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Geochemistry of organic-rich river waters in Amazonia: Insights on weathering processes of intertropical cratonic terrain

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A B S T R A C T

In this study, eight organic-rich rivers that flow through the Brazilian craton in the southwestern Amazon rainforest are investigated. This investigation is the first of its type in this area and focuses on the effects of lithology, long-term weathering, thick soils, forest cover and hydrological period on the dissolved load compositions in rivers draining cratonic terrain. The major dissolved ion concentrations, alkalinity (TAlk), SiO_2, trace element concentrations, and Sr isotope contents in the water were determined between April 2009 and January 2010. In addition, the isotopic values of oxygen and hydrogen were determined between 2011 and 2013. Overall, the river water is highly dilute and dominated by the major dissolved elements TAlk, SiO_2 and K^+ and the major dissolved trace elements Al, Fe, Ba, Mn, P, Zn and Sr, which exhibit large temporal and spatial variability and are closely correlated with the silicatic bedrock and hydrology. Additionally, rainwater and recycled water vapor and the size of the basin contribute to the geochemistry of the waters. The total weathering flux estimated from our results is 2–4 t $km^{-2}.yr^{-1}$, which is one of the lowest fluxes in the world. The CO_2 consumption rate is approximately 21 –61 10^3 mol km^{-2} yr^{-1}, which is higher than expected given the stability of the felsic to basic igneous and metamorphic to siliciclastic basement rocks and the thick tropical soil cover. Thus, weathering of the cratonic terrain under intertropical humid conditions is still an important consumer of CO_2.

1. Introduction

Weathering of stable, cratonic terrain results in thick weathering profiles that isolate the parent rock from weathering, especially under intertropical humid conditions (e.g., Bardossy and Aleva, 1990; Tardy and Roquin, 1998 and references therein). The rivers that drain these regions are considered silicatic, with low weathering flux and low CO_2 consumption (Gaillardet et al., 1997; Millot et al., 2002; Oliva et al., 2003; Zakarova et al., 2007 and references within) relative to the rivers that flow through (Xu and Liu, 2010) or originate in (Edmond et al., 1996; Boeglin and Probst, 1998; Gaillardet et al., 1999; Moquet et al., 2014) tectonically unstable mountainous regions where intense mechanical erosion occurs and high concentrations of dissolved and suspended matter are observed. To understand the roles of cratonic terrain in the chemical cycle, it is important to quantify the dissolved load exported from cratonic terrain, understand how the terrain weathers, determine the CO_2 consumption rates of the terrain, and identify the main parameters that control the river water chemistry. Studying these topics is particularly important in Amazonia because this region supplies approximately 20% of the water (Callède et al., 2004), 10% of the dissolved load (Gaillardet et al., 2007) and 3% of the suspended load (Milliman and Syvitski, 1992) to the global ocean.

In Amazonia, the geochemistries of the Solimões-Amazon River and their larger tributaries have been well documented (e.g., Stallard and Edmond, 1983, 1987; Allègre et al., 1996; Edmond et al., 1996; Gaillardet et al., 1997; Mortatti et al., Probst, 2003; Moquet

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et al., 2011). However, information regarding mid-to small-scale cratonic tributary basins remains scarce. The most thorough geochemical studies were conducted by Hieronymus et al. (1993), Edmond et al. (1996) and Sondag et al. (2010). Although these studies did not characterize the relationship between water chemistry and bedrock composition, they highlighted the following main characteristics of the rivers draining the cratonic terrain in Amazonia: i) low suspended material concentrations; ii) elevated dissolved SiO_2, K^+, Al and Fe concentrations; iii) a pH of less than 7; and iv) weathering rates between 3.5 and 5 m Ma^{-1}. However, the diversity of the mineral paragenesis of the Brazilian craton, the length of time over which weathering occurred, the thick intertropical soils, the forest cover and the regional seasonality all influence the chemistry of the rivers. Thus, the main goal of our paper was to ascertain how these various factors regulate the chemical composition of river water, the weathering flux, migration of the weathering front and the CO_2 consumption rate. To explore this problem, we determined the water chemistry in two mid-to small-scale rivers hosted in cratonic environments in southwestern Amazonia, Brazil. Our results are helpful for understanding the spatial and temporal tropical weathering processes in the silicate cratonic terrain of Amazonia. Specifically, our results demonstrate how the geochemistry of medium-to-small drainage basins and the chemistry of the river water in these basins reflect the local environment and influence the main river.

2. Study area

The study area is located in the southwestern region of the Amazon basin between 6 and 13°S and 59–62°W (Fig. 1). The sampled rivers generally flow from south to north and belong to the Aripuanã basin in the west and the Sucunduri basin in the east (Fig. 1). The Aripuanã and Sucunduri Rivers in these two drainage basins drain into the Madeira River, which is one of the main tributaries of the Amazon River. These rivers drain lateritic terrain covered by rainforest, have very low suspended material concentrations and are classified as either organic rich or black waters according to the biochemical classification of rivers presented by Sioli (1968).

The Aripuanã drainage basin covers an area of 109,000 km^2 and extends for approximately 900 km in a north-south direction (Fig. 1). The mean discharge of the Aripuanã River, which empties the Aripuanã basin, is 2164 m^3 s^{-1} at the gauging station. At the gauging station, the Aripuanã River (Fig. 1, site 1) is nearly 400 m wide. The Aripuanã River mainly drains the western part of the study area. The Acari River, which is nearly 100 m wide at the sampling site (Fig. 1, site 6), the Jatuarana and Juma Rivers (sites 2 and 5, respectively), which are less than 30 m wide, and Ig1 and Ig2 (sites 3 and 4, respectively), which are less than 10 m wide at the sampling site, are all tributaries to the Aripuanã River.

The Sucunduri basin covers an area of 12 700 km^2 and is approximately 500 km long from south to north. The Sucunduri River has a mean discharge of 193 m^3 s^{-1} at the gauging station, where it is approximately 200 m wide (Fig. 1, site 8). The main tributary of the Sucunduri River is the Camaiú River (Fig. 1 site 7), which is 70 m wide at the sampling site.

The geology of the two basins is characterized by a variety of Proterozoic and Paleozoic silicate rocks (CPRM, 2013; Reis, 2006 and Fig. 1). In the study area, siliciclastic sedimentary rocks are located in the upper reaches of the Aripuanã drainage basin; felsic volcano-sedimentary rocks and intrusive felsic intrusive rocks (tonalite, granodiorite, and granite) with minor basic rocks (charnockite, amphibolite, and gneiss) are located in the middle of the basin; and siliciclastic sedimentary rocks are located near the sampling sites. The small tributaries (samples 2, 3, 4, and 5) and the Camaiú River (sample 7) flow entirely over siliciclastic sedimentary rocks, while the Acari River (sample 6) flows over felsic volcanic rocks (Fig. 1). The Sucunduri drainage basin is almost entirely composed of siliciclastic sedimentary rocks (siltstone, sandstone, claystone, siliceous breaches and minor dark grey limestone) and felsic volcano-sedimentary rocks (Fig. 1). All of these rocks have undergone long-term weathering, and have developed a residual lateritic crust composed of hematite, goethite, kaolinite, gibbsite and, occasionally, Mn minerals covered by oxisols and spodosols (Silva et al., 2012).

The climate is hot and humid and is slightly drier from May to September. The mean annual temperature ranges from 25 to 27 °C, the relative humidity is approximately 85%, and the yearly rainfall is 2336 mm $year^{-1}$ (data from the Brazilian Water National Agency's pluviometric station in the city of Humaitá, near the study area, from 1998 to 2007). Based on this 10-year record of rainfall, we have identified four main seasons: a wet season (during April, October, November, December and January with a mean rainfall of 265 mm $month^{-1}$), a receding water season (during May, with a mean rainfall of 156 mm^{-1}), a dry season (June, July and August, with a mean rainfall of 54 mm $month^{-1}$) and a rising water season (during September, with a mean rainfall of 163 mm $month^{-1}$). The wet and dry seasons correspond to higher and lower river discharge. Human pollution does not significantly affect the region due to the very low population density (<5 individuals km^{-2}). However, some anthropogenic impacts may occur in the town of Apuí and along the road and in deforested areas.

3. Materials and methods

River water samples were collected monthly from April 2009 to January 2010 along the Transamazonica highway near the town of Apuí in southwestern Amazonia, Brazil (Fig. 1). In addition, a spring was sampled to evaluate the geochemical characteristics of the local groundwater and to determine its influence on the river water (Fig. 1). Samples were collected from the middle of each river. The Aripuanã and Sucunduri Rivers were sampled from a canoe, and the other rivers were sampled from bridges. Each water sample was collected in a plastic bag, from which a subsample of water was collected using a 20 ml syringe. Next, the sample was passed through a 0.45-μm Millex filter before storing in a polyethylene flask. Each flask was prepared by soaking in a 10% HNO_3 solution for 24 h, rinsing three times with ultrapure water and then rinsing again three times with the sampled water. Two flasks were used for each sample. In the first flask, 0.02 g of thymol was added to prevent bacterial action. The sample in the first flask was analyzed for major ions, total alkalinity and SiO_2. In the second sample flask, which was used for trace element analysis, two drops of bi-distillated HNO_3 were added to prevent precipitation.

Electrical conductivity, pH, total alkalinity (TAlk; samples at pH > 4.3 were titrated with sulfuric acid), SiO_2 (by spectrophotometry), cations (Na^+, K^+, Mg^{2+}, and Ca^{2+}) and anions (Cl^-, NO_3^-, and SO_4^{2-}) were determined for all samples with a reproducibility of ±5%. Ions were analyzed using a DIONEX ICS 900 ion chromatograph calibrated with a DIONEX standard-compliant solution. Trace elements (Ag, Al, As, Au, Ba, B, Be, Bi, Cd, Co, Cr, Cu, Fe, Ga, Ge, Hf, Hg, In, Mn, Mo, Ni, Nb, P, Pb, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Sn, Sr, Ta, Te, Tl, V, Zn, Zr, and Y) and rare earth elements (REEs) were determined for samples collected in December (high water), May (receding water), July (low water) and September (rising water) using inductively coupled plasma mass spectrometry (ICP-MS) at ACMELAB in Vancouver, Canada. TMDA-70 was used as a standard.