C. R. Geoscience xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Comptes Rendus Geoscience

www.sciencedirect.com

External Geophysics, Climate, and Environment (Hydrology, Hydrogeology)

Temporal variability and annual budget of inorganic dissolved matter in Andean Pacific Rivers located along a climate gradient from northern Ecuador to southern Peru

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ARTICLE INFO

Article history:
Received 25 May 2016
Accepted after revision 6 November 2017
Available online xxx

Handled by François Chabaux.

Keywords:
Pacific Rivers
Andes
C vs. Q relationships
Climate control
Riverine dissolved budget

ABSTRACT

In Ecuador and Peru, geochemical information from Pacific coastal rivers is limited and scarce. Here, we present an unedited database of major element concentrations from five HYBAM observatory stations monitored monthly between 4 and 10 years, and the discrete sampling of 23 Andean rivers distributed along the climate gradient of the Ecuadorian and Peruvian Pacific coasts. Concentration (C) vs. discharge (Q) relationships of the five monitored basins exhibit a clear dilution behavior for evaporites and/or pyrite solutes, while the solute concentrations delivered by other endmembers are less variable. Spatially, the annual specific fluxes for total dissolved solids (TDS), Ca^{2+}, HCO_3^-, K^+, Mg^{2+}, and SiO_2 are controlled on the first order by runoff variability, while Cl^-, Na^+ and SO_4^{2-} are controlled by the occurrence of evaporites and/or pyrite. The entire Pacific basin in Ecuador and Peru exported 30 Mt TDS·yr^{-1}, according to a specific flux of ~70 t·km^{-2}·yr^{-1}. This show that, even under low rainfall conditions, this orogenic context is more active, in terms of solute production, than the global average.

1. Introduction

Mountain ranges are key environments in global and regional biogeochemical cycles. They are the main sources of dissolved matter (including nutrients such as N and Si) provided to the oceans by the continents (Meybeck, 1976, 2003), and they are particularly active in the continental weathering budget and associated CO_2 consumption that control the climate over the geological timescale (e.g., Gaillardet et al., 1999; Godderis et al., 2017; Raymo and Ruddiman, 1992; Gaillardet et al., 1999; West et al., 2012). Moreover, these environments are occupied by 1480·10^6 inhabitants (~20% of the world population) over 25% of the

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https://doi.org/10.1016/j.crte.2017.11.002

Please cite this article in press as: Moquet J-S, et al. Temporal variability and annual budget of inorganic dissolved matter in Andean Pacific Rivers located along a climate gradient from northern Ecuador to southern Peru. C. R. Geoscience (2018), https://doi.org/10.1016/j.crte.2017.11.002

continents (Meybeck et al., 2001). They are, therefore, particularly sensitive to both water resource quality and quantity. However, global estimates of continents and mountains dissolved fluxes are generally based on the fluxes of major rivers (Meybeck, 2003; Milliman and Farnworth, 2011), and local, small equatorial rivers are generally misrepresented, because of the low availability of river chemistry data.

The Andes are the second main orogenic area in the world; however, estimates of hydrochemical budgets for this mountainous range are limited and generally focus on its eastern slope, in the Amazon basin (e.g., Armijos et al., 2013; Baronas et al., 2017; Bouchez et al., 2017; Dellinger et al., 2015; Guyot et al., 1993, 1996; Moquet et al., 2011, 2016; Torres et al., 2015, 2017 and references within) or in other Andean rivers, such as the Pilcomayo (Smolders et al., 2004). By contrast, geochemical information on Pacific Andean rivers in Ecuador and Peru is limited and scarce. This is mainly due to the difficulty in monitoring the abundant number of rivers in this area. According to a global discharge-TDS (total dissolved solids) relationship, the non-monitored Pacific basin TDS flux in Ecuador and Peru is estimated at ~30 Mt·yr^{-1} (Milliman and Farnworth, 2011). In situ hydrochemical data available in these regions focused on the local scale in various environments, as in glaciers in Peru (Fortner et al., 2011) and Argentina (Leon and Pedrozo, 2015), or in basins impacted by mining activity in Ecuador and Peru (e.g., Betancourt et al., 2005; Skierszkan et al., 2016). Only one TDS budget has been reported at the outlet of a Pacific Andean river in this area by Armijos et al. (2013) in the Esmeraldas basin. Considering the great importance of Pacific sea margin productivity (e.g., Mollier-Vogel et al., 2012), it is crucial to estimate fluxes of solutes delivered by rivers to this area to better estimate the availability of nutrient inputs and to better constrain regional elemental cycles. Moreover, the hydrology of this region is particularly affected by the El Niño Southern Oscillation (ENSO) events (e.g., Morera et al., 2017; Rau et al., 2017a). Therefore, through the study of concentration vs. discharge relationships ("*C*–*Q* relationships"), the sensitivity of dissolved matter production to changes in hydroclimatological conditions can be determined.

In the present study, we present inorganic dissolved matter fluxes in the Andean Pacific basins based on discrete sampling for solute measurements at 23 stations along the Pacific coast, from Ecuador to southern Peru. Moreover, we describe the TDS variability during the hydrologic cycle based on monthly samples for solute concentrations acquired between 2007 and 2010 at five gauging stations (SNO-HYBAM database). Based on this unedited database, we identified the main factors controlling TDS production as a function of time and space discharge variability in Andean rivers along the Pacific coast. More specifically, we first discuss the *C* vs. *Q* relationship of solute concentrations during the hydrologic cycle at the monitored stations. Second, we discuss the discrete TDS and solute-specific flux distributions along the north-south climate gradient. We finally estimate a TDS Pacific basins budget, and we compare it with the Andean basins budget of the Amazon.

2. Studied area

The 28 sampled basins are located on the western slope of the Andes, between 0.5°N and 18°S and 80.5°W–70°W, and along 2400 km of the Pacific coast from Ecuador to southern Peru. All headwaters of the studied basins are in the Andes and reached a maximum elevation of ~6500 m.a.s.l., and their outlets are located along the Pacific coast (Fig. 1, Table S1). The studied basins cover between 0.8 and 19.6 × 10^3 km^2 and represent approximately 40% of the total Pacific coast drainage area for Ecuador and Peru and approximately 54% of the Andean domain of this area (> 500 m.a.s.l.) (Table S1).

According to the 1:1,000,000 geological map of Ecuador (Baldock, 1982) and Peru (INGEMMET, 1999), the studied basins drain several types of lithologies that are variably dominated by volcanic rocks, sedimentary rocks, and plutonic and metamorphic rocks (Table S2, supplementary material). Volcanic rocks (e.g., andesites, basalts, and dacites) are present in all studied basins and cover between 8% and 70% of the basin, with a lower covered area in the central basins between the Santa and Chancay basins. However, active volcanos are only present in the Esmeraldas basin (Ecuador), as well as the southern basins in Peru from Ocoña to Sama basins. Plutonic and metamorphic rocks generally represent between 13% and 34% of the sampled basins. Silico clastic sedimentary rocks cover is highly variable, and represents between 11% and 74% of the sampled basins. When they are sensed, carbonates cover only a small part of the basins. With a relative surface ranging between 1% and 7% of the basins area, this lithology is significant only in the Tumbes, Cañete, and Chincha basins. The evaporite outcrop is not significant in the studied basins. However, even if carbonates and evaporites are not reported in lithological maps, they can occur in Andean formations (Rosas et al., 2007) or appear as neoformations in arid and semi-arid basins, similar to the Upper Madeira basins (Guyot et al., 1993; Magat, 1981). According to the Peruvian mining map (INGEMMET: geocatmin.ingemmet.gob.pe), pyrite is present in most of the studied basin; however, its relative abundance is not quantified.

The climate of Ecuadorian and Peruvian Pacific andean slopes depends on large-scale circulation patterns associated with the Andes cordillera, contrasting oceanic boundary conditions and landmass distribution (Garreaud et al., 2009). Rainfall is more abundant along the Ecuadorian and northern Peruvian coast and declines towards the south, where conditions of extreme aridity occur (Fig. 1; Garreaud et al., 2009; Rutlland et al., 2003). According to the TRMM rainfall data (1998–2009 period; freely downloaded from http://www.geog.ucsb.edu/~bodo/TRMM/), the mean rainfall for these studied basins ranges from 1570 mm·yr^{-1} in the Esmeraldas basin to 107 mm·yr^{-1} in the Sama basin, located at the extreme North and extreme South of the studied area, respectively (Fig. 1; Table S1). The studied basins are influenced by a strong rainfall seasonality and exhibit a decreasing latitudinal gradient in mean annual rainfall from north to south (Fig. 1). In addition, a rainfall gradient is observed following the elevation on the west–east axis. According to the Köppen–Geiger climate classification, semi-arid

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