The hydrochemical and isotopic signature of the Middle Paraná River downflow the confluence of Paraguay and Upper Paraná rivers: surface water mixing or groundwater inflow?

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The Paraná River basin is one of the largest hydrological systems in South America (~2.6 x 10^6 km^2). Most large rivers exhibit transverse and longitudinal inhomogeneities downflow the confluence of tributaries, which can be detected for tens or even hundreds of kilometers (e.g., Yang et al., 1996). A noticeable cross-sectional chemical asymmetry regarding the major dissolved constituents was earlier distinguished in the Middle Paraná River, after the confluence of its main tributaries, i.e., the Paraguay and Upper Paraná rivers (Drago and Vasallo, 1980). In this study we present new chemical and stable and radiogenic isotopic data of the Paraná River drainage basin in order to explain the dissimilar composition of water observed across the main channel of the Middle Paraná River.

Water chemistry (major and minor dissolved constituents) and isotopic signature ($\delta^{18}O$, $\delta^{2}H$ and ^{222}Rn) were analyzed in three cross-sections along the Middle Paraná River (Corrientes-Resistencia, Goya-Reconquista and Paraná-Santa Fe). Waters collected from main (Paraguay and Upper Paraná) and minor tributaries, as well as groundwater from some deep (~105 m bs) and shallow boreholes (~15 m bs) located near both river banks were also examined in order to assess the relative contributions of these sources to the Middle Paraná River.

Downflow the confluence of the Upper Paraná and Paraguay rivers a chemical and isotopic asymmetry was confirmed, mainly through the values of electrical conductivity (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 $\delta^{2}H$). Towards the western margin of the middle stretch, 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. We estimated, by means of Cl^{-} mass-balance, that after the confluence, at Corrientes-Resistencia, more than 80% of water in the western margin was supplied by the Paraguay River, whereas at the East it accounted for less than 15% of the total water budget. This chemical and isotopic variability remained detectable at least until ~225 km downflow, where differences between western and eastern margins were less evident. At ~580 km downflow the confluence, a slight inversion in the cross-sectional 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 eastern 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 sources represent between 0.5% and 6% of the total water inputs to the Middle Paraná River, revealing that the chemical asymmetry is mainly 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 Middle Paraná River, it may partially explain the higher concentrations of some trace elements (i.e., As, Fe, U, Ba and Sr) found in the eastern margin ~580 km downflow the confluence of Paraguay and Upper Paraná rivers.

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