Arsenal environmental-isotope laboratories 1964-2010 – more than 45 years production/application/interpretation of basic isotope-hydrological data for Central Europe

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Abstract

The hydrological application of isotope-ratio measurements is based upon variations of ^{2}H, ^{3}H and ^{18}O in the natural water cycle. Main targets of isotope-hydrological projects are the investigation of hydrological relationships, the hydrogeological situation, the residence times of groundwater, and the possible transport of pollutants. Isotope-hydrological data also play an important role in climate research. A good knowledge of the "isotopic environment" is necessary for the interpretation of isotope data. For this purpose, basic isotope data of all parts of the hydrological cycle have been gathered at the Vienna Arsenal for nearly fifty years. The emphasis was on the isotope ratios in precipitation as they represent the input values for isotopic investigations in the terrestrial part of the water cycle. The influence of climatic changes has become observable in the long-term isotope time series of precipitation and surface waters. This influence must also be taken into account when using isotope data from a longer time period in hydrology. Environmental ^{3}H values were around 10 TU in 2010, while slightly higher values can be observed in hydrological systems which still contain significant water portions from the sixties and seventies. Aside from a survey of the development of the "isotopic environment" in the last decades and a few key results, which helped to understand (isotope)hydrological processes, this paper includes some data sets meant for application purposes.

Umweltisotopenlaboratorien im Wiener Arsenal 1964-2010 – mehr als 45 Jahre Produktion/Anwendung/Interpretation von isotopenhydrologischen Basisdaten für Mitteleuropa.

Die hydrologische Anwendung von Isotopenverhältnismessungen beruht auf den in natürlichen Wässern auftretenden Häufigkeitsschwankungen von ^{2}H, ^{3}H und ^{18}O. Wichtigste Zielsetzungen von Isotopenuntersuchungen sind die Erforschung hydrologischer Zusammenhänge, der hydrogeologischen Verhältnisse, der Verweilzeit von Grundwässern und die Abschätzung eines möglichen Schadstofftransportes. Isotopenhydrologische Daten spielen auch eine wichtige Rolle in der Klimaforschung. Notwendig für die Interpretation isotopenhydrologischer Daten ist eine gute Kenntnis der „Isotopenumwelt". Hierzu wurden am Wiener Arsenal mehr als 45 Jahre lang Isotopenbasisdaten aus allen Teilen des natürlichen Wasserkreislaufes für Österreich erhoben. Der Schwerpunkt wurde dabei auf die Isotopenverhältnisse im Niederschlag gelegt, sie stellen die Eingangsgröße für Isotopenuntersuchungen im terrestrischen Teil des Wasserkreislaufes dar. In den langjährigen Messreihen von Niederschlägen und Oberflächenwässern zeichnet sich in den stabilen Isotopen inzwischen deutlich der Einfluss von Klimaänderungen ab, der auch bei der hydrologischen Verwendung von Isotopendaten aus mehrjährigen Zeiträumen zu berücksichtigen ist. Die ^{3}H-Werte lagen 2010 um 10 TU, lediglich in hydrologischen Systemen, die noch größere Wasseranteile aus den 60er und 70er Jahren enthalten, sind die Werte etwas höher. Neben einer Übersicht über die Entwicklung der „Isotopenumwelt" in den letzten Jahrzehnten und einigen Schlüsselresultaten für das Verständnis von (isotopen)hydrologischen Prozessen enthält diese Arbeit einige für den Anwender gedachte Datenzusammenstellungen.
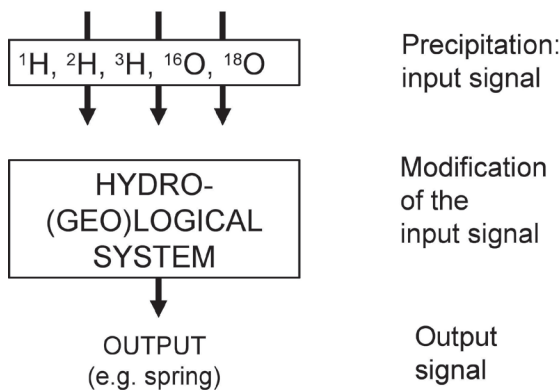
1. Introduction

In 1956, the physicist Johann Mairhofer was charged with the task of looking for applications of radionuclides for economical purposes at the "Bundesversuchs- und Forschungsanstalt Arsenal" (BVFA Arsenal, a federal testing and research institution in Vienna). After some attempts in different working fields (analysis of geological material, abrasion of gears, air exchange rates in railway coaches, etc.), groundwater tracing turned out to be the most promising application, also from the economical point of view. A lot of research work was done on the development of single-well methods for the measure-ment of groundwater flow parameters in the following years. With the purchase of a liquid scintillation counter in 1964, the application of environmental isotopes – primarily ^{3}H at that time – was also included in the hydrological research work (Figure 1). The laboratory work began with the development of an electrolytical enrichment unit for ^{3}H in water (Figure 2). All this occurred in close cooperation with the Isotope Hydrology Section of the IAEA in Vienna.

A monthly routine of precipitation sampling was initiated at various locations in Austria at that time, later on also daily

ISOTOPE HYDROLOGY

^1H, ^2H, ^3H, ^{16}O, ^{18}O

Precipitation:
input signal

HYDRO-
(GEO)LOGICAL
SYSTEM

Modification
of the
input signal

OUTPUT
(e.g. spring)

Output
signal

Methodology:

Comparison of the input and output signal, drawing
conclusions on the properties of the system
(= „dating": origin, age and way of the water)

Figure 1: Principle of the use of isotope measurements for the investigation of hydro(geo)logical systems.

sampling at the Arsenal, and in 1974 the whole ANIP (Austrian Network for Isotopes in Precipitation) with about 80 sampling stations was officially set up in cooperation with Fritjof Bauer from the "Bundesanstalt für Wasserhaushalt in Karstgebieten" (now part of the Environment Agency Austria). A surface water sampling program with about 20 sampling locations in Austria – where water quality was routinely measured by the "Bundesanstalt für Wassergüte" – completed the basic network for isotope measurements in 1976 (Rank, 1993). The whole net-

work has been in operation since that time without major interruptions. All the samples – measured and not measured – are stored in a sample bank. This sample bank allows us to produce up to 30 or 40 years long isotope records for many sampling locations within a few weeks if there is need for it.

Aside from ^3H records, long-term stable isotope records have since also become of interest, not only for hydrological applications but also for the tracing of climatological changes and the interpretation of isotope data in paleoclimatic research. During the nineties, we therefore began to develop a computer-aided environmental isotope data bank, ARIS (ARsenal ISotopes, Figure 3), which was mainly based on the analytical data from the precipitation and surface water sampling network, supplemented by groundwater data from various projects. Due to organizational changes a few years ago, this data base is now administrated by AIT (Austrian Institute of Technology). The isotope laboratories themselves are now also operated by AIT and were moved to Tulln.

A successful work in isotope hydrology was only possible by long-term cooperation with and the help of other institutions. The "Hydrographischer Dienst" and its stations helped us with precipitation-water sampling and providing us with hydro-meteorological data, the "Bundesanstalt für Wassergüte" with surface-water sampling. The IAD (International Association for Danube Research) and the governmental "Wissenschaftlich-Technische Zusammenarbeit" (bilateral cooperation between Austria and several Eastern-European countries) helped us to overcome the Iron Curtain and to cooperate with colleagues from Eastern Europe, especially with VITUKI Budapest. Highlights of this cooperation across the Iron Curtain were the long-term studies to achieve a better knowledge about the water balance of the Neusiedlersee (steppe-lake at the Austrian-Hungarian border, see section 4.2) and the participation in the Danube Expedition 1988, which allowed us, for the first time, to set up an isotope-hydrological survey for the whole Danube River.

For decades, the cooperation of several Central-European institutes within the International Association of Tracer Hydrology (ATH), a loose non-institutional cooperation, was important for the progress in tracer hydrology in Central Europe – including environmental-isotope methods. The ATH carried out several comparative studies to check the applicability and the reliability of tracers under different regional conditions.
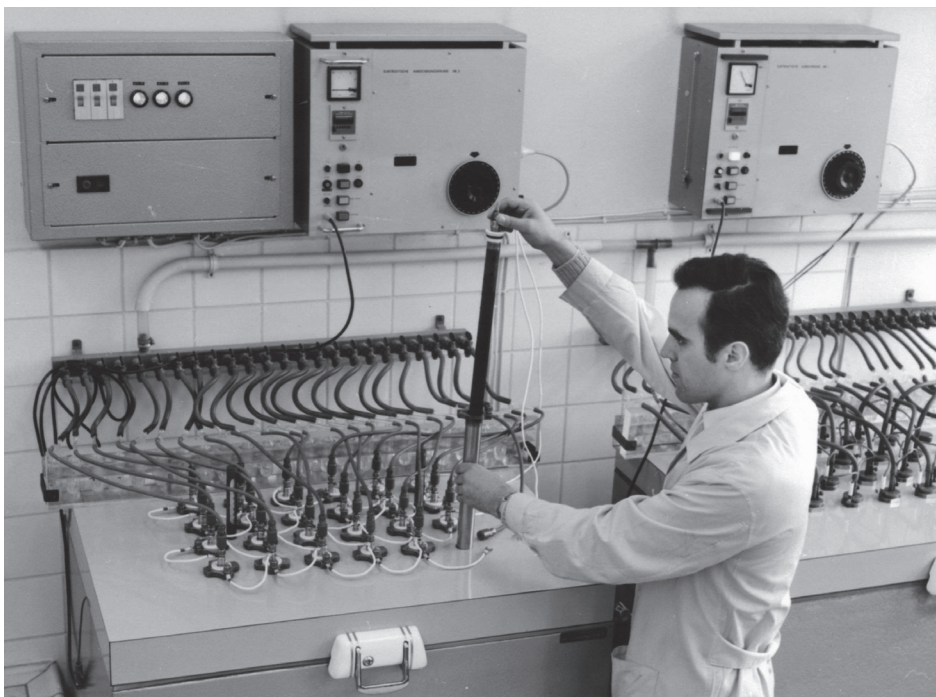

Figure 2: Former Arsenal ^3H laboratory in Vienna: electrolytic ^3H enrichment in water samples (electrolysis cell, cathode, cooling box, and control unit).
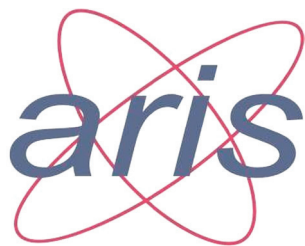
Figure 3: The ARsenal ISotope data base comprises about 200.000 isotope values (^{2}H, ^{3}H, ^{18}O, and ^{14}C) of water samples from the Austrian precipitation and surface water sampling network, as well as from various national and international projects of more than 40 years. This data base is now administrated by AIT.
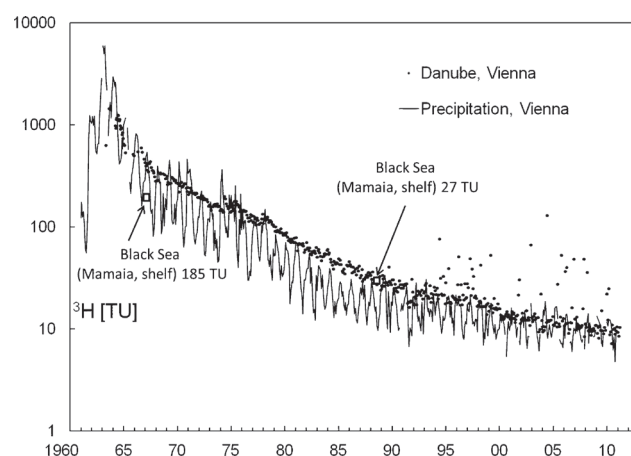

Figure 4: Passage of the nuclear-weapon test ^{3}H through the Upper Danube Basin: ^{3}H time series of precipitation (monthly mean values) and Danube (monthly grab samples) at Vienna. The sometimes higher ^{3}H content of Danube water since the 1990s is due to short-term releases from a nuclear power plant some 400 km upstream of Vienna. Figure 6 shows an example of such a ^{3}H pulse.

New tracing techniques and evaluation methods were developed and approved under field conditions since 1966. Such investigations were performed in the Eastern-Alpine area of Austria (1966), in the Swabian Alb of South Germany (1967-1969), in the Dinaric Karst of Northern former Yugoslavia (Slovenia, 1972-1975, 1993-1997), in the Jura and Alpine mountain regions of Switzerland (1977-1981), in the Northeastern Peloponnesus of Greece (1982-1986), and in the southern Black Forest of South Germany (1987-1992). A lot of research institutes from different countries participated in one or more of these investigation periods and, in this way, created a well experienced scientific network. There was a closer cooperation for decades between the Arsenal laboratories and the "Bundesanstalt für Wasserhaushalt von Karstgebieten", Vienna (now part of the Environment Agency Austria), the "Institut für Hydraulik, Gewässerkunde und Wasserwirtschaft" (Technical University of Vienna), the "Institut für Radiohydrometrie der GSF", Neuherberg (now Helmholtz Zentrum München, German Research Center for Environmental Health, Institute of Groundwater Ecology), the "Vereinigung für Hydrogeologische Forschungen", Graz

(now part of Joanneum Research), and, of course, the Isotope Hydrology Section of the IAEA, Vienna.

Last but not least, we appreciate the long-term support and encouragement of Prof. Erich Schroll, the former head of the "Geotechnisches Institut" in the BVFA Arsenal, during the "pioneer" phase of the isotope laboratories.

Basics of isotope hydrology can be found e.g. in Moser and Rauert (1980) or Mook (2000), and are thus not discussed in this paper. Stable isotope measurements were performed using isotope mass spectrometers equipped with automatic equilibration lines. All results are reported as relative abundance (δ^2H and δ^{18}O, respectively) of the isotopes ^{2}H and ^{18}O in permil (‰) with respect to the international standard VSMOW (Vienna Standard Mean Ocean Water). The accuracy of δ^2H and δ^{18}O measurements is better than ± 1.0 ‰ and ± 0.1 ‰, respectively. – The samples for ^{3}H measurement were electrolytically enriched and analyzed using low-level liquid scintillation counting (precision ± 5 %, 1 TU = 0.119 Bq/kg for water).

2. Long-Term Isotope-Hydrological Records

The impetus for developing isotope-hydrological methods and their use in hydrological applications came from the marking of the atmosphere – and as a consequence of precipitation water – with ^{3}H by the nuclear-weapon tests in the fifties and early sixties (^{3}H maximum in 1963). This ^{3}H pulse (Figure 4) has gone through all hydrological systems. A good knowledge of the input values is necessary for the hydrological applications (Figure 1), so the establishment of a national precipitation sampling network was the first presupposition. The Austrian Network for Isotopes in Precipitation (ANIP) was founded in 1972 (officially 1974). At some stations samples had already been taken since the 1960s. At the same time the IAEA established the GNIP (Global Network of Isotopes in Precipitation). About 70 stations ranging from 120 to 2250 m in altitude are presently in operation all over Austria with some preference given to the karst areas north and south of the Alpine mountain range (Figure 5 shows a map of the stations mentioned in this paper). Precipitation water is collected on a daily basis in ombrometers (500 cm²) and mixed to monthly samples. All samples not measured immediately are stored in 1 L bottles in special cellar rooms and are available for analysis in the future. The aim of ANIP is to provide input data for hydrological and hydrogeological investigations and a data-base for climatological research. ANIP has been integrated in the "Gewässerzustandsüberwachungsverordung-GZÜV" of the Austrian Federal Ministry of Agriculture, Forestry, Environment and Water Management since 2006 and the Environment Agency Austria is at present responsible for ANIP (ANIP, 2015; Kralik et al., 2003). Germany (Stumpp et al., 2014) and Switzerland (Schürch et al., 2003) have also been operating national isotope networks since many years. Some isotope-hydrological time-series of selected stations, but not routine networks, also exist from other neighboring countries in Central Europe.

The amount of precipitation in Austria is influenced significantly by the Alpine mountain range (400-3000 mm/a). The
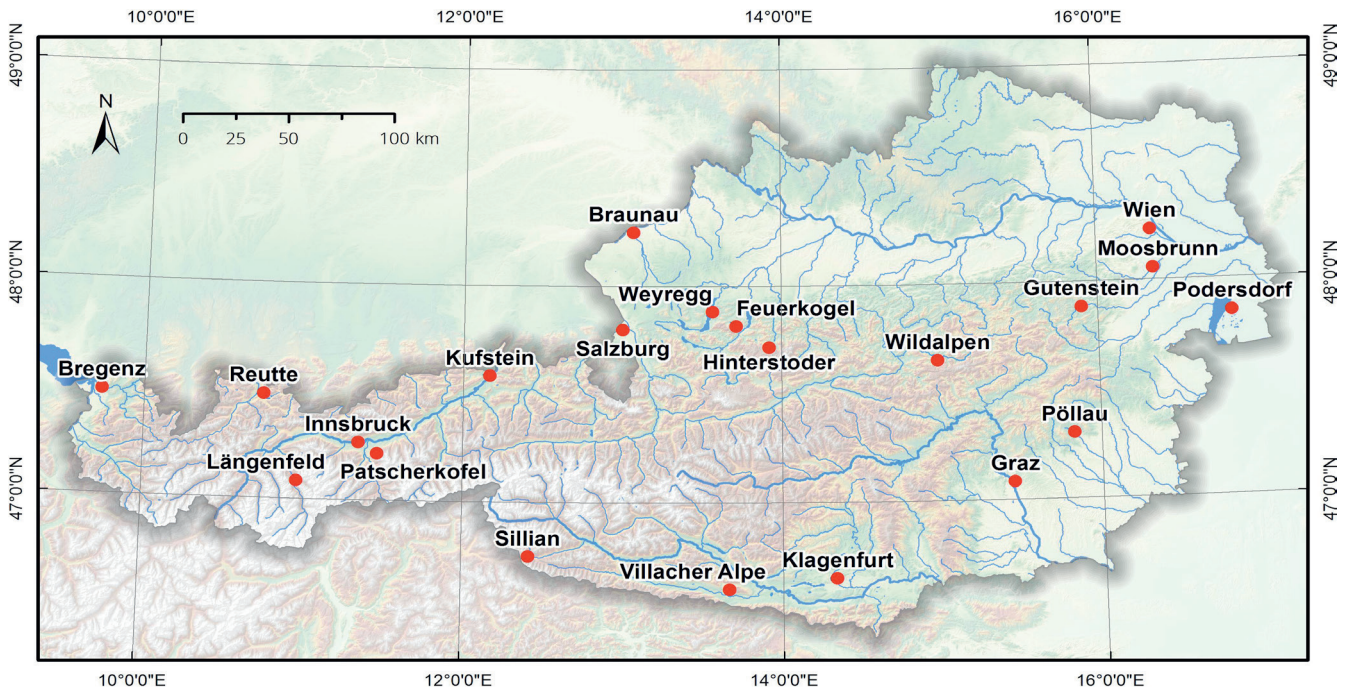
Figure 5: Selected sampling stations of the Austrian precipitation network which are mentioned in this paper.
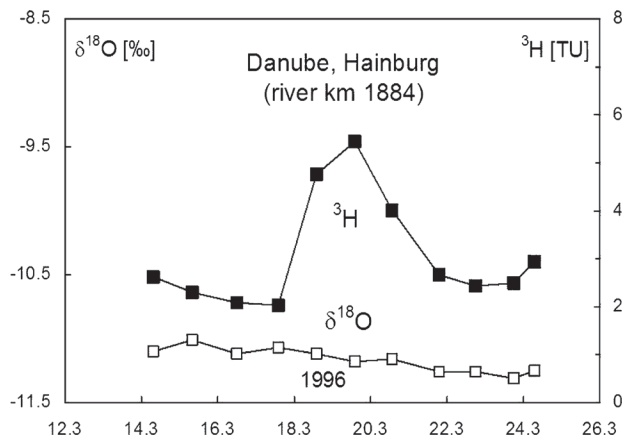

Figure 6: Example for a ³H contamination pulse in the Danube at Hainburg (river km 1884), probably the result of a ³H release from a nuclear power plant some 400 km upstream (Rank et al., 2000).

Figure 7: Passage of the nuclear-weapon test ³H through the groundwater body of the "Mitterndorfer Senke" (Southern Vienna Basin): ³H time series of precipitation water from Gloggnitz (annual mean values), completed with values from precipitation stations Ottawa (1960) and Wien Hohe Warte (1961-1964), and ³H values of the Fischa-Dagnitz-Quelle (spring), completed with data from Davis et al. 1967. The high ³H values in the early sixties are probably a consequence of local infiltration in the surrounding of the spring (dashed ellipse, see section 4.3).

amount of annual precipitation increases towards the mountain ranges. Strong regional differences exist between the windward and the lee side of the Alpine ranges. The Alps act as a weather divide and sharply distinguish precipitation events caused by different air flow directions. They are therefore a unique platform to study the origin of precipitating air masses and possible trends in air flow and precipitation patterns.

As mentioned before, the bomb tritium has been a tracer in all hydrological systems, in groundwaters (Figure 7) as well as in surface waters (Figure 4). Thereby, the long-term time series of ³H in precipitation served – and still serves – as input data for water-age dating models (Figure 1), the ³H time series of surface and groundwaters as output data (Table 1).

The density of the ANIP had proved to be extremely helpful in investigating local and regional ³H contaminations of preci-
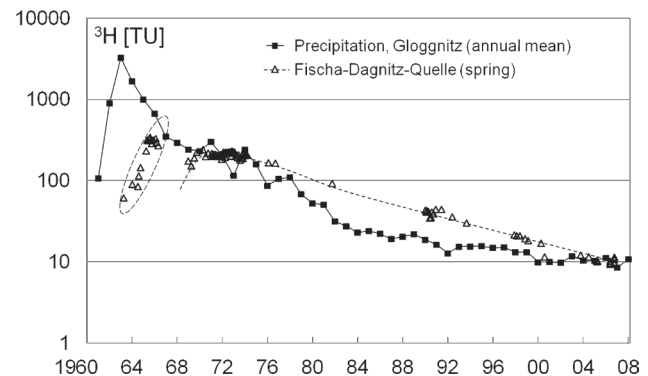
pitation water. Some of the rain samples collected in the Austrian Alps in May 1974, for instance, exhibited unusually high ³H concentrations (Bauer et al., 1975). The complete ³H distribution in precipitation could be reconstructed by analyzing all samples from May 1974 stored in the ANIP water sample bank (Figure 8, maximum at Hinterstoder). The alpine region east of Salzburg, about 20.000 km² in total, was affected. This unusual ³H distribution also offered the opportunity to study the feasibility of tree-ring analysis for detecting short-term effects (Kozák et al., 1993). A retrospective assessment of local environmental ³H contaminations might be required for various reasons, such as the verification of facility moni-

Table 1: ³H time series (yearly mean values from monthly samples) of precipitation (weighted mean) and surface waters in Austria. Precipitation station Villacher Alpe shows about 30 % lower ³H concentrations than Vienna, due to Mediterranean influence. – Values in brackets indicate that sampling did not cover the whole year.

	Precipitation water			Surface water	
year	Wien (Hohe Warte)	Villacher Alpe	Donau (Wien)	Neusiedlersee (Podersdorf)	Bodensee (Bregenz)
1961	(108)	-	-	-	-
1962	(905)	-	-	-	-
1963	(3278)	-	(1036)	-	-
1964	1666	-	(1009)	-	-
1965	(864)	-	(581)	-	-
1966	549	-	(527)	-	-
1967	316	-	378	-	-
1968	219	-	(306)	-	-
1969	236	-	(284)	243	-
1970	187	-	254	-	-
1971	259	181	218	(222)	-
1972	140	103	186	167	-
1973	110	94.5	160	133	-
1974	150	143	159	143	-
1975	142	87.8	157	130	-
1976	92.5	63.9	132	107	(168)
1977	86.1	74.5	115	87.7	144
1978	93.0	79.1	114	97.4	(132)
1979	56.2	45.3	91.1	77.9	119
1980	40.7	32.7	77.1	57.9	97.9
1981	42.8	46.4	66.2	(53.7)	83.6
1982	35.2	23.3	59.2	44.9	(71.9)
1983	28.0	21.2	53.9	36.5	62.2
1984	24.9	18.9	47.2	34.0	56.6
1985	20.8	18.4	(41.2)	(28.7)	(52.4)
1986	20.9	18.3	39.0	26.4	41.9
1987	19.5	15.5	33.1	23.3	38.2
1988	17.8	16.2	30.2	22.9	34.1
1989	26.0	17.1	29.6	22.3	31.4
1990	16.4	13.4	26.5	(21.3)	28.4
1991	16.3	12.3	23.1	18.9	27.2
1992	15.2	10.2	21.0	17.2	25.7
1993	16.5	10.5	22.9	(18.1)	22.5
1994	15.2	12.4	27.9	17.0	21.6
1995	15.4	12.1	21.7	16.0	20.3
1996	15.6	10.7	24.2	(16.1)	20.4
1997	15.8	10.6	26.3	15.5	18.4
1998	13.4	9.5	19.3	13.9	17.9
1999	12.4	10.5	19.4	13.3	15.7
2000	10.6	7.1	13.5	12.1	13.8
2001	12.2	7.5	15.0	11.3	13.1
2002	11.1	8.6	17.3	11.2	12.3
2003	9.6	8.5	13.1	(11.1)	11.4
2004	11.9	8.4	22.0	(10.7)	(11.5)
2005	11.8	8.7	16.3	(10.4)	10.3
2006	9.9	7.8	19.7	(10.8)	9.6
2007	9.3	8.1	14.3	(9.5)	9.0
2008	9.8	6.6	12.1	(9.3)	8.7
2009	10.4	7.5	10.2	(9.8)	8.3
2010	10.9	7.7	12.0	(9.8)	8.4

toring records or due to a lack of data. Tree-ring analysis is a possible candidate, since cellulose-bound ³H well reflects environmental levels and trees can usually be found in many areas. Data evaluation revealed a significant increase of the ³H concentration in 1974 tree rings in the exposed area (Figure 9), but the tree-ring values are probably not representative enough to serve as input data for isotope-hydrological modeling (e.g. influence of the vegetation period).

Tables 2 and 3 summarize basic data of some stations of the ANIP. The δ¹⁸O time series of the stations of the Austrian precipitation network show significant but not uniform long-term trends. While the 10-year running mean of some mountain stations exhibit a pronounced increase in δ¹⁸O of about 1 ‰ during the eighties, the change of δ¹⁸O at the valley stations is much slower (Figure 10). The differences in the δ¹⁸O values of sampling stations at similar altitudes can be explained by the origin of the air moisture. An Atlantic influence (moisture from NW) causes lower δ¹⁸O-values (e.g. Patscherkofel and Bregenz) than a Mediterranean one (e.g. Villacher Alpe and Graz). The main reason for this different ¹⁸O-content is the longer path of the Atlantic air masses over the continent along with the fact that the moisture becomes increasingly depleted in

Sampling station (Bundesland)	Latitude / Longitude (degrees)	Altitude (m asl)	Annual precipitation (mm)***	$\delta^{18}O$ [‰]		^3H [TU]
				1976-1985	2001-2010	2010
Braunau (O)	48.2539 / 13.0767	360	830	-10.62*	-9.35	11.0
Bregenz-Rieden (V)	47.4886 / 9.7364	430	1450	-10.86	-10.11	11.0
Feuerkogel (O)	47.8167 / 13.7239	1598	1767	-12.18	-11.33	11.2
Graz-Universität (St)	47.0769 / 15.4506	366	837	-9.11	-8.49	9.9
Gutenstein (N)	47.8756 / 15.8889	475	922	-10.65	-9.66	10.8
Innsbruck-Flugplatz (T)	47.2589 / 11.3553	577	912	-12.14**	-10.06	10.8
Klagenfurt-Flugplatz (K)	46.6458 / 14.3300	448	899	-10.46	-9.58	7.9
Kufstein(T)	47.5814 / 12.1736	495	1287	-11.65	n.a	11.1
Längenfeld (T)	47.0764 / 10.9700	1180	726	-12.61	-11.44	9.9
Moosbrunn (N)	47.9925 / 16.4519	186	520	-9.59	-9.19	10.4****
Patscherkofel (T)	47.2094 / 11.4617	2245	878	-14.11	n.a.	n.a.
Podersdorf (B)	47.8517 / 16.8431	120	489	-9.44	-8.21	10.4
Reutte (T)	47.4950 / 10.7253	870	1360	-11.77	-10.83	11.2
Salzburg-Flughafen (S)	47.7942 / 13.0017	435	1169	-10.57	-9.69	10.9
Sillian (T)	46.7458 / 12.4083	1075	1003	-11.55	n.a.	7.6
Villacher Alpe (K)	46.6036 / 13.6747	2135	1353	-11.39	-10.56	7.7
Weyregg (O)	47.8900 / 13.5719	469	---	-10.99	n.a.	11.1
Wien, Hohe-Warte (W)	48.2358 / 16.3519	203	609	-10.47	-9.37	10.9
Wildalpen (St)	47.6550 / 14.9817	610	1410	-11.61	-10.66	10.3

* 1978 – 1987, ** Innsbruck Universität, *** Long period average, **** 2008, n.a. not available

Table 2: Average $\delta^{18}O$ values (1976-1985 and 2001-2010) and mean ^3H content (2010) of some precipitation sampling stations in Austria.

	$\delta^{18}O$ (‰) 10-year mean 2001-2010												
Precipitation/surface water station	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	year
Wien Hohe Warte	-11.76	-13.01	-12.04	-9.17	-7.57	-6.45	-6.13	-7.36	-8.75	-10.88	-12.01	-13.52	-9.33
Villacher Alpe	-13.66	-13.60	-12.16	-10.56	-8.66	-8.10	-7.89	-8.78	-10.66	-10.59	-13.14	-14.34	-10.58
Donau Wien	-10.78	-10.88	-10.96	-11.10	-11.71	-11.70	-11.50	-11.14	-10.93	-10.89	-10.81	-10.91	-11.11
Neusiedlersee Podersdorf	-3.89	-3.74	-4.01	-3.80	-3.37	-2.28	-1.52	-1.24	-1.28	-1.61	-2.15	-2.95	-2.65
Bodensee Bregenz	-11.46	-11.48	-11.52	-11.60	-11.62	-11.63	-11.42	-11.19	-11.04	-11.17	-11.53	-11.45	-11.43

Table 3: Examples for $\delta^{18}O$ seasonality in precipitation (Vienna, Villacher Alpe: mountain station with Mediterranean influence), river (Danube) and lake water (Bodensee: recharge mainly by the alpine section of River Rhein; Neusiedlersee: shallow steppe lake) in Central Europe (10-year average values 2001-2010).

heavy isotopes due to successive rainout (continental effect).

The stable isotope variations in precipitation are a consequence of the isotope effects accompanying each step of the water cycle. The long-term stable-isotope records show a good correlation between fluctuations of isotope ratios in precipitation and surface air temperature, but also other influences such as changes in precipitation mechanisms are reflected (Figure 11, Rozanski and Gonfiantini, 1990; Rank and Papesch, 2005). The fluctuations of the ^{18}O-content of precipitation also correlate to a large extent with those of the North Atlantic Oscillation (NAO) index except during some years in which the influence of the amount of precipitation probably dominates the rain formation mechanisms (Kaiser et al., 2001).

The isotope input signal is damped in rivers (Figure 12).

Moreover, alpine rivers are characterized by a sharp $\delta^{18}O$ minimum in summer, due to the snowmelt in the mountains (retention of winter precipitation in the snow cover). The ^3H and ^{18}O high-resolution time series of the Danube at Vienna is one of the worldwide longest of a large river (Figures 4 and 13). It demonstrates that not only short-term signals (e. g. seasonal $\delta^{18}O$ variations or ^3H releases from nuclear facilities) but also long-term changes of isotope ratios in precipitation are transmitted through the catchment and can be detected in the river water (see section 4.1). The complete Danube isotope-data set 1963-2005 can be found in Rank et al. (2012).

The long-term changes in the isotopic records of rivers (e.g. increase of $\delta^{18}O$ during the eighties) may help to trace hydro-climatic changes in these areas that would otherwise

be difficult to detect. The main reason for the increase of δ18O during the eighties is probably an increase of the environmental temperature. However, poor snow covers in the drainage areas during some winters and changes in the winter/summer distribution of precipitation also play a certain role for the long-term changes of isotope ratios in rivers.

3. Some Key Results Which Helped To Understand Hydrological And Isotope-Hydrological Processes

3.1 Hydrological events

A prerequisite for successful isotope investigations of single hydrological events are variations in the isotope ratios of the input – the precipitation (Figure 14). The deviation of isotope ratios for single precipitation events from the average yearly course depends on the origin of the humid air masses and on the respective climatic conditions during the precipitation events.

Even within one and the same event, changes in the isotope ratios can be observed over time, and can cover a range in the magnitude of the seasonal variations of the monthly mean values (Figure 15). Therefore, in order to get representative isotope input data, sampling must cover the whole precipitation event.

Assuming an adequate depth of precipitation, the suitability of a single precipitation event for isotope-hydrological investigations increases with the deviation of the isotope ratios in precipitation water from the mean values in the hydrological system under consideration. As a result of seasonal variations in the δ18O value of precipitation, the greatest deviations of the δ18O value of single precipitation events from the mean value of the system can be expected in winter and in summer (Figure 12). Precipitation in Central Europe during the winter often takes the form of snow, and does not directly reach runoff. Mid-summer is therefore the most favorable period for such research.

The daily values do not show any significant correlation with the amount of precipitation. We also did not succeed in establishing simple correlations between isotope ratios in precipitation and weather situations. One reason for these difficulties in the interpretation of the data may be that precipitation events in the Alpine region are often a consequence of the collision of air masses of different origin (Atlantic, Mediterranean, continental, influence of local evaporation). The isotopic composition of
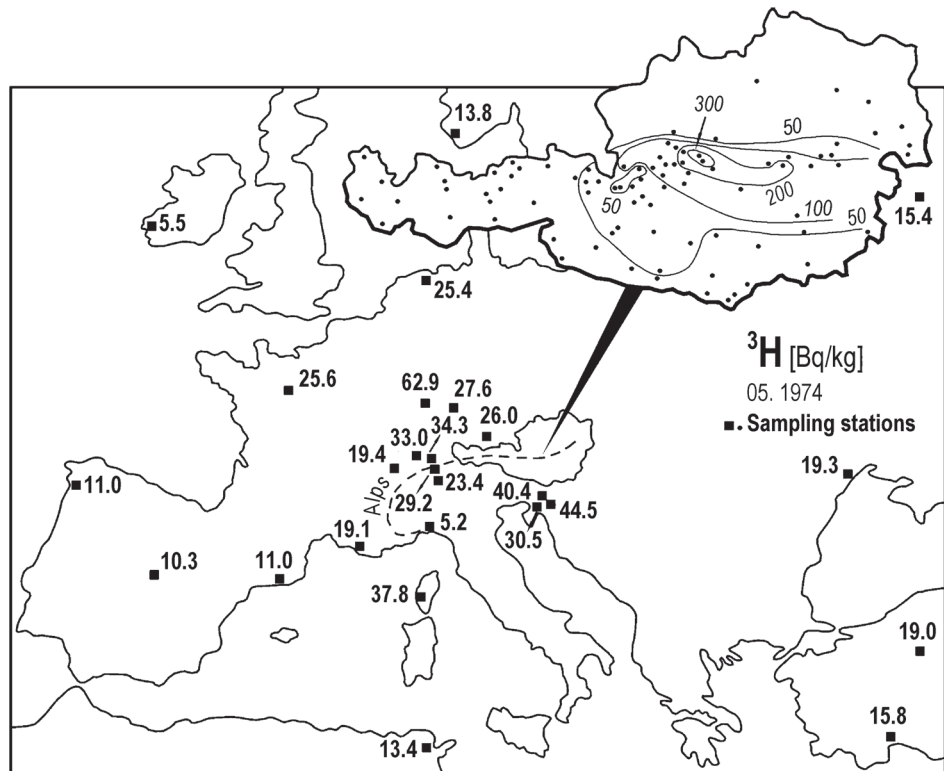

Figure 8: 3H content of precipitation (monthly mean values) in May 1974 in Austria and Europe (Rank and Sas-Hubicki 1984; IAEA/WMO, 2015).1 Bq/kg equals 8.39 TU. The origin of this 3H peak could not be identified, probably a 3H release in Western Europe.
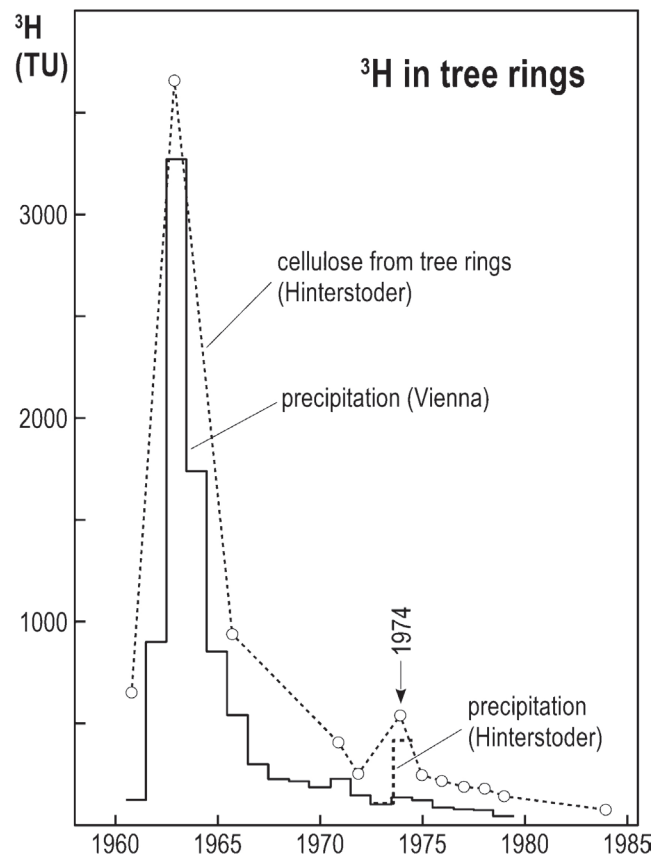

Figure 9: 3H chronology in tree rings: 3H content of cellulose from tree rings at Hinterstoder, indicating the 3H maximum in Hinterstoder precipitation in May 1974.
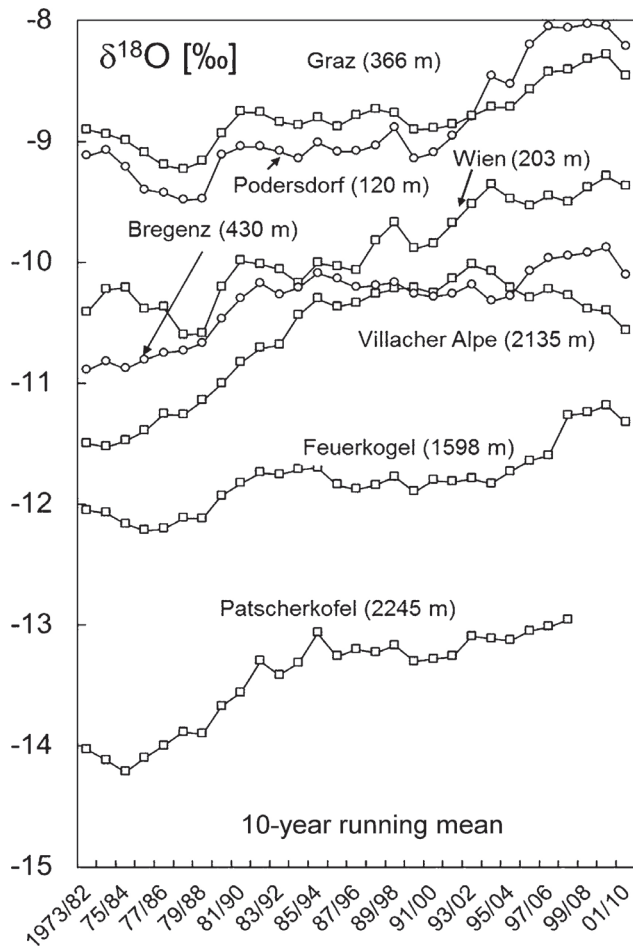
Figure 10: Long-term δ¹⁸O variations (10-year running means) at several stations of the Austrian Network of Isotopes in Precipitation, ANIP (Rank and Papesch, 2005, updated). Mountain stations show lower δ¹⁸O values than valley stations (altitude effect), stations with significant Mediterranean influence (e.g. Villacher Alpe and Graz) higher values than stations with predominant Atlantic influence (e.g. Patscherkofel and Bregenz, continental effect). The general increase of δ¹⁸O values during the last decades is mainly a consequence of the increasing environmental temperature. But also changes in the seasonal distribution of precipitation may play some role (winter precipitation has low, summer precipitation has high δ¹⁸O values). This climatic signal – especially the significant δ¹⁸O increase during the 1980s – is more pronounced in mountain regions.

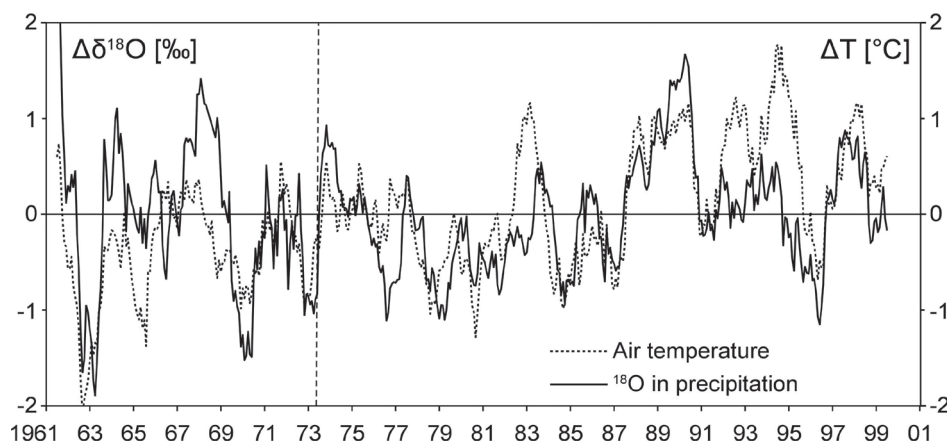precipitation water can also change significantly during such an event, not only due to isotopic effects (e.g. amount effect) but also as a result of a change in the origin of the moisture (see example in Figure 15). So these events cannot be described as easily as the rainout from a passing cloud. For a satisfactory interpretation of the daily data it is necessary to analyze the meteorological conditions during several days before the precipitation event, also including backward-trajectory calculations (Kaiser et al., 2001).

3.2 Insight into a karstic system

The Schneealpe is located some 100 km southwest of Vienna in the Northern Calcareous Alps. This plateau bearing karst massif (90 km²) consists mainly of Triassic limestone and dolomite, with a thickness of up to 1000 m, and with underlying impermeable layers (lower Triassic Werfen Formation, Figure 16). The karst water is used for the water supply of Vienna. In the years 1965-68, a 9.7 km long gallery was driven through this karst massif at the base of the carbonate rock. This gallery allowed, for the first time, the study of hydrological conditions in the depths of an alpine karstic aquifer. The result of hydrological and chemical investigations during the construction of the gallery showed a zonal structure of the aquifer with a core of old water in the depths of its central part (Bauer, 1969; Gattinger, 1973). The ³H results from gallery waters indicate the inhomogeneity of the water flow within the karst massif (Figure 16). There are channels with very high flow velocities directly adjacent to zones containing old water. Isotope data from the period between 1967 and 1990 were used for modelling the flow dynamics in this karst massif (Maloszewski et al., 2002).

The catchment area of the Wasseralmquelle (802 m a.s.l.) is situated in the NE part of the Schneealpe karst massif. The mean annual amount of precipitation in this area is 1.058 mm/a while the mean evaporation loss is 374 mm/a. Calculations from long-term isotope records from the Wasseralmquelle showed that the reservoir water in this karst system has a mean residence time of about 26 years, determined from ³H records, while the short-term component has a transit time of 1.2 months, including retention time in the snow cover (Maloszewski et al., 2002).

For these calculations, the karstic reservoir is approximated by two different parallel flow systems, which provide water from the surface to the karst springs. The first flow system, with a high storage capacity, consists mainly of mobile water in the fissures and quasi-immobile water in the porous matrix. The water enters this system through the whole surface of the catchment area and is collected in the drainage chan-
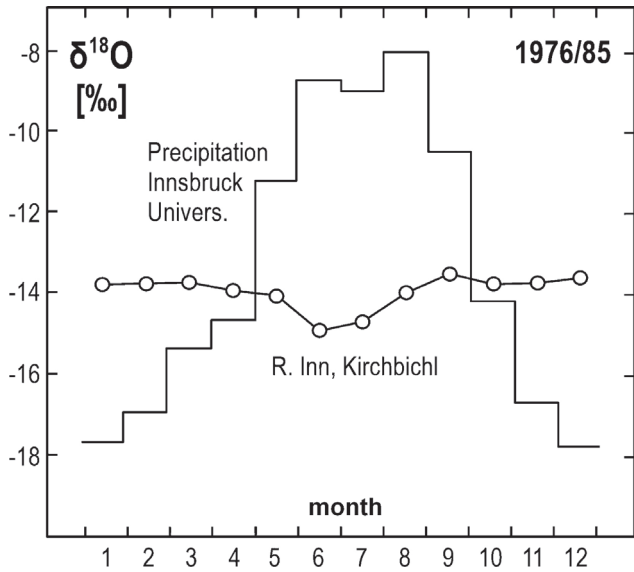

Figure 11: Long-term fluctuations of isotopic composition of precipitation (Δδ ¹⁸O [‰]) and surface air temperature (ΔT [°C]) in Austria. Running 12-month mean of seven meteorological stations (δ¹⁸O up to 1973: data of Vienna, temperature data from Auer et al., 2001).

Figure 12: Typical seasonality of monthly δ¹⁸O values of precipitation and (alpine) rivers in Central Europe (average values 1976-1985; Rank et al., 1990).
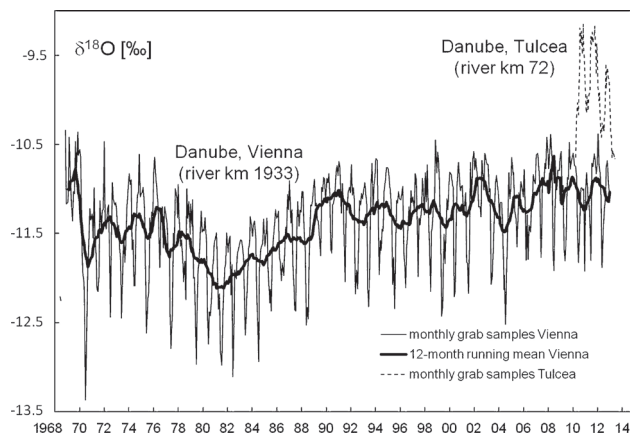

Figure 13: δ¹⁸O time series of the Danube River at Vienna (monthly grab samples, 12-month running average; Rank et al. 2012, updated) and Tulcea.

Figure 14: Pöllau test area: Daily precipitation depth P, δ¹⁸O values of daily precipitation in November 1991 (used in section 3.5).

Figure 15: Variations of δ¹⁸O and deuterium excess in precipitation during a rain event in Vienna (Arsenal), Aug. 6-9, 1985.

Figure 16: Cross-section through the Schneealpe (karst massif in the Eastern Alps). Variations in the ³H content of the karstic aquifer indicate a wide-ranging age distribution of the waters in the karst massif. While the short-term components of the spring waters have mean residence times of a few weeks, some gallery waters are more than 50 years old.

nels connected with the karst springs. These channels separately create a second flow system with a high velocity, a small groundwater volume and a very short mean transit time of the water. This system is connected with sinkholes, which introduce precipitation water directly into this system. As a result, in the karst springs, there is a mixture of two water components: (1) water flowing from the surface through fissured/porous medium to the drainage channels and then to the springs; and (2) water flowing directly from the sinkholes through the drainage channels to the springs. The conceptual model of the water flow in the karstic catchment area of the Wasseralmquelle is shown in Figure 17. This special form of the model for the Wasseralmquelle system also includes some infiltration of water from the channel system into the fissured-porous aquifer, since low precipitation depths (< 20 mm) do not lead to any increase in the discharge at the spring (Steinkellner, 1997). In this case, all precipitation water infiltrates into the fissured-porous matrix.
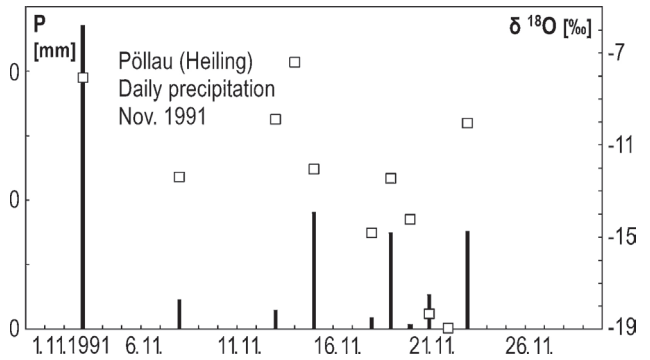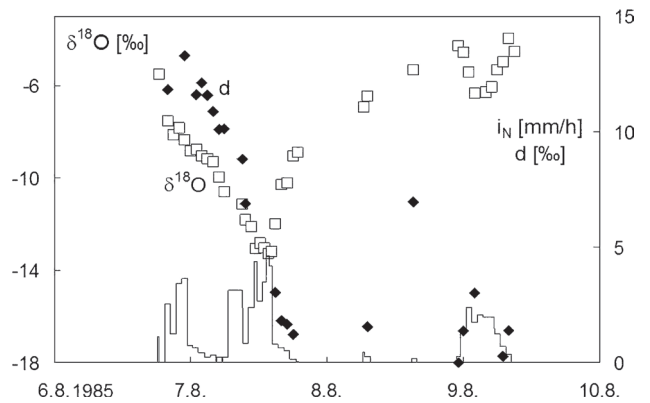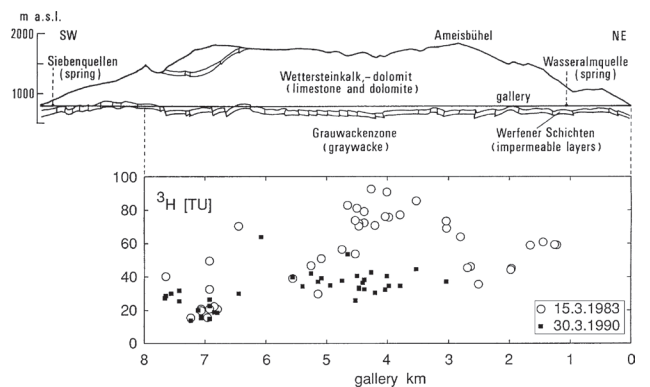
In terms of the isotopic composition, precipitation events may be understood as natural areal tracing experiments. The more the isotopic composition of precipitation water differs from the isotopic signature in the karst system, the more suitable this event is for the investigation of discharge components, provided that the amount of precipitation is not too low (see section 3.1).

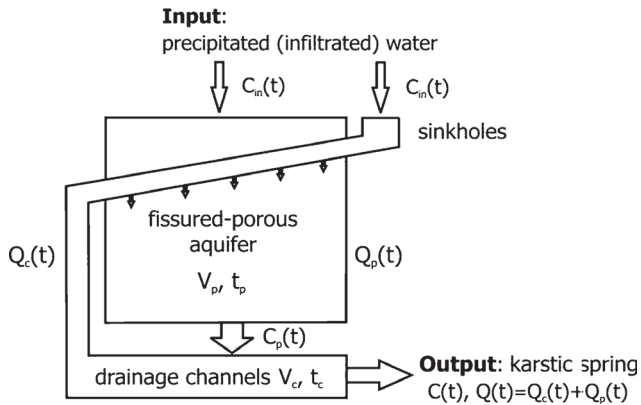An example of such an investigation is shown in Figure 18.

Figure 17: Conceptual model of water flow in the karstic system of the Wasseralmquelle, modified after Maloszewski et al. (2002). C = isotopic concentration, Q = discharge, V = volume, t = (mean residence) time.
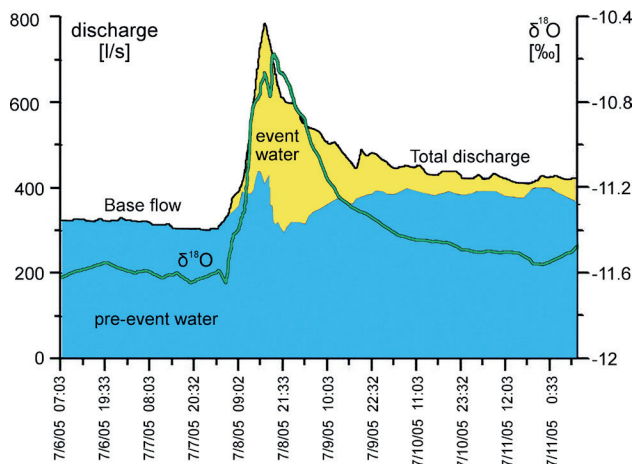

Figure 18: Wasseralmquelle: Separation of discharge components for a precipitation event on the basis of $\delta^{18}O$ data.

Heavy rainfalls during July 7 and 8, 2005, led to a discharge increase from 300 l/s up to 800 l/s. Contemporaneous changes in $\delta^{18}O$ and electrical conductivity showed that event water contributed to the increase in discharge from the beginning. The separation of discharge components yielded a content of up to 50 % event water in the discharge of the Wasseralmquelle during the discharge peak. The increase in base flow (pre-event water) persists after the discharge peak. The karst-water level in the matrix is obviously raised by infiltrated event-water and this leads to a larger base flow component. The results of the separation calculation indicate that about 8 % of the total precipitation water from the drainage area had passed through the spring three days after the precipitation event (Rank et al., 2006).

The discharge of the Wasseramlquelle during hydrological events shows a clear two-component case. Although the base-flow water has a mean residence time of 26 years (calculated from tritium record), event water from precipitation or snow melting appears in the spring after a few hours contemporaneous with the first increase in the discharge. Most of the additional discharge at the beginning consists of event wa-

ter. Apparently, this water reaches the spring through "quick" channels in the karst system.

Based on the isotopes, the electric conductivity and the temperature, the spring waters from the different outlets in the spring galleries have the same origin. This is evidence for a relatively large well mixed karstic reservoir, at least in the vicinity of the spring and when base-flow conditions are prevailing.

The data suggest that the electric conductivity of spring water is probably not a suitable parameter for the separation of short-term discharge components, at least for the Wasseralmquelle. The electric conductivity of the infiltrating precipitation water obviously increases relatively quickly in the karstic system. The calculations using electric conductivity gave unrealistically low short-term discharge components (50 % or more lower than with ^{18}O).

3.3 Water movement in the unsaturated zone during storm events: Preferential flow paths and the role of adhesive water in a sandy soil of the Great Hungarian Plain

Infiltration processes were studied at the lysimeter station Komlos near Kecskemét, in the context of the scientific-technologic cooperation between Austria and Hungary (Blaschke et al., 2000; Rank et al., 2001). Target of the work was a better understanding of the seepage in the sandy soil of the Great Hungarian Plain and the assessment of the groundwater recharge from local precipitation. A further target of the study was the investigation of the role of adhesive water in the water transport.

Storm events were simulated at four cylinder lysimeters (60, 110, 160, and 260 cm deep, surface 1 m²). During the summer and autumn of 1996 and 1997, eight tracing experiments were performed at intervals of approximately one month. Each time, 100 l of traced water were poured onto the top of the lysimeters within a few minutes, thus simulating a storm with a precipitation depth of 10 cm. ^3H, ^{18}O, NaCl and nitrate were used as tracers.

The soil in the investigation area predominantly consists of fine sand with very meager vegetation. Within the area of the lysimeter station there was no vegetation at all, here the top layer was replaced by a 10 cm thick sand layer. Permeabilities of about 2.10^{-4} to 1.10^{-5} m/s were estimated from the grain size distribution. The sand consists mainly of quartz with some carbonate and feldspar. Total porosity amounts to 39 % .

The first tracer experiment with water with low $\delta^{18}O$ (-14.55 ‰) pursued two targets. First the characteristics of the lysimeters should be roughly investigated by applying water with a $\delta^{18}O$ value deviating strongly from that in the lysimeters (~ -8 ‰), so that the main experiment with tritium tracing (2nd experiment) could be exactly calculated. Further, applying ^3H-free water should reduce and homogenize the ^3H content of the water in the lysimeters in order to make the evaluation of the ^3H experiment easier. Additionally, a low ^3H level permits the use of a relatively low ^3H concentration. The
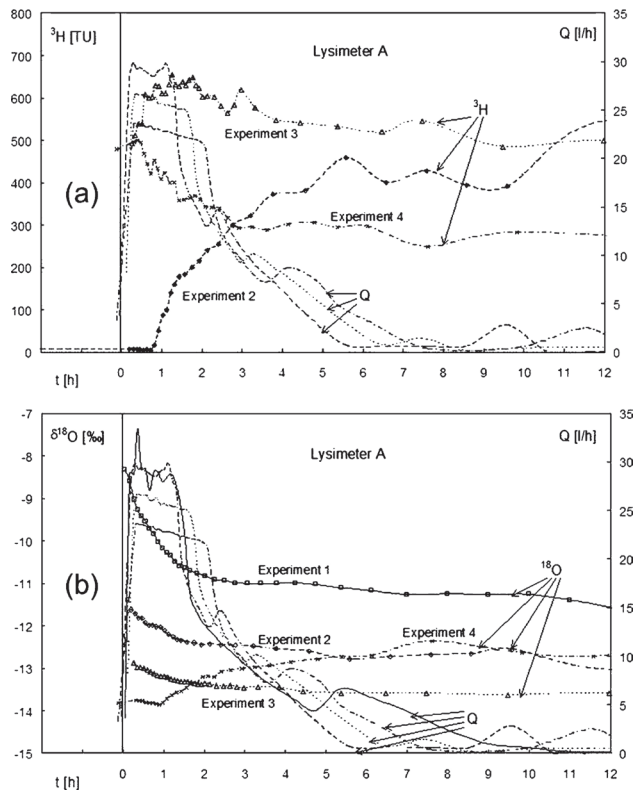
Figure 19: Lysimeter station Komlos (Hungary), Lysimeter A: (a) Experiments 2-4: ³H content in the discharge and discharge hydrograph for the first 12 hours after irrigation. (b) Experiments 1-4: δ¹⁸O in the discharge and discharge hydrograph for the first 12 hours after irrigation (δ¹⁸O of irrigation water: experiments 1-3: -14.55‰, experiment 4: -8.34‰).
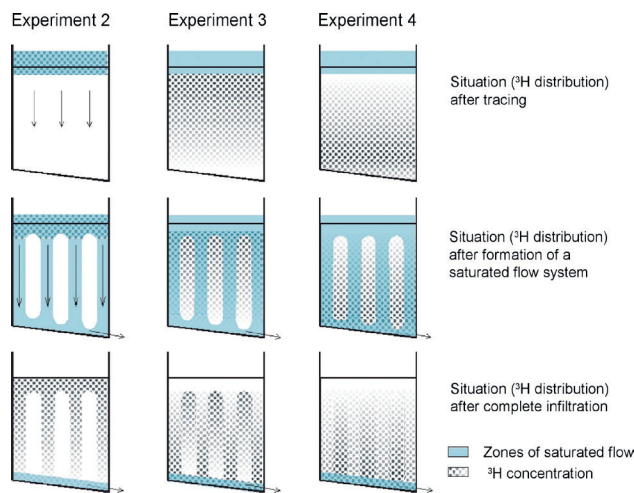

Figure 20: Lysimeter station Komlos: Conceptual model of the formation of preferential flow paths in lysimeter A

most important result from the first experiment was that the seepage water at the bottom of the lysimeters contained a very high portion of former adhesive water. As a consequence, a larger number of experiments than previously planned (2 experiments) had to be conducted in order to achieve a reasonable recovery of the tracer.

Experiment 2 (³H tracing) is to be regarded as main experi-

ment, which additionally permitted a quantitative evaluation. The ³H concentration of the irrigation water was chosen in such a way that it exceeded the previous concentration in the lysimeters by at least a factor of 100. On the other hand, the ³H concentration of the irrigation water should be kept as low as possible to reduce the risk of contaminating the lysimeter site (underground laboratory) and water samples due to inevitable splash-water losses. The ³H content of the water in the lysimeters before the experiment was below or at about 10 TU. About 1500 TU were chosen as the injection concentration, thus allowing the detection of a portion of less than 1 % of the traced water. As base water the same water with low ¹⁸O content was used as in experiment 1. The following experiments served above all to increase the recovery of the injected ³H. Additionally, NaCl (experiment 3) and NO3 (experiment 4) were tested as tracers.

Approximately one month before the start of the experiments the cocks at the base of the lysimeters were opened, so that the seepage water could run out. At the same time the lysimeters were covered with plastic foil to prevent the influence of evaporation and precipitation. The lysimeters remained like this for the entire duration of the investigations. The foils were only removed for a short time to apply the irrigation water at the beginning of each experiment.

The shallowest lysimeter A yielded the most interesting results. Figures 19a and 19b show the discharge hydrographs and the isotope concentration curves from the experiments 2-4 (³H) and 1-4 (¹⁸O), respectively, for the first 12 hours after irrigation. First the slightly inclined plateaus during the maximum discharge are noticeable, which obviously reflect a state of saturation. The inclination corresponds obviously to the decrease of the water level over the lysimeter body, until complete infiltration of the irrigation water into the lysimeter body abruptly ends the state of saturation (end of the plateau) and the discharge rapidly decreases. A closer view on the position of the ³H maxima during the different experiments shows that the maximum is achieved in experiment 2 (³H tracing) at the end of the discharge of the main quantity of water (after approximately 10 h), in experiment 3 – highest value – much earlier (approximately 2 hours after the beginning of the experiment) and that in experiment 4 the ³H maximum moves to the beginning of the experiment (Figure 19a).

A summary of these experimental results leads to the following conceptual model for the water movement in lysimeter A (Figure 20): A saturated zone is formed in the upper part of the lysimeter body after irrigation. Air displaced by the infiltrating water can initially escape through the outlet at the bottom of the lysimeter. With the increase in discharge – a few minutes after the irrigation – a saturated zone is formed also at the bottom of the lysimeter and the remaining air in the lysimeter can no longer escape. Preferential flow paths (Figure 20 center) and a more or less stationary status (plateau of the discharge curves) develop. These preferential flow paths are, however, not to be interpreted as macropores (e.g. wormholes), since the isotope concentration in the discharge indicates a large portion
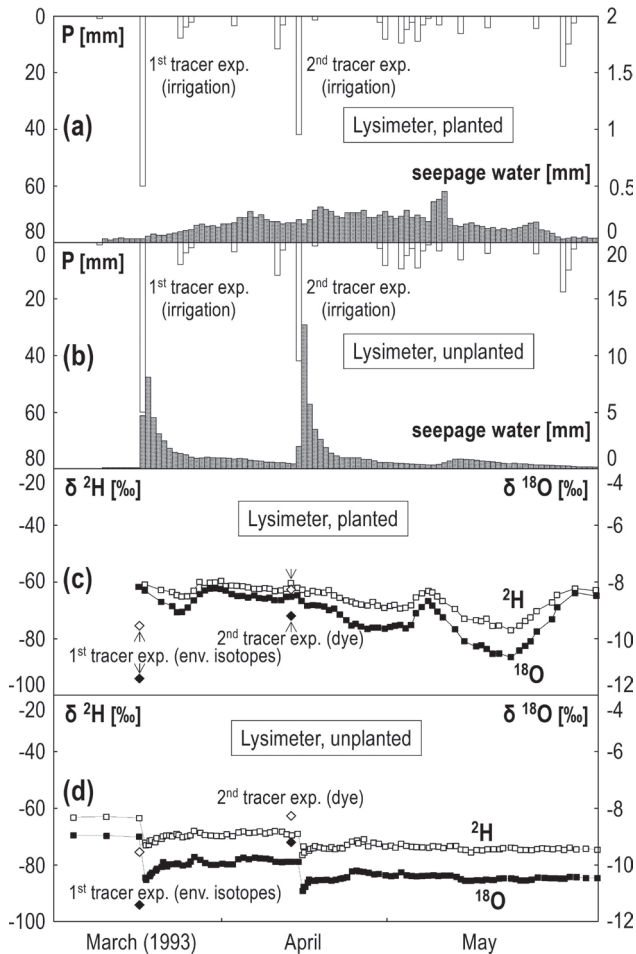
Figure 21: Lysimeter station Wagna (Leibnitzer Feld, Styria): Tracer experiments in 2 lysimeters, one planted, one fallow. Irrigation and precipitation amounts (P) compared to the discharge of the lysimeters tanks, (a) planted, (b) fallow; δ²H and δ¹⁸O values of the discharge, (c) planted, (d) fallow.

of former adhesive water (see e.g. the low ³H content in Figure 19a, experiment 2). This is also confirmed by the relatively small recovery of the traced water after the tracing experiment (13 % after experiment 2). These preferential flow paths are thus to be regarded as part of the matrix (Ritsema et al., 1993), the water movement in these flow paths is again in the form of a front. The seeping water mixes continuously with the adhesive water and a part of the mixture propagates.

The distribution and extent of the dry soil bodies is probably coincidental and might differ between experiments. If one assumes that at the end of the plateau of the discharge curve (= end of the state of saturation) there is still as much water in the lysimeter as is necessary for maintaining saturation conditions, then the volume of the dry bodies in the lysimeter can be estimated from the effective porosity and the cumulative discharge at this time. The residual water mass is approximately 45 l, the effective porosity approximately 15 % (total porosity 39 % , adhesive water 24 %) and the total volume of the lysimeter body approximately 600 l. An air volume of about 45 l results from this, i.e. approximately half – once more, once less – of the usable pore volume remains dry during the sa-

turation phase. The saturation flow in the preferential flow paths breaks down after the complete infiltration of the irrigated water. The entrapped air can again escape and percolation again gradually takes place in the entire cross section of the lysimeter. Thus former adhesive water from the air-filled parts arrives at the discharge and additionally dilutes the water coming from the tracing experiment (reaching the lower part of the lysimeter over the preferential flow paths). This leads to a decrease of the tracer concentration in the discharge, although the major part of the tracer is still in the lysimeter.

The different position of the three maxima in the ³H concentration curve is easy to explain on the basis of these considerations: In experiment 2 (³H tracing) the applied tracer is at the surface of the lysimeter. It will thus take a certain time until a part of the traced water – diluted with former adhesive water – arrives at the outflow over the preferential flow paths. At the beginning of experiment 3 the centre of the ³H plume has shifted downwards, with the highest ³H concentration however within the upper part (Figure 20 top centre). The way to the outlet is shorter and the dilution along the preferential paths smaller, therefore the ³H maximum in the discharge is achieved earlier and is higher than in experiment 2 (Figure 20 centre centre). The ³H free water from experiment 3 already follows on the preferential flow paths. At the beginning of experiment 4 a large part of the injected ³H has already passed the lysimeter and the centre of the ³H plume continues to shift downward. Water with a higher ³H concentration arrives directly at the outlet with the formation of preferential flow paths. In the course of the further experiments the ³H content decreases continuously, since the highest ³H concentrations are found at the bottom of the lysimeter.

Conclusion: Experiments simulating heavy rain events clearly showed the difference between propagation of the wetting front and the movement of individual water molecules in the unsaturated zone of a sandy soil. The discharge largely consists of former adhesive water, which is displaced by the infiltrating rain water. In the case of a contamination of the unsaturated soil zone, this causes a strong – temporary – retention of the dissolved material only by the seepage mechanism, even without adsorption. There is no indication of a typical more-velocities mechanism, which can be found in a more fine-grained soil (macropores, micropores). There is evidence of temporary formation of preferential flow paths in a more or less homogeneous sandy soil after heavy rain events, at least when the depth to water table is small. The reason is not the existence of macro- and micropores, but the distribution pattern of the entrapped soil air. This air cannot escape as long as the water saturation of the uppermost soil layer continues after a rain event.

3.4 Water movement in the unsaturated zone during storm events: Influence of vegetation on the seepage process (lysimeter station Wagna, Styria)

Tracing experiments at the lysimeter station Wagna in a large groundwater field in southern Styria should improve the

knowledge of the solute transport processes on the seepage path through the unsaturated zone (Fank and Harum, 1994). The soil there consists mainly of loamy sands with high field capacities and high permeabilties under saturated conditions. Differences between solute transport and water movement in the unsaturated zone were investigated with the help of stable-isotope tracing, which should bring a detailed description of the seepage process (Rank and Papesch, 1994). One lysimeter was covered with vegetation (rape), the other was fallow after a monoculture of maize. After a winter without snow cover and a long dry period, both lysimeters were irrigated with water of an isotopic composition significantly different from that in the lysimeter tanks (Figure 21, 60 mm in 2 hours). This water had been taken from a mountain lake ($\delta^{18}O$ -11.4‰), about 2.5‰ lower in $\delta^{18}O$ than the water in the tank soil (about 9‰, local precipitation). Local groundwater (-9.19‰, 42 mm) with several chemical tracers was used for the second irrigation on 15 April (Fank and Harum, 1994). Dry weather conditions prevailed throughout the entire investigation period (Figures 21a and 21b, small amounts of precipitation). The amounts of irrigation water corresponded to a normal summer thunderstorm event.

The outflow of seepage water from the lysimeter tanks shows the influence of different cultivation on the infiltration behavior. The outflow of the lysimeter without vegetation is characterized by a quick response after irrigation (Figure 21b) and a pronounced maximum followed by a typical depletion curve during the following dry period until the second tracer experiment. The outflow peak after the second irrigation is even higher, in spite of the lower amount of irrigation, due to the higher saturation of the soil before the experiment. The following decrease in outflow is similar to that after experiment 1. The low $\delta^2H/\delta^{18}O$ signal already appears in the first outflow sample taken one day after irrigation (Figure 21d), the portion of labelled irrigation water is about 2/3. This portion diminishes during the following decrease in outflow to about 50% until experiment 2. After irrigation 2, nearly unmixed water from irrigation 1 is pressed out and the portion of water from experiment 1 remains higher than before irrigation 2. These results correspond to the results of electric conductivity measurements (Fank and Harum, 1994). After the tracing experiment a quick dewatering of a macroporous system occurs, but the bigger part of the irrigation water is stored in the soil. The second irrigation again leads to dewatering of the macropores (piston-flow behavior). Irrigation water of experiment 1, stored in the microporous system, dominates in the outflow also during the following period.

The outflow from the lysimeter covered with vegetation (rape) during the whole winter is significantly lower with a strong damping of the hydrograph, reaching its peak 20 days after the first irrigation experiment. This is due to the high water consumption of the plants and processes of interception and evapotranspiration (Figure 21a). The reaction of the outflow was quicker after the second irrigation experiment, af-

ter 4 days, due to the higher saturation before the irrigation. The interpretation of the isotope record (Figure 21c) is more difficult than for the fallow lysimeter. The most probable scenario is that a small portion of the irrigation water reaches the outflow through preferential flow paths (macropores) after both irrigation experiments in each case, with a minimum in the second half of March and a maximum in the first half of May. Aside from these two peaks, the portion of low $\delta^2H/\delta^{18}O$ water from the first tracing experiment increases continuously to a maximum of 70-80% in the second half of May. Thereafter, water from the second irrigation becomes dominant.

The results of the isotope tracing experiment lead to the conclusion that water is transported mainly through a microporous system in the unsaturated zone. Strongly dependent on vegetation, a more (fallow) or less (covered with vegetation) developed macroporous system becomes effective. In general, the results indicate the propagation of water fronts through the lysimeter body corresponding to piston flow or dispersion models.

3.5 Conceptual runoff model for small catchments in the crystalline border mountains of Styria, as developed from isotope investigations of single hydrological events

Isotope-hydrological investigations in small catchments in the crystalline Styrian border mountains (Eastern Alps, Austria) during storm events showed that a two-component runoff model (direct runoff, base flow) cannot sufficiently explain the course of the runoff isotope data during the events (Rank et al., 2003).

The weathered layer, which covers the slopes of the crystalline hills, is between one and several meters thick. The „Ringkogel" near Hartberg, the slopes of which are the source of numerous small springs (discharge ≤ 1 l/s), was chosen as a test area (Figure 22). Several springs were sampled on a monthly basis for isotope analysis from July 1991 to November 1992 (Figure 23).

Sampling on 21 November 1991 took place after severe storms. Discharge from the springs was higher than usual. In the springs of the crystalline zone, which primarily exude fissure water, there was a significant, short-term rise in $\delta^{18}O$ (Figure 23, springs H9 and H15), while the springs in the Tertiary zone exhibited no $\delta^{18}O$ variation. The mean residence time of the base-flow water of the springs ranged between 7 and 13 years. Although the higher $\delta^{18}O$ value in the Ringkogel springs on 21 November initially suggested that the runoff contained a high amount of water from summer precipitation, which had been stored for several months, the results of the ^3H investigations placed this assumption in question. On November 21st, a common feature of all fracture springs was a significant ^3H minimum (decrease at H9 from 36 to 28 TU, at H15 from 28 to 20 TU), while spring H18 in the Tertiary zone indicated no change in either ^{18}O content, or in ^3H content. Summer precipitation, characterized by the seasonal ^3H maximum, can therefore not be responsible for the raised ^{18}O content on November 21st.
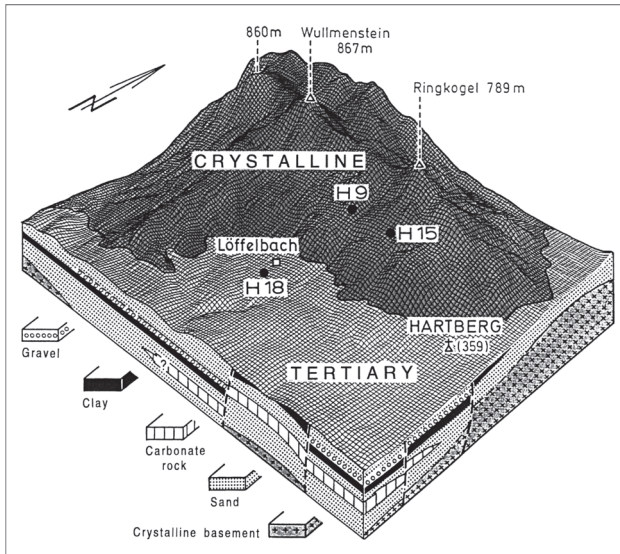
Figure 22: Geological situation in the Ringkogel test area (Häusler, 1995). The shists and gneisses of the Ringkogel crystalline are plunging under the Tertiary series towards the south. The Tertiary is formed by a series of sands, limestones, mudstones and gravels that is quickly changing, both horizontally and vertically (diagram area about 8 km x 6 km).

Figure 23: Ringkogel test area: $\delta^{18}O$, electric conductivity (EC), and discharge (Q) of two fracture springs in the Ringkogel area (H9, H15) and one spring in the Tertiary zone (H18). The fracture springs show a quick, significant increase of the $\delta^{18}O$ value after the storms in November 1991, which cannot be attributed to the direct runoff of precipitation water.

A more precise explanation of the composition of the discharge water on 21 November was provided by a thorough analysis of the input – the precipitation. To facilitate this, attempts were made to reconstruct the hydrological situation in November 1991, utilizing precipitation data from the neighboring Pöllau Basin (Figure 14). On November 4th, the region experienced significant storms (45 mm of precipitation in the Pöllau test area), with a $\delta^{18}O$ value unusually high for this season and a low ^3H content, which corresponded to the usual seasonal values (approximately 5 TU). The rain which fell immediately prior to the sampling had, in contrast, a low $\delta^{18}O$ value, and can therefore be elimi¬nated as a possible cause for the $\delta^{18}O$ maximum in the spring water on 21 November. This precipitation water can therefore have had little, or no, direct influence on the runoff of 21 November.

Apparently, the infiltrating precipitation water from November 4th was primarily stored in the unsaturated zone, raising the moisture content of the soil, but not significant-ly contributing to a short-term rise in the spring discharge. Later on, such water can be mobilized by further storms, quickly reaching springs and/or small creeks.

The electric conductivity of the spring water during the storm period proved not to be very indicative (Figure 23). While the springs H9 and H15 behave similarly with respect to their isotope ratios and discharge, significant differences can be observed in their respective conductivities. For H9, the value is lower, and hardly changes, even during the storm period, while H15, with a higher initial value, exhibits a clear maximum in November 1991. The cause of this behavior could be the influence of agriculture on the weathered layer in the drainage area of H15. Corresponding to the following concep-tual model, during the storm period, the longer path of trans-
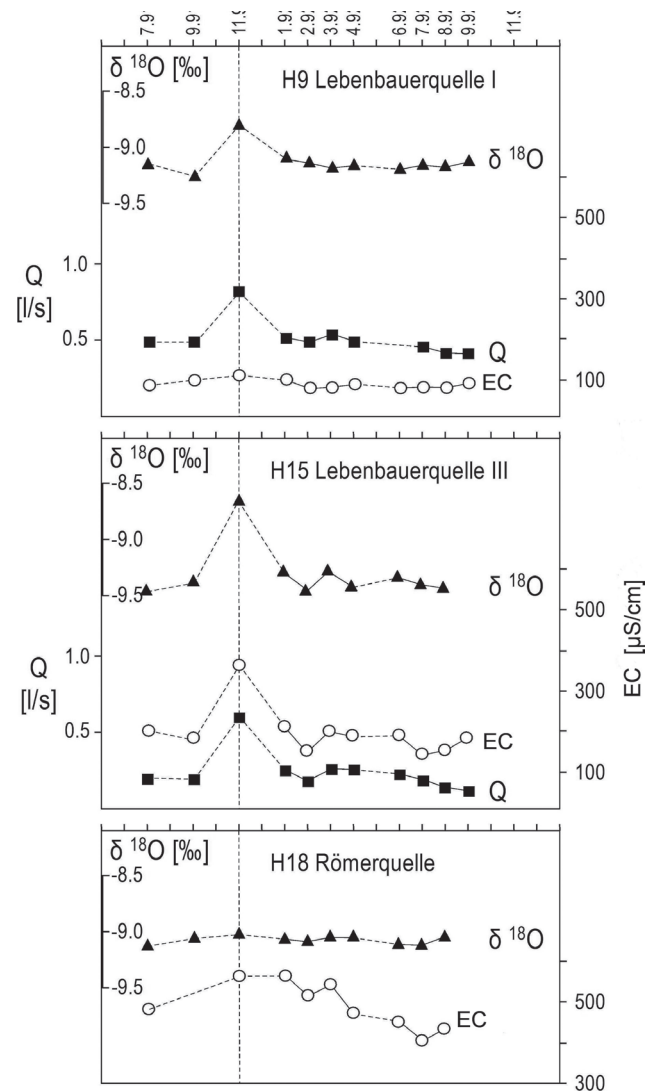
port for the infiltrating precipitation water in the weathered layer probably led to a rise in electric conductivity.

The findings of the isotope investigations in the Ringkogel region point towards a conceptual hydrogeological model of runoff generation during storms in the area of the crystal-line border mountains of eastern Styria. An essential share of the water discharged on 21 November 1991 from the Ring-kogel springs (fracture springs) could be attributed to the storm of 4 November 1991, not to the storms of the previous day. Following a brief storage period, the discharge to the springs of this precipitation water did apparently not occur via the joint aquifer system (mean residence time of the water approximately 10 years), but rather via the otherwise unsa-turated zone of the weathered layer.

Normally, the weathered layer is unsaturated (Figure 24, „Low precipitation rate"). The infiltrating precipitation water
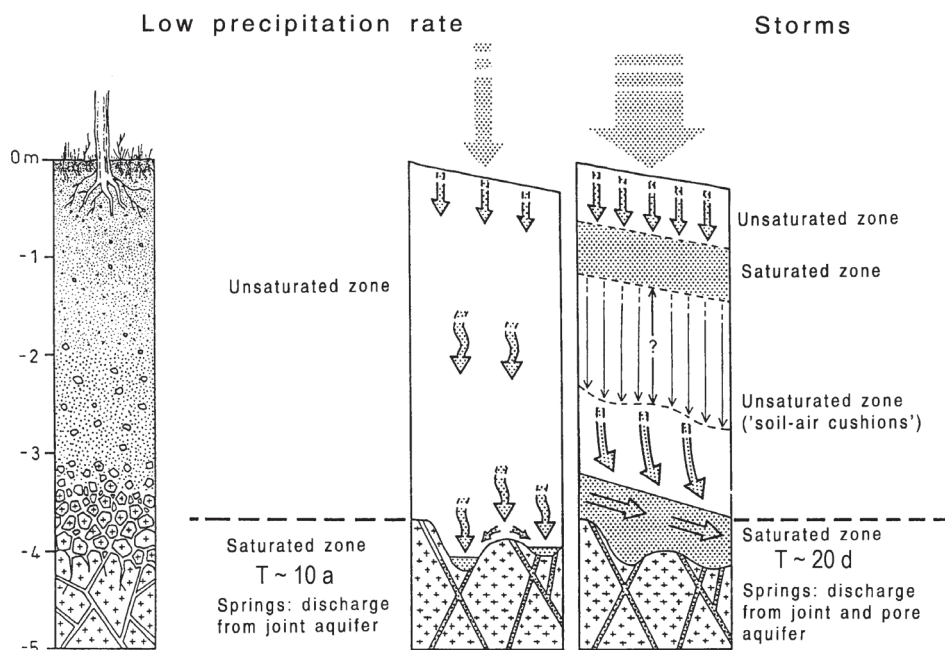
Low precipitation rate

Storms

Figure 24: Conceptual hydrogeological model for the generation of runoff during storm events in the crystalline border mountains of Styria. Normally, the infiltrating water enters the joint aquifer. Provided that the soil moisture is high enough, a saturated zone will be formed above the joint aquifer during storms, and young water will quickly reach the springs and creeks. Thereby, pressure transmission via „soil-air cushions" obviously plays a certain role, also. T = mean residence time.
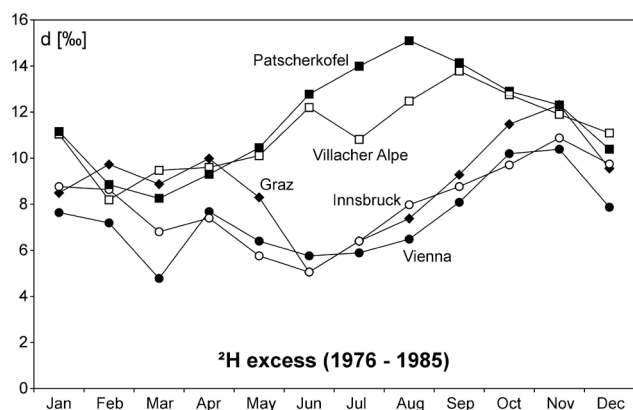

Figure 25: Seasonal variations of deuterium excess (d) in precipitation at different locations and altitudes in Austria (north: Patscherkofel 2245 m asl, Innsbruck 577 m; south: Villacher Alpe 2135 m, Graz 366 m); average values 1976-85.

of 4 November is stored primarily in the unsaturated zone and increases the moisture content of the soil. It does not, however, contribute significantly in the short term to a rise in the discharge from the springs. Under the influence of additional storms (16 and 20 November), a saturated zone developed above the joint aquifer, because the joint aquifer was either full or the infiltrating precipitation water could not seep into the joint aquifer quickly enough (Figure 24, „Storms"). Following the slope, this water quickly reaches the spring area where it mixes with the water of the base flow.

The fact that the runoff of 21 November contained no notable amounts of water from the most recent precipitation event leads to the conclusion that precipitation waters from conse-

cutive storms infiltrate the soil as fronts (Figure 24). Between the fronts, „soil-air cushions" are formed temporarily, which on the one hand prevent the short term mixing of the waters from consecutive storms, while on the other hand, the formation of a saturated zone above the fissured water system is encouraged through pressure transmission, and the water is pressed out towards the springs. The pressure transmission through soil-air cushions also has the effect that, during storm events, the discharge from springs and creeks rises sharply with no notable delay, and a discharge peak develops. Laboratory investigations have confirmed that soil-air cushions can assume such a pressure transmission function (Bergmann et al., 1996).

The finding that discharge peaks during precipitation events are created essentially through the pressing out of water stored underground, and are not primarily attributable to the direct runoff of precipitation water, leads to the conclusion that precipitation water infiltrates the soil to a greater extent than originally assumed.

By the time of the next measurement series in January 1992, the isotope ratios of the majority of the Ringkogel springs had returned to the base-flow values; that is, the springs were again being fed primarily from the joint aquifer (Figure 23).

The results of the observations of this event in the Ringkogel test area lead to the conclusion that, after storm events, water may be pressed out that cannot be attributed to either the base flow before the event (primarily fissure water with a higher residence time) or to the actual precipitation event itself. The fact that the measurement series at the Ringkogel springs by chance took place at a particularly favorable time – greatly varying isotope ratios for consecutive precipitation events – did however enable the origin of this „third" runoff component from the normally unsaturated zone to be determined. Due to the lack of local precipitation data, no quantitative statements as to runoff composition were possible.

3.6 Deuterium excess in the Eastern Alps

Deuterium excess (d = $\delta^2H - 8 * \delta^{18}O$) has widely been used as an additional parameter to identify the source region of water vapour. However, it turns out that a simple relationship cannot be established due to secondary fractionation processes, like snow formation or partial evaporation of raindrops below the cloud base. From the long-term time series
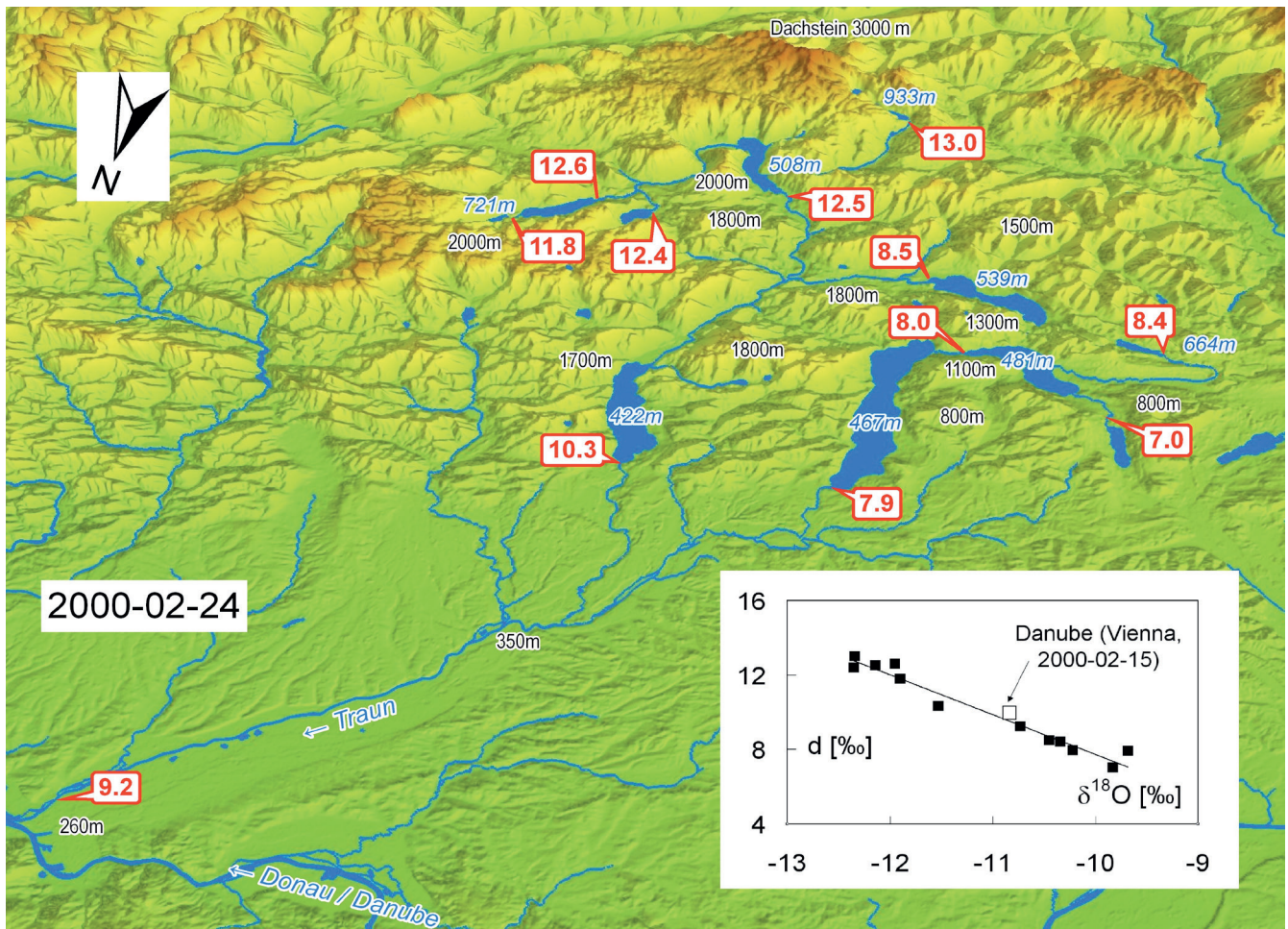
Figure 26: Deuterium excess (red numbers) in alpine lakes of the River Traun system (Upper Austria, diagram area about 150 km x 110 km). Black numbers: elevation asl, blue: elevation of lake surface. Insert: correlation between deuterium excess and δ¹⁸O in lake water.

a significant difference in the behavior of the deuterium excess at mountain (Patscherkofel, Villacher Alpe) and valley stations has been observed (Figure 25). There is a slight increase in the yearly mean of the deuterium excess with increasing altitude of the sampling station, an effect, which has been observed by several authors (e.g. Schotterer et al., 1993; Holko, 1994; Gonfiantini et al., 2001). But moreover, the seasonal pattern of the deuterium excess is quite different. While the valley stations (e.g. Innsbruck) exhibit the expected minimum in summer, the mountain stations show a distinct maximum (ca. 15 ‰) between June and October. This is also the period with the seasonal maximum of precipitation. An unexpected result is that there are no significant differences between the northern and the southern stations, stations with Mediterranean influence like Villacher Alpe and Graz show more or less the same deuterium excess pattern as the northern stations.

These differences occur even if the horizontal distance between the mountain and valley station is only a few kilometers (Figure 25: Patscherkofel and Innsbruck). From this we concluded, that the reason for the lower d-values at the valley stations is obviously evaporation and/or isotopic exchange with air moisture during the falling of the raindrops. Froehlich

et al. (2008) discussed this in detail.

In a further step, it was investigated whether the Mediterranean influence could be the reason for the higher d-values at the mountains. This could be excluded from trajectory studies for two mountain stations (Kaiser et al., 2001). The last step was to look for the response in surface and ground waters. Mountain lakes ("Salzkammergut", River Traun system) seemed to be good investigation objects for this purpose (Figure 26). They are relatively deep, cold, and have a high through flow (mean residence time of a few years) and so evaporation influence on isotope ratios is negligible in most cases. These lakes become well mixed in late winter, so samples from the outflow of the lakes taken at this time deliver more or less yearly mean isotopic values. The measured data showed a clear correlation between δ¹⁸O values and deuterium excess (between 7 and 13 ‰). From this an altitude effect of about 0.43 ‰ per 100 m can be calculated for the deuterium excess (taking into account an altitude effect of -0.25 ‰ per 100 m for δ¹⁸O) (Rank and Papesch, 2005).

This has some consequences for the interpretation of deuterium excess data from mountainous regions in isotope-hydrological applications:

• The relatively big variations of the deuterium excess in precipitation in the Alps (higher values at the mountains, lower

values in the valleys and forelands) are mainly a consequence of the local orographic conditions and not the result of a different origin of the air masses transported into the mountainous region.

• Therefore, in the Alps, the deuterium excess is probably not a reliable tool to trace the origin of air masses and moisture coming from further away. For this purpose – e.g. to distinguish between Atlantic and Mediterranean origin – $\delta^{18}O$ (or $\delta^{2}H$) values and also ^{3}H data are a suitable instrument.

• The water of the rivers coming from mountainous regions is a mixture of mountain and valley precipitation, so that the resulting deuterium excess is more or less "normal" when the river leaves the mountainous region.

3.7 Environmental-isotope study at a research landfill in the Southern Vienna Basin (Breitenau)

Understanding of the pollutants transport at a landfill presupposes information about the water movement. With respect to environmental isotopes, the Breitenau Experimental Landfill in the Southern Vienna Basin (see also section 4.3) offered several indicators which facilitate the study of water movement in waste bodies and in the bottom liners. They are in part random (^{3}H contamination of the leachate by a ^{3}H source contained in the waste), in part attributable to the water used in the construction of the bottom liner, and in part emerge from the landfill itself (strong shift of the ^{2}H content of the leachate as a result of the anaerobic decomposition). Therefore, infiltrating precipitation water clearly differs in several isotope parameters from the leachate.

The purpose of this landfill research project was to observe the long term behavior of deposited rubbish from conditions of total encapsulation to those shown when rubbish is deposited in a reactor type landfill (with accelerated anaerobic decomposition in the presence of water) under natural environmental conditions. The site permitted the gathering of comprehensive data about milieu induced reactions and the reaction products, landfill gas and leachate. Since the construction of the Breitenau Experimental Landfill in 1987-1988, leachate samples were taken at regular intervals and stored in a deep-frozen state. In 1991, an isotope survey investigation was initiated that initially encompassed leachate samples from every second month (Rank et al., 1992). This sample material provided a unique opportunity to pursue the chronological development of the environmental isotope contents in the leachate since the waste was the first deposited. In this manner it has been possible, for example, to observe the transition from aerobic to anaerobic decomposition.

A source of ^{3}H that appeared to be contained in the waste (e.g. watches) led to a strong ^{3}H tracing of the leachate (up to 3000 TU). ^{3}H concentrations up to 1000 TU were found in methane formed from the microbial decomposition of organic material in the landfill. ^{3}H measurements at several municipal landfills led to the conclusion that elevated ^{3}H concentrations may occur in the leachate of more or less every younger landfill.

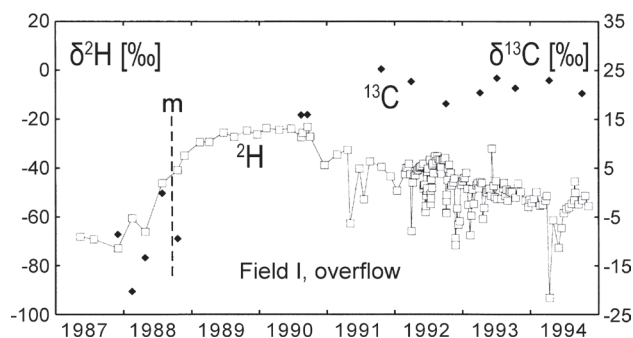The beginning of the methanogenic phase is characterized by

Figure 27: Research field Breitenau: ^{2}H content of leachate and ^{13}C content of dissolved inorganic carbon (DIC); m = beginning of methanogenic phase.

a strong enrichment of ^{2}H in the leachate (Figure 27) accompanied by a depletion of ^{2}H in methane. Since 1991, short term infiltrations of precipitation water through leakages in the covering of the waste body have caused distinct ^{2}H minima. The long term trend shows a slight decrease of the ^{2}H enrichment due to decreasing microbial activity and the increasing influence of precipitation water. The $\delta^{13}C$ value of the dissolved inorganic carbon rises to about +20‰ in the methanogenic phase.

The ^{3}H content of the leachate water below the bottom liner (silt-clay-gravel mixture) has shown an increasing influence of water from the waste body since 1991, superimposed by sharp peaks from time to time. This suggests leakage becoming active from time to time when a saturated zone exists in the lower part of the waste body above the bottom liner.

The goal of the entire isotope investigation was to make statements, on the one hand, about the passage of the leachate through the mineralogical barrier, and, on the other hand, about how the water from a single precipitation event passes through the waste body, depending upon which material covers the landfill. Analysis of isotopes of hydrogen, carbon and oxygen was found to be a useful tool to investigate water movement and gas formation in the waste body as well as to identify groundwater contamination by leachate and landfill gas migration.

4. Some Remarkable Regional Results

4.1 Isotopic composition in river water in the Danube River system

The Danube River, with a catchment area of 817 000 km², a length of 2857 km and a long-term discharge at its mouth of about 6500 m³/s, is the second largest river in Europe (Figure 28). The catchment area at Vienna (Upper Danube Basin) is about 103 000 km². The mean annual flow rate is around 1900 m³/s, with a seasonal variation typical for alpine rivers (a minimum of 1300 m³/s in November and a maximum of 2700 m³/s in July). The amount of precipitation in the Upper Danube Basin shows a distinct gradient with the altitude. It rises from 650-900 mm/a in the lowland areas to more than 3000 mm/a in the high mountain ranges exposed to the west and north. For the stations located in the lowland areas, summer precipi-

Figure 28: The Danube Basin river system with indication of the proposed sampling points at the Iron Gate and Tulcea as well as the sampling points of the Austrian network for isotopes in river water (Table 4), where long-term isotope records are available (based on ESRI ArcGIS 9.3).

Figure 29: $\delta^{18}O$ records of the Danube, some tributaries and the alpine section of the Rhine (12-month running mean). All the alpine rivers show a similar long-term pattern (R. Inn, R. Drau and Rhine). This isotopic signal dominates also in the Danube at Vienna. The upper Danube (Ulm, data from Rank et al., 1998) and the River March show a somewhat different isotopic behavior.

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 variation: delayed runoff of winter precipitation (snow cover, Figure 12), residence time of groundwater discharged to the river, confluence with tributaries, evaporation from lakes in the river system as well as anthropogenic influences on the hydrological regime (e.g. reservoirs, irrigation). Therefore, isotope ratios 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 (Gibson et al., 2002).

The comparison of long-term trends of stable isotope ratios in precipitation and river water (Figures 10, 13 and 29) reveals that, in the case of the Upper Danube Basin, river water quite well reflects the isotope trends of precipitation. Not only short-term signals (e. g. seasonal $\delta^{18}O$ variations or ^{3}H releases from nuclear facilities) but also long-term changes of isotope ratios in precipitation are transmitted through the catchment, for instance the significant increase of $\delta^{18}O$ values during the eighties. The different sources of air moisture (Atlantic, Mediterranean) are also clearly represented isotopically in the river system. The alpine rivers Drau (Mediterranean influence) and Inn (Atlantic influence) differ significantly in their $\delta^{18}O$ values (Figure 29, Table 4).

It becomes evident from the long-term trend curves for river water and precipitation at Vienna (Figure 30) that the

tation represents more than 60 % of the annual precipitation. For high-altitude stations, winter precipitation is more important, although it is stored on the surface as snow cover until spring and summer, when melting takes place.

The isotopic composition of hydrogen and oxygen in river water is mainly determined by the isotopic composition in

		Sampling location	Latitude / Longitude (degrees)	Drainage area (km²)	MQ (m³/s)	δ¹⁸O [‰] 1976-1985	δ¹⁸O [‰] 2001-2010	³H [TU] 2010
Rivers	Donau (Danube)	Engelhartszell (O-1)	48.5046 / 13.7361	77 090	1400	-11.82	-11.12	14.1
		Wien (O-5)	78.2662 / 16.3695	101 731	1915	-11.75	-11.11	12.0
		Hainburg (O-9)	48.1507 / 16.9407	104 178	---	n.a.	n.a.	13.9
	Drau	Neubrücke (O-10)	46.6211 / 14.5481	11 052	---	-11.86	-11.07	7.3
	Inn	Kirchbichl (O-13)	47.5233 / 12.0939	9 319	289	-14.01	-13.26	8.1
		Schärding (O-12)	48.4361 / 13.4417	25 664	729	-12.84	-12.00	8.3
	Leitha	Deutsch-Brodersdorf (O-14)	47.9384 / 16.4784	1 599	10	-10.74	-10.40	8.7
	March	Angern (O-15)	48.3840 / 16.8356	25 624	107	-9.88	-9.28	33.9
	Mur	Spielfeld (O-16)	46.7106 / 15.6361	9 480	140	-11.49	-10.72	7.9
	Salzach	Salzburg (O-18)	47.8169 / 13.0375	4 426	176	-13.12	-12.32*	8.8
	Ill	Gisingen (O-11)	47.2609 / 9.5790	1 281	65	-13.46	-12.54*	8.8
	Rhein (Rhine)	Lustenau (O-17)	47.4482 / 9.6590	6 110	232	-13.58	-12.64	8.1
Lakes	Bodensee	Bregenz (O-19)	47.5067 / 9.7480	---	---	-12.30	-11.43	8.4
	Fuschlsee	Fuschl am See (O-20)	47.7982 / 13.2997	---	---	-10.58	-10.01	8.3
	Neusiedlersee	Podersdorf (O-22)	47.8605 / 16.8292	---	---	-3.41	-2.65	9.8

*) average value 2003-2010

Table 4: Surface water sampling sites in Austria: long-term average δ¹⁸O values (1976-1985 and 2001-2010) and average ³H content 2010 on the basis of monthly grab samples (Danube river system, Rhine river system, lakes).

δ¹⁸O signal is delayed in the Danube by approximately one year with respect to precipitation (Rank et al., 1998). Because of the relatively low amplitude of long-term changes of δ¹⁸O (δ²H) in precipitation and in river water, this approach is useful to assess the mean transit time of the fast component of the flow. For the Danube, the mean transit time derived from comparisons of δ¹⁸O trend curves for precipitation and river water at Vienna is around one year. The agreement of the trend curves is partly excellent while there are also some discrepancies, most likely due to the specific distribution of precipitation amount for low and high altitude portions of the catchment during this period.

The ³H background concentration in Danube water at Vienna has decreased to about 10 TU in recent years, which is close to the natural level (Figure 4). All river water values exceeding about 12 TU should be the consequence of human activities. In most cases these contaminations show short-term character (Wyhlidal et al., 2014). This can clearly be seen, for instance, from the long-term ³H record of the Danube at Vienna (Figure 4). An example of such a short-term contamination peak is shown in Figure 6. The source for this ³H peak was probably a nuclear power plant (NPP Isar 2) some 400 km upstream of the sampling point. Although the ³H pulse had passed several dams, the half-width of the ³H peak was only about 2 days. On the Rhine River, such ³H peaks originating from NPP releases were used for determining travel time and dispersion of contamination pulses (Krause and Mundschenk, 1994).

Residence times for the upper Danube are estimated to be about 3-5 years using ³H data (Rank et al., 1998; Yurtsever, 1999), but the results are still not satisfactory. Using the climatic signal of the long-term δ¹⁸O time series of the Danube was tried as a new approach for getting information about the age of base-flow water (Rank et al., 2014). In a first attempt, δ¹⁸O trends of precipitation and Danube water at Vienna were compared on the base of 10-year averages. Thus, short-term and seasonal variations play only a minor role. The climatic
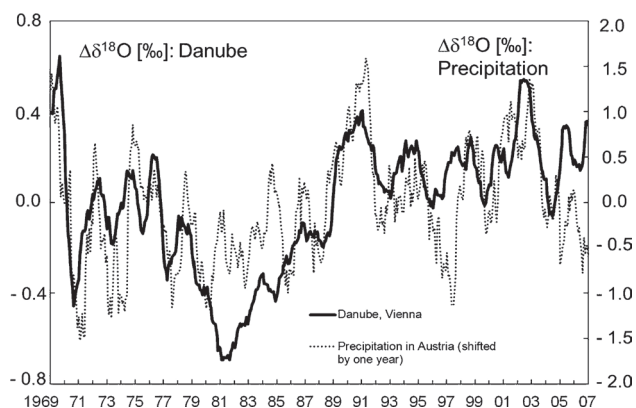

Figure 30: Comparison of the long-term trend curves of δ¹⁸O, expressed as departures from the long-term mean value, for the Danube and for precipitation at Vienna, shifted by 1 year.

signal in the Danube showed a shift of about 3 years, probably the mean residence time of the base flow.

The spatial variation of δ¹⁸O in river water in the Danube Basin is shown in Figure 31, with lower values in mountainous regions and higher values in lowland tributaries. The δ¹⁸O value of the Danube increases from -10.8 ‰ after the confluence of the upper Danube (mainly lowland drainage area, higher δ¹⁸O value) and Inn River (mainly alpine drainage area, lower δ¹⁸O value) up to -9.6 ‰ at the mouth. This increase (1.2 ‰) is due to the decreasing influence of runoff contributions from 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 δ¹⁸O 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 the strong influence of evaporation on the lake water (Rank et al., 2009).

The δ¹⁸O record exhibits three significant changes along the river (Figure 31): firstly, at the confluence of upper Danube and Inn. The second change is caused by the inflow of the tributa-
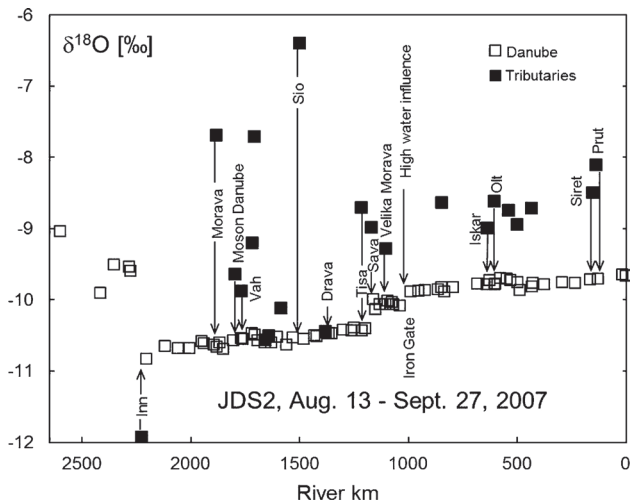
Figure 31: Longitudinal δ¹⁸O profile of the Danube (river km 2600, Ulm – river km 0, Black Sea) and δ¹⁸O values of tributaries at confluence (Aug. 13 – Sept. 27, 2007).

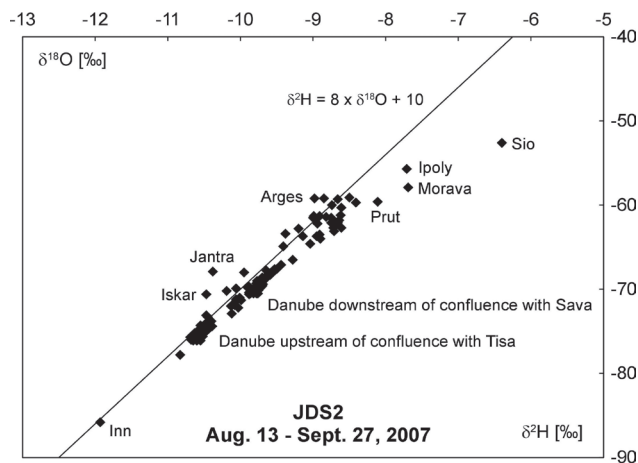**Figure 32:** δ²H-δ¹⁸O diagram for river water samples from the Danube Basin.
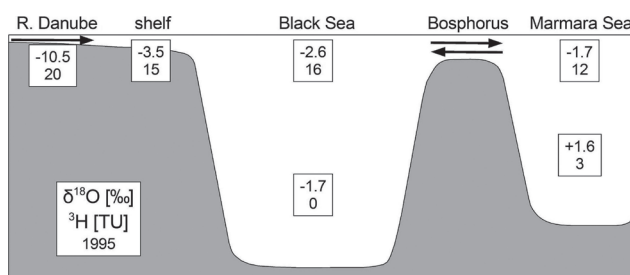

Figure 33: Schematic overview of the isotopic composition in the waters of the Danube – Black Sea – Bosphorus – Marmara Sea system (Rank et al., 1999).

ries Tisa and Sava with their higher ¹⁸O 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, 2007, resulting in slightly higher δ¹⁸O values for the Danube between the Iron Gate and river mouth.

The δ²H-δ¹⁸O diagram (Figure 32) shows that most of the

values lie close to the Global Meteoric Water Line ($\delta^2H = 8*\delta^{18}O + 10$) which suggests that surface water evaporation along the Danube river course is minor and its influence on the isotopic composition of river water may be neglected for the main stream and the majority of tributaries. Only River Sio carries water significantly influenced by evaporation – isotopic signal below the meteoric water line – because it contains water from Lake Balaton. But also the tributaries Ipoly, Morava and Prut show slightly pronounced evaporation effects, probably due to the presence of reservoirs in the river course. The higher deuterium excess values in the upper sections of the rivers Iskar, Jantra and Arges – isotopic signal above the meteoric water line – are probably due to the local orographic – mountainous – conditions (see section 3.6).

Since the isotopic composition of river water in the Danube Basin is mainly governed by the isotopic composition of precipitation in the catchment area, short- and long-term isotope signals from precipitation are transmitted through the whole catchment. The isotopic composition of Danube water in the delta region so should provide an integrated isotope signal for climatic/hydrological conditions and changes in the whole catchment. The aim of an investigation in 2009/2012 was to establish a representative isotope monitoring near the Danube Delta. The results showed that in terms of the isotope content the Danube River is fully mixed at the bifurcation of the Danube Delta arms (Rank et al., 2013). Therefore, routine sampling at only one location in the pre-delta region should be sufficient to obtain a representative isotope record for the whole Danube Basin. The δ¹⁸O time series from November 2009 to May 2012 (sampling twice a month) shows seasonal variations in the range of -9.8‰ ± 0.7‰ with a minimum in spring and a maximum in autumn (Figure 13). The values are generally higher than those from the Danube at Vienna, due to the major contribution of water from lower parts of the Danube River Basin. While the δ¹⁸O time series of Vienna is characterized by a sharp negative peak in summer (snowmelt in the Alps), the δ¹⁸O values of the Danube at Tulcea show lower values in spring (influence of winter precipitation) and higher values in autumn (summer precipitation). The ³H results exhibit the influence of short term contaminations due to human activities. The expected "environmental" ³H content of river water in Central Europe would be about 10 TU. During this investigation, ³H values up to 100 TU were observed in the pre-delta section. This indicates short terms releases of ³H from local sources such as nuclear power plants in the Danube river system.

The Danube water isotope time series will serve as a basic data set for hydrological investigations as well as for assessing future impacts within the Danube Basin. This includes climatic/hydrological changes (e.g. temperature changes, change of precipitation distribution) as well as anthropogenic impacts on the hydrological regime (e.g. reservoirs, change in land use). All these changes will more or less be reflected in the isotopic composition of river water. Since the Danube River is the most important inflow into the Black Sea, it might also be of interest to follow the Danube`s isotopic signal in

the shelf zone of the Black Sea (Figure 33, Rank et al., 1999) in order to detect the origin of possible contaminations.

4.2 Assessment of groundwater inflow to the Neu-siedlersee (shallow steppe-lake)

The Neusiedlersee is a steppe-lake situated near Vienna at the Austrian/Hungarian border (latitude 16° 45', longitude 37° 50') were the outlying hills of the Eastern Alps slope into the Pannonian Plain. The water surface is at 115.5 m above sea level and the total area is almost 300 km², of which about 180 km² are covered by reeds. The mean water depth is about 1 m. Originally, the steppe-lake was without discharge. However, today the water level is regulated by a channel (Einserkanal). In 1965, Austria and Hungary agreed upon a minimum discharge to stabilize the water level. The water balance of the lake is preferably determined by precipitation and evaporation including the indeterminate subterranean inflow. The lake has disappeared more than once in its history, most recently about 150 years ago.

Little was known of the subterranean inflow to the Neusiedlersee. A conceptual model of the very complicated hydrogeological conditions, partly determined by Quaternary tectonics, did exist (Gattinger, 1975), but in the past groundwater inflow has only been taken as a remainder in the water balance equation. Accordingly, the estimated values varied widely.

An Austrian/Hungarian project in the 1980s was an attempt to learn more about the subsurface inflow by a more accurate investigation of the lake-side areas and the interrelationships of groundwater and lake water, and subsequently to arrive at a quantitative estimation. Moreover, it was of interest to what extent nutrients and noxious substances flow into the lake with the groundwater on account of the intensive agricultural utilization of the surroundings (vineyards) and tourism. The results of the study were also important with regard to considerations of how to prevent the lake from possibly drying up again, which may be caused by a series of very dry years (Boroviczeny et al., 1992).

In the Neusiedlersee area, with its complicated hydrogeological conditions, the measurement of environmental isotopes has proved to be a useful instrument in the investigation of the interrelationships of groundwater and surface water. The use of isotope methods is aided by the great differences of the surface water and groundwater isotopic composition, which is due to a high evaporation rate over the shallow Neusiedlersee. Thus, more information on the mechanism of the previously rather speculatively estimated subterranean inflow to the Neusiedlersee could be obtained.

Taking into account all hydrological and isotope-hydrological data leads to a tentative conceptual model of hydrological conditions and interrelationships of ground water and lake water at the eastern side of Neusiedlersee (Figure 34a). According to this, shallow groundwater is to be found in Quaternary layers, obviously influenced by precipitation and evaporation. A continuous aquifer cannot be certified. Where the aquifer does exist in the lake-side area, it is thin. In the assumed
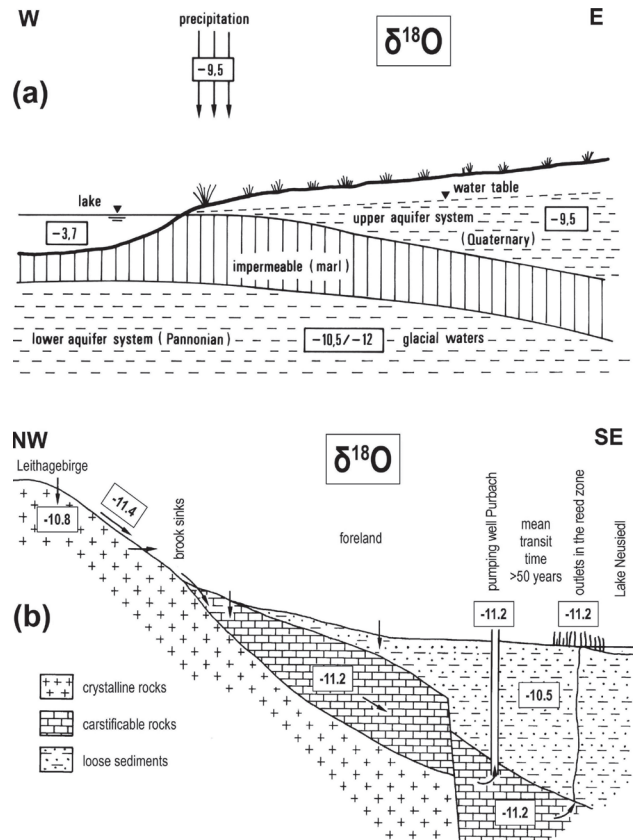

Figure 34: Generalized conceptual models of the hydrogeological conditions at the eastern (a) and western (b) lake-side of the Neusiedlersee ($\delta^{18}O$ data from 1980-1985).

recharge zone, horizontal permeability, water-table gradient and aquifer thickness – relevant parameters for a subterranean inflow to the lake – are very small. From this it follows that precipitation water in this area (Seewinkel) mainly evaporates after a certain residence time in the ground and that inflow to the lake from shallow groundwater can be estimated to be very low. At various depths in Tertiary layers another, again non-homogeneous, aquifer is to be found. The water of this aquifer has long residence times and hardly moves. Therefore, one may assume that no considerable recharge takes place from the second aquifer either. Distinct connections between the upper and lower aquifer may be excluded.

The south-eastern flank of the crystalline anticline of the Leithagebirge is overlain by limestone and conglomerates generally dipping south-eastwards under marls and clays of the Neogene (Figure 34b). Little creeks coming from the upper Leithagebirge feed a widely ramified karstic water system, preferably outside the vegetation period. The water of this system is, therefore, characterized by low $\delta^{18}O$ values (winter precipitation). A few little seepage springs could be identified in the reed belt of the lake, where karst water reaches the subsoil of the lake through clefts. The mean residence time of this water is about 100 years. No such outlets could be found in the open lake.

The geohydrological analyses revealed the aquifer transmissivities throughout the region to be extremely low, parti-
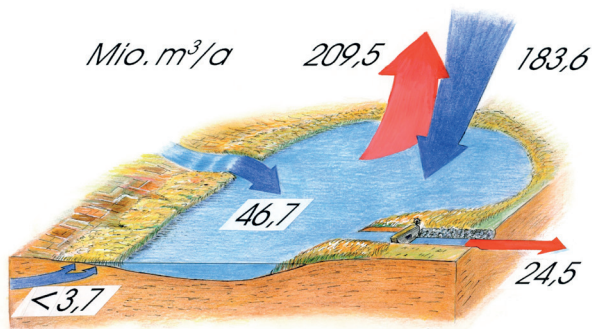
Figure 35: Water balance of the Neusiedlersee including high-water runoff. The subterranean inflow plays no significant role for the water balance.
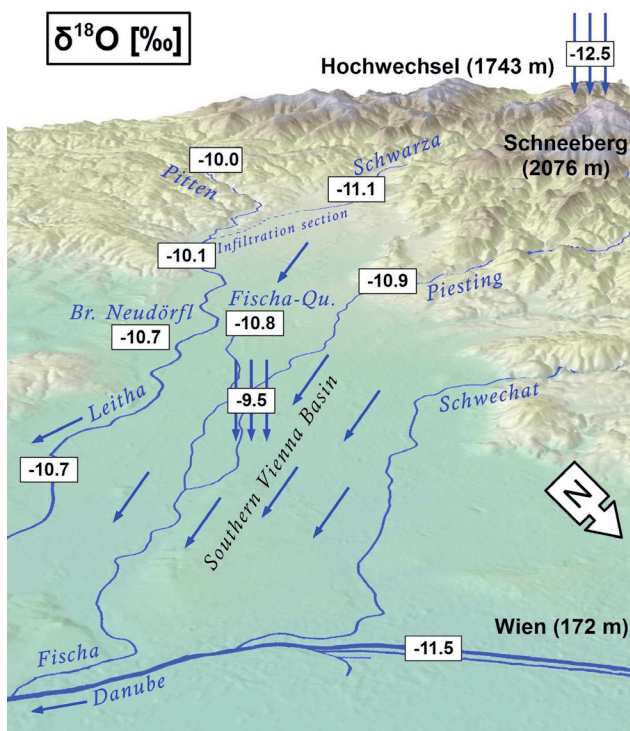

Figure 36: Southern Vienna Basin: $\delta^{18}O$ values of precipitation, surface and groundwater (yearly mean values 1998, diagram area about 30 km x 60 km).

cularly in the vicinity of the lake. Due to the large terrestrial evapotranspiration and the rather low annual precipitation, the groundwater recharge throughout the catchment is low. In the deeper usually artesian layers, which are frequent in this region, groundwater recharge is extremely low.

The results of all investigations indicate that the subsurface inflow amounts to a maximum of 1-2 % of the positive water balance components of the Neusiedlersee. This means that – opposed to previous assumptions – the lake´s water balance is not influenced significantly by subsurface inflow (Figure 35, Boroviczeny et al., 1992). The most important controls are precipitation directly on the lake surface and evaporation from the lake surface. A certain influence can be attributed to surface inflows and surface outflow.

The study provided a general survey of the groundwater regime in the Neusiedlersee area. The results of the study can serve as a basis of individual investigations for water resources management in this region.

4.3 Determination of groundwater flow velocity in the Southern Vienna Basin from a long-term environmental isotope record

The "Mitterndorfer Senke" in the youngest zone of subsidence in the Southern Vienna Basin contains an important groundwater occurrence with regional water-supply facilities (Figure 36). The depression filled with Pleistocene gravels and sands is about 40 km long, 2 to 8 km in width and 50 to 150 m deep. Up to 13 m³/s of river water infiltrate the alluvial cones in the most southern part of the "Mitterndorfer Senke" from the crossing rivers. The contribution of local precipitation to groundwater recharge is very low due to strong evaporation in this area (up to 600 mm/a). The fill in the "Senke" acts very much like a pipeline, transmitting water readily from the main recharge area south-west of Wiener Neustadt to points of surface discharge in the northern part of the basin (Davis et al., 1967). For many years, a plume of chlorinated hydrocarbons has been moving from the industrial plants in the most southern part of the depression towards the Danube. The determination of the groundwater flow velocity in the depression became important in this connection.

A survey of the $\delta^{18}O$ values of precipitation, surface water and shallow groundwater in the Southern Vienna Basin is given in Figure 36. A spring (Fischa-Dagnitz-Quelle) with a discharge of 350 l/s is situated at a distance of about 20 km from the infiltration sections. A long-term environmental isotope record (³H) exists for this spring (Figure 7, values since the early sixties). There is a shift of 8 to 10 years between the ³H-maxima in precipitation and in the spring.

From these data, an estimation of groundwater flow velocity may be gained by comparing the ³H-record of precipitation (input from infiltration section of rivers) with the ³H-record of the Fischa-Dagnitz-Quelle, since the contribution of local precipitation to groundwater recharge is nearly negligible. This was proved by a three year series of ¹⁸O measurements at the Fischa-Dagnitz-Quelle (1971/73, Figure 37). The lower $\delta^{18}O$ in the spring water, compared to local precipitation, confirms that the spring water is coming from a higher part of the catchment area. A rough estimate shows a mixture of about 2/3 water of type Schwarza River and 1/3 of type Pitten River (Figure 36). The $\delta^{18}O$ variation of two-weekly and monthly samples, respectively, is below the measurement accuracy, $< \pm 0.1‰$. This means that the mean residence time of the water is at least 8 years, according to a model calculation using the $\delta^{18}O$ amplitude ratio of spring water and precipitation (e.g. Moser and Rauert, 1980). No short-term influences are visible. Therefore, the higher ³H values of the spring from the mid-sixties (Figure7) were not included in the age calculation model. On the one hand, ³H contents of precipitation and – old – groundwater differed by up to more than a factor of 1000
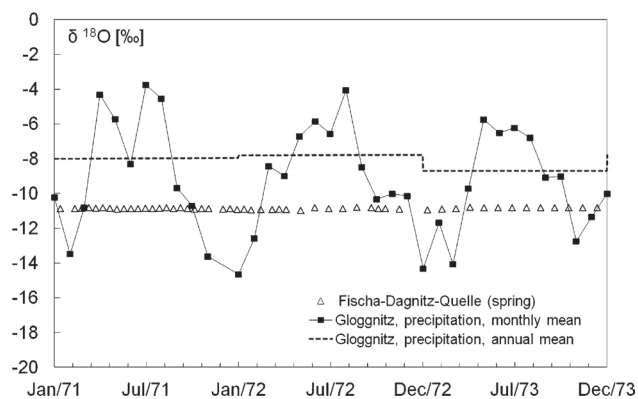
Figure 37: $\delta^{18}O$ time series of precipitation (station Gloggnitz) and Fischa-Dagnitz-Quelle (spring) 1971-1973.
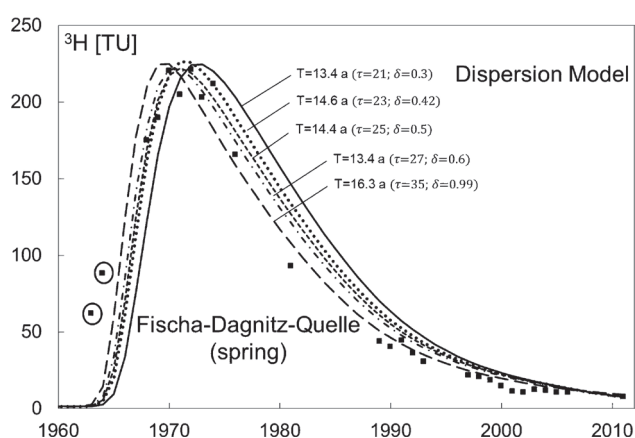

Figure 38: Fischa-Dagnitz-Quelle: Selected results of ^3H water-age calculations using a lumped-parameter method with a one-box model approach (dispersion model), variation of model parameters δ (dispersion parameter) and τ (Etcheverry and Vennemann, 2009), excluding ^3H values of 1963 and 1964. The calculated mean residence time of groundwater, T, in the Fischa-Dagnitz-Quelle lies between 13.5 and 16.5 years.

at that time, so only a few percent of rain water infiltrating in the closer proximity of the spring could be the reason for these elevated ^3H concentrations. On the other hand, unusually high precipitation amounts at that time probably increased the local infiltration influence on the top of the large groundwater body of the "Mitterndorfer Senke".

The results of a preliminary lumped-parameter model calculation are shown in Figure 38. The calculated mean residence time of spring water lies between 13.5 and 16.5 years, including the ^3H age of the river water before the infiltration process. The infiltrating river water consists mainly of snowmelt water of the same year and water from heavy rainfalls. This means that the age of the infiltrating water should be less than one year. Taking into account a distance of about 20 km between infiltration sections and the spring, this result leads to an average groundwater flow velocity of about 1.2 km per year.

More detailed environmental-isotope studies in this area are in progress at AIT and at the Environment Agency Austria by M. Kralik.

5. Conclusions and Outlook

The Arsenal environmental-isotope laboratories 1964-2010 contributed considerably thereto that isotope methods have become a routine tool in the solution of hydrological and hydrogeological problems in Austria and some neighboring regions. The work done there also contributed to the general understanding of hydrological and isotope-hydrological processes. The environmental-isotope measurements gained over the course of more than 45 years of laboratory work are included in a databank with more than 200.000 isotope values at the AIT. This database comprises several of the worldwide longest environmental-isotope records of precipitation, surface and groundwater and is a basis on which future work in isotope hydrology can be built.

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