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The dissolved chemical and isotopic signature downflow the confluence of two large rivers: The case of the Parana and Paraguay rivers

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SUMMARY

The Paraná River basin is one of the largest hydrological systems in South America (~2.6×10^6 km^2). Downflow the confluence of tributaries, most large rivers exhibit transverse and longitudinal inhomogeneities that can be detected for tens or even hundreds of kilometers. Concordantly, a noticeable cross-sectional chemical asymmetry in the dissolved load was distinguished in the Middle Paraná River, after the confluence of its main tributaries (i.e., the Paraguay and Upper Paraná rivers). Water chemistry and isotopic signature in three cross-sections along the Middle Paraná River, as well as from main and minor tributaries, and some deep (~105 m bs) and shallow boreholes (~15 m bs) located near both river banks, were analyzed in order to define the extent of mixing and identify possible contributions from groundwater discharges. Downflow the confluence of the Upper Paraná and Paraguay rivers a chemical and isotopic asymmetry was observed, mainly through the values of EC, major ions (Ca^{2+}, Na^+, Mg^{2+}, Cl^- and SO_4^{2-}), some trace elements (Fe, U, Th, Ba, Sr, As and REE) and stable isotopes ($\delta^{18}O$ and δ^2H). Toward its western margin, higher elemental concentrations which resembled that of the Paraguay River were measured, whereas at the eastern border, waters were more diluted and preserved the chemical signature of the Upper Paraná River. This variability remained detectable at least until ~225 km downflow the confluence, where differences between western and eastern margins were less evident. At ~580 km downflow the confluence, a slight inversion in the transverse chemical asymmetry was observed. This trend switch can be the result of the input of solutes from minor tributaries that reach the main channel from the East and/or may be due to higher groundwater discharges from the East bank. A mass balance model was applied, as a first approach, to estimate the groundwater inflow using the geochemical tracer ^{222}Rn. The results indicate that groundwater contributions represent between ~0.5% and 6% of the total water inputs to the Middle Paraná River under baseflow conditions. This implies that the chemical asymmetry in the Middle Parana River is mostly due to the incomplete mixing of the main tributaries. Though the influence of groundwater is not a determining factor in the chemical variability of the river, it may partially explain the higher concentrations of some trace elements found in the eastern margin ~580 km downflow the confluence.

1. Introduction

Large rivers play a significant role in continental denudation as they transport the erosion products from the continents to the oceans. Potter (1978) considered that area of drainage basin, river length, volume of transported sediments and water discharge are the four main characteristics that define a large river, and used the first two to identify the 50 largest rivers of the world. Later, Meade (1996) listed the 25 rivers that present the largest discharges of water and suspended sediments to the world oceans. Recently, Milliman and Farnsworth (2011) published an extensive data base containing global rivers discharge and sediments fluxes from the continents to the oceans, and listed 12 rivers that account for ~25% of the total continental areas draining into the world oceans, and discharge ~35% of the freshwater reaching the ocean.

In South America, the large rivers Amazonas, Orinoco and Paraná are responsible for the greatest discharge of freshwater (i.e., ~8000 m^3 yr^{-1}) into the Atlantic Ocean (Milliman and Farnsworth, 2011). In turn, Tundisi (1994) pointed out that these three rivers supply about 13% of the total suspended solids delivered by all world rivers to the oceans (i.e., 570 Mt yr^{-1}, Milliman and Farnsworth, 2011).

The Paraná River is about 4000 km long and its drainage basin, the second largest in South America, has an area of 2.6×10^6 km^2

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(Orfeo and Stevaux, 2002). Its average annual discharge is about 17,000 $m^3\ s^{-1}$ (Pasquini and Depetris, 2007) and on the average it delivers 530 $km^3\ yr^{-1}$ of water to the Río de la Plata estuary (Pasquini and Depetris, 2010). The Paraná River transports $6.2 \times 10^4\ t\ yr^{-1}$ of dissolved load and $9 \times 10^7\ t\ yr^{-1}$ of total suspended solids to the Atlantic Ocean (Milliman and Farnsworth, 2011).

Most large rivers exhibit inhomogeneities in four dimensions: longitudinal (i.e., downstream), transverse, vertical and temporal. The first two, are frequent features observed downflow the confluence with tributaries, where parallel water bodies can be distinguished (Yang et al., 1996). A number of methods have been used to study these inhomogeneities. For example, remotely sensed data (i.e., airborne and satellite multispectral images) were used to study the visual mixing downflow the confluence of two large rivers (e.g., Lane et al., 2008; Matsui et al., 1976). Chemical tools include the use of dye tracers (e.g., Caplow et al., 2004) and surveys of naturally occurring dissolved chemical compounds (e.g., Leibundgut et al., 2009).

Several studies reported field data showing a transverse chemical asymmetry in large rivers. For instance, Pawellek (1995) identified a chemical asymmetry in the Danube River due to the incomplete mixing of the Iller and Lech rivers, and established that once the volume of the main course exceeded that of its tributaries by a factor of 10–15, the chemical composition became homogenous. Transverse chemical variations in the Amazon River were reported by Aucour et al. (2003) downflow the confluence of the Negro and Solimões rivers, using major elements and organic carbon concentrations. A few kilometers upstream this confluence, Bouchez et al. (2010) also found cross-sectional heterogeneities in the confluence of the Purús and Solimões rivers. Lateral chemical and isotopic heterogeneities are also caused by groundwater discharges, as it was determined at the confluence of the Garonne and Ariège rivers in the SW of France, as well as in the confluence of the Ganges and Yamuna rivers in northern India (Lambs, 2004).

Drago and Vassallo (1980) first reported a noticeable cross-sectional chemical asymmetry in the middle stretch of the Paraná River that was recognized up to ~200 km downstream the confluence of its main tributaries, i.e. the Paraguay and Upper Paraná rivers. Based only on data from major dissolved composition, these authors found that water flowing near the western margin was saltier than water from the eastern border, and attributed this behavior to the influence of the tributaries that imparted their own chemical signatures. Furthermore, on the basis of remote sensing images, Lane et al. (2008) determined that the mixing length in the Middle Paraná River varied between 8 and 400 km.

The goal of this paper is to identify the factors that control the transverse chemical asymmetry detected in the Middle Paraná River downflow the confluence of the Paraguay and Upper Paraná rivers, using new evidences that include major and trace dissolved components and isotopic tracers ($\delta^{18}O$, δ^2H and ^{222}Rn). In addition, the inputs of water from the different hydrological compartments that interact in this river stretch were quantified using a model based on ^{222}Rn mass-balance.

2. Study area

The Paraná River drainage basin (Fig. 1) constitutes one of the largest in South America. It covers an area of about $2.6 \times 10^6\ km^2$ (Orfeo and Stevaux, 2002) and supplies about 80% of the total discharge of the Río de la Plata. Its northernmost water sources, at the

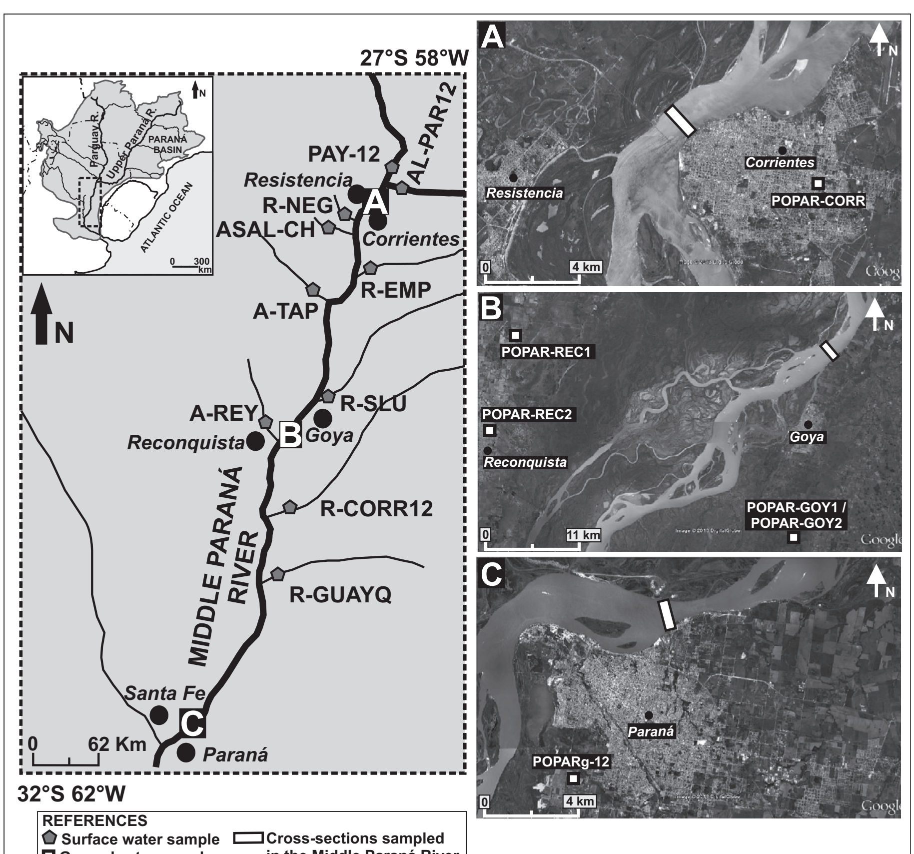

Fig. 1. Map of the Middle Paraná drainage basin showing the location of surface and groundwater sampling sites. Cross-section A: Corrientes–Resistencia (27°27′35″S); Cross-section B: Goya–Reconquista (29°03′45″S); and Cross-section C: Paraná–Santa Fe (31°42′10″S). The sampling station names are indicated in Table 1.