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GRAIN SIZE ANALYSIS AND CLAY MINERAL ASSOCIATIONS IN BOTTOM SEDIMENTS FROM PARANA RIVER BASIN

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Abstract: Three different clay mineral assemblages are detected in mud-sandy bottom sediments of the Paraná Basin of Argentina. A dominant Kaolinite association, with sources areas in the Upper Amazon, north-east of the study area and within the Brazilian Shield (also with subordinated crystalline Illite); an Illitic- Smectitic and Interlayer I/S association, from the Andean Cordillera and the Chaco Plains in the north-west and mainly represented by the Bermejo and Pilcomayo Rivers; a southern Illitic-Chlorite dominant, but with lower crystallinity index than in the northern area, whose source is in the Pampean Plains to the west of Argentina. Mixed layer clays (Illite/Smectite) were also detected in this southern sector. These clay mineral associations reflect not only the climate but the source rock composition in these three main geographical areas. The tributaries of the lower Paraná River Basin show a dominant Illitic-Smectitic clay mineral association that has been eroded and transported from the Pampean Plains. In this contribution, three main clay mineral associations (Illite-Chlorite, Smectite-I/S, and Kaolinite) in stream sediments of the Paraná River and tributaries within a wide area of Argentina are described and their provenance is interpreted on the basis of controlling factors, climate and provenance.

Keywords: bottom sediments, grain size, clay minerals, Paraná River and tributaries.

Resumen: Se describen tres asociaciones de argilominerales presentes en sedimentos de fondo limo-arcillosos del río Paraná y algunos de sus tributarios en Argentina. Una asociación con Caolinita (con Illita cristalina subordinada) y con áreas de aporte hacia el noreste de la zona de estudio, en el Alto Amazonas y el Macizo Brasileño, una asociación de Illita-Esmectita e interestratificado Esmectita/ Illita, procedente de la Cordillera Andina y las Planicies del Chaco ubicadas hacia el noroeste y representadas por los ríos Bermejo y Pilcomayo y una asociación de Illita-Clorita dominante, de menor índice de cristalinidad que las del área norte, procedente de las Planicies Pampeanas de Argentina hacia el oeste. Argilominerales interestratificados de tipo Illita/ Esmectita son también descriptos en este sector sur. Las asociaciones de arcilla reflejan tanto la influencia del clima como a la litología y composición de estas áreas de aporte. Los tributarios del río Paraná Inferior muestran una composición de argilominerales dominante, de tipo Illita-Esmectita con proveniencia de las Planicies Pampeanas. En esta contribución tres asociaciones de argilofacies (Illita-Clorita, Illita-Esmectita interestratificado y Caolinita) en los sedimentos de fondo de los tributarios del Río Paraná son analizadas e interpretadas en base a los principales factores de control como clima y procedencia.

Palabras clave: sedimentos de fondo, textura, argilominerales, Río Paraná y tributarios.

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INTRODUCTION

The Del Plata Basin is the second largest in South America and comprises Argentina, Uruguay, Brazil, Bolivia and Paraguay (Fig. 1). The three main rivers are: Paraná (4352 km long), Paraguay (2459 km) and Uruguay (1600 km) which contains the widest estuary of the world, the Río de la Plata (256 km wide). The annual discharge reaching the Atlantic Ocean is 23,000 $m^3 s^{-1}$.

The Paraná River is the sixth largest river of the world, with a basin of 2.600.00 km^2, a mean annual discharge of 17,000 $m^3 s^{-1}$ and suspended load of 118.7 million tons yr^{-1} (Orfeo and Stevaux, 2002). This basin also passes through a great variety of geological units, like the Andes Mountains, the Chaco-Pampean Plains, the Eastern Plains, the Jurassic-Cretaceous Area and the Brazilian Shield (Iriondo, 1988). These well differentiated geologic and climatic environments are important controlling factors in the sedimentology and clay mineralogy of the area and their fingerprints can be traced along the basin (Bertolino and Depetris, 1992). Previous clay researchers showed that clay mineral assemblages are excellent indicators of lithology, climate, weathering and topography in the source areas, but also give important clues about different types of fluvial transport and sedimentation processes (Potter *et al*., 2005).

The grain size of the sediments in the basin is dominated by silt and clay sizes (Orfeo, 1999; Iriondo, 2004). There are also vast amounts of colloids and clay aggregates circulating in the basin, which is characteristic of the wash load (Konta, 1985). This river´s suspended matter plays an important role in the sediment budgets and nutrient production in downstream floodplain environments. The Bermejo and the Pilcomayo rivers, two of the most important tributaries of the Paraná Basin, are good examples: the former, with only 5% of the total water discharge provides 56 % of the total sediment suspended load (more than 50 million tons yr^{-1}), the latter is one of the largest active mega-fluvial fans in the world (Latrubesse and Ramonell, 1994) running eastward from the Andean Cordillera, crossing extended swampy areas.

Taking into account the fact that most of the continental rocks exposed to weathering in large river basins have suffered previous weathering cycles (Gaillardet *et al*., 1999; Barnes and Pelletier, 2006), the relationship between weathering intensity, climate parameters and dissolved river loads (derived from silicate weathering) becomes highly complex.

The dynamics of fine bottom fluvial sediments in the Paraná Basin also play an important role in environmental studies, as they may act as transporting agents and sinks of pollutants (Horowitz, 1985; Ronco *et al*., 2001; Camilión *et al*., 2003; Manassero *et al*., 2004). Although long transport distances of mud favour both mixing and recycling of particles from different sources, it is possible to establish the broad paleogeographic setting of the source and infer transport paths (Potter *et al*., 2005).

The objective of this contribution is to discuss the main grain size characteristics of bottom sediments from the upper, middle and lower sectors of Paraná River Basin, and to describe the primary compositional trends and the clay-provenance, based on standard clay mineral composition data. The study was undertaken within a major project for the water quality assessment program of selected sections of the Paraná, Paraguay rivers and their tributaries (SADS, OPS, PNA, UNLP, 2005).

METHODOLOGY

The fine grained fraction of the stream bed sediments (upper 20 cm) from equivalent positions (100 to 200 m upstream of the tributary mouths) of different rivers discharging into the Paraná River Basin (Fig. 1; Table 1) was analysed and compared using standardized methods for grain size determination, as well as sand and clay mineral composition. The cores, taken in both margins using a bottom sampler (Wildco, Wild Life Supply Company), were divided in an upper layer (S) (0-10 cm) and a lower layer (I) (10-20 cm) for most of the samples. When sample core recovery was over 20 cm long, a middle sample (M) was also separated and analyzed. The sieving and settling velocity technique, with previous cement removal (Day, 1965; Carver, 1971) was performed for grain size analysis. Statistical parameters were also calculated following Folk and Ward (1957) and Carver (1971). Organic matter content was determined by the dichromate oxidation method followed by filtration according to Allison (1965).

Prior to clay fraction separation, the 38 carbonate free samples were treated for removal of organic materials with hydrogen peroxide, and properly dispersed by using sodium hexametaphosphate (Carver, 1971). The clay fraction was separated from the aqueous suspension and oriented clay slides were prepared by pipetting the clay suspension onto glass slides. The X-ray diffraction analysis was conducted sequentially on air-dried, glycolated and heated to 550 °C samples on

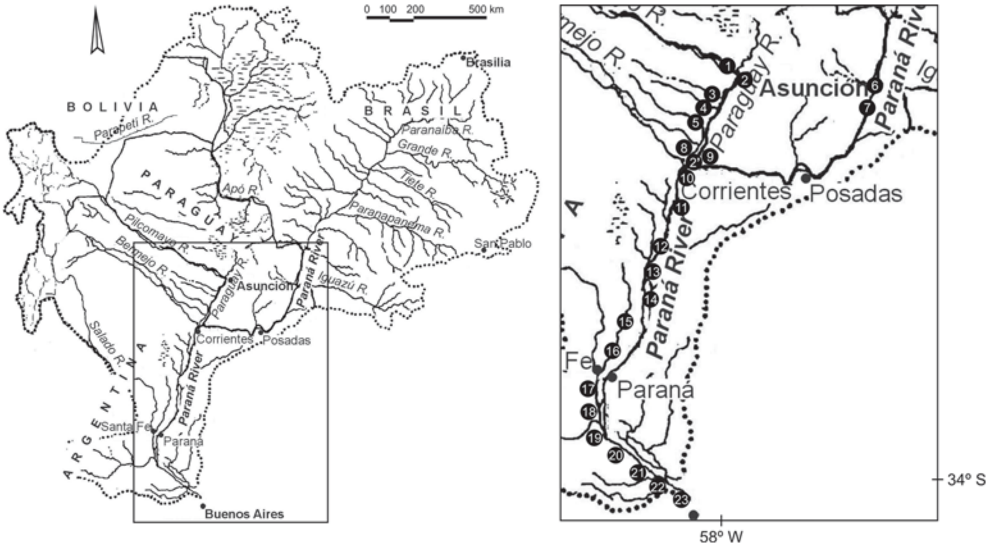

Figure 1. Paraná River Basin in Argentina and selected rivers and creeks with indication of sampling locations, **Upper Sector**: Pilcomayo (1), Paraguay (2), Montelindo (3), Pilagá (4), Bermejo (5), Iguazú (6), Paraná (7), Negro (8) and Uruguaí (9), **Middle Sector;** San Lorenzo (10), Sta. Lucía (11), Corrientes (12), Guayquiraró (13), Feliciano (14), Salado (15), Coronda (16), Carcarañá (17), Ludueña (18), Saladillo (19) and Pavón (20), **Lower Sector:** Del Medio (21), Arrecifes (22) and Areco (23).

Figura 1. Cuenca del Paraná en Argentina, ríos y arroyos seleccionados, con indicación de los sitios de muestreo, **Sector Superior**: Pilcomayo (1), Paraguay (2), Montelindo (3), Pilagá (4), Bermejo (5), Iguazú (6), Paraná (7), Negro (8) y Uruguaí (9), **Sector Medio;** San Lorenzo (10), Sta. Lucía (11), Corrientes (12), Guayquiraró (13), Feliciano (14), Salado (15), Coronda (16), Carcarañá (17), Ludueña (18), Saladillo (19) y Pavón (20), **Sector Inferior:** Del Medio (21), Arrecifes (22) y Areco (23).

X-Ray diffractometer (Cu K α radiation with Ni-filter, 36 KV, 18 mA). The clay minerals were identified by their characteristic basal reflections (Brindley and Brown, 1980; Moore and Reynolds, 1989). Semi-quantitative estimations of relative concentrations of clay minerals were based on the peak area method (Biscaye, 1965). The peak areas of glycolated samples were first computed under 17 Å for smectite, 12 Å for the interlayer illite/smectite, 10 Å for illite and 7 Å for chlorite and kaolinite. Percentage evaluation was based on peak height and area, corrected by factors depending on the crystallinity of the mineral (Moore and Reynolds, 1989). Sand optical petrography was carried out using standard methods in polarized microscope and immersion liquids of known refraction indexes.

RESULTS AND DISCUSSION

Bottom sediments from the studied sites of the Paraná Basin are typical clayly-silty facies, with a variable content of organic matter, ranging between 0.4 and 13% (dry weight), with 5.7% average content. Sands are mainly composed by quartz, feldspar and lithic fragments, while clays exhibit a typical illite, kaolinite and smectite predominance.

Grain size analysis and sand mineralogy

The analysis of grain size data (Table 2; Fig. 2) from cores and statistical parameters of the core samples show that most of the samples have a bimodal pattern, with main frequencies both in the coarse (silt or fine sand) and finer fractions (clays). The mean grain sizes vary from very fine sand (3-4 Φ) to very coarse to coarse silt (5-6 to 4-5 Φ) with poor to moderate sorting (standard deviation), high kurtosis and positive skewness.

The statistical grain size parameters (Table 3) of these tributaries of the Paraná Basin do not show strong differences and suggest typical and prevailing fluvial sedimentary processes with well defined rolling-sliding, saltation and suspension populations, according to important changes in the hydraulic regime. As observed by Orfeo (1999) for small rivers of the Chaco-Pampa plain, the grain size of the bed sediments is relatively homogeneous.

Previous contributions (Stevaux, 1994; Orfeo, 1999; Orfeo and Stevaux, 2002) showed that the bed load sediment is constituted mainly of medium (60-80%) and fine (20-40%) sand. Their interpretation of the cumulative frequency curves of the bed sediments suggested that saltation is the dominant transport mecha-

Sites (figure between parenthesis refer to numbering according Fig. 1)	*Sampling date*	*Water depth (m)*	*Location*
Río Pilcomayo (mouth) (1)	07/12/2004	3	25º 21´ 13" S/57º 40´ 05" W
Río Paraguay (2)	07/01/2005	3	25º 21´ 53" S/57º 39´ 04" W
Río Paraguay (mouth) (2´)	09/12/2004	1,5	27º 17´ 15" S/58º 36´ 43" W
Arroyo Monte Lindo (3)	08/12/2004	2,5	25º 52´ 43" S/57º 52´ 30" W
Riacho Pilaga (4)	08/12/2004	3	26º 04´ 52" S/57º 59´ 14" W
Río Bermejo (5)	09/12/2004	3	26º 52´ 13" S/58º 23´ 04" W
Río Iguazú (6)	04/01/2005	1	25º 35´ 35" S/54º 34´ 49" W
Río Paraná (7)	04/01/2005	1,5	25º 35´ 27" S/54º 35´ 35" W
Río Negro (8)	09/12/2004	2,5	27º 24´ 07" S/58º 47´ 53" W
Río Uruguay (9)	06/01/2005	1,5	25º 52´ 33" S/54º 33´ 30" W
Arroyo San Lorenzo (10)	14/12/2004	1	32º 43´ 11" S/60º 43´ 39" W
Río Santa Lucía (11)	11/12/2004	3	29º 04´ 34" S/59º 13´ 32" W
Río Corrientes (12)	12/12/2004	3	30º 01´ 00" S/59º 32´ 12" W
Río Guayquiraró (13)	12/12/2004	1	30º 20´ 31" S/59º 30´ 49" W
Río Feliciano (14)	13/12/2004	2	31º 06´ 25" S/59º 52´ 44" W
Río Salado (15)	13/12/2004	1	31º 39´ 20" S/60º 44´ 39" W
Río Coronda (16)	14/12/2004	1	32º 28´ 40" S/60º 47´ 52" W
Río Carcarañá (17)	14/12/2004	3	32º 26´ 37" S/60º 48´ 20" W
Arroyo Ludueña (18)	14/12/2004	1	32º 54´ 25" S/60º 40´ 37" W
Río Saladillo (19)	14/12/2004	3	32º 59´ 58" S/60º 36´ 52" W
Arroyo Pavón (20)	13/01/2005	0	33º 14´ 30" S/60º 26´ 26" W
Arroyo del Medio (21)	13/12/2004	0	33º 19´ 50" S/60º 18´ 14" W
Río Arrecifes (22)	13/12/2004	0	33º 49´ 02" S/59º 35´ 32" W
Río Areco (23)	13/01/2005	0	34º 03´ 22" S/59º 18´ 07" W

Table 1. General information on sediment sampling points and samples.
Tabla 1. Información general sobre los puntos de muestreo de sedimentos y muestras.

nism (96-99%) in the river channels. The samples analyzed here show that the sand fraction is mainly composed of stable minerals that resist weathering and transport, like quartz (90%) with minor amounts of chalcedony, potassium feldspar and plagioclase. Heavy minerals are rare (2%) and are composed of magnetic and non magnetic opaque minerals (see also Passeggi, 1996). Besides, Marengo *et al*. (2005) have shown, in a relatively small area within the Province of Santa Fe, that in a 2 km fluvial transport distance along the Pampean Plains, silts with abundant glass shards (40-60%) decrease these values to 5% and increase the relative proportion of quartzose sand to 30%. The analysis of 35 loose and very fine sand bottom sediment-samples by optical microscopy agrees with this data, demonstrating also that quartzose sources are located mainly in the Brazilian Shield and glass-shard sources are spread not only in the Pampean Plains but in the Andean Cordillera as well.

Clay mineralogy

The distribution patterns of the clay mineral association in mud and sand are indicative of provenance and climate, both in recent and ancient sediments (Millot, 1970; Robert and Kennett, 1994; Dingle and Lavelle, 2000; Zuther *et al*., 2000; Suresh *et al*., 2004). They have been a useful guide to paleoclimatic settings because hydrolysis of rock-forming silicates in tropical conditions can change rapidly in response to climate (Yuretich *et al*., 1999). And since all samples are mixtures from various sources, only the four groups of mayor clay minerals (Irion and Zollmer, 1999) are used in this study.

Stream	*Grain size interval (µm)*								
	> 500	250 - 500	125 - 250	63 - 125	31.5 - 63	15.6 - 31.5	7.8 - 15.6	3.9 - 7.8	< 3.9
Pilcomayo S.	0.19	0.82	1.56	10.24	9.34	19.50	11.91	12.50	33.94
Pilcomayo I.	0.00	0.00	0.50	20.44	44.30	0.49	6.07	7.02	21.14
Pilcomayo M	0.00	0.00	5.32	10.11	4.48	11.00	12.07	3.86	53.19
Paraguay S.	0.00	0.00	0.37	7.22	35.74	2.94	14.30	8.74	30.68
Paraguay I.	0.00	0.00	0.66	12.45	30.11	14.57	0.71	2.88	38.61
Paraguay mouth	0.00	0.05	0.18	2.46	43.00	6.65	7.81	30.31	9.30
Montelindo	0.00	0.12	1.80	13.23	27.20	4.73	19.73	7.94	25.28
Pilagá	0.00	0.00	0.00	32.20	28.40	10.67	0.90	3.32	24.40
Bermejo S.	0.00	0.00	0.10	0.05	1.00	9.35	14.74	11.50	63.26
Bermejo I.	0.00	0.00	0.00	0.27	1.66	8.97	7.62	10.49	78.47
Iguazú S.	0.00	5.95	18.49	5.83	28.56	3.32	19.78	2.12	15.94
Iguazú I.	0.00	8.46	27.81	6.14	7.01	4.92	27.78	1.78	16.08
Paraná S.	0.00	0.77	14.09	24.34	9.10	8.50	2.19	2.85	38.16
Paraná I.	0.00	0.88	17.81	29.58	5.12	4.62	7.48	5.66	28.84
Negro S.	0.00	0.00	0.46	20.90	57.41	3.53	1.29	2.70	13.71
Negro I.	0.00	0.15	0.48	6.73	18.36	6.15	38.52	19.09	10.51
Uruguaí S.	0.00	0.26	1.41	5.27	4.46	21.60	13.86	32.58	20.02
Uruguaí I.	0.00	0.00	1.10	7.89	2.76	16.83	22.11	28.23	21.07
San Lorenzo	0.00	0.00	1.29	2.57	23.58	11.21	12.32	0.18	48.85
Santa Lucía	0.00	3.87	37.18	4.97	13.52	5.56	5.56	8.29	21.04
Corrientes	0.00	26.18	33.41	7.48	4.53	3.39	0.15	14.66	10.19
Guayquiraró	0.00	7.22	11.79	5.42	11.14	20.27	8.83	8.83	26.29
Feliciano	0.00	0.43	1.47	7.69	33.73	8.31	25.27	3.38	19.72
Salado S.	0.00	0.00	0.56	0.47	3.69	10.32	14.84	1.49	68.63
Salado I.	0.00	0.00	0.14	0.07	18.71	14.14	7.93	12.60	46.41
Coronda S.	0.00	0.26	2.23	13.03	25.67	17.05	9.49	5.03	27.24
Coronda I.	0.00	0.14	2.74	9.39	17.48	15.50	10.51	7.95	36.27
Carcarañá	0.00	0.40	1.93	4.04	23.03	15.89	6.82	5.84	42.03
Ludueña	0.00	0.00	0.65	0.65	28.90	10.15	0.10	10.80	48.76
Saladilo S.	0.00	16.80	3.06	0.00	25.31	7.48	1.77	37.73	7.70
Saladillo I.	0.00	1.11	7.15	1.19	3.50	32.02	9.34	35.71	8.62
Pavón	0.00	36.10	11.18	9.78	15.42	11.34	1.34	4.73	10.04
del Medio S.	0.00	8.64	1.02	33.24	23.06	10.10	3.53	0.15	20.26
del Medio I.	0.00	28.60	2.68	5.41	17.64	17.64	11.28	7.52	26.87
Arrecifes S.	0.00	0.00	2.45	2.16	23.81	8.19	8.61	11.32	53.46
Arrecifes I.	0.00	1.20	0.28	0.37	6.79	8.63	11.82	3.76	67.22
Areco	0.00	7.51	4.36	9.86	12.47	22.80	2.82	27.36	12.81

Table 2. Grain size data for the 38 sediment-bottom samples of the Paraná River Basin. S: upper layer; I: lower layer; M: middle layer.
Tabla 2. Datos de granulometría de 38 muestras de sedimentos de fondo de la Cuenca del Río Paraná y tributarios. S: capa superior; I: capa inferior; M: capa media.

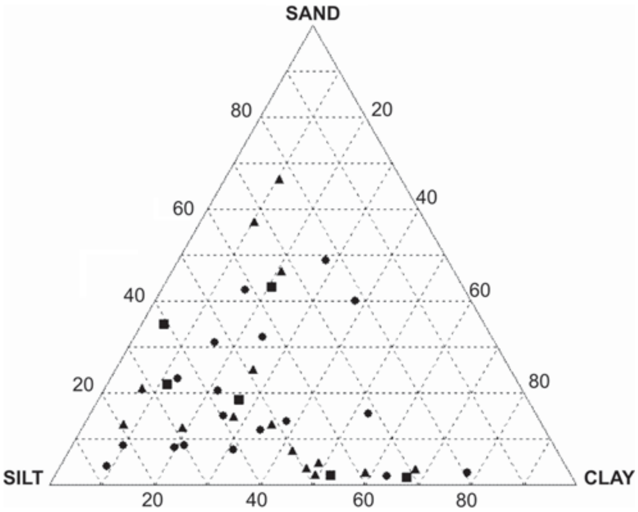

Figure 2. Sand- Silt- Clay ternary diagrams for the studied Paraná River Basin bottom sediments. Samples are identified as Upper, Middle and Lower sector with full circles, triangles and squares, respectively.

Figura 2. Diagramas ternarios Arena-Limo-Arcilla para sedimentos de fondo estudiados de la Cuenca del Río Paraná. Las muestras se identifican como Paraná Alto, Medio y Bajo con círculos, triángulos y cuadrados rellenos, respectivamente.

Previous studies on the Paraná Basin suspended sediments (Depetris and Griffin, 1968; Bertolino *et al*., 1991, Bertolino and Depetris, 1992, Bonetto *et al*., 1994) have shown the mean mineralogical composition as a percentage of the total clay fraction, with a dominant illitic-smectitic composition for the Bermejo, Pilcomayo and Paraguay, with higher kaolinite contents in the Upper Paraná sector. There is a large variation in the content of the four different clay minerals within the 38 sediment-bottom studied samples, with variations in the order of magnitude for each individual mineral group. (Table 4; Figs. 3 and 4).

The principal clay minerals in the bottom sediments are then, illite-chlorite, smectite+interlayer illite/smectite and kaolinite (Fig. 5). Much is known of these clay minerals in modern environments (Millot, 1970; Johnson and Reynolds, 1986; Weaver, 1989; Ferrel *et al*., 1998), so a brief description of their general characteristics is provided.

Illite-chlorite dominant clay facies: The studied sets of samples show strong illite dominance, with more than 50 % containing a maximum of 80% (Figs. 3 and 4, Table 4) in the Upper Parana: Bermejo, Negro, Montelindo, Uruguaí (also samples from Pilcomayo and Paraguay); Middle Paraná: San Lorenzo, Salado, Coronda, Carcarañá, Saladillo; and in the Lower Paraná: Del Medio, Arrecifes, Areco. The mean grain size of this clay facies is fine silt (Fig. 3) with relatively moderate to poor sorting.

Dominant clay minerals of immature soils that have undergone little chemical weathering are associated with chlorite and random mixed-layer clays. Illite is derived directly from the erosion of unweathered parent rocks. These clay minerals are characteristics of cold regions and deserts marked by very low rates of weathering and areas of steep topography where mechanical erosion interferes with soil formation. All the sedimentary rocks are included within the depositional model of the Pampa Loess, where winds derived from the Patagonian ice field in the SE, during the late Quaternary, formed a large sand sea and loess belt behind it. The source rocks of these sediments are both the Andean Cordillera and the Pampean plains (Iriondo, 1997). It is important to emphasize that although sediments have abundant glass shards, they are fresh and not yet altered to smectite (Marengo *et al*., 2005).

Sharp X-ray diffraction peaks showing good crystallinity in illite are also indicative of physical degradation of rocks rich in biotite as a mineral precursor from gneisses, granulites and granitoids (Damiani *et al*., 2006).

The chlorite clays, like the previously described clay minerals, are also formed by the physical weathering of low-grade metamorphic and basic source rocks rich in Mg, under a cold climate (Ehermann *et al*., 1992). They generally represent less than 10% of the clays in the bottom sediments (Fig. 3 and Table 4). The results agree with previous research on suspended sediments from different sector of the Paraná Basin (Bertolino and Depetris, 1992; Bonetto *et al.,* 1994). In the analyzed set of samples, chlorite is relatively more abundant in the Upper Paraná, in agreement with a survey by Bonetto and Orfeo (1984), the source areas probably being both the Andean Cordillera and basic rocks from the Brazilian Shield (maximum detected values of 20%).

Illite-Smectite and associated interlayer Illite/Smectite dominant clay facies: The streams with more than 50 % of smectite plus I/S (Figs. 3 and 4; Table 4) are, for the Upper Paraná: Pilcomayo, Pilagá and Paraguay; for the Middle Paraná: Corrientes, Guayquiraró; and for the Lower Paraná: Arrecifes. The mean grain size of this clay facies is fine to coarse silt (Fig. 3) with relatively moderate to poor sorting. Bertolino *et al*. (1991) and Bertolino and Depetris (1992) have studied the

Sample	*Mean*	*Sorting*	*Skewness*	*Kurtosis*
Pilcomayo S.	6,0	1,8	6,2	7,8
Pilcomayo I.	5,2	2,1	6,7	8,0
Pilcomayo M	6,4	2,0	5,5	7,4
Paraguay S.	5,9	1,7	6,2	8,3
Paraguay I.	5,6	1,8	6,6	8,8
Paraguay mouth	5,3	1,4	5,9	5,4
Montelindo	5,7	1,8	5,6	8,3
Pilagá	5,0	2,0	6,2	9,6
Bermejo S.	7,2	1,0	6,8	1,6
Bermejo I.	7,4	0,9	7,3	1,4
Iguazú S.	4,4	2,2	4,6	11,5
Iguazú I.	4,5	2,2	3,8	12,5
Paraná	4,6	2,2	6,8	14,1
Negro S.	4,7	1,5	4,0	2,4
Negro I.	5,7	1,4	4,8	3,5
Uruguaí S.	6,3	1,2	5,7	3,2
Uruguaí I.	6,3	1,3	5,9	3,6
San Lorenzo	6,2	1,6	5,8	7,3
Santa Lucía	4,5	2,4	5,2	14,9
Corrientes	3,5	2,4	4,6	11,7
Guayquiraró	5,0	2,4	5,9	12,1
Feliciano	5,5	1,7	5,2	5,0
Salado S.	7,2	1,2	6,4	3,0
Salado I.	6,6	1,5	5,7	5,5
Coronda S.	5,4	1,8	6,3	8,8
Coronda I.	5,9	1,8	6,0	8,8
Carcarañá	6,0	1,8	6,1	9,0
Ludueña	6,4	1,7	5,3	7,9
Saladilo S.	4,5	2,4	5,7	9,4
Saladillo I.	5,9	1,3	6,0	4,0
Pavón	3,3	2,4	3,3	11,1
del Medio S.	4,8	2,0	4,3	5,0
del Medio I.	5,3	2,2	6,0	10,4
Arrecifes S.	6,4	1,8	5,4	8,2
Arrecifes I.	7,1	1,4	6,2	4,0
Areco	5,1	2,1	5,8	9,0

Table 3. Statistical parameters of the samples grain size analysis.
Tabla 3. Parámetros estadísticos del análisis granulométrico de muestras.

mineralogy of the clay-sized suspended load from headwater tributaries of the Bermejo, Pilcomayo and Paraguay Rivers and established a clay mineralogy signature for each basin identifying sources and transport paths, with results and interpretations that are consistent with the ones proposed in this contribution.

This detrital clay mineral forms from alteration of volcanic rocks and also, in poorly drained tropical to

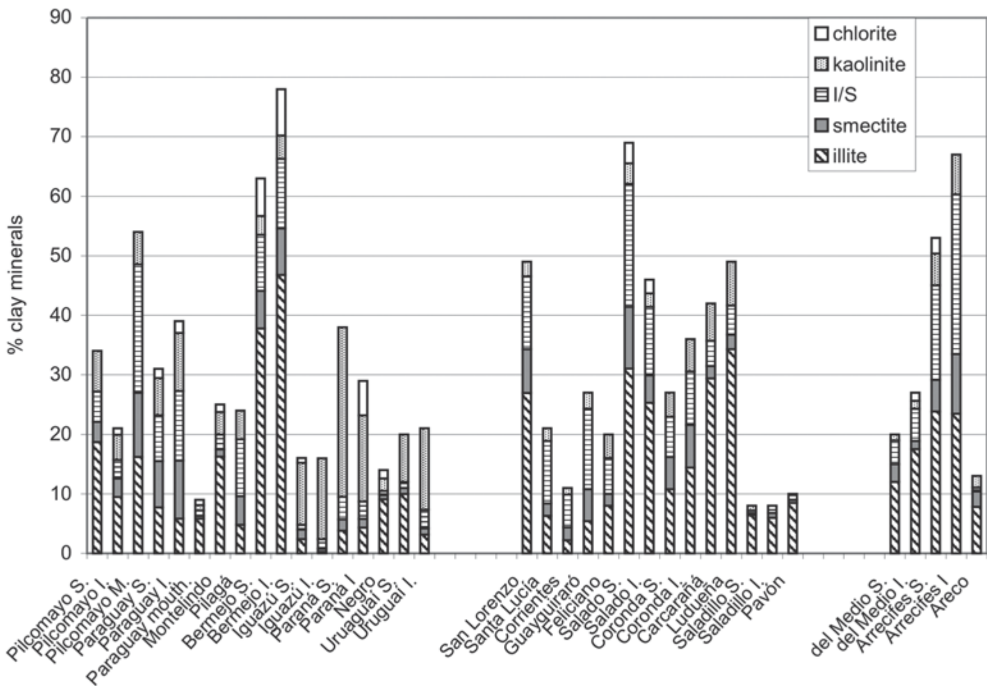

Figure 3. Distribution of clay mineral associations in sampling sites of the Paraná River Basin.
Figura 3. Distribución de las asociaciones de argilominerales en los sitios de muestreo de la Cuenca del Río Paraná.

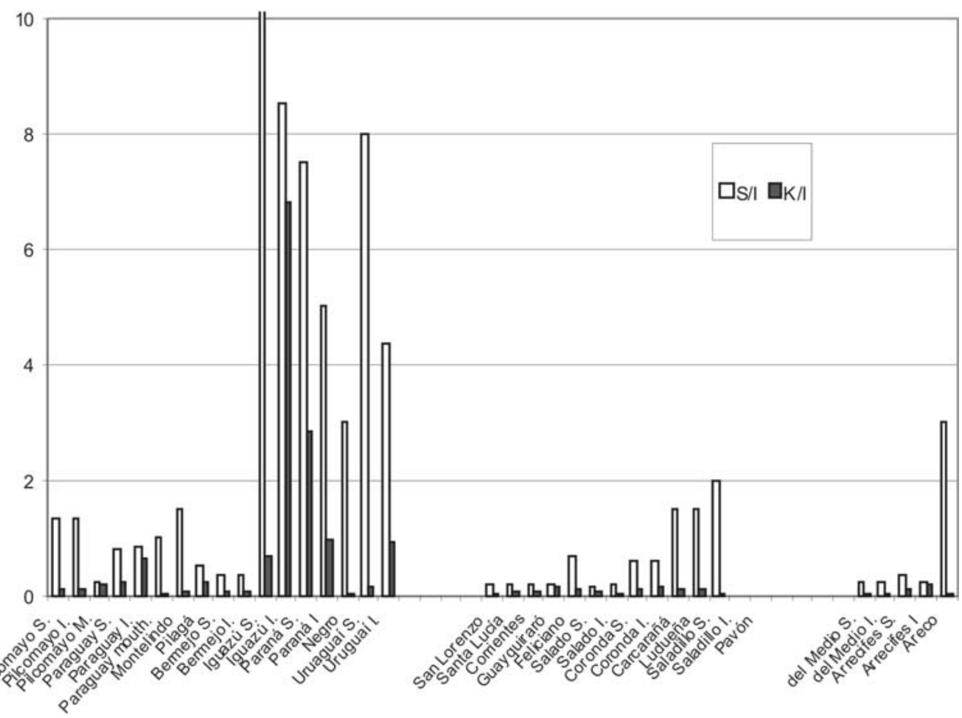

Figure 4. Clay mineral ratios (Smectite/ Illite and Kaolinite/Illite) of bottom fluvial sediments in sampling localities of the Paraná River Basin.
Figura 4. Relación entre arcillas (Esmectita/ Illite y Caolinita/ Illita) en los sitios de muestreo de sedimentos de fondo de la Cuenca del Río Paraná.

Stream	*Illite*	*Smectite*	*I/S*	*Kaolinite*	*Chlorite*
Pilcomayo S.	55	10	15	20	0
Pilcomayo I.	45	15	15	20	5
Pilcomayo (mouth)	30	20	40	10	0
Paraguay S.	25	25	25	20	5
Paraguay I.	15	25	30	25	5
Paraguay M.	65	5	10	10	10
Montelindo	65	5	10	15	5
Pilagá	20	20	40	20	0
Bermejo S.	60	10	15	5	10
Bermejo I.	60	10	15	5	10
Iguazú S.	15	10	5	65	5
Iguazú I.	2	3	10	85	0
Paraná S.	10	5	10	75	0
Paraná I.	15	5	10	50	20
Negro	65	5	5	15	10
Uruguay S.	50	5	5	40	0
Uruguay I.	15	5	15	65	0
San Lorenzo	55	15	25	5	0
Santa Lucía	30	10	50	10	0
Corrientes	20	20	50	10	0
Guayquiraro	20	20	50	10	0
Feliciano	40	10	30	20	0
Salado S.	45	15	30	5	5
Salado I.	55	10	25	5	5
Coronda S.	40	20	25	15	0
Coronda I.	40	20	25	15	0
Carcaraña	70	5	10	15	0
Ludueña	70	5	10	15	0
Saladillo S.	80	5	5	10	0
Saladillo I.	75	10	15	0	0
Pavón	85	5	10	0	0
del Medio S.	60	15	20	5	0
del Medio I.	65	5	20	5	5
Arrecifes S.	45	10	30	10	5
Arrecifes I.	35	15	40	10	0
Areco	60	20	5	15	0

Table 4. Clay mineral composition and relative abundance of main clay associations in % in bottom sediments of the Paraná River Basin.
Tabla 4. Composición de argilominerales y abundancias relativas porcentuales de asociaciones de arcillas en sedimentos de fondo de la Cuenca del Río Paraná.

subtropical areas of low relief marked by flooding during humid seasons, and subsequent concentration of solutions in the soil during dry seasons. Today smectite is the dominant mineral formed in the Lower Amazon Basin (Millot, 1970). In this case, the main source areas for this mineral seem to be the Andean Cordillera and the Chaco Plains in the Upper Paraná. Bertolino and Depetris (1992) also proposed the following order of abundance illitee» smectitee» chloritee» kaolinite for the clay suspended load of the headwaters of Bermejo River.

On the other hand, random mixed layer clay illite/smectite is tied to the degradation of the previous and abundant smectitic clays. They have been interpreted

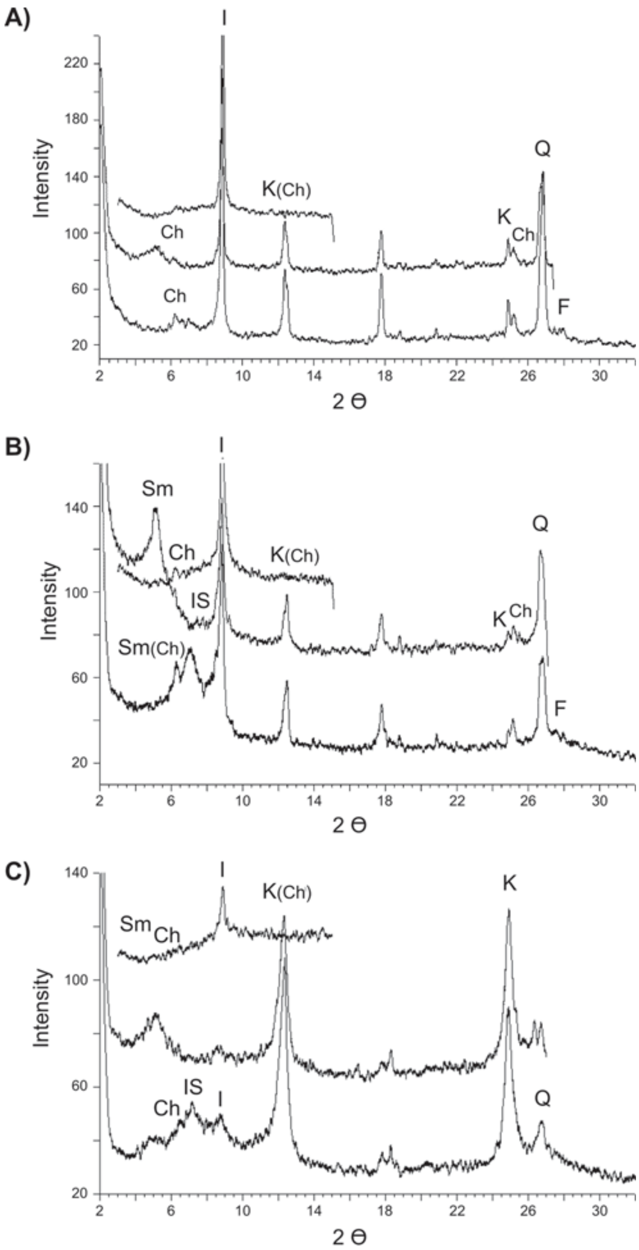

Figure 5. Selected examples of X-ray diffractograms plotted after background correction of digital data showing peaks used to calculate clay mineral percentages. A-illite, B-Smectite, and C-Kaolinite dominant facies. Specimens air dried, saturated with ethylene glycol, and heated to 375ºC.

Figura 5. Difractogramas de Rayos X corregidos por fondo a partir de datos digitales con picos característicos. A- Illita, B-Esmectita, C- Argilofacies de Caolinita dominante. Las muestras fueron secadas, glicoladas y calcinadas a 375ºC.

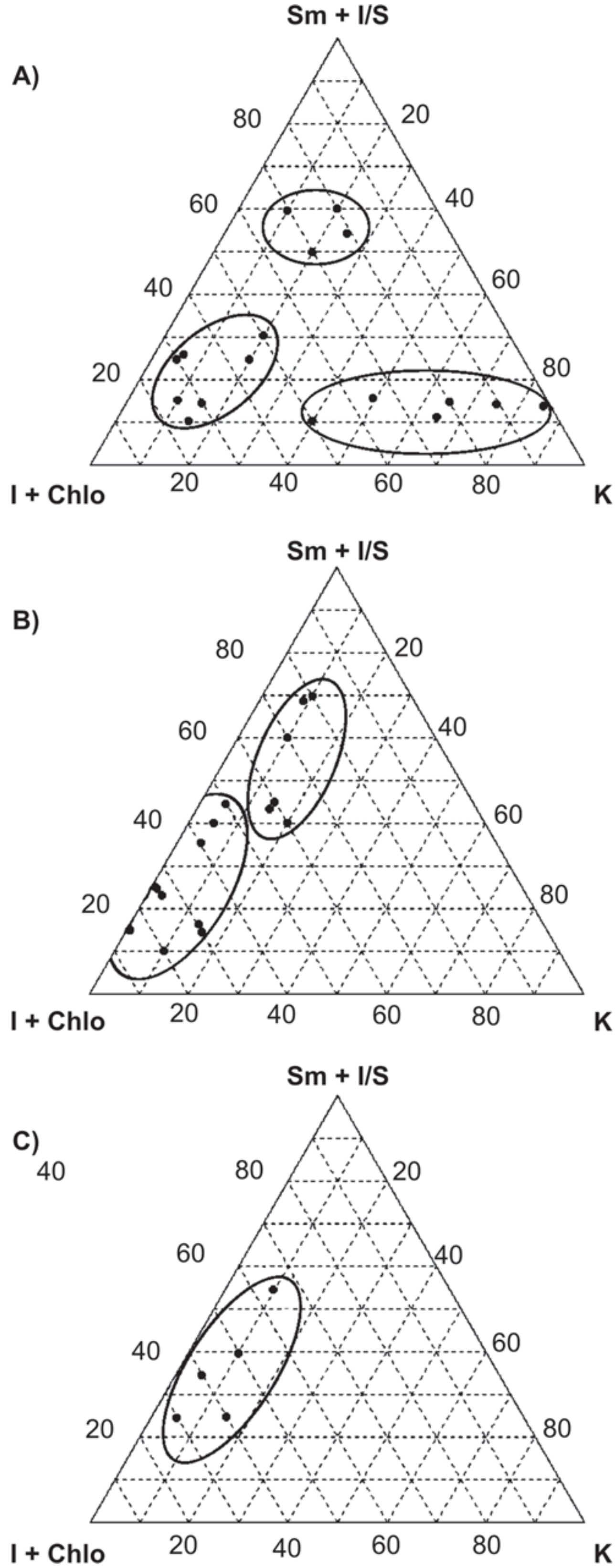

Figure 6. Provenance ternary plots of Illite-Smectite+ Illite/ Smectite-Kaolinite+ Chlorite in sampling sites of the Paraná River Basin.

Figura 6. Diagramas ternaries de procedencia de Illita-Esmectita+ Illita/ Esmectita- Caolinita+ Clorita en sitios de muestreo Cuenca del Río Paraná.

as the product of alteration of smectite by weathering (Johnsson and Reynolds, 1986), although a diagenetic origin may not be discarded. They also are relatively more abundant in tributaries of the middle sector of the Paraná Basin due to their association with loess deposits and recently formed paleosoils (Figs. 6 and 7).

Kaolinite dominant clay facies: In the studied samples, only big rivers like the Paraguay, Paraná, Uruguaí and Iguazú (Figs. 3 and 4, Table 4) clearly show this upper Amazon influence with more than 50% of kaolinite (maximum of 85%). The mean grain size of this clay facies is very close to fine sand (Fig. 3) with moderate to poor sorting.

This mineral typically develops in tropical soils on well-drained surfaces of diverse rocks receiving high precipitation. It is the dominant clay mineral in the Upper Amazon Basin (Millot, 1970) and is widely distributed in sediments in adjacent oceanic areas (Biscaye, 1965). This clay mineral could represent 30% of the clay content in the Upper Paraná River (Bonetto *et al.*, 1994). The source rocks are generally old igneous (granites) or metamorphic feldspar rich rocks exposed to high precipitation and tropical weather and associated with paleosoils (Dingle and Lavelle, 2000). Kaolinite is the main clay mineral component of lateritic soils and the upper part of the Mesozoic basalts in the Paraná Basin. Kaolinite might be also formed by hydrothermal alteration or diagenesis as well as chemical-weathering under tropical to temperate climate (Jeong and Yoon, 2001).

Previous studies (Bertolino and Depetris, 1992) have also stressed that for the clay-sized suspended load, the dominant tropical environment within the Río Paraguay headwaters of the Mato Grosso (Brazil) region, along with the marine beds and volcanic and intrusive rocks exposed in this area, have an important role as source of the kaolinite-smectite fine grained minerals. Bertolino *et al.* (1991) also described the presence of regular kaolinite/smectite (R1) for the Bermejo River.

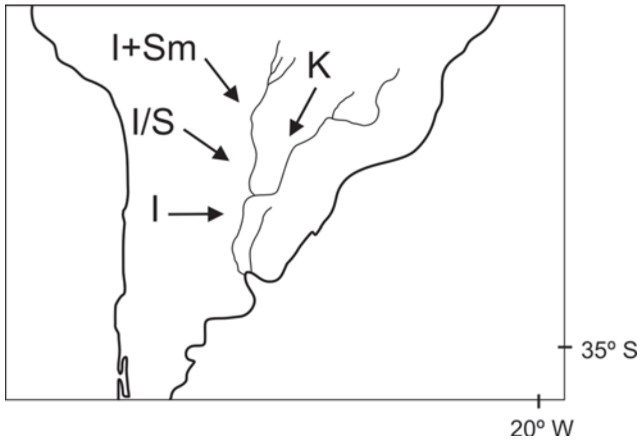

Figure 7. Simplified scheme of fine sediment sources for the Paraná River Basin.
Figura 7. Esquema simplificado de áreas de aporte de sedimentos finos de la Cuenca del Río Paraná.

Sediment source areas

The clay mineral composition is controlled by the interplay between different source rocks and the main sedimentary processes taking place in the streams sediment deposition, like the size-sorting processes and bed load structures.

When observing the distribution the clay mineral associations of the tributaries plotted in ternary diagrams from the upper, middle and lower Paraná (Figs. 6 and 7), it can be confirmed a greater homogeneity in the clay mineral composition of the studied tributaries. This tendency could also be reflected within the Paraná River itself, considering examples from other big river basins (Yuretich *et al.*, 1999). The clay mineral composition in fine sediments from the studied tributaries of the Upper Paraná sector exhibits higher variability, while to the south, is only represented by a single Illitic-Smectitic association.

In addition, the fine sediment clay composition of all tributaries shows: a) an increase of the estimated Illite crystallinity index in tributaries of the upper basin like the Iguazú, Uruguaí, and the Paraná itself, showing the imprint of the Brazilian Shield (from mica rich rocks like gneisses and granitoids); and b) a variable random Illite/ Smectite mixed layer clays associated to sources like Sub Andean region and the loess deposits and paleosoils (Fig. 7). Cratons and passive margins tend to be small donors of sediments (Potter *et al.*, 2005), with a more clear imprint (shown here by Kaolinite abundance and high Illite crystallinity index), while in contrast, active margins provide more complex clay associations (with variable Smectite/ Illite index).

CONCLUSIONS

The dynamics of bottom fluvial sediments play an important role both in sedimentary and environmental studies, considering that they may act as transporting agents and sinks of pollutants. The size of the component particles is one of the fundamental textural characteristics of all fragmented deposits and their lithified equivalents.

The study of grain size data and statistical parameters of the cores, from distal positions of tributaries of the Paraná River Basin, shows a moderate to poor sorting with predominant transport saltation and suspension processes. The first related to the abundance of fine sands and silts and the latter to the clay mineral one.

Three clay mineral associations are detected in the fine sediments of the tributaries of Paraná River. An Illite- Chlorite clay facies with source-areas in the Pampa Plains, with scarce and subordinated mixed layers clays like Illite/ Smectite. An Illite-Smectite+Illite/ Smectite clay facies, coming from both, the Andean Cordillera and the Chaco Plains, and mainly present in the Bermejo and Pilcomayo Rivers. A last Kaolinite clay facies, coming mainly from Brazilian sources could also be detected. They have subordinated Illite with good crystallinity index. This last association shows a typical imprint of a passive continental margin.

The present study contributes with regional knowledge at the level of clay mineral distribution, provenance, transport and deposition in sediments from surface bodies of water discharging in a highly complex and large river system like the Paraná River Basin.

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