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Environmental and artificial tracers in hydrogeology

title: **Stable carbon pattern in Belgrade catchment area, Serbia**

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INTRODUCTION

Rivers are important regulators of carbon (sinking or evaporating) which influence transport fluxes of nutrients and pollutants, production of organic matter, precipitation of carbonates or evaporate. In the catchment area, rivers undergo major changes in spatial and seasonal scale and are also influenced by anthropogenic activities. In order to distinguish between carbon sources we have to know the isotopic composition of the various contributors and understand the isotopic fractionation processes in the water. Dissolved inorganic carbon (DIC) in freshwater systems originates mainly from dissolution of carbonate minerals, soil CO₂ derived from root respiration and from microbial decomposition of organic matter (often mainly of terrestrial origin but also including aquatic production), and exchange with atmospheric CO₂. The major processes removing riverine DIC are carbonate mineral precipitation, CO₂ degassing, and aquatic photosynthesis. The isotopic composition of dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$) in freshwater systems, together with its concentration, is widely used to trace organic matter production and decomposition and presents a powerful tool to study the sources of carbon as well as the impacts of biological recycling of the carbon (Jedrysek et al., 2006). There are three major types of particulate organic matter (POM) in the riverine system: natural terrigenous materials consisting mainly of soils and bedrock-derived sediments, anthropogenic wastes and autochthonous materials from the aquatic system. The isotopic composition of suspended particulate organic carbon ($\delta^{13}\text{C}_{\text{POC}}$) reflects the relative proportions of allochthonous terrestrial organic matter (probably dominated by detritus from C3 plants and C3 plant-dominated soils), and autochthonous particles (derived from plankton and algae, aquatic macrophytes, and fragments and faecal materials from invertebrates and fish in the river) (Deines, 1980). These two sources can, in theory, be distinguished based on the ratio of organic carbon (OC) to organic nitrogen (molar C:N) (Kendall et al., 2001).

In this work, we have studied the stable isotopic composition of DIC and POC in the surface and ground waters of Belgrade area in order to use ¹³C natural abundance as a complementary tracer to improve the current knowledge of atmospheric and geochemical processes governing water quality.

STUDY AREA AND MEASUREMENTS

Belgrade (44° 49' 7" N, 20° 28' 5" E), the capital of Serbia, is situated in south-eastern Europe on the Balkan Peninsula and lies at the point where the Sava River merges into the Danube. It is the largest urban settlement in Serbia with 1.6 million inhabitants spreading over the area of 763.87 km². Downstream part of Sava alluvium and Danube-Sava interfluvies characterized by natural bank-filtered area, supplying drinking water for Belgrade, covering about 40-50% of its demand. The Sava and the Danube rivers' valley presents a region for Belgrade combined water supply using three-quarters of groundwater exploited from alluvial sediments using 99 wells with horizontal drains settled along the river Sava River and one quarter of water tapped from the main stream of the Sava and partly from the Danube. Considering the size (wells are placed in line of 50 km along the left and right river banks), the total capacity is about 4 m³/s (Fig. 1).

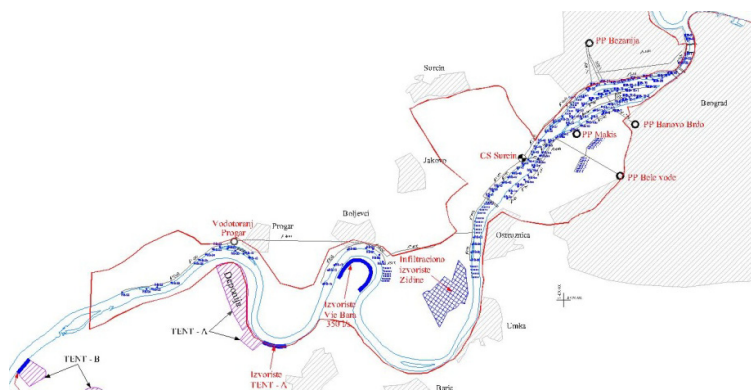


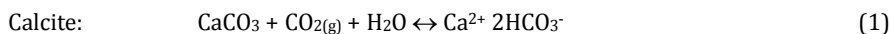
Figure 1. Map of surface and groundwater sources in Belgrade area.

Hydrological and geophysical properties of the Belgrade alluvial aquifer indicates a large accumulation of groundwaters in Upper Quaternary sediments (thickness up to 25 m) generally fed from two sources: by filtration of the river water along the bank and by infiltration of the precipitation through the surface layer or along the edges of the aquifer. The aquifer mainly consists of sandy-gravel, sand and has less permeable upper layer. The total depths of Quaternary sediments are 25 to 30 m. Hydraulic conductivity values of the water-bearing layer mostly range from 10^{-9} to 10^{-5} m/s. On the significant part of the alluvial plane, aquifer is divided with a less permeable layer-aquitard (Dimkic et al., 2007). In some locations floor is made of limestones dating from lower-Cretaceous and Sarmat. In the area of Ostruznica village alluvial aquifer lies over upper-Cretaceous (Ostruznica) flysch.

Collected samples of surface and groundwater were analyzed for major chemical parameters (HCO_3^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , NO_3^- , SO_4^{2-} , Cl^- , SiO_2) in the laboratory of Jaroslav Černi Institute for Development of Water Resources, Serbia as well as measurements of the water quality parameters pH, specific conductivity (SC), and temperature (T) in the field. Analyses of stable carbon isotopes of DIC and POC have already been described in previous work (Ogrinc et al., 2008). The measurements were performed on Europa Scientific 20–20 with ANCA SL preparation module for solid and liquid samples and/or ANCA TG preparation module for trace gas samples in the Department of Environmental Sciences at Jožef Stefan Institute, Ljubljana, Slovenia. All stable isotope results are reported using conventional delta (δ)-notation in per mil (‰) relative to the V-PDB standard. The precision of measurements were 0.2‰ for $\delta^{13}\text{C}_{\text{DIC}}$ and $\delta^{13}\text{C}_{\text{POC}}$. The partial pressure of CO_2 ($p\text{CO}_2$) and mineral saturation states for calcite and dolomite were calculated using the PHREEQC speciation program (Parkhurst, Appelo, 1999).

RESULTS AND DISCUSSION

Water samples were collected in March, May and July of 2008 and 2009 in the area of Belgrade from surface water (the Sava River, lake and channels) and groundwater (piezometers and production wells). Most of the water samples were Ca–Mg– HCO_3^- type with an evident correlation between Ca^{2+} ($r = -0.59$) and Mg^{2+} ($r = -0.79$) ions with measured pH. High concentrations of dominant dissolved ions such as HCO_3^- , Ca^{2+} , and Mg^{2+} is affected by carbonate (calcite and dolomite) dissolution by carbonic acid indicating by (eq. 1 and 2).



Most of analyzed samples have a 2:1 mole ratio of HCO_3^- to $\text{Ca}^{2+} + \text{Mg}^{2+}$ (Fig. 2a) according to the stoichiometry of the reactions (see Eq. 1 and 2) and the predominance of dolomite dissolution in groundwater aquifer (Fig. 2b). Saturation index (S.I.) calculated for analyzed water samples indicated that surface waters and half of groundwaters were saturated (S.I. = 0) and super-saturated (S.I. > 0) with respect to calcite while less than half of the groundwaters were under-saturated (S.I. < 0) with respect to calcite.

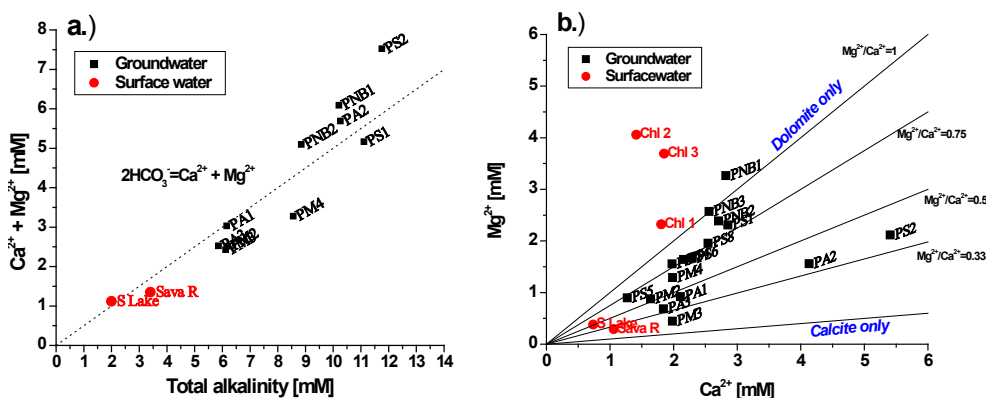


Figure 2. a) $\text{Ca}^{2+} + \text{Mg}^{2+}$ ratio versus alkalinity; line 1:2 indicates weathering of carbonates. b) Mg^{2+} versus Ca^{2+} indicates the dominance of dolomite dissolution in groundwater aquifer.

The $\delta^{13}\text{C}_{\text{DIC}}$ in analyzed area is highly variable and distinct between surface water (-11.8 to -4.9‰) and groundwater (-16.8 to -10.8‰) indicating different evolution pathways of carbon. The values for the Sava River ($\delta^{13}\text{C}_{\text{DIC}} = -11.2 \pm 0.8\text{‰}$, $n = 3$) containing predominantly groundwater with $\delta^{13}\text{C}$ values of the HCO_3^- fraction of -11‰ with varying amounts of additional biogenic CO_2 are in excellent agreement with results obtained near its mouth in 2006 (Ogrinc et al., 2008). Enriched values found for $\delta^{13}\text{C}_{\text{DIC}}$ in channels and lake in the range of -9.8‰ to -4.9‰ (Fig. 3a) pointed out an occurrence of intensive photosynthetic activity of phytoplankton in summer which is significantly controlled by water temperature ($r^2 = 0.9$). On average, the $\delta^{13}\text{C}_{\text{DIC}}$ values in groundwaters were lower than in stream waters, with rather uniform mean values of $-12.9 \pm 0.8\text{‰}$ ($n = 20$) and -12.8 ± 1.1 ($n = 17$) for operation wells (Fig. 3b.) and for piezometers (Fig. 3c), respectively. These values are the combined average $\delta^{13}\text{C}$ values of the soil CO_2 , originating mainly from the decomposition of C_3 plant cover organic matter ($\delta^{13}\text{C}$ about -28‰) and the other half as a result of carbonate dissolution from parent materials such as limestone ($\delta^{13}\text{C}_{\text{Ca}} \sim 0.0\text{‰}$) and dolomite ($\delta^{13}\text{C}_{\text{Mg}} \sim 2.0\text{‰}$). The exceptions are the operation well (WM2) and piezometer (PNB1) with more depleted values of -16.8 and -15.5‰ , respectively. Consideration of the proportion of dissolved CO_2 species of DIC indicated the increase of $\text{CO}_2(\text{aq})$ in respect to HCO_3^- that is caused probably by the process of microbial respiration. The bacteria present in contaminated waters are readily able to transform components of the crude oil ($\delta^{13}\text{C} \sim -30\text{‰}$) into inorganic carbon (Medina-Bellver et al., 2005), which leads to a decrease in the $\delta^{13}\text{C}_{\text{DIC}}$ relative to the value in unpolluted water.

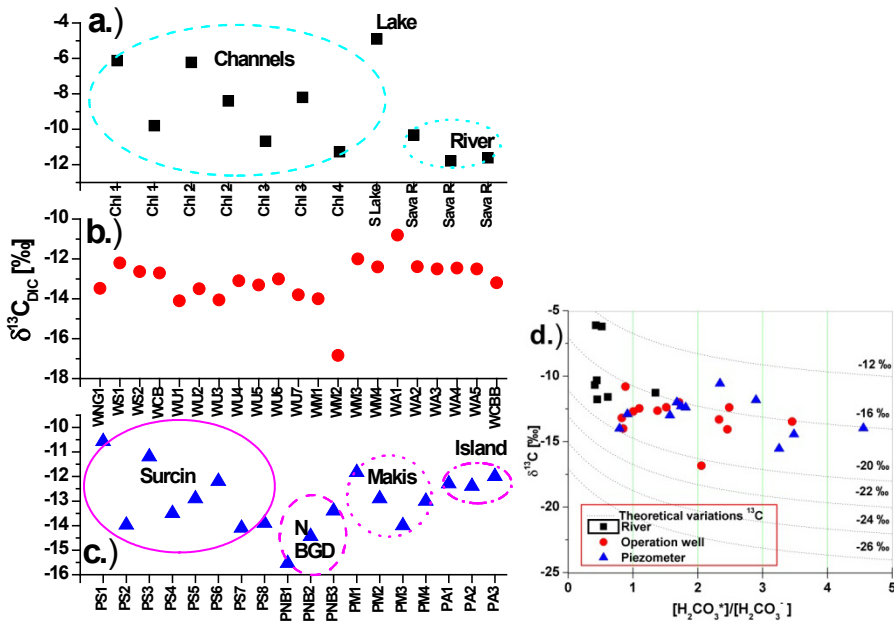


Figure 3. Spatial variations of $\delta^{13}C_{DIC}$ and $\delta^{13}C_{POC}$ in a) surface waters, b) operation wells, c) piezometers, and d) relationship between the $\delta^{13}C_{DIC}$ and the ratio $[H_2CO_3^*]/[H_2CO_3]$ in Belgrade area.

The variations of $\delta^{13}C$ values are controlled by the proportions of the concentrations of aqueous CO_2 [$H_2CO_3^*$] and of bicarbonate ions [$H_2CO_3^-$] in solution. The relationship between the $\delta^{13}C_{DIC}$ in surface and groundwater of the Belgrade area and the ratio $[H_2CO_3^*]/[H_2CO_3^-]$ is plotted in Fig. 3d. In the same diagram, the theoretical variations of $\delta^{13}C_{DIC}$ in equilibrium with different isotopic composition of soil CO_2 calculated as a function of the concentrations of dissolved carbonate species together with their respective $\delta^{13}C$ values and from the temperature dependence of isotope enrichment factors are plotted (Amiotte-Suchet et al., 1999). All samples are in apparent isotopic equilibrium ($\delta^{13}C_{DIC} = -16\text{‰}$) with ^{13}C enriched gaseous soil CO_2 . The DIC is not in isotopic equilibrium with the soil CO_2 originated from C3 vegetation (-23 to -24‰). The enrichment in ^{13}C of the DIC is caused by the dissolution of carbonate from limestone and dolomite and by isotopic equilibration with the atmospheric CO_2 as well (open system). At a given sampling date, the $\delta^{13}C$ values appear to be more or less controlled by the relative ratio of $H_2CO_3^*$ to $H_2CO_3^-$. Nevertheless, the trends of points often cross the theoretical curves, indicating that the isotopic composition of the gaseous phase is spatially changing.

$\delta^{13}C$ signatures of suspended POC in analyzed waters varied between -38.3 and -25.0‰ . The majority of values were observed in a narrow range of -29.6 to -25.0‰ , averaging at $-27.8 \pm 1.1\text{‰}$ ($n=16$) indicating that the main source of POC in the river system is soil OC. Markedly more depleted $\delta^{13}C_{POC}$ values of -38.1‰ , -38.3‰ , and -35.1‰ found in operating well (WA4), piezometer (PS8), and channel (Chl1) respectively, are associated with the presence of anaerobic bacterial decomposition of organic matter producing very depleted methane with $\delta^{13}C$ values between -50 and -80‰ (Sivan et al., 2007). At the locations where bacterial activi-

ties were observed, a strong positive linear relationship ($r = 0.94$, $n=7$) between the carbon isotopic compositions of DIC and POC is obtained probably due to a major fraction of POC was derived from allochthonous matter.

CONCLUSIONS

The major solute composition of analyzed surface and groundwaters was dominated by carbonic acid dissolution of calcite and dolomite. The $\delta^{13}\text{C}_{\text{DIC}}$ of about -13‰ is in agreement for value originated from dissolution of soil carbonate minerals by soil organic CO_2 derived from C3 land vegetation. Negative $\delta^{13}\text{C}$ values below -14‰ would be indicative of biological activity, i.e. a relatively large contribution of biogenic (soil) CO_2 with low $\delta^{13}\text{C}$.

The POM from surface waters showed considerable variations in carbon isotopic compositions depending on the potential sources of organic matter. It seems that most important source of the particulate organic matter is soil which is not bioavailable.

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