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## RARE EARTH ELEMENTS (REE) IN THE URBAN WASTEWATER OF COTONOU (BENIN, WEST AFRICA)

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1 **Abstract:** The rare earth element (REE) contamination of urban wastewater, which was  
2 collected from open sewers and the inlet of a wastewater treatment plant in Cotonou (Benin),  
3 was assessed. The drinking water distributed to the inhabitants of Cotonou and water samples  
4 from private wells were also analyzed. The sampling occurred between October and December  
5 2016 and the samples were analyzed by ICP-MS. Although the only magnetic resonance  
6 imaging facility in Cotonou opened in November 2016, pollution by anthropogenic gadolinium  
7 (Gd), which is included in phase contrast agents, was observed: there was 30 to 620 times more  
8 Gd in wastewater samples than in drinking and well water samples. Europium was another REE  
9 presenting positive anomalies. It is hypothesized that the europium came from the leachates of  
10 solid waste piles in the street. In the absence of any wastewater treatment, the REEs found in  
11 the wastewater are spread to the aquatic environment. It would be interesting to monitor the  
12 wastewater REEs over the long term. So far, the aquifers used for water provision have not  
13 been polluted by the anthropogenic REEs.

14 **Keywords:** Drinking water, Gadolinium, Rare-earth elements, Wastewater, Well water.

15

## 16 1. INTRODUCTION

17 Accessibility to clean water for all is one of the 17 millennium development goals (MDGs) set  
18 by UNO in 2015 in its 2030 agenda for sustainable development (UN-water, 2017). This goal  
19 implies the improvement of sanitation infrastructure and control in many countries. Wang et al.  
20 (2014) reviewed the gaps in the current practices for water and wastewater treatment in Africa,  
21 as well as the efforts needed to achieve the MDGs. These authors insisted on the insufficient  
22 infrastructure and the poor operation and maintenance of sewerage systems. The situation is  
23 worsened by rapid, ongoing urbanization and climate change (Koop and van Leeuwen, 2017).  
24 According to the UN-Water report (2017), on average, high-income countries treat  
25 approximately 70% of the municipal and industrial wastewater they generate. That percentage  
26 drops to 38% in upper-middle-income countries (15% of African countries) and to 28% in  
27 lower-middle-income countries (33% of African countries). In low-income countries (50% of  
28 African countries), only 8% of the municipal and industrial wastewater undergoes treatment of  
29 any kind before it is discharged into the aquatic environment.

30 Sanitation primarily concerns the removal or degradation of macropollutants, such as  
31 suspended matter, organic matter and nutrients (nitrogen, phosphorus), whose concentrations  
32 are increased by human activities. However, micropollutants that are toxic at low doses should  
33 also be addressed. According to Sibanda et al. (2015), the quality of South African aquatic  
34 ecosystems is deteriorating not only due to the discharge of macropollutants and pathogens (as  
35 also stressed by Luyt et al., 2012, Singh and Lin, 2015) but also due to the presence of metals  
36 and endocrine-disrupting compounds (EDCs). Metals in water systems can have a natural or  
37 anthropogenic origin, and those of anthropogenic ones can originate from domestic  
38 (Atinkpahoun et al., 2018), industrial etc. sources (e.g., mining (Affum et al., 2016; du Preez et  
39 al., 2016; Olias et al., 2017; Atibu et al., 2018) or metal factories (Belabed et al., 2017)). They  
40 can be directly ingested by humans through drinking water (Elumalai et al., 2017) or indirectly

41 ingested by the consumption of freshwater edible resources (fish, crustaceans) in which metals  
42 bioaccumulate (Ajani et al., 2015; Somerset et al., 2015; Gbogbo et al., 2017). One of the  
43 difficulties for extended data collection is the lack of the laboratory infrastructure necessary to  
44 support the extensive monitoring of micropollutants over the African continent (Madikizela et  
45 al., 2017; Gwenzi and Chaukura, 2018).

46 Rare earth elements (REEs) represent a specific group of 15 metals ranging from lanthanum to  
47 lutetium. They are generally subdivided into two groups, light REEs (LREEs, from La to Eu)  
48 and heavy REEs (HREEs, from Gd to Lu). The REE signature in pristine waters is partially  
49 inherited from rocks and sediments. REEs are increasingly used in high-tech devices (e.g.,  
50 liquid crystal displays, communication devices, and solar panels) and to manufacture contrast  
51 agents for medical use, electric motors, batteries, catalysts, magnets, lamp triphosphors,  
52 phosphorescent paints, and other items. The concentrations of REEs have increased in the  
53 hydrosphere and in tap water (Gonzalez et al., 2014), and they have been recognized as potential  
54 micropollutants (Pagano et al., 2015; Hermann et al., 2016, Ebrahimi and Barbieri, 2019).  
55 Gadolinium (Gd) is certainly the most publicized REE, and large positive Gd anomalies (i.e., a  
56 concentration higher than that can be expected from the natural content in the crust) have been  
57 detected in Europe, Asia, Australia and America (Kulaksiz and Bau, 2011a; Merschel et al.,  
58 2015; Campos and Enzweiler 2016). The Gd concentration has also seemed to increase over  
59 time in Berlin (Germany) tap water (Tepe et al., 2014), in San Francisco Bay (California) (Hatje  
60 et al. (2015) or in the Garonne Estuary (Lerat-Hardy et al., 2019). Positive Gd anomalies have  
61 been detected in two tributaries of the Hérault River (France) and in some wells supplying  
62 drinking water, corresponding to an excess of anthropogenic Gd in the water up to 15.4 pM (i.e.  
63 2.4 ng/L) (Rabiet and al., 2009). Anomalies have also been detected for lanthanum (Kulaksiz  
64 and Bau, 2011b, 2013; Klaver et al., 2014; Merschel and Bau, 2015; Song et al., 2017; Pignotti  
65 et al., 2017), samarium (Kulaksiz and Bau, 2013; Merschel and Bau, 2015; Song et al., 2017)

66 and cerium (Hissler et al. 2015). Data from Africa are limited, but Ayedun et al. (2017) have  
67 reported that some REEs they found in Lagos State (Nigeria) could be related to leaching from  
68 wastes dumpsites. Similar to other metals, REEs accumulate in aquatic plants (Chua, 1998) and  
69 fish (Mayfield and Fairbrother, 2015) and can impede the development of fish embryos and  
70 larvae (Cui et al., 2012, Trifuoggi et al., 2017). Fears are emerging with regard to harmfulness  
71 of Gd to humans, particularly with the introduction of more stringent treatment of organic  
72 micropollutants in treatment plants, which may lead to a release of Gd from chelates used in  
73 medicine (Port et al., 2008). For REE other than Gd, concern has been recently raised in the  
74 vicinity of REE mining activities (Romero-Freire et al., 2018; Edahbi et al., 2019) with human  
75 health threatening conditions related to water resources and agricultural production (Li et al.,  
76 2013; Hao et al., 2016; Liu et al., 2019), prompting for more epidemiological surveys (Huo et  
77 al., 2017; Gwenzi et al., 2018).

78 In Benin, the access rates to sanitation are 17% and 61% in rural and urban areas, respectively  
79 (pS-Eau, 2018). A total of 70% of households discharge their wastewater in nature, and 20.1%  
80 of households discharge their wastewater in courtyards (INSAE, 2016). In the case of Cotonou  
81 (Figure 1), the economic capital of Benin and the largest city in the country (680,000  
82 inhabitants), most households (57%) dispose their wastewater in nature and 9.6% dispose their  
83 wastewater in courtyards. In addition, 7.2% and 3.5% dispose their wastewater in closed and  
84 open sewers (INSAE, 2016), respectively, which discharge the waste without any treatment  
85 into the lagoon (Cotonou Channel) or shallows. For populations with access to an individual  
86 sanitation system, septic water is collected in tanks or latrines and graywater is collected in  
87 sumps (21%). This situation only partially fulfills its role of preserving and protecting human  
88 health because the water table is near the surface in Cotonou and can be easily contaminated by  
89 infiltration. There are also some collective sanitation systems, such as the Vie Nouvelle  
90 wastewater treatment plant, but they do not function properly.

91 Based on this literature review, there appear to be few studies examining REE in wastewater to  
92 assess their contribution to the pollution of water resources, and no such studies have been  
93 conducted on the wastewater of Cotonou. Thus, the objective of this study was to evaluate the  
94 baseline REE content of urban wastewater in Cotonou. Urban wastewater means domestic  
95 wastewater or the mixture of domestic wastewater with industrial wastewater and/or runoff rain  
96 water. Our work focused on the wastewater from open sewers (which discharge wastewater  
97 into Lake Nokoué) in Cotonou and on the domestic wastewater of the Vie-Nouvelle  
98 neighborhood. The case of the gadolinium receives specific focus, as it is used as a contrast  
99 agent in magnetic resonance imaging (MRI), and the only MRI facility in Benin opened in  
100 Cotonou in November 2016.

101

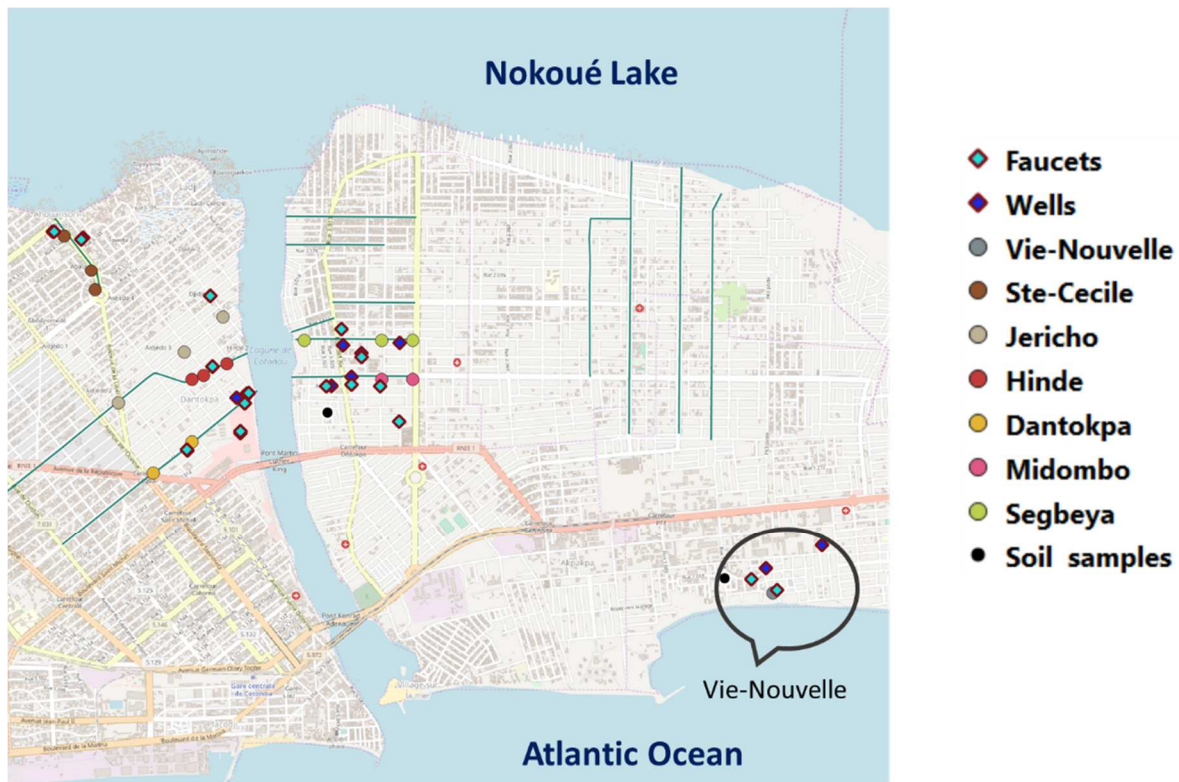
## 102 **2. MATERIALS AND METHODS**

103 Any data treatment was performed using Microsoft Excel.

### 104 **2.1 Description of study area**

105 Cotonou's watershed (6°20'N and 2°20'E) covers an area of 79 km<sup>2</sup> and extends 10 km to the  
106 west and 6 km to the east. The urban area, composed of 13 districts (INSAE, 2005), is bounded  
107 on the north by Lake Nokoué and on the south by the Atlantic Ocean. It is separated into two  
108 parts (western and eastern) by the Cotonou channel, which is the extension of Lake Nokoué  
109 towards the sea (Figure 1). The underground hydrological structure is complex, vertically as  
110 well as horizontally, with risk of saline water intrusions in the water table, originating from the  
111 ocean and Lake Nokoué (McInnis et al., 2013).

112



114

115 *Figure 1: Location of wastewater and drinking water sampling points in the city of Cotonou.*

116 *The map was drawn using QGIS 3.6 (<https://www.qgis.org>) and is based on original data*

117 *from SOGEFI (<https://www.sogefi-sig.com>).*

118 According to the 4<sup>th</sup> census of the population in 2013, the city has a population of 680,000  
 119 inhabitants. A total of 51% of the households in the city have access to drinking water provided  
 120 by SONEB (Société Nationale des Eaux du Bénin) at home, and 46% visit other houses for this  
 121 water. The water consumption is approximately 60 L/day/inhabitant. Some populations use this  
 122 drinking water for all purposes, and others use it in addition to well water. The sewage system  
 123 of Cotonou has a length of 306 km, with 30 subwatersheds in its western zone and 20  
 124 subwatersheds in its eastern zone. Table 1 presents the characteristics of the open sewers where  
 125 sampling was conducted (MUHA, PUGEMU and IGIP AFRIQUE, 2014).



126 *Table 1: Characteristics of open sewers and subwatersheds of Cotonou*

Sewers	Characteristics
<b>Western zone</b>	
Jericho and Hinde	329 ha. Located in the central part of the city between the Aïdjèdo, Gbégamey, Fignon and Dantokpa districts. The road network is almost completely asphalted or paved, and the density of the secondary and tertiary drains is very important.
Dantokpa	102 ha. Located in the city center. The main channel crosses the market area; the watershed is almost impermeable due to the very high rate of urbanization and the road surface.
S <sup>te</sup> Cécile	269 ha. The watershed is largely impermeable due to the high rate of urbanization and the presence of paved or tarred roads.
<b>Eastern zone</b>	
Segbeya	51 ha. Several drains connected to the main channel.
Midombo	36 ha. Similar characteristics as Segbeya.

127

128           The Vie-Nouvelle neighborhood, where the sampling of domestic wastewater was made  
 129 over 24 hours, is a small housing complex of 50 villas and 316 apartments built as part of a  
 130 low-income housing project initiated by the Benin Government in the 1970s. The apartments  
 131 (approx. 1,200 inhabitants) are connected to a collection and treatment system for domestic  
 132 wastewater (graywater and septic wastewater).

133           The only medical MRI scanner in Benin is in a private medical facility in Cotonou  
 134 (Zongo-Nima district). It started to operate at the end of November 2016.

135

## 136 **2.2 Sampling**

137 The wastewater sampling campaigns were conducted by dry weather between October and  
138 December 2016. For each open sewer a composite sample was prepared by mixing equal parts  
139 of three grab sub-samples collected in the upstream, middle and downstream regions of the  
140 sewer. Figure 1 shows the three sampling points on each open sewer. The sub-samples were  
141 collected in one-liter polyethylene bottles, with a sampler consisting of a jar attached to a rope.  
142 The sewer sampling campaigns were repeated six times between October and December 2016  
143 (Oct 18, Oct 31, Nov 14, Nov 25, Dec 18, Dec 22).

144 At Vie-Nouvelle, a 24 h sampling campaign (one 1L sample per hour) was conducted at the  
145 inlet of the wastewater treatment plant with an automatic sampler (Avalanche, Isco, Lincoln,  
146 NE, USA) in October 2016. A time-based composite sample was made for this sampling site.  
147 All samples were stored at 4°C and transported to the laboratory for analysis within 24 hours.

148 At all wastewater sampling sites, SONEB-delivered drinking water grab samples (1L at faucets)  
149 and well water grab samples (1L) were collected in April 2017. Soil samples were collected in  
150 five locations (Figures 1 and SII - Supplementary Information), dried in air for three days, sieved  
151 at 2 mm and ground.

152

## 153 **2.3 Analyses**

154 Wastewater sample turbidity was measured with a Wagtech (Thatcham, UK) turbidimeter. The  
155 chemical oxygen demand (COD) and ammonium of wastewater samples were analyzed  
156 according to the NF-T 90-101 and NF-T 90-015 (i.e., Nessler method) methods, respectively.  
157 Filtration (0.45 µm pore size) was done prior to the ammonium determination. For the drinking  
158 water and well water samples, dissolved organic carbon (DOC) and dissolved total nitrogen  
159 (DTN) were analyzed after filtration (0.45 µm pore size) on a VCHN (Shimadzu, Noisiel,

160 France) by catalytic oxidation at 680°C and infrared detection of the produced carbon dioxide.  
161 The NO<sub>x</sub> resulting from the oxidation was reacted with ozone, and the total dissolved nitrogen  
162 was finally quantified via luminescence. Calibration was done with potassium hydrogen  
163 phthalate for DOC and potassium nitrate for DTN.

164 The dissolved organic matter of the drinking water and well water samples was characterized  
165 optically. The UV-visible absorbance spectrum of each filtrated sample was measured between  
166 200 and 700 nm using an Anthélie Light UV-visible spectrophotometer (Secomam, Alès,  
167 France) in a quartz cuvette (volume = 3.5 mL, optical path length = 1 cm). The blank was  
168 performed with ultra-pure water for solvent correction. Synchronous fluorescence spectra were  
169 obtained with a F-2500 fluorometer (Hitachi, Krefeld, Germany) equipped with a Xenon lamp,  
170 by using FL Solution 2.0 software. A fixed gap (50 nm) between the excitation and emission  
171 wavelengths ( $\lambda_{\text{ex}}$  and  $\lambda_{\text{em}}$ , respectively) was used, with the excitation wavelength varying  
172 between 230 and 600 nm (wavelength step = 1 nm). The 50 nm gap was selected as a  
173 compromise to optimize the resolution of both the tryptophan-like fluorescence and the humic-  
174 like fluorescence (Reynolds, 2003). A quartz cuvette was used (volume = 3.5 mL, optical path  
175 length = 1 cm). No correction for the inner-filter effect or the Rayleigh and Raman diffusion  
176 was performed, and the spectra were collected at the natural pH of the sample. The blank was  
177 performed with ultra-pure water. The fluorescence intensities were expressed in Raman units.  
178 Deconvolution of the spectra was performed using the procedure developed by Assaad et al.  
179 (2015), i.e., four fluorophores were extracted from the spectra: F1 ( $\lambda_{\text{exc}} = 280$  nm,  $\lambda_{\text{em}} = 330$   
180 nm), F2 ( $\lambda_{\text{exc}} = 300$  nm,  $\lambda_{\text{em}} = 350$  nm), F3 ( $\lambda_{\text{exc}} = 320$  nm,  $\lambda_{\text{em}} = 370$  nm) and F4 ( $\lambda_{\text{exc}} = 355$   
181 nm,  $\lambda_{\text{em}} = 405$  nm).

182 The REEs (lanthanum (La), cerium (Ce), neodymium (Nd), samarium (Sm), europium (Eu),  
183 gadolinium (Gd), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm) and lutetium

184 (Lu)) were measured by inductively coupled plasma mass spectrometry (ICP-MS) in  
185 accordance with the NF EN ISO 17294-1 and NF EN ISO 17294-2 standards on a Thermo-  
186 Scientific ICAPQ ICP-MS. A natural river water certified reference material (SLRS-6 (NRC-  
187 CNRC)) was used to test the REE analytical procedure (Table 2).

188 Table 2: Test of the SLRS-6 reference material

	Reference value (ng/L) (Yeghicheyan et al., 2019)	% Error
La	248.3	0.86
Ce	292.7	0.05
Pr	59.1	0.55
Nd	227.8	1.15
Sm	39.5	1.86
Eu	7.26	7.07
Gd	31.6	2.37
Tb	4.07	16.13
Dy	21.9	3.97
Ho	4.3	6.13
Er	12.4	5.46
Tm	1.79	0.79
Yb	11.2	2.39
Lu	1.91	2.72

189

190 Total metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were measured by inductively coupled  
191 plasma atomic emission spectroscopy (ICP-AES with argon plasma) (Thermo Instruments,  
192 Courtaboeuf, France). A quality control was run every ten samples. The metal and REE  
193 analyses were carried out on previously mineralized samples. For the digestion (40 min at  
194 180°C under 9 bars in a microwave system equipped with PTFE vessels or tubes), 5 mL of  
195 ultra-pure nitric acid was added to liquid samples (20 mL) and to soil samples (0.15 mg, in  
196 triplicate). The final volume of the mineralized samples was 50 mL. Rhenium and rhodium  
197 were used as internal standards for soil analysis.

198 The Eu anomaly was calculated using Eq 1.:

$$199 \quad Eu_{anom} = Eu_N / \sqrt{Sm_N \cdot Gd_N} \quad Eq. 1$$

200 where  $Sm_N$  and  $Gd_N$  are the normalized concentration in Sm and Gd, respectively. A ratio  
201 greater than 1 indicates a positive anomaly. The Eu anthropogenic excess was calculated using  
202 Eq. 2. (Rabiet et al., 2009):

$$203 \quad Eu_{anth} = Eu_{meas} - Eu_{nat} = Eu_{meas} - (Eu_{meas} / Eu_{anom}) \quad Eq. 2$$

204 Unfortunately it was not possible to calculate anomalies related to Gd, due to the lack of Tb  
205 data.

206

## 207 **3. RESULTS AND DISCUSSION**

### 208 **3.1 General characteristics of water and wastewater samples**

209 The average pollution characteristics of the wastewater samples are given in Tables S11 and S12  
210 (Supplementary Information). The COD and ammonium concentrations in open sewers were relatively  
211 low when the Vie-Nouvelle exhibited a very high COD concentration: the high pollution concentration  
212 in Vie-Nouvelle can be related to a low consumption of water in the housing complex. As the samples

213 were collected during dry weather, dilution by rain water in the open sewers is unlikely. However,  
214 infiltration from the water table can be expected due to its low depth and the deterioration of the open  
215 sewers: this can explain the low pollution concentration in the open sewers.

216 Al and Fe were the metals with the highest concentrations in Vie-Nouvelle (6 mg/L and 7 mg/L,  
217 respectively), but in the open sewers, the concentrations of Mn ( $300 \mu\text{g/L} \pm 200 \mu\text{g/L}$ ) could be higher  
218 than those of Al ( $360 \mu\text{g/L} \pm 280 \mu\text{g/L}$ ). In terms of heavy metals, Cu and Zn are expected to be present  
219 in significant concentrations (up to  $908 \mu\text{gCu/L}$  and  $224 \mu\text{gZn/L}$  in Vie-Nouvelle), but Cr, Ni and Pb  
220 are present in high concentrations in some samples: up to  $40 \mu\text{g Cr/L}$  and  $36 \mu\text{g Ni/L}$  in Vie-Nouvelle  
221 and  $118 \mu\text{g Pb/L}$  in Hinde. However these values do not exceed the limits set by the Beninese legislation  
222 (MEHU, 2001). Adjahouinou and Fiogbe (2014) found slightly higher concentrations in Cu, Pb, Zn, and  
223 Cd in wastewater samples collected in the same neighborhoods.

224 Based on the 20 drinking water samples, the drinking water contained an average of  $1.1 \text{ mgC/L}$  ( $\sigma = 0.3$   
225  $\text{mgC/L}$ ) and  $0.9 \text{ mgN/L}$  ( $\sigma = 0.2 \text{ mgN/L}$ ), where  $\sigma$  is the standard deviation (Figure SI2). The drinking  
226 water synchronous fluorescence spectra revealed the presence of two fluorophores, F1 (protein-like  
227 fluorophore) and F4 (related to humic substances). It is likely that the presence of F1, indicative of  
228 biological activity, was due to biofilm development in the network.

229 The average concentrations of organic carbon and total nitrogen in the well water samples were  $7 \text{ mgC/L}$   
230 and  $18 \text{ mgN/L}$  (with maximal values at  $54 \text{ mg/L}$ ), respectively (Figure SI3). The organic carbon was  
231 mainly related to two fluorophores, F3 and F4, associated with humic substances (F3 and F4).  
232 Fluorophore F1 was more present in the well water samples than in the drinking water. The presence of  
233 F1 could be due to biological activity in the wells, which were eventually polluted by untreated  
234 wastewater. The UV-visible spectra exhibited high absorbances in the UV range ( $<220 \text{ nm}$ ). There was  
235 a reasonable correlation ( $R^2 = 0.62$ ) between the  $225 \text{ nm}$  maximum of the second derivation of the UV-  
236 visible spectra and the total dissolved nitrogen (Figure SI4). Based on the slope ( $486 \text{ (mgN/L)/(cm}^{-1}\text{nm}^{-2}$ )), it is likely that most of the nitrogen is in the form of nitrates (Pons et al., 2017). In such a case,  $18$   
237  $\text{mgN /L}$  corresponds to  $80 \text{ mg NO}_3^-/\text{L}$ , much higher than values found by Toure et al. (2018) in Mali  
238 (between  $23$  and  $40 \text{ mg NO}_3^-/\text{L}$  depending upon the season), Xiao et al. (2019) in China ( $22 \text{ mg NO}_3^-/\text{L}$   
239

240 in average but with a maximal value at 677 mg NO<sub>3</sub><sup>-</sup>/L) or Murray et al. (2018) in Maryland (< 4 mg  
241 NO<sub>3</sub><sup>-</sup>/L).

### 242 **3.2 REE concentrations**

243 Table 3 presents the concentrations of REEs in the wastewater samples of the different  
244 stations, as well as in both drinking water and well water. The values lower than the limit of  
245 quantification (LOQ) were not considered for the calculation of the average values. No effect  
246 of the MRI facility opening at the end of November 2016 could be detected, as all the Gd  
247 concentrations measured in December 2016 were lower than the LOQ (Table 4). Gd, Dy, Ho  
248 and Tm were mostly below the LOQ.

249 Table 3: REE concentrations ( $\mu\text{g/L}$ ): LOQ = Limit of quantification; min : minimum ; max = maximum ; aver = average ;  $\Sigma$  REE = sum of REE

		La	Ce	Nd	Sm	Eu	Gd	Dy	Ho	Er	Tm	$\Sigma$ REE
<b>LOQ</b>		0.0016	0.002	0.002	0.001	0.0002	0.0005	0.0003	0.0002	0.0003	0.0001	
	<b>min</b>	0.002	0.1	1.1	0.6	0.3	<LOQ	<LOQ	0.01	0.5	<LOQ	
<b>Ste Cécile</b>	<b>max</b>	3.0	2.0	6.0	1.8	0.3	<LOQ	<LOQ	0.01	1.8	<LOQ	<b>7</b>
	<b>aver</b>	1.0	1.3	2.3	1.0	0.3	<LOQ	<LOQ	0.01	1.1	<LOQ	
	<b>min</b>	0.6	1.9	2.2	1.0	0.3	7.3	5.2	0.05	0.7	<LOQ	
<b>Hinde</b>	<b>max</b>	17.6	12.9	29.7	7.6	1.8	7.3	5.2	1.0	3.9	<LOQ	<b>34</b>
	<b>aver</b>	4.1	4.9	7.4	2.3	0.8	7.3	5.2	0.4	1.7	<LOQ	
	<b>min</b>	0.8	2.7	1.8	0.7	0.4	2.6	1.7	0.1	0.6	<LOQ	
<b>Midombo</b>	<b>max</b>	7.7	10.1	13.5	3.9	06	2.6	1.7	0.4	2.2	<LOQ	<b>21</b>
	<b>aver</b>	3.0	5.7	4.4	1.5	0.5	2.6	1.7	0.2	1.3	<LOQ	
	<b>min</b>	2.6	3.4	0.3	1.1	0.4	1.8	<LOQ	0.07	0.42	<LOQ	
<b>Segbeya</b>	<b>max</b>	7.6	10.2	12.8	3.2	1.3	1.8	<LOQ	0.22	2.00	<LOQ	<b>21</b>
	<b>aver</b>	4.2	5.8	4.8	1.7	0.6	1.8	<LOQ	0.13	1.33	<LOQ	
	<b>min</b>	0.1	0.7	0.3	0.4	0.3	<LOQ	<LOQ	0.03	0.4	<LOQ	
<b>Dantokpa</b>	<b>max</b>	1.3	14.6	4.3	1.5	0.3	<LOQ	<LOQ	0.04	1.9	<LOQ	<b>10</b>
	<b>aver</b>	0.9	4.6	1.9	0.9	0.3	<LOQ	<LOQ	0.04	1.1	<LOQ	
	<b>min</b>	0.3	0.5	0.3	0.4	0.3	<LOQ	<LOQ	0.03	0.6	<LOQ	
<b>Jericho</b>	<b>max</b>	2.0	5.6	4.5	1.6	0.3	<LOQ	<LOQ	0.05	1.9	<LOQ	<b>8.5</b>
	<b>aver</b>	1.2	2.4	2.3	1.0	0.3	<LOQ	<LOQ	0.04	1.2	<LOQ	
	<b>min</b>	0.3	1.9	1.6	0.7	0.02	0.00	0.05	0.00	0.6	0.00	
<b>Cité Vie-Nouvelle</b>	<b>max</b>	102.2	279.3	153.3	44.5	14.3	48.7	39.1	7.8	21.9	2.3	<b>81</b>
	<b>aver</b>	12.1	31.1	18.3	5.1	1.4	4.9	4.4	0.8	2.8	0.4	
	<b>min</b>	0.02	0.003	0.03	0.01	0.003	0.01	0.01	0.003	0.01	0.001	
<b>Drinking water</b>	<b>max</b>	1.1	0.7	1.4	0.3	0.1	0.4	0.4	0.1	0.3	0.0	<b>1.37</b>
	<b>aver</b>	0.3	0.2	0.4	0.1	0.03	0.1	0.1	0.03	0.1	0.01	
	<b>min</b>	<LOQ	0.001	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	
<b>Well water</b>	<b>max</b>	0.1	0.2	0.1	0.02	0.01	0.03	0.02	0.01	0.02	0.003	<b>0.15</b>
	<b>aver</b>	0.02	0.05	0.03	0.01	0.003	0.01	0.01	0.002	0.01	0.001	



251 Table 4: Gd concentrations in the open sewers in Oct-Nov 2016 (prior to MRI opening) and  
 252 Dec 2016 (after MRI opening).

	Ste-Cécile	Hinde	Midombo	Segbeya	Danktopa	Jericho
Oct-Nov 2016	<LOQ	7.3	2.6	1.8	<LOQ	<LOQ
Dec 2016	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

253 The REE total concentration in the wastewater samples varied from 8 µg/L (Ste Cécile) to 82  
 254 µg/L (Vie-Nouvelle WWTP). Concerning the sewers, Hinde was the site with the highest REE  
 255 concentration (35 µg/L). Holmium was the REE with the lowest concentrations in all sites.  
 256 Thulium was not detected in any sewer, but it was detected in Vie-Nouvelle. Neodymium was  
 257 the REE with the largest concentrations in Ste Cécile, Hinde, Midombo and Segbeya. Cerium  
 258 was the REE with the largest concentrations in Dantokpa, Jericho and Vie-Nouvelle WWTP.

259 The drinking water, which came from deep aquifers, had a total REE concentration (1.36 µg/L)  
 260 higher than that of the well water samples (0.13 µg/L), which were pumped from the upper  
 261 water table. All the REEs under consideration were detected in the drinking water at all sites.  
 262 For the well water samples, Gd, Dy and Tm were not detected in Ste Cécile, which was also  
 263 true for the wastewater sampled in this neighborhood. Gd and Dy were not detected in Hinde,  
 264 and Sm was not detected in Midombo. All the REEs were detected in the well water samples  
 265 from Segbeya, Dantokpa, Jericho and Vie-Nouvelle. The REE concentrations in the drinking  
 266 water and well water were much lower than those in the wastewater samples: based on Vie-  
 267 Nouvelle wastewater, the ratios drinking water/wastewater varied between 30 (for Er) and 160  
 268 (for Ce) and the ratios well water/wastewater between 280 (for Er) and 620 (for Ce).

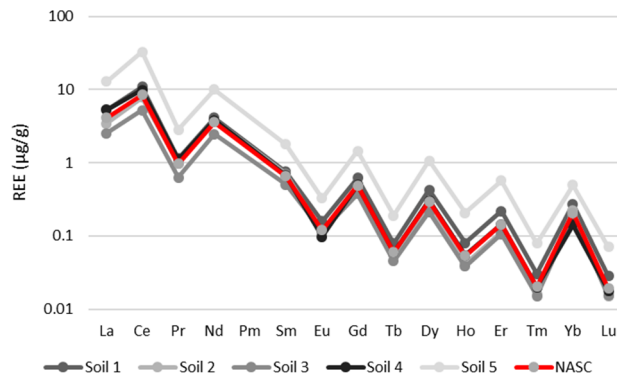
### 269 **3.3 REE normalized profiles**

270 The soil samples present REE profiles similar to those of NASC (North American Shales  
271 Composite) (Bau et al., 2018) except for one sample (P5), which is slightly apart from the water  
272 sampling area (Figure 2). The REE soil concentrations were of the same order of magnitude as  
273 Lake Nokoué sediments, studied by Yessoufou et al. (2017). Normalized REE ( $REE_N$ ) profiles  
274 were calculated, with NASC used as the reference (Figure 3). Deviations, such as enrichments  
275 of heavy REEs compared to light REEs and anomalies (deviation of an element compared to  
276 neighboring elements), can be detected in these profiles.

277 Anomalies are usually quantified by calculating the ratio between the normalized concentration  
278 of the element in the sample and the normalized concentration of that element in the case of no  
279 anomaly. The latter concentration is derived by averaging the normalized concentrations of the  
280 nearest neighbors of the deviating member (Riou, 1999; Olias and al., 2017). However, in the  
281 present case, many REE exhibit wastewater concentrations lower than their LOQ and their  
282 anomalies were not calculated. Eu anomalies ( $Eu_{anom}$  (Eq. 1.) could be safely calculated for  
283 drinking water (1.31), well water (1.70) and wastewater samples from Segbeya (1.62), Hinde  
284 (0.91) and Vie-Nouvelle (1.28), using Sm and Gd concentrations.

285 The negative anomaly of Eu for the Hinde wastewater sample can be due to the high Gd  
286 concentration of this sample.

287

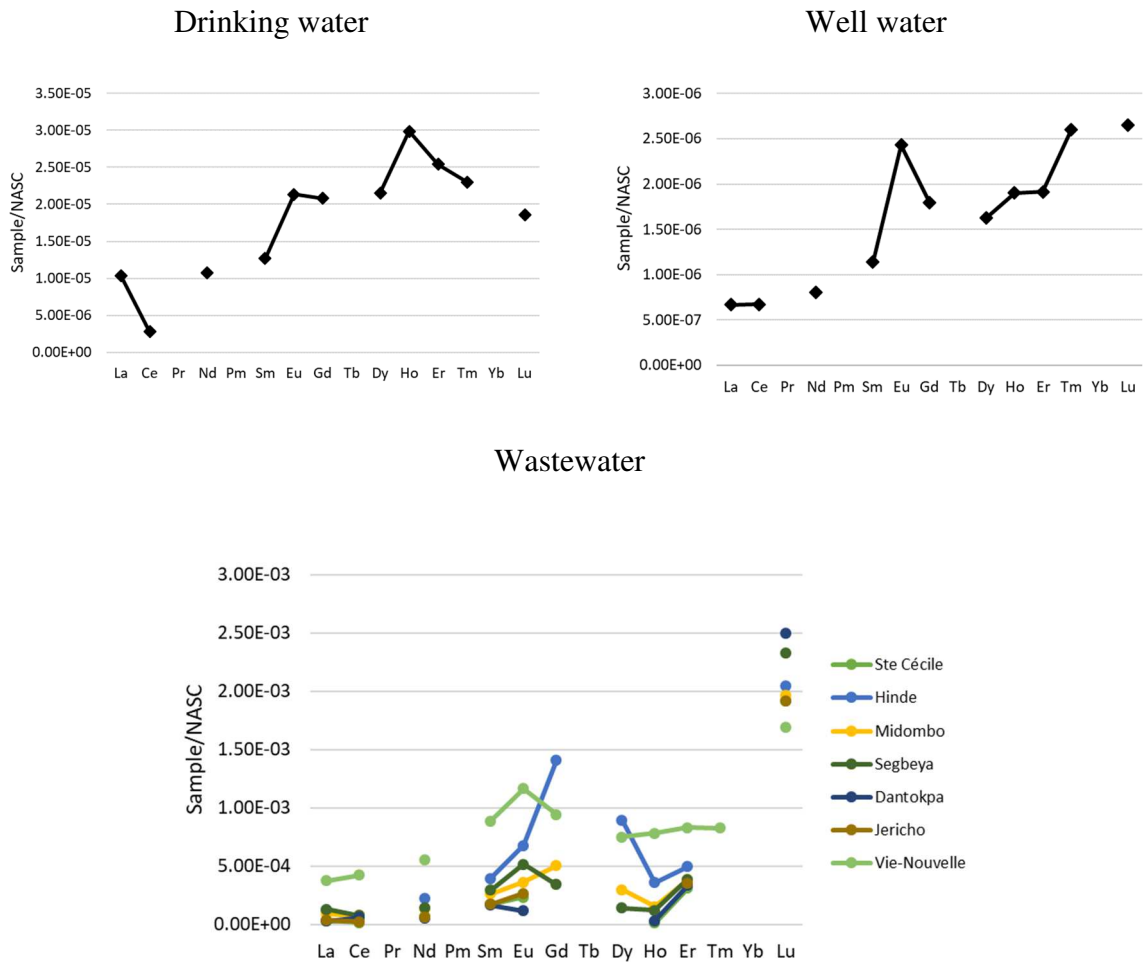


288

289

Figure 2: Cotonou soil REE profiles compared to NASEC

290



291

Figure 3: Normalized REE profiles in Cotonou drinking water (average), well water

292

(average) and wastewater

293 This means that the measured Eu proportions in these samples were different from those of the  
294 reference system (i.e. NASC) (Riou, 1999; Rabiet et al., 2009). Their presence could be due to  
295 the inorganic and organic ligands (e.g.,  $F^-$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$ ,  $PO_4^{3-}$ , fulvic and humic acids, proteins,  
296 and amino acids) in the environment that can complex more heavy REEs than light REEs (Riou,  
297 1999; Rabiet, 2009). According to Leleyter and al. (1999), heavy REEs and cerium are  
298 preferably associated with iron oxides. In terms of of total iron an average of 2.4 mg/L for open  
299 sewers wastewater and 6.9 mg/l for domestic wastewater in Vie-Nouvelle were found, with the  
300 highest value found in Segbeya (7.7 mg/L). The Fe content can facilitate REE complexation  
301 and explain the HREE richness of these samples. The Vie-Nouvelle wastewater, which had the  
302 highest Fe concentration, had the greatest enrichment  $La_N/Lu_N$ , while the Dantokpa sample,  
303 which had the lowest Fe concentration (728  $\mu g/L$ ), had the lowest  $La_N/Lu_N$  (0.01).

304 The SONEB drinking water and well water samples had  $La_N/Lu_N$  of 0.56 and 0.25, respectively;  
305 these values, which are less than 1, indicate an enrichment in HREE compared to LREE. REEs  
306 in natural waters come from the chemical alteration of soil minerals. With water, the main agent  
307 of this alteration consists of the partial or total dissolution of rocks or soils (Riou, 1999). This  
308 enrichment was observed in all sites. However, we note that the well water in Ste Cecile and  
309 Hinde presented an enrichment in LREE compared to HREE, with  $La_N/Lu_N$  ratios of 1.22 and  
310 1.28, respectively. This situation could be due to particular conditions within these wells, which  
311 would merit further investigation.

312 Although it was not possible to calculate Gd anomalies, challenging Gd values were observed  
313 in Hinde, Midombo, Segbeya open sewer samples and Vie-Nouvelle wastewater samples. They  
314 are much larger than the Gd concentrations of the drinking water and well water samples  
315 collected in the area. The highest concentration is detected in Vie-Nouvelle wastewater samples  
316 (up to 48.7  $\mu g/L$ ) when the drinking water highest concentration is 0.4  $\mu g/L$ . It is likely that

317 these high Gd values can be attributed to the presence of gadopentetic acid or other Gd salts  
318 used in medical MRIs. The Gd compounds, which are injected in a complex form into patients  
319 during examinations, are subsequently completely excreted by the patients and thereby  
320 contaminate wastewaters. The content of anthropogenic Gd is random because it depends on  
321 the number of people undergoing MRI examinations. Gadolinium had a significant correlation  
322 with COD ( $R^2= 0.9$ ) and no correlation with turbidity. It also had a significant correlation with  
323 ammonium (human pollution indicator) ( $R^2= 0.9$ ). This confirms that the gadolinium came from  
324 human pollution, in spite of the quasi-absence of MRI facilities in Benin. The only facility  
325 opened in November 2016 and was likely not fully operational at the time of the wastewater  
326 samplings. However, such facilities are available in neighboring countries (Togo, etc.); it is  
327 possible that patients traveled abroad for MRI examinations and returned home with Gd still in  
328 their bodies. Unfortunately, there are very few data in literature regarding the content of REE  
329 in untreated wastewater. In Verplanck et al. (2005) normalized Gd concentrations in primary  
330 influents of large WWTPs in USA of about  $5 \cdot 10^{-4}$  are given, but the water consumption is very  
331 different: between 200 and 700 L/day/person in USA, when in Cotonou it is about  
332 60L/day/person. So the comparison is difficult.

333 Wastewater samples from Segbeya and Vie-Nouvelle presented europium positive anomalies.  
334 The anthropogenic excess calculated for these sites are 0.25  $\mu\text{g/L}$  for Segbeya in sewer samples  
335 and 0.31  $\mu\text{g/L}$  in the Vie-Nouvelle domestic wastewater. The SONEB drinking water and well  
336 water samples also showed europium anomalies of 1.31 and 1.70, respectively, but did not have  
337 an excess (0.00  $\mu\text{g/L}$ ). It can be deduced that the drinking water and well water were not sources  
338 of anthropogenic europium excesses in wastewater.

339 This europium excess in wastewater could come from another source, which could be related  
340 to the management of solid wastes in Cotonou. Some sources of europium are fluorescent

341 lamps, television wastes, and smartphones (Rollat et al., 2016). The runoff of leachates from  
342 waste piles in the streets to open sewers and to the sewage network of Vie-Nouvelle, as well as  
343 wastes themselves, which are thrown in abundance into the sewers, can explain this pollution;  
344 lead (Youssao et al., 2011) and cadmium (Gbesso et al., 2015) pollution can be explained by  
345 this mismanagement of solid waste. Europium had a positive, significant correlation with  
346 turbidity ( $R^2 = 0.5$ ) and could be adsorbed to the suspended matter, as the heavy metals (Cr,  
347 Cu, Ni, Pb and Zn) found in abundance in the wastewater and sewers samples.

348 SONEB water also showed a negative cerium anomaly (0.27). This anomaly is often observed  
349 in continental and marine water samples (Riou, 1999; Loges et al; 2012; Göb et al., 2013; Bau  
350 et al., 2018) and has been linked to the nature of the rocks.

#### 351 **4. CONCLUSION**

352 Cotonou wastewater was affected by the presence of REEs, with an enrichment in heavy REEs  
353 compared to light REEs. The two main REE were gadolinium and europium. The pollution by  
354 anthropogenic Gd is due to the use of Gd chelates as contrast agents for MRI. Gd contamination  
355 is likely to increase in the next few years with the improved access to MRI facilities and the  
356 absence of wastewater treatment plants. The europium pollution could be related to the  
357 mismanagement of solid wastes, whose leachates were found in sewerage networks. The  
358 aquifers are not yet polluted by Gd and Eu.

359 In Benin and other African countries, the development of proper sanitation and solid waste  
360 management should help limit the dissemination of these ecotoxic substances in the aquatic  
361 environment and the food chain.

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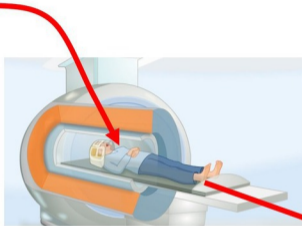
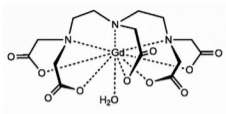
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