Journal of Hydrology 565 (2018) 365–373

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Research papers

Distribution of H and O stable isotopes in the surface waters of the Sava River, the major tributary of the Danube River

Nives Ogrinc[a,b,*], David Kocman[a], Nada Miljević[c,1], Polona Vreča[a], Janja Vrzel[a,b], Pavel Povinec[d]

[a] Department of Environmental Sciences, Jožef Stefan Institute, Ljubljana, Slovenia
[b] Jožef Stefan International Postgraduate School, Jamova 39, 1000 Ljubljana, Slovenia
[c] Jaroslav Černi Institute for Development of Water Resources, Belgrade, Serbia
[d] Department of Nuclear Physics and Biophysics, Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava, Slovakia

ARTICLE INFO

This manuscript was handled by Marco Borga, Editor-in-Chief, with the assistance of Daniele Penna, Associate Editor

Keywords:
Hydrology
Surface water
MRT
$\delta^{18}O$ spatial distribution
GIS
Sava River Basin

ABSTRACT

The presented paper describes spatial and temporal variations in extended stable isotope datasets of hydrogen and oxygen (δ^2H and $\delta^{18}O$) in the Sava River water that were used to estimate the mean residence time (MRT) of stream water using an exponential flow model. The re-examining MRT was < 2 years in the Slovenian part of the Sava River and was in a good agreement with previous estimates and with the MRT estimated in the Sava River at Ostružnica near Belgrade, Serbia. A MRT > 2.2 years was observed in the Danube River at Vinča also near Belgrade. The spatial distribution of $\delta^{18}O$ in precipitation over the Sava River Basin (SRB) was mapped based on the long-term weighted mean annual $\delta^{18}O$ values and established relationship with various geographical controls (latitude, longitude and altitude). The modelled $\delta^{18}O$ values in precipitation agree with the measured values in the surface river water at different locations indicating that the spatial variation in the isotopic composition of precipitation is the dominant factor controlling surface water isotope ratios over the SRB.

1. Introduction

Stable isotopes of hydrogen and oxygen are ideal independent environmental tracers for investigating hydrological problems relating to both surface and groundwater resources (Kendall and McDonnell, 1998; Gat, 1996; Tetzlaff et al., 2007; Koeniger et al., 2009; Reckerth et al., 2017; Šanda et al., 2017) and can be used successfully in studies of atmospheric circulation (Rozanski et al., 1992) and palaeoclimatic investigations (Thompson et al., 2000; An et al., 2001). In addition, isotope methods were introduced into catchment hydrology research as complementary tools to obtain important hydrological information on the following: recharge and discharge processes, flow and the interconnections between aquifers, and the sources and mechanism of pollution (Aggarwal et al., 2006a,b). For this purpose, a volunteer database on isotopic composition of river water termed the Global Network of Isotopes in Rivers (GNIR) was launched in 2007 by the International Atomic Energy Agency (IAEA) (Vitvar et al., 2007; Halder et al., 2015). The GNIR database supplements the existing IAEA Global Network of Isotopes in Precipitations (GNIP) monitoring programme established in 1961 (http://isohis.iaea.org). The GNIP has been traditionally used to provide information about the isotopic labeling of different local water sources typically based on local meteoric water lines. These datasets can be further used to develop various statistical and geostatistical tools that when combined with Geographical Information System (GIS) tools can be used to map the spatial variability in isotopic composition among the different components of the water cycle (e.g. Bowen, 2010; Dutton et al., 2005; West et al., 2008, 2014). Depending on the spatial coverage and temporal extent of the data available, various interpolation techniques can be used to map and model the geospatial distribution of stable isotopes in precipitation. These approaches usually take into account different geographical and meteorological controls on the isotopic composition of precipitation (e.g. Bowen and Wilkinson, 2002; Bowen and Revenaugh, 2003; Lykoudis and Argiriou, 2007; Dutton et al., 2005; Lykoudis et al., 2009; Bowen, 2010; Giustini et al., 2016). However, existing large-scale models do not capture the finer-scale regional complexity and variability. This is especially the case in catchments that cover a wide set of geographic and climatic conditions such as the Sava River Basin (SRB). For the surface waters, Bowen et al. (2011) developed a simple, "steady state," water balance model for surface water isotopic composition using GIS. They then used this model to evaluate the isotopic relationships between surface water and drinking water across the contiguous United States. Relatively accurate

* Corresponding author.
E-mail address: nives.ogrinc@ijs.si (N. Ogrinc).
[1] N. Miljević passed away in 2011.

https://doi.org/10.1016/j.jhydrol.2018.08.024
Received 14 March 2018; Received in revised form 27 July 2018; Accepted 9 August 2018
Available online 12 August 2018
0022-1694/

models for surface water isotope composition can also be developed in the absence of densely distributed surface water monitoring data and can be applied in poorly sampled regions, while in the case when monitoring data are available, the models can be improved through the incorporation of residual correction (Bowen et al., 2011).

In this paper a hydrological research of the surface water in the SRB is presented using stable isotopes of H and O. The SRB plays an important role in groundwater systems in Slovenia, Croatia, Bosnia and Herzegovina and Serbia. The results of the study can be widened from regional to continental scale, since the Sava River is the major tributary of the Danube River, which is a main source of groundwater in the Central Europe, and its main water supply body. Previous hydrological investigations in the SRB were mainly performed in Slovenia and near Belgrade in Serbia, while isotopes in precipitation were monitored at different locations mostly within the frame of short-term research projects (e.g. Vreča et al., 2006; Golobočanin et al., 2007; Ogrinc et al., 2008; Vreča and Malenšek, 2016). Long-term isotope data records (> 20 years) in precipitation are available only for Ljubljana (Vreča et al., 2014) and for Zagreb (Krajcar Bronić et al., 1998; Vreča et al., 2006) as a part of the GNIP. The isotopic variations in precipitation follow approximately the sinusoidal, seasonal pattern where winter months are dominated by colder air masses that bring more ^{2}H- and ^{18}O-depleted rain and snow and summer months with ^{2}H- and ^{18}O-enriched precipitation. The correlation between δ^2H and δ^{18}O in Ljubljana in Slovenia, Zagreb in Croatia and Belgrade in Serbia are high, i.e., $R^2 > 0.98$, $R^2 > 0.96$ and $R^2 > 0.97$, respectively, and Local Meteoric Water Lines (LMWL) (Vreča et al., 2006, 2014; Golobočanin et al., 2007) are close to the Global Meteoric Water Line (GMWL) (Craig, 1961). Assuming that precipitation in the Mediterranean area is characterized by higher *d*-excess values of up to 25‰ compared to 10‰ that are typical of Atlantic air masses (Cruz-San et al., 1992; Rozanski et al., 1993) the influence of the Atlantic air masses predominates in Ljubljana, Zagreb and Belgrade. The influence of Mediterranean air masses is also important and can contribute more than 20% of precipitation in the north western part of the SRB (Vreča et al., 2006).

In comparison to precipitation, surface water δ^2H and δ^{18}O values are generally less variable. They do exhibit seasonal differences, being generally ^{18}O-depleted during the winter, while ^{18}O-enriched precipitation affected summer δ^{18}O surface water values. The spatial variability in δ^{18}O values across Slovenia is consistent with the recharge regimes determined in the Sava River catchment (Hrvatin, 1998) changing from Alpine High Mountain in the upper parts with lower δ^{18}O values to Dinaric Alpine in the lower parts of the catchments where δ^{18}O values are higher and reflect reduced precipitation in this area (Ogrinc et al., 2008). Poor correlations between δ^{18}O values and river discharge ($R^2 = 0.03$) or temperature ($R^2 = 0.01$) were obtained suggesting that the factors influencing the δ^{18}O values of surface waters are multivariate and more complex. The mean residence time (MRT) of the main Sava River stream water in Slovenia was similar at all sampling locations with a mean value of 1.32 years and can be characterized as being relatively short indicating a negligible evaporation effect. However, the ^{18}O-enriched isotopic content below Šabac in the Sava's lower course is a consequence of increased evaporation from the reservoir due to climate conditions and the low river flow and velocity and/or growth rate of the phytoplankton biomass. The fraction of water lost by evaporation was estimated to be between 10 and 25% (Miljević et al., 2008).

Although some hydrological investigations have already been performed in the SRB, they were limited in area or in time periods. The study, therefore, is a follow-up of the above-mentioned research, focusing on extended isotope datasets from the Sava River and model the spatial distribution of stable isotopes in the SRB using various geographical controls (latitude, longitude and altitude) as predictor variables. The study had the following objectives: (1) to compare δ^2H and δ^{18}O values in the Sava River surface water at selected locations from its source to the confluence with the Danube River in Serbia; (2) to compare surface water MRT at sampling locations on the Sava River with prolonged isotope datasets in Slovenia; (3) to estimate the MRT of the Sava and Danube Rivers at Belgrade in Serbia using the temporal variability of δ^{18}O values in precipitation and surface water; (4) to investigate geographical controls on δ^{18}O values in precipitation and its spatial variations over the SRB; and (5) to investigate the relationship between precipitation and surface water δ^{18}O composition. Overall, the study aims to demonstrate the usefulness of routinely applied water stable isotopes as key tracers in hydrological studies, with an emphasis on their application in water management in relation to climatic and human impacts.

2. Materials and methods

2.1. Site description

The main characteristics of the Sava watershed are summarized in this paragraph according to the report of the International Sava River Basin Commission (ISRBC, 2016). The Sava River is one of the largest tributaries of the Danube River located at the junction area between the Southern Alps, the Dinaric Mountains and the Pannonian Plain. The river is 945 km long and drains a total of 95 719 km^2 of surface area contributing 12% of the Danube watershed area and 25% of the total discharge. It flows through four countries, while the basin area is shared among six countries: 12% of the drainage area belongs to Slovenia, 26% to Croatia, 39.3% to Bosnia and Herzegovina, 15.5% to Serbia, 7.1% to Montenegro and 0.2% to Albania. The general elevation of the SRB varies between approx. 70 m a.s.l. at the mouth in Belgrade (Serbia) and 2,864 m a.s.l. at source (Triglav, Julian Alps). The mean elevation of the basin is approx. 545 m a.s.l. and according to FAO classification, the dominant slope in the basin is moderately steep with a mean gradient of 15.8%.

The Sava catchment is situated within a broad region where the moderate climate of the northern hemisphere prevails. In the upper part of the SRB in Slovenia alpine climate prevails, while major parts are covered by a warm temperate fully humid climate, characterized by warm summers and classified as a Cfb climate (C-warm temperate; f-no dry season; b-warm summer) according to the Köppen-Geiger climate classification system (Kottek et al., 2006). The mean annual air temperature ranges from 5.7 °C (Rateče, Slovenia) to 12.6 °C (Belgrade, Serbia). Similarly, precipitation is highly variable and long-term average annual precipitation ranges from 600 mm to 2300 mm, with an average annual amount of about 1100 mm. The highest levels of precipitation were observed in the upper part of the SRB in Julian Alps and at upper parts of the catchments of the tributaries Kupa, Piva, Tara, Una, Vrbas, Drina and Lim Rivers. Areas experiencing the lowest amount of precipitation are the lowland areas of Slavonia, Srem, Semberija and the Kolubara River catchment.

The average discharge of the Sava River is 93 m^3/s in Ljubljana, 318 m^3/s at Zagreb, and 1620 m^3/s in Belgrade. The backwater effect of the Iron Gate Dam (Djerdap I) on the Danube River located cca. 225 km downstream from Belgrade can be also noticed during the low flow as far upstream as to the town of Šabac located 105 km upstream from Belgrade.

Fourty-one important groundwater bodies in the SRB were identified with 21% of them located in Slovenia, 44% in Croatia, 21% in Bosna and Herzegovina, 13% in Serbia and 1% in Montenegro. In Slovenia almost two thirds of the total groundwater storage capacity is located in the SRB. Hydropower generation, agriculture and industry can be identified as the main drivers causing hydrological alterations.

2.2. Sampling and analysis

Surface water samples were collected at four long-term water monitoring locations in Slovenia selected based on previous