



Long-term trends in hydrochemistry in the Paraíba do Sul River, southeastern Brazil

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SUMMARY

The Paraíba do Sul watershed is an important hydrological resource for southeastern Brazil, that has undergone extensive land use changes related to industrial, agricultural and urban activities. Over 11 years, between 1997 and 2007, a long-term study was conducted to evaluate hydrochemical variation in the basin outlet through estimations of annual fluxes and identification of their controlling factors. River water was classified as Na–HCO₃, with TDS ranging from 32 to 132 mg L⁻¹. Variation between seasons was found: cations, total alkalinity, electrical conductivity, dissolved oxygen, nitrate and chlorophyll “a” had increased values during the low discharge period, while concentrations of DOC, ammonium, nitrite, phosphate and SPM had increased values during the high discharge period. Chloride, sulfate, silica and pH showed no clear relationship with discharge. These patterns also were correlated with hydrological flow paths originating from different sources. Wavelet decomposition was used to characterize precipitation anomalies largely associated both with long-term climate factors (i.e. ENSO) and short-term climate responses from the two discharge periods that were studied. Distinct responses of fluvial hydrochemistry were observed including ENSO-induced fluctuation to be particularly strong for DOC, with annual flux varying approximately 60% around measured median value.

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1. Introduction

Riverine transport of dissolved and particulate materials is related to a large number of inter-linked processes involving climatic, hydrological, geological, physical–chemical and biogeochemical aspects across temporal and spatial scales. For instance, weathering plays a key role in the type and amount of dissolved and particulate loads (Berner and Berner, 1996), while in-channel hyporheic zones can significantly affect the migration of essential nutrients of fluvial food webs (Hinkle et al., 2001). Fluvial hydrochemistry also can be affected by anthropogenic factors, such as urban demands, and impacts from agricultural and industrial activities (Négre et al., 2007). In particular, expansion of population and economic activities, especially in developing countries, has led to widespread discharge of effluents to river waters.

In southeastern Brazil, several major urban areas (i.e. the São Paulo and Rio de Janeiro metropolitan regions) are concentrated in and associated with the watershed of the Paraíba do Sul River. Since the 1980s the Paraíba do Sul River has received considerable attention due its importance as a water source for agriculture, industry and human use for approximately 13 million inhabitants

and 5000 different types of industry especially for the State of Rio de Janeiro. Early studies of river water conducted in this catchment did not consider temporal changes, if any, resulting from this development, thereby making it difficult to understand the evolution of water quality and to discriminate between natural and human induced processes. In general, these studies have been restricted to internal reports from state and federal environmental agencies, though several studies by Pfeiffer et al. (1986), Azcue et al. (1986, 1988) and Malm et al. (1988) assessed the critical pathway of heavy metals contamination in this river through use of an integrated research methodology.

Beginning in the 1990s and more recently in this decade, several studies began to consider the temporal (Lacerda et al., 1993; Carvalho et al., 1999; Dittmar et al., 2012) and spatial (Carvalho et al., 2002; Lage Pinto et al., 2008; Souza et al., 2010) effects of land use in this watershed on riverine water. However, long-term changes, particularly those associated with global climate changes, have received limited study (Marengo and Alves, 2005).

Studies assessing long-term changes have been recognized as a key tool for understanding ongoing processes in watersheds and for providing an essential background for evaluation of rapid changes within industrialized and developing countries (Nihlgard, 1994; Chen et al., 2002; Clair et al., 2002, 2008; Zakharova et al., 2005; Yuan et al., 2007; Tao et al., 2010). Nowadays, long-term

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studies also have been placed into a broader context, as changes in global climate factors, such as the El Niño Southern Oscillation (ENSO) and other atmospheric-ocean processes have been shown to impact ecosystem-levels changes. The aim of this article is to evaluate the long-term variations of hydrochemistry at the outlet of Paraíba do Sul River Basin, through the estimation of annual riverine fluxes and the identification of their controlling factors.

2. Materials and methods

2.1. Study area

The Paraíba do Sul River (PSR) watershed occupies an area of 57,300 km² in the states of São Paulo, Minas Gerais and Rio de Janeiro and is located between the latitudes of 20°26' and 23°38'S and the longitudes of 41°00' and 46°30'W. The total length of the river channel is approximately 1150 km (Fig. 1). The area within the PSR watershed is highly urbanized, with a total population of close to 5 million residents. Water from this river is used by 13 million people, and approximately 160 m³ s⁻¹ of water is diverted from the PSR watershed for use by the Rio de Janeiro metropolitan region. Presently, vegetation cover in the PSR watershed is approximately 70% pastures, 27% agriculture and reforestation areas, and only 3% of the original Atlantic Forest.

The Paraíba do Sul River Basin can be divided into three macro-sectors (MME-DNAEE, 1995): 1. An upper basin sector with an area of 7300 km², where the river descends from an altitude of around 1800 m to 600 m through narrow and embedded valleys carved out of crystalline rocks; 2. A middle basin sector with an area of 27,500 km² and average elevation of 510 m; 3. A lower basin sector with an area of 22,500 km² that is mainly occupied by a coastal plain with numerous riverine meanders and islands.

The lithology of the middle and upper basins encompasses pre-cambrian rocks, with predominant granitoid gneisses, migmatites, biotite-gneiss and biotite schists, and localized occurrences of quartzite, marble, granitic and alkaline intrusions. The lower coastal plain basin is composed of Tertiary and Quaternary terrains (DNPM, 1983).

The climate type, according to the Köppen classification system, ranges from Cwb (tropical of altitude with cool summer and rainy summer) to CFB (subtropical with cool summers) and Aw (hot and humid with summer rains). For the entire basin, the average annual maximum temperature is 26–28 °C with a minimum between 15 and 17 °C. Average rainfall is 2000 mm year⁻¹ in the upper and middle Paraíba sectors and 1200 mm year⁻¹ in the lower basin.

Within the entire PSR basin, 6000 farms and 8500 different types of industrial production are found. Major industrial production, especially for steel, chemicals, food and paper, is concentrated in the middle and upper basin sectors and in the sub-basins of the Pomba and Paraíba rivers, tributaries of the main PSR. Extensive farming is the main activity in the lower basin sector, especially irrigated sugar cane production. Forty-seven different reservoirs and hydroelectric dams of varying sizes also are found throughout the basin.

2.2. Sampling and analytical methods

Samples were collected fortnightly from January 1997 to December 2007, at the basin outlet, in the municipality of Campos dos Goytacazes (Fig. 1). A glass bottle was used to collect depth-integrated water samples from the center of the river channel. Water samples were transferred to plastic bottles, and stored on ice during transport to the lab. Instantaneous discharges were estimated using river velocity and cross-sectional area measurements (General Oceanic model 2030 current meter).

Electrical conductivity (EC) and pH were measured *in situ*, while in the laboratory suspended particulate matter (SPM) was measured by filtering well-mixed water samples (approximately 250 ml per sample) through a pre-weighed 0.45 µm polysulfone membrane filter, which was dried to constant weight at 85 °C and subsequently reweighed.

A sub-sample of water was appropriately preserved for dissolved oxygen determination (Golterman et al., 1978). Total alkalinity was determined by automatic titration (Mettler 21). Sub-samples were filtered (GF/F Whatman) and stored in plastic bottles and frozen (–20 °C) prior to analysis. Silica, ammonium and phosphate were determined spectrophotometrically; nitrate and nitrite were determined by flow injection analysis (FIA/ASIA/ISMATEC); chloride and sulfate were determined by ion chromatography (Merck- Hitachi L-6200); sodium, potassium, calcium and magnesium were determined by ICP-AES (Varian). Dissolved organic carbon (DOC) was determined with a TOC-5000 Shimadzu analyzer after filtration (GF/F membranes; Sharp et al., 1983). These membranes also were used for spectrophotometric determination of chlorophyll “a” by ethanol extraction (Nush and Palme, 1975). All analytical procedures were performed in triplicate with an analytical coefficient of variation below 10%. Analytical control was made by charge balance and a test was used for the ionic charge balance (meq L⁻¹) that, in general, had acceptable values.

Annual river loads were calculated by multiplying fortnightly instantaneous discharges by the associated dissolved and particulate concentrations, to estimate elemental loads for a sampling day. These calculated values were considered to be constants for the successive days until new measurements from the next sampling campaign. Daily loads were added together to obtain the annual river loads.

Hierarchical cluster analysis of chemical data was performed using Euclidean distance as measure of similarity, in the R statistical environment. Data columns were normalized to unit length and the median of the data was taken from cluster centers. The low frequency components of the discrete wavelet decomposed signals were considered as long term trends. Meyer wavelet was used as a basis and the calculations were also performed in R environment. The wavelet analysis approach was preferred over Fourier methods due to its intrinsic ability to deal with non-stationary signals, such as those originating from complex systems, like river catchments (Mallat, 1999; Milne et al., 2009; Pasquini and Depetris, 2007, 2010).

3. Results

The hydrochemical characteristics of the Paraíba do Sul River (PSR) during the sampling period are presented in Table 1. Piper diagrams were used for the chemical characterization of riverine water (Fig. 2) and based on these diagrams water in the PSR can be classified as largely Na–HCO₃⁻ with no distinctions resulting from discharge at different times of the year. Calcium, the second largest cation found in river water varied between 20% and 50% during the sampling period. HCO₃⁻ dominated the chemical composition of water in the PSR (as shown in the anion ternary diagram), with only a small contribution by chlorine. These hydrogeochemical characteristics (observed in the Piper diagrams) reflect a watershed lithology that is dominated by rocks of gneiss-granitic composition. Compared to other tropical watersheds, the chemistry of the PSR was similar to large rivers such as the Niger, Congo, Amazon and Orinoco (as shown in the Gibbs diagram; Fig. 3) plotting in the rock dominance domain, with TDS ranging from 32 to 132 mg L⁻¹ (with a mean of 60 mg L⁻¹), and Na/(Na + Ca) ratio between 0.3 and 1.0 (with a mean value of 0.6).

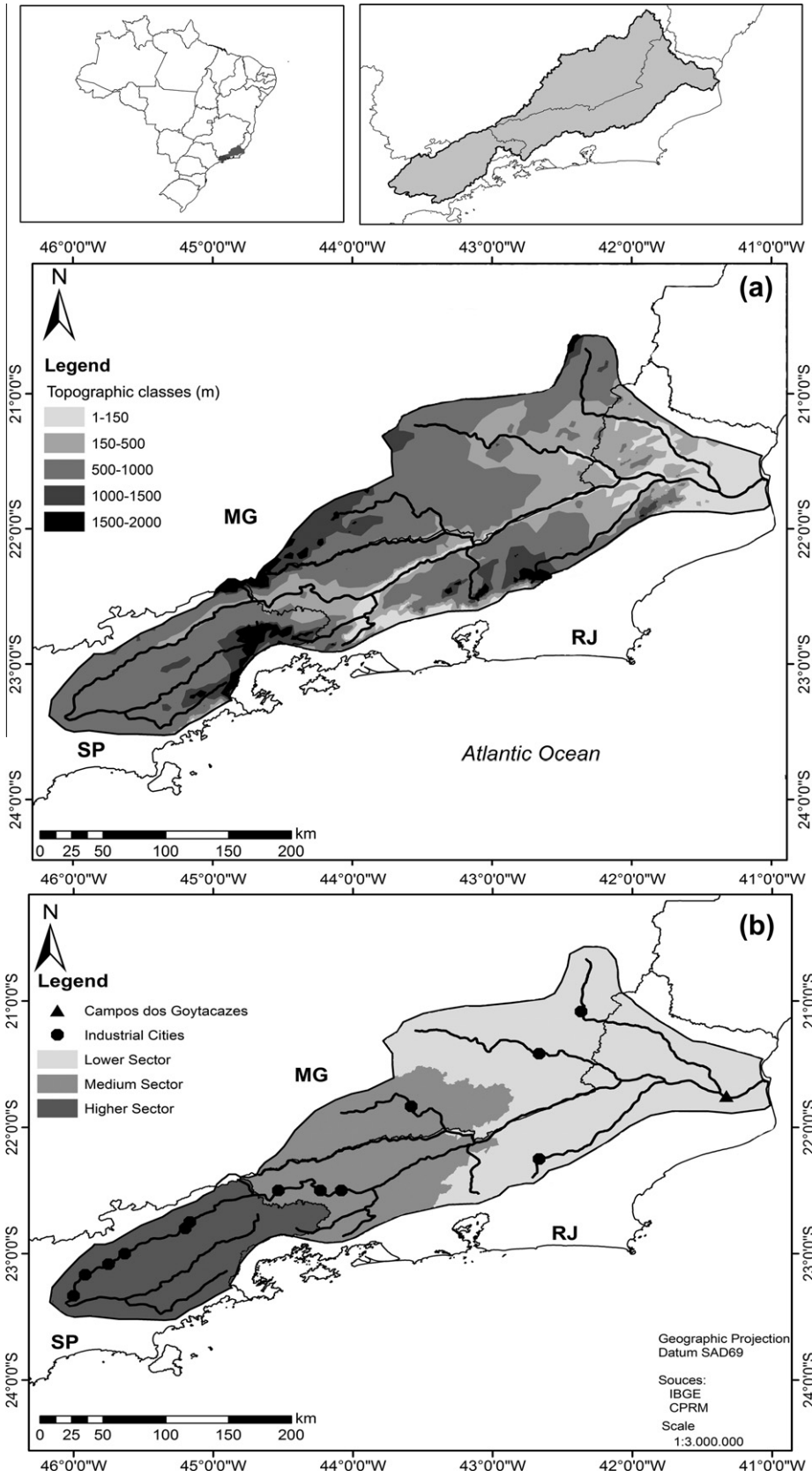


Fig. 1. Location and topographic map of the Paraíba do Sul River watershed (a). The main industrial cities along the basin sectors (b).

Table 1
Summary of the hydrochemical characteristics of Paraíba do Sul River in the basin outlet.

	Max	Min	Mean	Median	SD
Q ($\text{m}^3 \text{s}^{-1}$)	7500	115	758	542	728
pH	9.74	5.15	6.92	7.00	0.69
Cond ($\mu\text{S cm}^{-1}$)	147	33.8	66.1	65.4	11.9
DO (mg L^{-1})	11.2	4.6	7.7	7.7	1.0
DOC (mg L^{-1})	6.3	0.4	2.9	2.7	1.3
SPM (mg L^{-1})	230	1.0	37.3	22.7	39.3
DOC (mg L^{-1})	6.3	0.4	2.9	2.7	1.3
Chl-a ($\mu\text{g L}^{-1}$)	35.5	0.3	3.4	1.7	5.1
N- NO_2^- (μM)	2.47	0.05	0.47	0.29	0.44
N- NO_3^- (μM)	110	8.7	35	35	12
N- NH_4^+ (μM)	14	0.1	2.1	1.5	1.9
P- PO_4^- (μM)	3.19	0.08	0.68	0.62	0.4
SiO_2 (mg L^{-1})	13.5	2.0	6.2	6.2	1.5
HCO_3^- (mg L^{-1})	35.8	11.3	21.3	21.4	2.9
Cl^- (mg L^{-1})	43	1.2	5.0	4.5	3.7
SO_4^{2-} (mg L^{-1})	8.5	0.9	3.2	3.0	1.1
Na^+ (mg L^{-1})	14.8	1.0	5.5	5.5	1.6
Ca^{+2} (mg L^{-1})	7.0	1.7	3.7	3.7	0.8
K^+ (mg L^{-1})	3.7	0.4	2.0	2.0	0.6
Mg^{+2} (mg L^{-1})	2.5	0.4	1.4	1.4	0.3

3.1. Hydrochemical temporal variation in the Paraíba do Sul River Basin outlet

The time series of discharge and measured parameters are presented in Figs. 4–7, and the hierarchical clustering analysis of the data set is presented in Fig. 8.

Notwithstanding the large spatial variation of precipitation volume over the whole basin, the PSR discharge shows a remarkable regularity along a year (high discharge from November to February and low discharge from May to October; Fig. 4). Long term assessment of discharge revealed that the period between 1998 and 2002 was affected by negative precipitation anomalies that resulted in less pronounced duration and magnitude of high flow periods and increased duration of dry periods, culminating in the lowest instantaneous discharge values measured during our study in October 2002 ($115 \text{ m}^3 \text{ s}^{-1}$). By arbitrarily using the instantaneous discharge median value ($540 \text{ m}^3 \text{ s}^{-1}$) as a threshold between high and low discharge periods, we can see that this extended dry period was longer than 3 months in several studied years, though a positive precipitation anomaly prevailed in 1997, 2003, 2004, 2005 and 2007. Analysis of long-term variation in SPM showed a remarkable response (Fig. 4), which readily responded to every variation in instantaneous discharge, so that its maximum and minimum concentrations along the study period were associated with corresponding discharge values.

Seasonal variation of dissolved oxygen was characterized by higher concentrations during low discharge periods, which also was associated with maximum chlorophyll “a” concentrations. However, no clear trends in long-term variation of dissolved oxygen were found, except for several anomalous fluctuations in concentrations that were observed at the end of 2005 and the beginning of 2006 (Fig. 4). Chlorophyll “a” annual variation was characterized by several high values during low discharge periods, with the maximum each year found between August and October (Fig. 4). Long-term patterns of chlorophyll “a” showed no relationships with annual precipitation anomalies during the studied period.

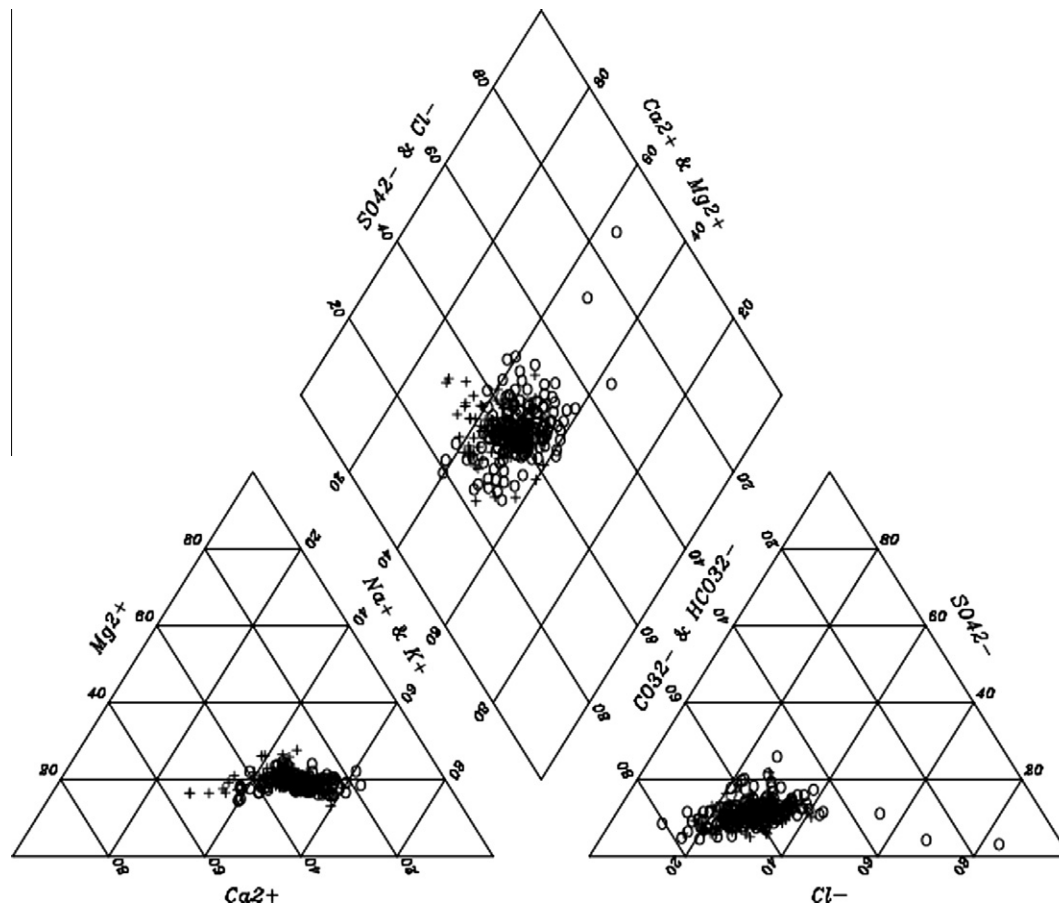


Fig. 2. Piper diagram showing the composition of for major ions in the PSR outlet. Plus signals refer to the high discharge periods and open circles to low discharge periods.

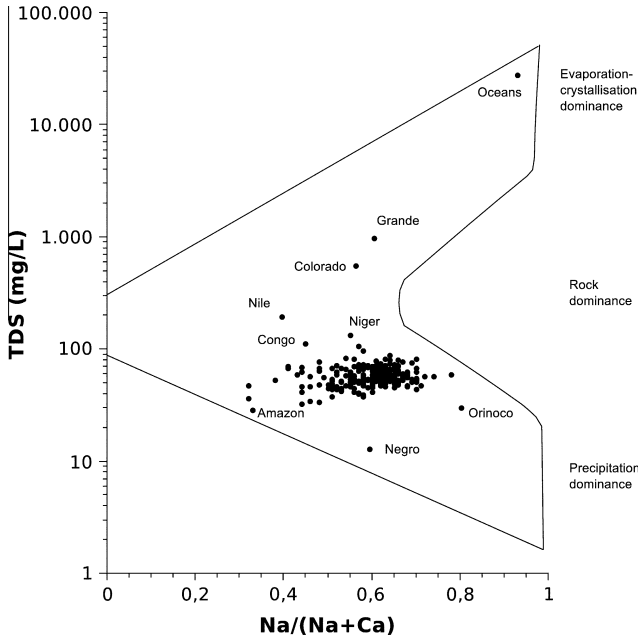


Fig. 3. Gibbs diagram for the PSR data set and principal rivers of the world (Gibbs, 1970).

Electrical conductivity (EC; Fig. 5), an indicator of major ions concentrations in riverine water, was found to have a similar pattern as Na^+ , K^+ , Mg^{2+} , and to a lesser extent, Ca^{2+} , all of which constituted a common cluster in the cluster analysis (Fig. 8). Their seasonal variations were characterized by increased concentra-

tions during low discharge periods and higher concentrations after only a few weeks during the start of the flood periods. However, these increased concentrations were not long lasting, as they sharply decreased during peak discharge. Analysis of long-term variation of EC and major cations revealed that during years with a negative precipitation anomaly (e.g. 1999 and 2006), the maximum concentrations observed during the beginning of high discharge period were enhanced.

Total alkalinity also was found to have a similar seasonal pattern as these cations, with increased concentrations during the low and rising discharge stages, followed by a sharp decrease in concentrations during high discharge periods. However, in several years (e.g. 2001, 2004 and 2007) lower concentrations were still observed during high discharge periods (Fig. 4). Long-term variation in total alkalinity showed no trend at all. No seasonal variation was found for pH (Fig. 4), though long-term variation revealed an acidification process that started in 2001 and extended until 2006. However, during 2007, the pH of river water returned to its normal pH range. Both total alkalinity and pH also were included in the same cluster of cations in the cluster analysis (Fig. 8).

Dissolved inorganic nitrogen (DIN) compounds (N-NH_4^+ , N-NO_2^- and N-NO_3^-) and their seasonal variation revealed two different behaviors, as ammonium and nitrite were positively associated with instantaneous discharge, while nitrate showed an inverse pattern (Fig. 6). Maximum DIN concentrations were found during the initial runoff events each year and just before maximum annual discharge. Ammonium and nitrite concentrations were consistently elevated during high flow conditions, whereas nitrate concentrations appeared to be affected by dilution. Nitrate was by far the most abundant form of DIN (92% of all DIN), followed by ammonium (6%) and nitrite (<2%). Analysis of inter-annual variation revealed a complex pattern for ammonium and nitrite, with

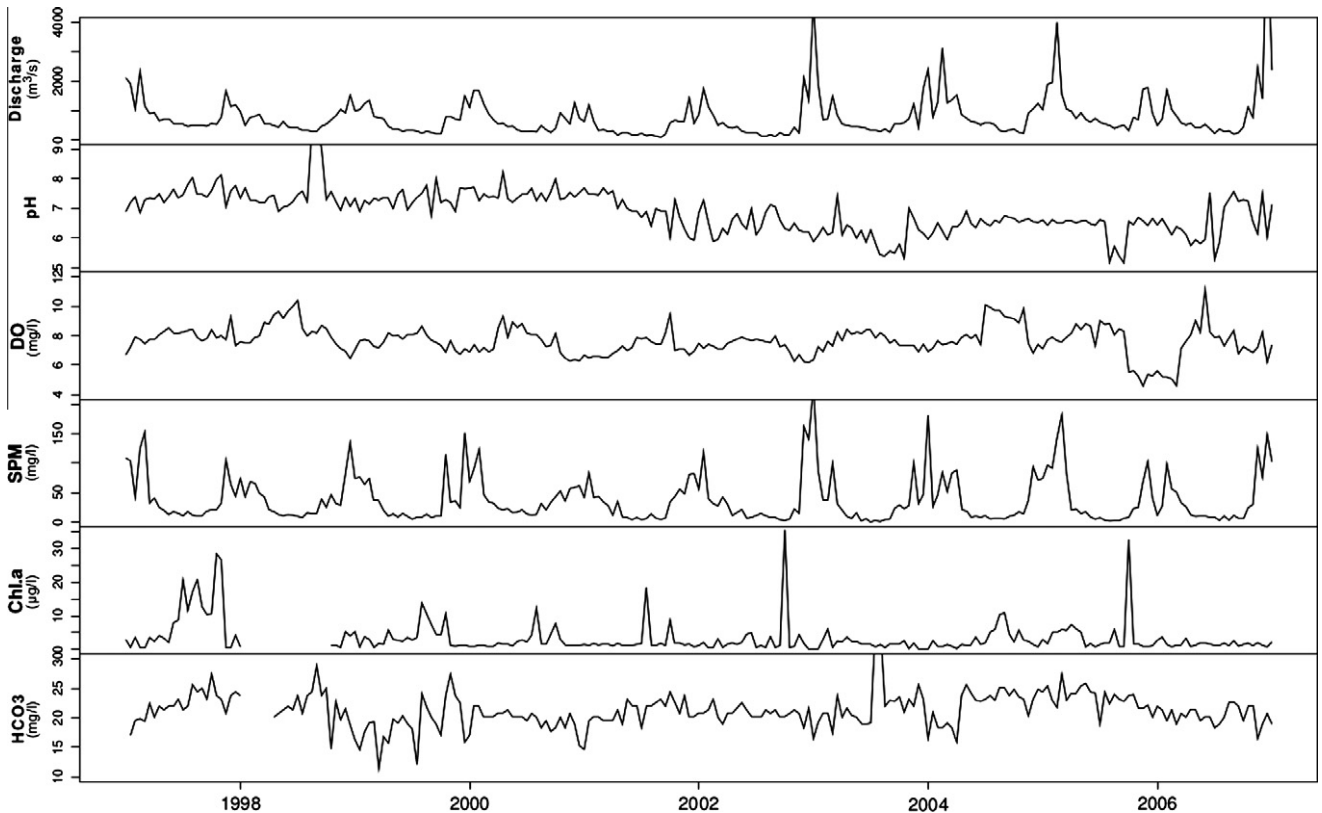


Fig. 4. Temporal variation of parameters measured in the PSR outlet: instantaneous discharge, pH, dissolved oxygen, suspended particular matter, total alkalinity, and chlorophyll “a”.

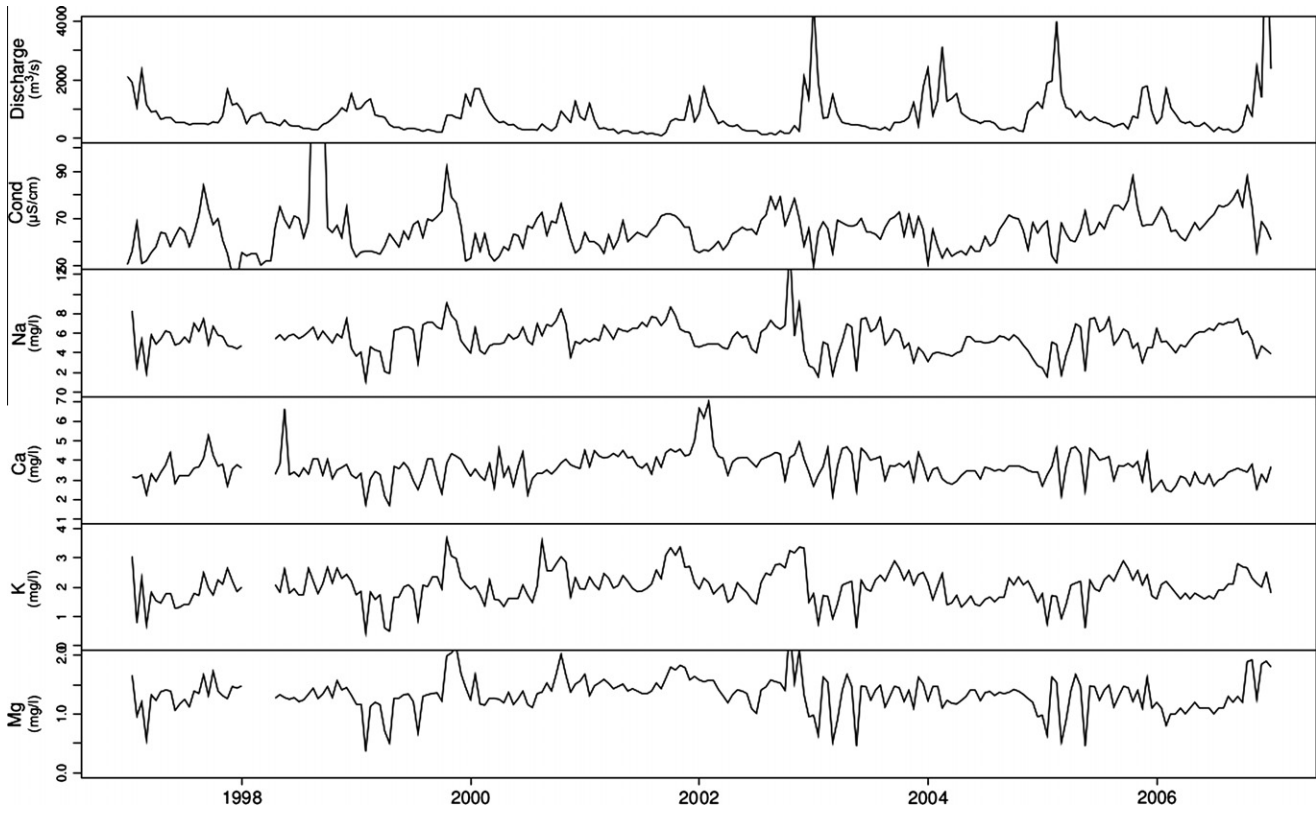


Fig. 5. Temporal variation of parameters measured in the PSR outlet: instantaneous discharge, electrical conductivity, and cations.

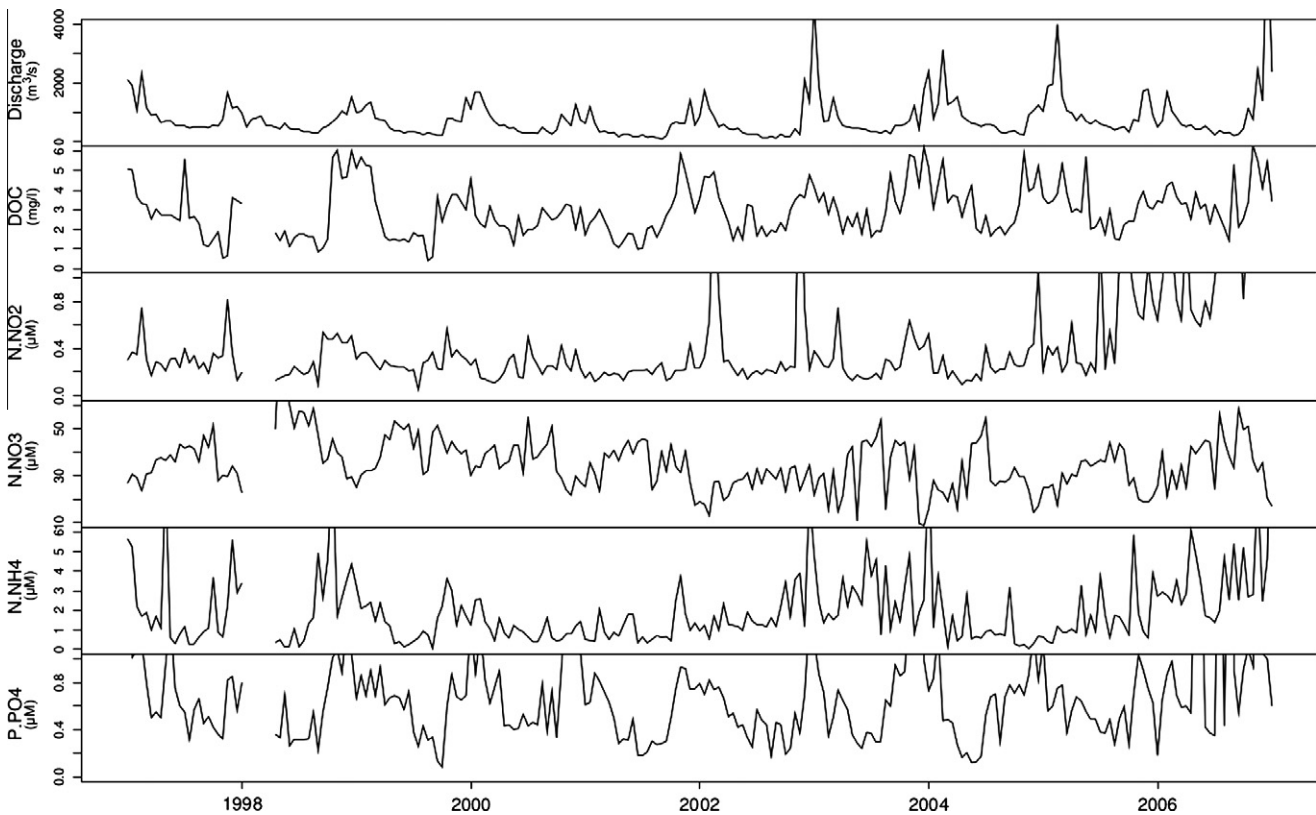


Fig. 6. Temporal variation of parameters measured in the PSR outlet: instantaneous discharge, DOC, nitrogen, and phosphorus compounds.

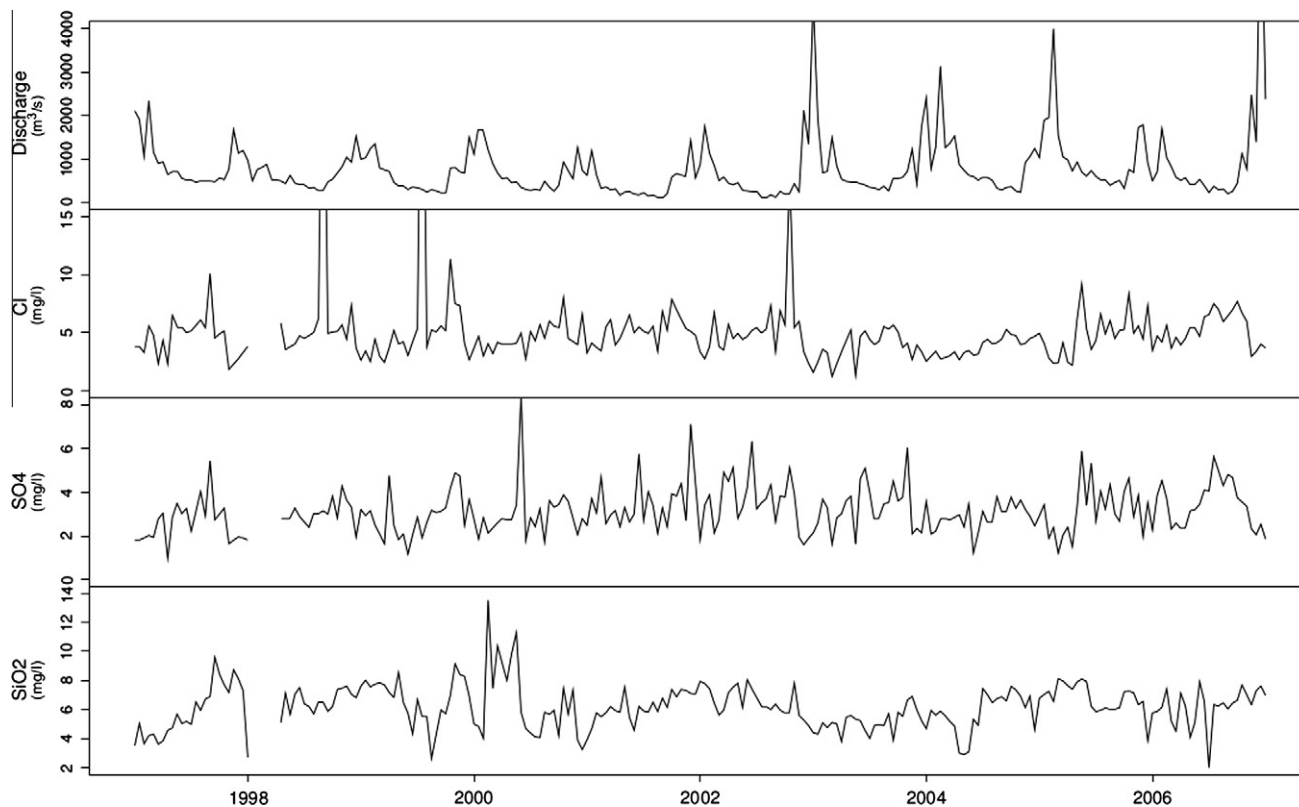


Fig. 7. Temporal variation of parameters measured in the PSR outlet: instantaneous discharge, chloride, sulfate, and dissolved silica.

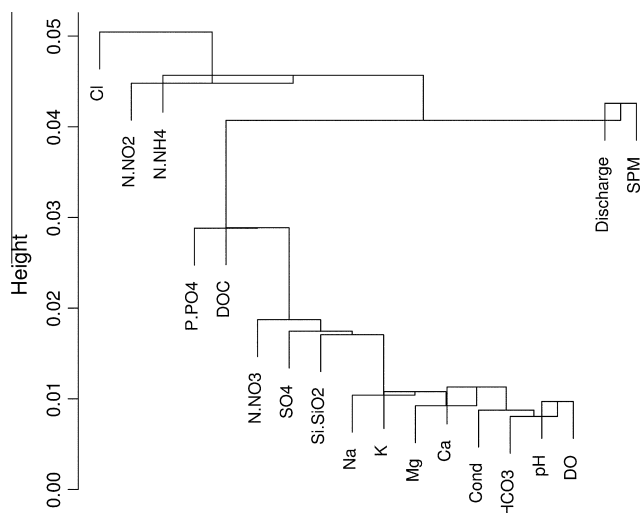


Fig. 8. Hierarchical cluster analysis of the data set.

anomalous isolated peaks and long periods when concentrations increased dramatically (e.g. between 2005 and 2007). However, nitrate tended to be lower during years with high annual discharges. This contrasting behavior also was visible in the cluster analysis, with nitrite and ammonium grouped apart from nitrate (Fig. 8).

DOC and phosphate also were found to be positively associated with instantaneous discharge and were grouped together in the cluster analyses (Fig. 8). DOC generally showed a sharp increase at the start of the rising water stage, followed by a decrease in concentrations with decreasing discharge (Fig. 6). Long-term variation in DOC was found to include an increase in minimum values during years of high discharge, as observed between 2003 and 2005. Be-

sides the remarkable association of phosphate with instantaneous discharge at the annual scale, at the long-term scale several phosphate concentration peaks occurred during 2006 and 2007.

No seasonal variation was found for dissolved silica (SiO_2), with lower concentrations occurring in both high (e.g., 2000 and 2004) and low (e.g., 1999 and 2006) flow periods (Fig. 7). This lack of correlation indicated that SiO_2 concentrations were not solely a function of discharge. Long-term variations also did not indicate any particular patterns, though silica is grouped with nitrate and sulfate in cluster analysis.

Despite no significant correlation in long-term variation, chlorine and sulfate showed some similarities, as they tended to have low concentrations during high discharge periods (Fig. 7). However, no general patterns with discharge were identified, with only erratic concentrations peaks appearing to be independent of year and discharge. In the cluster analysis both species are clearly separated, with chlorine more closely associated with ammonium and nitrite in an isolated group.

3.2. Long-term fluxes and export of SPM and dissolved elements in the Paraíba do Sul River Basin

Table 2 illustrates the annual export fluxes for the analyzed parameters. Inter-annual variation was found to be very large, with total dissolved solid fluxes varying between 14.9 (2001) and 35.3 (2005) $\text{ton km}^{-2} \text{year}^{-1}$. Relative amplitude (i.e., the ratio between maximum and minimum annual flux) was high for nitrite and ammonium (by a factor of 10 or more) and SPM (by a factor of approximately 4), whereas the others chemical elements were between 2 and 3. Nitrite and ammonium concentrations strongly increased from 2005 to 2007, which helps to explain the anomalous long-term variation of their annual fluxes.

As a consequence of its direct association with instantaneous discharge, almost 80% of annual flow of SPM occurs during high

Table 2
Export fluxes of dissolved and particulate materials in the Paraíba do Sul River Basin outlet; Q (runoff) in mm y^{-1} ; N-NO_3^- , P-PO_4^{3-} , N-NO_2^- , N-NH_4^+ , in $\text{kg km}^{-2} \text{y}^{-1}$; others in $\text{ton km}^{-2} \text{y}^{-1}$.

	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Na^+	2.3	1.4	1.7	2.1	1.5	1.5	1.7	2.1	2.6	2.0	2.4
Ca^{2+}	1.5	0.9	1.1	1.4	1.0	1.3	1.5	1.7	2.2	1.1	1.7
K^+	0.88	0.53	0.65	0.81	0.59	0.67	0.80	0.97	1.05	0.78	1.09
Mg^{2+}	0.56	0.34	0.43	0.55	0.37	0.42	0.50	0.65	0.72	0.48	0.87
SiO_2	6.1	3.4	5.3	5.6	3.0	4.1	4.9	5.9	8.6	5.1	7.1
HCO_3^-	10.2	5.4	6.5	7.7	4.8	5.9	9.3	10.4	13.7	7.7	10.0
SO_4^{2-}	1.6	0.7	1.0	1.1	1.4	0.9	1.3	1.4	1.7	1.3	1.3
Cl^-	2.0	1.4	1.8	1.7	1.3	1.3	1.3	1.7	2.5	1.9	2.1
DOC	1.7	0.8	1.3	1.0	0.7	1.0	1.7	2.0	2.0	1.5	1.7
SPM	31.8	13.1	18.4	24.4	11.1	18.5	42.6	31.5	42.8	19.7	46.5
N-NO_3^-	242	158	182	195	113	96	191	181	215	188	230
N-NH_4^+	21.9	8.9	10.3	7.3	3.9	5.7	21.3	16.0	9.9	19.7	35.3
N-NO_2^-	2.9	1.0	1.6	1.4	0.7	2.2	2.1	2.0	4.4	6.5	10.5
P-PO_4^{3-}	14.4	5.2	7.6	10.7	4.9	5.6	12.5	8.7	12.1	12.9	12.9
Q	534	335	344	393	238	286	456	507	583	385	486

discharge periods, from November to February each year. Therefore, long-term variations in the volume of precipitation induced sharp responses in SPM annual fluxes. Other elements like cations, which are affected by dilution resulting from increased water runoff, were less affected by annual precipitation anomalies.

However, in 1998 the flux of most dissolved elements and SPM was lowest, except cations and sulfate that were found to have the lowest flux level in 2001. Maximum fluxes measured during the studied period were obtained in 2005 for anions, silica, Na^+ , K^+ and SPM, and in 2007 for nitrite, ammonium, Ca^{2+} and Mg^{2+} .

4. Discussion

The riverine transport of dissolved and particulate materials is generally related to a large number of interactions involving land use, climatic, hydrological, physical, chemical and biogeochemical aspects. Seasonal patterns observed in the PSR basin outlet were related to hydrological responses such as the distribution and quantity of rainfall and could be analyzed according to the three component hydrological approach described by Tardy et al. (2004): 1. Quick flow within the upper portion of soils; 2. Slow runoff flowing within deeper soil horizons or on large flooded plains in the lower basin; and 3. Groundwater discharge located below the water table and delayed in time. Each pathway exerts a large influence on the transport of solutes and SPM to the river channel.

4.1. Factors controlling the seasonal variation of hydrochemistry in the Paraíba do Sul River

The main sources of cations for riverine waters are from soils and rocks weathering in which cations leach through hydrological flowpaths described above. The relative contribution of each flowpath varies depending on precipitation and discharge conditions. As seen in Fig. 5, during low discharge periods cations and EC had the highest values, which were associated with a progressively higher contribution of groundwater input as the low water period proceeded. Concentrations of cations in riverine water during this stage were close to the expected hydrochemical characteristics of the groundwater reservoir. However, unlike the expected dilution effect induced by increasing instantaneous discharge, the abundance of dissolved cations and the measured EC of riverine water continued to increase at the beginning of each rising water period, before decreasing in concentration close to peak water flow. According to Tardy et al. (2004) this “lag effect” between cations and EC and increasing discharge is related to the quick runoff that

appears as soon as the discharge starts to increase at the beginning of the wet season and leads to the high flux of several solutes and SPM from soils to riverine water.

Chloride and sulfate also generally followed similar patterns as cations, especially in 1999, 2003 and 2005 (Fig. 7). Their main natural sources in the PSR basin include atmospheric inputs and weathering of localized sedimentary rocks, especially in the middle basin sector. These elements also exhibited high standard deviation, with several isolated peaks of high concentrations during the study period, generally in the low water periods of each year. In particular, these high standard deviations were found for chloride concentrations and were likely associated with a complex suite of anthropogenic inputs, such as disposal of untreated sewage, fertilizers and industrial effluents.

In contrast, the limited responses of total alkalinity and pH to seasonal discharge reflect the suite of inter-linked processes that are more difficult to quantify (Fig. 4). The lowest total alkalinity values were always associated with high discharge periods, as observed in 1999, 2001, 2004 and 2007, and likely reflect the same sources and flowpaths of cations described above. Other control factors of total alkalinity and pH were associated with in-channel biogeochemical processes, such as photosynthesis, respiration, decomposition, and typical hyporheic anaerobic processes (i.e., organic matter mineralization, denitrification and ammonification) that are enhanced by areas of extensive sedimentation in the PSR basin, particularly in the lower sector of the basin (Pezzine and Ovalle, 2009).

Trends in dissolved silica, as described by lack of correlation with river discharge, indicate that this element was primarily controlled by chemical weathering of silicates (Fig. 7). Terrestrial plants also take up considerable quantities of silica from soil solutions, and return it to soil from litterfall as biogenic silica (Derry et al., 2005). After being flushed from soils the dissolved silica enters the river channel, where diatoms, a major component of riverine phytoplankton, absorb significant amounts of silica to build their external structures (called “frustules”). The growth of diatoms in the river channel during low flow conditions also were likely stimulated by eutrophication, as suggested by high chlorophyll “a” values, resulting in a large scatter of silica concentrations during the entire period of low flow, even with maximum yields of groundwater during this period.

Seasonal patterns of dissolved inorganic nitrogen (DIN) – nitrate, ammonium, and nitrite – likely were affected by microbial activity and oxidation processes of organic matter in catchment soils, which comprise a suite of soluble organic and inorganic compounds that accumulate in the soil profile during the dry season (Fig. 6), leading to available ammonium and organic nitrogen.

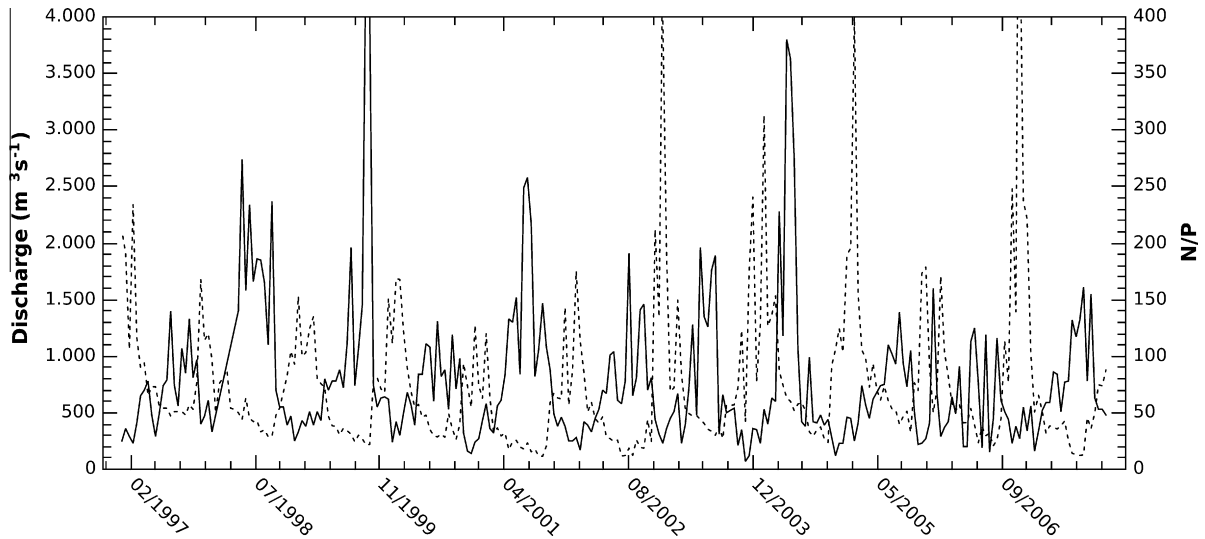


Fig. 9. Temporal variation of instantaneous discharge (dashed line) and N/P_a (solid) in the PSR outlet.

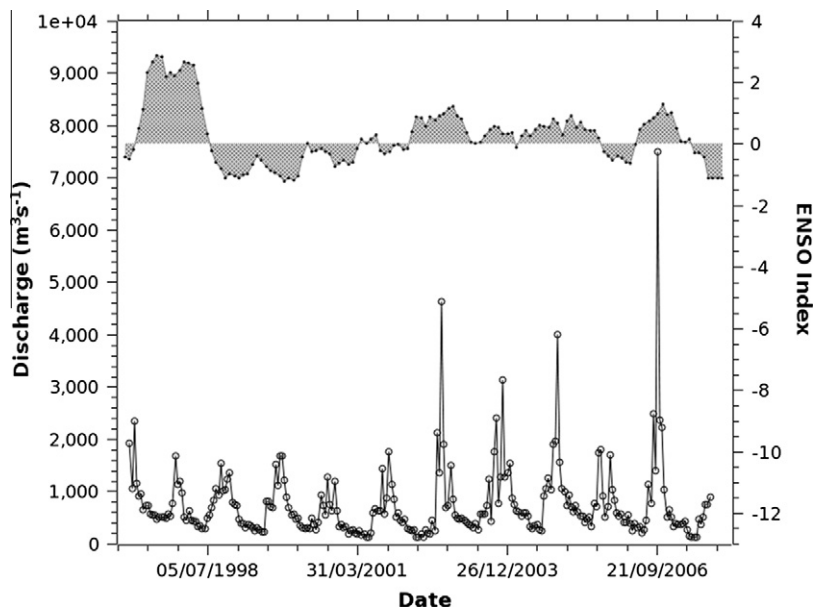


Fig. 10. Relation between instantaneous discharge in PSR and ENSO Index (EI); negative values of the EI represent the cold ENSO phase, La Niña, while positive EI values represent the warm ENSO phase, El Niño; NOAA, 2011. http://www.cdc.noaa.gov/people/klaus.wolter/MEI/#ref_wt1; accessed 07/02/2012.

Nitrogen retention in soils results primarily from plant uptake and microbial immobilization, while geochemical processes, such as ammonium adsorption, generally play a less important role. In N-enriched systems, as agricultural areas, there is less competition for available N between microorganisms and plants, and the total input from fertilizers and internal mineralization may exceed biological requirements, allowing nitrification to occur. Once formed, nitrate that is not removed from denitrification in anoxic zones and biological uptake moves quickly in the soil into groundwater and the river channel (Van Miegroet, 1994). Consequently nitrogen leaching in soils is mostly in the form of nitrate.

Following the first rainfall of rainy season, a large flux of solutes is released from the watershed into river water, with surface and sub-surface flows promoting rapid leaching of ammonium, and, to a lesser extent, nitrite, thereby minimizing the residence time of nitrogen in the soil to undergo denitrification and leading to elevated concentrations of nitrogen compounds in riverine water with increased discharge (Fig. 6). As noted by Figueiredo et al. (2011) ni-

trate concentrations clearly decreased during increased periods of discharge, as surface and sub-surface flows increased their contribution to river channel. This result indicates that most of the nitrate entering the PSR during low flow conditions was likely from diffuse groundwater discharge. Moreover, point sources along the watershed also provided a significant amount of the DIN from treated and untreated wastewater that was diluted during high discharge periods.

In well-oxygenated riverine water, ammonium and nitrite undergo nitrification, while nitrate can be denitrified in the hyporheic zone, due to advection of water through the water/sediment interface and anaerobic condition of the fine sandy bottom sediments. During low flow conditions large sedimentation areas emerged in the river channel, especially in the lower basin sector of PSR. Porewater in those sediments were anoxic only a few centimeters below the surface ($E_h -120$ mV) with high total alkalinity (up to 115 mg L^{-1}), and dominance of reduced forms of DIN ($\text{NO}_3/\text{NH}_4 + -\text{NO}_2 < 0,1$) compared to riverine waters (up to 19), revealing a

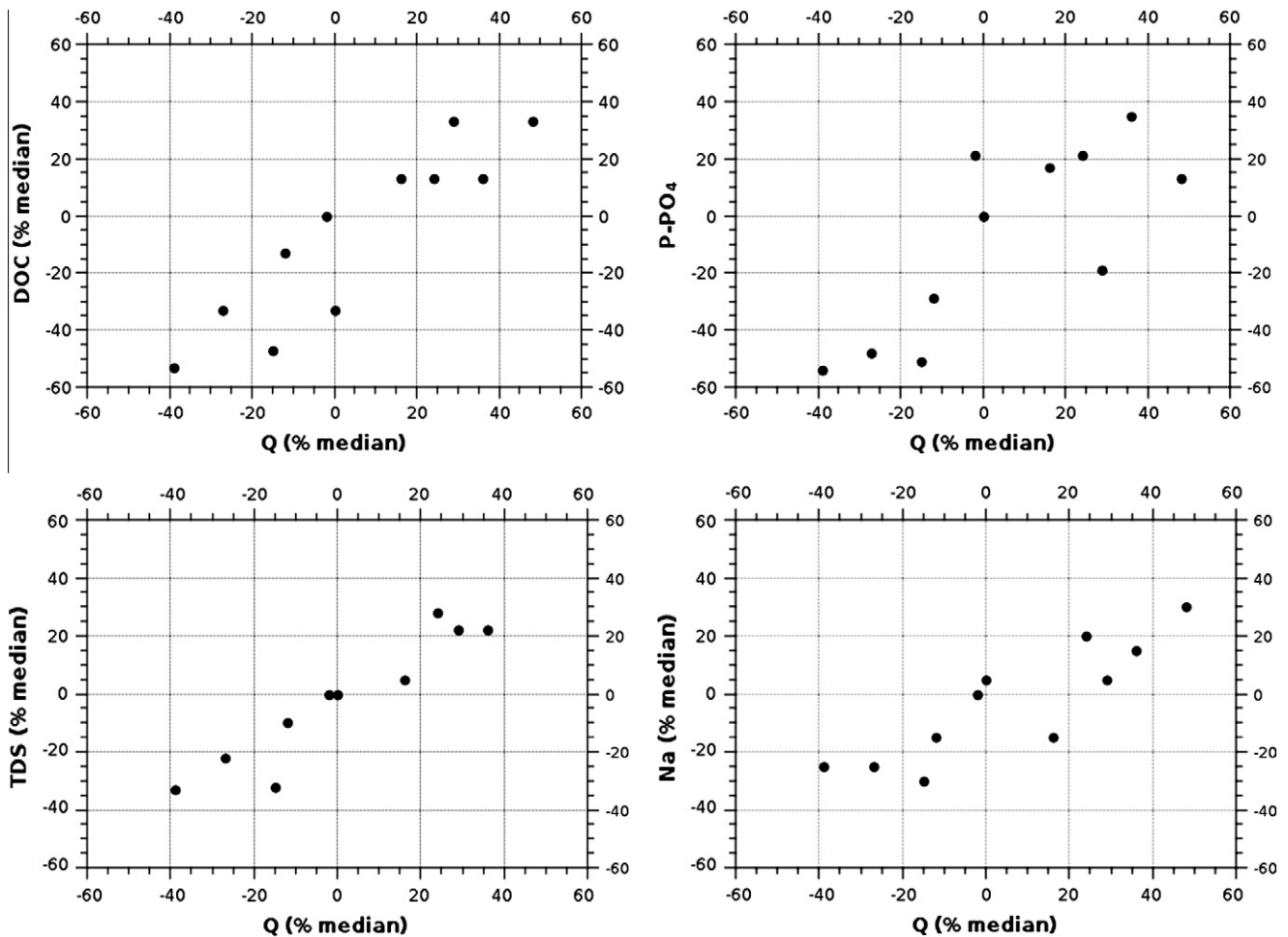


Fig. 11. Variation of annual fluxes related to median values (values in %); negative values are related to La Niña events and positive to El Niño events.

“hyporheic-like” biogeochemical environment with heterotrophic microbial activity that was characteristic of a typical denitrification site (Pezzine and Ovalle, 2009). In the beginning of flood period, bottom sediments are partially resuspended and porewater advection achieve its maximum, thus contributing to the onset of peak levels of ammonium during the water rising stage.

The linkage between annual variation of DOC and river flow is commonly described in the literature (Clair et al., 2008). In this study, during low flow conditions, DOC concentrations were sustained by diffuse contribution from groundwater. During the rising limb of the hydrograph there was a change in the relative contribution of hydrological components, with two flowpaths other than groundwater emerging – a quick flow that moved within the upper portion of soils and a slow runoff that flowed within the deeper horizons of soils. These flowpaths promoted a sharp increase in DOC concentrations in riverine waters, with maximum annual values occurring just before peak river discharge (Fig. 6). Such transient flowpaths promoted leaching and flushing of organic material not only from agricultural and natural soils, but also from floodplain and fluvial islands that accumulated organic debris from aquatic macrophytes and benthic algae.

Seasonal variation in phosphate concentrations in river water, a major by-product of soil organic matter decomposition, was associated with multiple biogeochemical processes that occurred in upper soils, as well as in-channel processes, including biological assimilation and sorption to sediments (House, 2003). The delivery of diffuse P loads, including from agricultural areas, is largely due to the strong affinity of phosphorus for particles, and is generally

associated with surface runoff. The P load from point sources, like untreated sewage, is highly bioavailable and is delivered along with readily degradable organic materials. Once in the river, soluble phosphorus undergoes numerous transformations, involving particles, sediments, the water column and biota.

During low discharge conditions, phosphate delivery by diffuse groundwater inputs to riverine waters is probably overwhelmed by untreated sewage contribution. However, the net uptake by sediments through sorption/precipitation processes and the biological uptake by phytoplankton (and in a less extend benthic algae) rapidly depletes available phosphate in riverine waters (Fig. 6). As the rainy season begins, P-enriched porewater flushed from both remobilization of bottom sediments and surface and sub-surface runoff from agricultural and natural terrains results in a sharp increase of dissolved phosphate that remains during the high water period, though with less intensity than other water chemical elements.

The high concentration of nitrate leads to a mean N:P ratio (74:1) higher than what could be attributed to phytoplankton. The seasonality dynamic is notable, with lower values observed during high discharge periods (Fig. 9), indicating that there is an excess of available nitrogen relative to phosphorous for primary production. Despite this limitation, primary production in riverine waters is high, with chlorophyll “a” levels reaching up to $35 \mu\text{g L}^{-1}$ (Fig. 4), especially during low discharge periods. Even with high nutrient input and the high dilution and flushing by river flow, the Paraíba do Sul estuary is classified as mesotrophic, with low susceptibility to eutrophication (Cotovicz et al., 2012).

4.2. Factors controlling the long-term variation of hydrochemistry in the Paraíba do Sul Basin outlet

After establishing the role of hydrological mechanisms in seasonal material inputs to fluvial channel, it is necessary to evaluate the response of these systems across years, especially years with precipitation anomalies (Eimers et al., 2008). Precipitation anomalies in South America are strongly affected by large-scale climatic events such as ENSO (El Niño/Southern Oscillation), the most important coupled ocean–atmosphere phenomenon to cause global climate variability on inter-annual time scales. The influence of this inter-annual oscillation on discharge variability (Pasquini and Depetris, 2007, 2010) and also in sediment transport and fish biology (Smolders et al., 2002) has been observed in several South American large rivers.

In this study, variation in long-term discharge measurements was found to be related to both positive and negative precipitation anomalies associated with ENSO phenomena (Fig. 10). For example, from 1998 to 2002 the PSR watershed was under the influence of La Niña, with predominant negative precipitation anomalies. As described earlier, the duration and intensity of the high flow period of the PSR was decreased during this time compared to other years. The cumulative effect of a sequence of years with negative precipitation anomalies induced a critical situation during the low flow period in 2002, when large sedimentation areas emerged in the lower reaches resulting in fragmentation of the river channel into a mosaic of interconnected eutrophic ponds with lentic character-

istics, ideal condition that gave rise to a bloom of cyano-bacteria (chlorophyll “a” and *Anabaena cf spiralis* density up to $36 \mu\text{g L}^{-1}$ and $21,000 \text{ ind mL}^{-1}$, respectively;) that compromised the water supply of almost 200,000 inhabitants of the municipality of Campos dos Goytacazes for several days. This bloom was the most intense one seen during the studied period, though it was not an episodic event. Chlorophyll “a” peaks have generally occurred during low discharge periods, notably during La Niña years (Fig. 4), but this was the first time that harmful phytoplankton species prevailed. For the years of 2003, 2004, 2005 and 2007 a positive precipitation anomaly was prevalent as a result of an El Niño event of low-to-medium intensity. During the same period, a great flood occurred in January 2007 with instantaneous discharge rising to approximately $7500 \text{ m}^3 \text{ s}^{-1}$. This long-term coupling between fluvial discharge and atmospheric phenomena reinforces the necessity of determining fluctuations in riverine transport and their potential linkages with precipitation anomalies (Eimers et al., 2008).

As a result of these findings, we feel confident in describing the long-term variation of elemental fluxes of the PSR as strongly influenced by ENSO (Table 2). Using median fluxes values as a reference, we noted that cations, which are related to groundwater discharge, were less affected by precipitation anomalies, with inter annual variation around 30% (Fig. 11). On the other hand, compounds related to surface/sub-surface transient flowpaths that are activated during the wet season, such as nutrients and DOC, were found to be more variable (up to 60%), mainly during La

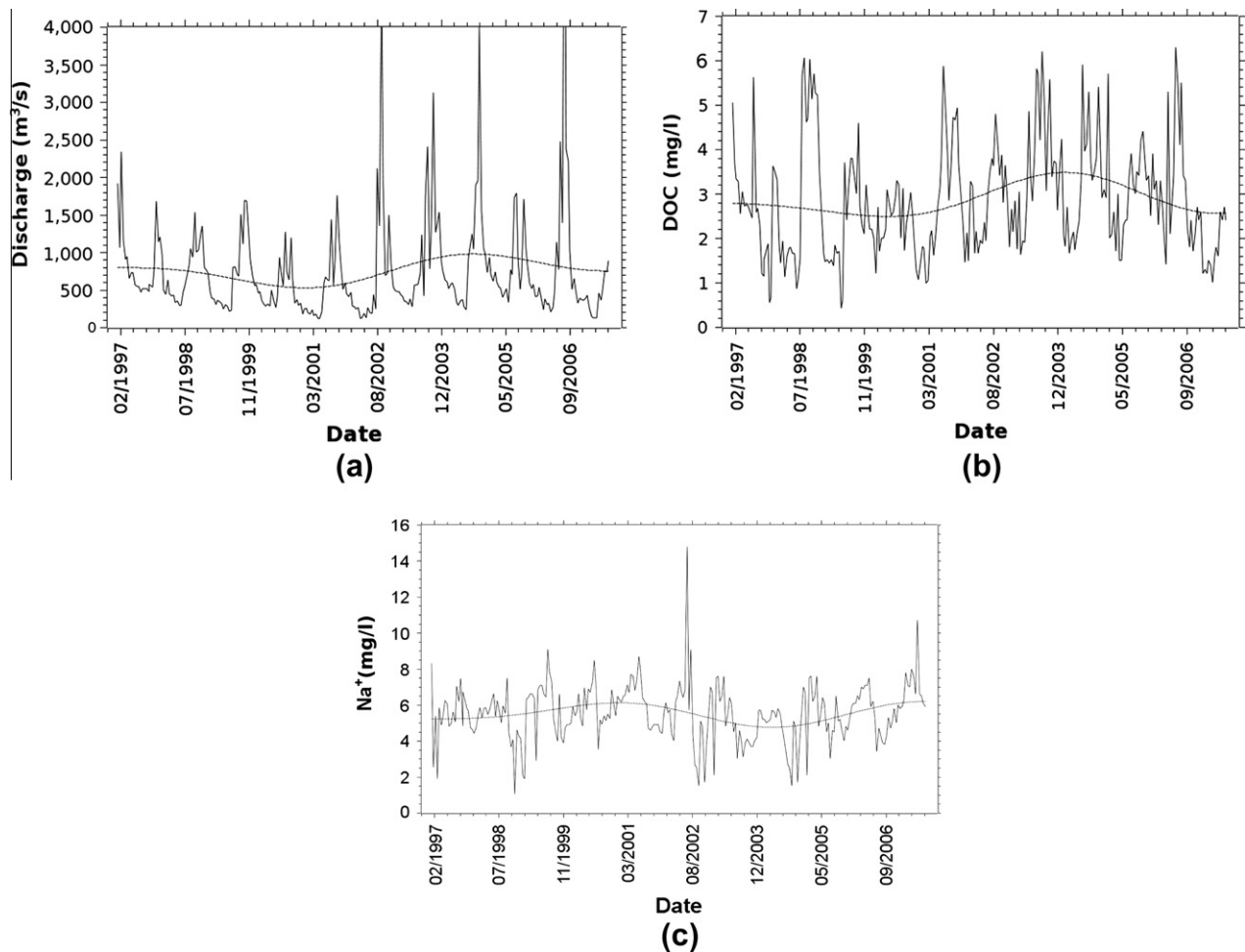


Fig. 12. Time series of discharge (a) and interannual trends of DOC (b) and Na (c) obtained from wavelet analysis using the Meyer scaling function.

Niña years, when negative precipitation anomalies drastically reduced the effectiveness of transport capacity of these hydrological mechanisms.

In this context, one might consider that the transport of dissolved species is affected by not only precipitations anomalies, but also by their mobilization from soils and by in-channel transformations rates. In fact, microbial degradation of soil organic matter and nutrient release rates in tropical regions are directly dependent on water availability, increasing with high rainfall (Austin and Vitousek, 2000). In-channel processes, like nitrification/denitrification in hyporheic zones, also are affected by moisture conditions. Changes in redox conditions in sedimentation areas are associated with fluctuations in water-saturated zones, affecting retention/release and reduction/oxidation processes. The consequences of cumulative years of positive or negative precipitation anomalies on the rates of these processes are complex to evaluate, with the dissolved annual fluxes measured in PSR result from a suite of inter-connected biogeochemical reactions.

4.3. Determination of long-term hydrochemical trends in the Paraíba do Sul Basin outlet by wavelet analysis

As discussed above, variations in river flow and subsequent variations in hydrological flowpaths exerted a strong control on water chemistry and mass fluxes, principally those which exhibit strong hydrological controls including SPM, DOC, ammonium, and nitrite. As a result, there is need to understand the factors that regulate changes in mass fluxes at inter-annual scales. In this context, we used wavelet decomposition (with an approximation at level 7) to analyze time series data at different frequency scales and cluster analysis to identify the representative parameters of the main hydrological mechanisms responsible for the river runoff dynamics. DOC was chosen to represent both surface and subsurface flowpaths (Fig. 12b) and Na was chosen to indicate diffuse groundwater contributions (Fig. 12c) to the riverine water.

The wavelet analysis indicated general patterns associated with precipitation anomalies induced by ENSO dynamics (Cavalcanti et al., 2005), as described above, though different responses were found for this climatic event. As DOC represents a transient hydrological flowpaths, it is natural that the pattern of its concentrations tended to increase during periods of positive precipitation anomalies associated with the El Niño phase of ENSO and to decrease during periods of negative precipitation anomalies (associated with the La Niña phase of ENSO; Fig. 12b). This pattern is nearly identical to the patterns exhibited by discharge (Fig. 12a), with only a small advance in phase. Consequently, the clustering algorithm assigned DOC (as well as PO_4^{3-}) and discharge (along with SPM) to different clusters, although they may represent the same hydrological mechanism.

In contrast, Na which represents a continuous and diffuse input of groundwater, showed an opposite pattern to the one shown by DOC, as higher relative contributions of groundwater to river runoff were found during La Niña years (Fig. 12b).

5. Conclusions

The seasonal pattern of instantaneous discharge at the outlet of the PSR basin has shown a remarkable covariance with rainy and dry periods. Consequently, we found that dissolved loads in the PSR exhibited consistent and yearly temporal variation during the study period, with significant inputs coming from groundwater, as identified from hydrochemical measurements. In contrast to the expected dilution effect during rising discharge periods, the abundance of dissolved cations and electrical conductivity of riverine water continued to increase until after peak river dis-

charge. This pattern was likely associated with transient flowpaths emerging at the beginning of the rainy season that induced a lag effect between peak flow and minimum concentrations of these dissolved compounds in riverine waters. Dissolved silica, as well as cations and total alkalinity, originates from chemical weathering of the dominant granitic composition rocks of the watershed. Once flushed from soils to the river channel, dissolved silica concentrations are strongly affected by diatoms that absorb significant amounts, mainly during low discharge periods, when highest amounts of chlorophyll "a" occur. Therefore there was no direct correlation between dissolved silica content and discharge.

Seasonal patterns of DOC, phosphate and the reduced forms of dissolved inorganic nitrogen have a strong linkage to transient hydrological flowpaths, and we found that their concentrations reached their maximum values at the very beginning of the rising water phase. The main source of these compounds is the mineralization of organic matter in natural and agricultural soils of the watershed. Though soil organic matters plays an important role as a source of nitrate to riverine waters, point and diffuse anthropogenic inputs also delivery large amounts of nitrate into the river channel, resulting in a pattern inversely related to discharge. In-channel processes such as primary production, nitrification/denitrification and sorption/desorption in sedimentation areas, strongly affect not only the speciation, but also the amount of dissolved nutrients in riverine waters.

Long-term trends of instantaneous discharge have shown a steady decrease in instantaneous discharge from 1998 to 2002, when negative precipitation anomalies prevailed, mostly related to the ENSO phenomenon. Concentrations of cations were found to be highest during these dry years, which are associated with La Niña. During this period groundwater is by far the most important contributor to the total discharge of the PSR. Additionally, the long-term behavior of dissolved nutrients, like DOC, that are intrinsically related to transient flowpaths tended to increase during the El Niño phase of ENSO. The impact of ENSO phases on inter-annual variation of fluvial fluxes delivery to the estuary ranged from approximately 30% for cations and nearly 60% for dissolved nutrients.

The long term study of PSR hydrochemistry revealed a chronic eutrophication scenario, which associated with the siltation of the river channel in the lower basin sector, favored algae blooms when a negative precipitation anomaly prevailed. During this study the system also suffered acute environmental disruptions associated to toxic spills (e.g., Hoag, 2003), with the impacts extending to the adjoining coastal shelf. In spite of the impacts related to anthropic activities all along the basin, PSR waters present strong resilience and can be regarded as crucial for water supply as well as for estuarine and coastal food webs (Costa et al., 2009).

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References

- Azcue, J.M.P., Pfeiffer, W.C., Fizman, M., Malm, O., 1986. Heavy metals in drinking waters from the Paraíba do Sul-Guandu river System (PSR-GR). *Water Sci. Technol.* 19 (7), 1181–1188.
- Azcue, J.M.P., Pfeiffer, W.C., Marino, C., Fizman, M., Malm, O., 1988. Heavy metals in foods from the Paraíba do Sul River valley, Brazil. *J. Food Compos. Anal.* 1, 250–258.

- Austin, A.T., Vitousek, P.M., 2000. Precipitation, decomposition and litter decomposability of *Metrosideros polymorpha* in native forests on Hawaii. *J. Ecol.* 88, 129–138.
- Berner, E.K., Berner, R.A., 1996. *Global Environment: Water, Air and Geochemical Cycles*. Prentice Hall, New Jersey, pp. 376.
- Carvalho, C.E.V., Salomão, M.S.M.B., Molisani, M.M., Rezende, C.E., Lacerda, L.D., 2002. Contribution of a medium-sized tropical river to the particulate heavy-metal load for the South Atlantic Ocean. *The Science of the Total Environment* 284, 85–93.
- Carvalho, C.E.V., Ovalle, A.R.C., Rezende, C.E., Molisani, M.M., Salomão, M.S.M.B., Lacerda, L.D., 1999. Seasonal variation of particulate heavy metals in the Lower Paraíba do Sul River, RJ, Brazil. *Environ. Geol.* 37 (4), 297–302.
- Cavalcanti, I.F.A., Souza, C.A., Kousky, V.E., Barbosa, E.B.M., 2005. Desvios de Precipitação na Região Sudeste do Brasil. <<http://energia1.cptec.inpe.br/portalfpop2.shtml>> (accessed 07.12.11).
- Chen, J., Wang, F., Xia, X., Zhang, L., 2002. Major element chemistry of the Changjiang (Yangtze River). *Chem. Geol.* 187, 231–255.
- Clair, T.A., Dennis, I.F., Vet, R., Laudon, H., 2008. Long-term trends in catchment organic carbon and nitrogen exports from three acidified catchments in Nova Scotia, Canada. *Biogeochemistry* 87, 83–97.
- Clair, T.A., Ehrman, J.M., Quillet, A.J., Brun, G., Lockerbie, D., Ro, C.U., 2002. Changes in freshwater acidification trends in Canadá Atlantic Provinces: 1983–1997. *Water Air Soil Pollut.* 135, 335–354.
- Costa, L.S., Huszar, V.L.M., Ovalle, A.R.C., 2009. Phytoplankton functional groups in a tropical estuary: hydrological control and nutrient limitation. *Estuaries Coasts* 32, 508–521.
- Cotovicz, L.C., Brandini, N., Knoppers, B.A., Mizerkowski, B.D., Sterza, J.M., Ovalle, A.R.C., Medeiros, P.R.P., 2012. Assessment of the trophic status of four coastal lagoons and one estuarine delta, eastern Brazil. *Environ. Monit. Assess.* 184 (7). <http://dx.doi.org/10.1007/s10661-012-2791-x>.
- Dittmar, T., Rezende, C.E., Manecki, M., Niggemann, J., Ovalle, A.R.C., Stubbins, A., Bernardes, M.C., 2012. Continuous flux of dissolved black carbon from a vanished tropical forest biome. *Nat. Geosci.* 8, 1–5.
- Derry, L.A., Kurtz, A.C., Ziegler, K., Chadwick, O.A., 2005. Biological control of terrestrial silica cycling and export fluxes to watersheds. *Nature* 433, 728–731.
- DNPM / Departamento Nacional de Produção Mineral. 1983. Projeto RADAMBRASIL, Levantamento de Recurso Naturais 32, Folhas SF.23/24. Ministério de Minas e Energia, pp. 780.
- Eimers, M.C., Watmough, S.A., Buttle, J.M., 2008. Long-term trends in dissolved organic carbon concentration: a cautionary note. *Biogeochemistry* 87, 71–81.
- Figueiredo, R.O., Ovalle, A.R.C., Rezende, C.E., Martinelli, L.A., 2011. Carbon and nitrogen in the lower basin of Paraíba do Sul River, southeastern Brazil: element fluxes and biogeochemical processes. *Amby-Agua* 6 (2), 7–37.
- Gibbs, R., 1970. Mechanisms controlling world water chemistry. *Science* 170 (3962), 1088–1090.
- Golterman, H.L., Clymo, R.S., Ohnstad, M.A.M. 1978. *Methods for Physical and Chemical Analysis of Fresh Waters*. Oxford Blackwell Scientific Publications, pp. 215.
- Hinkle, S.R., Duff, J.H., Triska, F.J., Laenen, A., Gates, E.B., Bencala, K.E., Wentz, D.A., Silva, S.R., 2001. Linking hyporheic flow and nitrogen cycling near the Willamette River – a large river in Oregon, USA. *J. Hydrol.* 244, 157–180.
- Hoag, H. 2003. Toxic spill threatens Brazilians rivers: Fishes, animals and people at risk after caustic soda leak. *Nature*, April 4, doi: <http://dx.doi.org/10.1038/news030331-11>.
- House, W.A., 2003. Geochemical cycling of phosphorus in rivers. *Appl. Geochem.* 18 (5), 739–748.
- Lacerda, L.D., Carvalho, C.E.V., Rezende, C.E., Pfeiffer, W.C., 1993. Mercury in sediments from the Paraíba do Sul River continental shelf, SE Brazil. *Marine Pollution Bulletin* 26 (4), 220–222.
- Lage Pinto, F., Oliveira, J., Da Cunha, M., Souza, C., Rezende, C.E., Azevedo, R., Vitoria, A., 2008. Chlorophyll “a” fluorescence and ultrastructural changes in chloroplast of water hyacinth as indicators of environmental stress. *Environ. Exp. Bot.* 64, 307–313.
- Mallat, S., 1999. *A Wavelet Tour of Signal Processing*, second ed. Academic Press, New York, NY.
- Malm, O., Pfeiffer, W., Fiszman, M., Azcue, J., 1988. Transport and availability of heavy metals in the Paraíba do Sul-Guandu river system, Rio de Janeiro state, Brazil. *The Science of the Total Environment* 75, 201–209.
- Marengo, J.A., Alves, L.M., 2005. Hydrological Tendencies of the Paraíba do Sul River Basin. *Brazilian Journal of Meteorology* 20 (2), 215–226.
- Milne, A.E., Macleod, C.J.A., Haygarth, P.M., Hawkins, J.M.B., Lark, R.M., 2009. The wavelet packet transform: A technique for investigating temporal variation of river water solutes. *Journal of Hydrology* 379, 1–19.
- Négrel, P., Roy, S., Petelet-Giraud, E., Millot, R., Brenot, A., 2007. Long-term fluxes of dissolved and suspended matter in the Ebro River Basin (Spain). *J. Hydrol.* 342, 249–260.
- Nihlgard, B.J., Swank, W.T., Mitchell, M.J., 1994. Biological processes and catchment studies. In: Moldan, B., Cerny, J., (Eds.), *Biogeochemistry of Small Catchments: A Tool for Environmental Research*, SCPE 51, John Wiley & Sons Ltd., pp. 133–162.
- Nush, E.A., Palme, G., 1975. Biologische Methoden für die Praxis der Gewässeruntersuchung 1- Bestimmung des Chlorophyll a und Phaeopigmentgehaltes in Oberflächenwasser. *GWV* 116 (12), 562–565.
- Pasquini, A.L., Depetris, P.J., 2007. Discharge trends and flow dynamics of South American rivers draining the southern Atlantic seaboard: an overview. *J. Hydrol.* 333, 385–399.
- Pasquini, A.L., Depetris, P.J., 2010. ENSO-triggered exceptional flooding in the Parana River: where is the excess water coming from? *J. Hydrol.* 383, 186–193.
- Pezzine, A., Ovalle, A.R.C., 2009. Characterization of sediment and physico-chemical parameters in an area of sediment deposition in the Paraíba do Sul River (RJ): its similarity with the dynamics of hyporheic areas. *Geochimica Brasiliensis* 23 (2), 255–276.
- Pfeiffer, W.C., Fiszman, M., Malm, O., Azcue, J.M., 1986. Heavy metal pollution in the Paraíba do Sul River, Brazil. *The Science of the Total Environment* 58, 73–79.
- Sharp, J.H., Peltzer, E.T., Alperin, M.J., Cauwet, G., Farrington, J.W., Fry, B., Karl, D.M., Martin, J.H., Spitz, A., Tugrul, S., Carlson, C.A., 1983. Measurement of dissolved organic carbon in natural waters. *Procedures subgroup report. Mar. Chem.* 41, 37–49.
- Smolders, J.P., Guerreiro Hiza, M.A., Van Der Velded, G., Roelofs, J.G.M., 2002. Dynamics of discharge, sediment transport, heavy metal pollution and sábalo (*prochilodus lineatus*) catches in the lower Pilcomayo River (Bolivia). *River Research and Applications* 18, 415–427.
- Souza, T.A., Godoy, J.M., Godoy, M.L.D.P., Moreira, I., Carvalho, Z.L., Salomão, M.S.M.B., Rezende, C.E., 2010. Use of multitracers for the study of water mixing in the Paraíba do Sul River estuary. *J. Environ. Radioact.* 101, 564–570.
- Tao, Y., Wei, M., Ongley, E., Jingsheng Li, Z., 2010. Long-term variations and casual factors in nitrogen and phosphorus transport in the Yellow River, China. *Estuar. Coast. Shelf Sci.* 86 (3), 345–351.
- Tardy, Y., Bustillo, V., Boeglin, J.L., 2004. Geochemistry applied to the watershed survey: hydrograph separation, erosion and soil dynamics. A case study: the basin of Niger River, Africa. *Appl. Geochem.* 19, 469–518.
- Van Miegroet, H., 1994. The relative importance of sulfur and nitrogen compounds in the acidification of fresh water, In: Steinberg, C.E.W., Wright, R.F., (Eds.) *Acidification of Freshwater Ecosystems: Implications for the Future*, John Wiley & Sons, pp. 33–50.
- Yuan, F., Miyamoto, S., Anand, S., 2007. Changes in major element hydrochemistry of the Pecos River in the American Southwest since 1935. *Appl. Geochem.* 22, 1798–1813.
- Zakharova, E.A., Pokrovsky, O.S., Dupré, B., Zaslavskaya, M.B., 2005. Chemical weathering of silicate rocks in Aldan Shield and Baikal Uplift: insights from long-term seasonal measurements of solute fluxes in rivers. *Chem. Geol.* 214, 223–248.