5. ISOTOPIC INVESTIGATIONS

5.1. ENVIRONMENTAL ISOTOPE INVESTIGATIONS

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5.1.1. Introduction

The environmental isotopes deuterium (²H), oxygen-18 (¹⁸O) and tritium (³H) are suitable for tracing the origin of the water in the hydrological cycle because they are constituents of the water molecule. Therefore, the use of environmental isotope techniques may, in addition to conventional investigation methods, provide further insight into the storage properties of natural hydrological systems. Information can be derived about the mean altitude of catchment areas and mean residence times (transit times) of subsurface water by applying specific models. As a major part of this study, the ¹⁸O content is presented in time series of precipitation and runoff samples. The investigation of single hydrological events (e.g. storms, snow melt) was one of the main targets of the use of isotope methods within the karst research program 1993-96 in Slovenia. The location of the sampling points (precipitation stations, springs and sinkholes) are documented in Figure 5.1.

The 3H and ^{18}O analyses were performed at the Geotechnisches Institut, Bundesforschungs- und Pruefzentrum Arsenal, Vienna and at the GSF Institute of Hydrology, Neuherberg. The measuring accuracy (2σ criterion) of 3H values corresponds to 8 % and the detection limit is ca. 0.5 TU. The $\delta^{18}O$ values are given as relative %o -deviation from the international standard water V-SMOW. The measuring accuracy (2σ criterion) is equal to 0.1 %o in the $\delta^{18}O$ scale.

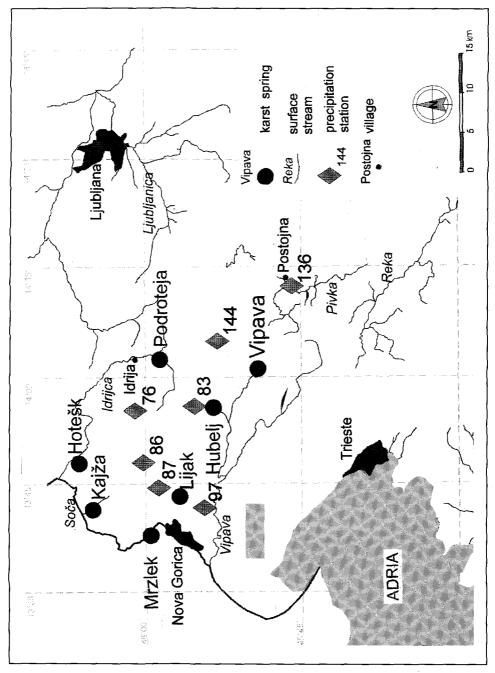


Fig. 5.1: Location map of the precipitation stations, springs and sinkholes of the area under investigation sampled for isotope measurements.

5.1.2. Precipitation

The precipitation was collected at six stations, usually in monthly intervals. The stations are spread over the research area at different altitudes. In Table 5.1, the locations of the precipitation sampling points are listed together with the altitude above sea level.

Name of the station	Code No.	Altitude [m]
Vojsko	76	1070
Lokve	86	965
Trnovo	87	789
Bilje	97	50
Postojna	136	555
Podkraj	144	799

Tab. 5.1: Precipitation stations.

5.1.2.1. Seasonal variation

The δ^{18} O contents of the monthly precipitation samples are documented in Figure 5.2. The expected seasonal variations can be seen, but are overlapped by irregularities in single months.

At one station (Lokve) the twofold running mean over three months is used to visualise the sinusoidal wave of the isotopic content in precipitation (Fig. 5.3). The relative high δ^{18} O -values in the summer months are followed by lower δ^{18} O -values in the winter months. Considering the whole observation period of three years, a general trend towards lower δ^{18} O -values is obvious.

Using the isotope content as the input function, the precipitation amount has to be taken into account. As an example, Figure 5.4 shows the δ^{18} O-values as an input function recalculated by the following equation:

$$\delta^{18}O_{cal} = \left(\delta^{18}O_{i} - \delta^{18}O_{mean}\right) \frac{P_{i}}{P_{mean}} + \delta^{18}O_{mean} \quad [\%6]$$
 (1)

P_{mean}: mean monthly precipitation amount

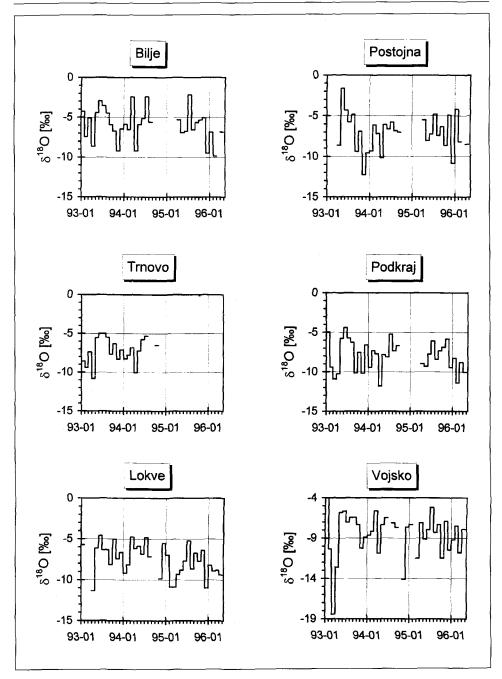


Fig. 5.2: Seasonal variation of $\delta^{18}O$ -contents (monthly means) in precipitation from Slovenian meteorological stations.

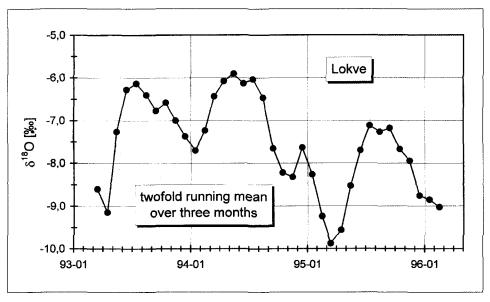


Fig. 5.3: Twofold running mean over three months of $\delta^{18}O$ -contents in precipitation from the meteorological station Lokve.

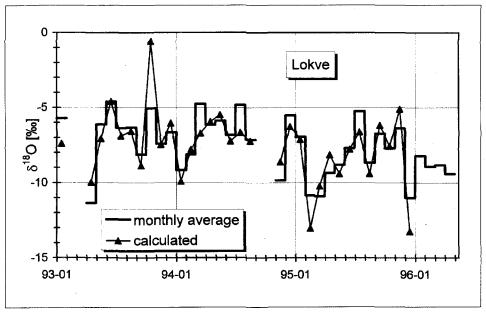


Fig. 5.4: Comparison of $\delta^{18}O$ -contents in precipitation of monthly average and calculated after Eq. 1 from the meteorological station Lokve.

Besides the precipitation amount, Eq. (1) also considers the difference between the $\delta^{18}O$ content in the precipitation of a single month and the mean weighted $\delta^{18}O$ -value estimated over the whole observation period. It can be seen that relatively higher $\delta^{18}O$ -values occur at the beginning of the investigation (1993) in comparison with the $\delta^{18}O$ -values towards the end of the observation period (1995).

5.1.2.2. Short term variation

A prerequisite for successful isotope investigations of single hydrological events are variations in the isotope content of the input - the precipitation. The deviation of the $\delta^{18}O$ -values for single precipitation events from the average yearly course depends on the origin of the humid air masses, as well as on the respective climatic conditions during the precipitation events.

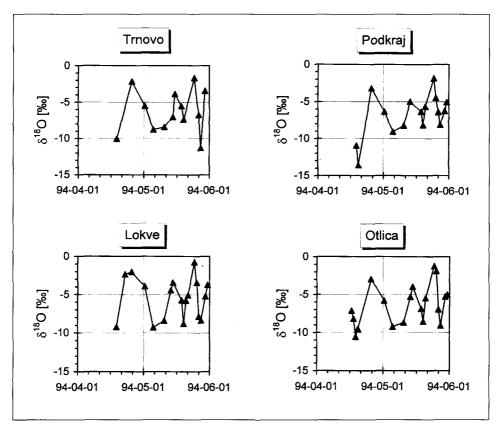


Fig. 5.6: Variation of $\delta^{18}O$ -contents in daily precipitation from Slovenian meteorological stations (observation period April to May 1994).

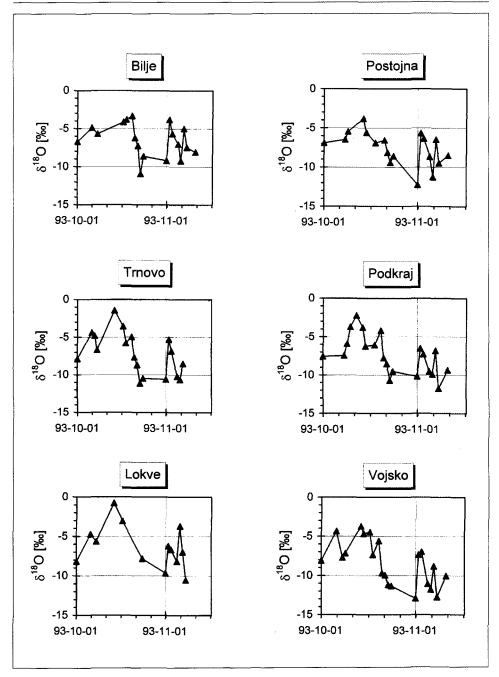


Fig. 5.5: Variation of $\delta^{18}O$ -contents in daily precipitation from Slovenian meteorological stations (observation period October to November 1993).

Figure 5.5 depicts the variations in the $\delta^{18}O$ content of daily precipitation at the six sampling stations during the period of October/November 1993. Significant precipitation events occurred with $\delta^{18}O$ content, which differed considerably from one another. These events normally provide useful input signals, which can be followed within the hydrological system. Furthermore it can be recognised that a general pattern is given in the $\delta^{18}O$ variation at all stations. This demonstrates the possibility of using this precipitation data as a regional input. In Figure 5.6, the $\delta^{18}O$ contents of single precipitation events from three sampling stations are plotted together with the results from the precipitation station Otlica. The observation period was from middle of April to the end of May 1994. The $\delta^{18}O$ -values, specially in May, scatter up to 10 % from one event to the following. Therefore, the use of these events as a pronounced isotopic input signal is limited.

Further examples are given in chapter 5.1.4 together with the δ^{18} O-values of the discharge of the karst springs Vipava, Hubelj and Lijak.

5.1.3. Altitude Effect

Figure 5.7 shows the correlation between the weighted annual average of the δ^{18} O-values in the precipitation and the altitude (Tab. 5.1) of the corresponding sampling stations for different years. For the stations Bilje, Postojna, and Podkraj, the results of each of the three years could be used, for Vojsko two years and for Lokve only one year. The isotope results obtained from the

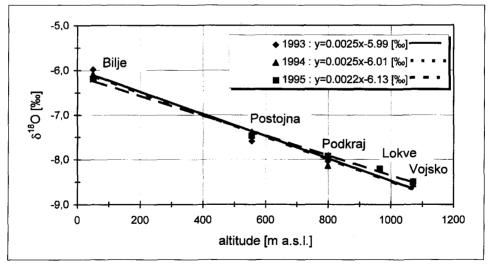


Fig. 5.7: Correlation of $\delta^{18}O$ -contents in precipitation from Slovenian meteorological stations and altitude for the years 1993, 1994, and 1995.

precipitation at Trnovo did not fit the ¹⁸O content - altitude correlation at all. Calculating the mean value from the three years, an altitude correlation which will be used for further calculations, is obtained as follows:

$$\delta^{18}O = -0.0024 A - 6.03 \ [\%_o] \tag{2}$$

with A = altitude in meter above sea level.

5.1.4. Long-term observation

The observation period for the isotope investigations was on the order of three years for most of the selected karst springs. The main objectives were to estimate the mean altitude of the catchment areas of the springs and to calculate the transit time of the water.

5.1.4.1. Altitude of the catchment

For the estimation of the mean altitude of a catchment area, the average δ^{18} O-value was calculated over the whole observation period and Eq. (2) applied. In particular, two sinkholes and seven springs were investigated. The uncertainty of the calculated altitude of the catchment areas results from the 2σ criterion of the δ^{18} O-values.

Sinkholes

Figure 5.8 shows the δ^{18} O variation of the water from the sinkholes Banjšice and Čepovanski Potok. These two sinkholes are located at an altitude of 667 m a.s.l. and 608 m a.s.l., respectively. The resulting altitudes of their catchment areas are listed in Table 5.2.

Tab. 5.2: Estimated mean altitude of the	he catchment area of	two sinkholes
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Name of the sinkhole	δ¹8O [‰]	Altitude [m]
Banjšice	-7.76 ± 0.17	720 ± 70
Čepovanski Potok	-8.28 ± 0.14	940 ± 60

Taking the altitude of the sinkholes themselves into account the following can be concluded:

The catchment area of the water disappearing in the sinkhole Banjšice covers an altitude range from 670 m up to 770 m. In contrast, the catchment area of the water in the sinkhole Čepovanski Potok ranges from 600 m up to

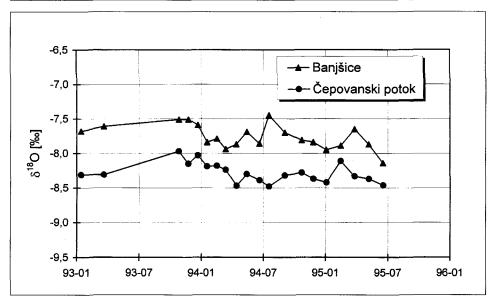


Fig. 5.8: Seasonal variation of $\delta^{18}O$ -contents of water from the sinkholes Banjšice and Čepovanski Potok.

nearly 1200 m. This estimation presupposes that the altitude of the catchment area starts at the location of the sinkhole. With these altitude ranges the catchment areas of the waters of these two sinkholes can be geographically fixed.

Karst springs

In Figure 5.9 the seasonal variations of the $\delta^{18}O$ content of the water from the springs Kajža, Hotešk, and Podroteja are plotted. Besides the corresponding sinusoidal fluctuations of the $\delta^{18}O$ -values, a difference in the absolute values can be recognised.

The seasonal variations of the $\delta^{18}O$ content of the water from the springs Hubelj, Mrzlek, and Vipava are documented in Figure 5.10. In comparison to the curves in Figure 5.9, the seasonal fluctuations of the $\delta^{18}O$ content of the water are similar, meanwhile the absolute values vary roughly between -8 and -9 ‰ . During 1995, a continuous increase of the $\delta^{18}O$ -values in the water of all three springs is obvious. This was caused by an increase in the $\delta^{18}O$ -values in the precipitation, documented e.g. in Figure 5.4 for the Lokve precipitation station.

The calculated altitudes of the catchment areas of the individual springs are listed in Table 5.3.

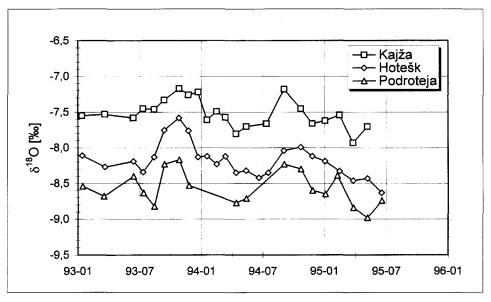


Fig. 5.9: Seasonal variation of $\delta^{18}O$ -contents of water from the karst springs Kajža, Hotešk, and Podroteja.

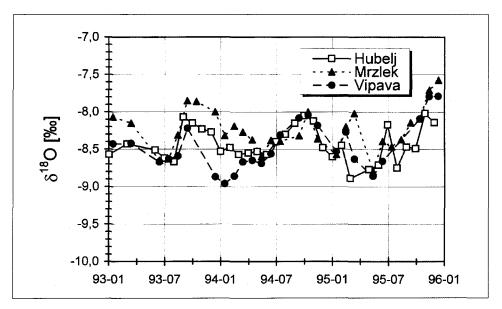


Fig. 5.10: Seasonal variation of $\delta^{18}O$ -contents of water from the karst springs Hubelj, Mrzlek, and Vipava.

Name of the spring	δ ¹⁸ Ο [‰]	Altitude [m a.s.l.]
Kajža	-7.52 ± 0.20	620 ± 80
Hotešk	-8.18 ± 0.24	900 ± 100
Mrzlek	-8.24 ± 0.29	920 ± 120
Hubelj	-8.43 ± 0.23	1000 ± 100
Vipava	-8.46 ± 0.33	1010 ± 140
Podroteja	-8.57 ± 0.24	1060 ± 100

Tab. 5.3: Estimated mean altitude of the catchment area of the six springs.

Soča River

The $\delta^{18}\text{O}$ -values of the water from the Soča river shows the analogue seasonal variation as observed in the water of the springs (Fig. 5.11). From the average $\delta^{18}\text{O}$ -value (-8.46 ± 0.30 ‰), the mean altitude of the catchment area was estimated to 1010 ± 130 m a.s.l.. The general trend over the whole observation period, which was mentioned for the $\delta^{18}\text{O}$ content of precipitation samples, is also obvious in the $\delta^{18}\text{O}$ -values of the river water with a delay of the winter precipitation possibly caused by a temporal storage of the snow cover.

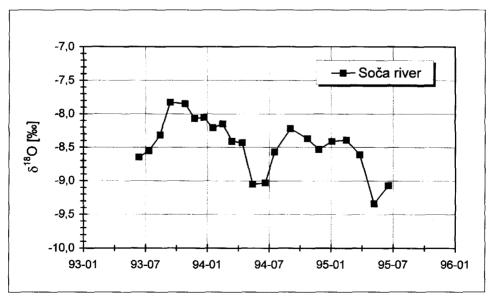


Fig. 5.11: Seasonal variation of $\delta^{18}O$ -contents of water from the Soča river.

5.1.4.2. Mean residence time

In the literature, several mathematical models known as so-called Black-Box-Models are used to estimate the mean transit times from long term isotopic observations (MALOSZEWSKI & ZUBER 1982, 1996). Considering the hydrological situation in the area under investigation, the dispersion model (DM) seems to be applicable for the interpretation of the isotope data obtained during base flow conditions. Since the groundwater system is under steady state conditions, the relation between input and output concentration of the nonradioactive tracer is given by the following convolution integral:

$$C_{out}(t) = \int_{0}^{t} C_{inp}(\tau) g(t - \tau) d\tau$$
 (3)

where C_{inp} and C_{out} are the input and output concentrations as functions of time, t, respectively, and g(t) is the weighting function defining the transit time distribution in the system. The g(t) function for the dispersion model is defined as follows (MALOSZEWSKI & ZUBER 1982):

$$g(t) = \frac{1}{\sqrt{4\pi P_D(t/T)}} \frac{1}{t} \exp\left[-\frac{(1-t/T)^2}{4P_D(t/T)}\right]$$
(4)

The main parameter of this model is the mean transit time of water (T), which is defined as

$$T = \frac{V}{Q} \tag{5}$$

where Q is the mean volumetric flow rate through the system and V is the volume of water in the system. P_D is the dispersion parameter, which describes the variance of the transit time distribution.

With stable isotopes, a simpler procedure can be applied, if the isotopic input curve can be approximated as a sinusoidal function with the period of one year (see chapter 5.1.2.1):

$$C_{inn}(t) = A_n \sin(\omega t) \tag{6}$$

where w=2p / (year), and A_n is the mean amplitude of the input function. Introducing Eq. (6) in Eq. (3) yields:

$$C_{out}(t) = B_n \sin(\omega t + \varphi) \tag{7}$$

where B_n is the mean amplitude of the output function, and ϕ is the phase shift, which in the case of the dispersion model is equal to:

$$\varphi = T \left[(1 + 3P_D) - \sqrt{1 + (3P_D)^2} \right]$$
 (8)

The mean transit time can be calculated from the amplitude ratio $f = B_n / A_n$ as:

$$T = \frac{1}{\omega} \sqrt{-\frac{\ln f}{P_D}} \tag{9}$$

The values of parameters φ and f are determined directly from experimental data. By using the Eqs. (8) and (9) iteratively, the mean transit time of water (T) and the dispersion parameter (P_D) can be calculated.

The amplitude A_n (input function) was estimated from the $\delta^{18}O$ variation in precipitation at representative stations shown in Figure 5.2. The $\delta^{18}O$ output function of the selected karst springs are plotted in Figures 5.9 and 5.10. These data are the basis for the estimation of the amplitude B_n of the karst springs under investigation.

Tab. 5.4: Mean transit time (T) and dispersion parameter (P_D) calculated for selected springs.

Name of the spring	T [months]	P _D [-]
Kajža	5.4	0.28
Hotešk	5.5	0.30
Podroteja	5.5	0.29
Hubelj	5.8	0.25
Mrzlek	5.0	0.25
Vipava	4.4	0.30

The evaluation of the ${}^{3}H$ data gives similar results. The ${}^{3}H$ values of monthly samples from the Vipava spring correspond with the actual ${}^{3}H$ content of precipitation, thus may indicate a relatively short mean residence time of the spring water in the underground (Fig. 5.12). There is no significant increase/decrease of the ${}^{3}H$ content even during low water periods. Only the seasonal variations of the ${}^{3}H$ content in precipitation (see also Fig. 5.12) are reflected in the ${}^{3}H$ graph of the Vipava spring. A mean transit time of about 0.4 years may be estimated from the comparison of the ${}^{3}H$ amplitudes of precipitation and spring water. This corresponds with the results above concluded from the $\delta^{18}O$ -values.

However the mean transit times of around 5 months (see Tab. 5.4) seem to be too low considering the hydrogeological situations. Therefore a mixture of two water components, having mean transit times of weeks (karstic channels) and mean transit times of years (outflow from the karst massif) could not be excluded. While, to separate these two components a longer observation period is necessary.

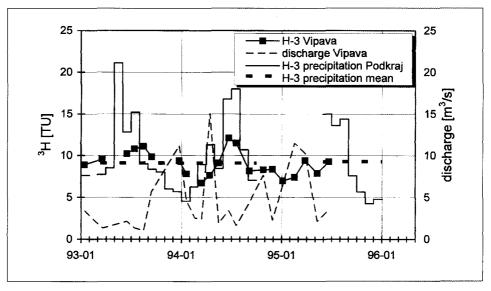


Fig. 5.12: Discharge and ³H content of monthly samples from Vipava spring together with the monthly and weighted mean ³H-values of precipitation at the meteorological station Podkraj.

5.1.5. Short term observation

In addition to a quantitative approach to the course of hydrological events, isotopic investigations also provide insight into the age structure of waters. Such knowledge helps in drawing conclusions on storage processes in hydrological systems and on the composition of the runoff; that is on the relative shares of base flow, direct runoff following storm events, and interflow. Distinguishing the components of runoff is an important basis for hydrological assessment of potable water reserves in a particular region.

To apply this method, an adequate amount of precipitation is necessary as well as a distinct difference in the isotope content of the water components mentioned above. Considering the seasonal variations in the ¹⁸O content in precipitation, major deviations in the ¹⁸O content from single precipitation events from the mean value of the system can be expected in winter and in summer. In the area under investigation, precipitation in winter generally takes the form of snow, and does not directly reach runoff. Therefore, mid-summer would be the most favourable period for such research.

As mentioned above, isotope data can be used to estimate the portion of water flowing directly through the karstic channels. To do this, the isotope content has to be monitored in the karstic springs before and during a discharge event and in the precipitation producing this event.

The travel time through the karstic system of the fast-flow portion of a precipitation event can be estimated from the time delay between the respective peaks in precipitation and discharge, assuming a piston flow model. The percentage of direct flow water (d) is obtained by calculating the simple mixing equation using the δ^{18} O-values of precipitation and discharge as follows:

$$d = \frac{C_{DE} - C_{BF}}{C_{PE} - C_{BF}} \tag{10}$$

with: C_{DE} = weighted mean $\delta^{18}O$ content in discharge event

 C_{PE}^{DE} = weighted mean $\delta^{18}O$ content in precipitation event

 $C_{BF} = \text{mean } \delta^{18}O$ content in discharge before the event at base flow conditions

5.1.5.1. Vipava spring

For the Vipava spring, the determination of the direct water component was only possible from the isotopic data obtained during the event on 17 November 1995.

The discharge measurements of the Vipava spring from October 1995 until March 1996 are plotted in Figure 5.13 together with the precipitation amount of the meteorological station Podkraj. The precipitation and discharge are in phase, only with the low values a shift of some days can be recognised. Isotope data from the single precipitation events are shown in Figure 5.14. Unfortu-

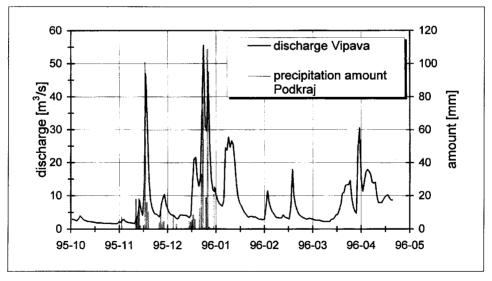


Fig. 5.13: Monthly precipitation amount from the meteorological station Podkraj and daily discharge of the Vipava spring (No. 4/7).

nately no precipitation samples are available from 1996. As can be seen in Figure 5.14, the rain event on the 17 November 1995 with 101 mm has a δ^{18} O-value of -4.86 %. The percentage of the direct water component was calculated for this event (see Tab. 5.5). The 18 O content of the heavy rainfalls on 24 and

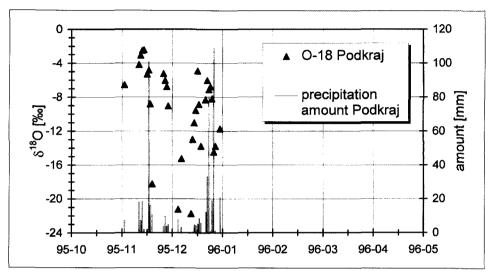


Fig. 5.14: Monthly precipitation amount and $\delta^{18}O$ -content of precipitation from the meteorological station Podkraj.

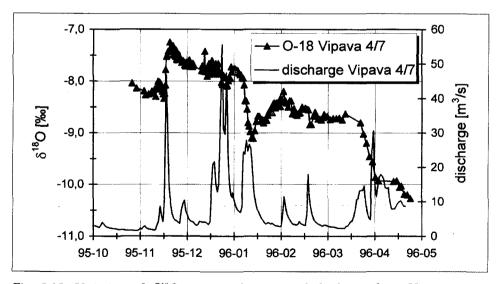


Fig. 5.15: Variation of $\delta^{18}O$ -content of water and discharge from Vipava spring No. 4/7.

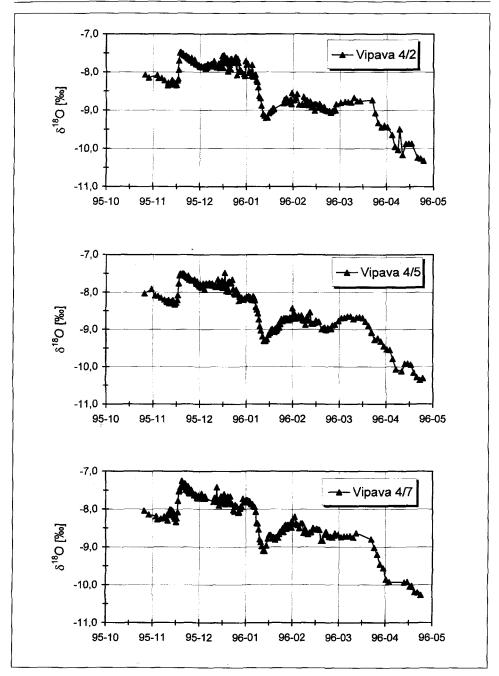


Fig. 5.17: Daily variation of δ^8 O-content of water from Vipava springs at sampling points No. 4/2, 4/5 and 4/7 (see Fig. 4.12).

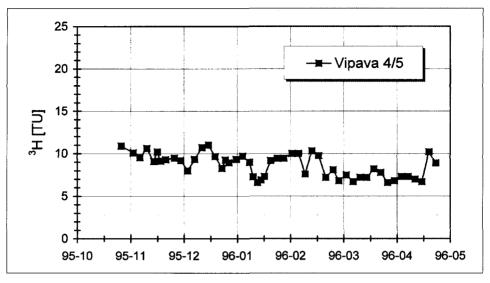


Fig. 5.18: Daily variation of the ³H content of water from the Vipava spring.

27 December 1995 are scattered around the $\delta^{18}\text{O}$ -values of the discharge and therefore no separation is possible here. In Figure 5.15 the ^{18}O content and the discharge of the Vipava spring at sampling point 4/7 are shown. Measurable changes in the ^{18}O content correspond with high discharge values, except those at the end of December, which is explained above.

During the observation period October 1995 to April 1996 three individual springs of the Vipava system were sampled. The δ^{18} O-values for these spring waters are shown in Figure 5.17. The temporal curves of the 18 O content demonstrate the general spatial distribution pattern. The average values of the 18 O content of the three springs (4/2, 4/5 and 4/7) differ only slightly over the observation period. Using the altitude relation (see chapter 5.1.3) one can estimate that the mean altitude of the catchment area of Vipava spring 4/7 is ca. 50 m lower in comparison to the two other springs.

Also the 3H data of the Vipava spring 4/5 values (Fig. 5.18) exhibit some variations during the period November 1995 - April 1996, but these changes are not as significant as those of the δ^{18} O-values.

5.1.5.2. Hubelj spring

For the Hubelj spring, two events could be taken into account: 28 August 1995 and 20 September 1995.

As input function, concerning the Hubelj spring, the meteorological station Otlica was used for the hydrograph separation. The precipitation amount

(Otlica) and the discharge measurements (Hubelj) are illustrated in Figure 5.19. Again there is a good correlation with an obvious shift of one day during heavy precipitation events. Taking the mean δ^{18} O-value of the Hubelj spring water into consideration, the precipitation events (Fig. 5.20) from 26 to 28 of August 1995 (166 mm) and from 20 to 22 of September 1995 (73 mm) with δ^{18} O-values of -6.67 ‰ and -7.40 ‰, respectively, were used for runoff

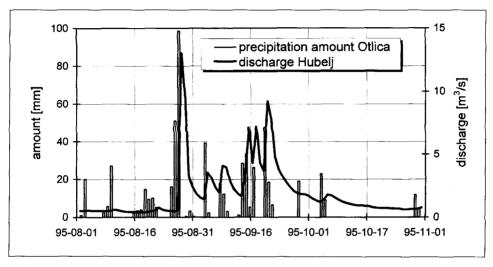


Fig. 5.19: Monthly precipitation amount from the meteorological station Otlica and daily discharge of the Hubelj spring.

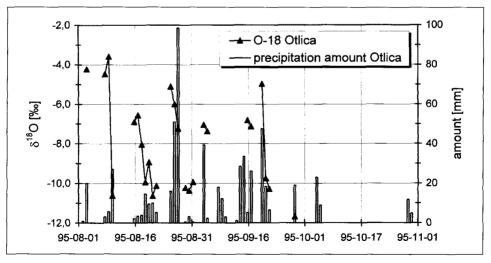


Fig. 5.20: Monthly precipitation amount and $\delta^{18}O$ -content of precipitation from the meteorological station Otlica.

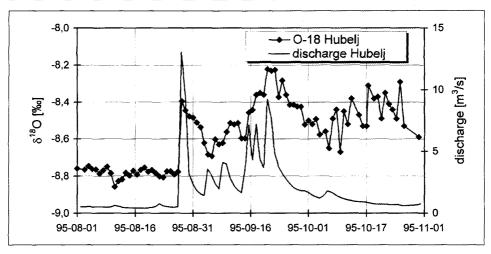


Fig. 5.21: Daily variation of $\delta^{18}O$ -content of water and discharge from the Hubelj spring.

separation. The reaction in the ¹⁸O content of the discharge in the Hubelj spring is given in Figure 5.21 and the results are summarised in Table 5.5.

5.1.5.3. Additional karst springs

Besides these two main spring systems Vipava and Hubelj, five additional karst springs were sampled on a daily basis during the spring of 1994.

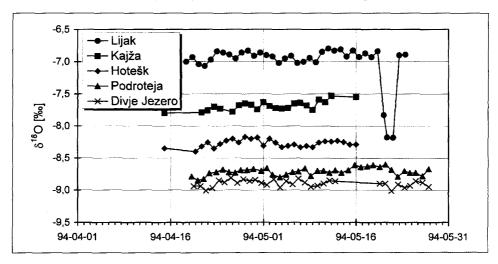


Fig. 5.22: Daily variation of $\delta^{18}O$ -contents of water from the karst springs Lijak, Kajža, Hotešk, Podroteja, and Divje Jezero.

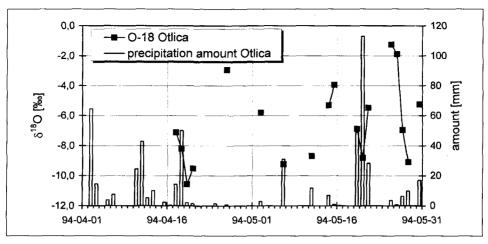


Fig. 5.23: Daily precipitation amount and $\delta^{18}O$ -content of precipitation from the meteorological station Otlica.

The temporal variations of the δ^{18} O-values are shown in Figure 5.22. It was only possible to calculate the direct runoff portion with the data obtained from the Lijak spring water during the 19 May 1994 event (see Tab. 5.5). The precipitation amount and the discharge values are documented together with the corresponding isotope data in Figure 5.23 and 5.24.

For the springs Podroteja and Divje Jezero, the ¹⁸O content of precipitation and discharge were too close together and Eq. (10) could not be applied. The karst springs Kajža and Hotešk were not sampled during the mentioned precipitation event.

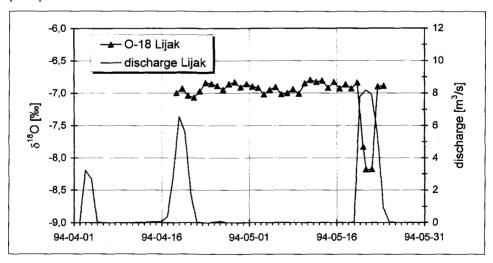


Fig. 5.24: Daily variation of $\delta^{18}O$ -content of water and discharge from the Lijak spring.

Hubeli

Hubeli

5.1.5.4. Results

The results obtained by calculating the portion of direct water component during single events of selected springs using ¹⁸O contents are summarised in Table 5.5. The travel time between precipitation event and discharge response are on the order of one to two days (see Fig. 5.13 and 5.19).

Name of the C_{BF} [%o] C_{PE} [%0] C_{DE} [%o] Date of d [%] spring event Lijak 1994-05-19 -6.85-8.63 -8.15 73 1995-11-15 Vipava -8.20 -4.90-7.5021

-8.78

-8.36

1995-08-28

1995-09-20

-8.42

-8.22

-6.67

-7.40

17

15

Tab. 5.5: Portion of direct water component during single events of selected springs calculated using ¹⁸O contents.

The portions of direct runoff in Hubeli and Vipava spring range between 15 % and 20 %, with slightly higher values indicated for the Vipava spring. In contrast, the water of the Lijak spring shows a pronounced portion of precipitation water.

The δ^{18} O-values of the karst springs shown in Figure 5.22 could also be used to calculate the mean altitude of the catchment areas of these individual springs. This is due to the fact that the discharge was very low during the observation period, as shown by the discharge measurements of the Podroteja spring (Fig. 5.25).

The average δ¹⁸O-content was calculated for the period of 15 April to 15 May 1994. The uncertainty of the calculated altitude of the catchment areas results once more from the 2σ criterion of the δ^{18} O-values.

Name of the spring	δ¹8Ο [‰]	Altitude [m a.s.l.]
Lijak	-6.92 ± 0.08	370 ± 30
Kaiža	-7.69 ± 0.07	690 ± 30

Tab. 5.6: Estimated mean altitude of the catchment area of the five springs

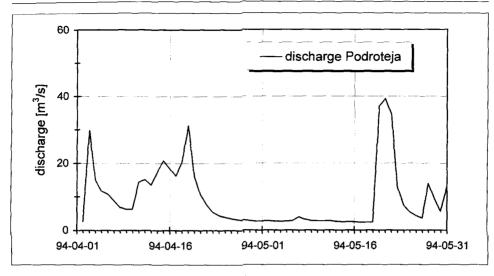


Fig. 5.25: Daily variation of discharge from the Podroteja spring.

The estimated mean altitudes of the catchment areas of the given springs are in agreement with the altitudes calculated by the δ^{18} O-values of the yearly variation (see chapter 5.1.4).

5.2. DISSOLVED INORGANIC CARBON ISOTOPE COMPOSITION OF WATERS

(J. URBANC, B. TRČEK, J. PEZDIČ, S. LOJEN)

The objective of this research is to determine whether the isotope composition of TDIC in water and the chemical composition of water in the outflow from a karst aquifer can be used to interpret the carbon isotope composition and partial pressure of soil CO₂ in the aquifer's recharge area. Further, an attempt was made to establish which model of carbonate rock dissolution in water can be applied to interpret initial conditions and define the degree of accuracy with which the initial conditions can be described if the only data available are those of the isotopic and chemical composition of water in the outflow from a carbonate aquifer. Thus, in our research, the carbon isotope composition and partial pressure of soil CO₂ measured in the recharge area of a karst aquifer were compared to the values, calculated from the isotopic and chemical composition of water in the outflow from aquifer.

Previous observations have shown that the formation of soil CO₂ is to the greatest extent conditioned by soil temperature (BILLES et al. 1971; DORR & MUNNICH 1980; KIEFER & BROOK 1986; WOOD et al. 1993), by the