Introduction

Oxygen and hydrogen stable isotope ratios of the water molecule ($^{18}\text{O}/^{16}\text{O}$ and $^{2}\text{H}/^{1}\text{H}$) are by their nature excellent tracers of the physical processes affecting water such as evaporation, condensation, snow melting and mixing of waters of different origin [4, 9]. Isotope methods were introduced into catchment hydrology research in the 1960s as complementary tools to conventional hydrological methods for addressing questions such as the fate of precipitation, its pathway to the stream and its residence time in the catchment [19]. Isotope methods were introduced into catchment hydrology research in the 1960s as complementary tools to conventional hydrological methods for addressing questions such as the fate of precipitation, its pathway to the stream and its residence time in the catchment [19]. Measurements of the isotopic composition of water sources coupled with river discharge data can provide insight into the effects of basin-integrated hydroclimate forcing on water cycling. The water in a river originates from different surface (recent precipitation) and subsurface (groundwater) sources, and its isotopic composition is determined by contributions from each of them, with their individual isotopic signatures. Studies of oxygen and hydrogen isotopes in rivers and their tributaries have many applications, such as identification of the source(s) of water and assessment of their mixing proportions [24], and estimation of evaporation losses [16].

The River Sava Basin is located between the southern edges of the Alps, North-Eastern part of the Dinaric Mountains and the Southern part of the Pannonian lowland; it is shared by five states, Bosnia-Herzegovina, Croatia, Montenegro, Serbia and Slovenia. The Sava represents the North-Western boundary of the Balkan Peninsula and connects three European capitals: Ljubljana (Slovenia), Zagreb (Croatia), and Belgrade (Serbia). As the Danube’s longest right-hand...
tributary (total length of 945 km) it contributes approximately 25% to the Danube’s total discharge and drains 95,719 km² of surface area (including 115 km² in Northern Albania), of which 15687 km² belongs to the territory of Serbia [10]. The Sava starts in the Julian Alps region of North-Western Slovenia and is created by two headwaters, the Sava Dolinka (45 km long) with source elevation at 1222 m a.s.l., and the Sava Bohinjka (31 km long) at an elevation of 805 m asl that have their confluence between the towns of Lesce and Radovljica.

At the start of its journey to Belgrade, the Sava has an average discharge of about 45 m³/s (near the town of Lesce) and increases to a value of 384 m³/s in Crnac (amongst others the Kupa, Una, Vrbas, Bosna, and Drina rivers) contribute to the average discharge of 1722 m³/s before merging with the Danube. The maximum discharge is observed during April (2630 m³/s) and the minimum in September (1370 m³/s) [27]. As a result of its strongly fluctuating discharge, the water levels and water depths also vary strongly during the year. The flatter part of the basin (altitudes between 70 and 400 m) covers 21.9% of its total area in the middle and lower courses. The climate in this basin varies from Alpine to Pannonian, and to moderate continental characterized by hot summers and moderately cold winters with regular heavy snowfall (annual precipitation 600–1300 mm) [20] and temperatures ranging from –20°C to 40°C.

The upper course of the River Sava is composed of massive Triassic and Jurassic limestone and dolomite, which alternate with massive dolomite and conglomerates composed of dolomite [22]. Its high hydro-electric production potential, up to 3.2 billion kWh, has not been utilized until lately. In terms of its major ion chemistry, the Sava is a typical Ca-HCO₃ river [23].

The Sava Valley is a natural route for land traffic, which includes the Belgrade–Zagreb railway and highway, and routes of oil and gas pipelines from Croatia to Serbia. As a result of all this traffic and the densely populated and industrialized areas it flows through, the river is much polluted. The main sources of contamination are composed of dolomite [22]. Its high hydro-electric production potential, up to 3.2 billion kWh, has not been utilized until lately. In terms of its major ion chemistry, the Sava is a typical Ca-HCO₃ river [23].

Ongoing the sand and gravel mining over the past 10 to 15 y has resulted in a drop of the average water level of the Sava at certain locations of the order of one metre. This decrease in water level has a considerable impact on the environment (forestry and agriculture). The Sava basin hosts the largest complex of alluvial wetlands in the Danube Basin (Posavina – Central Sava Basin) and large lowland forest complexes in Serbia. The Sava basin is of great significance for the Danube River Basin because of its outstanding biological and landscape diversity.

Generally, there is a paucity of experience in the use of stable isotopes for investigating the River Sava catchment hydrology. A significant focus of research has coupled hydrochemical parameters with stable isotope techniques to study the watershed in Slovenia at 41 locations [18]. In view of exploration of the River Sava for water supply, estimation of the origin and dynamics of the Sava's discharge, the water levels and water depths also vary strongly during the year. The flatter part of the basin (altitudes between 70 and 400 m) covers 21.9% of its total area in the middle and lower courses. The climate in this basin varies from Alpine to Pannonian, and to moderate continental characterized by hot summers and moderately cold winters with regular heavy snowfall (annual precipitation 600–1300 mm) [20] and temperatures ranging from –20°C to 40°C.

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Table 1. River Sava tributaries on Serbian territory with some characteristic parameters (total drainage area, total length, distance from the confluence point with the Sava) together with relevant gauging stations

<table>
<thead>
<tr>
<th>River</th>
<th>Total drainage area (km²)</th>
<th>Total length (km)</th>
<th>Station</th>
<th>Distance from the river confluence (rkm)</th>
<th>Annual discharge for 2006 (m³/s)</th>
<th>Mean</th>
<th>Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drina</td>
<td>19,226</td>
<td>346</td>
<td>Radalj</td>
<td>85.5</td>
<td>390</td>
<td>1800</td>
<td></td>
</tr>
<tr>
<td>Bosut</td>
<td>2913</td>
<td>186</td>
<td>Batrovci</td>
<td>35.9</td>
<td>11.4</td>
<td>11.4</td>
<td></td>
</tr>
<tr>
<td>Kolubara</td>
<td>3639</td>
<td>123</td>
<td>Beli Brod</td>
<td>39.2</td>
<td>25.4</td>
<td>323</td>
<td></td>
</tr>
<tr>
<td>Topčiderka</td>
<td>138</td>
<td>30</td>
<td>Rakovica</td>
<td>5.3</td>
<td>0.77</td>
<td>15.8</td>
<td></td>
</tr>
</tbody>
</table>
river with small inclination in its lowest section. The short River Kolubara, due to its many long tributaries, creates a relatively large branched system within the river drainage area (3639 km²), passing through an immense lignite deposit which in the Neogene was a huge bay of the Pannonian Sea. The River Topčiderka originates from the Northern section of Kosmaj mountain at an altitude of 192 m and enters the urban section of Belgrade. It drains an area of 138 km² (out of which 70% is agricultural land) and empties into the Čukarica Bay of the Sava, at an altitude of 69 m.

A 4-day campaign to examine the water and sediment quality in the Serbian stretch of the Sava was carried out from 21–23 August 2006 (Fig. 1). Samples were collected at four locations: Jamena, Smederevska Mitrovica, Šabac and Ostružnica. The research ship ‘ARGUS’ was used to perform the longitudinal survey in collaboration between the Republic Hydrometeorological Service of Serbia and the Management for Environmental Protection of Serbia. The ship is normally used for water quality surveys, and is equipped with sampling devices, on-board field instrumentation and laboratory equipment [15]. A list of sampling locations, listed from upstream to downstream together with the actual flow rates on the date of sampling, is summarized in Table 2.

Grab water samples were collected from the ship with a bucket in the middle of the river, and near the left and right banks, and then analyzed for a range of physicochemical parameters, namely pH, electrical conductivity (EC), dissolved oxygen (DO), nitrate (NO₃⁻) phosphorus (total-P), for biological parameters (chlorophyll-a, phytoplankton, zooplankton) and for stable isotopes (²H and ¹⁸O). Sampling, preservation and analytical protocols for determination of the physicochemical and biological parameters were conducted in accordance with standard methods for surface waters [1, 29, 30]. Classification of chemical parameters was made following the ICPDR standard classification [14]. River water samples for determination of stable isotope ratios were collected and stored according to standard procedures [4] and analyzed in the Department of Environmental Sciences at the Jožef Stefan Institute, Ljubljana, Slovenia, by a Varian MAT 250 mass spectrometer. The isotopic ratios of hydrogen and oxygen (²H/¹H and ¹⁸O/¹⁶O) are expressed in the conventional delta (δ) notation relative to V-SMOW (Vienna-Standard Mean Ocean Water) [13]. The oxygen isotopic composition was determined by means of the water-CO₂ equilibration technique [7], while the isotopic composition of hydrogen was determined using reduction of water over hot (800 °C) chromium [11]. All measurements were done in duplicate or triplicate. The precision of the measurements was better than ±0.1‰ for δ¹⁸O and ± 1‰ for δ²H.

### Results and discussion

The stable isotope composition of the Sava river water has previously been measured on Serbian territory at Jamena in 1998 [21] and at Ostružnica during the period 2003–2005 [12]. These data demonstrated that the mean δ¹⁸O value increases downstream, probably as a result of interaction of tributaries draining lowlands (with ¹⁸O-enriched isotope signatures) and the storage effect of large swamps (e.g. Obędska Bara) and ponds in the flood plain of the river. During this survey, the measured isotopic composition of Sava water along the main stem (near the left and right banks and in the middle of the river) in Serbia varied over a narrow range from −66‰ to −61‰ for δ²H, and from −9.1‰ to −8.5‰ for δ¹⁸O (Table 3). Recorded values are in the observed range of variability measured in Slovenia [22], indicating that the isotopic signal from high elevation

### Table 2. Sampling locations and their characteristics (latitude, longitude, elevation, distance from the confluence point with the Danube, drainage area upstream of the sampling site, discharge and flow velocity) during the campaign in August 2006

<table>
<thead>
<tr>
<th>SC</th>
<th>Location</th>
<th>Distance from the river confluence (rkm)</th>
<th>Latitude (°N); Longitude (°E)</th>
<th>Elevation (m a.s.l.)</th>
<th>Drainage area (km²)</th>
<th>Discharge (m³/s)</th>
<th>Flow velocity (m/s)</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Jamena</td>
<td>195.0</td>
<td>44 52 42 19 05 21</td>
<td>84</td>
<td>64,073</td>
<td>660</td>
<td>0.53</td>
<td>21/08/2006</td>
</tr>
<tr>
<td>2</td>
<td>Sremska Mitrovica</td>
<td>136.4</td>
<td>44 57 55 19 36 01</td>
<td>80</td>
<td>87,996</td>
<td>852</td>
<td>0.52</td>
<td>22/08/2006</td>
</tr>
<tr>
<td>3</td>
<td>Šabac</td>
<td>103.6</td>
<td>44 46 17 19 42 16</td>
<td>79</td>
<td>89,490</td>
<td>750</td>
<td>0.42</td>
<td>23/08/2006</td>
</tr>
<tr>
<td>4</td>
<td>Ostružnica</td>
<td>17.0</td>
<td>44 43 19 20 18 15</td>
<td>78</td>
<td>95,283</td>
<td>792</td>
<td>0.28</td>
<td>23/08/2006</td>
</tr>
</tbody>
</table>

SC – sample code; rkm – river kilometre.

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Fig. 1. Map of sampling locations along the River Sava and its tributaries during the campaign in August 2006. The numbers represent sampling locations.
precipitation upstream is not preserved in the isotopic composition of the Sava downstream. The electrical conductivity and pH of the water also varied over a narrow range from 390 to 410 μS/cm and from 8.4 to 8.7, respectively. The sampling period was characterized by stable weather conditions with high air and water temperatures (24.1–28.2 °C and 21.2–24.4 °C, respectively), no precipitation and a low water regime.

The average value obtained for the isotope content from two independent determinations with its 2-σ uncertainty is illustrated by the error bars in Fig. 2a. It is apparent in most cases that the error bars overlap the values of samples taken at the left and right banks and mid-stream at the same location, indicating that there is no difference in the isotopic content between those samples within experimental error. Thus, the river water samples taken at the middle and right bank at the Jamena location (1), all samples at the Smederevska Mitrovica location (2) and at the mid-river location of Sabac (3) appeared to be isotopically the same stream water with an average value of −9.0 ± 0.1‰ for δ18O and −65 ± 1.0‰ for δ2H. The case is similar with the samples taken near the left and right bank locations at Sabac (3) and Ostružnica (4). The mean values for those samples of −8.7 ± 0.1‰ for δ18O and −63 ± 2‰ for δ2H reflect the same degrees of evaporation. On the other hand, an obvious discrepancy was observed for the sample taken near the left bank at the Jamena location (1). The enrichment in 18O (δ18O = −8.6‰) and 2H (δ2H = −61‰) contents might be the result of either incomplete mixing processes between stream water and adjacent still waters, or evaporation [31] since the river is shallow with the depth ranging between 1.3 and 2.4 m on the stretch upstream between the confluence with the Drina (rkm 177) and the border with Croatia. It is assumed that evaporation could be the consequence of inundation of floodplain areas (Drina mouth with Bosut forest) occurring during April/May 2006 [28].

Further, the stable isotope data comprising measurements of the rivers Drina, Sava, and Danube at the Badovinci, Jamena, Ostružnica, and Vinča locations are summarized in Table 4. Seasonal variations in the river waters are shown in Fig. 3. On the δH vs. δ18O plot, water samples from the Sava and the Drina taken in winter-spring 1998 lie on or close to the global meteoric water line (GMWL) [5] and the local meteoric water line (LMWL) [12], as well as samples taken from the Sava in Slovenian part in August 2006. The River Sava shows ~1‰ depletion in δ18O in spring samples relative to the autumn ones [12]. Summer Sava samples collected during this survey are enriched in heavy isotopes and slightly off the LMWL, indicating substantial evaporation. The evaporation line (LEL) is defined by a slope of 5.6 ± 0.5 (n = 18; r = 0.94), significantly less than that of the LMWL (7.8 ± 0.2). The intercept between the evaporation line and the
LMWL presents the initial stable isotopic composition of the non-evaporated water body. This composition was found to be similar to that of water taken in May, a month in which it is assumed that evaporation does not take place. For comparison, the mean values of δ²H and δ¹⁸O values with the corresponding standard deviations of the Sava (Ostružnica) and the Danube (Vinča) during our regular isotopic monitoring programme for 2006 are illustrated. The annual average δ values for 2006 were obtained from the monthly composite samples prepared from a portion of weekly composites taken at the actual time and flow conditions. Therefore, from the annual average at Ostružnica for 2006 evaporation (which occurs occasionally) is not in evidence. However, δ values found during this summer survey are in the range of standard deviations of the annual average δ values. The δ values measured for the lowland part of the Sava in Slovenia also lie in these ranges, whereas the values for the high mountain area in Slovenia fall in the range of standard deviations for the Danube, indicating their high mountain isotopic signature which is lost in the lowest course of the Sava.

Table 4. Stable isotopic parameters of the Drina, Sava and Danube

<table>
<thead>
<tr>
<th>River</th>
<th>Location</th>
<th>Latitude (°N); Longitude (°E)</th>
<th>Time</th>
<th>δ²H  (‰)</th>
<th>δ¹⁸O  (‰)</th>
<th>d-excess (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drina</td>
<td>Badovinci</td>
<td>44 47 05; 19 21 20</td>
<td>December 1997–June 1998</td>
<td>−69 ± 1</td>
<td>−10.0 ± 0.1</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>Jamena</td>
<td>44 52 4; 19 05 21</td>
<td>December 1997–June 1998</td>
<td>−70 ± 4</td>
<td>−10.0 ± 0.4</td>
<td>10.4</td>
</tr>
<tr>
<td>Sava</td>
<td>Ostružnica</td>
<td>44 43 54; 20 19 02</td>
<td>August 2006</td>
<td>−62 ± 1</td>
<td>−8.8 ± 0.1</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Annual mean 2006*</td>
<td>−65 ± 4</td>
<td>−9.4 ± 0.3</td>
<td>10.2</td>
</tr>
<tr>
<td>Danube</td>
<td>Vinča</td>
<td>44 46 06; 20 37 33</td>
<td>August 2006</td>
<td>−73 ± 1</td>
<td>−10.2 ± 0.1</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Annual mean 2006*</td>
<td>−70 ± 4</td>
<td>−10.0 ± 0.3</td>
<td>10.0</td>
</tr>
</tbody>
</table>

* From the isotopic monitoring programme for 2006.

We performed the detailed evaporation calculations described by Gammons [8] for the weather conditions during our survey. The key variables that influence this calculation were set at δ¹⁸O₀ = −9.8‰ and δ²H₀ = −69‰ for the initial stable isotopic composition of the water body, and an average surface air temperature of 22.6°C. Estimated water vapour compositions yields values of δ¹⁸Owv = −19.8‰ and δ²Hwv = −138‰. The LELs begin at the isotopic composition of Sava water in May, and deviate at progressively higher degrees of evaporation due to kinetic isotopic effects that are augmented by decreasing relative humidity (Fig. 4). The value of the relative humidity, h, that gives the best fit to the isotopic data for river water (solid squares) is somewhere between 0.6 and 0.4. This compares well with the average annual relative humidity of 0.7 for Sremska Mitrovica in August 2006 based on data of the Republic Hydrometeorological Service of Serbia. The fraction of water lost to evaporation, F, could be estimated to be approximately between 10 and 20%. The samples at the left side bank (1 – Jamena and 3 – Šabac) were the most evaporated, having lost about 25% of their initial water (F = 0.6).

The d-excess value (d = δ²H − 8δ¹⁸O) [6] calculated from the mean values of the River Sava data for Jamena (1998) and during the sampling period of January–December 2006 (Ostružnica) is close (10.3 ± 0.1‰) to the +10‰ value (Table 4) that is generally observed over the northern hemisphere from air masses of the mid-latitude oceanic areas. Slightly lower d-excess...
values of 8.5 ± 0.1‰ for samples collected from the Sava at Ostružnica and the Danube at Vinča in August 2006 (Table 4) were calculated. At sampling point 3 (Šabac), the d-excess values are different for all three sampling locations (3L, 3M, 3R). The d-excess is the lowest (d = 7.0) at the sampling location 3L, indicating the evaporation effect (see Fig. 4). However, the other two sampling locations (especially 3R) are located in areas where groundwater recharge through the river bed is possible, being situated on an alluvial plain. This is further supported by the increase in d-excess from the left to the right river bank (Table 3).

The concentration of dissolved oxygen (DO) in surface waters is an indicator of the water quality and the impact of pollutant loads of various sources and discharges. According to the ICPDR classification, all the parameters examined matched the first and the second class of water quality. DO varied from 8.0 to 10.5 mg/l and correspondingly the oxygen saturation (OS) from 95% to 120%. Generally, DO was lower near the banks than in mid-river, while still waters along the Sava show the effects of eutrophication. The growth rate of the phytoplankton community is affected by the availability of sunlight, carbon dioxide, nutrients such as nitrates and phosphates, and trace elements. Because the level of nutrients expressed as nitrogen-to-phosphorus ratio (N/P) ranged from 14.6 to 23.7, phosphorus was in deficient and limited algal growth [26]. Thus, phytoplankton biomass varied between 34 and 183 μg/l [3]. This parameter measured along the Sava during the survey shows a good negative correlation with dissolved oxygen (DO) concentration ($r^2$ = 0.77, n = 11) and a weak positive correlation ($r^2$ = 0.30, n = 11) with δ18O, reflecting downstream variations in flow velocity (0.52 to 0.28 m/s, Table 2) and river morphology.

Conclusions

The River Sava on Serbian territory was sampled over a length of 188 km during a four-day campaign and the oxygen and hydrogen stable isotopic composition determined were compared with results from other seasons. The results obtained led to the following observations and conclusions.

This downstream survey demonstrated the potential of the stable isotope content to identify areas of significant evaporation processes in river water. Based on δ values, the higher isotopic signal in the summer clearly shows increased evaporation caused by higher temperatures characteristic of a plain river with meanders at the altitude of approximately 70 m. The δ18O-enriched isotopic content below the location of Šabac in the Sava’s lower course is the consequence of increased evaporation occurring in the reservoir due to weather conditions and the low flow and velocity/or growth rate of the phytoplankton biomass. The fraction of water lost by evaporation was estimated to be between 10 and 20%, whereas at the surface of the river at the left hand locations (Jamena and Šabac) about 25% evaporated. The influence of tributary catchment effects upon the isotopic signature of the River Sava in the stretch through Serbia could not be detected, probably due to low water regime and insufficient discharge at the time of observation.

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References