Rare earth elements in surface waters and sediments of the Mgoua watershed, south western Cameroon

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Abstract

The concentrations and distribution spectra of 14 stable rare earth elements (REE) were studied for surface waters \((n = 30)\) and sediments \((n = 30)\) of the tropical zone Mgoua watershed in southwest of Cameroon. Samples were analyzed using the inductively coupled plasma mass spectrometer (ICP-MS) method. The \(\sum\)REE concentrations of the surface waters vary from 0.11 to 6.60 \(\mu\)g/L with an average value of 1.18 \(\mu\)g/L. This average is 150 times lower than the average values of the Post-Archean Australian Average Shale (PAAS). In the sediments, the concentrations range from 282.12 to 727.67 ppm with an average value of 550.05 ppm, making it 2.5 times higher than the PAAS. Rare earth spectra normalized to PAAS are spread out and show heavy rare earth enrichment; positive Eu anomalies; negative, low, or no Ce anomalies; and a gradual decrease in heavy earths in river and well waters and sediments, but are sawtooth with strong negative Ce anomalies in effluent waters and sediments. A low rare earth fractionation is noted in river and well waters \([(La/Yb)_{N} \sim 0.35–1.19]\), while it is high in effluent waters \([(La/Yb)_{N} \sim 0.42–56.99]\); a slight depletion of rare earths in all environments \([(La/Sm)_{N} \sim 0.69–2.35]\), as well as a depletion of heavy rare earths \([(Gd/Yb)_{N} \sim 0.58–1.94]\). In the sediments, the same characteristics are found with elemental ratio values differing slightly \([(La/Yb)_{N} \sim 1.15–1.99]\); \([(La/Sm)_{N} \sim 0.75–1.36]\); and \([(Gd/Yb)_{N} \sim 1.15–2.01]\). This study shows that the Mgoua watershed does not have a high concentration of REE, although in the sediments they are well above the average PASS value while they are insignificant in the waters.

Keywords Rare earth elements · Waters · Sediment · Rivers-effluents-wells · Mgoua watershed

Introduction

Rare earth elements (REE) are valuable resources because they are used worldwide in hundreds of applications, including medicine (e.g., magnetic resonance imaging (MRI) and X-ray scanners), military operations (e.g., communications, guidance, and control systems), energy (e.g., catalytic converters and rechargeable batteries for hybrid cars), and consumer products (e.g., televisions, computers, camera lenses, and other electronic devices) (Kulaksiz and Bau 2007; Tepe et al. 2014; Ma et al. 2019). Rare earth elements are composed of fourteen naturally occurring elements ranging from lanthanum (La) to lutetium (Lu). They are called “the lanthanides” and are known to have the tendency to occur in the same ores (Armstrong-Altrin et al. 2018; Ongboye et al. 2019; Ndjigui et al. 2021; Liu et al. 2021). Generally, in the environment, light REE (LREE: La, Ce, Pr, Nd, Sm, Eu, Gd) tend to have higher affinities for fine and coarse particles, while heavy REE (HREE: Tb, Dy, Ho, Er, Yb, and Lu) are more easily complexed by dissolved ligands (Censi et al. 2004; Deng et al. 2017). These characteristics lead to several geochemical applications of REE. For example, once the concentrations of REE in a sample are normalized against appropriate standards (e.g., chondrite, PAAS, and...
UCC), anomalies in the abundance of one element relative to other REE can be quantitatively assessed and then used, for example, as tracers (Ekoa Bessa et al. 2018;Ndjigui et al. 2013, 2021; Armstrong-Altrin 2020; Dang et al. 2021; Ramos-Vázquez and Armstrong-Altrin 2021a,b).

The majority of rare earth production and processing currently occurs in China (which accounted for over 90% of global rare earth production in 2010), with the Bayan Obo mine in Inner Mongolia being the largest operating REE mine in the world (Elishkaki and Graedel 2014). Many processing steps are required, including separation of individual rare earths, rare earth metal processing, and manufacturing. For instance, permanent magnet production caused 30% of rare earth production (Binnemans et al. 2013). Furthermore, although global demand for REE is increasing, supply is declining and recycling of REE-containing waste is becoming an increasingly important activity (Schulze and Buchert 2016; Cox and Kynicky 2018; Ndjigui et al. 2021; Armstrong-Altrin et al. 2021a, b). As a result, REE contamination is no longer limited to areas in the immediate vicinity of mining operations, but has also been reported in surface waters and sediments that are not in close proximity to mining activity (Tepe et al. 2014; Bonnail et al. 2017; Ongboye et al. 2019).

The distribution and behavior of REE have been characterized for a number of large tropical river watersheds such as the Amazon, Congo, Mekong, and Sepik (Egashira et al. 1997), but little or no information is available on the distribution and behavior of REE in the rivers of the Mgoua watershed in the city of Douala, southwestern, Cameroon. Tropical watersheds are marked by intense physical and chemical weathering processes, high dilution, shorter water residence time, and seasonal fluctuations (Ekoa Bessa et al. 2022). Due to high and intense precipitation, tropical rivers pour a large amount of sediment into rivers and oceans and carry a unique REE distribution signature compared to high pH rivers in high latitudes.

The very rapid growth in the extraction and use of REE worldwide may have resulted in new sources of REE in the environment: one would expect varying concentrations and patterns of REE to appear in environmental repositories such as water and sediment. The Mgoua watershed is in the humid tropics and contributes significantly to dissolved and particulate inputs to the Atlantic Ocean via the Wouri River in tropical Central Africa. Contamination of natural resources is one of the major challenges associated with industrial development and urbanization in Central Africa and particularly in Cameroon. Detailed documentation of REE concentration is important to distinguish between pristine and contaminated natural systems. In this study, we present and discuss REE data and PAAS-normalized models for sediments and surface waters of the Mgoua watershed. The aim of this study is to assess the current environmental behavior of REE in the Mgoua watershed, particularly in water and sediments. The ICP-MS method was used to measure the concentrations and patterns of REE in surface water and sediments collected in the Mgoua watershed in order to distinguish their possible sources in this watershed.

### Study area

The Mgoua watershed is located between parallels 4°00’ and 4°02’ North and between meridians 9°42’ and 9°45’ East in the lowlands of the Cameroon coast (Fig. 1). It covers an area of 780 ha and is the site of some socio-environmental challenges experienced by most cities in developing countries in sub-Saharan Africa. The climate is equatorial humid coastal, influenced by the Atlantic Ocean. The Mgoua watershed is characterized by rainfall of 4000 mm/year due to its proximity to Mount Cameroon (4100 m) (Njueya et al. 2012). There are two main seasons: a long rainy season of about 9 months (March to November) and a relatively short dry season of about 3 months (December to February) (Belmonte 1966). The average annual temperature oscillates around 27.5 °C. Hydrologically; the area is typified by a vast lagoon-marsh complex with a very dense dendritic to sub-parallel hydrographic network (Baltzer 1982). The soils are dominated by ferrallitic soils, hydromorphic soils, poorly evolved soils and crude mineral soils. The base content of these soils is very low and their pH is acidic (on average 5.5) (Njueya et al. 2012). Geologically, the Mgoua watershed is located in the large Douala sedimentary basin lying on a Precambrian basement composed of magmatic (ancient syntectonic intrusive granites) and metamorphic (crystalline schists, biotite, and amphibole gneiss) formations. These basement formations are found on the Northern part of the remobilized and restructured Eburnian Congo Craton (Ngueutchoua et al. 2019). Overlying this basement, are sedimentary series that present a low-slope relief characterized by formations of secondary, tertiary, and quaternary ages and representing a multi-layered aquifer system with a sandy, silty, and/or sandy-clay fractions (Ngueutchoua et al. 2019). These sedimentary formations are composed of conglomerates, conglomeratic sandstones, and arkosic sandstones, interbedded with thin limestones and black to dark gray shales. On these often permeable sediments are found numerous industries straddled along many waterways (such as River Wouri and the Mgoua watershed) that have been transformed to dumping grounds.

### Sampling and analytical methods

#### Sampling

Water samples were collected from rivers, wells, and effluents at ten different stations. At each station, three
representative samples were collected, making a total of 30 samples. Accordingly, the five river stations (WR1 to WR5) sampled summed up to fifteen samples; the three water wells stations (WW1 to WW3) gave nine samples; and the two industrial effluent stations (WE1 and WE2) produced six samples. The polyethylene sample bottles used to collect water for the determination of the REE were cleaned with nitric acid diluted to 10%, then rinsed abundantly with Milli-Q water, dried at 80 °C in the oven and then preserved. The samples taken are then fixed with 2% nitric acid and transported in a cooler at 4 °C. Upon arrival at the laboratory, they were kept in a refrigerator at the same temperature until the day of the analyses.

Same protocol used to sample water was deployed to collect sediments at the various stations that water was sampled such that triplet set of sediment collected at each station culminated in a total of thirty (30) sediment samples. They are labeled SR1 to SR5 for rivers/streams; SW1 to SW3 for sediments inside wells; and SE1 and SE2 for sediments near effluents (Table 1). The samples taken were transferred into clean plastic bags of 100-ml capacity. Prior to this, the bags were washed, soaked in 1 M HCl, then rinsed several times with Milli-Q water, and dried before collecting the samples. This was to avoid the risks of contamination. The collected sediment samples were homogenized and stored at 4 °C, then transported to the laboratory.

**Analytical methods**

Water was analyzed for a certain number of elements (REE) using a Perkin Elmer 5100 ZL equipment and inductively coupled plasma mass spectrometer (ICP-MS) method, at the Geosciences et Environnement de Toulouse (GET) on 25 ml of diluted sample filtrate. To minimize, a lanthanum chloride solution was used in the air-acetylene flame. The concentration of each element was determined directly using a calibration curve (Aubert and Pinta 1971).

About 5 g of the sediment samples were ground and then pulverized in a flask made of 99.8% alumina. The sediment powders were prepared for ICP-MS analysis for REE by acid dilution. They were treated in an acidic HCl and HClO₄ mixture at 120 °C in Teflon boxes for 1 week, then in dilute nitric acid (HNO₃) and finally dried. The residue was then dissolved in an acid mixture (HCl + HClO₄) and dried for a second time before being dissolved in a mixture of three (3) acids (HNO₃, HCl and HF) at 100 °C. The solution samples were analyzed using a Perkin Elmer Elan 9000 ICP-MS. For the 1 M 100 analysis, the average weight

**Table 1** The location and coordinates of the sampling sites

| Stations   | Locality       | North latitude | East longitude |
|------------|----------------|----------------|----------------|
| WR1 and SR1| Axe lourd      | 04°00’36”      | 09°44’18”      |
| WR2 and SR2| Bongogo        | 04°01’18”      | 09°44’29”      |
| WR3 and SR3| Nettoy Cam     | 04°01’30”      | 09°43’68”      |
| WR4 and SR4| Oyack          | 04°01’30”      | 09°44’30”      |
| WR5 and SR5| Aeroprot       | 04°00’45”      | 09°44’09”      |
| WW1 and SW1| Axe lourd      | 04°00’34”      | 09°44’14”      |
| WW2 and SW2| Oyack          | 04°01’00”      | 09°44’00”      |
| WW3 and SW3| Tergal         | 04°02’00”      | 09°44’00”      |
| WE1 and SE1| Carrefour CCC  | 04°02’06”      | 09°43’30”      |
| WE2 and SE2| Chococam       | 04°02’08”      | 09°43’54”      |

WR water river; WW water well; and WE water effluent
SR sediment river; SW sediment well; and SE sediment effluent
of the instrument responses for three (3) certified reference samples prepared in the same manner as unknown was compared to the values obtained by the unknown solution instrument for each element. The nominal zero concentration was equal to the measured response from the blank.

Results

The concentrations of the surface waters and sediments of the Mgoua watershed are presented in Tables 2 and 3. Physico-chemical parameters, major, minor, and trace elements in surface waters and sediments of this basin have been described in previous studies (Ndjama et al. 2008, 2021).

REE concentrations in water

Surface water $\sum$REE concentrations range from 0.11 to 6.60 µg/L with an average value of 1.18 µg/L which are on average more than 150 times lower than the Post-Archean Australian Shale (PAAS) values. They are listed in Table 2 and follow the order: La > Ce > Nd > Pr > Gd > Sm > Dy > Er > Yb > Ho > Tb > Eu > Tm > Lu. The river water recorded the lowest concentrations of $\sum$REE, the highest being the waters of the wells that are farthest from the rivers, followed by those of the effluents. The sum of the values of REE in the rivers ranged from 0.11 to 0.44 µg/L, with an average of 0.21 µg/L. The concentrations of $\sum$REE in river water follow the following order: Ce > La > Nd > Pr > Gd > Dy > Sm > Yb > Er > Eu > H
### Table 2: Statistical data of analytical results of surface waters of the Mgoua watershed (µg/kg)

| REE | Rivers | Effluents | Wells |
|-----|--------|-----------|-------|
|     | WR1 \((n = 3)\) | WR2 \((n = 3)\) | WR3 \((n = 3)\) | WR4 \((n = 3)\) | WR5 \((n = 3)\) | Avg. \((n = 15)\) | WE1 \((n = 3)\) | WE2 \((n = 3)\) | Avg. \((n = 6)\) | WW1 \((n = 3)\) | WW2 \((n = 3)\) | WW3 \((n = 3)\) | Avg. \((n = 9)\) |
| La  | 0.0413429 | 0.0330459 | 0.0294819 | 0.0428789 | 0.0805659 | 0.0454631 | 1.4656 | 0.0604639 | 0.76303195 | 0.0962369 | 0.043212 | 1.2501919 | 0.4632136 |
| Ce  | 0.0470044 | 0.0570034 | 0.0371364 | 0.0893174 | 0.1919344 | 0.0844792 | 0.0186529 | 0.1114014 | 0.14896315 | 0.2843994 | 0.1326644 | 2.5126834 | 0.9765824 |
| Pr  | 0.0048022 | 0.0062642 | 0.0034145 | 0.0107739 | 0.0216365 | 0.0093782 | 0.2745834 | 0.016251 | 0.1454172 | 0.0349394 | 0.016724 | 0.3142651 | 0.1210995 |
| Nd  | 0.02135 | 0.03231 | 0.020895 | 0.045302 | 0.085332 | 0.0410378 | 0.0341721 | 0.073304 | 0.05373805 | 0.184344 | 0.072971 | 1.39279 | 0.550035 |
| Sm  | 0.003054 | 0.0034479 | 0.00182083 | 0.0065745 | 0.0079595 | 0.00457135 | 0.142974 | 0.0105095 | 0.079731 | 0.031954 | 0.0095666 | 0.34818 | 0.1275687 |
| Eu  | 0.0032161 | 0.0031319 | 0.0015121 | 0.0023166 | 0.0056105 | 0.00279384 | 0.0120405 | 0.00149792 | 0.048537 | 0.031954 | 0.0095666 | 0.34818 | 0.1275687 |
| Gd  | 0.003054 | 0.0032975 | 0.0057413 | 0.069642 | 0.0160338 | 0.00701816 | 0.060803 | 0.0194461 | 0.0217632 | 0.031954 | 0.0095666 | 0.34818 | 0.1275687 |
| Tb  | 0.00037216 | 0.00053558 | 0.00042112 | 0.0097629 | 0.0026263 | 0.00098629 | 0.0293539 | 0.002764 | 0.1605895 | 0.0038608 | 0.0018093 | 0.042373 | 0.1631437 |
| Dy  | 0.0041395 | 0.0066854 | 0.0031104 | 0.0056959 | 0.0114496 | 0.00621616 | 0.0043463 | 0.0220975 | 0.0132219 | 0.0256975 | 0.0107425 | 0.2502955 | 0.0957585 |
| Ho  | 0.00090815 | 0.00090851 | 0.0072319 | 0.011864 | 0.030014 | 0.0034553 | 0.238025 | 0.0045313 | 0.141669 | 0.0050473 | 0.0023313 | 0.05048 | 0.0192862 |
| Er  | 0.0026688 | 0.0023657 | 0.003046 | 0.005272 | 0.0058307 | 0.00383664 | 0.0044777 | 0.00894755 | 0.0069756 | 0.0171942 | 0.0088284 | 0.148171 | 0.0580643 |
| Tm  | 0.00049935 | 0.0004186 | 0.004426 | 0.0008067 | 0.0010328 | 0.00664001 | 0.0129447 | 0.0015869 | 0.0072658 | 0.0021863 | 0.00087378 | 0.0180178 | 0.00702716 |
| Yb  | 0.003054 | 0.0034479 | 0.00182083 | 0.0065745 | 0.0079595 | 0.00457135 | 0.0018984 | 0.005095 | 0.00620395 | 0.0200703 | 0.0087455 | 0.1092465 | 0.04602077 |
| Lu  | 0.0032214 | 0.00056873 | 0.0006475 | 0.0010592 | 0.0093732 | 0.0070698 | 0.0120405 | 0.00149599 | 0.0067682 | 0.032722 | 0.001467 | 0.056101 | 0.00678233 |

∑REE: 0.13 0.15 0.11 0.22 0.44 0.21 2.21 0.34 1.27 0.73 0.32 6.60 2.55

A = LREE (La, Ce, Pr, Nd, Sm and Eu)

B = HREE (Gd, Tb, Dy, Ho, Er, Tm and Lu)

Ce/Ce* = \((C_{La_{sample}}/C_{La_{PAAS}})^{1/2}(P_{Pr_{sample}}/P_{Pr_{PAAS}})^{1/2}\)

Eu/Eu* = \((E_{Yb_{sample}}/E_{Yb_{PAAS}}) \times (S_{Gd_{sample}}/S_{Gd_{PAAS}})^{1/2}\)

C = \((L_{Yb_{sample}}/L_{Yb_{PAAS}}) \times (T_{Sm_{sample}}/T_{Sm_{PAAS}})^{1/2}\)

D = \((L_{Sm_{sample}}/L_{Sm_{PAAS}}) \times (T_{La_{sample}}/T_{La_{PAAS}})^{1/2}\)

E = \((G_{Yb_{sample}}/G_{Yb_{PAAS}}) \times (G_{Sm_{sample}}/G_{Sm_{PAAS}})^{1/2}\)
Table 3  Statistical data of analytical results of sediments of the Mgoua watershed (ppm)

| REE | Rivers | Effluents | Wells |
|-----|--------|----------|-------|
|     | SR1 \((n = 3)\) | SR2 \((n = 3)\) | SR3 \((n = 3)\) | SR4 \((n = 3)\) | SR5 \((n = 3)\) | Avg. \((n = 15)\) | SE1 \((n = 3)\) | SE2 \((n = 3)\) | Avg. \((n = 6)\) | WW1 \((n = 3)\) | SW2 \((n = 3)\) | SW3 \((n = 3)\) | Avg. \((n = 9)\) |
| La  | 119.35 | 84.77 | 68.91 | 157.12 | 69.30 | 99.89 | 168.57 | 72.83 | 120.70 | 128.31 | 161.24 | 181.05 | 156.87 |
| Ce  | 231.31 | 162.02 | 124.47 | 298.80 | 132.46 | 189.81 | 298.92 | 156.27 | 227.60 | 263.87 | 295.15 | 301.21 | 286.74 |
| Pr  | 25.49 | 17.01 | 13.40 | 32.76 | 14.28 | 20.59 | 39.29 | 18.09 | 28.69 | 28.09 | 38.21 | 42.91 | 36.40 |
| Nd  | 90.75 | 58.59 | 44.55 | 115.16 | 48.71 | 71.55 | 138.94 | 56.79 | 97.87 | 110.58 | 131.15 | 129.98 | 123.90 |
| Sm  | 15.61 | 9.75 | 7.56 | 18.53 | 8.59 | 12.01 | 23.09 | 14.09 | 18.59 | 19.51 | 21.87 | 25.90 | 22.43 |
| Eu  | 1.46 | 1.11 | 1.06 | 1.54 | 1.74 | 1.38 | 1.89 | 1.78 | 1.835 | 1.60 | 1.96 | 2.01 | 1.86 |
| Gd  | 14.52 | 8.55 | 7.03 | 16.45 | 8.08 | 10.93 | 20.09 | 10.23 | 15.16 | 16.35 | 19.20 | 22.19 | 19.25 |
| Tb  | 1.76 | 0.92 | 0.87 | 1.89 | 1.03 | 1.29 | 1.99 | 1.11 | 1.55 | 1.86 | 1.97 | 2.09 | 1.97 |
| Dy  | 10.43 | 4.97 | 5.47 | 11.27 | 5.94 | 7.62 | 13.83 | 7.37 | 10.6 | 11.91 | 13.96 | 14.18 | 13.35 |
| Ho  | 2.12 | 0.92 | 1.03 | 2.19 | 1.06 | 1.46 | 2.87 | 1.61 | 2.24 | 2.20 | 2.96 | 2.90 | 2.69 |
| Er  | 6.89 | 2.79 | 3.33 | 7.29 | 3.15 | 4.69 | 7.95 | 4.58 | 6.27 | 6.99 | 7.56 | 7.87 | 7.47 |
| Tm  | 1.04 | 0.42 | 0.48 | 1.13 | 0.45 | 0.70 | 1.41 | 0.85 | 1.13 | 1.14 | 1.81 | 1.98 | 1.64 |
| Yb  | 7.64 | 3.15 | 3.45 | 7.63 | 2.83 | 4.94 | 7.80 | 3.08 | 5.44 | 7.69 | 7.98 | 7.88 | 7.85 |
| Lu  | 1.25 | 0.51 | 0.51 | 1.26 | 0.41 | 0.79 | 1.03 | 0.888 | 0.96 | 1.48 | 1.38 | 1.52 | 1.46 |
| \(\Sigma\)REE | 529.62 | 355.48 | 282.12 | 673.02 | 298.03 | 427.65 | 727.67 | 349.57 | 538.62 | 601.58 | 706.4 | 743.67 | 683.88 |
| A  | 483.97 | 333.25 | 259.95 | 623.91 | 275.08 | 395.23 | 670.7 | 319.85 | 495.28 | 551.96 | 649.58 | 683.06 | 628.20 |
| B  | 45.65 | 22.23 | 22.17 | 49.11 | 22.95 | 32.42 | 56.97 | 29.72 | 43.34 | 49.62 | 56.82 | 60.61 | 55.68 |
| A/B | 10.61 | 14.99 | 11.72 | 12.70 | 11.98 | 12.19 | 11.77 | 10.76 | 11.42 | 11.12 | 11.43 | 11.26 | 11.28 |
| Ce/Ce* | 0.93 | 0.95 | 0.91 | 0.92 | 0.93 | 0.93 | 0.81 | 0.95 | 0.88 | 0.97 | 0.83 | 0.76 | 0.85 |
| Eu/Eu* | 0.46 | 0.57 | 0.68 | 0.42 | 0.98 | 0.62 | 0.41 | 0.70 | 0.56 | 0.42 | 0.45 | 0.39 | 0.42 |
| C  | 1.15 | 1.99 | 1.47 | 1.52 | 1.81 | 1.59 | 1.60 | 1.75 | 1.68 | 1.23 | 1.49 | 1.70 | 1.47 |
| D  | 1.11 | 1.26 | 1.32 | 1.23 | 1.17 | 1.22 | 1.06 | 0.75 | 0.91 | 0.96 | 1.07 | 1.02 | 1.02 |
| E  | 1.15 | 1.64 | 1.23 | 1.30 | 1.73 | 1.41 | 1.56 | 2.01 | 1.79 | 1.29 | 1.46 | 1.70 | 1.48 |

A = LREE (La, Ce, Pr, Nd, Sm and Eu)
B = HREE (Gd, Tb, Dy, Ho, Er, Tm and Lu)

Ce/Ce* = \(\left(\frac{Ce_{\text{sample}}}{Ce_{PAAS}}\right)\left(\frac{La_{\text{sample}}}{La_{PAAS}}\right)^{1/2}\left(\frac{Pr_{\text{sample}}}{Pr_{PAAS}}\right)^{1/2}\)

Eu/Eu* = \(\left(\frac{Eu_{\text{sample}}}{Eu_{PAAS}}\right)\left(\frac{Sm_{\text{sample}}}{Sm_{PAAS}}\right)^{1/2}\left(\frac{Gd_{\text{sample}}}{Gd_{PAAS}}\right)^{1/2}\)

C = \(\frac{(La/\text{Yb})_{\text{N}}}{(La_{\text{sample}}/La_{PAAS})/(\text{Yb}_{\text{sample}}/\text{Yb}_{PAAS})}\)

D = \(\frac{(La/Sm)_{\text{N}}}{(La_{\text{sample}}/La_{PAAS})/(Sm_{\text{sample}}/Sm_{PAAS})}\)

E = \(\frac{(Gd/\text{Yb})_{\text{N}}}{(Gd_{\text{sample}}/Gd_{PAAS})/(\text{Yb}_{\text{sample}}/\text{Yb}_{PAAS})}\)
o > Tb > Lu > Tm. The values of the $\sum$REE in the effluent waters range from 0.34 to 2.21 µg/L with an average of 1.27 µg/L. In this environment, the sum of the REE is superior in relation to those of the rivers with an order that can change, according to the sequence below: La > Ce > Pr > Sm > Nd > Tb > Ho > Dy > Gd > Eu > Tm > Er > Lu > Yb. The gradual increase in $\sum$REE concentrations from the flooded areas to groundwater indicates hydraulic connection between the wells, the effluent and the main river channel. Rare earth element concentrations ranged from 0.32 to 6.60 µg/L with an average of 2.55 µg/L. These REE concentrations in well water are different and higher than those in river water and effluents. They follow this order: Ce > Nd > La > Gd > Pr > Dy > Er > Sm > Yb > Eu > Ho > Tb > Tm > Lu (Fig. 2).

The PAAS normalized spectra (Taylor and McLennan 1985) of river, effluent, and well water samples are shown in Fig. 3. The PAAS normalized values resulted in the spread of REE spectra for all river and well samples as well as one sample from the Bongongo site (WE2.1) with LREE enrichment, positive Eu anomalies, slight to no negative Ce anomalies, and a gradual lowering of HREE in the river water (Fig. 3a, c). The normalized HREE to PAAS spectra of the effluent waters differ from those of the river and well waters in that they are not flattened, but are saw tooth-shaped (Fig. 3b) with strong negative Ce anomalies.

The normalized ratios of some elements to PAAS vary from one environment to another. Low rare earth fractionation is observed in river and well waters [(La/Yb)$_N$ ~ 0.35–1.19 with an average of 0.7], while it is high in effluent waters [(La/Yb)$_N$ ~ 0.42–56.99 with an average of 28.71]. LREE depletion is found in water samples from all environments studied [(La/Sm)$_N$ ~ 0.69–2.35 with an average of about 1.27]. Similar depletion of heavy rare earths is visible in all studied samples- the results of (Gd/Yb)$_N$ ratio are between 0.58–1.94 (Table 2).

**REE concentrations in sediments**

Sediment $\sum$REE concentrations range from 282.12 to 727.67 ppm with a mean value of 550.05 ppm. These values are listed in Table 3 and are about 2.5 times higher than the PAAS values (Taylor and McLennan 1985). These concentrations follow this order: Nd > Ce > Gd > La > Pr > Er > Yb > Tm > Ho > Dy > Sm > Lu > Tb. River sediments have lower average REE concentrations (~282.12–673.02 ppm) with an average of 427.65 ppm. These $\sum$REE concentrations in river sediments follow this order: Nd > Ce > Gd > La > Pr > Er > Yb > Tm > Ho > Dy > Sm > Tb > Lu. The effluent sediments recorded REE concentrations that varied from one site to another. They are higher in the sediments from the Carrefour CCC site compared to those from the Chococam site. The $\sum$REE values in the sediments ranged from 349.57 to 727.67 ppm, with an average of 538.62 ppm. These $\sum$REE concentrations in effluent sediments follow the same order as the overall sediment average. In well sediments, REE values are increasingly spiking as one moves away from the waters near the harvested sediments. They range from 601.58 to 743.67 ppm with an average of 683.88 ppm. In this environment, the sum of the REE is higher than those of the river sediments and effluents with an order that can change, and is presented as follows: Nd > Ce > Gd > La > Pr > Er > Yb > Tm > Ho > Eu > Sm > Dy > Tb > Lu.

The PAAS-normalized REE spectra (Taylor and McLennan 1985) for sediments from the different environments are shown in Fig. 4. The river and well sediments show REE...
spectra that are spread out and similar in having higher concentrations of LREE, a negative anomaly of Eu, a slight upward convexity centered on the intermediate REE for the river sediments, and a more pronounced one for the effluent and well sediments. As with the effluent waters, the rare earth spectra normalized to the PAAS of the effluent sediments show a sawtooth pattern with pronounced negative Ce anomalies.

The normalized ratios of some elements to PAAS are almost similar from one environment to another. Thus, a weak rare earth fractionation is observed in the collected sediment sites \([\text{La/Yb}}_N \sim 1.15–1.99]\); a slight depletion of rare earths is observed in the sediment samples of all the studied sites \([\text{La/Sm}}_N \sim 0.75–1.36]\); and a similar depletion of heavy rare earths is visible in all the studied samples: the results of the ratio \([\text{Gd/Yb}}_N\) are between 1.15 and 2.01 (Table 3).

**Discussion**

The concentrations of REE are higher in sediments \((\Sigma\text{REE} \sim 550.05 \text{ ppm})\) than in waters \((\Sigma\text{REE} \sim 1.18 \mu\text{g/L})\), and are likely due to preferential removal and transport of soluble mineral phases in water and enrichment in sediments. Both waters and sediments showed slight enrichment of Gd that is likely due to the relatively immobile behavior of Gd in waters and sediments. Due to the predominance of
sand and silt grain size fractions (Ndjama et al. 2008), the contact time of percolating water in fluvial environments is generally short. The high water flushing conditions in the study area prevent the accumulation of concentrated acidic solutions in these different waters and reduce the dissolution and mobilization of resistant REE bearing phases in the Mgoua Basin waters. Such conditions favor the enrichment of REE in the sediments and the distribution of REE according to the relative elemental composition of the REE-bearing minerals (e.g., apatite, monazite) and the total REE balance in the surrounding sedimentary rocks (Ngueutchoua et al. 2019; Ndjigui et al. 2021).

Rare earth concentrations in well water were observed to be significantly higher than those in river and effluent water. In terms of dissolved REE removal, the concentration progressively increases from upstream of the rivers to the effluent and continues to increase downstream in the wells. Thus, the change in REE concentration appears to be a function of the change in dissolved solids, i.e., the REE-TDS relationship. This is in agreement with Sholkovitz and Szymczak’s (2000) observation that REE concentrations decrease with increasing salinity in tropical rivers in the Littoral region (Ndjama et al. 2008). Other variables that determine the concentrations and chemical forms of REE in waters are pH and TDS. The pH, TDS, and trace element concentration data for the study area were presented in a previous study (Ndjama 2014). The slightly acidic pH and low redox potential favored the dissolution of REE in the Mgoua watershed in Douala. Overall, the different spectra of REE in surface waters such as the depletion of some REE (Nd to Dy) in the waters and a slight negative anomaly of Eu in the river waters, are likely due to the variation in pH (5.08 to 7.62) and TDS (233 to 1259, mg/L) between the river, effluent, and well hydrochemical compartments.

It appears that high pH and reducing conditions favor the adsorption/precipitation of REE in the still environment (Ekoa Bessa et al. 2021). Low pH and TDS in river water increase the solubility of REE. The spectra of REE in river and well water showed similarity to the spectra of EARs in the Mgoua watershed sediments, revealing the signature of source rocks. However, the predominant pH-TDS conditions in the effluent waters resulted in significantly different REE spectra from the sediments.

The surface sediments from the surrounding streams and in the sedimentary rocks of the watershed area show a similarity in distribution spectra with a dominance of the sandstone from the Douala Sedimentary Basin (DSB). The sedimentary rocks (especially the sandstones) of the DSB (Ngueutchoua et al. 2019), the sediments of river Sanaga (Nanga Bineli et al. 2021), and the sediments of Lake Ossa (Ekoa Bessa et al. 2021) all near the study site have similar spectral signatures to the sediments in this study. Even the sediments of river Dibamba (Sonfack et al. 2021) that are further away from the study site are completely similar to the sediments in this study (Fig. 5). Overall, the REE spectra of the surface waters followed the REE spectra of the sediments but with a large discrepancy due to the high concentrations in the sediments compared to the waters and the prevailing pH-TDS conditions.

The large rivers of the equatorial zones, the calm environments, and the lakes of these regions do not present a Ce anomaly. On the other hand, an Eu anomaly is observed in most tropical rivers. The Eu anomaly gradually changes from positive in water to negative in sediment, as shown in Fig. 6. Larger changes in the Eu anomaly are observed in surface waters compared to sediments. This transition in the Eu anomaly indicates the preferential dissolution of Eu-bearing minerals. The Ce anomaly is observed to be weak.
and the variation is not as significant as that of Eu. The Ce anomaly changes from positive to negative anomaly depending on the materials such as PAAS, sediments and surface water. Thus, it appears that under the high pH-TDS conditions of the Mgoa watershed, there is Ce adsorption/precipitation. The lack of significant negative Ce anomaly is also likely due to the early stages of weathering during which REE fractionation is less pronounced. Middelburg et al. (1988) suggest that significant REE fractionation occurs during the advanced stages of alteration which is not the case in this study.

A comparison of dissolved REE concentrations in the surface waters of the two largest tropical rivers of the Amazon (Gaillardet et al. 1997) and Congo (Bau et al. 2006)
reveals that REE concentrations are higher in the waters of the larger rivers compared to the waters of the Mgoua basin. Principal component analysis of the water REE data from two principal components representing 99.33% and 95.86% of the total variances for water and sediment, respectively, reveals two groups for each. The projection of 14 variables from 30 sampling points in three distinct environments onto the two-dimensional space is shown in Fig. 7. The length and position of the line on the projection shows the degree of association between the variables.

Most of the REE variables are distributed on the positive PC1 axes and on the positive and negative PC2 axes, forming two groups based on enrichment and depletion. Regarding waters (Fig. 8a), in the first group, variables consisting of 3 LREE (Sm, La, and Pr) and 4 HREE (Lu, Tm, Tb, and Ho) plot away from zero and confirms enrichments on spectra normalized to the PAAS (Fig. 3). In the second group, the LREE dominate the group with 4 elements (Eu, Ce, Gd, and Nd), with three elements of the HREE (Er, Dy, and Yb) well-defined and confirms depletions on normalized spectra relative to PAAS (Fig. 3), as well as the ratios between elements. In the sediments, the two groups formed differ from those formed with the water samples. The first group is composed of triplet LREE (Eu, Sm, and Pr) and HREE (Tm, Ho, and Dy) that plot close to zero and confirms the enrichments on the normalized spectra with respect to PAAS (Fig. 4). Similarly, in the second group, the elements form 2 quadruplets of LREE (Gd, La, Nd, and Ce) and HREE (Er, Tb, Yb and Lu), which like the previous group, are close to zero and confirms the depletion observed on the spectra of the sediments normalized with respect to PAAS (Fig. 4). In both water and sediment, Eu is distant from the other elements due to its anomalous nature on rare earths. This element has shown variations probably due to the most Ph-TDS sensitive features among the rare earths (Henderson 1984; Wilde et al. 1996).

3- The spectra of REE of surface waters are not very similar to those of sediments, with a large discrepancy due to the high concentrations in sediments and under the effect of the predominant conditions of pH-TDS.

4- Surface sediments on various streams and sediments show similarity in the distribution spectra of the sandstone rocks of the BSD and the surrounding large streams and lake environments where they originate.

5- The REE of the Mgoua Basin have negative Ce and positive Eu anomalies in the waters, whereas we have negative Ce and Eu anomalies relative to the PAAS in the sediments. Similarly, statistical analysis depicted that most of the REE variables were distributed in two groups based on non-preferential enrichment/depletion.

Conclusions

This study, whose main goal is to determine the REE concentrations in the waters and sediments from three distinct environments (rivers, effluents and wells) in the Mgoua watershed located in the city of Douala in the African tropics, reveals that:

1- In this coastal area, REE concentrations are generally low and cannot be of economic interest, although in the sediments they are above the average PASS values, they do not reach the thresholds of exploitability.

2- Comparisons of REE in the different environments show enrichment for waters and sediments in the order wells < rivers < effluents with depletion/enrichment in LREE and HREE.

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Declarations

Ethics approval 1. Armel Zacharie Ekoa Bessa, hereby consciously assures that for the manuscript “Rare earth elements in surface waters and sediments of the Mgoua watershed, southwestern Cameroon,” the following is fulfilled: (1) This material is the authors’ original work, which has not been previously published elsewhere. (2) This paper is not currently being considered for publication elsewhere. (3) This paper reflects the authors’ research and analysis truthfully and completely. (4) This paper properly credits the meaningful contributions of co-authors and co-researchers. (5) The results are appropriately placed in the context of prior and existing research. (6) All sources used are properly disclosed (correct citation). Copying of text must be indicated as such using quotation marks and giving proper reference. (7) All authors have been personally and actively involved in substantial work leading to this paper and will take public responsibility for its content. The violation of the Ethical Statement rules may result in severe consequences. I agree with the above statements and declare that this submission follows the policies of Arabian Journal of Geosciences as outlined in the Guide for Authors and the Ethical Statement.

Consent to participate By signing below, I am indicating my consent to participate in the research. I understand that the data collected from my participation have been used primarily for a Ph.D work of the first author, and will also be used in summary form for journal publication, and we consent for it to be used in that manner.

Conflict of interest The authors declare no competing interests.
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