Austrian Journal of Earth Sciences | Volume 102/2 | 170 - 180 | Vienna | 2009

Isotopic composition of river water in the Danube Basin - results from the Joint Danube Survey 2 (2007)

Dieter RANK[1)*], Wolfgang PAPESCH[2)], Gerhard HEISS[2)] & Roland TESCH[2)]

KEYWORDS

isotope hydrology
Danube Basin
river water
deuterium (^{2}H)
tritium (^{3}H)
oxygen 18 (^{18}O)

[1)] Center for Earth Sciences, University of Vienna, 1090 Wien, Austria;
[2)] Austrian Institute of Technology - AIT, 2444 Seibersdorf, Austria;
[*)] Corresponding author, dieter.rank@univie.ac.at

Abstract

Grab samples of river water were collected for isotope measurements (^{2}H, ^{3}H, ^{18}O) from all sampling points of the Joint Danube Survey 2 (JDS2), organized by the International Commission for the Protection of the Danube River (ICPDR), and the simultaneous national sampling campaigns on several tributaries. Since only very few isotope data were existing especially from the lower Danube, the main objective of this isotope study was to provide a basin-wide basic isotope data set for hydrological applications and a base line of isotope data for assessing future impacts within the Danube Basin. δ^{18}O values range from -13.1 ‰ (Inn, alpine river) up to -6.4 ‰ (Sio, discharge of Lake Balaton, evaporation influence). The δ^{18}O value of the Danube increases from -10.8 ‰ after the confluence of Inn River and upper Danube up to -9.6 ‰ at the mouth in the Black Sea, with a major change after the inflow of the rivers Tisa and Sava. The isotopic composition of river water in the Danube Basin is mainly governed by the isotopic composition of precipitation in the catchment area, evaporation effects play only a minor role. The expected actual ^{3}H content of river water in Central Europe would be about 10 TU, values up to 40 TU in the Danube and 250 TU in the tributaries are clear evidence for discontinuous releases of ^{3}H from local sources (mainly nuclear power plants) into the rivers.

Beim „Joint Danube Survey 2 (JDS2)“, organisiert von der Internationalen Kommission zum Schutz der Donau (IKSD), und den gleichzeitigen nationalen Probenahmekampagnen an wichtigen Nebenflüssen wurden Flusswasserproben für Isotopenanalysen aus dem gesamten Donaueinzugsgebiet entnommen. Da es vor allem von der unteren Donau bis dahin nur wenige Isotopendaten gab, war das Hauptziel dieser Isotopenstudie einen beckenweiten Isotopenbasisdatensatz zu erhalten: einerseits für hydrologische Anwendungen und andererseits als Basislinie für die Abschätzung der Auswirkungen künftiger hydrologischer und klimatischer Änderungen im Donauraum. Die gemessenen δ^{18}O-Werte reichen von -13.1 ‰ (Inn, alpiner Fluss) bis -6.4 ‰ (Sio, Abfluss des Plattensees, Verdunstungseinfluss). Der δ^{18}O-Wert der Donau beträgt nach dem Zusammenfluss von Inn und oberer Donau -10.8 ‰ und nimmt bis zur Mündung ins Schwarze Meer auf -9.6 ‰ zu, der Zufluss von Theiss und Save führt dabei zu einem signifikanten Anstieg des δ^{18}O-Wertes in der Donau. Die Isotopenzusammensetzung im Flusswasser im Donaueinzugsgebiet wird im Wesentlichen durch die Isotopenzusammensetzung im Niederschlag im Einzugsgebiet bestimmt, Verdunstungseffekte spielen nur eine untergeordnete Rolle. Für Flusswasser in Mitteleuropa wären im Untersuchungszeitraum ^{3}H-Werte um 10 TU zu erwarten, Werte von bis zu 40 TU in der Donau und bis zu 250 TU in den Zuflüssen deuten auf Kurzzeitabgaben von ^{3}H aus lokalen Quellen – vorwiegend Kernkraftwerken - in die Flüsse hin.

1. Introduction

The Danube is the second largest stream in Europe spanning between its source and its mouth in the Black Sea a total of 2857 km and covering an overall catchment area of 817000 km² with an average discharge of about 6500 m³/s at its mouth (Fig. 1). The core activity of the Joint Danube Survey 2 (JDS2), which had been organized by the International Commission for the Protection of the Danube River (ICPDR), focused on the Danube River and on the mouths of the main tributaries. 96 sampling points were selected for water sampling, starting near Ulm (river km 2600) on Aug. 13, 2007 and reaching the Black Sea (river km 0) on Sept. 27, 2007 (sampling points see Fig. 2). In parallel with the core activity on the Danube River, longitudinal surveys on some major tributaries were performed at the national/regional level: Morava, Drava, Tisa, Sava, Velika Morava, Arges, Olt, Jantra, Iskar, Russenski Lom, and Prut.

Isotope ratios of hydrogen and oxygen in river water are indicators for hydrological processes in the catchment (e.g. formation of base flow), for interactions between river water and groundwater, for mixing processes in a river, for travel time and dispersion of short term pulses (e.g. pollution pulses) as well as for hydrological/climatic changes in the drainage area of a river. The investigation of such topics requires a good knowledge of the “isotopic environment”. At that time existed several regional isotope studies on river water in the Danube Basin (e.g. Hadzisehović et al. 1992, Miljević et al. 2008, Pawellek et al. 2002, Rank et al. 1998) and one more extensive on the Danube between Vienna and the Black Sea (Rank et al. 1990). Since there was a lack of isotope data especially from the lower part of the Danube Basin, the JDS2 was a welcome opportunity to improve the data base for environmental isotopes in this region (Newman et al. 2008).

The isotopic composition of hydrogen and oxygen in river

water is mainly determined by the isotopic composition in precipitation water in the drainage area (altitude effect, continental effect, seasonal variations, storms; see e.g. Mook 2000; Rank and Papesch, 2005). Several hydrological parameters and processes modify this isotopic signature and its temporal variations: delayed runoff of winter precipitation (snow cover), residence time of groundwater discharged to the river, confluence with tributaries, evaporation from lakes in the river system, climatic changes (change in environmental temperature, spatial and temporal change of precipitation distribution in the drainage area, etc.) as well as anthropogenic influences on the hydrological regime (e.g. reservoirs, irrigation).

Figure 1: Danube Basin river system (based on ESRI ArcGIS 9.3).

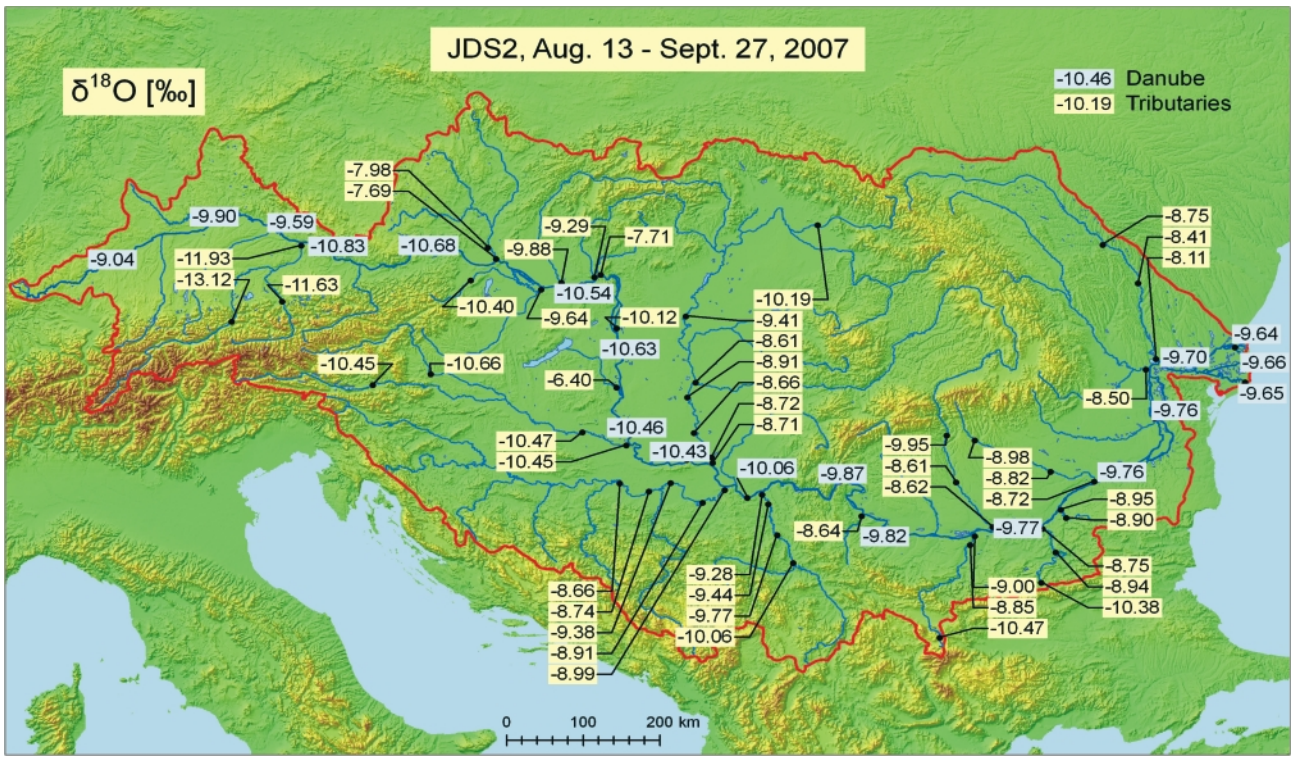

Figure 2: $\delta^{18}O$ of river water in the Danube Basin (Aug. 13 – Sept. 27, 2007).

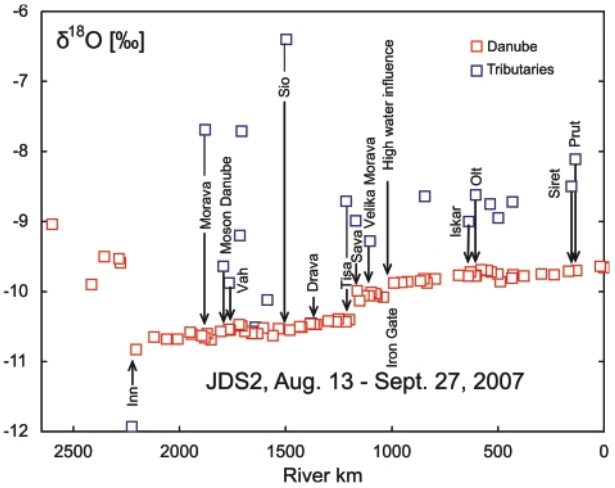

Figure 3: Longitudinal $\delta^{18}O$ profile of the Danube (rkm 2600, Ulm – rkm 0, Black Sea) and $\delta^{18}O$ values of tributaries at confluence (Aug. 13 – Sept. 27, 2007).

2. Methods

One liter PET bottles were filled with river water from the middle of the stream at the sampling points of JDS2 and the national sampling campaigns and brought to the isotope laboratories of the Austrian Institute of Technology (AIT) in Seibersdorf. The amount of sample water enabled measurement of stable isotope ratios as well as determination of tritium content. Stable isotope measurements were performed using isotope mass spectrometers Finnigan MAT 251 and DeltaPlusXL equipped with automatic equilibration lines. All results are reported as relative abundance (δ^2H and $\delta^{18}O$, respectively) of the isotopes ^2H and ^{18}O in permil (‰) with respect to the international standard VSMOW (Vienna Standard Mean Ocean Water). The accuracy of δ^2H and $\delta^{18}O$ measurements is better than ± 1.0 ‰ and ± 0.1 ‰, respectively. – The samples for ^3H measurement were electrolytically enriched and analyzed using low-level liquid scintillation counting (precision ± 5%, 1 TU = 0.119 Bq/kg for water).

3. Results

The results of ^2H, ^3H, and ^{18}O measurements of river water samples from JDS2 are listed in Table 1 (Danube) and Table 2 (tributaries). Some data from the Austrian network for isotopes in rivers from the same time period are also included. Deuterium excess d is calculated from

$$d = \delta^2H - 8 \times \delta^{18}O \quad (1)$$

with d being deuterium excess, δ^2H and $\delta^{18}O$ the stable isotope composition of the water sample. With d = 10 ‰, equation (1) describes the general relation between δ^2H and $\delta^{18}O$ in precipitation (Global Meteoric Water Line, see Craig, 1961; Mook, 2000). On average, precipitation water in Central Europe also exhibits a deuterium excess of about 10 ‰.

The spatial distribution of $\delta^{18}O$ in river water in the Danube Basin is shown in Fig. 2, with lower values in mountainous regions and higher values in lowland tributaries. The $\delta^{18}O$ value of the Danube increases from -10.8 ‰ after the confluence of upper Danube (mainly lowland drainage area, higher $\delta^{18}O$ value) and Inn River (mainly alpine drainage area, lower $\delta^{18}O$ value) up to -9.6 ‰ at the mouth (Fig. 2 and 3). This increase is due to the decreasing influence of runoff contributions from

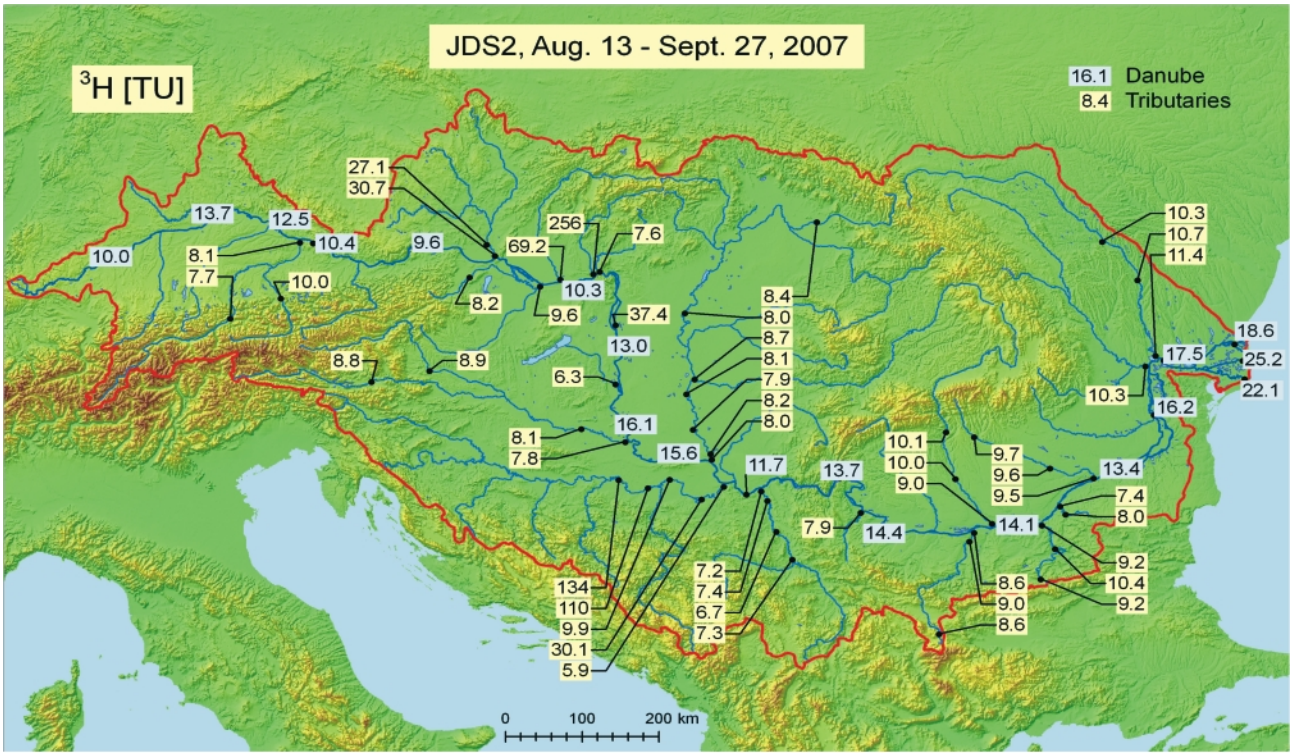

Figure 4: ^3H content of river water in the Danube Basin (Aug. 13 – Sept. 27, 2007).

the alpine part of the drainage area and the corresponding increase of lower elevation contributions. The Inn River with its alpine catchment has the lowest $\delta^{18}O$ value (-13.1 ‰) in the whole Danube Basin. The highest value (-6.4 ‰) was found for River Sio with the discharge from Lake Balaton. The enrichment in heavy isotopes is due to strong evaporation influence on the lake water.

It must be emphasized that the different samples had not been taken at the same time in all parts of the catchment, but within a time span of about six weeks. So hydrological conditions could possibly have changed during the sampling campaign, as it had happened by a heavy rain event in the alpine part of the Danube Basin during Sept. 5 -7, 2007 (see discussion).

The ^3H distribution resulting from the JDS2 water samples (Fig. 4 and 5) can be regarded as representative only for those parts of the river system where local ^3H releases into the rivers do not play a significant role. Since such releases are usually in the form of short term pulses, the ^3H content measured in the river water depends very much on the moment when the sample is collected. The ^3H content of actual precipitation in Central Europe would lead to a ^3H concentration of about 10 TU in river water and slightly lower in tributaries, the drainage area of which is influenced by Mediterranean air masses (Rank and Papesch, 2005) . The samples from JDS2 showed ^3H values up to 40 TU in the Danube and up to 250 TU in the tributaries (Fig. 4 and 5). The reasons for these higher values are obviously discontinuous releases from local sources (mainly nuclear power plants, NPPs) into the rivers.

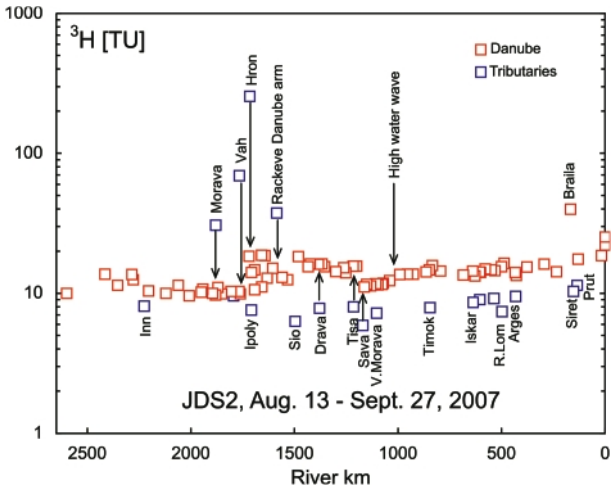

Figure 5: Longitudinal ^3H content profile of the Danube (rkm 2600, Ulm – rkm 0, Black Sea) and ^3H content of tributaries at confluence (Aug. 13 – Sept. 27, 2007).

Results of ^2H, ^3H, and ^{18}O analyses of JDS2 Danube samples and calculated ^2H excess d.

River km	Sampling point	Sample no.	Date of sampling	Discharge [m^3/s]	δ^2H [‰]	^3H [TU]	$\delta^{18}O$ [‰]	d [‰]
2600	Upstream Iller	JDS1	13.08.2007 13:00		-64,6	10.0 ± 0.9	-9,04	7,7
2415	Kelheim, gauging station	JDS2	15.08.2007 09:00		-69,8	13.7 ± 1.0	-9,90	9,4
2354	Geisling power plant	JDS3	15.08.2007 16:52		-67,6	11.4 ± 0.9	-9,50	8,4
2285	Deggendorf	JDS4	16.08.2007 12:30		-67,6	13.6 ± 1.0	-9,53	8,6
2278	Niederalteich, downstream Isar confluence	JDS5	16.08.2007 14:10		-68,3	12.5 ± 0.6	-9,59	8,4
2204	Jochenstein	JDS7	17.08.2007 10:40	1180	-77,8	10.4 ± 0.5	-10,83	8,8
2120	Upstream dam Abwinden -Asten	JDS8	18.08.2007 08:50	1450	-76,1	10.0 ± 0.5	-10,65	9,1
2061	Upstream dam Ybbs -Persenbeug	JDS9	18.08.2007 13:55	1600	-76,0	11.4 ± 0.6	-10,68	9,4
2008	Oberloiben	JDS10	18.08.2007 20:30	1660	-75,7	9.6 ± 0.5	-10,68	9,7
1950	Upstream dam Greifenstein	JDS11	19.08.2007 12:45	1620	-75,0	10.2 ± 0.5	-10,58	9,6
1942	Klosterneuburg	JDS12	19.08.2007 16:30	1645	-75,8	10.7 ± 0.6	-10,61	9,1
1895	Wildungsmauer	JDS13	21.08.2007 11:20	1915	-75,4	10.0 ± 0.5	-10,63	9,6
1881	Upstream Morava, Hainburg	JDS14	21.08.2007 16:00	1925	-75,8	9.7 ± 0.5	-10,66	9,5
1869	Bratislava	JDS16	22.08.2007 10:50	1759	-76,1	11.0 ± 0.6	-10,60	8,7
1852	Gabcikovo reservoir	JDS17	23.08.2007 09:00		-75,7	9.9 ± 0.5	-10,69	9,8
1806	Medvedov/Medve	JDS18	23.08.2007 15:00	1771	-74,8	10.3 ± 0.5	-10,57	9,8
1768	Komarno/Komarom	JDS20	24.08.2007 12:30	1577	-74,8	10.3 ± 0.5	-10,54	9,5
1761	Iza/Szony	JDS22	24.08.2007 17:20		-74,3	9.9 ± 0.5	-10,55	10,1
1719	Sturovo/Esztergom	JDS23	25.08.2007 09:15	1460	-74,5	18.4 ± 0.9	-10,47	9,3
1707	Szob	JDS26	25.08.2007 16:30		-75,0	14.1 ± 0.7	-10,49	8,9
1692	Upstream end of Szentendre Island	JDS27	26.08.2007 12:00		-75,0	14.7 ± 0.7	-10,57	9,6
1692	Upstream end of Szentendre Island, arm	JDS28	26.08.2007 13:00		-75,2	10.6 ± 0.5	-10,57	9,4
1659	Upstream Budapest	JDS29	27.08.2007 12:00		-75,3	18.7 ± 0.9	-10,60	9,5
1658	Budapest, old Danube, end of S. arm	JDS30	27.08.2007 14:00		-75,1	11.1 ± 0.6	-10,57	9,5
1632	Downstream Budapest	JDS32	29.08.2007 14:00	1330	-76,1	12.8 ± 0.6	-10,60	8,7
1605	Adony/Lorev	JDS33	29.08.2007 19:10		-75,6	15.1 ± 0.7	-10,52	8,6
1560	Dunaföldvar	JDS35	30.08.2007 13:20		-75,2	13.0 ± 0.6	-10,63	9,8
1533	Paks	JDS36	30.08.2007 17:55	1382	-75,1	12.5 ± 0.6	-10,53	9,1
1481	Baja	JDS38	31.08.2007 15:30	1423	-76,1	18.3 ± 0.8	-10,55	8,3
1434	Hercegszanto	JDS39	01.09.2007 15:20	1415	-74,8	15.5 ± 0.7	-10,50	9,2

Table 1

Results of ^{2}H, ^{3}H, and ^{18}O analyses of JDS2 Danube samples and calculated ^{2}H excess d.

River km	Sampling point	Sample no.	Date of sampling	Discharge [m^3/s]	$\delta^{2}H$ [‰]	^{3}H [TU]	$\delta^{18}O$ [‰]	d [‰]
1424	Batina	JDS40	01.09.2007 18:10	1410	-75,3	16.2 ± 0.8	-10,51	8,8
1384	Upstream Drava	JDS41	02.09.2007 16:30		-74,9	16.1 ± 0.8	-10,46	8,8
1367	Downstream Drava, Erdut/Bogojevo	JDS43	03.09.2007 08:30	2050	-74,0	16.2 ± 0.8	-10,47	9,8
1355	Dalj	JDS44	03.09.2007 10:10	2010	-74,7	15.5 ± 0.8	-10,47	9,1
1300	Ilok/Backa Palanka	JDS45	03.09.2007 15:30	2160	-74,4	14.3 ± 0.7	-10,42	9,0
1262	Upstream Novi Sad	JDS46	04.09.2007 11:00	2090	-74,2	15.2 ± 0.7	-10,43	9,2
1252	Downstream Novi Sad	JDS47	04.09.2007 13:00		-74,4	14.0 ± 0.7	-10,39	8,7
1216	Upstream Tisa, Stari Slankamen	JDS48	05.09.2007 09:00	2240	-74,5	15.6 ± 0.8	-10,43	8,9
1200	Downstream Tisa/upstream Sava, Belegis	JDS50	05.09.2007 17:10	2460	-73,8	15.6 ± 0.8	-10,40	9,4
1159	Downstream Sava/upstream Pancevo	JDS52	07.09.2007 14:00		-71,3	11.0 ± 0.6	-9,99	8,6
1151	Downstream Pancevo	JDS53	07.09.2007 17:05		-72,0	11.6 ± 0.6	-10,13	9,0
1132	Grocka	JDS54	08.09.2007 10:15		-71,2	11.3 ± 0.6	-10,06	9,3
1107	Upstream Velika Morava	JDS55	08.09.2007 09:00		-71,4	11.6 ± 0.6	-10,06	9,1
1097	Downstream Velika Morava	JDS57	09.09.2007 09:40		-71,0	11.5 ± 0.6	-10,01	9,1
1077	Starapalanka/Ram	JDS58	09.09.2007 12:40		-72,2	11.6 ± 0.6	-10,03	8,0
1071	Banatska Palanka/Bazias	JDS59	09.09.2007 16:40	3200	-71,4	11.8 ± 0.6	-10,06	9,1
1040	Irongate reservoir, Golubac/Koronin	JDS60	10.09.2007 12:00		-71,9	12.3 ± 0.6	-10,08	8,7
991	Donji Milanovac	JDS61	10.09.2007 15:54		-70,6	13.6 ± 0.7	-9,88	8,4
954	Irongate reservoir, Tekija/Orsova	JDS62	11.09.2007 10:00		-70,3	13.7 ± 0.7	-9,87	8,7
926	Vrbica/Simijan	JDS63	11.09.2007 19:30		-69,9	13.7 ± 0.6	-9,86	9,0
865	Iron Gate II	JDS64	13.09.2007 13:05		-70,1	14.2 ± 0.7	-9,85	8,7
849	Upstream Timok, Rudujevac/Gruia	JDS65	13.09.2007 17:30	4780	-70,5	14.7 ± 0.7	-9,82	8,1
834	Pristol/Novo Selo Harbour	JDS67	14.09.2007 09:00		-70,4	15.8 ± 0.7	-9,88	8,6
795	Calafat	JDS68	14.09.2007 12:25	4829	-70,2	14.4 ± 0.7	-9,82	8,4
685	Downstream Kozloduj	JDS69	15.09.2007 12:40		-70,0	13.5 ± 0.7	-9,77	8,2
640	Upstream Iskar, Bajkal	JDS70	15.09.2007 16:50		-70,5	14.4 ± 0.7	-9,78	7,7
629	Downstream Iskar	JDS72	16.09.2007 09:30		-69,7	13.3 ± 0.7	-9,72	8,1
606	Upstream Olt	JDS73	16.09.2007 13:30		-69,3	14.2 ± 0.7	-9,78	8,9
602	Downstream Olt	JDS75	16.09.2007 18:30		-69,5	14.1 ± 0.7	-9,77	8,7
579	Downstream Turnu Magurele/Nikopol	JDS76	17.09.2007 10:45	5930	-69,4	14.8 ± 0.7	-9,69	8,1
550	Downstream Zimnicea/Svistov	JDS77	17.09.2007 14:45	5740	-69,6	14.7 ± 0.8	-9,70	8,0
532	Downstream Jantra	JDS79	18.09.2007 13:00		-69,8	14.5 ± 0.7	-9,72	8,0
500	Upstream Ruse	JDS80	18.09.2007 17:20		-70,1	15.5 ± 0.8	-9,75	7,9
488	Downstream Ruse/Giurgiu	JDS82	20.09.2007 14:15	6321	-70,5	16.4 ± 0.8	-9,86	8,4
434	Upstream Arges	JDS83	21.09.2007 08:00		-70,2	14.1 ± 0.7	-9,81	8,3
429	Downstream Arges, Oltenita	JDS85	21.09.2007 13:10	6420	-70,5	13.4 ± 0.7	-9,76	7,6
378	Chiciu/Silistra	JDS86	21.09.2007 18:45		-69,9	15.4 ± 0.7	-9,78	8,3
295	Upstream Cernavoda	JDS87	22.09.2007 14:10		-69,6	16.2 ± 0.8	-9,75	8,4
235	Giurgeni	JDS88	23.09.2007 09:30		-69,3	14.3 ± 0.7	-9,76	8,8
167	Braila	JDS89	23.09.2007 13:10	5910	-68,8	39.8 ± 1.7	-9,71	8,9
130	Reni	JDS92	24.09.2007 17:30		-68,6	17.5 ± 0.8	-9,70	9,0
18	Vylkove, Kilia arm	JDS93	25.09.2007 12:50		-67,8	18.6 ± 0.9	-9,64	9,3
0	Sulina, Sulina arm	JDS95	26.09.2007 13:45		-68,8	25.2 ± 1.1	-9,66	8,5
0	Sf. Gheorghe, Sf. Gheorghe arm	JDS96	26.09.2007 17:30		-68,7	22.1 ± 1.0	-9,65	8,5

TABLE 1 CONTINUED

Results of ^{2}H, ^{3}H, and ^{18}O analyses of JDS2 samples from Danube tributaries and calculated ^{2}H excess d.

Mouth rkm	Sampling point	River km	Sample no.	Date of sampling	$\delta^{2}H$ [‰]	^{3}H [TU]	$\delta^{18}O$ [‰]	d [‰]
	Inn, Kirchbichl		148118	16.08.2007	-95,5	7.7 ± 0.5	-13,12	9,5
	Salzach, Salzburg		148133	20.08.2007	-82,2	10.0 ± 0.6	-11,63	10,8
2225	Inn	4,2	JDS6	16.08.2007 21:00	-85,8	8.1 ± 0.5	-11,93	9,6
	March, Angern		148117	16.08.2007	-61,8	27.1 ± 1.3	-7,98	2,0
1880	Morava	0,08	JDS15	21.08.2007 18:30	-57,9	30.7 ± 1.4	-7,69	3,6
	Leitha, Deutschbrodersdorf		148116	26.08.2007	-74,3	8.2 ± 0.5	-10,40	8,9
1794	Moson Danube Arm, end	0,1	JDS19	23.08.2007 18:00	-68,4	9.6 ± 0.5	-9,64	8,7
1766	Vah	0,8	JDS21	24.08.2007 09:15	-69,7	69.2 ± 3.0	-9,88	9,3

TABLE 2

Results of ^{2}H, ^{3}H, and ^{18}O analyses of JDS2 samples from Danube tributaries and calculated ^{2}H excess d.

Mouth rkm	Sampling point	River km	Sample no.	Date of sampling	$\delta^{2}H$ [‰]	^{3}H [TU]	$\delta^{18}O$ [‰]	d [‰]
1716	Hron	0,5	JDS24	25.08.2007 12:30	-62,8	256 ± 11	-9,20	10,8
1708	Ipoly	0,7	JDS25	25.08.2007 14:15	-55,7	7.6 ± 0.4	-7,71	6,0
	Rackeve Danube arm	Start	JDS31	29.08.2007 12:00	-74,6	18.6 ± 0.9	-10,51	9,5
1586	Rackeve Danube arm	End	JDS34	30.08.2007 10:50	-72,9	37.4 ± 1.6	-10,12	8,1
1497	Sio	1	JDS37	31.08.2007 12:30	-52,6	6.3 ± 0.4	-6,40	-1,4
	Drava, Neubrücke		148138	29.08.2007	-72,9	8.8 ± 0.5	-10,45	10,7
	Mur, Spielfeld		148130	16.08.2007	-75,8	8.9 ± 0.6	-10,66	9,5
	Drava, D. Miholjac	77	JDS-DR1	02.09.2007 17:30	-73,1	8.1 ± 0.4	-10,47	10,7
1379	Drava	1,4	JDS42	02.09.2007 18:00	-73,3	7.8 ± 0.4	-10,45	10,3
	Tisza, Tiszabecs		JDS-TI1	31.08.2007 10:00	-70,2	8.4 ± 0.4	-10,19	11,3
	Tisza, Szolnok		JDS-TI2	31.08.2007 10:30	-64,9	8.0 ± 0.4	-9,41	10,4
	Tisza, Szeged		JDS-TI3	31.08.2007 12:20	-62,7	8.7 ± 0.4	-8,61	6,2
	Tisa, Martonos	152	JDS-TI4	05.09.2007 09:15	-63,5	8.1 ± 0.4	-8,91	7,8
	Tisa, Novi Becej	66	JDS-TI5	05.09.2007 10:15	-62,1	7.9 ± 0.4	-8,66	7,2
	Tisa, Titel	9	JDS-TI6	05.09.2007 10:30	-62,7	8.2 ± 0.4	-8,72	7,1
1215	Tisa	1	JDS49	05.09.2007 10:55	-63,1	8.0 ± 0.5	-8,71	6,6
	Sava, downstream Zupanja	254	JDS-SA1	07.09.2007 08:00	-59,3	134 ± 6	-8,66	10,0
	Sava, Jamena	195	JDS-SA2	07.09.2007 10:00	-60,0	110 ± 5	-8,74	9,9
	Sava, Sremska Mitrovica	136,4	JDS-SA3	07.09.2007 10:05	-63,4	9.9 ± 0.5	-9,38	11,6
	Sava, Usce	62	JDS-SA4	07.09.2007 10:10	-61,3	30.1 ± 1.3	-8,91	10,0
1170	Sava	7	JDS51	07.09.2007 10:15	-61,3	5.9 ± 0.4	-8,99	10,6
	Velika Morava, Varvarin	237,2	JDS-VM1	08.09.2007 10:00	-69,9	7.3 ± 0.4	-10,06	10,6
	Velika Morava, Bagrdan	154,1	JDS-VM2	08.09.2007 10:05	-69,0	6.7 ± 0.4	-9,77	9,2
	Velika Morava, Ljubicevski Most	34,8	JDS-VM3	08.09.2007 10:10	-67,1	7.4 ± 0.4	-9,44	8,4
1103	Velika Morava		JDS56	08.09.2007 10:12	-66,5	7.2 ± 0.4	-9,28	7,7
845	Timok	0,2	JDS66	13.09.2007 20:30	-61,8	7.9 ± 0.4	-8,64	7,3
	Iskar, before reservoir	320	JDS-IS1	15.09.2007 11:00	-70,6	8.6 ± 0.5	-10,47	13,2
	Iskar, Orehovica	17,7	JDS-IS2	15.09.2007 14:00	-59,2	9.0 ± 0.5	-8,85	11,6
637	Iskar	0,3	JDS71	15.09.2007 18:45	-61,5	8.6 ± 0.5	-9,00	10,5
	Olt, upstream Ramnicu Valcea	163	JDS-OL1	16.09.2007 09:10	-68,0	10.1 ± 0.6	-9,95	11,6
	Olt, downstream Slatina	61	JDS-OL2	16.09.2007 09:15	-60,3	10.0 ± 0.6	-8,61	8,6
605	Olt	0,4	JDS74	16.09.2007 16:45	-61,2	9.0 ± 0.5	-8,62	7,8
	Jantra, Yabalka, Gabrovo	131,7	JDS-JA1	18.09.2007 09:00	-67,9	9.1 ± 0.5	-10,38	15,1
	Jantra, Karanci	51,2	JDS-JA2	18.09.2007 10:00	-62,2	10.4 ± 0.5	-8,94	9,3
537	Jantra	1,0	JDS78	18.09.2007 10:50	-62,1	9.2 ± 0.5	-8,75	7,9
	Beli Lom, Pisanec	37	JDS-RL1	20.09.2007 10:15	-63,7	8.0 ± 0.5	-9,14	9,4
	Rusenski Lom, Basarbovo	10	JDS-RL2	20.09.2007 11:30	-64,0	7.9 ± 0.5	-8,90	7,2
498	Rusenski Lom		JDS81	20.09.2007 12:45	-63,7	7.4 ± 0.5	-8,95	7,9
	Arges, upstream Pitesti	234	JDS-AR1	21.09.2007 09:00	-59,2	9.7 ± 0.6	-8,98	12,6
	Arges, upstream Bucharest	121	JDS-AR2	21.09.2007 09:05	-61,4	9.6 ± 0.5	-8,82	9,2
432	Arges		JDS84	21.09.2007 10:00	-61,8	9.5 ± 0.5	-8,72	8,0
154	Siret	1,0	JDS90	23.09.2007 16:00	-59,1	10.3 ± 0.5	-8,50	8,9
	Prut, Ungheni	404	JDS-PR1	23.09.2007 13:00	-61,5	10.3 ± 0.5	-8,75	8,5
	Prut, Bumbata, Leova	220	JDS-PR2	23.09.2007 15:00	-59,7	10.7 ± 0.5	-8,41	7,6
135	Prut	1,0	JDS91	23.09.2007 18:40	-59,6	11.4 ± 0.6	-8,11	5,3
8	Bystroe canal, Kilia arm		JDS94	25.09.2007 09:50	-67,8	30.8 ± 1.4	-9,53	8,4

Table 2 continued

4. Discussion

4.1 Hydrological conditions during the JDS2 sampling period

Low water conditions were prevailing in the Danube during the first half of the JDS2 sampling period, from Ulm (rkm 2600) down to the Iron Gate (about rkm 1000) and also during the sampling campaigns on the largest tributaries, Inn, Drava, Tisa, and Sava (Fig. 6). Heavy storms in the upper Danube Basin on Sept. 5 – 7 led to a high water situation on the upper Danube. The discharge at Vienna (rkm 1491, Fig. 7) increased from about 1500 m^3/s to more than 7000 m^3/s (yearly mean about 1900 m^3/s). The high water wave reached the sampling ships in the region of the Iron Gate. Since the storms did not

affect the lower Danube Basin, Danube discharge downstream of the Iron Gate increased only by a factor slightly more than 2 and showed with 6000 – 7000 m^3/s values in the order of the yearly mean. The high water wave was probably also damped to a certain extent during passing the Iron Gate Danube section with its two reservoirs.

4.2 Stable isotopes (δ^2H, $\delta^{18}O$) in river water

The $\delta^{18}O$ record exhibits three significant changes along the river (Fig. 3): firstly, at the confluence of upper Danube and Inn. The second change is caused by the inflow of the tributaries Tisa and Sava with their higher ^{18}O content. The third significant change in stable isotope ratios in the region of the Iron Gate cannot be attributed to the inflow of tributaries. It is obviously caused by the extreme precipitation event in Central Europe during Sept. 5 – 7, resulting in slightly higher $\delta^{18}O$ values for the Danube between Iron Gate and river mouth. The comparison of the $\delta^{18}O$ values of precipitation event water at Vienna (-9.8 ‰, Sept. 5-7) and the yearly mean values of precipitation at Vienna (2006: -9.7 ‰, 2007: -9.6 ‰) showed that the $\delta^{18}O$ value of the event water lay close to the yearly mean values. Without a prominent differential ^{18}O signal in rain water, there should also be only a minor influence of the high water wave on the $\delta^{18}O$ values of the lower Danube. From Fig. 3 a maximum increase of 0.2 – 0.3 ‰ in $\delta^{18}O$ can be assessed for the JDS2 water samples downstream of the Iron Gate, where the high water wave had reached the sampling ships. Approaching the Danube delta, this amount had probably become even lower because all (relatively small) tributaries of the lower Danube had significantly higher $\delta^{18}O$ values than the Danube and therefore their influence on the $\delta^{18}O$ value of the Danube was reduced by the high water wave. The total increase of 1.2 ‰ in $\delta^{18}O$ between Inn confluence and mouth of the Danube is mainly due to the decreasing influence of alpine runoff contributions and a corresponding increase of lower elevation contributions.

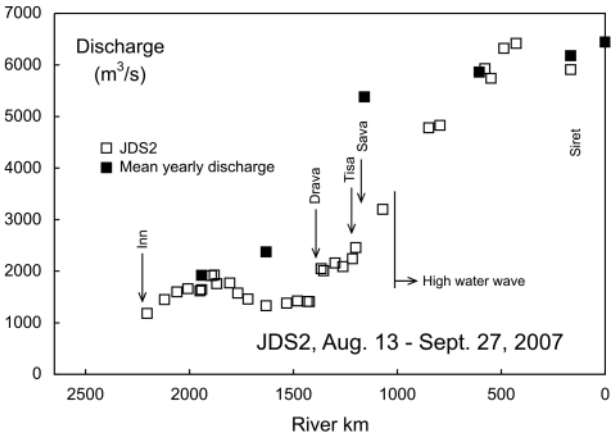

Figure 6: Joint Danube Survey 2 (Aug. 13 – Sept. 27, 2007): discharge at the time of sampling (see Table 1) and some mean yearly discharge values (from László ffy, 1967).

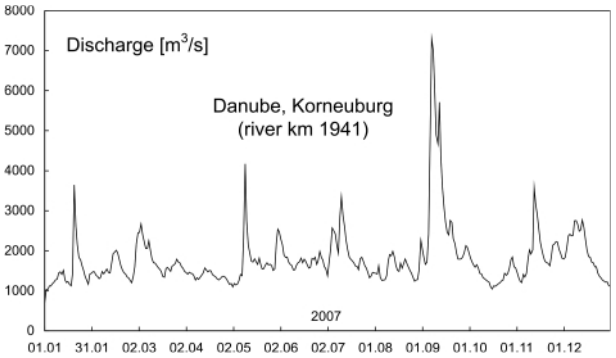

Figure 7: Danube discharge at Korneuburg (upstream of Vienna) 2007 (BMLFUW 2009).

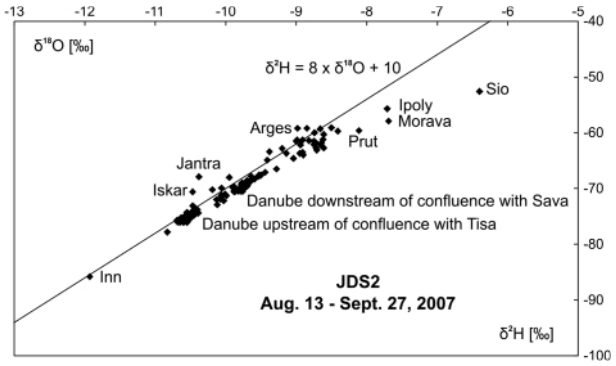

Figure 8: Joint Danube Survey 2 (Aug. 13 – Sept. 27, 2007): δ^2H-$\delta^{18}O$ diagram for river water samples from the Danube Basin.

The δ^2H-$\delta^{18}O$ diagram (Fig. 8) shows that most of the values lie closely to the Global Meteoric Water Line which suggests that surface water evaporation along the Danube river course is minor and may be neglected for the Danube and the majority of tributaries. Only River Sio carries water significantly influenced by evaporation because it contains discharge of Lake Balaton water. The tributaries Ipoly, Morava and Prut show also slightly pronounced evaporation effects, probably due to the existence of reservoirs in the river course. The presence of water influenced by evaporation in those tributaries is identified by the position of the isotopic signal below the meteoric water line (When water undergoes evaporation, the residual water becomes progressively more enriched in ^{18}O than in ^2H and so the isotopic signal does not follow the meteoric water line). Local orographic (mountainous) conditions are probably the reason for the higher deuterium excess values (isotopic signal above the meteoric water line) in the upper sections of the rivers Iskar, Jantra and Arges. Such a dependence of the deuterium excess on the orographic situation was found in the Austrian Alps where mountain and valley precipitation differed significantly in their deuterium excess as consequence of re-evaporation processes (higher d values on mountains, lower d values in valleys; Kaiser et al., 2001; Rank and Papesch, 2005; Froehlich et al., 2008).

The first longitudinal isotope record for the Danube originates from the ship-based scientific excursion organized by the “Internationale Arbeitsgemeinschaft Donauforschung” (IAD, International Association of Danube Research) in March 1988 (Rank et al., 1990). Although the surveys 1988 and 2007 were

performed in different seasons (March and Aug./Sept., respectively), the $\delta^{18}O$ values from both surveys seem to be comparable with each other. Regarding the seasonal $\delta^{18}O$ variation in Danube water, both sampling periods lie outside the typical summer minimum caused by the snowmelt in the high alpine parts of the catchment (Fig. 9). Therefore, we could expect $\delta^{18}O$ values close to the yearly means in both cases.

The comparison of the 1988 data with the data from JDS2 exhibits a significant increase in heavy isotope content during the last 20 years (Fig. 10). Even if we take into account that part of this difference is due to seasonal effects and the influence of precipitation events, the remaining part of the increase is clear evidence for hydrological/climatic changes in the drainage area of the Danube. It is probably mainly the increase of environmental temperature during the last decades which led to an increase of heavy isotope concentration in precipitation in Central Europe, as a consequence of the strong temperature dependence of isotope fractionation during evaporation and condensation processes (Rozanski and Gonfiantini, 1990; Rank and Papesch, 1996, 2001, 2005). This isotopic trend in precipitation is reflected in the long-term $\delta^{18}O$ record of the Danube (significant $\delta^{18}O$ increase during the 1980s, Fig. 11).

The deuterium excess record exhibits relatively uniform d values along the course of the Danube, values lying between 8 and 11 ‰ (Fig. 12). Such values are usually found in precipitation water in Central Europe and are close to d = 10 ‰ which characterizes the Global Meteoric Water Line. There are slight differences between the records of 1988 and 2007 on the lower Danube which may be attributed to the influence of the storm event of Sept. 5 - 7, 2007 in the upper Danube Basin. The difference becomes most pronounced around river km 500 coincident with the discharge maximum of the high water wave. The prevailing isotope characteristics within the storm event seem therefore to be mainly responsible for the differences between the two deuterium excess records. Among all the tributaries investigated, River Sio exhibits the lowest deuterium excess because it bears lake water influenced by strong evaporation effects, as previously mentioned in the discussion of the $\delta^{2}H$-$\delta^{18}O$ diagram. Also the tributaries Morava, Ipoly, Tisa and Prut show significant lower d values than the Danube, probably due to the existence of reservoirs in the river course where the water is exposed to considerable evaporation.

4.3 Tritium(^{3}H) content of river water

River water in most parts of the Danube Basin reflects the actual environmental ^{3}H level of about 10 TU with precipitation as input. The influence of Mediterranean air moisture in some basin parts leads there to slightly lower values. All river water values exceeding about 12 TU should be the consequence of human activities. In most cases these contaminations show short-term character. This can clearly be seen, for instance, from the ^{3}H distribution in the Sava River (Fig. 4) or from the long-term ^{3}H record of the Danube at Vienna (Fig. 11). An example for such a short-term contamination peak is shown in Fig. 13 (Rank et al., 2000). The source for this ^{3}H peak was probably a nuclear power plant (NPP Isar 2) some 400 km upstream of the sampling point. Although the ^{3}H pulse had passed several dams, the half-width of the ^{3}H peak was only about 2 days. On the Rhine River such ^{3}H peaks originating from NPP releases were used for determining travel time and dispersion of contamination pulses (Krause and Mundschenk, 1994).

In some cases it is easy to identify the source of the ^{3}H contamination pulses, like NPP Dukovany for Morava, NPP Bohunice for Vah, NPP Mohovce for Hron, NPP Krško for Sava and NPP Isar 2 for upper Danube. For the lower sections of the Danube, it is more difficult to identify the source because all NPPs upstream of the sampling point are possible candidates. The highest ^{3}H content in the Danube during JDS2, for instance, was found at Braila (40 TU), a single significant higher value between lower concentrations upstream and downstream. The nearest NPP is Cernavodă, some 120 km upstream, but one cannot be sure if this had been the source. In

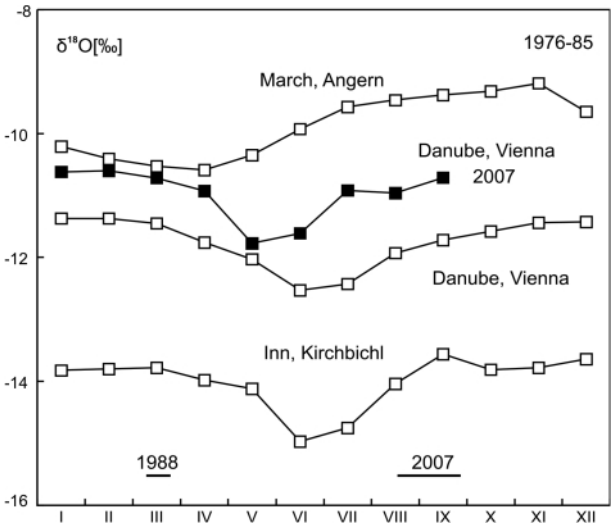

Figure 9: Average seasonal $\delta^{18}O$ variations 1976-85 in Austrian rivers and $\delta^{18}O$ variation in Danube water at Vienna 2007, with indication of sampling periods 1988 and 2007.

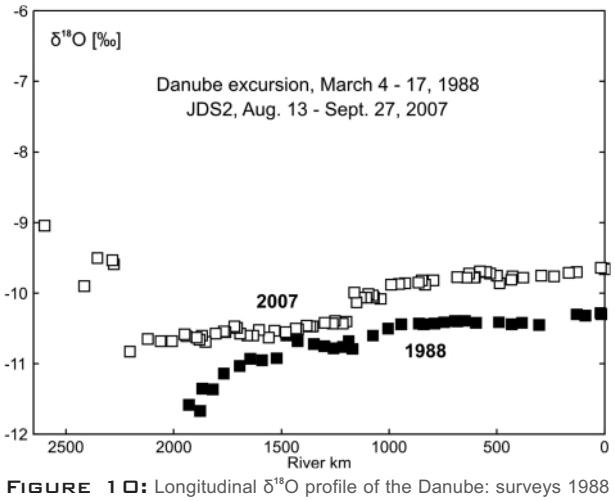

Figure 10: Longitudinal $\delta^{18}O$ profile of the Danube: surveys 1988 and 2007.

such cases, the identification of the ^3H source requires sampling with good temporal and spatial resolution.

The influence of the storm event of Sept. 5 - 7, 2007, and the following high water wave on the ^3H concentrations in the lower Danube can easily be assessed. The ^3H content of the event water at Vienna (11.2 ± 0.6 TU, precipitation water Sept. 5 - 7, 2007) is similar to the yearly mean value of precipitation at Vienna (2006: 10.2 TU, 2007: 9.3 TU). If one approximately uses 10 TU as concentration of the additional discharge in the lower Danube, a ^3H content of about 60-70 TU can be assessed for the ^3H maximum at Braila (40 TU, Fig. 5) without the additional event water.

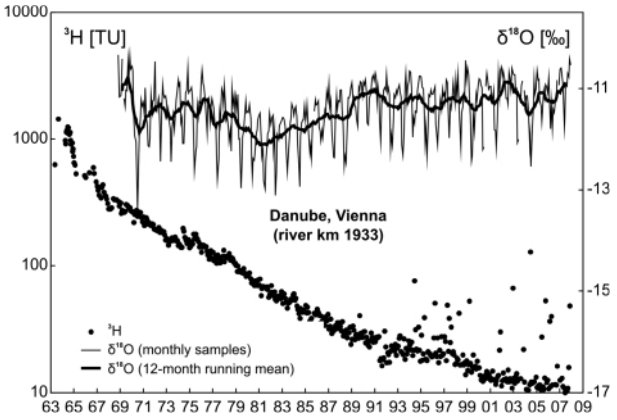

Figure 11: Long-term ^3H (monthly grab samples) and $\delta^{18}O$ (monthly grab samples and 12-month running mean) records of the Danube at Vienna. The sometimes higher ^3H content of Danube water during the last years is probably due to releases from a nuclear power plant some 400 km upstream of Vienna.

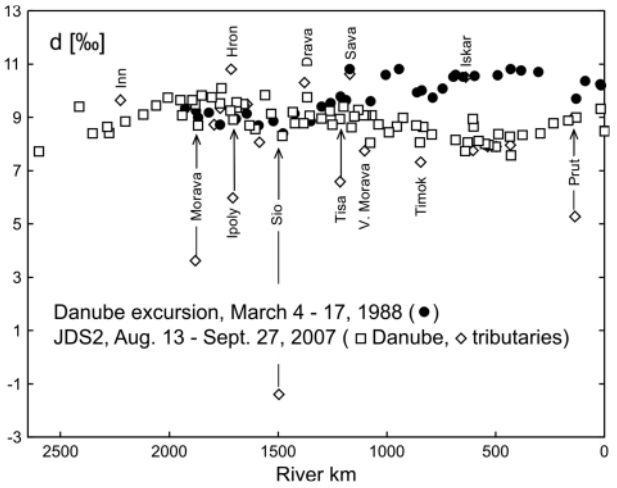

Figure 12: Longitudinal deuterium excess (d) profile of the Danube (1988 and 2007) and d values of tributaries at confluence (2007).

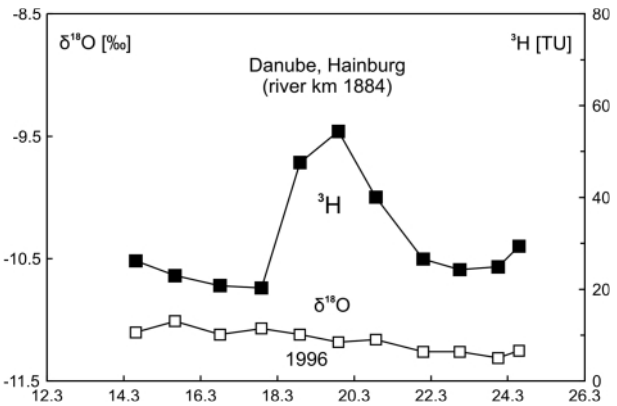

Figure 13: Example for a ^3H contamination pulse in the Danube at Hainburg (rkm 1884), probably the result of a release from a nuclear power plant some 400 km upstream (Rank et al., 2000).

^3H concentrations of river water in 2007 were generally lower than in 1988 (Fig. 14). This reflects the general decrease of the environmental ^3H level (Fig. 11). While in the 1988 record only the inflow of Tisa and Sava, and the higher ^3H concentration in the wastewater plume of the NPP Kozloduj caused significant changes in the ^3H concentration profile of the Danube, the 2007 record exhibits much more quick changes of ^3H concentration in the Danube stream, probably due to the operation of several NPPs along the Danube (Isar 2, Dukovany, Bohunice, Mohovce, Paks, Krško, Kozloduj, and Cernavodă).

5. Outlook

The isotope data set generated from the JDS2 river water samples is a useful basis for isotope hydrological applications. An important actual research trend is the tracing of hydrological processes in the catchment of a river by isotope investigations of river water. The main topic thereby is the formation and age structure of base flow (groundwater contribution to river discharge). The results of this study show that evaporation effects play only a minor role for the isotopic composition of river water in the Danube Basin. Thus isotopic signals in precipitation water are transmitted through the whole catchment and can be used for such basin-wide hydrological research.

A classical application is the investigation of interactions between river water and groundwater, e.g. assessment of the portion of bank filtration water in pumping wells of water supplies. Prerequisite for such applications is a significant differential isotope signal between river and groundwater. Since the Danube stream carries a substantial portion of water from high elevations, this prerequisite is fulfilled for δ^2H and $\delta^{18}O$ values along the whole river course. The distinct difference between $\delta^{18}O$ values of Danube and tributaries from the lower parts of the catchment area is a proof for this.

Different isotope signatures – stable isotope ratios as well as ^3H concentrations – in the main stream and in tributaries enable the investigation of mixing processes of tributary and main stream water. Inn River and upper Danube, for instance, would be ideal candidates for such an investigation, they differ by more than 2 ‰ in $\delta^{18}O$ at their confluence. But also smaller tributaries, which carry ^3H pulses from releases from nuclear power plants, offer good possibilities for mixing studies (Morava, Vah, Hron).

^3H releases from nuclear power plants at the Danube and ist tributaries, as detected in this study, can also be used for stu-

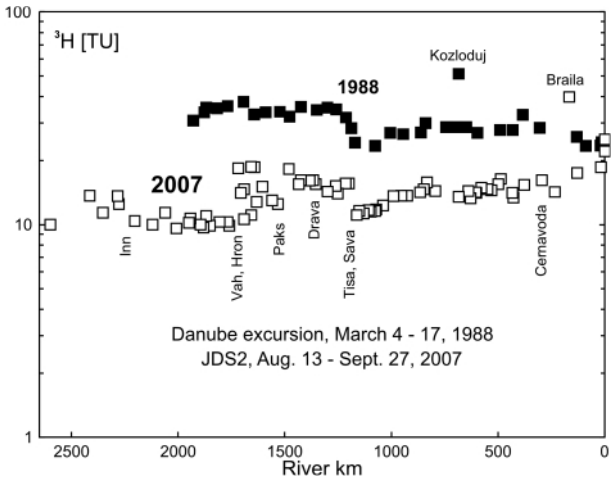

Figure 14: Longitudinal ^{3}H content profile of the Danube: surveys 1988 and 2007.

dying travel time and dispersion of contamination pulses in the Danube. This could be a basis for the development of emergency measures in case of pollution accidents in the catchment area.

Besides the use for hydrological investigations, the JDS2 isotope data set can serve as a base line of isotope data for assessing future impacts within the Danube Basin. This includes hydrological/climatic changes (e.g. temperature changes, change of precipitation distribution) as well as anthropogenic impacts on the hydrological regime (e.g. reservoirs, changes in land use). All these changes will be reflected in the isotopic composition of river water and its temporal behaviour.

Acknowledgements

We would like to thank the members of the JDS2 sampling team on the ships on the Danube and of the national sampling teams on the tributaries for providing us with good quality water samples for isotope analysis, as well as Joachim Heindler and Peter Kostecki for sample analyses.

References

BMLFUW, 2009. Bundesministerium für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft, Abteilung VII/3-Wasserhaushalt (HZB), personal communication.

Craig, H., 1961. Isotopic variations in meteroric waters. Science, 133, 1702-1703.

Froehlich, K., Kralik, M., Papesch, W., Rank, D., Scheifinger, H. and Stichler, W., 2008. Deuterium excess in precipitation of Alpine regions – moisture recycling. Isotopes in Environmental and Health Studies, 44, 61-70.

Kaiser, A., Scheifinger, H., Kralik, M., Papesch, W., Rank, D. and Stichler, W., 2001. Links between meteorological conditions and spatial/temporal variations in long-term isotope records from the Austrian precipitation network, IAEA-CN-80/63, Vienna.

Krause, W. and Mundschenk, H., 1994. Zur Bestimmung von Fließgeschwindigkeiten und longitudinaler Dispersion im Mittel- und Niederrhein mit $^3H^1HO$ als Leitstoff. Deutsche Gewässerkundliche Mitteilungen, 38, 128-143.

Hadžisehović, M., Miljević, N., Šipka, V. and Golobočanin, D., 1992. Environmental tritium of the Danube basin in Yugoslavia. Environmental Pollution, 77, 23-30.

Lászlóffy, W., 1967. Die Hydrographie der Donau (Der Fluss als Lebensraum). In: R. Liepolt (ed.), Limnologie der Donau. E. Schweizerbart´sche Verlagsbuchhandlung, Stuttgart, 16-57.

Miljević, N., Golobočanin, D., Ogrinc, N. and 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.

Mook, W.G., 2000. Environmental Isotopes in the Hydrological Cycle. Technical Documents in Hydrology, 39, Vol. 1, UNESCO, Paris, 280 pp.

Newman, B., Papesch, W., Rank, D. Vitvar, T., Hudcova, H., Aggarwal, P. and Groening, M., 2008. Isotope survey of the Danube. In: International Commission for the Protection of the Danube River, Joint Danube Survey 2, Final Scientific Report. ICPDR, 209-214.

Pawellek, F., Frauenstein, F. and Veizer, J., 2002. Hydrochemistry and isotope geochemistry of the upper Danube River. Geochimica et Cosmochimica Acta, 66, 3839-3854.

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

Rank, D. and Papesch, W., 1996. Die Isotopenverhältnisse im Donauwasser als Indikatoren für Klimaschwankungen im Einzugsgebiet. Limnologische Berichte der 31. Arbeitstagung der Internationalen Arbeitsgemeinschaft Donauforschung, Wissenschaftliche Referate, 1, 521-526, Göd/Vácrátót.

Rank, D. and Papesch, W., 2001. Isotopenverhältnisse im natürlichen Wasserkreislauf – Indikatoren für Klimaänderungen. In: Barbara-Gespräche Payerbach 1998, Geoschule Payerbach, Wien, 241-255.

Rank, D. and Papesch, W., 2005. Isotopic composition of precipitation in Austria in relation to air circulation patterns and climate. In: IAEA, Isotopic composition of precipitation in the Mediterranean Basin in relation to air circulation patterns and climate. IAEA-TECDOC-1453, Vienna, 19-36.

Rank, D., Papesch, W. and Rajner, V., 1990. Tritium(^{3}H)- und Sauerstoff-18(^{18}O)-Gehalt des Donauwassers zur Zeit der Internationalen Donaubereisung 1988. In: Internationale Arbeitsgemeinschaft Donauforschung (ed.), Ergebnisse der Internationalen Donau¬expedition 1988, Wien, 307-312.

Rank, D., Papesch, W., Rajner, V. and Tesch, R., 2000. Kurzzeitige Anstiege der ^{3}H-Konzentration in Donau und March. Limnological Reports der 33. Konferenz der Internationalen Arbeitsgemeinschaft Donauforschung, Osijek, Croatia, 35-40.

Rozanski, K. and Gonfiantini, R., 1990. Isotopes in climatological studies. IAEA Bulletin 32, No. 4, Vienna, 9-15.

Received: 10. March 2009
Accepted: 2. November 2009

Dieter RANK[1)*)], Wolfgang PAPESCH[2)], Gerhard HEISS[2)] & Roland TESCH[2)]

[1)] Center for Earth Sciences, University of Vienna, 1090 Wien, Austria;

[2)] Austrian Institute of Technology - AIT, 2444 Seibersdorf, Austria;

[*)] Corresponding author, dieter.rank@univie.ac.at