

Rare earth elements and yttrium in water sources of the Distrito Federal, Central Brazil: baseline data for water quality monitoring

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Abstract

Rare earth elements and yttrium (REY) were evaluated in water supply sources of the Distrito Federal, Central Brazil, to establish baseline data for water quality monitoring. Tap water was collected from the distribution system of two water sources: Lakes Paranoá and Descoberto, while groundwater samples were obtained from porous and fractured aquifers. Sampling was carried out during the rainy and dry seasons. REY were preconcentrated as HDMEP–H₂DMEP complexes using C18 solid-phase extraction columns and quantified by inductively coupled plasma mass spectrometry. The highest total REY concentrations were observed in the porous aquifer during the rainy season (944.0 ± 33.7 ng/L). Elevated gadolinium (Gd) concentrations were also recorded during this period in the porous aquifer (25.4 ± 2.9 ng/L) and in tap water from Lake Paranoá (22.9 ± 2.1 ng/L). The presence of anthropogenic Gd was identified in the porous aquifer; however, the high variability limits a clear distinction between natural and anthropogenic sources. Positive anomalies for La (La/La* from 1.2 to 1.7) and Gd (Gd/Gd* from 30.40 to 21.12) were observed in tap water from Lake Paranoá, linked to fertilizer runoff and wastewater-based sources, respectively, as Gd has been associated with emerging contaminants as contrast agents used in exams. A positive Ce anomaly (Ce/Ce* = 2.9 ± 0.3) was detected only in tap water from Lake Descoberto, suggesting a contribution from agricultural sources. These results indicate that REY analysis can complement conventional water quality monitoring, especially when traditional parameters are insufficient to identify potential contamination sources.

Keywords: anthropogenic gadolinium; environmental monitoring; groundwater; rare earth elements; water quality.

Elementos de terras raras e ítrio em fontes de água do Distrito Federal, região Centro-Oeste do Brasil: dados de referência para o monitoramento da qualidade da água

Resumo

Os elementos terras raras e o ítrio (ETR+Y) foram avaliados em fontes de abastecimento de água do Distrito Federal, Brasil Central, com o objetivo de estabelecer dados de referência para o monitoramento da qualidade da água. Amostras de água tratada foram coletadas no sistema de distribuição de duas fontes de abastecimento, os lagos Paranoá e Descoberto, enquanto amostras de água subterrânea foram obtidas em aquíferos porosos e fraturados. As coletas foram realizadas durante os períodos chuvoso e seco. Os ETR+Y foram pré-concentrados na forma de complexos HDMEP–H₂DMEP utilizando colunas de extração em fase sólida C18 e quantificados por espectrometria de massas com plasma indutivamente acoplado. As maiores concentrações totais de ETR+Y foram observadas no aquífero poroso durante o período chuvoso ($944,0 \pm 33,7$ ng/L).

Concentrações elevadas de gadolínio (Gd) também foram registradas nesse período no aquífero poroso ($25,4 \pm 2,9$ ng/L) e na água tratada proveniente do Lago Paranoá ($22,9 \pm 2,1$ ng/L). A presença de Gd de origem antrópica foi identificada no aquífero poroso; entretanto, a alta variabilidade dos dados limita uma distinção clara entre fontes naturais e antrópicas. Anomalias positivas de La (La/La* variando de 1,2 a 1,7) e de Gd (Gd/Gd* variando de 30,40 a 21,12) foram observadas na água tratada do Lago Paranoá, associadas, respectivamente, ao escoamento de fertilizantes e a fontes relacionadas a efluentes sanitários, uma vez que o Gd tem sido associado a contaminantes emergentes, como agentes de contraste utilizados em exames médicos. Uma anomalia positiva de Ce (Ce/Ce* = $2,9 \pm 0,3$) foi detectada exclusivamente na água tratada do Lago Descoberto, sugerindo contribuição de fontes agrícolas. Esses resultados indicam que a análise de ETR+Y pode complementar o monitoramento convencional da qualidade da água, especialmente em situações nas quais os parâmetros tradicionais são insuficientes para identificar potenciais fontes de contaminação.

Palavras-chave: água subterrânea; elementos terras raras; gadolínio antropogênico; monitoramento ambiental; qualidade da água.

1 Introduction

Rare earth elements (REE) comprise the lanthanides (from La to Lu, $Z = 57-71$), with concentrations ranging from 66 mg/kg (Ce) to 0.3 mg/kg (Lu) in the Earth's crust. They are among the least soluble elements at rock-soil-water interfaces (Sager; Wiche, 2024). REE are widely used to study rock formation and differentiation, hydrothermal alteration, weathering processes (Rollinson, 1994), and hydrological dynamics (Abreu *et al.*, 2024; Boester; Rude, 2020; Iwatsuki *et al.*, 2017; Leite *et al.*, 2023; Möller; Dulski; De Lucia, 2021; Sholkovitz, 1993). This versatility is largely due to the gradual decline in ionic radius and the increasing atomic number across the lanthanide series, known as lanthanide contraction (Sager; Wiche, 2024). Moreover, REE have ionic radii similar to Ca^{2+} (Ca^{2+} 100 pm, La^{3+} 103.1 pm) and typically form trivalent cations under certain biogeochemical conditions, except Ce and Eu, which can also exist in the tetravalent and divalent states. As a result, REE exhibit strong interactions with negatively charged surfaces, such as organic and inorganic ligands. These interactions increase as the ionic radius decreases, particularly in soil environments (Cao *et al.*, 2001). For example, REE undergoes weak hydrolysis in water at pH 5 to 7 (Bentouhami *et al.*, 2004), forming complexes with PO_4^{3-} , CO_3^{2-} , SO_4^{2-} , Cl^- , and F^- (Millero, 1992). REE can compete with other cations depending on ionic strength and pH (Bentouhami *et al.*, 2004). In groundwater, their concentration ranges from 1 to 100 ng/L, with most of the REE bound to colloidal particles of quartz, clay, iron hydroxides, calcite, and humic substances. They also form complexes with CO_3^{2-} , Cl^- , and F^- (Iwatsuki *et al.*, 2017). The concentration of REE^{3+} and $(\text{REECl})^{2+}$ species decreased with increasing molecular weight, whereas the levels of $\text{REE}(\text{CO}_3)^{2-}$ increased, and $(\text{REECO}_3)^+$ remained constant. At low redox potential ($-0.40 < E_h < -0.25$ V), a positive Eu anomaly is observed without a Ce anomaly, while in the E_h range from -0.1 to $+0.26$ V, a positive Ce anomaly was registered in water.

Furthermore, fractionation occurs between light REE (LREE – La to Sm) and heavy REE (HREE – Eu to Lu) depending on the biogeochemical and complexation processes in the environment (Sager; Wiche, 2024). This fractionation is attributed to both lanthanide contraction and the increasing covalence resulting from the progressive filling of their 4f electron shell. During rock weathering, the weathered products tend to become enriched in LREE relative to the parent rock, as HREE complexes are more soluble, while LREE is retained through adsorption or incorporation into secondary minerals (Sholkovitz, 1995).

Additionally, yttrium is usually included in lanthanide investigations (REY), even though it is not a lanthanide, due to its trivalent state in aqueous solutions and its similar ionic radius to $\text{Ho}(+III)$. As a result, Y exhibits identical chemical properties to the lanthanides and is often considered alongside them, positioned between Dy and Ho in normalized REE distributions (Yang *et al.*, 2020). Y–Ho fractionation occurs through the preferential Ho-scavenging onto Fe-oxyhydroxides compared to Y, as well as the selective incorporation of Ho into CaCO_3 in the water of the Dead Sea, Israel

(Censi *et al.*, 2017). Moreover, some lakes, rivers, and groundwater exhibit light REY decay (LREY), with positive La and Y anomalies and negative Ce anomalies (Lawrence *et al.*, 2006; Lawrence; Jupiter; Kamber, 2006). This REY fractionation is attributed to complexation with CO_3^{2-} ligands and dissolved organic carbon species. Additionally, the bonding is stronger for HREY than LREY (Johannesson; Lyons, 1994).

Over the last 20 years, REE anomalies have been recorded in Europe's rivers, lakes, groundwater, tap water, and estuaries (Boester; Rde, 2020; Duvert *et al.*, 2015; Knappe *et al.*, 2005; Kulaksiz; Bau, 2007, 2011, 2013), North America (Bau; Knappe; Dulski, 2006), and Australia (Lawrence; Jupiter; Kamber, 2006). Gd anomalies have been observed in the natural waters of European rivers since 1996, attributed to anthropogenic activities, particularly from hospital sewage (Bau; Knappe; Dulski, 2006; Knappe *et al.*, 2005; Kulaksiz; Bau, 2007). These anomalies are linked to Gd-based contrast agents (CABGd) used in clinical analyses by nuclear magnetic resonance imaging (Bau; Knappe; Dulski, 2006). These Gd compounds are not removed in wastewater treatment plants (WWTP) due to their high stability, and thus, they are transferred to surface waters through clearwater discharge from WWTP (Kulaksiz; Bau, 2011).

Considering the extensive use of REEs in forestry, high technology, medical treatments (such as REE chelates and Gd-DTPA), and fertilizer, monitoring their environmental availability is crucial. Natural and anthropogenic REE can have cumulative and synergistic detrimental effects, altering natural distribution, particularly in aquatic systems, and disrupting biogeochemical cycles (Sager; Wiche, 2024). Furthermore, Gd-based contrast agents are highly bioaccessible due to their stability in the gastrointestinal tract, making them potentially bioavailable (Souza *et al.*, 2021).¹

This enhanced bioavailability has prompted recent literature to raise critical concerns regarding the role of REYs as emerging environmental contaminants capable of inducing bioaccumulation and cellular toxicity in aquatic organisms. Reflecting this scenario, a comprehensive review conducted by Albarano *et al.* (2025) using species sensitivity distribution (SSD) curves established that all ten major REEs evaluated exhibit hazardous concentrations (HC_5 and HC_{50}) below 100 $\mu\text{g/L}$, indicating that they pose a potential ecological concern even at low ambient levels. Based on the calculated HC_5 values, the authors proposed a decreasing toxicity prioritization order of Dy (0.03 $\mu\text{g/L}$) > Ce (0.15 $\mu\text{g/L}$) > Sm (0.29 $\mu\text{g/L}$) > La (0.64 $\mu\text{g/L}$) > Y (0.81 $\mu\text{g/L}$) > Gd (0.95 $\mu\text{g/L}$). Elements such as Gd and Ce, which are frequently linked to anthropogenic anomalies from medical effluents and agricultural inputs, respectively, display high toxicity toward aquatic invertebrates (e.g., arthropods and echinoderms), potentially impairing fundamental cellular and molecular mechanisms. In light of this increasing anthropogenic input and latent toxicity, establishing baseline data for public water supplies becomes imperative to anticipate ecological risks and safeguard environmental health.

In Brazilian waters, REE distributions are influenced by the lithology of hydrographic basins (Gaillardet *et al.*, 1997; Merschel *et al.*, 2017; Sholkovitz, 1995), while positive Gd anomalies have been increasingly linked to anthropogenic contributions in aquatic environments. In Northeast Brazil, along the coast of Salvador City, Gd anomalies have been detected in seawater near the submarine sewage outfalls, decreasing with distance from the point source (Pedreira *et al.*, 2018). Similar anomalies were found in the surface waters of the Paraguau River and its estuarine zone (Andrade *et al.*, 2020). In Fortaleza City, Gd anomalies were recorded in wastewater outfall areas and two local river estuaries, indicating significant contributions of anthropogenic Gd (Gd_{anth}) to the ocean (Da Costa *et al.*, 2021). In Southeast Brazil, unexpected Gd_{anth} anomalies in surface waters were attributed to raw sewage leakage from underground effluent pipes (De Paula Marteleto; Enzweiler, 2021). Gd anomalies have also been documented in groundwater from Campinas and So Carlos (So Paulo State) linked to Gd inputs from local wastewater treatment systems (Abreu *et al.*, 2024; Leite *et al.*, 2023). In Central Brazil, anomalous Gd was registered in Lake Parano, associated with effluents from two WWTPs in Braslia (Distrito Federal, DF) (Amorim *et al.*, 2019; Merschel *et al.*, 2015). Between 2013 and 2017, an estimated 5 ± 1 kg of Gd_{anth} was present in the lake, with 14.1 g of Gd_{anth} removed daily at the lake's outlet. These findings suggest that Gd levels have remained stable over four years, likely due to changes in the lake's hydrology.

Given the reported evidence, the widespread use of REE, global and local incentives for their exploration, and the strategic location of DF as a natural divider between three major Brazilian

hydrographic basins with extensive agricultural activities (covering approximately 70% of the DF), monitoring REE variations in the aquatic environments is important. This study aims to establish baseline data on rare earth elements and yttrium (REY) in water supply sources, including tap water and groundwater, to support water quality monitoring in the Distrito Federal, Central Brazil.

In this study, Section 2 describes the materials and methods, including the study area, sampling locations, water collection procedures, and the quantification of aquatic parameters, rare earth elements, and yttrium (REY). Section 3 presents the results and discussion, focusing on water hydrogeochemistry and on the variations, enrichments, and potential anomalies of REY used to distinguish between different water sources. Section 4 concludes by emphasizing the importance of REY in differentiating waters from distinct lithological regions, as well as the role of anthropogenic gadolinium as a potential tracer of water mixing, particularly in waters affected by effluent inputs.

2 Material and methods

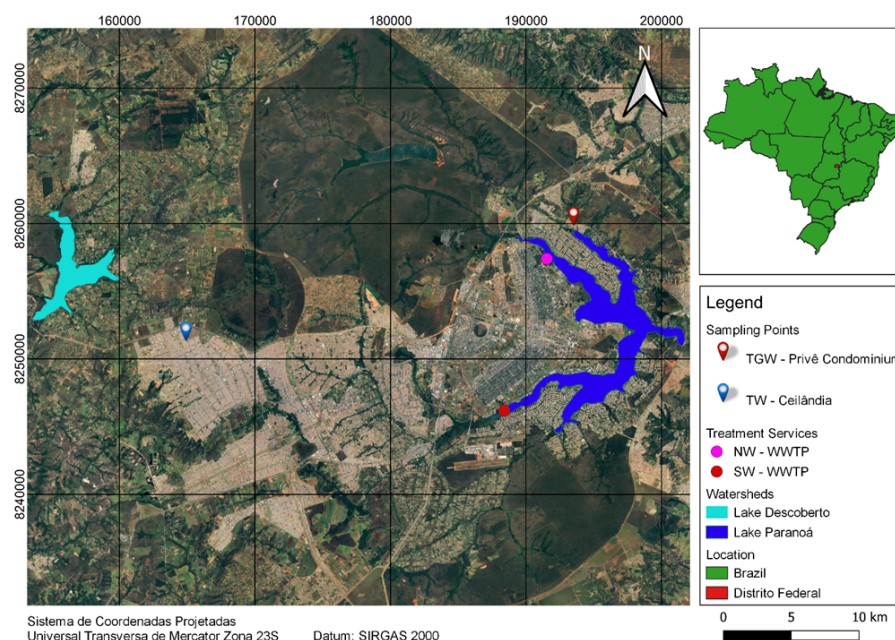
This section describes the study area, including the location of the water supply systems in the Distrito Federal (DF), the local climate and its rainfall regime, the sampling sites, and the geological setting. In addition, the procedures for material cleaning, water sampling, and the quantification of physicochemical parameters, as well as rare earth elements and yttrium (REY), are presented, including their respective limits of detection and quantification.

2.1 Study area and sampling

DF is located in the central region of Brazil, covering an area of 5,802 km² and with a population of approximately 3 million, of whom around 97% reside in urban areas, resulting in a population density of more than 450 inhabitants/km². This region is a natural divider between three major Brazilian hydrographic regions: the Tocantins/Araguaia, São Francisco, and Paraná watersheds. The area hosts two primary types of aquifers, porous and fractured, and includes an important aquifer recharge area (Codeplan, 2020).

The water supply systems (WSS) in the DF are managed by the Environmental Sanitation Company of the Distrito Federal (Caesb). There are five main WSS: Torto/Santa Maria/Bananal/Paranoá, Descoberto, Brazlândia, Sobradinho/Planaltina, and São Sebastião. In urban areas, these systems serve 99% of the population, while in rural areas, only 15% depends on Caesb systems. Instead, individual shallow wells are frequently used in rural regions, often without proper water quality control (Codeplan, 2020). Among these systems, Torto/Santa Maria/Bananal/Paranoá and Descoberto include Lakes Paranoá and Descoberto, respectively. Lake Paranoá, an artificial reservoir built in 1959, was created for energy generation, recreational activities, and maintaining the city's humidity during the dry season (Abbt-Braun *et al.*, 2014). It now houses one water treatment plant (WTP), operated since 2017, and two WWTPs (Figure 1). Lake Descoberto hosts only one WTP.

Figure 1 – Water sampling site locations in Distrito Federal, Central Brazil. Distrito Federal Subdistricts (map in green)



Source: prepared by the authors.

The DF region has well-defined dry and rainy seasons (INMET, 2025). The rainy season extends from October to April, accounting for 43% of total annual precipitation, while the dry season extends from May to September, contributing only 2.4% of total annual precipitation. The annual precipitation is 1477.4 mm, with an average temperature of around 21 °C.

In this study, water samples were collected from two locations in the DF. The first site was a residential condominium, Privê, in the eastern portion of DF, supplied by water from Lake Paranoá (Figure 1). At this site, three samples were collected: two groundwater samples (one from the porous aquifer and the other from the fractured aquifer) and one tap water sample. These samples were collected during the rainy season (January 2023) and the early dry season (May 2023). The second site was a residential complex in Ceilândia, located in the western portion of DF, which primarily receives its water supply from Lake Descoberto (Figure 1). One tap water sample was collected during the dry season (September 2023) at this site.

The water samples collected in this study are situated within the Paranoá Group, which covers approximately 65% of the DF. This group comprises various rock types, including quartzite, metasilite, slate, sandy metarhythmite, medium quartzite, clayey-clayey metarhythmite, and a psammo-pelite-carbonate unit (Codeplan, 2020). Additionally, the tap water collected in Ceilândia falls within the Araxá group, which occupies about 5% of the DF and comprises muscovite and various schists. The soils in the region are predominantly ferralsols, characterized as red, highly weathered, very deep, well-drained, dystrophic, and acidic, with clay content ranging from 15 to 80%. Due to these properties, fertilizers are often required for agricultural cultivation.

2.2 Aquatic parameters and REY quantification

In this study, all procedures from sampling to analysis were performed using ultra-clean techniques, employing the reagents and standard solutions outlined in Amorim *et al.* (2019). Only double-distilled acids (HNO₃ and HCl; Merck, Germany) were used for REY analysis.

Water samples were collected in 1-L polyethylene bottles and filtered in the laboratory using a polyethylene filtration system (Nalgene, USA) with cellulose acetate membranes (47 mm diameter) of different porosities: 0.45 µm for ion analysis and 0.22 µm for REY analysis. The filtered samples were acidified with 6 mol/L HCl to a pH of approximately 2.0 for REY analysis.

Aquatic parameters, including pH, dissolved oxygen (DO), total dissolved solids (TDS), conductivity, and temperature, were measured *in situ* using a multiparameter probe (Hanna, HI7609829). Alkalinity was determined by titration with 0.1 mol/L H₂SO₄, as described in Standard

Methods (Eaton *et al.*, 2005). Cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and NH_4^+) and anions (F^- , Cl^- , SO_4^{2-} , NO_3^- , and PO_4^{3-}) were analyzed by ion chromatography (Compact IC Flex, Metrohm, Switzerland). Detection limits (DL) for ions were calculated by dividing the quantification limit (QL) by 3, with the QL being derived from the first point of the calibration curve. These results are presented in Table 1.

Table 1 – Detection and quantification limits of cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NH_4^+) and anions (F^- , Cl^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) measured by ion chromatography

Cations	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+
DL (mg/L)	0.3	0.3	0.3	0.3	0.3
QL (mg/L)	1.0	1.0	1.0	1.0	1.0
Anions	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
DL (mg/L)	0.03	0.08	0.03	0.3	0.16
QL (mg/L)	0.1	0.25	0.1	1.0	0.5

Source: prepared by the authors.

REY was separated from interfering Ba in solution using a Sep-Pak C18 column (Waters, USA) impregnated with the complexing agent HDMEP-H2DMEP, as adapted from Shabani, Akagi and Masuda (1992) and performed by Amorim *et al.* (2019). Aliquots of 1.0 L of the water samples were passed through the cleaned C18 column using a peristaltic pump (flow rate of 12 mL/min). Then, 10 mL of 0.01 mol/L HCl was added to remove interfering Ba. REYs were eluted with 40 mL of 6 mol/L HCl. The eluate was evaporated at 180°C and recovered in 20 mL of a 0.5 mol/L HNO_3 solution for quantification by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500ce). An internal standard (In 1.0 µg/L) was added to monitor ICP-MS fluctuations. Instrumental conditions, REE quantification procedures, Ba interference correction equations, Ba removal efficiency, as well as method precision and accuracy, were previously validated using the SLRS-6 river water certified reference material, as described by Amorim *et al.* (2019). Quantification was performed using the following isotopes: ^{89}Y , ^{139}La , ^{140}Ce , ^{141}Pr , ^{144}Nd , ^{147}Sm , ^{153}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{174}Yb , and ^{175}Lu . Detection and quantification limits for REEs were established by adopting the lowest calibration concentration as the quantification limit (10 pg/L) and accounting for the method preconcentration factor (Amorim *et al.*, 2019). The REE concentrations measured in SLRS-6 (Table 2) were consistent with values reported in international intercalibration exercises (Yeghicheyan *et al.*, 2019), thereby confirming the high accuracy of the analytical procedure.

The red balloon marks the Privé residential condominium, where tap water and groundwater (TGW – porous and fractured aquifers) were collected in January (rainy season) and May (beginning of the dry season) of 2023. The blue balloon marks the residential location in Ceilândia, where tap water (TW) was collected in September 2023 (dry season). The pink and red circles represent the wastewater treatment plants in Lake Paranoá, located at the North Wing (NW-WWTP) and South Wing (SW-WWTP) of Brasília. The blue of the two watersheds are Lake Paranoá and Lake Descoberto.

Table 2 – Intercalibrated concentrations of rare earth elements in the SLRS-6

Element	Concentration of REE (ng/L) in SLRS-6	
	Yeghicheyan <i>et al.</i> (2019)	Amorim <i>et al.</i> (2019)
La	248.3 ± 12.1	233 ± 3
Ce	292.7 ± 15.1	276 ± 1
Pr	59.1 ± 1.9	59 ± 1
Nd	227.8 ± 9.4	226 ± 3
Sm	39.5 ± 1.7	39.6 ± 0.8
Eu	7.3 ± 0.4	7.3 ± 0.5
Gd	31.6 ± 2.5	31 ± 2
Tb	4.1 ± 0.3	3.3 ± 0.2

Dy	21.9 ± 1.1	23.1 ± 0.8
Ho	4.3 ± 0.3	4.4 ± 0.2
Er	12.4 ± 0.7	13 ± 1
Tm	1.8 ± 0.2	1.8 ± 0.1
Yb	11.2 ± 0.7	11.0 ± 0.6
Lu	1.9 ± 0.2	1.6 ± 0.2

Source: Yeghicheyan *et al.* (2019) and Amorim *et al.* (2019).

3 Results and discussion

This section presents the results and discussion, focusing on water hydrogeochemistry and REY variations, enrichments, and anomalies to distinguish different water sources.

3.1 Hydrogeochemistry of water

The aquatic parameters and ion concentrations were measured in most samples, except in the tap water from Lake Descoberto. Significant variations in temperature (24°C – 26 °C) and pH were observed, with pH values below 6, except in fractured aquifers, where pH was 7.7 during the dry season. In groundwater, higher concentrations of dissolved oxygen (DO around 4 mg/L), conductivity (ranging from 107 to 129 $\mu\text{S}/\text{cm}^3$), and TDS (ranging from 57 to 65 mg/L) were recorded during the rainy season when the water is influenced by local runoff. However, only conductivity exhibited temporal variation in tap water from Lake Paranoá, with higher values during the dry season (127 $\mu\text{S}/\text{cm}^3$), likely associated with the evaporation process during this period.

Spatiotemporal variations of cations were observed in the water. In groundwater, the highest values of Na^+ (17.36 ± 0.05 mg/L, $n = 2$) and Ca^{2+} (5.0 ± 1.5 mg/L, $n = 2$) were observed in the porous aquifer during the dry and rainy periods, respectively. Moreover, a lower concentration of NH_4^+ (0.64 ± 0.06 mg/L, $n = 2$) was recorded in this sample during the rainy season. In the fractured aquifer, K^+ was quantified with a maximum value in the rainy period (20.9 ± 2.3 mg/L, $n = 2$), and a low Ca^{2+} concentration was registered only in the dry period (1.8 ± 1.6 mg/L, $n = 2$). In the tap water from Lake Paranoá, the maximum concentrations of cations (in mg/L) were recorded during the dry period, in the following decreasing order: $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+$ (13.66 ± 0.09 , 10.10 ± 0.30 , 2.78 ± 0.04 , $n = 2$, respectively).

The water alkalinity in this study was mainly attributed to HCO_3^- as determined by the H_2SO_4 titration method. This analysis was performed only during the rainy season, and the HCO_3^- concentration (in mg/L) followed this decreasing order: tap water from Lake Paranoá (54.7) > porous aquifer (11.1) > fractured aquifer (5.3). Furthermore, no significant temporal variation of anions was observed in the samples. However, a spatial variation was noted for the Cl^- ion, which was predominant in the fractured aquifer (16.4 ± 0.1 mg/L, $n = 2$) and tap water from Lake Paranoá (11.5 ± 0.2 mg/L, $n = 2$), characteristic of the local lithology. The highest values of NO_3^- (15.1 ± 0.1 mg/L, $n = 2$) and SO_4^{2-} (7.32 ± 0.03 mg/L, $n = 2$) were recorded in the porous aquifer, where a septic tank is located upstream of the well, and in tap water from Lake Paranoá, respectively. Moreover, SO_4^{2-} originates from the natural dissolution of soils and rocks and water treatment processes, such as aluminum sulfate as a coagulant precursor. According to Brazilian Resolutions (Brasil, 2021), the maximum allowable value of NO_3^- is 10 mg/L, and for SO_4^{2-} concentrations vary from 250 to 400 mg/L depending on the resolution. Therefore, the water from a porous aquifer should not be available for human consumption without proper treatment, considering the nitrate concentrations. The PO_4^{3-} concentration in all water samples was below the DL (1.0 mg/L).

3.2 Rare earth elements and yttrium (REY) variation

The REY concentration in the water samples (Table 3) was higher than the QL, highlighting the effectiveness of this study's pre-concentration and quantification methods.

Spatiotemporal variations of REY were observed in the waters (Table 3). The maximum concentrations of ΣREY (944.0 ± 33.7 ng/L) and high values of all individual REE and Y were recorded in the porous aquifer during the rainy season. These values were supported by the sum of light REE ($\Sigma\text{LREE} = 804.5 \pm 32.2$ ng/L) and of heavy REE plus yttrium ($\Sigma\text{HREY} = 139.5 \pm 10.0$ ng/L). In comparison, the ΣREE concentration in the porous aquifer was about twenty times smaller

than the maximum concentrations (ranging from 23.2 to 18.8 $\mu\text{g/L}$) recorded in groundwater from Campinas City during the rainy season (Abreu *et al.*, 2024). Among the REE, Ce presented the highest concentration (301.8 ± 23.2 ng/L), while Lu had the lowest (0.85 ± 0.1 ng/L). During the rainy season, the REE concentrations are primarily associated with colloidal particles from river water, influenced by erosion and runoff, reflecting the dissolution of minerals during aquifer recharge (Duvert *et al.*, 2015). Additionally, among the aquifers, the fractured one presented the lowest ΣREY concentration, suggesting limited water-rock interaction, regardless of the season (31.5 ± 4.3 ng/L in the rainy season, 69.8 ± 1.8 ng/L in the dry season).

The maximum Gd concentrations were observed in the porous aquifer (25.4 ± 2.1 ng/L) and tap water from Lake Paranoá (22.9 ± 2.1 ng/L), mainly during the rainy season. These concentrations are comparable to the Gd levels recorded in the surface water of Lake Paranoá in 2017 (22.40 ± 0.04 ng/L), near the WWTP (Amorim *et al.*, 2019), and in tap water samples from Berlin, Germany (ranging from 11.4 to 27.3 ng/L) (Kulaksiz; Bau, 2011; Tepe; Romero; Bau, 2014). However, those values are lower than the Gd concentration observed in the groundwater of Campinas and São Carlos Cities, where the maximum values ranged from 0.291 to 0.590 $\mu\text{g/L}$ (Abreu *et al.*, 2024; Leite *et al.*, 2023), as well as in tap water from Salvador City (0.46 ± 0.04 $\mu\text{g/L}$) (Souza *et al.*, 2021).

There is no significant temporal variation of REY in tap water from Lake Paranoá. However, ΣHREY was twice as high as ΣLREE (Table 3). A high ΣLREE value was observed in tap water from Lake Descoberto, primarily due to the presence of Ce (116.8 ± 6.7 ng/L), Nd (18.0 ± 1.0 ng/L), and La (17.7 ± 1.1 ng/L). These values are below the concentrations reported in rivers (Gaillardet; Viers; Dupré, 2014), suggesting a local lithological contribution. Additionally, the La, Ce, and Nd values in this study are close to those reported in Lake Paranoá and its tributaries (La varied from 1.13 to 43.1 ng/L; Ce ranged from 1.30 to 74.5 ng/L and Nd varied from 0.94 to 34.4 ng/L) (Amorim *et al.*, 2019), except in the porous aquifer, where the concentrations of these elements were six times higher than the maximum values recorded in the surface waters of Lake Paranoá.

Overall, the REY results in the fractured aquifer are consistent with the variations observed in the literature, with ΣREE concentrations ranging between 1 and 100 ng/L. However, in the porous aquifer, La, Ce, and Nd values (Table 3) were higher than the average concentrations reported in river waters (Ce = 262 ng/L, Nd = 152 ng/L, and La 120 ng/L) (Gaillardet; Viers; Dupré, 2014). The high values of La, Ce, and Nd measured in the porous aquifer are similar to those observed in some wells in Campinas City (Abreu *et al.*, 2024). However, these authors also recorded high concentrations of these elements in other groundwater wells. High ΣREE concentrations were observed in the tributaries of the southern part of Lake Paranoá, particularly for La, Ce, and Nd (Amorim *et al.*, 2019). Positive Ce anomalies are likely associated with enriched mineral colloids, such as Fe or Mn oxyhydroxides (Loges *et al.*, 2012), or by Ce derived from soils enriched by agricultural activities (Sager; Wiche, 2024). Another hypothesis for high concentrations of La and Ce may be related to domestic sewage contamination in the aquifer recharge areas, mostly due to the absence of wastewater collection and treatment systems. In this city region, wastewater from most households is primarily managed by septic tanks, which can leak or overflow.

Table 3 – Mean concentration (ng/L, n = 2) of rare earth elements and yttrium (REY) in tap water and groundwater (porous and fractured aquifers) samples obtained during the rainy (January 2023) and dry (May 2023) periods in the Distrito Federal, Central Brazil

REY	Rainy season			Dry season			
	Fractured aquifer	Porous Aquifer	Tap water (Lake Paranoá)	Fractured aquifer	Porous Aquifer	Tap water (Lake Paranoá)	Tap water (Lake Descoberto) ^a
	Mean $\pm$ sd	Mean $\pm$ sd	Mean $\pm$ sd	Mean $\pm$ sd	Mean $\pm$ sd	Mean $\pm$ sd	Mean $\pm$ sd
La	7.1 ± 0.6	259.3 ± 23.3	3.5 ± 0.2	17.7 ± 1.6	134.4 ± 23.7	2.6 ± 0.2	17.7 ± 1.6
Ce	9.6 ± 3.9	301.8 ± 32.8	5.7 ± 1.0	15.04 ± 0.1	141.6 ± 26.0	4.4 ± 0.7	116.8 ± 9.2
Pr	1.3 ± 0.1	49.0 ± 6.5	0.87 ± 0.02	3.8 ± 0.4	23.5 ± 4.0	0.642 ± 0.003	4.8 ± 0.40
Nd	4.8 ± 0.7	167.3 ± 19.7	3.5 ± 0.1	13.5 ± 1.3	79.3 ± 11.1	2.5 ± 0.2	18.0 ± 1.4
Sm	0.74 ± 0.0	27.0 ± 3.6	0.69 ± 0.01	2.32 ± 0.02	12.4 ± 1.3	0.539 ± 0.004	3.3 ± 0.3
ΣLREE	23.6 ± 4.0	804.5 ± 32.2	14.3 ± 1.0	52.2 ± 1.7	391.3 ± 26.3	10.8 ± 0.5	160.6 ± 6.9
Eu	0.16 ± 0.03	5.1 ± 0.5	0.16 ± 0.01	0.5 ± 0.01	2.4 ± 0.2	0.15 ± 0.04	0.67 ± 0.07

Gd	0.9 ± 0.2	25.4 ± 2.9	22.9 ± 2.1	2.9 ± 0.2	14.4 ± 2.0	17.1 ± 1.0	3.9 ± 0.3
Tb	0.11 ± 0.0	2.8 ± 0.4	0.091 ± 0.002	0.4 ± 0.02	1.76 ± 0.12	0.13 ± 0.04	0.49 ± 0.05
Dy	0.59 ± 0.2	13.9 ± 1.9	0.51 ± 0.01	1.7 ± 0.1	6.3 ± 0.8	0.48 ± 0.01	1.8 ± 0.15
Y	5.2 ± 1.3	74.8 ± 13.7	3.48 ± 0.2	9.5 ± 1.1	26.9 ± 4.1	2.5 ± 0.1	9.0 ± 1.1
Ho	0.13 ± 0.1	2.6 ± 0.3	0.12 ± 0.01	0.36 ± 0.03	1.2 ± 0.2	0.15 ± 0.04	0.4 ± 0.04
Er	0.38 ± 0.2	6.8 ± 1.0	0.39 ± 0.04	1.0 ± 0.1	3.5 ± 1.0	0.4 ± 0.02	1.2 ± 0.1
Tm	0.05 ± 0.0	1.0 ± 0.1	0.09 ± 0.01	0.15 ± 0.01	0.44 ± 0.2	0.106 ± 0.0	0.18 ± 0.01
Yb	0.22 ± 0.06	6.0 ± 0.9	0.7 ± 0.1	0.79 ± 0.04	2.2 ± 1.4	1.113 ± 0.0	1.09 ± 0.06
Lu	0.04 ± 0.01	0.85 ± 0.1	0.11 ± 0.00	0.12 ± 0.01	0.35 ± 0.18	0.13 ± 0.05	0.19 ± 0.03
ΣHREY	7.8 ± 1.4	139.5 ± 10.0	28.6 ± 2.1	17.6 ± 0.8	59.6 ± 3.5	22.3 ± 0.7	19.1 ± 0.8
ΣREY	31.5 ± 4.3	944.0 ± 33.7	42.9 ± 2.3	69.8 ± 1.8	451.0 ± 26.5	33.1 ± 0.9	179.7 ± 6.7

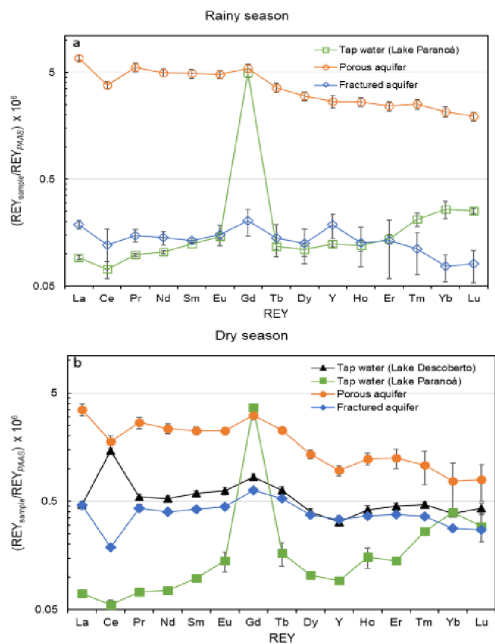
^aThis tap water was collected in September 2023, corresponding to the last month of the dry season in Distrito Federal, Brazil Central. ΣLREE is the sum of the mean concentrations and their respective standard deviations (sd) of the light rare earth elements (La, Ce, Pr, Nd, Sm); ΣHREY is the sum of the mean concentrations and their respective standard deviations (sd) of the heavy rare earth elements plus yttrium (Eu, Gd, Tb, Dy, Y, Ho, Er, Tm, Yb, Lu). Source: research data.

3.3 Assessment of REY enrichment and anomalies

To assess the enrichment levels between LREE and HREE and identify potential REY anomalies, the concentrations were normalized to Post Archean Australian Shale (PAAS) data (McLennan, 1989). This approach offers insights into REY anthropogenic and geological contributions in various environmental samples (Merschel *et al.*, 2015).

Regarding Figure 2, negative Ce anomalies were observed in all waters, except in the tap water from Lake Descoberto during the dry season, where Ce exhibited a positive anomaly. A negative Y anomaly was detected in all samples during the dry period, while a positive Y anomaly was observed only in the fractured aquifer during the rainy period. Additionally, a strong positive Gd anomaly was present in the tap waters of Lake Paranoá for both seasons, while a smaller positive Gd anomaly was noted in other samples.

Figure 2 – Shale-normalized REY (REY_{SN}) patterns of tap water and groundwater from Distrito Federal, Central Brazil



Water samples were collected during (a) the rainy season (January 2023) and (b) the dry season (May 2023), except the tap water from Lake Descoberto, collected in September 2023. Source: prepared by the authors.

La, Ce, and Gd anomalies were assessed numerically using the La/La*, Ce/Ce*, and Gd/Gd* ratios. La, Ce, and Gd concentrations in the water samples were compared with their expected natural concentration (La*, Ce*, Gd*). The values for La*, Ce*, Gd* were calculated according to the equations (Kulaksiz; Bau, 2013; Merschel *et al.*, 2015):

$$\log \log La_{SN}^* = (2 \log Nd_{SN} - \log Eu_{SN}) \quad (1)$$

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

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

For the Y anomaly, the Y/Y* ratio was calculated according to Equation 4 (Fazio *et al.*, 2007):

$$Y^* = \frac{Y}{\frac{2Y_{SN}}{(Dy_{SN} + Ho_{SN})}} \quad (4)$$

The Gd anthropogenic (Gd_{anth}) was calculated according to Equation 5 (Merschel *et al.*, 2015):

$$Gd_{anth} = Gd_{measured} - Gd_{SN}^* \quad (5)$$

In all equations, SN represents the shale-normalized concentrations (using PAAS).

The Yb_{SN}/Pr_{SN} ratio was used to assess the relative enrichment between HREE and LREE. Regardless of the sampling period, most samples displayed LREE enrichment, as the values for this ratio were ≤ 0.70, except in the tap water from Lake Paranoá (Table 4). An HREE enrichment was observed in this sample, with the Yb_{SN}/Pr_{SN} ratio varying between 2.66 ± 0.5 and 5.43 ± 0.02 during the rainy and dry seasons, respectively. This enrichment was also found in the surface waters from branches of Lake Paranoá and its dam (Amorim *et al.*, 2019) as well as in the Atibaia and Jaguari rivers in Southeast Brazil (Mortatti; Enzweiler, 2019). The enrichment of HREE over LREE is associated with carbonate complexes that bond with HREE more readily than with LREE, which influences the lanthanide contraction in the aquatic environment (Sholkovitz, 1995). The waters of Torto Creek (in Lake Paranoá) flow into the sampling site, suggesting that they may act as potential tracers of natural REY. Furthermore, HREE enrichment is characteristic of weathered water with low pH, where the adsorption of dissolved REE onto suspended particles is more significant for the LREE fraction, rendering them less available in the aqueous phase (Sholkovitz, 1993).

A slight positive anomaly in the Y/Y* ratio was observed only in the fractured aquifer during the rainy season, which may be associated with the weathering of local lithology (Möller; Dulski; De Lucia, 2021).

The La/La* ratios ranged from 1.2 to 1.7 in most water samples, except for the tap water from Lake Descoberto (La/La* = 1.0 ± 0.1) (Table 4). These values are similar to those observed in the surface water of Lake Paranoá (ranging from 1.18 to 1.72) (Merschel *et al.*, 2015). The contribution of La in these waters is likely associated with agricultural activities in rural areas of DF (EMATER, 2024), where fertilizers such as phosphorite, superphosphate, or P-fertilizer enriched in La and Ce are commonly used (Sager; Wiche, 2024). Another potential source could be hospital waste, as La is used in certain medical treatments (Aktar; Toyoda, 2024).

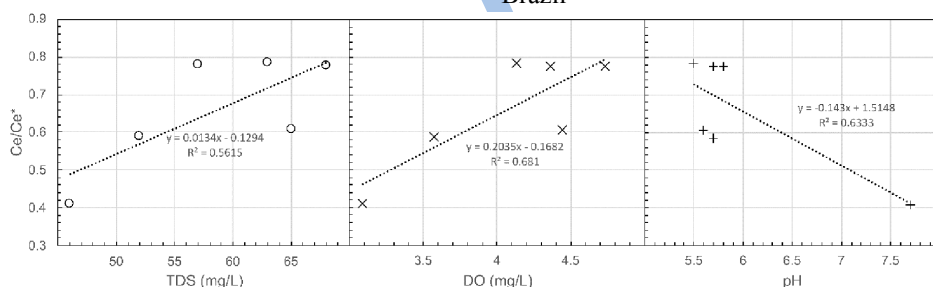
Table 4 – Values of Yb_{SN}/Pr_{SN} and La_{SN}/Pr_{SN} ratios, anthropogenic Gd (Gd_{anth}), Gd (Gd/Gd*), Ce (Ce/Ce*), La (La/La*), and Y/Y* intensity anomalies as observed in the water samples collected during rainy (January 2023) and dry (May or September 2023) seasons in Distrito Federal, Central Brazil

Anomalies	Rainy season			Dry season			
	Fractured Aquifer	Porous Aquifer	Tap water (Lake Paranoá)	Fractured Aquifer	Porous Aquifer	Tap water (Lake Paranoá)	Tap water (Lake Descoberto) ^a

^a the tap water from Lake Descoberto was collected in September/2023.
Source: research data.

Ce/Ce* ratio was lower than 1 in most water samples (Table 4), suggesting an oxidative environment, as supported by a good correlation ($R^2 = 0.681$; $n = 6$) between Ce/Ce* ratio and DO (Figure 3). Under these conditions, dissolved Ce^{3+} may be oxidized to the insoluble Ce^{4+} form, favoring adsorption/precipitation involving inorganic colloids (Deluca *et al.*, 2020; Loges *et al.*, 2012). The precipitation of cerianite (CeO_2) in the surface waters (Dia *et al.*, 2000; Seto; Akagi, 2008) can also be catalyzed by microorganisms (Akagi; Masuda, 1998). On the other hand, Ce^{3+} remains soluble and mobile (Möller; Dulski; De Lucia, 2021), as observed in the investigated samples, where a fair correlation ($R^2 = 0.5615$, $n = 6$) between Ce/Ce* ratio and TDS was registered (Figure 3). Moreover, Ce anomalies were more pronounced at acidic pH values (< 5.7) with a good correlation ($R^2 = 0.6333$; $n = 6$) observed between these variables (Figure 3). The composition of REE in the dissolved fraction ($< 0.22 \mu m$ filtrate) of river waters is mainly influenced by surface reactions (Sholkovitz, 1995). The pH-dependent fractionation order of REEs is consistent with chemical models of REE partitioning between solutions and surfaces.

Figure 3 – Linear correlation between calculated Ce/Ce* ratio and total dissolved solids (TDS), dissolved oxygen (DO), and pH in the waters (tap water and groundwater) sampled in 2023 at Distrito Federal, Central Brazil



Source: prepared by the authors.

The tap water from Lake Descoberto showed a Ce/Ce* ratio of 2.91, which is closer to the value observed in Lake Paranoá (2.09) (Amorim *et al.*, 2019). This positive anomaly has been previously recorded in unfiltered samples. In contrast, filtered samples from Lake Paranoá exhibited negative to neutral anomalies, suggesting that suspended particulate matter in the lake is enriched in Ce (Merschel *et al.*, 2015). This Ce enrichment is likely related to fertilizers (Sager; Wiche, 2024), as around 70% of DF is rural and engaged in agricultural activities (Emater/DF, 2024), as also registered in Torto Creek, which drains farming areas and urban settlements around Lake Paranoá (Amorim *et al.*, 2019). Additionally, Ce enrichment in the tap water from Lake Descoberto could also be linked to water alkalinity (Bau; Möller, 1993), although this was not evaluated in the present study. The pH and alkalinity values in the surface water of this reservoir remain relatively stable (Portela *et al.*, 2020).

A significant positive Gd anomaly was observed in the tap water supplied from Lake Paranoá (Figure 2), indicating its anthropogenic origin. This is consistent with findings in the surface water of Lake Paranoá (Merschel *et al.*, 2015; Amorim *et al.*, 2019). The anomaly is evident as the Gd/Gd* ratios ranged from 30.40 to 21.12, and the Gd_{anth} varied between 22.23 and 16.30 ng/L, representing 97% and 95% of total Gd in the tap water during both sampling periods (Table 4). Gd/Gd* values

ranging from 41.68 to 68.37 and Gd_{anth} concentrations between 22.1 and 33.6 ng/L were reported in the surface water of Lake Paranoá (Amorim *et al.*, 2019), which receive effluents from NN-WWTP and SW-WWTP (Figure 1). Since Gd originating from clinical exams has been used as a tracer for water contamination by domestic wastewater (De Paula Marteleto; Enzweiler, 2021; Möller; Dulski; De Lucia, 2021), the origin of Gd_{anth} in the tap water from Lake Paranoá is associated with the use of REE-based chelates in clinical exams. The presence of Gd_{anth} in the supply of water has also been documented in other countries. For example, concentrations ranging from 1.38 to 93.9 ng/L were reported in tap water samples from fast-food franchises in Germany (Schmidt *et al.*, 2019). In Poland, levels up to 11.45 ng/L were reported in water supply systems (Wysocka; Rogowska; Kostrz-Sikora, 2023), while other studies showed that Gd_{anth} often enters surface and groundwater systems, eventually reaching water treatment facilities (Brünjes; Hofmann, 2020; Kulaksiz; Bau, 2011; Tepe; Romero; Bau, 2014).

In groundwater, the Gd_{anth} concentrations were lower than those observed in the tap water from Lake Paranoá (Table 4). However, in the porous aquifer, where NO_3^- concentrations exceeded the Brazilian Resolution limit of 10 mg/L (Brasil, 2021), Gd concentration ranged from 25.4 ± 2.1 to 14.4 ± 2.0 ng/L (Table 4). During the rainy and dry seasons, Gd_{anth} varied between 3.37 and 4.18 ng/L, accounting for 13% and 29% of total Gd, while Gd/Gd^{*1} ratio ranged from 1.15 to 1.41, respectively. Natural Gd anomalies are typically characterized by Gd/Gd^* values between 1.0 and 1.5 (Bau; Knappe; Dulski, 2006) or up to 1.4 in surface water (Rabiet *et al.*, 2009). In contrast, a Gd/Gd^* ratio between 1.3 and 1.4 indicates an anthropogenic source of Gd anomalies in groundwater (Abreu *et al.*, 2024). This was evident in two groundwater samples from the alluvial plain of Campinas City, where Gd/Gd^{*2} values exceeding 1.8 were linked to Gd contamination from sewer systems. Furthermore, discrete anthropogenic Gd anomalies were observed in groundwater samples from São Carlos City, with Gd/Gd^{*2} ratios ranging from 1.24 to 1.27, indicating either older or more recent leaks from sewer systems (Leite *et al.*, 2023).

It is worth mentioning that in the aforementioned Brazilian groundwater studies, Gd anomalies were calculated using the interpolation of the normalized concentration of its neighboring REEs, samarium (Sm) and terbium (Tb), employing Equation 6 (Lawrence *et al.*, 2006):

$$Gd^{*2} = \frac{Gd}{(0.33 Sm_{SN} + 0.67 Tb_{SN})} \quad (6)$$

In the present study, the groundwater samples exhibited Gd/Gd^{*2} ratios ranging from 1.2 ± 0.1 to 1.5 ± 0.6 , with Gd_{anth} values between 3.9 ± 2.2 and 6.7 ± 9.5 ng/L, representing 26% and 27% of total Gd in the porous aquifer (Table 4). However, the contribution of anthropogenic Gd from Lake Paranoá in this groundwater remains uncertain due to the high variance in the results. Furthermore, our findings support previous research demonstrating that anthropogenic Gd behaves conservatively in the hydrosphere (Boester; Rüdé, 2020; De Paula Marteleto; Enzweiler, 2021; Kulaksiz; Bau, 2007; Merschel *et al.*, 2015). These results corroborate previous research, indicating that this conservative behavior makes Gd_{anth} a valuable tracer for investigating interactions between surface waters and groundwaters, particularly in contexts where municipal wastewater influences water supply systems (Abreu *et al.*, 2024; Boester; Rüdé, 2020; Leite *et al.*, 2023), and tap water quality (Kulaksiz; Bau, 2011; Tepe; Romero; Bau, 2014).

4 Conclusion

This study demonstrates that REY signatures are effective geochemical tracers for distinguishing among water sources in the Distrito Federal, Central Brazil, including tap water and groundwater. By characterizing the distinct REY behaviors—such as the LREE enrichment in the porous aquifer, the conservative behavior of HREE in surface-derived tap water, and the low concentrations in the fractured aquifer—this research provides a framework for monitoring water-rock interactions and seasonal hydrodynamic variations.

An important contribution of this work is the clear differentiation between the region's two main water supplies: the tap water from the Lake Paranoá system, marked by a pronounced anthropogenic

Gd anomaly, and the tap water from the Lake Descoberto system, characterized by lithogenic Gd and positive Ce anomalies likely linked to regional agricultural practices.

For the local community and managers in the Distrito Federal, these findings offer a powerful tool for environmental monitoring, helping to safeguard drinking water quality and track wastewater impacts or agricultural runoff. Regionally and scientifically, this study serves as a pioneering reference for assessing anthropogenic anomalies (e.g., Gd and Ce) in drinking water and groundwater systems.

Notably, since the REY concentrations quantified in this study are in the nanogram-per-liter (ng/L) range, current levels remain significantly below known toxicity thresholds, indicating a safe scenario for public supply and serving as an early warning indicator. Nonetheless, given the persistence and bioaccumulation potential of elements like Gd in biological systems, continuous monitoring of these waters stands as a fundamental preventive measure for future public health management.

As a pioneering baseline study, the primary focus here was establishing initial geochemical characterization and validating REY signatures as tracers. While these inferred origins are robustly supported by literature, future research would benefit from expanding sampling points and conducting direct source tracking—such as analyzing hospital effluents, wastewater, and specific fertilizers. Ultimately, this expanded dataset will provide the fundamental prerequisite to supply and calibrate future quantitative hydrogeochemical and transport models as continuous monitoring networks are established in the region.

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Conflicts of interest

No conflicts of interest are disclosed.

Contributions to the article

DUTRA-MAIA, P.: Conceptualization, Supervision, Writing original draft, review & edition. **AMORIM, A. M.:** Writing - review & edition, Data acquiring, Methodology, Validation. **OLIVEIRA, J. L. L.:** Data acquisition, Methodology, Investigation, Validation. **CUNHA, L. S.:** Writing - review & edition. **SODRÉ, F. F.:** Writing - review & edition, Supervision, Funding Acquisition.

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