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# High rates of rock organic carbon oxidation sustained as Andean sediment transits the Amazon foreland-floodplain

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## Author Contributions:

MD, RGH and AJW designed the research and obtained funding. All authors contributed to fieldwork and sample collection. MD undertook the geochemical analysis of materials for this work. MD analyzed and interpreted the data with RGH. MD and RGH wrote the manuscript with input from all authors.

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The authors declare no competing interests.

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Carbon cycle; weathering; rivers; Amazon; Andes; Organic carbon

## 41 **Abstract**

42 The oxidation of organic carbon contained within sedimentary rocks (“petrogenic” carbon, or  
43 hereafter  $OC_{\text{petro}}$ ) emits nearly as much  $CO_2$  as is released by volcanism, thereby playing a key  
44 role in the long-term global C budget. High erosion rates in mountains have been shown to  
45 increase  $OC_{\text{petro}}$  oxidation. However, these settings also export un-weathered material that may  
46 continue to react in downstream floodplains. The relative importance of  $OC_{\text{petro}}$  oxidation in  
47 mountains versus floodplains remains difficult to assess as disparate methods have been used  
48 in the different environments. Here, we investigate the sources and fluxes of rhenium (Re) in  
49 the Rio Madre de Dios to quantify  $OC_{\text{petro}}$  oxidation from the Andes to the Amazon floodplains  
50 using a common approach. Dissolved rhenium concentrations ( $n=131$ ) range from 0.01 to 63  
51  $\text{pmol.L}^{-1}$  and vary depending on lithology and geomorphic setting. We find that  $>75\%$  of the  
52 dissolved Re derives from  $OC_{\text{petro}}$  oxidation and that this proportion increases downstream. We  
53 estimate that in the Andes,  $OC_{\text{petro}}$  oxidation releases  $11.2^{+4.5}/_{-2.8} \text{ tC km}^{-2} \text{ yr}^{-1}$  of  $CO_2$ , which  
54 corresponds to  $\sim 41\%$  of the total  $OC_{\text{petro}}$  denudation (sum of oxidized and solid  $OC_{\text{petro}}$ ). A Re  
55 mass balance across the Rio Madre de Dios shows that 46% of  $OC_{\text{petro}}$  oxidation takes place in  
56 the Andes, 14% in the foreland-lowlands, and 40% in the Andean-fed floodplains. This  
57 doubling of  $OC_{\text{petro}}$  oxidation flux downstream of the Andes demonstrates that, when present,  
58 floodplains can greatly increase  $OC_{\text{petro}}$  oxidation and  $CO_2$  release.  
59

## 60 **Significance Statement:**

61 Erosion and weathering play key roles in Earth’s carbon cycle, controlling climate over millions  
62 of years by transferring  $CO_2$  to and from the atmosphere. Weathering of sedimentary rocks in  
63 mountains can release  $CO_2$  when ancient organic carbon in rocks is chemically broken down.  
64 However, mountain erosion also moves rock organic carbon that has not been broken down and  
65 is transported by rivers to lowland floodplains to an unknown fate. Here we use rhenium in  
66 rivers to quantify rock organic carbon weathering in the Andes and adjacent floodplain. Erosion  
67 in the Andes leads to high rates of  $CO_2$  release. However,  $CO_2$  release doubles when including  
68 the floodplains. The presence or absence of floodplains next to mountains governs  $CO_2$  release  
69 by weathering.  
70

## 71 **Main text:**

## 73 **Introduction**

74 Substantial climatic changes have occurred throughout geologic time, with the evolution of the  
75 carbon cycle and the planet’s habitability modulated by the interplay between tectonic, climatic,  
76 erosional and biological processes. Over long timescales ( $>10^5$  years), the abundance of  $CO_2$  in  
77 the atmosphere is determined by the balance of the major carbon sources and sinks (1). It has  
78 been widely debated how the Earth system responds to transient imbalances in the long-term  
79 carbon (C) cycle, with much focus of prior research on the  $CO_2$  sink associated with the  
80 chemical weathering of silicate minerals (1, 2). However, recent studies have highlighted the  
81 potential importance of changes in  $CO_2$  fluxes linked to oxidative weathering (OW) reactions  
82 of sedimentary rocks on the continents (3–5). Although receiving less attention to date, OW of  
83 reduced phases in sedimentary rocks is central to both the C and O cycles (6, 7). Carbon dioxide  
84 release and  $O_2$  consumption can result from both (i) oxidation of fossil (i.e. “rock-derived” or  
85 “petrogenic”) organic matter ( $OC_{\text{petro}}$ ) and (ii) the OW of sulfides that produces sulfuric acid,  
86 which can be neutralized by carbonate minerals, or by the carbonate buffer of continental waters  
87 leading to net  $CO_2$  release to the atmosphere (8, 9).

88 The export of particulate  $OC_{\text{petro}}$  by rivers in their sediment load has been documented  
89 in many places (10–16), but only a few field-based studies have estimated the rate of OW of  
90  $OC_{\text{petro}}$  (3). The highest fluxes of OW of  $OC_{\text{petro}}$  (reported as a yield per catchment area, of 5 to

91 30 tC.km<sup>-2</sup>.yr<sup>-1</sup>) have been measured in small high standing islands composed of sedimentary  
92 rocks such as in Taiwan (17) and New Zealand (4), as well as in catchments from major  
93 mountain ranges (0.5 to 5 tC.km<sup>-2</sup>.yr<sup>-1</sup>) like the Yamuna (18), Swiss Alps (19) and in the  
94 Mackenzie River basin (20). This reflects the role of physical erosion rate in mountains that can  
95 continuously supply OC<sub>petro</sub> to oxygenated surface waters and the atmosphere (17, 21). A  
96 consequence is that, in combination with carbonate weathering by sulfuric acid, CO<sub>2</sub> release by  
97 OC<sub>petro</sub> oxidation can be larger than CO<sub>2</sub> consumption by silicate weathering in many erosive  
98 settings (3), challenging the idea that chemical weathering in mountain belts is a long-term  
99 carbon sink (22–24).

100 While physical erosion can enhance the supply of reduced phases to OW reactions and  
101 increase the weathering flux (8, 17, 25), the overall intensity of weathering can also decline  
102 (26), meaning that erosive catchments can also export very large amounts of ‘unweathered’  
103 particulate OC<sub>petro</sub> (7). These particulate fluxes can be very high, for instance reaching 250  
104 tC.km<sup>-2</sup>.yr<sup>-1</sup> (13, 26). The subsequent fate of this material is critical to governing how physical  
105 erosion and weathering impact the carbon cycle. It has been proposed (10, 14) that this OC<sub>petro</sub>  
106 can be largely oxidized in floodplains when present (e.g. in the Amazon and Ganges  
107 floodplain), because of the long residence time of sediments and the warm and oxidative  
108 conditions that prevail in the floodplains relative to upstream mountainous area. Hence, the  
109 mountain catchments underlain by sedimentary rocks with river floodplains could have greater  
110 net CO<sub>2</sub> release from OW than mountain catchments without floodplains. Over 10<sup>5</sup>-10<sup>6</sup> year  
111 timescales, the configuration of continental drainages can shift dramatically (27) and young,  
112 high standing mountain ranges potentially operate differently in terms of OW and CO<sub>2</sub> release  
113 relative to mountain ranges with floodplain drapes.

114 Despite the recognition of these geomorphological controls on OW (3), the relative  
115 contributions of mountain versus floodplain weathering to OC<sub>petro</sub> oxidation and CO<sub>2</sub> release  
116 remains unknown. This knowledge gap arises in part because different methods have been used  
117 to assess OW of OC<sub>petro</sub> in mountain catchments (4, 17) versus floodplains (10, 14). In mountain  
118 catchments, dissolved rhenium (Re) fluxes have been used for quantifying OC<sub>petro</sub> oxidation  
119 fluxes (17), whereas studies on floodplains have used sediment fluxes and radiocarbon content  
120 of river sediments (Bouchez et al., 2010). Both methods have benefits and drawbacks.  
121 Dissolved Re fluxes are easier to measure because water discharge is usually known with more  
122 precision than sediment flux. On the other hand, there are large uncertainties on the source of  
123 dissolved Re and on the estimation of the Re/OC<sub>petro</sub> ratio of the bedrock (20). Because water  
124 and sediments integrate over different spatial and temporal scales, their direct comparison can  
125 also be problematic. Overall, the influence of floodplains on the global OC<sub>petro</sub> budget remains  
126 an open question (3, 28).

127 To resolve these issues, here we investigate the source and fluxes of dissolved and  
128 particulate rhenium (Re) in the Madre de Dios watershed, part of the larger Amazon Basin. We  
129 focus on an elevation transect ranging from the high Andes to the low-elevation floodplains  
130 and use Re to quantify the flux of CO<sub>2</sub> released by OC<sub>petro</sub> oxidation. These catchments have  
131 been well-characterized by previous studies in terms of erosion rates and their major dissolved  
132 load (11, 23, 29), and benefit from time-series samples over a range of river discharges. Most  
133 importantly, this setting provides an opportunity to determine the rate of OC<sub>petro</sub> oxidation in  
134 each of the different geomorphological settings (mountain, foreland, floodplain) within a single  
135 river basin.

136

## 137 **Study site**

138 The Madre de Dios watershed (124,231 km<sup>2</sup> at the confluence with the Rio Beni in Bolivia) is  
139 one of the main headwaters of the Amazon basin (30), the largest river basin in the world. The  
140 precipitation in the Madre de Dios region is between <1000 and >6000 mm.yr<sup>-1</sup> and the mean

141 annual temperature varies with elevation from 4 to 25°C (30–32). The Rio Madre de Dios  
142 drains: i) the eastern flank of the Andes in Peru with elevations from 1300 m to 6300 m, ii) the  
143 mountain front with elevations from 500 m to 1300 m, iii) the foreland corresponding to  
144 elevations of less than 500 m, in which river basins are not Andean-fed but had undergone some  
145 recent uplift associated with the Fitzcarrald Arch, and iv) the Andean-fed floodplains, which  
146 are the low-relief environments adjacent to active river channels from rivers originating from  
147 the Andes and where sediments are deposited and exchanged with the main channel. The  
148 bedrock in the headwaters is primarily composed of Paleozoic and Mesozoic sedimentary and  
149 metasedimentary rocks (with  $[OC_{\text{petro}}] \sim 0.4$  to  $0.6\%$ ) and some minor granitic intrusions in the  
150 Andes (23). Observations from the neighboring Beni catchment with similar lithologies to the  
151 Madre de Dios show that this  $OC_{\text{petro}}$  is a mixture of disordered and graphitic carbon (10).

152 To characterize the spatial variability of dissolved Re concentrations ( $[Re]_{\text{diss}}$ ) across  
153 the Madre de Dios River basin (Fig. 1A), we studied a large number of small tributaries draining  
154 each geomorphological setting that have been subject to prior work on water, sediment and  
155 carbonate and silicate weathering fluxes (11, 23, 29, 33–35). To characterize the dissolved Re  
156 sources, we sampled stream, spring and lysimeter waters from small first-order catchments in  
157 each geomorphological setting (referred as Wayqecha Small Catchment “WAY-SC”, Villa  
158 Carmen Small Catchment “VC-SC” and CICRA Small Catchment “CICRA-SC”; Burt et al.,  
159 2022). To examine the downstream evolution of  $OC_{\text{petro}}$  weathering processes across these  
160 geomorphic settings, we studied in detail four main nested sub-catchments that define a  
161 geomorphic gradient from the Andes to the Foreland-floodplain: the Rio Kosñipata at  
162 Wayqecha in the Andes (referred as “WAY”, altitude 2250 m); the Rio Kosñipata at San Pedro  
163 in the Andes (“SP”, altitude 1360 m); the Alto Madre de Dios at Manu Learning Center  
164 (“MLC”, altitude 479 m) at the transition between the Andes and the Foreland; and the Madre  
165 de Dios at CICRA-Los Amigos research station (“CICRA”, altitude 217 m). Time series  $[Re]_{\text{diss}}$   
166 and discharge data from the years 2010-2011 are used to characterize changes in Re  
167 concentration during the hydrological cycle. The measured annual runoff for the year 2010-  
168 2011 was  $3065 \text{ mm}\cdot\text{yr}^{-1}$  at the “WAY” site (Upper Andes) to  $2796 \text{ mm}\cdot\text{yr}^{-1}$  at SP. The  
169 suspended sediment flux (a proxy for erosion rate) at San Pedro (SP) measured during the same  
170 period is  $3500 \text{ t}\cdot\text{km}^{-2}\cdot\text{yr}^{-1}$  (11), similar to the estimated suspended sediment load from the  
171 Andean area of the entire Madre de Dios watershed ( $3208 \text{ t}\cdot\text{km}^{-2}\cdot\text{yr}^{-1}$ ; 35). Finally, to integrate  
172 weathering processes over large areas and establish a Re mass-budget, we studied several large  
173 tributaries with Andean-fed floodplains that drain all geomorphic settings (Rios Manú,  
174 Colorado, Chiribi, Inambari and Tambopata).

## 175 **Results**

176 Rhenium concentrations were measured on water samples collected from several field  
177 campaigns, including (i) from the Madre de Dios mainstem and major tributaries sampled  
178 under different flow conditions in 2012 and 2013 (23, 34, 38), and again at high and low flow  
179 in March and May 2019 (35), (ii) from time-series samples collected at four nested catchment  
180 sites (areas 50 to  $27\,830 \text{ km}^2$ ) in 2010 and 2011 at various hydrological conditions (29, 33), and  
181 (iii) from another time series of samples collected from smaller first-order catchments ( $<1 \text{ km}^2$   
182 area) across the elevation gradient (36). The time-series dataset is used to characterize the  
183 relationship between Re concentration and instantaneous runoff.

### 185 **Spatial variability of dissolved Re concentrations**

186 Rhenium concentrations in dissolved samples ( $n=133$ ) range from  $0.01$  to  $63 \text{ pmol}\cdot\text{L}^{-1}$ , with  
187 spatial variability depending on the sample type, bedrock lithology and geomorphic setting  
188 (Fig. 1B; Dataset S1). Rivers have  $[Re]_{\text{diss}}$  ranging from  $0.1$  to  $9.5 \text{ pmol}\cdot\text{L}^{-1}$ . The rainwater  
189 sample collected in the Andes has  $[Re]_{\text{diss}}$  below detection limit ( $[Re]_{\text{diss}} < 0.05 \text{ pmol}\cdot\text{L}^{-1}$ ) while  
190  $[Re]_{\text{diss}}$  in the throughfall sample from the same location is  $0.36 \text{ pmol}\cdot\text{L}^{-1}$ . Lysimeter samples

191 from first-order small catchments in the Andes and in the Foreland have also very low  $[\text{Re}]_{\text{diss}}$ ,  
192 ranging from 0.09 to 0.12  $\text{pmol.L}^{-1}$  ( $n=4$ ). In contrast, the two hot springs samples from Aguas  
193 Caliente have very high  $[\text{Re}]_{\text{diss}}$  (39  $\text{pmol.L}^{-1}$  and 63  $\text{pmol.L}^{-1}$ ). However, the  $[\text{Re}]_{\text{diss}}$  of the Alto  
194 Madre de Dios downstream of the hot springs is unchanged compared to  $[\text{Re}]_{\text{diss}}$  upstream of  
195 the hot springs, suggesting that their contribution to the Re budget is negligible.

196 In terms of lithology, small rivers draining mostly granitic rocks in the High Andes have  
197 lower Re concentrations ( $0.56\pm 0.44 \text{ pmol.L}^{-1}$ ,  $1\sigma$ ,  $n=6$ ) than rivers draining sedimentary rocks  
198 ( $2.90\pm 2.06 \text{ pmol.L}^{-1}$ ,  $1\sigma$ ,  $n=25$ ). Rivers draining the mountain front composed of mostly  
199 granites also have lower  $[\text{Re}]_{\text{diss}}$  ( $1.32 \text{ pmol.L}^{-1}$ ,  $n=2$ ) than those draining sedimentary rocks  
200 ( $3.88\pm 1.12 \text{ pmol.L}^{-1}$ ,  $1\sigma$ ,  $n=10$ ).

201 We observe a notable geomorphic control on  $[\text{Re}]_{\text{diss}}$  for the tributaries and first-order  
202 catchments draining specific settings, but not for the nested catchments (Fig. 1B). Tributaries  
203 draining sedimentary rocks in the High Andes and Mountain front have significantly higher  
204  $[\text{Re}]_{\text{diss}}$  ( $3.22\pm 1.82 \text{ pmol.L}^{-1}$ ,  $1\sigma$ ,  $n=38$ ) than those draining the foreland ( $0.70\pm 0.53 \text{ pmol.L}^{-1}$ ,  
205  $1\sigma$ ,  $n=9$ ). For first-order catchments,  $[\text{Re}]_{\text{diss}}$  is the highest in the High Andes (0.12 to 0.48  
206  $\text{pmol.L}^{-1}$ ), as compared to  $<0.15 \text{ pmol.L}^{-1}$  in the Mountain front and Foreland. In contrast, no  
207 significant change in  $[\text{Re}]_{\text{diss}}$  downstream is observed for nested catchments, although the  
208 average concentration at WAY ( $3.76\pm 0.76 \text{ pmol.L}^{-1}$ ,  $1\sigma$ ,  $n=6$ ) is slightly higher than at the SP  
209 site ( $2.59\pm 0.44 \text{ pmol.L}^{-1}$ ,  $1\sigma$ ,  $n=7$ ). We note that in March 2019,  $[\text{Re}]_{\text{diss}}$  was higher ( $4.22$   
210  $\text{pmol.L}^{-1}$ ) at SP than the average  $[\text{Re}]_{\text{diss}}$  of time-series measurements from the 2010-2011  
211 period, perhaps related to a large landslide in this catchment in the intervening period. At the  
212 foreland-floodplain site (CICRA),  $[\text{Re}]_{\text{diss}} = 3.69\pm 0.98 \text{ pmol.L}^{-1}$  ( $1\sigma$ ,  $n=9$ ). For the main  
213 tributaries of the Madre de Dios, we observe the highest  $[\text{Re}]_{\text{diss}}$  in the Manù (1.5 to 9.5  $\text{pmol.L}^{-1}$ ),  
214 lowest  $[\text{Re}]_{\text{diss}}$  in the Chiribi and Colorado rivers (0.5 to 2.2  $\text{pmol.L}^{-1}$ ), and intermediate  
215  $[\text{Re}]_{\text{diss}}$  in the Alto Madre de Dios (3.4 to 4.7  $\text{pmol.L}^{-1}$ ), Inambari (3.3  $\text{pmol.L}^{-1}$ ) and the  
216 Tambopata (2.3  $\text{pmol.L}^{-1}$ ).

217

### 218 **Temporal variability of dissolved Re concentrations**

219 In the four nested-catchments,  $[\text{Re}]_{\text{diss}}$  generally decreases with increasing instantaneous runoff,  
220  $Q$ , except for the high-altitude Andean site (WAY) where  $[\text{Re}]_{\text{diss}}$  shows no clear relationship  
221 with runoff (Fig. 1C). The relationship can be modeled using a power law  $[\text{Re}]_{\text{diss}} = a \times Q^b$ ,  
222 with  $a$  and  $b$  as the two fitted constants. For our samples, we observe a decrease of the  $b$  value  
223 from the Andes ( $-0.09\pm 0.12$  in WAY,  $-0.15\pm 0.08$  in SP;  $1\sigma$ ) to the mountain front ( $-0.40\pm 0.06$   
224 in MLC) and the foreland-floodplain ( $-0.46\pm 0.08$  in CICRA), indicating a more chemostatic  
225 behavior of Re in the Andes, and more dilutional behavior in the Foreland-floodplain. This  
226 decrease of the  $b$  value with elevation is similar to that observed for most major elements (29).

227

### 228 **Re concentrations in solids**

229 The Re concentration in bedloads ( $[\text{Re}]_{\text{BM}}$ ) from Andean rivers draining shales ranges from  
230 0.12 to 0.50 ppb with an average of  $0.28\pm 0.06$  ppb ( $\pm 2\text{SE}$ ,  $n=14$ ; Fig. 2). These are higher than  
231 the Re concentration in Andean soil samples (39) collected close the SP site  $0.07\pm 0.07$  ppb  
232 ( $\pm 2\text{SE}$ ,  $n=3$ ) and in the Foreland-floodplain  $0.04\pm 0.01$  ppb ( $\pm 2\text{SE}$ ,  $n=4$ ). The  $[\text{Re}]_{\text{BM}}$  is slightly  
233 higher in WAY (0.31 to 0.36 ppb) compared to SP (0.23 to 0.26 ppb). Two rock samples were  
234 analyzed: [Re] of the  $\text{OC}_{\text{petro}}$  and sulfur-rich sedimentary rock sample is almost 100 times higher  
235 (4.61 ppb) than the igneous rock (0.06 ppb). The  $[\text{Re}]/[\text{OC}]$  ratio in bedloads and rocks vary  
236 from  $0.27\times 10^{-7}$  to  $2.65\times 10^{-7} \text{ g.g}^{-1}$  with an average of  $0.93\pm 0.38\times 10^{-7} \text{ g.g}^{-1}$  ( $\pm 2\text{SE}$ ,  $n=16$ ; Fig. 2).  
237 The average  $[\text{Re}]/[\text{OC}]$  for the Kosñipata stream (WAY and SP sites) is  $0.80\pm 0.12\times 10^{-7} \text{ g.g}^{-1}$   
238 ( $\pm 2\text{SE}$ ,  $n=5$ ). This  $[\text{Re}]/[\text{OC}]$  ratio value is similar to bedload from New Zealand Southern Alps  
239 (4) but lower than bedloads from Taiwan (17), the Yamuna River (18) and the Mackenzie River  
240 (20).

241

## 242 Discussion

243 Our aim is to determine the rates and controls of OW of OC<sub>petro</sub> across the transition from the  
244 Andes Mountains to Amazon floodplain in the Madre de Dios basin. To do so, we need to  
245 characterize the source, behavior, and fluxes of dissolved Re. Following previous studies (4,  
246 17, 19, 20, 40), the OC<sub>petro</sub> oxidation yield ( $J_{OC_{petro-ox}}$ , tC km<sup>-2</sup> yr<sup>-1</sup>) can be estimated from:

247

$$248 J_{OC_{petro-ox}} = J_{Re} \times f_c \times ([OC]/[Re])_{solids} \times (1 - f_{graphite}) \quad [1]$$

249

250 Where “ $J_{Re}$ ” is the dissolved Re yield (in g km<sup>-2</sup> yr<sup>-1</sup>), the product of the Re concentration  
251 and runoff ( $J_{Re} = [Re]_{diss} \times Q$ ), while “ $([OC]/[Re])_{solids}$ ” is the OC/Re ratio in sedimentary rocks  
252 being weathered (in g.g<sup>-1</sup>), “ $f_c$ ” is the fraction of dissolved Re deriving from the oxidation of  
253 OC<sub>petro</sub> and “ $f_{graphite}$ ” is the proportion of graphite in the rocks that may be resilient to OW (14).

254

### 255 Dissolved Re source and yield

256 To determine the OC<sub>petro</sub> oxidation flux using the Re proxy, we must first quantify the  
257 proportion of dissolved rhenium derived from OC<sub>petro</sub> oxidation relative to other potential Re  
258 sources (rainwater, carbonates, sulfides, silicates, carbonates; ref.18). Following the approach  
259 developed in ref. (20), we use the  $[Re]/[SO_4^*]$  and  $[Re]/[Na^*]$  ratios to do so ( $[Na^*]$  and  $[SO_4^*]$   
260 are concentrations corrected for atmospheric-derived contributions). In general sulfides have  
261 low Re/SO<sub>4</sub> (41) and silicates low Re/Na relative to OC<sub>petro</sub> (20), and both Na and SO<sub>4</sub> are  
262 conservative soluble species in the Madre de Dios catchment (34, 35, 38). In analogy with  
263 studies on silicate and carbonate weathering, here we use local constraints on the end member  
264 compositions, using the combination of water samples from first-order catchments and  
265 tributaries (e.g. refs. 39, 40), combined with river sediments and rocks (23, 44) (Materials and  
266 Methods).

267 We find that small Upper Andes tributaries draining shales have a large range of  
268  $[Re]/[SO_4^*]$  and  $[Re]/[Na^*]$  ratios that can be interpreted as a mixing trend between sulfides and  
269 OC<sub>petro</sub> weathering, with limited Re contribution from silicate weathering (Fig. 3). In contrast,  
270 Andean tributaries draining granites, and rivers draining the foreland, have ratios that can be  
271 mostly explained by a mixture between silicates and OC<sub>petro</sub> (Fig. 3). A mixing analysis  
272 (Materials and Methods) shows that the fraction of dissolved Re derived from OC<sub>petro</sub> oxidation,  
273  $f_c$  (Equation 1), is >0.75 in the Andes (sites WAY and SP) and increases downstream to >0.90.  
274 Seasonal variability of the Re source is small but significant (less than 20% variability), with  
275 higher proportion of Re derived from OC<sub>petro</sub> oxidation in the Andes at higher runoff. This could  
276 reflect the larger contribution of shallow groundwaters from the unsaturated zone above the  
277 sulfide OW front (19). The fraction of Re derived from sulfide OW decreases from ~0.15-0.25  
278 in the Andes (WAY and SP) to <0.05 in the Foreland-floodplain (CICRA). The fraction of Re  
279 derived from silicate weathering is generally <0.05 but reaches ~0.2 for rivers draining only the  
280 foreland (e.g. Los Amigos River). Altogether, this shows that in the Madre de Dios basin, the  
281 majority of dissolved Re is derived from OC<sub>petro</sub> oxidation, confirming observations in other  
282 catchments where sedimentary rocks dominate the geology (19, 20, 45).

283 Calculation of dissolved Re yield ( $J_{Re}$ ) can be done in several ways, i.e. using average  
284  $[Re]_{diss}$  (4, 17, 18, 46), discharge-weighted average  $[Re]_{diss}$  (41) or rating curve-derived  $[Re]_{diss}$   
285 (19) and annual or instantaneous water discharge estimates. Here, these methods return similar  
286 results (Materials and Methods; Dataset S3). Therefore, we take advantage of paired  $[Re]_{diss}$   
287 and discharge measurements (at the four nested catchment sites and at the main tributaries) and  
288 use discharge-weighted average  $[Re]_{diss}$  and annual water discharge to derive dissolved Re  
289 yield. For the main tributaries, the highest  $J_{Re}$  is in the Manu River catchment ( $2.0^{+0.9}/_{-0.7}$  g km<sup>-2</sup>  
290 yr<sup>-1</sup>) and the lowest for the Las Piedras river ( $0.3 \pm 0.1$  g km<sup>-2</sup> yr<sup>-1</sup>). For the nested catchments,

291 the Re yield is  $2.1 \pm 1.0 \text{ g km}^{-2} \text{ yr}^{-1}$  and  $1.3 \pm 0.2 \text{ g km}^{-2} \text{ yr}^{-1}$  for WAY and SP sites respectively,  
292 and  $1.6 \pm 0.4 \text{ g km}^{-2} \text{ yr}^{-1}$  for the Foreland-floodplain (CICRA) site. Although there is slight  
293 decrease with elevation, the main result is that the specific Re yield of the Rio Alto Madre de  
294 Dios does not change, within uncertainty, when the Rio Alto Madre de Dios (Andes) reaches  
295 the Foreland-Floodplains.

296

### 297 **Rates and control of $\text{OC}_{\text{petro}}$ oxidative weathering in the Andes**

298 We compute the  $\text{OC}_{\text{petro}}$  oxidative weathering rate (Equation 1) using the parameter  
299 values defined above (Dataset S3). As we have no constraint on  $f_{\text{graphite}}$  in this setting, we do  
300 not account for this term here. To estimate the uncertainties, we use Monte Carlo  
301 simulations with 10 000 resolutions of the equation with distribution sampling of values within  
302 the errors of each parameter (4). The estimated  $\text{OC}_{\text{petro}}$  oxidative weathering fluxes based on  
303 dissolved Re yield are  $16.7^{+11.9}_{-8.8} \text{ tC km}^{-2} \text{ yr}^{-1}$  for the WAY site and  $11.2^{+4.5}_{-2.8} \text{ tC km}^{-2} \text{ yr}^{-1}$   
304 for the SP site. The lower uncertainty on the  $J_{\text{OC}_{\text{petro-ox}}}$  for SP is due to a higher precision on the  
305 water flux at this site (33).

306 It has been proposed that physical erosion rate is a major control on the rate of OW (3,  
307 8), with a potential role for landslide erosion supplying fresh mineral surfaces (24). The present-  
308 day erosion rate of the Rio Kosñipata is high, with values between 1200 and 3500  $\text{t.km}^{-2}.\text{yr}^{-1}$   
309 (11) and frequent landslides (47). The  $J_{\text{OC}_{\text{petro-ox}}}$  for the Kosñipata are much higher than in the  
310 Mackenzie ( $0.45$  to  $1.01 \text{ tC km}^{-2} \text{ yr}^{-1}$ ) and the Swiss Alps ( $3.6$  to  $5.7 \text{ tC km}^{-2} \text{ yr}^{-1}$ ) characterized  
311 by lower erosion rates, and more similar to rivers in New Zealand and Taiwan ( $4$  to  $30 \text{ tC km}^{-2}$   
312  $\text{yr}^{-1}$ ) which have higher erosion rates (3). Results from this study thus confirm the general  
313 control of erosion rate on the rate of  $\text{OC}_{\text{petro}}$  oxidation (3), though other factors can also play an  
314 important role (3, 48). The un-weathered solid  $\text{OC}_{\text{petro}}$  export at the SP site has been determined  
315 previously to be  $16.1 \pm 1.4 \text{ tC.km}^{-2}.\text{yr}^{-1}$  using sediment samples collected across the same time  
316 period (11). These fluxes imply that  $41 \pm 10\%$  of the total bedrock  $\text{OC}_{\text{petro}}$  is oxidized in the  
317 Andes, and the remainder is exported downstream. This  $\text{OC}_{\text{petro}}$  weathering intensity value is  
318 slightly lower than in the Mackenzie River basin (50%), similar to the Swiss Alps (19) and  
319 higher than in Taiwanese rivers (<20%) (17).

320 Our estimate of the flux of  $\text{OC}_{\text{petro}}$  oxidation in the Rio Kosñipata is the first attempt to  
321 quantify the  $\text{CO}_2$  emission from weathering of  $\text{OC}_{\text{petro}}$  in the Andes. This estimate can also be  
322 compared with other carbon fluxes relevant to the long-term carbon cycle in the Andes in the  
323 Kosñipata catchment. In the SP catchment, the rate of biospheric organic carbon ( $\text{OC}_{\text{bio}}$ ) export  
324 in river suspended sediments is  $12.6 \pm 0.4 \text{ tC km}^{-2} \text{ yr}^{-1}$  (11), which is slightly higher than the  
325  $\text{OC}_{\text{petro}}$  oxidative weathering yield. At the same site, the yield of carbon release associated with  
326 carbonate weathering by sulfuric acid is  $\sim 6 \text{ tC km}^{-2} \text{ yr}^{-1}$  (23), 45% lower than the rate of  $\text{CO}_2$   
327 release by  $\text{OC}_{\text{petro}}$  oxidation. Together, the OW of reduced phases ( $\text{OC}_{\text{petro}}$  and sulfides) in  
328 Andean sedimentary rocks release about  $17 \text{ tC km}^{-2} \text{ yr}^{-1}$  to the atmosphere, confirming that OW  
329 of sedimentary rocks in mountain belts is a large source of  $\text{CO}_2$  to the atmosphere.

330

### 331 **Oxidative weathering in the foreland and in the Andean-fed floodplains**

332 Once the  $\text{OC}_{\text{petro}}$  that survived OW in the Andes has reached the foreland and the floodplains,  
333 it can undergo further OW during transport and deposition in the floodplains (10). It has been  
334 suggested that this process can be a large source of  $\text{CO}_2$  to the atmosphere in the neighbouring  
335 Beni catchment (10) and in the Ganges floodplain (14). Here we take several approaches to  
336 isolate the weathering signal from the foreland (here defined as <500 m) versus the Andean-  
337 fed floodplain (<500 m and low relief adjacent to active river channels where Andean-derived  
338 sediments are exchanged). First, we assess the  $\text{OC}_{\text{petro}}$  weathering flux in the foreland by using  
339 data from the Las Piedras river catchment, since it drains the foreland exclusively with no  
340 Andean contribution. The  $[\text{Re}]_{\text{diss}}$  concentration at Las Piedras ( $1.24 \pm 0.35 \text{ pmol.L}^{-1}$ , 2SE) is



341 low like the two other medium-size foreland rivers, the Blanco ( $0.36 \pm 0.06 \text{ pmol.L}^{-1}$ ) and the  
342 Los Amigos ( $0.50 \pm 0.16 \text{ pmol.L}^{-1}$ ). The  $[\text{Re}]/[\text{OC}]$  ratio of bedrock in Las Piedras can be  
343 reasonably assumed to be equivalent to the Andean-derived bedload from the Rio Kosñipata,  
344 given that the foreland-floodplain region is predominantly underlain by Andean-derived  
345 sediments (23). Using this, we calculate a  $J_{\text{OCpetro-ox}}$  of  $1.9^{+1.2/-0.8} \text{ tC.km}^{-2}.\text{yr}^{-1}$  which is about 6  
346 times lower than in the Andes and similar to the rate measured in the Mackenzie River basin  
347 (20).

348 To estimate the  $\text{OC}_{\text{petro}}$  weathering flux in the floodplains, we attempt a mass-balance  
349 at the scale of the whole Madre de Dios catchment ( $118\,459 \text{ km}^2$  at El Sena station near  
350 Riberalta, Ref. 36). Assuming the  $J_{\text{OCpetro-ox}}$  from SP (Upper Andes) is representative of the  
351 Andean area ( $40\,868 \text{ km}^2$ ; defined as  $<500 \text{ m}$ ) of the Madre de Dios, we calculate a total Andean  
352  $J_{\text{OCpetro-ox}}$  of  $0.46^{+0.18/-0.11} \text{ MtC.yr}^{-1}$ . This assumption is justified as the SP catchment has similar  
353 erosion rates as the inferred Andean erosion rate for the whole Madre de Dios River (37). The  
354 contribution from foreland weathering ( $<500 \text{ m}$ ;  $77\,591 \text{ km}^2$ ) can be estimated using the  $J_{\text{OCpetro-ox}}$   
355 from the Las Piedras River ( $19\,630 \text{ km}^2$ ) as  $0.15^{+0.09/-0.06} \text{ MtC.yr}^{-1}$ . The total  $J_{\text{OCpetro-ox}}$  at the  
356 mouth of the Madre de Dios is  $1.00^{+0.43/-0.28} \text{ MtC.yr}^{-1}$ . Hence, the contribution of Andes +  
357 Foreland is lower than the total  $J_{\text{OCpetro-ox}}$  of the Madre de Dios at its mouth by  $0.39^{+0.16/-0.11}$   
358  $\text{MtC.yr}^{-1}$ , which we attribute to weathering in the floodplain. This mass-balance indicates that  
359  $\sim 46\%$  of the total  $\text{OC}_{\text{petro}}$  oxidation takes place in the Andes,  $\sim 40\%$  in the floodplains, and  $\sim 14\%$   
360 in the foreland-lowlands (Fig. 4A).

361 The deposition and weathering of sediments in the floodplain constitutes a different  
362 mechanism compared to upland weathering (29, 49). Sediment and water exchange and storage  
363 during floodplain transit by rivers can result in long sediment residence times (50), and  
364 influence water flux, and redox state, which could all facilitate OW (7). In addition, the warmer  
365 climatic conditions in the floodplain relative to the Andes could be important in setting reaction  
366 rates (21), while the length of floodplains and their channel migration rates (51) could also be  
367 important controlling variables. Scaled laboratory experiments have been used to suggest that  
368 in-situ oxidation during within river transport is small (52) meaning reactions in sediment stores  
369 of floodplains are likely to be of most importance (53).

370 Our paired instantaneous  $[\text{Re}]_{\text{diss}}$  and discharge measurements from the same sampling  
371 trips (in 2013 and 2019, both wet and dry seasons) covering both upstream and downstream  
372 floodplain sections constrain the location of  $\text{OC}_{\text{petro}}$  oxidation reactions in the floodplains  
373 between MLC and CICRA (Fig. 4B). The  $\sim 85 \text{ km}$  long section of the river along the course of  
374 the Alto Madre de Dios floodplain, between the Mountain Front (MLC) and the confluence  
375 with the Rio Manu, is mostly braided and multi-channel, with mobile channel bars comprised  
376 of sand and fine gravel. Measurements show a significant increase of  $J_{\text{Re}}$  (Re flux). Water  
377 isotopes indicate lack of significant water, and therefore likely Re, contribution from tributaries  
378 in this river reach (see Materials and Methods). Hence, we attribute this  $J_{\text{Re}}$  increase (from 4 to  
379  $30\%$ , Fig. 4B) to weathering of  $\text{OC}_{\text{petro}}$  from Andean sediments transiting in the floodplains (SI  
380 Appendix). The same calculation can be done using mean annual Re flux, but with a larger  
381 uncertainty. We calculate that the mean annual  $J_{\text{Re}}$  increases by  $31 \pm 20\%$  which corresponds to  
382 a flux of  $\text{CO}_2$  release through  $\text{OC}_{\text{petro}}$  oxidation in the floodplain reach between MLC (Mountain  
383 front) and AMdD of  $0.03 \pm 0.01 \text{ MtC.yr}^{-1}$ . In comparison, the  $\text{CO}_2$  release through  $\text{OC}_{\text{petro}}$   
384 oxidation in the Andean part of the Alto Madre De Dios catchment is  $0.08 \pm 0.02 \text{ MtC.yr}^{-1}$ . As  
385 the solid  $\text{OC}_{\text{petro}}$  load at MLC is  $0.12 \pm 0.01 \text{ MtC.yr}^{-1}$  (Ref. 32, assuming similar solid  $\text{OC}_{\text{petro}}$   
386 yield as at SP), this would suggest that  $\sim 25\%$  of Andean-derived solid  $\text{OC}_{\text{petro}}$  is oxidized before  
387 reaching the confluence with the Rio Manu over a floodplain length of  $85 \text{ km}$ .

388 In contrast, in the section between AMdD and CICRA ( $\sim 180 \text{ km}$  long), where a larger,  
389 single channel meanders through the floodplain, we observe no significant Re flux increase in  
390 wet seasons (2013 and 2019) and dry season 2019. For the dry season in 2013, we even observe

391 a small decrease of Re yield along the section (Fig. 4B). Similarly, using mean annual  $J_{Re}$ , we  
392 calculate no significant increase in  $OC_{petro}$  oxidation, within uncertainties (Fig. 4B, SI  
393 Appendix), in this section nor in the CICRA-PM section (~170 km long). Over the transit from  
394 MLC to CICRA, the isotopic composition of sulfate suggests minimal sulfate reduction (36),  
395 suggesting that oxygen is available for OW weathering along this river reach. In addition, the  
396 warm tropical climate could drive higher reaction rates and  $OC_{petro}$  oxidation (21). Therefore,  
397 the apparent limited floodplain weathering could reflect an exhaustion of reactive  $OC_{petro}$   
398 supplied from Andean erosion upstream. Regardless of the mechanisms at play, the Rio Madre  
399 de Dios example shows that high rates of  $OC_{petro}$  oxidation in the mountain headwaters can be  
400 matched by OW in the foreland (Fig. 4). A large proportion of floodplain weathering appears  
401 to happen over a relatively short-length scale (~<85 km) after exiting the Andes.

402 Finally, for the section furthest downstream, PM-Ribe (~560 km long), calculation using  
403 mean annual  $J_{Re}$  show a 10% increase in Re flux. This may reflect OW of reactive  $OC_{petro}$   
404 supplied by the Inambari and/or the Tambopata, in combination with a longer time sediments  
405 spend in this long floodplain section (e.g. see ref. 50). Yet, this observation should be  
406 interpreted with caution due to the large uncertainty ( $\pm 13\%$ ) associated with our calculation.  
407 Additional work on this part of the catchment is necessary to refine these calculations.

408

## 409 **Implications for the long-term carbon cycle**

410 Previous studies on the Amazon River found significant  $CO_2$  release from  $OC_{petro}$   
411 oxidation during the transit of fluvial sediments in the Madeira floodplain (10, 11). They found  
412 that the solid  $OC_{petro}$  flux from the Madeira at the confluence with the Amazon is much lower  
413 than the solid  $OC_{petro}$  supplied by the Beni at the mountain front and transported through the  
414 plain. They estimated a  $CO_2$  emission of  $0.50 \text{ MtC.yr}^{-1}$  across the Rio Beni floodplain. Our Re-  
415 based estimate of  $OC_{petro}$  oxidation during the transit of Madre de Dios sediments in the  
416 floodplain ( $0.39^{+0.16}/_{-0.11} \text{ MtC.yr}^{-1}$ ) is of similar magnitude. The total  $CO_2$  emission from  $OC_{petro}$   
417 oxidation in the whole Madre de Dios catchment ( $1.00^{+0.43}/_{-0.28} \text{ MtC.yr}^{-1}$ ) is more than twice the  
418 silicate weathering  $CO_2$  drawdown ( $0.43^{+0.22}/_{-0.09} \text{ MtC.yr}^{-1}$ ; ref. 53). Considering that sulfide  
419 oxidation also contributes to the carbonate weathering flux (23), the net  $CO_2$  balance during  
420 weathering in the Madre de Dios catchment appears to be tipped firmly toward being a  $CO_2$   
421 source (3).

422 Our findings from the Rio Madre de Dios catchment allow us to postulate a broader role  
423 for floodplain weathering in enhancing the  $CO_2$  release by  $OC_{petro}$  oxidation. Uplift and  
424 exhumation of sedimentary rocks in a mountain range can increase the supply of  $OC_{petro}$  to an  
425 oxygenated weathering zone (17, 21) and increase the rates of  $OC_{petro}$  oxidation and  $CO_2$   
426 release, as we observe in the Andes (Fig. 4). However, the overall weathering intensity can be  
427 low, with only ~20% to 50% of  $OC_{petro}$  oxidized, meaning there is further potential for  $CO_2$   
428 release. On high standing mountain islands, floodplains are short. For instance, in Taiwan rivers  
429 have floodplains <40 km long, and many are shorter than 5 km, and there un-weathered  $OC_{petro}$   
430 is re-buried offshore (16). However, if the tectonic setting permits the growth of a larger  
431 continental floodplain, additional  $OC_{petro}$  oxidation is very likely to occur even if just ~100 km  
432 in length based on our findings (Fig. 4). In this case, only extremely refractory  $OC_{petro}$  escapes  
433 oxidation (10). While future work will need to establish how temperature and  $O_2$ -supply impact  
434  $OC_{petro}$  oxidation rates in floodplains (7, 21), our results suggest that the formation of floodplain  
435 adjacent to a mountain range allows more complete  $OC_{petro}$  oxidation during sediment transit.  
436 Over multi-million year timescales, the growth and waning of riverine floodplains and  
437 continental sediment storage (27) could thus act as a powerful carbon cycle modifier throughout  
438 Earth's history.

439

## 440 **Materials and methods**

441 The materials and methods are summarized here; further details are provided in SI Appendix. All data  
442 used in this study are reported in Datasets S1–S5.

443

444 **Sample collection and discharge measurements.** Major cation and anion concentration data of  
445 samples from 2010 to 2013 are from Torres et al., (2015, 2016). Detailed information on the sampling  
446 protocol can be found in those studies. In summary here, for the four main nested catchment sites (WAY,  
447 SP, MLC and CICRA, Fig. 1), time-series samples were collected between 2010 and 2011 using a clean  
448 PP bottle and filtered on site with 0.2  $\mu\text{m}$  porosity nylon filter (29). At these sites, water discharge was  
449 measured at the same time as sampling by monitoring water levels manually and converting to discharge  
450 using a rating curve. At the SP site, river level was monitored with a water level logger that recorded  
451 river level measurements every 15 min (33). At other localities, samples were collected on fieldtrips in  
452 2012, 2013, 2016 and 2019 (Dataset S1). Water samples were collected from the river surface using  
453 clean bucket and transferred to 10 or 20 L plastic bags before filtration. Samples were filtered within 24  
454 to 48h of collection with 0.2 $\mu\text{m}$  porosity polyethersulfone (PES) filters. The discharge (“Q”) at CICRA  
455 was measured during each sampling trip using an Acoustic Doppler Current Profiler (ADCP, RD1  
456 Sentinel GED154 in March 2013 and SonTek M9 in August 2013 and in March and May 2019). In  
457 2019, the discharge of the Alto Madre de Dios, Rio Manù, Chiribi and Colorado were also measured by  
458 ADCP. All discharge measurements are from Torres et al., (2017) and Burt et al., (2021)

459

460 **Re concentration measurements in water and sediments.** The dissolved Re concentrations were  
461 measured following the same protocol as described in ref. (19). Briefly, dissolved Re concentrations  
462 ( $[\text{Re}]_{\text{diss}}$ ) were measured by direct calibration against a set of seven standards with varying Re  
463 abundances and similar matrixes to river water, by quadrupole inductively coupled plasma mass  
464 spectrometry (Q-ICP-MS, Agilent Technologies 7900). Calibration standards and samples were doped  
465 with 0.025 mg/L concentration of internal standard Tb and Bi to correct for instrumental drift and matrix  
466 drift. Accuracy and precision of the measurements was assessed by repeated measurements of various  
467 riverine standard reference materials, in particular reference materials SLRS-5 and SLRS-6 at various  
468 dilutions. The standards confirmed better than 10% accuracy and precision. For sediment samples, the  
469 rhenium concentrations were determined using the method in ref. (55). A mass of 0.2 to 0.5g was  
470 digested using a mixture of 3 mL 27M HF and 3 mL 16M  $\text{HNO}_3$  for 24 to 48h at 120°C on a hot plate.  
471 Digested solutions were processed through AG1-X8 resin to separate Re from the rest of the matrix.  
472 Rhenium concentrations were then measured with a Neptune MC ICP-MS at Durham University.

473

474 **Dissolved Re yield calculations.** Several methods can be used to determine dissolved ion yields  
475 depending on the number of paired water discharge (Q) and concentration measurements, their  
476 frequency and the behavior of the element of interest in relation with discharge (56). Previous studies  
477 with large datasets of Re concentration and discharge (19, 20) have used a rating curve approach to  
478 quantify dissolved yields, by fitting power law functions to the trends in the data and using this  
479 relationship to predict predicted for each daily discharge value and annual fluxes. Other studies have  
480 used discharge-weighted average concentration (41) or average concentration of several measurements  
481 (4, 17, 18, 46) combined with annual water discharge estimates.

482 The four nested catchments in our dataset have between five and nine Q and  $[\text{Re}]_{\text{diss}}$  data pairs  
483 for each catchment (Fig. 1C). For the large tributaries (Manu, Colorado, Chiribi, Alto Madre de Dios),  
484 our dataset includes 4 paired Q and  $[\text{Re}]_{\text{diss}}$  measurements each. For all the sites, we use three different  
485 methods to calculate the Re yield and uncertainties: i) mean  $[\text{Re}]_{\text{diss}} \pm \text{SE}$  multiplied by annual discharge;  
486 ii) discharge-weighted mean  $[\text{Re}]_{\text{diss}} \pm \text{SE}$  multiplied by annual discharge; and iii) average of measured  
487 instantaneous Re fluxes,  $J_{\text{Re}} \pm \text{SE}$ . The advantage of the first method is that it includes more  $[\text{Re}]_{\text{diss}}$   
488 measurements (since the instantaneous discharge was not measured for all samples). The disadvantage  
489 is that there is a potential bias toward high concentration by not weighting to discharge. The third method  
490 is useful if annual discharge is not known, however it has the disadvantage of being less accurate because  
491 instantaneous fluxes vary more than instantaneous concentrations (56). Discharge values and  
492 uncertainties are reported in Dataset (S3). For the WAY and SP catchments, we use annual discharge  
493 values from Clark et al., (2014), determined over the year 2010. In addition, we use average annual  
494 discharge values dataset for the main tributaries of the Madre de Dios that were determined by water  
495 balance over the period 1968-1982 (57). They calculate a total discharge at the mouth of the Madre de

496 Dios (Riberalta) of  $6369 \text{ m}^3 \cdot \text{s}^{-1}$  which are very close (only 12% higher) to the discharge measured during  
497 the 2002–2011 period ( $5661 \text{ m}^3 \cdot \text{s}^{-1}$ ; Vauchel et al., 2017). For CICRA, the discharge can be estimated  
498 by adding the annual discharge values of the Manu, Alto Madre de Dios, Colorado from Abastos Lara,  
499 (1987) and considering that the Rio Chiribi contributes 7.5% of the total discharge in CICRA (see  
500 Dataset S5). This gives a value of  $2165 \text{ m}^3 \cdot \text{s}^{-1}$ . For instantaneous discharge of the main tributaries (Alto  
501 Madre de Dios, Manù, Chiribi and Colorado) that were measured or calculated during the 2013 and  
502 2019 sampling trip, we use values from previous studies (34, 35).

503 Calculation of uncertainty is done by a Monte Carlo simulation (run 10 000 times for each  
504 watershed). As the calculated distributions follow skewed rather than normal distributions, we report  
505 the median value (50th percentile) with the uncertainty range defined by the 16th and 84th percentiles  
506 (equivalent to 68% of the entire population; SI Appendix). Comparison between the various methods  
507 shows good agreement between the different methods for the different sites within uncertainties (Dataset  
508 S3). The third method gives larger uncertainty compared to methods 1 and 2. This could reflect the  
509 lower number of samples used, the uncertainty on the discharge measurement or an imbalance between  
510 the discharge during the 1968-1982 period and the 2010-2020 period. When quantifying  $\text{OC}_{\text{petro}}$   
511 oxidation fluxes from the dissolved Re flux for all sites, we use the second method (discharge-weighted  
512  $[\text{Re}]_{\text{diss}}$ ) when possible and the first method (mean  $[\text{Re}]_{\text{diss}}$ ) otherwise.

513  
514 **Source partitioning of dissolved rhenium.** To quantify the  $\text{OC}_{\text{petro}}$  oxidation flux using dissolved Re,  
515 we need to: i) correct for Re inputs from precipitation and/or atmospheric deposition; ii) quantify the Re  
516 input from non- $\text{OC}_{\text{petro}}$  sources (i.e. sulfide, carbonate and silicate minerals). Solutes in precipitation can  
517 come from dissolution of sea salts, dust or biogenic particles. The  $[\text{Re}]/[\text{Cl}]$  ratio ( $\sim 7.5 \times 10^{-5} \text{ pmol} \cdot \mu\text{mol}^{-1}$ )  
518 of the ocean is very low (58) compared to the  $[\text{Re}]/[\text{Cl}]$  of rivers from the Madre de Dios. The  $[\text{Cl}]_{\text{diss}}$   
519 in rivers from this study are also low, indicating that the proportion of Re derived from sea salts is very  
520 small. While we have only one rainwater sample from the upper Andes, its  $[\text{Re}]_{\text{diss}}$  was below detection  
521 limit of the measurement session ( $< 0.05 \text{ pmol} \cdot \text{L}^{-1}$ ), supporting this conclusion. Among all the samples,  
522 the lowest measured  $[\text{Re}]_{\text{diss}}$  and  $[\text{Re}]/[\text{Cl}]$  ratio correspond to a lysimeter sample in the Foreland  
523 (PER19-38) with values of  $0.009 \text{ pmol} \cdot \text{L}^{-1}$  and  $1.4 \times 10^{-3} \text{ pmol} \cdot \mu\text{mol}^{-1}$  respectively. The  $[\text{Re}]/[\text{Cl}]$  ratio  
524 of this sample is  $\sim 20$  times higher than the  $[\text{Re}]/[\text{Cl}]$  ratio of the ocean. The major element concentration  
525 for this sample is in the range of the average composition of rainwater from the Andes from Torres et  
526 al., (2015). Hence, we use this sample as representative of the maximum Re/Cl ratio of rainwater. For  
527 calculating the proportion of Re derived from each source we used the following mass-balance. For the  
528 contribution of the rain:

$$530 \quad [\text{Re}]_{\text{rain}} = \left( \frac{\text{Re}}{\text{Cl}} \right)_{\text{rain}} \times [\text{Cl}]_{\text{cycl}} \quad [1]$$

531  
532 Where  $(\text{Re}/\text{Cl})_{\text{rain}}$  is the proposed elemental ratio between Re and the Cl in the rain ( $1.4 \times 10^{-3} \text{ pmol} \cdot \mu\text{mol}^{-1}$ )  
533 and  $[\text{Cl}]_{\text{cycl}}$  is the cyclic chlorine concentration. Since the marine evaporite contribution is small or  
534 negligible in the Madre de Dios catchment (23, 29), we consider that  $[\text{Cl}]_{\text{cycl}} = [\text{Cl}]_{\text{riv}}$ . The concentration  
535 of any element X corrected for rainwater and evaporite inputs is referred as “[X\*]”. We find that the  
536 proportion of riverine Re deriving from rainfall is negligible, being generally less than 0.5%, with a  
537 maximum of 6%. For  $\text{SO}_4$  rain concentration we use a  $(\text{SO}_4/\text{Cl})$  value of 0.53 corresponding to the  
538 median value of precipitation data from Torres et al., (2015). This value is only slightly lower than the  
539 lowest  $(\text{SO}_4/\text{Cl})$  measured in our dataset (sample PER19-38, value of 0.60).

540 We then move to quantify the proportion of dissolved rhenium derived from  $\text{OC}_{\text{petro}}$  oxidation  
541 relative to other potential Re sources (sulfides, silicates, carbonates). Previous work has suggested  
542 carbonates are not a major source of dissolved Re (18). If the Re/Ca of carbonates is  $\sim 5 \times 10^{-5} \text{ pmol} \cdot \text{mol}^{-1}$   
543 (18),  $< 1\%$  of total dissolved Re in the studied rivers here can be accounted for by carbonate weathering  
544 (a maximum proportion using this Re/Ca ratio and assuming all dissolved Ca in the Madre de Dios  
545 catchments is derived from carbonates). We therefore follow the approach developed in Horan et al.,  
546 (2019), that uses the  $(\text{Re}/\text{SO}_4)^*$  and  $(\text{Re}/\text{Na})^*$  ratio to characterized Re input from sulfides, silicates and  
547  $\text{OC}_{\text{petro}}$ .

548 Sulfides have low Re/S (Miller et al., 2011) and silicates low Re/Na relative to  $\text{OC}_{\text{petro}}$  (Horan  
549 et al., 2019) and both Na and  $\text{SO}_4$  are conservative soluble species in the Madre de Dios catchment

550 (Baronas et al., 2017; Torres et al., 2017; Burt et al., 2021). Assuming that all the  $[\text{SO}_4^{2-*}]$  is derived  
 551 from pyrite oxidation (i.e. no evaporite contribution, Torres et al., 2016), we estimate the Re  
 552 concentration derived from sulfide oxidation:

$$554 \quad [\text{Re}]_{\text{diss.sulfides}} = \left( \frac{\text{Re}}{\text{SO}_4^{2-}} \right)_{\text{sulfides}} \times [\text{SO}_4^{2-*}] \quad [2]$$

555  
 556 Where  $(\text{Re}/\text{SO}_4^{2-})_{\text{sulfides}}$  is the sulfide composition. Then we can determine the concentration of  
 557 Re deriving from silicate weathering ( $[\text{Re}]_{\text{diss.sil}}$ ) using sodium and assuming that all the  $[\text{Na}^*]$  is derived  
 558 from silicate weathering:

$$560 \quad [\text{Re}]_{\text{diss.sil}} = \left( \frac{\text{Re}}{\text{Na}} \right)_{\text{silicates}} \times [\text{Na}^*] \quad [3]$$

561  
 562 Where  $(\text{Re}/\text{Na})_{\text{sil}}$  is the silicate signature. Then we attribute the excess Re to the oxidation of  
 563  $\text{OC}_{\text{petro}}$ , calculated as:

$$564 \quad [\text{Re}]_{\text{diss.OC}} = [\text{Re}^*] - [\text{Re}]_{\text{diss.sulfides}} - [\text{Re}]_{\text{diss.sil}} \quad [4]$$

565  
 566 In analogy with studies on silicate and carbonate weathering, we use small tributaries (e.g.  
 567 Gaillardet et al., 1997; Galy and France-Lanord, 1999) and/or sediment composition (23, 44) to  
 568 constrain local weathering end-members  $[\text{Re}]/[\text{SO}_4]$  and  $[\text{Re}]/[\text{Na}]$  ratio values (20). Small Andean  
 569 tributaries draining sulfur-rich metasedimentary rocks display two orders of magnitude variability in  
 570  $[\text{Re}]/[\text{SO}_4^*]$  and  $[\text{Re}]/[\text{Na}^*]$  ratios and are positively correlated. Several Andean rivers with low  
 571  $[\text{Re}]/[\text{SO}_4^*]$  values (Fig. 3) have similar composition to the median Re/S values of pyrite from the  
 572 literature ( $1.8^{+4.2}/_{-1.7} \times 10^{-3} \text{ pmol.}\mu\text{mol}^{-1}$ , Miller et al., 2011) with the lowest  $[\text{Re}]/[\text{SO}_4^{2-}]$  ratio  
 573 corresponding to a lysimeter sample (PER19-97) in the riparian area of a small catchment ( $[\text{Re}^*]/[\text{SO}_4^{2-}]$   
 574  $]^* = 2.2 \times 10^{-4} \text{ pmol.}\mu\text{mol}^{-1}$ ) and a river sample (r2400) from another small catchment in the Andes  
 575 ( $[\text{Re}^*]/[\text{SO}_4^{2-}]^* = 4.8 \times 10^{-4} \text{ pmol.}\mu\text{mol}^{-1}$ ). They both have high  $\text{SO}_4$  concentration indicating a high rate  
 576 of sulfide oxidation. The  $[\text{Re}]/[\text{SO}_4^*]$  ratio of these samples is similar to the sulfide-oxidation rich  
 577 sample in the Mackenzie basin (Horan et al., 2019). Hence, this suggests that the Re and  $\text{SO}_4$   
 578 composition of these rivers is dominated by sulfide oxidation of pyrite and that they can be used as end-  
 579 member values for  $(\text{Re}/\text{SO}_4)_{\text{sulfides}}$ . The lowest  $(\text{Re}/\text{SO}_4)^*$  value ( $2.2 \times 10^{-4} \text{ pmol.}\mu\text{mol}^{-1}$ ) measured here  
 580 could represent the most “pure” sulfide oxidation end-member and higher  $[\text{Re}]/[\text{SO}_4^*]$  for other rivers  
 581 would be explained by a small contribution of Re from rock organic carbon oxidation. Alternatively, it  
 582 is possible that the Re/S from the local bedrock is variable and explains the range of  $[\text{Re}]/[\text{SO}_4^*]$   
 583 observed in rivers dominated by sulfide oxidation. A third possibility is that the very low  $[\text{Re}]/[\text{SO}_4^*]$   
 584 and  $[\text{Re}]/[\text{Na}^*]$  of some samples is due to non-conservative behavior and removal of dissolved Re  
 585 because some of these rivers have low pH values (as low as 3.5) and  $\text{ReO}_4^-$  is less stable under acidic  
 586 conditions (60). However, this cannot explain the low  $[\text{Re}]/[\text{SO}_4^*]$  value of sample PER19-3 ( $3.5 \times 10^{-3}$   
 587  $\text{ pmol.}\mu\text{mol}^{-1}$ ) which has pH value of 8. Considering the above discussion we consider  $(\text{Re}/\text{SO}_4)_{\text{sulfides}}$   
 588 ranging from  $2 \times 10^{-4}$  to  $4 \times 10^{-3} \text{ pmol.}\mu\text{mol}^{-1}$  that encompass the range of  $[\text{Re}]/[\text{SO}_4^*]$  of Andean rivers  
 589 that we identified as typical of sulfide oxidation.

590  
 591 Rivers draining mostly granites (sulfide-poor and no  $\text{OC}_{\text{petro}}$ ) have low Re/Na but an order of  
 592 magnitude higher  $[\text{Re}]/[\text{SO}_4]$  ratios relative to Andean tributaries draining shales (Fig. 3). Interestingly,  
 593 rivers and lysimeter samples from the foreland have similar composition as rivers draining granites. For  
 594 Foreland rivers, especially at low elevations, deeply weathered soils and high weathering intensity  
 595 probably leads to almost complete oxidation of pyrite due to its fast kinetics, and therefore we expect  
 596 the chemical composition of those samples to be less influenced by OW of pyrite than Andean rivers.  
 597 Altogether, rivers draining granite and the foreland have ratios that are inferred to reflect mostly mixing  
 598 between weathering of silicates and weathering of  $\text{OC}_{\text{rock}}$ . These observations are supported by river bed  
 599 sediment samples. For Andean rivers, the  $[\text{Re}]/[\text{Na}]$  ratio of river bed sediments is similar to the low  
 600  $[\text{Re}]/[\text{Na}^*]$  of small tributaries draining granites (lowest value is  $2.2 \times 10^{-3} \text{ pmol.}\mu\text{mol}^{-1}$  for sample  
 601 PER19-26) and of samples from small first-order catchments draining the foreland (lowest value is  
 602  $1.5 \times 10^{-3} \text{ pmol.}\mu\text{mol}^{-1}$  for sample PER19-35). In addition, one rock sample, corresponding to an igneous

603 rock (a granophyre), has a very low [Re]/[Na] ratio of  $4.3 \times 10^{-4}$  pmol. $\mu$ mol<sup>-1</sup>, similar to the crystalline  
604 rock endmember [Re]/[Na] ratio value in the Himalaya ( $2 \times 10^{-4}$  pmol. $\mu$ mol<sup>-1</sup>, Ref. 18). Hence, we  
605 consider here a [Re]/[Na] ratio between  $4 \times 10^{-4}$  and  $2 \times 10^{-3}$  pmol. $\mu$ mol<sup>-1</sup> for silicates, which spans the  
606 range of lowest [Re]/[Na] values from local solid and river samples.

607 Using Eq. (1-4) and the range of above defined (Re/SO<sub>4</sub>)<sub>sulfides</sub> and (Re/Na)<sub>silicates</sub> values for our  
608 study area, we can calculate [Re]<sub>diss.OC</sub> for each sample. The calculation of [Re]<sub>diss.OC</sub> is done by a Monte  
609 Carlo simulation (run 10 000 times for each river) assuming random distribution of (Re/SO<sub>4</sub>)<sub>sulfides</sub> values  
610 between  $2 \times 10^{-4}$  and  $4 \times 10^{-3}$  pmol.mol<sup>-1</sup> and (Re/Na)<sub>silicates</sub> values between  $4 \times 10^{-4}$  and  $2 \times 10^{-3}$  pmol. $\mu$ mol<sup>-1</sup>  
611 (SI Appendix; Dataset S4). Fractions of dissolved Re derived from OC<sub>petro</sub> OW ( $f_c = [\text{Re}]_{\text{diss.OC}} / [\text{Re}]_{\text{diss}}$ )  
612 are reported in Dataset S3.

613  
614 **Floodplain mass-balance of dissolved Re.** The section of the Alto Madre de Dios river between MLC  
615 (mountain front) and AMdD (confluence with Manu River) has relatively minimal tributary input. Over  
616 three sampling trips, we observe an increase in the Re concentration between MLC and AMdD by 3%  
617 (March 2013), 26% (March 2019) and 12% (May 2019). There is also a systematic increase in Re/Na  
618 and Re/SO<sub>4</sub> ratio. The Re concentration of sub-Andean tributaries is about 0.8 ppt, which is higher than  
619 the Re concentration at MLC and could explain part of the observed increase. The contribution of water  
620 and weathering inputs from sub-Andean-foreland tributaries can be assessed using  $\delta$ D and  $\delta^{18}$ O since  
621 tributaries (PER19-53, Rio Carbon, Rio Pini Pini) have higher  $\delta$ D (-54.9 to -70.2‰) and  $\delta^{18}$ O values (-  
622 8.2 to -10.4 ‰) compared to the Alto Madre de Dios at MLC ( $\delta$ D ~ -72.5‰ and  $\delta^{18}$ O ~ -10.6‰). The  
623  $\delta$ D and  $\delta^{18}$ O of the Alto Madre de Dios does not change significantly which indicates that any Re  
624 contribution from these tributaries is too small to explain the observed 26% increase in Re concentration  
625 in 2019. Therefore, we conclude that this increase is due to ongoing OC<sub>petro</sub> oxidation of sediment during  
626 transit and/or within the floodplain between MLC and AMdD.

627

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636

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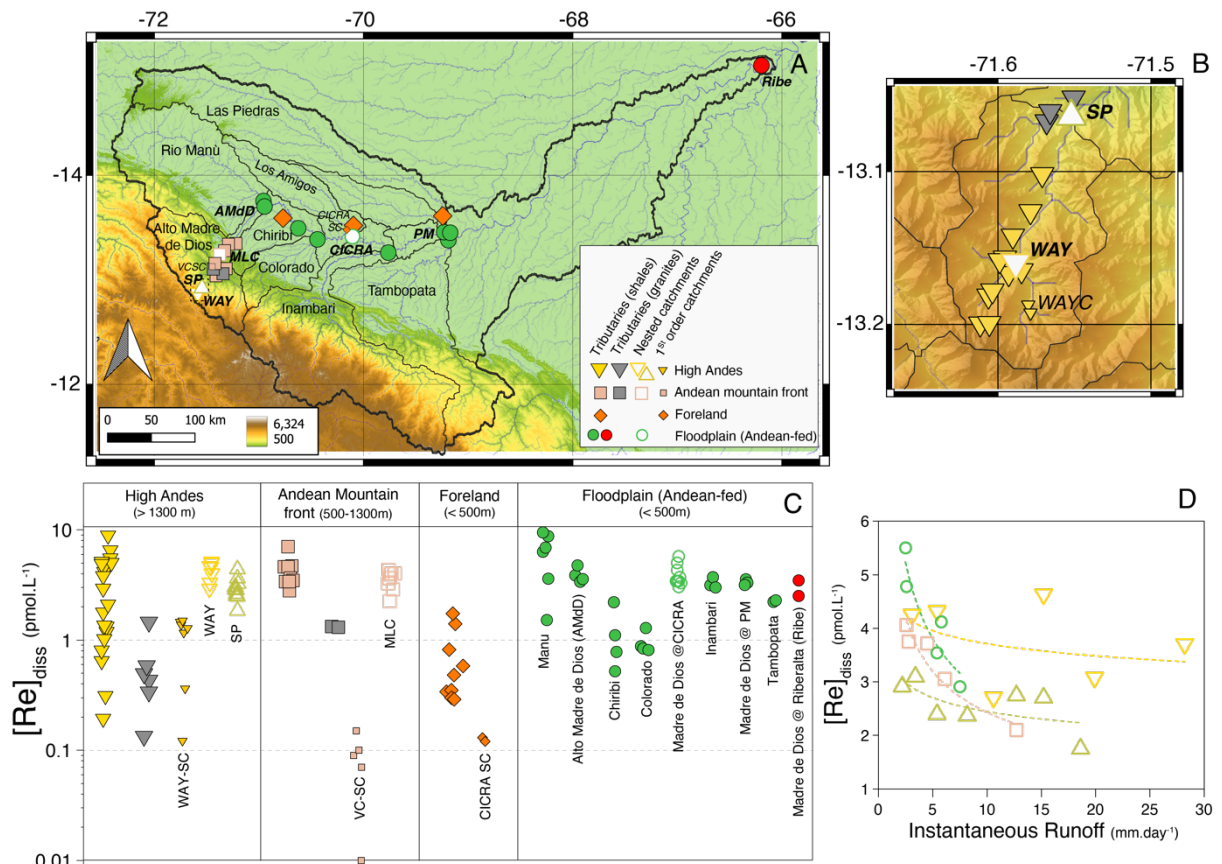
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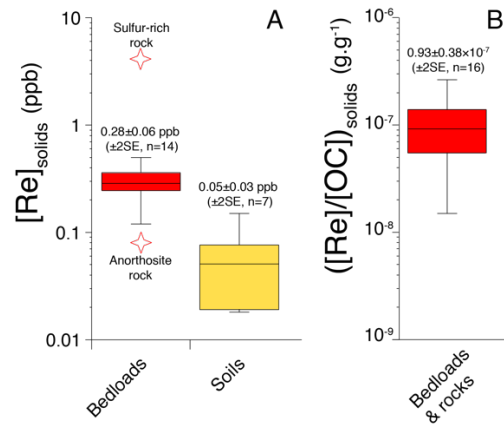
803 **Figures**

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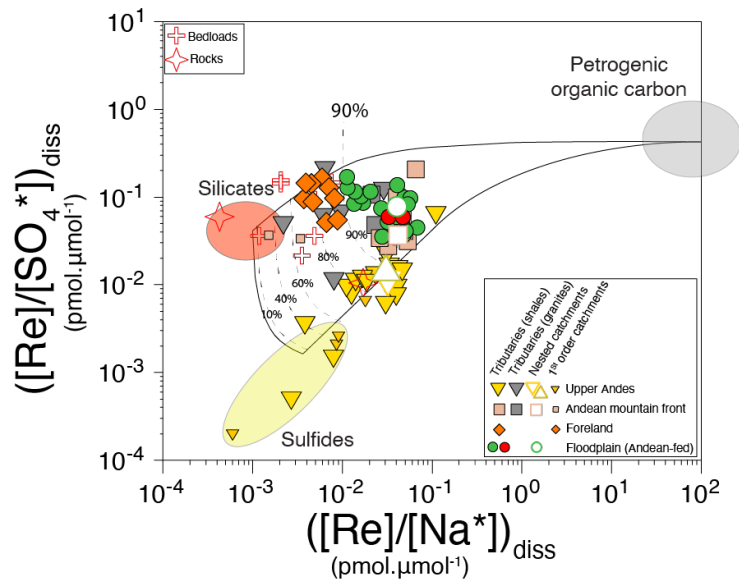
805 **Figure 1.** (A) Map of the Madre de Dios River basin with the location of the samples from this study. (B) Inset  
 806 showing the location of the samples in the High Andes. (C)  $Re$  concentration (in pmol.L<sup>-1</sup>) in the various  
 807 geomorphic settings for all river samples from this study. The  $[Re]_{diss}$  from the two hot springs samples are not  
 808 shown. (D)  $[Re]_{diss}$  versus instantaneous runoff  $W$  (water discharge normalized by catchment area, mm day<sup>-1</sup>) at  
 809 the time of sampling for the main nested catchments of this study (WAY, SP, MLC and CICRA).  
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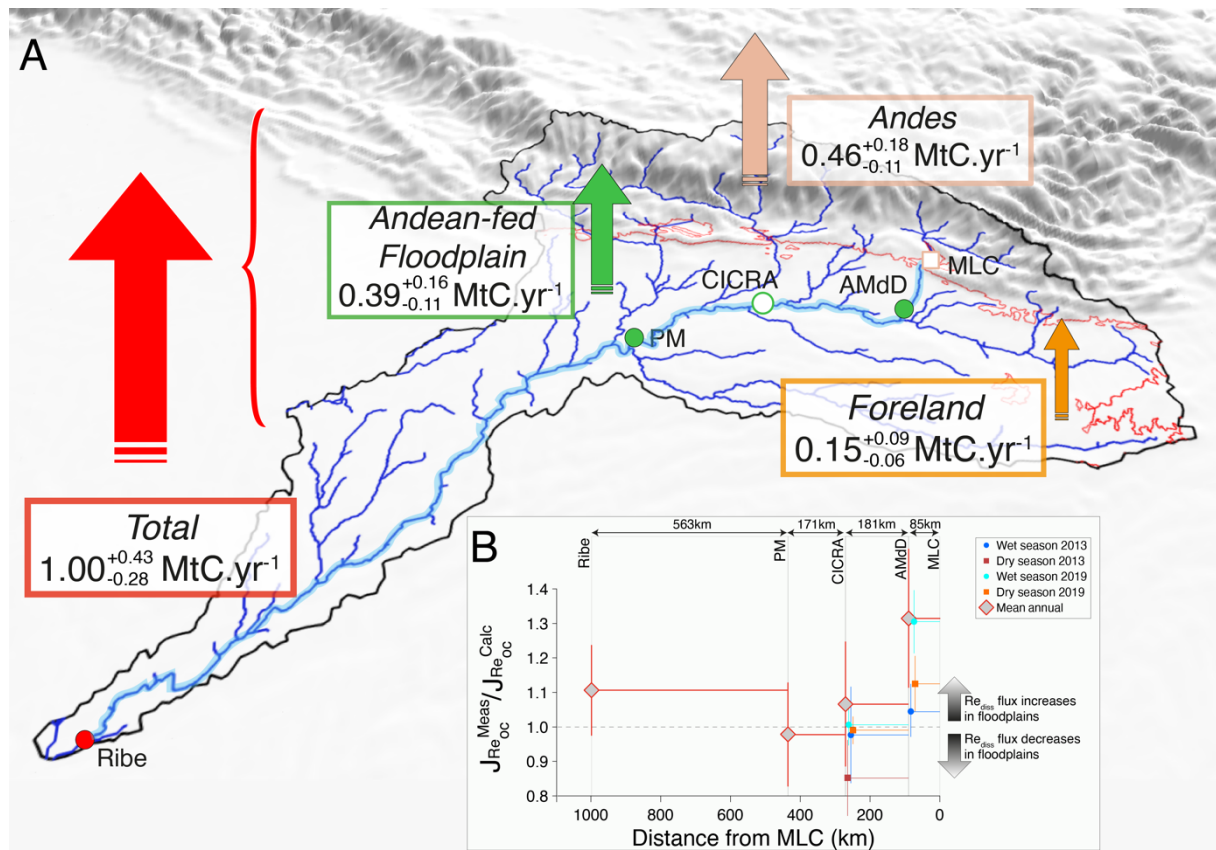
821 **Figure 2.** (A) Rhenium concentration in solids ( $[Re]_{solids}$ ): rock samples (red stars), bedloads (red box) and soils  
 822 (yellow box). The middle line in boxes is the average value, upper and lower box limits correspond to the  $\pm 2SE$   
 823 values, the upper and higher bars represent extreme data points. (B) Average  $\pm 2SE$  and extreme values of the  
 824  $[Re]/[OC]$  ratio in bedloads and rocks.  
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 851 **Figure 3.** Rhenium to sodium,  $[Re]/[Na^*]$ , and rhenium to sulfate,  $[Re]/[SO_4^*]$ , ratios ( $\text{pmol } \mu\text{mol}^{-1}$ ) for river  
 852 waters from this study (High Andes = triangles; Andean Mountain front = square; Foreland = diamond; circles =  
 853 Foreland-Floodplains). For the four nested-catchments, only the average values are represented. The red crosses  
 854 correspond to the river sediments (bedloads) and bedrocks from the Kosnipata River basin. The shaded ovals show  
 855 the ranges of elemental ratios associated with the rock weathering end-members (sulfides, silicates and  $OC_{\text{petro}}$ ).  
 856 The lines correspond to the mixing proportions between the rock weathering end-members, with the average  
 857 proportion of Re derived from  $OC_{\text{petro}}$  weathering shown (in %).

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**Figure 4.** (A) Estimated net contribution (vertical arrows) of each geomorphic zones to the total flux of  $OC_{\text{petro}}$  oxidation and associated  $CO_2$  release at the scale of the whole Madre de Dios River basin. MLC=Mountain Front, AMdD=Alto Madre de Dios, PM=Madre de Dios at Puerto Maldonado, Ribe=Madre de Dios at Riberalta. The red squiggly line corresponds to the 500m elevation. (B) Ratio between the measured dissolved rhenium flux derived from  $OC_{\text{petro}}$  oxidation ( $J_{\text{Re-OC}}^{\text{meas}}$ ) and the predicted flux ( $J_{\text{Re-OC}}^{\text{calc}}$ ) using the tributary mixing model (SI Appendix) as a function of the channel distance from MLC. A value  $>1$  can be interpreted as  $OC_{\text{petro}}$  oxidation in the floodplain. Vertical bars represent the uncertainties. This studied floodplain transect correspond to the channel highlighted in light blue on panel A.