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1                                   **Tropical mangrove forests as a source of**  
2                                   **dissolved rare earth elements and yttrium.**

3                                   Duc Huy Dang<sup>1,2\*</sup>, Zhirou Zhang<sup>1</sup>, Wei Wang<sup>1</sup>, Benjamin Oursel<sup>3</sup>,  
4                                   Farid Juillot<sup>4,5</sup>, Cecile Dupouy<sup>3,5</sup>, Hugues Lemonnier<sup>6</sup>, Stephane Mounier<sup>7</sup>

5                                   <sup>1</sup>Trent School of the Environment, Trent University, Peterborough, Canada.

6                                   <sup>2</sup>Department of Chemistry, Trent University, Peterborough, Canada.

7                                   <sup>3</sup>Aix Marseille Université, Université de Toulon, CNRS, IRD, MIO, Marseille, France

8                                   <sup>4</sup>Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Sorbonne Université,  
9                                   UMR CNRS 7590, MNHN, ERL IRD 206, Paris, France

10                                   <sup>5</sup>Institut de Recherche pour le Développement (IRD), Centre IRD Noumea, Nouvelle-Calédonie

11                                   <sup>6</sup>IFREMER, IRD, Université de la Nouvelle-Calédonie, Université de La Réunion, UMR 92200  
12                                   ENTROPIE, Nouméa, Nouvelle-Calédonie

13                                   <sup>7</sup>Université de Toulon, Aix Marseille Université, CNRS, IRD, MIO, Toulon, France

14  
15                                   **\*Corresponding author: [huydang@trentu.ca](mailto:huydang@trentu.ca)**

16 **Abstract:** Rare earth elements (REEs) and Y are commonly used as geochemical proxies for  
17 water chemistry, history of the continental crust and provenance studies. At the continent-ocean  
18 interface, the estuarine geochemistry of REEs is commonly considered to be driven by a large-  
19 scale removal. Consequently, the river-borne flux of dissolved REEs to the marine budget is  
20 assumed as a minor fraction. Here, we report a significant release of dissolved REEs, together  
21 with a fractionation between light, heavy REEs and Y, in the tropical mangrove estuaries of New  
22 Caledonia. These observations were associated with internal recycling within the redox-dynamic  
23 mangrove system. The possible contribution of groundwater can be ruled out based on water  
24 stable isotopes. These findings imply that tropical mangrove estuaries act as a sizeable source of  
25 REEs and Y to the ocean rather than as a buffer zone. We extrapolated our data toward global  
26 dissolved fluxes of REEs and Y through the mangroves. This preliminary calculation suggests  
27 that the mangrove system supplies 2.6-5% of global river-borne dissolved Nd, a REE with the  
28 most comprehensive mass balance. Therefore, oceanic mass balance budget models may need to  
29 consider this atypical system as an input to balance the global distribution of REEs and Y.

30 **Keywords:** Rare earth elements, yttrium, water stable isotopes, mangrove, estuary.

## 31 **1. Introduction**

32 Over the past decade, rare earth elements (REEs or the lanthanide series), Y and REE isotopes  
33 have received significant attention in geochemistry as tracers of the geological history of the  
34 continental crust and provenance study (Bayon et al., 2015). In paleoenvironmental studies, REEs  
35 are also commonly used as proxies to reconstruct water chemistry and oxygen saturation as per  
36 the distinct behaviour of Ce during redox transitions (Auer et al., 2017; Wallace et al., 2017). The  
37 fractionation between the light REEs (LREEs), heavy REEs (HREEs) and the non-lanthanide Y  
38 can also highlight the mechanisms of particle transport, sediment deposition and even geological  
39 features (e.g., iron formation) over the Earth's history (Bayon et al., 2015; Planavsky et al.,  
40 2010). More recently, because of the implication of REEs in novel technologies, REE anomalies  
41 (increased in concentrations of a specific REE relative to its neighbouring REEs) could also be  
42 used as a proxy for emission sources (Dang and Zhang, 2021; Ma et al., 2019; Tepe et al., 2014).  
43 However, the environmental chemistry of REEs remains fragmented, mostly regarding their  
44 anomalous behaviour across the river-estuarine-coastal water mixing zone where the  
45 fractionation between LREEs and HREEs is often associated with the redistribution of REEs  
46 among the dissolved and particulate fractions and the formation of stable dissolved complexes  
47 (Nozaki et al., 2000; Sholkovitz and Szymczak, 2000; Sholkovitz, 1995). As a consequence, the  
48 ocean mass budget of REEs remains unbalanced with missing fluxes at the global scale (Arsouze  
49 et al., 2009; Garcia-Solsona and Jeandel, 2020; Pourret and Tuduri, 2017; Tachikawa et al.,  
50 2003).

51 The interpretation of estuarine REE behaviour is fundamental to highlight their geochemistry at  
52 the continent-ocean interface. One conventional feature derived from decades of investigation on  
53 REEs' estuarine geochemistry is that large-scale removal of dissolved REEs (especially LREEs)  
54 occurs in the estuarine mixing zone (Elderfield and Greaves, 1982; Lawrence and Kamber, 2006;  
55 Nozaki et al., 2000; Pourret and Tuduri, 2017; Sholkovitz, 1995). This phenomenon minimizes  
56 the effective continental flux of REEs to the ocean and subsequently affects the marine budget  
57 calculations of REEs (Nozaki et al., 2000). Various factors would lead to such extensive removal  
58 of REEs. These include planktonic uptake, coprecipitation with ferromanganese oxyhydroxides  
59 and salt-induced coagulation of colloids (Hoyle et al., 1983; Nozaki et al., 2000; Sholkovitz and  
60 Szymczak, 2000). However, a limited number of publications pointed out a supply of dissolved

61 REEs in the mid-estuary zones (Lawrence and Kamber, 2006; Nozaki et al., 2000). This REE  
62 release could be associated with desorption from terrigenous suspended particles or  
63 remineralization in the estuarine system.

64 Moreover, most of the estuarine systems investigated so far for REEs geochemistry were major  
65 well-oxygenated riverine systems. However, it has been demonstrated that REEs cycling in  
66 marine waters can be impacted by redox variations (Bau et al., 1997). This process is particularly  
67 important as it can increase the effective continental REE flux to the oceans through enhanced  
68 supply to the water column upon dissolution of REEs-bearing oxyhydroxide phases. Therefore,  
69 further insights on REE behaviour across the redox-sensitive estuarine mixing zone are needed to  
70 strengthen our understanding of the REE geochemistry at the continent-ocean interface.

71 Tropical mangrove forests are of great interest to investigate these environmental conditions.  
72 First, they cover a large surface area (150,000 km<sup>2</sup>) where complex hydrological processes  
73 balance abundant precipitation, surface runoff, and evaporation (Spalding, 2010). Moreover, the  
74 combination of elevated and annually constant temperature patterns with high bioavailability of  
75 natural organic matter boosts bacterial respiration, promoting hypoxia (Dubuc et al., 2019). To  
76 date, very limited studies on REEs focused on this critical ecosystem as it is generally assumed  
77 that the mangrove systems act as a buffer zone retaining trace elements and thus contribute a  
78 minor input for REEs to the oceans (Marchand et al., 2012).

79 Here, we investigated REE internal cycling within two estuarine mangrove systems in the  
80 subtropical region of New Caledonia. We meticulously measured dissolved REEs and Y over a  
81 24-hour cycle in mangrove stations during a dry season and the spatial variations across the  
82 estuary in a rain season. To track whether additional water masses alter the mixing between the  
83 fresh and seawater endmembers, we also measured stable water isotopes ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) to assess  
84 the hydrologic regime. We compared the stable water isotopes in these mangrove systems with  
85 other river waters collected in southeastern New Caledonia to verify the signature of the  
86 freshwater endmembers. Altogether, the data highlights REE behaviour during the estuarine  
87 mixing and document the mangrove forest's role on REE cycling at the continent-ocean interface.  
88 This dataset will help answer whether the REE continental flux from the tropical mangrove-  
89 dominated estuaries should be included in the REE marine budget.

90           **2. Materials and Methods**

91           **2.1. Study site description**

92           In the Southwest Pacific Ocean, New Caledonia is surrounded by the Coral Sea (**Figure 1A,B**).  
93           The main island “Grande Terre” is 400 km long and 64 km wide with a semi-arid tropical climate  
94           along the west coast. The whole island is also bordered by a coral reef enclosing a lagoon of over  
95           20,000 km<sup>2</sup>. The rich reef diversity and associated ecosystems were inscribed as a UNESCO  
96           World Heritage Site in 2008. On the other hand, most of the island is mountainous with vast  
97           ultramafic masses, schists and outcrops of basalt (Lillie and Brothers, 1970). Weathering of the  
98           ultramafic rocks’ surface led to the formation of thick lateritic regoliths (tens of meters) hosting  
99           deposits of transition metallic elements of prime economic importance (Dublet et al., 2014; Noël  
100           et al., 2014). Between the lucrative mineral-rich land and the sea of tremendous ecological  
101           importance, the mangrove system acts as a buffer zone to filter heavy metals from reaching the  
102           reef (Marchand et al., 2012).

103           The hydrological behaviour of the Grande Terre is clearly distinct between the southwestern and  
104           northeastern coasts because of the ‘rain-shadow’ effect across the central massif divide (Terry  
105           and Wotling, 2011) (**Figure 1B**). Accordingly, the southwestern coast (leeward) tends to be drier  
106           than the windward northeastern coast. Overall, the hydrologic regime is characterized by high  
107           annual variability of rainfall amount and extreme events. Moreover, high and steep watersheds  
108           are associated with flash floods and thus rapid water transfer to the lagoons (Desclaux et al.,  
109           2018).

110           The Voh-Kone region (Northwest of the Grande Terre, **Figure 1B**) is an area of great economic  
111           and ecological interest. The Koniambo Massif hosts a large mine (Koniambo mine, **Figure 1C**),  
112           one of the largest nickel reserves in New Caledonia. The ore is conveyed to a coastal smelting  
113           site (Koniambo Nickel SAS, **Figure 1C**). Besides, the hydrologic system mainly comprises of  
114           two major rivers (Temala and Voh) discharging into the mangroves, then the bays of Chasseloup  
115           and Vavouto, respectively. Moreover, the hydrologic system comprises also of relatively smaller  
116           streams, such as the Coco River. These small tributaries have their flows significantly reduced  
117           during the dry season.

118 This study focused on the Temala and Coco Rivers (**Figure 1C**) in the Voh region. The Temala  
119 River originates from outside of the Koniambo Massif and discharges into Chasseloup Bay. It is,  
120 therefore, considered not impacted by mining activities. On the other hand, the Coco River's  
121 sources are in the Koniambo Massif hosting the Koniambo Mine. Along its course toward  
122 Vavouto Bay, the Coco River meanders parallelly to the ore conveyor. The Koniambo Nickel  
123 SAS smelting site is indeed only ca. 1.2 km away from the stream (**Figure 1 C**). Therefore, it is  
124 highly probable that this river is subject to anthropogenic impacts. Besides this contrasted  
125 exposition to anthropogenic sources, the natural geological settings of both rivers also differ. The  
126 Temala River catchment is made of soils developed on volcano-sedimentary rocks (cherts,  
127 basalts), whereas the Coco River catchment is composed of Ni-laterites developed on ultramafic  
128 rocks (peridotites) (Merrot et al., 2019).

129 We also investigated river waters (Dumbea, Coulee, Tontouta, Pirogue, **Table 1**) around Noumea  
130 in the Grande Terre's Southeast (**Figure 1B**) as a reference site for hydrological assessment using  
131 salinity and water isotope mixing.

## 132 2.2. Water sampling

133 We organized multiple sampling trips to investigate the hydrologic regime and REE cycling. The  
134 two first sampling campaigns were organized in June 2019 (dry season) and March 2020 (rain  
135 season) to collect samples in the Voh-Kone region (Temala and Coco Rivers). We also collected  
136 samples in four southeastern rivers (Dumbea, Coulee, Tontouta, Pirogue) in January, March,  
137 October and November of 2018. The March samples were collected during and after the Hola  
138 tropical cyclone while other samples are collected during the dry season.

139 During a dry season (June 2019), the first campaign aimed for a high-temporal resolution  
140 sampling in the mangrove forests (sites C2 and T6, hereafter referred to as “mangrove stations”,  
141 **Figure 1C**). For that purpose, two automatic samplers (ISCO) were deployed during high tide (8-  
142 9h AM). The samplers were programmed to collect water samples one hour after installation to  
143 ensure the resettlement of resuspended sediments during deployment. The first water samples  
144 were collected at 9h AM at C2, and 10h AM at T6. Following samples were collected every hour.  
145 At the end of the 24-hour automatic sampling cycle, all samples were filtered (0.22  $\mu\text{m}$ , cellulose  
146 acetate, Sartorius) directly on site. The filtered waters for stable water isotopes were filled to the

147 top to avoid water-air exchange, while samples for elemental analysis were acidified to pH<2  
148 with ultra-trace HNO<sub>3</sub> (Merck). The samples were then immediately shipped by air to Trent  
149 University for analysis.

150 In 2020, during the rain season, a series of samples were collected across the salinity gradient  
151 along the Temala (T1-T8) and Coco (C1-C5) rivers (hereafter referred to as the “estuarine  
152 stations”, **Figure 1C**). An additional sample was collected in the lagoon to serve as a marine  
153 endmember (M, **Figure 1C**). The samples were treated with the same protocol as in 2019 before  
154 being shipped to Trent University.

155 All the filters, sampling and storing bottles were previously rinsed with 10% HCl and milli-Q  
156 water (18 MΩ cm) in the laboratory and with river or lagoon water in the field.

### 157 2.3. Water stable isotopes

158 Water stable isotopes (δ<sup>18</sup>O and δD, deuterium) were measured using a Liquid Water Isotope  
159 Analyzer (LWIA-24d, Los Gatos Research) at the Water Quality Center (Trent University,  
160 Ontario, Canada). The delta notation was calculated relative to the V-SMOW (Vienna-Standard  
161 Mean Ocean Water) standard.

$$162 \quad \delta^{18}O = \left( \frac{\left( \frac{^{18}O}{^{16}O} \right)_{sample}}{\left( \frac{^{18}O}{^{16}O} \right)_{V-SMOW}} - 1 \right) \times 1000 (Eq. 1)$$

$$163 \quad \delta D = \left( \frac{\left( \frac{D}{^1H} \right)_{sample}}{\left( \frac{D}{^1H} \right)_{V-SMOW}} - 1 \right) \times 1000 (Eq. 2)$$

164 Analytical recovery was assessed using two isotopic natural water reference materials (CRMs,  
165 Elemental Microanalysis, UK), covering the range of δ values found in natural waters (**Table**  
166 **S1**). Averages and standard deviations of each measurement (standards and samples) were  
167 calculated based on eight injections (i.e., n = 8, 750 nL each). We also used ultra-high purity  
168 water (18.2 MΩ cm) as an in-house standard to bracket every two samples to monitor analytical



169 drift and eliminate any memory effects. However, no correction was necessary. Analytical  
170 recovery of stable water isotopes is reported in **Table S1**.

#### 171 2.4.Elemental analysis

172 To accurately determine the concentrations of REEs and Y at the ng/L levels in complex  
173 environmental matrices (seawater), we have performed a preconcentration step using column  
174 chromatography before analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). A  
175 full description of the REE column chromatography and ICP-MS analysis were reported  
176 elsewhere (Dang and Zhang, 2021; Ma et al., 2019). Briefly, REEs and Y in the filtered water  
177 samples were preconcentrated using 0.2 mL Nobias Chelate-PA1 resin (Hitachi High-  
178 Technologies). An aliquot of 50 mL of samples buffered at pH 6 was loaded on previously  
179 washed and conditioned resin. The seawater matrix was then washed off with 40 mL 0.05 M  
180 acetate buffer solution (pH = 6). REEs and Y were collected by eluting 20 mL of a 1 M HNO<sub>3</sub>  
181 solution through the column. This aliquot was collected into a 30 mL PTFE vessel and  
182 completely evaporated on a hotplate at 100°C. A final 2 mL of 0.5 M HNO<sub>3</sub> was added to retake  
183 the REEs and Y.

184 All acids used to clean and wash the resins were double-distilled trace metal grade. The acetate  
185 buffer was also passed through the Nobias column for purification. We also meticulously  
186 checked procedural blanks and column recovery in every batch of 10 samples. Procedural blanks  
187 were between 0.1 to 29 pg of REEs and Y and significantly less than their mass in natural  
188 samples. Several aliquots (50 mL) of certified reference seawater CASS-6 (National Research  
189 Council of Canada, NRCC) were also repeated to test column recovery (Ma et al., 2019).

190 REEs and Y were determined using a triple quadrupole ICP-MS (8800 Agilent Technologies) at  
191 the Trent Water Quality Center. All REEs and Y were analyzed in MS/MS mode with O<sub>2</sub> as the  
192 reaction cell gas. Detection limits were in the range of 0.1-0.4 ng/L. Although there were no  
193 certified reference materials for REEs, we compared the REEs and Y concentrations measured in  
194 an NRCC natural water certified reference material (SLRS-6) to the values reported in a  
195 European interlaboratory calibration (Yeghicheyan et al., 2019). Excellent recovery was  
196 observed; the detailed data are reported in **Table S2**.

#### 197 2.5.Normalization of REE patterns and calculations of anomalies

198 A common practice in the scientific community to eliminate the Oddo-Harkins effect and  
 199 compare samples is to normalize the measured REE concentrations to geological materials (e.g.,  
 200 upper continental crust, shales, chondrite) or offshore seawater (Piper and Bau, 2013). Here, we  
 201 normalized the measured concentrations of dissolved REEs to Post-Archean Australian Shale  
 202 (PAAS (McLennan, 2001)) (Goldstein and Jacobsen, 1988; Ma et al., 2019; Piper and Bau,  
 203 2013). The shale-normalized concentrations are hereafter referred to as REE<sub>PAAS</sub>.

204 In the current literature, excess or depletion of an REE relative to its neighbouring REEs are  
 205 referred to as positive or negative anomaly of this element (REE/REE\*). Accordingly, the REE  
 206 anomalies could be determined by several approaches (e.g., arithmetic mean, geometric  
 207 extrapolations, modelling the shape of PAAS-normalized patterns, third-order polynomial fit).  
 208 Using all these approaches, Hatje et al. have demonstrated minor variability in the final results  
 209 (Hatje et al., 2016). Therefore, we calculated Ce, Eu, and Gd anomalies using the following  
 210 equations (arithmetic mean).

$$211 \quad Ce/Ce = \frac{2 \times Ce_{PAAS}}{La_{PAAS} + Pr_{PAAS}} \text{ (Eq. 3)}$$

$$212 \quad Eu/Eu = \frac{2 \times Eu_{PAAS}}{Nd_{PAAS} + Sm_{PAAS}} \text{ (Eq. 4)}$$

$$213 \quad Ce/Ce = \frac{Gd_{PAAS}}{0.33 \times Sm_{PAAS} + 0.67 \times Tb_{PAAS}} \text{ (Eq. 5)}$$

### 214 3. Results and Discussions

#### 215 3.1. Physical-chemical properties

216 At both mangrove stations (C2 and T6, **Figure 1B**), pH values varied within a narrow range (7.8  
 217  $\pm$  0.1, n = 48, **Table 1** and **Figure S1B**). Besides, the daily variations in salinity followed a  
 218 sinusoidal curve, typical of estuarine systems (**Figure 2A**). This variation pattern is more  
 219 noticeable at Temala with low tide (S = 26) recorded at 4h and 16h, and high tide (S = 33) at 22h.  
 220 However, the salinity pattern at Coco is significantly distinct, with two events marked by steep  
 221 drops at 13h, 19h and a third gradual decrease from midnight until 7h AM (1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> as marked  
 222 in **Figure 2A**). The variation range of salinity in Coco is also narrower (29.6 to 34.2) than in  
 223 Temala (26.0 to 33.0) (**Table 1**).

224 Temperature variations also help distinguish the two systems. Water temperatures increased from  
225 16.8°C at 11h and held constant at ca. 17.5°C at Temala (**Figure S1A**, average of  $17.3 \pm 0.2^\circ\text{C}$ ,  $n$   
226 = 24, **Table 1**). However, the temperature pattern at Coco showed broader variations (15.5°C to  
227 16.5°C, average of  $16.1 \pm 0.3^\circ\text{C}$ ,  $n = 24$ , **Table 1**) with temperature drops at 11h and 21h (**Figure**  
228 **S1A**). Minimums in water temperatures at Coco are lagged by two hours relative to the salinity  
229 minimums (13h and 19h, **Figure 2A**).

230 Across the entire estuaries (estuarine stations), salinities ranged from 0 to 34.9 for the river water  
231 and marine endmembers, respectively (**Figure 2B**). On the other hand, all the river samples  
232 collected from the Southeast of New Caledonia are freshwater with a salinity of zero (**Figure**  
233 **2C**).

### 234 3.2. Stable water isotopes and the hydrologic regime

235 *The  $\delta\text{D}$  and  $\delta^{18}\text{O}$  pairing.* As the mangrove stations have narrow daily salinity variations (**Table**  
236 **1**), so too is the range of stable water isotope compositions relative to the whole estuaries (**Figure**  
237 **2 D-I**). At the mangrove stations, the  $\delta\text{D}$ - $\delta^{18}\text{O}$  relationship has the equation of  $\delta\text{D} = 4.3 \times \delta^{18}\text{O} +$   
238  $5.5$  ( $n=40$ , **Figure S2**). The slope of  $4.3 \pm 0.6$  is typically lower than other tropical Pacific regions  
239 (5.1 to 6.5, Conroy et al. (2014)), and the global seawater average of 7.4 (Rohling, 2007). This  
240 indicates a strong influence of the evaporation process in the mangrove during the dry season.

241 Across the estuaries, the  $\delta\text{D}$ - $\delta^{18}\text{O}$  relationship of Coco and Temala waters aligns with  
242 southeastern rivers with the equation of  $\delta\text{D} = 4.8 \times \delta^{18}\text{O} - 4.6$  ( $n=29$ ,  $r^2=0.9$ , **Figure S2**). The  
243 slope ( $4.8 \pm 0.3$ ) is very similar to the mangrove stations ( $4.3 \pm 0.6$ ), only the intercepts differ (-  
244 5.3 across the estuary and +5.5 in the mangrove during the dry season).

245 According to the interpretation of the local evaporation line, as described by Wolfe et al. (2007),  
246 local surface waters often plot in linear clusters to the right of the Meteoric Water Line along a  
247 slope in the range 4 to 6. Our observations of consistent slopes ( $4.3 \pm 0.6$  and  $4.8 \pm 0.3$ ) fall into  
248 this conventional interpretation (**Figure S2**) considering the Local Meteoric Water Line (LMWL)  
249 of  $\delta\text{D} = 7.1 \times \delta^{18}\text{O} + 12.6$  (retrieved from the online isotopes in precipitation calculator,  
250 [www.waterisotopes.org](http://www.waterisotopes.org)).

251 To explain the difference in the intercepts (higher values in the dry season than the rain season),  
252 we calculated the deuterium excess (d-excess) using the conventional approach:  $d\text{-excess} = \delta D -$   
253  $8 \times \delta^{18}O$ . This variable is valuable as it quantifies the deviation of a given dataset from the Global  
254 Meteoric Water Line (GMWL) by differential kinetic fractionation effects between D and  $^{18}O$ .  
255 Such effects are related to humidity, moisture recycling and post-deposition process (Dansgaard,  
256 1964). Low d-excess tends to reflect slow evaporation due to high humidity, while high d-excess  
257 values indicate fast evaporation due to low humidity (Lee et al., 2003). This interpretation is  
258 coherent with our observations as high d-excess values ( $15.8 \pm 1.3\text{‰}$  and  $15.9 \pm 2.9\text{‰}$  at Coco and  
259 Temala, respectively) were observed at the mangrove stations in dry season while low d-excess  
260 values were typical of rain season and across the estuaries ( $0.4 \pm 5.8\text{‰}$ ) (**Table 2**).

261 ***Pairing  $\delta D$  and  $\delta^{18}O$  with salinity.*** The linear relationships between  $\delta^{18}O$ ,  $\delta D$  and salinity have  
262 been used to estimate the stable water isotope composition of a freshwater endmember, defined  
263 as the  $\delta^{18}O$  and  $\delta D$  values when salinity equals zero. This extrapolation should be interpreted  
264 with careful consideration of the contributions of regional precipitation, river water and runoff.  
265 However, it has been demonstrated that the extrapolated  $\delta^{18}O$  and  $\delta D$  of freshwater endmembers  
266 in the Great Barrier Reef (NE Australia) reflected the isotope composition of local river water  
267 with relatively insignificant contributions of regional precipitation and runoff (Munksgaard et al.,  
268 2012).

269 Accordingly,  $\delta^{18}O$  and  $\delta D$  values in the samples collected in the mangroves of Coco and Temala  
270 varied linearly with salinity (**Figure 3** and **Table 2**). In addition, all linear relationships  
271 converged to a common signature of the marine endmember (blue diamond in **Figure 3**). We  
272 extrapolated these linear relationships toward salinity of zero to determine the isotope  
273 composition of each river water endmember (**Table 2**). It is important to note that the  
274 interpretation of such relationships often requires a spatial and temporal assessment of the two  
275 systems (Conroy et al., 2017). As the samples were collected simultaneously in the dry season,  
276 the difference in water isotope composition between the freshwater endmembers at Coco and  
277 Temala can thus be only attributed to distinct water sources in each river system.

278 In the mangrove stations, the two linear regression lines are significantly distinct between Coco  
279 and Temala, except for a few stations at Temala that fall on the regression line of Coco (encircled

280 data, **Figure 3B**). These data represent the last samples collected during the high tide over the 24-  
281 hour series (3<sup>rd</sup> discharge event of the Coco River, **Figure 2A**). All physical-chemical properties  
282 and stable water isotopes of the two rivers overlap during this period (grey zone in **Figure 2 A,**  
283 **D, G**). This probably reflects a common blackish water mass formed during the high tide.  
284 Therefore, we excluded these data from Temala's  $\delta D$ -salinity regression because of the lack of  
285 more robust proxies to confirm this phenomenon and assuming that it may be minor. The  
286 exclusion of these three data did not affect the fact that the water isotope composition is  
287 significantly more depleted in the Coco River than Temala during the dry season. This depletion  
288 is more noticeable for  $\delta D$  ( $-72.9 \pm 8.9\text{‰}$  vs.  $-36.0 \pm 2.8\text{‰}$ , respectively) than  $\delta^{18}O$  ( $-9.9 \pm 1.7\text{‰}$  vs.  $-$   
289  $8.4 \pm 1.2\text{‰}$ , respectively) (**Table 2**).

290 However, across the estuaries and during the rain season, the  $\delta D$ -S and  $\delta^{18}O$ -S relationships for  
291 both river systems are significantly similar ( $p < 0.05$ ) and align along with consistent equations  
292 ( $\delta D = 1.0 \times S - 33.7$  and  $\delta^{18}O = 0.2 \times S - 5.2$ , **Table 2** and **Figure 3A**). Both the slopes and intercepts  
293 are close to the Temala mangrove during the dry season ( $\delta D = 1.0 \times S - 36.0$  and  $\delta^{18}O = 0.2 \times S - 8.4$ ,  
294 **Table 2**). This observation suggests that the hydrologic regime in the Temala River differs only  
295 slightly within seasons with relatively constant water isotope compositions of the river  
296 endmember ( $\delta D_{River}^{Temala} \sim -34$  to  $-36\text{‰}$  and  $\delta^{18}O_{River}^{Temala} \sim -5.2$  to  $-8.4\text{‰}$ ). These values are close  
297 to the four southeastern rivers over an annual cycle (**Figure 3A**) ( $\delta D_{River}^{SE} = -31 \pm 6\text{‰}$  and  
298  $\delta^{18}O_{River}^{SE} = -5.8 \pm 1.0\text{‰}$ , **Table 2**), confirming reasonably consistent  $\delta D$ -S and  $\delta^{18}O$ -S  
299 relationships and hydrologic regimes of major river systems along the western coast of New  
300 Caledonia.

301 It is important to note that the Coco River is a small tributary with a relatively dry riverbed with  
302 significantly decreased flow during the dry season. Consequently, the Coco River's isotopic  
303 compositions differ substantially during the dry and rain seasons (**Table 2**) due to less  
304 precipitation and enhanced evapotranspiration during the dry season.

305 In summary, the difference in stable water isotope composition between the Coco and Temala  
306 rivers is related to the natural effects of a depleted hydrologic reservoir with enhanced  
307 evaporation. This effect is naturally more noticeable in small reservoirs during the dry season,  
308 such as the Coco River than the major streams (Temala and the four southeastern rivers). Overall,

309 we observed a relatively conservative hydrologic system with the mixing of only two water  
310 masses: the river freshwater and the marine endmembers. Water isotopic data allow excluding the  
311 contribution of a third water mass (e.g., groundwater discharge) in these mangrove-dominated  
312 estuarine systems.

### 313 3.3. Rare earth element cycling in the mangrove system.

314 The PAAS-normalized REE patterns are typical of coastal seawater with a gradual enrichment of  
315 heavy REEs relative to light REEs (Hoyle et al., 1983; Nozaki et al., 2000; Piper and Bau, 2013)  
316 (**Figure 4**). Moreover, we observed a depletion of Ce but an enrichment of Eu and Gd relative to  
317 their neighbouring REEs that are commonly referred to as anomalies. The anomalies of Ce and  
318 Eu were already extensively discussed in the literature. The negative Ce anomaly was shown to  
319 develop progressively with increasing salinity as dissolved Ce(III) undergoes continued oxidation  
320 to insoluble Ce(IV) across the estuarine zone (Nozaki et al., 2000). The positive Eu anomaly was  
321 also reported in the dissolved fractions of various major rivers (Amazon, St Lawrence, Piper and  
322 Bau, (2013)) and the clay fractions of river sediments worldwide (Bayon et al., 2015). Several  
323 previous studies have recorded positive Eu anomaly in continental materials (e.g., suspended  
324 load, atmospheric aerosol and dust, Censi et al., 2004; Goldstein and Jacobsen, 1988). Therefore,  
325 the positive Eu anomaly observed in the dissolved loads was interpreted as the result of  
326 dissolution from suspended particles and formation of stable dissolved complexes during  
327 transport (Nozaki et al., 2000).

328 On the other hand, the Gd anomaly is commonly associated with anthropogenic emissions, such  
329 as medical sources (medical resonance imagery) or wastewater (Hatje et al., 2016; Tepe et al.,  
330 2014). We observed Gd anomaly ( $Gd/Gd^*$  up to 3.5) only during the dry season in the Coco  
331 river, in the first and second freshwater discharge events (**Figure S3** and **Figure 2A**). We have  
332 previously suggested that the 3<sup>rd</sup> event may be associated with a common brackish water at both  
333 Coco and Temala rivers formed during the high tide from 4h to 9h AM (**Figure 2A**), which is  
334 Gd-anomaly-free (**Figure S3D**). No Gd anomaly ( $Gd/Gd^* = 1$ ) was indeed observed in the  
335 marine endmember (blue diamonds, **Figure 4 C,D**). Given the absence of major medical facilities  
336 and considering the low population along the Coco river, a possible medical or wastewater origin  
337 for this Gd anomaly can be ruled out. However, the Coco River is associated with the nickel  
338 mined lateritic Koniambo regolith where a 13km long ore conveyor was built parallel to the river

339 and the Koniambo Nickel SAS smelting plant is adjacent to the Coco mangrove (**Figure 1C**).  
340 While there is no precedent study reporting Gd anomaly associated with lateritic ores extraction  
341 and processing, the Gd anomaly observed in the Coco river might be associated with those  
342 activities.

343 ***Estuarine mixing behaviors of REEs and Y.*** The REE concentrations in the marine endmembers  
344 are typically low; the sum of all REE concentrations ( $\Sigma$ REEs) approximates 6 ng/L. However,  
345 there was a significant difference in REE total concentrations between the two river endmembers,  
346 with Temala containing more REEs than Coco ( $\Sigma$ REEs of 24 and 2.6 ng/L, respectively). This  
347 trend was also observed at the mangrove stations (**Figure S3A**). The higher REE concentrations  
348 measured in the Temala River waters compared to the Coco River are directly associated with the  
349 geology of their watersheds. The Temala watershed is indeed made of soils developed on  
350 volcano-sedimentary rocks, whereas the Coco river meanders on lateritic soils developed on  
351 ultramafic rocks (**Figure 1C**) (Merrot et al., 2019). As volcanoclastic bedrock tend to contain  
352 higher REE and Y concentrations than the granitic regolith (Chapela Lara et al., 2018), the  
353 difference in the watershed's geology could be directly associated with higher REE  
354 concentrations in Temala river waters than Coco.

355 Moreover, we did not observe any REEs and Y removal during estuarine mixing between the  
356 rivers and the marine endmember, as commonly assumed for REE estuarine geochemistry (see  
357 section 1). In fact, we measured very high REE concentrations in the mangrove forest (salinity  
358 range of 25-33, see La concentrations in **Figure 5A**). The high REE (La) concentrations in the  
359 mangrove area seem to be conservatively mixed with the freshwater mass ( $y=0.6x+3.5$ ,  $r^2 = 0.97$ )  
360 and the marine endmember ( $y=-5.2x+183$ ,  $r^2 = 0.84$ ). This situation was not reported previously.  
361 It is commonly assumed that approximately 60-90% of REEs are removed from the low salinity  
362 region of an estuary by flocculation/coagulation of dissolved organic-bound Fe and colloidal  
363 materials depleting REEs from the dissolved pool (Lawrence and Kamber, 2006; Pourret and  
364 Tuduri, 2017; Sholkovitz and Szymczak, 2000; Sholkovitz, 1995). Minor releases of REEs  
365 during an estuary mixing were only reported in the turbid-clear water transition zone ( $S=12-15$ )  
366 in the Chao Phraya estuary (Thailand) (Nozaki et al., 2000) and the mid-salinity zone of the  
367 Elimbah Creek (Australia) (Lawrence and Kamber, 2006). Such REE release was attributed to  
368 several mechanisms, including desorption from suspended particles, coastal erosion, and

369 mineralization during early diagenesis. In addition, the reductive dissolution of ferromanganese  
370 oxides has been shown to significantly release REEs into the porewater, although LREEs tend to  
371 sorb back onto the newly formed ferromanganese oxides at the sediment-water interface (Och et  
372 al., 2014).

373 Although the La-salinity biplots (**Figure 5A**) could be interpreted as mixing of three water  
374 masses (river, mangrove forest, and marine), stable water isotopes (**Figure 3**) allow to rule out  
375 the possibility of a third water mass in the estuaries of Coco and Temala. Thus, the high La  
376 concentrations in the mangrove are instead explained by specific biogeochemical processes  
377 leading to the substantial release of dissolved REEs. Given the subtropical weather condition and  
378 the high availability of fresh organic matter in the mangrove forest (Noël et al., 2014), it is highly  
379 probable that bacterial activity contributes to this REEs solubilization in the sediments porewater  
380 (Och et al., 2014). In the mangrove system, the tidal conditions with water pushing up through  
381 the porous sediment (seawater circulation cell, **Figure 6A**) would then favour REE  
382 remobilization to the water column. A previous study has demonstrated significant fluxes of  
383 REEs from such a seawater circulation through diagenesis-active sediments (i.e., organic matter  
384 degradation and reductive dissolution of ferromanganese oxides (Paffrath et al., 2020), **Figure 6**).  
385 Other processes such as passive diffusion fluxes or sediment resuspension events induced by  
386 waves and tides (Dang et al., 2020) or bioturbation could also contribute to the REE release  
387 towards the water column (**Figure 6 C**). At a larger scale of the Northwestern Mediterranean Sea,  
388 upward diffusion of REEs (Nd) from sediment porewater counts for 30% of the Nd marine  
389 budget (Garcia-Solsona and Jeandel, 2020). Moreover, given the organic matter-rich surface  
390 waters in the mangrove system and the high affinity between REEs and dissolved organic carbon  
391 (Davranche et al., 2004; Marsac et al., 2010; Pourret and Davranche, 2013), it is also highly  
392 possible that the formation of stable organic complexes could contribute to maintaining REEs in  
393 solution in this mid-salinity region (25-33).

394 ***Fractionation of HREEs/LREEs and elemental ratios.*** All the water samples collected showed  
395 a progressive enrichment of HREEs relative to the PAAS shale (**Figure 4**). This is consistent  
396 with the conventional REE behaviours in the aquatic environment where the fractionation  
397 between the dissolved and particulate loads of HREEs and LREEs leads to this characteristic  
398 REE curve (Piper and Bau, 2013). Therefore, elemental ratios between representative HREEs and



399 LREEs (e.g., Er/Nd (Nozaki et al., 2000), Nd/Lu (Sholkovitz, 1995), Ho/Er (Lawrence and  
400 Kamber, 2006)) could help determine whether this fractionation occurs in the freshwater  
401 endmember or the estuary. As the interpretations using different ratios are very similar, we  
402 choose to discuss only the Er/Nd (weight ratios).

403 The Er/Nd ratios in both UCC (Rudnick and Gao, 2003) and PAAS (McLennan, 2001)  
404 approximate 0.08, while those in the river endmembers are significantly above this value (0.2 and  
405 0.3 at Temala and Coco, respectively, **Figure 5B**). This indicates that the fractionation between  
406 HREEs and LREEs occurred in the freshwater system. It is important to note that such  
407 fractionation is pH-dependent. At the pH range observed in Temala and Coco rivers (7.7-7.9,  
408 **Table 1**), REE adsorption on particles is enhanced, leading to significant fractionations by  
409 preferential LREE removal (Sholkovitz, 1995). Furthermore, the measured Er/Nd in the estuarine  
410 samples varied with salinity along the conservative mixing line of Temala (**Figure 5B**),  
411 suggesting no further fractionation (Lawrence and Kamber, 2006). This is consistent with the  
412 occurrence of dissolved organic-REE complexes in the mangrove waters, as previously  
413 suggested. Previous studies have demonstrated that the presence of dissolved organic matter  
414 significantly reduced REE sorption on ferromanganese oxides and the subsequent fractionation  
415 between LREEs and HREEs (Davranche et al., 2005, 2004).

416 On the other hand, a negative departure from the conservative mixing line (i.e., Er/Nd ratios  
417 decreased) was noticed at the mangrove stations (black arrow in **Figure 5B**). This indicates a  
418 preferential release of LREEs (Nd) relative to the HREEs (Er). This observation is in agreement  
419 with the hypothesis that LREEs previously bound to the solid fraction are released toward  
420 solution when the oxide phases undergo reductive dissolution (Bau et al., 1997). High REEs  
421 concentrations in porewater promote upward diffusion from the sediments by the seawater  
422 circulation cell or diffusive flux (**Figure 6**).

423 Furthermore, variations in the Y/Ho ratios are also of great interest. Although these two elements  
424 have similar ionic radii, their electronic configurations differ. Yttrium has no f-electron while Ho  
425 has 10 electrons filling up the f orbitals (Lawrence and Kamber, 2006). Therefore, the ability to  
426 form strong surface and solution complexes using the f orbitals (Byrne and Lee, 1993) drives the  
427 fractionation of this pair during weathering, riverine transport or in the marine environment

428 (Lawrence and Kamber, 2006; Nozaki et al., 2000). As a result, Ho tends to form more stable  
429 surface complexes than Y (Bau et al., 1997; Byrne and Lee, 1993; Lawrence and Kamber, 2006).  
430 Therefore, two conditions could lead to Y/Ho fractionation during estuarine mixing. First,  
431 coagulation, flocculation and sedimentation of Ho-bearing colloidal particles preferentially  
432 remove Ho from solution. Second, as Y tends to form weaker surface complexes than Ho, this  
433 fractionation is enhanced by the salt effect (competition for surface sorption sites), which favors  
434 Y release from colloidal particles toward solution. Both processes were well documented in the  
435 literature to support the increase in the Y/Ho ratio during the estuarine mixing (**Figure 6B**)  
436 (Lawrence and Kamber, 2006).

437 The Y/Ho ratio in the Temala river endmember (28.4) approximates UCC and PAAS (25.3  
438 (Rudnick and Gao, 2003) and 27.2 (McLennan, 2001), respectively), indicating that there was no  
439 significant fractionation between Y and the REEs in the Temala river (**Figure 5C**) (Lawrence and  
440 Kamber, 2006). However, in the Coco river endmember, the Y/Ho ratio is significantly lower  
441 (18.6). A situation where Y-Ho fractionation leads to lower Y/Ho ratios relative to the UCC is  
442 scarcely reported in the literature. While considered a minor process in natural water systems, it  
443 was previously reported by Bau et al. in the slightly acidic solutions of low complex-forming  
444 capacity of a stream from an abandoned mine (Bau et al., 1995). Interestingly, the Coco River,  
445 where this phenomenon is suspected to occur, is connected to the Koniambo mine.

446 In the estuary, we also observed the conventional Y/Ho fractionation (**Figure 6B**) as the Y/Ho  
447 ratios were beyond the conservative mixing lines (**Figure 5C**). However, the positive departure is  
448 even more noticeable in the mangrove forest, with Y/Ho reaching up to 80 (black arrow in  
449 **Figure 5C**). This suggests that additional processes took place in the mangrove forest area,  
450 further fractionating this pair. A previous study has suggested that the fractionation between Y  
451 and Ho could be redox driven (Bau et al., 1997). Accordingly, a redox change is expected to  
452 occur at the sediment-water interface (**Figure 6C**) where the upward diffusive flux from  
453 mangrove sediments confronts the freshly formed ferromanganese oxyhydroxides. As discussed  
454 previously, these reactive surfaces tend to further remove Ho relative to Y. Such preferential  
455 removal of Ho increases the Y/Ho ratios as observed in **Figure 5C**.

#### 456 3.4. Calculations of REE flux from the mangrove systems

457 Fluvial fluxes of dissolved constituents in the oceans are essential to balance their marine budget.  
458 The current ocean box models for REEs consider major inputs as river-borne dissolved and  
459 particulate load, atmospheric dust, groundwater discharge, porewater diffusion and dissolution of  
460 reworked sediments (Arsouze et al., 2009; Garcia-Solsona and Jeandel, 2020; Tachikawa et al.,  
461 2003).

462 Goldstein and Jacobsen have suggested a simple empirical approach to calculate the dissolved  
463 REEs flux ( $R_i^{eff.}$ ) from the continent (Goldstein and Jacobsen, 1988) as detailed in the following  
464 equation.

$$465 \quad R_i^{eff.} = C_i^R \times F_R \times \phi_i \times CF \quad (Eq. 6)$$

466 where  $C_i^R$  is the dissolved concentration of an element in the continental endmember (ng/L),  $F_R$  is  
467 the annual river discharge,  $\Phi_i$  is the effective factor, and CF is a correction factor to convert the  
468 final units into kg/year.

469 Here, we applied this calculation to our preliminary dataset to determine whether the fluxes of  
470 REEs and Y from the tropical mangrove system could be of interest in the global oceanic budget.  
471 Therefore, it is important to note a few assumptions in this simple calculation. First, because of  
472 the conservative mixing of REEs and Y between the mangrove system and the seawater (**Figure**  
473 **5A**), we can assume a full effective factor (i.e., absence of estuarine removal or  $\Phi_i = 1$ ). Second,  
474 the local Water Agency (DAVAR, Service de l'eau) monitored the hydrologic regime of the local  
475 river systems. According to the most recent report, the monthly discharges of the rivers in the  
476 leeward side (southwestern, e.g., Boghen, Poya, Pouembout-Boutana Rivers) of Grand Terre in  
477 2019 and 2020 average 18.6 m<sup>3</sup>/s in February and 0.6 m<sup>3</sup>/s in May (the month preceding the two  
478 sampling campaigns) (DAVAR Service de l'eau, 2020). The variability of the river discharge that  
479 could differ Coco and Temala, although not individually determined, could be consisted within  
480 the variability of major river systems of the leeward sides. Third, the concentrations of REEs and  
481 Y of the mangrove endmember ( $C_i^R$ ) are those of the samples with salinity in the range of 25-34  
482 (the mangrove forest, **Figure 5A**). Finally, the calculated fluxes ( $R_i^{eff.}$ ) of dissolved REEs and Y  
483 from the mangrove system are reported with standard deviations reflecting the errors propagating  
484 through the calculations and variability of all variables.

485 Accordingly,  $R_i^{eff.}$  values of Temala and Coco in the dry and rain seasons are reported in **Table**  
486 **S3** while the annual average fluxes are showed in **Table 3**. The fluxes of REEs and Y are  
487 significantly higher in the rain season and dry season (**Table S3**), as reported in other major  
488 estuarine systems (Pourret and Tuduri, 2017). Overall, the annual averages of REE and Y fluxes  
489 from the Coco and Temala range from 0.05 (Lu) to 16.1 (Y) kg per year (**Table 3**).

490 To extrapolate our data toward a general perspective of the global mangrove system, we first  
491 normalized the calculated fluxes to mangrove watershed surface areas ( $S_w$ , km<sup>2</sup>) and the fraction  
492 of vegetation coverage ( $f_v$ ). Equation 7 allows the calculation of area-normalized fluxes of REEs  
493 and Y from the two mangrove forests ( $R_i^{S-MF}$ , kg/yr/km<sup>2</sup>).

$$494 \quad R_i^{S-MF} = \frac{R_i^{eff.}}{S_w \times f_v} \text{ (Eq. 7)}$$

495 The watershed of the Voh region has a vegetation coverage of approximately 43±16% (Taureau  
496 et al., 2019), thus  $f_v = 0.43$ . The surfaces of the Temala and Coco watersheds ( $S_w$ ) approximates  
497 163 km<sup>2</sup> and 42 km<sup>2</sup>, respectively (FalconBridge NC, 2001). The calculated area-normalized  
498 fluxes of REEs and Y range from  $1.6 \times 10^{-3}$  (Lu) to 0.4 (Y) kg/yr/km<sup>2</sup>.

499 From the  $R_i^{S-MF}$  values, we attempted an extrapolation to the global surface of mangroves  
500 (150,000 km<sup>2</sup>) (Spalding, 2010) and thus calculated the global fluxes of dissolved REEs and Y  
501 from this unique ecosystem (**Table 3**). These global fluxes calculated for the mangrove systems  
502 could then be compared to the published global river-borne dissolved Nd loads (Arsouze et al.,  
503 2009; Garcia-Solsona and Jeandel, 2020; Tachikawa et al., 2003). Currently, the Nd oceanic  
504 budget is the most comprehensive as extensive studies reported both Nd concentrations and  
505 isotope composition to calibrate its ocean box models. In these models, the river inputs of  
506 dissolved Nd range from 260 to 500 tons per year (or Mg per year) (Rousseau et al., 2015;  
507 Tachikawa et al., 2003). Relative to these values, we estimate that the mangrove systems supply  
508  $13.3 \pm 5.6$  tons per year of dissolved Nd, representing 2.6-5 % of the total river input of dissolved  
509 Nd. Compared to other sources (e.g., dust dissolution of 400 tons of Nd per year, Nd release from  
510 suspended particles of  $5,700 \pm 2,600$  ton per year) (Arsouze et al., 2009; Rousseau et al., 2015;  
511 Tachikawa et al., 2003), the mangrove systems appear to be a minor source. However, it is  
512 important to note that even though this study documents a significant release of REEs and Y

513 within the mangrove system for the first time, we assess only two small mangrove systems  
514 representing <1% of the global mangrove surface. Further studies are therefore required to better  
515 characterize the contribution of the mangrove system to the global marine budget.

#### 516 **4. Implications for the role of mangrove on REE cycling and oceanic budgets.**

517 The conventional estuarine REE behaviour often implies a sharp removal of REEs when a  
518 riverine water mass enters an estuary. However, our data revealed a significantly release of  
519 dissolved REEs and Y (7.3 times for Y, 6.4 times for La and 3.3 times for Lu) in the mangrove  
520 system. Although other water masses could supply REEs to the water column (e.g., groundwater  
521 discharge (Kim and Kim, 2011)), our stable water isotopes data confirm a sole binary mixing  
522 between the fresh and seawater endmembers in the mangrove estuaries of New Caledonia. This  
523 release of REEs and Y has thus to be associated only with internal recycling or biogeochemical  
524 processes within the mangrove forests. This dataset thus strengthens the hypothesis that tropical  
525 mangroves act as a source of dissolved REEs and Y to the marine system.

526 This finding first redefines the role of tropical mangroves in the cycling of trace elements at the  
527 continent-ocean interface. While mangrove forests are often referred to as a buffer zone to filter  
528 trace metals from reaching the open sea (Marchand et al., 2012), this assumption might be valid  
529 only for the particulate loading. This specific ecosystem produces large amounts of organic  
530 matter that is bioavailable for bacterial degradation (Marchand et al., 2012) and thus boosts early  
531 diagenesis. These biogeochemical processes lead to the complex recycling of REE-bearing  
532 phases. The reductive dissolution of ferromanganese oxides occurs within the subsurface layers  
533 of the sediments and is thus responsible for releasing trace elements (Dang et al., 2015, 2014).  
534 However, the redox boundary at the seawater-sediment interface leads to forming a thin layer of  
535 newly formed Fe- and Mn-oxyhydroxides with large reactive surface areas that efficiently sorb  
536 trace elements and thus minimize their upward diffusive flux (Dang et al., 2015; Rigaud et al.,  
537 2013). Although we could not evaluate the relative amounts of REEs being diffused upward from  
538 the sediment porewaters relative to REEs retained at the interface, the diel variation in oxygen  
539 concentrations associated with hypoxia events in the mangrove (Dubuc et al., 2019) strongly  
540 suggests that the fraction of REEs being retained would be minor regarding the low stability of  
541 Fe- and Mn-oxyhydroxides in such redox-dynamic conditions (Bau et al., 1995).

542 Over the past 30 years, several works aimed to understand and revisit REE behaviour during  
543 estuarine mixing and accumulation in sediments (Bayon et al., 2015; Lawrence and Kamber,  
544 2006; Sholkovitz and Szymczak, 2000; Sholkovitz, 1995). This first dataset reporting REEs  
545 release in a tropical mangrove may provide an important insight into the contribution of  
546 mangrove forests to the oceanic budgets and mass balance of REEs and Y. However, these box  
547 models remain unbalanced with a significant missing flux (e.g., 800 Mg per year) (Tachikawa et  
548 al., 2003). Pourret and Tuduri (2017) recently suggested the continental shelves as a potential  
549 resource of REEs to be included in the oceanic mass balance of REEs. Moreover, mangrove is  
550 growing in 123 tropical and subtropical countries and covers a total surface of 150,000 km<sup>2</sup>  
551 (Spalding, 2010). Our simple flux calculation suggests that this atypical system supplies a  
552 significant proportion of REEs toward the oceans (2.6-5% of the global dissolved loading).  
553 However, it remains uncertain about the representativity of the Coco and Temala systems of the  
554 global mangroves. Therefore, further research on the REE cycling within mangrove systems is  
555 needed to determine whether the mangrove estuaries should be considered a significant input in  
556 ocean mass budget to balance the global REE distribution.

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565

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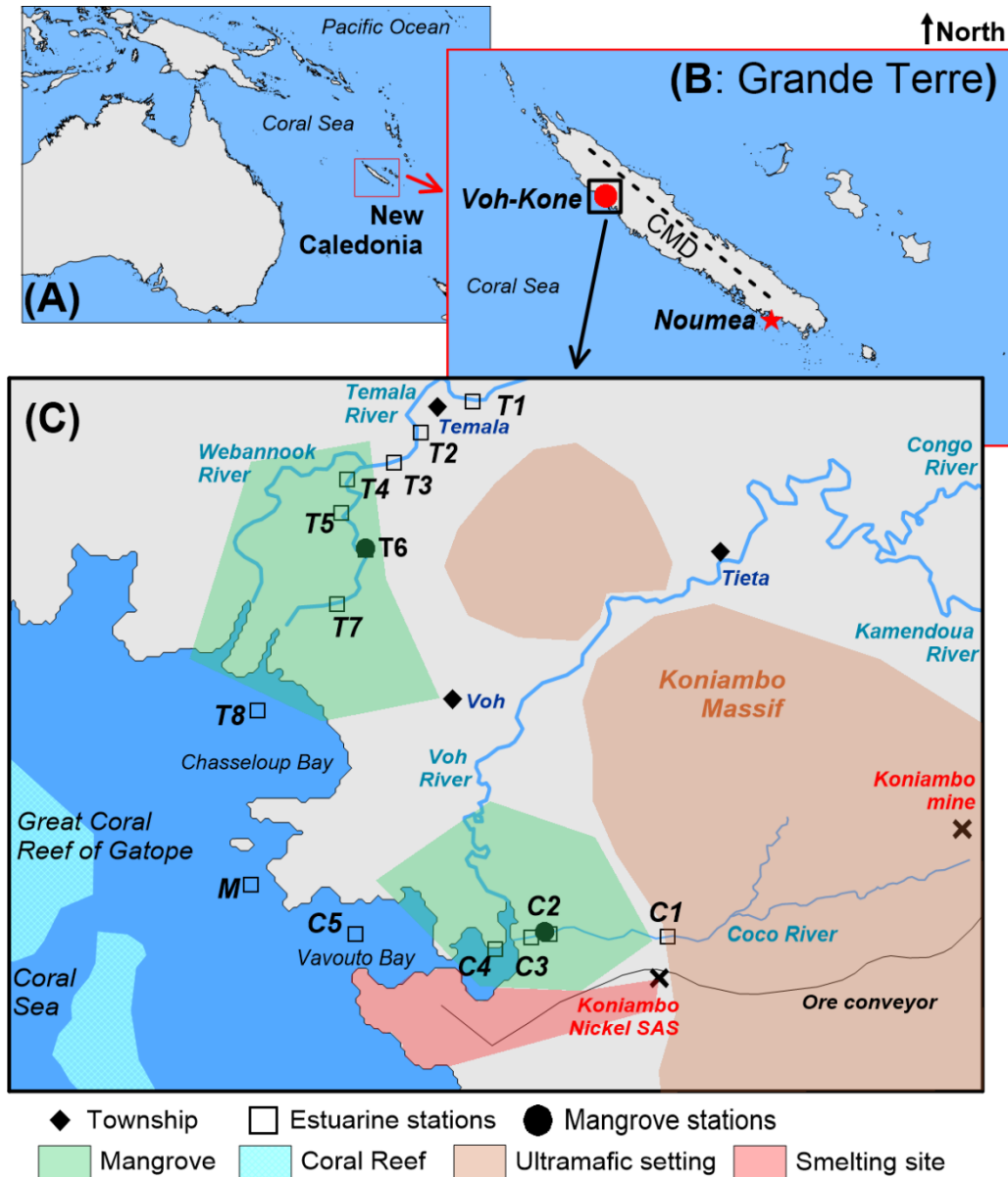
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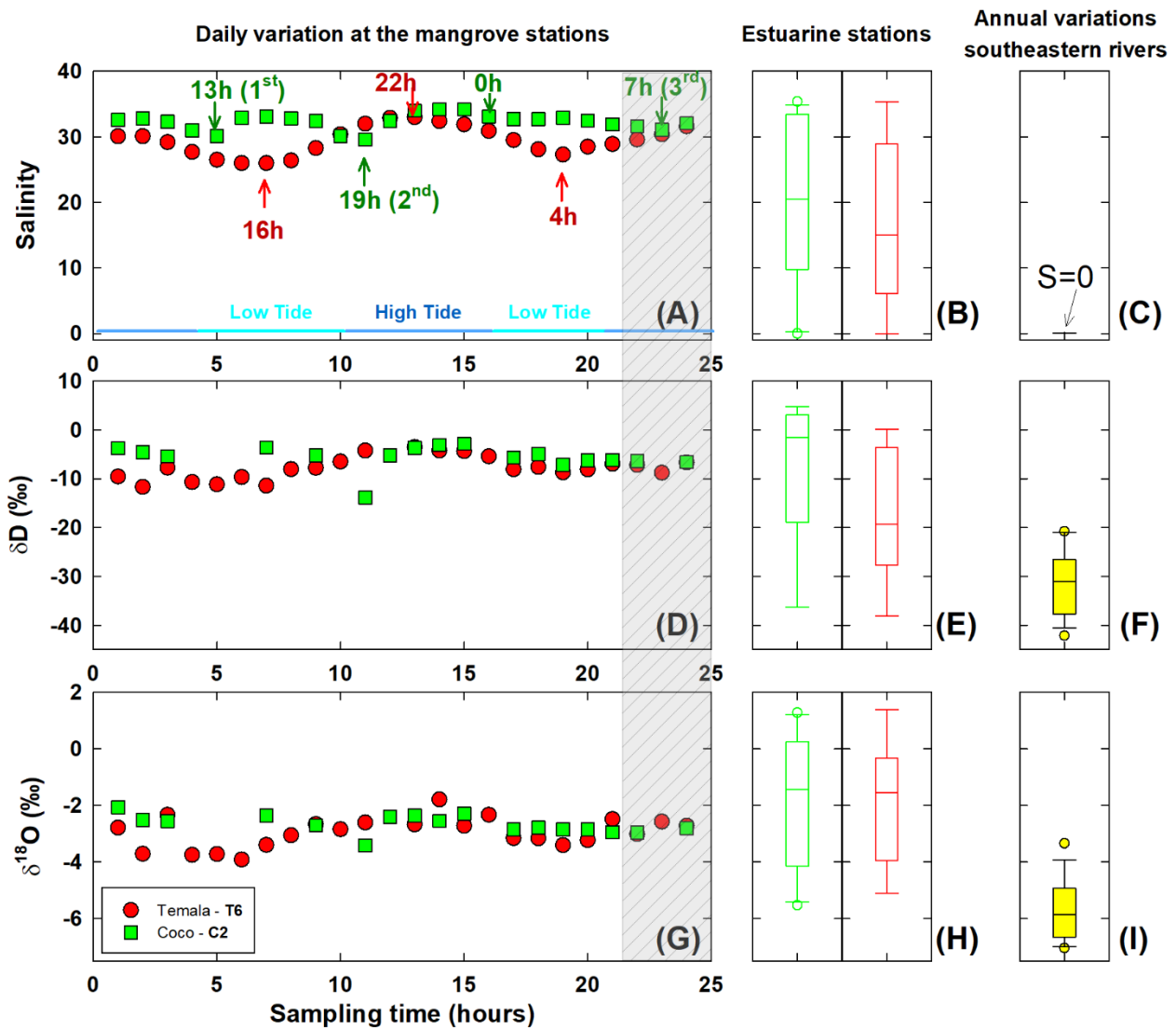
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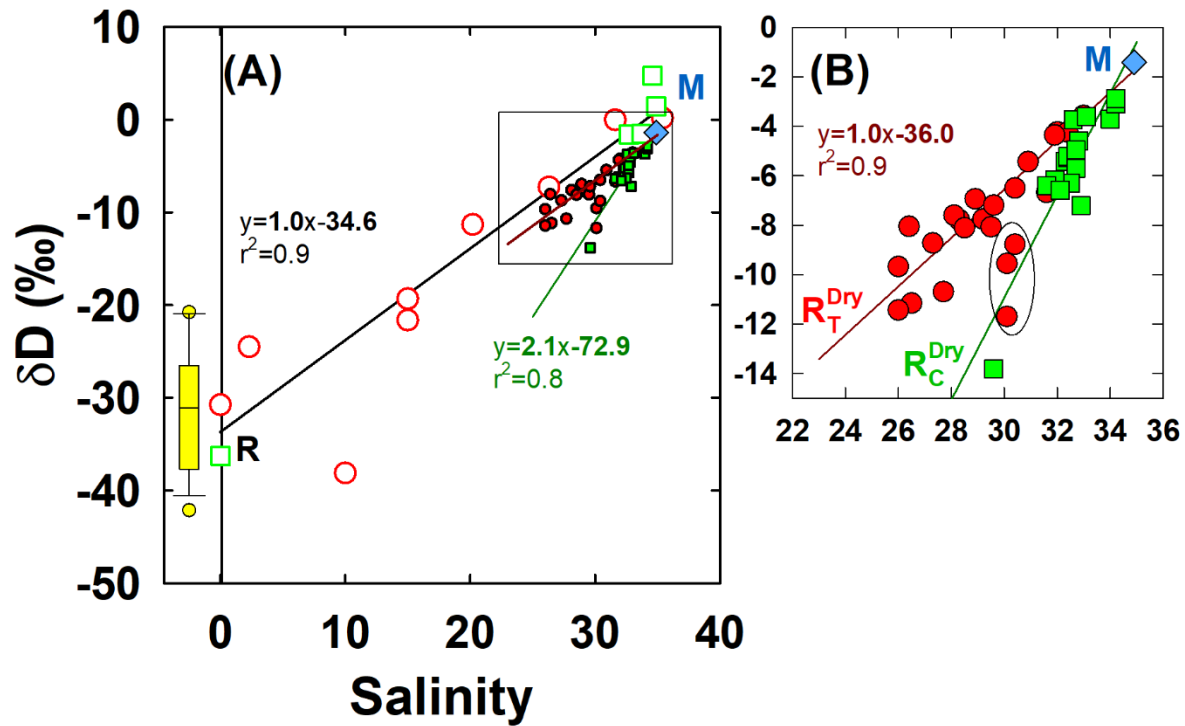
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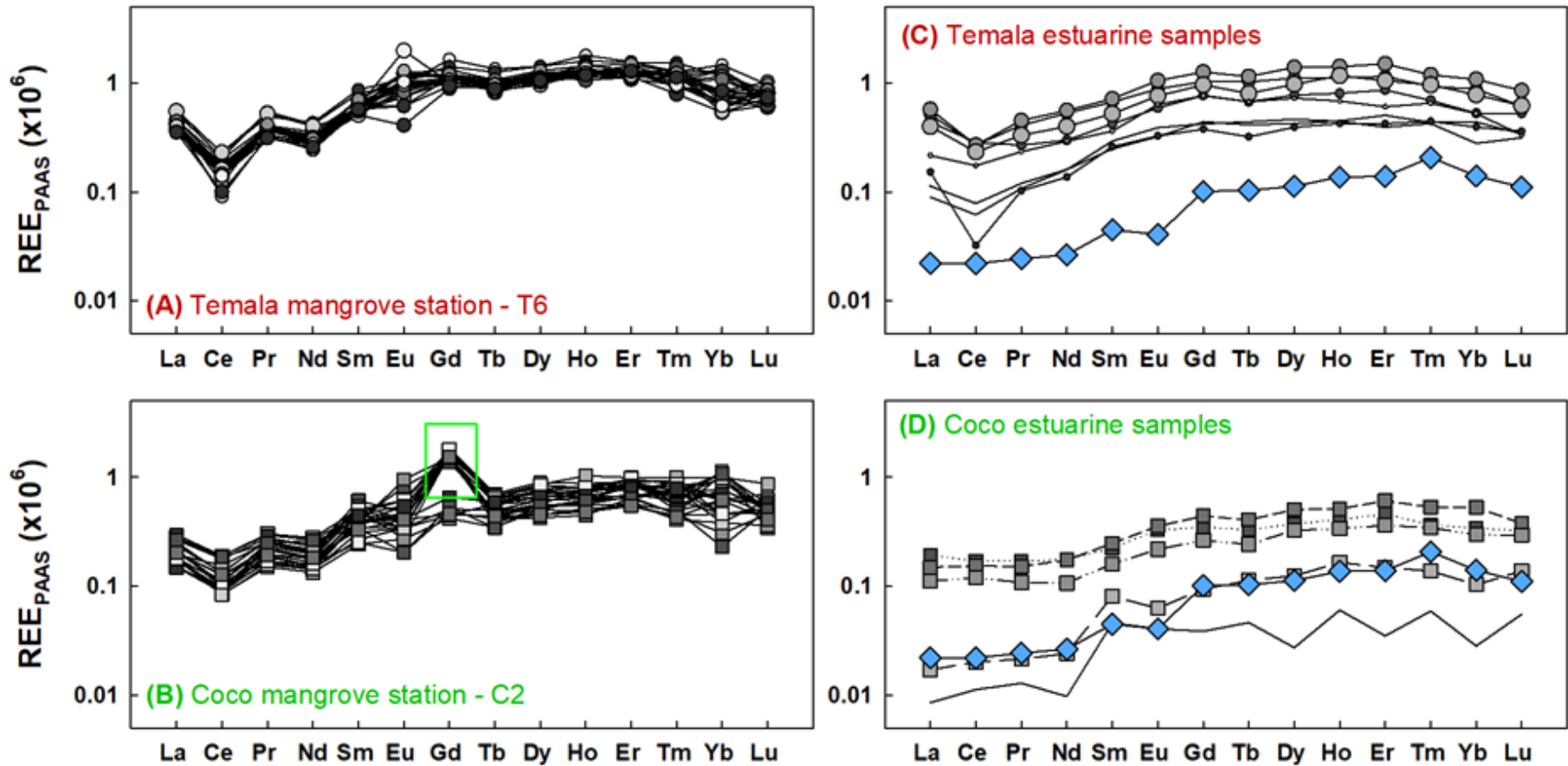
**Figure 1:** Map of New Caledonia (A), the two regions under investigation: Voh-Kone region (red circle) and four rivers in the Southeast of Grande Terre (red star), around Noumea (B), and a zoom into the Voh-Kone region with sampling locations (C). The position of the CMD (Central Massive Divide) in B is approximative. The southwestern basins of the CMD are considered leeward while the northeastern are windward. See text for more details on the study sites.



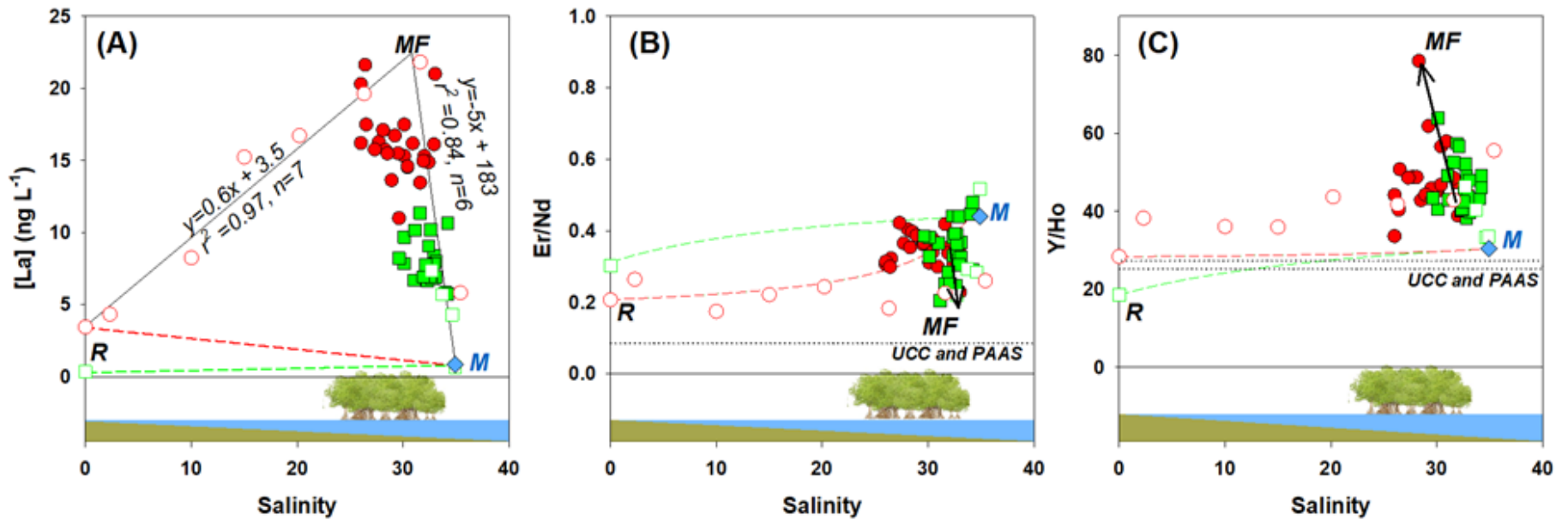
**Figure 2:** Variations in salinity,  $\delta D$  and  $\delta^{18}O$  in waters collected from the Temala (red symbols) and Coco (green symbols) Rivers of the Voh-Kone regions and four rivers of the Southeast (yellow boxes). Left panels (A, D, G) show the daily variations recorded within 24 hours in the mangrove forest (stations T6 and C2). The arabic numbers (1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup>) indicates the three events where freshwaters were discharged from the Coco river toward the lagoon. The greyed zone shows the last samples collected of the 24-hour series during high tide where all physical-chemical properties and stable water isotopes of the two rivers overlaps. Those data are excluded from the  $\delta D$ -salinity regression of Temala River as justified in text. Middle box plots (B, E, H) summarize the spatial variations of Temala and Coco estuaries. The right box plots (C, F, I) show the annual variations of the four rivers in the Southeast of New Caledonia. For all box plots, the horizontal lines in boxes show median values while box boundaries indicate the 25<sup>th</sup> and 75<sup>th</sup> percentiles. The whiskers demark the 10<sup>th</sup> and 90<sup>th</sup> percentiles and scatters are values of the 5<sup>th</sup> and 95<sup>th</sup> percentile range.



**Figure 3:** (A)  $\delta D$ -Salinity biplots of all waters collected from the Coco (green symbols), Temala (red symbols) and the box plot of four rivers in the Southeast (yellow, salinity = 0, see legend of Figure 2 for more details). Samples collected in the mangrove forests (full red and green symbols), across the estuaries (open red and green symbols) and the marine endmember (blue diamond) are also shown. A zoom in the Coco and Temala system during dry season is provided in panel (B). Their respective regression lines are shown in red (Temala) and green (green) while the black regression line represents all samples from Temala and Coco estuaries. The regression for Temala River excludes the data (encircled in B) that are observed on the Coco River regression lines. See text for justification.

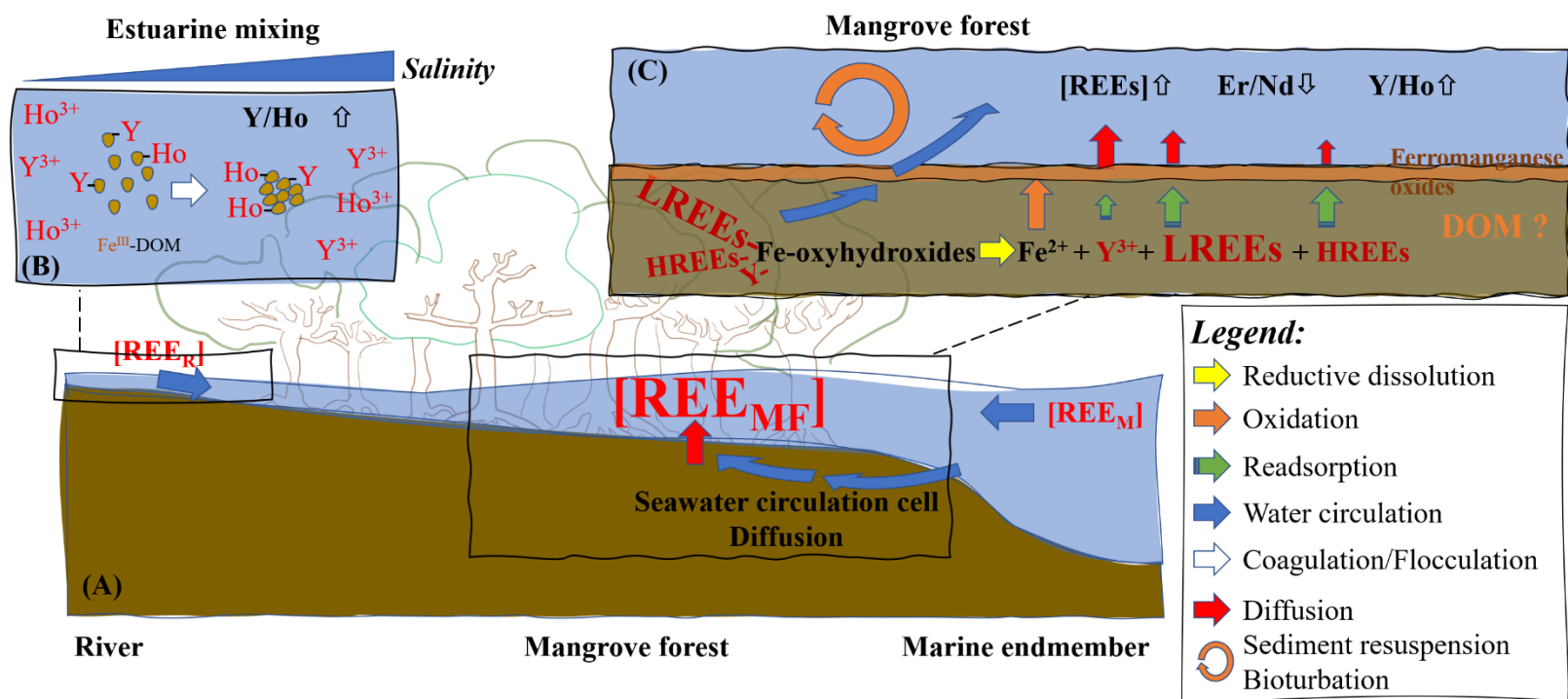


**Figure 4:** Rare earth element patterns in the waters of the mangrove stations (T6 and C2) at Temala (A) and Coco (B), and across the estuarine mixing of Temala (C) and Coco (D). The blue diamonds show the REE patterns in the marine endmember. The gray intensity of the symbols in panels A and B is associated with the 24-h time-series (black symbols corresponding to the first sampling). The symbol size in panels C and D reflect the salinity (small symbols reflecting freshwater). The green rectangle in B demarks Gd anomalies observed in Coco River water.



**Figure 5:** Variations of La concentrations (A), Er/Nd (B) and Y/Ho (C) ratios as the function of salinity at Temala (red symbols) and Coco (green symbols). Samples in the mangrove forests are shown by full symbols while estuarine samples are presented as open symbols. The blue diamond symbols represent the marine endmember. The horizontal dotted lines show the values in the Upper Continental Crust (UCC) and PAAS shale. The dotted green and red lines are conservative mixing line for Coco and Temala estuaries, respectively.





**Figure 6:** Schematic representation of the REE cycle in tropical mangrove-dominated estuaries (A). Panels (B) and (C) provide a zoom into the mechanisms occurring across the estuarine mixing and within the mangrove forest, respectively. In (B), the flocculation of either dissolved organic  $\text{Fe}^{\text{III}}$  complexes ( $\text{Fe}^{\text{III}}\text{-DOM}$ ) or colloidal particles is presented.

**Table 1:** Variations in the physical-chemical properties of water collected over a 24-hour cycle in the dry season in the Temala (T6) and Coco (C2) mangrove forest.

Parameters	Temala (n=24)			Coco (n=24)		
	Range	Average	SD	Range	Average	SD
Temperature	16.8-17.7	17.3	0.2	15.5-16.6	16.1	0.3
pH	7.7-7.9	7.8	0.1	7.6-8.0	7.7	0.1
Salinity	26.0-33.0	29.5	2.1	29.6-34.2	32.3	1.2

**Table 2:** Summary of the  $\delta D$ -S and  $\delta^{18}O$ -S relationships in the Coco and Temala rivers during rain and dry seasons. Values in brackets show the  $r^2$  values. The stable water isotope compositions of the Coco and Temala endmembers ( $\delta D_i$  and  $\delta^{18}O_i$ ) were calculated by the extension of the  $\delta D$ -S and  $\delta^{18}O$ -S relationships. For the Southeastern rivers and the marine endmembers, the  $\delta D_i$  and  $\delta^{18}O_i$  values were calculated as the average of all river samples with salinity = 0 and the values recorded at station M, respectively. For the See text for more details.

	Endmembers	$\delta D$ -S relationship	$\delta^{18}O$ -S relationship	$\delta D_i$ (‰)	$\delta^{18}O_i$ (‰)	d-excess (‰)
Mangrove stations – Dry season	Coco (n=17)	$y=2.1x-72.9$ (0.8)	$y=0.2x-9.9$ (0.6)	$-72.9\pm 8.9$	$-9.9\pm 1.7$	$15.8\pm 1.3$
	Temala (n=19)	$y=1.0x-36.0$ (0.9)	$y=0.2x-8.4$ (0.6)	$-36.0\pm 2.8$	$-8.4\pm 1.2$	$15.9\pm 2.9$
Estuarine stations – Rain season	Temala and Coco (n=15)	$y=1.0x-34.6$ (0.9)	$y=0.2x-5.0$ (0.9)	$-34.6\pm 1.9$	$-5.0\pm 0.4$	$0.4\pm 5.8$
	Marine (n=1)			$-1.6\pm 0.2$	$-2.1\pm 0.2$	
Freshwater stations	Southeastern rivers (n=14)			$-31.2\pm 6.2$	$-5.8\pm 1.0$	

**Table 3:** The fluxes ( $R_i^{eff}$ , kg/yr) of REEs and Y from the two mangrove systems in New Caledonia (NC) and the extrapolation toward the global flux (ton, or Mg per year).

	Annual fluxes from mangroves in NC		Global flux
	Temala	Coco	
<b>Y</b>	16.1±4.6	6.1±1.3	42.1±21.2
<b>La</b>	6.2±1.2	2±0.6	14.8±7.6
<b>Ce</b>	6.4±1.7	3.9±1.3	22.8±14
<b>Pr</b>	1.1±0.3	0.4±0.1	3.0±1.5
<b>Nd</b>	5.5±1.1	1.8±0.4	13.3±5.6
<b>Sm</b>	1.2±0.2	0.4±0.1	2.9±1.4
<b>Eu</b>	0.3±0.1	0.1±0	0.8±0.7
<b>Gd</b>	1.6±0.4	0.6±0.3	4.2±3.3
<b>Tb</b>	0.3±0	0.1±0.03	0.6±0.3
<b>Dy</b>	1.8±0.4	0.6±0.2	4.5±2.7
<b>Ho</b>	0.4±0.1	0.1±0	1.0±0.6
<b>Er</b>	1.1±0.3	0.5±0.2	3.1±1.8
<b>Tm</b>	0.1±0.03	0.1±0.02	0.4±0.3
<b>Yb</b>	0.8±0.3	0.4±0.2	2.4±2.5
<b>Lu</b>	0.1±0.03	0.05±0.01	0.3±0.2