

Isotopic tracing of groundwater at Žitný ostrov (SW Slovakia)

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Abstract

Geostatistical analysis of experimental isotope data has been carried out with the aim to study spatial variations in the distribution of water isotopes and radiocarbon in groundwater of Žitný ostrov (Rye Island), which is the largest reservoir (about 10 Gm³) of groundwater in the Central Europe. Subsurface water profiles showed enriched $\delta^{18}\text{O}$ levels at around 20 m water depth and depleted values below 30 m, which are similar to those observed in the Danube River. The core of the subsurface ¹⁴C profile represents contemporary groundwater with ¹⁴C values above 80 pMC.

1. Introduction

Stable and radioactive isotopes have been extensively used as environmental tracers during the last decades to study the water cycle, to better understand the origin, dynamics and interconnections of the different elements of the hydrologic cycle. It has been possible to study the present day distribution

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of water isotopes in the atmosphere, in the rain water, river water, groundwater, and then trace past isotopic compositions affecting many processes, such as atmospheric circulation, rain and snow formation, groundwater formation, ecology and paleoclimatology [1]. Radioactive and stable isotopes have been used to address key aspects of the water cycle, *e.g.* the origin, dynamics and interconnections of the different elements of the water cycle [2,3]. Fortunately with the development of the IAEA's Global Network of Isotopes in Precipitation (GNIP) database it has been possible to use isotopes in hydrological, ecological and climate studies, as input functions have been available for many areas of the world [4]. Many isotope data have been collected and several isotope databases have been developed. The GNIP database (www.GNIP.IAEA.org) has provided key data for the application of isotopes in hydrology, but also in climatic and ecological studies. Recently this monitoring activity has been enlarged to isotopes in the total water cycle, and the new isotope database (Isotope Hydrology Information System (ISOHIS), www.ISOHIS.IAEA.org), also covering groundwater data, together with the GNIP database enables to study dynamics and spatial characteristics of groundwater.

It is possible to trace the origin and pathways of different water masses on the bases of the developed isotopic maps, covering temporal and spatial distribution of hydrochemical and isotope data. Recently new geostatistical tools have been developed to integrate isotope data into a relational database covering also hydrogeology and hydrochemistry, which using GIS would be possible to visualize, and in this way to create temporal-spatial isotope maps of groundwater [5,6]. Such an integrated attempt will gather new information on temporal and spatial variability of groundwater, on its dynamics, on anthropogenic and climatic impacts, and on its vulnerability. From the existing and new $\delta^2\text{H}$ - $\delta^{18}\text{O}$ data obtained in the framework of the project, as well as from other data on isotopic composition and trace elements in groundwater, using results from Slovak institutions it will be possible to produce isotope maps of groundwater of Slovakia, and after their analysis to gather new information on groundwater.

Stable isotopes [7] and radiocarbon [8–10] have been applied in a few groundwater studies in Slovakia, however, there has not been done yet an integrated research, which would cover in full complexity all Slovakia (Fig. 1), not to speak that such a research should also cover the Central European countries. Some previous isotope hydrology work in Slovakia, *e.g.* on mineral and thermal waters [8] contributed to understanding of origin of these waters, however, temporal and spatial information has been missing, which could better characterize specific groundwater localities, groundwater



Fig. 1: The map of Slovakia with topography and the main river system. The Žitný ostrov is bordered by the Danube River on the south, and the Malý Dunaj (Small Danube) on the north (dashed line).

ages, infiltration areas, recharging characteristics of groundwater reservoirs, a danger of their contamination, climatic changes, etc., all important facts for the protection and correct exploitation of groundwater from the long-term perspective.

In this paper we report results on the spatial radiocarbon and stable isotope (^{18}O and ^{13}C) variability of groundwater found at the Žitný ostrov, SW Slovakia.

2. Hydrogeology background

The Žitný ostrov with the area of 1200 km^2 covers the territory of the Danube Plane from Bratislava at NW to Komárno at SE (Fig. 1). It is bordered on the north by the river Small Danube, and on the east by the river Váh. The territory of the Žitný ostrov is of great economical significance as it represents the largest reservoir of groundwater in the Central Europe (about 10^{10} m^3 , what represents potential $\sim 18\text{ m}^3\text{ s}^{-1}$). In 1987 the territory of the Žitný ostrov was declared as the National protected water resources territory of Slovakia. There are several groundwater sources situated at the territory of the Žitný ostrov, which are delivering drinking water to Bratislava as well as to many other places of the south western Slovakia.

3. Samples and analytical methods

The sampling sites were identical with groundwater sources regularly monitored by the Slovak Hydrometeorological Institute in the south-western Slovakia (Fig. 2). Sampling campaigns were carried out in November 2008 and in June 2009, visiting 38 boreholes. Groundwater samples were taken from deepest horizons. Description of the wells is presented in table 1. The sampling of water from boreholes was carried out in such a way that inflows were isolated from their overlying and/or underlying strata. All pipes of each borehole are cemented above perforation, so the wells are technically prevented from inflows of waters into the borehole from its sealed part. This, however, cannot prevent mixing of waters during their flow in aquifers. Such cases can occur especially in discharge areas, when waters of deep flow may be influenced by a shallow groundwater. During groundwater sampling in situ measurements of basic physical and chemical parameters (groundwater temperature, air temperature, pH, electrical conductivity (EC), oxidation-reduction potential (Eh), concentration of dissolved oxygen, and oxygen saturation) were carried out as well. Water samples for radiocarbon analysis of ~ 50 l volume were collected directly from the source. Bicarbonates were extracted as soon as possible by precipitation with barium chloride. Produced BaCO_3 was stored in polyethylene containers and transported to the laboratory. Simultaneously small volume water samples (1 l) were collected for analysis of tritium and stable isotopes. Table 1 describes the sampling sites as well as the shallow wells.

Laboratory analyses included: analysis of stable isotopes (^{18}O , ^{13}C), preparation of gas fillings and ^{14}C activity measurement. A few ml of carbon dioxide liberated from the BaCO_3 sample used for the determination of the isotopic ratio of $^{13}\text{C}/^{12}\text{C}$. $\delta^{13}\text{C}$ values are expressed relative to the VPDB standard (in ‰). $^{18}\text{O}/^{16}\text{O}$ isotopic ratio was analyzed directly in water samples [11], and the $\delta^{18}\text{O}$ data are reported relative to VSMOW (in ‰). Relative uncertainties were below 0.2‰ (at 1 σ). For ^{14}C analysis carbon dioxide was released from barium carbonate by addition of H_3PO_4 . Methane [12] synthesized from carbon dioxide was used as a filling gas of the low-level proportional counter [13]. Measuring time of samples was from forty to sixty hours. In addition to each water sample, samples of background and of radiocarbon standard (NIST Oxalic Acid) were also measured. ^{14}C results are expressed as percent modern carbon (pMC) relative to the NIST (National Institute of Standards and Technology, Gaithersburg, USA) ^{14}C standard. All ^{14}C data were corrected for $\delta^{13}\text{C}$. Relative uncertainties were below 10% (at 1 σ). Department of Nuclear Physics of the Faculty of Mathematics,

Table 1: Groundwater sampling sites at the Žitný ostrov.

St. n.	Locality	Proge depth (m)	Sampling year	GPS position
1	VLKY	30.48	2008	N48 08 50.0 E17 21 26.0
2	MALINOVO	54.66	2008	N48 08 47.7 E17 18 30.7
3	VYDRANY - KVETOSLAVOV	72.70	2008	N48 02 39.9 E17 20 42.0
4	ŠAMORÍN - ČILISTOV	88.46	2008	N48 00 29.9 E17 18 47.0
5	ROHOVCE - ŠTRKOVEC	83.28	2008	N47 58 44.3 E17 25 14.4
6	KALINKOVO	57.06	2008	N48 03 42.4 E17 12 31.6
7	OL'DZA	67.33	2008	N48 05 39.8 E17 25 16.2
8	ŠAMORÍN - MLIEČNO	69.92	2008	N48 00 20.1 E17 20 53.1
9	VRAKÚŇ	78.50	2008	N47 55 18.2 E17 38 00.6
10	DOBROHOŠŤ	80.50	2008	N47 59 35.6 E17 20 38.2
11	VOJKA	30.64	2008	N47 58 39.1 E17 22 57.5
12	GABČÍKOVO	25.14	2008	N47 53 08.0 E17 33 49.6
13	KL'ÚČOVEC	50.33	2008	N47 47 28.3 E17 41 56.8
14	KLIŽSKÁ NEMÁ	26.90	2008	N47 45 22.5 E17 47 43.0
15	HORNÁ POTŇ	35.78	2008	N48 04 09.5 E17 31 54.7
16	ČUŇOVO	66.91	2008	N48 02 42.8 E17 11 32.0
17	ROVINKA	62.26	2008	N48 06 28.2 E17 13 31.3
18	PODUNAJSKÉ BISKUPICE	23.65	2008	N48 07 46.1 E17 13 22.8
19	VEL'KÝ MEDER	35.14	2009	N47 52 07.2 E17 45 30.2
20	MLIEČANY	24.24	2009	N47 57 44.1 E17 35 40.3
21	VEL'KÉ BLAHOVO	28.71	2009	N48 03 03.5 E17 36 17.2
22	ORECHOVÁ POTŇ	20.80	2009	N48 02 15.8 E17 33 43.8
23	SAP	46.45	2009	N47 48 40.5 E17 38 00.4
24	ČALOVEC KAMENIČNÁ	10.89	2009	N47 49 36.5 E18 00 38.5
25	KAMENIČNÁ PIESKY	15.22	2009	N47 51 01.3 E17 59 14.8
26	OKOČ-ASZÓD	15.53	2009	N47 55 50.4 E17 52 25.6
27	JAHODNÁ	34.92	2009	N48 03 51.1 E17 41 17.2
28	JELKA	25.42	2009	N48 09 45.9 E17 29 55.4
29	KOMÁRNO	9.75	2009	N47 46 22.1 E18 05 39.7
30	KOMÁRNO	7.91	2009	N47 45 20.9 E18 07 56.0
31	ZLATNÁ N. OSTROVE	15.60	2009	N47 45 59.8 E17 57 12.9
32	KAMENIČNÁ	7.93	2009	N47 49 12.2 E18 02 13.2
33	DVORNÍKY N. OSTROVE	8.90	2009	N47 59 49.4 E17 39 34.6
34	HORNÝ ŠTÁL-ŽELEZ. STANICA	11.01	2009	N47 56 57.8 E17 44 04.1
35	PATAŠ MILINOVICE	7.80	2009	N47 51 42.1 E17 40 08.8
36	ZEMIANSKA OLČA	6.32	2009	N47 49 03.8 E17 53 00.9
37	ZEMIANSKA OLČA	6.01	2009	N47 51 17.3 E17 54 15.9
38	KOLÁROVO	8.98	2009	N47 55 53.6 E17 57 27.4

Table 2: Stable isotope and radiocarbon data.

St. n.	Locality	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)	^{14}C pMC
1	Vlky	-10.553	-15.406	89.62
2	Malinovo	-10.954	-15.406	93.47
3	Vydrany-Kvetoslavov	-10.941	-12.786	82.63
4	Šamorín-Čilistov	-10.863	-15.201	97.17
5	Rohovce-Štrkovec	-10.657	-15.557	80.44
6	Kalinkovo	-10.618	-15.165	105.51
7	Ol' dza	-10.825	-16.810	91.24
8	Šamorín- Mliečno	-10.702	-14.793	76.47
9	Vrakuň	-11.119	-13.510	97.11
10	Dobrohošť	-10.8	-10.656	78.88
11	Vojka	-10.669	-15.738	98.69
12	Gabčíkovo	-10.893	-14.911	92.41
13	Kl'účovec	-10.917	-11.728	86.48
14	Klizská Nemá	-10.275	-17.529	43.81
15	Horná Potôň	-10.585	-14.393	82.52
16	Čunovo	-10.548	-19.224	84.81
17	Rovinka	-11.018	-13.060	90.76
18	Pod. Biskupice - N. Košariská	-10.82	-15.244	72.86
19	Komárno	-10.584	-15.849	86.83
20	Komárno	-10.094	-14.134	80.22
21	Čalovec - Kameničná	-12.219	-11.080	31.54
22	Kameničná	-9.102	-15.859	90.05
23	Zlatná na Ostrove	-11.041	-11.485	72.92
24	Zemianska Olča	-10.273	-12.150	93.59
25	Zemianska Olča	-9.279	-12.541	86.62
26	Kameničná - Piesky	-10.276	-12.044	69.86
27	Kolárovo	-10.927	-13.933	99.58
28	Okoč - Aszód	-10.423	-12.623	81.16
29	Sap	-11.034	-10.791	90.36
30	Paraš - Malinovice	-10.712	-11.600	82.24
31	Čalovo - Vel'ký Meder	-11.056	-10.621	63.02
32	Horný Štál - žel.stanica	-10.659	-12.053	89.62
33	Mliečany	-11.312	-11.502	83.95
34	Dvorníky na Ostrove	-10.612	-12.692	93.85
35	Jahodná	-11.148	-11.425	80.80
36	Vel'ké Blahovo	-10.46	-12.664	89.41
37	Orechová Potoň	-10.916	-11.608	84.99
38	Jelka	-10.727	-12.986	79.49

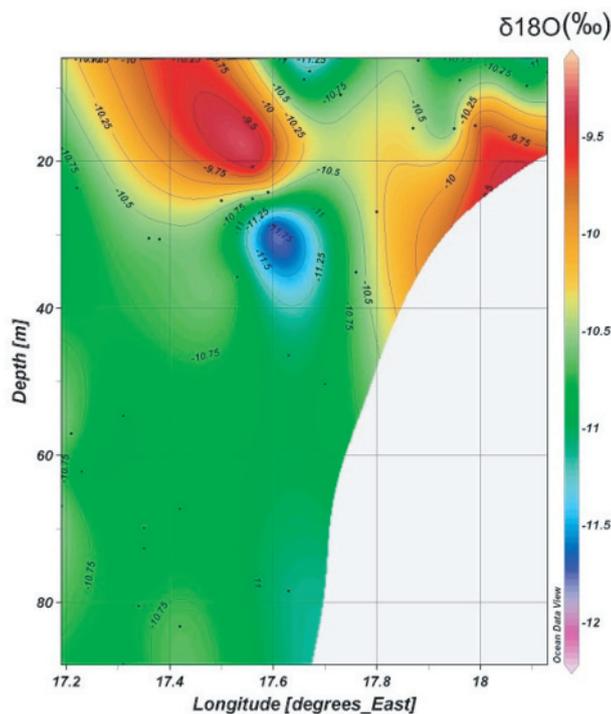


Fig. 3: Vertical distribution of $\delta^{18}\text{O}$ (in ‰) with longitude in groundwater of Žitný ostrov.

Physics and Informatics of the Comenius University in Bratislava has over 40 years of experience in radiocarbon measurements [14]. Quality management of all analyses has been assured by analysis of reference materials, and by participation in intercomparison exercises.

4. Results and discussion

The position of sampling sites and isotope data are presented in table 1 and 2, respectively. The spatial distribution of $\delta^{18}\text{O}$ in surface and subsurface waters with longitude of the Žitný ostrov area is presented in Fig. 3. While the bottom samples are depleted in $\delta^{18}\text{O}$ values, generally below -10.5‰ , similar to the Danube values, the subsurface core observed at around 20 m water depth shows enriched $\delta^{18}\text{O}$ values between -10.0‰ and -9.5‰ . However, the surface samples (up to 10 m water depth) show again depleted $\delta^{18}\text{O}$ values, close to the values observed for the Danube river

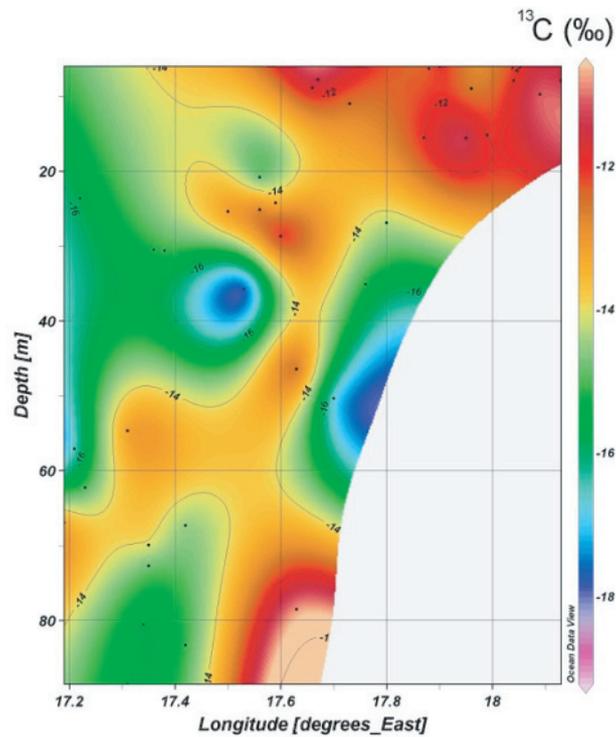


Fig. 4: Vertical distribution of $\delta^{13}\text{C}$ (in ‰) with longitude in groundwater of Žitný ostrov.

system. The obtained data are in good agreement with isotope data measured for the Danube river system (values between -10.92‰ and -12.26‰ for Danube, and between -0.57‰ and -11.39‰ for Malý Dunaj). As expected, the Danube river system is the main source of shallow groundwater observed at Žitný ostrov. It is possible that surface and shallow subsurface waters showing enriched $\delta^{18}\text{O}$ values may be due to land irrigation, which has been often used in this agriculturally heavily industrialized region. Fig. 4 also shows a similar profile for $\delta^{13}\text{C}$. Here we see enriched $\delta^{13}\text{C}$ levels in surface waters, and a depleted layer at water depths around 40 m. From the subsurface radiocarbon profile with longitude also shown in Fig. 3 we can see a subsurface core of about 50 pMC at around 60 m water depth, while the surface samples up to 10 m water depth show ^{14}C values above 80 pMC, representing contemporary groundwater (Fig. 5).

This has been a first attempt to construct isotope maps and to study surface and subsurface distribution of isotopes in groundwater of Slovakia.

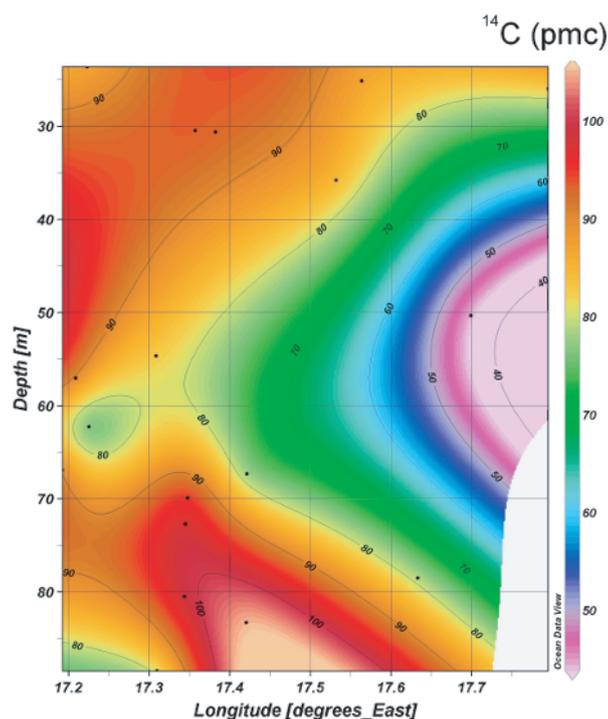


Fig. 5: Vertical distribution of ^{14}C (in pMC) with longitude in groundwater of Žitný ostrov.

More groundwater samples from the Žitný ostrov area will be collected and analysed during 2010 and 2011 expeditions, which will help to improve the spatial density of isotope data, and thus contribute to better understanding of the Žitný ostrov groundwater system. We hope that this new research approach will improve the capability and efficiency in using isotopic tools for deeper evaluation, more rigorous assessment and more efficient management of water resources in the region.

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