The geochemical signature of suspended sediments in the Parana River basin: Implications for provenance, weathering and sedimentary recycling

Verena Agustina Campodonico *, María Gabriela García, Andrea Inés Pasquini

Centro de Investigaciones en Ciencias de la Tierra (CICTERRA), Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Universidad Nacional de Córdoba (UNC), Av. Vélez Sarsfield 1611, X5016CGA, Córdoba, Argentina

ABSTRACT

The Paraná River basin is one of the largest hydrological systems in South America. The present study focuses on the mineralogical and chemical composition of the suspended sediments exported by the Paraná River to the Atlantic Ocean, with the aim of analyzing their provenance, the chemical weathering signature and the likelihood of sedimentary recycling. The particulate matter of the Middle Paraná River and its main tributaries (i.e., the Paraguay and the Upper Paraná rivers) is mostly composed of quartz, plagioclase, K-feldspar, and clays, such as illite and kaolinite. Different geochemical approaches indicate that the suspended sediments transported by the Paraná River preserve the chemical signature of its sources and its composition is not significantly modified during transport. These sediments are mainly supplied by acidic arc sources located in the Andean headwaters of the Bermejo and Pilcomayo rivers (and transported by the Paraguay River); and by tholeiitic basalts outcropping in the headwaters of the Upper Paraná River. The incomplete mixing of both main tributaries produces a transverse geochemical asymmetry in the particulate material of the Middle Paraná River, which was detected ~32 km downflow the confluence. The suspended load transported by the Paraguay River (which includes the contributions from the Bermejo and Pilcomayo rivers) indicates incipiently to moderately weathering, whereas the particulate matter exported by the Upper Paraná River reveals a higher degree of chemical alteration. This is the result of the different lithology and climatic regimes that prevail in the headwaters of both tributaries. The weathering signature of the Middle Paraná River's suspended load resembles that of the Paraguay River, which in turns supplies most of the particulate matter through the Bermejo River. This work also shows that the suspended load exported by the Paraná River basin has a mixed origin, where the chemical signatures from young materials derived from undifferentiated volcanic rocks, and from recycled materials affected by intracrustal differentiation can be distinguished.

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1. Introduction

Large rivers constitute the main pathways of solutes and suspended particles from the continents to the oceans, which result from continental denudation, i.e., the synergistic action of rock weathering and erosion. Milliman and Farnsworth (2011) found that rivers around the world discharge annually about 36,000 km³ of freshwater and more than 20 billion tons of solid and dissolved sediments to the global ocean. Numerous studies have focused on the magnitude and mechanisms that control continental denudation, for example, the classical works of Stallard and Edmond (1983), Milliman and Sivitsky (1992), McLennan (1993), Gaillardet et al. (1999a), among others.

Milliman and Farnsworth (2011) also pointed out that it is almost axiomatic to state that sediment production and transport in a drainage basin are controlled by its catchment size and geomorphology, bedrock geology, climate, vegetation cover and human activity. Most published data about concentration and composition of fluvial sediments is referred to suspended sediments, in part because measuring suspended loads is relatively easy, and because they record the chemical signature of their sources and the weathering conditions that prevail in the source areas. The chemical and mineralogical compositions of fluvial sediments reflect the parent lithology and the entire history of its modifications by weathering, recycling, transport, mixing, deposition and diagenesis (e.g., Weltje and von Eynatten, 2004). Several works have probed into the geochemical nature and factors controlling the concentration and composition of the suspended load of large rivers. For instance, Dupré et al. (1996), Gaillardet et al. (1997, 1999b), Picouet et al. (2002), Ramesh et al. (2000), Singh et al. (2005), Viers et al. (2008)

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* Corresponding author at: CICTERRA, Av. Vélez Sarsfield 1611, X5016CGA, Córdoba, Argentina.

E-mail address: vcampodonico@unc.edu.ar (V.A. Campodonico).

and Viers et al. (2009) analyzed the chemical composition of the suspended sediments transported by large rivers and the signature of weathering and erosion. The effects of transport and mineral sorting on sediment geochemistry have been evaluated in several works, such as those of Galy and France-Lanord (2001), Singh et al. (2005), Singh (2009) and Wu et al. (2013). Further, the geochemical record of clastic sediments has been widely used to analyze their provenance and the weathering conditions that prevail in the source areas (e.g., McLennan et al., 1993; Meinhold et al., 2007; Pasquini et al., 2005; Singh, 2009). For these purposes, immobile major and trace elements, such as Al, Fe, Ti, Th, Sc, Co and Zr, and rare earth elements (REEs), mainly carried in the suspended load of rivers, are particularly useful as they experience little fractionation during weathering. Sedimentary recycling has also been discussed in the literature by means of different geochemical approaches (e.g., Dellinger et al., 2014; Gaillardet et al., 1999b; McLennan et al., 1990, 1993, 2003; Meinhold et al., 2007; Potter et al., 2005).

The Paraná River is one of the largest rivers around the world (in the sense of Potter, 1978), inasmuch as it is about 4000 km long and its drainage basin, the second largest in South America (i.e., after the Amazon basin), has an area of 2.6×10^6 km^2 (Milliman and Farnsworth, 2011). In its middle stretch, the average annual discharge is about 18,800 m^3 s^{-1} at the city of Corrientes (mean for the period 1970–2012; Argentina's Subsecretaría de Recursos Hídricos, www.hidricosargentina.gov.ar) and the suspended sediment load is ~1.2×10^8 t yr^{-1} (calculated for December 1993–January 1999; Amsler and Drago, 2009). In the Paraná River basin, just a few works have analyzed the chemical and mineralogical composition of the suspended sediments (e.g., Bonetto and Orfeo, 1984; Depetris and Griffin, 1968; Depetris et al., 2003; Depetris and Pasquini, 2007), as well as their isotopic signature (e.g., Henry et al., 1996).

Another significant feature of large rivers is that they usually exhibit longitudinal (i.e., downstream), transverse, vertical and temporal heterogeneities. The first two are frequently observed downflow the confluence with large tributaries, leading to parallel "braids" of water bodies (Yang et al., 1996). Most studies reporting chemical asymmetries in large rivers are mainly focused on the dissolved load (e.g., Aucour et al., 2003; Bouchez et al., 2010; Lambs, 2004; Pawelleck, 1995). In a recent work, Campodonico et al. (2015) described a transverse chemical and isotopic asymmetry in the dissolved load of the Middle Paraná River, which was attributed to the unmixing of the main tributaries that imparted their own dissolved chemical signatures. The incomplete mixing of waters after the confluence with tributaries is also manifested through the concentration and composition of the particulate fraction. However, the suspended load has been scarcely used to explore the chemical heterogeneities in large rivers. For example, Aucour et al. (2003) and Laraque et al. (2009) examined the relative suspended sediment contributions of the Negro and Solimões rivers into the Amazon River. Bonetto and Orfeo (1984) measured in the Middle Paraná River at the city of Corrientes (i.e., ~32 km downflow the confluence of the Paraguay and Upper Paraná rivers) under baseflow conditions, a concentration of suspended sediments four times higher in the western margin compared to the eastern border. These authors also reported a nearly homogeneous concentration of suspended sediments at ~350 km downflow the confluence of the main tributaries.

In this work we report new data of the mineralogical and chemical composition of the suspended sediments of the Paraná River. The objectives of this paper are to infer the provenance of the suspended load, to analyze the imprint of chemical weathering in the basin, and to detect geochemical evidences of sedimentary recycling. Furthermore, the chemical composition of the suspended sediments is also used here to analyze the unmixing of the Middle Paraná's main tributaries, i.e., the Upper Paraná and Paraguay rivers, close to their confluence.

2. Study area

The Paraná River drainage basin (Fig. 1) covers an area of ~2.6×10^6 km^2 (Milliman and Farnsworth, 2011) and supplies ~80% of the total water discharge to the Río de la Plata estuary. The Upper Paraná River headwaters are placed at Serra dos Preneos (~45°W), close to the Atlantic coast in Brazil, whereas its westernmost water sources (i.e., the headwaters of the Pilcomayo, Bermejo and Salado rivers) are close to the Andes foothills (in western Argentina and Bolivia, ~65°W). The upper catchments of the Paraguay River are located at the Gran Pantanal, one of the largest wetlands in the world (Mato Grosso and Mato Grosso do Sul states, Brazil, ~15°S and ~55–60°W). The Upper Paraná and Paraguay rivers join near the city of Corrientes (Fig. 1) and the stretch encompassed between the confluence and the city of Diamante (32°04′11″S 60°38′16″W; Entre Ríos province, Argentina) is known as Middle Paraná River (Drago and Vassallo, 1980). The main contributor to the Middle Paraná River discharge is the Upper Paraná River, which supplies ~73% of the total water budget, whereas the Paraguay River (including the Bermejo and Pilcomayo rivers discharges) delivers the remaining 27% (Pasquini and Depetris, 2007). The relative contribution of the main tributaries is not uniform throughout the year due to the differences between the hydrological regimes of the Upper Paraná and Paraguay rivers. Hence, the freshwater contribution of the Paraguay River to the middle stretch is up to 34% during austral winter, and diminishes to ~19% in austral summer when the Paraná River reaches maximum flow (Depetris, 2007).

Fig. 1 also shows the lithology outcropping in the Paraná River basin. The Upper Paraná catchment is mainly covered by the Jurassic-Cretaceous tholeiitic basalts of the Serra Geral Formation and Cretaceous sandstones. Precambrian metamorphic rocks are also found in its headwaters. The Paraguay basin is covered primarily by Quaternary and recent fluvial deposits. At the Andes foothills, in the headwaters of the Pilcomayo and Bermejo rivers, outcrops of marine and continental sedimentary rocks, as well as of Precambrian metamorphic rocks and Quaternary intermediate volcanic rocks, can be found. A significant portion of the Paraná drainage basin, including the vicinity of the middle stretch, is covered by Quaternary deposits, mainly of fluvial and deltaic origin (Fig. 1).

The main course of the Middle Paraná River exhibits a multi-channelled pattern and it can be classified as braided of low sinuosity (Orfeo and Stevaux, 2002). This braided pattern is usually observed when the availability of bed sediments is higher than the suspended sediment load (Friend and Sinha, 1993). The floodplain of the middle and lowermost reaches of the Paraná River is 900 km long and ~30 km wide (Depetris and Kempe, 1993). It is a wetland composed of shallow streams, ponds, marshes and ox-bow lakes.

The atmospheric circulation over South America during austral summer is dominated by a monsoonal system (SAMS). The convection band, known as the South Atlantic Convergence Zone (SACZ), is a distinctive feature of the SAMS, and is placed along the north-eastern boundary of the Río de la Plata drainage basin (e.g., Garreaud et al., 2008). Also, during austral summer a low-level northerly/northeasterly jet that flows east of the Andes, transports large amounts of moisture between the Amazon and the Río de la Plata basin (e.g., Berbery and Barros, 2002). As a consequence of these continental climatic features, the mean annual rainfall is unevenly distributed over the Paraná basin. Maximum precipitation (2400 mm yr^{-1}) occurs along the eastern margin of the basin, whereas towards the west, along the 60–65°W strip, rainfall decreases to 400–800 mm yr^{-1} (Pasquini and Depetris, 2007). Mean temperatures in January (austral summer) are between 20–30 °C in the whole basin, while in July (austral winter) mean temperatures range from 15 to 25 °C in the northern and center portions of the basin, and from 10 to 15 °C in the South.

Milliman and Farnsworth (2011) estimated that the Paraná River transports on average 6.2×10^4 t yr^{-1} of dissolved load and
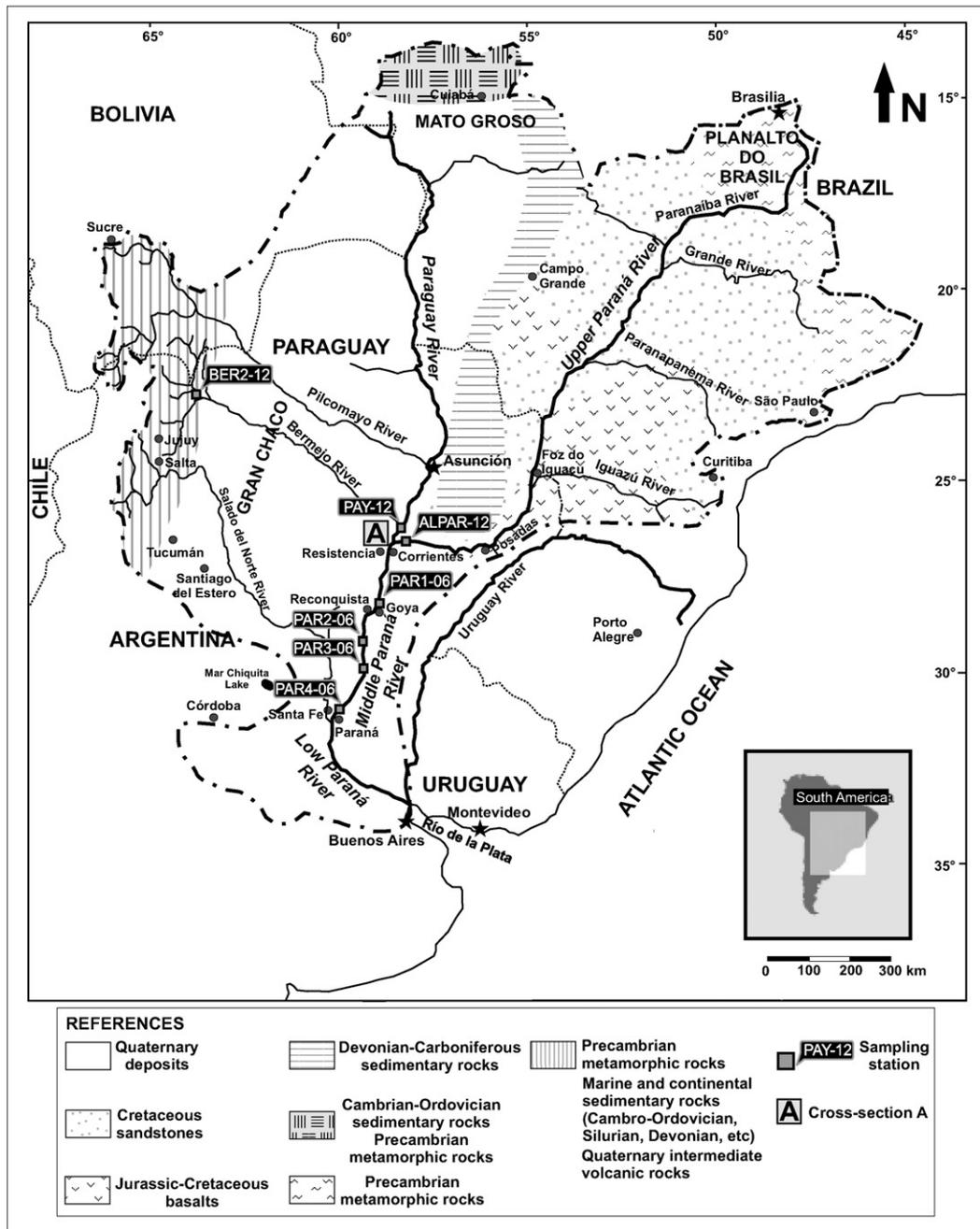
Fig. 1. Schematic geological map of the Paraná River drainage basin, showing the location of sampling sites.

9.0×10^7 t yr^{-1} of total suspended solids to the Atlantic Ocean. As pointed out above, Amsler and Drago (2009) measured in the middle stretch of the Paraná River a suspended sediment load of ~1.2×10^8 t yr^{-1} during December 1993–January 1999, of which ~90% is supplied by the Bermejo River, whose concentration often exceeds 5 g L^{-1} (Depetris, 2007). However, during austral summer, intense rainfall events occur at the Andes headwaters where friable sedimentary rocks with steep slopes are abundant, increasing the suspended sediment concentrations to 100 g L^{-1} between December and February (Amsler and Drago, 2009).

Depetris and Griffin (1968) determined that the <2 μm size fraction of the suspended sediment load in the Paraná's lowermost reaches was composed of illite ≫ smectite > kaolinite > chlorite. Besides, these authors established that the coarser size fraction (2–20 μm) was mainly composed by K-feldspar, plagioclase, mica and quartz.

3. Materials and methods

Suspended sediment (SS) samples were collected from the main channel of the Middle Paraná River and its tributaries (Upper Paraná, Paraguay and Bermejo rivers), under baseflow conditions (Fig. 1, Table 1). In order to analyze the contribution of the main tributaries (i.e., the Paraguay and Upper Paraná rivers) to the middle stretch's SS chemical signature, three samples were collected from the centre and close to both river banks along a cross-section located at Resistencia-Corrientes (27°27′35″S), named cross-section A (Fig. 1). Suspended sediments were also taken from the middle stretch of the Paraná River at Goya (29°06′0.0″S, 59°16′60.0″W), Esquina (30°01′06.7″S, 59°33′26.1″W), La Paz (30°43′38.6″S, 59°38′19.5″W) and Paraná (31°42′50.0″S, 60°30′35.6″W) cities. For the current analysis, a previous dataset reported in Depetris and Pasquini (2007) was also considered.

Table 1

Chemical composition of the suspended sediments transported by the Middle Paraná River and its tributaries. Weathering indices and REE UCC-normalized relationships are also included.

River	Middle Paraná R.							Upper Paraná R.	Paraguay R.	Bermejo R.
	Section A			Goya	Esquina	La Paz	Paraná			
	East	Centre	West							
Sample n°	PARC2-11	PARC2-31	PARC2-51	PAR1-06	PAR2-06	PAR3-06	PAR4-06	ALPAR-12	PAY-12	BER2-12
Location	27°27′43.6″ S	27°27′30.8″ S	27°27′4.3″ S	29°06′0″ S	30°01′6.7″ S	30°43′38.6″ S	31°42′50.0″ S	27°17′03.9″ S	27°16′19.1″ S	23°14′51.7″ S
	58°50′41.5″ W	58°50′51.0″ W	58°51′12.7″ W	59°17′0″ W	59°33′26.1″ W	59°38′19.5″ W	60°30′35.6″ W	58°31′45.9″ W	58°35′48.5″ W	64°08′14.9″ W
SiO_2	57.40	68.48	67.73	69.02	68.16	70.82	69.45	54.42	68.06	68.35
Al_2O_3	23.61	17.54	17.83	21.31	17.76	15.90	16.79	25.56	17.66	15.80
$Fe_2O_{3(T)}$	11.17	7.28	7.10	3.26	6.91	6.02	6.33	12.73	6.93	5.75
MnO	0.16	0.11	0.12	0.49	0.09	0.09	0.09	0.15	0.13	0.13
MgO	1.01	1.26	1.49	1.12	1.42	1.41	1.48	1.12	1.50	1.88
CaO	0.92	0.73	0.79	0.83	0.78	0.74	0.75	0.86	0.82	0.83
Na_2O	0.56	0.83	0.94	1.48	1.02	1.12	1.07	0.42	0.93	1.53
K_2O	1.61	2.40	2.84	1.71	2.63	2.68	2.86	1.60	2.85	3.89
TiO_2	3.04	1.17	0.95	0.45	0.99	0.99	0.95	2.68	0.89	1.56
P_2O_5	0.51	0.21	0.21	0.33	0.24	0.23	0.23	0.46	0.22	0.29
Sc	29.0	17.0	15.0	6.0	15.0	15.0	16.0	32.0	14.0	13.0
Ba	489.0	542.0	549.0	392.0	493.0	558.0	575.0	524.0	541.0	663.0
Sr	87.0	110.0	121.0	686.0	100.0	122.0	125.0	84.0	120.0	129.0
Y	38.0	35.0	32.0	25.0	30.0	37.0	35.0	39.0	31.0	29.0
Zr	242.0	280.0	207.0	62.0	218.0	326.0	251.0	268.0	191.0	229.0
Cr	110.0	70.0	60.0	230.0	60.0	100.0	120.0	110.0	60.0	70.0
Co	58.0	22.0	17.0	15.0	14.0	14.0	14.0	48.0	17.0	33.0
Ni	60.0	30.0	30.0	100.0	<20.0	40.0	<20.0	60.0	30.0	30.0
Cu	200.0	70.0	40.0	180.0	60.0	50.0	30.0	190.0	30.0	40.0
Rb	79.0	112.0	127.0	55.0	119.0	134.0	137.0	87.0	132.0	157.0
Nb	49.0	24.0	20.0	7.0	15.0	17.0	17.0	49.0	22.0	30.0
Hf	6.9	7.1	5.9	2.7	5.7	8.3	6.5	7.5	5.3	6.6
Ta	2.7	1.4	1.3	0.6	1.3	1.6	1.4	2.5	1.2	1.9
Tl	0.6	0.7	0.8	<0.1	0.7	0.7	0.5	0.4	0.7	0.9
Pb	35.0	31.0	29.0	629.0	70.0	76.0	416.0	52.0	28.0	31.0
Th	12.4	13.3	13.8	7.0	13.0	15.1	14.5	14.4	13.5	14.0
U	3.4	3.6	3.8	3.2	5.0	3.7	4.0	3.8	3.9	3.7
Cs	7.6	8.7	9.5	3.9	9.0	9.5	10.1	9.1	9.8	8.8
La	49.5	44.9	45.2	23.8	38.6	46.5	43.6	56.6	44.6	44.5
Ce	95.8	89.6	88.5	53.2	85.8	102.0	96.3	114.0	85.4	87.3
Pr	10.9	10.5	10.4	6.0	9.3	10.9	10.4	12.6	10.1	10.1
Nd	42.3	40.3	40.9	23.3	33.9	40.3	38.2	48.4	38.3	37.2
Sm	8.6	8.1	8.0	4.8	6.7	7.8	7.4	9.5	7.7	7.5
Eu	2.1	1.7	1.6	1.0	1.6	1.8	1.7	2.3	1.6	1.4
Gd	6.9	6.5	6.3	4.9	6.2	7.5	7.0	7.8	6.3	6.0
Tb	1.1	1.0	1.0	0.7	1.0	1.2	1.1	1.2	1.0	1.0
Dy	6.8	6.0	6.0	4.2	5.8	6.9	6.4	7.2	5.8	5.5
Ho	1.3	1.2	1.1	0.8	1.1	1.3	1.2	1.4	1.1	1.1
Er	3.7	3.4	3.2	2.4	3.3	3.9	3.6	4.0	3.2	3.2
Tm	0.6	0.5	0.5	0.4	0.5	0.6	0.5	0.6	0.5	0.5
Yb	3.9	3.4	3.2	2.3	3.1	3.8	3.4	3.9	3.1	3.1
Lu	0.6	0.5	0.5	0.3	0.5	0.6	0.5	0.6	0.5	0.5
La_N/Yb_N	0.93	0.97	1.04	0.76	0.91	0.90	0.94	1.06	1.06	1.05
Eu_N/Eu_N^*	1.29	1.11	1.06	1.00	1.15	1.12	1.14	1.27	1.09	1.01
Ce_N/Ce_N^*	0.91	0.92	0.90	1.00	1.04	1.03	1.03	0.95	0.90	0.93
Weathering indices										
CIA	85.6	77.4	75.1	79.3	75.5	72.9	73.5	87.5	74.8	66.3
ICV	0.77	0.84	0.88	0.56	0.86	0.94	0.91	0.73	0.89	1.19
αCa	12.3	10.9	8.1	3.7	8.6	9.0	8.6	11.5	7.3	12.8
αNa	6.4	6.5	5.7	2.2	4.4	4.6	4.6	9.4	5.5	3.3

Major oxides in % and trace elements in ppm.

Major oxides recalculated to 100%.

Total iron as Fe_2O_3.

$Eu_N/Eu_N^* = Eu/(Sm * Gd)^{0.5}$ (McLennan, 1989).

$Ce_N/Ce_N^* = Ce/(1/3Nd + 2/3La)$ (Elderfield et al., 1990).

N denotes normalization to UCC (McLennan, 2001).

During sampling, about 20 L of surface water were filtered using a Millipore 142 mm Pressure Filter System with 1.5 atm of N_2 as inlet gas. The suspended sediments were pre-concentrated on 0.45 μm cellulose acetate membrane filters (Millipore Corp.), air-dried for 24 h and stored in sealed plastic bags.

Mineral composition was identified by X-ray diffraction (XRD) and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) measures. XRD analyses were performed with a Philips X´ Pert PRO X-ray diffractometer operating at 40 kV and 40 mA using Cu-Ká radiation. XRD data were obtained for random samples in the 2θ range from 4 to 65° (step size: 0.02; 1 s/step). The mineralogical interpretation was done using the software X´Pert HighScore, installed on the X-ray diffractometer. SEM/EDS studies were performed with a Carl Zeiss Sigma FE-Scanning Electron Microscope. The samples were

prepared in graphite stubs and coated with gold. In addition, SEM was coupled with focused energy dispersive X-Ray analysis (EDS, AZTec. Oxford), in order to perform the elemental semi-quantification

The major chemical composition and the concentration of some selected trace elements, such as Ba, Be, Sc, Sr, V, Y and Zr, were measured by ICP-OES, whereas the remaining trace elements were determined by ICP-MS. The analytical work was performed at Activation Laboratories Ltd. (ACTLABS, Ontario, Canada). For chemical analyses samples were fused with lithium metaborate/tetraborate and then diluted with 5% HNO_3. For each group of samples, one blank and 14 reference materials were analyzed (NIST 694, DNC-1, LKSD-3, W2a, SY4, CTA-AC, BIR1a, NCS DC86312, ZW-C, NCS DC70014, NCS DC70009, OREAS 100a, OREAS 101a, JR-1), certified by the CANMET Materials Technology Laboratory, the Intytut Chemii I Techniki Jadrowej, and the USGS. The accuracy of standard measures ranged between 1 and 10% in most cases.

4. Results and discussion

4.1. Mineralogy

The most abundant minerals in the studied SS samples are quartz, plagioclase, K-feldspar, and clays such as illite and kaolinite. Fig. 2A shows, as an example, the mineralogical composition of the Paraná River SS in cross-section A. In the Bermejo River, vermiculite was also identified, whereas the presence of carbonates was only recognized in the centre of cross-section A (Fig. 2A). Certainly, the mineralogical composition determined here is similar to that pointed out by Depetris and Griffin (1968).

The mineralogy of the SS was similar in both river banks downflow the confluence of the Paraguay and Upper Paraná rivers (i.e., at cross-section A). SEM–EDS analyses reveal that the Paraguay and Upper
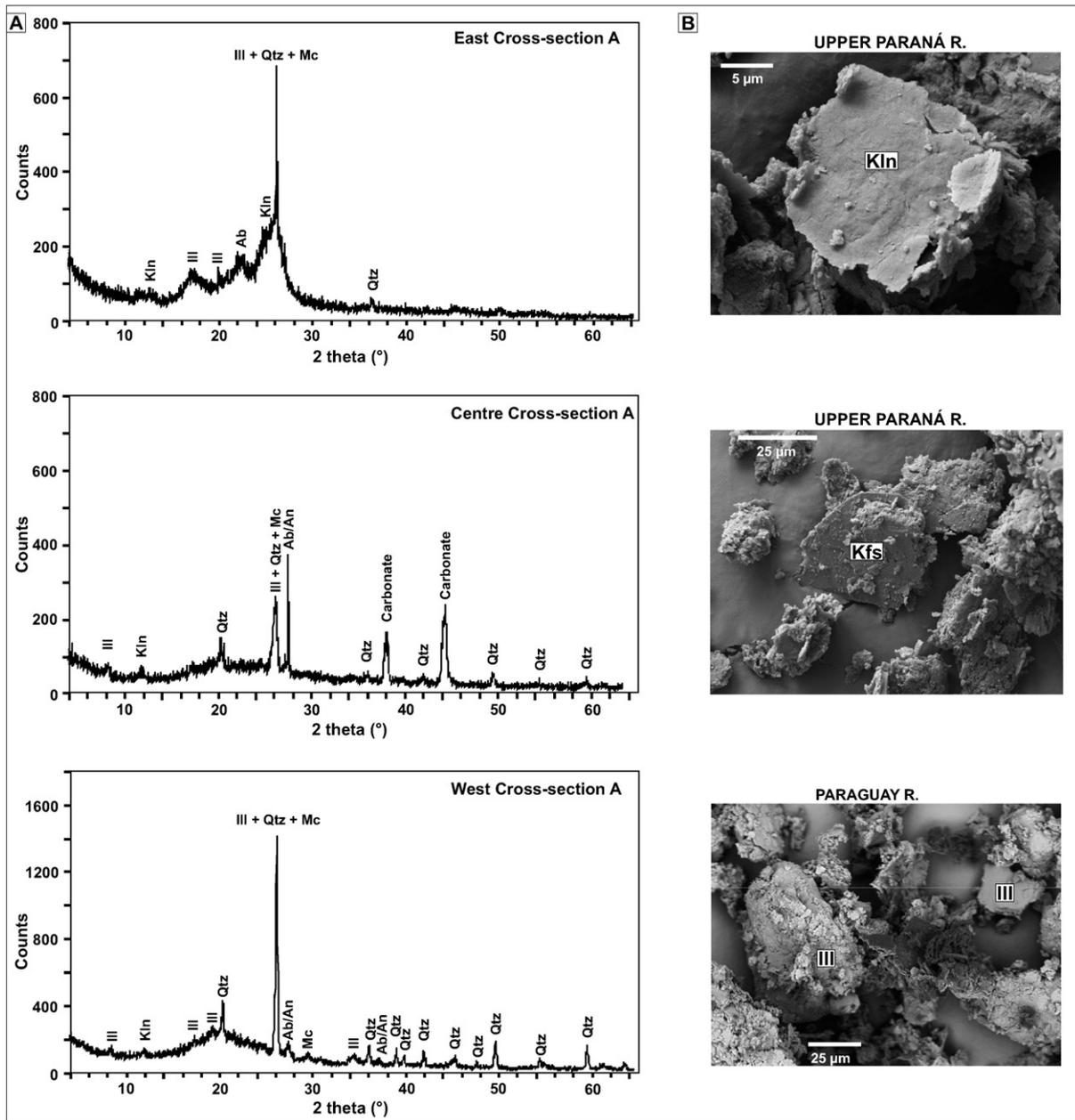
Fig. 2. A) X-ray diffractograms of the Middle Paraná River suspended sediments from the river banks and centre of cross-section A. The XRD of the Paraguay River resembles that of the West, whereas the XRD of the Upper Paraná River is similar to that of the East. B) SEM images of the suspended solids transported by the Paraguay and Upper Paraná rivers. These images reveal that they are mainly composed of altered aluminosilicates with abundant clayed coatings. Ill = illite; Kln = kaolinite; Qtz = quartz; Mc = microcline; Ab = albite; An = anorthite; Kfs = K-feldspar.

Paraná suspended loads are mainly composed of altered aluminosilicates with abundant clayed coatings (Fig. 2B). In general, mineral aggregates in the Paraguay River are larger than those observed in the Upper Paraná River.

Potter et al. (2005) established that clay mineralogy reflects the geological and climatic characteristics prevailing at a drainage basin's headwaters. Following this idea, illite in the Paraná River's SS is mostly supplied by the Andean tributaries Bermejo and Pilcomayo. These two rivers' headwaters extend over the Andes region, where large outcrops of sedimentary rocks are found and climatic semiarid conditions prevail. On the other hand, the Upper Paraná and Paraguay rivers, which drain the tropical Brazilian Shield and tholeiitic basalts, are likely the main contributors of kaolinite.

4.2. Geochemistry

The concentrations of major and trace elements measured in the suspended load of the Middle Paraná River and its main tributaries are shown in Table 1.

In order to classify the analyzed sediments, the ratio log (Fe_2O_3/K_2O) was plotted against the ratio log (SiO_2/Al_2O_3) in the Herron's (1988) diagram for clastic rocks (Fig. 3), which can further be applied to unconsolidated fine- to coarse-grained sediments. In terrigenous sands and shales, the SiO_2/Al_2O_3 ratio is a geochemical indicator of mineralogical maturity and it separates quartz-rich sandstones from clay-rich shales, with other sandstones showing intermediate values. The ratio of total iron (expressed as Fe_2O_3) to K_2O separates lithic fragments from feldspars in a wide variety of sandstones (Herron, 1988). According to the Herron's (1988) diagram, SS in the Middle Parana River basin are mineralogically immature, as most of the analyzed samples have log SiO_2/Al_2O_3 ratios of ~0.5 (Fig. 3). This is consistent with the presence of feldspars in the sediments (Fig. 2A). Downflow cross-section A, the log SiO_2/Al_2O_3 ratio remains almost constant or slightly increases. In all cases, SS in the Middle Paraná River, along with those collected in the Paraguay River, plot between the fields of mudstones and wackes. SS from the Bermejo, Pilcomayo, and Upper Paraná rivers, as well as from the eastern margin of cross-section A, are in turn classified as iron mudstones (Fig. 3). The SS of the Paraguay River that plot within the fields of lith-arenite and sublith-arenite, probably reflect the relative mineralogical maturity of the northern Mato Grosso's soils, whereas the SS from the Andean tributaries classified as iron sands reveal the capacity of these rivers to transport coarser and heavier materials, as it was already pointed out by Depetris and Pasquini (2007).
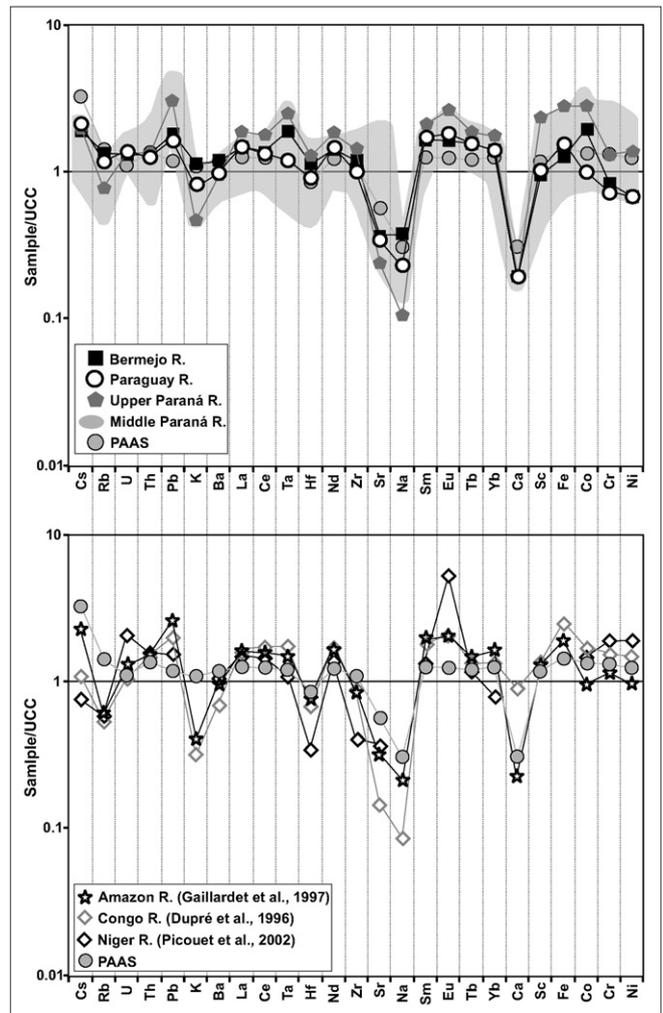
Fig. 4. Extended UCC-normalized spidergrams of suspended sediments from A) the Middle Paraná River (shaded area) and its main tributaries, and B) other world's large rivers (i.e., Amazon, Congo and Niger rivers, references in the graph). On the X-axis elements are ranked in order to obtain a monotonic decrease of UCC abundances (McLennan, 2001) when normalized to Primitive Mantle concentrations (Hofmann, 1988). UCC composition from McLennan (2001); PAAS: Post-Archean Australian Shales composition from McLennan (1989).
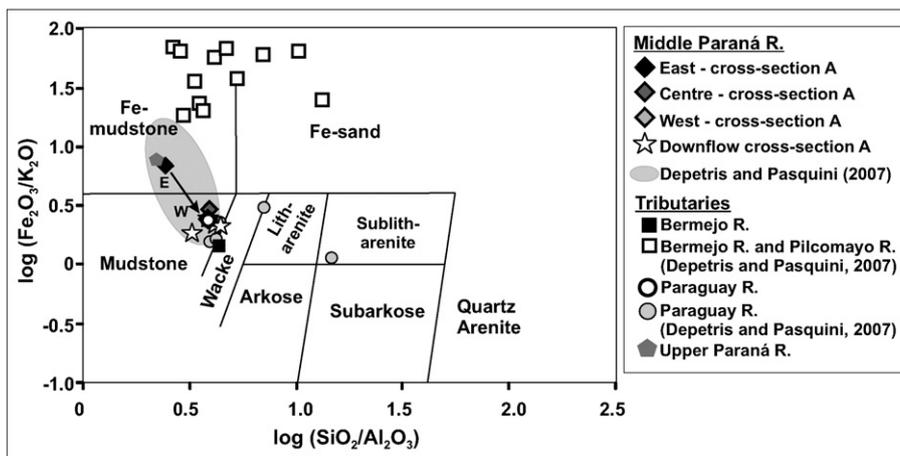
Fig. 3. Herron's (1988) geochemical classification diagram for the suspended sediments transported by the Middle Paraná River and its tributaries (i.e., Bermejo, Paraguay and Upper Paraná rivers). The dataset reported in Depetris and Pasquini (2007) is included for the analysis.

Fig. 4A shows the upper continental crust (UCC; McLennan, 2001) normalized extended patterns for the SS of the Middle Paraná, Paraguay, Upper Paraná and Bermejo rivers. The UCC-normalized Post Archean Australian Shales (PAAS, McLennan, 1989) pattern is also included. The shadowed area spans the compositional variability of SS in the middle stretch of the Paraná River (the transverse heterogeneities observed along cross-section A will be addressed further in this section). The X-order of elements in the diagram corresponds to the progressive enrichment of elements, from Ni to Cs, in the UCC with respect to the Earth's primitive mantle (Hofmann, 1988). For comparison, Fig. 4B shows the UCC-normalized extended patterns of the SS exported by some other world large rivers, such as the Amazon (Gaillardet et al., 1997), Congo (Dupré et al., 1996) and Niger (Picouet et al., 2002). According to this figure, the SS transported by the Middle Paraná River and its tributaries (Fig. 4A), show a PAAS-like composition, and are generally depleted in K, Sr, Na, and Ca with respect to the UCC composition. These elements are highly mobile during the early stages of chemical weathering and they are usually enriched in the dissolved phase. Conversely, less mobile elements such as Cs, Th, Pb, REE, Ta, Fe, and Co are slightly enriched in the analyzed SS. These elements are concentrated in the SS due to the removal of the most soluble elements from the bedrock.

The SS transported by large rivers generally display, in terms of absolute abundance, REEs concentrations that are close to those reported for the UCC (Viers et al., 2009). This is the case of the Middle Paraná River and its main tributaries, where the REEs abundances (Table 1) are, in average, about 1.6 times higher than the UCC. The UCC normalized-REEs patterns in the analyzed suspended sediments are shown in Fig. 5. In spite of the absolute variations, the UCC-normalized REEs spidergram shows similar patterns (Fig. 5), with a slight enrichment in middle REEs (MREEs; Sm to Dy), as well as a slight depletion in light REEs (LREE) compared to MREE and heavy REEs (HREE) ($La_N/Yb_N <1$; Table 1). MREEs enrichment in the SS may reflect the presence of organic matter (e.g., Tricca et al., 1999; Aubert et al., 2001), which represents about 4% of the annual suspended load according to long-term measurements of POC performed in the Middle Paraná River (Depetris, 2005). However, MREEs enrichment can also originate in sediments containing Fe-Mn oxyhydroxides (e.g., Johannesson and Zhou, 1999) or trace amounts of apatite (e.g., Hannigan and Sholkovitz, 2001). The particulate matter of the Middle Paraná River and its tributaries also
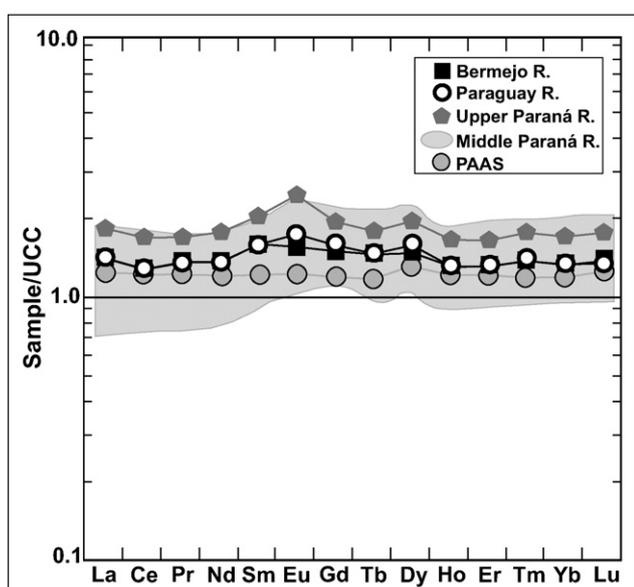
exhibits a slightly positive Eu anomaly (average $Eu_N/Eu_N^* = 1.14$; Table 1), which may be caused by a preferential retention of Eu-bearing minerals such as plagioclase and K-feldspar. Finally, most samples show a slightly negative Ce anomaly (average $Ce_N/Ce_N^* = 0.90$; Table 1), which is also concordant with the occurrence of organic matter in the suspended load.

The transversal heterogeneity in the chemical composition of the dissolved load transported by the Middle Paraná River was analyzed in a recent contribution (Campodonico et al., 2015). This variability was attributed to the incomplete mixing of waters draining the main tributaries (i.e. Paraguay and Upper Paraná rivers). A similar heterogeneity was identified here regarding the suspended load. Fig. 6 shows the concentration of selected elements in the SS of the Middle Paraná River, after the confluence of the main tributaries, i.e., along cross-section A. At this cross-section, the composition of the SS from the eastern border was similar to the Upper Paraná River, whereas on the western margin it resembled that of the Paraguay River, reflecting the geochemical signature of their respective drainage basins. Indeed, a trend of decreasing concentrations was observed from West to East for Ba, Sr, K and Rb, while Fe, Ti, Sc, Y and Nb exhibited an opposite trend (Fig. 6). Other elements such as Al, Co, Cr, Y, and Cu (not shown in the figure) show a similar increasing trend from the western bank to the eastern one. The mafic rocks (i.e., tholeiites) of the Upper Paraná basin are the major suppliers of the elements concentrated in the eastern border, whereas the Andean sedimentary rocks are probably the main sources of Ba, Sr, K and Rb. Longitudinal variations were not identified in the chemical composition of SS, with the exception of a slight increase in the concentration of a few elements such as Ba, Rb, Nb, Cs and Sc in the flow direction.

4.3. Provenance

Classical studies such as those of Dickinson et al. (1985) and Potter (1978) have documented the linkage between the mineralogy of sedimentary rocks and sediments and their provenance. Likewise, several discrimination models have been proposed to characterize sedimentary rocks in relation with the tectonic settings. Some other approaches however, consider that geochemical information, better than mineralogical composition, is a more accurate tool to analyze the relationship between composition, provenance and tectonic setting (e.g., Bathia, 1983; Roser and Korsch, 1986). In concordance, the geochemistry of suspended sediments has been widely used to determine provenance and weathering processes (e.g., Depetris and Pasquini, 2007; Gaillardet et al., 1999b; Singh et al., 2005). One of the major concerns in analyzing sediment provenance is recycling. Sediments exported from the continents to the oceans could have passed more than once through the exogenous cycle (e.g., Gaillardet et al., 1999b), which leaves a footprint in its mineralogy and chemistry, thus blurring in some cases the results obtained in the provenance analyses.

Though some traditional discrimination diagrams use major elements to infer the provenance of sedimentary rocks and sediments such as those of Bathia (1983) and Roser and Korsch (1986), several authors have recently found that these plots are not always reliable (e.g., Armstrong-Altrin and Verma, 2005; Borges et al., 2008; Caracciolo et al., 2012). Instead, several trace elements ratios and plots seem to be more appropriate to identify sedimentary provenance (e.g., Cullers, 1988, 1994; Pasquini et al., 2005; Singh, 2009; Toulkeridis et al., 1999). Among them, diagrams involving REEs, Th, Sc and high field strength elements are especially useful, as these elements have very short residence times in the water column, and are transferred (almost) quantitatively into the sedimentary record (Mishra and Sen, 2012). La and Th are more abundant in siliceous rocks, whereas Sc and Co are more concentrated in basic rocks. Thus, ratios such as La/Sc, Th/Sc, La/Co, Th/Co are good indicators of the chemical signature of rocks sources (e.g., Cullers, 1988).

Fig. 5. UCC-normalized REE spidergram of suspended sediments from the Middle Paraná River (shaded area) and its tributaries (i.e., Bermejo, Paraguay and Upper Paraná rivers). UCC composition from McLennan (2001); PAAS: Post-Archean Australian Shales composition from McLennan (1989).
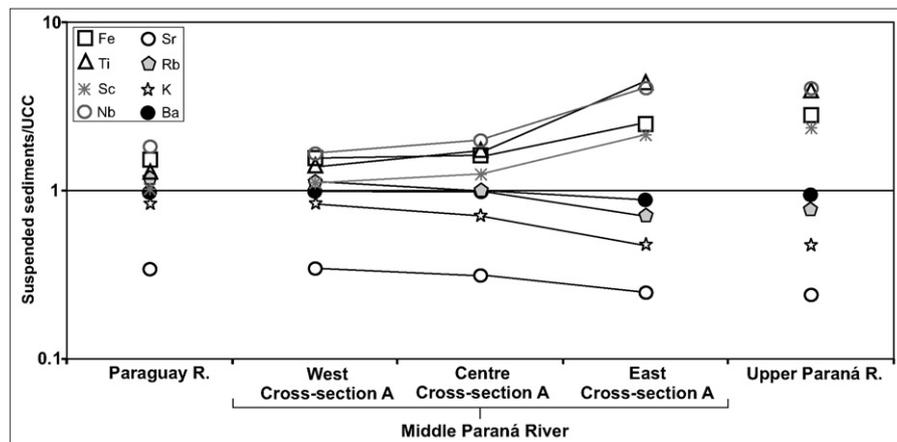
Fig. 6. Transverse variability of some major and trace elements in the suspended load of the Middle Paraná River at cross-section A. Sr, K and Rb increase from East to West, whereas Fe, Ti, Sc, and Nb show an opposite trend.

Fig. 7 shows the La—Th—Sc compositional triangles for the SS transported by the Middle Paraná River and its main tributaries. As seen in the figure, the SS cluster around the field of continental arcs (Fig. 7A), which generally encompasses a wide compositional range of igneous source rocks (i.e., from granitic to basaltic) (Fig. 7B). Samples from the Upper Paraná and from the eastern margin of cross-section A plot separated from the mentioned cluster of samples towards a more basic extreme, thus reflecting the signature of the tholeiitic basalts that outcrop in the upper catchments of the Paraná River (Fig. 7B). According to these results, the particulate matter transported by the Middle Paraná River seems to preserve the chemical signature of the rock sources as its composition is not substantially modified.

Fig. 8 corresponds to the discrimination diagram proposed by Floyd and Leveridge (1987), which uses the La/Th ratio vs. Hf to distinguish different arc compositions and sources. Sediments derived from acid arcs have low and uniform La/Th ratios and Hf contents of about 3–7 ppm (Floyd and Leveridge, 1987). With the progressive dissection of the arc and the erosion of its plutonic roots and continental basement of ancient (meta)sedimentary rocks, the Hf content increases due to the release of zircon, its main host phase (Floyd and Leveridge, 1987). The SS exported by the Middle Paraná River and its main tributaries exhibit low La/Th ratios (<5) and Hf concentrations of about 2.7–8.3 ppm (Table 1), which suggest that they derive predominantly from acidic arc sources and evidence the influence of an old sedimentary component (Meinhold et al., 2007).

The most outstanding feature of the REE distribution in sediments and sedimentary rocks is the remarkable uniformity of its patterns (e.g., McLennan, 1989), which resemble, in general, the UCC composition. The main factor controlling the concentration of REEs in clastic sediments is provenance; hence the REE patterns of the source may be preserved in sedimentary rocks and sediments (e.g., Cullers, 1994; Taylor and McLennan, 1985). Fig. 9 shows the UCC-normalized REE patterns of the Middle Paraná River SS, which are not only close to the composition of tholeiites from the Paraná basin (Depetris, personal communication), but also of young intermediate volcanic rocks (i.e., mean Andean andesites; http://www.geokem.com). Though Depetris et al. (2003) proposed that the SS of the Middle Paraná River preserve a dominantly Andean REE signature, as the Bermejo River is the main contributor of particulate matter, it can be seen that the REE composition of the suspended load delivered by the Paraná River to the Atlantic Ocean results from the mixture of both rock sources and it is not significantly modified.
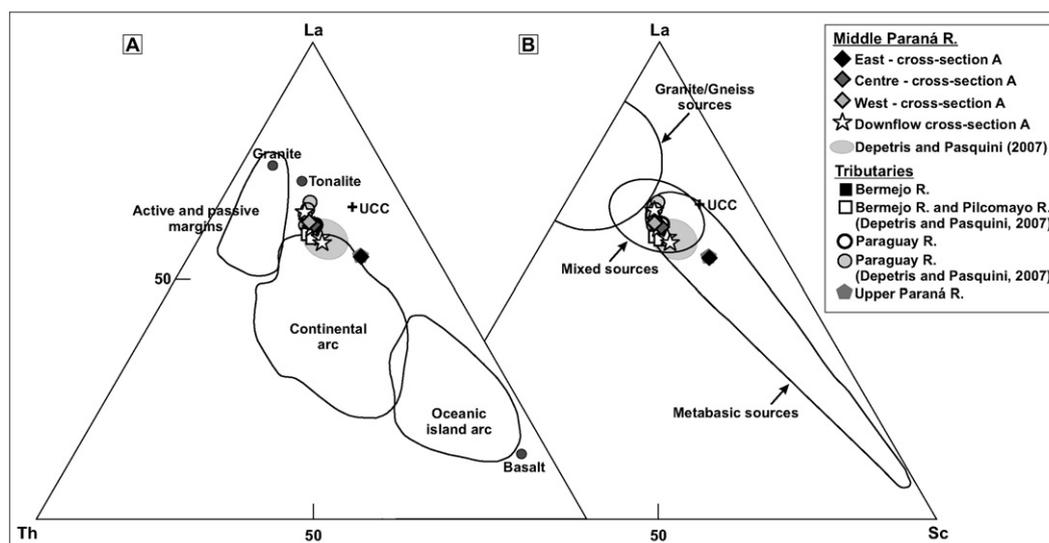
Fig. 7. La—Th—Sc ternary diagrams illustrating A) the tectonic setting (Bathia and Crook, 1986) and B) the sources of the suspended sediments transported by the Middle Paraná River and its tributaries. The dataset reported in Depetris and Pasquini (2007) is also included for the analysis.
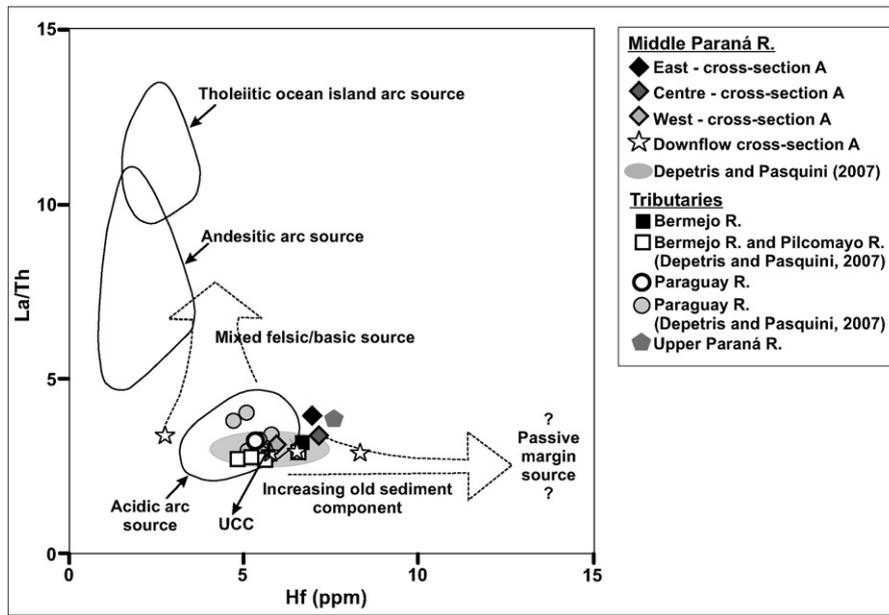
Fig. 8. La/Th vs. Hf discrimination diagram (Floyd and Leveridge, 1987) illustrating the sedimentary provenance of the particulate matter transported by the Middle Paraná River and its tributaries. The dataset published in Depetris and Pasquini (2007) is also included.

4.4. Chemical weathering and sedimentary recycling

Numerous weathering indices have been proposed in the literature to evaluate element mobility during chemical alteration (e.g., Depetris et al., 2014 and references therein). In general, these indices compare the concentration of an immobile element with several mobile components. The chemical index of alteration (CIA; Nesbitt and Young, 1982)

Fig. 9. UCC-normalized REE spidergram of the suspended sediments from the Middle Paraná River. The UCC-normalized REE patterns of tholeiites from the Paraná basin (Depetris, personal communication) and Andean andesites (http://www.geokem.com) are also included. UCC composition from McLennan (2001).

is one of the most commonly used indices, and it is calculated in molar proportions as:

$$CIA = 100 \left[Al_2O_3 / \left(Al_2O_3 + CaO^* + Na_2O + K_2O \right) \right] \quad (1)$$

where CaO^* represents the Ca in the silicate fraction only, adjusted for some other Ca-bearing minerals such as carbonates and apatite. Because carbonates were not identified in the analyzed sediments (with the exception of only one sample), its contribution was considered negligible and the corresponding correction for carbonates was not applied, while apatite corrections were made using the concentrations of P_2O_5. The UCC has a mean CIA of 47 (McLennan, 1993), whereas significantly weathered materials, such as the suspended load of large rivers, have CIA values of ~80. Clays have CIAs close to 100.

The index of compositional variability (ICV; Cox et al., 1995) is another ratio similar to CIA that considers the abundance of alumina relative to other major cations:

$$ICV = (Fe_2O_3 + K_2O + Na_2O + CaO + MgO + MnO + TiO_2)/Al_2O_3 \quad (2)$$

Silica is excluded to avoid problems with quartz dilution. Non-clay silicates have higher ICVs compared to clay minerals, thus compositionally mature fine-grained sediments, dominated by clays and poor in non-clay silicates, show low ICVs.

McLennan (1993) estimated a mean CIA value of 81 for the sediments exported by the Paraná River. One decade later, Depetris et al. (2003), calculated CIA values which ranged between 57 and 66 for the Andean tributaries and a discharge-weighted mean CIA value of ~71 for the Paraná River. Table 1 shows the calculated CIA and ICV values of the SS analyzed in this study. Clearly, the Bermejo River exhibits CIA and ICV values that denote incipient weathering, whereas the Paraguay and Middle Paraná rivers show higher indices, which indicate, as a first approach, moderate weathering. It is also interesting to point out the differences in the weathering indices estimated for the SS of cross-section A, as shown in Fig. 10. This figure corresponds to a bivariate plot of CIA vs. ICV values, where the segments of the theoretical evolution of a mean tholeiite from the Upper Paraná basin (Iacumin et al., 2003) and a mean Andean andesite (http://www.geokem.com) are also included. The SS of the Upper Paraná River and the eastern border of cross-section A plot over the tholeiite line, whereas the Andean
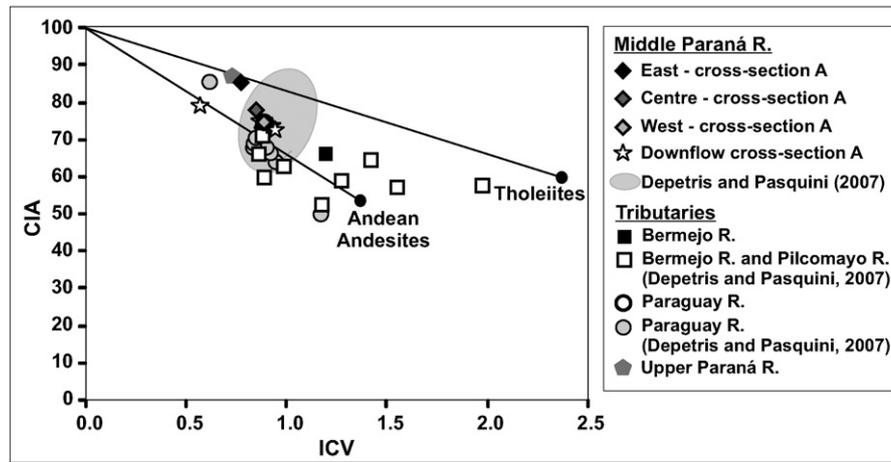
Fig. 10. CIA vs. ICV plot for the suspended sediments transported by the Middle Paraná River and its tributaries. The lines of the theoretical evolution of a mean tholeiite from the Upper Paraná basin (Iacumin et al., 2003) and a mean Andean andesite (http://www.geokem.com) are also plotted. The dataset published in Depetris and Pasquini (2007) is included for the analysis.

tributaries, the Paraguay River and the western border of cross-section A cluster around the theoretical Andean andesite evolution line (Fig. 10), indicating the weathering imprint of these source rocks. The dispersion observed in Fig. 10 for several samples of the Bermejo and Pilcomayo rivers, was attributed by Depetris and Pasquini (2007) to the presence of different supplying sources in their upper catchments, apart from the Andean andesites. As expected, the SS of the Middle Paraná River downstream cross-section A also plot close to the mean Andean andesite line, reflecting the dominant contribution of the Bermejo River to the suspended load of the Paraná River.

As CIA and ICV indices indicate the extent of weathering of a rock or sediment in a general sense, Gaillardet et al. (1999b) proposed the alpha (α) weathering index on the basis of a large set of chemical information of the suspended loads carried by several large rivers around the world. This index is calculated for each mobile element whose concentration is compared with that of an immobile element with a similar magmatic compatibility in the sense of Hofmann (1988). For instance, ratios between elements with similar magmatic compatibilities, such as Sm/Na, are expected to be less variable than ratios between elements of contrasting magmatic compatibilities, such as Th/Na. The α indices for Na and Ca were calculated here for the analyzed SS by means of Eqs. (3) and (4). Though Gaillardet et al. (1999b) defined the alpha indices using the UCC composition as unweathered source rock (because it represents the mean composition of the suspended sediments of large rivers), based on the previous provenance analyses, samples from the Upper Paraná and the eastern margin of cross-section A were normalized to tholeiites outcropping in the Upper Paraná basin (Iacumin et al., 2003), while the remaining samples were normalized to Andean andesites (http://www.geokem.com).

$$\alpha_{Na} = (Sm/Na)_{sed}/(Sm/Na)_{source\ rock} \qquad (3)$$

$$\alpha_{Ca} = (Ti/Ca)_{sed}/(Ti/Ca)_{source\ rock} \qquad (4)$$

From the definition of these indices, it follows that a value $\alpha_i = 1$ means that there is not chemical weathering, whereas $\alpha_i > 1$ indicates a lower concentration of element i in the sediment compared to the source rock and $\alpha_i < 1$ implies an enrichment of element i in the sediment with respect to the source rock. Thus, the higher the α value, the greater degree of chemical weathering exhibits the sediment.

Table 1 shows the α_{Na} and α_{Ca} for the Middle Paraná River and its tributaries, calculated as indicated above. The values of α_{Na} are, in general, less than 5, and they are significant lower than those determined in other large tropical rivers, such as the Orinoco-α_{Na} = 25- and Amazon-α_{Na} = 15 to 20- (Gaillardet et al., 1999b); thus

reinforcing the notion of an incipient to moderate weathering imprint. On the other hand, α_{Ca} values are generally less than 10, although this index exhibits more variability. The Bermejo River has $\alpha_{Ca} > 10$, whereas the Paraguay and the Middle Paraná rivers (downstream cross-section A) show lower values (Table 1). This can be interpreted as a result of the varied lithology outcropping in the Bermejo River basin, rather than an indicator of significant chemical alteration. Here again, it is interesting to focus on the variation of the alpha indices in cross-section A. The SS transported by the Upper Paraná River as well as those of the eastern margin of cross-section A, have α_{Na} and α_{Ca} considerable higher than the western tributaries (with the exception of the Bermejo River's α_{Ca}) and the Middle Paraná downstream this cross-section (Table 1), also indicating a higher degree of weathering for the eastern rock sources.

According to all the weathering indices calculated here, the Upper Paraná River transports a more weathered suspended material than the Bermejo and Paraguay Rivers. The weathering signature of the Middle Paraná River resembles that of the Paraguay River, which in turns supplies most of the particulate load.

Al_2O_3—CaO^* + Na_2O—K_2O plot (A-CN-K, where oxides are expressed in molar proportion and CaO^* represents the CaO in the silicate fraction only) has been extensively used in the literature to evaluate the extents of chemical weathering (e.g., Nesbitt and Young, 1982, 1989). In this diagram, the theoretical composition of plagioclase (Pl) and K-feldspar (Kfs) plot at 50% of the Al_2O_3 apex, defining the "feldspar line", which represents the initial path to weathering. On the other hand, at the Al_2O_3 apex, which represents highly weathered materials, the theoretical composition of most clay minerals is plotted (Nesbitt et al., 1996). Arrow C corresponds to the theoretical evolutionary path of UCC, which aims to the alumina-rich extreme. The vertical line on the left of the graph represents CIA values. Fig. 11A shows the ternary plot (A-CN-K) for the SS of the Paraná River basin; data from Depetris and Pasquini (2007) were included for comparison. The SS from the tributaries show a considerable dispersion, from incipient weathered to moderate weathered terms, whereas the SS of the Middle Paraná River show a spread-out trend towards illite composition and cluster in the upper portion of the triangle, overlapping the field of SS samples reported by Depetris and Pasquini (2007). On the other hand, the relationship CIA vs. Al/Si ratio, which is a proxy of mineral sorting (Fig. 11B), shows that the Al/Si ratios of SS are positively correlated with CIA values ($r^2 = 0.84$; Fig. 11B), indicating that CIA increases with decreasing grain size (increasing Al/Si), as this index varies substantially depending on the proportion of clay minerals in the sample. As it was already pointed out above, the SS of the Upper Paraná River and the eastern border of cross-section A register a higher degree of chemical alteration in agreement with the values of the
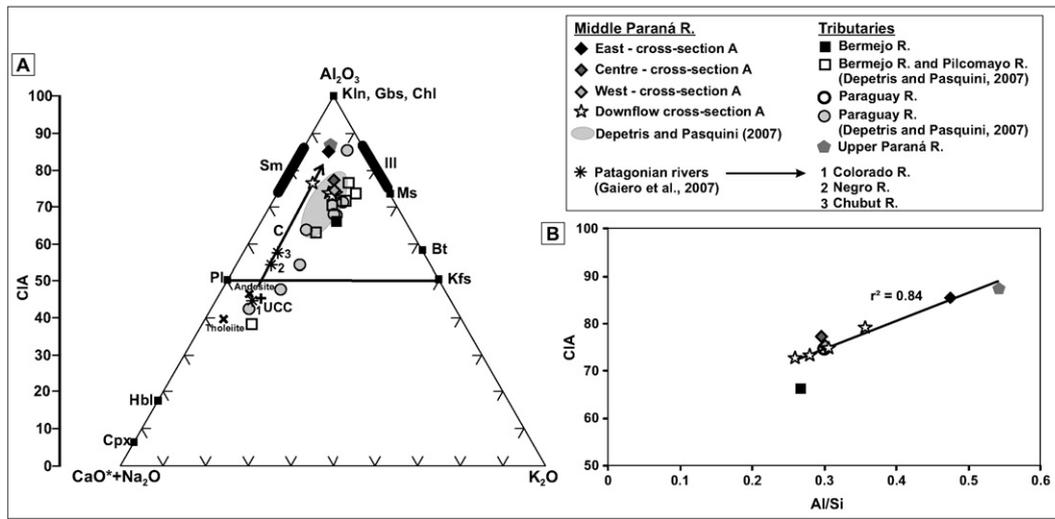
Fig. 11. A) A-CN-K ternary diagram for the suspended load transported in the Paraná River basin. Suspended sediments from Patagonian rivers (i.e., Colorado, Negro and Chubut rivers; Gaiero et al., 2007) are plotted for comparison. The supplementary vertical axis of CIA, the theoretical evolutionary path of UCC (arrow C) and the dataset reported in Depetris and Pasquini (2007) are also included. The UCC composition is from McLennan (2001). Cpx: clinopyroxene; Hbl: hornblende; Pl: plagioclase; Kfs: K-feldspar; Bt: biotite; Ms: muscovite; Ill: illite; Sm: smectite; Kln: kaolinite; Gbs: gibbsite; Chl: chlorite. B) Correlation CIA vs. Al/Si ratio for the Paraná River SS and tributaries.

calculated weathering indices. Fig. 11A also includes for comparison data of SS transported by three Patagonian rivers to the Atlantic Ocean (Gaiero et al., 2007), which show signs of incipient weathering. These rivers, with headwaters located in the Andean Patagonia, have been subjected to a typical weathering-limited denudation regime in the sense of Carson and Kirkby (1972). In such circumstances, there is an efficient transport of material that precludes the production of intense weathered products, as it is shown in Fig. 11A.

Several authors have postulated that the SS exported from the continents to the oceans generally contain a significant proportion of recycled materials, i.e., sediments that have passed more than once by the exogenous cycle (e.g. McLennan, 1993; Gaillardet et al., 1999b). Depetris et al. (2014) highlighted that weathering indices are not only useful to analyze the degree of chemical alteration but can also assist in establishing the likelihood that a river-transported sediment load has a significant proportion of recycled material. According to these authors, if the CIA is high and the ICV is low, then the cause could be either intense weathering in the source area or significant recycling of previously weathered material.

As it was pointed out above, different geochemical approaches have been discussed in the literature to analyze weathering processes and sedimentary recycling (e.g., Gaillardet et al., 1999b; McLennan et al., 1990, 1993, 2003; Meinhold et al., 2007). Diagrams in Fig. 12 were

proposed by McLennan et al. (1993); they used the ratios Th/U vs. Th (Fig. 12A) and Th/Sc vs. Zr/Sc (Fig. 12B) to analyze weathering processes and recycling. Uranium is easily mobilized during weathering and sedimentary recycling when the insoluble species U(IV) is oxidized to the soluble species U(VI). This process results in a loss of U and, consequently, in increasing Th/U ratios. Upper crustal rocks exhibit an average Th/U ratio of 3.8 (McLennan, 2001), whereas Th/U values greater than 4 in sedimentary rocks may indicate intense weathering in the source areas or sediment recycling (Bhuiyan et al., 2011). The relationship Th/Sc vs. Zr/Sc has been used in the literature to show the likelihood of sediment recycling in turbidites placed along active margins (McLennan et al., 2003). In such a framework, the enrichment of Zr is often interpreted as a clear signal of recycling, whereas in first-cycle sediments the ratios Th/Sc and Zr/Sc show an overall positive correlation, depending on the nature of the source rock. The Th/U ratios range between 2.0 and 6.0 for the SS transported by the Middle Paraná River and its tributaries. In general, the SS from the Bermejo, Pilcomayo and Paraguay rivers follow a normal weathering trend, whereas samples from the Middle Paraná River exhibit Th/U ratios close to the UCC (Fig. 12A). On the other hand, the Th/Sc vs. Zr/Sc plot reveals that the sediments exported by the Paraná basin to the Atlantic Ocean contain an unspecified proportion of recycled material (Fig. 12B); particularly those generated in the western tributaries of the Paraguay River, at
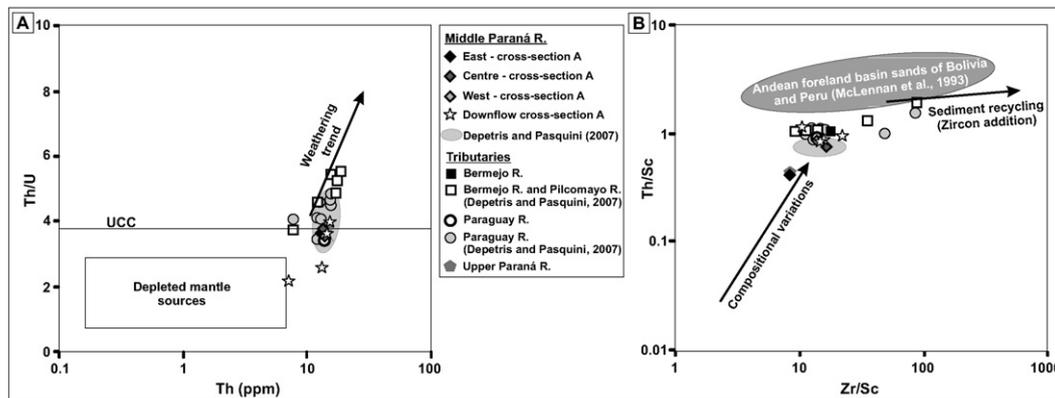
Fig. 12. Discrimination diagrams (McLennan et al., 1993), illustrating weathering and sedimentary recycling of the suspended sediments exported by the Middle Paraná River and its tributaries. The dataset published in Depetris and Pasquini (2007), and the Andean foreland basin sands of Bolivia and Perú (McLennan et al., 1993) are also plotted for comparison. A) Th/U vs. Th. B) Th/Sc vs. Zr/Sc.
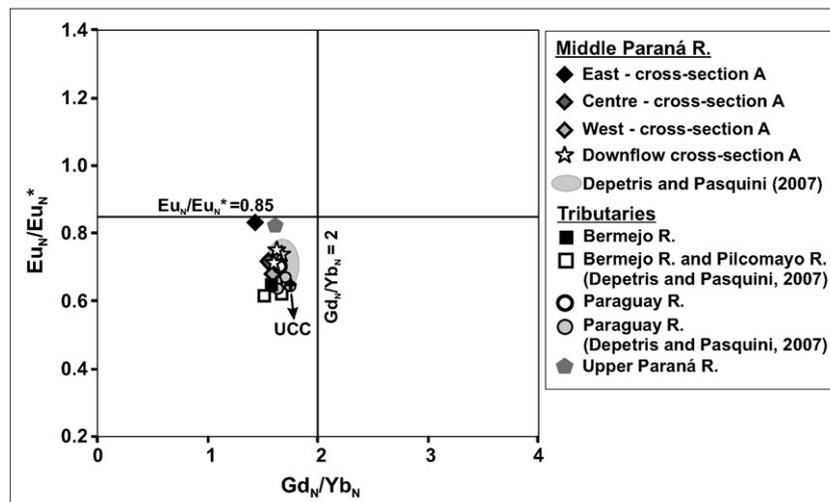
Fig. 13. Eu_N/Eu_N^* vs. Gd_N/Yb_N plot for the suspended sediments transported in the Paraná River basin. In this figure, N denotes normalization to chondrite (Taylor and McLennan, 1985). The dataset reported in Depetris and Pasquini (2007) is also included for the analysis.

the Bermejo and Pilcomayo headwaters. Fig. 12B also includes the composition of Andean foreland basin sands of Bolivia and Perú (taken form McLennan et al., 1993), where the upper catchments of the Pilcomayo and Bermejo rivers are located. McLennan et al. (1993) clearly pointed out that these sands evidence recycled sedimentary components.

Different REE ratios were also used in the literature to analyze sedimentary recycling. Fig. 13 shows the fractionation of REEs, represented by the ratio Gd_N/Yb_N, vs. Eu_N/Eu_N^*, where N denotes normalization to chondrite (Taylor and McLennan, 1985). The Eu anomaly is usually inherited form the rock sources (McLennan et al., 1993). Basic rock sources imprint weak Eu_N/Eu_N^* in the sediments, whereas strong Eu anomalies are attributed to felsic lithologies (e.g., Bhuiyan et al., 2011). The particulate matter analyzed here has Eu_N/Eu_N^* values <0.85, and Gd_N/Yb_N ratios <2.0 (Fig. 13), which are characteristic of PAAS-like sediments (McLennan, 1989). Furthermore, Gd_N/Yb_N and Eu_N/Eu_N^* ratios are similar to the corresponding mean values for the UCC. The negative Eu anomalies values indicate that the source rocks have undergone intracrustal differentiation, such as partial fusion or fractional crystallization (e.g., Meinhold et al., 2007).

As a first approach, Gaillardet et al. (1999b) estimated that ~86% of the SS delivered by the Paraná River to the Atlantic Ocean is derived from recycled continental rocks. McLennan et al. (1993) established that recycled sedimentary rocks have been influenced by intracrustal geochemical differentiation, which includes partial melting and/or crystal fractionation, and is characterized by fractionation of plagioclase, Eu anomalies (normalized to chondrite) values ranging between 0.6 and 0.8, and Gd/Yb ratios <2. Furthermore, fractionation and enrichment of heavy minerals, particularly zircon, may be associated to sedimentary recycling. Though Gaillardet et al. (1999b) calculated the percentage of recycled material for the Paraná basin using the ratio of predicted suspended concentrations over measured concentrations, the geochemical tools used in this study also confirm the presence of this type of material, mainly in the Andean tributaries (i.e., Bermejo and Pilcomayo rivers). Thus, the suspended load exported by the Middle Paraná River evidences a mixed origin, where the chemical signature of two sources can be recognized: 1) young materials, derived from undifferentiated volcanic rocks, and 2) old or recycled materials, that have suffered intracrustal differentiation.

5. Concluding remarks

The chemical and mineralogical composition of the suspended sediments transported by the Paraná River and its tributaries were

analyzed in order to constrain their provenance and to detect the signature of weathering and sedimentary recycling in the drainage basin.

The suspended sediments from the Middle Paraná River and its tributaries are compositionally immature, with SiO_2/Al_2O_3 ratios ~0.5, and are mainly composed of quartz, plagioclase, K-feldspar, and clays, such as illite and kaolinite. While illite is likely inherited and supplied by the Andean tributaries, the presence of kaolinite can be explained by the contributions from the Upper Paraná and Paraguay rivers. On the other hand, the crystalline rocks that outcrop in the basin supply the detrital minerals (i.e., quartz, plagioclase and K-feldspar). The suspended matter exported by the Paraguay and Middle Paraná rivers are classified as mudstones and wackes on the Herron's (1988) diagram, whereas the sediments transported by the Bermejo, Pilcomayo, and Upper Paraná rivers plot as iron mudstones.

The Middle Paraná River and its tributaries transport sediments with a PAAS-like chemical composition. The mineralogical and chemical analyses indicate that the they preserve the chemical signature of their sources, which is reflected by the transverse heterogeneity detected ~32 km downflow the confluence of the Paraguay and Upper Paraná rivers, where the incomplete mixing of both tributaries occurs. The concentrations of Ba, Sr, K and Rb are higher in the western margin, while Al, Fe, Ti, Sc, Y, Nb, Co, Cr and Cu, are more enriched in the sediments flowing towards the eastern border. The former set of elements is supplied by the Andean sedimentary rocks, whereas the latter are usually concentrated in basic rocks, such as the tholeiites outcropping in the Upper Paraná basin. In the flow direction, Ba, Rb, Nb, Cs and Sc show a trend of increasing concentrations, which has been correlated with a relative increase in the proportion of clays towards the mouth.

The suspended sediments composition is not substantially modified during transport, revealing that they preserve the chemical signature of the rock sources. Hence, the analyzed particulate matter which is mainly supplied by the Andean tributaries, derives predominantly from acidic arc sources. On the contrary, the sediment load from the Upper Paraná River and the eastern margin of cross-section A, clearly reflect the chemical signature of the tholeiitic basalts that outcrop in the upper catchments of the Paraná River.

Weathering indices (CIA, ICV and α), as well as other geochemical tools (as the A-CN-K plot), indicate that the Bermejo, Pilcomayo and Paraguay rivers transport from incipiently to moderately weathered sediments, reflecting the varied lithology outcropping in their respective basins. Conversely, the particulate load exported by the Upper Paraná River reveals the higher degree of chemical alteration that exhibit the eastern rock sources (tholeiites). As expected, the suspended sediments from the Middle Paraná River show a similar

weathering signature when compared to the Paraguay River, which in turns supplies most of the suspended load.

The current analysis suggests that the suspended load exported by the Paraná River basin to the Atlantic Ocean has a mixed origin, where two distinctive chemical signatures can be recognized: the one from young materials derived from undifferentiated volcanic rocks, and that corresponding to old or recycled materials affected by intracrustal differentiation. Future efforts should be addressed to quantify the sediment recycling and the "true" present day denudation rate within this large river basin.

Acknowledgments

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