



## **Distribution of Environmental Isotopes in the Upper Juzna Morava River Catchment**

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Natural variations in concentrations of  $2\text{H}$  (deuterium),  $3\text{H}$  (tritium) and  $^{18}\text{O}$  (oxygen-18) in river water, springs and precipitation in the upper catchment of the Juzna Morava River (southeastern Serbia) are presented. The studied mesoscale ( $350\text{ km}^2$ ) mountainous basin (runoff  $200\text{ mm/yr}$ ) includes only the nearby small right tributaries (Golema, Crnovrska, Jelasnicka Rivers) of the Juzna Morava River, which belongs to the Velika Morava catchment (Danube river basin). Elevation in this catchment varies from  $390$  to  $1923\text{ m}$  above mean sea level. It is situated mostly in the Morava massif, consisting of Paleozoic gneiss, mica schists, amphibolites and greenstone (metagabbros, metadiabases, calc-schists, quartz and other chlorite schists) complexes.

The region is characterized by a transitional regime between moderate continental and Mediterranean climate. The mean annual precipitation of  $614\text{ mm}$  ( $10\text{--}15\%$  as snow) and air temperature of  $10.8\text{ }^{\circ}\text{C}$  at the meteorological station Vranje ( $42^{\circ}33'\text{N}$ ,  $21^{\circ}55'\text{E}$ ,  $432\text{ m asl}$ ) about  $19\text{ km}$  from the watershed at elevation of  $1923\text{ m}$  were recorded for the 30-year period, 1961-1990. The changes in precipitation amount with elevation are considerable reaching  $1000\text{ mm}$  at  $1300\text{ m asl}$ . The individual 'grab' samples of stream and groundwater from various sites and monthly-composite precipitation were collected during the period 1988-1990.

The objectives of this study were spatial and temporal variability in  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$  and  $^3\text{H}$  of the rivers and compare the river isotopic data with available precipitation isotope data and discuss the origin of the spatial distributions in  $\delta$  values. The  $^{18}\text{O}$  and  $^2\text{H}$  in local precipitation fluctuated in a wide range of values, ranging from  $-16.9$  to  $-4.9\text{ ‰}$ , for  $\delta^{18}\text{O}$  and from  $-114.7$  to  $-33.3\text{ ‰}$ , for  $\delta^2\text{H}$  exhibiting a seasonal variation from low isotope ratios in winter (November-February) and high ratios in summer (May-

September). The  $^3\text{H}$  concentrations in atmospheric waters were pretty constant (11-30 TU) with slightly pronounced maximum in May-June (40- 75 TU). There is a weak positive correlation between tritium content and altitude ( $r^2 = 0.71$ ), as well as and monthly amount of precipitation ( $r^2 = 0.33$ ).

The "local " meteoric water line (LMWL) generated from weighted analyses of samples collected at 4 adjacent precipitation monitoring sites from different altitudes was  $\delta^2\text{H}_{LMWL} = (7.3 \pm 0.2) \delta^{18}\text{O} + (7 \pm 2)$  with  $n=41$ ,  $r^2=0.988$ . The slope is lower than for the global MWL reflecting the humidity of the local air mass (72% on average). The average deuterium excess value (d-excess) as an indicator of original air mass source for the region was  $14 \pm 1 \text{ ‰}$ . The gradients for altitude effects calculated from the relations  $\delta^{18}\text{O}(\delta\text{D}) = f(\text{altitude})$  for precipitation are  $-0.22 \pm 0.2 \text{ ‰}/100\text{m}$  for  $\delta^{18}\text{O}$  and  $-1.73 \pm 0.04 \text{ ‰}/100\text{m}$  for  $\delta\text{D}$ .

The stream samples integrate the isotopic compositions of waters derived much farther upstream. The values for river waters under investigation ranged from -10.87 to -9.27 ‰ for  $\delta^{18}\text{O}$ , and from -76.8 to -66.2 ‰ for  $\delta^2\text{H}$ . The unweighted linear regressions of individual streams made of small datasets (4-7 number of samples collected per site) gave the slopes between 3 and 23, with an average of 10.7. We combined data for 24 samples in a single equation of the LMWL for river water,  $\delta^2\text{H}_{RWL} = (7.6 \pm 1.4) \delta^{18}\text{O} + (4 \pm 14)$  ( $r^2=0.76$ ). Nevertheless, the position of the data points along the ranges of  $\delta$  values is presented according to the elevation of the collecting site. The similarity in slopes and intercepts for precipitation and river water (the difference 0.3 and 3 ‰, respectively) reflects some regional characteristic of mixing of precipitation and groundwater, pointing out that large-scale isotopic signatures of precipitation have been preserved in the river isotopic compositions over the same area. The obtained significant seasonal variations of  $\delta$  values in the Juzna Morava, Golema, Crnovrska, and Jelasnicka Rivers water suggest that the main source of their streamflows are from recent precipitation. The average d-excess for the stream water was 8.2 ‰, while for the elevation below 500 m asl the value was less than 8 ‰. The d-excess values showed obvious correlation with  $\delta^2\text{H}$  values ( $r^2= 0.77- 0.99$ ). In addition, river water showed seasonal temperature variations as well as some springs (shallow groundwater). The  $\delta^{18}\text{O}$  of stream water is influenced by altitude and temperature. The calculated isotopic altitude effect was smaller ( $-0.13 \text{ ‰}/100\text{m}$ ) than in the case of precipitation. The  $\delta^{18}\text{O}$ -stream temperature gradients for the tight fits ( $r^2= 0.67- 0.92$ ) were between 0.03 and 0.05 ‰/°C.

LMWL for cold springs in the region was  $\delta^2\text{H}_{RWL} = (4.67 \pm 0.8) \delta^{18}\text{O} - (25 \pm 8)$  for 24 samples with a correlation  $r^2=0.78$ . Linear regression between average tritium concentration in cold springs and elevation of their discharge showed the tendency of increasing tritium content (coefficient of correlation of 0.98 for 5 springs), which can

be attributed to different water age and capacity of the spring reservoir.