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THEMATIC ISSUE

Hydrochemical and sedimentological dynamics in a subtropical plain river: assessment by multivariate statistical analysis

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Abstract Understanding the transport dynamics of sediments and soluble components is critical when ecosystems could be adversely affected. This study examined some environmental factors influencing the spatial and temporal variations of water–sediment interactions in Negro River, northeast of Argentina, a subtropical plain fluvial system with anthropogenic influence. Samples of water and bottom sediments were collected from four sampling stations in four sampling campaigns spread over 2 years. Chemical parameters, including pH, conductivity, major ions, concentration of suspended sediments, extractable major cations and particle size of sediments, were determined. The experimental data were interpreted by classical hydrogeochemical methods and statistical methods. Multivariate statistical tools were applied to reduce the dimensionality of the data set and to evaluate the relative importance of combinations of environmental variables on sediment dynamics. The results showed that the variability of the hydrochemistry and the sediment chemistry is controlled by longitudinal and seasonal factors, whereas differences across the river section were nonsignificant. The concentration of suspended solids and the abundance of fine-grained materials in bottom sediments were inversely correlated with the concentration of some metals with agglutinant and coagulant properties in sediments. This corroborates the presence of fine particle aggregates, also evidenced by classical grain-size analysis. Thus, particle disaggregation by chemical methods is not recommended, as it could lead to misinterpretation when the objective is to evaluate the dynamics of sediments in natural environments. This study highlights the importance of analyzing multiple dimensions (spatial and temporal) to understand the dynamics of fluvial sediments, especially in plain rivers.

Keywords Chaco—Argentina · Transport processes · Plain rivers · Multivariate analysis · Principal component analysis

Introduction

The interaction between river water and solid materials (soils and rocks) defines the hydrochemical and geochemical characteristics of the basin, which have a direct influence on fluvial ecosystems. Fluvial systems drain the continental areas and mobilize the weathering products to the ocean. River basins occupy 69 % of the terrestrial surface and transport near 19 billion tons of materials each year, approximately 20 % of which are carried in solution (Nanson and Gibling 2003). The transported materials

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(natural and anthropogenic) must be carefully investigated to know their source and fate, especially when ecosystems could be negatively affected. The transport dynamics of sediments and solutes is determined by a complex set of interacting variables, such as lithology, weather and topography.

Fine-grained sediments tend to be together (aggregation) forming flocs with different possibilities of transport and different settling velocity. The process of aggregation depends on the type and concentration of the sediment, the flow conditions and the ionic concentration in the water column, mainly salinity (Mehta et al. 1989; Berlamont et al. 1993; Huang et al. 2006). Berlamont et al. (1993) indicated that the sediment structure of the flocs (i.e., size, density and shape) defines the rate of erosion and/or the settling velocity. However, some of these properties may vary both spatially and seasonally, due to different levels of turbulence, floc aggregation or disaggregation rates, suspended sediment concentration and hydrochemistry.

The anions carbonate, bicarbonate and hydroxide, and to a lesser extent borate, silicate and phosphate, are key regulators of water alkalinity (Abarca 2007). These ions are often associated with the more abundant cations Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}. Some metal ions such as iron, aluminum, magnesium and calcium, as well as organic matter, behave as cementing agents and contribute to the formation of aggregates of particles.

Sediments also affect the water quality of rivers, behaving as reservoirs and as transport and dispersal agents of different fluvial materials (Zhu et al. 2008; Horowitz 1991). A large number of chemical and biological reactions occur in river water bodies. These reactions frequently result in variations of pH and redox potential that can subsequently cause the release of chemical elements from the sediments to the water column. The biogeochemistry along a sediment–water interface is regulated by the movement of fluids along and across the interfaces (Cardenas and Wilson 2007).

Droppo et al. (1997) highlighted the fundamental ecological role of flocs in aquatic systems in regulating the overall water quality through physical, chemical and biological activity. Thus, the study of the transport dynamics of fine grain sediments is important because many nutrients and pollutants (such as heavy metals and pesticides) sorbed to them by adsorption phenomena and, to a lesser extent, by absorption further increase the density and settling rate of particulate matter (Domínguez-Chicas et al. 2004). The most important parameters that determine these bonding processes are: organic carbon content, clay abundance, humidity, pH, cation exchange capacity and temperature (Porta et al. 2003).

Sediment transport phenomena have special interest in river hydrology because they may help solve both environmental and engineering issues (McLaren and Bowles 1984; Habibi 1994; Ackermann and Schubert 2007; Symader et al. 2007; among many others). The transport dynamics of suspended sediments requires special attention because these sediments are responsible for establishing zones of accumulation and re-suspension of contaminants, as well as for increasing the residence time thereof in the system. The transport by traction of clastic grains and suspended particles depends on factors such as flow intensity, water density and viscosity, and the size, shape and density of the sediment particles (Perillo 2003). Generally, more rounded, smaller and less dense particles are transported more easily (Spalletti 1986).

When multiple environmental factors are analyzed, a large set of data are generated. In these cases, multivariate statistical techniques have been successfully applied (Massart et al. 1988; Wenning and Erickson 1994; Dixon and Chiswell 1996; Suárez 2012; Kumarasamy et al. 2014; Ogwueleka 2015). Multivariate analysis is useful to reduce the dimensionality of the data set, to evaluate the relative importance of combinations of variables and to facilitate the understanding of multiconstituent chemical and physical measurements (Vega et al. 1998; Helena et al. 2000; Rodrigues et al. 2010; Cid et al. 2011; and references therein).

Wiens (2002) noted that, in studies on river systems, it is important to consider both longitudinal and lateral dimensions, as well as seasonal variations. The climate variations could be extreme and affect various fluvial factors (Viles and Goudie 2003).

The aim of this research was to evaluate both longitudinal and lateral dimensions, as well as seasonal variations, in relation to some environmental factors, including rainfall pattern, topography, geology and soils, which influence the dynamics of sediments and of the more soluble elements (i.e., sodium, potassium, calcium, magnesium). The study also aimed to evaluate the influence of hydrochemistry on suspended solids and chemical composition of bottom sediments and to analyze the effect of hydrochemistry of the Negro River (Chaco, Argentina) on the behavior of sediments. To achieve these goals, hydrogeochemical variables and granulometric characteristics of the bed sediments were investigated and three-way multivariate statistical tools were applied.

Materials and methods

Study area

The Negro River, located in the northeast of Argentina in the geological province known as the Chaco-Pampeana Plain, is a tributary of the Paraná River and drains a region with increasing anthropic influence owing to the development of many cities, mainly in the lower part of the basin. To investigate the characteristics and variability of the riverbed sediments along the basin and simultaneously evaluate the effect of different degrees of anthropogenic influence on the water and sediments of this river, a study area that comprised the defined channel of the basin (500 km^2) was selected. The basin section investigated is located in the east of Chaco Province and covers the area located between 27°04′32″S–59°27′23″W and 27°25′42″S–58°57′42″W, integrating the alluvial paleofan of the Bermejo River (Argollo and Iriondo 2008). The slope of the river is 0.32 m/km. Paoli and Giacosa (1983) showed that 35 % of the continental area of Argentina is geomorphologically composed of plains, mostly flooded, where river systems do not behave within the parameters established for typical rivers. Fertonani and Prendes (1983) proposed that these hydrological units, not developed under the traditional concept of watersheds, should be named as "Non-Typical Hydrological Systems." These hydrological systems are characterized by not defined boundaries and not organized river networks. The surface runoff takes the shape of an erratic laminar flow, and the pathway is determined by the micro-topographic differences, the land cover and even the wind direction. In these plain areas with homogeneous lithology, where rivers have low energy to transport sediments, materials are mainly mobilized in suspension (Blasi 1981).

Owing to its low slope, the Negro River is included within "Non-Typical Hydrological Systems." Changes in its flow depend on the amount and distribution of rainfall in the basin (Poi Neiff, 2003). At present, the Negro River is regulated, and the typical discharges thus vary between 20 and 80 m^3 s^{-1}; for that reason, there are no regular direct discharge measurements and the pluvial precipitations offer an indirect option to estimate its discharges.

Typically, the streams of this region, including the one studied here, do not show large textural variations in their bed sediments, probably due to the lithological and granulometric homogeneity of the basins. Sandy–silty beds, as well as silty–sandy and clayey–silty types, are common and almost always poorly to moderately sorted with high organic matter content (Orfeo 1999). Also, in these types of rivers, the suspended sediments are inversely related to the water level.

The climate is subtropical humid with variable annual rainfall that affects the hydrological regime of this river system. The basin studied lies between isohyet 900 mm in the west and isohyet 1300 mm in the east, near its mouth. The rainy season begins in November and ends in March, and the dry season is between July and August (Morello 1983).

The studied stretch of the Negro River flows in the Chaco Province through an important Argentinean wetland of 508,000 hectares, recognized as a RAMSAR site in 1994, with number 1366 (RAMSAR 2015). RAMSAR sites are wetlands of international importance and represent a valuable reservoir of freshwater that captures sediments, purifies water, absorbs pollutants, regulates floods and supports a vast biological diversity with a worldwide ecological relevance. The abundant vegetation that grows in these wetlands and the organic matter in different states of decomposition have significant effects on the dynamics of local rivers (Orfeo 2006). Local courses show considerable variations in flow velocity, sediment transport, erosion and sedimentation rate, among other hydro-sedimentological variables, owing to the contributions of these wetlands (Neiff and Orfeo 2003).

Figure 1 shows the four sampling stations (SS) selected. They represent different typical scenarios in the longitudinal profile of this fluvial system. SS1 is located in the swampy headwaters area, characterized by low discharge, low land use and abundant populations of aquatic plants throughout the year. SS2 and SS3 are located in the canalized stretch of the basin with higher discharge, medium anthropogenic influence and abundant vegetation during most of the year. SS4 is located near the mouth, with more than twice higher discharge than the previous river sections; it is located downstream the urban area and receives high anthropogenic impact due to domestic and industrial effluents (mainly cryogenic and dairy industries), which in previous studies were identified as responsible for water quality degradation (Poi de Neiff et al. 2003; Ruberto 1999). The abundance of vegetation in this section varies along the year, with larger populations in the rainy periods. In its headwaters, river width varies between 8 and 15 m and the depth between 1 and 3 m, depending on the seasonal period, whereas in its mouth, the width varies between 60 and 100 m and the depth between 3 and 5 m.

The study area has saline and saline–alkaline soils, due to the saline groundwater and the natural saline content of the soil, along with the occasional water deficit observed in the region (OAS 1977; Ledesma and Zurita 1995). The levee and floodplain areas are also conditioned by salinity and sodicity. The Negro River flows through mollisol soils. Smith (1986) described these soils as rich in organic matter and alkaline ions, with dominance of Ca^{2+} and Mg^{2+} ions, often with horizons rich in clay (forming aggregates), as well as horizons rich in calcium–magnesium carbonates (15 % or more), and natric horizons (more than 15 % of exchangeable Na$^+$).

Sampling

Water and bed sediments were collected at the four sampling stations described above, during two hydrological periods, the rainy and the dry seasons, in 2009 and 2010.

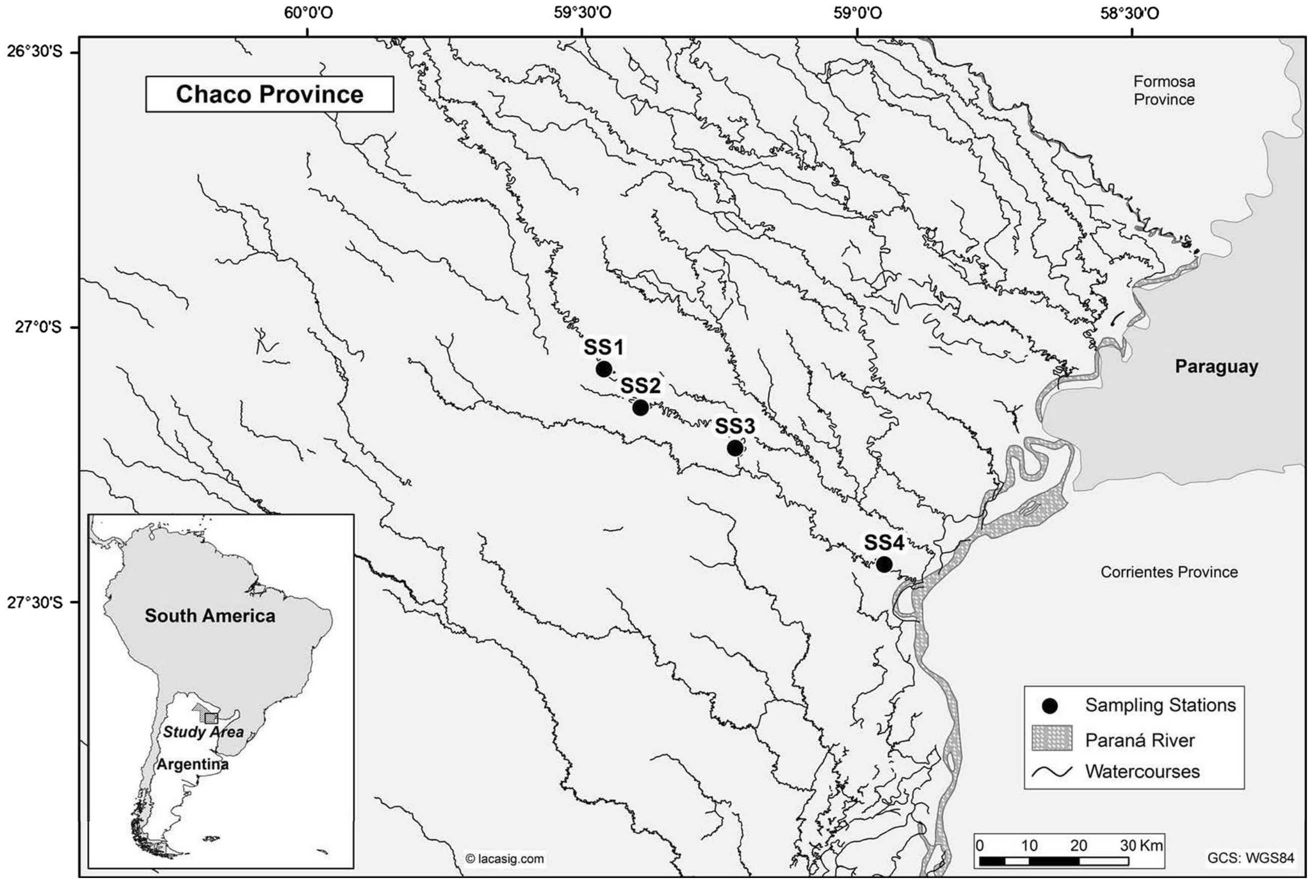


Fig. 1 Location of sampling stations

Therefore, the data collected allowed evaluating the spatial and temporal effects on the composition of river water and bed sediments. In July 2009, the discharge of the Negro River was extremely low because of the poor rainfall recorded during the previous years. In December 2009 and July 2010, the rainfall and the discharge increased progressively. Therefore, these sampling campaigns can be considered representative of medium flow conditions. Samples collected in December 2010 are representative of higher discharge as the rainfall was almost twofold higher than the first field campaign.

Temperature, electrical conductivity (as a direct indicator of the concentration of dissolved salts) and the water pH were measured in situ, using portable sensors (EC/TDS Hanna HI 98311 and pH meter Hanna HI 98128).

A Van Dorn bottle was used to take three replicated water samples, each collected in individual polyethylene bottles. One subsample was immediately filtered through cellulose nitrate disks (pore size 0.45 µm) acidified to pH 2 by addition of HCl and used to determine metal contents (Ca, Mg, Na, K) and total hardness. The second subsample was directly stored at 4 °C, without addition of chemical preservatives, and used to determine major anions (bicarbonate, chloride and sulfate). The third subsample was kept at its natural pH and temperature and used to analyze the concentration of suspended solids (CSS) by filtering through 0.45-µm pre-weighed cellulose acetate disks (Pedrozo and Orfeo 1986; APHA 1998; Orfeo 1999, 2006; Suárez et al. 2010).

In order to evaluate the longitudinal and cross variations of the particle size and chemical composition, bottom sediments were sampled at the four sampling stations from the middle of the channel and both margins of the river bed using a core sampler. The samples were transported refrigerated to the laboratory and stored at 4 °C until their analysis.

Samples were labeled as CX-SSY, where X means the sampling campaign (1–4) and Y means the sampling station (1–4).

Analytical procedures

The grain size of bed sediments was analyzed in three steps to evaluate the presence of fine particles aggregated forming flocs: (T1) without pre-treatment, representing the distribution of sediment grain-size classes closer to the natural environment; (T2) with removal of organic matter using an oxidant in cold and hot conditions to remove the sediment aggregation caused by organic matter (Lafleur et al. 1980); and (T3) with chemical oxidation as in (T2) followed by a chemical dispersant (40 % sodium hexametaphosphate) to eliminate the binder effect of salts (Lafleur et al. 1980). The grain size of the bed sediments was analyzed by means of classical procedures (Galehouse 1971; Ingram 1971; McManus 1988), using the Udden–Wentworth grain-size scale with the modifications proposed by Friedman and Sanders (1978).

To estimate the mobility of metals bound to bottom sediments in natural conditions, they were extracted with distilled water, following method 1312 (USEPA 1994).

Major anions and cations in water and sediments were determined according to APHA (1998). Magnesium, sodium, potassium and iron were quantified by atomic absorption spectrometry (Varian Spectra AA300) using an air–acetylene flame. Calcium was estimated from the data of hardness (titrimetry). Chloride was determined by titration according to argentometric method 4500 Cl-B (APHA 1998). The analytical results of bed sediments are referred to as dry weight.

Quality controls included reagent blanks, duplicate samples (APHA 1998) and analysis of certified reference material (Pond Sediment, National Institute for Environmental Studies, Tsukuba Ibaraki, Japan). Agreement with certified values was between 16 and 32 % as relative bias. Rainfall records of each sampling station were provided by the APA (2010).

The experimental results were interpreted by multivariate statistical techniques. Software packages SPSS 20, MINITAB 13.0 and MATLAB 6 were used for all statistical calculations. Analytical results below the method detection limit were replaced prior to calculations by a random value between zero and the detection limit.

N-way principal component analysis (PCA) was applied. This statistical method takes into account the three-dimensional structure of the data matrix and separates the information corresponding to each dimension: sampling stations, investigated variables and sampling campaigns, thus allowing an easier interpretation of the information (Smilde et al. 2004; Singh et al. 2006; Pardo et al. 2008). PARAFAC (Bro 1997) is one of the most common models to perform three-way PCA and is based on the decomposition of the matrix $\underline{\mathbf{X}}$ according to

$$x_{ijk} = \sum_{f=1}^{NF} a_{if} b_{jf} c_{kf} + e_{ijk}$$

where a_{if}, b_{jf} and c_{kf} are the elements of the loading matrixes **A**, **B** and **C** with $(n_{\text{sites}} \times F)$, $(n_{\text{var}} \times F)$ and $(n_{\text{time}} \times F)$ dimensions, respectively, carrying the information contained in the three modes of $\underline{\mathbf{X}}$. F is the number of significant factors needed to explain the maximum information and must be kept as low as possible. The mathematical feasibility of the model is determined by the core consistency parameter that must be near 100 % (Bro 1997). The N-way toolbox for MATLAB (Anderson and Bro 2000) was used in this study.

Results and discussion

Hydrochemistry of the Negro River

Table 1 summarizes the mean value and standard deviation of the ten variables measured in the 16 river water samples collected from the four stations in the four sampling campaigns achieving a first approximation to the data set variation. The high dispersion observed (high standard deviations) and the lack of normality for most variables indicate that the samples had different chemical composition, thus pointing out the presence of temporal and/or spatial variations.

Table 1 Descriptive statistics and Kolmogorov–Smirnov normality test (p value) of the variables measured in water samples collected at four sites in four sampling campaigns

Parameter	Units	Mean	Median	SD	Min.	Max.	p value*
pH	pH units	6.64	6.55	0.46	6.05	7.50	0.200
Conductivity	µS cm^{-1}	318	218	234.45	88	840	0.001
Alkalinity	mg $CaCO_3$ L^{-1}	83	83	36.80	29	166	0.200
Cl^-	mg L^{-1}	22.5	14.5	23.75	4.0	98.0	0.009
SO_4^{2-}	mg L^{-1}	27.4	13.0	30.10	2.0	105.0	0.019
Ca^{2+}	mg L^{-1}	16.5	13.2	9.23	5.3	36.0	0.008
Mg^{2+}	mg L^{-1}	6.6	5.9	4.36	2.0	16.0	0.200
Na^+	mg L^{-1}	25.9	16.5	28.66	0.4	105.0	0.003
K^+	mg L^{-1}	17.4	16.5	3.31	12.0	26.0	0.011
CSS	mg L^{-1}	146.1	76.0	193.7	30.0	815.0	0.000

* p value <0.05 indicates non-normal distribution of the variable

The ionic concentration was similar to that of other local rivers, reported previously by several authors (Lancelle et al. 1986; Bonetto et al. 1998; Villar and Bonetto 2000; MSAN OPS PNA UNLP 2005; Depetris and Pasquini 2007). The MSAN OPS PNA UNLP (2005) has indicated an abundance order of $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ and an abundance order of $(Na^{+}K^{+}) > (Ca^{2+}Mg^{2+})$ when the concentration of dissolved load increases. In Paraná River (the final collector of the Negro River), Depetris and Pasquini (2007) found an abundance order of major anions of $HCO_3^{-} > Cl^{-} > SO_4^{2-}$ and an abundance order of major cations of $(Na^{+}K^{+}) > Ca^{2+} > Mg^{2+}$.

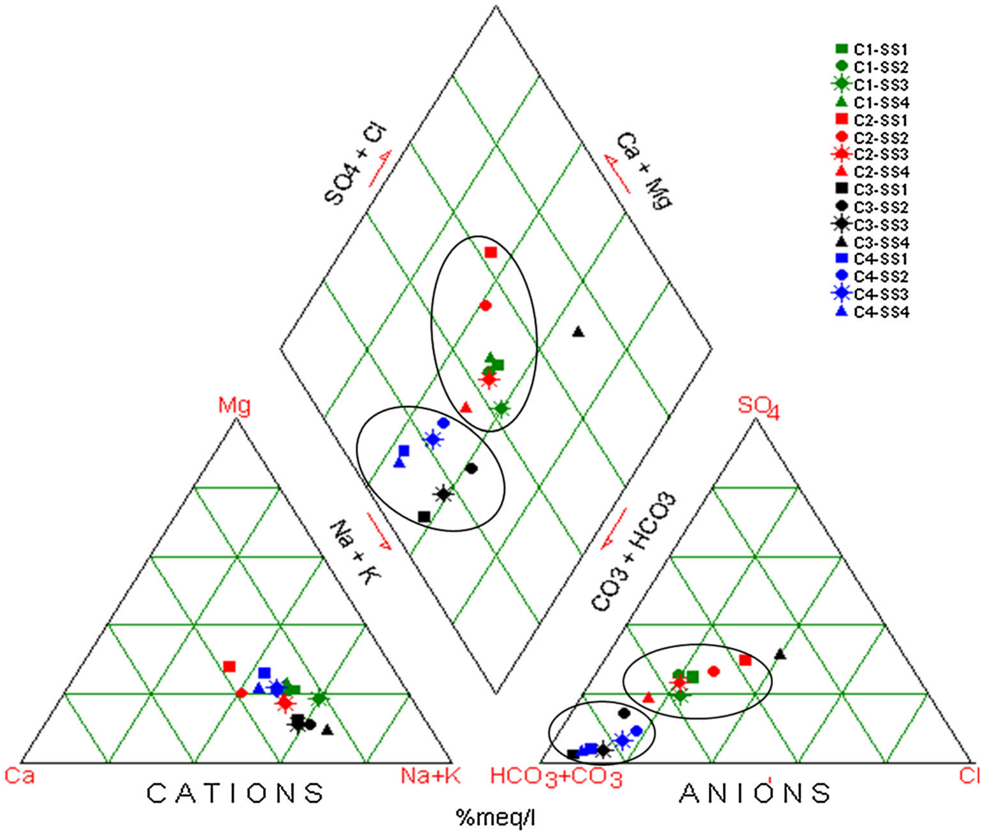
In the Negro River, the abundance order was found to be similar: $HCO_3^{-} > SO_4^{2-} > Cl^{-}$ for major anions and $Na^{+} > K^{+} > Ca^{2+} > Mg^{2+}$ for major cations. Potassium concentration was significantly higher than that found in the works mentioned above. However, the same works relate these events to exceptional periods. According to APHA (1998), the concentration of ion K in the Negro River corresponds to salty water classification.

The hydrochemical data of the four campaigns are presented by a Piper (1944) diagram in Fig. 2. According to the concentration of major anions and major cations, the water of the Negro River was classified mainly as sodium–potassium bicarbonated. Two main groups, mostly differentiated by the anionic composition, were found: one comprising samples collected during campaigns C1 and C2 and the other comprising those collected during campaigns C3 and C4. Samples collected during the lowest rainfall periods (campaigns C1 and C2) showed the lowest concentrations of carbonates, as well as the highest concentrations of sulfates and chlorides. The salty groundwater and the saline and saline–alkaline soils as well as the presence of tanneries in the study area could be responsible for the high concentrations of sulfates and chlorides, which contribute to increasing the water conductivity of this river system.

Samples collected during the highest rainfall periods (campaigns C3 and C4) showed highest concentrations of carbonates. This suggests washing processes of surface soils, coincident with the regional soils rich in calcium–magnesium carbonates as well as in sodium (Smith 1986; OAS 1977; Ledesma and Zurita 1995).

Several authors have highlighted the wide rainfall variation in the region as well as its effect on the hydrochemical characteristics and fluvial dynamics (Bielsa and Fratti 1981; Morello 1983; Lancelle et al. 1986; Patiño and Orfeo 1986, 1997; Ruberto 1999; Poi de Neiff et al. 2003; Suárez et al. 2010). Figure 3 shows the historical rainfall records for each sampling station (APA 2010). In 2009, rainfall was considerably lower than in 2010, so higher ionic concentration and low sediment transport could have

Fig. 2 Hydrochemical classification (Piper 1944)



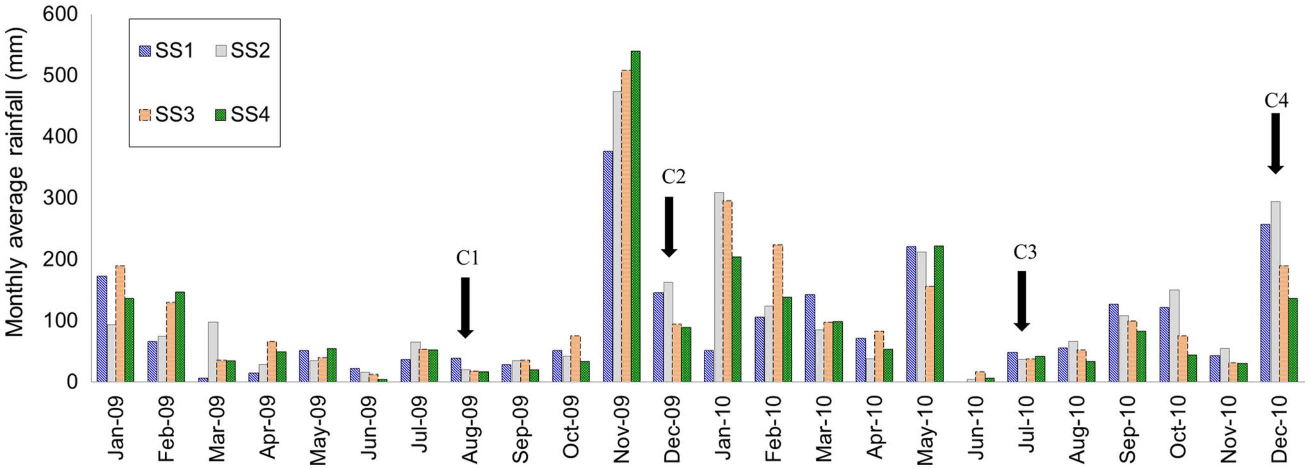
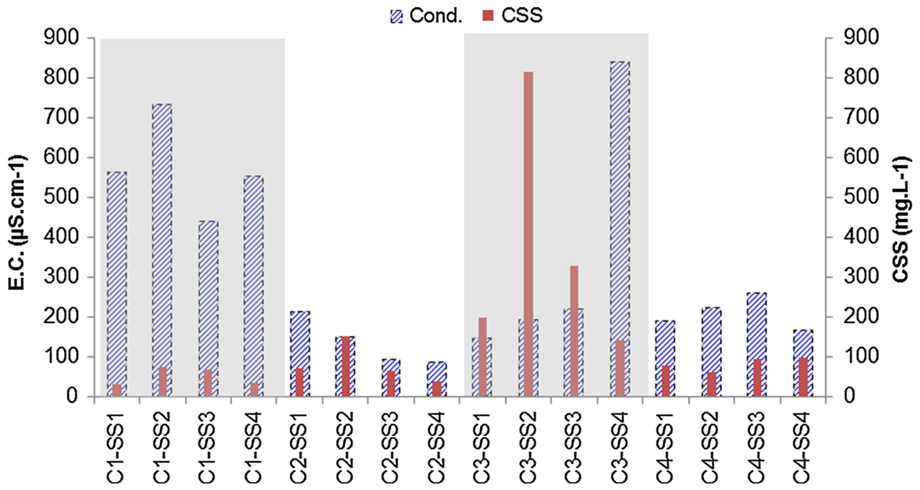


Fig. 3 Rainfall records of the four sampling stations in the four sampling campaigns

Fig. 4 Variation in conductivity and concentration of suspended solids (CSS)



predominated. In 2010, rainfall was higher during both the dry and the rainy seasons, so dilution processes, washing of surface soils and sediment transport could have been increased.

Figure 4 shows the variation in the conductivity and concentration of suspended solids (CSS). The gray background indicates the campaigns carried out during dry periods, whereas the background in white color indicates those carried out during rainy periods. An inverse variation was found between these two variables regulated by seasonality; the same relation has been pointed out by other authors for local rivers (Patiño and Orfeo 1997; Suárez et al. 2010).

The lowest CSS was recorded in SS1 and SS4 (river head and mouth, respectively). In SS1, the low concentrations appeared to be related to a high ion concentration, due to low flow rate and the saline soils of the area. Long water residence time, because of the flat topography, increases the ion exchange processes between the bottom sediments and the water column; this factor encourages an increase in the water conductivity and aggregation processes, as well as a subsequent increase in settling velocity of suspended sediments.

In SS4, the high conductivity appeared to be mainly related to the human activity upstream and soil washing. The decrease in the CSS near the mouth is also related to dilution processes, since the flow rate in SS4 was more than twice higher than that found near the head. During C3, high CSS values were recorded at all sampling stations. The increase seems to be a result of strong washing of surface soils, since the maximum rainfall was recorded in the region during this sampling campaign.

During the low water period, most of the channel and water-logged areas are rapidly colonized by aquatic vegetation, bringing abundant organic matter that is added to the incoming organic matter from the wet highlands (Orfeo 1999). Therefore, the dry season usually generates high CSS. The high CSS corresponds to minimal discharge, and therefore, the overall sediment transport is low (Orfeo 2006). However, in some rivers (mostly with saline hydrochemical composition), this trend is reversed. In the Negro River and most of the rivers located in this region, the CSS maintains a negative correlation with the hydrometric level (Orfeo 2006; Suárez et al. 2010). Highly saline streams with low flow velocity during the low water period have a positive correlation with the discharge. This is interpreted as a consequence of an active ionic exchange among clay particles, since the saline concentration is more influential in the decrease in CSS than organic matter (Suárez and Orfeo 2015). This is because the increase in the water conductivity induces the aggregation of fine sediments, generating floccules of larger size thus increasing the velocity of settling processes. In contrast, in rainy periods, the high flow dilutes the concentration of salts, and the CSS also decreases.

Analysis of sediment physicochemical characteristics

Table 2 summarizes the mean descriptive statistical information of the six chemical variables analyzed in bottom sediments. Sediment samples were collected during the four sampling campaigns at the four sampling stations. During sampling campaigns 2, 3 and 4, sediments were collected from the middle of the channel and both margins of the river bed, but in the first sampling campaign only sediments from the channel center were collected. Thus, 40 samples were collected and analyzed. The order of abundance was defined as Na > Mg > K > Fe > Ca > Mn. Similar values have been found in MSAN PAHO NAP UNLP (2005) for other local rivers.

As in the case of the water samples, the high dispersion of the parameters investigated points to the occurrence of strong temporal and/or spatial variations. Besides, most parameters were not normally distributed (p value < 0.05).

Figure 5 shows granulometric composition diagrams of the four sampling stations, taking into account the three analytical steps mentioned above. Points in the diagram represent average percentages of each granulometric fraction.

In step T1, the sandy-silty fraction predominated and the clay fraction was poorly represented. In T2, when the organic matter was eliminated, the proportion of fine grains (<2.0 µm), mainly silts, increased and the sand fraction was subordinate. In step T3, the frequency of sand and silt decreased significantly, while the clay fraction predominated. The granulometric abundance diagrams confirmed that the occurrence of particles greater than 62 µm is a consequence not only of the presence of sand grains, but also of the existence of fine

Table 2 Descriptive statistics and Kolmogorov–Smirnov normality test (p value) of the variables measured in 40 bottom sediment samples

Parameter	Units	Mean	Median	SD	Min.	Max.	p value*
Fe	mg kg^{-1}	65.1	6.2	133.9	0.10	621.9	0.001
Mn	mg kg^{-1}	8.0	0.4	24.6	0.03	143.4	0.000
K	mg kg^{-1}	151.4	117.3	116.0	32.9	520.2	0.050
Na	mg kg^{-1}	271.7	228.2	202.6	57.0	825.9	0.056
Mg	mg kg^{-1}	185.4	103.4	269.8	0.40	1414.0	0.016
Ca	mg kg^{-1}	27.2	13.4	40.2	0.19	223.2	0.013

* p value <0.05 indicates non-normal distribution of the variable

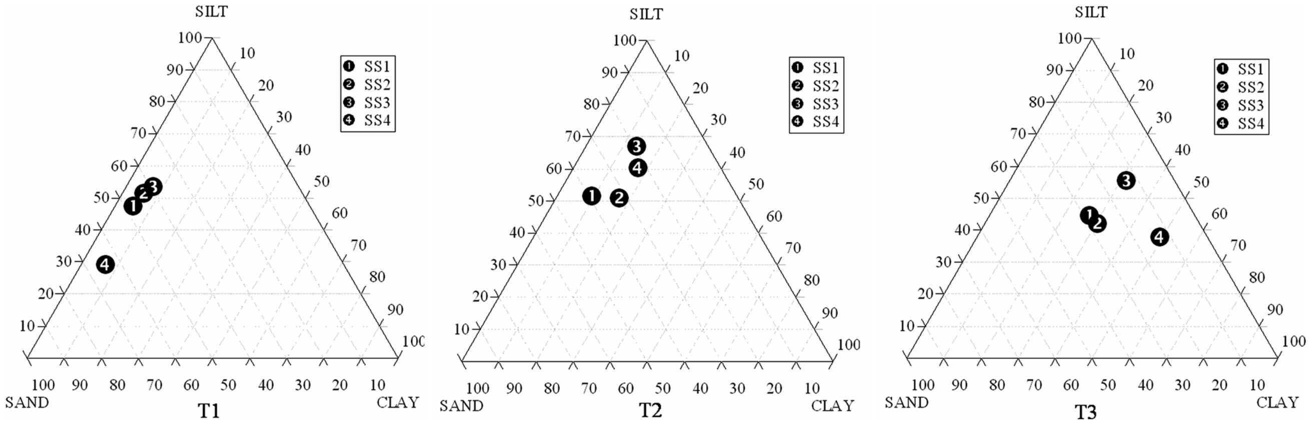


Fig. 5 Granulometric diagrams of bottom sediments in the three steps analyzed

sediment aggregates. This aggregation process is strongly related to the presence of fine particles in Negro River sediments, as well as to the high conductivity and the abundant organic matter.

Assessment of variation factors influencing the hydro-sedimentological dynamics by multivariate statistical analysis

The Kolmogorov–Smirnov normality test demonstrated that water variables were not normally distributed, thus revealing the existence of non-random effects on the variables investigated. A representation of the experimental results in box and whisker plots showed non-symmetric distributions and the existence of outliers for most variables, possibly caused by extreme variations of the flow during rainy and dry periods.

High dispersion, non-normal distributions and occurrence of outliers were also observed in most chemical variables of sediments. The iron and magnesium ions, which are widely important as natural cementing agents, were some of the most abundant leachable metals found in the bottom sediments of the Negro River.

The descriptive statistical analysis, as well as the hydrochemical and granulometric diagrams presented above, showed that data variations are controlled by both temporal and spatial factors. The chemometric analysis allowed elucidating the factor with strongest influence on sediment behavior and water ionic concentration. It also allowed establishing the linkage between hydrogeochemical variables and CSS, in relation to the presence of aggregates in bottom sediments.

To evaluate the contribution of the different sources of variation (longitudinal spatial, cross-spatial and temporal) to the variability of the analytical results, the nonparametric Mann–Whitney test was applied (Hari et al. 1991; Chagas and Suzuki 2005; Thomas and Aitchison 2006; Chae et al. 2007).

The Mann–Whitney test for water data evaluated seasonality (dry/rainy periods) and longitudinal distribution (head/middle/mouth) as sources of variation. The results showed that the significant differences among all variables are likely to be linked to seasonality.

For sediment variables, the effect of seasonality, longitudinal and transversal distribution (between both margins and to the center of the channel) was evaluated by the Mann–Whitney significance test. The results indicated that seasonality and longitudinal distribution further explain the variations in all the parameters analyzed. Since transversal variations were not significant, only the data of samples taken from the center of the channel were used in multivariate analysis. Thus, the dimensionality of the data set was reduced, allowing the integration into a single table sediment and water variables.

A total of 17 variables were selected for the PARAFAC statistical analysis: the hydrochemical data (identified with the chemical symbol), the water-leachable metals measured in sediment extracts (indicated with the chemical symbol followed by number 2), the percentage of fine-grained materials (<62 μm) obtained by granulometric step analysis 1 (indicated as FGM-1) and the CSS (expressed in mg L^{-1}). Since the granulometric variables (expressed as percentages) were fully correlated (their sum was 100 %), only the variable “FGM” was used in the multivariate analysis.

PARAFAC three-way PCA was applied to the three-dimensional matrix $\underline{\mathbf{X}}$ $n_{ss} = 4$ sampling stations $\times$ $n_v = 17$ variables (both water and sediment) $\times$ $n_c = 4$ sampling campaigns. This method decomposes the three-way data set into three matrixes $\mathbf{A}$ ($n_{ss} \times F$), $\mathbf{B}$ ($n_v \times F$) and $\mathbf{C}$ ($n_c \times F$), which contain the information corresponding to sampling station, variables analyzed and sampling campaigns, respectively. The appropriate number of factors of the model (F) was selected by means of the core consistency parameter (Stanimirova et al. 2006) implemented in the N-way toolbox for MATLAB (Anderson and Bro 2000; Pravdova et al. 2001). The optimal complexity was found for a two-factor model (core consistency = 100 %) which explained 51.5 % of the variance of the data matrix.

Figure 6 shows a summary of the components of the PARAFAC model, i.e., the loadings of the three matrixes: sampling stations (**A**), variables analyzed (**B**) and sampling campaigns (**C**). Similarly to classical PCA, the interpretation of multi-way PCA models like PARAFAC is based on the existence (or absence) of correlations between the loadings of the N different modes, found by simultaneously comparing, within each factor, the magnitudes and signs of the loadings of each PARAFAC mode.

The first factor of PARAFAC B mode, related to the 17 variables measured, presented large positive B1 loadings for pH, conductivity and most major anions and cations in the water column. Soluble metals in sediments had a minor contribution to this mode. Hence, factor B1 can be related to water hydrochemistry. The hydrochemical variables contributing positively to B1 mode were correlated with all the sampling points, which also presented positive A1 loadings. On the other hand, the temporal (seasonal) information (C1 factor loadings) showed that this factor was only positively contributed by the first sampling campaign, which took place during a severe drought period, thus highlighting the strong effect of seasonality, related to the precipitation regime, on water hydrochemistry in all sampling points.

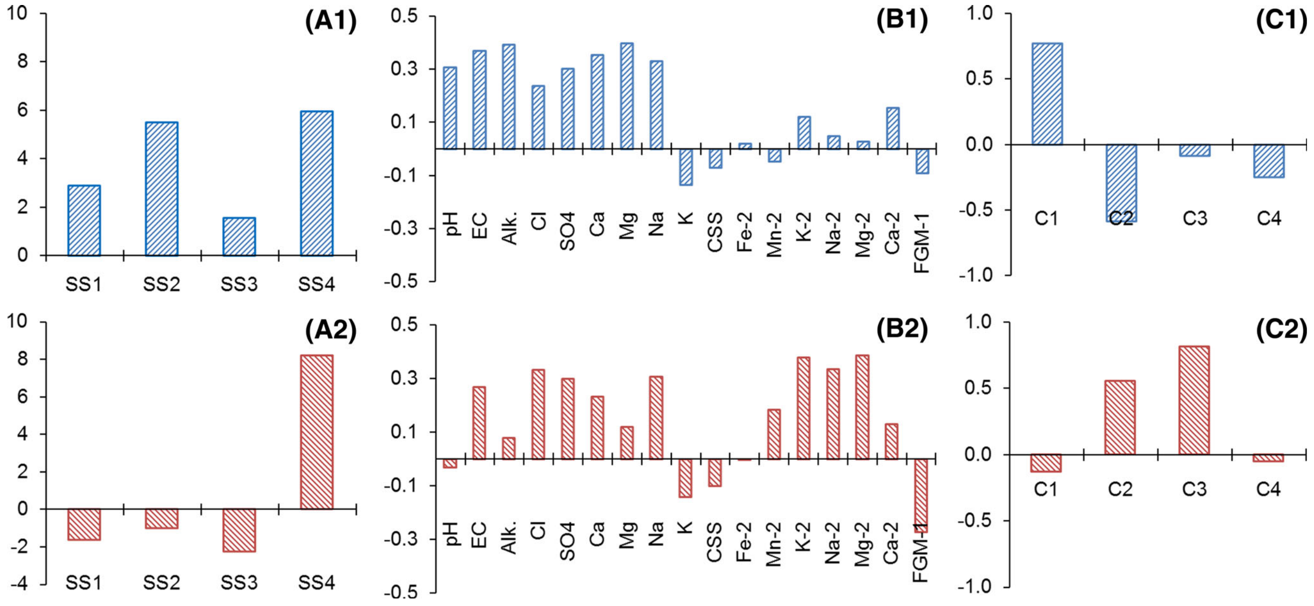


Fig. 6 PARAFAC model loadings: *A1, A2* Sampling stations; *B1, B2* Variables analyzed; *C1, C2* Sampling campaigns. Numbers 1 and 2 refer to the two factors of the PARAFAC model

The second PARAFAC factor had positive B2 loadings for all variables except for pH, K, CSS and FGM-1. All the variables with positive loadings were correlated with site SS4 and sampling campaigns C2 and C3. This factor, which seemed to be related to both the chemical composition of water and the leachable cations in sediments, is thus very strongly dependent on spatial location and seasonality.

As it can be observed, CSS behaved oppositely to ionic variables (mainly in the second factor), indicating the occurrence of coagulation processes and floc formation, which decreased the occurrence of suspended solids in the water column. This is supported by previous studies (Orfeo 1999, 2006; Suárez et al. 2010; Suárez and Orfeo 2015). A similar behavior was found for FGM-1, which decreased when the water ionic constituents and the extractable cations with hardening properties, such as Mg, Ca and Fe, increased. This opposite trend indicates the formation of aggregates that behave like larger-grained sediments, as observed in the ternary diagrams of particle size abundance. Potassium in water (K) behaved inversely to potassium in sediment (K-2), with opposite loadings in both B factors. This seems to be related to two properties of this ion: It is more strongly adsorbed than Na on the surface of clay minerals and organic matter, and it is readily incorporated into clay mineral lattices because of its large size (GAE 2015).

The spatial changes observed are related to human activity, which generates significant variations in water conductivity in the longitudinal profile, with maximum concentrations in SS4. Meanwhile, the seasonal changes observed are mainly related to an increase in water conductivity as well, with higher concentrations during dry periods.

Conclusions

The hydrochemistry and the sediment chemistry of the Negro River are controlled by both temporal and spatial factors. The statistical analysis demonstrated the absence of cross-sectional variations in the chemical composition of the river bed sediments.

The surface waters of the Negro River are mainly sodium bicarbonated, with a relative abundance sequence of $HCO_3^- > SO_4^{2-} > Cl^-$ for anions and $Na^+ > K^+ > Ca^{2+} > Mg^{2+}$ for cations. Compositional variations are partially controlled by the longitudinal spatial dimension, although the seasonal dimension was more significant for most variables. The chemical composition of the water fluvial system investigated is attributable to the leaching processes of surface soils and sediments.

In bottom sediments, the extracts obtained by water leaching indicate the cationic abundance as Na > Mg > K > Fe > Ca > Mn. The spatial (longitudinal) dimension was the most significant factor influencing the geochemistry and concentration of suspended sediments. The grain-size analysis evidenced the occurrence of particle aggregates.

The longitudinal spatial variability of the hydrochemical and sedimentological characteristics of the Negro River was strongly conditioned by the sampling site located close to the river mouth due to a higher anthropic influence (discharge of industrial and domestic wastes), with the plain topography resulting in longer water residence times, and weathering of soils. These factors had the most important effects on the increase in conductivity in the streamwise direction.

The seasonal factor was responsible for the increased electrical conductivity of the water column during low flow periods coincident with the dry season. An inverse variation occurred between water electrical conductivity and the concentration of suspended solids, which is explained by coagulation–flocculation processes of the finest-grained fractions (clays) and the consequent increase in the sedimentation velocity.

The concentration of suspended solids in the water column and the predominance of fine-grained materials in sediments were inversely correlated with the concentration of some metals with agglutinant and coagulant properties in sediments. This corroborates the presence of sediment aggregates, also observed in classical grain-size analysis.

The flat topography determines slow water flow and large water residence time, thus increasing the ion exchange processes between the sediments and the water column and the sedimentation of fine-grained materials caused by aggregation processes stimulated by water salinity.

This study highlights the importance of analyzing multiple dimensions (spatial and seasonal) to understand the dynamics of river sediments, and the sediment-associated materials, especially in plain rivers, as well as the usefulness of multivariate statistical methods in data interpretation, which have provided an easy visualization of the relationships existing among variables in the large and complex databases obtained. Multivariate statistics also proved to be a useful tool to corroborate the presence of fine particle aggregates.

It is concluded that it is not recommended to apply classical techniques of sediment particle disaggregation (chemical oxidation to remove organic matter and chemical dispersants to break down associated particles), as these treatments could lead to misinterpretation when the objective is to evaluate the dynamics of sediments in the natural environment.

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