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An anoxic event and other biogeochemical effects of the Pantanal wetland on the Paraguay River

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Abstract

The Paraguay River was sampled throughout the annual cycle at two sites located downriver from most of the Pantanal, and major tributaries were occasionally sampled close to their entry into the Pantanal. The floodplains strongly modulate the discharge regime and substantially reduce runoff by enhancing evapotranspirative losses. Contact of the river water with the floodplain results in depletion of dissolved O_2, oversaturation of CO_2 and CH_4, loss of suspended sediments, and reduced export of N and P. Oxygen depletion and associated chemical changes are most marked when river water first contacts the floodplain; in 1995, the water remained anoxic throughout the river channel for 6 weeks, causing massive fish mortality. Bottle incubations showed that the rate of O_2 consumption by the river water during the anoxic event was high at first (7.2 μM h^{-1}) but declined exponentially over several hours and was not stimulated by organic carbon and nutrient additions. The O_2 demand may be due largely to bacterial CH_4 oxidation; the concentration of CH_4 in the river was particularly high (~31 μM) at the time of the incubations. The O_2 depletion corresponded with higher concentrations of most major ions, Si, and dissolved organic carbon but was not accompanied by elevated concentrations of inorganic N and P, H_2S, or most of the 46 dissolved trace elements that were measured. In contrast to O_2 depletion and associated chemical changes, sediment retention by the floodplains was greatest at maximum river stages. Most chemical weathering of minerals seems to take place in the upland drainage basins rather than on the floodplains, and most major solutes display conservative mixing in the river–floodplain system.

The importance of floodplains to the hydrology, biogeochemistry, and ecology of large rivers has been increasingly recognized (e.g. Lewis and Saunders 1989; Junk et al. 1989; Richey et al. 1991). Floodplains regulate riverine discharge by temporarily storing water during flood stages and can enhance water loss by evapotranspiration and infiltration (Richey et al. 1989; Sutcliffe and Parks 1989). During passage of river water through floodplains and coastal deltas, sediment retention and loss or transformation of solutes can potentially alter the fluvial transport of elements from landscapes to the oceans (Meybeck 1988). Floodplains are also ecologically important because they support much of the biological diversity and production in riverine ecosystems (Junk et al. 1989; Sparks 1995). The physical and biological interactions between the floodplain and its parent river must be understood to evaluate the environmental impact of river regulation projects as well as to restore degraded riverine ecosystems.

The upper Paraguay River drains the Pantanal wetland, a vast complex of internal deltas (Welcomme 1985) that delays and potentially modifies runoff from the drainage basin. The Paraguay River is expected to show stronger floodplain effects than most other rivers because of the high degree of river–floodplain contact. An improved understanding of river–floodplain interactions is important for the Paraguay River in particular because a major navigation project known as the Paraguay–Paraná Waterway or Hidrovia is currently under consideration, and this project may require channel modifications that could alter the natural hydrological dynamics of the region (Ponce 1995).

The objective of this study is to evaluate the effects of the extensive floodplains on the biogeochemistry of the Paraguay River at its outflow from the region. We analyze comprehensive chemical data collected over the course of a year. We also examine the O_2 demand and hydrochemical changes during a natural anoxic event in the river that corresponded

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with initial inundation of the floodplain after the dry season. Elemental transport rates are calculated and compared with data from rivers in other geographical regions, and a regional water and solute budget is constructed to show the most important effects of the floodplain on fluvial transport of materials from the basin.

Study site

The Pantanal is generally defined as the floodplains of the upper Paraguay River above the Apa River (22°S). The Paraguay River flows along the western side of the Pantanal, collecting water from several major tributaries as well as from diffuse floodplain inputs (Fig. 1). The upland drainage basin surrounding the Pantanal occupies 359,000 km² and consists of elevated plateaus and low mountains to the north, east, and southeast (mostly 250–1,200 m asl), and plains to the west (EDIBAP unpubl. rep.). The land subject to inundation in the Pantanal is low lying (80–150 m), and much of the floodplain is composed of alluvial fans that slope gradually toward the Paraguay River (Klammer 1982). The area subject to seasonal flooding covers ~300 by 400 km (~137,000 km²) and is located mostly in Brazil, with smaller areas to the west in Bolivia and Paraguay. Our study is concerned with the 363,500 km² of the drainage basin that lies above Porto Esperança (Fig. 1), which includes most of the Pantanal.

The mean annual discharge of the Paraguay River at Porto Esperança (Fig. 1) was estimated at 1,412 $m^3 s^{-1}$ by EDIBAP (unpubl. rep.), corresponding to a mean runoff rate of 123 mm yr^{-1}, although the years used for that estimate (1964–1972) spanned an unusually prolonged drought. The high interannual variability of rainfall in the region results in variability in the flooding regimes, as reflected by the river stage record from Ladário, near Corumbá (Fig. 2). In the vicinity of Corumbá and Porto Esperança, the Paraguay River has a mean slope of 3 cm km^{-1} and is moderately sinuous with occasional islands (Ponce 1995). Several large lakes (shown in black in Fig. 1) are close to the Paraguay River and are hydrologically linked to the river (Calheiros and Hamilton 1996).

Rivers in the Brazilian uplands deliver most of the water and sediment to the Pantanal; the western side of the drainage basin has no major tributaries and contributes relatively little runoff (EDIBAP unpubl. rep.). Upon entering the Pantanal, most of the tributary rivers lose water to the floodplain through distributaries and overbank flow, often regaining some of the water before their confluence with the Paraguay River. Flooding originates not only from the tributaries that drain surrounding uplands but also from delayed drainage of rain that falls directly on the floodplain (Hamilton et al. 1996).

The climate of the Pantanal is tropical with a marked wet season, although temperatures are reduced significantly during winter, particularly during the occasional influx of polar air masses from the south (IBGE 1989). Mean monthly air temperature at Corumbá ranges between 21.4 and 27.4°C. Rainfall and potential evapotranspiration (PET) show a pronounced seasonal cycle in the region with excesses from November to March as shown by means for four stations within the Pantanal (Fig. 3). The mean annual rainfall and PET at the four stations within the Pantanal during nondrought years were 1,295 and 1,471 mm, respectively. Most of the upland areas surrounding the Pantanal show a similar seasonal cycle, although rainfall is significantly higher in some parts of the surrounding uplands, particularly in the north (EDIBAP unpubl. rep.).

Records of riverine discharge from the uplands to the Pantanal were compiled by EDIBAP (unpubl. rep.). Figure 3 shows the mean monthly sum of inflow discharges for the principal tributaries during the three nondrought years for which complete data are available, plotted together with the outflow discharge at Porto Esperança for the same period. Storage of water on the floodplain results in the ~4-month delay between the peak inflow and outflow and the attenuated outflow hydrograph.

Fluctuations in inundation area in the Pantanal have recently been estimated for a 9-yr period from satellite observations of passive microwave emission, using the 37-GHz polarization difference measured by the scanning multichannel microwave radiometer (Hamilton et al. 1996). The mean seasonal cycle of floodplain inundation and drainage reflects the cumulative difference between rainfall, riverine inflows, and outflows (Fig. 3). Comparison of the cumulative excess water volume (inflows + rain − evapotranspiration − outflow) with the inundation area for each month shows that the mean depth of water on the floodplain does not exceed 0.5 m throughout the year.

The hydrology and hydrochemistry of the upper Paraguay River and its adjacent floodplains remain little affected by human activities. Human impact has been mainly through the introduction of cattle and the increased use of fire during the last 200 yr, which have influenced the vegetation throughout the region (Prance and Schaller 1982). The river system is largely unregulated, with the only significant dam located on a tributary of the Cuiabá River. Water pollution probably has little effect on the hydrochemistry of the rivers within the Pantanal, although increased soil erosion resulting from recent agricultural development of the uplands may be significant. Human population density is low in the Pantanal and in most of the surrounding uplands (<2 km^{-2}: IBGE 1989).

The geology of the uplands is complex with significant areas of Precambrian, Paleozoic, and Mesozoic formations (RADAMBRASIL 1982). The thick alluvial deposits of the Pantanal are derived largely from the readily erodible sandstones forming the pediments to the east (Klammer 1982). Geological maps produced by RADAMBRASIL (1982) indicate that carbonate rocks cover ~2% (8,000 km²) of the drainage basin above Porto Esperança, mainly in the western and southern parts of the basin; comparable information for the Bolivian portion of the basin is not available. Floodplain soils are variable but generally contain more clay in areas subject to riverine overflow and tend to be sandy on the higher parts of the alluvial fans, including many areas subject to flooding by local rainfall (RADAMBRASIL 1982).

The vegetation of the basin includes cerrado savanna, semideciduous forest, xeric scrub, and gallery forest. A substantial fraction of the upland basin has recently been de-

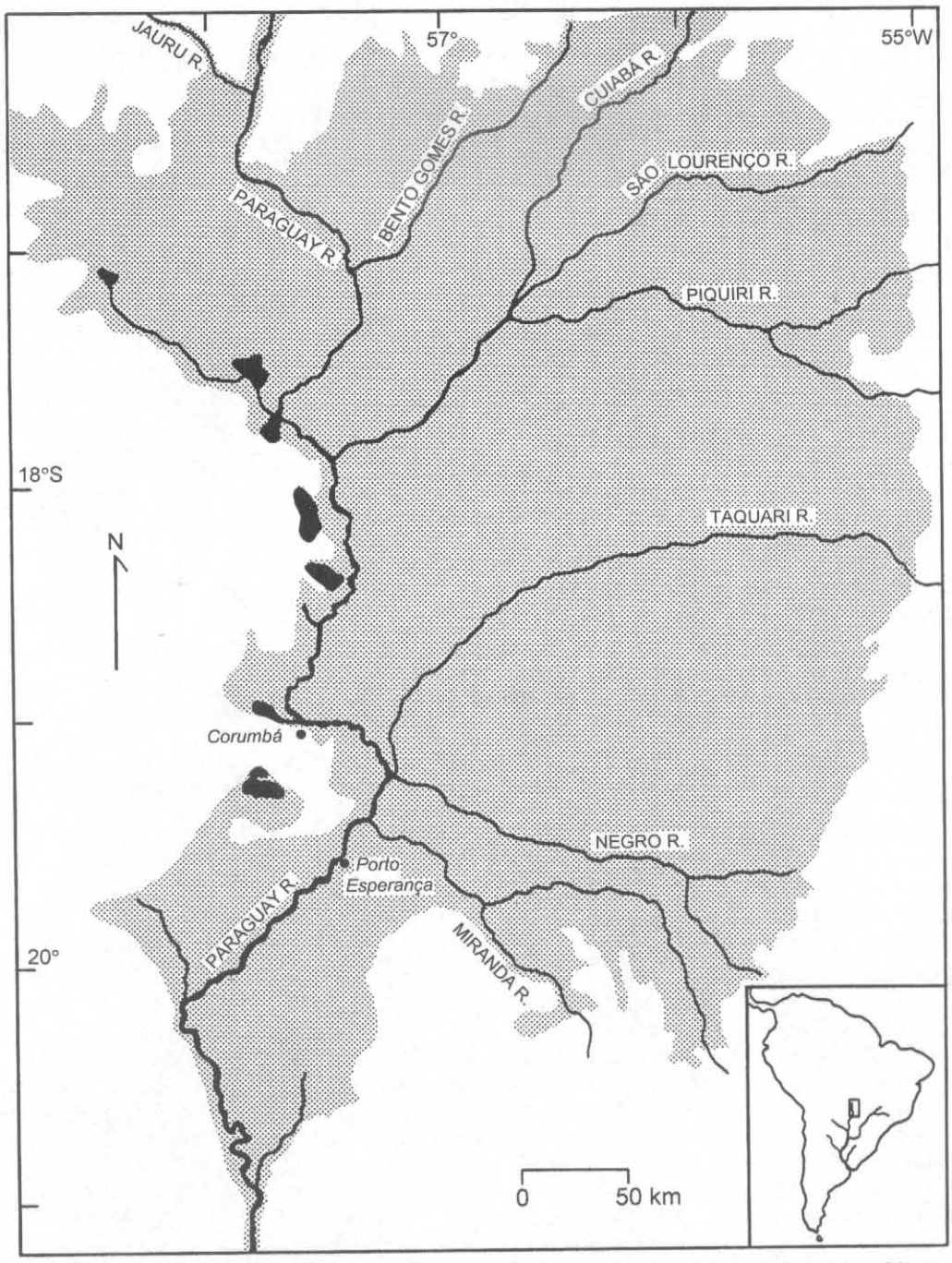

Fig. 1. Map of the upper Paraguay River and the Pantanal wetland (stippled area is subject to inundation). Most of the region is in Brazil, with smaller areas in Bolivia and Paraguay to the west of the Paraguay River. The Paraguay River was sampled just above Corumbá and above Porto Esperança.

forested for grazing or agricultural uses, but the floodplains are used mainly for cattle grazing during the dry season. On the floodplains, aquatic or semiaquatic vascular plants grow profusely during the flood season and are dominated by floating and rooted emergent forms that can tolerate fluctuating water levels (Prance and Schaller 1982). Many of these aquatic plant communities die back in the dry season—becoming replaced by terrestrial species—although some aquatic forms assume a terrestrial phase and remain dominant (Junk 1993). Natural river levees are often covered with a dense semideciduous gallery forest, behind which there are commonly lower-lying areas covered by marshes, shrublands, or palm forests.

The biogeochemistry of the Paraguay River remains little studied (Hamilton 1994). A few studies have examined the chemical composition of the river, sampling in the vicinity

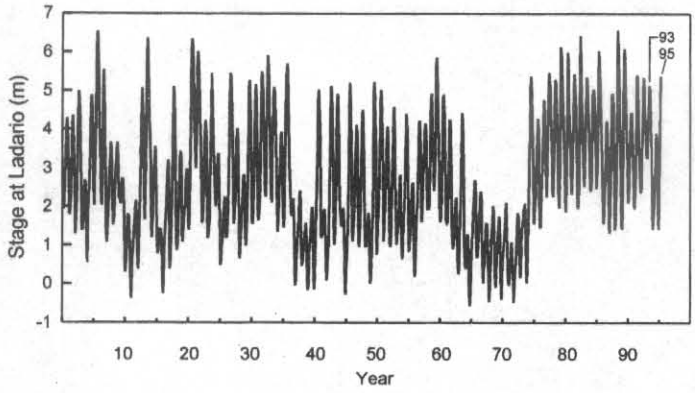

Fig. 2. Mean monthly stage of the Paraguay River at Ladário (near Corumbá) between January 1900 and March 1995. Two of the years for which data are analyzed in this study are marked on the plot. Stage was measured by the Brazilian Navy.

of Corumbá in the Pantanal (Alexandre 1982; Calheiros and Hamilton 1996) or close to its mouth, which is below the confluence of several other significant tributaries (Bonetto et al. 1981). Brazilian government sampling programs have measured sediment discharge of the rivers throughout the region (EDIBAP unpubl. rep.; Ponce 1995). Hamilton et al. (1995) analyzed the biogeochemistry of the wetland waters of the Pantanal.

Methods

The Paraguay River was sampled 1–2 km upstream of Corumbá and 2 km upstream of Porto Esperança (Fig. 1). Although the sampling period spanned 2 yr (1992–1993) at the Corumbá site and only 1 yr (1993) at the Porto Esperança site, we analyze data for the latter site here because it is downriver from all significant tributary inputs within the Pantanal and thus represents most of the export of water and materials from the Pantanal region. The Porto Esperança site was also better for transport estimates because almost all of the discharge flows within the main channel at that point.

Samples were collected from the Porto Esperança site at intervals of 4–6 weeks between December 1992 and November 1993. This sampling interval was judged to be acceptable based on the gradual changes in hydrochemistry that we had observed during the previous year of biweekly sampling at Corumbá. Surveys at the Porto Esperança site showed ions and gases in the river channel to be well mixed vertically, but that water from the Miranda River and its floodplain was not yet fully mixed across the channel, resulting in slightly elevated ion concentrations toward the left bank. Samples were therefore collected from middepth at three equally spaced points across the channel, and these were analyzed separately. Data presented in this study are means for the three sampling points.

The Paraguay River was also sampled at the Corumbá site on seven dates during an anoxic event from 15 February to 30 March 1995. These data will be compared to the regular sampling performed at the same site throughout 1992–1993, when the main channel of the river was not anoxic. Rivers flowing from surrounding uplands into the Pantanal were

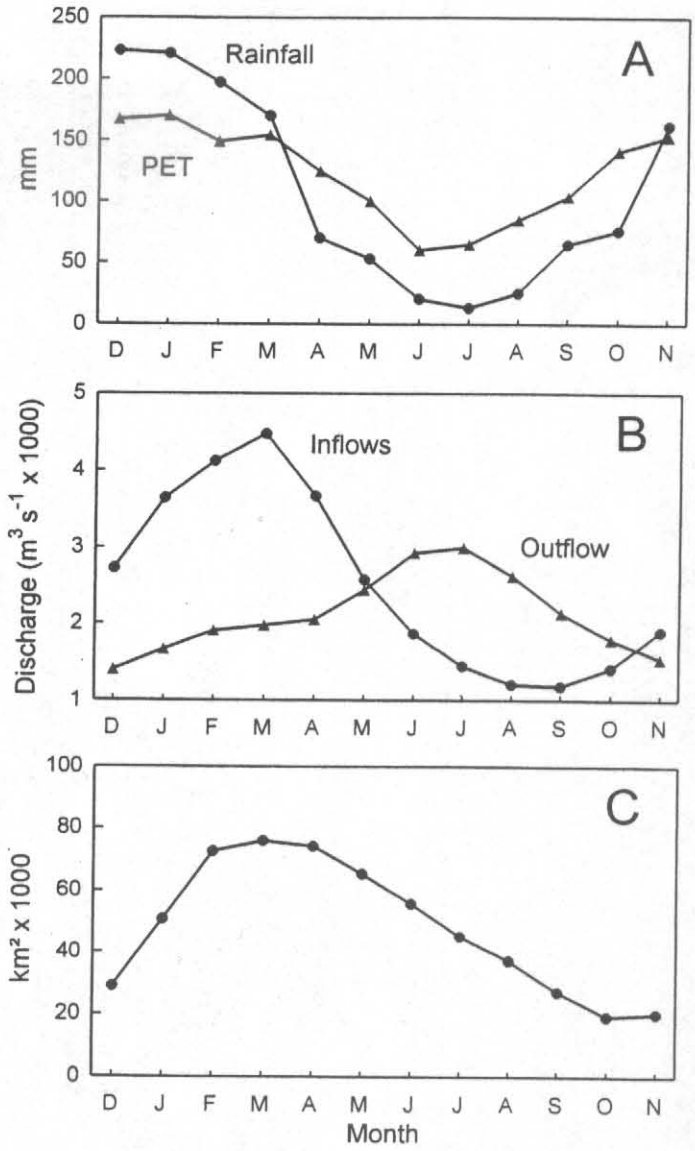

Fig. 3. Regional water fluxes in the Pantanal. A. Rainfall and Thornthwaite potential evapotranspiration (PET). Data are monthly means for four sites within the Pantanal, each of which has 3–6 yr of data during 1976–1982 (data from Cadavid Garcia 1984). B. Comparison of the sum of the 11 principal riverine inflows to the Pantanal with the outflow discharge at Porto Esperança. Data are monthly means for 3 yr (1974–1976); inflow data are from EDIBAP (unpubl. rep.) and outflow data were calculated from daily stage records using the rating curve from that period. C. Mean seasonal cycle of flooded area above Porto Esperança, determined from satellite observations of passive microwave emission (Hamilton et al. 1996).

sampled on occasion during their high-water phases. Most of these rivers were sampled close to the upland–floodplain boundary, with the exception of the Miranda River, which was sampled regularly at Passo do Lontra, located below the confluence of the Aquidauana River (the tributary of the Miranda River shown in Fig. 1).

Water samples were obtained with a vertical Van Dorn sampler, and filtration, pH measurement, and preservation of

Table 1. Summary of analytical methods, including definition of abbreviations used throughout the text.

Variable	Method	Reference
Sample filtration for solute analyses	Gelman Supor membrane filters (0.45-μm pore size)	—
Dissolved O_2 and temperature	Polarographic O_2 sensor with thermistor; Winkler analyses	Wetzel and Likens 1991
Dissolved CO_2	Calculated from pH, DIC, and/or Gran ANC	Skirrow 1975; Hamilton 1994
Dissolved inorganic carbon (DIC)	Acidification and gas chromatography	Stainton 1973; Hamilton 1994
Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe, Mn	Atomic absorption; standard protocols	—
Cl^- and SO_4^{2-}	Ion chromatography; standard protocols	—
Acid-neutralizing capacity (assumed ~HCO_3^-)	Gran titration between pH 4 and 3	Cantrell et al. 1990
Soluble silica (Si)	Molybdenum blue method; manual or by flow injection	Wetzel and Likens 1991
Dissolved organic C (DOC)	Persulfate digestion and gas chromatography	McDowell et al. 1987
pH	Closed-system measurement with low-ionic strength electrode	Hamilton 1994
NH_4^+	Phenolhypochlorite colorimetric method	Wetzel and Likens 1991
$NO_3^- + NO_2^-$	Cadmium reduction and colorimetric analysis	Wetzel and Likens 1991
Total dissolved N (TDN) and P (TDP)	Combined persulfate digestion and colorimetric analysis	Valderrama 1981
Particulate P (PP)	Ignition of material on glass-fiber filters; colorimetric analysis	Andersen 1976
Total suspended solids (TSS)	Gravimetric analysis on glass-fiber filters (1-μm pore size)	—
Specific conductance (Cond)	4-electrode cell; values corrected to 25°C	—
Particulate organic C (POC) and N (PON)	Elemental analyzer; glass-fiber filters; no acid pretreatment	—
Trace elements (except Fe and Mn)	Inductively coupled plasma mass spectrometry	*See text*

subsamples were performed on the day of collection. Sample processing and chemical analysis are summarized in Table 1 and detailed by Hamilton (1994) and Hamilton et al. (1995); a few additional measurements that were not included in those references are described below.

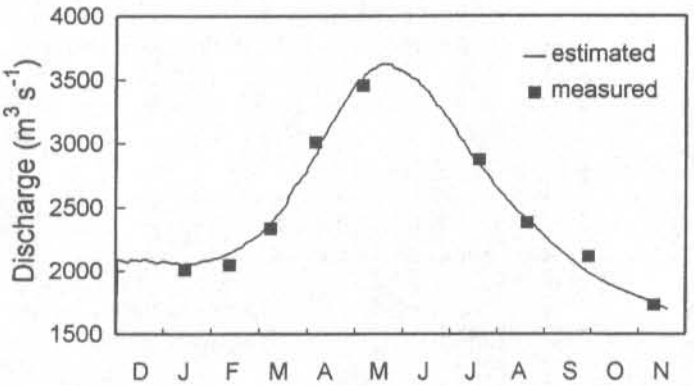

Fig. 4. Discharge hydrograph for the Paraguay River at Porto Esperança during the sampling period (December 1992–November 1993). Symbols show the discharge measurements used to produce a stage–discharge relation that estimated daily discharge (solid line) from daily stage records.

Discharge was determined on most collection dates. We measured velocity (means for 20 and 80% depth) at five equally spaced points across the channel, with an electromagnetic flowmeter suspended from an anchored boat. Discharge was calculated as the sum of the products of velocity and cross-sectional area for each subsection. Mean depth and velocity were calculated from discharge and the width and cross-sectional area of the channel. Previously published discharge data collected by Brazilian government agencies (e.g. EDIBAP unpubl. rep.) span mostly lower river stages than we observed, and published data extend only to 1979. We therefore used our 1993 discharge measurements to produce a stage–discharge relationship that predicts discharge at Porto Esperança from stage measured upriver at Ladário (near Corumbá), where the best stage record is available for the study period (Fig. 4). We used this rating curve to interpolate between measurement dates, obtaining daily discharge estimates for calculation of discharge-weighted means and elemental transport.

Our point samples of total suspended solids (TSS) from middepth probably underestimated the total sediment concentration because the vertical distribution of suspended sediments is nonuniform in rivers, with higher concentrations toward the bottom (Meade and Stevens 1990). The TSS concentrations for Porto Esperança provide an estimate of wash

load but do not reflect the bed material load and therefore provide only an approximate indication of the total sediment discharge in the river channel.

Dissolved (filterable) trace metals were determined by inductively coupled plasma mass spectrometry (ICP-MS) on samples from 1993 and 1995 that had been filtered (0.45-μm Supor membrane), preserved with ultrapure HNO_3 upon collection, and stored in new acid-washed polyethylene bottles. Analyses were performed in June 1995 on a VG PlasmaQuad instrument equipped with an ultrasonic nebulizer. Calibration was achieved by simultaneous analysis of 1.0- and 2.0-ppb standards containing most of the elements, and indium was added to the samples as an internal standard. Analysis of blanks poured in the field using the same bottles and acid did not reveal problems with contamination, although we did not test the nonmetallic Van Dorn sampler for leaching effects. Fe and Mn were measured by atomic absorption (flame or graphite furnace, depending on concentration) within 12 months of collection.

Total dissolved solids (TDS) was calculated from individual analyses, expressing concentrations as dry residue following Hem (1985), with the additional inclusion of organic matter estimated as mg dissolved organic carbon (DOC) liter^{-1} times 2.5. Acid-neutralizing capacity as determined by Gran titration was assumed to be equivalent to HCO_3^-. The concentration of ionized organic acids was estimated from pH and DOC using the model of Oliver et al. (1983).

Oxygen consumption assays were performed twice during the 1995 anoxic event with river water collected at the Corumbá sampling site. The nearly anoxic water was collected with minimal aeration by siphoning from ~10 cm beneath the surface in the middle of the river. Immediately afterward at the field laboratory, the sample was diluted with air-equilibrated deionized water to bring the O_2 concentration to 20–25% saturation. The sealed, entirely full 12-liter container was mixed by inversion; subsamples were then dispensed by siphon into glass 120-ml serum bottles, taking care to avoid aeration. Six of these bottles were randomly selected for immediate analysis of O_2 by Winkler titration, and triplicate sets of three samples were subsequently analyzed for O_2 over the course of incubation in the dark at 25°C. The first experiment (2–3 March) determined the time course of O_2 consumption. In the second experiment (7–8 March), we added N (10 μM as NH_4Cl), P (10 μM as KH_2PO_4), and organic carbon (18 μM C as sucrose) to sets of subsamples in an attempt to stimulate microbial respiration rates, measuring O_2 after an incubation period of ~6 h.

Discharge-weighted mean concentrations for the Paraguay River were calculated by linear interpolation of concentrations between sampling dates, summation of the products of daily discharges and concentrations over all days of the year, and division of the sum by the annual discharge (Lewis and Saunders 1989). Specific transport (kg ha^{-1} yr^{-1}) was computed by division of the total mass transport by the area of the drainage basin above Porto Esperança (363,500 km^2. EDIBAP unpubl. rep.).

Results

Discharge, concentrations, and transport—The discharge of the Paraguay River was much higher during the study than the previously reported mean discharge of 1,412 m^3 s^{-1} (EDIBAP unpubl. rep.). Our 1993 discharge measurements (Fig. 4), when used to develop an empirical stage–discharge relation that allows interpolation between sampling dates, yielded an annual mean of 2,500 m^3 s^{-1} for the study period. This discharge corresponds to a specific runoff rate of 6.9 liters s^{-1} km^{-2} or 217 mm yr^{-1}. The mean depth and velocity of the river ranged between 5.2 to 7.7 m and 0.56 to 0.82 m s^{-1} and show the same seasonal pattern as the discharge hydrograph.

We used our 1993 stage–discharge relation to calculate elemental transport rates because our data correspond with the chemical measurements and are representative of runoff during the nondrought conditions that have predominated during much of the past century (Fig. 2). Discharge-weighted mean concentrations and specific transport rates of chemical constituents in the Paraguay River at Porto Esperança are presented in Table 2. On the basis of its specific runoff and mean annual air temperature, the Paraguay River basin fits into Meybeck's tropical contrasté or savanna category. Table 2 provides data compiled by Meybeck on tropical savanna and global rivers for comparison. Insofar as possible, Meybeck's data represent rivers in their natural state with minimal anthropogenic interference and without sediment retention by dams (Meybeck 1988).

The Paraguay River carries water that is ionically dilute and low in suspended solids. Ca^{2+}, Mg^{2+}, and HCO_3^- are the dominant ions, Cl^- and SO_4^{2-} are present at relatively low concentrations, and the pH is circumneutral (Table 2). The sum of cations (558 μeq liter^{-1}) nearly equals the sum of anions (559 μeq liter^{-1}) when ionized organic acids are included, which are estimated at 39 μeq liter^{-1} (7% of the anion equivalents) and thus exceed the concentrations of Cl^- and SO_4^{2-}. After including estimates for organic acids, analyses for individual dates show cation : anion charge ratios of 0.96–1.03 and good agreement between measured and calculated conductance (Miller et al. 1988), indicating that our ion analyses were accurate and likely included all of the principal ionized species other than organic acids.

Total C, N, and P concentrations in the Paraguay River are low compared with other rivers (Table 2), and this is explained largely by the lower concentrations of particulate forms of these elements. Carbon and nitrogen are dominated by dissolved forms, but phosphorus is primarily particulate. Occasional analyses of NO_3^- and NH_4^+ indicated that most of the soluble N is present in organic form. The concentration of soluble Si is high compared with global rivers but is close to the mean for savanna rivers.

The Paraguay River seems to be lower in TSS than comparable rivers (Table 2), although sampling differences make quantitative comparisons of sediment concentrations difficult (Meade 1988). The TSS concentration in Table 2 (12.5 mg liter^{-1}) is for the middle of the water column, corresponding with the chemical analyses. The particulate material carried in the water column of the Paraguay River averages 4.9% C by weight (Table 2), corresponding to ~12% organic matter (Cahill et al. 1987), which is typical of rivers with comparably low TSS concentrations (Ittekkot 1988). The C:N mass ratio of the particulate material averaged 8.5, which is close to the global mean. Algae were sometimes visible in

Table 2. Discharge-weighted mean concentrations (mg liter^{-1}) and specific transport (kg ha^{-1} yr^{-1}) of the Paraguay River (PR) at Porto Esperança, compared with mean values for tropical savanna rivers (SR) and global rivers (GR) from Meybeck (1979, 1982, 1988). Acid-neutralizing capacity was assumed equal to HCO_3^-, and TSS is the concentration at middepth. Silica is expressed as Si rather than SiO_2.

	Concentration			Transport		
Variable	PR	SR	GR	PR	SR	GR
Ca^{2+}	4.96	6.3	13.4	10.77	10.0	50.2
Mg^{2+}	2.39	2.6	3.25	5.19	4.2	12.5
Na^+	1.58	5.0	5.15	3.43	8.1	19.3
K^+	1.73	1.8	1.3	3.76	3.0	4.9
HCO_3^-	30.89	30.0	52	67.00	53.5	194.7
Cl^-	0.35	4.2	5.75	0.76	6.8	21.5
SO_4^{2-}	0.14	3.7	8.25	0.31	4.3	30.9
Free CO_2-C	2.04	—	—	4.42	—	—
DOC	4.00	—	5.50	8.69	—	—
POC	0.61	—	4.50	1.33	—	—
DOC + POC	4.61	—	10.00	10.02	7	30
TDN	0.264	—	0.375	0.57	—	—
PN	0.072	—	~0.5	0.16	—	—
TDN + PN	0.336	—	~0.8	0.73	—	~3
TDP	0.012	—	—	0.025	—	—
PP	0.110	—	—	0.240	—	—
TDP + PP	0.122	—	~0.5	0.265	—	~2
Si	7.46	6.73	4.86	16.18	11.0	18.2
TSS	12.5	—	450	27.12	900	1,762
Total Fe	1.11	—	—	2.40	—	—
TDS	52.9	—	—	114	—	—
Conductance	56 μS cm^{-1}	—	—	—	—	—
pH	6.89	—	—	—	—	—

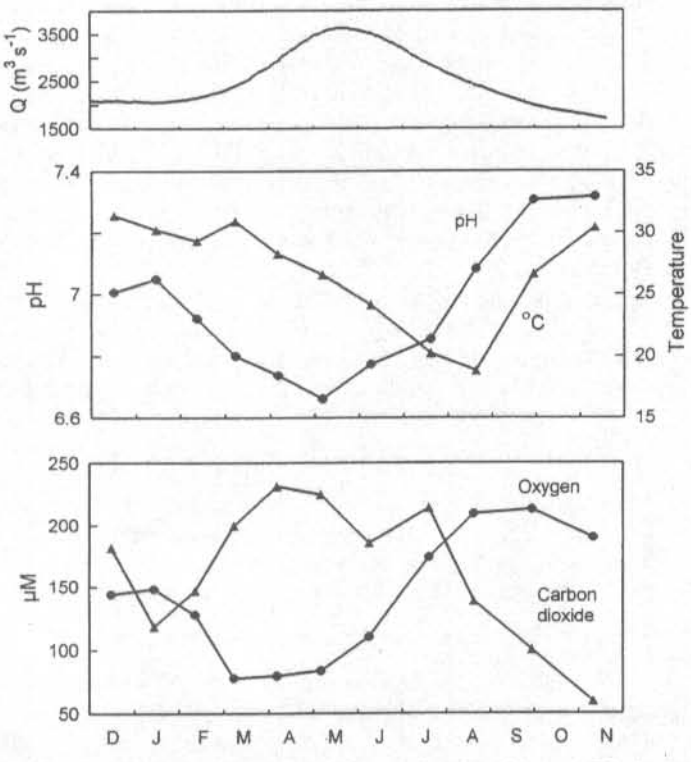

Fig. 5. Water temperature, pH, and dissolved O_2 and CO_2 in the Paraguay River at Porto Esperança. Discharge (Q) from Fig. 4 is shown along the top.

water samples, particularly at falling stages, but did not appear to comprise most of the organic material. Total particulate Fe, as measured by atomic absorption in acidified samples, comprises a substantial fraction of the total particulate material, averaging 5.9% by weight (filterable Fe was subtracted from Fe measured in unfiltered samples to estimate total particulate Fe). Particulate carbonates that are soluble in acid are essentially absent from the suspended material in the Paraguay River, and the calcite disequilibrium index indicates consistent undersaturation in the river (range, −1.8 to −2.5; Hamilton 1994).

Seasonal patterns—Most chemical variables show gradual seasonal changes over the course of the year in the Paraguay River at Porto Esperança (Figs. 5–8). Gradual changes were also observed in our more frequent sampling of the river above Corumbá (Hamilton unpubl. data), which displayed seasonal changes during the 2 yr of sampling that resemble those observed at Porto Esperança during 1993.

Temperature and the biologically active dissolved gases have pronounced seasonal patterns in the river (Fig. 5). Dissolved O_2 was undersaturated and CO_2 was highly oversaturated with respect to the atmosphere: for the 11 sampling dates, the mean O_2 concentration was 142 μM (=4.5 mg liter^{-1}) and the mean CO_2 concentration was 164 μM (=7.2 mg liter^{-1} as CO_2), corresponding to a CO_2 partial pressure of 5,040 ppmv (range, 2,000–7,400 ppmv). Seasonal changes in pH are driven largely by changes in dissolved CO_2. In the Paraguay River at both sampling sites as well as in the floodplain waters, the period of greatest deviation

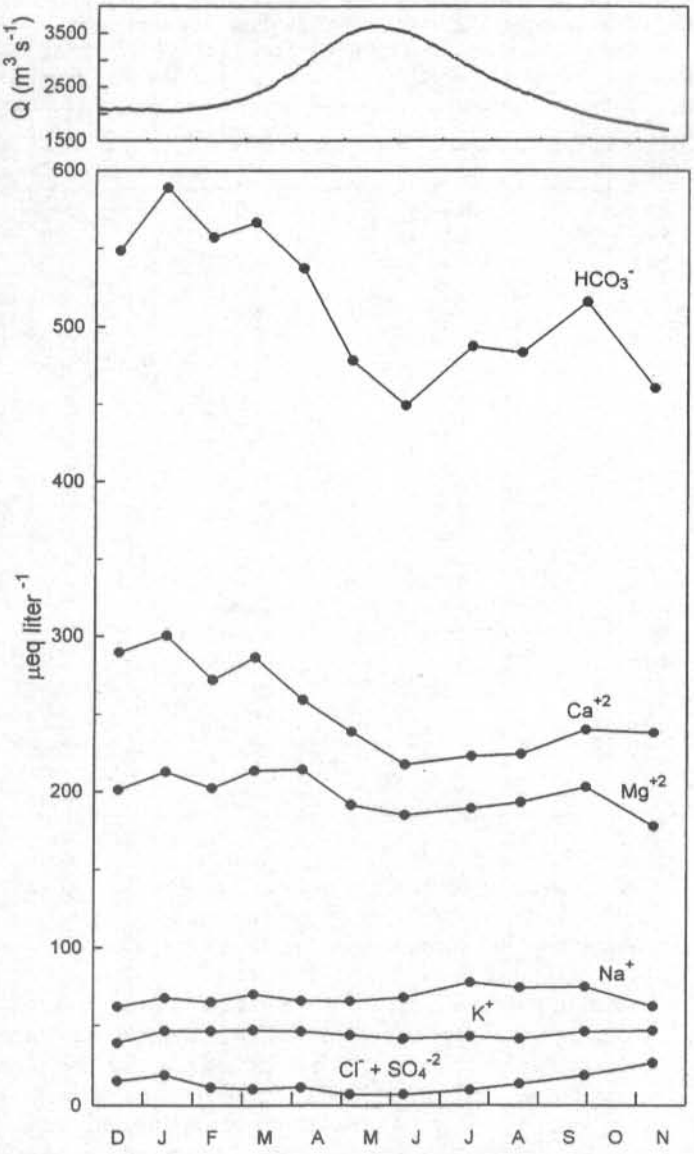

Fig. 6. Major ionic solutes in the Paraguay River at Porto Esperança. Discharge (Q) from Fig. 4 is shown along the top.

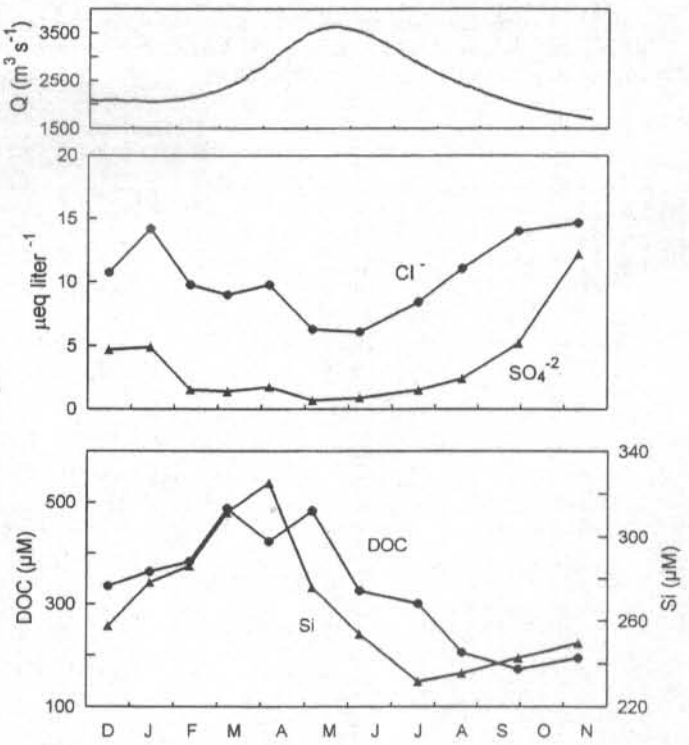

Fig. 7. Cl^-, SO_4^{-2}, soluble Si, and DOC in the Paraguay River at Porto Esperança. Discharge (Q) from Fig. 4 is shown along the top.

of O_2 and CO_2 concentrations from atmospheric equilibrium corresponds with rising water levels, as the flood waters first contact most of the floodplain (Fig. 5; also Hamilton 1994; Calheiros and Hamilton 1996).

Seasonal variation is also evident for the major ions (Figs. 6, 7). HCO_3^- and Ca^{2+} had higher concentrations during the rising limb of the hydrograph than during the falling limb, whereas K^+, Na^+, and Mg^{2+} varied relatively little. Concentrations of Cl^- and SO_4^{2-} were lowest at peak discharge, and the ratio of Cl^- to SO_4^{2-} changed seasonally (Fig. 7). Soluble Si and DOC had higher concentrations during the rising limb of the hydrograph, coincident with the minimum O_2 concentrations (Fig. 7).

The concentration of TSS at middepth in the water column is inversely correlated with discharge (Fig. 8), even though the mean velocity in the river channel increased at high discharge. Rivers flowing into the Pantanal from the uplands do not show this pattern, which probably results largely from the sedimentation of particulates during residence of water in floodplain environments (Ponce 1995; Hamilton et al. 1996). At the beginning of the sampling period (December), the river was still in contact with some of its floodplain. By the end of the sampling period in November, when there was little floodplain inundation along the river, TSS had increased considerably and the river water appeared turbid and clay colored. Concentrations of particulate C, N, and P showed seasonal patterns that resemble that of TSS (data not shown).

The composition of the particulate matter changes seasonally. Concentrations of total Fe and Mn had very similar seasonal patterns with minima at the falling limb of the hydrograph (Fig. 8). Analysis of filtered samples indicated that most of the total Fe and Mn was removed by filtration through a 0.45-μm membrane. Fe comprised a significant proportion of the TSS, especially during February and March when the river water appeared distinctly rust colored (Fig. 8). Organic C was also an important component of the TSS, with the highest percentage during the falling limb of the hydrograph when TSS concentrations were relatively low.

Observation of a natural anoxic event—The seasonal patterns described above show that elevated concentrations of solutes and greater deviations of dissolved gases from atmospheric equilibrium correspond with the initial contact of river water with the previously dry floodplain. The dry season in late 1992, which preceded the year of regular sam-

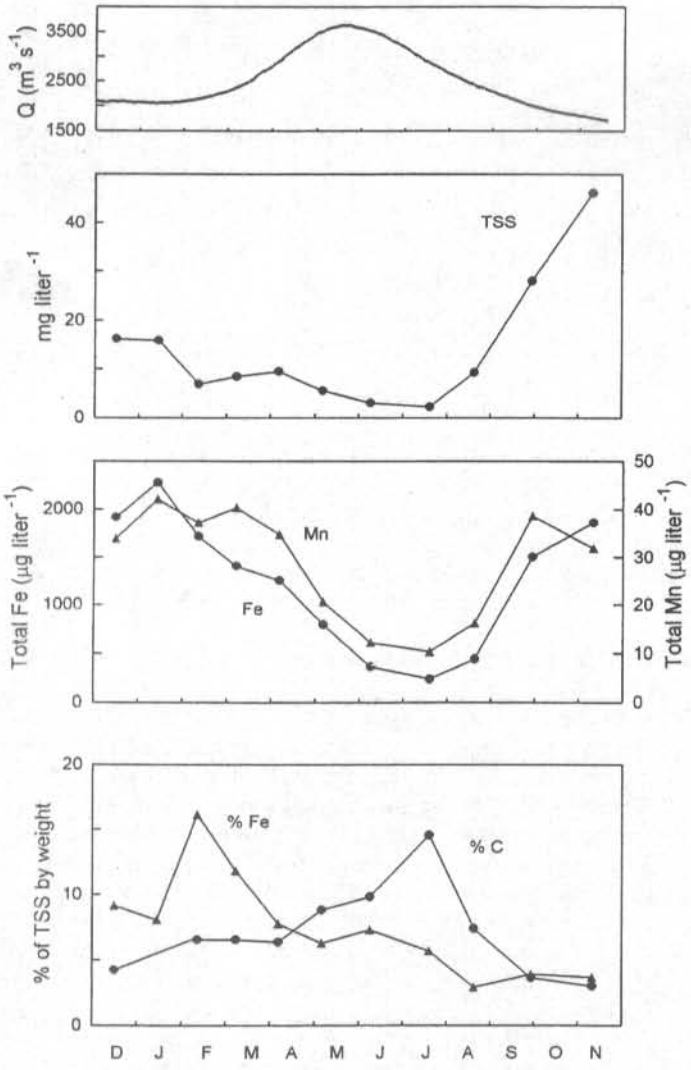

Fig. 8. TSS (at middepth), total Fe and Mn, and the percentage contribution of Fe and organic C to TSS in the Paraguay River at Porto Esperança. Discharge (Q) from Fig. 4 is shown along the top.

pling in 1993, was particularly wet, as is evident from the river stage record (Fig. 2). The dry season of late 1994 was more marked, although not unusually so. Sampling of the Paraguay River at Corumbá in early 1995, as the rising waters first contacted the previously dry floodplain, revealed that the river water became virtually anoxic throughout the water column for a 6-week period (15 February–30 March; Table 3).

During the anoxic event in 1995 we observed the mortality of many species of fishes in the river and in floodplain waters. Fish kills are known to occur occasionally in the Pantanal (Calheiros and Hamilton 1996), particularly after severe dry seasons, but they did not occur in the river during our previous sampling in 1992–1993. The distribution of reported fish kills provides an indication of the regional extent of the phenomenon. According to local residents, the fish kills began in January 1995 in the northern Pantanal, near the confluence of the upper Paraguay and Bento Gomes rivers (Fig. 1). The fish kills extended into the floodplain and

Table 3. Changes in the hydrochemistry of the Paraguay River above Corumbá during a natural anoxic event (February–March 1995) compared with the range observed during two seasonal cycles (February 1992–November 1993) in which the river remained oxic throughout the year. The table shows ranges for oxic water and means for anoxic water. The number of measurement dates is 29 for oxic water and seven for anoxic water unless noted in parentheses; some analytes were determined for only a few dates that represented the seasonal cycle. Most of these data are for the Corumbá sampling site, which is upriver of the Porto Esperança site (na, not available).

	Oxic water	Anoxic water
Cond. (µS cm^{-1})	43–52	63
Dissolved O_2 (µM)	67–246	<1
Dissolved CO_2 (µM)	37–314	430
Dissolved CH_4 (µM)	0.1–0.9	17
pH	6.52–7.36	6.55
Ca^{2+} (µeq liter^{-1})	157–241	271
Mg^{2+} (µeq liter^{-1})	128–189	210
Na^+ (µeq liter^{-1})	45–83	54
K^+ (µeq liter^{-1})	35–51	86
HCO_3^- (µeq liter^{-1})	337–461	571
Cl^- (µeq liter^{-1})	3.9–17	21
SO_4^{2-} (µeq liter^{-1})	0.8–13	1.3
Si (µM)	192–273	290
DOC (µM)	164–692	935
NH_4^+ (µM)	na	<1
$NO_3^- + NO_2^-$ (µM)	0.6–5.5 (4 dates)	<1 (6 dates)
TDN (µM)	13–24 (11 dates)*	25
TDP (µM)	<1 (11 dates)*	0.8

* Measured at the Porto Esperança sampling site.

generally progressed in the downriver direction, eventually reaching Corumbá and later developing in Nabileque—the region downriver of Porto Esperança. By that time the fish kills in the northernmost areas, which had lasted about 2 months, had ceased. The stage of the Paraguay River at Ladário increased from 3.8 to 6.2 m over the course of the anoxic event in the river near Corumbá.

During the fish kills the water was dark, due to the elevated DOC and the low levels of inorganic particulates and algae, and stagnant floodplain waters had an oily surface film. Precipitated Fe oxides were abundant in the surface film and also became visible in the river water as O_2 concentrations increased at the end of the event. As river water inundated the floodplain, some of the terrestrial vegetation that had colonized the floodplain during the dry season died, and the remains of aquatic plants from the previous flood season were flooded for the first time since the water had receded. At the same time, however, emergent vascular plants responded to the flooding with rapid growth.

Our observations of the changes in hydrochemistry during the anoxic event were qualitatively similar to those observed at rising stages in previous years but reached more extreme levels (Table 3). Concentrations of most of the major ions (except Na^+ and SO_4^{2-}), dissolved CO_2 and CH_4, DOC, and Si exceeded the annual range that had been observed previously. Dissolved N and P did not increase in concentration.

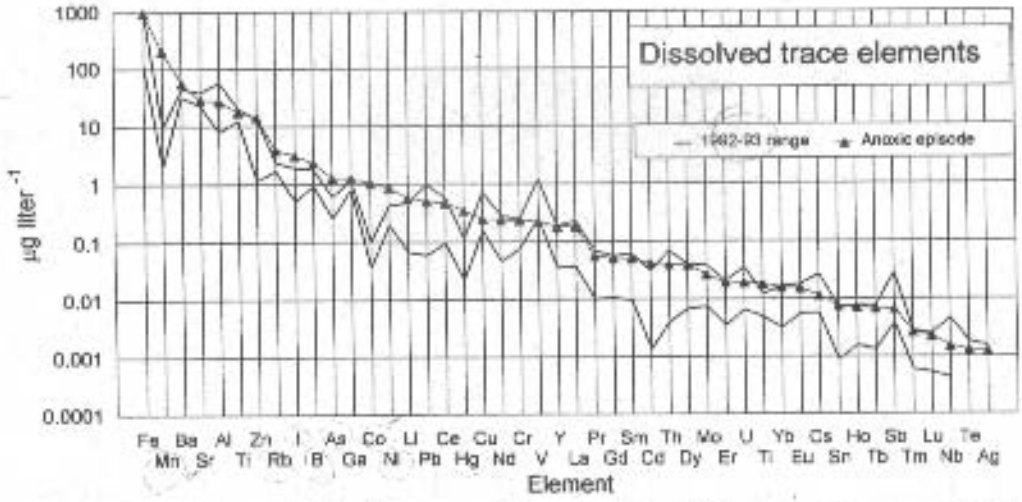

Fig. 9. Trace elements in filtered Paraguay River water. The solid lines show the range observed in the Paraguay River at Porto Esperança (10 dates in 1993), and the symbols show the mean for three dates during the anoxic event of February–March 1995 (samples from above Corumbá).

Dissolved sulfide was not detectable (<0.5 µM) by the methylene blue method during the anoxic event nor was it found during 1993 in a survey of floodplain waters throughout the southern Pantanal (Hamilton 1994).

Dissolved trace elements were measured in samples from the 1995 anoxic event as well as in samples collected throughout 1993 from the Paraguay River at Porto Esperança to reveal increases that might have contributed to the fish mortality (Fig. 9) The concentrations of most elements did not greatly exceed their previously observed ranges during the anoxic event. Two exceptions are Mn and Co, which increased by about an order of magnitude. Other elements that increased in concentration include Hg, Ni, As, B, I, and Rb.

In the incubations of river water in bottles, the rate of O_2 consumption tapered off over time (Fig. 10). In the first experiment the O_2 saturation in the samples had been raised from ~3 to 23% by mixing with air-equilibrated deionized water. The average rate of O_2 consumption over the ensuing 24-h period was 1.6 µM h^{-1}, and during the first 2 h the rate was 7.2 µM h^{-1}. In the second experiment 5 d later, we observed a slightly lower rate of O_2 consumption with no detectable stimulation of respiration by the addition of NH_4^+, PO_4^{3-}, or organic C (as sucrose), either separately or together (Table 4).

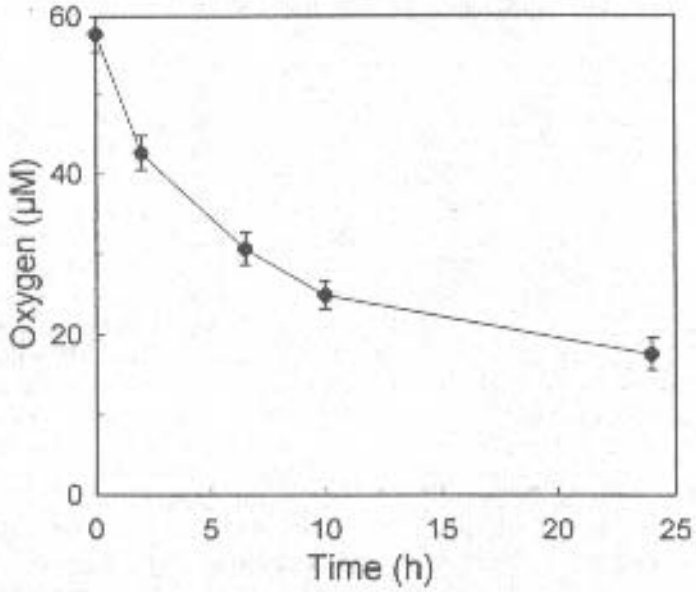

Fig. 10. Consumption of dissolved O_2 in bottle incubations of river water during the 1995 anoxic event (means ± SD). After O_2-saturated water was added, the rate of O_2 consumption tapered off over time.

Chemistry of inflowing rivers—Information on the hydrochemistry and discharge of inflowing rivers is summarized in Table 5. Considerable variation is evident among the tributary rivers, reflecting the variable geology of their upland drainage basins. In particular, the abundance of calcareous rocks in the Miranda River basin results in elevated ion concentrations. In contrast, rocks in the basins of the Taquari

Table 4. Results of an O_2 consumption assay performed with Paraguay River water collected during the 1995 anoxic event (7 March). The O_2 consumption rate over the 5.75-h period (3.2 µM h^{-1}) was slightly lower than that observed over the first 6 h in the first experiment (4.0 µM h^{-1}; Fig. 10).

Treatment	µM O_2 (mean ± SD)
Initial	55±2
Final (after 5.75 h):	
No additions	37±1
NH_4^+ added	37±3
PO_4^{3-} added	37±1
Organic C added	38±2
All of above added	36±1

Table 5. Hydrochemistry and discharge of major inflows to the Pantanal. Solute data are based on occasional samples that we collected at high water in 1992, 1993, or 1995. Mean discharges (Q) are long-term means from EDIBAP (unpubl. rep.) and are included here to indicate the relative importance of the various rivers (na, data not available). River abbreviations: JAUR, Jauru; UPAR, upper Paraguay; CUIA, Cuiabá; BENT, Bento Gomes; SAOL, São Lourenço; PIQU, Piquiri; TAQU, Taquari; MIRA, Miranda; NEGR, Negro.

	JAUR	UPAR	CUIA	BENT	SAOL	PIQU	TAQU	MIRA	NEGR
Q (m^3 s^{-1})	86	382	286	7	113	130	268	151	56
No. samples	2	2	2	2	3	9	2	12	1
Cond. (μS cm^{-1})	87	45	53	47	44	11	29	155	30
Ca^{2+} (μeq $liter^{-1}$)	374	207	234	139	140	29	125	902	70
Mg^{2+} (μeq $liter^{-1}$)	246	165	178	176	114	26	67	527	85
Na^{+} (μeq $liter^{-1}$)	214	51	81	111	75	14	23	109	25
K^{+} (μeq $liter^{-1}$)	56	27	32	46	81	17	57	55	70
HCO_3^- (μeq $liter^{-1}$)	840	423	468	402	326	80	260	1,516	180
Cl^- (μeq $liter^{-1}$)	16	8	15	32	46	5	4	26	9
SO_4^{2-} (μeq $liter^{-1}$)	20	5	13	1	18	3	5	13	15
Si (μM)	315	204	186	225	252	171	309	393	238
DOC (μM)	999	508	91	455	105	112	109	291	97

and Piquiri rivers are mostly sandstones that yield relatively few solutes to the runoff, but these basins export high concentrations of sediment (RADAMBRASIL 1982; Ponce 1995). The most dilute runoff is produced in the Piquiri drainage basin; in the Correntes River, a tributary of the Piquiri, specific conductance was as low as 3.5 μS cm^{-1}.

Discussion

The biogeochemistry of the upper Paraguay River is strongly influenced by its contact with the floodplains of the Pantanal. The high water storage capacity of the floodplain dampens the discharge hydrograph of the river (Fig. 3) and modulates short-term changes in the hydrochemistry of the river. Contact of river water with the floodplain also results in hydrochemical changes, the most important of which include consumption of dissolved O_2, retention of sediments and particulate organic material, and transformation and loss of inorganic nutrients. These floodplain effects are discussed below. Additionally, we present a regional mass balance analysis which suggests that the floodplains have little effect on the export of most major solutes from the drainage basin, and that most chemical weathering of minerals takes place in the upland drainage basins.

Oxygen depletion and associated changes—The natural anoxic event described here appears to be unprecedented in the literature on other large rivers (Kempe 1982), although some smaller tropical rivers that flow across extensive floodplains are known to become depleted in dissolved O_2 at rising water (Townsend 1994). We observed anoxia in the Paraguay River at Corumbá in only 1 of the 3 years of sampling, but local inhabitants attest to the occasional occurrence of fish kills, and the river stage record shows that the hydrological conditions that preceded the 1995 anoxic event are common (Fig. 2). In general, it appears that in densely vegetated floodplains such as those of the Paraguay, Amazon, and Orinoco rivers, net O_2 consumption by the aquatic environment potentially results in deoxygenation of the river water (Richey et al. 1988; Vásquez 1992; Hamilton et al. 1995). Rivers in which a large proportion of the discharge contacts floodplain environments with abundant emergent vegetation are thus most likely to become depleted in O_2.

The effects of the floodplain on the river might be expected to be strongest at the highest river levels, when the exchange of water between the floodplain and the river is greatest, rather than at rising stages. Also, the ability of air–water gas exchange to reaerate floodplain and river waters is diminished as the depth of the water column increases (Devol et al. 1995). In the Amazon River, which also has extensive floodplains, minimum O_2 concentrations (to ~100 μM) correspond with maximum stage (Devol et al. 1995), whereas respiration rates for suspended bacteria are maximal at low stages (Benner et al. 1995). The results of this study indicate that some of the effects of the floodplain on the Paraguay River, such as O_2 consumption (Fig. 5), are most marked during the rising limb of the hydrograph and are less evident at equivalent stages during the falling limb.

Two additional factors may explain the timing of the floodplain effects in the Pantanal. One is that leaching of soils and detritus and decomposition of labile organic matter are likely to be greater upon initial contact of flood waters with the previously dry floodplain, which contains abundant plant remains from the previous wet season as well as terrestrial plants that do not withstand flooding (Junk et al. 1989; Calheiros and Hamilton 1996). Another factor that may be important is the seasonal cycle of temperature; water temperature typically falls from ~30°C to 15–20°C or less over the course of the flood wave (Fig. 5; Hamilton 1994), which would considerably reduce rates of aquatic metabolism, and the stronger cold fronts typical of June–August correspond with the senescence of many of the dominant species of emergent vascular plants in floodplain waters (Da Silva 1990). Senescence of these emergent plant populations may result in more organic matter for aquatic decomposition, but it would also reduce the demand for dissolved O_2 by their submersed roots (Hamilton et al. 1995) and increase rates of air–water gas exchange by the reduction of their dense canopies. Light penetration into the water column increases with the demise of the plant canopies, allowing greater growth of submersed vascular plants and algae and thereby shifting the overall aquatic metabolism toward a

more autotrophic state. Thus the interaction of these factors could produce the observed seasonal pattern of maximum deoxygenation and leaching of solutes at rising water in the Paraguay River, followed by higher O_2 concentrations and lower solute inputs from the floodplain during peak and falling stages.

Retention of riverborne sediments and particulate organic material, in contrast to the other floodplain effects, seems greatest at maximum river stages, when concentrations of TSS and particulate forms of C, N, and P were minimal despite the increased velocity of the river (Fig. 8). Sedimentation in quiescent floodplain environments may be a largely physical phenomenon that would have its greatest effect on the sediment load of the river at the highest stages when the largest proportion of riverine discharge passes through the floodplains. The difference between sediment discharge of the rivers flowing into the Pantanal and the sediment discharge of the Paraguay River at Porto Esperança shows that much of the total fluvial sediment inputs to the Pantanal is retained on the floodplains (Ponce 1995). The inverse correlation between TSS concentrations and discharge in the Paraguay River has rarely been reported for large rivers, which typically display maximum sediment concentrations and transport at high discharges (e.g. Meade 1988; Lewis and Saunders 1989); its occurrence in the Paraguay River underscores the importance of the floodplains in this riverine system.

Increased concentrations of free CO_2 accompany O_2 depletion in the Paraguay River, and significantly decrease the pH of the river water (Fig. 5). The annual mean partial pressure of 5,040 ppmv CO_2 is at the upper end of the range in a compilation of CO_2 data for 24 large rivers by Kempe (1982). Among major rivers of the world, comparably high concentrations have been reported only in polluted rivers of densely populated regions and in the Paraná River below the confluence with the Paraguay River (Depetris and Kempe 1990). The high CO_2 concentrations in the Paraguay River are explained by the combination of high rates of heterotrophic metabolism by vascular plants and microbes, reduced air–water gas exchange in floodplain environments, and the absence of readily soluble particulate carbonates to react with the free CO_2 (Kempe 1982; Hamilton et al. 1995). Under these conditions, dissolved CO_2 concentrations reflect a quasi-steady state in which net biological generation of CO_2 is balanced by gas evasion to the atmosphere. Comparison of O_2 and CO_2 deviations from atmospheric equilibrium shows considerable "excess CO_2" that cannot be accounted for by the observed consumption of dissolved O_2; the sources of this CO_2 probably include root respiration by aquatic vascular plants as well as anaerobic bacterial metabolism, as discussed by Hamilton et al. (1995) and Devol et al. (1995).

The O_2 consumption rates measured in the bottle assays suggest that O_2 consumption by the river water could account for the observed O_2 depletion during the anoxic event, although it is possible that the increased O_2 availability in the assays stimulated oxidation rates compared to the in situ conditions. The first assay showed high O_2 consumption rates at first, but these rates were not sustained for long under the conditions of the experiment, even though O_2 concentrations remained adequate to support aerobic respiration (Fig. 10). Addition of labile organic carbon and inorganic N and P failed to stimulate O_2 consumption rates in the river water, suggesting that these factors were not limiting. These observations contrast with results from the Amazon River, where respiration rates were observed to remain constant in bottle incubations for many hours and were stimulated by addition of organic carbon (Benner et al. 1995). The O_2 consumption rate that we observed during the first 2 h of the experiment (7.2 μM h^{-1}) is much higher than the range observed over the course of the year in the Amazon River (0.1–1.6 μM h^{-1}: Devol et al. 1995).

The rate of O_2 consumption required to maintain O_2 concentrations near zero in the river can be estimated if we assume that air–water gas exchange would continually replenish the O_2 (Devol et al. 1995). The rate of O_2 invasion across the air–water interface (F) can be estimated from the stagnant-boundary-layer model of gas exchange (Broecker and Peng 1982):

$$F = D/z([O_2]_{eq} - [O_2]_{obs}),$$

where D is the molecular diffusion coefficient for O_2 (2.25×10^{-4} m^2 d^{-1} at 30°C), z is the thickness of the theoretical boundary layer in m, $[O_2]_{eq}$ is the concentration of O_2 at atmospheric equilibrium, and $[O_2]_{obs}$ is the concentration observed in the river (nearly zero in this case). If we assume that the theoretical boundary-layer thickness for large rivers is in the range of 50–100 μm (Devol et al. 1987, 1995), the rate of O_2 invasion into anoxic water would be 0.6–1.1 mol m^{-2} d^{-1}. Division of this rate by the mean depth of the river above Corumbá (~8 m) yields the equivalent volumetric rate of O_2 consumption that would be required to balance the O_2 invasion. The river water would therefore have to consume O_2 at a rate of 3–6 μM h^{-1} to maintain the anoxic conditions, which is comparable to the initial rate that we measured in the river water during the anoxic event, providing further evidence that most of the O_2 was consumed in the water column rather than in the sediments or in the adjacent floodplain.

The exponential decline over time in the rate of O_2 consumption in the bottles (Fig. 10) suggests that the processes consuming O_2 became limited by the depletion of substrates or reactants. However, the observation that O_2 consumption was not stimulated by additions of carbohydrate or available N and P (Table 4) suggests that some other factor must have become limiting and that aerobic respiration by microbes may not have been responsible for the O_2 consumption. Two alternative possibilities are inorganic chemical oxidations and CH_4 oxidation. The potential inorganic reductant that was most abundant in the river water during the anoxic event was Fe (Table 3, Fig. 9). The concentrations of filterable and total Fe as measured by atomic absorption were 26 and 70 μM near the time of the experiments (5 March) and had varied little during the previous 2 weeks. A significant fraction of the oxidizable Fe(II) in freshwaters can exist in particulate as well as dissolved phases (Lovely 1991), and the oxidation of Fe(II) is rapid at circumneutral pH (Stumm and Morgan 1981). Even if all of the 70 μM of Fe were initially present as Fe(II), its oxidation to Fe(III) could only account for ~17 μM of the ~40 μM of O_2 consumed over the course

of the first experiment (Fig. 10), because ~1 mole of O_2 is consumed for every 4 moles of Fe(II) that are oxidized (Stumm and Morgan 1981; Balistrieri et al. 1992). Thus, Fe oxidation could have been significant but the concentration initially present in the water was insufficient to account fully for the O_2 consumption observed in the bottles.

Methane oxidation is carried out by specialized bacteria in hypoxic waters that are generally unable to utilize more complex organic substrates such as carbohydrates (Cicerone and Oremland 1988); thus, the addition of sucrose to the bottle incubations might not have affected the activity of CH_4 oxidizers. The concentration of dissolved CH_4 in the river was 31 μM near the time of the experiments (mean for 27 February and 5 March). The overall reaction catalyzed by CH_4 oxidizers consumes 8 moles of O_2 for every 5 moles of CH_4 consumed (Wetzel 1983). The oxidation of 31 μM of CH_4 by methanotrophic bacteria would have consumed ~50 μM of dissolved O_2, and thus CH_4 oxidation alone can account for the O_2 consumption observed in the bottles. Oxygen depletion by the microbial oxidation of CH_4 has not been implicated in the literature as a cause of fish kills, but dissolved CH_4 is rarely measured in fisheries investigations.

The maintenance of such high rates of O_2 consumption in the river, whether due primarily to chemical or biological demand, must have required a continual source of reduced inorganic substances or CH_4 to the river water that was not present in the bottle assays. Contact of the river with the floodplain is the likely cause of the elevated rates of O_2 consumption in the river. Evidence for the role of the floodplain is provided by the following observations: O_2 became depleted in reaches that receive floodplain waters returning to the river but not in reaches that mainly lose water to the floodplain; floodplain waters tend to be depleted in dissolved O_2 and have high concentrations of dissolved CH_4, particularly upon initial inundation but also at other times (Hamilton et al. 1995; Calheiros and Hamilton 1996); and the surface area of the bottom of the river channel was not changing around the time of the anoxic event, whereas the area of inundated floodplain was rapidly increasing because the river had breached its banks.

On the basis of the limited data available, the concentrations of inorganic N and P seem to be lower in the Paraguay River than in similar rivers that lack such extensive floodplains (Table 2). This is expected because several studies have demonstrated reductions in concentrations of nutrients as river water passes through floodplain environments, where processes such as sedimentation, biotic assimilation, and denitrification can be important (e.g. Engle and Melack 1993; Hamilton and Lewis 1987, 1990). In other large rivers such as the Amazon and Orinoco, however, it is not clear whether there is enough contact of river water with the floodplain to reduce substantially the concentrations of inorganic N and P carried by the rivers above their deltas (Lewis and Saunders 1989; Devol et al. 1995).

Elevated concentrations of inorganic N and P were not observed during the anoxic event in the Paraguay River (Table 3). This observation is interesting because concentrations of PO_4^{3-} and NH_4^+ are commonly elevated in anoxic waters of lakes and eutrophic rivers, where sources such as decomposition of organic matter and release from the sediments typically exceed rates of autotrophic nutrient uptake (Wetzel 1983). The low nutrient concentrations in anoxic waters of the Pantanal may be explained by the abundance of emergent vascular plants with their roots suspended in the water column. These plants could take up nutrients from anoxic waters because their roots are supplied with atmospheric O_2 via the lacunar system of their emergent stems (Hamilton et al. 1995). The anoxic conditions could even enhance the availability of nutrients to emergent plants with roots in the water column, favoring their rapid growth at this time.

Concentrations of most of the dissolved trace elements do not appear to be unusual in the Paraguay River considering the geology of its basin and the low level of anthropogenic disturbance, although there are few data available from tropical regions for comparison (Meybeck 1988; Furch 1976). During the anoxic event, most dissolved trace elements remained at concentrations similar to or only slightly above the range observed during oxic conditions (Fig. 9) and are therefore unlikely to be responsible for the fish mortality. As expected, elements with more soluble reduced forms such as Fe and Mn showed elevated concentrations during the anoxic event, although Mn increased much more than Fe, possibly because it is not as rapidly reoxidized as Fe (Stumm and Morgan 1981). The elevated concentration of Co in the anoxic waters may be explained by the solubilization of Mn oxides, because Co is known to coprecipitate with Mn in aquatic ecosystems (Hem 1985). Although Mn and Co were elevated compared with oxic conditions, their concentrations remained within the range that has been observed in other rivers (Hem 1985), suggesting that these metals probably did not reach toxic levels.

The high proportion of Fe in the suspended solids (Fig. 8) may result from precipitation of iron oxyhydroxides; anoxic floodplain waters accumulate soluble Fe(II), which is then subject to precipitation when these waters enter the relatively oxic river channels. Amorphous Fe precipitates were commonly observed on submersed surfaces where floodplain waters flowed into rivers or lakes. Thus some of the inorganic suspended material that is present in the Paraguay River during inundation of the floodplain may originate within the floodplain rather than in the upland drainage basins.

Regional water and solute balances—Differences in concentrations and transport rates between the Paraguay River and other large rivers may be due to processes within the floodplains of the Pantanal, or they may be explained by other characteristics of the drainage basin, such as its geology or continental location. For example, the major ion composition of river water is determined largely by chemical weathering and is therefore particularly subject to influence by the lithology of the drainage basin (Gibbs 1967). A regional mass balance approach provides insight into the effects of the Pantanal on runoff and on hydrologic export of major solutes from the drainage basin.

The first step in the mass balance approach is to formulate a regional water balance. A water balance that is concurrent with our river sampling period could not be compiled because the hydrological monitoring program in the region is presently inadequate. More complete hydrological data were collected by Brazilian government programs from approxi-

Table 6. Regional water balance for the Pantanal above Porto Esperança (Paraguay River sampling site). The monthly data from Fig. 3 were used to produce this average annual balance, which applies to nondrought years. PET, Thornthwaite potential evapotranspiration.

	Flux, 10^6 m^3
Riverine inflows	78,221
Rain on flooded land	62,455
PET from flooded land	−69,607
Balance of above	71,069
Riverine outflow	65,804

mately the late 1960s to the early 1980s. Previously published compilations of these hydrological data have been for periods that spanned the prolonged drought of 1964–1973 (UNESCO 1973; EDIBAP unpubl. rep.). The water balance described here is based on the data presented in Fig. 3 and thus excludes data collected during the drought years to be consistent with conditions during our sampling period.

We define the Pantanal for the present purposes as all floodplain upriver of our Paraguay River sampling site (Porto Esperança: Fig. 1). We use the term outflow to refer to water discharge at Porto Esperança. Upriver of Porto Esperança, the drainage basin includes 123,000 km^2 of floodplain and 240,000 km^2 of uplands. We have excluded the southernmost subregion known as Nabileque, which comprises 13,660 km^2 or ~10% of the region that is traditionally referred to as the Pantanal (Hamilton et al. 1996).

The hydrological data in Fig. 3 are summarized in the form of a regional water balance in Table 6. Rainfall and evapotranspiration were assumed to affect only the flooded land surface that was estimated by remote sensing. Runoff from dry floodplain to flooded floodplain was assumed to be negligible, which is reasonable given the very low slopes. Evapotranspiration was assumed to approach its potential maximum rate (PET) in flooded areas (Fennema et al. 1994). The water balance is only approximate because the data are not exactly coincident and because the meteorological data were collected at only four stations. Nonetheless, the results are instructive because they reveal that the fluxes via rain and evapotranspiration are typically of similar magnitude to the total riverine inflow and outflow. The runoff coefficient, or the proportion of rainfall that leaves the drainage basin as riverine discharge, has been estimated to vary between 0.07 and 0.15 for the entire upper Paraguay River basin (EDIBAP unpubl. rep.; Ponce 1995). This unusually low runoff coefficient is explained by the retention of water in the floodplains where losses by evapotranspiration are enhanced.

The balance between riverine inflows, rainfall on the flooded land, and evapotranspiration from the flooded land is only 8% greater than the measured riverine outflow, indicating that the water balance is likely to be approximately complete (Table 6). Exchanges between surface waters and groundwater within the Pantanal must not be large relative to the other fluxes or exchanges must be roughly balanced across the region over the course of the year. UNESCO (1973) also concluded from varied lines of evidence that there were no large-scale transfers of water between surface waters and deep aquifers within the Pantanal.

Table 7. Solute budget for the Pantanal, based on the water budget (Table 6), discharge-weighted means for inflowing rivers (calculated from the data in Table 5), and annual volume-weighted means for rain at a site in the central Amazon (Lesack and Melack 1991). Rain was assumed to contain negligible amounts of Si. Predicted outflow concentrations were obtained by dividing the total mass of inputs (via rivers and rain) by the volume of riverine outflow. The predicted outflow concentrations can be compared with the observed outflow concentrations for the Paraguay River at Porto Esperança (from Table 2); P:O, ratio of predicted to observed concentrations.

	Inflowing rivers	Rain	Outflow		
			Predicted	Observed	P:O
Ca^{2+} (μeq liter^{-1})	246	1.5	294	248	1.18
Mg^{2+} (μeq liter^{-1})	168	1.1	201	197	1.02
Na^{+} (μeq liter^{-1})	62	2.1	76	69	1.10
K^{+} (μeq liter^{-1})	39	0.6	47	44	1.07
HCO_3^{-} (μeq liter^{-1})	475	0	565	507	1.11
Cl^{-} (μeq liter^{-1})	12	3.6	18	10	1.77
SO_4^{2-} (μeq liter^{-1})	10	3.9	16	3	5.20
Si (μM)	242	~0	288	266	1.08

We formulated a regional solute budget based on the annual water budget combined with our data on the chemistry of the major tributaries (Table 5) and published data on the chemical composition of continental rain. The solute budget was calculated only for major ions and Si because the synoptic sampling of the tributary rivers is inadequate to characterize nutrient concentrations, which are typically more variable. The contribution of each inflowing river was weighted by its long-term mean annual discharge, based on data of EDIBAP (unpubl. rep.), to estimate the discharge-weighted solute concentration of inflowing water (Table 7). The contribution of rain as a source of solutes to the region was estimated from the rainfall onto flooded land surfaces (Table 6) and the volume-weighted mean concentrations reported by Lesack and Melack (1991) for a site in the central Amazon. These Amazon rain measurements are the most comprehensive data currently available for continental South America and should resemble rain chemistry for the Pantanal because the Pantanal is also continental and receives much of its moisture from the Amazon Basin (IBGE 1989). Also, samples of 13 rain events collected at Corumbá showed similar ion chemistry. The sum of mass inputs by inflowing rivers and rainfall was divided by the volume of outflow at Porto Esperança to yield the predicted concentrations of solutes in the outflowing water.

The regional solute budget suggests that the floodplains of the Pantanal do not have a large effect on the export of most of the major ions and Si from the drainage basin (Table 7), although this conclusion must be regarded as tentative because the data on tributary rivers are sparse and the rain data are from the Amazon basin. Two ions that do seem to show losses in the floodplains are Cl^{-} and SO_4^{-2}. These two ions are the least abundant of the major solutes, so their budgets are the most affected by rain inputs (Table 7). Loss of SO_4^{-2} in the Pantanal is likely given the large difference

between predicted and observed concentrations. A plausible retention pathway would be reduction of SO_4^{2-} to S^{2-} by anaerobic respiration in anoxic floodplain environments, followed by precipitation of S^{2-} with dissolved metals such as Fe(II). Loss of S by emission of H_2S to the atmosphere seems less likely to be important because H_2S was not detected in waters of the region. The $Cl^- : SO_4^{2-}$ ratio is highest during maximum floodplain inundation (Fig. 7), suggesting greater relative loss of SO_4^{2-} at that time. The apparent loss of Cl^- is harder to explain; Cl^- is generally regarded as conservative in most aquatic environments. Several investigators have noted that Cl^- is an important electrolyte in the tissues of aquatic vascular plants (Hutchinson 1957), but K^+ is also important and does not show the same retention. The concentrations of Cl^- in rain reported by Lesack and Melack (1991) exceed Na^+ concentrations and seem high for such a continental location, but the rain in the Pantanal would have to be substantially lower in Cl^- than Na^+ for the solute budget to be balanced.

The approximate balance between fluvial inputs and outputs of major weathering products such as Ca^{2+}, K^+, Si, and HCO_3^- (Table 7) suggests that the yield of these solutes from weathering of the alluvial sediments in the Pantanal is small compared to the weathering yields from the upland drainage basins. Other large-scale fluxes of these solutes that might take place in the floodplains, such as precipitation or dissolution reactions or biotic uptake and release, are either absent or in balance. Evidence is accumulating that most major ions generally display conservative behavior in the dilute floodplain waters of many South American rivers (Gibbs 1967; Forsberg et al. 1988; Hamilton and Lewis 1990), although biotic uptake and release can be important for some elements at certain times (e.g. K^+ and Cl^- release during aquatic plant decomposition at falling stages: Hamilton and Lewis 1987). Most major ions in the Pantanal may behave conservatively because: fluvial sediments are already highly weathered by the time they are deposited in the floodplains; the contact between surface waters and underlying sediments is much lower in the floodplain than the contact between groundwater and the soil and rock matrix in an upland drainage basin; and the strongly heterotrophic metabolism in the aquatic environments of the floodplain maintains oversaturation of dissolved CO_2 and thereby precludes precipitation of $CaCO_3$.

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