

Geochemical behavior of Rare Earth Elements (REE) in urban reservoirs: the case of Funil Reservoir, Rio de Janeiro State, Brazil

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Abstract

Rare earth elements (REE) have unique chemical properties, which allow their use as geochemical tracers. In this context, the present study aims to assess the role of Funil Reservoir on REE biogeochemical behavior. We collected water samples upstream of the reservoir (P-01) in the city of Queluz, inside the reservoir (P-02) and downstream of Funil Reservoir (P-03) in the city of Itatiaia, RJ. In the field, physicochemical parameters were measured using a probe (pH, temperature, electrical conductivity, and dissolved oxygen). In the laboratory, water samples were filtered (0,45 μm) and properly packed until chemical analysis. Chlorophyll a concentrations were determined by a spectrophotometric method and suspended particulate matter (SPM) by a gravimetric method. Ionic concentrations were determined by ion chromatography technique and REE concentrations were determined by ICP-MS. Chlorophyll a concentrations were higher in Funil Reservoir. Ionic concentrations in Queluz (P-01) suggest anthropic contamination. The sum of REE in the dissolved fraction ranged from 2.12 to 12.22 $\mu\text{g L}^{-1}$. A positive anomaly of La in Queluz indicates anthropic contamination. The observed patterns indicate that Funil Reservoir acts as a biogeochemical barrier, modifying the fluvial transport of REE. Nonetheless, another factor that probably influences REE behavior is the algal bloom that occurs in reservoirs during the rainy season. The seasonal behavior of algae can influence REE biogeochemistry through the incorporation and release of trace metals.

1. Introduction

The unique and similar geochemical behavior of the rare earth elements (REE) results from the similar electronic configuration and makes them ideal tracers for many biogeochemical processes (Tranchida et al., 2011). In aquatic systems, determining REE concentrations associated with dissolved and particulate fractions allow inferring their rock origins, weathering, water mass circulation in the marine environment, column water scavenging and bioavailability of these elements (Goldstein and Jacobsen, 1987; Goldstein and Jacobsen, 1988; Elderfield et al., 1990; Sholkovitz, 1991; Negr el et al., 1993; Tricca et al., 1999; Ingri et al., 2000; Xu and Han, 2009).

Many studies have been conducted in recent decades to better understand REE composition and fractionation in distinct marine environments, including estuaries, oceans and hydrothermal veins (Haley et al., 2004) aquatic environments (Goldstein and Jacobsen, 1988; Elderfield et al., 1990; Dupr e et al., 1996; Gaillardert et al., 1997; Douglas et al., 1999; Viers et al., 2000; Tosiani et al., 2004; Xu and Han, 2009). Nonetheless, the geochemical controls on REE distribution in tropical environments are relatively scarce compared to their temperate counterparts. In the modern world, REE is largely employed in several technological applications owing to its unique magnetic, phosphorescent, and catalytic properties. The universal REE may result in their releasing and contamination in the environmental, while other human interventions in the landscape can alter natural erosion and runoff dynamics of rivers and estuaries, leading to changes in physicochemical properties, such as grain-size, texture, and eventually influence the distribution of trace elements (Gomes et al., 2013; Bisi et al., 2012; Patchineelam et al., 2011). The

anthropogenic factor in the natural cycling of the REE deserves better mitigation, particularly in fluvial courses modified by dams (Tang and Johannesson, 2010).

Human actions in drainage basins affect the pulse, magnitude and nature of water flow and the transport of elements in fluvial waters. As an example, human activities such as logging, agriculture and livestock production increase surface runoff and transport in drainage basins. Dams increase breath and water supply, as well as sediments and nutrients. Dams retain and transform materials, altering the natural flux of material, changing the capacity of transport (Souza et al., 2011).

Considering the influence of dams on biogeochemical cycles, this study aims to assess the hole of Funil Reservoir on REE biogeochemistry in this section of the Paraíba do Sul drainage basin. Indeed, REE has been frequently used to evaluate anthropogenic influences and sources for river waters or sediments (Benabdelkader, 2019; Bau and Dulski, 1996; Fuganti et al., 1996; Xu et al., 2012; Gallelo et al., 2013). The natural distribution of REE in water, soil, and sediment from densely industrialized and populated regions can be altered by anthropogenic influences (Nozaki et al., 2000; Elbaz-Poulichet et al., 2002; Oliveira et al., 2003; Kulaksiz and Bau, 2007; Di Leonardo et al., 2009; Rabiet et al., 2009).

2. Material And Methods

Study area: Paraíba do Sul drainage basin, in southeastern Brazil, occupies 57,000 km² and covers important Brazilian states such as São Paulo, Rio de Janeiro and Minas Gerais. This drainage basin is located in a rural and metropolitan area, with the original Atlantic forest restricted to parks and reserves. The course of Paraíba do Sul River began to be modified by fluvial transport in 1950, with the creation of Santa Cecília Reservoir, where waters from Paraíba do Sul were pumped (160 m²/s) to supply the metropolitan area of Rio de Janeiro (INEA, 2013). The hydro energy systems of Furnas are located in this drainage basin area, represented by Funil Reservoir and Light Company, which control five reservoirs: Santa Cecília, Vigário, Santana, Tocos and Lajes.

Funil Reservoir (Fig. 1) is located in Paraíba do Sul River, in the city of Itatiaia, Rio de Janeiro (State). The Granite of Funil characterizes the geology of this region. This area is 50 km² in size and corresponds to a type I granite, incipiently deformed to not deform, monzogranite composition (Chappell, 1974). This granite is characterized by the presence of magnetite, pyrite, and molybdenite. The study area is distinguished by yellow dystrophic oxisols, sedimentary alluvial soils, and podzolic lithosols. The soil of the region is also recognized by its clay minerals typical of acid soils with high Al contents and low permeability (Governo do Estado do Rio de Janeiro, 1997).

Experimental settings: We collected subsurface water samples using a Van Dorn water sampler at three different sampling points: (P-01) located 18 km upstream of the reservoir, in the city of Queluz, São Paulo (State); (P-02) located in Funil Reservoir; and (P-03) located 6 km downstream of the reservoir, in the city of Itatiaia, Rio de Janeiro (State). *In situ*, physicochemical data were measured using a probe (Hanna

Instruments – HI9829). Then, water samples were correctly packed into Teflon flasks and transported to the laboratory in ice coolers.

In the laboratory, water samples were filtered through cellulose acetate membranes (0.45 μm) to obtain the respective dissolved (< 0.45 μm) and particulate fractions (> 0.45 μm). After the filtration step, ion concentrations in dissolved fractions were determined using Ion exchange chromatography (Dionex ICS-2000 Ion Chromatograph with Dionex AS40 Automated Sampler). The anionic species measured were fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrate (NO_3^-), sulfate (SO_4^{2-}), and phosphate (PO_4^{3-}). Gradient separations were performed with KOH eluent, AS-19 column, AG-19 guard column and ASRS-300 electrolytic suppressor (all Dionex and 2 mm).

Metal concentrations were determined in a distinct dissolved fraction acidified with HNO_3 (Suprapur®, Merck) and in SPM samples by ICP-MS (Agilent 7500ce).

The chosen isotope list was: ^{27}Al , ^{55}Mn , ^{56}Fe , ^{45}Sc , ^{89}Y , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{172}Yb , ^{175}Lu , and ^{232}Th . The analysis was run with Octapole Reaction System (ORS) equipped with a low-flow MicroMist nebulizer connected to a refrigerated quartz Scot mist chamber. Nickel samplers and skimmer cones were used. The internal standard used was Rhodium. The determination of Fe isotope m/z 56 was made using the ORS system with the introduction of He gas for the elimination of ArO interference.

All reagents used in Ion Chromatography and ICP-MS analysis were analytical grade. The solutions were prepared with ultrapure water (resistivity < 18.2 $\text{M}\Omega\text{ cm}$) obtained from a Milli-Q Reference System (Millipore).

The acetate cellulose membranes with particulate fraction were designed to quantify the SPM by using gravimetric method (Carmouze, 1994). Chemical determination of chlorophyll a in filters was performed by a spectrophotometric method (Shimadzu UV-1800) after 90% acetone extraction (Carmouze, 1994).

3. Results And Discussion

Table 1 summarizes all physicochemical data. Overall, a similar electrical conductivity and SPM concentration behavior was observed from upstream (P-01) to downstream (P-03). Chlorophyll a concentration detaches from the other physicochemical data with concentrations four times occurring in Funil Reservoir (P-02). Furthermore, according to CONAMA 357/2005, values of chlorophyll a concentration within Funil Reservoir (P-02) are above the reference value. This behavior probably reflects seasonal algal blooms in Funil Reservoir, as reported by other authors (Barbosa, 2005; Novo et al., 2006; Rudorff, 2006; Londe, 2008; Costa, 2009; Vidal, 2012).

Table 1. Physicochemical parameters, concentration of suspended particulate matter (SPM) and chlorophyll a at different ingestion points.

		Temperature (°C)	pH	Conductivity (µS/cm)	DO (mg/L)	TDS (mg/L)
<i>Rainy Season</i>						
Queluz	Average	23.67	6.9	74.67	5.58	37.33
	SD	2.31	0.29	14.53	1.65	7.31
Funil	Average	25.20	8.0	74.50	6.02	37.33
	SD	2.66	1.12	5.05	1.67	2.88
Itatiaia	Average	23.67	6.7	70.17	3.91	42.50
	SD	2.10	0.23	10.52	0.85	17.33
<i>Dry Season</i>						
Queluz	Average	20.49	6.66	91.00	5.96	45.60
	SD	1.52	0.24	8.92	1.49	4.41
Funil	Average	22.43	7.60	74.66	7.09	37.66
	SD	1.58	1.50	6.97	1.70	3.44
Itatiaia	Average	20.77	6.90	81.80	5.48	41.20
	SD	1.94	0.18	6.83	1.07	3.34

Ion concentrations are presented in Table 2. Comparing the three sample stations, the high concentrations of chloride nitrate and sulfate found in Queluz (P-01) suggest an anthropic influence, despite all values being within the standards established by Brazilian environmental legislation (CONAMA 357/2005). In Funil Reservoir (P-02), ionic concentrations diminish, likely due to ion incorporation by algae or water column scavenging, which increases seasonally in the reservoir (Barbosa, 2005; Novo et al., 2006; Rudorff, 2006; Londe, 2008; Costa, 2009; Vidal, 2012).

Table 2. Ionic concentrations at sampling points, expressed in mg.L⁻¹.

	Fl ⁻	Cl ⁻	Br ⁻	NO ₃ ⁻	PO ₄ ⁻³	SO ₄ ⁻²
Queluz	0.075	5.710	0.036	3.520	0.057	10.300
Funil	0.080	4.410	0.010	2.040	0.010	7.307
Itatiaia	0.072	4.440	0.010	2.700	0.010	6.610

In line with previous studies (Gomes et al., 2013), iron and aluminum concentrations in the dissolved phase (Fig. 2) seem to be derived from the weathering of aluminosilicate mineral assemblies of the material from the middle Paraíba do Sul watershed geology. These high concentrations are probably due to the entrainment of soil and erosion of fluvial margins. However, the lowest concentrations of Fe, Al and Mn in Funil Reservoir (P-02) indicate that this reservoir acts as a biogeochemical barrier, promoting the removal of these elements via sorption on surface particles and subsequent decantation (Von Sperling, 1990). Concentrations of Fe, Al and Mn in Itatiaia (P-03) indicate the influence of drainage basin washing, as was found in Queluz (P-01) (Gomes et al., 2013).

Evaluating the SPM fraction (Fig. 3), Al concentration was more elevated upstream (P-01) and downstream (P-03) of the reservoir, and there is a significant reduction of Al inside Funil Reservoir (P-02). Accordingly, Al data probably indicates clay mineral deposition inside the Funil Reservoir (P-02).

The REE concentrations in the dissolved fraction in the Funil Reservoir sample (Table 3) were four to six times higher than other sample stations. In all of them, light REE concentrations were higher than heavy REE, especially in Funil Reservoir (P-02). Such a pattern agrees with experimental studies conducted in lacustrine environments, where hydrodynamical conditions favor a depletion of medium and heavy REE typically observed (Sultan and Shazili, 2009).

Table 3. Concentrations of rare earth elements associated with the dissolved fraction at different sampling points.

	Queluz	Funil	Itatiaia
La	0.35	8.87	0.52
Ce	0.84	0.35	1.04
Pr	0.098	0.06	0.14
Nd	0.35	0.05	0.052
Sm	0.062	0.06	0.089
Eu	0.05	0.05	0.05
Gd	0.065	2.48	0.095
Tb	0.05	0.05	0.05
Dy	0.05	0.05	0.057
Ho	0.05	0.05	0.05
Tm	0.05	0.05	0.05
Yb	0.05	0.05	0.05
Lu	0.05	0.05	0.05
ΣREE	2.12	12.22	2.76

Total REE concentration normalized by PAAS (Post Archean Australian Shales) in water samples reveals geochemical fractionation, characterized by a slight enrichment of heavy REE (Fig. 4).

Together, particulate and dissolved fractions evidence processes occurring in the water column of the Funil Reservoir that modify the dynamics of these elements. The formation of aqueous complexes, biological uptake and adsorption to colloids are potential processes responsible for REE fractionation between dissolved and particulate phases (Ronnback et al., 2008).

In dissolved fractions, REE curves overlap in shape and magnitude, while in the SPM, Funil reservoir samples distinguish for neighbor sampling stations with lower normalized values. This pattern could be explained by two reasons: the first is the incorporation of light REE by microalgae, that develop seasonally in Funil Reservoir according to many authors (Novo et al., 2004; Barbosa, 2005; Rudorff, 2006; Londe, 2008; Costa, 2009; Vidal, 2012); and the second is particle sedimentation in Funil Reservoir due to hydrodynamic processes and physicochemical conditions.

Algae are great accumulators and have been experimentally used for REE recovery, which are metals with high technological value destined for the use of high technology industries. The metals bioavailability for algae depends upon many factors: physicochemical parameters, pH, salinity, luminosity, SPM concentration, and organic matter contents (Karez et al., 1994). Furthermore, according to Karez et al. (1994), competition for dissolved metals in algal cell sites depends on biological factors.

Notwithstanding, Valittuto et al. (2006) demonstrated that biota have a keyhole in REE removal from the water column. Other authors identified correlations between REE concentrations in the dissolved phase and biota. In this way, some authors identify that the capacity of REE absorption from the soluble phase is probably related to physicochemical similarities between REE and Ca, which is an essential element for plants (Lakatos et al., 1999).

Observing the following graphic (Fig. 5) we can identify two anomalies: Tm and Eu. Tm anomaly could be justified by the geological settings of the study area, whose minerals are sources of REE, and thus, reflect weathering activity in drainage basins (Pereira et al., 2001).

According to Sultan and Shazili (2009), Eu anomalies are observed in most rivers and reflect the redox potential chemistry of this element (Ryu et al., 2007). This anomaly was higher in Funil Reservoir (P-02) when compared with other sample points; consequently, in Funil Reservoir (P-02) Eu is released and associated with the dissolved phase. We hypothesize that algal blooms leading to anoxic conditions in sediments may favor the Ce releasing through water pore diffusion.

Positive anomalies of Ce occur typically in tropical environments, where high temperatures are constant throughout the year, combining with precipitation, according to Sultan and Shazili (2009) (Table 4), probably due to reducing conditions that favor Ce anomalies. And analyzing La anomalies, high positive anomaly of La found in Queluz (P-01) suggests anthropic contamination (Bau, 1999).

Table 4. Occurrence anomalies of rare earth elements in the study area.

	Queluz	Funil	Itatiaia
Ce	1.157	1.315	1.05
Eu	1.036	1.157	1.061
La	54.083	5.407	13.287

4. Conclusion

According to the presented results, Funil Reservoir acts as a biogeochemical barrier, modifying the fluvial transport of rare earth elements associated with particulate and dissolved fractions of waters from the middle Paraíba do Sul River. Another factor that might influence REE biogeochemical behavior is the seasonality of algae. These algae can act through the uptake and release of REE, which behave exactly like other metals. Moreover, hydrochemical conditions can influence the dynamics of REE along this section of Paraíba do Sul River. The positive La anomaly suggests anthropic influence in Queluz (P-01).

Declarations

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Author contribution statement:

J.M.C.O.S.N. designed the study and prepared the figures and tables to present the data. J.M.C.O.S.N., S.R.P. and D.F.A. wrote the main text of the manuscript. All chemical analyses were performed by J.M.C.O.S.N., J.M.O.G. and A.C.A. The data analyses were performed by J.M.C.O.S.N. and S.R.P. The entire manuscript was reviewed by S.R.P., J.M.C.O.S.N., J.M.O.G. and D.F.A.

Competing Interest statement in your manuscript:

I declare that the authors have no competing interests as defined by Springer, or other interests that might be perceived to influence the results and/or discussion reported in this paper.

Data Availability statement:

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Figures

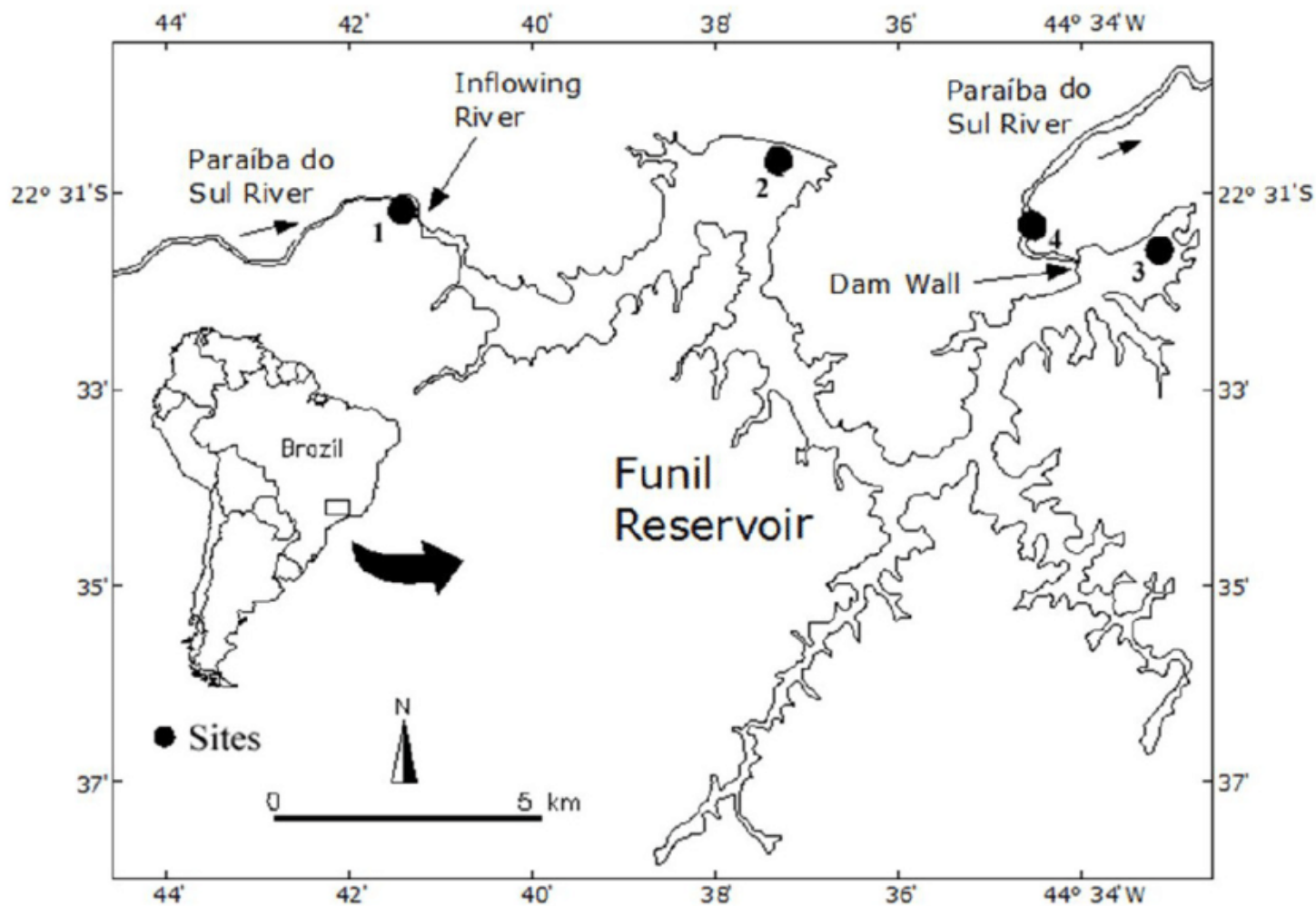


Figure 1

Map of the Funil reservoir indicating study area zones: 1. River upstream from the reservoir, 2. Upper reservoir, 3. Lower reservoir, and 4. River downstream of the reservoir (Araújo et al., 2017).

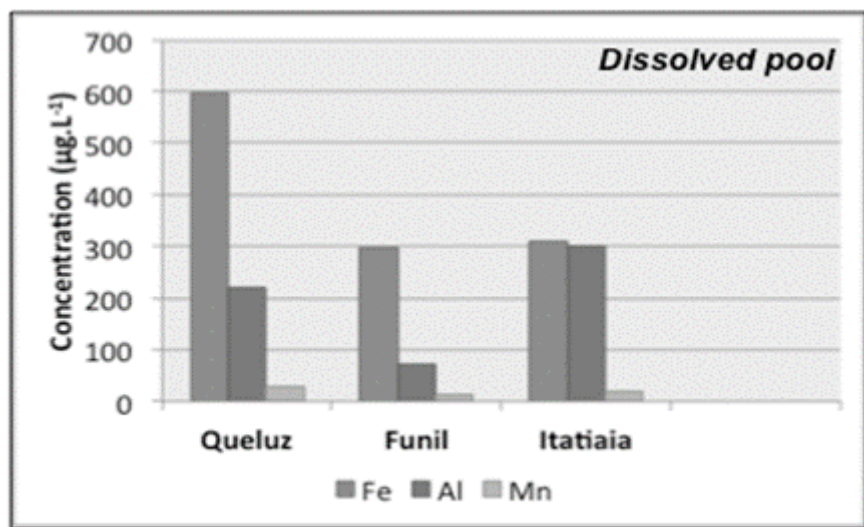


Figure 2

Comparative of Fe, Al, Mn concentrations (mg.L^{-1}) associated with dissolved pool in all sample points.

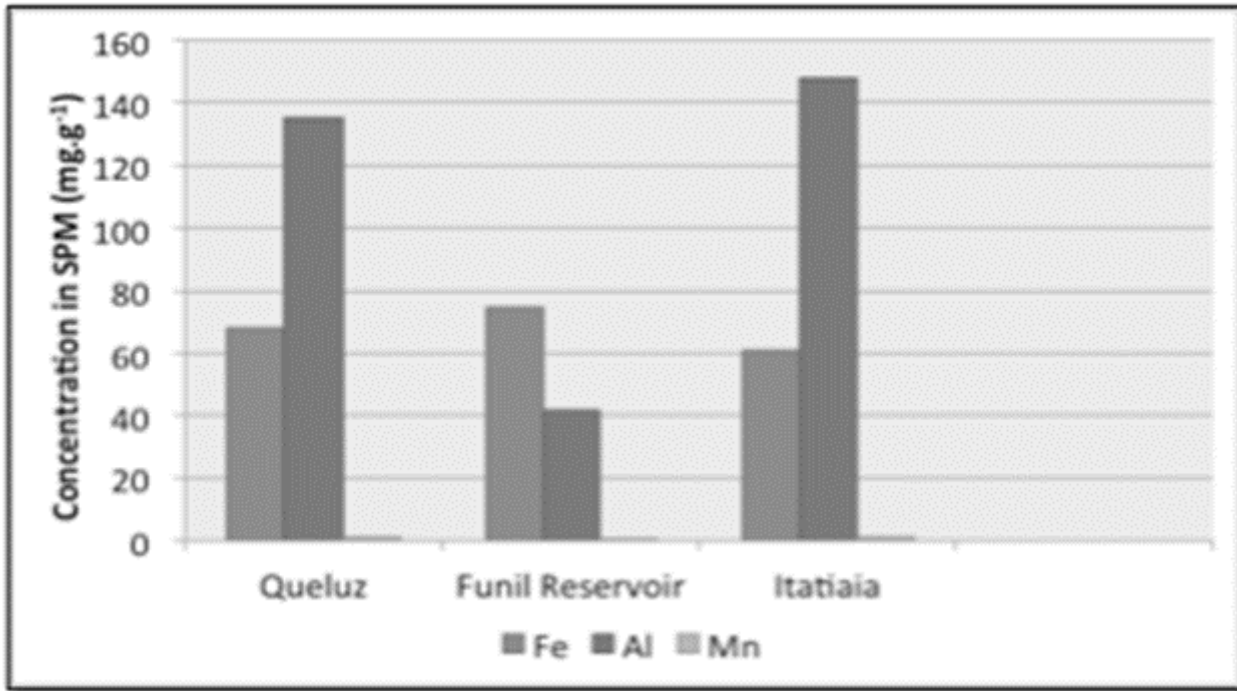


Figure 3

Comparative of Fe, Al, Mn concentrations (mg.g^{-1}) associated with particulate phase in all sample points.

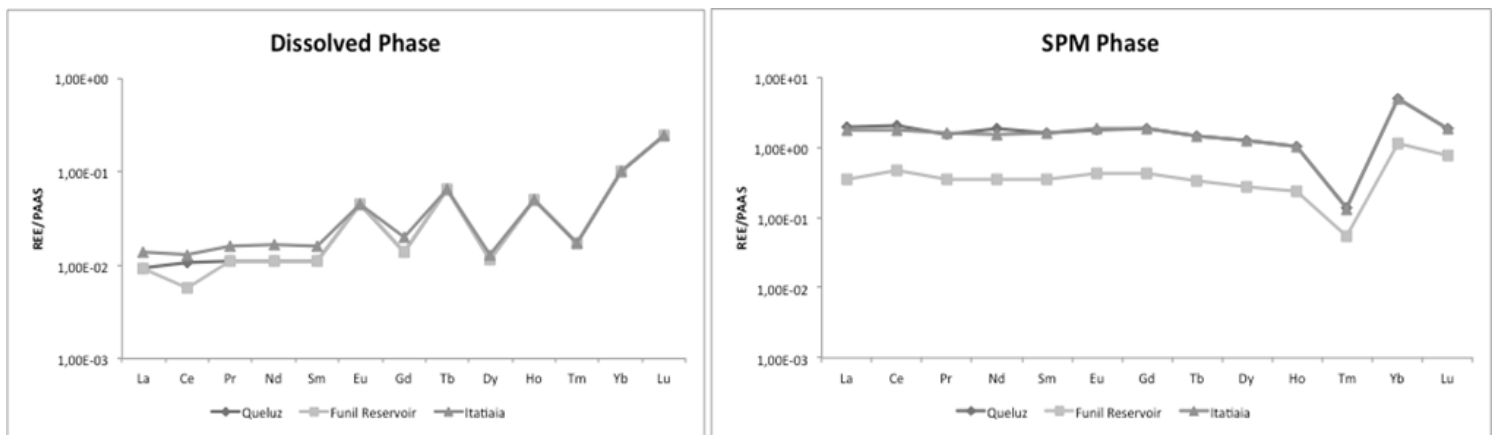


Figure 4

Concentrations of rare earth elements (REE) ($\mu\text{g.L}^{-1}$) associated with dissolved phase and SPM phase along the study area.

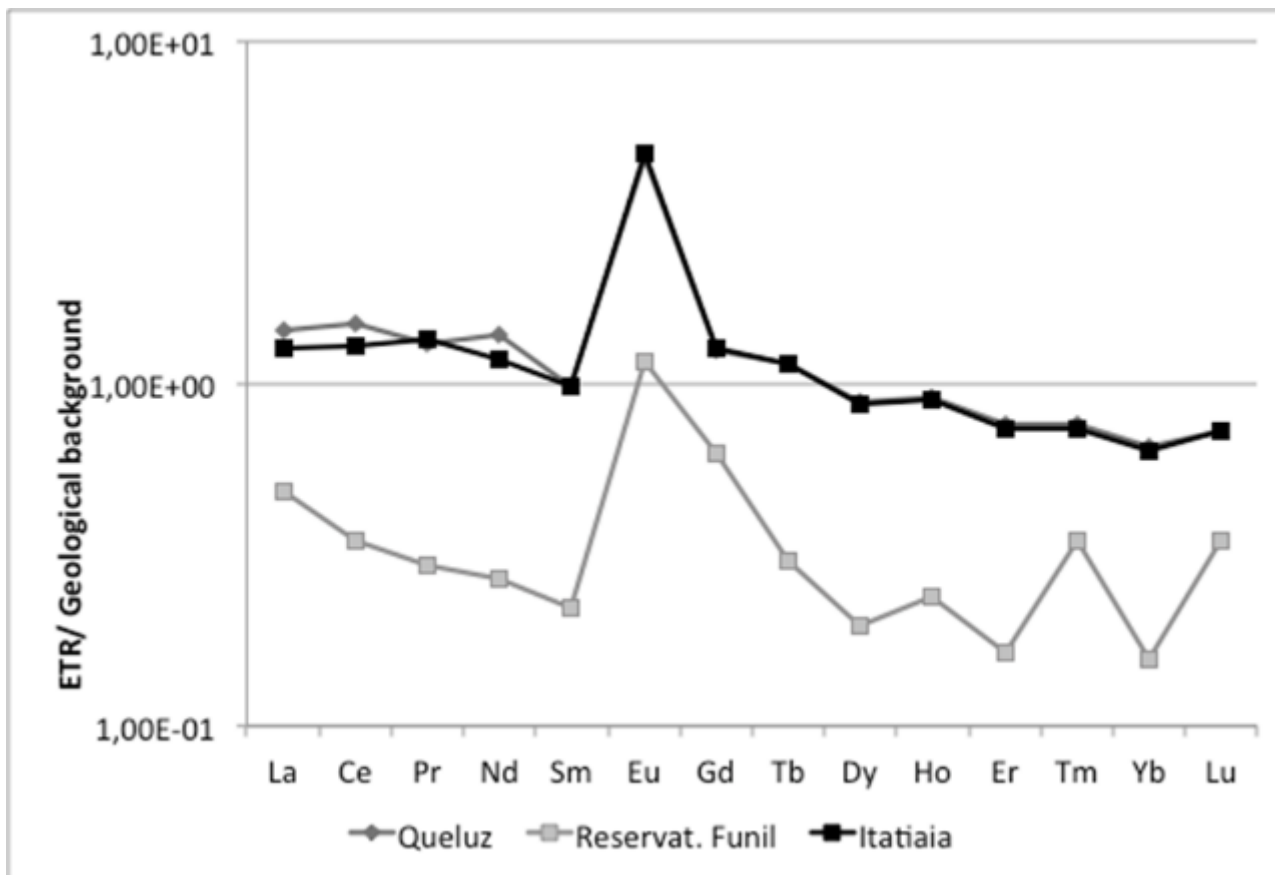


Figure 5

Rare earth elements (REE) concentrations normalized by PAAS associated with dissolved pool (left side) and particulate matter (right side).