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Bed and suspended sediment-associated rare earth element concentrations and fluxes in a polluted Brazilian river system

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Abstract

Rare earth elements (REEs) have been recently recognized as emergent pollutants in rivers. However, data regarding REE fluxes in association with either bed or suspended are scarce. To address this knowledge gap, we determined the concentrations and fluxes of La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, Lu, Dy, Er, Ho, Tb and Tm in bed and suspended sediment samples of a representative polluted Brazilian River. Sediment-associated data on REEs were placed in the context of corresponding background concentrations in soils under natural conditions along the Ipojuca watershed. Light rare earth elements (LREEs) comprised more than 94% of the total REEs associated with bed and suspended sediments. Suspended sediments accounted for more than 95% of the total REE flux. The Ce and Nd fluxes of about 7 t year^{-1} underscore the importance of including REEs in future estimations of global suspended sediment-associated element fluxes. In contrast, bedload often transported less than 0.0007 t year^{-1} of each REE. The main sources of pollution in the Ipojuca River are anthropogenic, likely due to domestic effluent and waste water from industrial and agricultural operations – major causes of sediment-associated Gd transport in polluted streams.

Keywords: lanthanides, environmental quality, sediment-associated transport, watershed management, water quality, bedload.

1. Introduction

Erosion in river basins transfers sediments to nearby streams and rivers. Globally, suspended and bed sediment loads respectively comprise 5-25% and 90% of total fluvial sediment transport, although the bed load can account for only 75% of the total load for some rivers (Yang 1996; Milliman and Farnsworth, 2011; Cantalice et al. 2013). Fluvial sediments are responsible for a major component of the sediment-associated flux of rare earth elements (REEs) reaching the world's oceans (Martin et al. 1976**)**. REE concentrations in sediments can be used to trace the recycling of the continental crust (Taylor and McLennan 1985) and to assess anthropogenic impacts on rivers (Viers et al. 2009, Hissler et al. 2015). REEs play an important role in the industrial production of several technological devices (i.e. smart phones, computer hard disks, fluorescent and light-emitting-diode (LED) lights, flat screen televisions and electronic displays) and in agricultural activities, yet these elements have only recently been recognized as potentially emergent pollutants in rivers (Hissler et al. 2015; Gwenzi et al. 2018; Censi et al. 2018; Cuss et al. 2018; Blinova et al. 2018; Xu et al. 2018), thereby requiring management decisions targeting contaminated sites (Kulaksiz and Bau 2013; Liang et al. 2014; Ramos et al. 2016; Blinova et al. 2018). Such management can be required since some REEs impact on human health; Gd accumulation, for example, can trigger kidney failure and anaphylactic shock followed by death in extreme cases (Ergun et al. 2006; Idee and Corot 2008; Kay 2008). Even where human health impacts are not reported, fluvial suspended and bed sediment transport govern the transfer of REEs and the environmental conditions of exposure imply a continuous contamination of the world's estuaries and oceans (Hannigan et al. 2010; Liang et al. 2014; Polyakov et al. 2009; Brito et al. 2018) and represent not only short- but also long-term pollution transfers in rivers (Taylor et al. 2003).

In Brazil, recent studies of REEs have focused on a wide range of soils (Silva et al. 2016; Paye et al. 2016), but there is no study integrating information on REE concentrations in soils and suspended and bed sediments. Here, in fact, data for sediment-associated REE fluxes remain scarce. Overall, REE concentrations in Brazilian soils are often lower than the values reported for soils elsewhere in the world or for the earth's crust (Wei et al. 1991; Tyler and Olsson 2002; Sadeghi et al. 2013). Moreover, data reported for Brazil are typically for soils enriched with light rare earth elements (LREEs) and this natural abundance is likely to have consequences for the geochemical characteristics of both suspended and bed sediments and especially in a multi-metal contaminated catchment, such as the Ipojuca River watershed (Silva et al. 2015a; Silva et al. 2017).

The Ipojuca River is one of the most polluted rivers in Brazil. For instance, suspended sediment-associated Pb fluxes have been reported as exceeding those in rivers affected by mining activities (Silva et al. 2015a). To date, most studies undertaken in the Ipojuca River watershed have focused on sediment-associated trace element fluxes, modelling point and non-point pollution and the contamination of water resulting from the sugarcane industry (Gunkel et al. 2007; Barros et al. 2013; Silva et al. 2015a). Since the Ipojuca River crosses semiarid and coastal regions, it provides a unique opportunity for studying sediments derived from different sources. The major pollution sources for the Ipojuca River include domestic effluents – known to be the major source of Gd in polluted streams (Verplanck et al. 2010; Hissler et al. 2015; Adebayo et al. 2018), urban/municipal wastes, hospital and domestic effluents derived from wastewater treatment plants and the applications of agrochemicals along its watercourse (SRH 2010).

Since data on the distribution and transport of REEs in conjunction with sediments are still scarce, a number of research questions remain, including: Are sediment-associated REEs derived primarily from natural or anthropic sources? What is the ratio between LREEs and heavy REEs (HREEs) transported in association with bed and suspended sediments? To address these questions, we determined both the concentrations and fluxes of La, Ce, Pr, Nd, Sm, Eu, Gd, Yb, Lu, Dy, Er, Ho, Tb and Tm in association with bed and suspended sediment samples in the Ipojuca River. To help with the interpretation of the sediment-associated data on REEs, we also determined the background concentrations of REEs in local soils under natural conditions.

2. Material and methods

2.1. Study area

The total length of the Ipojuca River is approximately 290 km, extending from a semiarid to a coastal zone (08°09’50’’– 08°40’20’’ S and 34°57’52’’– 37°02’48’’ W) and draining a catchment area of ~3,435 km^2 (Figure 1). The average annual rainfall in the study area ranges from 600 mm to 2,400 mm (SRH 2010). Soils are mostly derived from granites (36.74% Leptosols/Regosols, 32.10% Acrisols, 17.77% Planosols, 8.89% Ferralsols and 4.5% for the remaining soils; FAO/WRB, 2015). Average water discharge ranged from 0.29 m^3 s^{-1} to 25 m^3 s^{-1}, for upstream and downstream cross sections, respectively.

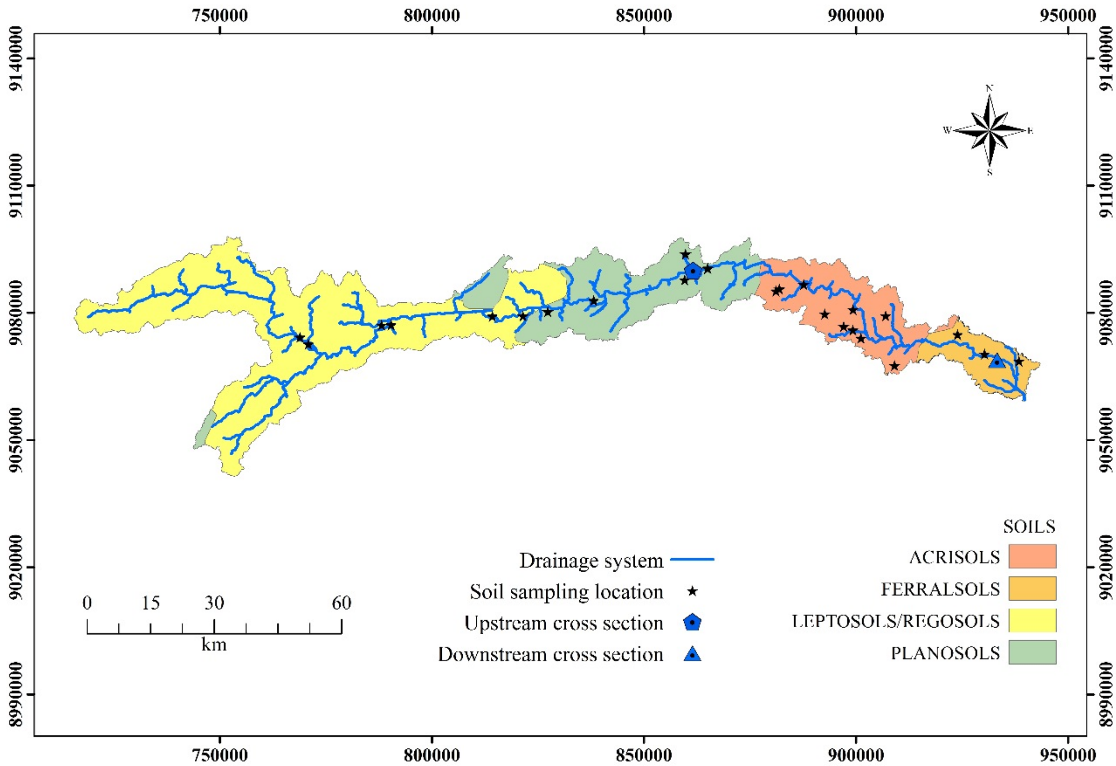

Fig. 1 Map of soils with the respective soil and sediment collection areas in the Ipojuca River watershed. Streamflow is intermittent for the first 100 km and this justifies the sampling design. Acrisols: soils with clay-enriched subsoil; Ferralsols: soils distinguished by Fe/Al chemistry; Leptosols: soils with limitations to root growth; Regosols: soils with little or no profile differentiation; Planosols: soils distinguished by Fe/Al chemistry - Stagnating water, abrupt textural difference (FAO/WRB, 2015)

2.2. Sampling sites and measurements

The background values for REEs in soils of the study watershed were determined at reference sampling sites (i.e. areas under native vegetation or with minimal anthropic influence). A total of 25 composite topsoil samples (i.e. uppermost 20 cm without the superficial organic layer and comprising 100 sub-samples) were retrieved, representing the diversity of soil classes and soil parent materials (Silva et al. 2015b).

Suspended sediment samples were collected from both the upstream (08º13’10’’ S–35º 43’09’’ W) and downstream (08º24’16’’ S–35º04’03’’ W) cross sections shown in Figure 1, using the method previously described by Silva et al. (2017). In short, these samples were collected using a US DH–48 sampler following the equal-width-increment (EWI) method in order to obtain a representative set of samples. A total of 120 samples were collected and used to create 24 composite samples. Both channel cross sections were sampled concurrently to ensure a consistent water discharge regime. The bedload was sampled using a BLH-84 sampler in the same vertical segments used to collect the suspended sediment samples. Suspended sediment (SSQ) and bedload (BQ) discharge were calculated following Horowitz (2003) and Gray (2005), respectively:

$$SSQ = \sum(SSC.Q).0.0864 \quad (1)$$

$$BQ = \sum\left(\frac{m}{wt}\right)L0.0864 \quad (2)$$

where Q is the water discharge in each vertical segment (m^3 s^{-1}), SSC is the suspended sediment concentration at each vertical (mg L^{-1}), 0.0864 is the data conversion factor to estimate t day^{-1}; m is the mass of sediment from bedload transport (g), w is the width of nozzle —US BLH-84, t is the sampling time of bedload transport (s), and L is the equivalent width (m).

The rare earth element fluxes in suspended sediments were calculated following the approach proposed by Horowitz et al. (2001). The REE flux for bedload was obtained by multiplying the amount of bed sediment crossing the site (Gray 2005) and its respective rare earth element concentration. To decrease the uncertainties related to the estimation of the REE flux, water discharge and sediment concentration were determined simultaneously during cross section measurements.

2.3. Chemical analysis

Aliquots (0.5 g each) of the soil, bedload and suspended sediment samples were grounded and passed through a 0.3-mm-mesh stainless steel sieve (ABNT nº. 50). Samples were then digested in Teflon vessels (12 mL acid solution - HNO_3:HCl, 3:1) in a microwave oven (USEPA 1998). This method extracts the REEs that are likely to become available over the medium- and long-term (Alloway 2013). This extraction is considered to represent the most ecologically- or environmentally-relevant fraction (REE contents in carbonates, sulfates, oxides and less labile phases) (USEPA 1998; Rauret et al. 1999; Rao et al. 2010; Löll et al. 2011).

Standard operation and analytical data quality assurance procedures were followed, including the use of calibration curves, high purity acids, curve recalibration, analysis of reagent blanks, and standard reference materials (2709a San Joaquin Soil and 2710a Montana I Soil; NIST 2002). All analyses were performed in duplicate. Concentrations of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu were determined by ICP-OES. Fe was also determined to provide further explanation regarding REE transport in suspended sediments. In order to improve sensitivity to REEs, we coupled a cyclonic spray chamber/nebulizer to the ICP-OES.

2.4. REE normalization and anomalies

Bed and suspended sediment samples were normalized to Post Archean Australian Shale (PAAS) (Taylor and McLennan, 1985). We selected PAAS as a standard to calculate REE anomalies since it is a common standard for fluvial sediments; also, it is comprised of sedimentary rocks that have been recycled several times under a wide range of geochemical conditions (Piper and Bau, 2013). Note that if normalized to North American Shale Composite (NASC), Post Archean Australian Shale (PAAS), World Shale Average (WSA), Upper Continental Crust (UCC), or Average Values for Sediments of World Rivers (ASSWR), the bed and suspended sediments from Ipojuca exhibit normalized curves (Figure 2) that are quite similar (Piper and Bau 2013).

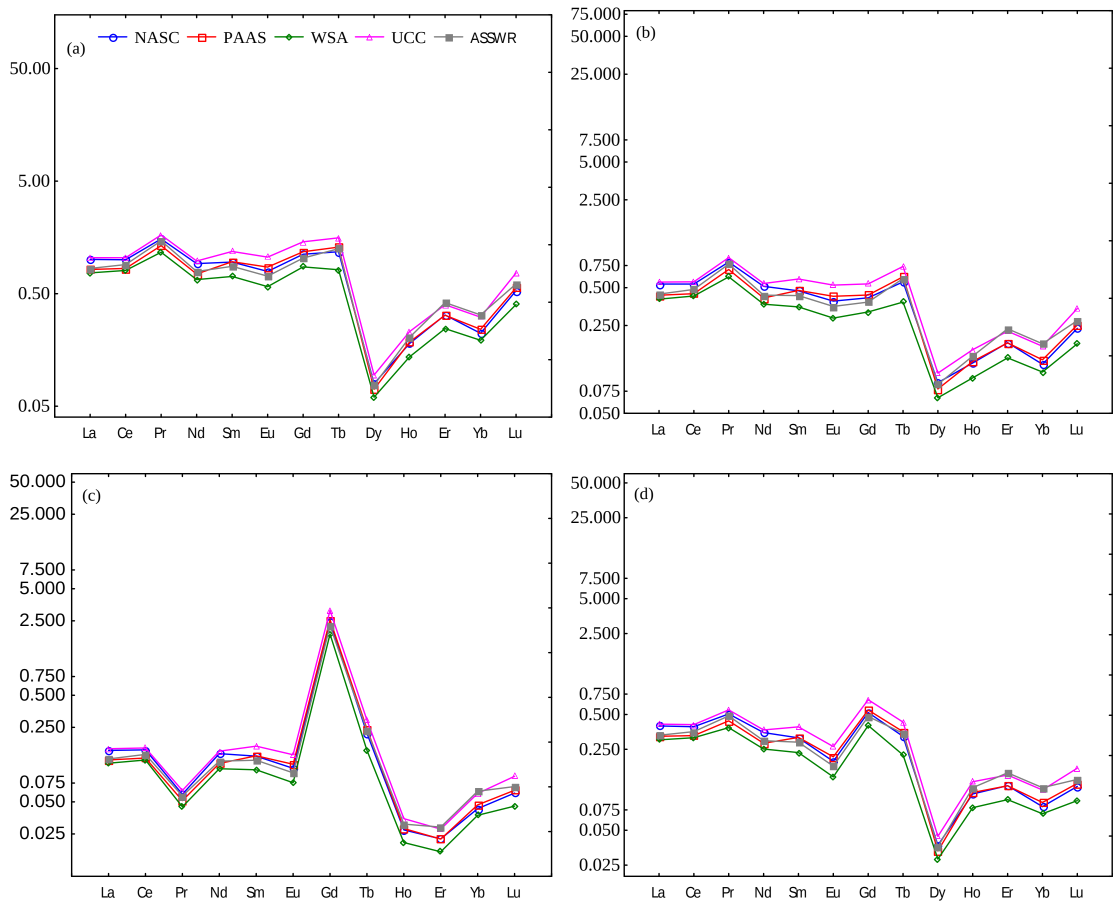

Fig. 2 Rare earth elements normalized to NASC, PAAS, WSA, UCC and ASSWR (mg kg^{-1}); (a) suspended sediments downstream; (b) bedload downstream; (c) suspended sediments upstream; (d) bedload upstream.

The Ce anomaly (Ce/Ce*), the ratio of the normalized Ce concentration to an expected normalized value from the interpolation of normalized La and Pr concentrations was calculated as:

$$Ce/Ce^* = \frac{2.[Ce]_{PAAS}}{[La]_{PAAS} + [Pr]_{PAAS}} \quad (3)$$

The Eu anomaly (Eu/Eu*) was calculated similarly, using normalized Eu concentrations and the concentrations of directly neighboring REEs (Sm and Gd) (Noack et al. 2014). The Gd anomaly (Gd/Gd*) was interpolated from the normalized concentrations of its two neighboring REEs (Sm and Tb) using the following equation proposed by Rabiet et al. (2009):

$$Gd/Gd^* = \frac{Gd_{PAAS}}{Sm_{PAAS}^{0.33} x\ Tb_{PAAS}^{0.67}}$$

(4)

The anthropogenic Gd concentration (Gd_{anth}) was calculated using the following equation proposed by Rabiet et al. (2009):

$$Gd_{anth} = Gd - Gd\ anomaly \quad (5)$$

where Gd is the normalized concentration in the sediment samples.

2.5. Granite analysis

Granite samples were coated with a 20 nm gold layer (model Q150R - Quorum Technologies) for mineral identification by scanning electron microscope (SEM) (TESCAN, VEGA-3 LMU) at an accelerating voltage of 15 kV. Afterwards, an energy dispersive X-ray spectroscopy (EDS) detector (Oxford Instrument, model: 51-AD0007) coupled with SEM was used to determine the elemental composition of the mineralogical assembly.

2.6. Statistical analysis

Descriptive and multivariate statistical techniques were carried out using STATISTICA 10 software. Principal component analysis (PCA) was used to distinguish the natural and anthropogenic origins of REEs in suspended sediment samples. Here, varimax rotation was applied to highlight the contribution of the most important variables. Statistical techniques were applied to the standardized data in order to improve interpretation and avoid misclassification.

3. Results and discussion

3.1. Concentrations of REEs in soil samples

The average REE concentrations in soils from the Ipojuca River watershed followed the order: Ce > La > Nd > Pr > Sm > Gd > Dy > Tb > Er > Eu > Yb > Ho > Lu > Tm (Table 1). The REE abundance was quite similar to that reported for a wide range of Brazilian soils (Silva et al. 2016; Paye et al. 2016). The average ∑LREE, ∑HREE and ∑REE contents were 127.15 mg kg^{-1}, 5.77 mg kg^{-1} and 132.92 mg kg^{-1}, respectively. These values were within the range reported for other soils (Tyler 2004; Hu et al. 2006; Laveuf and Cornu, 2009; Silva et al. 2016; Paye et al. 2016).

Table 1 Mean, minimum, maximum and standard deviations of REE concentrations in soil samples (n = 25) collected from the Ipojuca River watershed

	Mean	Min	Max	SD
La	29.86	10.83	75.65	16.73
Ce	59.39	17.60	134.05	32.55
Pr	11.47	3.35	27.20	6.26
Nd	21.63	5.88	44.80	10.57
Sm	4.27	1.05	7.65	1.90
Eu	0.52	0.10	1.05	0.22
Gd	3.03	0.58	7.78	1.68
Tb	0.64	0.03	1.13	0.26
Dy	0.88	0.12	1.92	0.48
Ho	0.15	0.01	0.40	0.11
Er	0.58	0.12	1.22	0.29
Tm	0.02	0.01	0.13	0.04
Yb	0.41	0.10	0.93	0.24
Lu	0.06	0.01	0.25	0.06
ΣLREE	127.15	39.76	289.85	66.71
ΣHREE	5.77	1.15	11.48	2.71
ΣLREE/ΣHREE	23.46	8.24	42.63	8.84
ΣREE	132.92	40.91	296.65	68.35
Ce/Ce*	0.71	0.52	1.11	0.11
Eu/Eu*	0.73	0.42	1.31	0.23
Gd/Gd*	0.81	0.46	1.78	0.29
$(La/Yb)_N$	7.45	1.80	30.55	7.40
$(Gd/Yb)_N$	5.16	1.55	13.50	3.16

LREE - light rare earth elements, HREE - heavy rare earth elements, REE - total earth elements; N = normalized to Post-Archean Average Australian Sedimentary rock (PAAS) (Nance and Taylor 1976). PAAS values used ($mg\ kg^{-1}$) La: 38; Ce: 80; Pr: 8.9; Nd: 32; Sm: 5.60; Eu: 1.10; Gd: 4.7; Yb: 2.8; Lu: 0.50; Dy: 4.4; Er: 2.9; Ho: 1.0; Tb: 0.77; Tm: 0.50

LREEs accounted for more than 95% of the total REEs in soil samples collected from across the Ipojuca River watershed. Ce, La and Nd, were the most abundant REEs, accounting for 44%, 22%, and 16% of the total REE concentrations, respectively (Table 1). The high concentrations of LREEs in the soil samples retrieved from the Ipojuca River watershed can be explained by the predominance of soils originating from granitic geology. This rock type includes bastnaesite in its mineralogical composition and thereby contains a large amount of REEs (Ce – 32%, La – 17%, Nd – 10%, Pr – 4%; Figure 3).

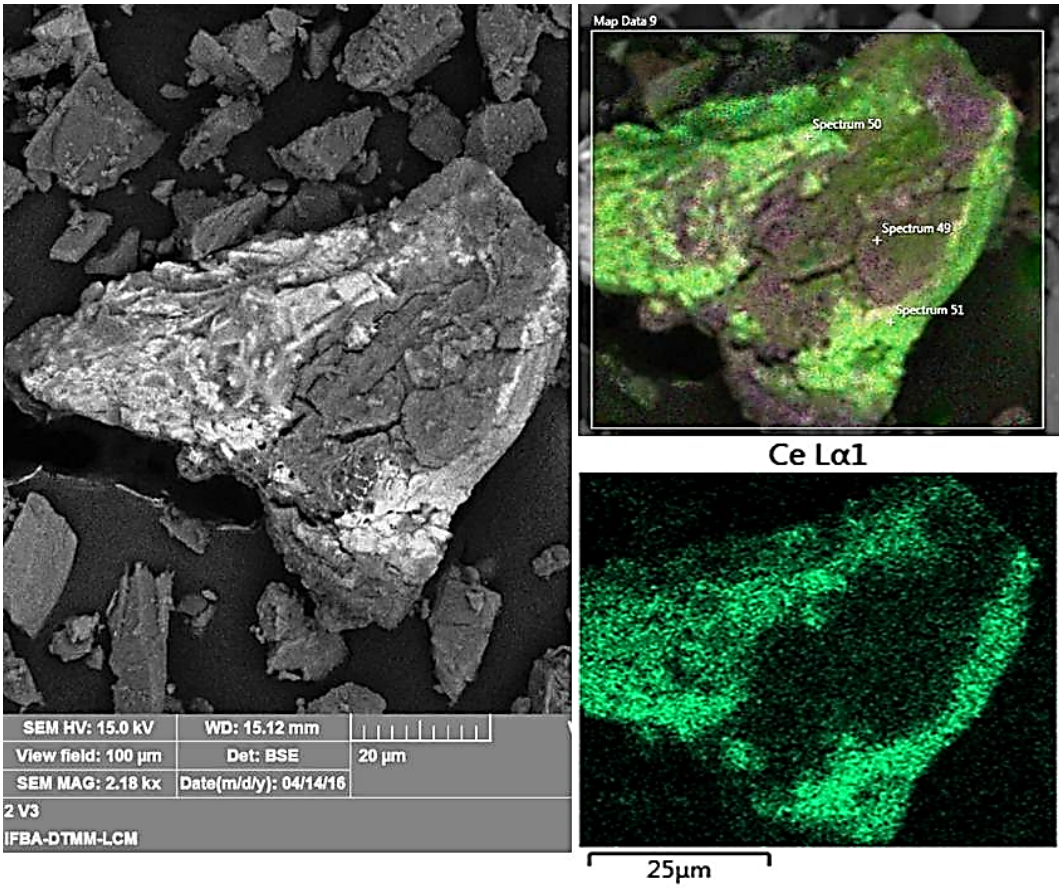

Fig. 3 Scanning electron microscope (SEM) image captured from titanite in I-type granite. Cross-section of titanite: spectrum 50 (Bastnaesite, Ce – 32%, La – 17%, F – 14%, Th – 9%, Al -8%, Nd – 8%, Si – 7%, Ca – 5%), spectrum 51 (Bastnaesite Ce – 34%, La – 19%, F - 18%, Nd – 10%, Th – 8%, Ca – 5%, Pr – 4%, Si – 2%, Al – 1%). Quantitative elemental map from a cross-section of titanite using SEM with energy-dispersive X-ray spectroscopy attached facilities (SEM-EDS)

Negative anomalies for Ce, Eu and Gd (mean values of 0.71, 0.73 and 0.81, respectively) were interpreted as indicative of Ce, Eu and Gd depletion. LREE enrichment was demonstrated by the $(La/Yb)_N$ and $(Gd/Yb)_N$ ratios (Table 1). The negative Ce, Eu and Gd anomalies might be related to the source material, indicating slow dissolution of primary minerals (Smith and Liu 2018; Silva et al. 2016; Alfaro et al. 2018; Cunha et al. 2018; Mao et al. 2017). Aubert et al. (2001) attributed the negative Eu anomaly to the slow dissolution of feldspar. Additionally, it may be also associated with the fractionation of plagioclase when Ca replaces Eu (Pepi et al. 2018; Pepi et al. 2016). Patino et al. (2003) observed that a negative Ce anomaly can develop during the weathering of basalts due to Ce^{4+} immobilization, CeO_2 precipitation or oxidative elimination of Ce^{4+} on Fe and Mn oxyhydroxides.

3.2 Concentrations of REEs in suspended and bed sediment samples

At the upstream channel cross section, the suspended sediment discharge ranged from 29.91 t day^{-1} to 150.35 t day^{-1} in the low and high water discharge periods, respectively. The suspended sediment discharge in the downstream cross section ranged from 7.67 t day^{-1} to 669.18 t day^{-1} for the same periods. The pH at the upstream and downstream cross sections ranged from 6.8-7.5, respectively.

Among the LREEs, Ce, La and Nd were present in the highest concentrations in both suspended and bed sediment samples (Figure 4). In the case of HREEs, the concentration of Gd was highest. At the upstream cross section, the ∑LREEs/∑HREEs ratio varied from 0.78 to 2.75 and 6.88 to 19.21 in the suspended and bed sediment samples, respectively. At the downstream cross section, an increase in sediment-associated REE content was observed, varying from 7.32 to 20.95 and 13.96 to 23.08 in the suspended and bed sediment samples, respectively. LREEs comprised more than 94% of the total REEs associated with the suspended and bed sediment samples (Figure 4). The maximum LREE enrichment in the sediment samples was similar to that observed in rivers draining the Himalayan mountains (Ramesh et al. 2000) and other large rivers around the world (Li et al. 2013), including those in Amazonia (Gerard et al. 2003).

LREE enrichment in the sediment samples of the Ipojuca River watershed was further supported by the $(La/Yb)_N$ ratio ranging from 2.74 to 3.79; LREEs showed a strong fractionation in the sediment samples. At the downstream cross section, the increase in the $(La/Yb)_N$ ratio reflected high erosion rates during the highest water discharge period in the Ipojuca River system. This hypothesis was also supported by the highest values of erosivity (5500 Mj mm ha^{-1} h^{-1} year^{-1} to 10,000 Mj mm ha^{-1} h^{-1} year^{-1}) reported for the coastal zone (Cantalice et al. 2009). Moreover, the widespread occurrence of soils highly susceptible to erosion could be expected to increase LREEs, as reflected by an increase of $(La/Yb)_N$ and LREE/HREE supply to the watercourse at the downstream sampling site. Thus, the removal of La and other LREEs from the drainage basin resulted in a high transport of these elements in association with the suspended sediment samples.

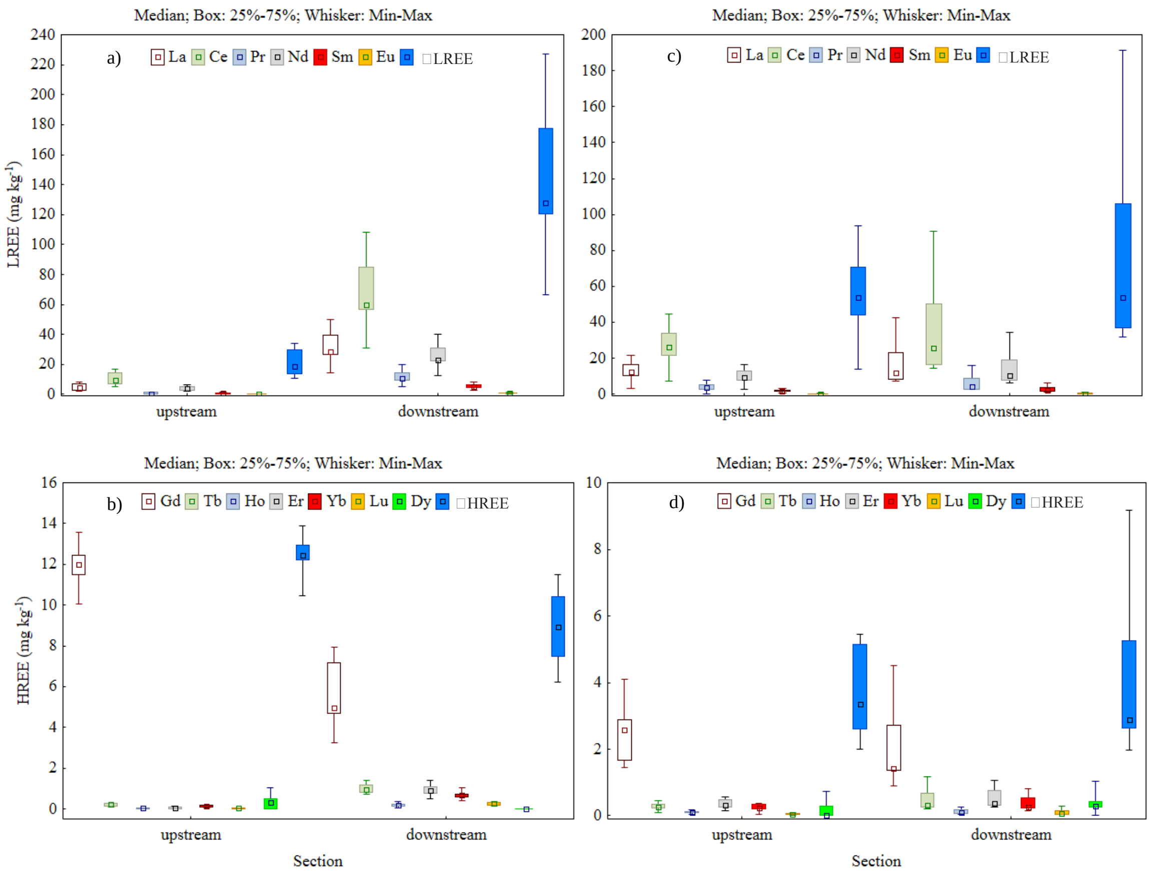

Fig. 4 Concentrations of LREEs and HREEs in suspended sediments (a and b) and bed sediment (c and d) samples

The predominance of LREEs observed for the reference soils across the Ipojuca River watershed (127.15 mg kg^{-1} ∑LREE, 5.77 mg kg^{-1} ∑HREE, 23.46 ∑LREE/HREE) is also reported for a wide range of Brazilian soils under natural conditions (Silva et al. 2016; Paye et al. 2016). LREEs accounted for more than 95% of the total REEs in the soil samples collected from across the Ipojuca River watershed. This abundance was very similar to that reported for suspended and bed sediments (94%). This finding suggests that REEs in sediment samples mainly originate from natural soil sources mobilized by soil erosion processes. In the fluvial environment, the enrichment of LREEs has been related to high adsorption on clay minerals, whereas HREEs are reported to form stable soluble complexes (Kuss et al. 2001; Caccia and Millero 2007).

Despite the high fractionation between ∑LREEs and ∑HREEs, the ∑REEs in the Ipojuca River was up to six times lower than that reported for Chinese and Taiwanese rivers (Kritsananuwat et al. 2015). In contrast, the LREEs and HREEs for the study river were up to 11 and 1.4 times higher than those reported for the Euphrates River (Kalender and Aytimur 2016). In coastal rivers, the relative enrichment of LREEs is reported to be mainly influenced by the high specific surface area of suspended sediments (Li et al. 2013) whilst HREEs have been reported to be predominantly transported in soluble, which is easily exhausted, as opposed to particulate form (**Åström** 2001; Pourret and Tuduri 2017; Kritsananuwat et al. 2015).

Except for the suspended sediment samples at the upstream cross section, negative Ce anomalies were often observed; at both cross sections, for example, Eu showed a negative anomaly, which in turn, might be indicative of the natural source suggesting this element had been supplied by the weathering of granites, a common rock type observed along the Ipojuca River watershed (Silva et al. 2015b). Intense weathering is likely to have resulted in the negative Ce anomaly (Ramesh et al. 2000; Prajith et al. 2015), while the negative Eu anomaly might be associated with sediments derived from local felsic rocks (Xu et al. 2012; Baturin et al. 2014; Odoma et al. 2015).

Beside the HREEs enrichment supported by the $(Gd/Yb)_N$ ratio ranging from 3.30 to 70.02, positive Gd anomalies were also observed (1.09-18.01) (Table 2). Such high values are in agreement with anthropogenic Gd dilution (-0.78) and the pH at the upstream and downstream cross sections ranged from 6.8-7.5, respectively. Here, the contamination triggered by wastewater is likely to have modified the REE distribution and resulted in the HREE enrichment and positive Gd anomalies (Rabiet et al. 2009). Several studies have shown that 95% of the positive Gd anomaly might by related to hospital and domestic effluents derived from wastewater treatment plants (Elbaz-Poulichet et al. 2002; Knappe et al. 2005; Bau et al. 2006; Rabiet et al. 2009; Hissler et al. 2015; Merschel and Bau 2015; Adebayo et al., 2018). The probable reason is the widespread use of stable and soluble Gd chelates as a contrasting agent in magnetic resonance imaging (de Campos and Enzweiler 2016). This anomaly is more obvious in rivers under low-discharge conditions and which drain areas with medium to high population densities (Bau et al. 2006); a typical situation encountered in the Ipojuca river.

Table 2 Average Ce, Eu and Gd anomalies, $(Gd/Yb)_N$ and $(La/Yb)_N$ ratios in suspended and bed sediment samples collected at the upstream and downstream channel cross sections

		Upstream		Downstream	
		Suspended Sediments	Bed sediments	Suspended Sediments	Bed sediments
Ce/Ce*	Mean	1.77	0.80	0.78	0.94
	Min.	1.07	0.76	0.75	0.78
	Max.	2.34	0.87	0.84	1.57
	SD	0.51	0.03	0.03	0.23
Eu/Eu*	Mean	0.08	0.89	0.81	0.49
	Min.	0.03	0.80	0.44	0.21
	Max.	0.14	1.02	1.05	0.65
	SD	0.04	0.08	0.19	0.15
Gd/Gd*	Mean	18.01	1.09	1.41	2.25
	Min.	11.96	0.99	0.80	1.43
	Max.	39.22	1.42	2.92	4.34
	SD	9.90	0.16	0.61	1.09
Gd_{anthro}	Mean	-0.78	0.96	4.50	1.27
	Min.	-14.38	-1.41	2.70	0.10
	Max.	3.04	2.20	6.60	3.83
	SD	6.36	1.09	1.21	1.21
$(Gd/Yb)_N$	Mean	70.02	3.30	5.13	7.50
	Min.	34.26	2.95	3.18	4.17
	Max.	157.87	3.97	10.80	19.66
	SD	46.34	0.33	2.27	4.75
$(La/Yb)_N$	Mean	2.74	3.17	3.36	3.79
	Min.	1.99	2.48	2.55	3.36
	Max.	3.61	3.81	4.13	4.72
	SD	0.55	0.44	0.48	0.41
LREE/HREE	Mean	1.66	18.06	16.22	14.31
	Min.	0.78	13.96	7.32	6.88
	Max.	2.75	23.08	20.95	19.21
	SD	0.74	2.95	4.48	4.20

(Ce/Ce*, Eu/Eu* and Gd/Gd*) = anomalies; Gd_{anthro} = anthropogenic Gd; SD = standard deviation.

Based on the abovementioned anomalies, REE concentrations in the study river were interpreted as being primarily derived from a natural source.

3.3. Suspended and bed sediment-associated REE fluxes

Suspended sediment-associated REE fluxes (t $year^{-1}$) at the upstream and downstream channel cross sections followed the order: Gd > Ce > La > Nd > Sm > Pr > Tb > Eu = Yb > Ho > Lu > Dy and Ce > Nd > La > Pr > Gd > Sm > Eu = Er > Yb > Tb = Dy > Ho = Lu. At both the upstream and downstream sampling sites, suspended sediment transported more than 99% of the total REE flux (Table 3). Thus, suspended sediment controls the total REE flux in the Ipojuca River watershed. Viers et al. (2009) also observed similar results studying several important rivers in the world. In contrast, bedload often transported less than 0.0007 t $year^{-1}$ of each REE and therefore did not play an important role in REE flux in the study river.

Table 3 REE fluxes (t year^{-1}) in association with suspended sediment

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb	Lu
U	0.13	0.28	0.01	0.1	0.02	0.003	0.33	0.004	0.0001	0.0007	0.001	0.003	0.0007
D	3.38	7.17	1.27	7.16	0.56	0.09	0.58	0.04	0.04	0.02	0.09	0.07	0.02

U = upstream cross section; D = downstream cross section

Except for Gd, the REE flux in the Ipojuca River mainly originated from natural sources as supported by normalization with PAAS, principal component analysis (Table 4) and scanning electron microscope (SEM) evidence (Figure 3). The latter showed a high concentration of REEs (mainly Ce and La) in soils derived from granites – one of the most predominant rock types encountered across the Ipojuca study catchment.

The Ce and Nd fluxes of ~7 t year^{-1} at the downstream cross section, were higher than those reported for Cd (0.018 t year^{-1}), Cr (2.9 t year^{-1}), Cu (2.9t year^{-1}), Hg (0.006 t year^{-1}) and As (0.9 t year^{-1}) by Silva et al. (2015a). The high Ce and Nd fluxes for the study river draws attention to the importance of including REEs in the future estimation of global suspended sediment-associated element flux. A high positive correlation between REEs and Fe in suspended sediments (REEs = 0.90 + 2.95*Fe; $R^2 = 0.95$; $p < 0.0001$) suggested that these elements were likely transported and mediated by oxyhydroxides (Johannesson et al. 2011; Shynu et al. 2011; Willis and Johannesson 2011). Interactions between REEs and Fe oxyhydroxides depend upon various processes such as adsorption, surface precipitation, oxidation and scavenging. Therefore, due to large specific surface areas, these mineral phases are very effective binding agents for REE, exerting control on their concentration and migration in aqueous systems (Davranche et al. 2004). According to Silva et al. (2015a), oxyhydroxides were also responsible for transporting high amounts of trace elements in suspended sediments of the Ipojuca watershed. Surprisingly, Gd showed one of the highest flux in association with suspended sediment at the downstream cross section; this estimate was higher than that reported for Cr (0.19 t year^{-1}), Cu (0.078 t year^{-1}), Ni (0.070 t year^{-1}), Hg (0.001 t year^{-1}) and As (0.028 t year^{-1}) by Silva et al. (2015a). This finding suggested that Gd was derived from anthropic sources. Further analysis is warranted to address the precise sources of Gd in suspended sediments of the Ipojuca River watershed.

PC1 and PC2 explained roughly 70% and 15% of the total variance in REEs in association with suspended sediment samples collected from the downstream cross section (Table 4). Here, PC1 is interpreted as reflecting REEs derived from natural sources reflecting the geological origin of the soils sampled, while PC2 is interpreted as Gd derived from anthropogenic sources.

Table 4 Loadings of REEs on significant principal components (PCs) for the suspended sediment samples collected from the downstream cross section

Variables	PC1	PC2
La	**0.99**	0.01
Ce	**0.99**	0.07
Pr	**0.99**	0.01
Nd	**0.99**	0.1
Sm	**0.98**	0.13
Eu	**0.99**	0.03
Gd	0.03	**0.95**
Tb	**0.7**	0.3
Dy	**0.86**	-0.06
Ho	**0.93**	0.24
Er	**0.92**	0.4
Yb	**0.9**	0.34
Lu	**0.82**	-0.39
Eigenvalues	10.55	2.21
EV (%)	70.35	14.78

EV = explained variance.

REEs with a high loading for PC1 were interpreted as being primarily derived from the erosion of natural sources. This interpretation is supported by the negative Ce and Eu anomalies and the LREEs / HREEs fractionation based on the $(La/Yb)_N$ and $(Gd/Yb)_N$ ratios that reduced downstream in the suspended and bed sediment samples, respectively. Gd was the only REE with a concentration related to anthropogenic activity. The major anthropogenic source of pollution in the Ipojuca River is domestic effluent – widely recognized as the major source of Gd in polluted streams (Verplanck et al. 2010; Hissler et al. 2015), although it is also likely to be derived more generally from urban/municipal wastes and the widespread use of agrochemicals along watercourses in the study catchment (SRH 2010).

4. Conclusions

Weathering processes govern the supply of LREEs and HREEs, except for Gd. The predominance of LREEs provided information about the erosion sources across the Ipojuca River watershed. LREEs comprised more than 94% of the total REE associated with suspended and bed sediment samples. Suspended sediment accounted for more than 95% of the total REE flux. The sediment-associated fluxes of Ce and Nd of about 7 t $year^{-1}$ draw attention to the importance of including REEs in future estimations of global element flux in association with suspended sediment delivery. Only the Gd concentration in sediments likely poses a threat to human health and aquatic life. Further research is warranted to investigate the forms and toxicity of sediment-associated Gd in the Ipojuca River.

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