

# Assessing rare-earth elements and anthropogenic gadolinium in water samples from an urban artificial lake and its tributaries in the Brazilian Federal District



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## ARTICLE INFO

### Keywords:

Rare-earth elements  
Lanthanides  
Gadolinium anomaly  
Cerium anomaly  
SLRS-6 CRM  
Emerging contaminants

## ABSTRACT

This work highlights the rare earth elements (REE) dynamic in water samples from Paranoá Lake and its tributaries in the Brazilian Federal District. Variation of anthropogenic Gd in Paranoá Lake after a 4 years laps time, characterization of regional REE background levels and possible contaminations in the tributaries were studied. REE were assessed by thulium (Tm)-spiked solid-phase extraction followed by ICP-MS. Method validation was performed using synthetic samples and the SLRS-6 reference material. The method was efficient to remove the interfering Ba (> 99.99%) with REE recoveries (SLRS-6) varying from  $81 \pm 6$  (Tb) to  $105 \pm 4\%$  (Dy). In the Paranoá Lake, water samples were enriched for high and middle REE ( $\text{Pr}_{\text{SN}}/\text{Yb}_{\text{SN}}$  varied from 0.15 to 0.39,  $\text{Dy}_{\text{SN}}/\text{Pr}_{\text{SN}}$  ranged from 1.10 to 2.25,  $\text{Dy}_{\text{SN}}/\text{Yb}_{\text{SN}}$  varied from 0.27 to 0.45) while the tributaries at Southern part of lake presented an enrichment of lower REE ( $\text{Pr}_{\text{SN}}/\text{Yb}_{\text{SN}}$  1.24 and 2.30;  $\text{Dy}_{\text{SN}}/\text{Pr}_{\text{SN}}$  0.80 and 0.49). Gd anomalies were observed in the Paranoá Lake samples, with high levels of anthropogenic Gd ( $\text{Gd}_{\text{anth}}$ ) nearby two wastewater treatment plants ( $33.6$  and  $22.1 \text{ ng L}^{-1}$ ). No significant increase in total anthropogenic Gd stock was observed compared to 2013 data. Positive Ce anomaly observed in the dissolved phase may be associated to mineral colloids (Fe or Mn oxy-hydroxides) or agricultural supplies, while positive La anomaly registered in waters requires further studies.

## 1. Introduction

Rare-earth elements (REE) belongs to the lanthanide series, that shows similar properties, such as high electropositivity and prevalence of the oxidation state  $3+$ , except in some cases for cerium (Ce) and europium (Eu) [1]. REE have been used as tracers of geological processes [2–7] because these elements can form stable complexes with organic and inorganic ligands, distinguishing the geological fingerprint of different rocks, minerals, or water bodies. This formation of REE complexes are related with the tetra-d effect, which presents a decay of the third ionization energy of Gd and Lu, and in the halfway through Nd to Pm and Ho to Er as the subsequent filling of the electrons in the orbital “f” increases as the atomic number became higher [8].

In geochemical studies, REE are commonly separated in three groups according to their masses: light REEs (LREE) formed by La, Ce, Pr, and Nd; middle REE (MREE), consisting of Sm, Eu, Gd, Tb and Dy; and heavy REE (HREE), that comprise the elements Ho, Er, Tm, Yb and Lu [9]. The distribution of these elements in waters is influenced by environmental conditions that control their surface/solution interactions, such as the pH, dissolved oxygen, the formation of colloids and the salinity [10]. REE determination in natural waters are non-trivial as their concentration levels are close to the detection limits of Inductively Coupled Mass Spectrometers (ICPMS) and as severe plasma-generated polyatomic interferences can lead to false apparent anomalies [11]. As a result, sample pre-concentration and interference attenuation/correction methods are often necessary. Besides, there is a lack of Certified

**Abbreviations:** REE, rare-earth elements; LREE, light REE; MREE, middle REE; HREE, heavy REE; GBCA, Gd-based contrast agents; WWTP, wastewater treatment plant; BB, Bananal Branch; TB1, Torto Branch 1; TB2, Torto Branch 2; RB, Riacho-Fundo Branch; LD, Lake Dam; BC, Bananal Creek; TC, Torto Creek; RC, Riacho-Fundo Creek; GC, Gama Creek; NW-WWTP, north wing WWTP; SW-WWTP, south wing WWTP; E-WTP, emergency water treatment plant; F-WTP, future WTP; SPE, solid-phase extraction; ICP-MS, inductively coupled plasma mass spectrometry; PAAS, post-Archean Australian Shale; CRM, certified reference material; LOQ, limit of quantification; SN, shale-normalized; MRI, magnetic resonance imaging

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<https://doi.org/10.1016/j.microc.2019.04.055>

Received 2 November 2018; Received in revised form 31 March 2019; Accepted 6 April 2019

Available online 23 April 2019

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Reference Waters available for REE and interlaboratory calibration is a common practice for measurements validation [12,13].

Several studies confirm the potential use of Gd as a tracer of anthropic activities in aquatic systems [14–21] due to the use of Gd-based contrast agents (CABGd) in clinical analyzes using nuclear magnetic resonance imaging [22]. The presence of REEs in Brazilian waters was already reported on studies focusing on the characterization of rivers and the lithology of hydrographic catchments [7,10,23–27]. Few studies were carried out to evaluate the presence of anthropogenic Gd in Brazilian waters [28–30]. In the Paranoá Lake, Merschel et al. identified the presence of anomalous Gd due to discharge of effluents from two wastewater treatment plants (WWTPs) of Brasília. However, samples from the tributaries of Paranoá Lake were not analyzed that exclude the possible sources of contamination from the drainage areas occupied by residential, agricultural and environmentally protected areas. Paranoá Lake is used for many activities, such as recreational, fishing, hydro-electrical, wastewater disposal, and for drinking water supplying since October 2017.

This work revisits REE distribution in Paranoá Lake including its main tributaries: Riacho-Fundo, Bananal, Torto, and Gama creeks. The aims of this study were to apply and validate a suitable Tm spiked REE analytical method in order to 1) assess the evolution of anthropogenic Gd in Paranoá Lake after a 4 years laps time and to 2) characterize regional REE background levels and possible contaminations in these tributaries.

## 2. Material and methods

### 2.1. Chemicals and reagents

All reagents were of analytical grade or superior. Hydrochloric and nitric acids (Merck, Darmstadt, Germany) were purified twice by sub-boiling distillation, firstly using a Distillacid™ BSB-939-IR system (Berghof, Eningen, Germany) and then using a two-bottle assembly made of PFA. Individual standards of Ba and REE (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) were purchased from Accustandard (New Haven, USA) in 2% HNO<sub>3</sub> solution. Ultrapure water was produced in a Milli-Q Academic system (Millipore, Bedford, USA) and used for rinsing plastic materials and for the preparation of diluted acid solutions. A multi-element stock solution containing 100 µg L<sup>-1</sup> of each analyte was prepared in a 0.5 mol L<sup>-1</sup> double-distilled HNO<sub>3</sub> solution. Working solutions were prepared by successive dilutions of the stock solution.

### 2.2. Study site and sampling

Fig. 1 shows the location of the sampling points in Paranoá Lake and its tributaries.

At Paranoá Lake, the sampling point at the Bananal Branch (BB) and Riacho-Fundo Branch (RB) were located immediately after the North-Wing and South-Wing wastewater treatment plants (NW-WWTP and SW-WWTP), respectively. Two sampling points were located in the Torto Branch, upstream (TB1) and downstream (TB2) of the Emergency water treatment plant (E-WTP) of Paranoá Lake, a compact plant in operation since October 2017 to provide an emergency supply for drinking water to the region [31]. Finally, a sampling point nearby the lake dam (LD) was located in the proximities of the Future water treatment plant (F-WTP) of the Paranoá Lake.

The sampling point at Bananal Creek (BC) is located in a more preserved region including the area of the National Park of Brasília [32] whereas Torto Creek (TC), also at the north, passes through an area with agricultural activities and some urban agglomerations. At the south, Riacho-Fundo Creek (RC) is considered the most urban polluted [33] tributary while Gama Creek (GC) passes through a mix of preserved, agricultural, and residential areas [32]. Sampling points in all tributaries were located in accessible areas as close as possible to the

creek outfall.

Surface water samples were collected in September 2017. Sampling was carried out using pre-cleaned polyethylene bottles, by direct immersion, or with the aid of a polyethylene bucket previously rinsed with the sample water on site. Sample pH and conductivity were determined on site using portable water analyzers (340i, WTW, Weilheim, Germany and Cond 6+, Eutech Instruments, Singapore, respectively). Immediately after the sampling, bottles were individually transferred to plastic bags to avoid cross contamination and maintained under refrigeration until transport to the laboratory. Samples were kept refrigerated for two days before further preparation steps.

### 2.3. REE extraction and quantification

In the laboratory, samples were filtered through 0.22 µm pore-sized cellulose acetate membranes (47 mm, Millipore, Bedford, USA) in a polycarbonate filtration device (Nalgene, Rochester, USA). Filtered samples were transferred to polyethylene bottles, acidified to pH 2 with a double-distilled HCl 6 mol L<sup>-1</sup> solution, and stocked under refrigeration (4 °C) until the extraction procedure. All labware and bottles were cleaned with 10% double-distilled HNO<sub>3</sub> and ultrapure water. After each sample filtration, the device was thoroughly washed with ultrapure water, rinsed with double-distilled HCl (6 mol L<sup>-1</sup>) and with ultrapure water.

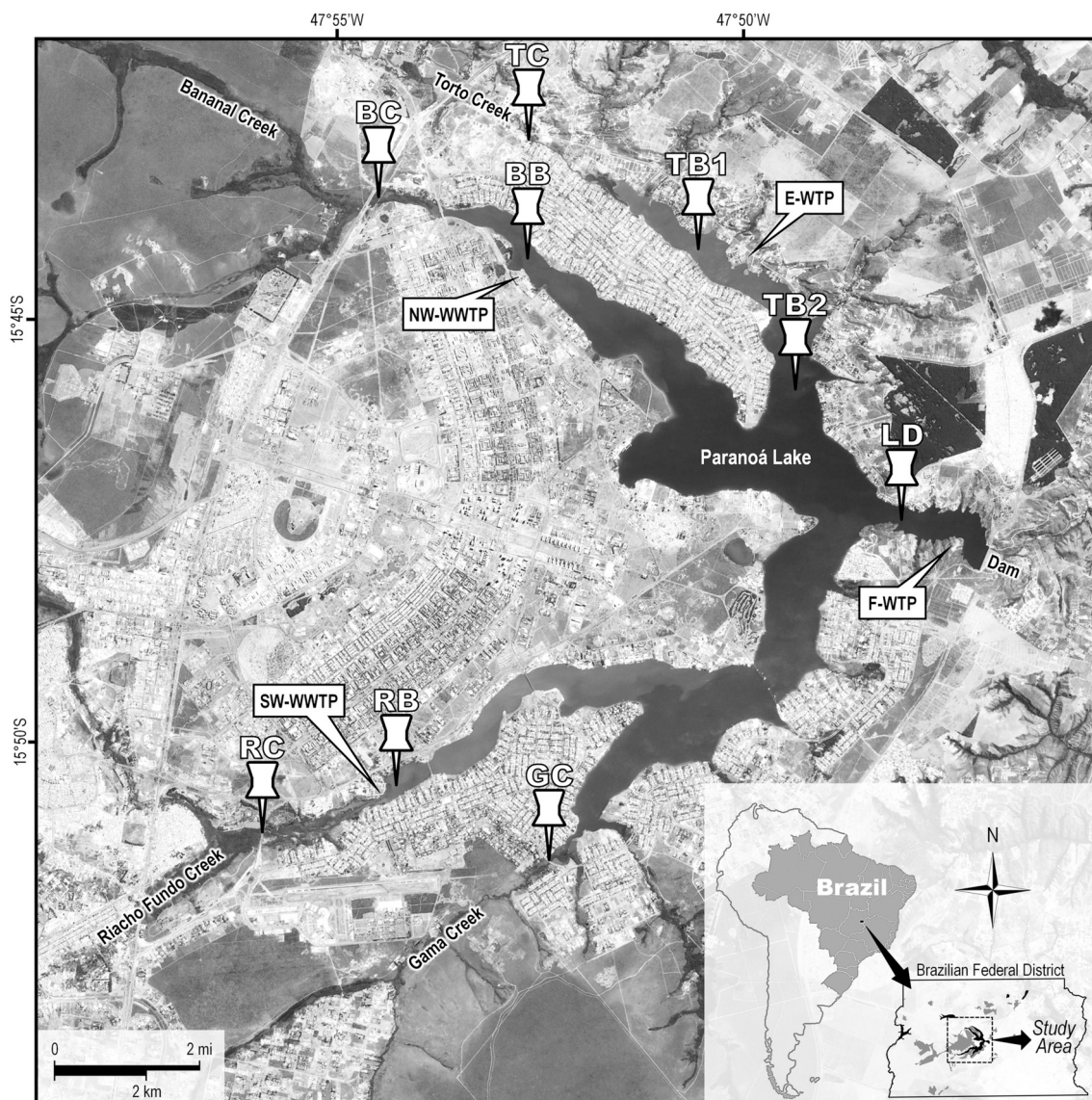
The extraction of REE from the filtered samples was performed using the method proposed by Shabani et al. [34] with some modifications, detailed in the Supplementary Material. REE were determined using an inductively coupled plasma mass spectrometer (ICP-MS) equipped with concentric nebulization and an octopole reaction system (Agilent 7500ce, Tokyo, Japan). Instrumental parameters used during the analysis are available in Table S1 of the Supplementary Material. The elements <sup>135</sup>Ba, <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>145</sup>Nd, <sup>149</sup>Sm, <sup>153</sup>Eu, <sup>158</sup>Gd, <sup>159</sup>Tb, <sup>163</sup>Dy, <sup>165</sup>Ho, <sup>166</sup>Er, <sup>169</sup>Tm, <sup>172</sup>Yb, and <sup>175</sup>Lu were quantified by internal calibration with In. Analytical curves were prepared using eight points with concentrations varying between 0.001 and 25.0 µg L<sup>-1</sup> for REE and from 0.1 to 10 µg L<sup>-1</sup> for Ba quantification. Due to the wide working range, analytical curves were presented and used on the logarithmic scale ( $\log y = b \times (\log x) + a$ ), where  $y$  was the intensity of the analytical signal,  $x$  the concentration of the analyte,  $b$  the slope and  $a$  the intercept. Correlation coefficient of the analytical curves varied between 0.997 and 0.999 for all elements, except for Lu (0.980).

Mathematical correction for isobaric interferences was automatically performed by the equipment software. The oxides interferences were corrected using an aqueous solution containing 10 µg L<sup>-1</sup> of the lanthanides (Ln) La, Ce, Pr, Nd, and Sm, and a second solution containing 10 µg L<sup>-1</sup> of Eu, Gd, and Tb, both prepared with double-distilled HNO<sub>3</sub> 0,5 mol L<sup>-1</sup>. The production ratios of lanthanide oxides (LnO<sup>+</sup>/Ln<sup>+</sup>) in both solutions (Table S2 of the Supplementary material) were used to correct the La oxides interferences as proposed by Aries et al. [35].

Two approaches for REE quantification were employed: one based on the addition of Tm as a surrogate standard [36–38], and other without Tm addition. The addition of Tm produces an anomaly in the REE patterns that serves as a surrogate internal standard for the quantification of the remaining REE [38] as shows the Eq. (1).

$$C_{REE}^* = \frac{C_{REE} \times C_{Tm}^{Add}}{C_{Tm}} \quad (1)$$

In Eq. (1),  $C_{REE}^*$  is the REE concentration calculated with the addition of Tm,  $C_{REE}$  is the REE concentration obtained from analytical curves (with internal standardization),  $C_{Tm}^{Add}$  is the concentration of Tm added to the sample and  $C_{Tm}$  is the concentration of Tm calculated by the analytical curve. As the concentration of Tm in the sample is altered, it is still possible to estimate the levels of natural Tm by the



**Fig. 1.** Map showing the sampling points in Paranoá Lake (BB: Bananal Branch, TB1 and TB2: Torto Branch, RB: Riacho-Fundo Branch, LD: Lake Dam) and its tributaries (BC: Bananal Creek, TC: Torto Creek, RC: Riacho-Fundo Creek, and GC: Gama Creek). The locations of the wastewater treatment plants at the North Wing (NW-WWTP) and South Wing (SW-WWTP) are also shown together with the Emergency and the Future water treatment plants (E-WTP and F-WTP, respectively). Water flows from west to east.

interpolation of its neighboring REE considering a geochemical standardized distribution of these elements in a sample according to Barrat et al. [36].

Apart from the REE quantification strategy, the distribution of these elements in the natural water samples was normalized with REE levels in the Post-Archean Australian Shale (PAAS) average values according to McLennan [39]. This procedure allows identifying the REE distribution patterns as well as anomalous concentrations [40].

### 3. Results and discussion

#### 3.1. Method validation

In order to verify the method accuracy, the solid phase extraction and interferences correction efficiencies an in-house synthetic solution reproducing natural REE concentration levels and the intercalibrated CRM SLRS-6 river solution were analyzed.

The synthetic natural water was produced in the laboratory to verify the method accuracy and to investigate the matrix effects due to the

interference. Five replicates taken from the same synthetic sample (1.0 L) were prepared in double-distilled HCl (pH 2) with REE and Ba concentrations similar to those reported by Gaillardet et al. [41], referring to the world average concentrations of trace elements found in rivers (Table S3). The removal of Ba is an essential step for the REE quantification by ICP-MS since the BaO formation in the plasma interfere in the Middle Rare Earth Elements (MREE) determination [13], specially Sm, Eu and Gd [34]. In this study, remaining Ba concentrations varied between < LOQ to  $9 \text{ ng L}^{-1}$  in the five replicates of synthetic water samples indicating an efficient Ba removal (> 99.99%).

Using Tm based quantification, nine of the 14 investigated REE present recoveries ranging from 90 to 105% (Table 1, Eq. (1)) values close to 80% were observed for Pr, Tb, and Lu and recoveries around 120% were observed for La and Tm.

The recoveries showed in Table 1 are similar to those reported by Shabani et al. [34], where values ranged from 54.5% (La) to 100.4% (Yb) for spiked synthetic samples. Using the same extraction procedure Bau and Dulski [42] reported recovery percentages between 92.4% (Yb) and 106% (Eu) and Hennebrüder et al. [43] reported recoveries varying

**Table 1**  
Recoveries percentages of the synthetic samples enriched with REE and Ba with and without Tm.

Element	Recovery (%)	
	Without Tm	With Tm
La	123 ± 20	117 ± 19
Ce	97 ± 6	93 ± 2
Pr	85 ± 6	81 ± 2
Nd	102 ± 8	97 ± 3
Sm	102 ± 8	97 ± 3
Eu	97 ± 7	92 ± 3
Gd	109 ± 8	104 ± 3
Tb	86 ± 7	82 ± 3
Dy	101 ± 7	96 ± 3
Ho	104 ± 7	99 ± 2
Er	105 ± 8	100 ± 4
Tm	nd	nd
Yb	103 ± 9	98 ± 4
Lu	85 ± 9	79 ± 10

nd = not detected.

from 82% (La) to 92% (Dy and Ho). Recoveries calculated without the addition of Tm were 5% higher than those obtained with the addition of Tm and exhibited higher relative standard deviations (50 to 75%) than the results obtained with Tm (Table 1). Thus, the quantification for REE in natural water samples was carried using of Tm as a surrogate due to the high precision and without compromising the accuracy.

The analytical method was also validated using the SLRS-6 river water certified reference material (CRM) from the National Research Council of Canada. Even though the natural REE concentrations are not yet certified for the SLRS-6, an intercalibration exercise involving nine international laboratories [44] was performed and the results are reported in Table S4 of the Supplementary material. 25 mL of the SLRS-6 CRM was diluted 50 times in ultrapure water allowing the analysis of two 500 mL replicates. This dilution was successfully proposed by Campos and Enzweiler [28] and reproduced in this work.

REE concentrations are in good agreement with those reported in the intercalibration exercise [44] (Table 2), satisfactory recoveries for 12 of the 14 REE investigated, varying between  $94 \pm 1\%$  (La) and  $105 \pm 3\%$  (Dy). Moreover, La recovery was better in the SLRS-6 CRM ( $94 \pm 1\%$ ) than those measured in the synthetic samples ( $117 \pm 19\%$ , Table 1), both tested with addition of Tm as a surrogate.

Tm recovery calculated by the interpolation Er and Yb concentrations, was not influenced by the addition of Tm since a highly accurate and precise value was reported ( $100 \pm 5\%$ , Table 2). Thus, the

**Table 2**  
Concentrations of rare earth elements in the SLRS-6 river water CRM obtained by intercalibration exercise [44] and by this study.

Element	Concentration of REE ( $\text{ng L}^{-1}$ ) of SLRS-6 CRM		Recovery (%) for this study
	Intercalibration Exercise [44]	This study	
La	248.3 ± 12.1	233 ± 3	94 ± 1
Ce	292.7 ± 15.1	276 ± 1	94.5 ± 0.4
Pr	59.1 ± 1.9	59 ± 1	100 ± 2
Nd	227.8 ± 9.4	226 ± 3	99 ± 1
Sm	39.5 ± 1.7	39.6 ± 0.8	100 ± 2
Eu	7.3 ± 0.4	7.3 ± 0.5	100 ± 7
Gd	31.6 ± 2.5	31 ± 2	99 ± 4
Tb	4.1 ± 0.3	3.3 ± 0.2	81 ± 5
Dy	21.9 ± 1.1	23.1 ± 0.8	105 ± 3
Ho	4.3 ± 0.3	4.4 ± 0.2	102 ± 5
Er	12.4 ± 0.7	13 ± 1	104 ± 9
Tm	1.8 ± 0.2	1.8 ± 0.1	100 ± 5
Yb	11.2 ± 0.7	11.0 ± 0.6	98 ± 6
Lu	1.9 ± 0.2	1.6 ± 0.2	83 ± 14

**Table 3**  
Concentrations ( $\text{ng L}^{-1}$ ) of REE in Paranoá Lake and its tributaries.

REE	Paranoá Lake Samples					Tributaries Samples			
	RB	BB	TB1	TB2	LD	RC	BC	TC	GC
La	4.53	1.73	4.99	1.13	3.82	38.1	7.76	4.28	43.1
Ce	10.1	2.00	19.4	1.30	6.06	74.5	12.78	9.92	83.9
Pr	0.98	0.21	1.08	0.16	0.38	8.56	1.77	0.80	9.60
Nd	4.12	0.94	4.30	0.84	1.65	34.4	7.73	3.27	36.9
Sm	0.86	0.23	0.83	0.36	0.38	6.54	1.59	0.56	6.15
Eu	0.17	0.06	0.19	0.06	0.09	1.29	0.38	0.11	1.17
Gd	34.4	22.4	10.0	9.15	9.52	9.54	2.07	0.52	5.01
Tb	0.10	0.03	0.08	0.03	0.05	0.68	0.24	0.05	0.54
Dy	0.10	0.20	0.40	0.19	0.23	3.62	1.37	0.26	2.52
Ho	0.13	0.05	0.07	0.11	0.05	0.73	0.32	0.07	0.50
Er	0.41	0.15	0.24	0.18	0.16	2.20	0.88	0.23	1.48
Tm	0.09	0.04	0.05	0.04	0.04	0.35	0.13	0.04	0.22
Yb	0.80	0.44	0.40	0.33	0.32	2.21	0.72	0.33	1.36
Lu	0.26	0.14	0.15	0.13	0.13	0.69	0.26	0.13	0.41
Total	57.1	28.6	42.2	14.0	22.9	183.4	38.0	20.5	192.9

RB: Riacho-Fundo Branch, BB: Bananal Branch, TB1 and TB2: Torto Branch, LD: Lake Dam, RC: Riacho-Fundo Creek, BC: Bananal Creek, TC: Torto Creek, and GC: Gama Creek.

standard distribution of the neighboring REE in the SLRS-6 CRM provides a good result for Tm recovery. However, lower recoveries were observed for Tb ( $80.5 \pm 5.6\%$ ) and for Lu ( $84.2 \pm 13.6\%$ ). Both elements also present relatively low recoveries in the experiments carried out using synthetic samples (Table 1).

In the natural and synthetic water samples the pre-concentration factor was  $50 \times$ . For the SLRS-6, 10 mL of the standard were diluted in followed by a 100-fold pre-concentration of the CRM. Outliers were excluded from the results by means of a Q-test, except for the SLRS-6 samples. Limits of quantification (LOQ) for the method were the lower standard concentration of the analytical curves divided by the pre-concentration factor. Thus, LOQ was  $10 \text{ pg L}^{-1}$  for the REE and  $0.1 \text{ ng L}^{-1}$  for Ba for the natural and synthetic samples.

### 3.2. REE in Paranoá Lake and its tributaries

Total REE concentrations ranged from  $57.1 \text{ ng L}^{-1}$  to  $14.0 \text{ ng L}^{-1}$  in the Paranoá Lake and from  $192.9 \text{ ng L}^{-1}$  to  $20.6 \text{ ng L}^{-1}$  in the tributaries (Table 3). Gd was the most abundant REE in four of the five samples from Paranoá Lake with concentrations varying between  $9.15 \text{ ng L}^{-1}$  (TB2) and  $34.4 \text{ ng L}^{-1}$  (RB). For the TB1 sample, however, Ce concentration ( $19.4 \text{ ng L}^{-1}$ ) was the highest, followed by Gd ( $10.0 \text{ ng L}^{-1}$ ). Total REE levels are commonly used to investigate the mobility and the sources of such elements in environmental compartments [45]. However, as urban wastewater discharges may also contribute to the presence of anthropogenic Gd in receiving waters [30], the evaluation of REE mobility becomes difficult [16].

In most of the tributaries, individual REE concentrations were higher than the levels registered for Paranoá Lake, except for Gd (Table 3). Low REE concentrations were registered for Bananal and Torto creeks, both located at the northern part of the lake, while high values, mainly for La, Ce and Nd, were observed for Riacho-Fundo and Gama creeks, in the south. Probably, this is associated to the local geochemical of rocks and sediments but this was not investigated in our study.

Fig. 2 presents PAAS-normalized REE concentrations for samples of Paranoá Lake and its tributaries. To understand the relative enrichment of LREE, MREE and HREE (Fig. 2),  $\text{Pr}_{\text{SN}}/\text{Yb}_{\text{SN}}$  (LREE/HREE),  $\text{Dy}_{\text{SN}}/\text{Pr}_{\text{SN}}$  (MREE/LREE) and  $\text{Dy}_{\text{SN}}/\text{Yb}_{\text{SN}}$  (MREE/HREE) ratios were calculated. In this study,  $\text{La}_{\text{SN}}/\text{Yb}_{\text{SN}}$  [4] ratio were not used since significant La anomalies were registered for some samples. The Paranoá Lake showed enrichment with  $\text{Pr}_{\text{SN}}/\text{Yb}_{\text{SN}}$  and  $\text{Dy}_{\text{SN}}/\text{Pr}_{\text{SN}}$  values varying respectively from 0.15 to 0.39 suggesting the presence of colloids in dissolved phase

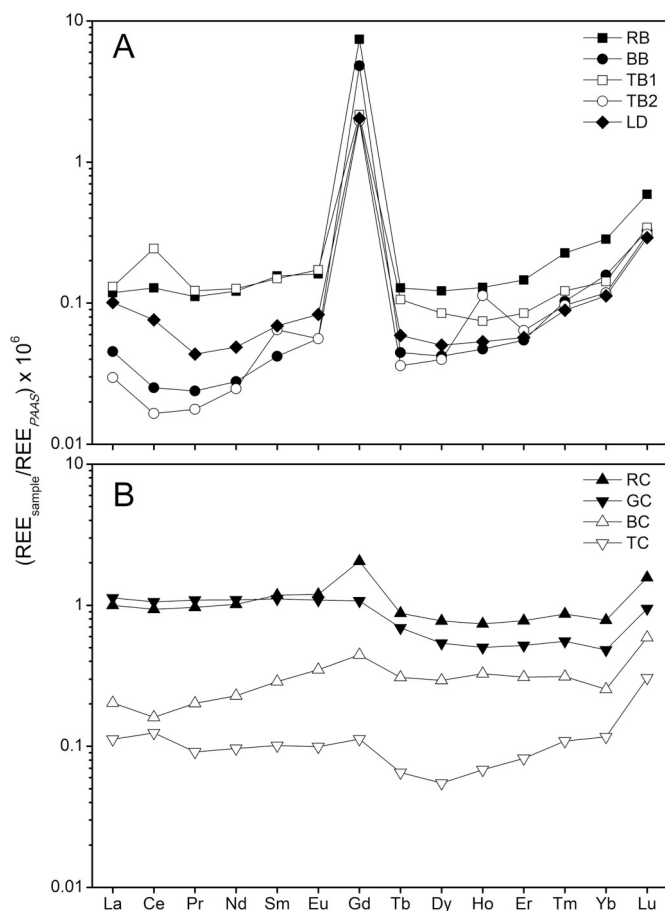


Fig. 2. Rare earth elements shale-normalized patterns (PAAS) of the samples collected in the Paranoá Lake (A) and its tributaries (B).

[5,10]. In the tributaries, flat REE pattern from MREE to HREE were observed for Riacho-Fundo (RC), Bananal (BC) and Gama (GC) creeks with  $D_{\text{YSN}}/P_{\text{rSN}}$  ratios close to 1 (0.99, 1.16, 1.11, respectively) indicating that ligands in the aqueous phase are able to interact equally with all elements of the lanthanide series. However, a LREE enrichment was observed in the Southern part of lake (RC and GC) with respective  $P_{\text{rSN}}/Y_{\text{bSN}}$  ratios of 1.24 and 2.30, and  $D_{\text{YSN}}/P_{\text{rSN}}$  ratios of 0.80 and 0.49. At low pH, the adsorption of dissolved REE onto suspended

particles is lower for the LREE fraction making them more available in the aqueous phase [10]. Contrastingly, in the Northern Paranoá tributaries, Torto Creek showed an enrichment in LREE ( $D_{\text{YSN}}/P_{\text{rSN}} = 0.60$ ) while Bananal Creek was enriched in MREE ( $D_{\text{YSN}}/P_{\text{rSN}} = 1.46$ ).

The water of the Paranoá Lake shows a significant positive Gd anomaly suggesting the anthropogenic source of this element as observed by Merschel et al. [30]. It is known that natural Gd can also present positive anomalies in minerals, such as lokaite, kimuraitte and permian limestones or in the aqueous media, due to the discontinuity of the stability constants of organocomplexes throughout the series of REE (tetra-d effect) [8]. In addition, the primary source of contamination is most likely related to the presence of CABGd residues in both raw and treated wastewaters since there is no significant industrial activity related to the use of Gd in the study area.

In the tributaries, Gd anomalies were less evident with PAAS-normalized because Gd levels are close to Eu and Tb normalized values for Gama, Bananal and Torto creeks (GC, BC and TC Fig. 2). However, Riacho Fundo Creek (RC) displayed a significant Gd anomaly. According to the most recent report from the National Water Agency (ANA) on Brasilia's wastewater management [46], two tributaries upstream of RC receive  $50 \text{ L s}^{-1}$  of treated sewage from a small treatment plant and  $21 \text{ L s}^{-1}$  of uncollected and treated wastewater which, combined, represent 3% of the tributary discharge. Consequently, this anomaly in RC sample is also most likely due to CABGd residues. Moreover, both RC and GC samples show high total REE concentrations ( $183.4 \text{ ng L}^{-1}$  and  $192.2 \text{ ng L}^{-1}$ , Table 3) without Gd anomaly in the GC sample even though this Creek drains an urbanized area that receive  $3.1 \text{ L s}^{-1}$  of untreated wastewater (only 0.2% of the tributary discharge).

To understand the intensity of the Gd anomaly, the concentration of Gd in the sample is compared with its expected natural concentration ( $Gd^*$ ). Several methods are available to estimate  $Gd^*$  [47] and we chose the method described by Kulaksiz et al. [40] (Eq. (2)) used by Merschel et al. [30] in the Paranoá Lake.

$$\log Gd_{\text{SN}}^* = (4 \log Eu_{\text{SN}} - \log Nd_{\text{SN}})/3 \quad (2)$$

In Eq. (2), SN stands for the shale-normalized (PAAS) values. Using this approach,  $Gd/Gd^*$  ratios higher than 1.5 indicate that anthropic activities have changed the natural levels of Gd [15]. The high  $Gd/Gd^*$  ratios are registered in the Riacho-Fundo (41.68) and Bananal branches (68.37) (Table 4) corroborating that effluents from NW-WWTP and SW-WWTP, respectively, are the main sources of anthropogenic Gd into Paranoá Lake. Moreover, anomalous Gd follows a similar pattern throughout the lake as samples collected at the Torto Branch (TB1 and

Table 4

Values of pH, conductivity (Cond.), anthropogenic Gd ( $Gd_{\text{anth}}$ ), Gd ( $Gd/Gd^*$ ), Ce ( $Ce/Ce^*$ ), and La ( $La/La^*$ ) intensity anomalies observed in samples from Paranoá Lake and its tributaries. Obtained data are compared with those registered by Merschel et al. [30] in 2013.

Sample	pH	Cond. ( $\mu\text{S cm}^{-1}$ )	$Gd_{\text{anth}}$ ( $\text{ng L}^{-1}$ )	$Gd/Gd^*$	$Ce/Ce^*_1$	$Ce/Ce^*_2$	$La/La^*$	Reference
RB	6.70	165.3	33.6	41.68	1.11	1.26	1.30	This study
	7.04	120.4	34.3	39.60	0.96	0.48	1.39	[30]
BB	6.25	165.0	22.1	68.37	0.77	1.27	3.27	This study
	7.17	88.5	13.4	30.04	1.06	0.53	1.52	[30]
TB1	6.24	115.4	9.2	11.35	1.92	2.05	1.41	This study
	7.45	83.4	7.4	18.51	0.84	0.42	1.18	[30]
TB2	6.81	120.8	8.8	26.80	0.72	1.54	2.72	This study
	7.35	85.4	9.0	39.08	0.78	0.39	1.72	[30]
LD	6.73	151.2	9.0	20.62	1.15	1.98	3.54	This study
	7.41	89.96	8.8	40.87	0.64	0.32	1.54	[30]
RC	6.63	135.2	3.70	1.63	0.95	1.02	1.15	This study
BC	6.30	52.2	0.20	1.10	0.79	0.92	1.37	This study
TC	6.44	69.9	0.060	1.12	1.23	1.46	1.19	This study
GC	6.53	39.9	ND	ND	0.95	0.97	1.03	This study

RB: Riacho-Fundo Branch, BB: Bananal Branch, TB1 and TB2: Torto Branch, LD: Lake Dam, RC: Riacho-Fundo Creek, BC: Bananal Creek, TC: Torto Creek, and GC: Gama Creek, ND: Not detected,  $Gd_{\text{anth}}$ : anthropogenic gadolinium,  $Gd/Gd^*$ : gadolinium anomaly calculated from Eq. (2),  $Ce/Ce^*_1$ : cerium anomaly calculated from Eq. (3),  $Ce/Ce^*_2$ : cerium anomaly calculated from Eq. (4), and  $La/La^*$ : Lanthanum anomaly calculated from Eq. (5).

TB2) and nearby the Lake Dam (LD) presented Gd/Gd\* ratios from 11.35 to 26.80, indicating a good lateral mixture of waters [30]. TB1 and LD sampling points are located respectively upstream of the Emergency and Future water treatment plants, respectively, indicating that the indirect water reuse in the lake may also consider the existence of possible diffuse sources (such as clandestine domestic effluents, agriculture and urban drainage waters) associated with adjacent areas in the catchment. According to the ANA report, 28% of the wastewaters from the North Lake and South Lake districts of Brasília are uncollected and untreated or treated by “individual” solutions [46].

Regarding Gd anomalies in the Paranoá Lake, our results are in accordance with those observed by Merschel et al. [30] in 2013. However, Gd/Gd\* ratios for the Bananal Branch was, at least, two times higher than those obtained in 2013 (Table 4). This result indicates a greater anthropogenic contamination in this branch over the years.

The concentration of anthropogenic Gd (Gd<sub>anth</sub>) was also calculated by the difference between the absolute Gd concentration (Table 4) and the Gd\*. The highest Gd<sub>anth</sub> levels were observed in Paranoá Lake branches nearby two wastewater treatment plants (RB = 33.6 ng L<sup>-1</sup> and BB = 22.1 ng L<sup>-1</sup>). The higher concentration in the RB point may be related to the higher average flow of the SW-WWTP (1.22 m<sup>3</sup> s<sup>-1</sup>) compared to the NW-WWTP (0.57 m<sup>3</sup> s<sup>-1</sup>) [48], suggesting that the main source of Gd is the WWTP.

Gd<sub>anth</sub> levels observed by Merschel et al. [30] and obtained in the present study are in the same order of magnitude for the Paranoá Lake samples (Table 4), except for a higher concentration in Bananal Branch (22.1 ng L<sup>-1</sup>) in the present study in comparison with the 2013 data (13.4 ng L<sup>-1</sup>). Gd anomaly in the tributaries was not expressive, except for the RC sample which presented a Gd/Gd\* ratio of 1.63 with Gd<sub>anth</sub> concentrations of 3.7 ng L<sup>-1</sup>. Fig. 3 shows the relationship between Gd<sub>anth</sub> and conductivity in the investigated samples as well as in the samples analyzed by Merschel et al. [30]. Beside characterizing non-contaminated (GC, BC and DC) and contaminated (RC) tributaries, it is observed that, despite the higher conductivity observed in 2017, of Gd<sub>anth</sub> levels are comparable for the majority of the lake samples including the one impacted by the SW-WWTP (RB). Considering the lake volume and typical Gd<sub>anth</sub> data from 2013 and 2017 (dashed rectangle in Fig. 3) it is estimated that 5 ± 1 kg of Gd<sub>anth</sub> are present in the lake. This absolute value is slightly inferior to the previous estimate of 6.1 kg but is analogous given the uncertainty. Thus, we conclude that Gd levels have not increased significantly in four years due to the hydrological turn-over of the lake. Merschel et al. [30] reported an increase of

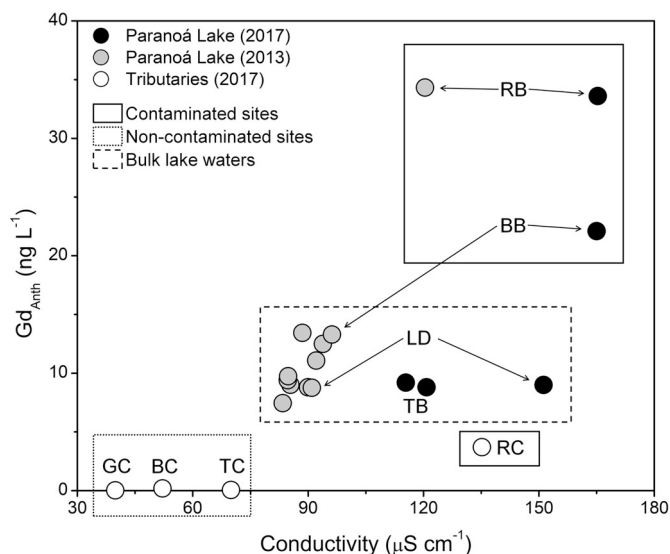


Fig. 3. Anthropogenic gadolinium against conductivity for Paranoá Lake samples collected in 2013 (Merschel et al. [30]) and in 2017 (this study).

up to 460% in the Gd<sub>Anth</sub> between November 2012 and July 2013 related to the increase on magnetic resonance imaging (MRI) exams. However, the authors did not relate this Gd behavior to the temperature stratification that is observed from April to June, isolating deep waters from the surface, whereas well mixed waters are observed from June to October [49]. In addition, based on a 10-year time series of the lake dam discharge (16.3 m s<sup>-1</sup>) [50] we estimate that 14.1 g of Gd<sub>anth</sub> are removed daily at the lake outlet.

Ce anomalies were numerically evaluated through Ce/Ce\* ratios, where Ce\* was calculated according to Eq. (3), as proposed by Kulaksiz and Bau [40].

$$\log Ce_{SN}^* = (\log La_{SN} + \log Pr_{SN})/2 \quad (3)$$

Although ratios lower than 1 is more commonly observed due to the oxidative behavior of Ce [2], the negative Ce anomalies observed in this study (Table 4) were rather limited. However, the Eq. (3) can induce a bias if La<sub>SN</sub> values are elevated compared to Pr<sub>SN</sub>. Considering the La behavior, Ce/Ce\* values may be systematically higher in our study in comparison to the data provided by Merschel et al. [30] in the Paranoá Lake, except for BB and TB2 which are numerically inferior but display high La<sub>SN</sub>/Pr<sub>SN</sub> ratios (1.9 and 7.3 respectively). Thus, an alternate equation to evaluate Ce anomalies [51] based on Pr<sub>SN</sub> and Nd<sub>SN</sub> may be used as follows:

$$\frac{Ce_{SN}}{Ce^*} = Ce_{SN}/(2Pr_{SN} - Nd_{SN}) \quad (4)$$

Considering Eq. (4), Ce/Ce\* values are higher than those observed by Merschel et al. [30] (Table 4). These results show negative anomalies (Ce/Ce\* between 0.32 and 0.53) while in our study positive Ce anomalies (Ce/Ce\* between 1.27 and 2.05) are registered in the Paranoá Lake. However, positive Ce anomalies were previously observed for unfiltered samples and negative to neutral anomalies in filtered sample indicating that suspended particulate matter (SPM) are enriched in Ce [30]. This Ce enrichment was attributed either to fertilizers [52] or to regional soils contributions, as Brasilia region has a large occurrence of lateritic soils that are known for their Ce anomalous content [53,54]. A transfer from SPM to the dissolved phase related to the alteration of E<sub>H</sub>-pH conditions, when compared to the previous study is unlikely given oxic characteristics of Paranoá surface waters and the slightly acidic pH values in our study (6.51 ± 0.21, Table 4) compared to slightly basic values obtained in the previous study (7.32 ± 0.17). Consequently, the presence of a positive Ce anomaly in the dissolved phase in our study can be explained either (i) by the presence of Ce enriched mineral colloids as Fe or Mn oxy-hydroxides [55] or (ii) by an enrichment in the truly dissolved phase due to the dissolution of Ce through lixiviation of soils enriched with agricultural supplies like fertilizers and correctives [56]. This hypothesis could be supported by high positive Ce anomalies registered in the Torto Creek (1.46) and in the Torto Branch samples (TB1 with Ce/Ce\* = 2.05 that is close to the Torto Creek and TB2 with Ce/Ce\* = 1.54) as Torto Creek drains an area with agricultural activities and some urban agglomerations. In contrast, the three other tributaries (RC, GC, and BC) displayed slightly negative to neutral Ce anomaly (Ce/Ce\* between 0.92 and 1.02) as drains preserved regions or a mix of preserved, agricultural and residential areas.

As mentioned earlier, some samples displayed high relative La concentration that difficult the evaluation of Ce anomalies based on La<sub>SN</sub> and Pr<sub>SN</sub> (Table 2). To investigate the possible La anomaly, La/La\* ratios were calculated based on the equation proposed by Kulaksiz et al. [40] to assess La\*, as follows:

$$\log La_{SN}^* = (2 \log Nd_{SN} - Eu_{SN}) \quad (5)$$

In this study La/La\* varied between 1.03 and 3.54 and values from Merschel et al. [30] varied between 1.18 and 1.72 (Table 4). Given the low blanks intensities obtained for La (Table S4 of the Supplementary material) as well as the good recoveries achieved from the SLRS-6 CRM,

La anomalies in this study are significant. However, attributing these significant yet limited La anomalies to human activities would be rather speculative and out of the scope of this study. La contribution from SPM matter or colloids to the dissolved phase (by analogy to Ce) can be ruled out as SPM La/La\* values calculated from Merschel et al. [30] dataset (applying Eq. (4) to unfiltered minus filtered data) shows values of  $1.35 \pm 0.17$  and Ce/Ce\* vs La/La\* in the dissolved phase exhibit a poor correlation ( $R^2 = 0.21$ ). Furthermore, La/La\* exhibit no significant correlation with Gd/Gd\* ( $R^2 = 0.40$ ) and shall not come from WWTP. Since an increase in these anomalies between 2013 and 2017 is observed, their monitoring in future studies and the use of Ce/Ce\* equations that do not include La<sub>SN</sub> are relevant.

#### 4. Conclusion

In the tributaries of the Paranoá Lake, high values of total REE was registered for Riacho Fundo and Gama creeks (RC and GC), mainly for La, Ce, and Nd. Besides, only RC, polluted tributary [33], displayed a significant Gd anomaly with  $3.70 \text{ ng L}^{-1}$  of anthropogenic Gd. Moreover, an enrichment of LREE was registered in the Southern part of lake while at the Northern part, the Creeks follow no distinguish between REE enrichment. These results suggest that REE variation is close to the local geochemical of rocks and sediments in the most of samples.

In the Paranoá Lake, we certified that the main sources of Gd anomalies were the South-Wing and North-Wing WWTPs located in the Riacho-Fundo (RB) and Bananal branches (BB), respectively. We estimated that  $5 \pm 1 \text{ kg of Gd}_{\text{anth}}$  were present in the lake from 2013 and 2017 year as well as  $14.1 \text{ g of Gd}_{\text{anth}}$  are removed daily at the lake outlet. Both estimates indicate that Gd levels have not increased significantly in four years due to the hydrological turn-over of the lake.

Positive Ce anomalies identified is probably associated to the enriched mineral colloids as Fe or Mn oxy-hydroxides [55] or by the Ce from the soils enriched with agricultural supplies. Even though the positive La anomaly was observed in some samples, we recommend the monitoring of this anomaly for future studies to understand their behavior in water.

#### Acknowledgments

The authors thank the National Institute of Criminalistic of Brazilian Federal Police for providing access to the ICP-MS used in this work and the Coordination for the Improvement of Higher Education Personnel (CAPES) for the fellowship to the first author.

#### Funding

This work was supported by the Brazilian National Research Council (CNPq) [Grant number 454494/2014-9].

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.microc.2019.04.055>.

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