Hydrogeochemical and isotopic characterization of groundwater at Žitný Island (SW Slovakia)

Z. Ženišová, P. P. Povinec, A. Šivo, R. Breier, M. Richtáriková, A. Ďuričková and A. L'uptáková

ABSTRACT

Hydrogeochemical investigations and spatial variations studies on the distribution of water isotopes and radiocarbon in the groundwater of Žitný Island (Rye Island) were carried out. Žitný Island represents the largest groundwater reservoir in Central Europe (about 10 Gm^3). The chemical composition of the groundwater of Žitný Island depends mainly on the chemical composition of Danube water, as well as on the length of its infiltration from the Danube River. The groundwater is characterized by potamogenic mineralization, and its chemical composition is influenced by anthropogenic contamination. Sub-surface water profiles showed enriched $\delta^{18}O$ levels up to around 20 m water depth, and depleted values for deeper waters. The observed isotopic composition of the groundwater is similar to Danube water, suggesting that the Danube River is the main source of the Žitný Island groundwater. The core of the sub-surface ^{14}C profile represents contemporary groundwater with ^{14}C values above 80 pMC.

Key words | carbon-13, carbon-14, groundwater, oxygen-18, Slovakia, Žitný Island

Z. Ženišová
A. Ďuričková
Department of Hydrogeology,
Faculty of Natural Sciences,
Comenius University,
842 15 Bratislava,
Slovakia

P. P. Povinec (corresponding author)
A. Šivo
R. Breier
M. Richtáriková
Department of Nuclear Physics and Biophysics,
Faculty of Mathematics,
Physics and Informatics,
Comenius University,
842 15 Bratislava,
Slovakia
E-mail: *povinec@fmph.uniba.sk*

A. L'uptáková
Slovak Hydrometeorological Institute,
833 15 Bratislava,
Slovakia

INTRODUCTION

Hydrogeochemical and isotope studies of groundwater have been carried out in the past with the aim to better understand its origin, formation, dynamics, climatic impacts, its vulnerability and protection against anthropogenic impacts in the world (Gonfiantini *et al.* 1999; Kendall & McDonnell 1999; Aggarwal *et al.* 2006a, b), and specifically in Central Europe (Rank *et al.* 1995; Deák 2003; Povinec *et al.* 2006; Schiavo *et al.* 2009). Recently, new geostatistical tools have been developed to integrate isotope data into a relational database covering also hydrogeology and hydrochemistry of groundwater. Using geographical information system, it has been possible to create temporal-spatial isotope maps of groundwater (Bowen *et al.* 2005; Aggarwal & Araguás-Araguás 2006).

Isotope data together with hydrographic data have been used for better characterization of specific groundwater regions, for studying groundwater ages, infiltration areas, recharging characteristics of groundwater reservoirs, impact of climatic changes and a danger of groundwater contamination (Vitvar *et al.* 2007; Ockenden *et al.* 2014; Szczucinska 2014; de la Torre *et al.* 2015). These have been important studies for the protection and sustainable exploitation of groundwater from the long-term perspective.

Although several isotope hydrology studies were carried out in Central Europe (Rank *et al.* 1995, 1998, 2009; Deák 2003; Vitvar *et al.* 2007; Miljević *et al.* 2008), including Slovakia (Malík *et al.* 1995; Michalko 1999; Franko *et al.* 2005, 2008; Povinec *et al.* 2010), information on temporal and spatial groundwater variations, and specifically isotope depth profiles, have been missing. Development of an isotope groundwater database for Central Europe is underway which will identify regions with limited data sets, where new sampling campaigns and isotope analysis will be carried out. It is believed that with recently

doi: 10.2166/nh.2015.187

developed geostatistical tools the evaluation, assessment and management of groundwater resources in the region will be improved.

In this paper we present a first attempt to apply geostatistical tools in studying spatial and vertical distribution of isotopes in the groundwater of Žitný ostrov (Rye Island) in South-West Slovakia. The territory of Žitný Island is of great economic significance as it represents the largest reservoir of groundwater in Central Europe (about $10^{10}\,m^3$, which represents potential $\sim 18\,m^3\,s^{-1}$). In 1987 the territory of Žitný Island was declared as the national protected water resources territory of Slovakia. The groundwater sources at Žitný Island are delivering drinking water to Bratislava as well as to many other places in South-West Slovakia. Žitný Island is also, because of its location, good soil and climatic conditions, the most important agricultural region of Slovakia. There is also located the largest Slovak water power plant (Gabčíkovo, established in 1992), which is producing 720 MW of electricity. The Gabčíkovo water system considerably influences the hydrology of the region, as well as the Danube River shipping conditions. The Gabčíkovo plant with the reservoir, and the inlet and outlet canals has a positive impact on regional groundwater conditions. Owing to the back water effect of the reservoir, the level of groundwater in the region of Bratislava has increased by about 2 m, with an important positive impact on all ecosystems in the region.

HYDROGEOLOGY OF ŽITNÝ ISLAND

Žitný Island, with an area of 1,200 km^2, covers the territory South-East of Bratislava (Figure 1), which is bordered on the north by the Small Danube River, and on the east by the Váh River. Žitný Island belongs to the Danube Plain where several wetplains are located. The relief is made of bottom lands, consisting mainly of fluvial, proluvial-wetplain and eolic-fluvial relief. The territory represents a flat terrain 129–136 m above sea level. The average annual precipitation during 1951–1980 was between 528 and 580 mm. The average annual evaporation from the soil surface at Žitný Island for the time interval between 1961 and 1990 was 450–500 mm. The total potential annual evaporation was between 700 and 800 mm.

Figure 1 | Map of Slovakia with topography and the main river system (Žitný Island is SE of Bratislava).

The territory of Žitný Island is located in the Danube basin with the core of the Gabčíkovo depression, bordered at the North-West by Small Carpathians, and from the South-East by a system of faults. There are three strata in the Quaternary filling: (i) bottom strata which is formed mostly by fine-grained sand gravel with frequently occurring clayey or silt sands up to clays with 10–350 m thickness; (ii) middle strata (the Danube gravel formation) from middle up to course-grained sandy gravels with sporadic intermediate layers of fine sediments up to a thickness of 160 m in the center of the depression; and (iii) top strata (bottom-land facies), mostly fine-grain Holocene sediments from 0.5 to 3 m thickness. The Quaternary sub-base is made of ruman, dak and pont sediments, mostly of gray up to gray-green weakly calcinated mica clays and dust with varying admixture of sand. The territory of Žitný Island is formed by terraces of fluvial sediments – clayey sands, sands, gravels, sand gravels and residual sands – and by bottom lands of fluvial sediments – sandy clay, clays, clayey sands and clayey gravels (Maglay *et al.* 2009). Quaternary sediments of Žitný Island may be allocated to lower, middle and upper Pleistocene and Holocene. The Pleistocene sediments have a thickness from 10 to 20 m south of Bratislava, 8–12 m at Komárno, and in the center of the depression at Gabčíkovo it is about 160 m. The sediments are mostly made of coarse gravels, sand gravels and sands without fine fractions, which indicate a dominance of stream-bed facies over bottom-land sediments. The Holocene sediments are formed by a diluvium enclosure of river bottom lands with admixture of gravel, and recent and fossil soils.

On the basis of statistical evaluation of the hydrographic data from 812 boreholes, the Žitný Island territory has been divided into four regions with the following hydraulics parameters: (i) a right-riverside of the Danube – a high value of median flow capacity ($2.03 \times 10^{-2}\ m^2\ s^{-1}$), and median filtration coefficient ($4.06 \times 10^{-3}\ m\ s^{-1}$), and an average value of specific strength ($12.6\ L\ s^{-1}$); (ii) an upper part – a lower value of median flow capacity ($5.01 \times 10^{-2}\ m^2\ s^{-1}$), and median filtration coefficient ($1.00 \times 10^{-2}\ m\ s^{-1}$), and an average value of specific strength ($28.0\ L\ s^{-1}$); (iii) a middle part – a highest value of median flow capacity ($1.55 \times 10^{-1}\ m^2\ s^{-1}$), and median filtration coefficient ($3.1 \times 10^{-2}\ m\ s^{-1}$), and an average value of specific strength ($93.25\ L\ s^{-1}$); and (iv) a lower part – a lowest value of the median flow capacity ($7.95 \times 10^{-3}\ m^2\ s^{-1}$), and median filtration coefficient ($1.59 \times 10^{-3}\ m\ s^{-1}$), and an average value of specific strength ($5.4\ L\ s^{-1}$).

A general trend in the flow of groundwater is mostly following the main rivers in the region (Danube, Small Danube and Váh). The Danube River during all its water levels in Žitný Island feeds groundwater in the region. Precipitation is influencing the groundwater regime of Žitný Island indirectly via elevated flow rates in rivers (as will be discussed later using isotope data). Increasing river flow rates have also been increasing the groundwater level, with different delays depending on the distance from the river. The groundwater regime of Žitný Island is thus mainly determined by interactions between Danube water (and other surface waters in the region) and groundwater in the region.

There are three types of hydrogeological boreholes at Žitný Island (Figure 2): (i) a basic monitoring network; (ii) boreholes in use for water supply; and (iii) presently not used boreholes. Boreholes of the basic monitoring network have piezometers located from 1 to 6 levels, enabling thus to study vertical distribution of contaminants (and isotopes) in groundwater (L'uptáková *et al.* 2007).

GROUNDWATER SAMPLING AND ANALYSIS

Groundwater sampling

The sampling sites were identical with groundwater sources regularly monitored by the Slovak Hydrometeorological Institute in Žitný Island (Figure 2). The sampling strategies were determined by development of a relational isotope database of groundwater of Slovakia (which will cover hydrogeological, hydrochemical and isotope data), determination of the catchments areas of groundwater at Žitný Island and contribution to the protection of groundwater against contamination from surface waters (e.g. from the Gabčíkovo water system), from agricultural fertilizers and industrial products (e.g. oil products from the Slovnaft refinery located in Bratislava). Two sampling campaigns were carried out, one in November 2008 and the second one in June 2009. Altogether 38 boreholes were visited. Groundwater samples were taken from different horizons. A description of the sampling wells is presented in Table 1.

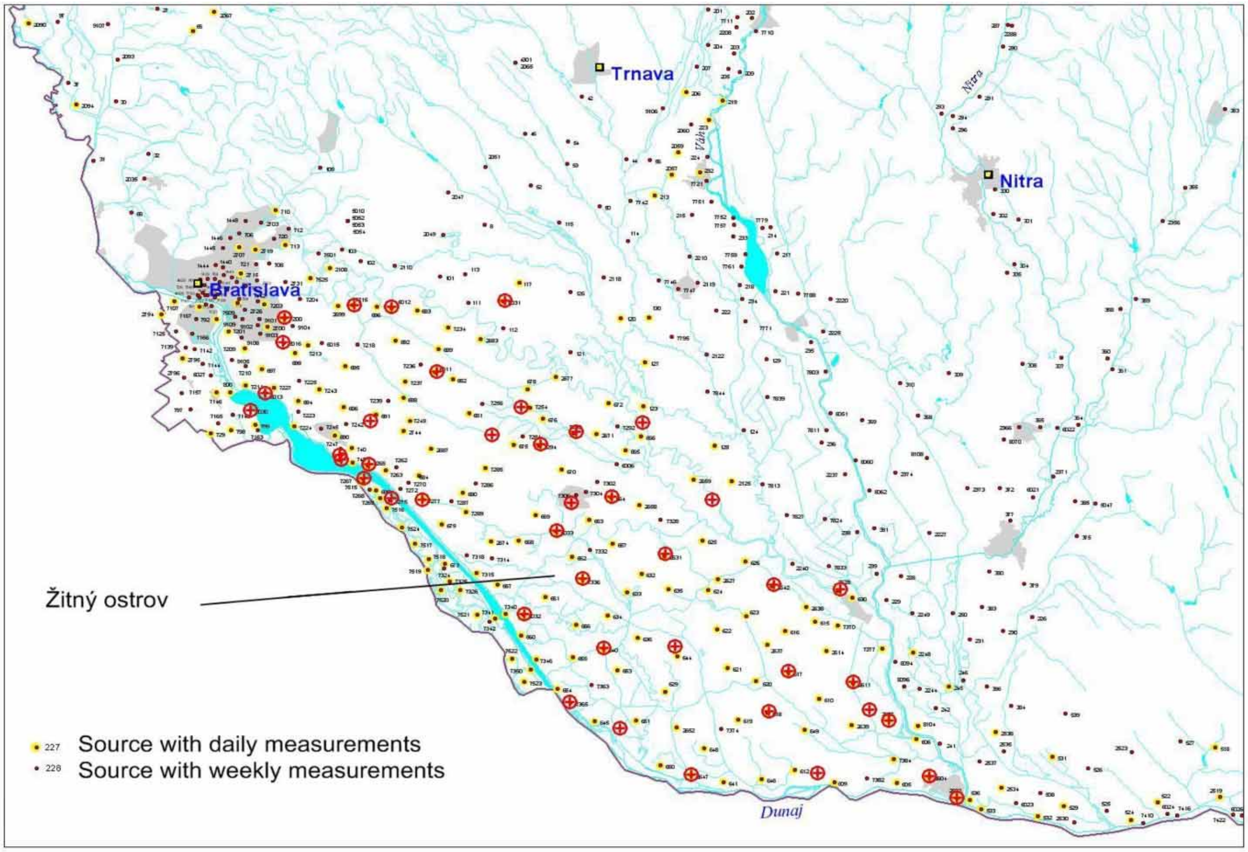

Figure 2 | Groundwater monitoring and sampling sources in Žitný Island (circles indicate the sampling sites).

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 protected 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, oxidation-reduction potential, concentration of dissolved oxygen and oxygen saturation) were carried out as well. Water samples for radiocarbon analysis (~50 L) 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.

Laboratory analyses

Laboratory analyses included analysis of stable isotopes (^{18}O, ^{13}C), preparation of gas fillings for proportional counters and ^{14}C activity measurements. A few mL of carbon dioxide liberated from the $BaCO_3$ sample was used for the determination of the isotopic ratio of $^{13}C/^{12}C$. The $\delta^{13}C$ values are expressed relative to the Vienna Pee Dee Belemnite standard (in ‰). $^{18}O/^{16}O$ isotopic ratio was analyzed directly in water samples. The $\delta^{18}O$ data are reported relative to Vienna Standard Mean Ocean Water (in ‰). Relative uncertainties were below 0.2‰ (at 1 σ). Stable isotope analyses were carried out using mass spectrometers at the Dionýz Štúr Geological Institute in Bratislava.

Table 1 | Groundwater sampling sites at Žitný Island

St. no.	SHMU[a] number	Number of area	Locality	Sampling year	GPS position	Probe depth (m)	Lower perfor. (m)	Upper perfor. (m)	Sampling level
16	603091	51	ČUŇOVO	2008	N48 02 42.8 E17 11 32.0	66.91	67.00	65.00	3
6	601393	52	KALINKOVO	2008	N48 03 42.4 E17 12 31.6	57.06	58.00	55.00	3
4	724891	52	ŠAMORÍN – ČILISTOV	2008	N48 00 29.9 E17 18 47.0	88.46	89.50	86.50	3
8	726591	52	ŠAMORÍN – MLIEČNO	2008	N48 00 20.1 E17 20 53.1	69.92	68.00	65.00	3
10	601092	52	DOBROHOŠŤ	2008	N47 59 35.6 E17 20 38.2	80.50	80.00	78.00	4
11	727491	52	VOJKA	2008	N47 58 39.1 E17 22 57.5	30.64	64.00	61.00	3
12	603291	52	GABČÍKOVO	2008	N47 53 08.0 E17 33 49.6	25.14	24.00	20.00	2
29	736591	52	SAP – PALKOVIČOVO	2009	N47 48 40.5 E17 38 00.4	46.45	45.00	42.00	1
17	601691	53	ROVINKA	2008	N48 06 28.2 E17 13 31.3	62.26	55.00	40.00	3
18	720092	53	PODUNAJSKÉ BISKUPICE	2008	N48 07 46.1 E17 13 22.8	23.65	50.00	47.00	3
3	724191	54	VYDRANY – KVETOSLAVOV	2008	N48 02 39.9 E17 20 42.0	72.70	71.50	68.50	2
7	601191	54	OL’DZA	2008	N48 05 39.8 E17 25 16.2	67.33	67.00	61.00	3
5	727791	54	ROHOVCE – ŠTRKOVEC	2008	N47 58 44.3 E17 25 14.4	83.28	84.50	81.50	3
9	733691	54	VRAKÚŇ	2008	N47 55 18.2 E17 38 00.6	78.50	77.00	74.00	4
15	725491	54	HORNÁ POTÔŇ	2008	N48 04 09.5 E17 31 54.7	35.78	34.00	31.00	3
37	729492	54	ORECHOVÁ POTÔŇ	2009	N48 02 15.8 E17 33 43.8	20.80	19.00	16.00	2
36	729394	54	VEL’KÉ BLAHOVO	2009	N48 03 03.5 E17 36 17.2	28.71	28.00	25.00	4
33	603391	54	MLIEČANY	2009	N47 57 44.1 E17 35 40.3	24.24	24.00	20.00	2
34	66490	54	DVORNÍKY N. OSTROVE	2009	N47 59 49.4 E17 39 34.6	8.90	–	–	1
13	736691	55	KL’ÚČOVEC	2008	N47 47 28.3 E17 41 56.8	50.33	52.00	50.00	2
14	264791	55	KLIŽSKÁ NEMÁ	2008	N47 45 22.5 E17 47 43.0	26.90	25.00	23.00	2
31	600491	55	VEL’KÝ MEDER	2009	N47 52 07.2 E17 45 30.2	35.14	33.00	30.00	3

(*continued*)

Table 1 | continued

St. no.	SHMU[a] number	Number of area	Locality	Sampling year	GPS position	Probe depth (m)	Lower perfor. (m)	Upper perfor. (m)	Sampling level
30	64090	55	PARAŠ – MILINOVICE	2009	N47 51 42.1 E17 40 08.8	7.80	–	–	1
32	263190	55	HORNÝ ŠTÁL-ŽEL. STANICA	2009	N47 56 57.8 E17 44 04.1	11.01	–	–	1
24	61890	55	ZEMIANSKA OLČA	2009	N47 49 03.8 E17 53 00.9	6.32	–	–	1
25	61790	55	ZEMIANSKA OLČA	2009	N47 51 17.3 E17 54 15.9	6.01	–	–	1
23	738191	55	ZLATNÁ NA OSTROVE	2009	N47 45 59.8 E17 57 12.9	15.60	–	–	1
21	605990	55	ČALOVEC-KAMENIČNÁ	2009	N47 49 36.5 E18 00 38.5	10.89	9.50	8.50	1
22	260790	55	KAMENIČNÁ	2009	N47 49 12.2 E18 02 13.2	7.93			1
26	261190	55	KAMENIČNÁ-PIESKY	2009	N47 51 01.3 E17 59 14.8	15.22	9.00	5.00	1
19	260290	55	KOMÁRNO	2009	N47 45 20.9 E18 07 56.0	7.91	–	–	1
20	260490	55	KOMÁRNO	2009	N47 46 22.1 E18 05 39.7	9.75	–	–	1
2	721593	56	MALINOVO	2008	N48 08 47.7 E17 18 30.7	54.66	49.50	44.50	3
1	601291	56	VLKY	2008	N48 08 50.0 E17 21 26.0	30.48	29.50	27.50	3
38	603191	56	JELKA	2009	N48 09 45.9 E17 29 55.4	25.42	24.00	20.00	2
35	600592	56	JAHODNÁ	2009	N48 03 51.1 E17 41 17.2	34.92	34.00	31.00	3
28	264290	56	OKOČ-ASZÓD	2009	N47 55 50.4 E17 52 25.6	15.53	14.00	10.00	1
27	262890	56	KOLÁROVO	2009	N47 55 53.6 E17 57 27.4	8.98	–	–	1

[a]Slovak Hydrometeorological Institute.

The radiocarbon measurements were carried out in the Department of Nuclear Physics and Biophysics of the Faculty of Mathematics, Physics and Informatics of the Comenius University in Bratislava. For ^{14}C analysis of groundwater samples, carbon dioxide was released from barium carbonate by addition of H_3PO_4. Methane (Povinec 1972) synthesized from carbon dioxide was used as a filling gas of the low-level proportional counter (Povinec 1978). Measuring time of methane samples was from 40 to 60 h. In addition to each water sample, samples of background and of radiocarbon standard (National Institute of Standards and Technology (NIST)) oxalic acid standard were also measured (Usačev *et al.* 1973). ^{14}C results are expressed as percent modern carbon (pMC) relative to the NIST ^{14}C standard. All ^{14}C data were corrected for $\delta^{13}C$. Relative uncertainties of ^{14}C measurements were below 10% (at 1 σ). Quality management of all analyses has been assured by analysis of reference materials, and by participation in intercomparison exercises.

Isotope data evaluation

The spatial isotope maps have been constructed using the Ocean Data View software, which reproduces well surface, as well as depth distributions of isotopes in the aquatic environment (Povinec *et al.* 2011). The present spatial resolution of the obtained maps is 5 km in the horizontal plane, and 10 m in the vertical plane.

RESULTS AND DISCUSSION

Hydrogeochemistry

The physical, chemical and isotopic characteristics of the collected groundwater samples are presented in Tables 2 and 3. The chemical composition of the groundwater of Žitný Island depends on the chemical composition of Danube River water (and also of Small Danube and Váh river waters), as well as on the length of infiltration of rivers waters into the groundwater. Although the groundwater samples were collected during summer and winter (however, at different sampling sites during different seasons), we did not observe a statistical difference in the stoichiometry of the samples collected during different sampling periods. The groundwater is characterized by potamogenic mineralization, and its chemical composition is influenced by anthropogenic contamination. The Quaternary environment, especially the alluvial sediments of the Danube, Small Danube and Váh rivers, has mostly silicate character (gravels, sand gravels and sands).

Total dissolved solids (TDS) and the contents of basic ions in groundwater depend on the intensity of anthropogenic contamination. The chemical composition of groundwater in Žitný Island changes with distance from the Danube River, as well as with the groundwater depth. The chemical analyses (Table 3, and a piper diagram presented in Figure 3) show that the basic hydrogeochemical type of groundwater is Ca-Mg-HCO_3, which is dominant on the whole area of Žitný Island, mainly in deeper levels, under 25 m. An expressive sulfates contamination appears in groundwater levels up to 25 m with dominant hydrogeochemical Ca-Mg-HCO_3-SO_4 type. TDS of groundwater (Table 3) ranges from the lowest values in fluvial zone of the Danube River (290 mg L^{-1}) to the highest values (1,091 mg L^{-1}) at the South-East of the Island. The pH values were between 6.88 and 7.93, and the water temperature between 10.5 and 15.7 °C (Table 2). The basic cations are calcium (35.5–140 mg L^{-1}) and magnesium (11.8–58.6 mg L^{-1}). The dominant anions are represented by HCO_3^- (188–677 mg L^{-1}). The values of SO_4^{2-} in deeper water layers are low (12.6–62.9 mg L^{-1}) with the exception of Gabčíkovo (94.4 mg L^{-1}). Higher values were observed in water layers up to 35 m (65.5–133 mg L^{-1}). The Cl^- contents are low (2.9–56 mg L^{-1}). Concentrations of NO_3^- are also low, often under the detection limit (<1.0 mg L^{-1}). This is connected with reduction conditions in alluvial deposits, following with reduction of NO_3^-. The highest value of NO_3^- (47.9 mg L^{-1}) is at the Komárno station (Table 3). Quality of groundwater is influenced by unfavorable oxidation-reduction conditions with high contents of Fe and Mn.

Under anthropogenically non-influenced conditions, groundwater is of Ca-Mg-HCO_3 type with TDS between 400 and 600 mg L^{-1}. In regions with anthropogenic influence, sulfites, chlorides and nitrates dominate among anions. Sodium and potassium dominate over calcium and magnesium in the cation group, and TDS is usually above 800 mg L^{-1}.

In the layer up to 25 m, groundwater is characterized by three chemical types: (i) a basic distinctly A_2 type (Ca-(Mg)-HCO_3) with average TDS of 426 mg L^{-1}, which is dominating in the fluvial zone of the Danube River; (ii) a basic-indistinctly A_2 type (Ca-(Mg)-HCO_3) with average TDS of 662 mg L^{-1}, typical for the central part of Žitný Island, in a continuous strip from Bratislava down to Kolárovo; and (iii) a mixed type with dominance of A_2 and $S_2(SO_4)$ components with average TDS of 911 mg L^{-1}, which is bordered from the south by the line Bratislava – Komárno, and from the north by the Small Danube up to the Váh River.

In the layer below 25 m, groundwater is characterized by three chemical types: (i) a basic distinctly A_2 type (Ca-(Mg)-HCO_3) with average TDS of 381 mg L^{-1}, which is dominating on the territory of Žitný Island; (ii) a mixed type with dominance of A_2 and $S_2(SO_4)$ components with average TDS of 680 mg L^{-1}, which is probably overlapping from the first layer; and (iii) a basic distinctly A_1 type (Na-HCO_3) with

Table 2 | Groundwater sampling sites – water parameters, stable isotopes and radiocarbon data

St. no.	SHMU number	N. area	Locality	Sampling date	Bottom depth (m)	T (°C)	EC (mS m^{-1})	pH	O_2 (mg L^{-1})	CO_2 (mg L^{-1})	HCO_3^- (mg L^{-1})	$\delta^{18}O$ (‰)	$\delta^{13}C$ (‰)	pMC (‰)
16	603091	51	ČUŇOVO	19.11.2008	54.65	12.1	55.4	7.61	1.7	4.32	189.53	−10.548	−19.224	84.81
6	601393	52	KALINKOVO	11.11.2008	60.00	11.7	45.4	7.58	2.2	8.72	204.48	−10.618	−15.165	105.51
4	724891	52	ŠAMORÍN – ČILISTOV	10.11.2008	90.00	12.8	44.9	7.56	1.6	4.32	238.43	−10.863	−15.201	97.17
8	726591	52	ŠAMORÍN – MLIEČNO	11.11.2008	69.92	11.5	48.4	7.56	2.0	9.81	250.66	−10.702	−14.793	76.47
10	601092	52	DOBROHOŠŤ	11.11.2008	80.50	11.8	44	7.87	1.6	6.54	235.38	−10.800	−10.656	78.88
11	727491	52	VOJKA	12.11.2008	66.91	11.4	47.3	7.67	2.2	6.54	195.64	−10.669	−15.738	98.69
29	736591	52	SAP – PALKOVIČOVO	15.6.2009	46.45	12.2	44.7	7.54	1.2	5.49	194.10	−11.034	−10.791	90,36
17	601691	53	ROVINKA	19.11.2008	62.26	10.5	43.1	7.75	2.0	2.18	235.38	−11.018	−13.060	90.76
18	720092	53	PODUNAJ. BISKUPICE	19.11.2008	55.00	10.5	59.4	7.56	6.0	5.45	290.40	−10.820	−15.244	72.86
7	601191	54	OL'DZA	11.11.2008	67.33	11.7	47	7.69	4.2	5.45	244.55	−10.825	−16.810	91.24
5	727791	54	ROHOVCE – ŠTRKOVEC	10.11.2008	83.28	11.2	52.2	7.70	2.2	4.32	238.43	−10.657	−15.557	80.44
9	733691	54	VRAKÚŇ	11.11.2008	78.50	11.8	35.6	7.79	2.0	2.18	201.75	−11.119	−13.510	97.11
15	725491	54	HORNÁ POTÔŇ	12.11.2008	35.78	11.3	70.4	7.52	3.9	9.81	275.12	−10.585	−14.393	82.52
37	729492	54	ORECHOVÁ POTÔŇ	16.6.2009	20.88	13.1	77	7.43	1.8	12.08	282.04	−10.916	−11.608	84.99
36	729394	54	VEL'KÉ BLAHOVO	16.6.2009	28.71	14.2	67.2	7.39	2.2	16.47	251.72	−10.460	−12.664	89.41
33	603391	54	MLIEČANY	15.6.2009	23.84	12.4	61.2	7.54	2.5	12.08	245.65	−11.312	−11.502	83.95
34	66490	54	DVORNÍKY N. OSTROVE	16.6.2009	8.55	12.8	97	7.31	3.5	20.86	321.47	−10.612	−12.692	93.85
13	736691	55	KL'ÚČOVEC	12.11.2008	50.33	15.8	34.5	7.93	3.6	1.09	201.75	−10.917	−11.728	86.48
14	264791	55	KLIŽSKÁ NEMÁ	12.11.2008	26.90	11.7	70.2	7.16	2.3	32.71	452.42	−10.275	−17.529	43.81
31	600491	55	VEL'KÝ MEDER	15.6.2009	35.14	12.8	40	7.63	2.6	3.29	224.42	−11.056	−10.621	63.02
30	64090	55	PARAŠ – MALINOVICE	15.6.2009	9.60	12.7	93.9	7.21	2.1	5.49	373.03	−10.712	−11.600	82.24
32	263190	55	HORNÝ ŠTÁL – ŽEL. ST.	15.6.2009	11.01	12.5	83.8	7.34	2.0	0	294.18	−10.659	−12.053	89.62
24	61890	55	ZEMIANSKA OLČA	11.6.2009	9.27	13.9	223	7.07	2.6	34	618.68	−10.273	−12.150	93.59
25	61790	55	ZEMIANSKA OLČA	11.6.2009	15.51	13.2	137.3	7.07	1.5	34	464.01	−9.279	−12.541	86.62
23	738191	55	ZLATNÁ NA OSTROVE	10.6.2009	16.50	14.7	103.6	7.39	1.5	0	530.73	−11.041	−11.485	72.92

(*continued*)

Table 2 | continued

St. no.	SHMU number	N. area	Locality	Sampling date	Bottom depth (m)	T (°C)	EC (mS m^{-1})	pH	O_2 (mg L^{-1})	CO_2 (mg L^{-1})	HCO_3^- (mg L^{-1})	$\delta^{18}O$ (‰)	$\delta^{13}C$ (‰)	pMC (‰)
21	605990	55	ČALOVEC – KAMENIČNÁ	10.6.2009	10.91	15.2	58	7.48	1.2	29.65	351.80	−12.219	−11.080	31.54
22	260790	55	KAMENIČNÁ	10.6.2009	5.98	15.6	98.1	7.32	1.7	21.96	606.55	−9.102	−15.859	90.05
26	261190	55	KAMENIČNÁ-PIESKY	11.6.2009	10.00	13.8	91.3	7.09	2.2	36.23	476.14	−10.276	−12.044	69.86
19	260290	55	KOMÁRNO	10.6.2009	7.91	15.7	98.5	6.88	3.5	6.5	582.29	−10.584	−15.849	86.83
20	260490	55	KOMÁRNO	10.6.2009	9.76	13.2	88.8	7.34	1.4	17.57	464.01	−10.094	−14.134	80.22
2	721593	56	MALINOVO	10.11.2008	54.65	12.1	55.4	7.61	1.7	4.32	189.53	−10.954	−15.406	93.47
1	601291	56	VLKY	10.11.2008	30.50	12.4	53.6	7.46	1.5	10.79	250.05	−10.553	−15.406	89.62
38	603191	56	JELKA	16.6.2009	25.40	12.7	87.3	7.47	2.1	23.06	291.14	−10.727	−12.986	79.49
35	600592	56	JAHODNÁ	16.6.2009	34.92	12.7	51	7.59	1.2	5.49	248.68	−11.148	−11.250	80.80
28	264290	56	OKOČ-ASZÓD	11.6.2009	15.51	12.4	63.1	7.17	1.5	27.45	351.80	−10.423	−12.623	81.16
27	262890	56	KOLÁROVO	11.6.2009	9.00	13.7	73	7.28	1.4	13.18	327.54	−10.927	−13.933	99.58

average TDS of 626 mg L^{-1}, which is found in the South-East part of Žitný Island.

Spatial distribution of $\delta^{18}O$ in groundwater

Spatial distribution of $\delta^{18}O$ in shallow groundwater (top 25 m) with latitude and longitude of Žitný Island area is presented in Figure 4. Although the data density is still very limited, we can see regional differences in the $\delta^{18}O$ distribution. The eastern part of Žitný Island shows enriched $\delta^{18}O$ values (up to −9.5‰). The rest of the region shows, however, depleted values (below −10.5‰), which are in agreement with $\delta^{18}O$ data measured for the Danube River (Pawellek *et al.* 2002; Michalko *et al.* 2011). The enriched $\delta^{18}O$ values observed at the east may be due to larger evaporation losses (river runoff in this part of Žitný Island is small), and also due to land irrigation (Kompári *et al.* 2012), which has been often used in this agricultural region.

Vertical distribution of $\delta^{18}O$ in groundwater with latitude and longitude of Žitný Island is also presented in Figure 4. While the bottom samples (below 40 m) are depleted in $\delta^{18}O$ values, generally below −10.5‰, the subsurface core observed at around 20 m water depth shows enriched $\delta^{18}O$ values between −10.0 and −9.5‰. However, the sub-surface samples (up to 10 m water depth) on the north and north-east side of the island show again depleted $\delta^{18}O$ values, close to the values observed for the Danube River system (from −12.4 to −10.2‰; Michalko *et al.* 2011).

The measured $\delta^{18}O$ values in the Danube River (Bratislava) have been varying during the year showing maxima (up to −10.2‰) in winter and minima (down to −12.4‰) in June (Michalko *et al.* 2011). The June minimum (also accompanied by the largest river flow rates) should be associated with melting of Alpine snow. A $\delta^{18}O$ in Alpine precipitation as low as −18‰ was observed by Pastorelli *et al.* (2001). The $\delta^{18}O$ values in shallow wells situated close to the Danube River should be therefore following this temporal variation (with a time delay of a few years; Michalko *et al.* 2011).

On the contrary, the measured $\delta^{18}O$ values in precipitation in south-west Slovakia varied from about −15‰ during winter to about −5‰ during summer (caused by evaporation losses of ^{16}O), with average annual values for

Table 3 | Groundwater chemical composition of the Žitný Island area

St. no.	SHMU number	Locality	Number of area	Date of sampling	Chemical type	TDS[a]	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Ca^{2+}	Mg^{2+} (mg L^{-1})	Na^+	K^+	CO^2 free	CO^2 aggr.	$C^{org.}$
16	603091	ČUNOVO	51	6.11.2008	Ca-Mg-HCO_3	353.4	188.0	18.0	29.7	10.5	57.5	12.8	11.1	2.3	12.3	< 1.1	1.1
6	601393	KALINKOVO	52	5.11.2008	Ca-Mg-HCO_3	372.9	200.0	18.9	31.2	9.87	61.1	13.9	10.8	2.4	14.0	< 1.1	1.3
4	724891	ŠAMORÍN-ČILISTOV	52	18.9.2008	Ca-Mg-HCO_3	390.5	246.0	19.3	12.6	< 1.0	63.8	14.2	9.8	2.0	17.5	< 1.1	0.8
8	726591	ŠAMORÍN-MLIEČNO	52	5.11.2008	Ca-Mg-HCO_3	411.3	243.0	19.5	22.7	3.26	69.4	15.5	10.5	2.1	16.7	< 1.1	0.9
10	601092	DOBROHOŠŤ	52	4.11.2008	Ca-Mg-HCO_3	388.6	235.0	17.3	19.7	2.48	65.1	14.5	9.4	2.2	16.7	< 1.1	1.0
11	727491	VOJKA	52	22.9.2008	Ca-Mg-HCO_3	397.9	228.0	18.2	34.9	3.96	64.6	14.5	8.0	2.1	16.7	< 1.1	1.0
12	603291	GABČÍKOVO	52	10.11.2008	Ca-Mg-HCO_3-SO_4	524.5	256.0	20.8	94.4	1.29	91.8	22.5	8.7	1.9	15.8	< 1.1	0.8
29	736591	SAP-PALKOVIČOVO	52	23.9.2008	Ca-Mg-HCO_3	355.0	199.0	17.3	41.7	< 1.0	52.3	12.9	7.0	1.8	13.2	< 1.1	1.2
17	601691	ROVINKA	53	20.11.2008	Ca-Mg-HCO_3	395.5	232.0	14.4	36.5	< 1.0	66.1	18.8	4.9	1.4	14.0	< 1.1	0.5
18	601591	PODUNAJ. BISKUPICE	53	20.11.2008	Ca-Mg-HCO_3-SO_4	535.2	289.0	22.6	65.5	2.90	94.3	22.4	5.9	3.1	19.4	< 1.1	< 0.5
3	724191	VYDRANY-KVETOSL.	54	30.9.2008	Ca-Mg-HCO_3	386.8	220.0	17.6	33.7	4.56	66.2	15.4	5.0	1.1	5.28	< 1.1	0.5
7	601191	OL'DZA	54	4.11.2008	Ca-Mg-HCO_3	378.6	237.0	56.0	29.4	12.70	59.6	20.4	4.3	1.3	15.8	< 1.1	0.8
5	727791	ROHOVCE-ŠTRKOVEC	54	23.9.2008	Ca-Mg-HCO_3	435.0	231.0	22.5	48.4	5.06	70.5	16.8	8.0	1.4	15.8	6.6	0.6
9	733691	VRAKUŇ	54	23.9.2008	Ca-Mg-HCO_3	303.5	207.0	4.6	20.5	2.69	45.9	13.7	2.4	0.5	13.2	< 1.1	< 0.5
15	725491	HORNÁ POTÔŇ	54	24.9.2008	Ca-Mg-HCO_3-SO_4	604.7	288.0	26.0	80.6	40.8	102.0	26.1	5.8	1.6	21.1	< 1.1	0.5
37	729492	ORECHOVÁ POTÔŇ	54	24.9.2008	Ca-Mg-HCO_3-SO_4	678.3	293.0	37.6	117.0	33.2	104.0	30.1	11.5	3.0	9.7	< 1.1	0.6
36	729394	VEL'KÉ BLAHOVO	54	24.9.2008	Ca-Mg-HCO_3-SO_4	594.5	293.0	26.2	84.1	24.2	101.0	24.6	6.0	1.8	12.3	< 1.1	0.7
33	603391	MLIEČANY	54	20.11.2008	Ca-Mg-HCO_3-SO_4	534.4	256.0	24.1	85.7	14.20	87.9	25.9	6.9	2.4	5.3	< 1.1	< 0.5
13	736691	KL'ÚČOVEC	55	22.9.2008	Ca-Mg-HCO_3	290.9	209.0	3.3	12.0	< 1.0	39.2	11.8	9.9	0.9	15.8	< 1.1	< 0.5
14	264791	KLIŽSKÁ NEMÁ	55	10.11.2008	Ca-Mg-HCO_3	644.3	464.0	5.8	24.7	< 1.0	93.3	35.4	9.3	1.0	22.0	< 1.1	1.8
31	600491	VEL'KÝ MEDER	55	20.11.2008	Ca-Mg-HCO_3	341.6	226.0	5.5	23.7	< 1.0	53.7	15.5	7.6	1.3	16.7	6.6	< 0.5
23	738191	ZLATNÁ NA OSTR.	55	24.11.2008	Na-Ca-Mg-HCO_3-SO_4	958.4	549.0	29.4	124.0	< 1.0	68.4	36.5	109.0	1.7	23.8	< 1.1	1.7
21	605990	ČALOVEC-KAMENIČNÁ	55	25.9.2008	Ca-Mg-HCO_3	442.3	293.0	16.4	14.8	< 1.0	35.5	20.0	38.8	1.1	0.9	< 1.1	1.1
22	260790	KAMENIČNÁ	55	26.11.2008	Mg-Ca-K-HCO_3	926.4	634.0	2.9	60.1	5.56	55.1	58.6	10.8	94.2	33.9	< 1.1	1.4
26	261190	KAMENIČNÁ-PIESKY	55	25.9.2008	Ca-Mg-HCO_3-SO_4	798.2	445.0	22.9	108.0	< 1.0	125.0	36.7	24.7	1.7	39.6	42.9	1.8
19	260290	KOMÁRNO	55	27.11.2008	Ca-Mg-HCO_3	1091.5	677.0	26.8	60.1	47.90	146.0	38.7	19.0	39.4	64.7	< 1.1	2.4
20	260490	KOMÁRNO	55	24.11.2008	Mg-Ca-HCO_3	926.2	555.0	27.9	95.1	31.50	77.6	71.0	28.9	2.3	29.0	< 1.1	1.4
2	721593	MALINOVO	56	24.9.2008	Ca-Mg-HCO_3-SO_4	489.0	238.0	21.8	98.8	10.20	70.4	22.4	3.9	1.1	14.0	< 1.1	0.6
1	601291	VLKY	56	5.11.2008	Ca-Mg-HCO_3	434.6	232.0	25.3	35.0	1.97	71.2	16.2	14.5	2.4	16.7	< 1.1	1.3
38	603191	JELKA	56	30.9.2008	Ca-Mg-HCO_3-SO_4	803.5	305.0	57.0	133.0	35.8	140.0	38.0	16.4	3.8	9.7	< 1.1	1.0
35	600592	JAHODNÁ	56	24.9.2008	Ca-Mg-HCO_3	433.0	249.0	13.8	48.0	2.85	76.4	18.6	4.8	1.3	17.6	< 1.1	0.6
28	264290	OKOČ-ASZÓD	56	29.9.2008	Ca-Mg-HCO_3	580.5	342.0	12.7	62.9	< 1.0	107.0	23.7	7.9	0.9	26.4	2.2	2.6

[a]Total dissolved solids.

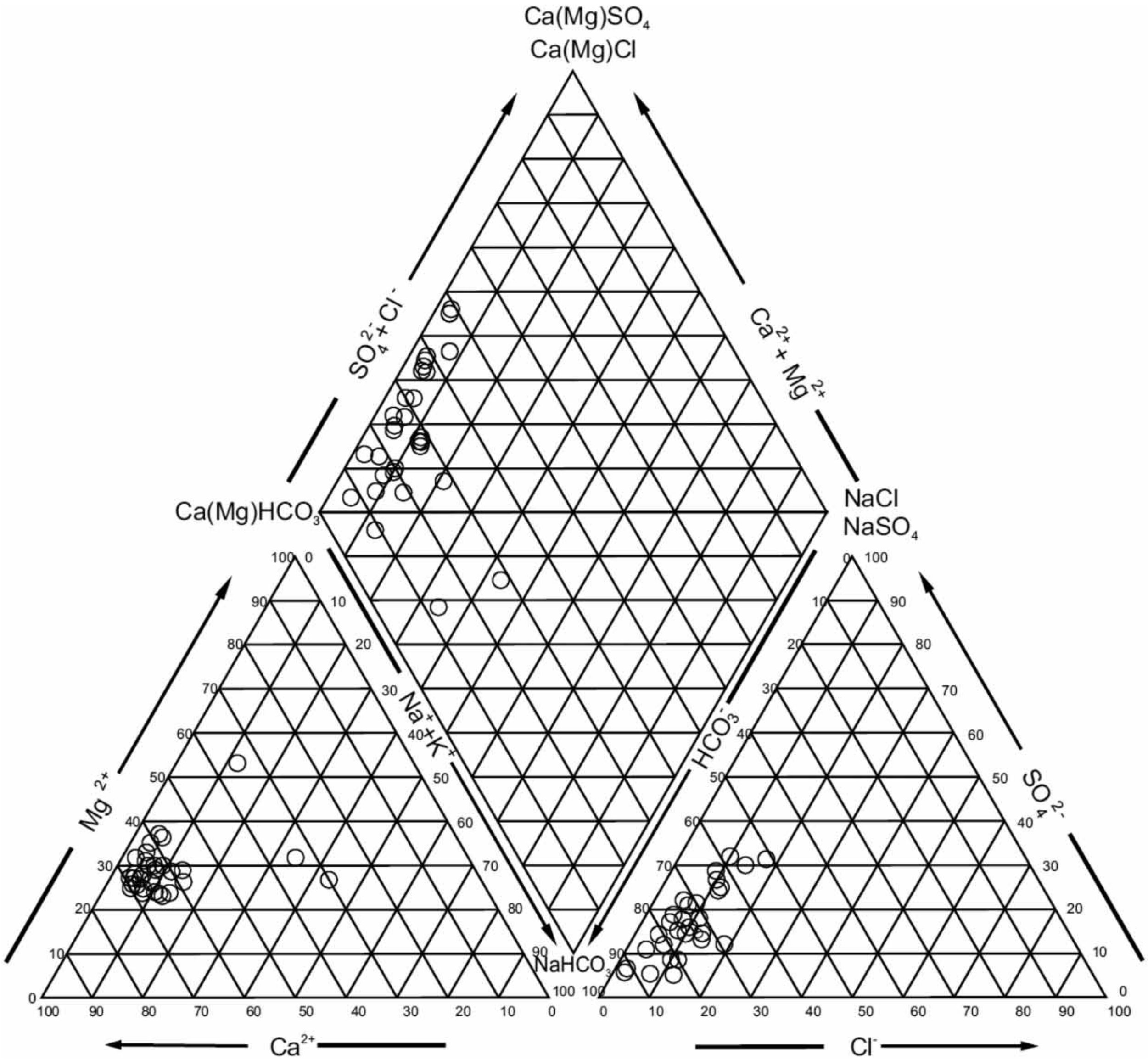

Figure 3 | Piper diagram.

Bratislava of −8.83‰, and for Topoľníky (situated at the center of Žitný Island) of −9.35‰ (Holko *et al.* 2012). Unfortunately, we do not have δ^{18}O sub-surface groundwater data available yet for the Žitný Island stations, which would be collected both during summer and winter seasons at the same stations at the same depth. The δ^{18}O data presented in Table 2 do not show large differences between groundwater samples collected in summer (top horizons down to 25 m with average value of −10.54‰) and in winter (deeper horizons <25 m with average value of −10.74‰). However, for proper temporal variations studies we would need new δ^{18}O results for top horizons in winter and bottom horizons in summer.

The obtained δ^{18}O groundwater data are in reasonable agreement with isotope data measured for the Danube River system indicating therefore that the Danube River should be the main source of groundwater observed at Žitný Island. As we already mentioned, precipitation should be influencing the groundwater regime of Žitný Island only indirectly via elevated flow rates in rivers. We

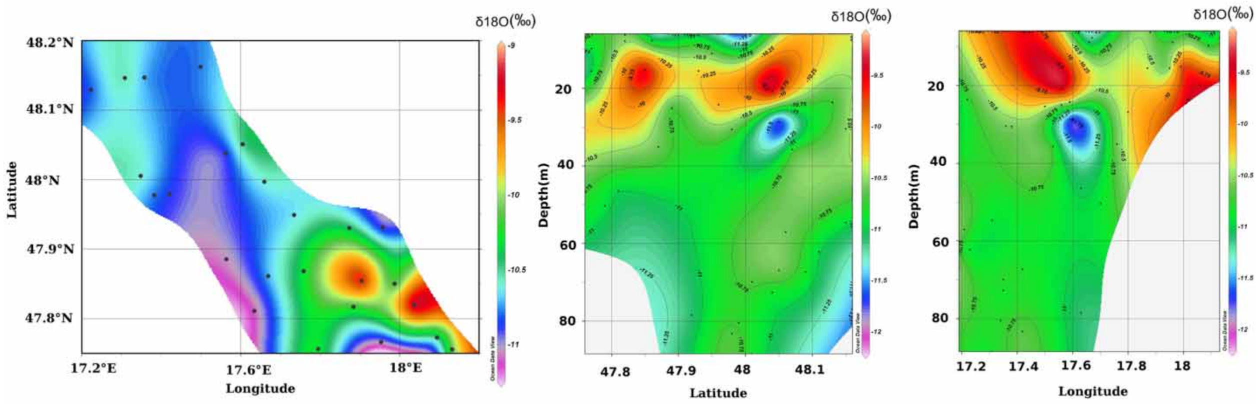

Figure 4 | Spatial distribution of $\delta^{18}O$ with latitude and longitude in groundwater of Žitný Island.

should get, however, a more-clear picture when summer/winter data are available for the same stations.

Spatial distribution of $\delta^{13}C$ in groundwater

Distribution of $\delta^{13}C$ with latitude and longitude of sub-surface (top 25 m) groundwater samples collected in Žitný Island is presented in Figure 5. Here we see mostly enriched $\delta^{13}C$ levels in surface waters of the central part of Žitný Island. The depth profile of $\delta^{13}C$ shows large variability – depleted values in the central and eastern parts of the Island at depths between 30 and 50 m (down to −19.22‰ at St. 6), but also enriched $\delta^{13}C$ values (−10.66‰ at St. 10 at 80 m depth, up to −10.62‰ at St. 31 at 35 m depth) in the central and eastern part of the Island. Quaternary aquifers which form the main hydrogeology structure of the area (Maglay *et al.* 2009) are usually represented by large variations in $\delta^{13}C$ values, which are connected with a large amount of carbonate materials, as observed, e.g. in the eastern part of the Island.

Spatial distribution of ^{14}C in groundwater

The spatial distribution of radiocarbon in sub-surface (top 25 m) groundwater with latitude and longitude of Žitný Island is shown in Figure 6. The surface samples up to 10 m depth at the western part of the Island show ^{14}C values above 80 pMC, representing contemporary groundwater. At the other regions, the observed values are also mostly >80 pMC, except at St. 21 (depth 10.9 m) on the east side of the Island, where a ^{14}C value of 31.5 pMC was measured. At around 60 m water depth a sub-surface core of about 50 pMC is well allocated at the eastern part of the Island as well. Neogene clays were found there a few meters below the surface (Maglay *et al.* 2009), which prevent

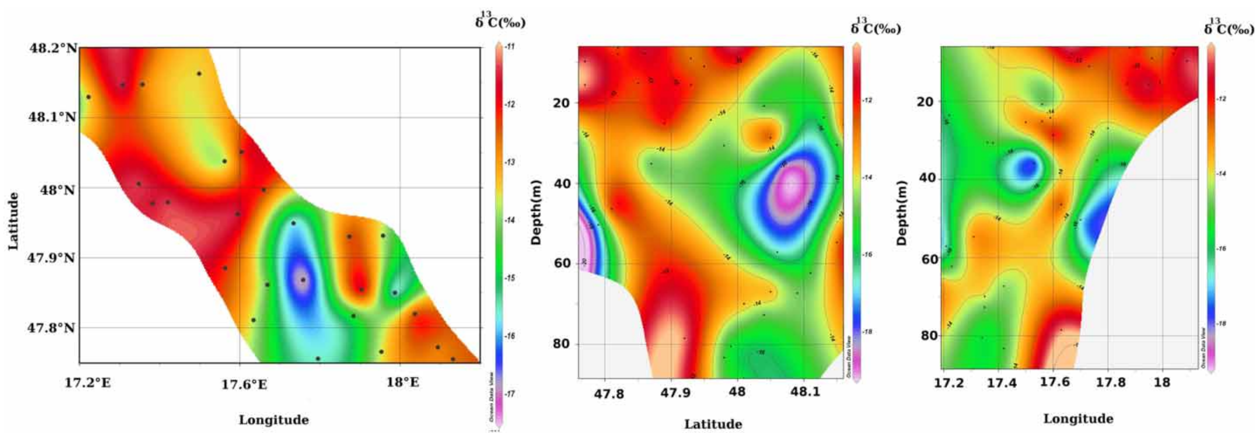

Figure 5 | Spatial distribution of $\delta^{13}C$ with latitude and longitude in groundwater of Žitný Island.

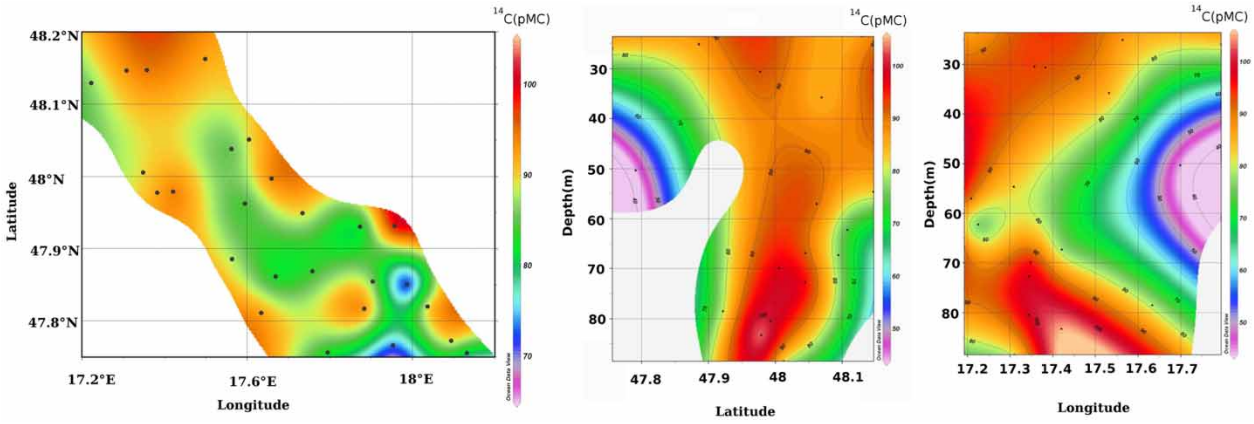

Figure 6 | Spatial distribution of ^{14}C with latitude and longitude in groundwater of Žitný Island.

a direct infiltration of groundwater of Danube origin to deeper layers. This indicates existence of a confined aquifer formed below the layer of Neogene clay sediments.

CONCLUSIONS

This has been a first attempt to construct isotope maps and to study spatial and vertical distribution of isotopes in groundwater of Slovakia. Groundwater samples collected during 2008–2009 in SW Slovakia, at the area called Žitný Island, improved the data density so that geostatistical methods of data treatment could be applied.

The chemical composition of groundwater of Quaternary sediments of Žitný Island depends on the chemical composition of Danube water, and also of Small Danube and Váh river waters, as well as on the length of infiltration of river waters into the groundwater. The groundwater is characterized by potamogenic mineralization, and its chemical composition is influenced by anthropogenic contamination.

The obtained results on spatial variability of ^{14}C, $\delta^{13}C$ and $\delta^{18}O$ suggest large isotopic heterogeneity in the groundwater of Žitný Island. While the bottom samples (below 40 m) are depleted in $\delta^{18}O$ values, generally below −10.5‰, the sub-surface core observed at around 20 m depth shows enriched $\delta^{18}O$ values between −10.0 and −9.5‰. However, the sub-surface samples up to 10 m depth on the north and north-east of the island show again depleted $\delta^{18}O$ values, close to the values observed for the Danube River system. In the ^{14}C profile a sub-surface core of about 50 pMC at around 60 m depth at the south-east of the island was observed, in agreement with expectations due to the presence of Neogene clay sediments there. The sub-surface samples up to about 20 m depth show ^{14}C values above 80 pMC, representing thus contemporary groundwater mostly supplied by the Danube River system.

The obtained groundwater isotope data are in good agreement with isotope data measured for Danube water indicating that the Danube River should be the main source of groundwater observed at Žitný Island. More groundwater samples from the Žitný Island area will be collected and analyzed during forthcoming expeditions, which will help to improve the spatial density of isotope data, as well as their seasonal characteristics, and thus contribute to better understanding the groundwater system of Žitný Island.

REFERENCES

Aggarwal, P. & Araguás-Araguás, L. 2006 *CRP Proposal – Geostatistical Analysis of Spatial Isotope Variability to Map the Sources of Water for Hydrology and Climate Studies*. IAEA, Vienna.

Aggarwal, P. K., Gat, J. R. & Froehlich, K. F. O. (eds) 2006a *Isotopes in the Water Cycle*. Springer, Heidelberg, 381 pp.

Aggarwal, P., Froehlich, K., Gonfiantini, R. & Gat, J. 2006b Isotope hydrology: a historical perspective from the IAEA. In: *Isotopes in the Water Cycle* (P. K. Aggarwal, J. R. Gat & K. F. O. Froehlich, eds). Springer, Heidelberg, pp. 3–8.

Bowen, G. J., Wassenaar, L. I. & Hobson, K. A. 2005 Global application of stable hydrogen and oxygen isotopes to wildlife forensics. *Oecologia* **143**, 337–348, doi:10.1007/s00442-004-1813-y.

Deák, J. 2003 Isotope-hydrogeology studies in Hungary focusing on the requirements of the EU Water Framework Directive.

In: *Proceedings of Isotopenmethoden in der Hydrogeologie und Wasserwirtschaft*, IAEA (International Atomic Energy Agency), Vienna, pp. 1–9.

de la Torre, M. L., Grande, J. A., Valente, T., Santisteban, M. & Cerón, J. C. 2015 Hydrochemical changes in a reservoir that receives water contaminated by acid mine drainage. *Hydrology Research* **46** (3), 303–312, doi:10.2166/nh.2014.114.

Franko, O., Šivo, A., Richtáriková, M. & Povinec, P. 2005 Radiocarbon ages of mineral and thermal waters in Slovakia, In: *19th International Radiocarbon Conference*, University of Oxford, Oxford, pp. 261–262.

Franko, O., Šivo, A., Richtáriková, M. & Povinec, P. 2008 Radiocarbon ages of mineral and thermal waters of Slovakia. *Acta Physica Universitatis Comennianae* **49**, 125–132.

Gonfiantini, R., Froehlich, K. & Araguás-Araguás, L. 1999 Isotopes in groundwater hydrology. In: *Isotope Tracers in Catchment Hydrology* (C. Kendall & J. McDonnell, eds). Elsevier, Amsterdam.

Holko, L., Dóša, M., Michalko, J., Kostka, Z. & Šanda, M. 2012 Isotopes of oxygen-18 and deuterium in precipitation in Slovakia. *Journal of Hydrology and Hydromechanics* **60** (4), 265–276.

Kendall, C. & McDonnell, J. 1999 *Isotope Tracers in Catchment Hydrology*. Elsevier, Amsterdam.

Kompári, L., Szucs, P., Fejes, Z., Palcsu, L. & Deák, J. 2012 Infiltration tests on irrigated agricultural areas. *Geosciences and Engineering* **1**, 99–104.

L'uptáková, A., Žákovičová, A., Kvapilová, L., Molnár, L'., Jančár, V., Mrafková, L. & Májovská, A. 2007 *Quality of Žitný Island Groundwater (2005–2006)*. SHMÚ, Bratislava, 79 pp. (in Slovak).

Maglay, J., Pristaš, J., Kučera, M. & Ábelová, M. 2009 *Geological Map of the Quarter of Slovakia*. MŽP SR, Bratislava (in Slovak).

Malík, P., Michalko, J., Mansell, S. J. & Fendeková, M. 1995 Stable isotopes in karstic groundwaters of Veľká Fatra mountains, Slovakia. In: *Proc. International Symposium on Isotopes in Water Resources Management*, IAEA, Vienna.

Michalko, J. 1999 Stable isotopes of hydrogen, oxygen and sulphur in the waters of Slovakia. *Slovak Geological Magazine* **5**, 63–67.

Michalko, J., Bodiš, D., Malík, J., Fajčíková, K., Grolmusová, Z. & Veis, P. 2011 Potential sources of strategic amounts of groundwater in the Bratislava region. *Mineralia Slovaca* **43**, 449–462.

Miljević, N., Golobočanin, D., Ogrinc, N. & Bondžić, A. 2008 Distribution of stable isotopes in surface water along the Danube River in Serbia. *Isotopes in Environmental and Health Studies* **44**, 137–148.

Ockenden, M. C., Chappell, N. A. & Neal, C. 2014 Quantifying the differential contributions of deep groundwater to streamflow in nested basins, using both water quality characteristics and water balance. *Hydrology Research* **45** (2), 200–212, doi:10.2166/nh.2013.035.

Pastorelli, S., Marine, L. & Hunziker, S. 2001 Chemistry, isotope values (δD, $\delta^{18}O$ $\delta^{34}S_{SO4}$) and temperatures of the water inflows in two Gotthard tunnels, Swiss Alps. *Applied Geochemistry* **16**, 633–649.

Pawellek, F., Frauenstein, F. & Veizer, J. 2002 Hydrochemistry and isotope geochemistry of the upper Danube River. *Geochimica et Cosmochimica Acta* **66** (21), 3839–3854.

Povinec, P. 1972 Preparation of methane gas filling for proportional ^3H and ^{14}C counters. *Radiochemical and Radioanalytical Letters* **9**, 127–135.

Povinec, P. 1978 Multiwire proportional counters for low-level ^{14}C and ^3H measurements. *Nuclear Instruments and Methods* **156**, 441–445.

Povinec, P. P., Aggarwal, P., Aureli, A., Burnett, W. C., Kontar, E. A., Kulkarni, K. M., Moore, W. S., Rajar, R., Taniguchi, M., Comanducci, J.-F., Cusimano, G., Dulaiova, H., Gatto, L., Hauser, S., Levy-Palomo, I., Ozorovich, Y. R., Privitera, A. M. G. & Schiavo, M. A. 2006 Characterization of submarine groundwater discharge offshore south-eastern Sicily. *Journal of Environmental Radioactivity* **89**, 81–101.

Povinec, P. P., Franko, O., Šivo, A., Richtáriková, M., Breier, R., Aggarwal, P. K. & Araguás-Araguás, L. 2010 Spatial radiocarbon and stable carbon isotope variability of mineral and thermal waters in Slovakia. *Radiocarbon* **52**, 1056–1067.

Povinec, P. P., Breir, R., Coppola, L., Groening, M., Jeandel, C., Jull, A. J. T., Kieser, W. E., Lee, S. H., Liong Wee Kwong, L., Morgenstern, U., Park, Y. H. & Top, Z. 2011 Tracing of water masses using a multi isotope approach in the southern Indian Ocean. *Earth and Planetary Science Letters* **302**, 14–26.

Rank, D., Pepesch, W. & Rainer, V. 1995 Environmental isotope study at research landfill (Breitenan, Austria). In: *Proc. International Symposium Isotopes in Water Resources Management*. IAEA, Vienna, pp. 379–381.

Rank, D., Adler, A., Araguás-Araguás, L., Froehlich, K., Rozanski, K. & Stichler, W. 1998 Hydrological parameters and climatic signals derived from long-term tritium and stable isotope time series of the River Danube. In: *Isotope Techniques in the Study of Environmental Change*. IAEA, Vienna, pp. 191–205, IAEA-SM-349.

Rank, D., Papesch, W., Heiss, G. & Tesch, R. 2009 Isotopic composition of river water in the Danube basin – results from the joint Danube survey 2 (2007). *Austrian Journal of Earth Sciences* **102** (2), 170–180.

Schiavo, M., Hauser, S. & Povinec, P. P. 2009 Stable isotopes of water as a tool to study groundwater-seawater interactions in coastal south-eastern Sicily. *Journal of Hydrology* **364**, 40–49.

Szczucinska, A. M. 2014 Spatial distribution and hydrochemistry of springs and seepage springs in the Lubuska Upland of western Poland. *Hydrology Research* **45** (3), 379–390, doi:10.2166/nh.2013.249.

Usačev, S., Povinec, P., Chudý, M. & Šeliga, M. 1973 Bratislava radiocarbon measurements I. *Radiocarbon* **15**, 443–450.

Vitvar, T., Newman, B. D., Aggarwal, P. & Garner, A. 2007 Application of environmental isotopes for studying stream/aquifer interactions in the Danube basin. *Water Science & Technology: Water Supply* **7** (3), 25–30, doi:10.2166/ws.2007.063.

First received 10 December 2014; accepted in revised form 22 December 2014. Available online 21 January 2015