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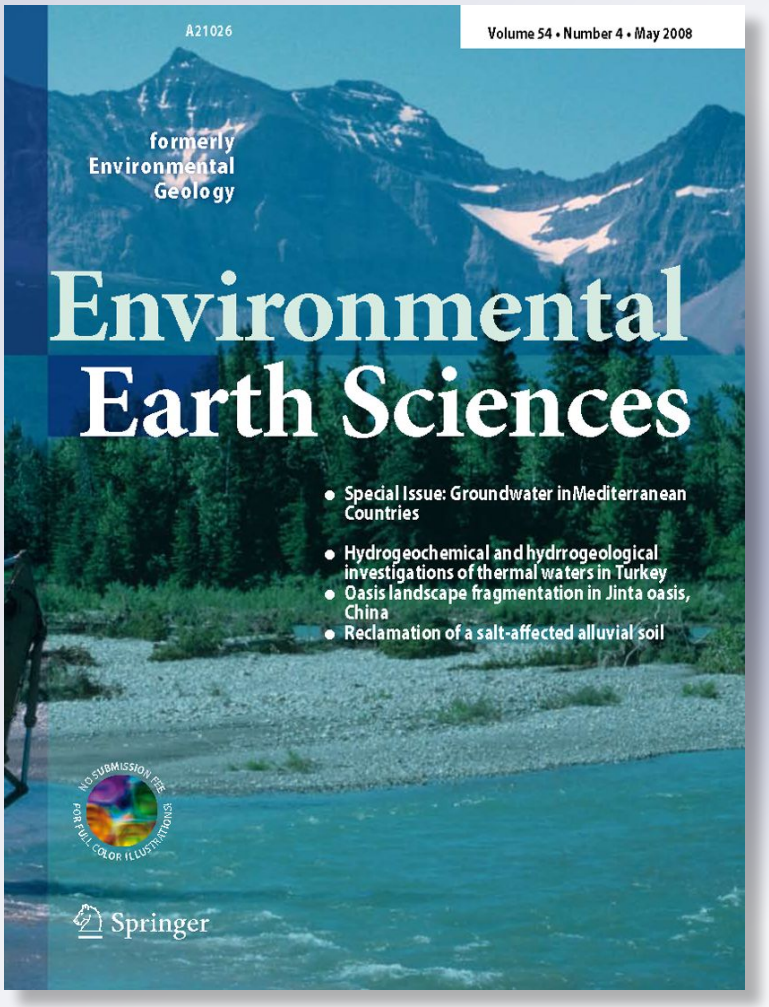

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SPECIAL ISSUE

Hydrochemical considerations and heavy metal variability in the middle Paraná River

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Abstract The Paraná River is one of the largest drainage systems in the Americas. Its hydrology is characterized by an active teleconnection with the ENSO, and by a significant discharge increase trend, evident since the mid-1970s. An Eh–pH data set collected in the Paraná's middle stretch suggests that large flood events, such as the one triggered by the 1982–1983 ENSO, are discernible in the plot, probably due to the influx of water draining flood plain water bodies. The total (particulate + dissolved) concentration of a set of heavy metals (Cr, Mn, Ni, Cu, Zn, As, Cd, and Pb) was determined in a downriver survey of the middle stretch. With the exception of Cu, Cd, and Pb, the metals exhibit a significantly increasing concentration trend towards the river mouth. The slopes of the regression lines imply that Zn and Ni, on one hand, and Mn and Cr, on the other would have common controlling sources. Another set of analyses were performed during the 1982–1983 flooding event; besides an increased variability observable during the flood arrival, most elements, with the only exception of Pb, did not show a variability coherent with the discharge series.

Keywords Water chemistry · Paraná River · ENSO · Total heavy metals · Hydrology

Introduction

There are two major pathways of heavy metals to the aquatic environment: those derived from natural sources and those for whom an anthropogenic origin is recognized. The first source group is basically determined by mineral weathering, geothermal and volcanic phenomena, and the mineralization of natural organic materials. In the second group mining, industry, agriculture, and other waste sources of different human-affected nature are found. The atmosphere mediates between those two major pathways and the environment in as much as it transports debris produced in each one of them.

In the middle Paraná River, the largest proportion of its sediment load is supplied by the Bermejo (often more than 70% of the middle Paraná's total suspended load) and Pilcomayo rivers, both are Andean tributaries of the Paraguay River. Considering the fact that most heavy metals are transported adsorbed onto organic particles and/or colloids, and that human intervention (i.e., direct heavy metal pollution) is not particularly significant in the headwaters of both rivers, it can be concluded that in the middle Paraná reach, natural sources of heavy metals are more significant than anthropogenic ones.

Heavy metal concentrations have been scantily explored in the Paraná River. There are some papers devoted to toxicity assessment: Cataldo et al. (2001); Gómez et al. (1998); and Villar et al. (1999a). Villar et al. (1999b) have also explored heavy metal concentration in macrophite tissue and sediments in the lower Paraná, whereas Giancoli Barreto et al. (2004) have experimented with extraction methods of heavy metals in the upper Paraná basin. Recently, Ronco et al. (2007) have related metal occurrence and textural-compositional properties in bottom sediments of the lower Paraná and de la Plata rivers. Depetris et al. (2003), and Depetris (2007), are additional contributions to the subject matter.

There is a continued interest in the world for a better understanding on the environmental dynamics of heavy

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metals (e.g., Soylak et al. 1999). Davutluoglu et al. (2011) studied metal pollution in the Seyhan River (Turkey) by means of indexes and compared their results with other world rivers.

In this paper, several characteristics of the Paraná drainage basin (including the chemistry of dissolved phases) are reported, as well as on the dynamics of a group of heavy metals determined in the middle Paraná River during the 1982–1983 ENSO flood, one of the most significant hydrological events throughout its recorded history. Also included is the lengthwise variability survey performed in 1985.

Materials and methods

In the period March 1981–November 1984, the middle Paraná River was mainly sampled at the main stem, in the Paraná-Santa Fe cross-section, about 600 km upstream from the mouth. Samples were collected with plastic pumping devices, from 1 m below the surface, in the center of the main channel. Simultaneously, pH, Eh, dissolved oxygen, conductivity, alkalinity, and other physicochemical parameters were determined. Another set of samples, in which the same parameters were measured, was collected in July 1985, following a downriver sampling scheme, from the city of Corrientes (about 1,600 km upstream from the mouth), downstream to the city of Paraná (about 600 km upstream from the mouth).

The speciation of a group of selected metals was determined by means of an electrothermal atomic absorption spectrometer fitted with an autosampler. Metals were determined in two fractions: in the dissolved phases (i.e., vacuum filtered with 0.45 μm pore-size cellulose acetate filters) and in the so-called "total recoverable metals" (i.e., the concentration of metals determined in an unfiltered sample after vigorous digestion). The difference between these two determinations supplied the "suspended metals" fraction.

Dissolved metals were determined in the acidified aliquot (with concentrated, ultra pure 99.999% HNO_3, until pH < 2.0, Sigma-Aldrich, St. Louis MO, USA). In most analyzed metals, no further pretreatment was required except for the addition of an optional matrix modifier, when required (e.g., Eaton et al. 1995).

Similarly, total recoverable metals were determined in a well-mixed, acid-preserved sample appropriate for the expected metals concentration, and then repeatedly treated with 5-ml aliquots of concentrated, redistilled, ultra pure (99.999%) HNO_3 (Sigma-Aldrich) until a light-colored residue remains. Afterwards, 1 + 1 redistilled HCl (Sigma-Aldrich) was added, following the widely known procedure described elsewhere, in several environmental analytical chemistry treaties (e.g., Eaton et al. 1995). This sample set was collected during the El Niño event, which determined the extraordinary 1982–1983 flood in the Paraná River (Pasquini and Depetris 2010, and references therein) and analyzed immediately thereafter.

Most detection limits for the analyzed elements fell within the 1–2.5 ppb concentration band. Precision is specified by the standard deviation (s) of the results; most s fell within ±0.1%.

The dissolved fraction of another set of samples collected in the Paraná and main tributaries during July 2002 was analyzed by ICP-MS. In this occasion, the samples were filtered in the field with a 0.22 μm pore-size cellulose filter and acidified until pH < 2 with redistilled, ultra pure (99.999%) HNO_3 (Sigma-Aldrich). The validity of the results for dissolved elements was checked with NIST-1640 (Riverine Water Reference Materials for Trace Metals certified by the National Research Council of Canada) and SRLS-4, carried out along with sample analysis. Reproducible results were obtained in selected samples. In most cases, analytical error was lower than 10%.

Geological and hydrological framework

The Paraná River basin (Fig. 1) has a drainage area of 2.783×10^6 km^2 (Tossini 1959) and it is the most important river system in the Río de la Plata drainage basin because it accounts for about 88% of its total drainage area (3.170×10^6 km^2), and almost 80% of its total discharge to the SW Atlantic Ocean (Pasquini and Depetris 2007).

Extended Jurassic–Cretaceous flood basalts and the adjoining Cretaceous sandstones are the most conspicuous features of the Phanerozoic mantle that covers a significant portion of the Río de la Plata drainage basin. The headwaters of the Bermejo and Pilcomayo rivers, western tributaries of the Paraguay River, exhibit thick beds of marine and continental sedimentary rocks as well as outcrops of metamorphic rocks, along with volcanic rocks of Quaternary age (Fig. 1). The abundance of friable sedimentary formations with steep slopes, in humid to semiarid climates, are critical factors determining the high sediment load that has been recorded mainly in the Bermejo drainage basin (Drago 2007). Potter and Hamblin (2006) have dealt with the morphological evolution of the Paraná River drainage basin.

The Paraná River delivers (mean for the period 1970–2008) an annual discharge of ~492 km^3 (~15,600 m^3 s^{-1}). The mean annual rainfall is unevenly distributed over the entire drainage basin. Maximum recorded rainfall (~2,400 mm year^{-1}) occurs along the eastern edge of the drainage basin. Rainfall (and some snowfall) decreases distinctly (800–400 mm year^{-1})

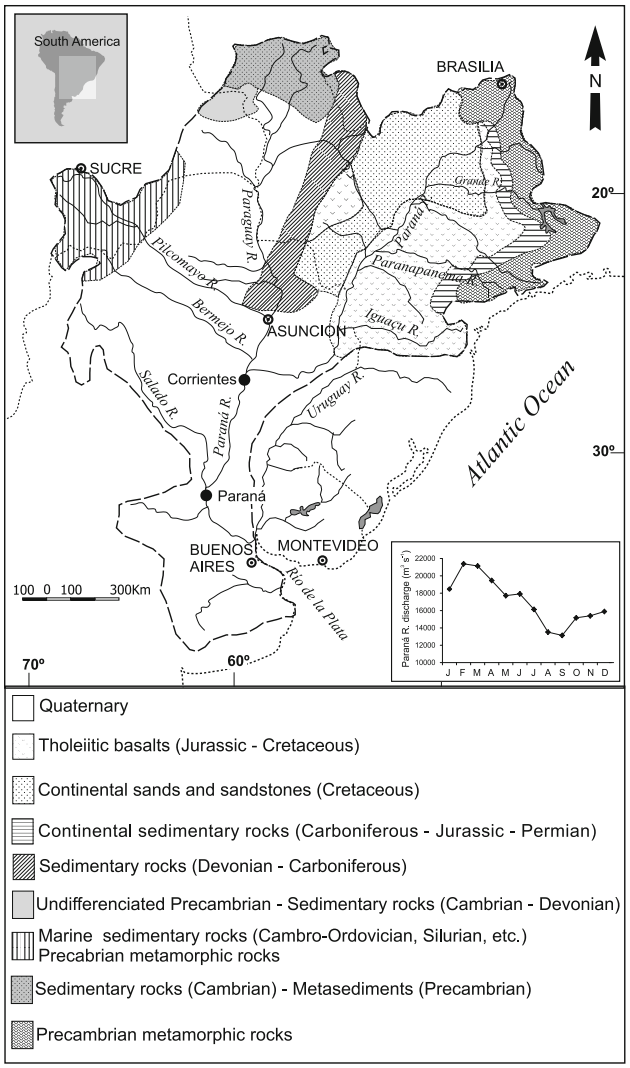


Fig. 1 Schematic geological map of the Paraná River drainage basin. Inset: mean hydrograph of the middle Paraná River

towards the northwestern and western edge of the basin (Fig. 1), along 60°–65°W. The northwestern tributaries (Pilcomayo and Bermejo rivers) reach maximum discharges in February–March (the end of austral summer). The Paraguay River reaches peak discharges in June–July (southern winter), and lastly, the Iguaçú River resembles the Paraná main channel, with top discharges during February–March (austral summer) and low water during the southern spring. More details on the relative contribution and dynamics of major tributaries have been considered elsewhere by Pasquini and Depetris (2007).

The summer circulation over South America is mainly controlled by a monsoonal system, whose major seasonal characteristic is the South Atlantic Convergence Zone (SACZ), positioned along the northeastern boundary of the Río de la Plata drainage basin (e.g., Robertson and Mechoso 2000). Another important feature in the regional climatic control is a low-level northerly/northeasterly jet that flows east of the Andes, and transports moisture along the corridor placed between the Andes and the Brazilian altiplano (e.g., Wang and Fu 2004).

There is unquestionable evidence that regional rainfall and river runoff has increased in the Río de la Plata drainage basin during the last third of the twentieth century. The discharge increase in the Paraná and Paraguay rivers, for example, has been pointed out by several workers (e.g., Genta et al. 1998; Robertson and Mechoso 1998; Collischonn et al. 2001; Boulanger et al. 2005; Dore 2005; García and Mechoso 2005); most authors place the breaking point around the early 70s.

In a recent contribution (Pasquini and Depetris 2007), the non-parametric Mann–Kendall trend test was employed (Mann 1945; Kendall 1975) on discharge time series and disclosed that some of Paraná's tributaries (Bermejo, Paraguay, Iguaçú, and Salado rivers) and the lowermost Paraná main stem station (at Paraná) exhibit significant positive trends ($p < 0.001$). Other gagging stations along the Paraná River main channel (i.e., Posadas and Corrientes) exhibited lesser levels of significance (Pasquini and Depetris 2007).

The seasonal Kendall test was also applied (Hirsch et al. 1982) to monthly flow data from rivers in the Río de la Plata drainage basin (Pasquini and Depetris 2007). Interestingly, the months that showed a significant flow increase were those of yearly low flow (southern winter). A discharge increase was also displayed during the high water period (southern summer), although we must add that such months were the least statistically significant. Further, the Paraná and all its tributaries have clearly reversed a negative discharge trend, discernible until about the mid-twentieth century, which was then replaced by the currently recorded increasing trend.

Figure 2 shows the continuous wavelet transform (CWT) (e.g., Nakkem 1999) spectral analysis applied to the Paraná River (at Paraná, 600 km upstream from the mouth) deseasonalized discharge time series for the over one hundred year-long period, 1904–2008. As pointed out by other authors (e.g., Labat et al. 2005; García and Mechoso 2005) the diagram shows a strong quasi-decadal frequency. It also shows potent interannual oscillations in the 2- to 7-year range that are frequently in phase with El Niño events in the equatorial Pacific. The wavelet spectra become very useful to illustrate the shifting in frequencies of interannual periodicities throughout the twentieth century. The 2- to 5-year analysis shows maximum power peaks for 1928 and 1980. Power drops markedly for the range from ~1935 to ~1970 but, precisely for that time range, power increases in the 5- to 7-year band.

Digging deeper into the hydrological signals of Paraná's headwater tributaries revealed that the Paraguay River is,

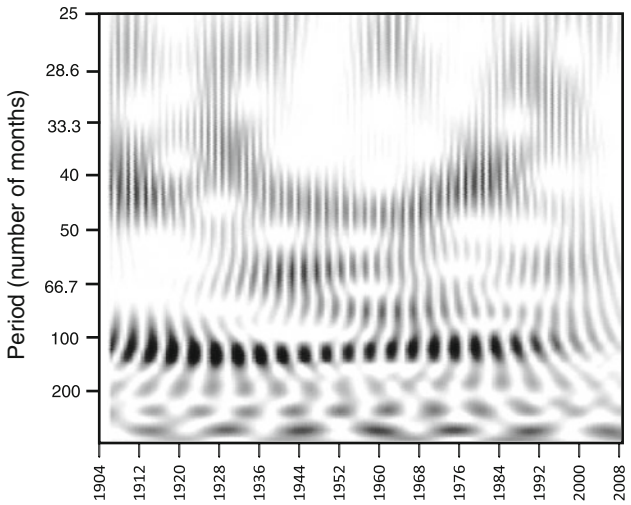


Fig. 2 Real part of the continuous Morlet wavelet spectrum of Paraná River (at Paraná, 600 km upstream from the mouth) deseasonalized monthly mean discharge. *Dark colors* represent high power

in relative terms, increasing its discharge at a higher pace than the upper Paraná River does. This increasing contribution observed in the Paraguay River can be followed fairly well with the isotopic signal ($\delta^{18}O$) determined in the middle Paraná expanse (Pasquini and Depetris 2010).

Overview of dissolved components

Water plays in the Earth surface system a central role because it operates as both, a reactant and as a transporting agent from land to sea of dissolved and particulate components. Water supply is unevenly distributed in the Paraná River drainage basin, and weathering exerts an unequal control in different upper catchments. Therefore, the dissolved chemical nature of the middle and lower Paraná River is determined not only by the dissimilar water volume contribution from Paraná's two main tributaries (i.e., the Upper Paraná and the Paraguay, Fig. 1), but also by various processes that govern their dissolved species concentrations (Depetris and Pasquini 2007). Generally, the Paraná River waters follow the order $HCO_3^- > Cl^- > SO_4^{2-}$ for the abundance of major anions whereas the order for major cations is $(Na^+ + K^+) > Ca^{2+} > Mg^{2+}$. The middle Paraná maintains an asymmetric chemical cross-section throughout a significant portion of its middle course, because the water flowing along its western margin has a higher ionic strength than the eastern one (Drago and Vassallo 1980). This characteristic may be not only determined by the diverse chemical signature of both, the Paraguay and the Upper Paraná rivers, but also by the combined influx of surface runoff and groundwater flow originating in the sediment-mantled Chaco-Pampa plain.

The total dissolved solids (TDS) load estimate for the middle Paraná River is $\sim$25 Tg year^{-1} (1 Tg = 10^9 g) (Depetris and Pasquini 2007 and references therein), about one-third of what appears to be its total mean sediment load. The upper Paraná delivers more diluted waters than the Paraguay, whose mean TDS concentration is usually twice as much as that of the upper Paraná River. If their mean discharge ratio ($\sim$2.3:1) is considered, the TDS load for the middle Paraná is supplied in about equal proportions by both major tributaries. Exceptional floods seem to cause significant dilution and only a slight increase of the TDS export rate: during the 1982–1983 ENSO-determined exceptional flood, the TDS load increased less than 10% (Depetris and Pasquini 2007, and references therein).

Clearly, large floods, such as the one determined in the Paraná River by the 1982–1983 ENSO event, generate significant changes in the geochemical functioning of complex hydrological systems. Figure 3 is an Eh–pH diagram in which a set of Eh–pH measurements performed in the middle Paraná River during the ENSO flood of

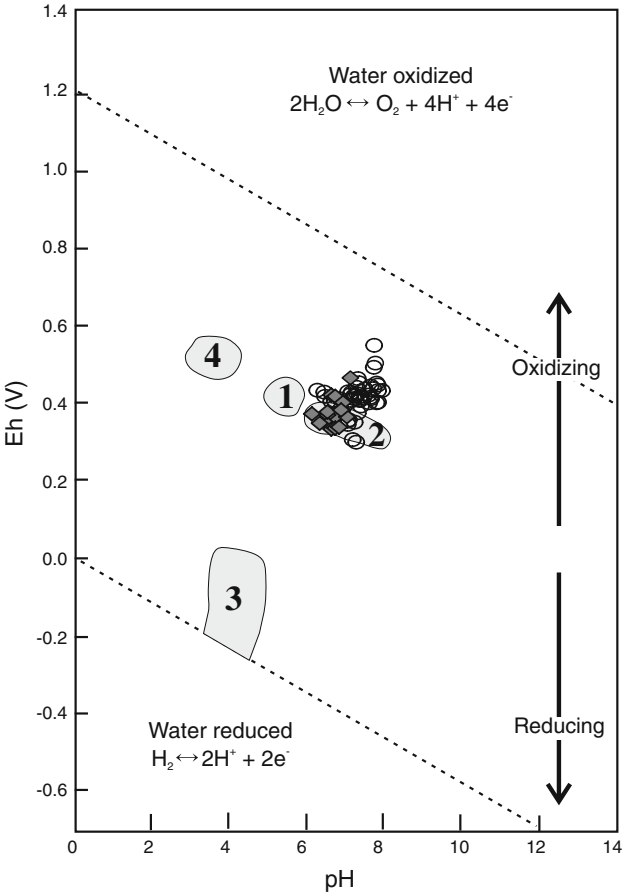
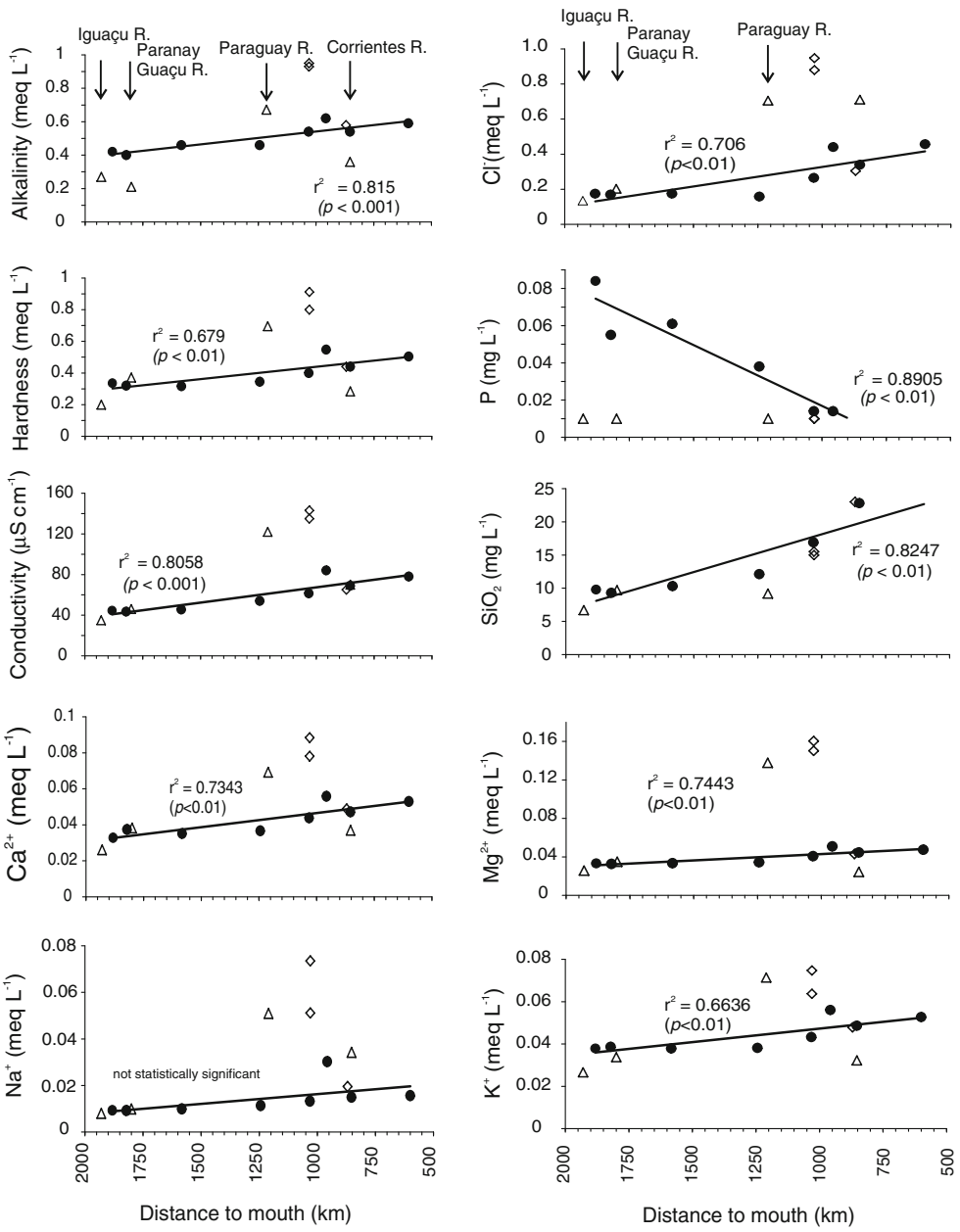


Fig. 3 Eh-pH diagram showing mean fields for different environment-types: *1* rain, *2* rivers, *3* waterlogged soils, *4* surface ocean water. Open circles: Paraná River data collected during the 1982–1983 flood; squares: Paraná River data collected during the 1985 downriver geochemical survey



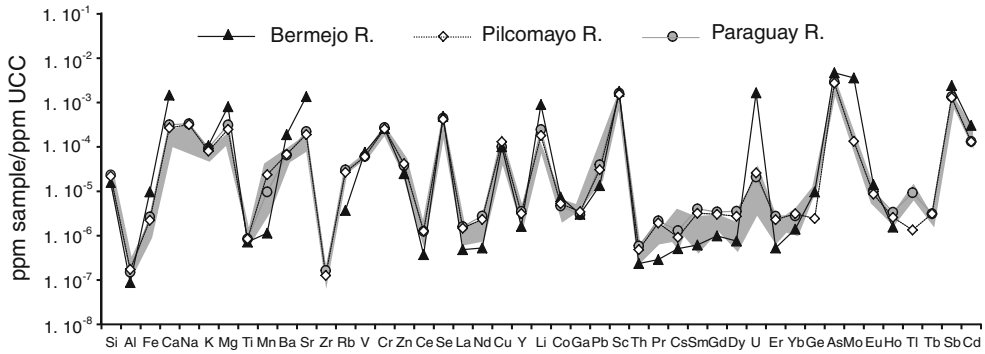


Fig. 4 Downstream variation of selected chemical parameters determined in the upper and middle Paraná River in July 1985. Squared correlation coefficients and corresponding significance levels are indicated in each case for the mainstream values. *Filled circles* correspond to mainstream samples; *triangles* indicate tributaries; *diamonds* indicate ponds and ox-bows in the riparian environment. Tributaries are indicated in the *uppermost graphs*

Fig. 5 UCC-normalized extended diagram of dissolved elements in the Paraná River and main tributaries. The *shaded area* corresponds to middle Paraná River data

Table 1 Total heavy metals concentration determined in a downriver geochemical survey of the middle Paraná River and associated riparian environments

River	Distance	Date	μg L^{-1} of total HM (dissolved + suspended)							
	km to mouth	d/m/y	Cr	Mn	Ni	Cu	Zn	As	Cd	Pb
Iguazú	1,927	21.7.85	1 ± 0.13	12.9 ± 0.6	2.41 ± 0.12	4.76 ± 0.2	26.8 ± 1.4	2.19 ± 0.47	0.29 ± 0.02	1.1 ± 0.14
Paraná	1,882	22.7.85	0.64 ± 0.03	8.65 ± 0.5	1.45 ± 0.12	8.62 ± 0.16	37.3 ± 1.9	2.08 ± 0.48	0.16 ± 0.03	<0.3
Paraná	1,822	22.7.85	1.36 ± 0.03	8.64 ± 0.7	1.63 ± 0.25	2.9 ± 0.22	45.5 ± 2.3	1.28 ± 0.39	0.1 ± 0.001	<0.3
Paranay Guazú	1,800	22.7.85	0.49 ± 0.02	8.64 ± 0.6	1.72 ± 0.03	1.84 ± 0.09	30 ± 1.5	0.59 ± 0.2	0.66 ± 0.09	4.8 ± 0.8
Paraná	1,583	23.7.85	0.65 ± 0.01	9.38 ± 0.8	2.58 ± 0.06	10 ± 0.34	26.8 ± 1.4	1.27 ± 0.16	0.92 ± 0.09	1.1 ± 0.2
Paraná	1,244	23.7.85	1.29 ± 0.62	8.93 ± 0.7	2.25 ± 0.19	2.49 ± 0.1	41.5 ± 2.2	1.43 ± 0.08	0.12 ± 0.02	2.2 ± 0.2
Paraguay	1,210	23.7.85	1.43 ± 0.3	42.86 ± 3	2.8 ± 0.27	2.75 ± 0.18	36.2 ± 1.9	2.43 ± 0.1	0.4 ± 0.02	5.2 ± 0.3
Paraná	1,032	24.7.85	1.86 ± 0.04	35 ± 1.6	2.87 ± 0.22	3.28 ± 0.24	54.1 ± 2.8	2.94 ± 0.07	0.28 ± 0.02	1.3 ± 0.2
Pato Cuá (pond)	1,030	24.7.85	1.29 ± 0.08	75.3 ± 3	1.55 ± 0.04	3.27 ± 0.2	58.2 ± 3	6.2 ± 0.43	0.25 ± 0.01	8.7 ± 0.3
Pato Cuá (stream)	1,030	24.7.85	2 ± 0.21	122.7 ± 6.6	3.29 ± 0.04	3.43 ± 0.3	44.1 ± 2.3	4.79 ± 0.29	0.42 ± 0.01	6.9 ± 0.2
Paraná	957	25.7.85	1.53 ± 0.03	44.3 ± 2	2.94 ± 0.1	3.71 ± 0.1	40.4 ± 2.1	3.58 ± 0.24	0.19 ± 0.4	1.1 ± 0.2
Aguará (pond)	870	25.7.85	1.41 ± 0.04	27.6 ± 1.6	5.2 ± 0.04	5.31 ± 0.24	40.4 ± 2	3.65 ± 0.36	0.43 ± 0.01	4.3 ± 0.4
Paraná	853	25.7.85	4.25 ± 0.12	51.3 ± 3.2	3.56 ± 0.1	4.21 ± 0.2	39.3 ± 2.1	3.99 ± 0.26	0.13 ± 0.03	1.6 ± 0.2
Paraná	601	30.7.85	14.2 ± 0.42	52.7 ± 4.1	3.44 ± 0.11	3.58 ± 0.18	101.4 ± 5	6.62 ± 0.49	0.14 ± 0.02	1.9 ± 0.2
Corrientes	853	25.7.85	8.18 ± 0.13	194.3 ± 15.2	2.81 ± 0.12	6.6 ± 0.22	50.9 ± 2.7	3.26 ± 0.37	0.12 ± 0.01	3.7 ± 0.5

Values are means ± standard deviations

1982–1983 was plotted. Where water is in contact with the atmosphere, e.g., rivers, rainwater, ocean surface water, and mine waters, Eh is oxidizing, with positive values. Figure 3 clearly shows that during the flood Eh tends to be more positive, probably due to organic reactions (e.g., organic decay, respiration, photosynthesis), or to redox reactions of common elements (e.g., manganese, iron and, sulphur), occurring mostly in ponds and small streams in the flood plain. In July 1985 (low water period), a downriver geochemical survey showed, under normal hydrological conditions (low waters), lesser oxidizing characteristics than during the high flood of 1982–1983 (Fig. 3). Figure 4 shows the variation of selected parameters measured in the same downriver geochemical survey (i.e., July 1985). Most variables showed concentrations with a significant increasing downstream trend due to the solute load supplied by tributaries, the extensive riparian domain and, probably, by groundwater seepage. Only phosphorous showed a negative trend, most likely determined by biological consumption.

In July 2002, another downriver geochemical survey of the middle Paraná River and major tributaries (Paraguay, Bermejo, and Pilcomayo rivers) was performed. Figure 5 shows a UCC-normalized (upper continental crust, McLennan 2001) extended diagram of a set of dissolved major and trace elements. The diagram (a.k.a. "spidergram") clearly

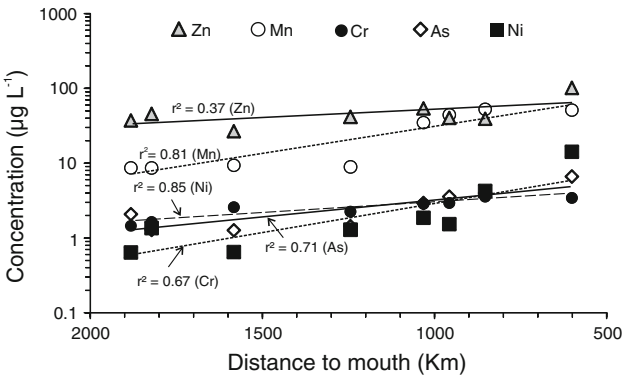


Fig. 6 Set of regression lines showing the spatial variability of selected heavy metals in the main channel of the middle Paraná River. Notice parallelism in *broken* and *full lines*

differentiates the insoluble elements, below 10^{-6} UCC-normalized concentrations (e.g., Al, Ti, Zr, etc.), from those with markedly soluble characteristics (e.g., Ca, Na, Mg, Ba, Sr, etc.). Other features worth mentioning are the differences in normalized abundances attributable to changes in lithology. For example, the dominance of sedimentary rocks in the Bermejo River upper catchments is seen in the concentrations of soluble elements such as Ca, Mg, Ba, and Sr; other elements, such as U and As are probably linked to volcanism, with significant presence all

Table 2 Total heavy metals concentration determined at Paraná (about 600 km upstream from the mouth) during the 1982–1983 ENSO-triggered flood

Sample date	Cr		Mn		Ni		Cu		Zn		As		Cd		Pb	
d/m/y	mg L^{-1}	% P	mg L^{-1}	% P	mg L^{-1}	% P	mg L^{-1}	% P	mg L^{-1}	% P	mg L^{-1}	% P	mg L^{-1}	% P	mg L^{-1}	% P
06/08/1982	6.6 ± 0.2	91	68.7 ± 1	87	8 ± 0.6	>99	5.7 ± 0.6	70	32.9 ± 0.2	>99	7.7 ± 0.3	>99	0.31 ± 0.03	42	7.9 ± 0.5	4
07/09/1982	7.5 ± 0.2	88	94.7 ± 1.5	96	9 ± 0.5	>99	6.4 ± 0.3	92	73.2 ± 1.5	90	n.d.	n.d.	0.77 ± 0.1	91	8.1 ± 0.2	96
23/09/1982	4.9 ± 0.2	90	77.9 ± 1	92	5.3 ± 0.4	99	n.d	n.d	26.2 ± 0.5	>99	3.3 ± 0.1	>99	0.74 ± 0.08	73	0.9 ± 0.1	67
07/10/1982	19.1 ± 0.2	97	42.5 ± 0.3	82	10.4 ± 0.8	56	2.6 ± 0.1	54	41.1 ± 3.7	29	0.5 ± 0.1	>99	1.27 ± 0.01	98	n.d.	n.d.
27/10/1982	32.3 ± 0.7	96	93.8 ± 3.1	99	0.8 ± 0.2	>99	4.9 ± 0.2	67	26.1 ± 0.7	74	1.3 ± 0.2	62	0.08 ± 0.01	>99	1.5 ± 0.1	80
24/11/1982	8.5 ± 0.3	93	96.1 ± 1.4	98	6 ± 1.2	75	43.6 ± 0.6	92	28.2 ± 1	80	3.1 ± 0.4	77	0.04 ± 0.005	>99	n.d.	n.d.
15/12/1982	6.1 ± 0.4	92	12 ± 0.2	>99	10 ± 0.8	39	n.d.	n.d.	22.7 ± 0.7	76	2.6 ± 0.4	77	0.23 ± 0.03	>99	7.2 ± 0.9	56
28/12/1983	5.6 ± 0.2	95	25 ± 0.6	72	4.1 ± 0.3	85	n.d.	n.d.	15.9 ± 0.3	58	6.3 ± 0.3	90	0.33 ± 0.04	>99	11.4 ± 0.3	68
03/02/1983	4.2 ± 0.1	95	16.3 ± 0.4	40	12.5 ± 0.7	>99	4.8 ± 0.3	52	30.5 ± 1.3	56	7.5 ± 0.4	93	0.13 ± 0.03	54	8.3 ± 0.4	14
23/02/1983	6.2 ± 0.1	97	30.7 ± 0.7	46	3.1 ± 0.8	45	3.3 ± 0.2	21	22.8 ± 1.6	49	4.5 ± 0.4	89	0.08 ± 0.01	38	6 ± 0.4	45
11/03/1982	2.9 ± 0.1	93	144 ± 1.8	>99	6.5 ± 0.5	83	6.6 ± 0.2	67	61.7 ± 2.9	81	4.8 ± 0.5	88	0.67 ± 0.01	94	12.6 ± 0.7	56
14/04/1983	31.2 ± 0.4	99	45.2 ± 0.2	86	7.3 ± 1	25	8.7 ± 0.2	74	22.3 ± 0.6	57	2.7 ± 0.03	>99	0.9 ± 0.01	6	9.5 ± 0.4	11
03/05/1983	8.4 ± 0.4	71	55 ± 0.7	>99	6.5 ± 0.4	63	10.2 ± 0.3	64	79.3 ± 1.4	>99	2.5 ± 0.1	>99	0.65 ± 0.07	46	9.9 ± 1.1	42
03/06/1983	5.3 ± 0.2	>99	54.7 ± 0.7	80	7 ± 0.5	>99	25.1 ± 1	70	34 ± 0.4	>99	7.1 ± 0.3	>99	0.4 ± 0.05	>99	8.4 ± 2.1	15
23/08/1983	2.2 ± 0.2	45	58.2 ± 0.9	95	16.2 ± 1.1	>99	11 ± 0.2	85	64.2 ± 1.5	63	6.6 ± 0.2	>99	0.53 ± 0.07	85	10.7 ± 0.3	51
21/09/1983	2.7 ± 0.2	48	112.1 ± 0.3	86	7 ± 0.1	57	3.9 ± 0.1	38	29.5 ± 0.2	84	5.6 ± 0.3	89	0.11 ± 0.01	45	1.8 ± 0.04	83
26/10/1983	5 ± 0.2	96	59.4 ± 0.8	94	14.3 ± 0.9	73	21 ± 0.2	89	45.4 ± 3.2	95	12.9 ± 1	93	0.3 ± 0.04	90	1.7 ± 0.2	71
06/12/1983	3.6 ± 0.2	83	101.8 ± 0.5	93	12.5 ± 0.5	74	30.5 ± 0.2	92	49.9 ± 1.3	76	8.2 ± 0.5	91	0.8 ± 0.09	80	1.4 ± 0.1	79
15/02/1984	8.5 ± 0.3	89	80 ± 1	91	11 ± 0.8	67	41 ± 0.4	92	50.3 ± 0.8	54	7.4 ± 0.3	93	0.1 ± n.d.	n.d.	1.6 ± 0.1	81
06/04/1983	2.8 ± 0.1	79	29.7 ± 0.9	>99	15.7 ± 0.3	76	20.5 ± 0.2	>99	66.1 ± 2.5	54	4.8 ± 0.1	88	1.1 ± 0.02	84	13.1 ± 1	60
30/05/1984	5.7 ± 0.4	>99	113.3 ± 4.5	>99	3.9 ± 0.2	>99	2.5 ± 0.1	>99	18.7 ± 0.2	>99	8.5 ± 0.3	>99	0.08 ± 0.02	>99	5.2 ± 0.2	60
01/08/1984	0.9 ± 0.1	>99	53.7 ± 1.2	31	6.8 ± 0.6	43	7.9 ± 0.4	39	27.3 ± 1.6	24	2.9 ± 0.3	83	0.26 ± 0.02	15	2.4 ± 0.1	75

% P percent of particulate fraction, *n.d.* not determined

along the Andes. Another important difference is the higher UCC-normalized concentration of dissolved RRE in the Paraná as a result of widespread basaltic outcrops. Paraguay and Pilcomayo rivers show a UCC-normalized pattern similar to the Paraná River.

Heavy metals concentrations

The dynamics of a set of heavy metals (Mn, Zn, As, Cr, Ni, Pb, Cd, and Cu) in the middle stretch of Paraná River was examined in two different opportunities: during the exceptional flooding event of 1982–1983, and later, in July 1985, in a downriver geochemical survey of the river.

Table 1 shows the variation of total heavy metal concentrations determined for a stretch of about 1,000 km of the middle course. Figure 6 shows the spatial variability of a set of elements that correlate significantly with the distance to the mouth. Incidentally, they all show an increasing trend towards the outflow. The slopes of the exponential equations that best describe the association between variables and distance to the mouth are relatively close in the case of Zn and Ni (5.0×10^{-4} and 6.0×10^{-4}, respectively) suggesting a similar controlling mechanism. Likewise, Mn and Cr exhibit comparable slopes (1.7×10^{-3} and 1.8×10^{-3}, respectively), also implying an analogous dynamics. Arsenic, which is probably influenced by As-rich groundwater seepage, shows a rate of concentration increase placed in between the abovementioned ranges. A significant correlation with the distance to the mouth is not verified for Pb, Cd and Cu. Significant squared correlation coefficients (Fig. 6) are

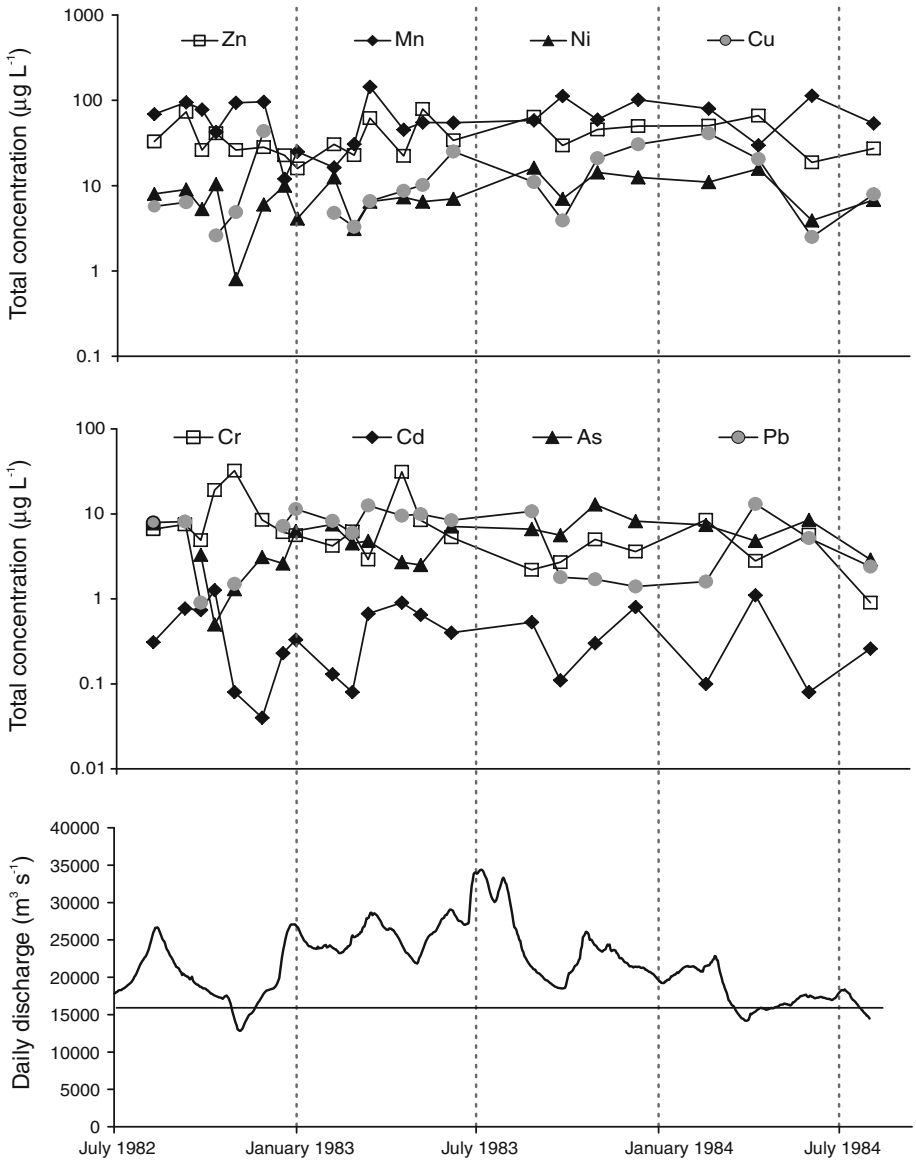


Fig. 7 Temporal variability of selected heavy metals measured at Paraná (about 600 km upstream from the mouth) during the 1982–1983 ENSO-triggered flood. The *bottom graph* corresponds to the daily river discharge determined at Paraná; *horizontal line* indicates mean discharge ($15{,}600\ m^3\ s^{-1}$)

variable and are supported by different levels of confidence: Zn, $p < 0.1$; Cr, $p < 0.05$; Mn, $p < 0.01$; As, $p < 0.01$; and Ni, $p < 0.001$.

Table 2 shows the total heavy metal concentration variation determined during the ENSO-linked flood of 1982–1983. With the only exception of Pb, which shows a mean partition coefficient that suggests a distribution of the element in roughly even proportions of particulate and dissolved phases, all the remaining elements evidence a dominance of particles as the main carrier for the exportation of metals to the sea. A good example of this is that of As, whose occurrence in the particulate phases is >90% in most cases (Table 2).

Figure 7 shows the temporal variability of the set of samples used for the determination of total heavy metals (Zn, Mn, Ni, Cu, Cd, As, and Pb) in the middle Paraná River, along with the daily discharge determined at Paraná, about 600 km upstream from the mouth. With the only exception of Pb, which shows a significant correlation with discharge ($r = 0.59$, $p < 0.05$), the remaining metals do not exhibit a coherent dynamics with the river flow. Furthermore, beside Cu that shows a significant correlation with the total suspended matter concentration ($r = 0.45$, $p < 0.05$) metals do not exhibit an association with the sediment load. The variability of metals appears enhanced during the onset of the ENSO-triggered flood (i.e., since late 1982 until mid-1983, Fig. 7). Afterwards, they seem to fluctuate, probably as a function of the interactions with the floodplain (i.e., the alternation of water flow entering and leaving the water bodies occupying the flood plain).

Conclusions

The Paraná River is the main stem of a system that shows and active teleconnection with the occurrence of ENSO events in the equatorial Pacific. Furthermore, the mean discharge has been increasing, mostly due to an increased contribution from the Paraguay River catchments, in the Mato Grosso.

Sediments are mainly supplied by the Andean tributaries of the Paraguay–Bermejo and Pilcomayo rivers, which also provide a relatively high proportion of dissolved solids (TDS). In terms of transported mass, the upper Paraná and the Paraguay supply a roughly equal TDS load to the middle Paraná stretch.

The Eh–pH data set shows that during the 1982–1983 exceptional flood episode, the samples plot outside of the mean field for river waters, thus suggesting that a significant mass of water draining the flood plain entered the Paraná's main stem altering the usual Eh–pH signature.

The downriver distribution of dissolved elements in the middle Paraná and main tributaries was also determined. Although the UCC-normalized extended elemental diagram clearly shows the control of relative mineral solubility, it is also evident the signature of the dominant lithology in different catchments.

In most measured heavy metals, a clear downriver increasing trend was discernible, which cannot be linked to an anthropogenic source. Although there are no clear sources, the analysis of the respective slopes suggests common sources for Zn and Ni, on one hand, and Mn and Cr, on the other.

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