Anthropogenic Gadolinium Anomalies in an Alluvial Plain with On-site Wastewater Treatment Systems in Campinas, SP, Brazil

Anomalias Antrópicas de Gadolínio em uma Planície Aluvionar com Sistemas de Saneamento In-situ em Campinas, SP, Brasil

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ABSTRACT

Gadolinium anomalies have become a well-established marker for the pollution caused by wastewater, but there is not yet a standardized method to estimate the anomaly. Here, we compare four different published equations, distinct threshold values and reference normalizing values to estimate Gd anomalies by applying them to the results of a hydrochemical investigation in an alluvial aquifer with on-site sanitation systems. We measured traditional wastewater markers (such as electric conductivity, NO_3–N, NH_4–N, Cl^-) and REE in groundwater samples collected from hand-dug wells in two seasons. The ratios of Gd normalized measured concentrations to Gd normalized geogenic concentrations (Gd_{SN}/Gd^*) estimated with the various methods ranged from 0.7 to 2.8. It turned out that the choice of the equation and the threshold value can affect the decisions about anthropogenic pollution's occurrence (or not). The normalizing values did not play a significant role in the decision. Based on measurement uncertainties and on the interpretation of hydrogeological conditions in the study area, a threshold value of 1.3 for defining anthropogenic Gd anomalies was deemed adequate for the study area. The occurrence of Gd anomalies higher than 1.8 in two wells, one in each season, reinforces the hypothesis that the groundwater is contaminated by the on-site sanitation systems in the study area, as intermittent detection of anthropogenic Gd is a characteristic of this pollution source.

Keywords: rare earth elements, water quality, septic systems, marker of anthropogenic pollution

RESUMO

As anomalias de gadolínio são reconhecidas atualmente como bons marcadores de poluição causada por água residuária. Apesar disso, ainda não existe um método padronizado para a sua estimativa. Neste artigo são comparadas quatro equações, diferentes limiares e diferentes valores de normalização para estimativa das anomalias de Gd em um estudo de caso realizado em um aquífero aluvionar onde existem sistemas de saneamento in-situ. As concentrações de marcadores tradicionais de poluição (tais como condutividade elétrica, NO_3–N, NH_4–N, Cl^-) e de elementos terras raras (ETR) foram medidas em amostras coletadas em poços cacimba. As razões entre a concentração normalizada de Gd medida e a concentração geogênica normalizada de Gd (Gd_{SN}/Gd^*) variou de 0,7 a 2,8. Verificou-se que a escolha da equação para estimativa da concentração geogênica, assim como o valor do limiar que define a anomalia podem afetar a decisão sobre a ocorrência (ou não) de poluição antropogênica. O valor de referência para normalização não teve papel relevante para esta decisão. Com base nas incertezas analíticas de medida e na interpretação das condições hidrogeológicas da área de estudo, o valor de 1,3 foi considerado adequado como limiar para a definição das anomalias de Gd na área de estudo. A ocorrência de anomalias de Gd acima de 1,8 em dois poços, uma em cada campanha de coleta, confirma que a poluição das águas do aquífero tem como fonte as fossas sépticas existentes na área de estudo, uma vez que a detecção intermitente de anomalias de Gd é uma das características deste tipo de fonte.

Palavras-Chave: elementos terras raras, qualidade da água, fossas sépticas, marcador de poluição antrópica

1 INTRODUCTION

The use of rare earth elements (REE) concentrations as water pollution markers is a growing tendency (KULAKSIZ; BAU, 2013; TEPE, *et al.*, 2014; HATJE, *et al.*, 2016; CAMPOS; ENZWEILER, 2016; LOUIS, *et al.*, 2020; MARTELETO; ENZWEILER, 2021). The REE comprise Sc, Y and the fifteen lanthanides (La-Lu), but frequently the term refers only to the last series, as in this article. This group of elements has a coherent chemical behavior and, due to the Oddo Harkins effect, the comparison of their concentrations is better done by division to a reference. When one of the normalized REE value differs from its neighbors, it is considered an anomaly. Cerium (Ce) and Europium (Eu) may present natural anomalies because they can occur in two valences and become decoupled from the remaining REE under specific oxy-reduction conditions. On the contrary, gadolinium occurs in geogenic conditions in only one oxidation state and is therefore not expected to present anomalies. Its introduction in the environment is related to its use in the form of gadopentetic acid ($Gd(DTPA)_2$) and other Gd chelates as contrast agents for enhancing magnetic resonance imaging (MRI) in hospitals and clinics since 1988 (KUMMERER; HELMERS, 2000). Such Gd chelates are highly stable both in the human body and remain soluble in wastewater and water bodies after excretion. Moreover, they are unaffected by regular sewage treatment. Therefore, Gd was proposed as an ideal tracer of raw wastewater and of wastewater treatment plants (WWTP) effluents (MOLLER *et al.*, 2000; 2002).

Bau and Dulski (1996) were the first ones to identify gadolinium anomalies in river water resulting from wastewater pollution. Since then, some methods have been proposed to estimate the Gd anomaly. Three aspects are relevant in the discussion about how to detect the occurrence of a Gd anomaly and how to estimate it: a) the best equations for each case study to estimate the geogenic (or natural) concentration of Gd, here addressed as Gd*, b) the criterion (or threshold value) to establish what should be considered an anomalous concentration and c) the reference values used for normalization. For water, the reference values are published shales REE average values.

This study compares different methods to estimate Gd anomalies discussing the consequences of using them to identify septic tank wastewater pollution in an alluvial aquifer in a peri-urban area with on-site sanitation systems (septic tanks and cesspools). Louis *et al.* (2020) have recently discussed the influence of the different calculation methods on the numerical value of the observed Gd anomalies in a different geological and land-use setting. We expanded the topic, also discussing the impact of the different REE normalizing values in use and the threshold value to assume the presence of an anthropogenic Gd anomaly, especially in groundwater.

The presence of geogenic Eu anomalies attributed to feldspar dissolution in previous studies in river water in the same watershed (CAMPOS; ENZWEILER, 2016; MORTATTI; ENZWEILER, 2019) prevented the use of methods that include Eu for the estimation of Gd geogenic concentrations.

2 ESTIMATION OF Gd ANOMALY

Bau and Dulski (1996) used equation (1) to estimate Gd anomaly in their pioneering work. This equation assumes that the difference between neighboring concentrations is constant (linear regression) and uses Sm and Tb to obtain Gd normalized geogenic concentration (Gd*)

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$$Gd^* = 0.33Sm_{SN} + 0.67Tb_{SN} \quad (1)$$

The subscript SN always indicates shale normalized geogenic concentrations of the elements.

Lawrence *et al.* (2006b) inspected their data on both linear–linear and log–linear plots and concluded that, overall, their REE patterns behaved more smoothly on log–linear plots. Therefore, they used equation (2) to estimate Gd*.

$$Gd^* = \left(Sm_{SN} \, . \, {Tb_{SN}}^2\right)^{1/3} \ (2)$$

Lawrence *et al.* (2006b) are among the few who compared Gd anomalies estimated with different equations. When using Eq. (1) and (2) they concluded that both yielded robust Gd anomalies. The differences in calculated anomalies for their samples were typically less than 2% (which is within the combined analytical uncertainties, according to the authors, who also tested Ce and Eu anomalies).

Both equations (1) and (2) have the advantage of requiring the measurement of only two other REE, besides Gd, to estimate the anomaly.

Möller *et al.* (2003) estimated Gd* using two procedures: one that considered the normalized concentrations of Eu and Tb and the other that fitted a third-order polynomial (as offered by the Excel® program) to the shale normalized concentrations of Pr, Nd, Dy, Ho and Er. They found out that the differences between the Gd anomalies given by both methods were within 25%, and commonly the results of both interpolation procedures were nearly identical. The authors deemed the fitting method as more adequate. Eu anomalies were absent in their water samples. Later on, Lawrence *et al.* (2009) proposed that the estimation should be done by fitting a third order polynomial to the nine non-anomalous REE: Pr, Nd, Sm, Tb, Dy, Ho, Er, Tm, Yb.

Kulaksiz and Bau (2007) found out that Gd behaved as a light REE (LREE, La, Ce, Pr, Nd) in river water in their study area and deemed that only LREE should be used to estimate Gd*, proposing Nd and Sm as extrapolating elements. Afterwards, the same authors used a linear regression of the normalized concentrations of Pr, Nd and Sm (KULAKSIZ; BAU, 2011) to estimate Gd*.

Kulaksiz and Bau (2011; 2013) proposed the use of the concentrations of Eu and Nd for the estimation of Gd anomalies. Merschel *et al.* (2015) also used the same elements in their study of Paranoá lake, Brasilia, Brazil. Hissler *et al.* (2015) proposed the use of Nd and Dy for the estimation of the Gd anomalies. In their study area REE showed an increasing trend from Nd to Dy during low flow. During high flow events Gd behaved as a middle REE (MREE: Sm, Eu, Gd, Tb).

Louis *et al.* (2020) compared the results for equation (1) and the methods proposed by Hissler *et al.* (2015) and Kulaksiz and Bau (2007; 2013). They found out that the different equations did not give the same value of Gd/Gd*, with the proposal of Hissler *et al.* (2015) tending to maximize the anomaly. Kulaksiz and Bau (2007; 2013) approaches tended to minimize it. However, in Louis *et al.* (2020) the results could be used in a qualitative way, as all four equations resulted in similar Gd anomalies allowing the comparison of the intensities of Gd anomalies among samples.

A second aspect to be considered is the criterion to establish what should be considered an anomalous concentration. The concentration of anthropogenic Gd (Gd_{anth}) is estimated by equation (3)

$$Gd_{anth} = Gd_{meas} - Gd_{nat} \qquad (3)$$

Where Gd_{anth} is the concentration of Gd in the water introduced from anthropogenic sources, Gd_{meas} is the Gd concentration measured in the sample, Gd_{nat} is the natural Gd concentration in the area, calculated as in equation (4).

$$Gd_{nat} = H.Gd^{*}.Gd_{norm} \qquad (4)$$

Where Gd_{nat} is the natural concentration of Gd, Gd* is the estimated natural Gd normalized concentration resulting from the interpolation, Gd_{norm} is the Gd concentration in the shale normalizer and H is the threshold that defines the limit above which Gd concentrations should be considered anthropogenic and not geogenic.

Bau and Dulski (1996) proposed, from a theoretical point of view, that H should be equal to 1. However, these authors pointed out that in their study area waters regarded as pristine showed Gd_{SN}/ Gd* ratios of 1.2 and 1.9 and hence, Gd_{SN}/ Gd* ratios above unity did not necessarily imply the presence of anthropogenic Gd anomalies. They stated that consideration of the complete REE pattern was essential.

Bau *et al.* (2006) proposed a distinction between natural and anthropogenic Gd anomalies. They studied water samples of several rivers and lakes in the USA and identified that they showed one continuous upward trend from La to Gd, then a step to a lower level and a second upward or flat trend from Tb to Lu. The Gd_{SN}/ Gd* ratios of these samples as estimated by equation (1) ranged from 1.15 to 1.47, which would in principle indicate an anthropogenic Gd anomaly. Therefore, they defined H=1.5 as the threshold to distinguish between a natural and an anthropogenic Gd anomaly in freshwater in their study area. Natural Gd anomalies would be characterized by Gd_{SN}/ Gd* between 1.0 and 1.5.

A similar approach was used by other researchers. Rabiet *et al.* (2005; 2006; 2009) studied the Hérault watershed in France. They considered 1.0 to be the threshold for natural anomalies and H=2.0 (RABIET *et al.*, 2005), H=1.5 (RABIET *et al.*, 2006) and H=1.4 (RABIET *et al.*, 2009) as the threshold for wastewater contamination. Petelet-Giraud *et al.*

(2009) studied the Dommel watershed in Belgium and Netherlands. They considered 1.0 to be the threshold for natural anomalies and H=1.3 to be the threshold for wastewater contamination. Lawrence *et al.* (2006b), applying equation (2), considered 1.0 to be the threshold for natural anomalies and H=1.23 to be the threshold for anthropogenic anomalies.

Kulaksiz and Bau (2011) estimated Gd* by linear regression of the normalized concentrations of Pr, Nd and Sm. They stated that a Gd_{SN}/ Gd* ratio above unity indicates a positive anthropogenic Gd anomaly because Gd behaves as an LREE. So, no HREE (Tb, Dy, Ho, Er, Tm, Yb, Lu) was included to estimate the background Gd.

Lawrence *et al.* (2009) concluded that a third order polynomial is the only method that makes no implicit assumption as to whether Gd behaves more like the LREE, or the HREE. According to them, such a distinction is usually unimportant when all samples are of a similar type, however, this is not expected to be the case, for instance, where natural waters are compared with WWTP effluents. They considered H to be equal to 1.1.

Möller *et al.* (2003) presented two explanations for the adoption of H=1.2 (instead of 1.0) as indication for the anthropogenic (medical) anomaly. In their study area dolomite and limestone of marine origin showed Gd_{SN}/ Gd* in the range of 1.1 to 1.2 and fertilizers widely used in agriculture showed Gd_{SN}/ Gd* in the range of 1.2 to 1.3.

Hissler *et al.* (2015) considered H=1.5 and Louis *et al.* (2020) decided for H=1.8 for their study area in France. Mortatti and Enzweiler (2019) and Marteleto and Enzweiler (2021) used H=1.2.

The third aspect that needs consideration is the normalizer used to properly compare the measured REE concentrations. Of special interest in this respect is the study of Lawrence *et al.* (2006b). They tested the robustness of the anomalies calculated relative to Mud from Queensland (MUQ) (KAMBER *et al.*, 2005) for sediments from individual waterways, and relative to the Post Archaean Australian Shale (PAAS) average as published by Taylor and McLennan (1985). They found out that, whilst the magnitude of the La, Ce and Gd anomalies varied according to the normalizer, the features themselves clearly persisted.

According to the present literature review, the most widely used normalizer when studying Gd anomalies is the PAAS. Bau and Dulski (1996); Moller *et al.* (2002); Möller *et al.* (2003); Knappe *et al.* (2005); Bau *et al.* (2006); Morteani *et al.* (2006); Kulaksiz and Bau (2011); Hissler *et al.* (2014); Merschell *et al.* (2015); Hissler *et al.* (2016); Campos and Enzweiler (2016); and Louis *et al.* (2020) used PAAS concentrations proposed by McLennan (1989). Hissler *et al.* (2016) used PAAS concentrations proposed by Taylor and Mc Lennan (1985). Mortatti and Enzweiler (2019); and Marteleto and Enzweiler (2021) used PAAS concentrations proposed by Pourmand *et al.* (2012). Lawrence *et al.* (2006a); Lawrence *et al.* (2006b); Lawrence *et al.* (2009) used MUQ concentrations proposed by Kamber *et al.* (2005) as normalizer. Rabiet *et al.* (2005; 2006; 2009); and Petelet-Giraud *et al.* (2009) used the North American Shale Composite (NASC) concentrations proposed by Haskin *et al.* (1968). Klaver *et al.* (2014) used NASC concentrations proposed by Hannigan and Sholkovitz (2001).

3 STUDY AREA

The study area comprises 0.25 km^2 of the 32 km^2 alluvial plain on the left riverbank of Atibaia River in Campinas, SP, southeast Brazil (Figure 1). Medium and low-income inhabitants have lived in the area from the early 1980's onwards (SIMPLICIO; ABREU, 2021). Campinas is the central city of a metropolitan area that has modern medical infrastructure. The nearest hospitals are located at about 11 km of the study area. According to Marteleto and Enzweiler (2021) they have MRI facilities and perform annually more than 8000 MRI exams.

The local climate is predominantly humid subtropical (Cwa), with rainy summers and dry winters. The average precipitation is 1,404 mm/year, with the highest precipitation records in January (273 mm) and the lowest in August (31.4 mm). The annual average temperature is 22.4 ºC (CEPAGRI, 2021).

Forty-five hand-dug wells in the study area supply water for domestic purposes other than drinking and cooking (ALENCAR, 2021). Most of them show poor sanitary protection. Only 26% of the wells lie more than 30 meters apart from any on-site sanitation system.

Recent unconsolidated sediments form the shallow phreatic aquifer of the alluvial plain. Its heterogeneous facies distribution contains fine and coarse sand and silt and clay-sized sediments, intercalated by fine or very fine micaceous sand lenses. They are deposited over Permo-Carboniferous sedimentary rocks of the Itararé Subgroup, Cretaceous igneous rocks of the Serra Geral Formation and Pre-Cambrian igneous and metamorphic rocks (Jaguariúna Complex) (SÃO PAULO, 2009).

Figure 1 shows the potentiometric map of the area in August 2019 (ALENCAR, 2021). The overall flux in the area is from NNE to SSW. The region near well W37 is a natural levee. The existing ponds are the result of abandoned sand mining sites that occurred in the alluvial plain in the 1970s (SIMPLICIO; ABREU, 2021). Throughout the whole study area, the hydraulic heads are generally 0.5 m lower in the dry season than in the wetter season. The south zone has evidence of anoxic conditions, with high Fe(t), Mn(t) and dissolved organic carbon (DOC) concentrations, while the northern area is under oxic conditions (ALENCAR, 2021). According to Rupias *et al.* (2021), high concentrations of Cl^{-}, Na^{+} and NO_3^{-} imply anthropogenic pollution, especially in the rainy season, when pollutants mobilization is higher. The prevalence of anoxic conditions can attenuate the NO_3^{-} concentrations in the southern area.

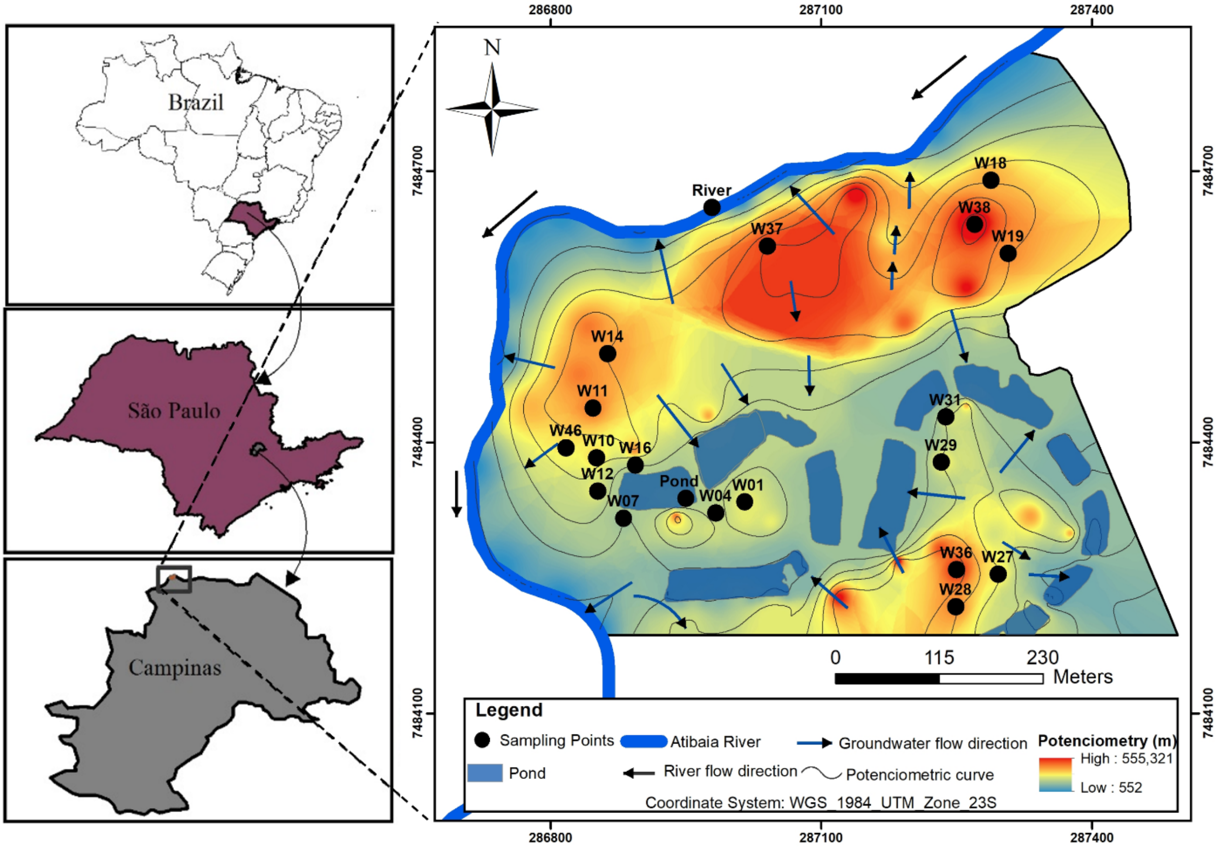

Figure 1 - Location of the study area, hydraulic heads in the dry season and location of the sampling points.

4 METHODS

Alencar (2021) and Rupias *et al.* (2021) performed the registration of the existing dug wells in the study area. Eighteen of these wells were sampled in April 2019 and in August 2019, not necessarily the same. Moreover, two samples from surface water bodies were collected in each campaign: one from the Atibaia river and one from one of the existing abandoned mining ponds. Of the eighteen samples collected from dug wells in each season, only thirteen (for each season) are discussed in this study, because some of the samples had most of the REE concentrations bellow the limit of quantification (LOQ) in both or in one of the seasons. All in all, for this study fifteen samples are available for each season: thirteen water samples from dug wells, one from the Atibaia River, and one from the abandoned mining pond. Ten sampling locations are common for both campaigns. Figure 1 indicates the sampling points.

Water was collected from the wells using plastic bailers. Electric conductivity and pH were measured in the field with a multisensor (YSI Pro-Plus). Sampled water was filtered across 0.22 µm pores cellulose acetate filters and stored in two 50 mL low-density polyethylene (LDPE, Nalgene) bottles and one 30 mL amber glass bottle, which have been previously cleaned with deionized water. One of the 50 mL filtered aliquot was acidified (1% v/v ultrapure HNO_3) in the field for preservation.

Major ions (NO_3^-, Cl^-, NH_4^+) concentrations were determined by ion chromatography (ICS-2500, Dionex). Dissolved organic carbon (DOC) was determined by measuring CO_2 after thermocatalytic oxidation by the non-purgeable organic carbon (NPOC) method (multi N/C® 2100/2100S, Analytik Jena), following ISO 8245 (1999). The measurement of major cations and trace elements concentrations, including REE, was done directly in the acidified aliquots by inductively coupled plasma mass spectrometry (ICP-MS, X Series II - Thermo Fisher Scientific). This paper discusses only the samples in which most of the REE concentrations are above the limit of quantification (LOQ).

The measured REE concentrations were ratioed against the respective PAAS values (POURMAND *et al.*, 2012). The estimates of Eu anomalies and Ce anomalies followed Equations (5) and (6) (LAWRENCE; KAMBER, 2006).

$$\frac{Eu}{Eu^*} = \frac{Eu_{SN}}{\left(Sm_{SN}{}^2.Tb_{SN}\right)^{1/3}} \quad (5)$$

$$\frac{Ce}{Ce^*} = \frac{Ce_{SN}}{(La_{SN}.Pr_{SN})^{1/2}} \quad (6)$$

Where the subscript SN indicates the PAAS normalized measured concentrations of each REE.

To estimate Gd anomalies, we compared four different methods (M), as reviewed in item 2 and summarized in Table 1. In the following they will be addressed as M1, M2, M3 and M4. As the normalizer adopted by Hissler *et al.* (2015) is not indicated, it was not included in this study.

The concentrations of anthropogenic Gd were then compared to the concentrations of traditional wastewater markers (NO_3-N, NH_4–N, Cl^-) to assure that the estimated Gd anomalies in the study area are effectively present.

Table 1 - Methods used for the estimation of Gd anomalies.

Method	Reference	Normalizer	Estimation of Gd_{SN}*	H $^{(*)}$
M1	Bau and Dulski (1996)	PAAS (McLennan, 1989)	Equation (1)	1.0
M2	Lawrence *et al.* (2006b)	MUQ (Kamber *et al.*, 2005)	Equation (2)	1.0
M3	Lawrence *et al.* (2009)	MUQ (Kamber *et al.*, 2005)	Third order polynomial fit of the normalized concentrations of nine not anomalous REE: Pr, Nd, Sm, Tb, Dy, Ho, Er, Tm, Yb.	1.1
M4	Kulaksiz and Bau (2011)	PAAS (McLennan, 1989)	Linear regression of the normalized concentrations of Pr, Nd and Sm	1.0

(*) threshold value proposed in the corresponding reference

5 RESULTS

The physicochemical parameters and the concentrations of NO_3^-, Cl^-, NH_4^+, DOC and REE of the 30 samples discussed in this paper are presented in tables 2 and 3. [NO_3^-] and [NH_4^+] are expressed as mg/L NO_3-N and NH_4–N, respectively.

5.1 PHYSICOCHEMICAL DATA

The pH of the groundwater was acid to neutral, ranging from 4.94 to 6.59 in the wet season and from 5.63 to 7.16 in the dry season. The electrical conductivity (EC) ranged from 52 to 409 µS/cm in the wet season and from 69 to 543 µS/cm in the dry season, with median values of 202 and 245 µS/cm, respectively. In the wet season, the Atibaia River's pH was 7.06 and EC was 113 µS. In the dry season, the pH was 7.08 and EC was 110 µS/cm. In the abandoned mining pond, the pH was 7.41 and EC was 195 µS/cm in the wet season. In the dry season, the pH was 7.57 and EC was 193 µS/cm.

5.2 TRADITIONAL WASTEWATER MARKERS

The 13 well samples of the wet season presented NO_3–N concentrations from below the LOQ to 13.6 mg/L, NH_4–N concentrations ranging from 0.29 to 3.87 mg/L, Cl^- concentrations varying from 2.53 to 34.4 mg/L and DOC ranged from 0.63 to 3.0 mg/L. In the Atibaia River the NO_3–N concentration was 1.60 mg/L, Cl^- concentration was 10.7 mg/L and DOC was 4.00 mg/L. In the abandoned mining pond, the NO_3–N concentration was below LOQ, Cl^- concentration was 8.75 mg/L and DOC was 5.70 mg/L.

Among the 13 wells tested in the dry season, NO_3–N concentrations ranged from below the LOQ to 9.60 mg/L, NH_4^-N concentrations ranged from 0.29 to 12.2 mg/L, Cl^- concentrations ranged from 4.53 to 52.5 mg/L and DOC ranged from 0.55 to 7.90 mg/L. In the Atibaia River the NO_3–N concentration was 2.60 mg/L, Cl^- concentration was 13.0 mg/L and DOC was 3.50 mg/L. In the abandoned mining pond, the NO_3–N concentration was below LOQ, Cl^- concentration was 9.12 mg/L and DOC was 9.40 mg/L.

The area where well W37 is located is a natural levee and shows good water quality throughout the year. This well is located more than 30 meters away from on-site sanitation systems, in a less densely populated area of the neighborhood and shows low concentrations of well-established wastewater markers.

5.3 RARE EARTH ELEMENTS RESULTS

The ΣREE concentrations of wet season 15 samples ranged from 0.186 µg/L to 23.2 µg/L, with a mean value of 4.2 µg/L. The ΣREE concentrations of the 15 samples collected in the dry season ranged from 0.186 µg/L to 5.8 µg/L, and mean value of 1.8 µg/L.

The REE normalized distributions are presented in Figure 2. The normalized La/Yb ratios varied from 0.1 to 3.6 in the wet season and from 0.3 to 2.0 in the dry season. Three different groups could be identified: a) similar to Atibaia River (LREE enriched) (wells W01, W11, W12, W14, W18, W19, W28, W37, W46 and the Atibaia River in the wet season, and wells W10, W14, W36, W37, W38, W46, the river and the mining pond in the dry season), b) enriched in HREE (wells W04, W27, W29 and W31 in the wet season, and wells W12, W27 and W29 in the dry season) and c) relatively flat patterns (wells W07, W11, W16 and W31 in the dry season). No spatial correlation between similar patterns could be identified either in the wet or in the dry season.

A positive Eu anomaly is present in most of the samples. Eu/Eu* ratios varied from 1.2 to 4.4 in the wet season and from 1.3 to 2.1 in the dry season. Positive or negative Ce anomalies were identified in some of the samples, with Ce/Ce* ratios ranging from 0.2 to 1.5.

5.4 ESTIMATES OF GADOLINIUM ANOMALIES

The Gd_{SN}/Gd^* ratios for the 30 samples estimated according to the different proposed methods are presented in table 4. Methods M1 and M2 result in similar Gd_{SN}/Gd^* values, but according to M1 (H=1.0, as in table 1) all 30 samples have anthropogenic contribution, while according to M2 (H=1.0, as in table 1), 26 samples contain anthropogenic Gd. On the other hand, M3 systematically underestimates Gd_{SN}/Gd^* values when compared to M1, as presented in Figure 3(a). Moreover, as the threshold (H) proposed by Lawrence *et al.* (2009) is 1.1, according to M3 only 17 of the samples show anthropogenic Gd anomalies. Method M4 provides even smaller values for Gd_{SN}/Gd^* (Figure 3(b)) and according to this method only 10 out of the 30 samples show anthropogenic Gd anomalies. In fact, with M4 some of the estimated ratios are bellow unity. The reason for this that the REE patterns in the study area are variable and different from the patterns of the area for which M4 was proposed. As described by Kulaksiz and Bau (2007), the pristine rivers in the area where M4 was applied commonly display dissolved REE patterns that are subdivided in two sections: they increase from La to Gd, show a step down from Gd to Tb, and increase again from Tb to Lu; They are HREE enriched and Gd obviously behaves as a light REE (LREE).In the alluvial plain of the study area the REE do not show this pattern and Gd does not necessarily behave as a LREE, which is an assumption for the use of M4. For this reason, method M4 was not further investigated in this research.

The influence of the normalizer on the Gd anomaly results was also tested. The Gd_{SN}/ Gd^* ratios estimated by fitting a 3rd order polynomial to the normalized concentration of the natural non-anomalous REE using four different shale values as normalizers are presented in table 5. For the wet season, estimates made using PAAS values published by Mc Lennan (1989) and NASC values are usually higher than those obtained either with MUQ or with PAAS values proposed by Pourmand *et al.* (2012). All normalizers result in relatively similar estimates for the dry season, with MUQ revealing slightly higher values for most samples.

5.5 THRESHOLD VALUE AND MEASUREMENT ANALYTICAL UNCERTAINTIES

As previously discussed, the threshold value is another aspect to be addressed to evaluate Gd anthropogenic concentrations. Mortatti and Enzweiler (2019) suggested the use of H=1.2 due to measurement uncertainties and, to a lesser degree, due to small differences in estimated Gd anthropogenic concentrations that arise from the use of different published normalizing values. The measurement uncertainty of our analytical procedure was estimated using a top-down approach (MAGNUSSON *et al.* 2017) using long term (more than one year) measurement results obtained for the reference material of river water (SLRS-5). For the REE, the relative measurement uncertainties (U) vary from 6.2% (La) to 29% (Tm), at a 95% confidence interval, with an average of 16%. In comparison, the uncertainties associated with the compiled values range from 11% (La) to 33% (Tm) (YEGHICHEYAN *et al.* 2013), with an average uncertainty of 17%.

In the hypothesis of a worst-case scenario for methods M1 and M2, with the measured concentrations of Sm and Tb being at the lower side of their measurement uncertainty interval and those of Gd on its higher side, the estimated Gd anomalies would increase systematically, between 38 to 40% for method M1, and 42% for method M2. Such outcome results from high Tb measurement uncertainty. Similarly, for method M3, if Gd concentrations were at the higher side of the uncertainty interval while those of Pr, Nd, Sm, Tb, Dy, Ho, Er, Tm and Yb had an opposite tendency, the estimated Gd anomalies would increase 25% to 33%, with the majority becoming 30% higher. In conjunction, the former suppositions are highly improbable but help proposing realistic threshold values for methods M1 and M2 as 1.4, and for method M3, like 1.3. In this scenario, W4 in the wet season and W36 and the Atibaia River in the dry season would have anthropogenic Gd according to the three estimation criteria.

Table 2 - Physicochemical parameters and concentrations of traditional wastewater markers, DOC and REE of the samples collected in the wet season.

Parameter	W1	W4	W11	W12	W14	W18	W19	W27	W28	W29	W31	W37	W46	River	Pond	LOQ*
EC (µS/cm)	120.0	220.1	126.6	277.6	113.6	144.2	138.6	218.0	197.1	409.2	333.4	52.0	274.40	112.6	194.7	-
pH	6.09	6.14	5.31	5.80	5.13	5.71	5.73	6.14	6.52	6.59	6.48	5.53	4.94	7.06	7.41	-
DOC (mg/L)	2.80	2.40	0.69	2.40	0.63	1.40	0.97	2.00	3.00	1.20	1.50	0.76	1.10	4.00	5.70	0.60
Cl (mg/L)	8.04	21.8	16.1	17.7	15.1	16.8	11.6	25.4	2.53	30.1	19.6	7.62	34.4	10.7	8.75	0.010
NH_4-N(mg/L)	0.43	3.87	<LOQ	0.29	<LOQ	<LOQ	<LOQ	0.33	0.94	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.040
NO_3-N(mg/L)	<LOQ	0.20	3.98	2.69	5.33	2.78	2.46	1.06	<LOQ	7.79	0.48	<LOQ	13.6	1.60	<LOQ	0.009
ΣREE (µg/L)	1.552	0.186	5.656	16.810	1.165	2.494	0.536	0.302	1.828	0.527	0.455	0.260	23.187	5.623	1.728	-
La (µg/L)	0.199	0.025	1.265	3.552	0.260	0.987	0.176	0.090	0.318	0.139	0.092	0.080	4.833	1.120	0.331	0.024
Ce (µg/L)	0.730	0.048	2.599	8.780	0.541	0.391	0.187	0.076	0.769	0.100	0.168	0.087	10.80	2.709	0.909	0.028
Pr (µg/L)	0.065	0.005	0.245	0.650	0.048	0.174	0.024	0.014	0.083	0.027	0.020	0.014	1.033	0.256	0.076	0.004
Nd (µg/L)	0.333	0.027	0.926	2.507	0.187	0.653	0.093	0.064	0.392	0.113	0.085	0,050	3.892	0.989	0.285	0.022
Sm (µg/L)	0.058	0.007	0.159	0.386	0.033	0.088	0.013	0.013	0.075	0.021	0.016	0,007	0.711	0.168	0.039	0.006
Eu (µg/L)	0.015	0.004	0.043	0.084	0.012	0.018	0.009	0.007	0.017	0.005	0.004	0,002	0.169	0.036	0.008	0.002
Gd (µg/L)	0.049	0.012	0.139	0.291	0.028	0.077	0.015	0.012	0.060	0.022	0.016	0,007	0.590	0.134	0.032	0.006
Tb (µg/L)	0.006	0.001	0.020	0.039	0.004	0.008	0,002	0.001	0.007	0.003	0.002	0,001	0.085	0.017	0.004	0.001
Dy (µg/L)	0.032	0.007	0.110	0.204	0.022	0.041	0,008	0.008	0.040	0.016	0.011	0,004	0.479	0.085	0.018	0.004
Ho (µg/L)	0.008	0.002	0.022	0.042	0.004	0.008	0,001	0.002	0.009	0.005	0.003	0,001	0.091	0.016	0.003	0.001
Er (µg/L)	0.025	0.011	0.061	0.124	0.012	0.023	0,005	0.006	0.026	0.023	0.012	0,003	0.249	0.046	0.012	0.002
Tm (µg/L)	0.004	0.002	0.008	0.017	0.002	0.003	0,001	0.001	0.003	0.004	0.002	<LOQ	0.032	0.006	0.001	0.001
Yb (µg/L)	0.025	0.028	0.052	0.116	0.011	0.019	0.003	0.007	0.024	0.040	0.021	0.003	0.198	0.036	0.008	0.001
Lu (µg/L)	0.004	0.006	0.008	0.019	0.002	0.003	0.001	0.001	0.004	0.009	0.004	<LOQ	0.028	0.005	0.001	0.001

* LOQ stands for Limit of Quantification.

Table 3 - Physicochemical parameters and concentrations of traditional wastewater markers, DOC and REE of the samples collected in the dry season

Parameter	W7	W10	W11	W12	W14	W16	W27	W29	W31	W36	W37	W38	W46	River	Pond	LOQ*
C (µS/cm)	239	197	81	183	90	175	218	383	543	310	69	69	107	110	193	-
pH	7.16	5.63	5.84	6.15	6.14	6.58	6.26	6.84	7.16	6.37	6.46	6.81	5.71	7.08	7.57	-
DOC (mg/L)	3.30	1.20	1.40	3.60	0.55	3.00	3.30	1.30	7.90	3.10	0.94	0.70	1.10	3.50	9.40	0.60
Cl (mg/L)	8.92	20.4	9.15	15.2	12.3	6.06	11.6	37.6	52.5	15.7	4.53	7.53	12.6	13.0	9.12	0.010
NH_4-N(mg/L)	0.45	<LOQ	<LOQ	0.96	<LOQ	0.29	0.87	<LOQ	12.2	3.70	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.040
NO_3-N(mg/L)	1.11	5.08	1.36	0.21	3.55	<LOQ	<LOQ	9.62	9.19	<LOQ	0.06	2.40	2.50	2.60	<LOQ	0.009
ΣREE (µg/L)	0.186	5.297	0.785	0.772	0.337	0.564	0.568	0.576	5.795	4.865	0.224	0.319	1.704	0.548	4.769	-
La (µg/L)	0.039	1.504	0.160	0.121	0.076	0.104	0.085	0.140	0.935	0.823	0.048	0.113	0.363	0.105	0.814	0.024
Ce (µg/L)	0.076	1,858	0.349	0.359	0.170	0.247	0.175	0.121	2.664	2.180	0.094	0.050	0.811	0.255	2.429	0.028
Pr (µg/L)	0.008	0.263	0.033	0.030	0.012	0.025	0.023	0.032	0.248	0.195	0.011	0.021	0.068	0.024	0.193	0.004
Nd (µg/L)	0.033	1.060	0.141	0.148	0.048	0.102	0.130	0.153	1.099	0.917	0.046	0.083	0.270	0.099	0.883	0.022
Sm (µg/L)	0.008	0.157	0.026	0.027	0.008	0.022	0.031	0.025	0.215	0.160	0.007	0.013	0.047	0.016	0.132	0.006
Eu (µg/L)	0.002	0.036	0.006	0.007	0.002	0.006	0.008	0.008	0.053	0.043	0.002	0.004	0.015	0.004	0.030	0.002
Gd (µg/L)	0.008	0.143	0.022	0.022	0.007	0.019	0.033	0.023	0.174	0.292	0.006	0.014	0.044	0.021	0.110	0.006
Tb (µg/L)	0.001	0.018	0.003	0.003	0.001	0.013	0.004	0.002	0.025	0.015	0.001	0.002	0.006	0.002	0.014	0.001
Dy (µg/L)	0.005	0.097	0.017	0.014	0.006	0.013	0.024	0.014	0.140	0.081	0.004	0.008	0.032	0.009	0.072	0.004
Ho (µg/L)	0.001	0.021	0.003	0.003	0.001	0.003	0.006	0.004	0.030	0.019	0.001	0.002	0.007	0.002	0.013	0.001
Er (µg/L)	0.003	0.065	0.011	0.013	0.003	0.009	0.021	0.017	0.091	0.060	0.003	0.005	0.020	0.005	0.036	0.002
Tm (µg/L)	<LOQ	0.009	<LOQ	<LOQ	<LOQ	0.001	0.003	0.003	0.014	0.009	<LOQ	0.001	0.003	0.001	0.005	0.001
Yb (µg/L)	0.003	0.057	0.010	0.019	0.003	0.009	0.021	0.028	0.095	0.061	0.002	0.004	0.017	0.005	0.032	0.001
Lu (µg/L)	0.001	0.010	0.002	0.004	<LOQ	0.002	0.004	0.006	0.015	0.011	<LOQ	<LOQ	0.003	0.001	0.004	0.001

*LOQ stands for Limit of Quantification.

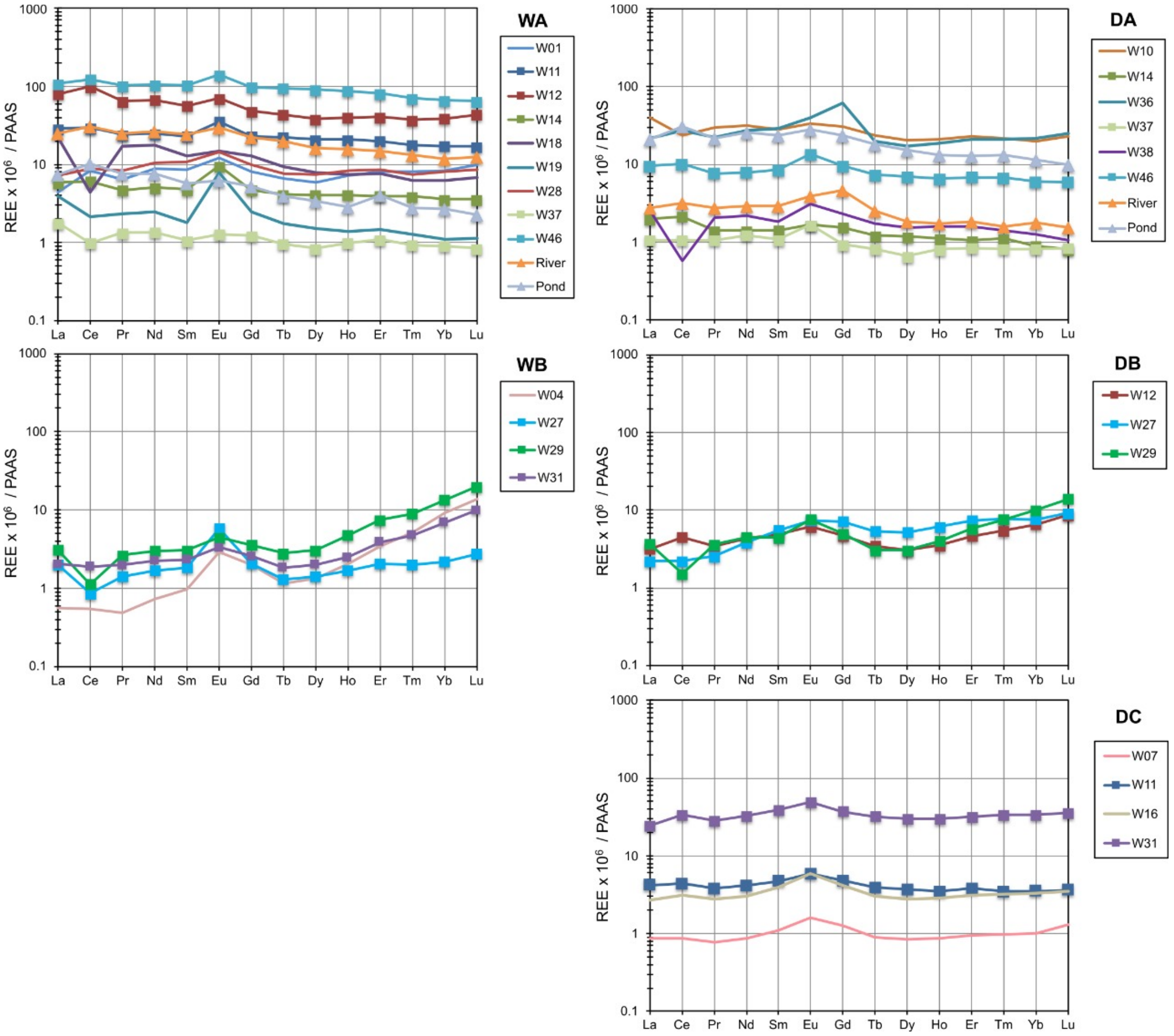

Figure 2 - Shale normalized plots of REE concentrations in the study area. WA. wet season, similar to Atibaia River (LREE enriched); WB. Wet season, enriched in HREE; DA. dry season, like Atibaia River (LREE enriched); DB. dry season, enriched in HREE; DC. Dry season, relatively flat patterns.

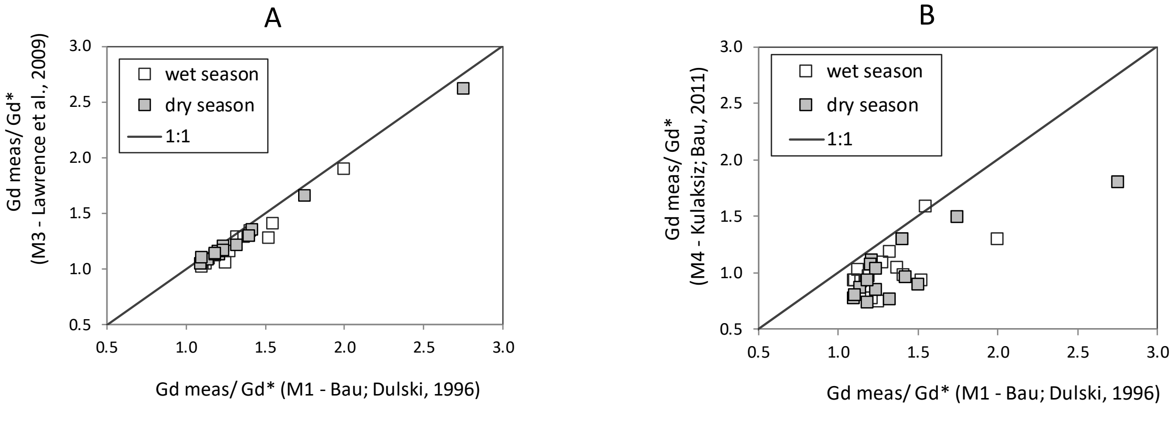

Figure 3 - Comparison of the Gd$_{SN}$/Gd* ratios estimated by different methods. A. M3 compared to M1; B. M4 compared to M1.

Table 4 - Gd_{SN}/ Gd* ratios estimated by methods M1, M2, M3 and M4

Wet season														
Method	W1	W4	W11	W12	W14	W18	W19	W27	W28	W29	W31	W37	W46	River	Pond
M1	1.2	2.0	1.1	1.1	1.2	1.3	1.5	1.5	1.2	1.4	1.4	1.4	1.1	1.1	1.3
M2	1.1	1.9	1.0	1.0	1.1	1.2	1.4	1.4	1.2	1.3	1.3	1.3	1.0	1.1	1.2
M3	1.1	1.9	1.0	1.0	1.1	1.3	1.4	1.3	1.1	1.3	1.3	1.3	1.0	1.1	1.2
M4	0.8	1.3	1.0	0.9	1.0	1.2	1.6	0.9	0.8	1.0	1.0	1.3	0.9	0.9	1.1
Dry season															
Method	W7	W10	W11	W12	W14	W16	W27	W29	W31	W36	W37	W38	W46	River	Pond
M1	1.5	1.2	1.1	1.2	1.2	1.2	1.3	1.4	1.1	2.8	1.1	1.4	1.2	1.7	1.2
M2	1.4	1.1	1.1	1.1	1.1	1.2	1.2	1.3	1.0	2.6	1.1	1.3	1.1	1.6	1.1
M3	1.4	1.1	1.1	1.1	1.2	1.2	1.2	1.3	1.0	2.6	1.1	1.3	1.2	1.7	1.1
M4	0.9	1.1	0.9	0.7	1.1	0.9	0.8	1.0	0.8	1.8	0.8	1.3	1.0	1.5	0.9

Table 5 - Gd_{SN}/ Gd* ratios estimated by fitting a 3rd order polynomial to the normalized concentrations of Pr, Nd, Sm, Tb, Dy, Ho, Er, Tm and Yb - comparison of four different normalizers.

Wet season															
Normalizer	W1	W4	W11	W12	W14	W18	W19	W27	W28	W29	W31	W37	W46	River	Pond
PAAS (McLennan, 1989)	1.1	2.1	1.2	1.2	1.1	1.3	1.6	1.4	1.2	1.4	1.5	1.4	1.1	1.2	1.3
MUQ	1.1	1.9	1.0	1.0	1.1	1.3	1.4	1.3	1.1	1.3	1.3	1.3	1.0	1.1	1.2
NASC	1.1	2.1	1.1	1.2	1.1	1.3	1.6	1.4	1.2	1.3	1.3	1.4	1.1	1.2	1.3
PAAS (Pourmand *et al.*, 2012)	1.1	1.8	1.0	1.0	1.1	1.2	1.5	1.3	1.1	1.2	1.3	1.2	1.0	1.0	1.2
Dry season															
Normalizer	W7	W10	W11	W12	W14	W16	W27	W29	W31	W36	W37	W38	W46	River	Pond
PAAS (McLennan, 1989)	1.5	1.3	1.1	1.1	1.2	1.2	1.2	1.3	1.0	2.6	1.1	1.5	1.3	1.8	1.1
MUQ	1.4	1.1	1.1	1.1	1.2	1.2	1.2	1.3	1.0	2.6	1.1	1.3	1.2	1.7	1.1
NASC	1.5	1.3	1.1	1.1	1.2	1.2	1.2	1.3	1.0	2.6	1.1	1.5	1.2	1.8	1.1
PAAS (Pourmand *et al.*, 2012)	1.3	1.1	1.0	1.1	1.1	1.1	1.2	1.3	1.0	2.5	1.0	1.3	1.1	1.6	1.1

6 DISCUSSION

Even though the maximum and the mean values for the ΣREE concentrations are smaller in the dry season, this tendency is not systematic when samples are considered individually. For instance, samples W07, W16, W31 and the pond have higher ΣREE concentrations in the dry season (samples W07 and W16 had most of the REE concentrations bellow the LOQ in the wet season and therefore their results are not included in this paper). Increased concentrations in the dry season could be a consequence of evaporation/evapotranspiration, especially for the mining pond. Samples W27, W31 and W37 show no significant change in REE concentrations in the two campaigns while all the other samples showed higher ΣREE concentrations in the wet season.

An increase of ΣREE concentrations in the wet season had been previously detected in the region by Mortatti and Enzweiler (2019), who studied the Atibaia and the Jaguari rivers REE concentrations. They attributed this fact to the association of the REE with colloidal particles of minerals added to the river water due to erosion and runoff. The release of colloidal particles from the alluvial sediments during recharge cannot be ruled out. Additionally, the REE content is known to reflect the mineral preferential dissolution that occurs during recharge (DUVERT *et al.* 2015), and this is enhanced during the wet season. The pH and DOC are known to control ΣREE concentrations, but no association could be observed in the study area. No spatial correlation between similar REE patterns could be identified either in the wet or in the dry season.

Considering the concentration of the traditional wastewater markers, a similar situation is detected. In some of the wells the concentrations are higher in the wet season and in other wells the concentrations are higher in the dry season. This varies from ion to ion and from well to well and reveals that the hydrogeochemical processes that are going on in the studied alluvial plain are complex, as revealed by other studies performed in alluvial plains, for instance, Santos Correa *et al.* (2022) and Zhang *et al.* (2022).

Regarding the method to estimate Gd anomalies, the choice of the equation to calculate the geogenic Gd concentration and the threshold value are critical issues to consider. In agreement with Lawrence *et al.* (2006b) previous observations, equations (1) and (2) lead to similar results. However, contrary to the findings of Möller *et al.* (2003); and Louis et al (2020), methods M3 and M4 yield different results, with M4 being inadequate for the investigated area, because Gd does not necessarily behave as a LREE.

The choice of the normalizer has little influence on the Gd_{SN}/Gd^* estimated values, when compared to the effect of the different equations proposed for geogenic Gd concentration estimation. However, the decision about the occurrence of anthropogenic Gd anomalies can be jeopardized by the choice of the normalizer in areas where most samples show Gd_{SN}/Gd^* very near to the threshold value, as in the case study presented in this paper.

Regarding the threshold value, for the study area 1.3 seems to be adequate for M3, as it encompasses possible measurement uncertainties and delivers similar results for the calculations performed with M1 and M2 with a threshold value of 1.4. This finding is corroborated by the Gd_{SN}/ Gd^* ratios calculated for W37 in the wet season. In this well no anthropogenic Gd concentrations are expected, as it is located far away from houses and from on-site sanitation systems in general. As the application of method M3 does not assume any specific REE normalized pattern for the calculations and uses the concentrations of nine elements, applying M3 with H=1.3 was deemed more appropriate for the study area.

Bearing the above in mind, wells W4 and W19 showed anthropogenic Gd anomalies in the wet season, while wells W7, W36 and the Atibaia River presented anthropogenic Gd anomalies in the dry season. The Gd anthropogenic concentrations estimated for these wells by M3 and H=1.3 are 0.004 µg/L for W4 and 0.001 µg/L for W19 in the wet season and 0.001 µg/L for W7, 0.147 µg/L for W36 and 0.005 µg/L for the Atibaia river in the dry season. Considering National Potability Level of 10 mg/L (Brazil, 2021) only one well (W46) showed NO_3–N concentrations above this limit and only in the wet season. However, NH_4–N concentrations exceeded NO_3–N concentrations in wells W1, W4 and W28 in the wet season and in wells W12, W16, W27, W31 and W36 in the dry season, indicating reducing conditions and/or recent contamination. The areas where water quality is more impacted by nitrogen compounds are about the same in both seasons and correspond to the more densely occupied areas.

Gd anomalies were not necessarily detected in the same wells where the highest concentrations of other traditional wastewater markers were detected, but they were detected in the same areas. As discussed by Oppenheimer *et al*. (2012) the likelihood of Gd anomaly detection within a small population wastewater system is low because of the single event administration of the gadolinium contrast agent. Therefore, Gd anthropogenic concentrations are not expected to be detected in every sampling point or all over the year. In the studied area, the intermittent detection of Gd anomalies, especially the anthropogenic Gd concentrations detected in wells W4 (wet season) and W36 (dry season), reinforce the evidence that groundwater in the study area receives pollution from the on-site sanitation systems.

7 CONCLUSION

By estimating Gd anomalies with different methods, we found out that the normalizers commonly used do not play a fundamental role in the decision about the occurrence (or not) of anthropogenic Gd concentrations, except if the Gd_{SN}/ Gd* ratios are near the threshold value. On the other hand, the equations and the threshold value adopted for the estimation of the Gd anomaly are important factors regarding the decision. In this study methods M1 and M2 lead to very similar results. However, methods M3 and M4 lead to different values and decisions regarding the occurrence of anthropogenic Gd in the study area.

In this study, threshold values to assume the presence of Gd anomalies were higher than the ones proposed for each of the original methods. With H = 1.4, methods M1 and M2 deliver very similar results. Method M3 (modified to adopt H = 1.3) was deemed more appropriate because the tested water samples present variable REE normalized patterns.

The results also point out that a community effort is needed to standardize the methods to estimate Gd anthropogenic anomalies, especially for areas where diffuse pollution dominates.

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