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Control of seasonal and inter-annual rainfall distribution on the Strontium-Neodymium isotopic compositions of suspended particulate matter and implications for tracing ENSO events in the Pacific coast (Tumbes basin, Peru)

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1 **Control of seasonal and inter-annual rainfall distribution on the Strontium-Neodymium**
2 **isotopic compositions of suspended particulate matter and implications for tracing**
3 **ENSO events in the Pacific coast (Tumbes basin, Peru)**

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22

23 **Keywords :**

24 River, Andes, Pacific basin, Sr and Nd radiogenic isotopes, suspended sediments, hydrology.

25

26 **Highlights**

- 27 ✓ Suspended sediments were sampled monthly in the Tumbes River along 2 hydrological years
- 28 ✓ ϵNd signatures indicates source provenance in relation with rainfall distribution
- 29 ✓ $^{87}\text{Sr}/^{86}\text{Sr}$ signatures is particularly sensitive to anomalous wet conditions
- 30 ✓ Nd and Sr isotopes are powerful tracers of paleo-ENSO and sediments dynamics

31

32 **Abstract:**

33 The geochemistry of riverine sediments exported to the oceans is important for paleo-
34 hydro-climatic reconstruction. However, climate reconstruction requires a good understanding
35 of the relationship between geochemistry and hydrological variability and sediment sources. In
36 this study, we analyzed the major elements, the strontium-neodymium radiogenic isotopes
37 signatures ($^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd) and the mineralogy of the suspended particulate matter (SPM)
38 sampled monthly during two hydrologic years (2007-2008, a wet year, and 2010-2011, a normal
39 hydrological year) upstream the Tumbes River outlet. The hydroclimate of this Ecuador-Peru
40 binational basin is particularly sensitive to ENSO (El Niño Southern Oscillation) events.

41 While mineralogy (dominated by illite) and the chemical alteration index (from 75 to
42 82) remain almost constant along the two hydrological years, $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7115 to 0.7176) and
43 ϵNd (-7.8 to -1.9) signatures are particularly sensitive to discharge and SPM concentration
44 variations. Along the hydrological year, two sources control the ϵNd variability : (1) volcanic
45 rocks, which dominate during the dry season, and (2) plutonic/metamorphic sources, whose
46 contribution increases during the wet season. This behavior is confirmed by the correlation
47 between ϵNd signature and the monthly rainfall contribution from volcanic area ($R=0.58$; p-
48 value <0.01), and also with the daily discharge at the outlet ($R=-0.73$; p-value <0.01). For most
49 of the samples, $^{87}\text{Sr}/^{86}\text{Sr}$ is less variable along the hydrological year. However, two exceptional
50 high discharge and SPM concentration conditions sampled exhibit more radiogenic (higher)

51 $^{87}\text{Sr}/^{86}\text{Sr}$ signatures when plutonic/metamorphic rocks derived sediments are released in
52 sufficient quantities to notably change the SPM isotopic Sr value of the Tumbes River.

53 Hence, this study demonstrates that $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd signatures can be used as
54 powerful proxies for paleoclimate reconstructions based on sediment core's analysis in relation
55 with spatial rainfall distribution and intensity in Pacific sedimentary basins submitted to the
56 diversity of ENSO events.

57

58 **1. Introduction**

59 The hydrological and hydro-sedimentological regime of the Andes are particularly
60 sensitive to extreme hydrological events like those related to the El Niño Southern Oscillation
61 (ENSO) system. The El Niño and its counterpart, La Niña (the two expressions of the ENSO)
62 are drivers of the strongest year-to-year climate fluctuations on the planet. They control the
63 hydrology and sediment production in Andean basins residing both along the Pacific coast
64 (Sulca et al., 2018; Rau et al., 2017; Lavado and Espinoza, 2014, Armijos et al., 2013) and in
65 Amazonian slopes (Espinoza et al., 2012). These events have been responsible for extreme
66 flooding in Pacific coastal areas (particularly in Northern Peru and in Ecuador) and droughts in
67 the Andes and in the Amazon region (Lavado and Espinoza, 2014; Sulca et al., 2018; Espinoza
68 et al., 2011). Importantly, the two main El Niño events of the last 40 years account for around
69 45% of the sedimentary flux exported to northern Peru Pacific Ocean (Moreira et al., 2017).
70 However, ENSO events present a large diversity associated with their tropical Pacific Sea
71 Surface Temperature (SST) anomaly patterns (e.g. Capotondi et al, 2015) and the variability
72 of these patterns can affect even the sign (positive or negative) of the precipitation anomalies
73 in northern Peru (Lavado and Espinoza 2014; Sulca et al 2018). Thus, predicting the impact of
74 extreme hydrological events associated with ENSO remains difficult because of the relatively
75 short time-scale of hydrological and riverine suspended matter export monitoring.

76 The reconstruction of paleo-ENSO events is necessary to understand the main forcing
77 on these events from the Pliocene (e.g. Wara et al., 2005) to Quaternary timescale, including
78 the Holocene (e.g. Carré et al., 2012). Paleo ENSO events have been identified in
79 onshore/continental geological record based on oxygen stable isotope compositions of
80 speleothems (e.g. Bustamente et al., 2016), authigenic calcite lake sediment cores (Bird et al.,
81 2011) and ice cores from the Ecuadorian and Peruvian Andes (e.g. Thompson et al., 2013). In
82 all of these studies, most of the geochemical tracers used to reconstruct paleo ENSO events in
83 the geological record were aimed at the identification of temperature (oceanic cores) or
84 precipitation (lake cores, speleothems, ice cores) anomalies based on stable isotope
85 geochemistry. To date, there has been little attempts to reconstruct paleo ENSO events based
86 on the identification of peak sediment fluxes linked to rainfall increase in the Andean coast,
87 which can be reflected in the sedimentary record by changes in the provenance of the associated
88 sediments. For instance, change in provenance based on Nd isotopic composition of the detrital
89 sediment fraction during the past 45,000 years have been used to reconstruct climate-driven
90 changes in the provenance of clays deposited along the Mozambique Margin (van der Lubbe et
91 al., 2016). Similarly, changes in the provenance of sediments deposited along the tropical South
92 American continental margin between Andes and shield regions, identified based on Nd-Sr
93 isotopic composition variations, were also used for reconstructing both erosional and associated
94 rainfall patterns on continental source regions during the Quaternary (e.g. Höppner et al., 2018).
95 Even more recently, variation of Nd isotopic composition of Amazon River suspended
96 particulate material (hereafter designated as “SPM”) during a one year hydrological cycle has
97 been related to seasonal changes in the rainfall distribution patterns across the Amazon basin
98 that are associated with latitudinal migrations of the Intertropical Convergence Zone (Rousseau
99 et al., 2019). The relationship between long-term (Holocene) climate change and changing
100 hydrology and sediment sources using Sr and Nd has been studied in the Nile basin (Woodward

101 et al., 2015). This work illustrates the benefits of using Sr and Nd isotopes in tandem to tease
102 out changes in catchment runoff and sediment delivery. However we have only identified 3
103 studies exploring Sr and Nd isotopes modern SPM variability along a hydrological year (Viers
104 et al., 2008; Mao et al., 2011; Rousseau et al., 2019). These studies reported significant
105 variability of the Sr and Nd signatures along the hydrological year. While ϵNd appears to mainly
106 trace the lithological composition of the SPM source, $^{87}\text{Sr}/^{86}\text{Sr}$ can track both the SPM source
107 (Mao et al., 2011) and grain size sorting effects due to either erosional processes (Viers et al.,
108 2008) or hydrodynamical floodplain sorting behavior (Rousseau et al., 2019).

109 In this scenario, the combined use of Sr and Nd isotopes in sedimentary rock as potential tracers
110 of paleo ENSO event may be particularly useful providing that isotopically contrasted rocks are
111 differentially eroded during ENSO and normal years. To explore this possibility, we present the
112 geochemistry and Nd and Sr isotopes composition of the SPM exported by the Tumbes River
113 along contrasted hydrological periods at both the seasonal (dry vs wet season) and inter-annual
114 (wet vs normal years) time scale. For this purpose, we have analysed monthly sampled SPM at
115 the lower reach of the basin along two hydrological cycles and interpreted the corresponding
116 data as function of discharge, SPM concentration, SPM fluxes, seasonal and inter-annual
117 rainfall distribution and geochemical characteristic of the SPM sources.

118

119 **2. Regional setting**

120 The Tumbes River basin is located in Southern Ecuador and Northern Peru (latitude -
121 79.35 and -80.70 decimal degrees). It drains the western slope of the Andes (between longitude
122 -3.47 and -4.25 decimal degree) over an area of $4.8 \cdot 10^3 \text{ km}^2$ including ~70% in the Andean
123 mountains above 500 m.a.s.l. (meter above sea level; Moquet et al., 2018). It originates in the
124 Andes (~ 3800 m.a.s.l.) and flows through a narrow coastal plain until its outlet to the Pacific
125 Ocean. The river drains three main lithologically-contrasted domains: a volcanic, a

126 plutonic/metamorphic and a sedimentary domain representing respectively 17, 25 and 58% of
127 the area (figure 1; table S1). The Upper Tumbes basin drains the volcanic domain which
128 consists in Cenozoic and Mesozoic volcanic rocks (elevation = 2014 ± 667 m.a.s.l.;
129 average \pm 1sd). They are composed of andesites, basalts, and locally derived pyroclastic rocks.
130 The mid-altitude Tumbes basin drains the Paleozoic plutonic and metamorphic domain
131 (elevation = 1036 ± 371 m.a.s.l.), which is mainly composed of schists, gabbro, granite and
132 intermediate intrusive rocks (Figure 1). The remaining part of the basin (elevation = 735 ± 333
133 m.a.s.l.) is formed by Cenozoic-Mesozoic mudstones, shales, and sandstones as well as locally
134 derived modern alluvial fan deposits and limestones (Figure 1).

135 The basin receives a rain amount of around 1000 mm.yr^{-1} which leads to a runoff of
136 around 750 mm.yr^{-1} (Lavado et al., 2012). The cumulative annual rainfall tends to increase with
137 elevation. The rainfall regime, and consequently the discharge regime, shows a strong
138 seasonality both in term of quantity and geographical distribution. The rainfall period occurs
139 during austral summer/fall between December and May (Segura et al., 2019), peaking between
140 February and April in relation to the southernmost position of the Intertropical Convergence
141 Zone (ITCZ) (Huaman and Takahashi, 2016; Figure 2). The rainfall period contributes to
142 around 85% of the annual discharge at El Tigre station (1985-2015 period; using data from
143 SENAMHI - Servicio Nacional de Meteorología e Hidrología -, PEBPT - Proyecto Especial
144 Binacional Puyango Tumbes - and HYBAM - Contrôle géodynamique, hydrologique et
145 biogéochimique de l'érosion/altération et des transferts de matières dans les bassins de
146 l'Amazonie, du Congo et de l'Orénoque). The relative contribution of the rainfall amount varies
147 also along the year. While the plutonic/metamorphic domain contribution is almost constant
148 along the year ($\sim 30\%$), the volcanic domain contributes more than $\sim 35\%$ along the September-
149 October-November period and decreases to $\sim 20\%$ during the rest of the year. Therefore, the

150 sedimentary area contributes between ~35% and ~50% of the total amount of rainfall received
151 by the basin during the dry and wet seasons, respectively (Figure 2).

152 The main anthropogenic activity is urbanization throughout the city of Tumbes located
153 close to the outlet of the basin, downstream the El Tigre hydrological station (Figure 1). Small-
154 scale gold mining activity has also been reported upstream in the Puyango and Portovelo-
155 Zaruma sub-basins (Marshall et al., 2018). But, overall, the anthropogenic influence is rather
156 small on sediment production at the Tumbes basin scale.

157

158 **3. Material and methods**

159 **3.1. Studied sites**

160 We analyzed the geochemistry and the mineralogy of the SPM sampled monthly during two
161 contrasted hydrologic years (2007-2008, a wet year, and 2010-2011, a normal hydrological
162 year) at the El Tigre hydrological station located near the Tumbes River outlet (fig. 1). We
163 compared these data with the daily discharge and the SPM concentration monitored at this
164 station and with the monthly rainfall data recorded over the basin (see next sections for details).
165 To identify potential source effects which can influence the geochemical and mineralogical
166 composition of the sediments sampled at the El Tigre station, we also performed a discrete
167 sampling of the riverine suspended matter of two Tumbes River tributaries representative of
168 two lithological environments: volcanic and plutonic/metamorphic areas. The Rio Calera at
169 Portovelo drains the volcanic domain and was sampled during 2016 wet season (high water
170 level). The Rio Marcabelli at Marcabelli village drains the plutonic/metamorphic domain and
171 was sampled during 2015 dry season (low water level) and 2016 wet season (high water level).
172 A sedimentary sub-basin (rio Pindo tributary at Buenavista) located downstream the volcanic
173 area and upstream the plutonic/metamorphic area has also been sampled twice (2015 dry season
174 and 2016 wet season) (table1, S1; figure 1). Note that we not considered this basin as
175 representative of the whole sedimentary area of the Tumbes basin because the sedimentary area

176 located downstream the plutonic/metamorphic area is expected to result on a mix from
177 plutonic/metamorphic and volcanic domains.

178
179 ***3.2. Hydrological and climate data***

180 The hydrological year was considered to be from September to August (Lavado et al.,
181 2012). Mean monthly rainfall was extracted from the PISCOv1.1 Database (Peruvian
182 Interpolated data of the SENAMHI's Climatological and Hydrological Observations; Lavado et
183 al., 2016) for the 1985-2015 period. This gridded rainfall dataset is available at a monthly
184 frequency for Peru and the regions close to the frontiers with a ~ 5 km resolution since January
185 1981. It results from the merging of two rainfall databases: (i) the national rain gauge dataset
186 from the SENAMHI and (ii) the remote sensing rainfall estimates of the Climate Hazards Group
187 Infrared Precipitation (CHIRP; see details in Lavado et al., 2016). This data is freely available
188 from the SENAMHI website
189 (<http://ons.snirh.gob.pe/SOURCES/.Peru/.SEAMHI/.PISCO/.Precipitation/.Monthly/.Precipitation/index.html?Set-Language=fr>). We extracted the monthly rainfall received by the whole
190 basin and by each of the 3 lithological domains (Figure 2) according to the delimitations defined
191 in the figure 1.

193 At the El Tigre SENAMHI/HYBAM station, daily river discharge was available for the
194 1963-2016 period . In the present study, we considered the 1985-2015 period as the reference.
195 Water levels were measured every 4 hours using a conventional hydrological method (Morera
196 et al., 2017). Gauging was accomplished monthly using a mechanical current meter. The daily
197 discharge record was then calculated from rating curves (discharge - water level relationship)
198 using the Hydraccess software (Vauchel, 2005). The daily discharge data are free available
199 from the HYBAM website (<http://www.so-hybam.org>) until july 2009. The remaining
200 discharge data was provided by the SENAMHI.

201

227 as the specific discharge ($\text{mm}\cdot\text{yr}^{-1}$) were calculated by dividing, respectively, the SPM flux and
228 the discharge by the total area of the basin at the El Tigre station.

229

230 ***3.5. Selection of the studied years***

231 Among the hydrological years for which we had access to sediment filters (2006-2011
232 period), we selected the wetter year (2007-2008 hydrological year) and a year close to the
233 median discharge (2010-2011 hydrological year) by comparison with the 30 discharge years
234 along the 09/1985-08/2015 period (Figure 3a, b). In term of annual discharge, with an annual
235 module of $170\text{m}^3\cdot\text{s}^{-1}$, the 2007-2008 year ranks as the 4th wetter year of this 30 years period and
236 exhibits, therefore, a return period of 7.8 years (Figure 3b). The 2007-2008 period featured to
237 La Niña conditions in the central Pacific, i.e. the Oceanic Niño Index (ONI,
238 <http://www.cpc.ncep.noaa.gov/data/indices/oni.ascii.txt>) was less than -0.5°C between April
239 2007 and June 2008 and less than -1°C between October 2007 and March 2008. It also presented
240 localized positive SST anomaly on the coast of Ecuador and Northern Peru between February
241 and April 2008, both of which promoted precipitation in both the coast and the highlands of
242 Southern Ecuador (Bendix et al., 2011). In the Piura river in Northern Peru (around 5°S), this
243 period produced the largest discharge after the extreme large-scale 1997-1998 and 1982-1983
244 El Niño and the 1925 coastal El Niño events, even more than other El Niño events. It was due
245 to the nonlinearity of the combination of the effects of the warm coastal and cool central Pacific
246 conditions (Takahashi and Martinez, 2017). Conversely, while the 2010-2011 period also
247 featured La Niña conditions in the central Pacific, it did not present warm coastal conditions.

248 Discharge records of El Tigre station indicate that the 2007-2008 year ($170\text{m}^3\cdot\text{s}^{-1}$) ranks
249 after the El Niño years of 1997-1998 ($387\text{m}^3\cdot\text{s}^{-1}$) and 1986-1987 ($261\text{m}^3\cdot\text{s}^{-1}$) and the La Niña
250 year of 2011-2012 year ($190\text{m}^3\cdot\text{s}^{-1}$) (Figure 3b). The lowest annual discharge value recorded
251 along this period ($52\text{m}^3\cdot\text{s}^{-1}$) corresponds to the 1989-1990 hydrological year. The 2010-2011

252 exhibits a module of $84 \text{ m}^3 \cdot \text{s}^{-1}$, close to the 1985-2015 period median value of $95 \text{ m}^3 \cdot \text{s}^{-1}$.
253 Moreover, the distribution of the daily discharge of the 2010-2011 period is similar to the 1985-
254 2015 period median distribution (Figure 3c, d). Therefore, the 2010-2011 year is considered as
255 a “normal” year in term of discharge distribution (Figure 3d). The higher daily discharge (half
256 upper daily discharge values) of the 2007-2008 year is close to the 90th percentile distribution
257 of the 1985-2015 period. In other words, during the 1985-2015 period only 10% of the years (3
258 years) exhibit higher daily discharge than the 2007-2008 year during the wet period (figure 3d).
259

260 **3.6. Mineralogy and Geochemistry**

261 *3.6.1. Sample treatments*

262 The 29 selected SPM filters were submerged in ultra-pure water and submitted from 3
263 to 5 sessions of ultrasonic baths of 30 minutes until all SPM was visually removed from the
264 filter. The filters were then discarded and the SPM was dried. Between 10 and 300 mg of SPM
265 was therefore recovered from each selected filters. The SPM of each sample was divided into
266 two aliquots. A small (2-3 mg) aliquot was used for X-ray diffraction analyses (DRX) and the
267 remaining sediment was digested for major element concentrations and for Nd and Sr isotopic
268 analyses. This second aliquot was first treated with H_2O_2 for 24h at ambient temperature, then
269 it was digested in $\text{HNO}_3 + \text{HF}$ for 36 h at $80 \text{ }^\circ\text{C}$, and in $\text{HCl} + \text{HNO}_3$ for 36 h at $120 \text{ }^\circ\text{C}$. Strontium
270 and Nd were separated by ion-exchange chromatography using Sr-SPEC, TRU-SPEC and LN-
271 SPEC resins (Eichrom®) according to the Pin et al. (1994) method. Ultrapure and bi-distilled
272 reagents were used for all digestion and separation steps.

273

274 *3.6.2. Sample analyses*

275 All analyses were performed at the Géosciences-Environnement-Toulouse (GET)
276 Laboratory - Observatoire Midi-Pyrénées (OMP). X-ray diffraction analyses were carried out

277 using a G3000 Inel diffractometer (40 kV, 30 mA) and Ni-filtered CuK α 1,2 radiation ($\lambda=1.5406$
278 Å). Due to limited amounts of material for some samples, we did not perform a glycol treatment
279 for clay mineral identification. We performed a semi-quantitative estimate of the chlorite, illite,
280 kaolinite and smectite abundance based on the Biscaye (1965) method (table S2).

281 Major element analyses were measured by ICP-OES (Horiba Jobin Yvon Ultima2).
282 Measurement accuracy was assessed by processing 5 and 10 mg of the GA basalt reference
283 material (CRPG; Centre de Recherches Pétrographiques et Géochimiques). The Chemical
284 Index of Alteration (CIA) is generally used to estimate the degree of weathering of a basin (e.g.
285 Viers et al., 2008; Rousseau et al., 2019). During weathering, alkali metal and alkaline earth
286 ions are released into solution, whereas alumina is preferentially retained in the weathered
287 material and the CIA is calculated as follows:

$$288 \quad \text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O}) \times 100 \text{ (molar proportions)}] \text{ Equation 2}$$

289 where CaO* is the CaO content in the silicate fraction.

290 The CIA of the GA reference standard is 59 (recommended value; CRPG) whereas we
291 obtained 55 and 61 for the two GA aliquot analyzed in the present study. An error of up to 4 in
292 this CIA molar ratio is therefore considered in our result presentation (table 1).

293 Neodymium and Strontium isotope measurements were conducted on a Triton Thermal
294 Ionization Mass Spectrometer. Neodymium isotope ratios were measured in static mode,
295 corrected for instrumental mass bias fractionation using a $^{146}\text{Nd}/^{144}\text{Nd}$ ratio of 0.7219. One
296 analysis of the La Jolla standard gave a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.511858 ± 16.10^{-6} ($\pm 2 \sigma$; internal
297 precision) in agreement with the recommended value of 0.511858 (Lugmair et al.,
298 1983). Repeated analyses of Rennes standard gave a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.511947 ± 10.10^{-6} to
299 0.511969 ± 16.10^{-6} (N=3; $\pm 2 \sigma$; external precision - 1 week) in agreement with the value
300 recommended by Chauvel and Blichert-Toft (2001) for the Rennes Nd standard ($^{143}\text{Nd}/^{144}\text{Nd} =$
301 0.511961 ± 13.10^{-6} ; 2σ). Neodymium isotopes are reported using the ϵNd notation, normalizing

302 samples to the CHondritic Uniform Reservoir (CHUR) value of $^{143}\text{Nd}/^{144}\text{Nd} =$
303 0.512638 (Jacobsen and Wasserburg, 1980):

$$304 \quad \epsilon Nd = \left(\frac{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{measured}}}{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}} - 1 \right) * 10^4 \quad \text{Equation 3}$$

305 Strontium isotope ratios were measured in dynamic mode, corrected for instrumental
306 mass bias using $^{88}\text{Sr}/^{86}\text{Sr} = 0.1194$. Repeated analyses of the NBS 987 standard gave a $^{87}\text{Sr}/^{86}\text{Sr}$
307 ratio of 0.710256 ± 15.10^{-6} (2σ , external precision, $N=6$ during two weeks) in agreement
308 with the value recommended by Hodell et al. (2007) ($^{87}\text{Sr}/^{86}\text{Sr} = 0.710240 \pm 15.10^{-6}$; 2σ).

309

310 3.6.3. Correlation analysis

311 All correlation analyses presented in the present study are performed along the whole
312 SPM dataset collected at the El Tigre station and analyzed ($N=21, 22, 23$ or 24 according to the
313 considered data). Only significant correlation at $p\text{-value} < 0.01$ are considered. Therefore, the
314 correlation is significant at $p\text{-value} < 0.01$ when $R > 0.526, 0.515, 0.505$ and 0.496 for $N = 21, 22,$
315 23 and 24 respectively. The best fit was observed considering relationships between discharge,
316 rainfall, SPM concentration and SPM flux according to logarithm scales and $^{88}\text{Sr}/^{86}\text{Sr}$, ϵNd and
317 the relative rainfall distribution by lithological areas according to linear scales.

318

319 4. Results

320 4.1. Hydro-sediment budgets

321 During the sampled years, the daily water discharge corresponding to sampling ranged
322 from $12 \text{ m}^3 \cdot \text{s}^{-1}$ (November 2010) to $736 \text{ m}^3 \cdot \text{s}^{-1}$ (March 2008) and the SPM concentration varies
323 from 2 to $7350 \text{ mg} \cdot \text{l}^{-1}$. The latter follows broadly a power law relationship with daily discharge
324 for discharge conditions up from around $40 \text{ m}^3 \cdot \text{s}^{-1}$ (figure 4). The SPM concentration remains
325 almost constant for discharge lower than this value (Morera et al., 2017). During the 2007-2008

326 and the 2010-2011 hydrological years, the Tumbes River exported 1835 and 190 t.km⁻².yr⁻¹ of
327 sediments at El Tigre station, respectively.

328

329 ***4.2. Mineralogy***

330 The DRX analyses show that the sampled SPM at El Tigre station are dominated by
331 illite (88±7% of the clays; ± 1 sd-standard deviation) followed by chlorite (9±2%) while
332 kaolinite and smectite represent less than 3% of the clays. This clay composition does not vary
333 with the seasonal hydrological variation. The sampled monolithological sub-basins exhibit
334 almost the same mineralogical composition (Figure S1; table S2).

335 According to these DRX analyses, feldspar and gibbsite are not detected in all samples
336 whereas quartz is systematically detected. However, as for clays, no relationship between quartz
337 abundance and discharge is observed. Interestingly, the monolithological volcanic and
338 sedimentary sub-basin samples can exhibit a slightly higher signal of amphibole, feldspath,
339 gibbsite and quartz (table S2).

340

341 ***4.3. Geochemistry***

342 The CIA of the El Tigre station SPM ranges between 75 and 82. This low variability reflects
343 a relatively homogenous chemical weathering state of the sediments. With values ranging from
344 71 to 87, the discrete sampling of monolithological volcanic, plutonic/metamorphic and
345 sedimentary basins exhibit the same range of CIA values (table 1). This spatial CIA
346 homogeneity from upstream to the basin outlet shows that no significant weathering processes
347 affect the exported sediments throughout their transport.

348 The εNd SPM values range from -7.8 to -1.9 and follow a seasonal behavior negatively
349 correlated with discharge and, therefore, the SPM concentration. The minimum εNd value is
350 observed during the rainy season (Figure 5). The ⁸⁷Sr/⁸⁶Sr isotopic composition of analyzed

351 SPM ranges from 0.7115 to 0.7176. The variability of $^{87}\text{Sr}/^{86}\text{Sr}$ is low for most of the samples
352 (0.7115 to 0.7139) with the exception of the March and April 2008 samples which exhibit
353 higher values (0.7176 and 0.7155 respectively). Interestingly, these two months correspond to
354 the highest SPM concentration recorded for the analyzed samples and correspond to high
355 discharge conditions (Table 1; Figure 5). The $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd values are significantly
356 negatively correlated ($R = -0.54$; $p\text{-value} < 0.01$) suggesting a first order opposite behavior.

357 The volcanic basin SPM sample has Nd and Sr isotope composition of respectively ϵNd
358 $= -0.3$ and $^{87}\text{Sr}/^{86}\text{Sr} = 0.7059$. By contrast the two samples from the plutonic/metamorphic basin
359 exhibits the lower Nd and the higher Sr isotope compositions ($\epsilon\text{Nd} = -10.1$ and -10.8 ; $^{87}\text{Sr}/^{86}\text{Sr} =$
360 0.7090 and 0.7092). The sampled sedimentary tributary exhibits slightly higher Nd isotope and
361 comparable Sr isotope compositions relative to the volcanic basin ($\epsilon\text{Nd} = 0.7$ and 2.7 ; $^{87}\text{Sr}/^{86}\text{Sr} =$
362 0.7058 and 0.7063 ; table 1).

363 Considering both hydrological cycles (figure 5, 6), Nd and Sr isotopic compositions are
364 significantly correlated ($p\text{-value} < 0.01$) with both discharge variability and SPM concentration.
365 In detail, the ϵNd is better negatively correlated with discharge variability ($R = -0.72$; figure 6a)
366 than with SPM concentration ($R = -0.58$; figure 6b) while $^{87}\text{Sr}/^{86}\text{Sr}$ is better correlated with SPM
367 concentration ($R = 0.75$; figure 6e) than with discharge ($R = 0.57$; figure 6d). As SPM
368 concentration depends on discharge variability (figure 4), both $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd signatures are
369 very well correlated with SPM fluxes ($R = -0.71$ and 0.72 respectively; figure 6c and g).
370 However, it is important to highlight that for Sr isotopes significant correlation is controlled by
371 two extreme discharges and SPM concentration values recorded during the wet hydrological
372 cycle (2007-2008; samples of March and April 2008; table 1).

373

374 **5. Discussion**

375 ***5.1. Homogenous mineralogical composition of the Tumbes River***

376 The SPM mineralogy values recorded in the Tumbes river and its monolithological sub-
377 basin tributaries are relatively homogenous (figure S1, table S2). This parameter is therefore
378 not discriminant for tracing the source variability of the riverine suspended sediments.
379 Interestingly, the mineralogical composition of the analyzed samples is enriched in illite and
380 depleted in kaolinite and smectite by comparison with those of the Peruvian and Ecuadorian
381 Andino-Amazonian basins. There, kaolinite, smectite and illite represent around $29\pm 14\%$ and
382 $40\pm 20\%$ and $26\pm 14\%$ ($\pm 1\text{sd}$) of the clays (among 30 river bank sediments samples from Napo,
383 Marañon and Ucayali basins; Guyot et al., 2007). As suggested by Liu et al. (2016) to explain
384 clay mineralogical composition diversity in fluvial sediments of South China Sea, physical
385 erosion and chemical weathering regimes can be invoked to explain this Andean Western vs
386 Eastern slope mineralogical contrast. Higher illite and chlorite content in the Pacific slope of
387 the Andes can be related to the stronger physical erosion recorded over this area (Armijos et
388 al., 2013; Morera et al., 2017) while high contents of smectite and kaolinite in Amazonian slope
389 can be attributed to the higher weathering intensity measured in the eastern slope of the Andes
390 (Moquet et al., 2011, 2014, 2018). In the Tumbes basin, geochemical tracers need to be used to
391 track SPM sources variability.

392

393 ***5.2. Geochemical signature as a proxy of SPM sources***

394 The SPM CIA values recorded in the Tumbes river and its monolithological sub-basin
395 tributaries are quite similar (table 1). Therefore, the CIA cannot be used for tracing the source
396 of the riverine suspended sediments. The ϵNd and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition of sedimentary
397 rocks or of riverine SPM have been proven to be robust tools for determining their provenance
398 (e.g., Allègre and Rousseau, 1984; McLennan et al., 1993; Krom et al., 2002; Goldstein and
399 Hemming, 2003; Faure and Mensing, 2004; Viers et al., 2008; Singh et al., 2008; Roddaz et al.,

400 2014; Höppner et al., 2018; Rousseau et al., 2019) when the sources are isotopically contrasted.
 401 However in some cases, these isotopic signatures can be controlled by grain size due to sorting
 402 effect especially for Sr isotopes (Blum and Erel, 2003; Bouchez et al., 2011; Roddaz et al.,
 403 2014; Bayon et al., 2015). In the Tumbes River and its tributaries, the mineralogy and the CIA
 404 do not vary. Moreover, no significant correlation is observed between mineralogy content, CIA
 405 and isotopic signatures. While almost constant mineralogy and CIA values reflect a quite
 406 homogenous weathering regime throughout the basin, SPM Nd and Sr isotope signature would
 407 be, to a first order, mainly controlled by source effect for most of the samples.

408 The Nd and Sr isotopic composition of Tumbes SPM have intermediate isotopic values
 409 between volcanic/sedimentary basins and plutonic/metamorphic basins, suggesting that they
 410 correspond to a mixing of these two sources endmembers. Interestingly, sampled SPM from
 411 plutonic/metamorphic sub-basins and from volcanic and sedimentary basins are particularly
 412 contrasted in term of $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd signatures. The volcanic and sedimentary basins SPM
 413 exhibit similar Sr-Nd isotopic composition as those of the Jurassic to Quaternary Andean
 414 volcanic rocks Andean (Scott et al., 2018; Ancellin et al., 2017) while the SPM from the
 415 plutonic and metamorphic area plots on the Subandean domain (Roddaz et al., 2005; Figure 7).
 416 A simple mixing equation between two endmembers (volcanic basin vs plutonic/metamorphic
 417 basin) based on Nd isotope ratio allows to estimate the proportion of SPM produced by the
 418 volcanic domain (or sediments in the case of the sedimentary basin) according to the following
 419 formula:

$$420 \quad \% \text{SPM}_{volc} = \frac{\epsilon \text{Nd}_{sample} - \epsilon \text{Nd}_{plu met}}{\epsilon \text{Nd}_{volc} - \epsilon \text{Nd}_{plu met}} \quad \text{Equation 4}$$

421 With $\% \text{SPM}_{volc}$ being the relative proportion of the Tumbes SPM derived from the
 422 volcanic domain and $\epsilon \text{Nd}_{volc}$, $\epsilon \text{Nd}_{plu met}$ and $\epsilon \text{Nd}_{sample}$, representing the ϵNd value of the
 423 volcanic basin, plutonic/metamorphic basin and Tumbes SPM respectively.

424 According to this calculation, around 24 to 74% of the Tumbes SPM are derived from
425 the volcanic endmember and the contribution of the volcanic endmember is negatively
426 correlated with the discharge (Figure 5 and 6). Indeed, volcanic/sedimentary and
427 plutonic/metamorphic material dominate the SPM production during the dry and wet period
428 respectively. In the next section, we describe the potential mechanism that explains this
429 relationship between Sr-Nd isotopic composition and hydro-climatic variables.

430

431 ***5.3. Relationship between Sr-Nd isotopic composition and hydro-climatic variables***

432 *5.3.1. Nd isotopic composition*

433 The observed correlations between Nd isotopic composition with SPM concentration and
434 discharge suggest that these isotopic compositions can be considered as good proxies of the
435 seasonal and inter-annual SPM fluxes variability in the Tumbes basin. Indeed, during both
436 analyzed hydrological years, Nd isotopes vary from volcanic to plutonic/metamorphic basin
437 endmembers signature at seasonal timescale (figures 5 and 6). During low water level period,
438 SPM Nd isotope signature is closer to the volcanic/sedimentary endmember while the
439 plutonic/metamorphic endmember appears to influence more the SPM geochemistry during
440 high level water season (figure 6a, d). These results suggest that SPM ϵ_{Nd} values are sensitive
441 to the distribution of rainfall throughout the studied basin. During the low discharge season,
442 maximum rainfall occurs more upstream the basin, in the volcanic domain and the upper
443 sedimentary domain, while during the high water stage, the proportion of rainfall received by
444 the lower part of the basin and the corresponding sediments generated from this area that
445 includes plutonic and metamorphic rocks, are higher (figure 2b). This interpretation is
446 confirmed when comparing the daily discharge, monthly discharge and ϵ_{Nd} signature with the
447 monthly relative rainfall distribution throughout the basin (figure 8e, f, g). The rainfall database
448 PISCO is only available at a monthly timescale. However, monthly discharge and rainfall can

449 serve as an appropriate representation of sampled daily discharge based on the observed high
450 correlation value between daily discharge and monthly discharge ($R=0.91$; figure 8i), the
451 monthly discharge and the monthly rainfall ($R=0.72$; figure 8b), and, therefore, between the
452 daily sampled discharge and the monthly rainfall ($R=0.68$, figure 8a). Thus, the contribution
453 from the volcanic area in terms of mean monthly rainfall was found to be significantly
454 (negatively) correlated to monthly discharge at the outlet ($R=-0.74$; figure 8e) and, therefore,
455 to the Nd isotopic composition of SPM sampled at the station ($R=0.58$; figure 8f). These results
456 demonstrate that the Nd isotopic composition of SPM is an excellent proxy of rainfall amount
457 (figure 8c) and spatial rainfall distribution (figure 8f) of the Tumbes basin which are linked to
458 the outlet discharge.

459

460 5.3.2. *Sr isotopic composition*

461 Whereas strontium isotopic composition also exhibits significant correlation with the
462 seasonal and inter-annual SPM fluxes variability in the Tumbes basin (Figure 6f), it is important
463 to highlight that this is essentially due to two extreme discharge and SPM concentration values
464 occurring during the wet hydrological year (2007-2008 year). Otherwise, the $^{87}\text{Sr}/^{86}\text{Sr}$ appears
465 less sensitive than ϵNd to the source variability in the Tumbes Basin.

466 Such Sr isotopes ratio anomalies have previously been reported for multi-millennial
467 rainfall events based on sediments cores records (e.g. Krom et al., 2002; Höppner et al., 2018)
468 and, in these cases, it was interpreted as a source effect. In the modern SPM Tumbes River, it
469 thus appears that only during extreme hydrological events the high $^{87}\text{Sr}/^{86}\text{Sr}$ typical of
470 plutonic/metamorphic rocks is released in sufficient quantities to notably change the SPM
471 $^{87}\text{Sr}/^{86}\text{Sr}$ value of the Tumbes River. A second possible explanation is that the $^{87}\text{Sr}/^{86}\text{Sr}$
472 fractionation can be affected by grainsize sorting (Bouchez et al., 2011). Indeed, in a given
473 geological context, finer (coarser) sediments can exhibit more (less) radiogenic Sr signature,

474 even when considering small grain size variability in a given grain size class. A third possible
475 explanation is that a larger proportion of the fresher part of these rocks are then eroded under
476 such extreme hydrological events, whereas under normal conditions, radiogenic Sr from these
477 rocks is rather leached through weathering. Suspended particulate matter grain size
478 measurements and concomitant geochemical analysis of the particulate and the dissolved
479 fraction of the same water samples would be required to evaluate these hypotheses.

480

481 5.3.3. *Suspended particulate matter Sr and Nd isotopic composition in South American rivers*

482 Suspended particulate matter Sr and Nd isotopic composition have also been measured
483 monthly in other South American large rivers. Interestingly, the SPM ϵ Nd measured at the
484 outlet of the Solimoes, the Madeira (Viers et al., 2008), the Amazon and the Orinoco outlets
485 (Rousseau et al., 2019) exhibits a low amplitude ranging from 0.8 (Orinoco) to 1.6 (Amazon ;
486 the amplitude being defined as the difference between the minimum and the maximum ϵ Nd
487 value recorded along the year in each river). These values are much lower than the amplitude
488 of 5.9 recorded in the Tumbes River (table 1; figure 7). Conversely these large rivers exhibit an
489 amplitude of $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging from 0.0041 (Solimoes) to 0.0134 (Madeira), thus much
490 higher than the Tumbes river (0.0024), when the two extreme values of the 2007-2008 year are
491 excluded (0.0061 when these two values are included). These differences can be explained, to
492 a first order, by the $^{87}\text{Sr}/^{86}\text{Sr}$ vs ϵ Nd isotopic mixing curve (figure 7). As the Tumbes river SPM
493 is predominantly derived from Andean volcanic lithologies, ϵ Nd variability is more sensitive
494 to SPM source changes, and therefore to hydrological variability, than $^{87}\text{Sr}/^{86}\text{Sr}$. Conversely, in
495 the large rivers of the Amazon and Orinoco Basins, the metasedimentary rocks contribute
496 proportionally more to the SPM composition (Viers et al., 2008; Rousseau et al., 2019).
497 Therefore, changes in SPM source along the hydrological year would affect more the $^{87}\text{Sr}/^{86}\text{Sr}$
498 SPM signature than the ϵ Nd. This observation highlights that the initial local lithology has

499 important implications in term of $^{87}\text{Sr}/^{86}\text{Sr}$ and ϵNd SPM sensitivity in response to source and,
500 therefore, to rainfall distribution variability.

501 To conclude, given the climatic and geological context studied here, variation in Nd and
502 Sr isotopic composition of SPM are, respectively, powerful proxies of the seasonal and inter-
503 annual discharge changes and these properties can be exploited for paleoclimate reconstruction
504 based on sedimentary records.

505

506 ***5.4. Implication for paleo ENSO and paleo extreme hydrologic event reconstruction***

507 Most of paleoclimate reconstruction based on Sr-Nd isotopic composition of marine
508 core sediments are based on a single SPM sampling of the different tributaries or rivers which
509 fed the marine sediments (e.g. Ehlert et al., 2013; Li et al., 2015; Höppner et al., 2018). The
510 dataset presented in this study can be used to improve this approach in Pacific coastal regions
511 affected by ENSO events. Being sensitive to seasonal rainfall distribution (mainly ϵNd) and
512 interannual high rainfall anomalies ($^{87}\text{Sr}/^{86}\text{Sr}$), these isotopic signatures may be particularly
513 interesting to reconstruct the paleoclimatology of the studied basin which is highly sensitive to
514 El Niño events (Morera et al., 2017). In addition, the results of this study can be extended
515 beyond the Tumbes River paleoclimate reconstruction and applied to other Peruvian and
516 Ecuadorian Pacific coast basins affected by the ENSO events. For instance, Nd and Sr isotopic
517 variability along Pacific margin sediments cores has previously been interpreted as a function
518 of the upwelling redistributions of the terrigenous sediments produced by rivers, which exhibit
519 contrasted signatures between 0° and 18°S (Ehlert et al., 2013). In the present study, we propose
520 a new and complementary perspective to interpret such records. The altitudinal and spatial
521 rainfall distribution over these basins also needs to be taken into account in order to interpret
522 the geochemistry of these marine core sediments. In fact, in Ecuador and Peru, the Pacific
523 coastal basins are characterized by similar lithological repartitions characterized by volcanic

524 rocks in elevated regions and plutonic and metamorphic rocks in lower elevated regions (Figure
525 A1). The sedimentary formations would result from their respective upstream erosion processes
526 either mixed, in case of contrasted lithology upstream, or homogenous, when this area drains
527 an homogenous lithological formation as it is the case for the sedimentary sub-basin sampled
528 in the present study. During ENSO events, the rainfall intensity and repartition are modified
529 and can either increase or decrease in both areas even if this effect decreases southward (Lagos
530 et al., 2008; Lavado and Espinoza, 2014). Indeed, according to Lavado and Espinoza (2014),
531 during strong El Niño events and coastal El Niño events, Northern Peruvian Pacific basins are
532 subjected to significant increases in rainfall from the coast to the high elevation areas, while the
533 rainfall decreases in the Southern Peruvian basins (especially in the elevated areas). However,
534 during La Nina events, positive rainfall anomalies are recorded in the upper part of the basins
535 (e.g. Sulca et al., 2018). Based on a regionalization of the rainfall data along the Peruvian
536 Pacific coast, Rau et al. (2017) highlighted that the main modes of influence of the ENSO
537 increased rainfall over downstream regions in Northern Peru during extreme El Niño events
538 and decreased rainfall over upstream regions along the Pacific slope during central Pacific El
539 Niño events. Given the results presented in this study, we expect more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ and
540 more negative ϵNd values during strong El Niño events for SPM of the northern basins because
541 of lower rainfall on volcanic rocks relative to downstream areas during these events. During the
542 La Nina events, higher rainfall in the more elevated areas occupied by volcanic rocks (high ϵNd
543 values) and low rainfall along the coast and downstream region would produce SPM with higher
544 ϵNd values and less radiogenic Sr isotopic compositions (Figure 9). As sediments fluxes depend
545 on rainfall amount especially during exceptionally rainy years (Morera et al., 2017), a
546 comparison of Sr and Nd isotopes with the sedimentation rate, can potentially indicate if a
547 relation exist between rainfall locations and rainfall amount during the period covered by the
548 core.

549

550 **6. Conclusion**

551 We investigated the geochemistry of the riverine SPM (Suspended Particulate Matter)
552 produced by the Tumbes River at a monthly frequency along two hydrological years, including
553 a wet (2007-2008) and a normal (2010-2011) year. We also analyzed the SPM of 2
554 monolithological tributaries representative of the lithological diversity of the basin (i.e. volcanic
555 and plutonic/metamorphic) and a sedimentary sub-basins located below the volcanic domain.
556 This constructed geochemical database, never produced so far for an Andean River, is
557 compared with the hydrology, climate and geology data available over the studied basin.

558 The clay mineralogy is almost homogenous with a CIA nearly constant along the
559 hydrological year, showing that these two parameters are not adapted to track the SPM sources
560 variability. However Sr and Nd isotopes signatures change during the hydrological year and
561 they covariate with discharge, SPM concentration and SPM fluxes. The variability of ϵNd (from
562 -7.8 to -1.9) along the two analyzed hydrological years is coherent with the spatial rainfall
563 distribution throughout the basin. Less radiogenic values are measured during rainy season
564 when the relative contribution of the upper part of the basin, dominated by volcanic rocks (a
565 more radiogenic endmember), is lower. Therefore, Nd isotope composition constitutes a direct
566 proxy of rainfall spatial distribution, which is related to SPM and water fluxes along the
567 hydrological year. With the exception of two samples, Sr isotope composition is less variable
568 along the studied periods ($^{87}\text{Sr}/^{86}\text{Sr}= 0.7115$ to 0.7139) as this isotope ratio traces only
569 exceptionally high hydrological conditions during exceptional high rainfall/discharge years.
570 The two exceptions of higher radiogenic Sr ($^{87}\text{Sr}/^{86}\text{Sr}= 0.7176$ and 0.7155) were measured
571 during abnormal hydrological conditions of March and April 2008 and can be most likely
572 attributed to higher contributions of the plutonic/metamorphic lithological domain.

573 Interestingly, these geochemical tracers are highly linked to hydrological and erosional
574 processes of the Tumbes basin.

575 These isotopic tracers are powerful proxies that can be used to reconstruct paleoclimate
576 based on either sediment cores from floodplains and/or continental margin basins as well as to
577 identify the main processes of seasonal SPM mobilization in the Tumbes basin. Moreover, these
578 tracers allow us to detect changes in rainfall and hydrological regimes both in terms of water
579 fluxes and rainfall distribution at the scale of the Tumbes River, which is a basin highly
580 sensitive to the diversity of ENSO events. Interestingly, the geology mapped along the whole
581 Pacific coast in Ecuador and Peru corresponds to the same geological distribution. Therefore,
582 the results of the present study can be generalized for these contexts and potentially allows
583 reconstructing paleo ENSO variabilities and other climate modes affecting the Pacific coast
584 climate from decadal to multi-millennial timescales.

585

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605

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List of figures:

752 Figure 1 : map of the Tumbes River basin : hydrological network, lithological domains, national
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754 @ Marcabelli - Plutonic and metamorphic area and 3 - a rio Pindo tribuary @Buenavista – a
755 sedimentary sub-basin).

756 Figure 2: a) monthly rainfall received by the Tumbes basin b) monthly relative contribution of
757 the rainfall received by the 3 lithological areas (defined on figure 1) in the Tumbes Basin along
758 the selected hydrological years (2007-2008 and 2010-2011). Source : monthly rainfall extracted
759 from PISCOv1.1 database (Peruvian Interpolated data of the SENAMHI's Climatological and
760 Hydrological Observations; Lavado et al., 2016)

761 Figure 3 : Hydrological characteristics of the selected years along the 1985-1986 to 2014-2015
762 period (30 years). a) Annual discharge along the 1985-2015 period. Red bars correspond to the
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764 the range among the 30 years period reference. b) Range of the annual discharge from the
765 wettest to the driest year. Red points correspond to the selected years. c) Hydrogram of the 30
766 years. d) Distribution of the daily discharge for the 90th, 50th and 10th percentiles (from the
767 lowest to the highest values). The daily discharge distribution of the 2007-2008 and 2010-2011
768 hydrological years are also reported. The daily discharge for the analyzed SPM samples are
769 reported (see the suppl mat for calculation details).

770 Figure 4 : Suspended Particulate Matter (SPM) concentration as function of daily discharge of
771 the Tumbes R. at El Tigre station along the 2006-2014 period. Data of the 2007-2008 and the
772 2010-2011 hydrological years are distinguished. The samples analyzed for geochemistry are
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774 reference for daily discharge upper than $40\text{m}^3.\text{s}^{-1}$.

775 Figure 5 : Variation of daily discharge (blue line), SPM concentration (brown line), ϵNd and Sr
776 isotopes composition (black line and squares) of the Tumbes River SPM at El Tigre station
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778 size. The relative contribution of SPM source calculated from the equation 4 is added for
779 reference (same symbol as ϵNd as it results from a proportional relationship). The abbreviation
780 Volc, PluMet and Sed refers to the values determined for SPM samples from the volcanic (ϵNd
781 = -0.3 and $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.7059), the plutonic/metamorphic (ϵNd = -10.1 and -10.8 ; $^{87}\text{Sr}/^{86}\text{Sr}$ =
782 0.7090 and 0.7092) and the sedimentary (ϵNd = 0.7 and 2.7; $^{87}\text{Sr}/^{86}\text{Sr}$ = 0.7058 and 0.7063) sub-
783 basins, respectively (see section 3.4 for details).

784 Figure 6 : ϵNd vs a) daily discharge; b) SPM concentration and c) daily SPM flux. $^{87}\text{Sr}/^{86}\text{Sr}$ vs
785 d) daily discharge; e) SPM concentration and f) daily SPM flux. Correlation coefficients
786 considerer all points of both hydrological cycles and are all significant (p-value<0.01). The
787 abbreviation Volc, PluMet and Sed refers to the values determined for SPM samples from the
788 volcanic, the plutonic/metamorphic and the sedimentary sub-basins, respectively (see section
789 3.4 for details).

790 Figure 7: $^{87}\text{Sr}/^{86}\text{Sr}$ versus ϵNd diagram for Tumbes R. and tributaries sediments (this study).
791 Volcanic rocks domains are extracted from Scott et al. (2018) and Ancellin et al. (2017) and
792 Subandean zone domain was defined by Roddaz et al. (2005). We also reported monthly
793 sampled SPM composition of the Madeira, the Solimoes (Viers et al. 2008), the Amazon and
794 the Orinoco (Rousseau et al., 2019). These values correspond to the modern composition.

795 Figure 8: a) daily discharge, b) monthly discharge, c) ϵNd and d) $^{87}\text{Sr}/^{86}\text{Sr}$ vs monthly rainfall.
796 e) daily discharge, f) monthly discharge, g) ϵNd and h) $^{87}\text{Sr}/^{86}\text{Sr}$ vs proportion of rainfall
797 received by the volcanic lithology (reported in fig.2). i) daily discharge vs monthly discharge.
798 Only significant correlation coefficients (p-value<0.01) are reported. They considered all points
799 of both hydrological cycles. The abbreviation Volc, PluMet and Sed refers to the values

800 determined for SPM samples from the volcanic, the plutonic/metamorphic and the sedimentary
801 sub-basins, respectively (see section 3.4 for details).

802 Figure 9 : schematic representation of the main SPM flux and their Nd and Sr isotope signature
803 in response to the extreme ENSO modes.

804 **List of tables:**

805 Table 1 : Suspended Particulate Matter (SPM) concentration, daily and monthly discharge (Q_j
806 and Q_{mens} respectively), Sr and Nd isotope signature ($\pm 2 \sigma$; 95% confidence level) and
807 Chemical Index Alteration (CIA) values of the sampled SPM. The CIA error is up to 4 (see
808 section 3.5.2. for details)

809

810 **Supplementary material:**

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812 S1: Tumbes River discharge distribution analysis.

813 To explore the daily discharge distribution of the sampled year reported in figure 3b and in the
814 section 2.4. We used the 1985-2015 daily discharge database recorded at El Tigre station. We
815 first ranges the daily discharge of each year from the lowest to the highest database. This range,
816 divided by the number of day of each year (365 or 364) is considered as the cumulative
817 frequency. We calculated the percentile 90, 50, and 10 of the 30 years for each cumulative
818 frequency value and we compare it to the daily discharge recorded along the selected years.
819 This analysis allows to explore the selected year discharge distribution for all the hydrological
820 condition. For example, it allows to identify if the 50% highest daily discharge of the sampled
821 years are closed to the 30 years median condition or if they are drier or wetter.

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825 **Figures :**

826 Figure S1 : Suspended Particulate Matter (SPM) clay mineralogical composition. Relative
827 proportion of clays mineralogical content of the monolithological basins and of the Tumbes
828 River at El Tigre station SPM. (D: Dry period; W : Wet period).

829 Figure S2: repartition of volcanic and Plutonic and metamorphic rocks along the Pacific coast
830 of Ecuador and Peru.

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832

833 **Tables :**

834 Table S1 : Characteristics of the Tumbes River at El Tigre station and its sampled tributaries

835 Table S2 : Mineralogical composition of the sampled Suspended Particulate Matter (SPM) in
836 the Tumbes R. and tributaries calculated from Biscaye (1965) method from DRX analyses.

837 LW : Low water ; HW : High water.

Table 1 : Suspended Particulate Matter (SPM) concentration, daily and monthly discharge (Qj and Qmens respectively), Sr and Nd isotope signature ($\pm 2 \sigma$; 95% confidence level) and Chemical Index Alteration (CIA) values of the sampled SPM. The CIA error is up to 4 (see section 3.5.2. for details)

type sample	Date (LW = low water / HW = High water)	Digested sample weight mg	SPM conc. mg.l ⁻¹	Qj m ³ .s ⁻¹	Qmens	⁸⁷ Sr/ ⁸⁶ Sr		¹⁴³ Nd/ ¹⁴⁴ Nd		εNd		CIA (error = 4)
						mean	±2 σ .10 ⁻⁶	mean	±2 σ .10 ⁻⁶	mean	±2 σ	
volcanic	28/02/2016 (HW)	256				0.705873	7	0.512622	21	-0.32	0.40	84
sedimentary	01/10/2015 (LW)	30				0.706347	18	0.512676	4	0.73	0.08	71
	27/02/2016 (HW)	19				0.705780	5	0.512775	7	2.66	0.15	87
plutonic/ metamorphic	27/02/2016 (LW)	7				0.729165	9	0.512118	2	-10.14	0.05	81
	01/10/2015 (HW)	12				0.729020	8	0.512083	5	-10.82	0.11	81
rio Tumbes	11/09/2007	6	23	17	18	-	-	0.512541	6	-1.89	0.12	80
rio Tumbes	11/10/2007	9	29	15	15	0.712726	8	0.512493	10	-2.83	0.19	80
rio Tumbes	11/11/2007	14	46	14	24	0.712700	9	0.512396	7	-4.72	0.14	82
rio Tumbes	11/12/2007	11	39	12	74	0.711989	8	0.512420	5	-4.25	0.10	80
rio Tumbes	11/01/2008	27	83	61	99	0.713399	9	0.512316	15	-6.28	0.30	79
rio Tumbes	11/02/2008	114	42	95	506	0.712309	10	0.512327	7	-6.06	0.14	77
rio Tumbes	11/03/2008	181	2665	475	581	0.717629	11	0.512240	5	-7.76	0.10	80
rio Tumbes	11/04/2008	92	2284	736	446	0.715501	17	-	-	-		75
rio Tumbes	11/05/2008	39	204	186	195	0.713068	8	0.512256	10	-7.46	0.19	78
rio Tumbes	11/06/2008	11	41	92	84	0.712805	6	0.512338	14	-5.86	0.27	80
rio Tumbes	11/07/2008	8	28	50	47	0.711790	9	0.512358	15	-5.46	0.29	79
rio Tumbes	11/08/2008	12	39	34	34	0.712213	8	0.512424	5	-4.17	0.10	81
rio Tumbes	11/09/2010	27	94	20	20	0.713872	11	0.512412	8	-4.41	0.15	82
rio Tumbes	11/10/2010	19	91	15	16	0.711846	9	0.512485	8	-2.98	0.15	81
rio Tumbes	11/11/2010	13	50	12	14	0.711565	9	0.512505	6	-2.59	0.11	81
rio Tumbes	11/12/2010	30	146	19	25	0.711876	8	0.512294	19	-6.70	0.38	81
rio Tumbes	11/01/2011	37	167	71	95	0.712520	10	0.512362	12	-5.39	0.24	81
rio Tumbes	11/02/2011	107	188	288	225	0.712581	6	0.512304	5	-6.52	0.10	77
rio Tumbes	11/03/2011	16	50	82	91	0.712700	1	0.512364	5	-5.34	0.10	80
rio Tumbes	11/04/2011	46	731	366	332	0.712518	7	0.512327	6	-6.07	0.12	81
rio Tumbes	11/05/2011	20	63	102	99	0.711504	8	0.512457	8	-3.52	0.15	80
rio Tumbes	11/06/2011	21	77	51	48	0.711646	11	0.512430	6	-4.06	0.12	80
rio Tumbes	11/07/2011	22	93	33	35	0.712390	15	0.512420	4	-4.25	0.08	81

rio Tumbes	11/08/2011	31	103	25	25	-	-	0.512514	9	-2.42	0.18	80
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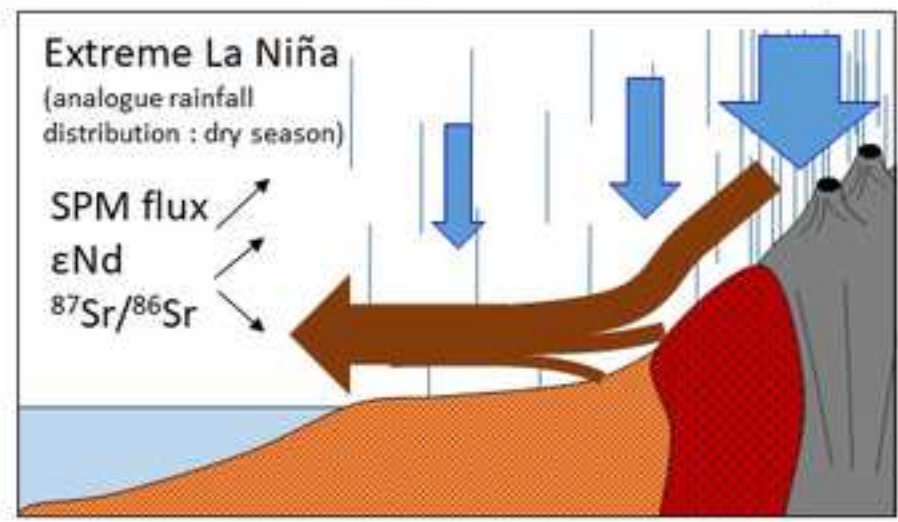
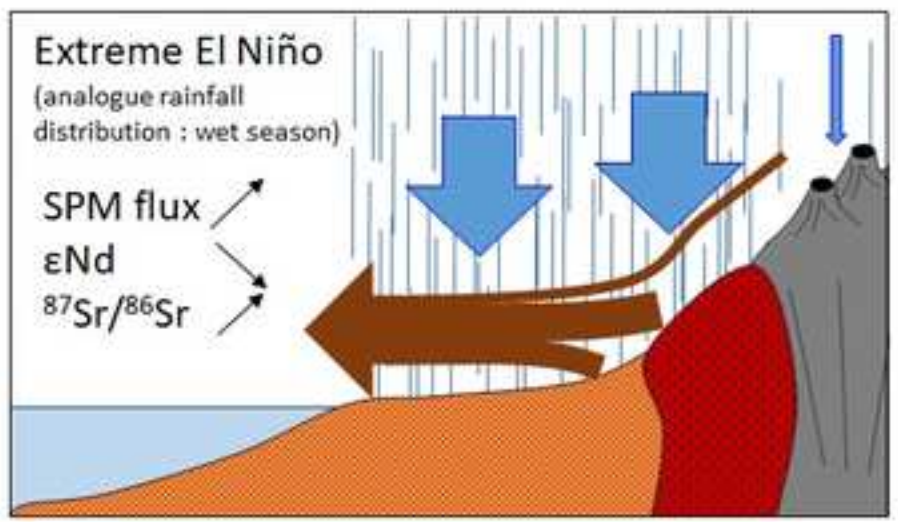
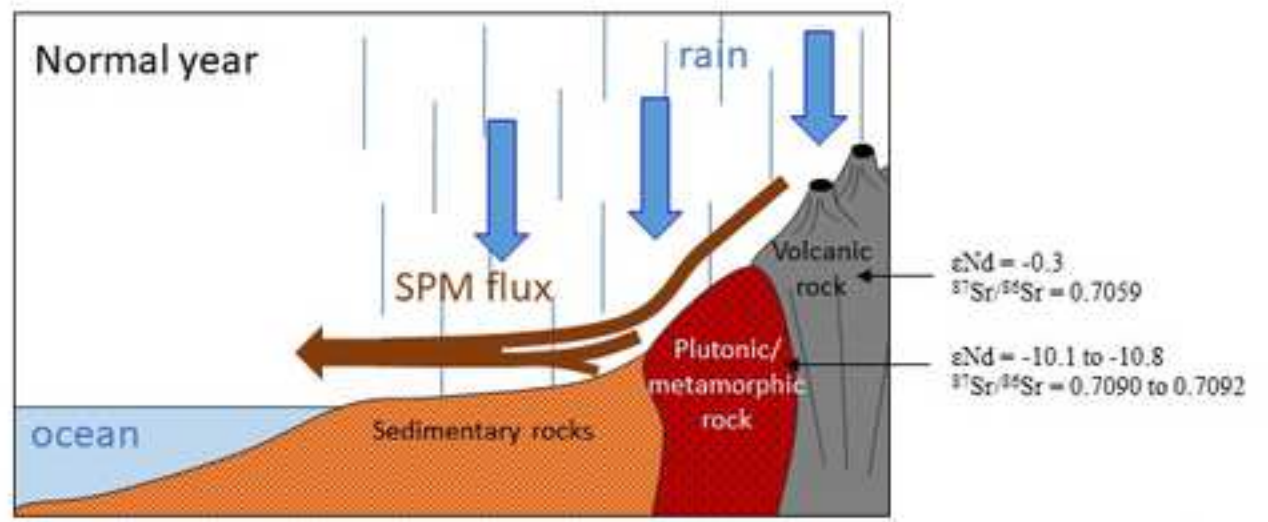
Table S1 : Characteristics of the Tumbes River at El Tigre station and its sampled tributaries

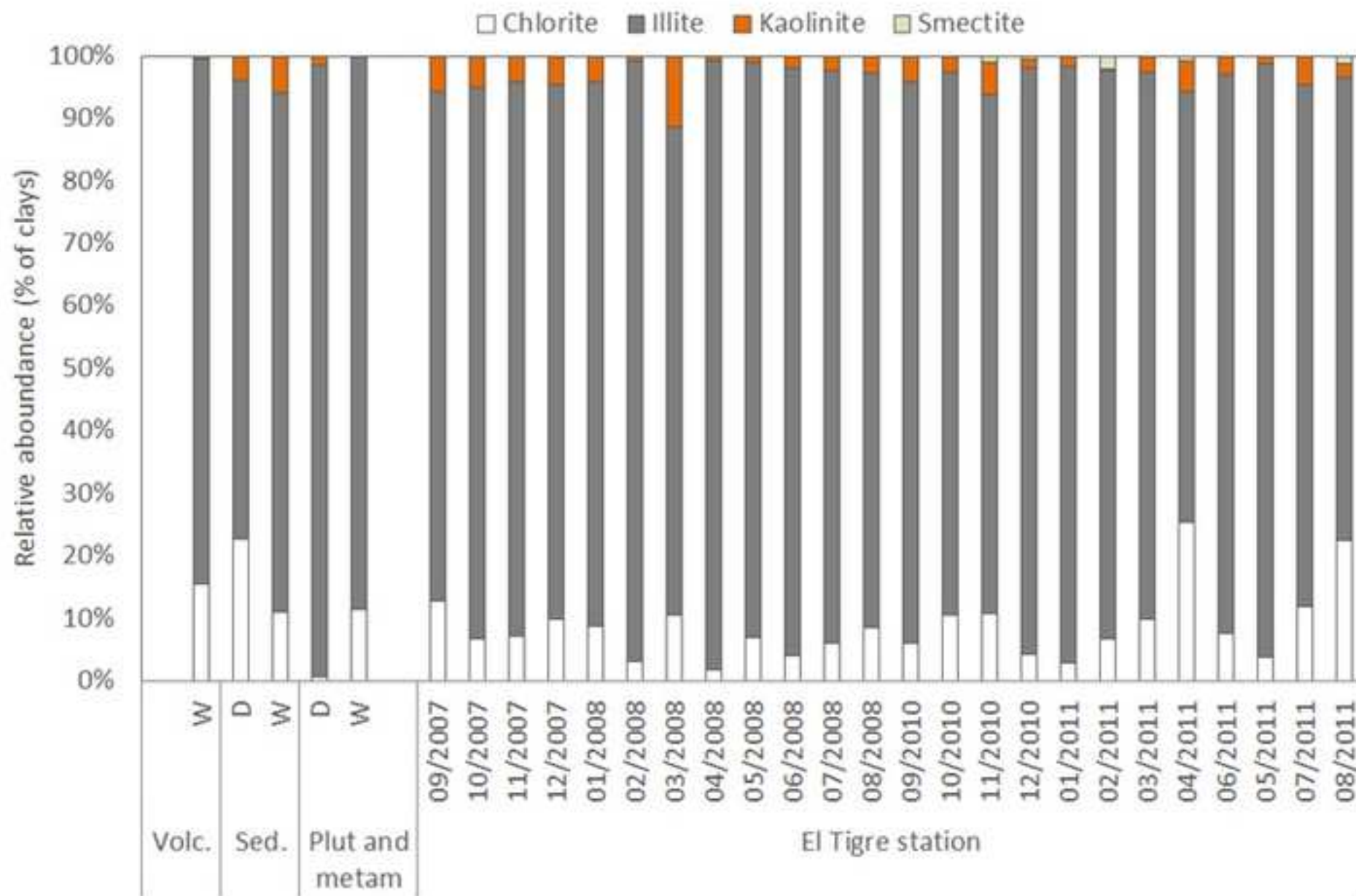
Country	River name	Sampled station Or Endmember	Lat. Decimal degree	Long.	Characteristics	variable	frequency	Monitoring or sampling period
Peru	Tumbes	El Tigre	-3.72	-80.47	Monitored station	Discharge	daily	1963-2016
						SPM concentration	10 days	2004-2014
						Mineralogical and geochemical analysis	monthly	2007-2008 and 2010-2011 hydrological years
Ecuador	Rio Calera @Portovelo	Volcanic	-3.7264	-79.635	Volcanic lithology			1 during 2016 wet (high water level) season
Ecuador	Rio Marcabelli @ Marcabelli	Plutonic/Metamorphic	-3.7699	-79.9183	Plutonic and metamorphic lithology	Mineralogical and geochemical analysis	discrete sampling	1 during 2015 dry (low water level) season and 1 during 2016 wet (high water level) season
Ecuador	rio Pindo tribuary @Buenavista	Sedimentary	-3.853	-79.7058	Sedimentary area			

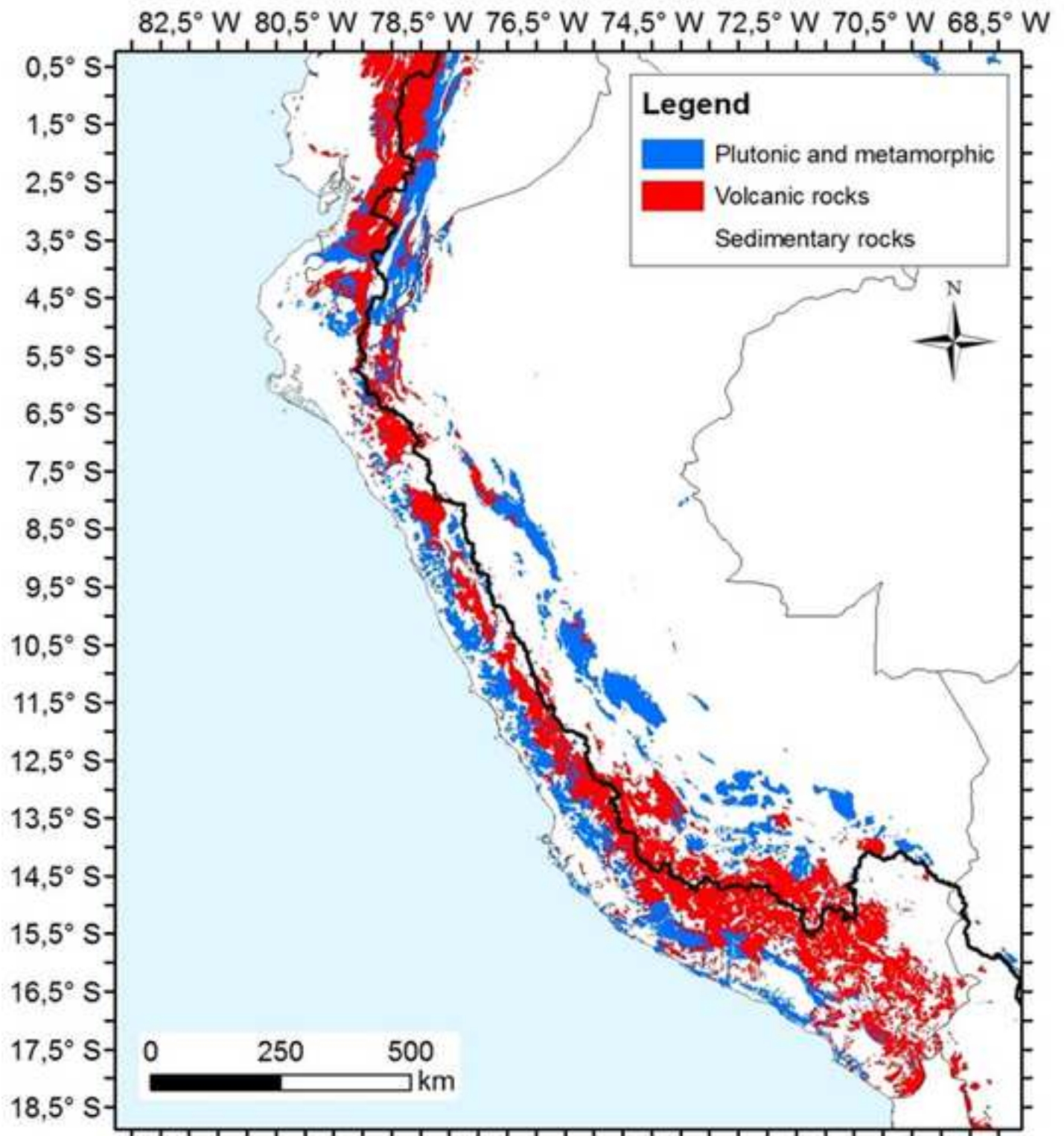
- 1 Table S2 : Mineralogical composition of the sampled Suspended Particulate Matter (SPM) in the
- 2 Tumbes R. and tributaries calculated from Biscaye (1965) method from DRX analyses. LW :
- 3 Low water ; HW : High water.

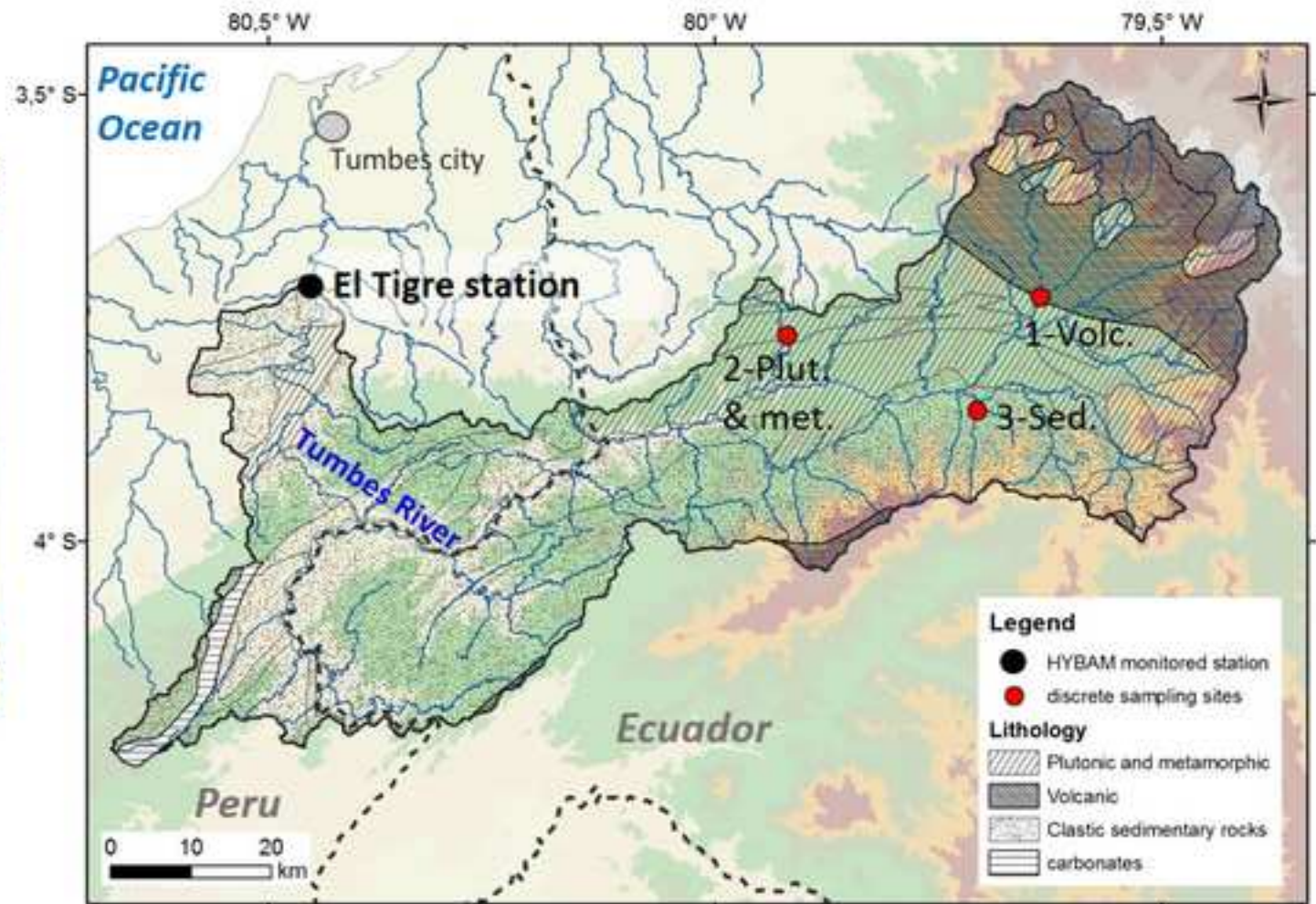
	date or sampling period	% clays				relative content (pic surface proportion/total signal)					
		Chlorite	Illite	Kaolinite	Smectite	index < 2µm	Amphibole (8.4-8.5 A)	Feldspath (3.2A)	Gibbsite (4.85 A)	Quartz (3.34 A)	
volcanic basin	28/02/2016 (HW)	16	84	1	0	0.611	0.022	0.100	0.111	0.156	
sedimentary basin	01/10/2015 (LW)	23	73	4	0	0.382	0.013	0.058	-	0.547	
	27/02/2016 (HW)	11	83	6	0	0.579	-	0.072	0.048	0.301	
plutonic/metamorphic basin	27/02/2016 (LW)	1	98	1	0	0.981	-	0.022	0.013	-	
	01/10/2015 (HW)	11	89	0	0	0.969	-	-	0.009	0.022	
Rio Tumbes @ El Tigre	09/2007	13	82	6	0	0.903	-	-	-	0.097	
	10/2007	7	88	5	0	0.931	-	-	-	0.069	
	11/2007	7	89	4	0	0.927	-	-	-	0.073	
	12/2007	10	85	5	0	0.877	-	0.035	-	0.087	
	01/2008	9	87	4	0	0.823	-	0.045	-	0.132	
	02/2008	3	96	1	0	0.799	-	0.061	-	0.140	
	03/2008	11	78	11	0	0.968	-	0.003	-	0.030	
	04/2008	2	97	1	0	0.912	-	-	-	0.088	
	05/2008	7	92	1	0	0.873	-	0.032	0.006	0.089	
	06/2008	4	94	2	0	0.899	-	0.058	-	0.043	
	07/2008	6	92	2	0	0.951	-	-	-	0.049	
	08/2008	8	89	3	0	0.967	-	-	-	0.033	
	09/2010	6	90	4	0	0.935	0.005	0.012	-	0.049	
	10/2010	11	87	2	0	0.952	-	0.027	-	0.024	
	11/2010	11	83	5	1	0.913	-	0.012	-	0.076	
	12/2010	4	94	1	0	0.959	-	-	-	0.041	
	01/2011	3	96	2	0	0.952	0.005	0.029	0.005	0.008	
	02/2011	7	91	0	2	0.855	-	0.034	0.005	0.106	
	03/2011	10	88	2	0	0.781	0.017	0.049	0.008	0.145	
	04/2011	25	69	5	1	0.574	0.006	0.169	0.010	0.241	
	06/2011	8	89	3	0	0.895	0.008	0.024	-	0.073	
	05/2011	4	95	1	0	0.722	0.018	0.090	-	0.170	
	07/2011	12	83	5	0	0.885	-	0.014	-	0.101	
	08/2011	22	74	2	1	0.899	0.009	0.019	-	0.072	
		mean	9	88	3	0	0.881	0.003	0.030	0.001	0.085
		± sd	6	7	2	1	0.090	0.005	0.038	0.003	0.053

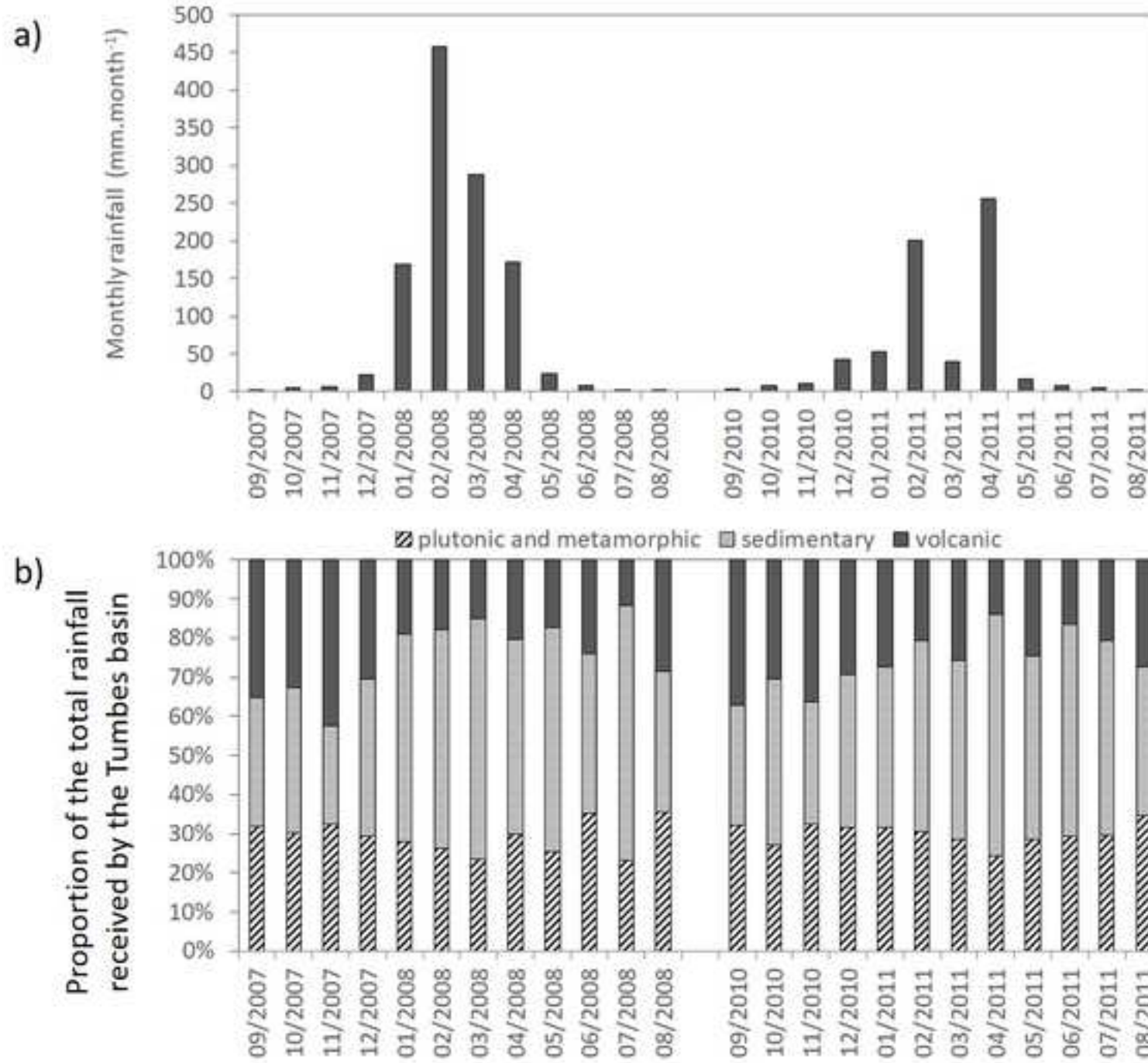
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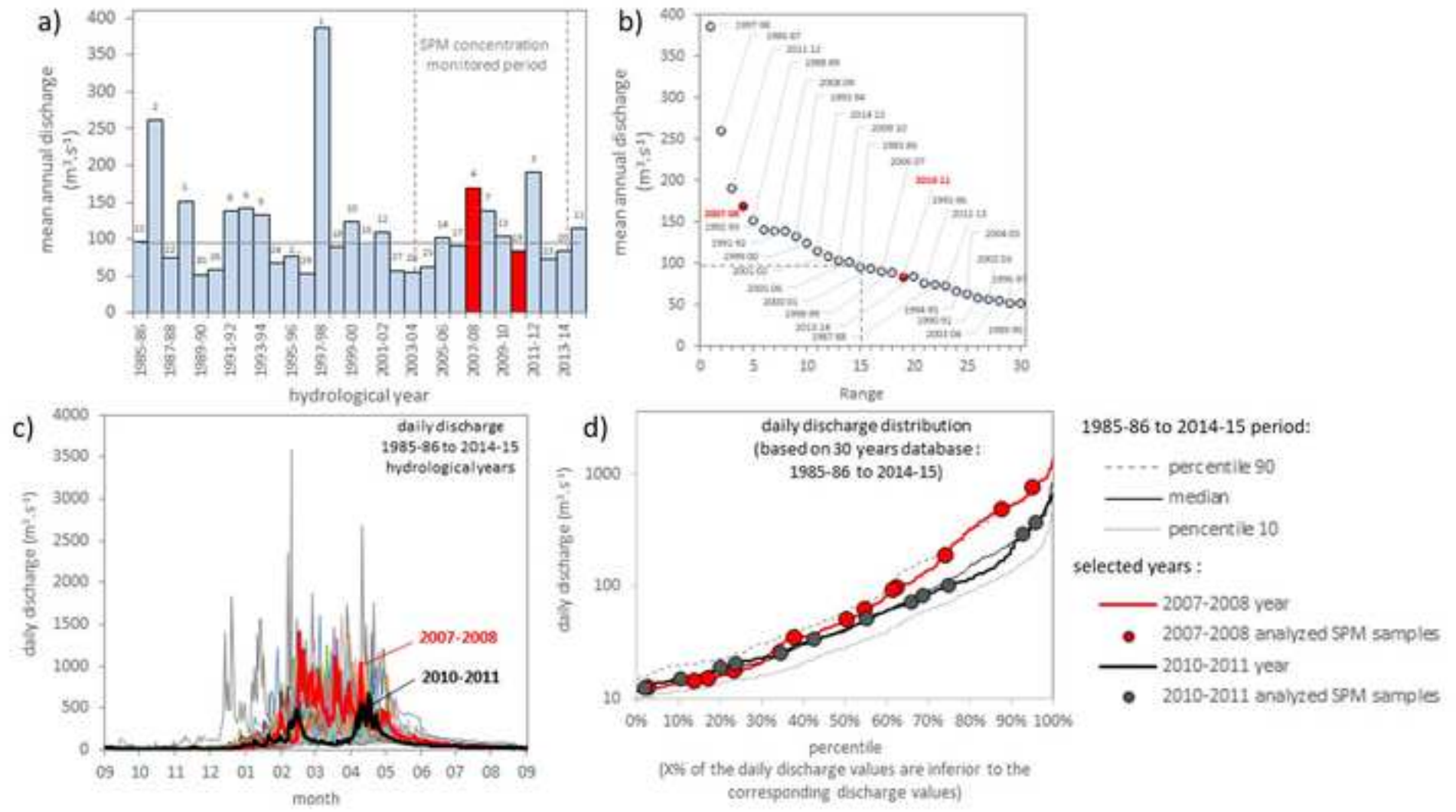












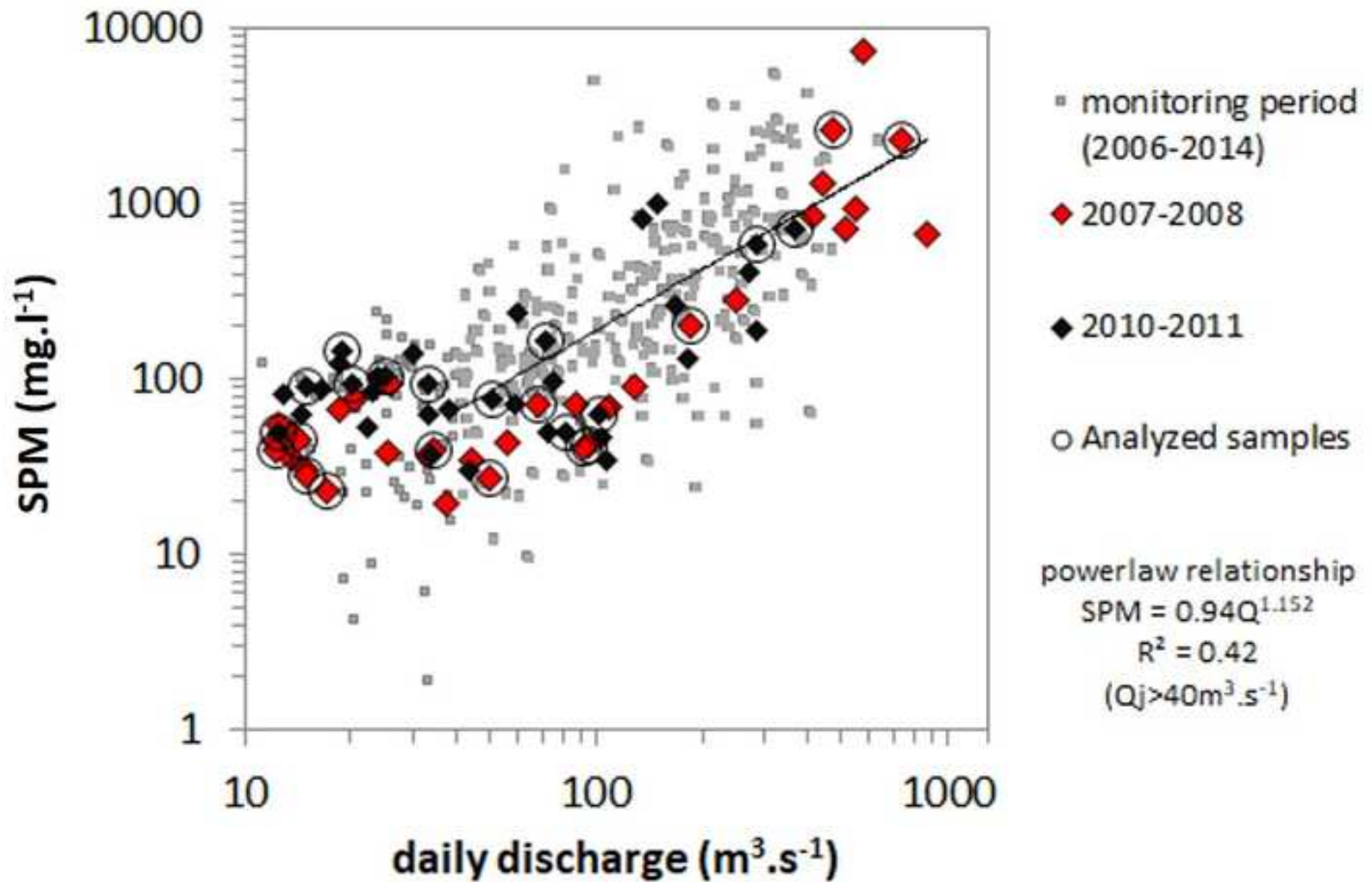
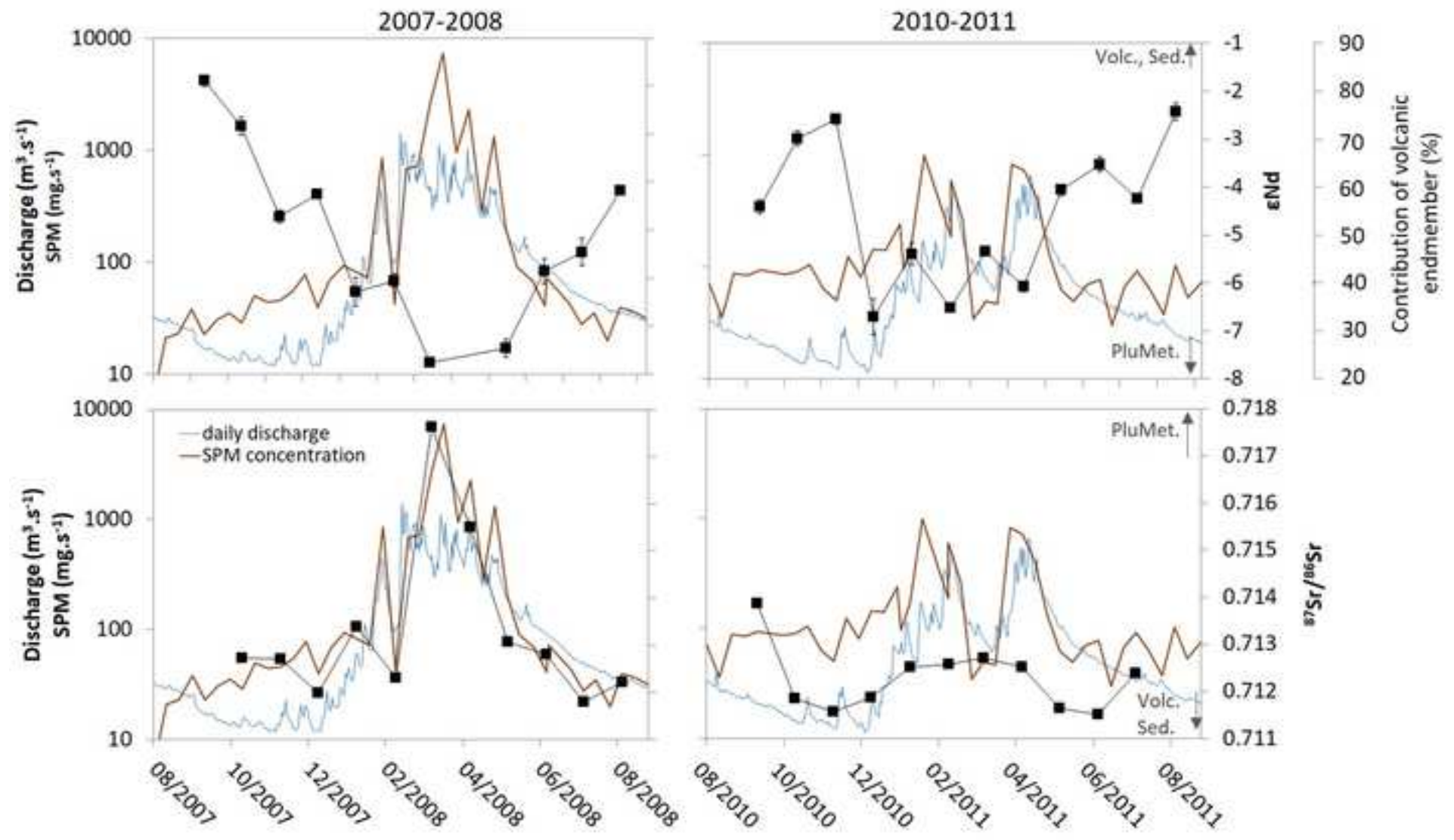
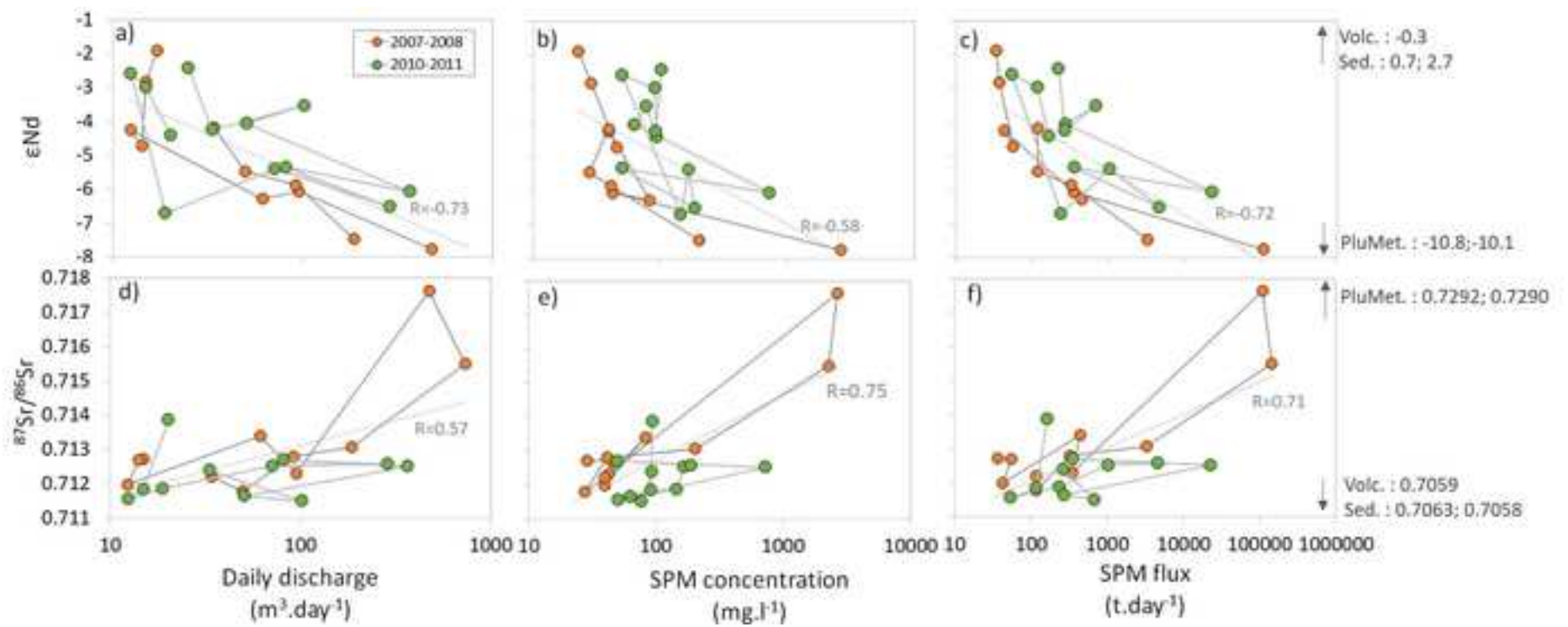
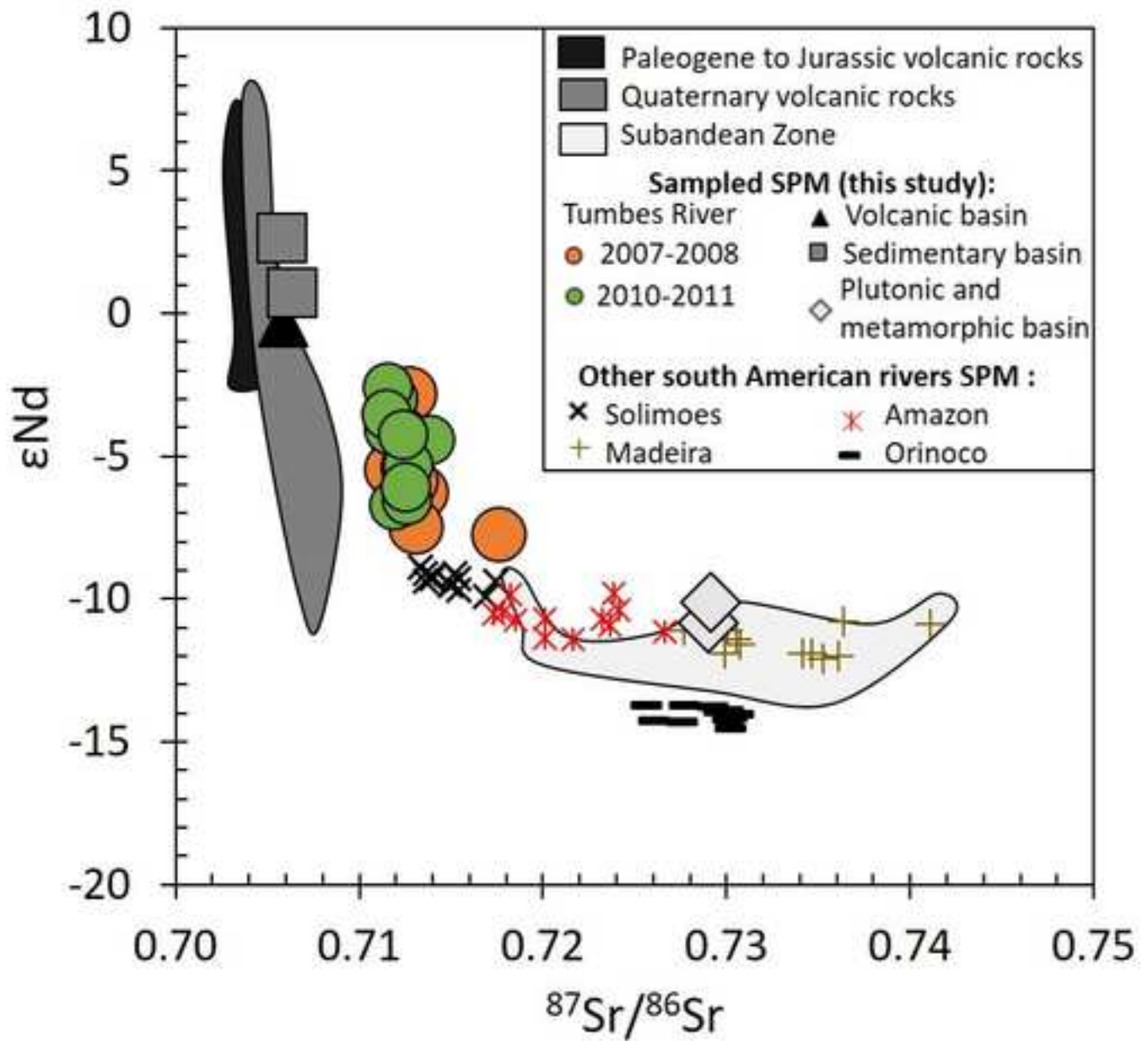
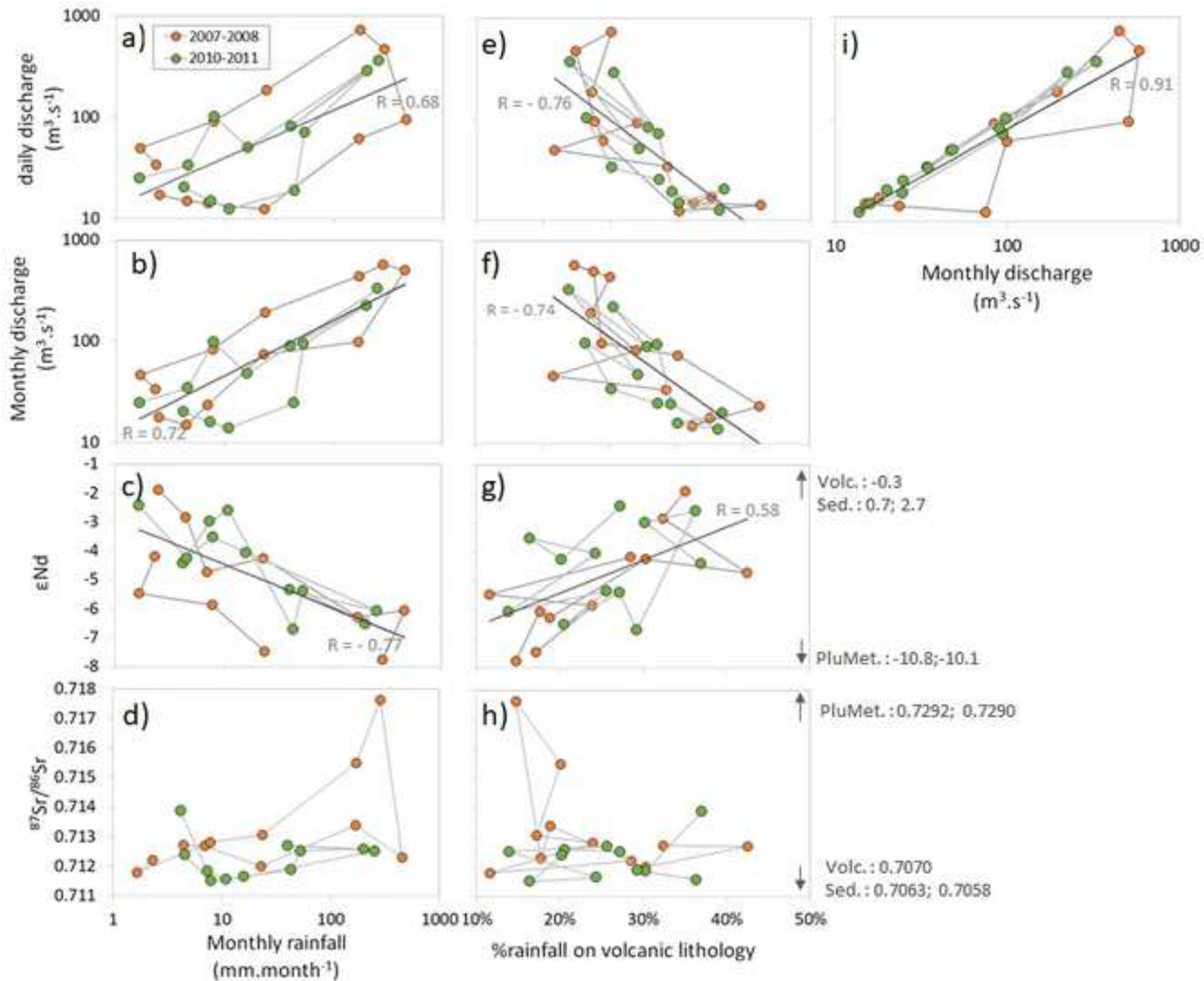


Figure 5









Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: