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ENVIRONMENTAL ISOTOPE INVESTIGATION
OF THE RIVER CATCHMENTS

N. Miljević

Vinča Institute of Nuclear Sciences, POB 522, Belgrade, Serbia

Introduction

The term environmental isotopes referees to isotopes, both stable and radioactive, that are present in the natural environment, either as a result of natural processes or introduced by anthropogenic activities. The original studies on isotopes in water were concerned with seawater and precipitation. During the transition of water from one phase to another (evaporation and condensation), the concentration ratio of the isotopes of an element (hydrogen and oxygen relevant in the hydrological cycle) changes, undergoes so-called isotope fractionation. Observing differences in especially the stable isotope composition are far from randomly distributed, they inform us about certain geochemical or hydrological process that took place relying on specific input pattern. Radioactive decay offers the possibility to determine an age, the time elapsed since the infiltration of the water. Isotope methods were introduced into catchment hydrology research in the 1960s as complementary tools to conventional hydrological methods for addressing questions of where water goes when it rains, what pathways it takes to the stream and how long water resides in the catchment [1]. The variety of isotopes used for this intention in isotope hydrology is presented in Fig. 1. Atmospheric thermonuclear weapon tests substantially increased the ^{3}H (tritium) content in the rapidly circulated parts of the hydrological cycle, with the peak around 1963 facilitating its use for the first systematic estimation of water age in catchments [2]. Stable isotopes of ^{2}H (deuterium) and/or ^{18}O (oxygen-18) have been common tools for assessing relative contributions of flow derived from uniquely labeled geographical sources or distributed components such as direct precipitation runoff, shallow and deep groundwater, surface waters including lakes and wetlands and water dating up to about five years of age, which typically occur in shallow aquifers connected to streams [3]. While nuclear explosion spike ^{3}H signal in natural systems decreases, the resolution of tritium method has declined and new tools needed for age determination. "New" methods using noble gases such as ^{3}He [4], ^{3}H/^{3}He [5], ^{85}Kr [6] and ^{222}Rn [7], solutes such as ^{35}S [8] and the anthropogenic compounds, chlorofluorocarbons (CFCs) [9] and SF_6 [10] have been developed for water dating methods from a few days up to decades. Solute isotopes such as ^{87}Sr [11], ^{13}C, ^{34}S and ^{15}N [12] have provided important information on bio (geo) chemical processes in the hydrological environment.
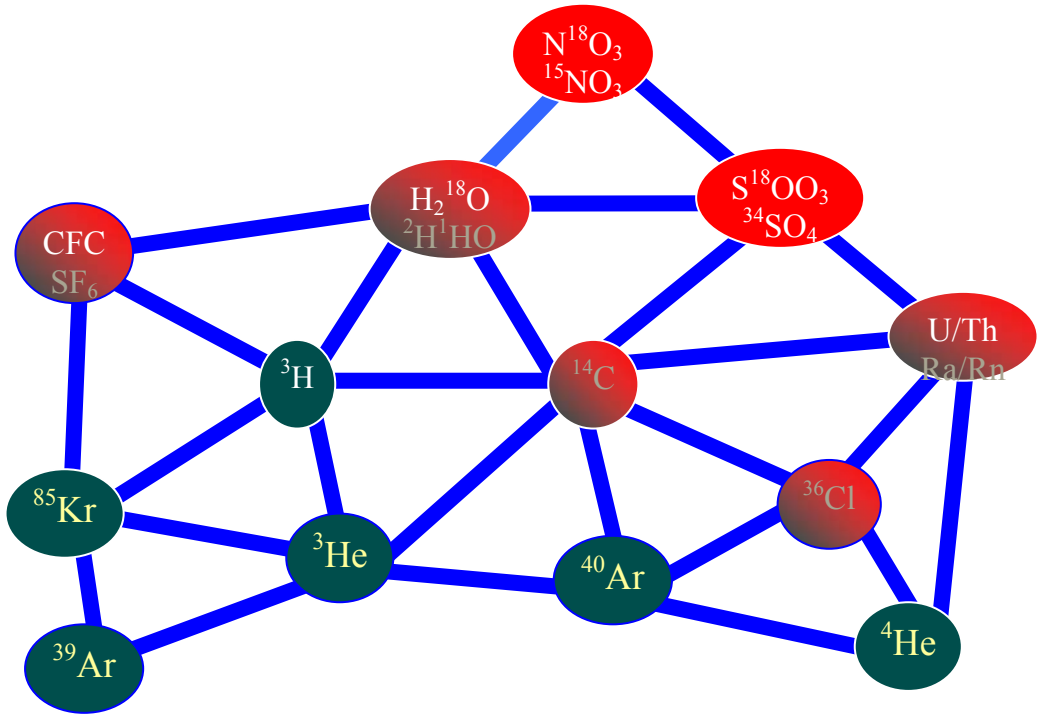
Fig. 1. Network of Isotope Hydrology

Analytical Techniques

Nuclear science has developed an array of methodologies and analytical techniques which use various isotopes of water to characterize water masses and trace their history and movement through the hydrological cycle. The observed variations of stable isotope composition within the water cycle are relatively small in absolute terms but can be measured with an adequate precision and accuracy by isotope ratio mass spectrometry (IRMS). The heavy isotope content of the sample is defined as the relative deviation from the adopted international reference standards and usually expressed in delta notation (δ) in permill (‰) [13]

$$\delta \ (isotope \ deviation) \quad = \frac{R_{sample} - R_{standard}}{R_{standard}} \ x \ 1000$$

where R is the isotope ratio of the heavy isotope to the more abundant light isotope ($^2H/^1H$, $^{13}C/^{12}C$, $^{18}O/^{16}O$). The most common chemical preparation treatments of the samples for deuterium measurements is the reduction of water to hydrogen with uranium [14], zinc [15], chromium [16] or equilibration of the sample with hydrogen gas using a platinum catalyst [17]. The ^{18}O abundance in water samples is usually measured using a modified CO_2/H_2O equilibration technique [3]. The

standard deviations of repeatability for ^2H and ^{18}O determinations are 1 and 0.1‰, respectively.

The radioactive sample is measured as an internal source, i.e. it is mixed with the counting medium, responsible for the operation of the instrument. Tritium content in water samples can be directly determined after electrolytic enrichment and mixing with a scintillating liquid (cocktail of various constituents) using liquid scintillation spectrometer (LSS) [18].

River Waters

River discharge consists mainly of two principal components, surface run-off of precipitation and groundwater seepage. Isotope signals in river discharge can potentially contribute to better understanding of the continental portion of the hydrological cycle including information such as water origin, mixing history, water balance, water residence times, surface-groundwater exchange and renewal rates, and evaporation-transpiration partitioning. Naturally occurring radioactive (Table 1) and stable (Table 2) isotopes of the elements of the water molecules and the components dissolved in water have increasingly been used to study the dynamics of surface water systems, their interaction with groundwater and vulnerability to pollution in river basins and catchment areas.

Table 1. Natural abundance, typical specific activities of radioactive isotopes used in river studies

Nuc.	Nature abundance	Standards/ Absolute value	Half-life [years]	Spec. act. [Bq/l]	Application
^3H	$< 10^{-17}$	NBS-SRM 4361 $^3H/^1H=6600$ TU	12.33	1.55×10^{-4}	Water balance and dynamics in river catchments, surface-groundwater interaction
^{14}C	$< 10^{-12}$	Oxalic acid 13.56 dpm/gC	5730	1.11×10^{-2}	Riverine carbon cycle, sediments dating, dating of flood events
^{238}U	0.9927		4.5×10^9	4×10^{-3}	Weathering, erosion and sedimentation

In addition, ^{232}Th and ^{230}Th are used in river studies [19], mostly combined with other uranium and thorium decay-series radionuclides such as isotopes of ^{226}Ra and ^{222}Rn.

Table 2. Natural abundance of stable isotope used in river studies

Isotope	Relevant isotope ratio	Average natural abundance	Standards/ Absolute value	Application
^{2}H	^{2}H/^{1}H	1.55×10^{-4}	V-SMOW 0.00015575	Water balance and dynamics in river catchments
^{13}C	^{13}C/^{12}C	1.11×10^{-2}	VPDB 0.0112372	Riverine carbon cycle, pollution
^{15}N	^{15}N/^{14}N	3.66×10^{-3}	atmospheric air	Pollution, biological processes
^{18}O	^{18}O/^{16}O	2.04×10^{-3}	V-SMOW 0.0020052 VPDB for carbonate 0.0020672	Surface-groundwater interaction
^{34}S	^{34}S/^{32}S	4.22×10^{-2}	VCDT 0.0441626	Pollution, salt depositional processes
^{87}Sr	^{87}Sr/^{86}Sr	0.709939	NBS 987 0.710245	Influence of tributaries on chemistry and pollution

V-SMOW - Vienna Standard Mean Ocean Water (water)
VPDB – Vienna Pee Dee Belammite (calcite)
VCDT - Vienna Canyon Diablo Troilite (FeS)

The stream δ^{18}O composition generally reflected the temporal pattern of the precipitation δ^{18}O composition with the signals significantly damped at all sites within the catchment. A two-year observation of the marked seasonal variation of ^{18}O content in monthly composite precipitation at the station Smederevska Palanka with high values in summer and more depleted ones during winter and strongly reduced amplitude in bimonthly grab river samples at locations Ljubicevski most and Varvarin are illustrated in Fig. 2. δ^{18}O of the Velika Morava river isotopic signal is controlled by the low δ^{18}O values of the input winter precipitation signal in the drainage area with a few month time lags.
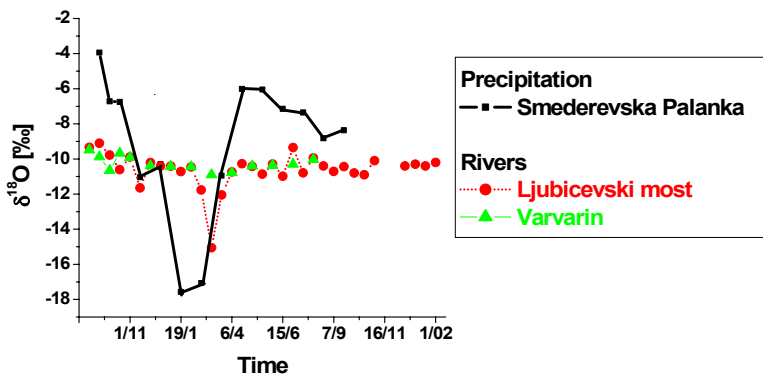
Fig. 2. Temporal variation of oxygen-18 composition in precipitation and river water in the Velika Morava catchment for the period September 2004 – February 2006

Mean Residence Time

The water "residence time" means the period of time that water molecules spend in the basin since the water molecule entered the catchment as recharge to when it exits at some discharge point (i.e., catchment outlet, monitoring well, and soil water sampler). During that time, water in the catchment is a mixture of the past recharges with different residence times, and the more appropriate term is the "mean residence time" (MRT) having not only important implications for flow pathways and storage, as well as for water quality, since many biogeochemical reactions are time-dependent.

The tracer composition of precipitation that falls uniformly on a catchment will be delayed by some timescale(s) before reaching the stream. More explicitly, the stream outflow composition at any time $\delta_{out}(t)$ consists of tracer, $\delta_{in}(t-\tau)$ past inputs lagged according to their residence time distribution $g(\tau)$ [20] it can be mathematically expressed by the convolution integral,

$$\delta_{out}(t) = \int_0^\infty g(\tau)\delta_{in}(t-\tau)d\tau$$

where τ are the lag times between input and output tracer composition. A range of models are available for assessing catchment residence times using tracer data [21, 22]. Seasonal trends in $\delta^{18}O$ in precipitation and stream water were modeled using periodic regression analysis [23] to fit seasonal sine wave curves to annual $\delta^{18}O$ variations in precipitation (Fig. 3a) and stream water (Fig. 3b) defined as

$$\delta^{18}O = X + A[\cos(ct-\theta)]$$

where X is the weighted mean annual measured $\delta^{18}O$ (‰), A is the estimated $\delta^{18}O$ annual amplitude (‰), c is the radial frequency of annual fluctuations

(0.017214 rad d^{-1}), t is the time in days after the start of the sampling period, and θ is the phase lag or time of the annual peak δ^{18}O in radians [24].
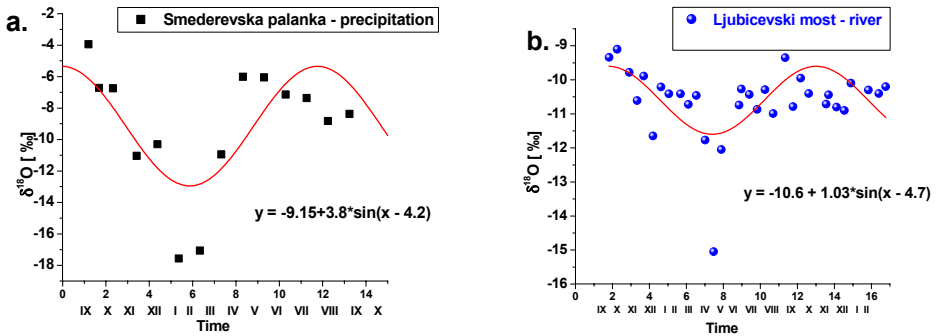

Figure 3. Fitted annual regression models to δ^{18}O for precipitation (a) and stream water (b) in the Velika Morava catchment

Sine wave models fitted to precipitation and stream water δ^{18}O variations were used to calculate MRT (T in month) expressed mathematically as

$$T = \frac{6}{\pi} \sqrt{(\frac{A_p}{A_r})^2 - 1}$$

where Ap is the amplitude of precipitation δ^{18}O (‰), and Ar is the amplitude of the river water δ^{18}O (‰). The preliminary estimated values within the Velika Morava catchment were in the range from short (3.5 months for Ljubicevski most) to longer MRTs (12 months for the Ibar) with 95% confidence limits.

River Water - Groundwater Interaction

Based on tritium content in precipitation, the Sava river and groundwater in the area of Makiš alluvial aquifer (~ 25 km^2) the infiltration rate and MRT of shallow groundwater body that serves for drinking water supply of Belgrade were determined [25]. The significant vertical age structure was found in the early pumping history of production wells (Fig. 4a). The "old" groundwater component (mean yearly tritium content of 17 TU) was identified in the upper water bearing layer, average thickness of about 10 m with a small infiltration. The lower layer, thickness between 10-15 m with
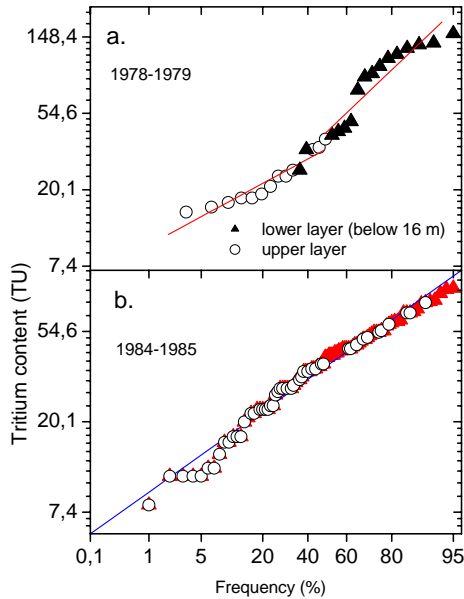
Fig.4. Frequency distribution of tritium content in water bearing layers during the production wells exploitation

means yearly value of tritium content of 51 TU was characterized by fast turnover exist. The origin of these groundwaters was dominated (~ 80%) by the Sava river water infiltration through the pumped wells. During exploitation the natural dynamics of groundwater flow had been changed with a preferential flow of young water into upper deposits (Fig. 4b). An efficient groundwater pathway could cause a non-acceptable contamination of the main aquifer. These findings were used in setting optimum strategies for a sustainable management of groundwater resource in this basin.

Conclusion

Isotopic abundance of light elements (hydrogen, carbon, nitrogen, oxygen, sulfur) as well as noble gases (helium, argon) is widely applied for identification of hydrological sources, flow paths under different flow conditions and estimation of mean catchment residence times. A more intensive merging of isotopic survey data in rivers is important to validate more accurate hydrological models related to water resources assessment (use of groundwater resources in the catchments), environmental studies and management.

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