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The geochemical signature of suspended sediments in the Parana River basin: Implications for provenance, weathering and sedimentary recycling

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A B S T R A C T

The Paraná River basin is one of the largest hydrological systems in South America. The present study focuses on the mineralogical and chemical composition of the suspended sediments exported by the Paraná River to the Atlantic Ocean, with the aim of analyzing their provenance, the chemical weathering signature and the likelihood of sedimentary recycling. The particulate matter of the Middle Paraná River and its main tributaries (i.e., the Paraguay and the Upper Paraná rivers) is mostly composed of quartz, plagioclase, K-feldspar, and clays, such as illite and kaolinite. Different geochemical approaches indicate that the suspended sediments transported by the Paraná River preserve the chemical signature of its sources and its composition is not significantly modified during transport. These sediments are mainly supplied by acidic arc sources located in the Andean headwaters of the Bermejo and Pilcomayo rivers (and transported by the Paraguay River); and by tholeiitic basalts outcropping in the headwaters of the Upper Paraná River. The incomplete mixing of both main tributaries produces a transverse geochemical asymmetry in the particulate material of the Middle Paraná River, which was detected ~32 km downflow the confluence. The suspended load transported by the Paraguay River (which includes the contributions from the Bermejo and Pilcomayo rivers) indicates incipiently to moderately weathering, whereas the particulate matter exported by the Upper Paraná River reveals a higher degree of chemical alteration. This is the result of the different lithology and climatic regimes that prevail in the headwaters of both tributaries. The weathering signature of the Middle Paraná River's suspended load resembles that of the Paraguay River, which in turns supplies most of the particulate matter through the Bermejo River. This work also shows that the suspended load exported by the Paraná River basin has a mixed origin, where the chemical signatures from young materials derived from undifferentiated volcanic rocks, and from recycled materials affected by intracrustal differentiation can be distinguished.

1. Introduction

Large rivers constitute the main pathways of solutes and suspended particles from the continents to the oceans, which result from continental denudation, i.e., the synergistic action of rock weathering and erosion. Milliman and Farnsworth (2011) found that rivers around the world discharge annually about 36,000 km^3 of freshwater and more than 20 billion tons of solid and dissolved sediments to the global ocean. Numerous studies have focused on the magnitude and mechanisms that control continental denudation, for example, the classical works of Stallard and Edmond (1983), Milliman and Sivitsky (1992), McLennan (1993), Gaillardet et al. (1999a), among others.

Milliman and Farnsworth (2011) also pointed out that it is almost axiomatic to state that sediment production and transport in a drainage basin are controlled by its catchment size and geomorphology, bedrock geology, climate, vegetation cover and human activity. Most published data about concentration and composition of fluvial sediments is referred to suspended sediments, in part because measuring suspended loads is relatively easy, and because they record the chemical signature of their sources and the weathering conditions that prevail in the source areas. The chemical and mineralogical compositions of fluvial sediments reflect the parent lithology and the entire history of its modifications by weathering, recycling, transport, mixing, deposition and diagenesis (e.g., Weltje and von Eynatten, 2004). Several works have probed into the geochemical nature and factors controlling the concentration and composition of the suspended load of large rivers. For instance, Dupré et al. (1996), Gaillardet et al. (1997, 1999b), Picouet et al. (2002), Ramesh et al. (2000), Singh et al. (2005), Viers et al. (2008)

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and Viers et al. (2009) analyzed the chemical composition of the suspended sediments transported by large rivers and the signature of weathering and erosion. The effects of transport and mineral sorting on sediment geochemistry have been evaluated in several works, such as those of Galy and France-Lanord (2001), Singh et al. (2005), Singh (2009) and Wu et al. (2013). Further, the geochemical record of clastic sediments has been widely used to analyze their provenance and the weathering conditions that prevail in the source areas (e.g., McLennan et al., 1993; Meinhold et al., 2007; Pasquini et al., 2005; Singh, 2009). For these purposes, immobile major and trace elements, such as Al, Fe, Ti, Th, Sc, Co and Zr, and rare earth elements (REEs), mainly carried in the suspended load of rivers, are particularly useful as they experience little fractionation during weathering. Sedimentary recycling has also been discussed in the literature by means of different geochemical approaches (e.g., Dellinger et al., 2014; Gaillardet et al., 1999b; McLennan et al., 1990, 1993, 2003; Meinhold et al., 2007; Potter et al., 2005).

The Paraná River is one of the largest rivers around the world (in the sense of Potter, 1978), inasmuch as it is about 4000 km long and its drainage basin, the second largest in South America (i.e., after the Amazon basin), has an area of 2.6×10^6 km^2 (Milliman and Farnsworth, 2011). In its middle stretch, the average annual discharge is about 18,800 m^3 s^{-1} at the city of Corrientes (mean for the period 1970–2012; Argentina's Subsecretaría de Recursos Hídricos, www.hidricosargentina.gov.ar) and the suspended sediment load is ~1.2×10^8 t yr^{-1} (calculated for December 1993–January 1999; Amsler and Drago, 2009). In the Paraná River basin, just a few works have analyzed the chemical and mineralogical composition of the suspended sediments (e.g., Bonetto and Orfeo, 1984; Depetris and Griffin, 1968; Depetris et al., 2003; Depetris and Pasquini, 2007), as well as their isotopic signature (e.g., Henry et al., 1996).

Another significant feature of large rivers is that they usually exhibit longitudinal (i.e., downstream), transverse, vertical and temporal heterogeneities. The first two are frequently observed downflow the confluence with large tributaries, leading to parallel "braids" of water bodies (Yang et al., 1996). Most studies reporting chemical asymmetries in large rivers are mainly focused on the dissolved load (e.g., Aucour et al., 2003; Bouchez et al., 2010; Lambs, 2004; Pawelleck, 1995). In a recent work, Campodonico et al. (2015) described a transverse chemical and isotopic asymmetry in the dissolved load of the Middle Paraná River, which was attributed to the unmixing of the main tributaries that imparted their own dissolved chemical signatures. The incomplete mixing of waters after the confluence with tributaries is also manifested through the concentration and composition of the particulate fraction. However, the suspended load has been scarcely used to explore the chemical heterogeneities in large rivers. For example, Aucour et al. (2003) and Laraque et al. (2009) examined the relative suspended sediment contributions of the Negro and Solimões rivers into the Amazon River. Bonetto and Orfeo (1984) measured in the Middle Paraná River at the city of Corrientes (i.e., ~32 km downflow the confluence of the Paraguay and Upper Paraná rivers) under baseflow conditions, a concentration of suspended sediments four times higher in the western margin compared to the eastern border. These authors also reported a nearly homogeneous concentration of suspended sediments at ~350 km downflow the confluence of the main tributaries.

In this work we report new data of the mineralogical and chemical composition of the suspended sediments of the Paraná River. The objectives of this paper are to infer the provenance of the suspended load, to analyze the imprint of chemical weathering in the basin, and to detect geochemical evidences of sedimentary recycling. Furthermore, the chemical composition of the suspended sediments is also used here to analyze the unmixing of the Middle Paraná's main tributaries, i.e., the Upper Paraná and Paraguay rivers, close to their confluence.

2. Study area

The Paraná River drainage basin (Fig. 1) covers an area of ~2.6×10^6 km^2 (Milliman and Farnsworth, 2011) and supplies ~80% of the total water discharge to the Río de la Plata estuary. The Upper Paraná River headwaters are placed at Serra dos Preneos (~45°W), close to the Atlantic coast in Brazil, whereas its westernmost water sources (i.e., the headwaters of the Pilcomayo, Bermejo and Salado rivers) are close to the Andes foothills (in western Argentina and Bolivia, ~65°W). The upper catchments of the Paraguay River are located at the Gran Pantanal, one of the largest wetlands in the world (Mato Grosso and Mato Grosso do Sul states, Brazil, ~15°S and ~55–60°W). The Upper Paraná and Paraguay rivers join near the city of Corrientes (Fig. 1) and the stretch encompassed between the confluence and the city of Diamante (32°04′11″S 60°38′16″W; Entre Ríos province, Argentina) is known as Middle Paraná River (Drago and Vassallo, 1980). The main contributor to the Middle Paraná River discharge is the Upper Paraná River, which supplies ~73% of the total water budget, whereas the Paraguay River (including the Bermejo and Pilcomayo rivers discharges) delivers the remaining 27% (Pasquini and Depetris, 2007). The relative contribution of the main tributaries is not uniform throughout the year due to the differences between the hydrological regimes of the Upper Paraná and Paraguay rivers. Hence, the freshwater contribution of the Paraguay River to the middle stretch is up to 34% during austral winter, and diminishes to ~19% in austral summer when the Paraná River reaches maximum flow (Depetris, 2007).

Fig. 1 also shows the lithology outcropping in the Paraná River basin. The Upper Paraná catchment is mainly covered by the Jurassic-Cretaceous tholeiitic basalts of the Serra Geral Formation and Cretaceous sandstones. Precambrian metamorphic rocks are also found in its headwaters. The Paraguay basin is covered primarily by Quaternary and recent fluvial deposits. At the Andes foothills, in the headwaters of the Pilcomayo and Bermejo rivers, outcrops of marine and continental sedimentary rocks, as well as of Precambrian metamorphic rocks and Quaternary intermediate volcanic rocks, can be found. A significant portion of the Paraná drainage basin, including the vicinity of the middle stretch, is covered by Quaternary deposits, mainly of fluvial and deltaic origin (Fig. 1).

The main course of the Middle Paraná River exhibits a multichannelled pattern and it can be classified as braided of low sinuosity (Orfeo and Stevaux, 2002). This braided pattern is usually observed when the availability of bed sediments is higher than the suspended sediment load (Friend and Sinha, 1993). The floodplain of the middle and lowermost reaches of the Paraná River is 900 km long and ~30 km wide (Depetris and Kempe, 1993). It is a wetland composed of shallow streams, ponds, marshes and ox-bow lakes.

The atmospheric circulation over South America during austral summer is dominated by a monsoonal system (SAMS). The convection band, known as the South Atlantic Convergence Zone (SACZ), is a distinctive feature of the SAMS, and is placed along the north-eastern boundary of the Río de la Plata drainage basin (e.g., Garreaud et al., 2008). Also, during austral summer a low-level northerly/northeasterly jet that flows east of the Andes, transports large amounts of moisture between the Amazon and the Río de la Plata basin (e.g., Berbery and Barros, 2002). As a consequence of these continental climatic features, the mean annual rainfall is unevenly distributed over the Paraná basin. Maximum precipitation (2400 mm yr^{-1}) occurs along the eastern margin of the basin, whereas towards the west, along the 60–65°W strip, rainfall decreases to 400–800 mm yr^{-1} (Pasquini and Depetris, 2007). Mean temperatures in January (austral summer) are between 20–30 °C in the whole basin, while in July (austral winter) mean temperatures range from 15 to 25 °C in the northern and center portions of the basin, and from 10 to 15 °C in the South.

Milliman and Farnsworth (2011) estimated that the Paraná River transports on average 6.2×10^4 t yr^{-1} of dissolved load and