Control of seasonal and interannual rainfall distribution on the Strontium-Neodymium isotopic compositions of suspended particulate matter in a basin submitted to the ENSO events (Tumbes River - Peru and Ecuador):

Target : "Geochemistry, Geophysics, Geosystems"

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Highlights

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

Abstract (<250 words):

The geochemistry of riverine sediments exported to the oceans is an important tool for the paleo-hydro-climate reconstitution but its interpretation requires a good understanding of its relationship with hydrological variability and provenance sources. In this study we analyzed the major elements, the $^{87}Sr/^{86}Sr$ and εNd signatures and the mineralogy of the SPM sampled monthly during two hydrologic years (2007-2008, a wet year, and 2010-

2011, a normal hydrological year) at the mouth of the Ecuador-Peru binational basin of the Tumbes River. This basin is particularly sensitive to the ENSO (El Niño South Oscillation) events.

While mineralogy and chemical alteration index remain almost constant along the two hydrological years studied, $^{87}Sr/^{86}Sr$ and εNd signatures are particularly sensitive to discharge and SPM concentration variabilities. Along the hydrological year, the εNd variability is controlled by two sources:, the volcanic rocks dominate during the dry period and the plutonic-metamorphic contribution increases during the wet period. This behavior is confirmed by the high correlation between εNd signature and volcanic area monthly rainfall contribution. For most of the samples, $^{87}Sr/^{86}Sr$ is less variable along the hydrological year due to low $^{87}Sr/^{86}Sr$ variability of volcanic material. However, the two exceptional discharge and SPM concentration conditions exhibit more radiogenic (higher) $^{87}Sr/^{86}Sr$ signature.

Hence, this study demonstrate that $^{87}Sr/^{86}Sr$ and εNd signatures can be used both as powerful proxies for paleoclimate reconstitution based on sediment cores analyses and as tools to better constrain the origin of the contemporaneous sediments in relation with spatial rainfall distribution and intensity in Pacific sedimentary basins submitted to ENSO events.

1. Introduction

The hydrological and hydro-sedimentological regime of the Andes are particularly sensitive to extreme hydrological events like those related to El Nino Southern Oscillation (ENSO) system. Indeed, the El Niño and and its companion La Niña, the two expressions of the ENSO, are drivers of the strongest year-to-year climate fluctuations on the planet. They control the hydrology and sediments production from Andean basins, both in Pacific coast (Sulca et al., 2018; Rau et al., 2016; Lavado and Espinoza, 2014, Armijos et al., 2013) and in Amazonian slopes (Guyot et al., 1994; Espinoza et al., 2012). In detail, these events caused extreme flooding in Pacific coastal area, and drought in the Andes, particularly in Northern Peru (Lavado and Espinoza, 2014; Sulca et al., 2018) and may account for 45% of the sedimentary flux exported to the Pacific Ocean for the last 40 years (Moreira et al., 2017).

Hovewer, the prediction of the impact of extreme hydrological events associated to ENSO is difficult because of the relative short time-scale of hydrological and riverine suspended matter export records. The reconstitution of paleo-ENSO events is necessary to understand the main forcing of these events from the Pliocene (e.g. Wara et al., 2005) to Quaternary timescale, including the glacial-intergalcial cycles (e.g. Rein et al., 2005) and the Holocene (e.g. Carré et al., 2012). Paleo ENSO events have been recognized in the onshore/continental geological record based on Oxygen stable isotope compositions of speleothems (Reuter et al., 2009; Apaestegui et al., 2014; 2018; Bustamente et al., 2016), δ18O on authigenic calcite from lake sediment cores (Bird et al., 2011) or Oxygen stable isotopes in ice cores from the Ecuadorian and Peruvian Andes (Hoffmann et al., 2003; Thompson et al., 2013). Offshore, in the Pacific Ocean, paleo ENSO events were identified by analyzing the Mg/Ca, d18O, d13C of planktonic foraminifera spanning the last 22kyr (Sadekov et al., 2013) or oxygen isotopes in Holocene fossil mollusk shells(Carré et al., 2012, 2014). Based on this literature review, most of the geochemical tracers used to reconstruct paleo ENSO events in the geological record seek to identified temperature anomalies based on stable isotope geochemistry. To date, there is little attempt to reconstruct paleo ENSO events based on the identification of peak of sediment fluxes linked to rainfall increase in the Andean coast which could be reflected in the sedimentary record by change in provenance of the associated sediments. For instance, change in provenance based on Nd isotopic composition of the detrital sediment fraction during the past 45,000 years have been used to reconstruct climate-driven changes in the provenance of clays deposited along the Mozambique Margin (van der Lubbe et al 2016). Similarly, changes in provenance of sediments deposited along the tropical South American continental margin between Andes and shield regions, identified based on Nd-Sr isotopic composition variation, were also used for reconstructing the erosional and associated rainfall patterns on continental source regions during the Quaternary (e.g. (Höppner et al., 2018; Zhang et al., 2015).And even more recently, variation of Nd isotopic composition of Amazon River suspended particulate material (termed hereafter SPM) during a one year hydrological cycle has been related to seasonal changes in the rainfall distribution patterns across the Amazon basin, associated with latitudinal migrations of the Intertropical Convergence Zone (Rousseau et al., in revision).

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

Regional setting

The Tumbes River basin is a basin located in Southern Ecuador and Northern Peru (latitude -79.35 and -80.70 decimal degrees). It drains the western slope of the Andes (between -3.47 and -4.25 decimal degree) over an area of 4.8 10^3 km^2 including ~70% in the Andean mountains above 500 m.a.s.l. (Moquet et al., 2018). It originates in the Andes (~ 3800 m.a.s.l.) and flows through a narrow coastal plain until its outlet to the Pacific Ocean. The river drains three main lithologically contrasted domains: the volcanic, the plutonic and metamorphic and the sedimentary domains representing respectively 17, 25 and 58% of the area (figure 1; Table 1). The upper Tumbes drains the volcanic domain which consists in Cenozoic and Mesozoic volcanic rocks. They are composed of andesite, basalts and, locally, pyroclastic rocks. The mid-altitude Tumbes basin drains the Paleozoic plutonic and metamorphic domain which is mainly composed by schists, gabbro, granite and intermediate intrusive rocks (Figure 1). Downstream, the remaining part of the basin is composed by Cenozoic-Mesozoic by mudstones, shales and sandstones. It may also consist locally of modern alluvial fan deposits and limestones (Figure 1).

The basin receives a rain amount of around 1000 $mm.yr^{-1}$ which leads to a specific discharge of around 750 $mm.yr^{-1}$ (Lavado et al., 2012). The cumulative annual rainfall tends to increase with elevation. The rainfall regime, and consequently the discharge regime, shows a strong seasonality, both in term of quantity and geographical distribution. The rainfall period occurs during austral summer, between December and May, in relation to the southernmost position of the Intertropical Convergence Zone (ITCZ,Segura et al., 2018). This period contributes to around 85% of the annual discharge at El Tigre station (1985-2015 period; SENAMHI, PEBPT and HYBAM). The relative contribution of the rainfall amount varies also along the year. While the plutonic and metamorphic domain contribution is almost constant along the year (~30%), the volcanic domain contribute to more than ~35% along the September-October-November (SON) period and decrease to ~20% during the rest of the year. Therefore, the sedimentary area contributes between ~35% and ~50% of the amount rainfall received by the basin during the wet and dry seasons, respectively (figure A1).

The main anthropogenic activity is urbanization, throughout the city of Tumbes located close to the outlet of the basin, downstream the El Tigre hydrological station (figure 1). Small scale gold mining activity has also been reported upstream in the Puyango and Portovelo-Zaruma sub-basins (Betancourt et al., 2005; Marshall et al., 2018). But overall, the anthropogenic influence is rather small????

2. Material and methods

2.1. Hydrological and climate data

Mean monthly rainfall was extracted from the PISCO Database (Peruvian Interpolated data of the SENAMHI's Climatological and hydrological Observations; Lavado et al., 2016) for the 1985-2015 period. The hydrological year is considered to be from September to August. At the El Tigre SENAMHI/HYBAM station, daily river discharge is available for the period (1963-2016). In the present study we considered the 1985-2015 period as the reference. Water levels were collected each 4 hours using a conventional hydrological method. Gauging was accomplished using a current mechanical meter in Peru. The daily discharge record was then calculated from rating curves (discharge - water level relationship) using the Hydraccess software (Vauchel, 2005).

2.2. *Suspended Particulate Matter measurements (SPM)*

For SPM concentration measurements, a 650 ml bottle of surface water (10-15 cm from the surface) was sampled each 10 days between 04/02/2004 and 21/04/2014 (387 samples). The sample is filtered through a pre-weighed filter of a 0.45µm pore size cellulose filter. The filter is dried at 80°C and weighted to determine the riverine SPM concentration.

2.3. Annual Flux calculation of monitored rivers

Annual SPM fluxes have been calculated based on the 10 days frequency of SPM concentration determinations and daily discharge records. The discharge values of the sampled days are representative of the hydrological conditions of each year recorded at the El Tigre station. We calculated the SPM flux of each sampled day according to the following formula:

$$F_d = C_d \times Q_d \qquad \text{Equation 1}$$

with F_d, C_d and Q_d the daily flux ($t.day^{-1}$), concentration ($mg.l^{-1}$) and discharge ($m^3.day^{-1}$) of the sampled day. Then, we interpolated the daily SPM flux values to estimate the monthly and the annual flux. According to Moatar et al. (2013) bias and imprecision method calculation, we estimated the proportion of SPM flux which transit by the station during 2% of the hydrological cycle (M2% = 0.5) and, based on their calibrated laws, we deduced the bias as less than 6% and the imprecision which ranges from -43% to 39% (see Moatar et al., 2013 for details). The SPM specific flux ($t.km^{-2}.yr^{-1}$) as well as the specific discharge ($mm.yr^{-1}$) were calculated by dividing, respectively, the SPM flux and the discharge by the total area of the basin at the El Tigre station.

2.4. Selection of the studied years

Among the hydrological years for which we had access to sediment filters (2006-2011 period), we selected the wetter year (2007-2008 hydrological year) and a year close to the median discharge (2010-2011 hydrological year) by comparison with the 30 discharge year along the 09/1985-08/2015 period. In term of annual discharge, with an annual module of $170 m^3.s^{-1}$, the 2007-2008 year ranks as the 4^{th} wetter year of the 30 years period and exhibits, therefore, a return period of 7.8 years. It ranges after the El Niño years of 1997-1998 ($387 m^3.s^{-1}$) and 1986-1987 ($261 m^3.s^{-1}$) and the La Niña year of 2011-2012 year ($190 m^3.s^{-1}$). The lowest annual discharge value recorded along this period ($52 m^3.s^{-1}$) corresponds to the 1989-1990 hydrological year. The 2010-2011 exhibits a module of $84 m^3.s^{-1}$, close to the 1985-2015 period median value of $95 m^3.s^{-1}$. The distribution of the daily discharge of the 2010-2011 period is similar to the 1985-2015 period median distribution (figure 2a, b). Therefore the 2010-2011 year is considered as a "normal" year in term of discharge distribution (figure 2b). The higher daily discharge (half upper daily discharge values) of the 2007-2008 year is close to the 90^{th} percentile distribution of the 1985-2015 period. In other terms, during the 1985-2015 period only 10% of the years (3 years) exhibit higher daily discharge during the wet period than the 2007-2008 year (figure 2b). This implies that, for 1985-2015 period, the 2007-2008 year is the 4^{th} wetter hydrological year both in term of annual budget and high daily discharge frequency.

To identify potential sources effects we also sampled the riverine suspended matter of three Tumbes River tributaries representative of each lithological environments: Volcanic, Plutonic and Metamorphic and Sedimentary areas (Table 1).

2.5. Mineralogy and Geochemistry

2.5.1. Sample treatments

The 30 selected SPM filters were immerged in ultra-pure water and 3 to 5 ultrasonic baths of 30 minutes were performed until all SPM was visually removed from the filters. Then, the filters were discarded and the SPM was dried. Between 10 and 300 mg of SPM were therefore available on each selected filters. The SPM was divided in two aliquots. A negligible weight of SPM (2-3 mg) aliquot was used for X-ray diffraction analyses (DRX) and the remaining sediment was digested for major and for Nd and Sr isotopic analyses. This second aliquot was first treated with H_2O_2 for 24h at ambient temperature, then it was digested in HNO_3+HF for 36 h at 80 °C, and in HCl+HNO_3 for 36 h at 120 °C. Sr and Nd were separated by ion-exchange chromatography using Sr–SPEC, TRU–SPEC and LN–SPEC resins (Eichrom®) according to the Pin et al. (1994) and Pin and Santos Zalduegui (1997) method. Ultrapure and bi–distillated reagents were used for all digestion and separation steps.

2.5.2. Sample Analyses

All analyses were performed at the Géosciences-Environnement-Toulouse (GET) Laboratory - Observatoire Midi-Pyrénées (OMP). XRD analyses were carried out using a G3000 Inel diffractometer (40 kV, 30 mA) and Ni-filtered CuKα1,2 radiation (λ=1.5406 Å). Due to limited amounts of material for some samples, we did not perform the glycol treatment, which enables the distinction of inflating clays. We performed a semi-quantitative estimate of the Chlorite, Illite, Kaolinite and Smectite aboundance based on the Biscaye (1965) method. Results are reported in Table 2.

Major element analyses were measured by ICP-OES (Horiba Jobin Yvon Ultima2). Sr and Nd concentrations were determined by Quadrupole ICPMS (AGILENT 7500 CE), using a four-point calibration and In/Re as internal standards to correct for instrumental drift and matrix effects. Measurement accuracy was assessed by processing 5 and 10 mg of the GA basalt reference material (CRPG; Centre de Recherches Pétrographiques et Géochimiques). Results, reported as Al ratios to limit uncertainties due to weight, are in within uncertainties ±10% by comparison with the reference value. The Chemical Index of Alteration (CIA) is generally used to estimate the degree of weathering of a basin (e.g. Li and Yang, 2010 and references within). During weathering, alkali metal and alkaline earth ions are released into solution, whereas alumina is preferentially retained in the weathered material. According to Nesbitt and Young (1982), CIA is calculated as following:

$$CIA = [Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O) \times 100 \text{ (molar proportions)} \quad \text{Equation 2}$$

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

The CIA of the GA referenced standard is 59 (CRPG) and the CIA of GA samples analyzed here is 55 and 61 for the two GA reference material analyzed samples in the present study. A 4% error is therefore considered in the CIA result presentation (table 3).

Nd and Sr isotope measurements were conducted on a Triton Thermal Ionization Mass Spectrometer. Nd isotope ratios were measured in static mode, corrected for instrumental mass bias fractionation using a $^{146}Nd/^{144}Nd$ ratio of 0.7219. One analysis of the La Jolla standard gave a $^{143}Nd/^{144}Nd$ ratio of 0.511858 ± 16.10^{-6} (±2 σ; 115 runs) in agreement with the recommended value of 0.511858 (Lugmair et al., 1983). Repeated analyses of Rennes standard gave a $^{143}Nd/^{144}Nd$ ratio of 0.511947±10.10^{-6} to 0.511969±16.10^{-6} (n=3; ±2 σ; 150 runs) in agreement with the value recommended by Chauvel and Blichert-Toft (2001) for the Rennes Nd standard ($^{143}Nd/^{144}Nd$ = 0.511961 ±13; 2σ). Nd isotopes are reported using the εNd notation, normalising samples to the Chondritic Uniform Reservoir (CHUR) value of $^{143}Nd/^{144}Nd$ =0.512638 (Jacobsen and Wasserburg, 1980):

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

Sr isotope ratios were measured in dynamic mode, corrected for instrumental mass bias using invariant ratio $^{88}Sr/^{86}Sr$ = 0.1194. Repeated analyses of the NBS 987 standard gave a $^{87}Sr/^{86}Sr$ ratio of 0.710256 ± 15.10^{-6} (2 σ, n=6) in agreement with the recommended value of 0.710240.

3. Results

3.1. Hydro-sediment budgets

During the sampling years, the water discharge corresponding to sampling ranged from 12 $m^3.s^{-1}$ (November 2010) to 736 $m^3.s^{-1}$ (March 2008) and the SPM concentration varies from 2 to 7350 $mg.l^{-1}$ and follows a powerlaw relationship with daily discharge for discharges conditions up to around $30m^3.s^{-1}$ (figure 3). The SPM concentration remains almost constant for discharge lower than this value (Morera et al., 2017). During the 2007-2008 and the 2010-2011 years, the Tumbes River exports 1835 and 190 $t.km^{-2}.yr^{-1}$ of sediments respectively. The SPM concentration variability follows the daily discharge (Figure 3).

3.2. Mineralogy

The DRX analyses show that the sampled SPM at El Tigre station are dominated by illite (88±7% of the clays; ± 1 sd) followed by the chlorite (9±2%) while kaolinite and smectite represent less than 3% of the clays. The composition of the clays does not vary with the seasonal hydrological cycle. The sampled sub-basins exhibit almost the same mineralogical composition (Figure 4; Table 2). The mineralogical composition of the analysed samples are similar to those of the Peruvian and Bolivian Andean basins of the Amazon (Guyot et al., 2007).

According to these analyses, the SPM grain size is mainly inferior to 2µm (88±9%). feldspath and gibbsite are not detected in all samples. Quartz relative abundance varies in phase with grain size <2µm abundance. However, as for clays, there is nono relationship with discharge . Interestingly, the monolithological sub-basin samples can exhibit lower proportion of SPM <2 µm and higher signal of amphibole, feldspath, gibbsite and quartz (Table 2).

3.3. Geochemistry

The CIA of the El Tigre station SPM ranges between 75 and 82. This low variability reflects a relatively homogenous chemical weathering state of the sediments. The discrete sampling of monolithological basins exhibit the same range of CIA values (Table 3; figure 5).

The εNd SPM values range from -7.8 to -1.9. The εNd SPM values follow a seasonal behavior in antiphase with the discharge and, therefore, the SPM concentration. The minimum εNd value is observed during the flood season (Figure 6). The $^{87}Sr/^{86}Sr$ isotopic composition of analysed SPM ranges from 0.7115 to 0.7176. The variability of $^{87}Sr/^{86}Sr$ is low for most of the samples (0.7115 to 0.7139) with the exception of the March and April 2008 samples which exhibit higher values (0.7176 and 0.7155 respectively). Interestingly these two months correspond to the highest SPM concentration recorded for the analyzed samples and correspond to high discharge conditions (Table 3; Figure 6).

The volcanic basin SPM sample has the higher Nd and lower Sr isotope composition of the sampled sediments. By contrast the two samples from the plutonic and metamorphic basin exhibit lower Nd and high Sr isotope compositions (Table 3). The sampled sedimentary tributary exhibits values similar to the volcanic basin(Table 3).

All correlation analyses presented here are performed along the whole dataset (N=21, 22, 23 or 24 according to the considered data) and significant at $p\text{-value}<0.01$ when they are presented. Considering both hydrological cycles (figure 6, 8), Nd and Sr isotopic compositions are significantly correlated ($p\text{-value}<0.01$) with both discharge variability and SPM concentration. In details, the εNd is better correlated with discharge variability (R=-0.72; figure 8a) than with SPM concentration (R=-0.59; figure 8b) while $^{87}Sr/^{86}Sr$ is better correlated with SPM concentration (R=0.75; figure 8e) than with discharge (R=0.57; figure 8d). As SPM concentration depend on discharge variability (figure 3), both $^{87}Sr/^{86}Sr$ and εNd signatures are very well correlated with SPM fluxes (R = -0.71 and 0.72 respectively; figure 8c and g).

4. Discussion

4.1.

The Tumbes SPM and basin tributaries CIA values are quite similar (Figure 5; Table 3). Therefore, the CIA cannot be used for tracing the source of the sediments. The εNd and $^{87}Sr/^{86}Sr$ isotopic composition of sedimentary rocks have been proven to be robust tools for determining the provenance of the sediments (McLennan et al., 1993; Faure and Mensing, 2004Allègre and Rousseau, 1984; Goldstein and Hemming, 2003; Roddaz et al., 2014; Hoppner et al., 2018) and riverine SPM (e.g. Viers et al., 2008; Singh et al., 2008; Rousseau et al., in revision) when the source of the sediments are isotopically contrasted. However in some cases, these isotopes signatures can be can be controlled by grain size due to sorting effect (.Bayon et al. (2015) Faure, 1986; Blum and Erel, 2003; Meyer et al., 2011). Bouchez et al. (2011) (Roddaz et al., 2014). In the Tumbes River and its tributaries the mineralogy and the CIA do not vary suggesting that sampled SPM are almost homogenous in term of the grain size class. SPM Nd and Sr isotope signature would be, at first order, mainly controlled by source effect for most of the samples.

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

$$\%\mathrm{SPM}_{volc} = \frac{-1}{\varepsilon\mathrm{Nd}_{volc} - \varepsilon\mathrm{Nd}_{plu\ met}} \times \varepsilon\mathrm{Nd}_{volc} - \varepsilon\mathrm{Nd}_{sample} + 1 \qquad \text{Equation 4}$$

With %SPMvolc the relative proportion of the Tumbes SPM derived from volcanic domain and $\varepsilon\mathrm{Nd}_{volc}$, $\varepsilon\mathrm{Nd}_{plu\ met}$ and $\varepsilon\mathrm{Nd}_{sample}$ the εNd value of the volcanic basin, plutonic and metamorphic basin and Tumbes SPM respectively.

According to this calculation, 24 to 74% of the Tumbes SPM are derived from the volcanic endmember and the contribution of the volcanic endmember co-vary with the discharge (Figure 6)..

4.2. Relationship between Sr-Nd isotopic composition and and hydro-climatic variables

The observed correlation between Sr-Nd isotopic composition with SPM concentration and discharge suggest that these isotopic composition can be considered as good proxies of the seasonal and inter-annual SPM fluxes variability in the Tumbes basin. However, it is important to highlight that for Sr isotopes this pattern is controlled by two extreme discharge and SPM concentration values occurring during the wet hydrological cycle (2007-2008). The $^{87}Sr/^{86}Sr$ is therefore more sensitive to anomalous hydrological conditions.

Indeed, during both analyzed hydrological cycles, Nd isotopes vary from volcanic to plutonic and metamorphic basin endmembers signature at seasonal timescale (figure 6, 8). During low water level period, SPM Nd isotope signature is closer to the volcanic endmember while the plutonic and metamorphic endmember appears to influence more the SPM geochemistry during high level water season. suggests that SPM εNd values are sensitive to the distribution of rainfall throughout the studied basin. Indeed, during the low discharge period the maximum of rainfall occurs upstream the basin, in volcanic domain (figure A1) while during the high water stage, the proportion of the sediments coming from the plutonic and metamorphic area and sedimentary areas and the proportion of rainfall received by this area, are higher (figure A1). This is confirmed when comparing the daily discharge, monthly discharge and εNd signature with the monthly relative rainfall distribution throughout the basin (figure 8, 9, A1). The rainfall database PISCO is only available at monthly timescale, however, sampled daily discharge are representative to the monthly discharge and monthly rainfall as it can be observed throughout the high correlation value between daily discharge and monthly discharge (r=0.88; figure 9a); the monthly discharge and the monthly rainfall (r=0.72; figure 9b) and, therefore, between the daily sampled discharge and the monthly rainfall (r=0.68). Indeed, the contribution of volcanic area in term of mean monthly rainfall is significantly correlated to monthly discharge at the outlet (r=-0.74; figure 9e) and therefore to the Nd isotopic composition of SPM sampled at the station (r=0.58; figure 9f). This results demonstrate that the Nd isotopic composition of SPM is an excellent proxy of rainfall amount (figure 9c) and rainfall distribution variability (figure 9f) of the Tumbes basin.

To conclude, variation in Nd and Sr isotopic composition of SPM variability are powerful proxies of the hydrological conditions. The εNd traces the spatial distribution of the rain throughout the basin which is linked to the outlet discharge. As $^{87}Sr/^{86}Sr$ is less sensitive than Nd to the source variability, this isotope ratio traces only exceptionally high hydrological conditions during exceptional years.

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4.3. Implication for paleo ENSO and paleo extreme hydrologic event reconstruction

Being sensitive to seasonal rainfall distribution (mainly εNd) and interannual hydrological/hydrodynamic anomalies ($^{87}Sr/^{86}Sr$), these isotopic tools may be particularly interesting to reconstruct the paleoclimatology of the studied basin which is highly sensitive to El Niño events Morera et al., 2017). In addition, the results of this study may not only be used for the Tumbes River paleoclimate reconstruction but also for the other Peruvian Pacific coast basins affected by the ENSO events. Nd and Sr isotopes variability along Pacific margin sediments cores has previously been interpreted as function of the upwelling redistributions of the terrigenous sediments produced by rivers which exhibit contrasted signature between 0° and 18°S (Ehlert et al., 2013). In the present study we propose a new and complementary perspective to interpret such records. The altitudinal spatial rainfall distribution over these basins need also to be taken into account to interpret the geochemistry of these marine core sediments. In fact, In Ecuador and Peru, the Pacific coastal basins are characterized by similar lithology repartition with volcanic rocks in elevated regions and plutonic and metamorphic rocks in lower elevated regions (figure A2). These latter? areas correspond to the rainfall repartitions anomalies occurring during ENSO events even if this effect decrease southward (Lagos et al., 2008; Lavado and Espinoza, 2014). Indeed, according to Lavado and Espinoza (2014), during the strong El Niño events and coastal El Niño events, northern Peruvian Pacific basins are submitted to significant increase of rainfall from the coast to the high elevation areas, while the rainfall decrease in the southern basins especially in the elevated areas. However, during La Nina events, positive rainfall anomalies are recorded in the upper part of the basins (e.g. Sulca et al., 2018). Based on a regionalization of the rainfall data along the Peruvian Pacific coast, Rau et al. (2017) highlighted that the main modes of influence of the ENSO increased rainfall over downstream regions in northern Peru during extreme El Niño events and decreased rainfall over upstream regions along the Pacific slope during central Pacific El Niño events. Indeed, during strong El Niño events, more radiogenic $^{87}Sr/^{86}Sr$ and more negative εNd values are expected to be found for SPM of the northern basins because of lower rainfall on volcanic rocks relatively to the downstream areas during these events. During the La Nina events, higher rainfall amount in the more elevated areas occupied by volcanic rocks (high ƐNd values) would produce SPM with higher ƐNd values and less radiogenic Sr isotopic composition.

In addition, the dataset presented in this study could be used to improve, paleoclimate reconstruction based on Sr-Nd isotopic composition of marine coresediments as most of the studies are based on a single SPM sampling of the different tributaries or rivers which produce the alimented the marine sediments (e.g. Ehlert et al., 2013; Li et al., 2015; Hoppner et al., 2018).

5. Conclusion

We investigated the geochemistry of the riverine SPM (Suspended Particulate Matter) produced by the Tumbes River at monthly frequency along two hydrological years, including a wet (2007-2008) and a normal (2010-2011) year. We also analyzed the SPM of 3 monolithological tributaries representative of the lithological diversity of the basin (i.e. volcanic, plutonic and metamorphic and sedimentary sub-basins). We compare this new and inedited geochemistry database with the hydrology, climate and geology data available over the studied basin.

The clay mineralogy and CIA are almost homogenous along the hydrological cycle, showing that no major changes of these variables occur along the hydrological cycle. Indeed, these two parameters are not adapted to track the SPM sources.

Sr and Nd isotopes signatures are variable during the hydrological year and they covariate with discharge, SPM concentration and SPM flux variability. ƐNd varies from -7.76 to -1.89 along the two analyzed hydrological year and this variability is coherent with the spatial rainfall distribution throughout the basin. Less radiogenic values are measured during rainy season when the contribution of the upper part of the basin, dominated by volcanic rocks (more radiogenic endmember), is lower. Therefore, Nd isotope composition constitute a direct proxy of rainfall distribution which is related to SPM and water fluxes along the hydrological year. With the exception of two samples, Sr isotope composition is less variable along the studied periods ($^{87}Sr/^{86}Sr$ = 0.7115 to 0.7139) because SPM are highly influenced by volcanic derivate material which exhibits a low Sr variability by comparison to the ƐNd. The two exceptions are high Sr values ($^{87}Sr/^{86}Sr$ = 0.7176 and 0.7155) measured during abnormal hydrological conditions of March and April 2007 probably due to higher contribution of metamorphic rocks domain less variable in term of ƐNd signature but highly variable to $^{87}Sr/^{86}Sr$. Interestingly, together these geochemical tracers are highly linked to hydrological and erosional processes of the Tumbes basin.

These isotopic tools are powerful proxies to either be use to reconstitute paleoclimate based on sediment core from floodplain and/or ocean, to identify the main processes of SPM mobilization seasonally and inter annually and to track anthropogenic impacts on SPM production in the Tumbes basin. Indeed, as these geochemical tracers represent erosional processes, they can easily be used to identify current or further changes in term of increase or decrease of SPM fluxes associated to anthropogenic activities like mining, agriculture and hydraulic infrastructure for example. Moreover, these tracers allow to identify the changes of rainfall and hydrological regimes both in term of water fluxes and rainfall distribution at the scale of the Tumbes River, which is a basin highly sensitive to ENSO events. Interestingly, the geology sensed along the whole Pacific coast in Peru respond to the same geological distribution. Therefore the results of the present study can be generalized for these contexts and allow to reconstruct paleo ENSO variabilities and other climate modes affecting the pacific coast climate from decadal to multimillenal timescales.

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List of figures:

Figure 1 : map of the Tumbes River basin : hydrological network, lithological domains, national boundaries and sampled stations.

Figure 2 : Hydrological characteristics of the selected years along the 1985-1986 to 2014-2015 period (30 years). a) Hydrogram of the 30 years. b) Distribution of the daily discharge for the 90th, 50th and 10th percentiles (from the lowest to the highest values). 2007-2008 and 2010-2011 daily discharge distribution are also reported. The daily discharge for which SPM samples are available are reported for the two selected hydrological years (see the supplementary material S1 for calculation details).

Figure 3 : SPM concentration as function of discharge of the Tumbes R. at El Tigre station (2006-2014 period; 2007-2008 and 2010-2011 hydrological years). The samples analyzed for geochemistry are identified for reference. The SPM vs daily discharge (Qj) powerlaw relationship is added for reference.

Figure 4 : Relative proportion of mineralogical content of clays of the monolithological basins and of the Tumbes River at El Tigre station. (D: Dry period; W : Wet period).

Figure 5 : CIA and A-CN-K diagram of rock plot analyses (Nesbitt and Young, 1982, 1984; Fedo et al., 1995). CaO* refers to the CaO in silicate minerals. All sample calculations are in mole numbers.

Figure 6 : Variation of daily discharge (blue line), SPM concentration (brown line), εNd and Sr isotopes composition (black line and scares) of the Tumbes River SPM at El Tigre station during the two selected hydrological cycles. Error bar of 87Sr/88Sr are included in the symbol surface. The relative contribution of SPM source calculated from the equation 4 is added for reference (same symbole than εNd as it results from a proportional relationship).

Figure 7. 87Sr/86Sr versus εNd(0) diagram for Tumbes R. and tributaries sediments. Volcanic rocks data are extracted from Scott et al. (2018) and Ancellin et al. (2017) and Sub andean zone domain was defined by Roddaz et al. (2005).

Figure 8 : εNd(0) vs a) daily discharge; b) SPM concentration and c) daily SPM flux. 87Sr/86Sr vs d) daily discharge; e) SPM concentration and f) daily SPM flux. Correlation coefficients considerer all points of both hydrological cycles and are all significant (p-value<0.01). Volc : volcanic basin; PluMet : plutonic and metamorphic basin; Sed : sedimentary basin.

Figure 9: a) daily discharge vs monthly discharge. b) Mounthly discharge, c) εNd(0) and d) 87Sr/86Sr vs mounthly rainfall. e) Mounthly discharge, f) εNd and g) 87Sr/86Sr vs proportion of rainfall received by the volcanic lithology (reported in fig.A1).Only significant correlation coefficients (p-value<0.01) are reported. They considerer all points of both hydrological cycles and are Volc : volcanic basin; PluMet : plutonic and metamorphic basin; Sed : sedimentary basin.

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Table 1 : Characteristics of the Tumbes River at El Tigre station and its sampled tributaries

Table2 : Mineralogical composition of the sampled SPM in the Tumbes R. and tributaries calculated from Biscaye (1965) method from DRX analyses. LW : Low water ; HW : High water.

Table 3 : SPM concentration, daily and monthly discharge, Sr and Nd isotope signature (±2; 95% confidence level), Chemical Index Alteration (CIA) values (equation 2) and X/Al ratios of the sampled SPM.

Supplementary material:

figure A1: a) monthly rainfall received by the Tumbes basin b) monthly relative contribution of the rainfall received by the 3 lithological areas (defined on the figure 1) in the Tumbes Basin along the selected hydrological years.

figure A2: repartition of volcanic and Plutonic and metamorphic rocks along the Pacific coast of Ecuador and Peru.

S1 : Discharge distribution analysis

To explore the daily discharge distribution of the sampled year reported in figure 2b and in the section 2.4. We used the 1985-2015 daily discharge database. We first ranges the daily discharge of each year from the lowest to the highest database. This range, divided by the number of day of each year (365 or 364) is considered as the cumulative frequency. We calculated the percentile 90, 50 and 10 of the 30 years for each cumulative frequency value and we compare it to the daily discharge recorded along the selected years. This analysis allows to explore the selected year discharge distribution for all the hydrological condition. For example, it allows to identify if the 50% highest daily discharge of the sampled year are closed to the 30 years median condition or if they are drier or wetter.

All correlation analyses performed in this study is related to significance relative to p-value <0.01.