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Published online: 16 Nov 2017.

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Gisela Mayora,[a] Melina Devercelli,[a] and María dos Santos Afonso[b]

[a]Instituto Nacional de Limnología (INALI-CONICET-UNL), Ciudad Universitaria, Santa Fe, Argentina; [b]Instituto de Química Física de los Materiales, Medio Ambiente y Energía (INQUIMAE-CONICET-UBA), Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires (DQIAQF-FCEN-UBA), Ciudad Universitaria, Buenos Aires, Argentina

ABSTRACT

Hydrosedimentological conditions of floodplain rivers can affect nutrient delivery processes. This study evaluated the effects of sedimentological and hydrological regimes on nitrogen (N) speciation and transport in the floodplain–river system of the Middle Paraná. Relations of sedimentological and hydrological regimes, assessed through turbidity and hydrometric level, with N speciation and concentration were analyzed. Simple linear regressions were performed to assess whether N load changed within the main channel in response to hydrological and sedimentological regimes. From the main channel to the floodplain, dissolved inorganic N decreased; however, the most isolated lake had the highest N concentration, almost totally in organic form. Turbidity was negatively associated with concentrations of nitrate-N (NO_3-N), nitrite-N (NO_2-N), and dissolved organic N (DON), and relative contributions of these N forms to total N (TN) but was positively correlated to particulate N (PN) and ammonium-N (NH_4-N). The hydrometric level was positively associated with DON concentration and its relative contribution at the main channel but negatively associated with DON, PN, and TN concentrations in the most isolated lake. Simple linear regressions showed that the sedimentological regime significantly explained all N forms but not TN load. Flooding increased TN and mainly DON load. The results show that the hydrosedimentological regime largely affects N transport and speciation. The sediment peak incorporates PN to the system and affects dissolved N speciation, probably through effects of suspended particles on redox reactions. The increase of N inputs to the fluvial system during the flood could be caused by DON exportation from the floodplain.

Introduction

Nitrogen (N) is among the most important nutrients in aquatic ecosystems because it is often a limiting factor for production in waterbodies (Carignan and Planas 1994, Jansson et al. 1996, Abell et al. 2010). N is present in different chemical (organic and inorganic) and physical (dissolved and particulate) forms with variable bioavailability; therefore, the ecological functioning of aquatic ecosystems depends both on its total supply and speciation (Mozdzer et al. 2010).

Transformations of N forms are generally mediated by the biota. The major N compounds available for macrophyte and phytoplankton uptake are present as dissolved inorganic forms (nitrite, nitrate, and ammonium), which are assimilated into organic constituents of cells (Okafor 2011). A large number of microorganisms can transform N forms through both assimilatory and dissimilatory processes, however, including nitrification and denitrification (Bothe et al. 2007) controlled by multiple environmental conditions, such as redox potential, temperature, hydrology, and concentration of suspended sediments (Burgin and Hamilton 2007, Alexander et al. 2009, Xia et al. 2013).

Floodplain river systems are characterized by a high heterogeneity of environmental conditions that affect N dynamic both temporally and spatially (Tockner et al. 1999, Ward et al. 2002). The decreasing trend of nitrate from the main channel to the more isolated floodplain lakes (Maine et al. 2004, Emmerton et al. 2008, Mayora et al. 2013) has been attributed to bacterial denitrification and N biological assimilation in floodplain waterbodies, which are characterized by high biological productivity and organic matter content. Consequently, floodplains are considered important sinking areas of the N transported by the river, mainly during high waters because of the increased exchange of materials between environments (Villar et al. 1999, Maine et al. 2004, Hoffmann et al. 2011,

Roach and Grimm 2011, Welti et al. 2012). Sediment peaks considerably increase the rates of N transformations because suspended particles favor the generation of microsites with particular conditions, stimulation of bacterial growth, and adsorption of nitrogenous molecules on their surfaces (Liu et al. 2013, Xia et al. 2013).

Floodplain rivers are subjected to increasing anthropogenic inputs of N and to hydrosedimentological alterations that could affect delivery processes (Hamilton 2010, Morée et al. 2013). In South America, these habitats have been comparatively less altered and are under-represented in studies of N load (Alvarez-Cobelas et al. 2008, Tockner et al. 2008), despite their importance in the amount of matter they transport to the sea (McClain and Gann 2010). The Paraná River, one of the largest floodplain fluvial systems of South America, discharges ~470 km^3 of water and 80×10^6 metric tons of suspended sediments to the sea per year (Drago 2007). At its middle stretch, most of the water discharge comes from the Upper Paraná River, whereas most of the suspended solids come from an Andean tributary (Amsler and Drago 2009). Hence, hydrological and sedimentological regimes are not coupled, individualizing their effects on N dynamics.

The aim of this work was to evaluate the N dynamic in the subtropical system of the Middle Paraná River in relation to the sedimentological and hydrological regimes and, particularly, to test their effects on the N speciation in a main channel–floodplain gradient and the N load in the main channel. The analyzed N forms included nitrite-N (NO_2-N), nitrate-N (NO_3-N), ammonium-N (NH_4-N), dissolved organic N (DON), and particulate N (PN). We hypothesized that (1) during high waters, inorganic N forms increase in the floodplain and organic N forms increase in the main channel because of the higher material exchange among environments; and (2) the sediment peak increases the load of PN in the main channel, whereas the flood increases the load of DON because of material inputs from the floodplain.

Materials and methods

Study sites

The subtropical Paraná River in central South America covers a basin area of 3.1×10^6 km^2 (Fig. 1a). The middle stretch of the river extends from its confluence with the Paraguay River (27°29′S; 58°50′W) to the city of Diamante (Argentina; 32°4′S; 60°32′W; Fig. 1b) and has a turbid main channel with suspended solids ranging from 20 to 310 mg L^{-1} (Bonetto et al. 1994). Along its right margin is a 10–50 km wide floodplain (13 000 km^2) comprising permanent and temporary waterbodies that flood with variable frequency. At least 1500 permanent lakes (mean area: 0.32 km^2, mean maximum depth: 1.46 m) developed

within the floodplain, mainly from the migration of secondary channels (Paira and Drago 2007). Nearly 75% of the water discharge is provided by the Upper Paraná River, whereas nearly 90% of the suspended sediments are supplied, through the Paraguay River, by Andean headwaters of the Bermejo River (Amsler and Drago 2009). The sediment peak occurs during the late summer, but hydrological phases are irregularly timed.

The study sites (Fig. 1c and d) are located within the Middle Paraná River system and include the main channel and 3 floodplain waterbodies: a lake directly and permanently connected to the main channel by a 0.65 km long channel (Lake 1); Miní Stream, a small secondary channel connected to several floodplain waterbodies; and a shallow lake indirectly connected to the fluvial system through the Miní Stream during high waters (Lake 2). The aquatic vegetation of both the Lake 1 and Miní Stream is generally restricted to the margins. Lake 2 is characterized by a large development of aquatic vegetation, generally dominated by *Ludwigia peploides* (Kunth) Raven.

Samplings and laboratory analysis

Samples were collected fortnightly from February to November 2012. Subsurface water samples were collected in triplicate at the center of the lotic environments and in the pelagic zone of the lakes. At the main channel, water samples were collected at a point far from tributaries that could locally influence water quality. This point is located 6 km downstream of the main channel section (31°42′–31°40′S; 60°29′–60°45′W), which is considered a control site where 85% of total water discharge passes through (Drago 1984). Water samples were refrigerated and processed within 24 h after sampling, except those for dissolved organic carbon (DOC) analysis, which were preserved by acidification with concentrated phosphoric acid and refrigerated until their analysis (ISO 8245, 1999) within 28 d after sampling. Conductivity, pH, temperature, and dissolved oxygen (HANNA portable checkers) were measured *in situ*.

Turbidity (formazin turbidity units [FTU]) was spectrophotometrically estimated with a HACH DR 2000 spectrophotometer used to estimate the sedimentological regime of the environments (Golterman 1975). A variable volume of water was filtered through Whatman GF/F glass-fiber filters with a vacuum pump; filters were stored at −20 °C up to 3 weeks for spectrophotometric analysis of chlorophyll *a* (APHA 2005). Filtered water samples were filtered again through Millipore filters (pore size: 0.45 μm) for analysis of NO_2-N by diazotization with sulfanilamide, NO_3-N + NO_2-N by reduction of NO_3-N with hydrazine sulfate and subsequent determination of NO_2-N (Hilton and Rigg 1983), NH_4-N by the indophenol blue method,
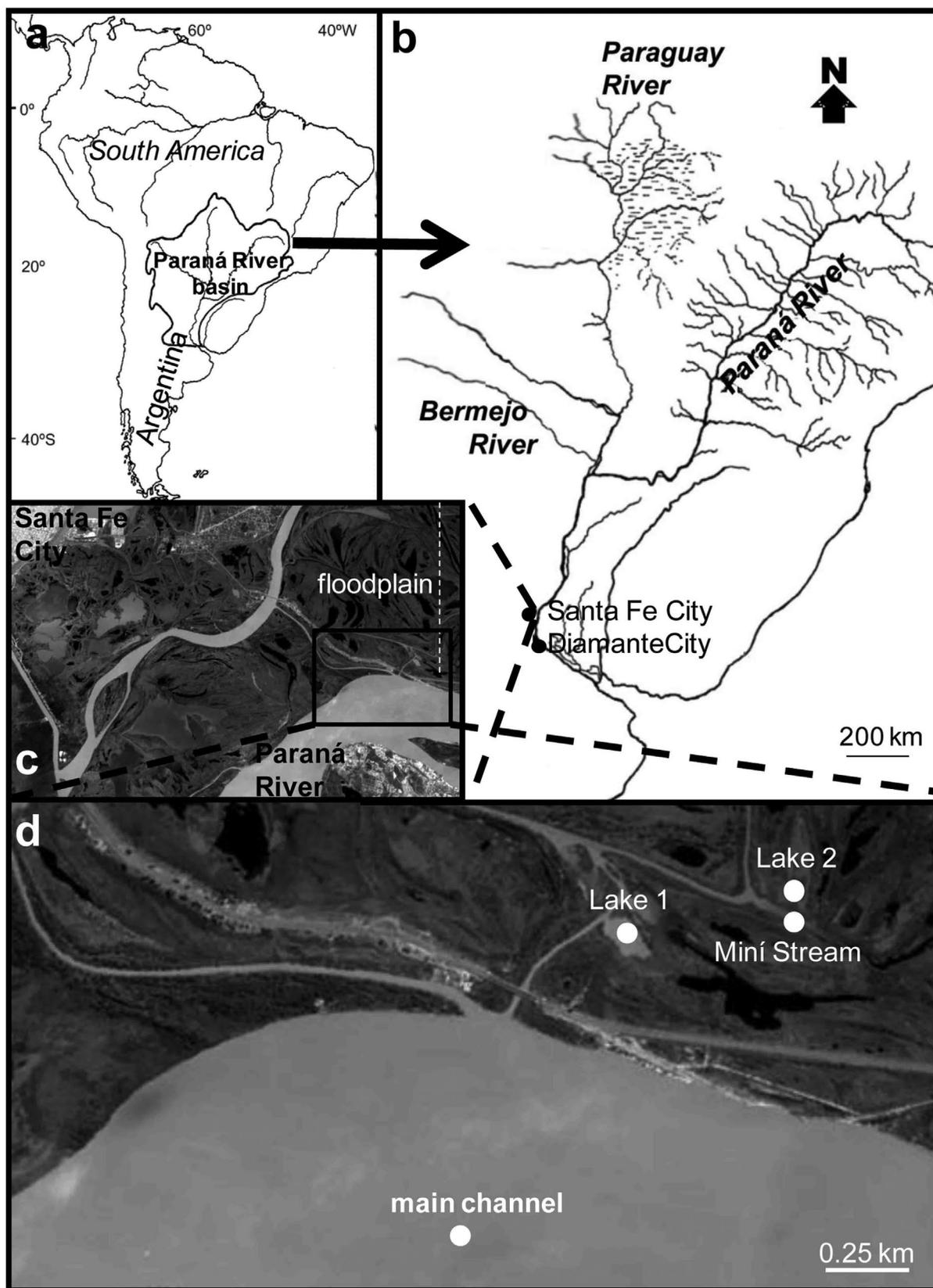
Figure 1. (a) Drainage basin of the Paraná River; (b) main tributaries and location of the study area; (c) detail of the main channel and floodplain at the study area; (d) sampling sites location (indicated by circle).

and total dissolved N (DN) by digestion with potassium persulfate (APHA 2005). Total N (TN) was determined from unfiltered water following the same digestion procedure. Dissolved inorganic nitrogen (DIN) was calculated as the sum of NO_3-N, NO_2-N, and NH_4-N; DON as the difference between DN and DIN; and PN as the difference between TN and DN. Contributions of each N form to the TN concentration, as well as contributions of dissolved N forms to the DN concentration (%), were calculated.

Depth of floodplain sites was measured *in situ* with an ultrasonic probe. In the main channel, the formation of migrating bed dunes up to 2.5 m in height (Reesink et al. 2015) precluded *in situ* depth as a suitable measure to evaluate its hydrological variations; therefore, its hydrometric level at the Paraná Harbor Gauge (informed by "Centro de Informaciones Meteorológicas", CIM-UNL) was used to estimate the hydrological regime of the system. Water discharge (Q; m^3 s^{-1}) was calculated following Toniolo (1999) as:

$$Q = 7.6206 \times 2.71828183^{PHL} + 2609.93 \times PHL + 6288.27, \quad (1)$$

where PHL is the hydrometric level of the main channel at the Paraná Harbor Gauge. Loads (metric tons d^{-1}) of different N forms were estimated as the product of Q × N concentrations.

The hydrometric level of the Bermejo River at the Mansilla Gauge was obtained from the Comisión Regional del Río Bermejo. Regression analyses were performed to assess the relationship between the hydrometric level of the Bermejo River (independent variable) and turbidity at the main channel of the Middle Paraná River (dependent variable). A delay of 5–30 d in turbidity values of the Paraná River with respect to hydrometric level of the Bermejo River (Alarcón et al. 2003) were evaluated at 1 d intervals to determine the best fit in the regression analysis.

Hydrological and sedimentological regimes were assessed through the river hydrometric level and turbidity at each site, respectively. A Kruskal-Wallis with Dunn's posttest was used to assess differences among the study sites with respect to limnological variables. Relations of hydrological and sedimentological regimes with concentrations of N forms as well as their percentages of contribution to TN and DN were analyzed with Spearman correlation using PAST software (Hammer et al. 2001). Simple linear regressions were performed with *RcmdrPlugin.HH* package in R software (R Development Core Team 2008) to assess whether the loads of analyzed N forms (dependent variables) changed in response to the hydrosedimentological regimes of the main channel (independent variables: hydrometric level and turbidity). Data were tested for normality and homogeneity of variance of residuals.

Results

Limnological variables and N speciation within the main channel–floodplain gradient

Chlorophyll *a* and DOC concentrations increased from the main channel to the most isolated floodplain lake, whereas dissolved oxygen and NO_3-N showed the opposite trend (Kruskal-Wallis: significant differences among Lake 2 and the other sites, $P < 0.001$; Table 1). Lake 2 had

Table 1. Mean values and ranges of variation (in brackets) of limnological variables and relative contributions of N forms to TN and DN at the main channel and floodplain environments of the Middle Paraná River sampled from February to November 2012. Cond = conductivity, Chl-*a* = chlorophyll *a*, DO = dissolved oxygen, n/d = not detected. Different letters indicate significant differences among environments according to Kruskal–Wallis test and Dunn's posttest ($P < 0.05$).

	Main channel	Lake 1	Miní Stream	Lake 2
Temp (°C)	20.5 (13.0–28.5)	19.8 (11.1–27.8)	19.3 (9.6–28.0)	17.9 (9.3–29.2)
pH	6.6 (5.2–7.7)	6.6 (5.7–7.3)	6.6 (5.6–7.3)	6.5 (5.4–8.9)
Cond (µS cm^{-1})	92 (69–115)	92 (71–121)	111 (81–165)	93 (39–139)
DOC (µM)	252 (199–336)[a]	259 (177–322)[a]	320 (201–441)[a]	858 (331–1266)[b]
Chl-*a* (µg L^{-1})	2.3 (0.5–8.8)[a]	3.8 (0.9–8.4)[a]	11.6 (1.7–33.5)[a]	11.6 (3.0–51.7)[b]
DO (mg L^{-1})	7.8 (6.4–9.9)[a]	7.5 (6.3–10.5)[a]	6.4 (4.9–8.5)[a]	2.9 (n/d–15.0)[b]
TN (µM)	78.8 (50.1–116.4)[a]	73.2 (43.2–112.3)[a]	68.8 (48.8–102.0)[a]	124.0 (50.7–315.6)[b]
DON (µM)	28.4 (3.9–65.6)[a]	27.3 (6.0–63.1)[a]	31.5 (3.1–66.6)[a]	66.6 (33.5–97.0)[b]
NO_3-N (µM)	19.4 (10.8–29.3)[a]	17.1 (10.3–24.1)[a]	10.6 (2.8–20.1)[b]	1.3 (n/d–6.6)[c]
NO_2-N (µM)	0.07 (n/d–0.15)[a]	0.07 (n/d–0.16)[a]	0.08 (n/d–0.23)[a]	0.02 (n/d–0.13)[b]
NH_4-N (µM)	3.8 (n/d–20.1)	3.8 (n/d–22.2)	5.2 (n/d–43.7)	2.8 (n/d–18.2)
PN (µM)	28.2 (0.9–84.5)	26.6 (2.3–81.8)	24.5 (1.0–78.2)	54.0 (1.3–220.6)
DON to TN (%)	37.3 (4.4–72.2)[a]	38.2 (10.5–73.7)[a]	47.5 (3.6–82.7)[ab]	60.2 (27.2–98.0)[b]
NO_3-N to TN (%)	25.4 (13.1–41.8)[a]	24.5 (14.3–55.7)[a]	15.5 (5.6–31.4)[a]	1.4 (0.0–6.3)[b]
NO_2-N to TN (‰)	1.0 (0.0–2.5)[a]	1.0 (0.0–2.8)[a]	1.2 (0.0–4.4)[a]	0.2 (0.0–1.2)[b]
NH_4-N to TN (%)	3.4 (0.0–14.3)	3.3 (0.0–18.7)	3.7 (0.0–13.1)	1.2 (0.0–3.7)
PN to TN (%)	33.7 (1.0–72.6)	33.9 (4.1–72.8)	33.2 (1.9–89.4)	37.1 (1.5–71.2)
DON to DN (%)	51.7 (12.0–75.2)[a]	54.0 (21.9–76.8)[a]	62.1 (22.0–93.0)[a]	94.6 (84.2–100)[b]
NO_3-N to DN (%)	39.4 (20.8–59.4)[a]	38.4 (22.3–72.5)[a]	28.0 (6.3–71.1)[a]	1.9 (0.0–8.2)[b]
NO_2-N to DN (‰)	1.3 (0.0–2.9)[a]	1.4 (0.0–3.0)[a]	1.8 (0.0–6.3)[a]	0.2 (0.0–1.6)[b]
NH_4-N to DN (%)	8.7 (0.0–39.0)	7.5 (0.0–39.1)	9.7 (0.0–47.4)	3.5 (0.0–15.8)

the highest TN, DON, and PN as well as the lowest DIN concentrations (Table 1). This waterbody differed significantly from the other sites in terms of the concentrations and relative contributions of dissolved N forms (except for NH$_4$-N) and TN concentration (Kruskal-Wallis: $P < 0.05$; Table 1).

Figure 2. Variations from February to November 2012 of (a) hydrometric level of the main channel and water depth of floodplain environments; (b) turbidity at each sampled site of the Middle Paraná River. Hydrosedimentological phases (LW1, HW, and LW2) are shown.

Variability of N speciation in relation to hydrosedimentological phases

Hydrological conditions at the Middle Paraná River changed from a low water phase (LW1, Feb–Apr 2012) to a high water phase (HW, May–Aug 2012) and back to a LW (LW2, Sep–Nov 2012; Fig. 2a). Lake 2 was connected to the fluvial system only during HW, whereas Lake 1 remained permanently connected but with higher lotic influence during HW. The turbidity peak at the main channel coincided with low waters (LW1: 84-288 FTU; Fig. 2b). The sedimentological regime at the main channel assessed through its turbidity (PTurb; FTU) was significantly explained by the hydrological state of the Bermejo River with an offset of 8 d ($r^2 = 0.86$; $P < 0.01$) according to the following exponential regression:

$$PTurb = 7.432e^{0.4821(BHL)}, \qquad (2)$$

where BHL is the hydrometric level of the Bermejo River (m). The turbidity peak was slightly attenuated at the floodplain waterbodies connected to the main channel (Fig. 2b). During LW1, turbidity also increased at Lake 2 (up to 370 FTU; Fig. 2b).

At the main channel, the hydrometric level was negatively associated with the relative contribution of NO$_3$-N to DN (NO$_3$-N:DN) and positively associated with the concentration and relative contribution of DON to TN and DN (DON:TN and DON:DN). These trends were similar to those of the more connected environments (Lake 1 and Miní Stream; Spearman: $P < 0.05$; Table 2). DON concentration increased during HW at all sites except at Lake 2, where it decreased (Fig. 3). In addition, at Lake 2 the river hydrometric level was negatively related to TN and PN concentrations (Spearman: $P < 0.01$; Table 2).

At all studied sites, turbidity was negatively associated with concentrations of dissolved N forms (except for NH$_4$-N) and/or their relative contributions to TN and DN

Table 2. Spearman correlation coefficients among indicators of the hydrosedimentological regime (river hydrometric level [HL] and turbidity at each site [Turb]) and N form concentrations and their relative contributions to TN and DN at the main channel and floodplain environments of the Middle Paraná River sampled from February to November 2012. Bold values = $P < 0.01$; regular type = $P < 0.05$.

	Main channel		Miní Lake		Miní Stream		Aislada Lake	
	HL	Turbidity	HL	Turbidity	HL	Turbidity	HL	Turbidity
TN							**−0.75**	**0.72**
DON	**0.72**		**0.69**			−0.60		
NO$_3$-N		−0.52		−0.57				
NO$_2$-N		**−0.74**		**−0.68**		−0.52		
NH$_4$-N		**0.88**		0.58				
PN		**0.74**				**0.69**	−0.55	**0.72**
DON:TN	0.64					**−0.72**		**−0.67**
NO$_3$-N:TN		**−0.74**						
NO$_2$-N:TN		**−0.74**		**−0.69**		−0.62		
NH$_4$-N:TN		**0.82**						
PN:TN		**0.81**		0.61		**0.80**		0.64
DON:DN	**0.66**		0.60		0.61	−0.53		
NO$_3$-N:DN	−0.56							
NO$_2$-N:DN		**−0.69**		−0.54				
NH$_4$-N:DN		**0.85**		**0.66**		0.54		

Figure 3. Mean concentrations of DON (▦), PN (▦) and DIN (▨) (bar graphs), and percentages of contribution to DIN of NO$_2$-N (■), NO$_3$-N (◧), and NH$_4$-N (□) (pie charts) during different hydrosedimentological phases (LW1, HW, and LW2; Feb–Nov 2012) at (a) the main channel of the Middle Paraná River; (b) Lake 1; (c) Miní Stream; (d) Lake 2. Note differences in y-axes scales.

(Spearman: $P < 0.05$; Table 2). By contrast, concentrations and contributions of PN and NH$_4$-N were positively correlated with turbidity (Spearman: $P < 0.05$; Table 2). LW1 concentrations and relative contributions were therefore lowest for NO$_2$-N and NO$_3$-N and highest for PN and NH$_4$-N (Fig. 3).

Effects of the hydrosedimentological regime on N transport within the main channel

Simple linear regression analysis showed that TN load within the main channel, and particularly DON, increased with hydrometric level ($r^2 = 0.41$, $P = 0.0131$ and $r^2 = 0.45$, $P = 0.0083$, respectively; Fig. 4). Turbidity explained significantly the loads of NO$_3$-N ($r^2 = -0.32$, $P = 0.0335$), NO$_2$-N ($r^2 = -0.68$, $P = 0.0003$), DON ($r^2 = -0.38$, $P = 0.0188$), NH$_4$-N ($r^2 = 0.49$, $P = 0.0056$), and PN ($r^2 = 0.30$, $P = 0.0428$; Fig. 5).

Discussion

The traditional theoretical framework maintains that floodplains act as nutrient sink areas, removing N from the main channel during floods (Villar et al. 1999, Maine
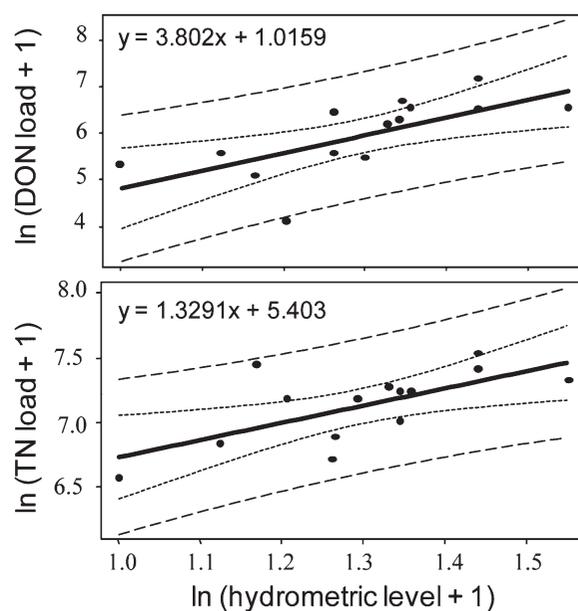
Figure 4. Scatter plots for the relationships between hydrometric level of the main channel (predictor variable) and N form loads (dependent variables). Solid lines are linear regression lines, dotted lines indicate 95% confidence intervals around regression lines, and dashed lines indicate 95% prediction intervals. Only significant relationships are shown ($P < 0.05$).
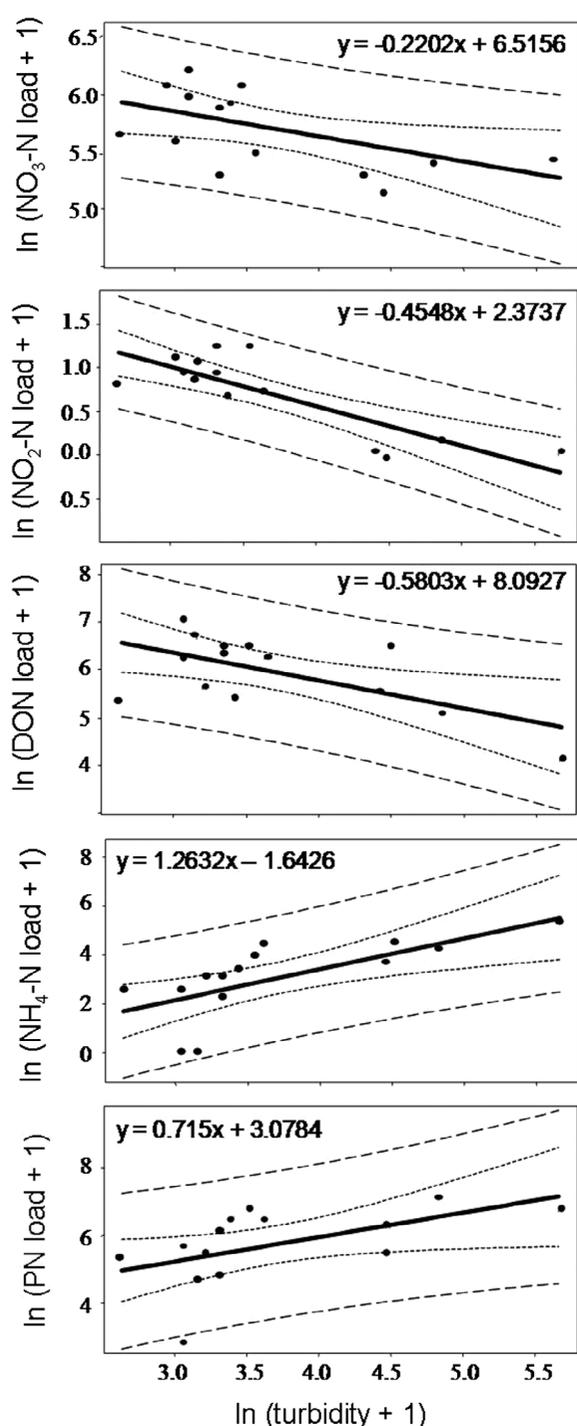
Figure 5. Scatter plots of the relationships between turbidity of the main channel (predictor variable) and N form loads (dependent variables). Solid lines are linear regression lines, dotted lines indicate 95% confidence intervals around regression lines, and dashed lines indicate 95% prediction intervals. Only significant relationships are shown ($P < 0.05$).

et al. 2004, Hoffmann et al. 2011, Roach and Grimm 2011, Welti et al. 2012), but we found that during HW, N inputs to the main channel increased. In this respect, the analysis of temporal and spatial variability of N forms allowed us to propose new hypotheses about the

processes governing N transformation and transport within floodplain rivers (Fig. 6).

Spatial variability of N speciation

During all studied hydrosedimentological phases, we found a decreasing DIN (mainly NO_3-N) concentration trend from the main channel toward the most isolated floodplain lake, as in previous studies (Maine et al. 2004, Emmerton et al. 2008, Mayora et al. 2013). The most isolated lake, however, had the highest N concentration, almost totally in organic form. Similarly, Devercelli et al. (2016) analyzed 22 environments with different degrees of hydrological connectivity to the main channel of the Middle Paraná River and observed the highest N concentrations at more isolated lakes despite their low NO_3-N concentration. The high N concentration suggests that its inputs are higher than its outputs in these alluvial waterbodies.

Most previous studies emphasized biological assimilation and denitrification as processes to remove NO_3-N from floodplain lakes (Villar et al. 1999, Saunders and Kalff 2001, Maine et al. 2004, Roach and Grimm 2011). The high biomass of aquatic macrophytes assimilates large quantities of DIN, which is immobilized as organic N and incorporated into bottom sediments after plant decay (Villar et al. 1999). Anaerobic conditions and high organic matter content promote denitrification, however, which reduces NO_3-N to gaseous N that is permanently lost from the waterbodies to the atmosphere (Burgin and Hamilton 2007). By contrast, N retained within biomass can be returned to the water column, either as PN, DON, or NH_4-N (excretes, exudates, detritus, and lixiviates; Wen and Peters 1994, Tyler et al. 2001, Aprile and Darwich 2013). The low DIN together with the high DON and PN concentrations at Lake 2 suggest that in highly vegetated areas of the floodplain, the N dynamic is largely affected by biological assimilation. We hypothesized that denitrification is comparatively less important in these sites, leading to low permanent N removal (Fig. 6). In addition, inputs of terrestrial N through surface runoff and flooding of riparian areas could increase the fraction of organic N at more isolated floodplain lakes (Hill et al. 1999), increasing the relation of N inputs to N outputs (Fig. 6).

The dissimilatory nitrate reduction to ammonium (DNRA) can also remove NO_3-N from floodplain lakes (Sgouridis et al. 2011, Welti et al. 2012). Similarly to denitrification, DNRA is promoted by anaerobic conditions and availability of organic carbon (electron donor) and prevails over denitrification when NO_3-N (electron acceptor) is in limited supply (Tiedje 1988, Porubsky et al. 2009, Enrich-Prast et al. 2016). High organic matter and low NO_3-N concentration in more isolated lakes of the Middle

Theoretical framework of nitrogen transformation and transport
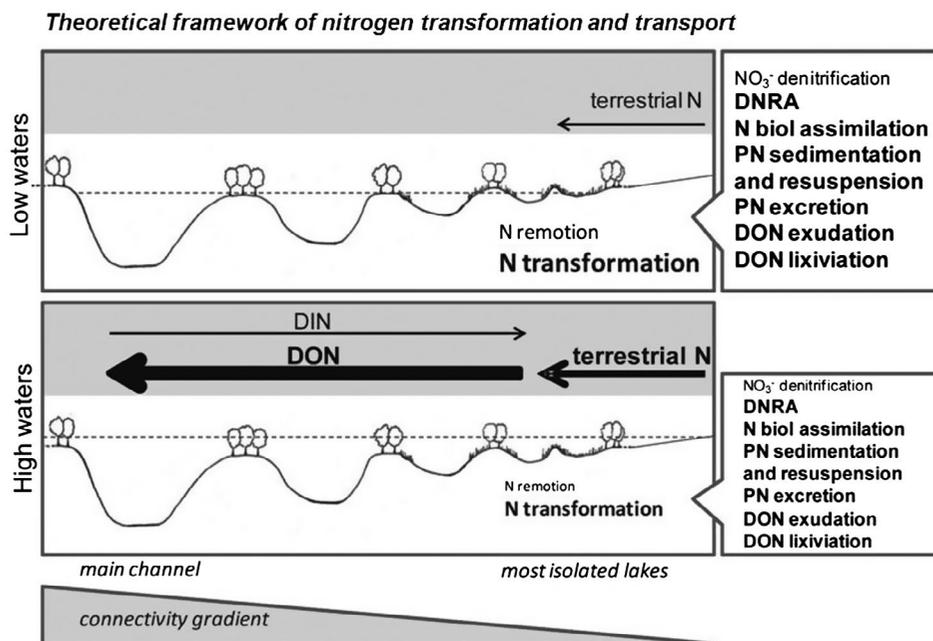
Figure 6. The main factors controlling transformation and remotion of N forms at the more isolated floodplain lakes and N exchanges within the main channel–floodplain gradient, according to the proposed hypothetical framework. These lists of N transformations and pathways are not exhaustive, but rather illustrate the relative importance of those considered most important. Arrows indicate N transport. The size of arrows and letter fonts indicate the relative importance of N transport and transformation in each hydrological phase and comparatively between low waters and high waters. DNRA = dissimilatory nitrate reduction to ammonium; N biol assimilation = N biological assimilation.

Paraná system could promote DNRA over denitrification, as noted in the proposed theoretical framework (Fig. 6). Because NH_4-N is more available biologically than NO_3-N, DNRA increases N recycling but not N removal from waterbodies (Sgouridis et al. 2011).

Effects of the hydrological regime on N speciation and transport

During floods, the fraction of organic N increased in the main channel and directly connected environments, as predicted, but in the most isolated lake, inorganic N decreased, contrary to expectations. In the last site, concentrations of NO_3-N and NO_2-N were undetectable during most samplings collected in high waters, suggesting a rapid removal of these anions after their input from the river.

Floods probably improved DON mobilization from more isolated floodplain lakes and riparian areas to the main channel (where both DON concentration and load increased with hydrometric level) by increasing hydrological connectivity among environments (Tockner et al. 1999). Similar results have been observed in other relatively pristine floodplain rivers (Saunders and Lewis 1988, Emmerton et al. 2008, Zurbrügg et al. 2013, Zuijdgeest et al. 2015). The increased DON load caused the transport of TN to rise during the flood; hence, the increasing

exchange of materials among the river and the floodplain during high waters was ineffective at decreasing the net input of N to the main channel. This finding is in contrast with traditional approaches indicating that floodplain lakes and riparian areas are important sinks of the N carried by the river. The concept of floodplain as an N sink during high flow has been based on the low concentration of NO_3-N and the high quantity of buried organic N at floodplain lakes as well as on the downstream decrease of NO_3-N along the main channel during floods (Hamilton et al. 1997, Tockner et al. 1999, Maine et al. 2004, Mugni et al. 2005, Hupp et al. 2009, Wolf et al. 2013).

The downstream decrease of NO_3-N along the main channel observed by Maine et al. (2004) in the Middle Paraná River during a flood could have been caused by incoming NO_3-N-poor water from the floodplain and by NO_3-N removal within the main channel itself (Alexander et al. 2009). Processes removing N from floodplain lakes and riparian areas (denitrification, biological assimilation and sedimentation of PN), however, are favored by higher development of bacteria and primary producers and increased residence time of water and N forms (Janauer and Kum 1996, Saunders and Kalff 2001, Alexander et al. 2009). N removal from the floodplain therefore likely increases during low water (Fig. 6) when the hydrological connectivity with the main channel is low, and therefore floodplain has no appreciable effect on N load in the river.

Despite the increasing hydrological connectivity during high waters, the influence of the floodplain on N load within the river could remain low because of the lower biota development and water residence time. During periods of high water discharge, N transport from floodplain waterbodies to the main channel would predominate (Fig. 6). Although floodplain lakes and riparian areas can remove NO_3-N, they can also export large amounts of DON during the connection phase (Fig. 6; Zurbrügg et al. 2013, Zuijdgeest et al. 2015). The main channel of the Upper Paraná River, which provides most of water discharge to the Middle Paraná River (Amsler and Drago 2009), is characterized by low N concentration (mean values ~30 μM; Roberto et al. 2009) compared with the middle stretch. Concentrations of N, however, and particularly of the organic fraction, are similar in more isolated floodplain lakes of both river stretches (Roberto et al. 2009), suggesting that the floodplain acts as a source of organic N to the main channel along its course, increasing the downstream N load, especially during high waters.

Unlike observations in the present study, some floodplains effectively act as sinks of N carried by the river during floods. This floodplain function has been assayed by mass balances for TN and measurements of denitrification rates during the connection phase (Fleischer and Stibe 1991, Windolf et al. 1996, Saunders and Kalff 2001, Roach and Grimm 2011, Welti et al. 2012). These floodplains have high NO_3-N concentrations, often from large anthropogenic inputs of inorganic N; therefore, their capacity for N removal could be due to positive effects on denitrification of both NO_3-N concentration (García-Ruiz et al. 1998, Koop-Jacobsen and Giblin 2010, Roach and Grimm 2011) and the NO_3-N to DOC ratio (Tiedje 1988, Scott et al. 2008, Porubsky et al. 2009, Nizzoli et al. 2010).

Effects of the sedimentological regime on N speciation and transport

The sediment peak was evidenced by high turbidity values from February to April during the Paraná River low water phase. In the middle stretch of the Paraná River, sediment peaks during the late summer were due to the arrival of the rainy season at the Andean headwaters of the Bermejo River, which constitutes its main source of suspended solids (Amsler and Drago 2009). Because Lake 2 was disconnected to the fluvial system during low waters, it did not receive inputs of sediments from the Bermejo River. The increased turbidity at this waterbody could have been caused by sediment resuspension through wind action as well as by phytoplankton development, processes occurring frequently in shallow floodplain lakes during low water (Izaguirre et al. 2001, Maine et al. 2004). Indeed, turbidity was positively associated with TN

and PN, hence probably coming from bottom sediments (Hamilton and Lewis 1990) or constituting compounds in algal cells (Reynolds 2006).

At the main channel of the Middle Paraná River and permanently connected environments (Lake 1 and Miní Stream), the sediment peak was associated with high concentrations and relative contributions of PN and NH_4-N attributed to the transport of vegetal detritus from flooded margins at the headwaters of the Bermejo River to the Middle Paraná system (Pedrozo and Bonetto 1987). Ammonification of organic N compounds can increase NH_4-N concentration. Moreover, the high concentration of suspended particles could have favored ammonification by increasing availability of surfaces where both ammonifying bacteria and DON can be adsorbed (Xia et al. 2013). This supposition is consistent with the low concentration of DON as well as of its relative contribution to TN and DN during periods with high turbidity. The sediment peak was also characterized by decreasing concentrations of NO_2-N and NO_3-N and relative contributions of these N forms to TN and DN. In turbid rivers, these ions can be largely removed by reduction because of the generation of particle microsites with low dissolved oxygen concentration (Liu et al. 2013). In addition, particle surfaces may contain metals that catalyze redox reactions (Choi et al. 2013) and act as reducing agents (Hou et al. 2015). As a result, we found that the sediment peak increased the transport of NH_4-N and PN but decreased the transport of other dissolved N forms, with no significant effect on TN load.

Conclusion

Variations in river N load and speciation were governed by hydrosedimentological conditions. The sediment peak incorporated PN and influenced dissolved N speciation by favoring production of NH_4-N and removal of other dissolved N forms, probably through effects of particles on redox reactions. Hence, the sedimentological regime affects N speciation but not N load. By contrast, the hydrological regime influenced N load, which rose during the flood because of an increasing DON load. The N net input to the main channel during periods with increasing hydrological connectivity among environments indicates that the floodplain can be a source of N to the river through DON exportation. Finally, DON is a significant component of the N pool and should be included in studies on N pathways.

Acknowledgements

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