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INFLUENCE OF RIVER WATER DIVERSION ON HYDROGEOCHEMISTRY AND REE DISTRIBUTION, RIO DE JANEIRO, BRAZIL

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Abstract: A previous study made by our group indicated that the changes in the rare earth element (REE) distribution pattern, within the upper 30cm of sediment column from Sepetiba bay, are related to Paraiba do Sul River (PSR) diversion. Here we show that REE fractionations in the water column are directly related with the construction of PSR and Guandu river watershed diversion system. Surface water samples were collected during the dry and wet season in specific sites along the transposition system. A tangential ultrafiltration system was used to obtain specific fractions: particulate (SPM load < 63 µm to > 0.1 µm) colloidal (colloidal load >10 kDa) and dissolved (dissolved load >1 kDa) fractions. The nutrients (H_4SiO_4, $PO4^{3-}$, F-, Cl^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, and Mg^{2+}) and REE were analyzed in each of fractions. The relatively large total REE concentrations found in the PSR diminished substantially when reaching the downstream section of the tributary, showing lower concentrations when compared to a nearby river unaffected by the diversion. Some of the factors that may control the self-purification of REE, include the trapping of the particulate fractions associated with suspended matter in dams along the basin, uptake of the dissolved fraction by aquatic plants in nutrient rich waters of the tributaries, and co-precipitation with oxides/hydroxides as the redox potential increased downstream from the water diversion.

Key words*:* particulate matter, ultrafiltration, colloidal fraction, rare earth elements, fluvial waters

1. INTRODUCTION

Rare earth elements (REE) have specific traits which may be used to indicate specific geochemical process. For example, REE's may be used as powerful tracers in aquatic systems, as well as to determine mixing rates between differing water masses (Viers et al., 2000; Tosiani et al., 2004; Xu & Han, 2009). The dissolved and particulate REE fractions are frequently associated with suspended particulate matter (SPM). In river waters the rare earth elements fractionation can indicate us about their origin and distribution pattern (Goldstein & Jacobsen, 1987, 1988; Elderfield et al., 1990; Sholkovitz, 1992; Negrél et al., 1993; Tricca et al., 1999; Ingri et al., 2000; Xu & Han, 2009).

In the past few decades, several studies have clearly deepened the discussion about composition and above all the pattern of fractionation and distribution of rare earths (Goldstein & Jacobsen, 1988; Elderfield et al., 1990; Dupré et al., 1996; Gaillardet et al., 1997; Douglas et al., 1999; Viers et al., 2000; Tosiani et al., 2004; Xu & Han, 2009). Despite the information provided in these studies, there is still a lack geochemical data concerning REE in fresh water systems, in particular from tropical and subtropical environments (Tang & Johannesson, 2010). Due to intense rainfall, subtropical/tropical rivers deliver a large amount of sediments to the oceans and carry a unique distribution of REE signature reflecting the geology of specific drainage basins (Sultan & Shazili, 2009). Rare earth elements are useful geomarkers owing to their trivalent state in most conditions, as such, they exhibit similar geochemical behaviors. However, Ce and Eu can be tetravalent and bivalent respectively, depending on the redox potential. These REEs are transitional in their atomic state and form tripositive ions in most compounds (Bell & Lott, 1972).

Specific concentrations of REEs are often associated with agricultural activities such as forestry, animal husbandry and aquaculture. Moreover, generally high concentrations of REEs are frequently related to bactericides, microelement fertilizers and animal feeds (Sun et al., 1994). For example, one of the principal components used for fertilizer is phosphogypsum, which are known to contain high concentrations of REEs. Furthermore, the large use of REE in ceramics, magnets, metallurgical alloys, glass and polishing, as well as specific medicines have been associated to greater concentrations of these group of elements and are regarded as a new contaminant of REEs. Gadolinium (Gd), used as a contrast agent in magnetic resonance imaging, has been touted a contaminant in rivers (Bau et al., 2006; Lawrence and Bariel 2010). Lanthanum and samarium have also been found to be a contaminant in the river waters (Kulaksız & Bau 2011; 2013). Furthermore, there is a tendency for REEs to accumulate in soil, water and within specific biota (Gorbunov et al., 1992). In Brazil, there are few studies reporting the concentration of REE in rivers, and most of these studies are in the region in Amazon Basin (Gaillardet et al., 1997; Küchler et al., 2000, Gerard et al., 2003, Barroux et al., 2006). A recent study has shown the contamination of Gd in a lake in central area of Brazil, due the discharge of wastewater effluents (Merschel et al., 2015). Indeed, large number of these REEs residues are characterized and categorized as environmental toxins (Qiang et al., 1994; Chua, 1998).

High concentrations of REE detected in plants have been related to contaminated soils. This is because plants have the ability to uptake REE through their roots and bioaccumulate (Ichihashi et al., 1992; Chua, 1998). Bioaccumulation of REEs in the various plant species of differing concentrations has been noted previously, for example Qiang et al., (1994) and Chua (1998). The capacity of plant species and agricultural yield to accumulate REE depends on the plant species and the REE contents of the substrate (Volokh et al., 1990; Ichihashi et al., 1992).

However, there are still relatively little data on the biological effects associated with REE. Based on bioaccumulation studies, bioassays in animals, plants and models, the few reported cases focused on the effects of human health after occupational exposures to REE (Sabbioni et al., 1982). In the absence of epidemiological studies of exposed occupational groups, the exposition of REEs may cause adverse effects, such as: growth inhibition, fertilization damage, cytogenetic effects and toxicity to specific organs such as liver, lungs and blood (Ding & Ma, 1984; Pagano et al., 2015; Thomas et al., 2014; Pagano et al., 2016; Yang et al., 2016; Wei et al., 2013).

In the present study, water quality assessments were undertaken by analyzing REE fractionation (particulate, colloidal and dissolved) along the Guandu tributary (Fig. 1). The aim of this work was to determine possible impacts caused by a major water diversion of one of the largest rivers in South-Eastern Brazil, the Paraíba do Sul River to the Guandu tributary watershed, which provides freshwater to the 14 million inhabitants of the metropolitan area of Rio de Janeiro.

2. HYDROLOGICAL SETTING

The transposition system was built in the 1950's, mostly by the diversion of 40% of the Paraíba do Sul river (Fig. 1) that discharges into the Guandu tributary to supply potable water which is used by three hydroelectric dams with a generation capacity of 612 MW. The portion of the diverted water along the Guandu tributary is treated for consumption in Rio de Janeiro, the second biggest water treatment plant of the world (ETA-Guandu). The remaining water is discharged into Sepetiba Bay, by the São Francisco canal and has become a significant additional source of water and dissolved as well as particulate material to the Bay (Silva-Filho et al., 2011).

The discharge from the diversion is pumped 33 m uphill into the Vigário Reservoir. From Vigário Reservoir, the subsequent fall to Sepetiba Bay is 390 m (Fig. 2). The distance between PSR and Sepetiba Bay is 94 km (Fig. 2). Sepetiba Bay is a 443 km^2 estuary, supporting extensive mangrove wetlands (Molisani et al., 2004; 2006). Three stations along the diversion system and one station in a nearby basin were selected for water sampling (Fig. 1). Station P-01 located upstream from PSR diversion; Station P-02 in the Vigario reservoir (VR); Station P-03 in the São Francisco canal (SF),

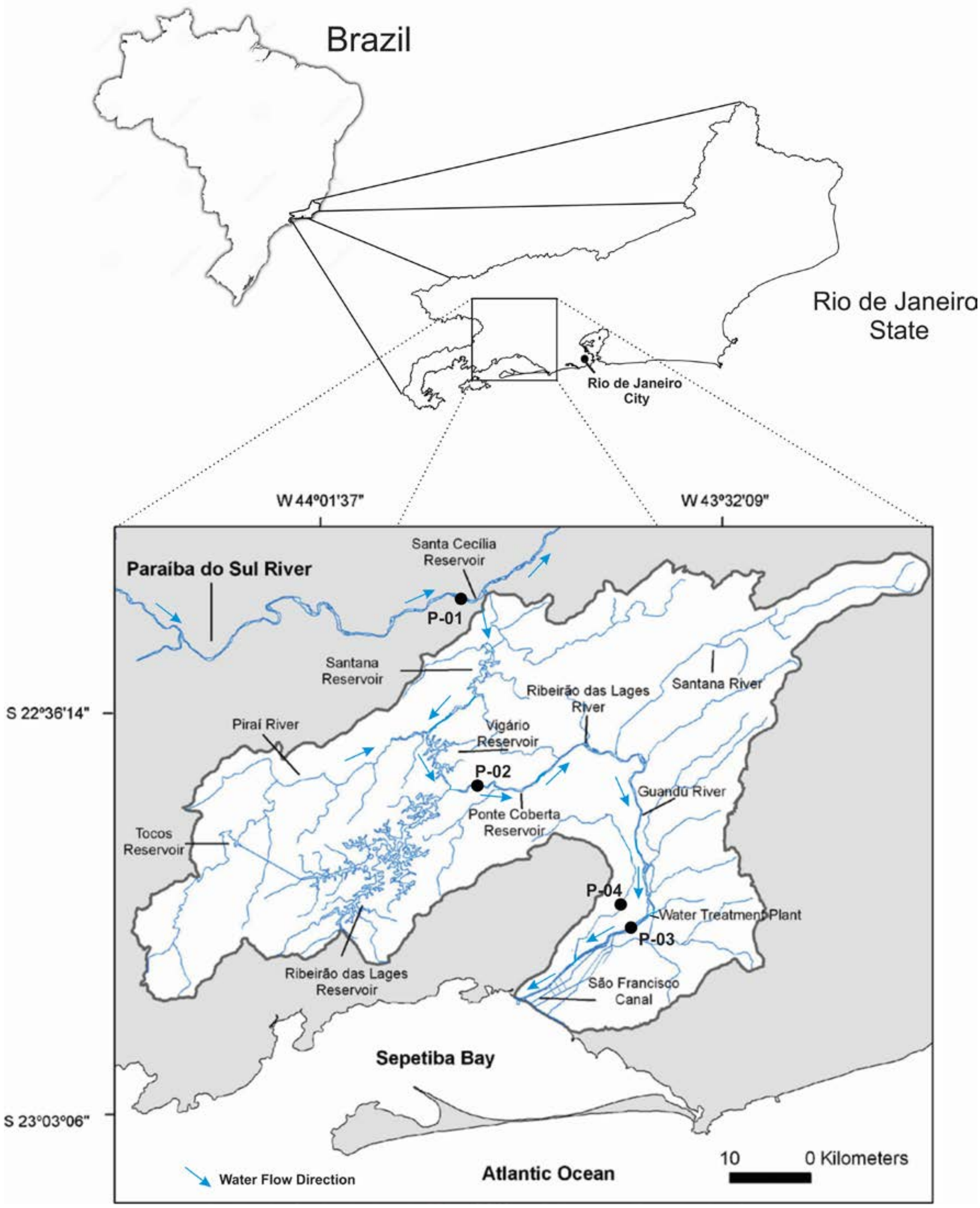

Figure 1. Map of the study area including sampling points (P-01 Paraiba do sul River; P-02 Vigario reservoir; P-03 São Francisco canal; P-04 Itingussu River) (Source: adaptation of Molisani et al., 2007).

approximately 20 km downstream the water treatment plant; and Station P-04 in the Itingussu river (IR), which is not directly impacted by the water diversion and located near the São Francisco site with similar distance to Sepetiba Bay. The P-04 station is considered for comparative purposes.

3. MATERIAL AND METHODS

The sampling locations are shown on Figure 1. Surface waters samples were collected during both: wet (February) and dry (July) seasons, 2010. Samples were collected using a Van Dorn bottle near the middle of the river channel. Physicochemical analyses (pH, Eh, dissolved oxygen, temperature) were conducted during samples collection with a multi-parameter probe (HI 9828-HANNA Instruments).

3.1 Tangential Filtration and REE Analyses

At each sampling station, 50L of water was filtered through 63µm polypropylene membrane and stored in high-density polyethylene (HDPE) containers for posterior ultrafiltration in the laboratory. Subsequently, the 50L collected at each site were immediately fractioned in tangential system (Pellicon 2 Millipore) with regenerated cellulose membranes 0.1 µm, 10 kDa, 1 kDa in the laboratory. The obtained fraction was divided in: particulate (***SPM load < 63 µm to >0.1 µm)*** colloidal ***(colloidal load >10 kDa)*** and dissolved (***dissolved load >1 kDa***) fractions. The different fractions were acidified with HNO_3 for ICP-MS (X SERIES 2 Thermo Fischer Scientific - Germany) analysis. Indium and rhodium were added as the internal standard. The whole procedure was performed in a clean laboratory, and Millipore-Q water (18.2 MΩ cm) and double sub-boiling distilled reagents were used throughout.

The ICP-MS operating procedures are listed as follows: R.F. Power: 1400 W; Plasma gas: 13 L min^1; Auxiliary gas: 0.7 L min^1; Nebulizer gas: 0.98 L min^1. In order to minimize isobaric interferences during ICP-MS operation, the monitored isotopes were: ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{158}Gd, ^{159}Tb, ^{164}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{174}Yb, and ^{175}Lu. The ICP–MS was calibrated by using a series of standards prepared from the REE multi-element stock solution (0.1 mg mL^{-1}) SpecSol®. The sample REE concentrations were calculated from their respective calibration curves (Johannesson et al., 2004). Blanks were measured between groups of samples throughout the entire analysis procedure.

These concentrations were relatively low for all REE (2–5%). The accuracy of analytical protocol was evaluated by analysis of certificated reference material SPS-SW-1 (Surface water) throughout the entire procedure for the analysis of rare earth elements in the sample set. The recovered results range from 85% (Pr) to 102% (Nd).

3.2 Nutrient Analyses

Subsamples were collected to determination the dissolved organic Carbon (DOC), dissolved inorganic silicate (H_4SiO_4) and dissolved phosphate (PO_4^{-3}), cations and anions concentrations (F^-, Cl^-, SO_4^{-3}, Na^+, K^+, Ca^{+2}, Mg^{+2}), as well as alkalinity. The DOC samples were collected in 100 mL glass bottles with air-tight caps and subsequently analyzed in the Hipertoc (Thermo Scientific) accord to 5310C Standard methods (1995). An aliquot of the subsample was filtered with Millipore 0.22µm filters for dissolved inorganic silicate (Si), dissolved phosphate, cations and anions (F^-, Cl^-, SO_4^{-2}, Na^+, K^+, Ca^{+2}, Mg^{+2}). The determination of dissolved inorganic silicate (Si), and dissolved phosphate was conducted according to Grasshoff et al., (1999). The ionic chromatography (Metrohm 850, 858) was used to determine the cations and anions concentrations. The alkalinity was determined in the unfiltered samples by titrimetric method according to the 2030 standard method (1995).

4. RESULTS

4.1 Physicochemical parameters and nutrients

Table 1 shows physicochemical parameters from the studied waters. During the wet season the Eh, temperature and pH showed slightly higher values in comparison to dry season (Table 1).

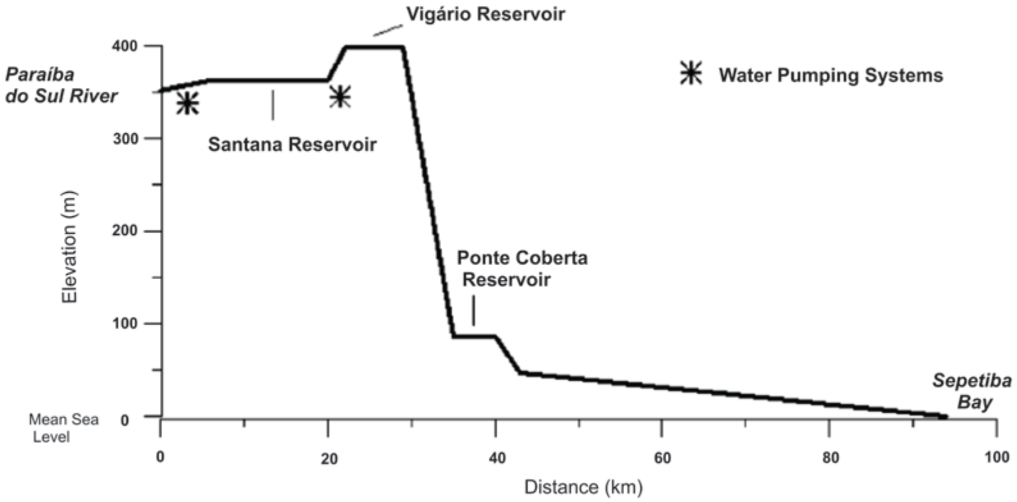

Figure 2. Graph indicating altitude and the water diversion from the Paraíba do Sul river (PSR) to the Sepetiba Bay, provision water to Rio de Janeiro metropolitan region. The bars on the graph indicate pumping stations. (Source: adaptation of Molisani et al., 2006).

Table 1. Physicochemical characterization of results found for each study site P-01 Paraiba do Sul river (PSR); P-02 Vigario reservoir (VR); P-03 São Francisco canal (SF); P-04 Itingussu river (IR). OD = Dissolved Oxygen

Study Site	pH	Eh (mV)	Temp. (ºC)	OD (mg . L^{-1})	Alkalinity (μEq . L^{-1})
Wet season					
P-01 (PSR)	6.6	51.3	27.8	4.2	2290
P-02 (VR)	6.6	112	27.4	6.4	428.7
P-03 (SF)	7.0	151.2	23.8	8.4	2600
P-04 (IR)	6.6	226.8	20.4	8.2	590
Dry season					
P-01 (PSR)	6.2	47.3	19.7	7.7	370.1
P-02 (VR)	6.3	90	19.3	6.3	768.8
P-03 (SF)	6.1	124.7	21.0	8.3	717
P-04 (IR)	6.1	111	16.5	9.0	700

Table 2. Major elemental cation and anion concentrations (mg L^{-1}) and nutrient results (mg L^{-1}) found for each study site P-01 Paraiba do Sul river (PSR); P-02 Vigario reservoir (VR); P-03 São Francisco canal (SF); P-04 Itingussu river (IR).

Study Site	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	F^{-}	Cl^{-}	SO_4^{2-}	NO_3^{-}	NO_2^{-}	NH_4^{+}	PO_4^{-3}	Si	DOC
Wet season													
P-01 (PSR)	38.61	11.66	50.56	27.41	2.29	34.9	47.27	0.34	0.03	0.06	0.07	3.5	3.20
P-02 (VR)	3.76	1.21	7.03	2.83	0.23	4.9	6.35	0.60	0.02	0.08	0.01	0.5	5.43
P-03 (SF)	43.53	13.28	96.16	29.26	2.42	65.8	78.41	0.46	0.79	27.9	1.90	12.7	7.19
P-04 (IR)	6.79	4.15	23.65	4.65	1.62	32.6	10.08	0.15	0.003	0.01	0.02	9.0	1.66
Dry season													
P-01 (PSR)	0.97	3.75	9.00	0.77	0.35	0.85	10.47	0.09	0.16	1.1	1.12	6.9	6.18
P-02 (VR)	8.18	4.34	8.28	3.34	0.25	0.79	9.83	0.08	0.11	0.9	0.97	6.6	15.2
P-03 (SF)	3.64	8.70	0.27	4.71	0.38	0.92	14.35	0.07	0.10	1.0	4.28	1.4	5.25
P-04 (IR)	2.85	5.58	2.04	0.96	0.03	0.39	1.25	0.02	0.05	0.2	0.07	7.2	2.01

During each campaign, all four sites maintained the same pH range. In the two periods, a gradual increase in Eh may be noted from the P-01 (PSR) to the P-03 (SF), and the highest values were found at the P-04 (IR) in the wet season. This parameter may play a role in the diminishing REE concentrations from the P-01 (PSR) to the P-03 (SF). In the wet season the highest Alkalinity values were found in the P-01 (PSR) station, which may be attributed to soil weathering and effluent discharge. The Paraiba do Sul River has several towns along its route that release large amount of domestic wastewater. During rainfall, an increase in the effluent discharge was noted as these towns use the same sewage and rainwater drainage system. Moreover, the watershed is highly anthropic, with the removal of native vegetation and replaced by pasture, which increases the erosive processes. At the P-03 (SF) the highest alkalinity may be attributed to sewage discharge and/or saline water intrusion from the Sepetiba Bay (Table 2). Regarding the major cation and anion concentrations (Table 2), higher values were noted in the wet season as compared to the dry season, an exception to this trend was in the Vigario Reservoir (P-02).

The higher cation and anion concentrations in the dry season at the Vigario Reservoir may be related to the life cycle of macrophytes which are associated to incorporate REEs within the vegetative structure (Chua, 1998). In the dry season, large proportions of these plants die, and the process of organic matter decomposition at the bottom of reservoir recycle the elements to water column. This process is corroborated by the DOC data, of which were twice as high in the Vigario Reservoir as compared to the Paraiba do Sul River.

5. DISCUSSION

The concentrations of the dissolved, colloidal and SPM REE decreased substantially from the P-01 (PSR) to the P-02 (VR) and to the P-03 (SF) stations (Fig. 3). The relatively low concentrations at the P-03 station total REE load are significant when compared to the nearby P-04 (IR), which is unaffected by the Paraiba do Sul River diversion (Fig. 1). Some of the main physicochemical differences in these two stations are that P-03 on the São Francisco canal (SF) receives water from the Guandu tributary, which is utilized for water consumption (water treatment) and subsequently acquires characteristics highly polluted as it flows through urban areas, eventually reaching the P-03 (SF) station. The chemical compositions of the two water courses, which subsequently reaching the P-03 (SF) and P-04 (IR), are substantially diverse. In order to corroborate this information, Table 2 presents the major ions concentrations in the studied sites and Table 3 the ratio among the main ions and Cl (Cl was chosen by the conservative behavior in fresh water) as described in Hem, (1985) and Drever (1997).

It may be noticed that the major ions and specifically element/Cl^- ratio show differences from the P-01 (PS) to the P-02 (VR) and P-03 (SF) as compared to the P-04 (IR) station (Tables 2 and 3). Despite the alterations along the Guandu tributary, the element/Cl^- ratios from the P-01 (PSR) are preserved until reaching the P-03 (SF) and the ion load is likely mixed by marine waters from the Sepetiba Bay.

One of the significant results in this study is the large nutrient content found the P-03 (SF) as compared to the P-04 (IR) (Table 2). Because of the anthropogenic modifications and subsequent differing chemical composition of the water along the Guandu tributary, aquatic plants are abundant, including species that typically proliferate in polluted waters (e.g., *Eicchornia azurea, Pistia statiotes, Salvinia auriculata* and *Eicchornia crassipes*). Although those plant species are in constantly in need of removal from hydroelectric dams and in some parts of São Francisco River, due to their rapid proliferation, they are efficient in the biological uptake of REEs (Chua, 1998; Valitutto et al, 2006).

5.1 REE Distribution

Figure 3 shows the REE signature (normalized by the Post-Archean Australian Shale) (McLennan, 2001) of the fractions from the four sampled stations. The major fraction of REE in P-01 (PSR) was noted in the dissolved load followed by SPM load during the dry season. On the other hand, most of the REE is in SPM, followed by dissolved fraction (Fig. 3), during wet season. The opposite is noted at the P-02 station (Vigario reservoir), which showed REEs major load at the dissolved fraction in both seasons, followed by colloidal phase during dry season, while in the wet season the greatest concentrations were in the SPM load (Fig. 3). This difference in the seasons may be related to an increase of SPM flux during the wet season. The P-03 station (São Francisco canal) also presented the major REE fraction in the dissolved load, followed by SPM fraction and colloidal load in the dry and wet season, respectively.

A drastic decrease in the SPM concentrations are noted as the water flows from the P-01 (PS), P-02 (VR) to the P-03 (SF), indicating REE retention processes along the tributary. If compared to the P-04 (IR), which has the same geological features (rock composition and structures) and equal distance to the Sepetiba Bay, the P-03 (SF) is depleted in the REE SPM fractionation. The dissolved fraction of REE appears to be more conservative. General REE concentrations decrease along the tributary, of the three species of REE considered in this study, though in different speciation ratios along the Guandu tributary. The results show different concentration rates between the Light REE (LREE) in the four studied sites (Fig. 3). In the dry season the colloidal and dissolved load are enriched in HREE, and the particulate loads are enriched in LREE. However, during the wet season the colloidal and dissolved load are enriched in LREE. The only exception was the P-02 station which showed HREE enrichment during both seasons.

Table 3. Major elemental/ Cl^- ratios (mg L^{-1}) found for each study site P-01 Paraiba do Sul river (PSR); P-02 Vigario reservoir (VR); P-03 São Francisco canal (SF); P-04 Itingussu river (IR).

Study Site	**Ca^{2+}/Cl^-**	**Mg^{2+}/Cl^-**	**Na^+/Cl^-**	**K^+/Cl^-**	**SO_4^{2-}/Cl^-**
Wet season					
P-01 (PSR)	1.1	0.3	1.4	0.8	1.4
P-02 (VR)	0.8	0.2	1.4	0.6	1.3
P-03 (SF)	0.7	0.2	1.5	0.4	1.2
P-04 (IR)	0.2	0.1	0.7	0.1	0.3
Dry season					
P-01 (PSR)	1.1	4.4	10.6	0.9	12.3
P-02 (VR)	10.4	5.5	10.5	4.2	12.4
P-03 (SF)	4.0	9.5	0.3	5.1	15.6
P-04 (IR)	7.3	14.3	5.2	2.5	3.2

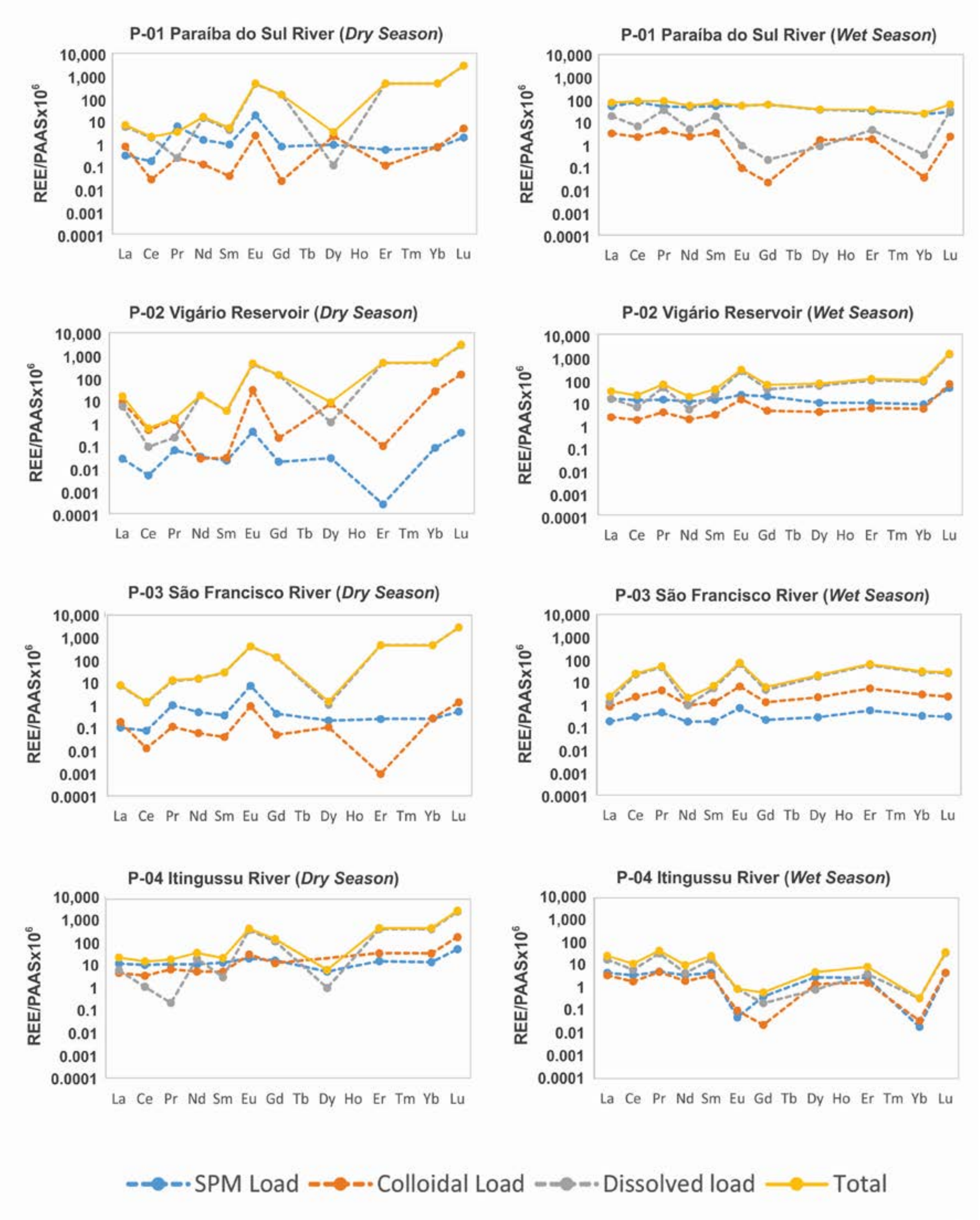

Figure 3. Rare earth element distribution in the three fractions studied and total at the four sites of this work (P-01 Paraiba do sul River; P-02 Vigario reservoir; P-03 São Francisco canal; P-04 Itingussu River).

According to Andersson et al., (2006), the enrichment of LREE in river water during the spring flood in a subartic boreal river was due the litter enrichment in LREE. Another interesting finding in this work was the large content of HREE presented by the colloidal fraction during the dry season (Fig. 3), compared to other studies (Ingri et al., 2000). Both the concentration and the extent of fractionation of dissolved trivalent REE in river water appear to be dependent on pH and on the colloidal particles occurrence (Ingri et al., 2000).

5.2. Physicochemical Controls on REE Behavior

It is known that hydroelectric dams decrease river flow energy, which may be responsible for the reduction of REE in the SPM fraction.

As the river flow energy decreases, the SPM precipitates along these stations. Another form of REE removal from the studied waters may also be the result of metal complexation in more oxidized environments (Eh>0), mainly through the formation of Fe (III) and Mn (IV) oxides/hydroxides and subsequent precipitation, as evidenced by the increment of Eh from the P-01 (PSR) to P-03 (SF) (Table 1). Under circumneutral and alkaline conditions, REE speciation is normally dominated by carbonate complexation (Schijf & Byrne, 2004). Therefore, the REE sorption by Fe (III) oxides/hydroxides may be related to the precipitation of REE-enriched Fe (III) / Mn (IV) oxides/hydroxides along the Guandu tributary and probably linked with Eh conditions. Although detrital monazite and apatite of probable igneous origin has been reported in the study area, Fe (III) oxides/hydroxides are ubiquitous, occurring as abundant coatings on mineral grains. Due to the fractionation patterns in the desorbable and exchangeable form of the REE, they may exhibit sorption by amorphous ferric hydroxide precipitation from Fe (III) oxides/hydroxides coatings on sediments (Davranche et al., 2004; Tang & Johannesson, 2010)

According to (Rönnback et al., 2008) a series of mechanisms may influence REEs behavior in waters, causing its fractionation between solution and solid interface. Moreover, the alkalinity conditions also may favor adsorption of REEs on particulates (He et al., 2010). As the P-03 (SF) is characterized by relatively high Eh and alkalinity, at least some of the reduction in the REE concentrations may be due to adsorption and sedimentation such as the Guandu tributary water reaches P-03 (SF) study site.

Increasing of water pollution may also affect the REE adsorption onto contaminants. Rare earth elements concentration is heavily dependent of high pH and low DOC concentration. REE adsorb onto organic-rich waters (Vagnetti et al., 2003). As the P-03 (SF) station is highly enriched in nutrients from untreated sewage discharge, REE adsorption and subsequent precipitation in this area is probable. Because REE may accumulate it is possible to suppose that contaminants transport and fate will influence its presence in the water bodies (Suzuki, 1997). The processes mentioned previously are important geochemical features that highlights the influence of anthropometry activities on REE behavior. So, the forms of these elements between the P-01 (PSR) until P-03 (SF) stations, reveals a strong self-purification in terms of the tributary's ability to remove the REE from the water column. Indeed, adsorption and eventual deposition of the SPM in areas with little energy, particularly in the dams, seems to be an essential self purification process of REE (He et al, 2010).

The role of organic colloids as important REE carriers in river water is apparent in this work as reflected by the concentrations of REE found in this fraction. Some of the geochemical processes that may influence REE retention by organic colloids within the tributary are the Eh variations, metal oxidation and the trapping of REE by colloids. Aqueous REE species are characterized by a high charge/ionic radius ratio which help sorption onto suspended colloidal materials (such as Fe and Mn-oxides/hydroxides and organic matter). As previously suggested (Viers et al., 1997), the affinity of REE to organic matter implies that in fresh water, the organic colloidal pool is probably of prime importance due to complexation.

One of the most interesting results found in this work is the likely influence of the colloidal organic matter on the REE behavior. This result is of broad significance as it demonstrates that the REE distribution in catchments is influenced by the hydrological and ensuing redox conditions. This suggests that REE may be affected by geochemical processes (redox, adsorption, complexation) occurring along the downstream study areas and therefore considered as non-conservative tracers. The different REE patterns display specific concentrations in each hydrological domain through chemical divergence along the tributary. Furthermore, the sensitivity of REE to redox variation, complexation or uptake onto sorptive surfaces strongly suggests that REE may be used as an indicator of environmental conditions along impacted river basins (Dia et al., 2000). As pointed out earlier, an increase in Eh was accompanied by a decrease in REE concentration in the P-03 (SF), which is interpreted as a factor in the flocculation processes (Lakind & Stone, 1989; Fergusson, 1990; Deng & Stumm, 1993; Chuan et al., 1996; Carroll et al., 1998) mainly due to that are known to be very effective scavengers of REE and of other trace elements (Trolard et al., 1995; Bau, 1999, Bau & Koschinsky, 2009; Dia et al., 2000). In summary, the chemical characteristics of the waters along the P-03 (SF) and the P-04 (MR) are substantially different, likely due to PSR river diversion at as well as the anthropogenic activities along the Guandu tributary, including input from Rio de Janeiro metropolitan region effluents. This study shows that these chemical characteristics play a role in REE fractionation.

5.3 Biological uptake

The biota plays a significant role in the REE uptake in this region as noted by Valitutto et al (2006). Rare earth elements with expected low bio-availability are known to bioaccumulated in macrophytes (Chua, 1998). Significant quantities of macrophytes have been document in this region, specifically *E. crassipes*, which is especially effective in REE uptake. Large amounts of these plants are consistently removed along the reservoirs and Guandu tributary. The capability of this macrophyte, commonly known as water hyacinth, for the uptake of REE via the root system has also been demonstrated in laboratory experiments (Chua, 1998). A study of REE uptake in P-02 (VR) area concluded that concentrations increased in the sequence of the following species: *E. azurea* < *P. stratiotes* < *S. auriculata* < *E. crassipes* (Valitutto et al., 2006). Many plant species, which show strong similarities with those observed in filtered water and in the suspended particulate fraction, indicated that there is no fractionation during the bio-uptake of REE. Indeed, the behavior of chemically similar REE groups becomes evident, being the more abundant in the dissolved water fraction (e.g. La, Ce, Nd, Pr), of which are also in higher concentrations in plant material (Lakatos et al., 1999). It has been demonstrated through laboratory experiments that the transfer of REE from nutrient solutions via root uptake by plants (including *E. crassipes*) increases linearly with the concentration of these elements in solution (Chua, 1998; Tagami & Uchida, 2006). This information may be pertinent in this study because the lowest REE concentrations in all three species of plants reported in previous studies are present in P-03 (SF), which contained the highest nutrient concentrations, and the lowest overall concentrations of REE in the combined fractions. These characteristics of the P-03 (SF) station may be explained by efficient biological uptake of the REE (especially the dissolved fraction) along the diversion system. Regarding the high REE concentrations observed in all species of the previous mentioned study, this finding may be related to the physicochemical similarities between REE and Ca, the later as an essential element to plants. Once absorbed by plants, REE may be transported to cells via Ca-proteins due to their similar effective ionic radius (Tagami & Uchida, 2006). This indicates that aquatic macrophytes, especially *E. crassipes* and *P. stratiotes*, may act as hyper-accumulators for REE under appropriate environmental conditions (Valitutto et al, 2006).

6. CONCLUSION

This study shows that the self-purification of REE-rich waters diverted to the Rio de Janeiro metropolitan region are explained by various geochemical, physical and biological process. The differences in the REE concentrations between the dissolved, colloidal and SPM REE from the upstream P-01 (PSR) to the downstream P-03 (SF) suggests a strong self-purification ability in terms of overall REE concentrations. Precipitation, influenced by the geochemical conditions and uptake by biota seems to be important self-purification mechanisms along the three sites of the study region, especially when compared to a geomorphologicaly similar river outside the Guandu tributary (P-04/IR). The reduction in stream energy caused by dams as well as the oxides/hydroxide sorption are likely significant factors influencing the REE scavenging along the hydrological system of this study. Biological uptake by aquatic plants, as previously reported, also play a significant role in the decrease in REE concentrations along the stations of this work. Some of the conclusions in this study were based on the comparison with a nearby river P-04 (IR), unaffected by the diversion and considered for comparative purposes as well as the hydrogeochemical characterization of the river water along the Guandu tibutary. The results of this study may be significant to support future studies using REE as geochemical tracers and to better understand anthropogenically impacted hydrological systems.

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