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POLLUTION ISSUES OF LARGE RIVERS

Relevance of the Paraná River hydrology on the fluvial water quality of the Delta Biosphere Reserve

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Abstract The increasing frequency of extreme events in large rivers may affect not only their flow, but also their water quality. In the present study, spatial and temporal changes in fluvial physico-chemical variables were analyzed in a mega-river delta during two extreme hydrological years (La Niña-El Niño) and related to potential explanatory factors. Basic water variables were evaluated in situ at 13 points (distant 2–35 km from each other) in watercourses of the Delta Biosphere Reserve (890 km^2) in the Lower Paraná River (Argentina) in nine surveys (October 2008–July 2010) without meteorological tides. Samples for laboratory analyses were collected from each main river. Multivariate tests by permutations were applied. The period studied was influenced by a drought, within a long period dominated by low flows combined with dry weather and wildfires, and a large (10 years of recurrence) and prolonged (7 months) flood. The hydrological phase, followed by the season and the hydrological year (according to the ENSO event) were the principal explanatory factors of the main water quality changes, whereas the drainage sub-basin and the fluvial environment (river or stream) were secondary explanatory factors. During the drought period, conductivity, turbidity, and associated variables (e.g., major ions, silicon, and iron concentrations) were maximal, whereas real color was minimal. In the overbanking flood phase, pH and dissolved oxygen concentration were minimal, whereas real color was maximal. Dissolved oxygen saturation was also low in the receding flood phase and total major ion load doubled after the arrival of the overbanking stage. The water quality of these watercourses may be affected by the combination of several influences, such as the Paraná River flow, the pulses with sediments and solutes from the Bermejo River, the export of the Delta floodplain properties mainly by the flood, the season, and the saline tributaries to the Lower Paraná River. The high influence of the hydrology of this large river on the Delta fluvial water quality emphasizes the relevance of changes in its flow regime in recent decades, such as the seasonality attenuation. Considering that the effects of extreme events differ among and within fluvial systems, specific ecohydrological evaluations and powerful appropriate statistics are key tools to gain knowledge on these systems and to provide bases for suitable management measures in a scenario of climate change and increasing human alterations and demands.

Keywords Physico-chemical assessment · Extreme events · Canonical analyses · Ecohydrology · Fluvial system · ENSO · South America · La Plata basin

Introduction

Large rivers are under increasing human pressures and more exposed to problems of multiple uses. Therefore, a multidisciplinary scientific assessment of their status is required to promote their integrated sustainable management in a context

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of climate change and increasing human impacts and demands (Habersack et al. 2014). The flood pulse concept predicts that the hydrological pulsing (periodic inundation and drought) is the main driving force in river-floodplain systems (Junk et al. 1989; Neiff 1990; Junk and Wantzen 2004). In temperate systems, the flood pulse is less regular than in tropical systems, thus increasing the variability within and between years in river flow characteristics, such as magnitude, duration, timing, frequency, and rate of change (Junk et al. 1989; Poff et al. 1997; Schemel et al. 2004). Moreover, in temperate and subtropical systems, water temperature or other seasonally changing variables may also be important ecological drivers (Tockner et al. 2000; Junk and Wantzen 2004).

Although water quantity and quality are closely linked, these two aspects are often deal with separately (Nilsson and Malm-Renöfält 2008). Likewise, direct links between flow magnitude and ecosystem responses have been widely studied, whereas indirect links mediated by water quality have been less studied (Nilsson and Malm-Renöfält 2008). Climate change and variability are expected to affect both the quantity and quality of water, creating competing demands for this resource from multiple sectors of the society. Studies on the effects of drought on water quality have increased mostly in North America, Europe, and Australia in the last years, but studies on these effects in Asia, Africa, and South America are so far scarce, according to a current review (Mosley 2015). The management of temperate and tropical rivers can be enhanced by determining how water quality is affected by flow on a site-by-site basis (SKM 2013).

The Paraná River, the second largest in South America, has been classified as one of the world's mega-rivers (Latrubesse 2008). This river generally flows in a north-south direction from tropical to temperate areas, contributing with ~75 % to the water discharged by the La Plata Basin (Fig. 1a, b) into the broad Río de la Plata estuary, which drains to the SW Atlantic Ocean. Due to the active teleconnection of its hydrology with the El Niño-Southern Oscillation (ENSO) phenomenon, extreme floods are more likely recorded with El Niño events, whereas normal to low flows are recorded with La Niña events (e.g., Pasquini and Depetris 2007). Many studies (e.g., Depetris and Pasquini 2007) have documented a major hydrological change in the Paraná River after the early 1970s. The relatively wet period that began around 1972–1973 was followed by a relatively dry period since the start of the new century (Puig et al. this Special Issue).

In the Middle Paraná River (Fig. 1b), a wide and complex floodplain interacts with the river during floods (Depetris and Pasquini 2007). In the last 320 km, the river splits into branches flowing through an extensive (17,500 km^2) fluvio-deltaic complex (Fig. 1c). This relatively low disturbed Delta is considered vulnerable to climate change. Also, it may be affected by human local uses, which are becoming intensified and diversified during the present relatively dry period, and by various anthropic activities within the rest of this large basin (Baigún et al. 2008).

In the lower Delta (Fig. 1d), the water quality depends not only on the different contributions of the main tributaries of the Paraná River, but also on processes such as the interaction with the island marshes (Villar et al. 2001; de Cabo et al. 2003). Within this geomorphic unit, the island territory (890 km^2) of San Fernando (Buenos Aires) (Fig. 1d, e) was designated as "Paraná Delta" Biosphere Reserve (MaB-UNESCO Program) in 2000. The management of this Biosphere Reserve is constrained by the scarce knowledge of the water quality of its watercourses, which support biodiversity and provide ecosystem services, such as water supply for inhabitants (Puig and Olguín 2011). In the lower Delta, several studies on water quality have been mainly performed upstream from the Reserve, in the Paraná de las Palmas R. (by Lima, Zárate and Otamendi) and in the Paraná Guazú R. (by Puerto Constanza), generally considering one river site (e.g., Bonetto et al. 1998; Villar and Bonetto 1998), but the knowledge about the Biosphere Reserve watercourses is very scarce. Our previous study (four samplings in four sites), carried out within the relatively wet period and including a large flood of average duration, has shown an association of fluvial water quality variables with hydrological stages and the consequent interaction degree with the island marshes (de Cabo et al. 2003). The present ecohydrological study is based on a more comprehensive sampling as well as on daily flow data provided by hydrological models for the two main river branches in the Delta Reserve. Although multivariate methods like clustering and Principal Component Analysis are increasingly used in water quality studies, a multivariate approach based on tests by permutations is currently followed in most ecological data analyses.

The aims of this study were to identify the main spatial and temporal variations in fluvial physico-chemical variables in the Delta Biosphere Reserve of the Paraná River at an intermediate spatial scale in two consecutive hydrological years with opposite extreme events (La Niña-El Niño), as well as to explore potential explanatory factors and quantify their respective contribution to the water quality variation following a multivariate statistical approach.

Methods

Study area

The Paraná River basin (drainage area: 2,600,000 km^2) drains a variety of landscapes and climatic regions in Brazil, Bolivia, Paraguay, and Argentina. The Upper Paraná River (Fig. 1b), which originates in Brazil, receives tributaries mainly from the coastal hills and contributes to the Lower Paraná River with

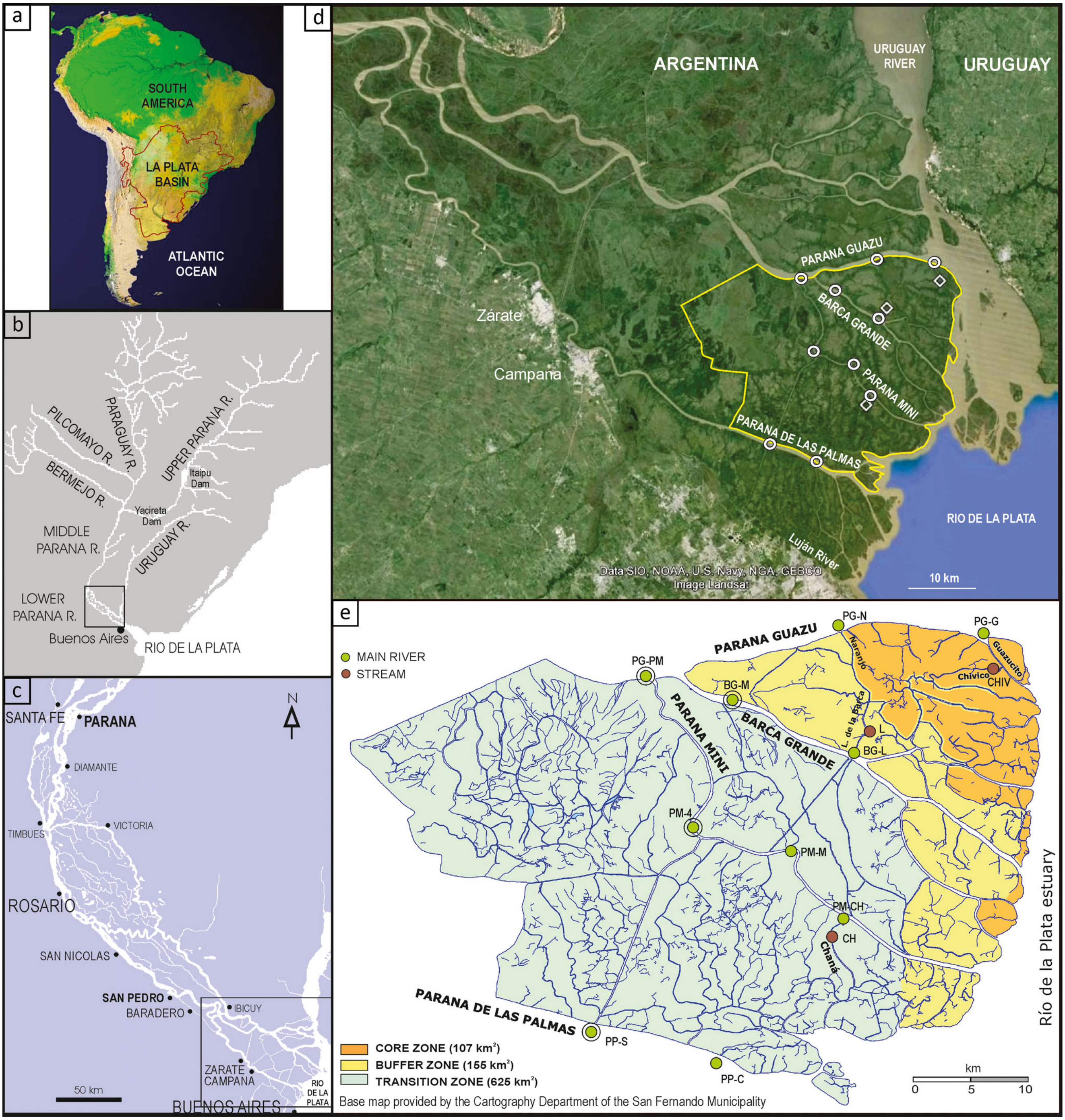

Fig. 1 La Plata Basin, Paraná River Delta, lower Delta and its Biosphere Reserve. **a** La Plata Basin contour. **b** La Plata Basin with the Uruguay River and main rivers of the Paraná River basin (southernmost large dams in the Paraná R. are indicated). **c** Lower Paraná River with main watercourses of the Delta (downstream Diamante city, 32°4′ S 60°32′ W). **d** Lower Delta including the Biosphere MaB Reserve "Paraná Delta" and sampling sites in main rivers (*circles*) and in streams (*rhombi*). **e** The Reserve with its three zones and sampling sites. Stream sites are distinguished by a different color and river sites sampled also for additional variables are indicated by a *double circle*

~75 % of its flow. The rest is mainly contributed by the Paraguay River, which drains the Gran Pantanal and receives the Bermejo and Pilcomayo rivers (Fig. 1b), with headwaters in the eastern slopes of the Andes. The slow passage of the summer floodwaters of the Paraguay River through the Pantanal delays their arrival at the lower river sector for 4 to 6 months (Hamilton et al. 1996), smoothing its flow (Fig. 2a). The suspended sediments supplied by the Upper Paraná River have decreased due to heavy damming (Amsler and Drago 2009). The Bermejo River supplies a large load of suspended sediments (mainly silt and clay) and a high proportion of dissolved solids to the Lower Paraguay River, due to heavy rains in the Andean headwaters from summer to middle autumn (Depetris and Pasquini 2007; Amsler and Drago 2009) (Fig. 2a). The mean Paraná River flow (1902–2010) is 16,700 m^3/s at the Paraná-Santa Fe section. In this sector, the river shows higher flow around autumn and lower flow around early spring (Depetris and Pasquini 2007). The Lower Paraná River begins where its last major tributary, the Salado River, joint it downstream from Santa Fe city (Fig. 1c). More details on the Paraná River and its flow regime are provided in Puig et al. (this SI).

The Delta starts near Diamante city and expands (from 18 to 60 km width) into the Río de la Plata estuary (Fig. 1c). The upper Delta and the middle Delta have numerous and various shallow lakes and, as a consequence of the flooding of vast areas, evidence an important capacity to soften downstream water pulses. In contrast, in the lower Delta (from the Ibicuy islands to the river mouth), the water is more efficiently conducted by main river branches and their network of distributaries (Puig et al. 2011) (Fig. 1d). The islands of the lower Delta, relatively higher and with natural levees, remain more protected from upstream floods, favoring the human settlement. In these islands, marshes dominated by emergent macrophytes (*Schoenoplectus californicus* or *Scirpus giganteus*) cover vast lowland areas (Kandus et al. 2006).

The drainage network of the Reserve is characterized by large rivers ending in deltaic fans, such as the Paraná Guazú and Paraná de las Palmas rivers, and small rivers with a dendritic pattern of distributaries in NW-SE direction (Fig. 1d, e). Small streams, internal to the islands and in many cases blind, are more numerous to the North, whereas large streams, providing better drainage conditions, prevail towards the SE. In general, the flow magnitude of the Paraná Guazú River is similar to that of the Paraná de las Palmas River during low waters, doubles it in normal flow periods and triples it during floods. The Paraná Guazú River conducts a higher proportion of floodwaters and receives flows from the Gualeguay and Nogoyá rivers and water in excess from the Ibicuy islands (Puig et al. 2011). The complex hydrological regime in the Reserve depends mainly on the flow of the Upper Paraná River and, to a lower extent, of the Paraguay River and on the influence of the Río de la Plata estuary, through astronomical semidiurnal microtides (few tens of centimeters) and meteorological tides. The latter (called "sudestadas" in Spanish) may be generated by persistent winds from the SE (up to 48 h) that raise the water level in the terminal Delta, due to their direction facing the dominant flow of rivers.

Sampling design and water quality assessments

Considering the scarce previous knowledge about the fluvial water quality of this complex region, the sampling design of this study focused on a broad spatio-temporal perspective: the three Reserve zones (Fig. 1e), the four main rivers, an intermediate spatial scale (1–100 km), and a sampling frequency of approximately two months. According to ecological criteria and logistical considerations, 13 sites were selected along a navigable path crossing the three Reserve zones (Fig. 1d, e). Almost half of these sites were located in areas with relatively higher human use (transition zone) and the rest, in areas with lower human use (core and buffer zones). At least two sites were considered in each main river (Paraná de las Palmas, Paraná Guazú, Paraná Miní, and Barca Grande). Also, a site in one stream for each Reserve zone was proposed as a first exploration of possible differences associated with the fluvial environment category (Fig. 1e). The distance between sites of the rivers was 5–35 km, whereas the distance from each stream site to the nearest main river site was only 2–3 km. The influence of the incoming flow of the Paraná River was maximized by the analysis of two hydrological years with opposite ENSO events, and the meteorological tidal influence was minimized avoiding sampling during days with "sudestada" events.

Nine surveys (usually two days of navigation) were carried out between October 2008 and July 2010 (dates in Fig. 2) by the SPA-1 scientific vessel through inter-institutional cooperation (Argentine Museum of Natural Sciences, Argentine Coast Guard and San Fernando Municipality). At each site, the geographic location (GPS), water transparency (Secchi disk depth), temperature, pH, conductivity, and dissolved oxygen (WTW multiparameter measurement from subsurface water collected with Niskin bottle) were determined. Also, from the second to the last survey, water samples in one of these sites per each main river (Fig. 1e) were collected according to standardized protocols (APHA 2005) and preserved at 4 °C until analyzed (<24 h) in the Central Laboratory of AySA (Argentine Water and Sanitation S. A.). Real color (spectrophotometry), turbidity (nephelometry), total alkalinity (potentiometry), chloride and sulfate (ion chromatography), and iron and silicon (ICP-AES) were determined following methods 2120C, 2130B, 2320, 4110B, and 3120B (APHA 2005), respectively, whereas hardness, calcium, magnesium, sodium and potassium (ion chromatography) were determined following method 14911 (ISO 1998).

Data analyses

Daily flows of the historical series (1902–2010) of the Paraná River at the Paraná-Santa Fe section (flow values derived by a curve for the closing section, i.e., including the main river channel, the Colastiné River and the Setúbal system), located 40 km north of the Delta region (Fig. 1c), were categorized in percentiles. The daily flow contribution to the estuary by the respective delta fan of the Paraná de las Palmas River and of the Paraná Guazú River (estimations derived by hydrological models) was also considered. Most sampling sites (except the two located in the Paraná de las Palmas R.) are in the network of distributaries of the Paraná Guazú River, thus being more influenced by the flow of this main river branch. The daily Paraná Guazú River flows during the two hydrological years studied were cross-correlated (Pearson index) with those of the mentioned series of the Paraná River. Then, the flows of this series several days before (according to the time lag analyzed by cross-correlation) to each sampling date were assigned to the respective range of percentiles. A similar analysis was performed considering the Paraná River series after the major hydrological change (1973–2010) for an additional categorization of samplings under extreme flows. The flood duration was compared with the mean number of days with flood per year in the historical series (1901–2010) of water levels at San Pedro gauge station (33°40′ S 59°43′ W, Fig. 1c), located near the middle of the Delta. All hydrological data were provided by the Argentine Water Institute (INA).

A set of data from 112 cases, corresponding to 9 dates × 10–13 sites (because not ever all streams could be sampled), of the five basic water quality variables (water transparency, temperature, pH, conductivity, and dissolved oxygen), and a dataset of 32 cases, corresponding to 8 dates × 4 sites (one per main river), of 11 selected variables (water transparency, temperature, pH, conductivity, dissolved oxygen, real color, turbidity, total alkalinity, hardness, iron, and silicon) were considered for multivariate analyses. In this last dataset, only physico-chemical variables having numerical values in all cases were included (potential risk variables are considered in Puig et al. this SI). Major ions were excluded to reduce the redundancy with conductivity.

A set of potentially explanatory factors was proposed. One temporal numerical variable was considered as an indicator of the overall hydrological situation in each sampling date: q= estimated "Paraná Guazú River flow" supplied to the estuary. Temporal categorical factors were as follows: per="season" (spring; summer; autumn; winter), ev=hydrological year according to the dominant "ENSO event" (Niña; Niño) and h=" hydrological phase" (drought; overbanking flow; flood; not extreme flow). Spatial categorical factors were as follows: a="fluvial environment" (river; stream), z="Reserve zone" (core; buffer; transitional), z2="zone by relative human use" (low, covering core and buffer zones; high), and d="drainage sub-basin" (Paraná de las Palmas; Paraná Guazú).

Multivariate dispersion (based on Euclidean distance) in groups of cases, defined by dates and by sites, was estimated and the homogeneity between groups was tested by permutations (Anderson 2006).

Redundancy Canonical Analysis (RDA) is a robust and powerful statistical method that models the set of response variables as a function of the set of explanatory (numerical or categorical) factors and may serve as a basis for variation partitioning (Borcard et al. 2011). RDA was applied on the standardized datasets (1) to test the significance of the relation between the multivariate structure of water quality variables and the proposed spatial and temporal factors, (2) to perform a parsimonious explanatory model, and (3) to quantify the explanatory power of each factor within this model. The significance of the RDA global model of water quality on the basis of all the explanatory factors proposed was tested (H_0: absence of linear relationship between both datasets) by permutations (one-tailed test), and also the significance of individual canonical axes (Borcard et al. 2011). Stepwise selection was applied to obtain a parsimonious RDA model. Multicollinearity was explored by computing the variance inflation factors (VIF) and thus, the explanatory factors with a VIF higher than 10 were sequentially removed from the analysis (Borcard et al. 2011). Variation partitioning (Borcard et al. 1992; Peres-Neto et al. 2006) was performed to quantify the various unique and joint fractions of the variation in water quality explained by each factor (or category of factors) of the parsimonious RDA model and finally, the corresponding Venn diagram was designed. Results were based on adjusted R^2 values, because these are independent of the sample size and number of explanatory factors and allow the comparison of results (Peres-Neto et al. 2006). All analyses were performed with R software version 2.15.2 (R Development Core Team 2008) using the "vegan" package (Oksanen et al. 2008).

Results

Characterization of the hydrological conditions

The samplings corresponded to two hydrological years (September-August period for this river) dominated respectively by a weak La Niña and a moderate El Niño events, after two hydrological years dominated by ENSO events in the inverse order (weak El Niño-moderate La Niña) (Fig. 2b), according to the Oceanic Niño Index (ERSST.v3b SST anomalies in the Niño 3.4 region). Along the two years studied, the flow at the Paraná-Santa Fe section varied (Fig. 2c) from 9469 m^3/s (May 23, 2009) to 39,178 m^3/s (February 15, 2010) (Fig. 2b), being categorized in the 10–20 and >95 percentiles, respectively, thus indicating that extreme hydrological conditions in both directions were attained during the studied period. The large magnitude of the flood corresponded to a recurrence time of 10 years (Puig et al. this SI). The flow of both main Paraná River branches evidenced a high correlation (r=0.99), being the Paraná de las Palmas flow much more stable (Fig. 2c). The estimated daily flow of the Paraná Guazú River varied between extreme values more than fourfold during the two years, and more than twofold among sampling dates (Fig. 2c).

The hydrological stage in each sampling was categorized with respect to the historical series of the Paraná River flow,

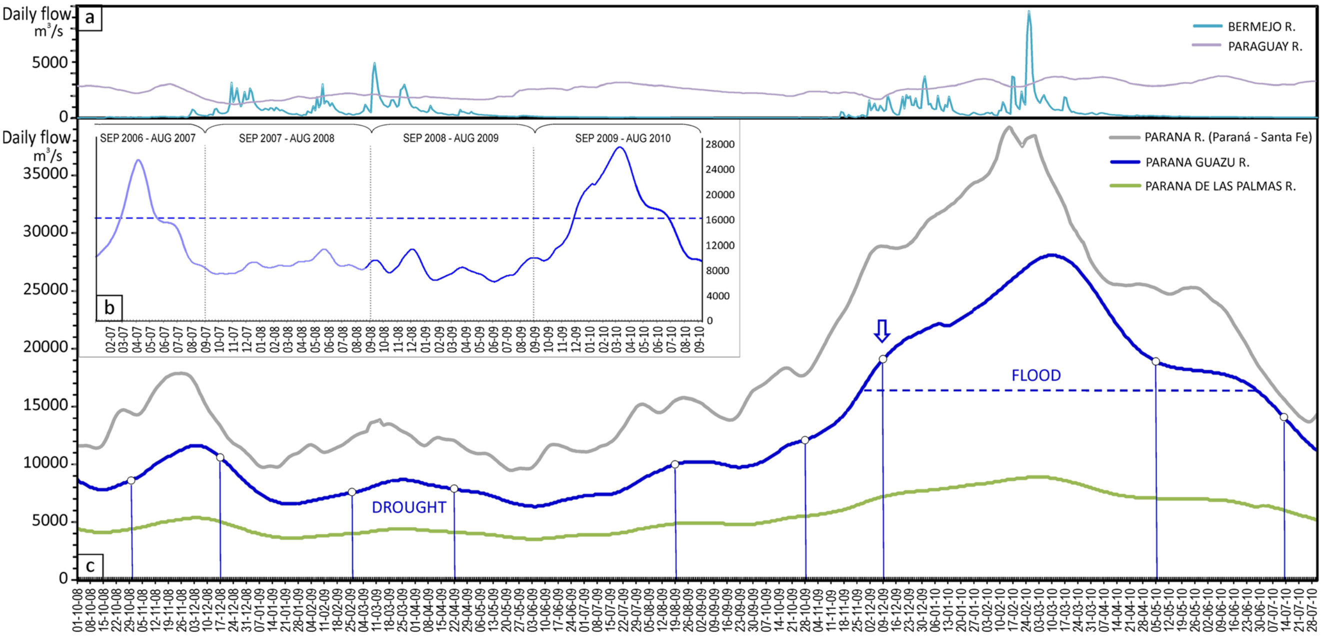

Fig. 2 Daily flows of the Paraguay, Bermejo and Paraná Rivers. **a** Flow of the Bermejo River at Pozo Sarmiento gauge station (23°13′ S 64°12 ′ W) and of the Paraguay River at Puerto Pilcomayo gauge station (25°25′ S 57°39′ W). **b** Estimated flow of the deltaic fan of the Paraná Guazú River in the two hydrological years of this study and in the two previous years. **c** Paraná River flow recorded at Paraná (31°41′ S 60°30′ W)-Santa Fe section and respective estimated flow of the deltaic fan of the Paraná Guazú River and of the Paraná de las Palmas River during the two hydrological years of this study. Paraná Guazú River flow at samplings dates: *circles* and *vertical lines*, flood condition: *horizontal blue line*, overbanking stage sampling: *blue arrow*

considering the mean time lag of 13 days (Pearson index: 0.995) estimated by cross-correlation between the recorded daily flows of the Paraná River and those estimated for the Paraná Guazú River (Fig. 2c). Two samplings (February and April 2009) corresponding to the drought stage (Fig. 2c) were categorized in the 20–30 percentile range considering the historical series (1902–2010) (Table 1). However, the first drought sampling was categorized in the <5 percentile and the subsequent one in the 10–20 percentile range, according to the series after the early 1970s change (1973–2010). Two samplings corresponding to the flood stage (Fig. 2c) were categorized in the 80–90 percentile range (Table 1), according to both historical series. The other samplings were categorized between these two extreme hydrological stages (Table 1). The first flood sampling (December 2009) was an initial overbanking flow stage, i.e., the recent overflow of the natural island levees, and the subsequent sampling (May 2010) corresponded to the flood receding phase (Fig. 2c). The duration of the 2009–2010 flood in the Delta (210 days) was around threefold the long-term average. The time between the maximum of this flood (March 2010) and that of the previous flood (of similar magnitude) (April 2007) was nearly three years, with two and a half years below the inundation stage (Fig. 2b).

General water quality results

Table 2 shows the mean and range values of the physical and chemical variables in the main rivers during the two hydrological years. The assessments encompassed a wide range of

Table 1 Characterization of the flow conditions in each Reserve sampling according to the percentiles of the historical series (1902–2010) of the Paraná River flow (m^3/s) recorded at the Paraná-Santa Fe section. Flow limits for percentile ranges and the corresponding assignation, considering a time lag of 13 days (see text), are included

Sampling in the Reserve	Paraná R. flow	Flow range	Percentile range
February 2009 April 2009	11,100 11,926	10,657–12,133	20–30
October 2008	12,366	12,133–13,738	30–40
August 2009	14,850	13,738–15,362	40–50
December 2008	17,115	15,362–17,166	50–60
October 2009 July 2010	18,144 18,322	17,166–19,455	60–70
December 2009 May 2010	25,951 25,506	21,968–26,078	80–90

Table 2 Mean and range values of water quality variables in main rivers in each sampling date. Data correspond to ten sites in the upper panel and to four sites (one per each main river) in the lower panel

	Oct 2008	Dec 2008	Feb 2009	Apr 2009	Aug 2009	Oct 2009	Dec 2009	May 2010	Jul 2010	Total
Temperature (°C)	22.6	26.6	26.8	22.6	15.1	21.4	23.8	19.5	15.0	21.5
	21.9–23.1	26.1–27.5	26.5–27.1	22.1–23.0	14.6–15.3	21.0–22.0	22.8–24.2	19.1–19.7	14.3–15.5	14.3–27.5
Conductivity (μS/cm)	117.5	121.2	149.4	152.5	101.2	101.6	117.9	134.5	139.8	126.2
	112–143	114–136	143–166	146–163	94–115	97–114	115–127	126–158	132–168	94–168
Dissolved oxygen (mg/L)	6.36	6.60	7.00	6.33	7.15	8.13	5.48	6.38	9.13	6.90
	6.06–6.69	5.97–6.85	6.58–7.95	5.83–6.64	6.83–7.67	7.59–9.20	4.98–5.94	5.57–6.68	8.70–9.40	4.98–9.40
Oxygen saturation (%)	73.7	82.2	86.8	73.4	71.0	92.2	64.9	69.5	90.6	78.3
	70.0–77.8	73.9–85.3	80.2–99.2	67.8–77.1	67.1–76.2	85.4–104.8	59.1–70.9	60.9–72.9	84.9–93.8	59.1–104.8
Transparency (cm)	40	40	14	10	40	33	36	37	31	31
	30–45	35–45	13–15	8–15	35–45	30–35	35–40	30–42	28–33	8–45
Real color		39.5	22.0	21.5	49.3	44.3	80.5	48.3	44.3	43.7
		36–43	19–26	17–26	40–63	41–48	77–86	41–51	36–49	17–86
Turbidity (NTU)		36	101	422	44	46	46	45	60	100
		33–38	85–110	390–442	40–50	45–50	45–50	40–50	50–75	33–442
Iron (mg/L)		1.9	7.0	14.0	2.1	3.1	3.0	1.7	2.5	4.2
		1.6–2.0	5.5–7.7	13.0–16.0	1.7–2.7	2.7–3.5	2.6–3.9	1.5–2.1	1.3–5.2	1.3–16.0
Silicon (mg/L)		7.8	18.5	46.0	9.3	14.8	8.6	7.4	10.3	15.3
		7.3–8.4	17.0–20.0	39.0–49.0	7.8–11.0	13.0–16.0	7.7–10.0	6.8–8.3	7.5–17.0	6.8–49.0
pH		7.7	7.7	7.9	7.7	7.4	6.8	7.0	7.2	7.4
		7.7–7.8	7.7–7.8	7.8–7.9	7.5–7.8	7.4–7.4	6.7–6.8	7.0–7.1	7.2–7.3	6.7–7.9
Hardness (mg/L CaCO$_3$)		25.0	40.3	46.5	27.8	22.5	31.8	30.0	40.5	33.0
		25–25	31–54	46–47	27–29	22–24	31–34	29–31	38–43	22–54
Alkalinity (mg/L CaCO$_3$)		28.6	38.4	44.7	28.3	24.8	32.2	34.5	32.6	33.0
		27–34	36–42	44–46	27–30	24–26	32–33	33–37	31–37	24–46
Chloride (mg/L)		12.0	15.2	12.2	7.8	8.4	11.1	11.4	12.7	11.3
		11.4–13.1	14.3–16.1	11.4–14.2	7.0–9.1	7.6–9.2	9.0–16.7	10.3–13.9	11.5–15.7	7.0–16.7
Sulfate (mg/L)		11.2	17.2	16.0	8.5	8.2	8.8	11.4	13.3	11.8
		10.5–12.4	16.3–18.5	15.0–17.9	7.8–10.2	7.5–9.7	8.1–10.7	10.4–14.0	12.0–16.8	7.5–18.5
Sodium (mg/L)		12.8	21.5	14.8	11.0	11.0	12.8	13.0	18.8	15.2
		12–15	10–35	14–17	11–11	11–12	11–15	12–16	16–24	10–35
Potassium (mg/L)		2.1	9.7	4.5	2.4	1.7	3.0	2.4	2.5	3.5
		2.1–2.2	7.4–14.0	4.1–5.5	2.3–2.4	1.6–1.7	2.8–3.1	2.3–2.4	2.3–2.7	1.6–14.0
Calcium (mg/L)		6.0	8.8	10.8	7.0	5.3	8.0	8.0	10.5	8.0
		6–6	6–12	10–11	7–7	5–6	8–8	8–8	10–11	5–12
Magnesium (mg/L)		2.4	4.4	4.6	2.5	2.1	2.9	2.7	3.5	3.1
		2.4–2.5	3.7–5.6	4.4–5.2	2.4–2.6	2.0–2.3	2.8–3.0	2.5–2.9	3.3–4.0	2.0–5.6

water temperature (14.3–27.5 °C) and two contrasting conditions of transparency (30–45 and 8–15 cm) (Table 2). The dissolved oxygen saturation was lower in the two flood samplings (mean: 65 % in December 2009 and 69 % in May 2010) (Table 2). The conductivity always evidenced higher values in the two sites of the Paraná de las Palmas River than in the other main river sites (Fig. 3a). Except for this persistent relative difference, a high spatial homogeneity among river sites in basic water variables was generally observed in each sampling date (Fig. 3a). In the two small streams from zones with lower human use, occasional differences were detected with respect to the nearest river (Fig. 3a), for example, in temperature (up to 3 °C lower in April) or in water transparency (up to 20 cm higher in December 2009). Also, low dissolved oxygen was recorded (December 2008: 4.3 mg/L in Lago de la Barca Stream) with a river pulse between bankfull and inundation flow and especially with the overbanking flow (December 2009: 1.3 mg/L in Lago de la Barca Stream and

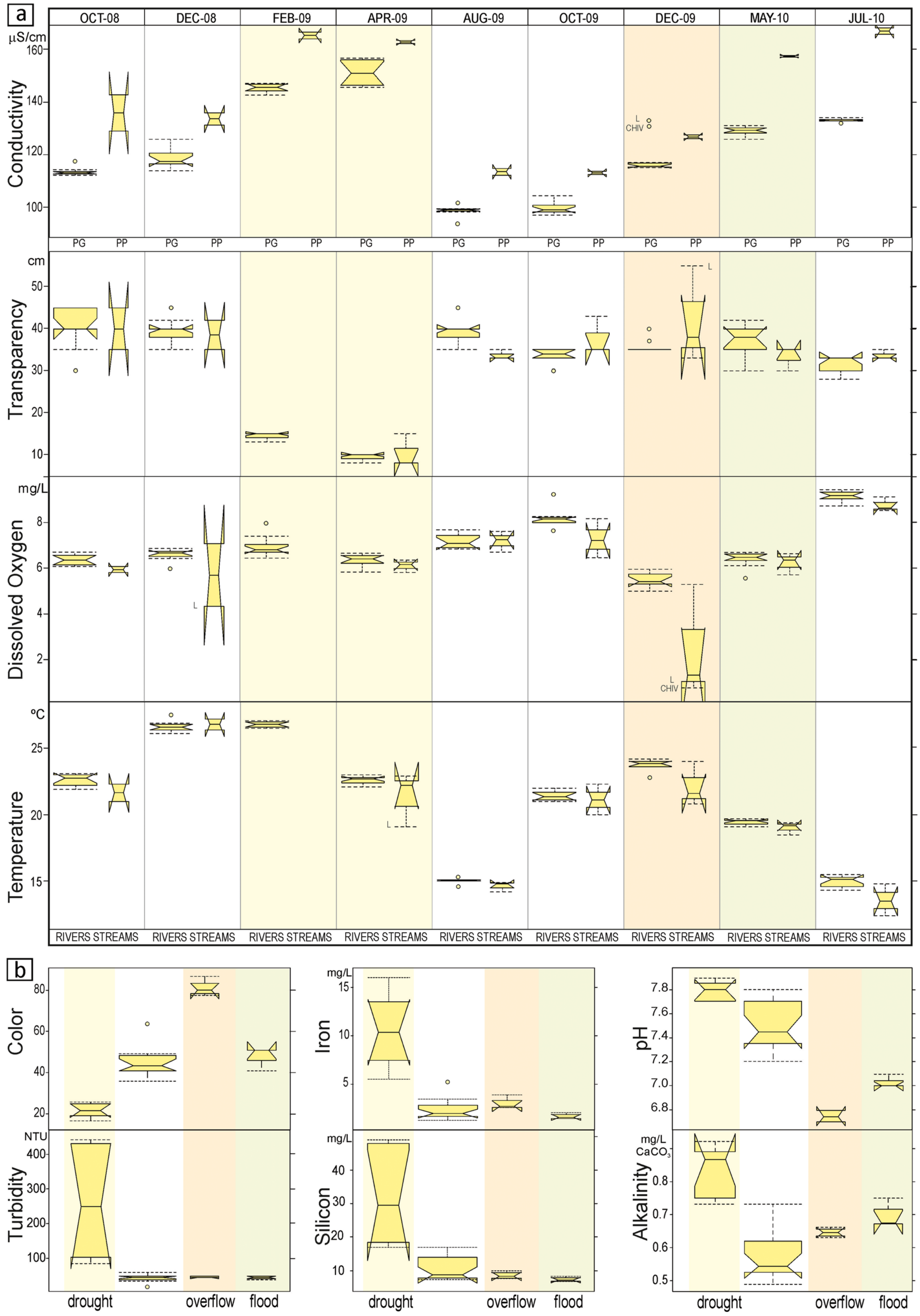

Fig. 3 Boxplots of selected water quality variables. **a** Basic variables in each sampling date considering conductivity in each sub-basin (PP: Paraná de las Palmas and PG: Paraná Guazú) and other variables in each fluvial environment (rivers and streams). **b** Variables in the four main rivers in each hydrological condition considered (site codes in Fig. 1e). *Notches* in each box indicate the confidence interval of the median value. Drought, overbanking, and flood conditions distinguished by color shading

0.78 mg/L in Chivico Stream) (Fig. 3a). In this last sampling, an increased conductivity, which exceeded that observed in all the other sites, was also detected in both streams (Fig. 3a). The real color was lower during the drought and higher with the overbanking flow (Fig. 3b). The turbidity, iron, and silicon showed higher values during the drought. The pH was lower with the overbanking flow, followed by the flood sampling, and higher during the drought. The alkalinity was higher during the drought and lower during not extreme flows (Fig. 3b).

Concentrations (meq/L) of major cations followed on average (Fig. 4a) and in general (Fig. 4b) the order: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$, whereas those of major anions followed the order: $HCO_3^- > Cl^- > SO_4^{2-}$ (considering that bicarbonate dominates the alkalinity in the pH range recorded). The sum of the average cations was 1.3 meq/L, which corresponds to medium diluted waters according to Meybeck (2003). The sum of major ions was higher in the Paraná de las Palmas River than in the other river sites in all samplings, a difference that was attenuated in the period of more diluted waters (Fig. 4b). The total major ion load (kg/s) showed only a slight decrease from December 2008–April 2009 to August and October 2009 samplings (Fig. 4b). In contrast, these loads doubled their values after the arrival of the overbanking flow (Fig. 4b), indicating the contribution from a relevant additional source.

The concentration (meq/L) of the total major ions was highly correlated with the conductivity evaluated in the field and in the laboratory (r=0.94). The expected inverse relationship between turbidity and transparency (Secchi disk estimation) approached an exponential curve (R^2=0.87), evidencing the better discrimination of the turbidity for cases of notably turbid waters in a river characterized by its naturally high suspended sediments. Real color was positively correlated with transparency (r=0.72) and negatively with turbidity (r=−0.60). Transparency and conductivity (r=−0.65), as well as dissolved oxygen and temperature (r=−0.52), showed inverse correlations, respectively. Many variables showed positive correlations among them. For example, large correlations were found between turbidity, iron, and silicon ($r \geq 0.95$) and between conductivity, sulfates, and alkalinity ($r \geq 0.84$).

Multivariate tests

The multivariate dispersion (distance to the respective centroid) between groups defined by the sampling dates and between those defined by the sites was homogeneous (nonsignificant tests) for both the 112 and the 32 cases. The mean and the range of the multivariate dispersion among sites considering basic water variables was higher with the overbanking flow and lower under drought samplings (Fig. 5). These multivariate distances were higher in sites from the Paraná de las Palmas River or from the small streams (Fig. 5).

After the stepwise selection procedure applied to both RDA models (112 and 32 cases), both zone categorizations (z and z2) resulted nonsignificant (Tables 3 and 4) and were removed. Considering the explanatory factors, the hydrological phase (h) showed a higher explanatory power than the Paraná Guazú flow (q), despite the significance of both hydrological factors. Therefore, the last factor was removed to reduce the VIF in the RDA models. Five of the proposed explanatory factors were retained in the parsimonious additive model (h+per+ev+d+a) selected to explain the multivariate structure of the five basic variables (112 cases). Four of these factors (fluvial environment had no meaning for this river

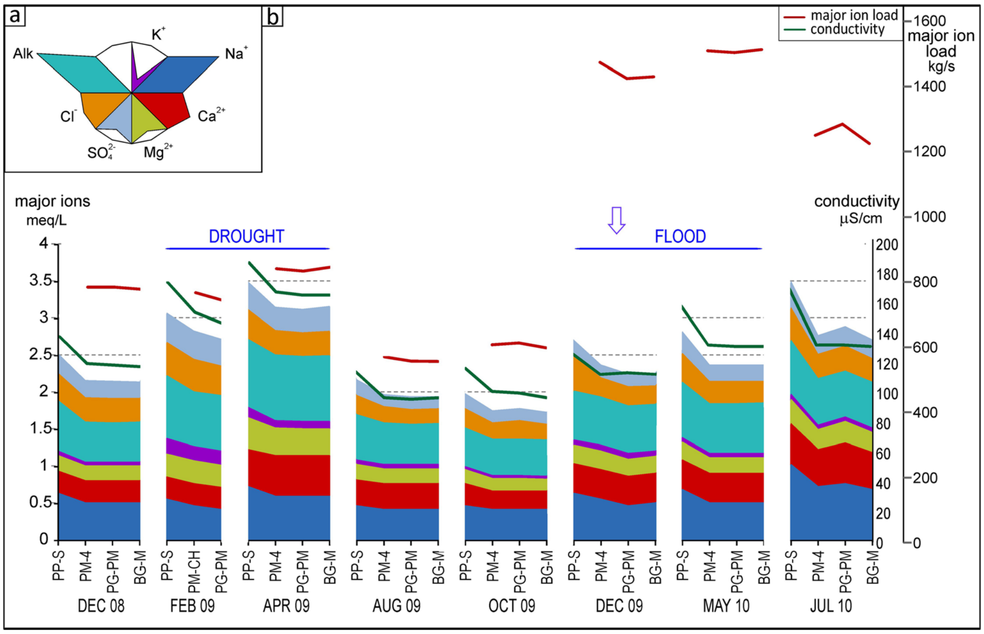

Fig. 4 Concentration (meq/L) and total load (kg/s) of major ions. **a** Maucha diagram (Maucha 1932) modified (total alkalinity instead of bicarbonate and carbonate; Silberbauer and King 1991) for the mean concentration of major ions. **b** Major ion concentration (graph of areas), conductivity (μS/cm) in the main rivers (site codes in Fig. 1e) and total load of major ions in the Paraná Guazú network sites (estimated considering the flow of this river branch) in each sampling date. Samplings during drought and flood (*horizontal blue line*) and the overbanking stage (*blue arrow*) are indicated

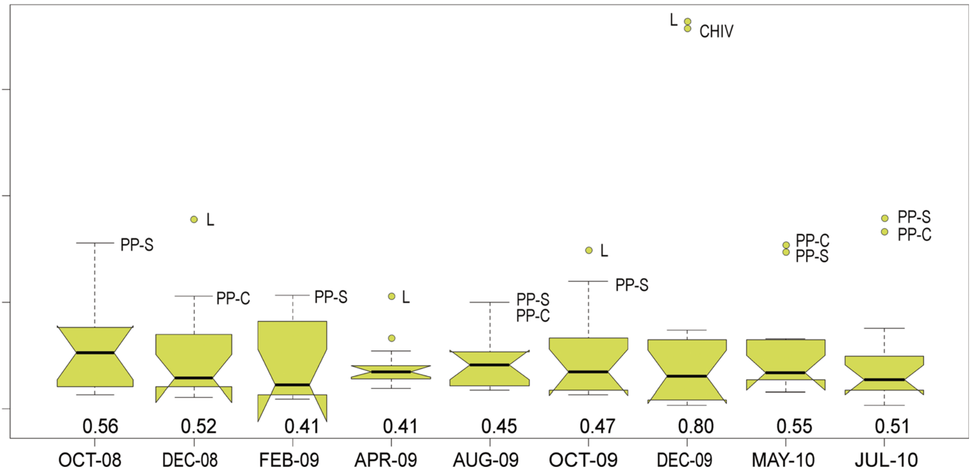

Fig. 5 Boxplots of multivariate dispersion (Euclidean distance) among sites on each sampling date considering basic water variables. *Notches* in each box indicate the confidence interval of the median value. Sites with higher multivariate dispersion (distance to the group centroid) in each date are shown (codes in Fig. 1e). The value of the mean multivariate dispersion is included under each boxplot

dataset) were retained in the parsimonious additive model (h+per+ev+d) selected to explain the multivariate structure of the 11 variables considered (32 cases). In both parsimonious models, all the explanatory factors retained were very highly significant ($p<0.001$) (Tables 3 and 4) and little redundant (VIF <10).

The parsimonious RDA model selected for the five basic water quality variables (112 cases) was very significant ($p<0.01$) and had an explanatory power (adjusted R^2) of 75.8 % and four very highly significant axes ($p<0.001$) (Table 5). The first two axes accounted for 56 % of the total variance and 74 % of the explained variance (Fig. 6a). The variables with higher loading on the first axis were water transparency, and, in inverse direction, conductivity and temperature, whereas those with higher loading on the second axis were dissolved oxygen, followed by temperature in the inverse direction (Fig. 6a, Table 5). Both samplings corresponding to the drought period (February and April) were distinguished towards one extreme position of the first axis, being characterized mainly by high conductivity and low water transparency (Fig. 6a, Table 2). The samples of the overbanking flow (December 2009) were distinguished with respect to the second axis by their low dissolved oxygen (Table 2), being two streams in far positions due to their strong hypoxia (Figs. 3a and 6a). One winter sampling (July) was distinguished towards the other extreme due to its high dissolved oxygen values (Figs. 3a and 6a, Table 2). Spatial differences within each sampling date were detected occasionally in one or both small streams (Figs. 3a and 6a). Also, both sites of the Paraná de las Palmas River, showing persistent higher conductivity values in each sampling (only exceeded in the overbanking flow by the two mentioned streams) (Fig. 3a), evidenced a trend to be located towards a higher conductivity in the ordination space (Fig. 6a).

The parsimonious RDA model selected for the 11 variables (32 cases) was very significant ($p<0.01$) and had an explanatory power (adjusted R^2) of 93.6 % and six very highly significant axes ($p<0.001$) (Table 6). The first two axes accounted for 69 % of the total variance and 74 % of the explained variance (Fig. 6b). The variables with higher loading on the first axis were turbidity, silicon, iron, and alkalinity, followed by hardness and conductivity, and, in the inverse direction, transparency, whereas the variables with higher loading on the second axis were dissolved oxygen, followed by temperature in the inverse direction (Fig. 6b, Table 6). Real

Table 3 Stepwise selection (999 permutations) results of potential explanatory factors in the RDA model based on the five basic physico-chemical variables (112 cases).

	Df	AIC	F	Pr (>F)
q (Paraná Guazú flow)	1	31.365	63.451	0.001***
fh (hydrological stage)	3	70.717	46.903	0.001***
fper (season)	3	88.292	60.535	0.001***
fev (ENSO event)	1	26.973	57.166	0.001***
fd (drainage sub-basin)	1	−5.426	17.686	0.001***
fa (fluvial environment)	1	−13.667	9.338	0.001***
fz2 (zone by human use)	1	−21.229	2.199	0.079
fz (Reserve zone)	1	−20.766	0.978	0.395

*** $p<0.001$

Table 4 Stepwise selection (999 permutations) results of potential explanatory factors in the RDA model based on 11 physico-chemical variables (32 cases)

	Df	AIC	F	Pr (>F)
fh (hydrological stage)	3	60.428	61.386	0.001***
fper (season)	3	46.304	36.745	0.001***
fev (ENSO event)	1	22.639	33.125	0.001***
fd (drainage sub-basin)	1	6.182	10.559	0.001***
fz (Reserve zone)	1	−2.936	0.718	0.626

*** $p<0.001$

Table 5 Results of the parsimonious RDA model (h+per+ev+d+a) based on the five basic physico-chemical variables (112 cases)

	RDA1	RDA2	RDA3	RDA4	RDA5[a]
Test of the RDA axes (999 permutations)					
Var	1.6886	1.2112	0.7483	0.1551	0.0843
F	160.9004	115.4159	71.3061	14.7833	8.0302
Pr (>F)	0.001***	0.001***	0.001***	0.001***	0.002**
Eigenvalues and their contribution to the variance[b]					
Eigenvalue	1.6886	1.2112	0.7483	0.1551	0.0843
Proportion explained	0.3377	0.2422	0.1497	0.0310	0.0169
Cumulative proportion	0.3377	0.5800	0.7296	0.7607	0.7775
Accumulated constrained eigenvalues					
Eigenvalue	1.6886	1.2112	0.7483	0.1551	0.0843
Proportion explained	0.4344	0.3116	0.1925	0.0399	0.0217
Cumulative proportion	0.4344	0.7459	0.9384	0.9783	1.0000
Scores of the water quality variables					
Temperature	−1.4641	−1.2033	0.9585	−0.2216	−0.2433
pH	−0.0241	0.3756	1.3670	0.1661	0.4022
Conductivity	−1.5355	0.7760	−0.4745	−0.5290	0.2453
Dissolved oxygen	0.7348	1.5804	0.7080	−0.2919	−0.3060
Transparency	1.7071	−1.0091	0.1098	−0.5378	0.1493

** $p < 0.01$, *** $p < 0.001$

[a] Only significant RDA axes are shown

[b] See in the text the values corrected by the R^2 adjusted to R^2 ratio

color and pH had a more similar load on both axes, but in the inverse direction. The higher number of variables considered in this analysis allowed a better distinction between sample groups of each date and especially between the most contrasting hydrological phases. The drought samplings (February and April) were positioned towards one extreme of the first axis (Fig. 6b), in association with high turbidity, alkalinity, conductivity, iron, silicon, hardness, and low transparency, and real color (Fig. 3). Both samplings showed similar conductivity and color values, whereas the April sampling showed higher alkalinity and pH and much higher turbidity, iron, and silicon than the February sampling (Table 2). Towards the other extreme of the first axis, August and October 2009 samplings showed lower conductivity values (Fig. 3a). With respect to the second axis, the samples of the overbanking flow (December 2009), showing the lowest dissolved oxygen and pH and the highest color (Fig. 3a, b), were positioned towards one extreme, whereas the winter samplings with high dissolved oxygen (mainly July) were positioned towards the opposite extreme (Fig. 6b). The flood sampling (May) was positioned in a direction similar to that of the overbanking flow (Fig. 6b), being characterized mainly by slightly higher alkalinity and pH than the previous sampling (Fig. 3b). The December 2008 sampling was positioned near the ordination space center (Fig. 6b), showing the lowest turbidity and, like the February sampling, the highest temperature (Table 2). The site of the Paraná de las Palmas was positioned towards a higher conductivity in the May sampling, and farther in the same direction in the following sampling (July) (Figs. 3a and 6b).

The variation explained (adjusted R^2) by unique and joint factors selected in both parsimonious models is shown in the respective Venn diagram (Fig. 7a, b). The temporal variation showed no joint effect (covariation) with the spatial variation. The four factors in common retained in both parsimonious models showed the same order in their unique explanation power: hydrological phase>season>ENSO event>drainage sub-basin. However, when comparing both models, in the model of 11 variables, the total explanation power was higher and the main joint fraction changed from hydrological phase and season to hydrological phase and ENSO event. Considering that hydrological aspects may be reflected by the hydrological phase and by the hydrological year (characterized according to the dominant ENSO event), the explanation power of both together increased from 43 % in the model of basic variables to 66 % in the model of 11 variables.

Discussion

In this study, the main temporal and spatial variations of fluvial water quality in the Paraná Delta Reserve were assessed and the respective additive contribution of significant explanatory factors was quantified. The hydrological stage was the

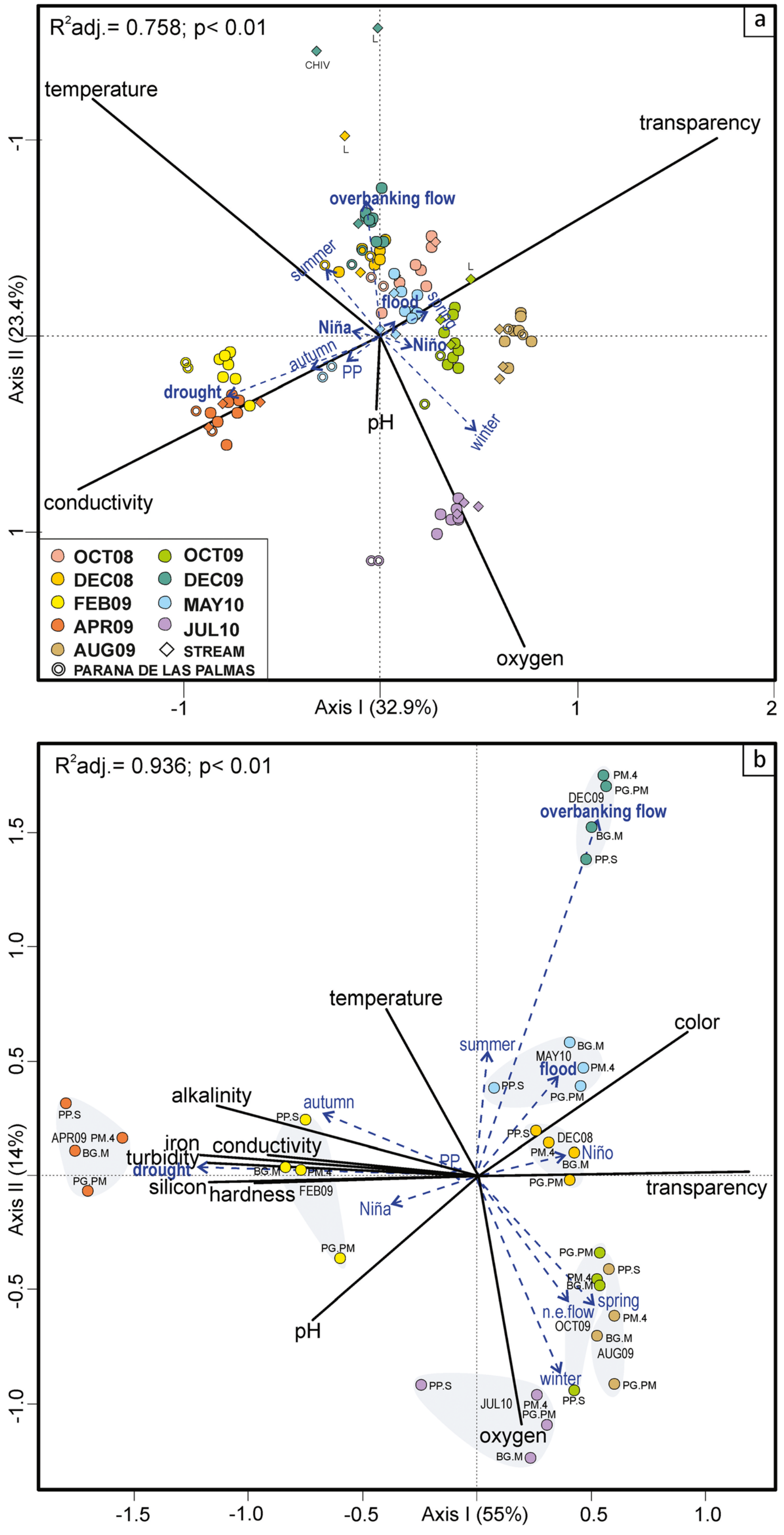

Fig. 6 Ordination diagrams (scaling 2 triplots; weighted averages scores, as recommended in Oksanen 2015) of the parsimonious Redundancy Canonical Analyses performed on **a** 112 cases of the five basic water quality variables and **b** 32 cases of 11 selected water quality variables. Sample forms colored according to the sampling date; water quality variables: *black lines*; explanatory factors: *blue arrows* (n.e.flow: not extreme flow). Site codes in Fig. 1e. Significance and explanatory power (R^2) of the respective model, as well as the variance explained by the two first axes are indicated

first explanatory factor of the water quality, the main changes being evidenced during the drought and with the overbanking flow. During the drought, the increase in conductivity, turbidity, and associated variables may be a consequence of the

Table 6 Results of the parsimonious RDA model (h+per+ev+d) based on 11 physico-chemical variables (32 cases)

	RDA1	RDA2	RDA3	RDA4	RDA5	RDA6	RDA7[a]
Test of the RDA axes (999 permutations)							
Var	6.1844	1.5704	1.2424	0.8420	0.3848	0.1387	0.0792
F	273.2546	69.3871	54.8954	37.2029	17.0033	6.1299	3.5007
Pr (>F)	0.001***	0.001***	0.001***	0.001***	0.001***	0.001***	0.007**
Eigenvalues and their contribution to the variance[b]							
Eigenvalue	6.1844	1.5704	1.2424	0.8419	0.3848	0.1387	0.0792
Proportion explained	0.5622	0.1428	0.1129	0.0765	0.0349	0.0126	0.0072
Cumulative proportion	0.5622	0.7050	0.8179	0.8945	0.9295	0.9421	0.9493
Accumulated constrained eigenvalues							
Eigenvalue	6.1844	1.5704	1.2424	0.8419	0.3848	0.1387	0.0792
Proportion explained	0.5901	0.1499	0.1186	0.0803	0.0367	0.0132	0.0076
Cumulative proportion	0.5901	0.7400	0.8586	0.9389	0.9756	0.9889	0.9964
Scores of the water quality variables							
Temperature	−0.4017	0.7335	0.7675	−0.5301	0.3073	−0.0571	
pH	−0.7266	−0.6313	0.7569	−0.0189	−0.3110	0.1419	
Conductivity	−0.9214	0.0948	−0.4756	−0.6752	−0.2194	−0.1771	
Dissolved oxygen	0.1912	−1.0867	−0.2771	−0.2260	0.3679	−0.1398	
Transparency	1.1875	0.0221	0.0427	0.0924	−0.3946	−0.1431	
Turbidity	−1.1846	0.0586	−0.0182	0.4695	−0.0475	−0.1636	
Real color	0.9180	0.6329	−0.3912	0.3039	0.1267	0.0154	
Silicon	−1.1814	−0.0271	0.0920	0.4299	0.0985	−0.1709	
Iron	−1.2174	0.0936	0.0863	0.3034	0.1309	0.0058	
Hardness	−0.9794	−0.0288	−0.5569	−0.0718	0.0911	0.2859	
Alkalinity	−1.1463	0.3081	−0.3735	−0.1474	−0.2494	0.0078	

** $p < 0.01$, *** $p < 0.001$

[a] Only significant RDA axes are shown

[b] See in the text the values corrected by the R^2 adjusted to R^2 ratio

reduced river flow in conjunction with the arrival (with some delay) of high particulate and dissolved loads supplied by flow peaks of the Bermejo River headwaters recorded from late December 2008 to early April 2009 (Fig. 2a). In the Middle Paraná River (near Santa Fe city), an increase in conductivity and suspended sediments was also recorded from February to April within the drought period (mean flow at Paraná: 11,526 m^3/s) of the 1999–2000 La Niña event (Devercelli 2010). The minimum real color values observed during the drought in the Reserve main rivers

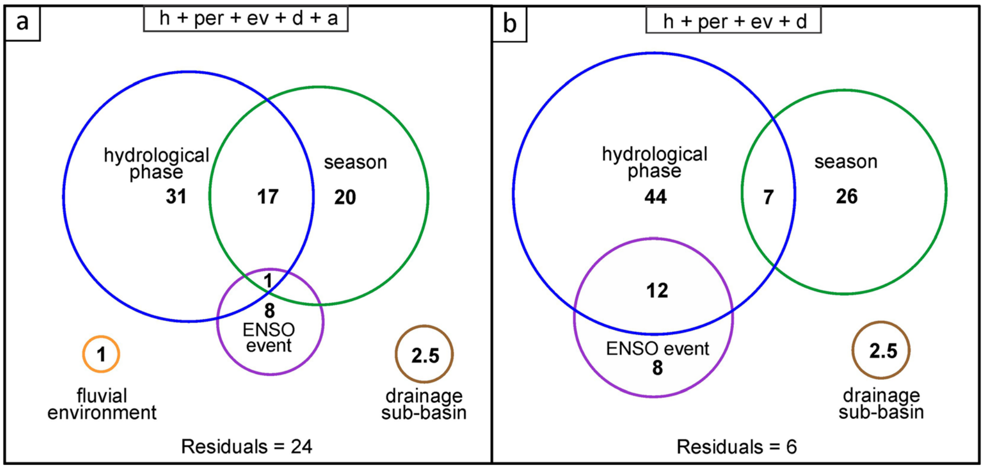

Fig. 7 Venn diagrams of the respective parsimonious additive model selected for **a** 112 cases of five basic variables and **b** 32 cases of 11 variables. The numbers (values <1 not shown) indicate the percentage of the water quality variation explained by each unique or joint explanatory factor in the respective model (on top). (ENSO event: hydrological year according to the dominant ENSO event)

(indicating low humic compounds) reflected their strong and extended disconnection from the Delta floodplain environments.

With the overbanking flow, the minimum values of dissolved oxygen and pH and the maximum values of real color recorded in the main rivers reflected the massive connection with deltaic marshes. These wetlands are characterized by water-saturated soils, litter accumulation by the high productivity and slow decomposition of emergent macrophytes, and the consequent water characteristics, such as dissolved oxygen depletion, low pH, and high concentration of dissolved organic matter (Villar et al. 2001). Likewise, minimum pH and dissolved oxygen saturation percentage in the onset of an extreme flood under a strong El Niño event (1997–1998) (Devercelli 2010), as well as increased export of dissolved organic matter from the floodplain by major floods (Depetris 2007), were found for the Middle Paraná River. The sharp increase in the total major ion load after the arrival of the overbanking flow indicates the contribution of a relevant additional source of salts. Only a low proportion of this load may be attributed to the Bermejo River, due to the low coincidence of the flow peaks of this river (Fig. 2a) (considering a time lag up to 2 months) with the sampling dates of the present study after the arrival of the overbanking flow (Fig. 2c). The non-linear dilution of the water conductivity with flood, due to the mobilization from solute sources of the floodplain, has been stated for the Middle Paraná River (Depetris 2007) and other river-floodplain systems, such as the Amazon River (Gibbs 1972) and a sub-basin of the Zambezi River (Zurbrügg et al. 2012). However, the degree of increase in the major ion load estimated in the present study (~100 %) clearly differed from the slight increase (<10 %) reported for the Middle Paraná River during the flood caused by the strong 1982–1983 El Niño event (Pasquini and Depetris 2007). This last-mentioned flood reached higher magnitude and exceptional duration (one year and a half). In addition, the different effects of the large flood studied may also be due to its specific previous conditions. The solute load mobilized was likely increased by its accumulation in Delta environments during the general low-flow conditions of two consecutive hydrological years dominated by La Niña events coupled with local uncommon dry weather that favored many fire foci, some of them with high intensity and persistence. These fire foci extended throughout 2008, with peaks in April and May and from August to November, and burned almost 15 % of the Delta surface (Salvia et al. 2012). In severely burned sites, the top soil layer showed a significant conductivity increase (Salvia et al. 2012). Also, several shallow lakes of the middle Delta showed high conductivity values (e.g., 3500 μS/cm in one lagoon previously affected by the fire) (Borro et al. 2010).

The season was the second explanatory factor of the water quality variation, even if the dataset became temperature-independent (i.e., by removing temperature and replacing dissolved oxygen concentration with dissolved oxygen saturation). In temperate zones, the river flow interacts with seasonal variations to drive ecologically significant changes in water quality, and therefore, droughts or floods in different seasons have markedly different ecological responses (e.g., Mosley 2015). The advance towards disentangling the joint effect of hydrological phases and seasons would require several years of data to provide different combinations of conditions, as was assessed in an ecosystem of the Danube River floodplain (Palijan 2015).

The hydrological year according to the dominant ENSO event also had a significant contribution as explanatory factor, besides the variation yet explained by the drought and flood stages. The two winter samplings, which were categorized in the same (not extreme) hydrological phase and showed similar water temperature, differed in conductivity and dissolved oxygen values. Therefore, water quality differences between the two winter samplings, one (August 2009) after a strong drought and the other (July 2010) after a strong flood, suggest that the influence of the ENSO event may extend after the extreme hydrological phase.

Considering the spatial variations, the persistent higher conductivity detected in the Paraná de las Palmas River may neither be attributed to the differing chemical signature of the Paraguay and the Upper Paraná rivers (because their incomplete mixing seems to disappear upstream Santa Fe-Paraná cities) nor to different contributions from groundwater discharges (only 0.5–6 % of the water inputs to the Middle Paraná River under baseflow conditions) (Campodonico et al. 2015). The Salado River contributes with high salinity (>1000 μS/cm) to the west margin of the Paraná River downstream from Santa Fe city. Thus, this tributary may be responsible for the conductivity asymmetry recorded in the Rosario (Fig. 1c) cross-section (O'Farrell et al. 1998), downstream of the split of the Paraná Pavón branch, which supplies waters that finally flow to the Paraná Guazú River. Moreover, other saline small rivers and streams, such as the Areco and Las Palmas (>1200 μS/cm) (Villar and Bonetto 1998), drain directly to the Paraná de las Palmas River. The minor spatial significant additional variation corresponding to occasional differences in some basic variables of the small streams indicated that several natural characteristics of these watercourses, such as width and orientation within the drainage network, prevail over the high spatial proximity (only 2–3 km) to the nearest main river site. The strong hypoxia, low pH, and increased conductivity (even above the usually higher values of the Paraná de las Palmas River) of these streams with the overbanking flow provided evidence of the local influence of the island environments on the main rivers.

The homogenization effect of flood among waterbodies within the floodplain and between the main river channel and the floodplain has been proposed as a general pattern for river-floodplain systems (Thomaz et al. 2007). However, during the same flood of this study (2009–2010), most of the physical and chemical variables showed a higher heterogeneity between the main channel and the floodplain in the Middle Paraná River (Mayora et al. 2013). The consideration of the spatial variability among deltaic watercourses in the present study (13 sites) may complement this discussion about spatial heterogeneity in river-floodplain systems. A different pattern was observed in conductivity (higher spatial range under different hydrological stages), transparency and dissolved oxygen (higher spatial range with the overbanking flow) (Fig. 3a). Besides the nonsignificant difference among dates in spatial multivariate dispersion, their mean and range considering basic water variables was higher in the overbanking flow and lower in the drought samplings (Fig. 5), thus following a pattern opposite to the generalization proposed.

This study clearly evidenced the dominant influence of the hydrology of the Paraná River on the water quality of the Reserve watercourses, at least under the extreme conditions assessed. Conversely, the high spatial homogeneity found in basic water variables among the Reserve river sites in each sampling, which were usually carried out through one and a half days, provides no evidence of the effect of daily astronomical tides on their subsurface water quality.

The importance of the flood in the export of the floodplain to watercourses, as part of the natural exchange process in fluvial systems, is widely recognized (e.g., Junk et al. 1989). However, specific geomorphological features of environments of floodplains and deltas may influence their physicochemical water characteristics (e.g., persistent versus occasional dissolved oxygen depletion), as has been pointed out for different sectors of the Paraná River (Maine et al. 2004), and the consequent water properties exported to the watercourses.

Notable changes in more water variables were recorded during the drought analyzed. Furthermore, more chemical and microbiological variables associated with water pollution, with potential consequences for the aquatic biota and for the island inhabitants, were recorded during the drought than during the flood (Puig et al. this SI). In concordance with these results, a recent review has pointed out that droughts have profound water quality effects (Mosley 2015). Most streams and rivers considered in that review also showed increased salinity during the drought, typically due to reduced dilution and concentration of mass. Conversely, the increased turbidity observed in the present study, likely due to a coincidence with high sediment loads from the Bermejo River, is not in agreement with that reported in most studies. Therefore, specific assessments are needed, because water quality effects of drought and floods can be quite variable and specific, depending on the characteristics of the water environments and their basins (Mosley 2015). The water quality was included in one of the four ecological low-flow principles proposed in a recent review (Rolls et al. 2012), indicating that the consequences are reflected in the biota distribution and abundance according to thresholds of water quality tolerances. The ecological effect of reduced flow in streams and rivers depends on the antecedent flow history (infrequently included in the assessments) and the antecedent water quality conditions that are driven by climate, flow regime and the surrounding landscape (Rolls et al. 2012).

The flow regime of the Lower Paraná River evidenced major changes after the early 1970s. The extremely low flows (10 % percentile of daily flows) disappeared and the flow seasonality attenuated progressively (Puig et al. this SI). Our previous study (de Cabo et al. 2003) was performed (1995–1996) within a marked wet period, characterized by more frequent large floods and very high year-to-year variability in the flood timing, which increased highly the probability of joint effect of different hydrological stages and seasons. In the current dry period (since the start of the new century), the spring flows, the number of reversals, and the variability in the flood onset date were higher than in the less altered period before the 1970s change (Puig et al. this SI). Some of these flow regime changes favor different combinations of hydrological stages and seasons or other drivers, with consequent different joint effects on water quality, as was the mentioned case of the relative contribution of the Bermejo River loads under drought and under flood.

Among the most widely predicted consequences of global climate change are increases in both the frequency and severity of a variety of extreme weather events, such as heavy rainfalls, floods, droughts, heatwaves, and wildfires, each of which can potentially impact water quality (Khan et al. 2015). The combination or the sequence of extreme events may be yet more important for water quality, but both issues have been identified as knowledge gaps (Khan et al. 2015). This study included a drought, in the last part of a period generally of low flows combined in 2008 with extreme dry weather and unusual wildfires, events with moderate (weeks to months) to long (years) post-effects (Khan et al. 2015), and a large (10 years of recurrence) and prolonged (7 months) flood, situations that may become more frequent in the future.

The projected increase in duration and frequency of dry periods in the Paraná basin until 2040 (Valverde and Marengo 2014) is in concordance with the increase in frequency of drought conditions predicted for most of the world's large rivers in the next 30–50 years (Mosley 2015). More studies are thus required to better understand the effects of droughts on water quality to prevent and/or manage adverse impacts (Mosley 2015), for example, in South America. In addition, recent modeling has provided evidence for the frequency of extreme El Niño events to double in the twenty-first century as result of greenhouse warming, leading to extreme events worldwide (Cai et al. 2014). These predictions are in agreement with the increase in the frequency of extreme conditions forecasted for South America (e.g., Torres and Marengo 2013).

The present study allowed gaining understanding of water quality at an intermediate scale in scarcely known deltaic watercourses, identifying potential explanatory factors and possible underlying processes. These findings provide valuable bases for suitable management measures as well as insights that should address various specific future research objectives.

Summary and conclusions

In this assessment of a fluvial deltaic zone of complex hydrology, temporal variations strongly prevailed over spatial ones at the scales and conditions considered. This prevalence evidences the relative influence of opposite hydrological extremes and seasons with respect to the low spatial heterogeneity of a deltaic distributary network dominated by a large river. The hydrological phase, followed by the season and the hydrological year (characterized by the dominant ENSO event) were the main significant explanatory factors of major changes in the water quality, whereas the drainage sub-basin and the watercourse category (river or stream) were secondary significant explanatory factors.

This study clearly evidenced the dominant influence of the Paraná River hydrology on the subsurface water quality of the Reserve watercourses, at least under the extreme conditions assessed. During the drought, the increase in conductivity, turbidity, and associated variables (e.g., major ions, alkalinity, hardness, silicon, iron values) was likely a consequence of the reduced Paraná River flow joint with particulate and dissolved loads from the Bermejo River. The minimum real color reflected a strong disconnection of watercourses from the Delta floodplain. Conversely, during the overbanking stage of the flood, the minimum dissolved oxygen and pH values and the maximum real color reflected the massive connection of watercourses with Delta marshes, evidenced mainly by the small streams. The sharp increase in the total major ion load with the flood, besides the Bermejo River supply, indicated the contribution of accumulated salts in the floodplain, likely intensified after a drought within a long period dominated by low flows combined with uncommon dry weather and extended Delta wildfires.

The fluvial water quality of the deltaic watercourses evaluated may be influenced by different drivers, such as the dilution-concentration effect (historically around autumn and early spring in the Delta, respectively) of the Paraná River flows; the sequence of flow pulses (usually from summer to middle autumn) of the Bermejo River, main source of sediments and solutes to the Delta; the exportation of water properties from the Delta floodplain, mainly in the flood onset; the season; and the different effect of tributaries to the Lower Paraná River. Recent changes in the flow regime of the Paraná River, such as the attenuation of seasonality, the increase in spring flows, and the higher variability in the flood onset date, favor different combinations in each year of hydrological phases and seasons or other drivers, and thus, different joint effects on water quality.

Despite the low spatial heterogeneity among deltaic watercourses in basic variables and their nonsignificant multivariate dispersion, some of these variables and the mean and the range of their multivariate dispersion differed or opposed (higher spatial heterogeneity under overbanking flow and lower under drought) to the pattern expected by the "homogenization effect of flood", proposed as a generalization for river-floodplain systems. These differences may be explained by the particularities of the floodplain or deltaic environments influencing properties exported by floods, as well as by other drivers, such as tributaries.

In agreement with the consideration that the effects of extreme events may be very specific, the variety of possible drivers identified and the particularities of the floodplain environments provide additional support for the appropriateness of water quality assessments not only in different large fluvial systems but also in different sectors of the same system.

The period studied was under the influence of a combination of extreme events: drought, dry weather and wildfires, with moderate to long post-effect, and a large (10 years of recurrence) supra-seasonal flood. The forecasted increase in frequency and severity of extreme weather events by the climate change will likely affect the fluvial water quality and consequently its biota. Therefore, the previous conditions as well as the combination or sequence of extreme events should be documented. Specific ecohydrological evaluations and the application of appropriate powerful statistical methods should also be emphasized as key tools to gain knowledge on the water quality of complex floodplain-river systems and to provide bases for suitable management measures in a scenario of climatic change and increasing human alterations and demands.

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