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1 Anomalous mercury isotopic compositions of fish and human  
2 hair in the Bolivian Amazon

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20

21 **ABSTRACT** We report mercury (Hg) mass dependent isotope fractionation (MDF) and non-mass  
22 dependent isotope fractionation (NMF) in hair samples of the Bolivian Esse Ejjas native people, and in  
23 several tropical fish species that constitute their daily diet. MDF with  $\delta^{202}\text{Hg}$  ranging from  $-0.40$  to  $-$   
24  $0.92$  ‰ for fish and  $+1.04$  to  $+1.42$  ‰ for hair was observed. Hair samples of native people with a fish  
25 dominated diet are enriched by  $+2.0 \pm 0.2$  ‰ in  $\delta^{202}\text{Hg}$  relative to the fish consumed. Both odd Hg  
26 isotopes,  $^{199}\text{Hg}$  and  $^{201}\text{Hg}$ , display NMF in fish ( $-0.14$  to  $+0.38$  ‰ for  $\Delta^{201}\text{Hg}$  and  $-0.09$  to  $+0.55$  ‰ for  
27  $\Delta^{199}\text{Hg}$ ) and in hair ( $+0.12$  to  $+0.66$  ‰ for  $\Delta^{201}\text{Hg}$  and  $+0.14$  to  $+0.81$  ‰ for  $\Delta^{199}\text{Hg}$ ). No significant  
28 difference in NMF anomalies is observed between Hg in fish and in human hair, suggesting that the  
29 anomalies act as conservative source tracers between upper trophic levels of the tropical food chain.

30 Fish Hg NMF anomalies are ten-fold lower than those published for fish species from mid-  
31 latitude lakes. Grouping all Amazonian fish species per location shows that  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$  regression  
32 slopes for the clear water Itenez river basin ( $0.95 \pm 0.08$ ) are significantly lower than those for the white  
33 water Beni river basin ( $1.28 \pm 0.12$ ). Assuming that the observed NMF originates from aquatic  
34 photoreactions, this suggests limited photodemethylation of monomethylmercury (MMHg) in the Beni  
35 river floodplains and insignificant photodemethylation in the Itenez river floodplains. This is possibly  
36 related to lower residence times of MMHg in Itenez compared to Beni river floodplains. Finally,  
37 significantly negative  $\Delta^{201}\text{Hg}$  of  $-0.14$  ‰ in Beni river fish suggests that the inorganic Hg precursor to  
38 the MMHg that bioaccumulates up the foodchain defines an ecosystem specific non-zero  $\Delta^{201}\text{Hg}$   
39 baseline. Calculation of photodemethylation intensities from Hg or MMHg NMF therefore requires a  
40 baseline correction.

41

## 42 **INTRODUCTION**

43 Mercury (Hg) is a globally distributed trace metal and its biogeochemical cycle and toxicity are largely  
44 controlled by its speciation. Excessive exposure to the neurotoxic organic form of Hg,

45 monomethylmercury (MMHg) may cause problems such as trembling, eyesight problems, coordination  
46 disorders and ultimately death [1]. In the Bolivian Amazon MMHg levels ranging from 4300 to 19520  
47  $\text{ng.g}^{-1}$  in hair of native people has been linked to elevated Hg in their fish diet [2, 3]. It is formed during  
48 inorganic Hg methylation by bacterial activities and abiotic reactions in aquatic systems [4]. In Bolivia,  
49 Hg is mainly released into the aquatic system by rock weathering and soil erosion, natural sources, but  
50 mercury input is increased by anthropogenic activities such as gold-mining, deforestation and  
51 agricultural slash and burn practices [5]. Riverine Hg transport mainly involves suspended particulate  
52 matter (SPM) [6] and it is during its transfer in floodplain lakes that Hg can be methylated and  
53 bioaccumulated in the foodchain [7, 8]. Comparative studies made in the Bolivian Andes [6] have  
54 suggested that Hg content in suspended sediments increased in human impacted areas compared to  
55 pristine valleys. However, there is a need to distinguish which of these Hg sources are responsible for  
56 high MMHg concentrations in the aquatic foodchain and consequently in human hair.

57 The natural fractionation of stable isotopes in the environment has already been studied for light  
58 elements, such as H, C, N, O and S. Recent analytical advances permit determination of the isotopic  
59 composition of heavier elements, such as Hg, using multi-collector ICP-MS [9, 10]. Hg has seven stable  
60 isotopes,  $^{196}\text{Hg}$ ,  $^{198}\text{Hg}$ ,  $^{199}\text{Hg}$ ,  $^{200}\text{Hg}$ ,  $^{201}\text{Hg}$ ,  $^{202}\text{Hg}$  and  $^{204}\text{Hg}$ , which can be fractionated during physical,  
61 chemical and biological processes such as methylation, vaporization, oxidation or reduction. Thus, Hg  
62 isotopic variations may aid in the identification of sources and transformations of this element in the  
63 environment. Two types of Hg stable isotope fractionation have been documented: i. Mass dependent  
64 fractionation (MDF), which expresses the relative differences in isotope masses on kinetic and  
65 equilibrium processes of chemical reactions and phase transformations, and ii. Non-mass dependent  
66 fractionation (NMF) of the odd isotopes,  $^{199}\text{Hg}$  and  $^{201}\text{Hg}$ , possibly as a result of nuclear field shift [11]  
67 or magnetic isotope effects [12]. Observations of MDF in natural samples span a remarkably wide range  
68 of 7 ‰ on the  $\delta^{202/198}\text{Hg}$  scale [13]. Large positive NMF anomalies, *i.e.* excess odd-isotope relative to  
69 MDF, have initially been observed in fresh water fish samples [14-16] and more recently in the marine  
70 fish certified reference material ERM-CE-464 tuna fish [17], and DORM-2 and DOLT-2 dogfish [15,

71 16]. Experimental photoreduction of Hg and MMHg [15] in the presence of fulvic acids has been shown  
72 to induce NMF and suggested to be possibly responsible for the Hg isotope patterns observed in fish.  
73 Bacterial methylation in sediments has been proposed as an alternative explanation for NMF in aquatic  
74 organisms, [16] yet recent bacterial methylation experiments show MDF only [18]. Negative NMF  
75 anomalies, i.e. odd-isotope deficits, have been documented indirectly in atmospheric Hg deposition,  
76 based on lichens [19], moss, peat and soil [20, 21]. Additional negative NMF signatures have been  
77 found in coal deposits [21] and sediments [22, 23], suggesting that a significant amount of atmospheric  
78 Hg has been incorporated in these geological reservoirs. Recently, liquid Hg evaporation has been  
79 shown to induce limited NMF [24]. However, the majority of biotic and abiotic reactions studied, such  
80 as microbial reduction and demethylation, abiotic atmospheric oxidation in a volcanic plume,  
81 hydrothermal HgS ore deposition, experimental abiotic reduction, derivatization, and Hg(0)  
82 volatilization do not induce NMF but only MDF [15, 17, 25-30].

83 In this study, we document Hg MDF and NMF in hair samples of the Bolivian Esse Ejjas native  
84 people, as well as in the tropical fish species that make up their daily diet. The specific objectives are to  
85 investigate Hg NMF in fish in relation to different physicochemical and hydrological properties of  
86 Amazonian rivers and floodplains. Secondly, we investigate the Hg isotopic variations between fish  
87 tissue and human hair as a first step in evaluating Hg isotopes as a metabolic process and/or Hg  
88 exposure tracer.

89

## 90 **MATERIALS AND METHODS**

### 91 **Itenez basin fish samples**

92 Fish samples were collected from several floodplain lakes adjacent to the San Martin river (13°18' S  
93 63°36' W and 13°18' S 63°33' W) and the Blanco river (13°15' S 63°43' W) in the Itenez river basin  
94 (Figure 1), at the Bolivia-Brazil border. Two species of fish were analyzed: 6 *Pygocentrus nattereri*,  
95 also known as “pirañas”, and 4 *Pellona castelnaeana*. *P. castelneana* is a strict piscivorous species that  
96 probably locally migrates between the river and the floodplain lake. *P. nattereri* is a sedentary species

97 and considered as a voracious predator although various studies reported that it also consumed more  
98 than 30% of vegetal material [31].

### 99 **Beni basin fish and hair samples**

100 Beni basin fish samples were caught in the Beni river at Puerto Salinas (14°15' S 67°30' W) and  
101 20 km downstream of the city of Rurrenabaque, in the Granja floodplain lake (14°16' S 67°28' W),  
102 regularly connected to the Beni river during periods of rising water and at the flood peak (Figure 1).  
103 Three fish species were analyzed: 9 *Pseudoplatystoma fasciatum*, locally named “surubi”, was obtained  
104 from both locations, while 5 *P. nattereri* and 6 *Salminus brasiliensis*, both sedentary and carnivorous  
105 species, were collected from the Granja floodplain lake only. *P. fasciatum* is a strict piscivorous and  
106 migratory species, often exhibiting the highest concentrations in Hg<sub>T</sub> [6] and one of the main fish  
107 species eaten by the local population. Hair of indigenous people was sampled in two different Esse Ejjas  
108 communities living along the banks of the Beni River: the community of Villa Copacabana (population  
109 A; 14°26' S 67°29' W) in 1998 (7 samples), and a family at Eyiyoquibo (population B; 14°25' S 67°33'  
110 W) in 2007 (7 samples) (Figure 1). Population A has an exclusive fish diet and leads a migratory  
111 existence along the Beni river limiting their contacts with the developed cities in the area, population B  
112 is permanently based in their village, practice limited agriculture, and are closer to the nearest town  
113 (Rurrenabaque: 30 min by direct road). Population B diet is consequently more diversified and besides  
114 fish includes fruits, rice, manioc, bread and meat.

### 115 **Analytical methods**

116 Total Hg concentrations (Hg<sub>T</sub>) were measured by atomic absorption after combustion and gold-trapping  
117 with a Milestone DMA-80. Isotopic analyses were performed at the Laboratoire des Mécanismes et  
118 Transferts en Géologie (Toulouse; France) by cold vapor multi-collector inductively coupled plasma  
119 mass spectrometer MC-ICP-MS (Thermo-Fisher Neptune). See reference [32] for details. Mass-bias  
120 was corrected with the exponential law, using Tl as internal standard by bracketing samples with NIST  
121 3133. Isotopic compositions are expressed in delta notation as follows

$$\delta^{x/198} = \left( \frac{{}^x\text{Hg}/{}^{198}\text{Hg}_{\text{sample}}}{({}^x\text{Hg}/{}^{198}\text{Hg}_{\text{NIST 3133 -1}} + {}^x\text{Hg}/{}^{198}\text{Hg}_{\text{NIST 3133 -2}}) / 2} - 1 \right) * 1000$$

122  
 123 where x is the isotope number, and the standard 1 is analyzed before the sample and standard 2 after the  
 124 sample. The reference material NIST 3133 used as a bracketing standard was at the same  $\text{Hg}_T$  and acid  
 125 concentrations as samples. Blank signals were typically below 1 % of those of samples. Non-mass  
 126 dependent fractionation is reported in "capital delta" notation as the difference between the measured  
 127  $\delta^{x/198}$  and the theoretically predicted  $\delta^{x/198}$  value using the relationship [33]:

$$\Delta^{x/198}\text{Hg} = \delta^{x/198}\text{Hg} - \beta * \delta^{202/198}\text{Hg}$$

128  
 129 where  $\beta$  is the equilibrium mass-dependent fractionation factor. Details on reference materials analyzed  
 130 and analysis uncertainties by DMA-80 and MC-ICP-MS can be found in the Supplementary Information  
 131 (SI).

132

## 133 **RESULTS AND DISCUSSION**

### 134 **Hg analyses in fish**

135 The  $\text{Hg}_T$  concentrations of freeze-dried *P. naterreri* and *P. castelnaena* samples from the Itenez river  
 136 basin range from 467-1140  $\text{ng.g}^{-1}$  and 706-1085  $\text{ng.g}^{-1}$  dry mass (d.m.), respectively (Table S1-S1). The  
 137  $\text{Hg}_T$  concentrations of the corresponding fresh-frozen samples range from 95-249  $\text{ng.g}^{-1}$  and 163-232  
 138  $\text{ng.g}^{-1}$  wet mass (w.m.) respectively, and are linearly correlated (slope = 3.78,  $r^2 = 0.99$ ,  $n = 24$ ) with  
 139 freeze-dried  $\text{Hg}_T$ . Mass loss of the fish samples upon freeze-drying was 70 %, which is consistent with  
 140 the wet and dry mass  $\text{Hg}_T$  concentration ratios. Variations in  $\delta^{202}\text{Hg}$  and  $\delta^{200}\text{Hg}$ , with  $\delta^{202}\text{Hg}$  ranging  
 141 from -0.70 to -0.40 ‰ are consistent with MDF (Figure S1-S1, Table S1-S1). Significant NMF was  
 142 observed for both odd isotopes, with  $\Delta^{199}\text{Hg}$  of +0.04 ‰ to +0.35 ‰ and  $\Delta^{201}\text{Hg}$  of +0.15 ‰ to +0.35  
 143 ‰ (Figure S1-S1).

144 The  $\text{Hg}_T$  concentrations of *P. fasciatum*, *P. naterreri* and *S. brasiliensis* fish samples from the Beni river  
 145 range from 1597 to 10315  $\text{ng.g}^{-1}$ , from 2376 to 9584  $\text{ng.g}^{-1}$  and from 1668 to 6458  $\text{ng.g}^{-1}$  dry mass,

146 respectively (Table S1-S1). Even for carnivorous or piscivorous species feeding at the upper trophic  
147 levels of the aquatic foodchain, these  $Hg_T$  levels are extremely elevated and easily exceed the EPA  
148 consumption limit [34] of  $100 \text{ ng.g}^{-1}.\text{d}^{-1}$  wet mass, corresponding to  $333 \text{ ng.g}^{-1}.\text{d}^{-1}$  dry mass for the  
149 muscles of consumed predator fish.

150 *P. fasciatum*, *P. naterreri* and *S. brasiliensis* of the Granja floodplain lake (Beni river) are  
151 characterized by  $\delta^{202}\text{Hg}$  values ranging from  $-0.92$  to  $-0.61$  ‰, from  $-0.61$  to  $-0.40$  ‰ and from  $-0.63$   
152 to  $-0.45$  ‰ respectively (Figure 2). In addition, significant odd isotope NMF is observed with  $\Delta^{199}\text{Hg}$   
153 and  $\Delta^{201}\text{Hg}$  values ranging from  $+0.36$  to  $+0.55$  ‰ and  $+0.24$  to  $+0.38$  ‰, respectively. The  $\delta^{202}\text{Hg}$   
154 values of *P. fasciatum* of the Beni river at Puerto Salinas range from  $-0.79$  to  $-0.59$  ‰, the  $\Delta^{199}\text{Hg}$   
155 values from  $-0.09$  to  $+0.27$  ‰ and the  $\Delta^{201}\text{Hg}$  values from  $-0.14$  to  $+0.19$  ‰.  $\delta^{202}\text{Hg}$  values for the  
156 pelagic *P. naterreri* ( $P = 0.74$ ) species are not significantly different between the Itenez and Beni river  
157 basins. In the Granja floodplain lake, the  $\delta^{202}\text{Hg}$  values between *P. naterreri* and *P. fasciatum* as well as  
158 between *S. brasiliensis* and *P. fasciatum* are significantly different ( $P = 0.003$  and  $P = 0.01$  respectively)  
159 but not between *P. naterreri* and *S. brasiliensis* ( $P = 0.54$ ). This may relate to different ecological  
160 factors such as foraging behavior (*P. naterreri* is pelagic while *P. fasciatum* and *S. brasiliensis* is  
161 benthopelagic species) and to trophic levels. The  $\Delta^{201}\text{Hg}$  values are not significantly different among the  
162 three Granja floodplain lake species. However, the  $\delta^{202}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  for *P. fasciatum* from the Beni  
163 river at Puerto Salinas are significantly lower than those from the Granja floodplain lake ( $P = 0.03$  and  $P$   
164  $= 0.013$  respectively).

### 165 **Hg NMF in fish**

166 Anomalies of the odd Hg isotopes have been related to both nuclear field shift (NFS) and magnetic  
167 isotope effects (MIE) [12, 35]. NFS induced anomalies depend on nuclear volume and shape properties,  
168 parameterized by the nuclear charge radius of individual isotopes. NFS isotopic fractionation has been  
169 estimated to induce a  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$  ratio between 2 and 3 depending on the choice of experimentally  
170 determined nuclear charge radii [20, 24, 36]. Experimental  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$  linear regression slopes of



171 1.00 for photoreduction of Hg(II) and of 1.36 for photodemethylation of MMHg, both in the presence of  
172 fulvic acids, have been reported and have been suggested to result from MIE effects [15].  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$   
173  $\Delta^{201}\text{Hg}$  ratios may therefore be a powerful means to distinguish NFS from MIE, as well as to identify  
174 different MIE inducing reactions. Bergquist and Blum [15] have shown that temperate lake fish samples  
175 containing predominantly MMHg have  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  up to +4.97 ‰ with a  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$   
176 regression slope of  $1.28 \pm 0.03$  (2 SE standard error). The similarity between MMHg photoreduction  
177 and fish MMHg  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$  ratios have led them to suggest that photochemical demethylation is  
178 the cause of Hg NMF observed in fish. Jackson *et al.* [16] have also observed positive Hg NMF  
179 anomalies ( $\Delta^{199}\text{Hg}$  up to +5.2 ‰) in crustaceans and fish from three Canadian lakes (Ontario, Shipikan  
180 and Cli) and have suggested bacterial methylation in sediments to be the main NMF inducing process.  
181 Recent bacterial methylation experiments however have only shown MDF and no NMF [18]. In  
182 addition, experimental works including biochemical reactions such as bacterial Hg(II) reduction and  
183 MMHg demethylation have shown complete absence of NMF [26, 27, 37] and theoretical  
184 considerations on biochemical radical chemistry have also indicated the unlikeliness of biochemical  
185 NMF [37, 38]. Therefore, we interpret our observed anomalies in Amazonian fish in the context of  
186 photochemical Hg and MMHg reduction, the only relevant process that has been shown to induce  
187 substantial NMF. Our observations (Figure 3) on tropical freshwater fish show similarities as well as  
188 differences with Bergquist and Blum's and Jackson *et al.*'s., temperate and boreal lake studies: i)  $\Delta^{201}\text{Hg}$   
189 values of tropical fish are lower (maximum of +0.38 ‰) than those observed in temperate freshwater  
190 (+3.89 ‰, [15]) and marine fish (+2.18 ‰, [17]), ii) several tropical fish carry limited, but significantly,  
191 negative  $\Delta^{201}\text{Hg}$  values down to -0.14 ‰, and iii) the ensemble of Beni river and floodplain lake fish  
192 species exhibits a  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$  slope of  $1.28 \pm 0.12$  (2 SD) (Figure 3,  $r^2 = 0.99$ ,  $n = 20$ ), similar to  
193 the mid-latitude lakes study [15].

#### 194 **Ecosystem specific Hg NMF baselines**

195 Itenez basin fish species show a lower  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$  slope of  $0.95 \pm 0.08$  (2 SD) ( $r^2 = 0.99$ ,  $n = 10$ )  
196 that is similar to the slope of 1.0 accompanying inorganic Hg photoreduction [15]. The negative  $\Delta^{201}\text{Hg}$   
197 values in fish suggest however that newly methylated Hg may have inherited anomalies i.e. the  
198 inorganic Hg precursor to MMHg already possessed a small but significant  $\Delta^{201}\text{Hg}$  anomaly  $\leq -0.14$  ‰.  
199 Supporting evidence for such an ecosystem specific negative baseline is provided by overbank sediment  
200  $\Delta^{201}\text{Hg}$  signatures of  $-0.15 \pm 0.10$  ‰ (2 SD) from the adjacent Mamore river basin which also drains the  
201 Andean cordillera [22]. It has been suggested that Hg NMF in fish can be used to calculate net  
202 photochemical demethylation extents. If we assume (as in ref. [15]) that i) the  $\Delta^{201}\text{Hg}$  baseline is 0 ‰,  
203 ii) that photodemethylation only takes place in water, and iii) that a  $\Delta^{201}\text{Hg}$  fractionation factor  
204  $10^3 \ln \alpha_{\text{Hg}(II)-\text{Hg}(0)}^{\Delta^{201}\text{Hg}}$  of 1.0057 corresponding to an experimental fulvic acid concentration of 10 mg C/L  
205 applies (supporting online information of ref. [15]), then the maximum  $\Delta^{201}\text{Hg}$  of +0.38 ‰ in Granja  
206 floodplain lake fish indicates MMHg losses via photoreduction of 5 ‰. On the contrary, if we assume  
207 that the Beni river  $\Delta^{201}\text{Hg}$  baseline is at least  $-0.14$  ‰, the calculated MMHg loss increases to 8 ‰.  
208 Despite the importance of a baseline correction, the largest uncertainty in the photodemethylation  
209 calculation remains the uncertainty of the NMF fractionation factor. Overall, photodemethylation in  
210 tropical floodplain lakes appears to be one order of magnitude less intense than in the cited mid-latitude  
211 lakes.

212 The negative sign of the Beni/Mamore Andean  $\Delta^{201}\text{Hg}$  baseline may suggest that a fraction of  
213 inorganic Hg, before being methylated, has already cycled through the atmosphere during a previous  
214 photoreductive process. It is well known that soils act as net sinks for atmospheric Hg deposition [39],  
215 Recent studies on the Hg isotopic composition of lichens, moss and peat suggest that atmospheric Hg  
216 deposition carries large negative  $\Delta^{201}\text{Hg}$ , down to  $-1.0$  ‰ [19-21]. Our suggestion then implies that  
217 Andean soils have acquired a small  $\Delta^{201}\text{Hg}$  of  $-0.14$  ‰ by mixing of non-anomalous bedrock Hg with  
218 negative anomalous atmospheric deposition. This soil Hg pool has subsequently been mobilized by  
219 weathering processes and deposited in the Amazon floodplains, sites of Hg methylation.

220

## 221 **Aquatic photoreduction of inorganic Hg and MMHg**

222 The  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$  slope of 0.95 for the clear water Itenez basin suggest that the MMHg carrying  
223 these NMF anomalies did not undergo significant photochemical demethylation. In addition, it may be  
224 possible that the inorganic Hg source for the Itenez fish MMHg did undergo photochemical reduction to  
225 acquire the range of positive  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  values on the  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$  slope of 0.95. The  
226 variation in Itenez fish  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  along the slope 0.95 line then reflects either i) a constant  
227 inorganic mercury  $\Delta^{199}\text{Hg} = \Delta^{201}\text{Hg}$  baseline, modified by local variations in inorganic Hg  
228 photoreduction, ii) mixing of MMHg produced from inorganic Hg reservoirs with variable  $\Delta^{199}\text{Hg} =$   
229  $\Delta^{201}\text{Hg}$  baselines between 0 and +0.5 ‰, or iii) different photodemethylation processes in tropical  
230 ecosystem resulting in different  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$  relationships than have been thus far observed.  
231 Variable positive baselines may have been induced over geological times, based on recent evidence of  
232 NMF signatures in geological reservoirs. Hydrothermal deposit  $\Delta^{199}\text{Hg}$  of up to +0.27 ‰ were observed  
233 in the Yellowstone hydrothermal field [40]. Of ultimate interest here is an explanation as to why  
234 photochemical demethylation result in different  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$  slopes in the Beni and the Itenez basin.  
235 In addition to this, within the Beni basin, fish NMF anomalies in the Granja floodplain lake are higher  
236 (+0.24 to +0.38 ‰ for  $\Delta^{201}\text{Hg}$ ) than in the Beni mainstream (-0.14 to +0.19 ‰ for  $\Delta^{201}\text{Hg}$ ) suggesting  
237 that MMHg photodemethylation mostly takes place in the floodplain lake. A qualitative explanation for  
238 these two observations may relate to the influence of regional geology and associated river water  
239 chemistry, and the hydrodynamics of the river-floodplain systems.

240 The observation of intensified MMHg photodemethylation in the floodplain lake correlates  
241 qualitatively with increased DOC levels (Beni river, 1-5 mg.L<sup>-1</sup>; Granja floodplain lake, 1-20 mg.L<sup>-1</sup>),  
242 increased water residence times and higher SPM (Granja floodplain lake, 8 – 1050 mg.L<sup>-1</sup> SPM with an  
243 average value of 100 mg.L<sup>-1</sup>; Beni river, 40 - 6300 mg.L<sup>-1</sup> SPM with an average value of 1400 mg.L<sup>-1</sup>).  
244 This is consistent with experimental studies that have showed that both  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  NMF

245 anomalies increase with DOC [15], and with the general notion that photoreduction rates are first order  
246 in light intensity [15, 41].

247 The inter-basin differences in floodplain lake MMHg photodemethylation involve differences in water  
248 chemistry. The Itenez river, similar to the Brazilian Tapajós river, drains the Pre-Cambrian shield with  
249 typically low SPM (1-227 mg.L<sup>-1</sup>). The Beni river, which drains the younger Andean cordillera, is a  
250 white water river with higher SPM (40 - 6300 mg.L<sup>-1</sup>) and dissolved solids. No difference was observed  
251 in net Hg methylation in periphyton between clear and white water floodplain lakes of the Amazon  
252 basin [42]. Moreover, DOC levels are not significantly different between the Granja floodplain lake (4.5  
253 mg.L<sup>-1</sup>) and the studied Itenez floodplain lakes (7.5 mg.L<sup>-1</sup>). The Granja floodplain lake area (0.90 km<sup>2</sup>)  
254 is approximately one order of magnitude larger than the Itenez floodplains (0.05 to 0.14 km<sup>2</sup>), for the  
255 same distance between floodplain lake and river, and the associated residence time of aqueous MMHg is  
256 probably higher in the Granja floodplain lake than in the Itenez floodplains. Given the difficulty in  
257 explaining all river and floodplain observations based on variations in SPM and DOC, we propose here  
258 that the aquatic MMHg residence time in a given water body is perhaps one of the key parameters in  
259 determining the evolution of Hg and MMHg NMF. MMHg residence times in the smaller Itenez  
260 floodplains are then insufficient to produce significant anomalies *via* photochemical demethylation. It is  
261 highly likely that the large MMHg NMF anomalies of +4.97 ‰ observed in Lake Michigan are due to  
262 the long MMHg residence time of approximately 72 years [43]. Finally, it should be noted that Hg(II)  
263 photoreduction by formic acid, a simple carboxylic acid, led to MDF but not NMF [29]. Clearly, our  
264 mechanistic understanding of photochemical NMF by MIE is insufficient, and more work is needed to  
265 map out the role of Hg complexation sites and chromophoric properties of organic ligands on Hg NMF,  
266 and in particular on the possible range  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$  ratios.

267

### 268 **Hg MDF and NMF in hair samples**

269 Hg<sub>T</sub> concentrations in hair of indigenous people, who have a daily fish diet, are elevated: from 6300 to  
270 23701 ng.g<sup>-1</sup> (Table S1-S1). The hair  $\delta^{202}\text{Hg}$  of native people living in Villa Copacabana (population A)

271 averages  $+1.15 \pm 0.16 \text{ ‰}$  (2 SD,  $n = 6$ ) and odd isotopes of Hg present positive anomalies of  $+0.19 \pm$   
272  $0.06 \text{ ‰}$  for  $\Delta^{199}\text{Hg}$  and  $+0.12 \pm 0.08 \text{ ‰}$  for  $\Delta^{201}\text{Hg}$  (2 SD,  $n = 6$ ). The hair  $\delta^{202}\text{Hg}$  of native people  
273 living in Eyiyoquibo (population B, all belonging to the same family), ranges from  $+1.04$  to  $+1.42 \text{ ‰}$   
274 and the odd isotope anomalies range from  $+0.25$  to  $+0.81 \text{ ‰}$  for  $\Delta^{199}\text{Hg}$  and from  $+0.15$  to  $+0.66 \text{ ‰}$  for  
275  $\Delta^{201}\text{Hg}$ . Both MDF and NMF signatures of hair of population A are remarkably homogeneous and  
276 reflect identical diet, mobility, and/or consanguinity. Whereas population A has an exclusive fish diet,  
277 population B diet is more diversified due to their proximity to the city of Rurrenabaque.  $\Delta^{201}\text{Hg}$  changes  
278 with age in population B (Figure 4), with the youngest people having the highest anomalies. In  
279 population A, this relationship was not observed, but  $\text{Hg}_T$  concentrations are also much higher than  $\text{Hg}_T$   
280 concentrations of population B, presumably due to exclusive fish diet. At present it is not possible to  
281 offer a conclusive interpretation for this age vs.  $\Delta^{201}\text{Hg}$  trend in the population B. Biochemical Hg  
282 NMF, in the form of bacterial methylation, has previously been suggested to contribute to Hg NMF  
283 observed in aquatic organisms [16]. Without well-constrained experimental evidence on non-  
284 photochemical, i.e. biochemical Hg NMF, we suggest that the observed  $\Delta^{201}\text{Hg}$  variation in population  
285 B is more likely due to i) dietary diversification, i.e. children of population B eat different food with  
286 different  $\Delta^{201}\text{Hg}$  than adults; in particular recent food aid programs to the Eyiyoquibo community in the  
287 form of conserved marine fish (sardines, tuna), which is known to have high  $\Delta^{201}\text{Hg}$  [15-17], may have  
288 shifted children's  $\Delta^{201}\text{Hg}$  to higher values than adults; and ii) a potential contamination of children from  
289 recent government vaccination programs. Some vaccines are known to be still stabilized with  
290 ethylmercury and only delivered to babies and young children [44]. The exact nature of a high  $\Delta^{201}\text{Hg}$   
291 food source requires further investigation.

292 A student t-test on  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  shows that the average anomalies of all analyzed Esse Ejjas  
293 hair are not significantly different from those of their main fish diet represented by *P. fasciatum*  
294 (respectively  $P = 0.525$  and  $P = 0.349$ ). In addition, the slope of  $\Delta^{199}\text{Hg} : \Delta^{201}\text{Hg}$  for hair is  $1.16 \pm 0.04$   
295 (2 SD) (Figure 3, excluding one outlier) which is not significantly different from the slope defined by

296 Beni basin fish (slope of  $1.28 \pm 0.12$ ):  $P = 0.11$  (ANCOVA test). NMF anomalies therefore appear to act  
297 as conservative source tracers for dietary MMHg exposure. In contrast,  $\delta^{202}\text{Hg}$  of Esse Ejjas hair are  
298 enriched in heavy isotopes by  $+2.0 \pm 0.2$  ‰ relative to *P. fasciatum*, suggesting that substantial MDF  
299 takes place during MMHg human metabolism. Excretion in faeces of light isotopes of Hg is one  
300 possible way, yet other metabolic reactions such as demethylation or blood-hair transfer should not be  
301 excluded. The direction of fractionation is similar to that for the lighter elements C, and N, which are  
302 typically enriched by several ‰ per trophic level increase. As humans and *P. fasciatum* define  
303 approximately one trophic level difference, MMHg metabolism is potentially accompanied by  $\sim +2$  ‰  
304 per trophic level enrichment of heavier Hg isotopes in  $\delta^{202}\text{Hg}$ . The striking similarity in population B  
305  $\delta^{202}\text{Hg}$  (and  $\Delta^{201}\text{Hg}$ ) compositions, despite a much larger variation in Beni basin *P. fasciatum*  $\delta^{202}\text{Hg}$   
306 (and  $\Delta^{201}\text{Hg}$ ) suggests that the metabolic process responsible for the large MDF does not vary much  
307 from one individual to another. If this is valid for MMHg metabolism in humans in general, then a  $+2.0$   
308  $\pm 0.2$  ‰ correction may be applied to human hair  $\delta^{202}\text{Hg}$  to find the average dietary MMHg  $\delta^{202}\text{Hg}$   
309 signature. Such an approach may be of use in future human MMHg exposure studies.

310

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319

320 **Supporting Information available**

321 Detailed study area and detailed experimental including sample treatment prior to analysis, analytical  
322 methods and delta values.

323

324

325 **References**

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458 **Figures**

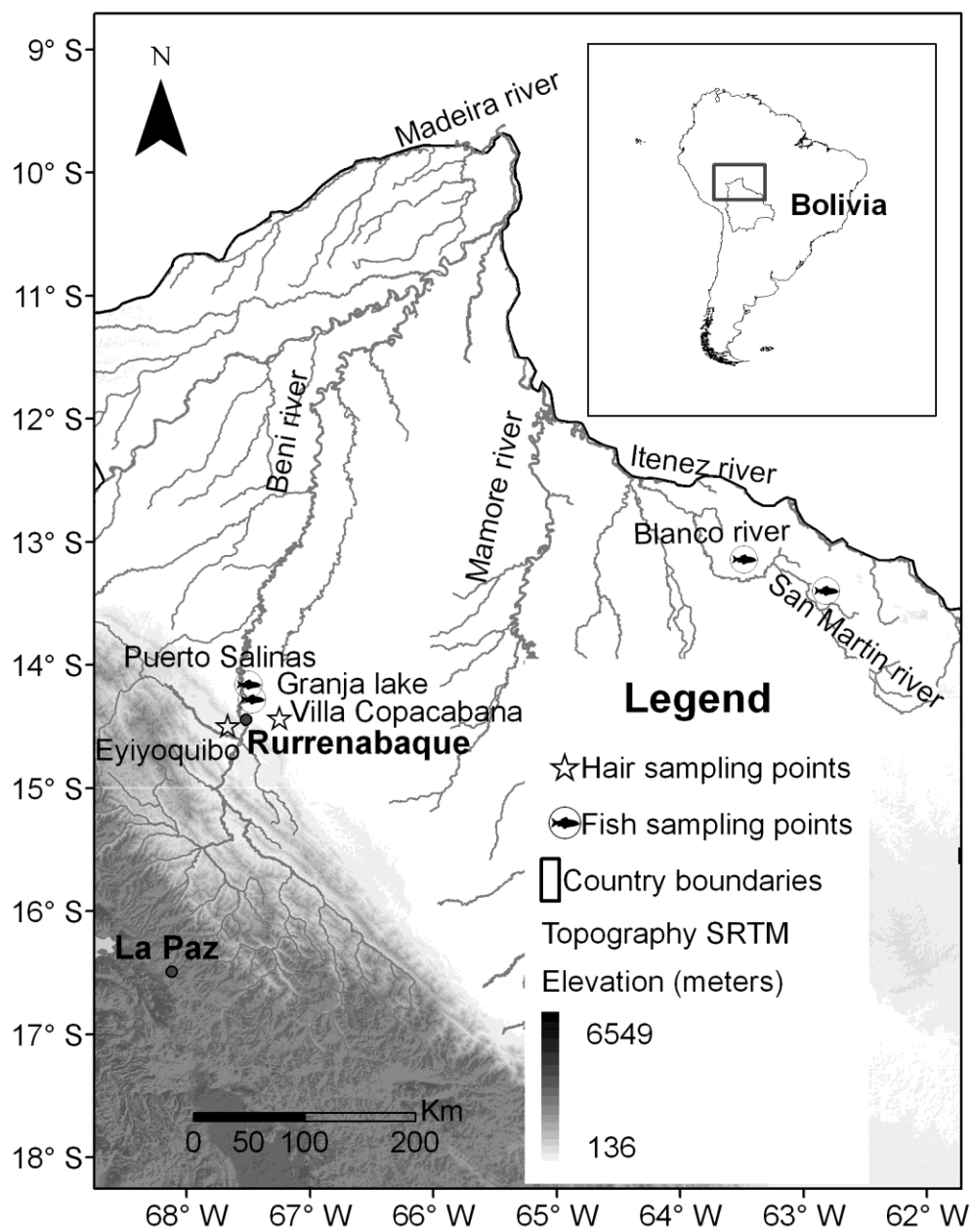
459 **Figure 1.** Study area and location of hair and fish sampling points.

460 **Figure 2.** NMF anomaly  $\Delta^{201}\text{Hg}$  plotted as a function of  $\delta^{202}\text{Hg}$  in fish and hair samples collected in the  
461 Beni river basin: *Pseudoplastyma fasciatum*, *Pygocentrus nattereri* and *Salminus brasiliensis* from  
462 Puerto Salinas (A) and Granja floodplain lake (B), native people, Esse Ejjas, hair from Villa  
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464 and *Pellona castelnaeana* (C). Error bars represent external reproducibility (2 SD). Human hair  $\delta^{202}\text{Hg}$   
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468 **Figure 3.** Linear correlations between  $\Delta^{199}\text{Hg}$  and  $\Delta^{201}\text{Hg}$  (‰) for: (A) fish samples from two basins:  
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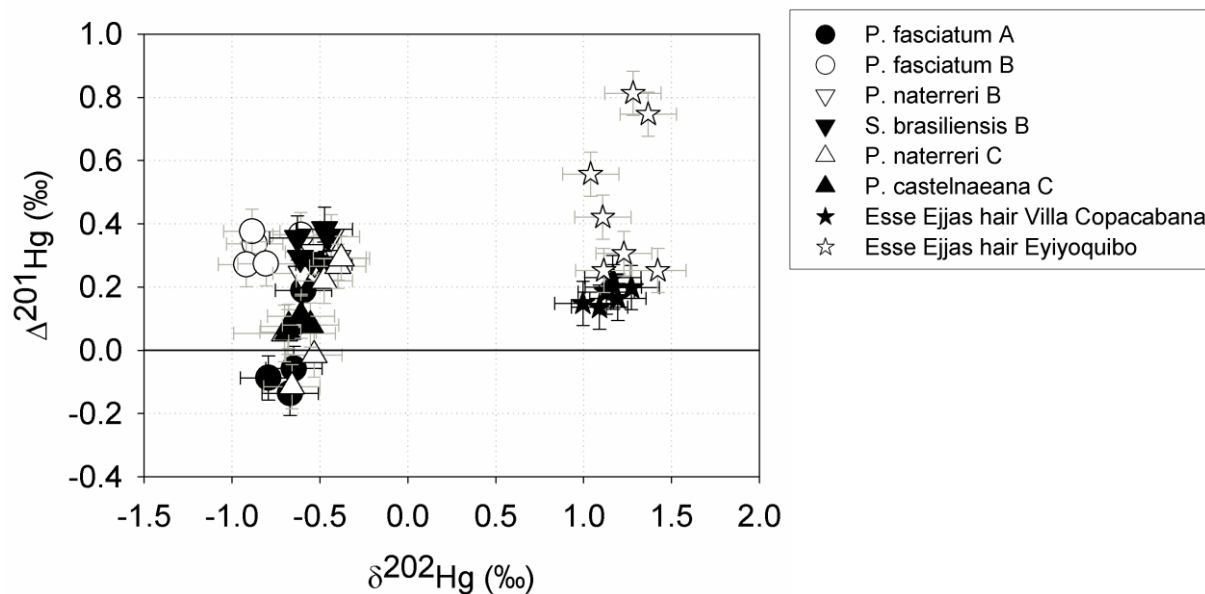
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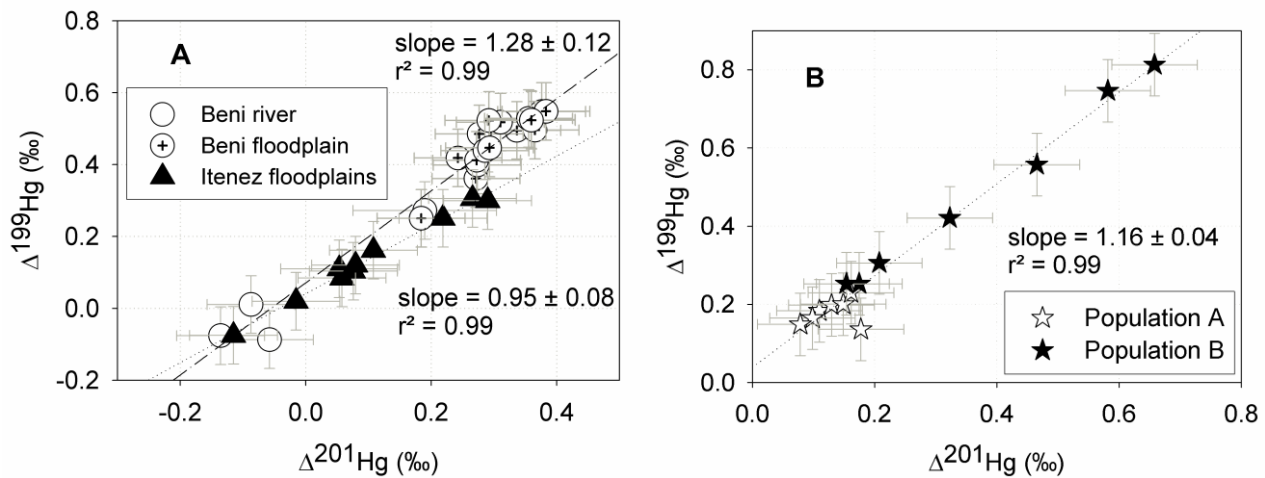
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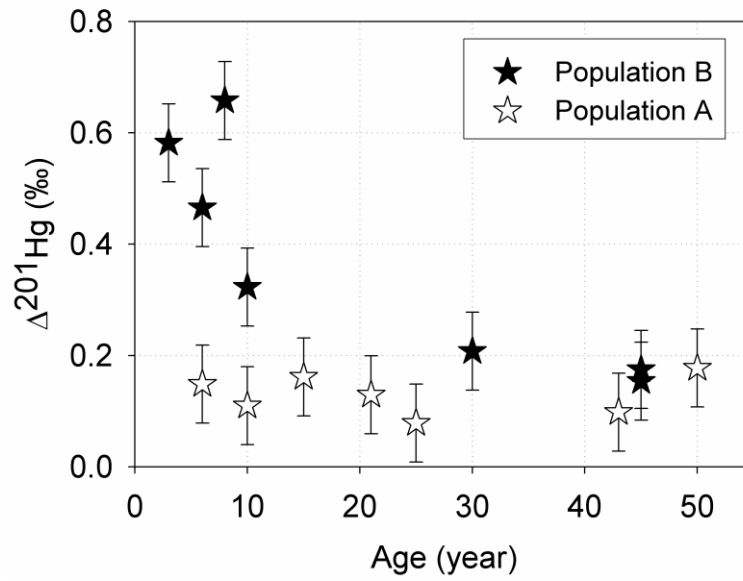
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537	<b>Table of Contents Brief:</b> Hg non-mass dependent fractionation evidence in hair samples of the
538	Bolivian Esse Ejjas native people and in tropical fish species that constitute their daily diet.
539	