Arch. Hydrobiol. 142 4 433–450 Stuttgart, July 1998

River-floodplain interactions: nutrient concentrations in the Lower Paraná River

Carlos A. Villar[1]*, Laura de Cabo[2], Panchabi Vaithiyanathan[3] and Carlos Bonetto[1]

Instituto de Limnología "Dr. Raúl A. Ringuelet"

With 3 figures and 4 tables in the text

Abstract: Changes in water chemistry along the lower 500 km stretch of the Paraná River were assessed. The water composition of the river and of a representative floodplain marsh were compared. Short-term changes in nutrient concentrations were monitored in marsh enclosures filled with river water in order to simulate the nutrient dynamics under floodplain inundation. Experiments were performed by resuspending river suspended matter (SM) in synthetic river water acidified to floodplain pH values and short term changes in soluble reactive phosphorus (SRP) and calcium recorded. Marsh water exhibited strong depletions of oxygen and nitrate. Dissolved free CO_2 was an order of magnitude higher and pH lower than in river waters. In the marsh, the net heterotrophic metabolism below the water surface seems to be the most plausible explanation for such features. The lack of a significant downstream increase in nitrate concentration in the river, in spite of large cultural inputs, was consistent with the low nitrate concentrations observed in marsh waters and the fast nitrate disappearance in enclosure experiments, suggesting large losses by denitrification. A decrease in SM along the Lower Paraná River would indicate high sediment retention within the floodplain. Calcium, bicarbonate, and soluble reactive phosphorus (SRP) concentrations were higher in the marsh than in the river. High marsh SRP concentrations are likely to originate from the weathering of river SM upon sedimentation, in response to the reducing and acidic marsh environment. The observed release of calcium and SRP upon acidification of SM is consistent with the higher contents observed in the marsh. Downstream increases in calcium, bicarbonate, and SRP along the river course

[1] **Authors' addresses:** Inst. Limnol. "Ringuelet". CC 712 (1900) La Plata, Argentina. *Becario CIC.

[2] Museo Argentino de Cs. Nat. "Bernardino Rivadavia". Angel Gallardo 470 (1405) Buenos Aires, Argentina.

[3] Duke University Wetland Center. 16139 Okeechobee Blvd. Loxahatchee, FL-33470, U.S.A.

0003-9136/98/0142-0433 $ 4.50

suggest the effect of a large water exchange between the river and its floodplain. The downstream increase in the P content of SM was correlated to SRP concentration. Mean inorganic nitrogen/SRP ratio, by weight, decreased from 8 in the upmost sampling site, to 3.6–3.8 close to the river mouth, being 0.6–0.8 in the floodplain marsh. The TOC and POC correlations to hydrometric level and the fact that both parameters attained their maxima at the receding stage after the flood peak, suggest the floodplain origin of the river organic loading. Conductivity, sodium, potassium, chloride, and sulphate increased from Santa Fe to Rosario, without further changes downstream, suggesting an important contribution from the Salado River, a tributary of high salinity that merges with the Paraná River downstream from Santa Fe.

Introduction

With an area of 3.1×10^6 km^2 and a mean water discharge of 20,000 m^3 s^{-1} at the mouth, the Paraná River watershed is the second largest hydrographic system in America, after that of the Amazon River. The Paraná River itself and the Paraguay River, its main tributary, are fringed by a 10–50 km wide floodplain, roughly half of which is occupied by a complex network of lentic habitats, and the rest covered by marshes and riparian forests. About 300 km upstream from the mouth, the river is divided into two main branches delimiting a delta of roughly 15,000 km^2. The region differs from the upper stretches in that marshes occupy a much larger area than lakes within the plain (roughly 80 % of the total area) and, because of tidal influence, a large and variable amount of water is exchanged daily between the river and its floodplain, its magnitude depending on hydrometric level, tidal amplitude, and wind action.

Floodplain environments differ from most aquatic habitats in that dramatic changes in water chemistry and biotic communities occur in response to periodic perturbations by the flood phase of the river. Nutrients supplied by rivers have been invoked to explain the high productivity of floodplain environments (Junk et al. 1989, Villar et al. 1996). Within the Paraná River Basin, attention has been focused on understanding the major nutrient sources and pathways within floodplain lakes in relation to the hydrologic regime in Middle (Pedrozo et al. 1992, Carignan & Neiff 1992) and Lower Paraná reaches (Bonetto et al. 1994). However, except for the recent contribution of Hamilton et al. (1997) for the Paraguay River, the net influence of the processes occurring in the floodplain environment on the river main course has been scarcely reported. The present study examines the influence of river-floodplain interactions on nutrient content along the lower 500 km stretch of the Paraná River, and relates observed patterns to the biogeochemical nature of floodplain marshes.

Materials and methods

The basin

The Upper Paraná River drains a tropical area covered by humid evergreens and deciduous forests. The headwaters drain sandstones from the old Precambrian Brazilian Shield. Downstream, the river drains iron-rich lateritic soils developed over Jurassic-Cretaceous basalts. About 1,200 km upstream from its mouth, the Paraná River joins its main tributary, the Paraguay River, to form the Middle Paraná River (Fig. 1). The Paraguay River drains the Pantanal wetland, a 10^5 km^2 marshy environment shared by southern Brazil and northern Paraguay. About 150 km upstream from the confluence, the Paraguay River joins its main tributary, the Bermejo River. The latter drains the Puna highlands, the oriental slope of the Andes, and the arid and semiarid Chaco plain. The high erosion rates occurring in the Andes determine that the Bermejo River contributes most of the suspended matter of the Lower Paraná River (PEDROZO et al. 1988). The Lower Paraná River joins the Uruguay River to form the Río de la Plata Estuary.

Study area

Downstream from Rosario (Fig. 1) the Paraná River is divided into two main branches, the Paraná Guazú (left arm) and the Paraná de las Palmas (right arm), delimiting a delta of approximately 15,000 km^2. The right arm delimits an area of intense agricultural activity, large cities (up to 2 million inhabitants) without sewage treatment, and industries (meat, leather, metallurgic, and petrochemical processing plants). The left arm drains a marshy environment without major human settlements.

The Lower Paraná stretch was sampled on six occasions, from Nov. 93 to Apr. 95, at Santa Fe, Rosario, Brazo Largo (left arm), and Otamendi (right arm), located 500, 300, 50, and 40 km upstream from the river mouth, respectively (Fig. 1). Two samplings were performed during floods: Nov. 93 and Apr. 95, the former in coincidence with the flood peak and the latter at the receding stage. Three samplings were performed at mean water level (Feb., Jun., and Dec. 94), and another one at an unusually low water phase (Set. 94).

A floodplain marsh representative of the deltaic region, at Puerto Constanza, on the left side of the Paraná Guazú River, 60 km upstream from the river mouth, was regularly sampled. Samples were taken bimonthly in the river and in two sites of the marsh, about 50 m from the river edge (riverside site) and about 800 m inside the marsh (inner floodplain site). The marsh was covered by a dense stand of emergent macrophytes, dominated by *Cyperus giganteus* and *Scirpus californicus*.

Analytical procedures

Surface water samples were taken in the navigation channel. Dissolved oxygen was determined with a YSI 51B recorder and pH with an Orion 250A pH meter. Water samples were filtered through Whatman GF/C filters, and carried in ice to the laboratory. Dissolved nutrients were determined in the filtrate. Soluble reactive phosphorus

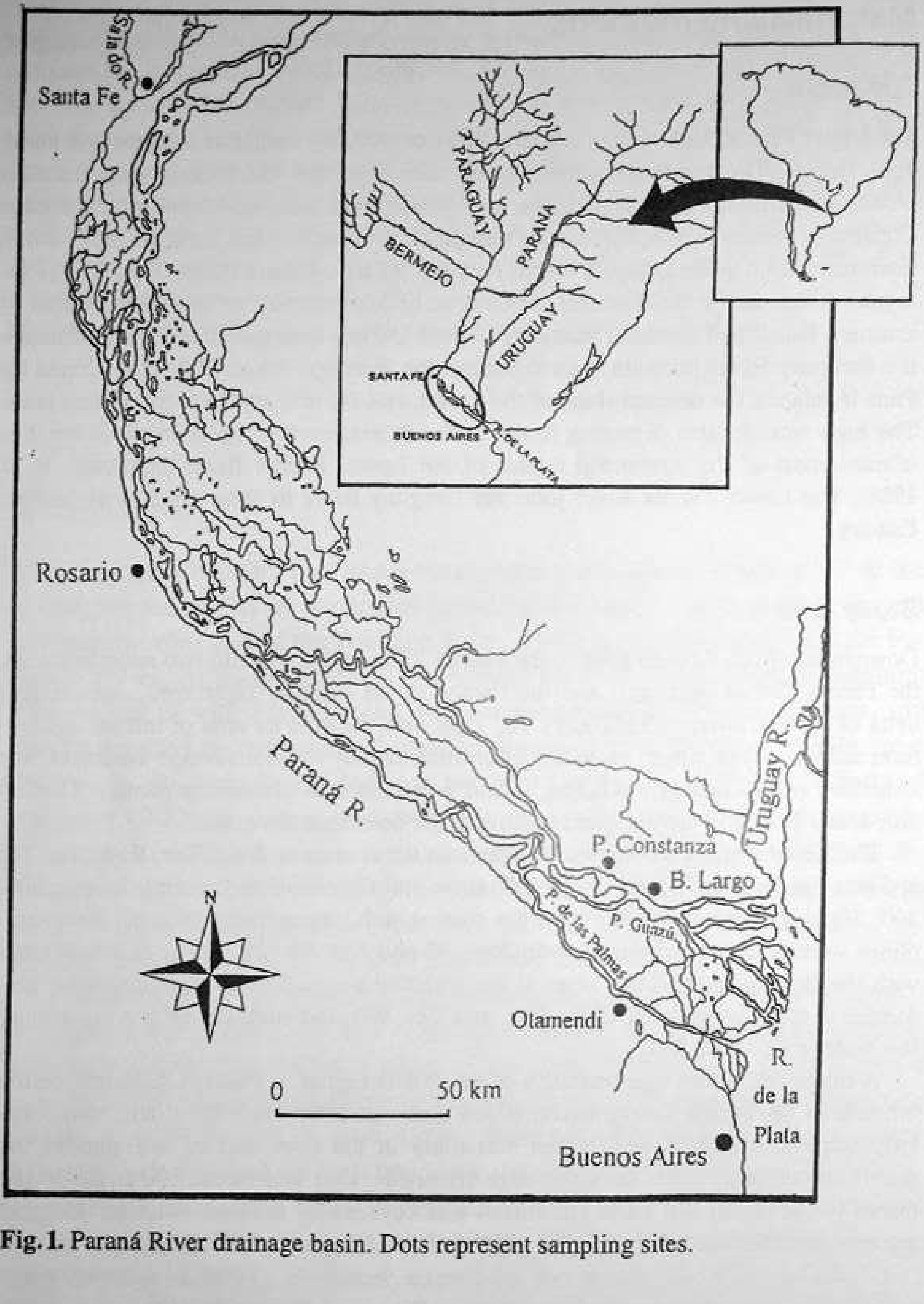

Fig. 1. Paraná River drainage basin. Dots represent sampling sites.

(SRP) (molybdate-ascorbic) and nitrates plus nitrites (cadmium reduction followed by diazotation) were determined following Strickland & Parsons (1972). Ammonium (indophenol blue) was measured according to Mackereth et al. (1978). Calcium and magnesium (EDTA), sodium and potassium (flame photometry), bicarbonate (Gran titration), sulphate (turbidimetry), and chloride (silver nitrate titration) were determined following APHA (1985). The concentration of dissolved free CO_2 was calculated from pH, bicarbonate, and major ions measurements following WETZEL & LIKENS (1990). Suspended matter (SM) was determined as the weight difference after filtration through Whatman GF/C filters. The filters were heated to 550 °C for two hours previous to use. Particulate organic carbon (POC) was determined after GOLTERMAN et al. (1978) by digestion of the filters used for SM determination. Total organic carbon (TOC) (GOLTERMAN et al. 1978) and total phosphorus (TP) (ANDERSEN 1979) were determined in unfiltered water samples fixed in the field with sulphuric acid.

SM was obtained at the laboratory by decantation of river water in 25-litre polyethylene containers (10–15 days). The supernatant was discharged by siphoning and the concentrated sediment dried in the oven at 60 °C. TP in river SM was measured by acid digestion after heating at 550 °C (ANDERSEN 1979). Carbon and nitrogen were determined with a C-N-H analyzer.

Suspended matter weathering under acidic conditions

An experiment was performed to asses SM weathering under pH changes similar to those recorded in river water upon mixing with floodplain marsh water. A suspension ($1\,g\,l^{-1}$) was prepared by resuspending Bermejo River SM, sampled at Puerto Velaz, a few km upstream from its confluence with the Paraguay River, in synthetic water resembling the mean ionic composition of the Lower Paraná River, but without SRP. Two litres of fresh suspension were slowly titrated with an autoburette from an initial pH of 8 to successively lower values until a final pH of 5.5 was attained. At several intermediate pH values, 40-ml subsamples were taken, filtered and analyzed for SRP and calcium concentrations.

Enclosure experiments

Experiments were performed at Puerto Constanza marsh in order to mimic the changes in nutrient concentration occurring when river water inundates the floodplain. Cylinders, 80 cm in diameter, were set in the floodplain marsh. The marsh soil has a superficial organic layer, about 25 cm deep, followed by a clay layer which retarded water exchanges between the cylinders and the external environment. One enclosure was set on Dec. 93 and remained in place during the whole study period (Enc. 1, Table 4). No sign of damage was observed in the vegetation within the enclosure. A second cylinder was set on Dec. 94 at a vegetation-free site (Enc. 2, Table 4). Six experiments were performed, involving the replacement of the floodplain water inside the cylinders by river water. Care was taken to minimize disturbances of the water-sediment interface. The water was thoroughly mixed and a sample representing the initial condition was taken. Changes in nutrient concentrations inside the cylinders were monitored for a few hours. Nitrate depletion rates were estimated as the difference between initial and final nitrate concentrations divided by the duration (in hours) of each experiment. This figure, times the enclosure water volume represents the total mass change per enclosure, which in turn was divided by the surface of the cylinder to calculate nitrate depletion rate per unit area.

Statistical analysis

Chemical data of the Lower Paraná River at each sampling site were compared by using randomized block analysis of variance (SOKAL & ROHLF 1979). Sites were considered the main factor and sampling dates the blocking factor. Whenever significant differences were detected, places were compared between each other by Tukey contrasts (SOKAL & ROHLF 1979). The same analysis was performed to compare river and marsh waters. Pearson correlations were calculated among all measured parameters in the Lower Paraná River. The statistical software utilized was SYSTAT (1990).

Results

Changes in water chemistry along the Lower Paraná River

Table 1 summarizes the water composition of the Paraná River from Santa Fe to Otamendi. Oxygen concentration behaved similarly to pH, both being correlated ($r = 0.71$, $p<0.01$), decreasing during floods and increasing during low-water periods. Oxygen ranged from 5.6 to 9.0 $mg\,l^{-1}$, and was inversely correlated to water level ($r = -0.69$, $p<0.01$), POC ($r = -0.55$, $p<0.01$) and TOC ($r = -0.42$, $p<0.05$). During floods (Nov. 93, Apr. 95), a significant downstream decrease in oxygen concentration was observed. Water pH fluctuated around neutrality (6.1–7.9) and was inversely correlated to water level ($r = -0.77$, $p<0.01$), POC ($r = -0.87$, $p<0.01$), and TOC ($r = -0.73$, $p<0.01$).

Conductivity, sodium, potassium, chloride, and sulphate concentrations increased from Santa Fe to Rosario ($p<0.05$), without further significant downstream changes. These variations were not related to those of the hydrometric level (except for potassium).

Bicarbonate was correlated to calcium ($r = 0.82$, $p<0.01$), TOC ($r = 0.63$, $p<0.01$), and water level ($r = 0.43$, $p<0.05$). The first two variables increased downsteam ($p<0.05$). Calcium was correlated to TP and SM ($r = 0.53$ and 0.44, $p<0.05$, respectively). DOC was the main organic component, the DOC/POC ratio was 2.5. TOC was correlated to POC ($r = 0.64$, $p<0.01$), and both variables were also correlated to water level ($r = 0.72$ and 0.58, $p<0.01$, respectively). Prominent TOC and POC maxima occurred soon after the flood peak (Apr. 95), during the receding stage.

SM showed important variations (43–253 $mg\,l^{-1}$), the highest concentrations corresponding to Feb.–Apr., about one month after the flood period of the Bermejo River. SM content decreased downstream ($p<0.05$), being roughly 20–70 % lower at Otamendi than at Santa Fe. The decrease was more marked at the highest hydrometric levels. Table 2 shows C, N, and P content of river SM at each sampling site. A significant downstream increase in P content was determined ($p<0.05$), while an apparent downstream increase in C and N content was not statistically significant.

Table 1. Limnological parameters measured at the Lower Paraná River.

	Height m	T °C	Cond. µS cm^{-1}	D.O. mg l^{-1}	pH	S.M. mg l^{-1}	Secchi cm	SRP µg l^{-1}	TP µg l^{-1}	N-NH_4^+ µg l^{-1}	N-NO_3^- µg l^{-1}	TOC mg l^{-1}	POC mg l^{-1}	HCO_3^- mg l^{-1}	SO_4^{2-} mg l^{-1}	Cl^- mg l^{-1}	Ca^{2+} mg l^{-1}	Mg^{2+} mg l^{-1}	K^+ mg l^{-1}	Na^+ mg l^{-1}
Santa Fe																				
Nov. 93		24	95	7.6	7.1	68	–	36	84	15	234	4.7	1.1	34.3	4.0	7.3	4.1	3.5	3.3	8.1
Feb. 94		28	73	7.2	7.2	237	13	30	703	33	137	4.5	1.6	55.8	12.0	3.5	10.0	7.5	2.1	4.8
Jun. 94		20	68	8.4	7.7	90	19	30	153	14	417	4.2	0.3	36.5	5.5	1.7	6.0	4.7	1.8	4.8
Sep. 94		22	68	8.1	7.6	66	26	21	108	26	120	4.3	0.9	29.7	2.7	3.8	4.3	3.7	1.9	5.2
Dec. 94		30	72	7.2	6.6	82	–	32	168	21	179	5.1	1.5	32.6	3.9	9.0	4.6	3.7	2.0	7.1
Apr. 95		23	92	7.2	6.2	249	8	28	430	21	213	9.3	2.6	51.6	3.5	4.0	9.2	4.6	2.6	3.0
Rosario																				
Nov. 93	4.6	23	168	7.4	7.0	106	17	69	176	26	174	6.2	1.9	41.9	9.2	17.2	4.9	3.5	4.1	20.2
Feb. 94	3.6	28	102	7.4	7.4	253	12	28	519	28	164	4.7	2.3	43.1	13.0	10.0	8.4	3.6	2.1	8.7
Jun. 94	3.2	18	178	8.8	7.6	85	19	60	188	26	333	4.9	0.2	47.6	16.0	23.7	8.6	3.7	2.7	24.9
Sep. 94	2.3	21	138	9.0	7.6	67	20	29	151	22	129	4.8	0.9	36.8	5.0	15.5	6.0	4.7	2.2	21.9
Dec. 94	3.7	29	158	6.9	6.9	60	18	45	199	20	144	4.8	1.3	38.5	11.0	26.0	6.6	3.6	2.4	22.3
Apr. 95	5.0	22	194	6.8	6.8	123	12	45	276	15	93	8.9	1.0	63.3	8.9	22.8	9.5	5.8	3.3	24.0
B. Largo																				
Nov. 93		21	142	5.6	6.8	71	21	76	154	24	107	5.7	1.4	39.3	6.0	13.1	9.2	3.0	3.8	16.4
Feb. 94		27	144	7.4	7.1	223	8	46	508	45	133	4.3	1.7	40.6	26.0	17.2	8.4	3.6	2.6	14.7
Jun. 94		17	181	9.0	7.8	66	18	60	174	23	317	4.7	0.3	52.3	11.0	23.3	9.5	3.7	2.7	25.1
Sep. 94		21	142	7.5	7.7	63	24	40	161	36	190	4.0	0.7	38.7	6.0	16.8	6.9	4.9	2.2	21.4
Dec. 94		29	156	7.0	6.8	54	–	53	226	22	181	4.5	1.3	38.4	10.4	26.0	6.9	3.9	3.5	22.3
Apr. 95		21	140	5.8	6.1	102	12	45	252	31	117	8.9	1.8	56.1	6.5	14.4	9.5	4.8	3.0	16.4
Otamendi																				
Nov. 93		23	195	6.6	7.2	43	–	88	130	19	152	4.7	0.8	48.2	9.6	19.7	6.5	3.5	4.1	24.8
Feb. 94		25	173	7.2	7.1	161	8	40	357	42	181	4.2	1.4	43.1	28.0	20.2	9.2	3.1	2.7	21.3
Jun. 94		18	234	9.0	7.9	69	17	70	212	30	333	4.4	0.2	63.0	38.0	28.3	10.4	3.7	3.0	30.2
Sep. 94		21	175	8.3	7.4	54	–	41	156	34	195	7.4	0.6	45.3	6.0	20.2	6.9	5.0	2.4	26.1
Dec. 94		28	158	6.5	6.8	46	20	61	190	25	221	4.2	1.1	40.3	12.0	25.0	6.3	4.3	2.7	22.3
Apr. 95		21	154	5.6	6.3	111	12	66	309	24	92	9.8	2.0	63.4	7.5	14.7	10.4	4.8	3.6	20.1

Table 2. Carbon, nitrogen and phosphorus content of suspended matter in the Lower Paraná River.

		C (%)	N (%)	P ($\mu g\ g^{-1}$)
Santa Fe	Nov. 93	1.43	0.15	660
	Feb. 94	0.66	0.08	677
	Jun. 94	1.01	0.12	635
	Sep. 94	1.04	0.11	677
	Dec. 94	1.04	0.13	602
	Apr. 95	0.68	0.08	620
Rosario	Nov.93	1.67	0.15	710
	Feb. 94	0.64	0.08	677
	Jun. 94	1.28	0.10	692
	Sep. 94	1.01	0.11	675
	Dec. 94	1.18	0.15	650
B. Largo	Nov. 93	1.70	0.16	762
	Feb. 94	0.75	0.09	712
	Jun. 94	1.18	0.11	712
	Sep. 94	1.18	0.13	702
	Dec. 94	1.43	0.18	723
	Apr. 95	0.80	0.10	655
Otamendi	Nov. 93	1.90	0.19	797
	Feb. 94	0.65	0.08	700
	Jun. 94	1.06	0.10	700
	Sep. 94	1.15	0.12	737
	Dec. 94	1.36	0.16	657
	Apr. 95	1.01	0.12	750

Total P was correlated to SM ($r = 0.91$, $p<0.01$). Unlike SM, an apparent downstream decrease in TP was not significant. SRP increased downstream ($p<0.05$), being its concentration correlated to the P content of SM ($r = 0.70$, $p<0.01$, Fig. 2).

Nitrate was the main N pool, representing about 80–85 % of the inorganic N pool. Its concentration was directly correlated to oxygen ($r = 0.46$, $p<0.05$) and inversely to POC ($r = -0.54$, $p<0.05$). Nitrate decreased downstream in three out of six samplings, two of which coincided with flood periods (Nov. 93, Apr. 95).

Suspended matter weathering under acidic conditions

Fig. 3 shows the changes in SRP and calcium concentrations measured after resuspending Bermejo River SM in water of similar ionic composition to that of the Lower Paraná River, subsenquently acidified from pH 8 to pH 5.5, a range consistent with values measured in the river and in floodplain marshes.

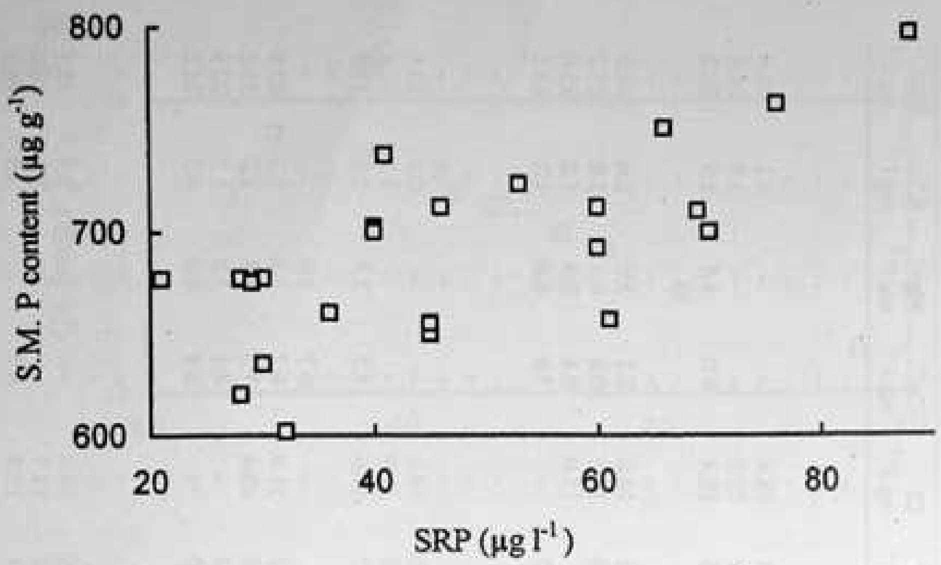

Fig. 2. Relationship between P content of suspended matter and water SRP concentration in the Lower Paraná River.

Dissolved calcium increased from 12.3 to 13.7 mg l^{-1}, while SRP increased from about 15 to approximately 50 µg l^{-1} in response to acidification.

Comparison between river and floodplain water

Table 3 summarizes the coastal water composition of the Paraná Guazú River at Puerto Constanza, together with that of two sites at the floodplain marsh. The water depth in the floodplain was 20–30 cm during most of the study period; however, the water level occasionally dropped below the sediment surface. Dense macrophyte coverage shade prevented phytoplankton growth within the marsh. Surface water temperature ranged from 7 to 25 °C. In spite of the shallowness of the marsh, there were frequent vertical variations; on Dec. 8, 93, temperature decreased from 25 °C at the surface to 21 °C at the bottom, 17 cm deep. Oxygen concentrations were low throughout the year in both marsh sites, and significantly lower than in the river ($p<0.01$). Surface oxygen concentrations usually ranged from 0.4 to 3.7 mg l^{-1}, peaking in winter. Vertical variations were often recorded, with oxygen exhaustion occurring near the sediment surface. Dissolved free CO_2 concentrations were consistently very high throughout the year, being an order of magnitude higher in the floodplain (36–303 mg l^{-1}) than in the river (1.3–16.9 mg l^{-1}). Water pH was significantly lower in the marsh than in the river ($p<0.01$), without significant differences between floodplain sites. Bicarbonate concentration was higher in the riverside floodplain site than in the inner floodplain site, and in the river ($p<0.01$), without significant differences between the latter two sites. Calcium concentration was higher in the riverside than in the inner floodplain marsh ($p<0.05$). SRP concentrations were higher in the riverside marsh, intermediate

Table 3. Limnological parameters measured at the riverside, inner floodplain marsh, and Paraná Guazú River at Puerto Constanza. Slashes separate surface and bottom values.

		T °C	D.O. mg l^{-1}	pH	Cond. µS cm^{-1}	N-NH_4^+ µg l^{-1}	N-NO_3^- µg l^{-1}	SRP µg l^{-1}	CO_2 mg l^{-1}	HCO_3^- mg l^{-1}	SO_4^{2-} mg l^{-1}	Cl^- mg l^{-1}	Ca^{2+} mg l^{-1}	Mg^{2+} mg l^{-1}	K^+ mg l^{-1}	Na^+ mg l^{-1}
Riverside	Aug. 93	–	–	6.0	164	35	98	10	–	–	–	–	–	–	–	–
	8 Sep. 93	–	5.1	–	–	40	4	23	–	–	–	–	–	–	–	–
	14 Sep. 93	–	–	6.8	166	9	34	29	–	–	–	–	–	–	–	–
	28 Sep. 93	12.0	3.7	6.5	199	–	13	312	48.3	78.7	2.3	18.4	–	–	4.1	18.6
	Oct. 93	18/16	1.4/0.4	6.4	135	10	6	114	51.7	73.6	4.2	12.0	–	–	2.8	14.5
	Dec. 93	22.0	0.6	6.5	193	30	10	300	36.5	71.0	4.5	18.4	9.0	4.5	2.5	20.2
	Apr. 94	–	–	–	–	9	7	71	–	–	–	–	–	–	–	–
	May 94	16.0	0.9	6.3	–	14	16	41	–	–	–	–	–	–	–	–
	Jul. 94	7/7	3/2.4	6.0	–	9	9	27	102.4	47.1	7.2	16.0	8.1	3.9	2.6	16.9
	Oct. 94	15.0	0.6	6.4	145	14	4	303	38.1	52.4	8.0	14.2	10.8	4.1	3.8	17.2
	Dec. 94	23.0	2.0	5.5	282	181	26	42	113.7	22.9	–	15.0	6.4	9.9	1.2	25.0
	Feb. 95	22.5	0.4	6.1	112	59	18	108	52.4	66.0	7.2	–	7.9	6.0	2.2	14.0
Inner floodplain	Aug. 93	–	–	5.8	110	49	18	17	–	–	–	–	–	–	–	–
	8 Sep. 93	16.0	4.6	6.1	–	75	9	15	–	–	–	–	–	–	–	–
	14 Sep. 93	16.0	–	6.5	142	21	108	27	–	–	–	–	–	–	–	–
	28 Sep. 93	13.0	0.7	6.0	132	–	3	104	94.1	49.5	2.5	10.3	–	–	0.7	13.9
	Oct. 93	18/15	2.2/0.2	6.3	136	23	3	167	40.9	47.0	3.5	13.0	–	–	3.3	15.1
	Dec. 93	–	–	–	–	–	7	84	–	53.3	3.7	15.0	7.7	3.8	2.9	17.5
	Apr. 94	–	–	–	–	61	3	61	–	–	–	–	–	–	–	–
	May 94	17.0	1.2	5.7	–	10	17	37	–	–	–	–	6.7	3.0	–	–
	Jul. 94	7.5	4.2/3.8	6.2	–	4	7	19	40.9	30.2	8.1	31.0	6.7	3.0	2.2	23.6
	Oct. 94	13.0	1.7	5.8	143	6	4	72	142.3	47.2	6.0	20.4	7.3	4.3	1.2	25.1
	Dec. 94	17.5	0.8	5.7	126	86	0	144	303.5	21.5	15.0	–	4.1	3.8	1.2	22.6
	Feb. 95	18.1	1.1/1.0	6.0	143	45	0	88	71.6	41.3	17.0	–	6.9	6.4	4.5	21.2
Paraná River	Aug. 93	–	–	7.3	143	22	173	17	–	–	–	–	–	–	–	–
	8 Sep. 93	–	–	7.1	–	97	184	19	–	–	–	–	–	–	–	–
	14 Sep. 93	–	–	7.5	147	28	289	24	–	–	–	–	–	–	–	–
	28 Sep. 93	–	–	7.5	144	–	202	47	2.1	38.1	5.6	14.0	–	–	2.1	15.8
	Oct. 93	–	–	7.5	139	49	239	53	2.0	36.8	6.8	12.7	–	–	2.8	15.5
	Dec. 93	25.0	5.6	7.1	–	32	150	64	5.3	43.1	7.5	17.7	8.2	–	3.5	19.8
	May 94	19.0	–	6.9	–	35	245	33	–	–	–	–	–	–	–	–
	Jul. 94	14.0	9.1	7.7	–	17	146	29	1.6	42.5	10.2	12.6	8.7	3.5	2.3	15.5
	Oct. 94	20.0	8.3	7.7	140	19	131	38	1.3	40.0	9.3	16.7	6.9	4.4	2.4	20.4
	Dec. 94	25.0	7.1	6.9	107	26	284	63	5.8	29.7	13.0	14.0	5.7	3.7	–	–
	Feb. 95	26.8	6.0	6.6	98	16	126	44	16.9	44.1	6.3	10.7	8.0	4.8	2.4	10.4

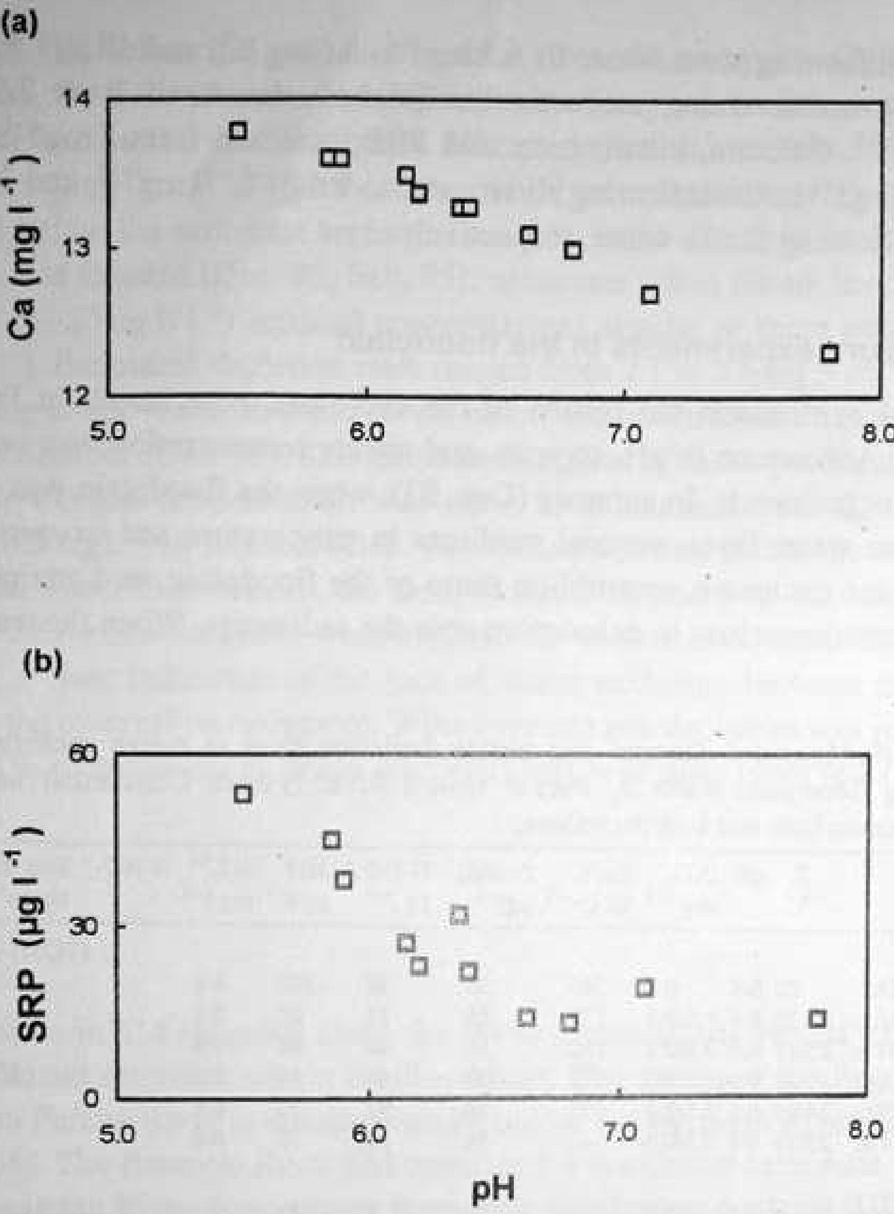

Fig. 3. Effect of pH on calcium (**a**) and SRP (**b**) release from suspended matter of the Bermejo River resuspended in SRP-free synthetic water of the Lower Paraná River.

in the inner floodplain site, and lower in the river ($p<0.01$). A large SRP variation range was observed in the riverside marsh, showing winter minima ($10\,\mu g\,l^{-1}$ on Aug. 93 and $27\,\mu g\,l^{-1}$ on Jul. 94) and spring maxima ($312\,\mu g\,l^{-1}$ in Set. 93 and $303\,\mu g\,l^{-1}$ in Oct. 94). Nitrate exhibited a large significant decrease from the river to both floodplain sites ($p<0.01$), while ammonium did not show significant differences between sites. The inorganic N/SRP ratio, by weight, decreased from 3.6 in the river to 0.5–0.7 in the floodplain marsh. Conductivity, as well as major ions concentrations did not differ significantly among marsh sites and river. On Dec. 8, 93, inflowing river water and outflowing marsh water were sampled during a tidal cycle. Water pH, oxygen, and nitrate concentrations decreased from $7.1\,mg\,l^{-1}$, $6.6\,mg\,l^{-1}$, and $150\,\mu g\,l^{-1}$

in the inflowing river water to 6.5 mg l^{-1}, 0.6 mg l^{-1}, and 10 µg l^{-1} in the outflowing marsh water, respectively. Sulphate decreased from 7.5 mg l^{-1} to 4.6 mg l^{-1}. Calcium, bicarbonate, and SRP increased from 8 mg l^{-1}, 43 mg l^{-1}, and 64 µg l^{-1} in the inflowing river water to 9 mg l^{-1}, 71 mg l^{-1}, and 300 µg l^{-1} in the outflowing marsh water, respectively.

Enclosure experiments in the floodplain

Table 4 synthesizes the results of the enclosure experiments at Puerto Constanza. A decrease in pH, oxygen, and nitrate concentration was evident in all of the experiments. In summer (Dec. 93), when the floodplain was covered by a 20-cm water layer, vertical gradients in temperature and oxygen developed inside the enclosure, resembling those of the floodplain, and attaining oxygen concentrations close to exhaustion near the sediments. When the water level in

Table 4. Measured changes and nitrate depletion rates in marsh enclosures after replacing floodplain water by Paraná Guazú River (Puerto Constanza) water. Slashes separate surface and bottom values.

	T °C	pH	D.O. mg l^{-1}	Cond. µS cm^{-1}	$N\text{-}NH_4^+$ µgl^{-1}	$N\text{-}NO_3^-$ µg l^{-1}	SRP µg l^{-1}	SO_4^{2-} mg l^{-1}	$N\text{-}NO_3^-$ Dep. Rate mg $m^{-2}h^{-1}$	Water depth cm
Dec. 93										
Marsh 8 hs	22	6.4	0.6	166	30	10	300	4.6		
Marsh 13 hs	24/20	6.4	1.8/0.3	173	25	15	95	5.1		
Marsh 17 hs	25/21	6.0	0.9/0.2	192	34	12	92	4.9		
Enc.1 8 hs	22	6.6	6.0	172	40	147	44	7.6	3.3	20
Enc.1 13 hs	24/20	6.1	2.8/2.1	173	30	92	33	6.8		
Enc.1 17 hs	25/21	6.1	2.2/0.5	–	38	20	55	6.0		
Jul. 94										
Marsh 13 hs	7	6.0	3/2.4	–	9	9	27	7.2		
Enc. 1 16 hs	12	7.1	9.6/9	–	21	138	45	10.1	2.4	18
Enc. 1 19 hs	10	6.7	6.0	–	16	98	32	9.7		
Oct. 94										
Marsh 12 hs	15	6.4	0.6	145	14	4	303	8.0		
Marsh 19 hs	16	6.2	0.7	–	20	3	308	7.5		
Enc. 1 12 hs	20	6.5	8.0	140	24	160	35	9.0	3.5	14
Enc. 1 16 hs	20/18	6.0	3.0	–	12	64	30	9.0		
Enc. 1 19 hs	18	5.9	2.0	–	13	29	38	9.0		
Dec. 94										
Marsh 16 hs	23	5.5	2.0	282	181	26	42	44.0		
Enc. 1 12 hs	26	6.6	7.6	115	86	240	62	13.0	2.1	10
Enc. 1 16 hs	29	6.4	7.8	117	64	187	45	15.0		
Enc. 1 20 hs	25	6.1	5.8	116	70	162	47	16.0		
Feb. 95										
Marsh 12 hs	23	6.1	0.4	112	59	18	108	7.2		
Enc. 1 13 hs	26	6.8	6.8	100	35	76	62	6.7	3.6	15
Enc. 1 17 hs	24/22	6.4	2.4/2.6	102	16	12	47	6.1		
Enc. 2 13 hs	26	6.7	6.6	97	16	68	47	6.1	3.6	15
Enc. 2 17 hs	23	6.5	6/6.2	91	13	25	33	5.8		

the marsh fell below the sediment surface (Dec. 94), oxygen depletion was less severe. On Feb. 95, vertical temperature and oxygen variations developed within the enclosures in a few hours. Nitrate depletion was related to that of oxygen, ranging from 30–32 % of the initial concentration when the water level fell below the sediment surface (Dec. 94), to 84–86 % in summer when the plain was flooded (Dec. 93, Feb. 95), occasions when nitrate inside the enclosure (20–25 $\mu g\,N\,l^{-1}$) attained concentrations similar to those outside (12–18 $\mu g\,N\,l^{-1}$). Estimated depletion rates ranged from 2.1 to 3.6 $mg\,N\,m^{-2}\,h^{-1}$, corresponding lower values to water levels below the sediment surface and higher values to summer (Dec. 93). SRP decreased in most of the experiments, except whenever oxygen concentration was close to exhaustion near the sediment surface (0.5 $mg\,l^{-1}$) in summer (Dec. 93). Concentrations inside the enclosures were often lower than outside. On Dec. 93, Oct. 94, and Feb. 95, large differences in SRP concentrations were attained between marsh water and the enclosures, a clear indication of the lack of water exchange between the enclosure and the external environment. Whenever oxygen depletion was important, a 10–20 % decrease in sulphate concentration was also observed (Dec. 93, Feb. 95).

Discussion

The decrease in SM recorded along the lower stretch of the Paraná River indicates sediment retention within the floodplain. The sediment loading entering the Lower Paraná River is mainly contributed by the Bermejo River (PEDROZO et al. 1988). The Bermejo River SM contains 1.4 % calcium carbonate, and that of the Paraguay River downstream from their confluence contains 0.07 % (CARIGNAN & VAITHIYANATHAN 1997). Emergent macrophyte production within the floodplain is large, being the above ground biomass 1.8–3 $kg\,m^{-2}$ (VILLAR et al. 1996) and the below ground biomass 11 $kg\,m^{-2}$ (VILLAR 1997). After each growing season most of the produced biomass senesces during winter and decomposes at the marsh surface. High rates of heterotrophic metabolism and reduced air-water gas exchange, due to large macrophyte coverage, determine the observed oxygen depletion and CO_2 supersaturation. Our findings are coincident with those reported for the Pantanal wetland by HAMILTON et al. (1995), who suggested that root respiration of emergent macrophytes provides roughly 40 % of the water CO_2 concentration. At our study site, the five times larger below than above ground biomass would have also contributed significantly to CO_2 supersaturation. Increased CO_2 concentrations lead to water acidification (STUMM & MORGAN 1981, HAMILTON et al. 1995, 1997). Ionized organic acids produced by anoxic decomposition of organic matter inside the marsh litter might also contribute to the observed floodplain acidity. Riverine particulate material retained by the marsh undergoes partial dissolution in response to the acidic and CO_2 oversaturated environment (STUMM & MORGAN 1981), leading to higher calcium and bicarbonate concentrations in the marsh, consistent with the observed release of calcium when the Bermejo River SM was acidified to the pH prevailing in the floodplain. Within this context, the higher calcium and bicarbonate concentrations in the riverside rather than in the inner floodplain marsh may reflect higher SM retention in the riverside strip. The trend towards a pH increase by carbonate dissolution from inflowing river SM seems to be low relative to the large flux of CO_2 originated by the heterotrophic activity occurring in the marsh. The downstream increase in calcium and bicarbonate along the Lower Paraná River seems to be supplied, at least partially, by water exchange with the floodplain. Inputs of acidic water from the floodplain did not produce a concomitant downstream decrease in the river pH. It is likely that the presence of particulate carbonate provides the river with a buffer capacity strong enough to counteract the acidity and free CO_2 contributed by the floodplain.

The TOC and POC correlations to hydrometric level and the fact that their maximum concentrations were attained at the receding stage, immediately after the flood peak, when organic matter rich waters drained from the floodplain, suggest the floodplain origin of the organic loading. DE PETRIS & KEMPE (1993) suggested that most of the organic matter loading entering the Middle Paraná River was supplied by the floodplain and by the Paraguay River. Furthermore, HAMILTON et al. (1997) conclude that the organic matter loading of the Paraguay River originates mainly from the Pantanal wetland.

The increase in conductivity, sodium, potassium, chloride, and sulphate from Santa Fe to Rosario may be explained by the contribution of the Salado River, a tributary of comparatively modest discharge but high salinity (MAGLIANESI & DE PETRIS 1970), which joins the Paraná River downstream from Santa Fe. The Salado River drains an arid environment of saline soils and groundwater, northwest of the Lower Paraná River. The lack of changes downstream from Rosario is indicative of the conservative behaviour of these elements.

The higher SRP concentration in the marsh than in the river may be attained by P released from river SM upon deposition within the floodplain environment. The enclosure experiment of Dec. 93 showed an initial decrease followed by a subsequent increase in SRP concentrations when oxygen concentration declined to near zero. Outside the enclosure a high SRP concentration was measured simultaneously with oxygen exhaustion, suggesting iron-bound P release after reduction of the sediment surface. The general trend towards measuring higher SRP concentrations in coincidence with oxygen depletion in the marsh, and the fact that SRP decreases when oxygen was not depleted in the enclosure experiments, provide further evidence of the importance of reduction-induced iron liberation from the marsh surface in determining the SRP concentrations in the overlaying water. The simultaneous release of calcium and SRP from the Bermejo River SM in response to pH reduction, also suggests the contribution of calcium-bound P. These results are consistent with the lower iron and calcium-bound P observed in the marsh sediments than in the river SM reported by BONETTO et al. (1994).

The contribution of cultural inputs to the observed downstream increase in SRP concentration remains uncertain. If a per capita input of $2\,g\,P\,d^{-1}$ (VOLLENWEIDER 1968, OECD 1982) is assumed, the effect of the daily sewage loading from cities (ca. 2 million inhabitants) to a river having a discharge of $20{,}000\,m^3\,s^{-1}$, should increase the TP concentration in roughly $2\,\mu g\,P\,l^{-1}$, an irrelevant amount when compared to the overall mean of $274\,\mu g\,P\,l^{-1}$ at Santa Fe. Even assuming that most of this P is readily mineralized to SRP, the expected increment is small when compared to the mean increase from $30\,\mu g$ SRP l^{-1} at Santa Fe to $61\,\mu g$ SRP l^{-1} at Otamendi. If point sources were the main input, then P and hydrometric level should be inversely correlated, since inputs are diluted during floods and concentrated during low-water periods. On the contrary, we observed that the highest SRP concentrations were coincident with a flood (Nov. 93), whereas the lowest values occurred at the lowest hydrometric level (Set. 94). Since mean SRP concentrations in the floodplain were three times higher than in the river, the present evidence suggests that the downstream SRP increase along the Lower Paraná River is mainly originated by the water exchange between the river and its floodplain. The Lower Paraná River SM exhibits a significant P-adsorption capability as shown by the concomitant increments in P content and water SRP. The liquid-solid equilibrium exchange reactions have a significant influence on the regulation of SRP concentration in water. Within the studied stretch, an increase in equilibrium SRP concentration of about $35\,\mu g\,l^{-1}$ is attained together with a simultaneous increase of $100\,\mu g\,g^{-1}$ in the P content of SM (Fig. 2). Assuming an overall mean SM concentration of $132\,mg\,l^{-1}$, would indicate that $13\,\mu g\,l^{-1}$ are stored in particulate form. Therefore, roughly 30 % of SRP inputs to the river would be retained in the particulate fraction, partially counteracting dissolved-P enrichment. However, it remains readily available whenever the equilibrium conditions are modified.

The contribution of inorganic N from cultural inputs to the Lower Paraná stretch foresees the same limitations as for SRP. A rough estimate of sewage point sources may be derived from population density and per capita contribution (VOLLENWEIDER 1968, OECD 1982). Such contribution was considered to be about 5 times larger for N than for P, representing roughly $20\,\mu g\,N\,l^{-1}$. The right margin of the river has areas of intensive agriculture. Unlike P, which is strongly adsorbed to the clay fraction of the soil, urea, the main N fertilizer used, is transformed to nitrate in the soil and leached to rivers by rains. In the

Upper Paraná River, peaks of nitrate were detected in coincidence with the elevating limb of the hydrograph, and interpreted as leaching from soils at the beginning of the wet season in the Upper Paraná Basin (PEDROZO & BONETTO 1989). The mean inorganic N concentrations were 346 $\mu g\,N\,l^{-1}$ in the Upper Paraná River (PEDROZO & BONETTO 1989), 231 $\mu g\,N\,l^{-1}$ in the Paraguay River (PEDROZO et al. 1988), and 366 $\mu g\,N\,l^{-1}$ in the Bermejo River (PEDROZO & BONETTO 1987), resulting a discharge-weighed mean of 328 $\mu g\,N\,l^{-1}$ for the Middle Paraná River, at Corrientes, while the mean inorganic N concentration measured in the present study at Brazo Largo decreased to 204 $\mu g\,N\,l^{-1}$. The lack of significant changes in nitrate concentration along the Lower Paraná River, in spite of cultural inputs, is consistent with the low concentrations determined in floodplain waters throughout the year and with the fast nitrate depletion observed in all of the enclosure experiments, suggesting large nitrate sinks of riverborn nitrates within the floodplain environment. The main pathways for nitrate removal at the soil-water interface include biological assimilation, dissimilatory nitrate reduction to ammonium, and denitrification. Under conditions of anaerobic organic sediments in contact with a suboxic water layer, there is a large demand for nitrates to be used as electron acceptors. D'ANGELO & REDDY (1993) suggest that most of the $^{15}N\text{-}NO_3^-$ (roughly 90 %) applied to Lake Apopka sediment-water cores was lost by denitrification. Freshwater marshes have the potential to remove large inputs of inorganic N by denitrification (LINDAU et al. 1991). Ammonium inputs may also be lost through coupled nitrification-denitrification. REDDY at al. (1989) showed that oxygen transport through the air spaces (aerenchyma) of aquatic macrophytes into the root zone supports the nitrification of ammonium, with nitrate diffusing into the adjacent anaerobic zone, where it undergoes denitrification. MINZONI et al. (1988) measured fast nitrate depletion together with a large recovery of N_2O in enclosures similar to ours, by adding nitrate to simulate a fertilization event in a rice field. Similarly to this environment, our floodplain marsh also attains a large macrophyte production in a shallow-water column in contact with an organic rich substratum, and receives large nitrate inputs from the river. The fast nitrate depletion, involving a time scale of hours, in all of our enclosure experiments suggests losses by denitrification.

BONETTO et al. (1994) and VILLAR et al. (1996) presented evidence of N limitation for macrophyte growth within the floodplain. Mean inorganic N/SRP ratio, by weight, decreased from 8 in the upstream most sampling site, to 3.6–3.8 close to the river mouth, while it was as low as 0.6–0.8 in the floodplain marsh. The downstream inorganic N impoverishment and SRP enrichment seems to be a consequence of the river-floodplain interaction, resulting from the combination of an important SM loading from the river together with a large macrophytic organic production in the marshes.

Acknowledgements

This research was possible thanks to the financial support of the International Foundation for Science (IFS). "Prefectura Naval Argentina" provided boating facilities to sample the Paraná River at Santa Fe and Rosario. The "Estación Agronómica Delta" of the "Instituto Nacional de Tecnología Agropecuaria" (INTA), provided boating facilities and the hydrometric records at Otamendi. Dr. Mari Dos Santos made valuable comments on the reviewed manuscript.

References

Andersen, J. (1979): An ignition method for determination of total phosphorus in lake sediments. – Water Research **10:** 329–331.

APHA (1985): Standard Methods for the examination of water and wastewater. – Amer. Publ. Health Assoc., N.Y., 1268 pp.

Bonetto, C., De Cabo, L., Gabellone, N., Vinocur, A., Donadelli, J. & Unrein, F. (1994): Nutrient dynamics in the deltaic floodplain of the Lower Paraná River. – Arch. Hydrobiol. **131:** 277–295.

Carignan, R. & Neiff, J. J. (1992): Nutrient dynamics in the floodplain ponds of the Paraná River (Argentina) dominated by the water hyacinth *Eichhornia crassipes.* – Biogeochemistry **17:** 85–121.

Carignan, R. & Vaithiyanathan, P. (1997): Phosphorus availability in the Paraná floodplain lakes (Argentina): Influence of pH and phosphate buffering by fluvial sediments. – Limnol. Oceanogr. (in press).

D'Angelo, E. & Reddy, K. (1993): Ammonium oxidation and nitrate reduction in sediments of a hypereutrophic lake. – Soil Sc. Soc. Amer. J. **57:** 1156–1163.

De Petris, P. & Kempe, D. (1993): Carbon dynamics and sources in the Paraná River. – Limnol. Oceanogr. **38:** 382–395.

Golterman, H., Clymo, R. & Ohnstad, M. (1978): Methods for the physical and chemical examination of freshwaters. – Blackwell Sci. Publ., Oxford, 166 pp.

Hamilton, K., Sippel, S., Calheiros, D. & Melack, J. M. (1997): An anoxic event and other biogeochemical effects of the Pantanal wetland on the Paraguay River. – Limnol. Oceanogr. **42:** 257–272.

Hamilton, K., Sippel, S. & Melack, J. M. (1995): Oxygen depletion and carbon dioxide and methane production in waters of the Pantanal wetland of Brazil. – Biogeochemistry **30:** 115–141.

Junk, W., Bailey, P. & Sparks, R. (1989): The flood pulse concept in river-floodplain systems. – In: Proceedings of the International Large River Symposium (LARS). – Can. Spec. Publ. Fish. Aquat. Sci. **106:** 110–127.

Lindau, C., De Laune, R., Jiraporncharoen, S. & Manajuti, D. (1991): Nitrous oxide and dinitrogen emissions from *Panicum hemitomon* freshwater marsh soils following addition of ^{15}N labelled ammonium and nitrate. – J. Freshwat. Ecol. **6:** 191–198.

Mackereth, F., Heron, J. & Talling, J. (1978): Water analysis: some revised methods for limnologists. – Freshwat. Biol. Assoc. Sci. Publ. **36:** 120 pp.

Maglianesi, R. & De Petris, P. (1970): Water chemistry of the Lower Salado River (Santa Fe, Argentina). – Physis **80:** 19–32.

MINZONI, F., BONETTO, C. & GOLTERMAN, H. L. (1988): The nitrogen cycle in shallow water sediment systems of rice fields. Part I: The denitrification process. – Hydrobiologia **159:** 189–202.

OECD (1982): Eutrophication of waters. Monitoring, assessment and control. – Organization for Economic Co-operation and Development, Paris, 154 pp.

PEDROZO, F. & BONETTO, C. (1987): Nitrogen and phosphorus transport in the Bermejo River (South America). – Rev. Hydrobiol. Trop. **20:** 91–99.

– – (1989): Influence of river regulation on nitrogen and phosphorus mass transport in a large South American River. – Regul. Rivers: Res. & Managem. **4:** 59–70.

PEDROZO, F., BONETTO, C. & ZALOCAR, Y. (1988): A comparative study of phosphorus and nitrogen transport in the Paraná, Paraguay and Bermejo Rivers. – In: TUNDISI, G. (ed.): Monografías em Limnología Vol. 1. Simposio: Limnología e Manejo de Represas, pp. 91–117.

PEDROZO, F., DIAZ, M. & BONETTO, C. (1992): Nitrogen and phosphorus in the Paraná River floodplain waterbodies. – Arch. Hydrobiol./Suppl. **90:** 171–185.

REDDY, K., PATRICK, W. & LINDAU, C. (1989): Nitrification-denitrification at the plant root-sediment interface in wetlands. – Limnol. Oceanogr. **34:** 1004–1013.

SOKAL, R. & ROHLF, F. (1979): Biometría. Principios y métodos estadísticos en la investigación biológica. – H. Blume Ediciones, Madrid, 832 pp.

STRICKLAND, J. & PARSONS, T. (1972): A practical handbook for seawater analysis. – Bull. **167**. J. Fish. Res. Bd. Canada, Ottawa, 311 pp.

SYSTAT (1990): SYSTAT: The System for Statistics. – SYSTAT Inc., Evanston.

STUMM, W. & MORGAN, J. J. (1981): Aquatic Chemistry. – Wiley, New York, 780 pp.

VILLAR, C. (1997): Interacción río-valle aluvial: intercambio de nutrientes y contaminantes. – Doctoral Dissertation, Universidad de Buenos Aires. Buenos Aires, Argentina, 182 pp.

VILLAR, C. DE CABO, L. & BONETTO, C. (1996): Macrophytic primary production and nutrient concentrations in a deltaic floodplain marsh of the Lower Paraná River. – Hydrobiologia **330:** 59–66.

VOLLENWEIDER, R. (1968): Scientific fundamentals of the eutrophication of lakes and flowing waters, with particular reference to phosphorus and nitrogen as factors in eutrophication. – OECD Technical Report, Paris, 159 pp.

WETZEL, G. & LIKENS, G. (1990): Limnological analysis. 2nd ed. – Springer-Verlag, New York, 391 pp.

Submitted: 12 June 1997; accepted: 5 February 1998.