



## ***Chemical dynamics of the Sava riverine system – A stable isotopic approach***

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In our investigation we observed some differences and changing trends on natural (climate, precipitation, bedrock, soils, vegetation) and direct anthropogenic (land use, industry, population, water and waste water management, agriculture) influences moving along the Sava until its confluence.

The presented data includes the results from two sampling period performed in October 2005 and May 2006 at 33 locations along the Sava River basin. Factor analysis of the entire chemical data and isotopic dataset suggests three dominant factors as controlling parameters, tentatively interpreted as geological (conductivity,  $\text{HCO}_3^-$ , Ca, Mg, Sr,  $\delta^{13}\text{C}_{DIC}$ ), biogenic ( $\text{SiO}_2$ ,  $\text{O}_2$ ,  $\text{NO}_3^-$ ,  $\delta^{13}\text{C}_{DIC}$ ,  $\delta^{13}\text{C}_{POM}$ ) and anthropogenic (pH, Na, K, Cl,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\delta^{15}\text{N}_{POM}$ ,  $\delta^{15}\text{N}_{NO_3}$ ,  $\delta^{34}\text{S}_{SO_4}$ ) influences. In terms of its major ion chemistry, the Sava river is a typical Ca- $\text{HCO}_3$  river. Dissolution of carbonates the primer source of conductivity is closely coupled with the riverine carbon cycle. It was found that carbonate weathering and soils are the main sources of dissolved inorganic carbon (DIC) in the system. It was also found that the river actively degasses  $\text{CO}_2$  to the atmosphere and represents the source of  $\text{CO}_2$  to the atmosphere. While the upper part of the Sava river is mainly controlled by weathering of minerals, the lower part in Slovenia and partially in Croatia, is anthropogenically influenced mainly by agricultural activity. The agricultural activity could be detected by higher concentrations of  $\text{NO}_3^-$  ions which reached up to 0.12 mM in Croatia. The highest concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  ions were determined in the River Bosna, one of the main tributary of the river Sava. Higher concentrations of  $\text{Na}^+$  and  $\text{Cl}^-$  ions were probably due to the influence of salt mine Tuzla, while higher

$\text{SO}_4^{2-}$  concentrations were the consequence of mine activity.

$\delta^{15}\text{N}_{POM}$  and  $\delta^{15}\text{N}_{NO_3}$  give further insights regarding the sources of nitrate in the riverine system. At the upper part, we found higher  $\text{NO}_3^-$  concentrations and particulate matter relatively enriched in  $\delta^{15}\text{N}$  while in the lower part a decreasing  $\delta^{15}\text{N}$  values (in fall sampling between +1.8‰ and +9.6‰) were observed. The  $\delta^{15}\text{N}_{NO_3}$  values determined in May 2006 ranged between 3.8‰ and 13.7‰. Low value of  $\delta^{15}\text{N}$  is characteristic of ammoniacal fertilizer and soil nitrate and was determined in Črnac in Croatia. Knowing the present anthropogenic conditions (population, land-use and agricultural activities) in the next step we will additionally focus on lower basin and tributaries to investigate transport and fate of agricultural contaminants and nutrient enrichment effected on aquatic biota in the Sava River.

We also estimated the percentage of pollution by including all major ions contributing to the pollution status of the river. The average percentage of pollution of the Sava river was not changing seasonally and was estimated to be 14.2 % and 13.2 % in October 2005 and May 2006, respectively. The average percentage of pollution in tributaries is higher comparing to the main stream of the Sava river reaching up to 45% in Bosna tributary in May 2006. Higher % of pollution of 25.3% and 30.1% was also observed in Kamniška Bistrica and Savinja in October 2005, respectively.