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NITRATE POLLUTION OF A KARSTIC GROUNDWATER SYSTEM IN SVATÝ JAN POD SKALOU, CZECH REPUBLIC

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Abstract - *Due to increasing agricultural activity after the 1960's both shallow and deep water resources in the Czech Republic including karstic systems have been contamined by infiltrating nitrate. Nitrate content of one of the largest spring (19L/s) now varies from 50 to 60 mg/L. To specify the sources of nitrate pollution and collect sufficient data for the prediction of possible future development, flow dynamics, chemical and isotopic composition ($\delta^{18}O$ in water, $\delta^{15}N$ in nitrate) were monitored in the spring and precipitation together with potential sources of pollution (fertilizers, solutes in soil profile). Observed data were modelled by a simple mixing cell model to specify system parameters (volume and mean residence time).*

1. INTRODUCTION

It has been observed that modern agricultural practices involving extensive application of manure and chemical fertilizers have increased nitrate concentrations in shallow and deep groundwater. The monitored spring was used as a source of high quality water for production of bottled water in the past. Production did not continue after the 1960s because of problems with water quality. The nitrate content of the studied spring varies now from 50 to 60 mg /L. To identify the sources of nitrate pollution and evaluate parameters of the karstic system, the stable isotopes ^{18}O and ^{15}N were used together with monitoring of flow dynamics, water chemistry and soil composition. From the space and time variations of stable isotopes as natural tracers of infiltrating precipitation and nitrate, we can specify the pollutant pathways and the size of the groundwater reservoir that may enable prediction of future evolution of water quality of the source.

2. SITE DESCRIPTION

The Bohemian Karst is an extensive karst area formed by Devonian limestone and located in the south-west surroundings of Prague, is known for numerous outflows of karstic water. These springs usually occur near the boundaries between limestone and underlying volcanic (diabases), volcanoclastic (tuffs and tuffaceous rocks) and non-karstic sedimentary rocks (shales). The springs having the largest discharges are, moreover, typically controlled by local or regional faults. The Bohemian Karst represents local elevation with the altitudes in the range from 500 m a.s.l. to about 200 m a.s.l., crosscut by the deep valleys of the Berounka river and the Kaèák stream. The annual precipitation averages 570 mm and the average year temperature varies, depending on the location and altitude, between 7.5 and 9 °C.

The largest of the karstic springs (all branches together above 19 L/s during minimum discharge) discharges in Svatý Jan pod Skalou village, a local pilgrimage place with a large Baroque church and monastery. The spring is characterized by relatively small discharge variability and, during most periods, very stable and relatively high temperature in the range between 11.4 and 11.6 °C, which is higher than the local average annual temperature. The spring infiltration area consists of several quite different parts. A small valley directly above the spring represents its geographical catchment with an area close to 1 km^2. This forested

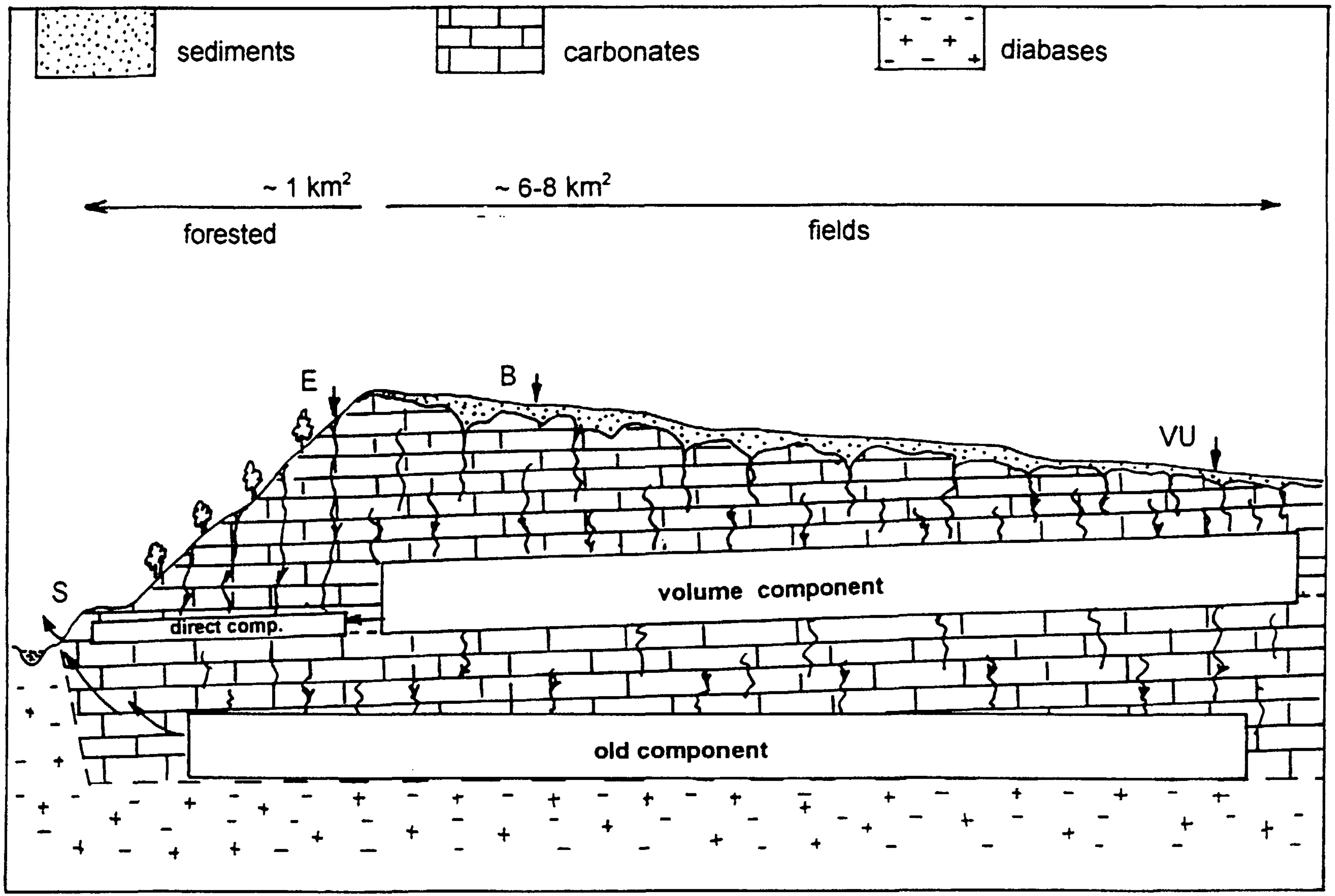

Fig. 1. Schematic cross-section of the karstic groundwater system: S spring, E tracer experiment site, B Bubovice soil profile, VU Vysoký Újezd soil profile.

land (oak-hornbeam assemblage) is characterized by steep slopes and contains several swallow holes which act as periodic ponores (sinking streams in a swallow holes) during large precipitation events. Some abandoned limestone quarries are present in this area, too. The spring discharge which does not decrease below 19 L/s suggests that the real (hydrological) catchment of the spring must be much larger than this small geographical one. The average groundwater unit yield for limestones of the Bohemian Karst is close to 2.8 $L.s^{-1}.km^2$ [1]. Using this value the total spring infiltration area should be in the range between 5 and 7 km^2. The spring infiltration area thus clearly comprises another (dominant) part with slow infiltration and a deep karstic-type reservoir. Analysis of the geological situation shows that the spring infiltration area probably follows the NW flank of a syncline of limestones trending in a NE direction, underlies and overlies by non-karstic rock types (see Fig. 1). At the surface this area is characterized mostly by flat country covered by fields with intensive agricultural activity. This flat elevated surface represents an old peneplain of Cretaceous period. Remnants of Cretaceous marine sandstone occur in the NE part of the study area. The surface of karstic rocks below this peneplain is deeply weathered and, as seen in outcrops in some quarries, very morphologically complex. Depressions in this fossil karst surface were filled with younger Cretaceous and Tertiary sediments. Surface waters from this area are drained now by the Bubovický potok Creek and by the Karlický potok Creek to the SW and SE.

The extent of forests and cultivated fields in the study area is shown on Fig. 1. In the past mostly organic fertilizers (dung, dung-water) were used on the fields. Starting from late 1960s artificial fertilizers started to be overused by local state-controlled Unified Agricultural Cooperatives. In the period from 1968 to 1989 most fields in the area received from 90 to 110 kg N/ha/year. After 1989, as a result of political changes and decreased state support of agriculture, the quantity of fertilizers used decreased dramatically to recent average value 35 kg of N/ha/year (during the last five years liquid fertilizer DAM 390 has been applied at about 100 L/ha „on leaves" during the beginning of vegetational period complemented once per 3 years by 40 t of dung/ha). The significant change in the quantity of applied fertilizers, which occurred after 1989 represents, the unique opportunity to study the changes of nitrate pollution in the deep karstic aquifer.

3. METHODS

Starting on November 1, 1994 regular measurements of temperature, discharge and $\delta^{18}O$ of the spring and precipitation on the possible recharge area have been performed. Precipitation was sampled using PE funnels installed at the recharge area and cumulative (3 or 7 days) samples were collected. The sampling period was twice a week in the first year and once a week in the second year. During large precipitation events the period was shortened to 12 hours to obtain a detailed record of flow dynamics. The $\delta^{18}O$ of water was measured by the standard equilibrium method [2]. The spring water chemistry and $\delta^{15}N$ of nitrate was measured every six or eight weeks. Other water sources, such as springs, streams and wells in the recharge area were monitored bi-monthly for chemistry and $\delta^{15}N$ of nitrate. Only some precipitation samples were monitored for chemistry and $\delta^{15}N$ of nitrate and ammonium to estimate the range of values for infiltrating water. All types of applied fertilizers were analyzed for their $\delta^{15}N$ values. Soil samples for soil extracts were taken from two soil profiles at the sites with different application of fertilizers and different distance from the recharge site (near Bubovice and Vysoký Újezd villages). Samples represent three levels (0-25 cm, 25-70 cm and 70-110 cm or 70-140 cm), corresponding to A, Bv and C horizons. The sampling was done in June 1996, about three months after snow melting and a few small precipitation events. Samples of soil were placed into PE sampling bags and frozen on site at -80°C using dry ice in cooling boxes for transportation. Upon transportation to the laboratory, the samples were stored in a refrigerator at -16°C. A 500 g sample of soil was extracted with 1L of 1M KCl solution at room temperature by stirring the suspension for about 30 minutes. The extract was filtered through prefilter and fine filter and the filtrate volume was measured. The solution was checked for ammonium and nitrate content, conserved by an addition of thymol and stored in a refrigerator for steam distillation. Solution aliquots were alkalized with MgO and steam distilled (nitrate with the addition of Devarda alloy) into a small excess of diluted sulfuric acid. Ammonium sulphate was dried and stored for $\delta^{15}N$ analyses.

The $\delta^{15}N$ analyses were performed by flash combustion in Fisons 1108 elemental analyzer coupled to Mat 251 isotope ratio mass spectrometer via open-split interface ConFlo I in continuous flow regime. Sample size was from 0.5 to 1mg of N. External reproducibility of $\delta^{15}N$ measurement was 0.15‰, however, overall reproducibility of steam distilled samples was about 0.4 ‰.

4. RESULTS AND DISCUSSION

4.1. Flow dynamics

Figure 2 shows the discharge and temperature patterns of the studied spring. The studied hydrological year 1994-95 had high monthly precipitation totals during May and June while the several years before were characterized by precipitation much below long-term average (about 80% of normal). As a result of this, the discharge during autumn 1994 and winter 1994/1995 was extremely low. The discharge of autumn of 1995 was about 25 % higher when compared to 1994.

During the largest precipitation event of the monitored period (from 1. to 2. June, 1995, 59.1 mm of precipitation) local floods occurred in the study area. During this event a new swallow hole appeared in the upper part of the geographical catchment of the Svatý Jan pod Skalou karstic spring (about 1050 m from the spring site) and was immediately used for a simple tracer experiment using NaCl solution as a tracer [3]. This tracer experiment enabled calculation of some parameters of the lowest part of the unknown underground stream system. The discharge of the spring was 24.5 l/s during the experiment. The tracer signal appeared between 19 and 20 hours after injection into the swallow hole, peaked after 26 hours and returned to background level after 37 hours. Supposing no tracer loss in the system the total possible spring discharge (including the branches which were not monitored) was calculated at 36.9 l/s. The volume of water-filled cavities between injection point and discharge (distance 1050 m, altitude difference 127 m) is in the range from 1680 to 2430 m^3.

Based on the hydrograph analysis of the spring, three components of the karst system can be identified [4]. The first one (a short time component) represents the dominant effect of drainage of well conduit parts with a volume close to the traces experiment cavity volume. The second component (a volume component) dominates in the middle parts of the hydrograph's recession and characterizes the emptying of well-connected karstified fractures. Its volume corresponds to $3\ 10^5$ or $4\ 10^5$ m^3. The third component (an old component) represents matrix flow from deeply infiltrated precipitation into deeper parts of the synclinal structure. Its residence time is not known up to now. The tritium concentration for very steady base flow (winter 1994-95) was 23 TU, which is about 12 TU above recent precipitation

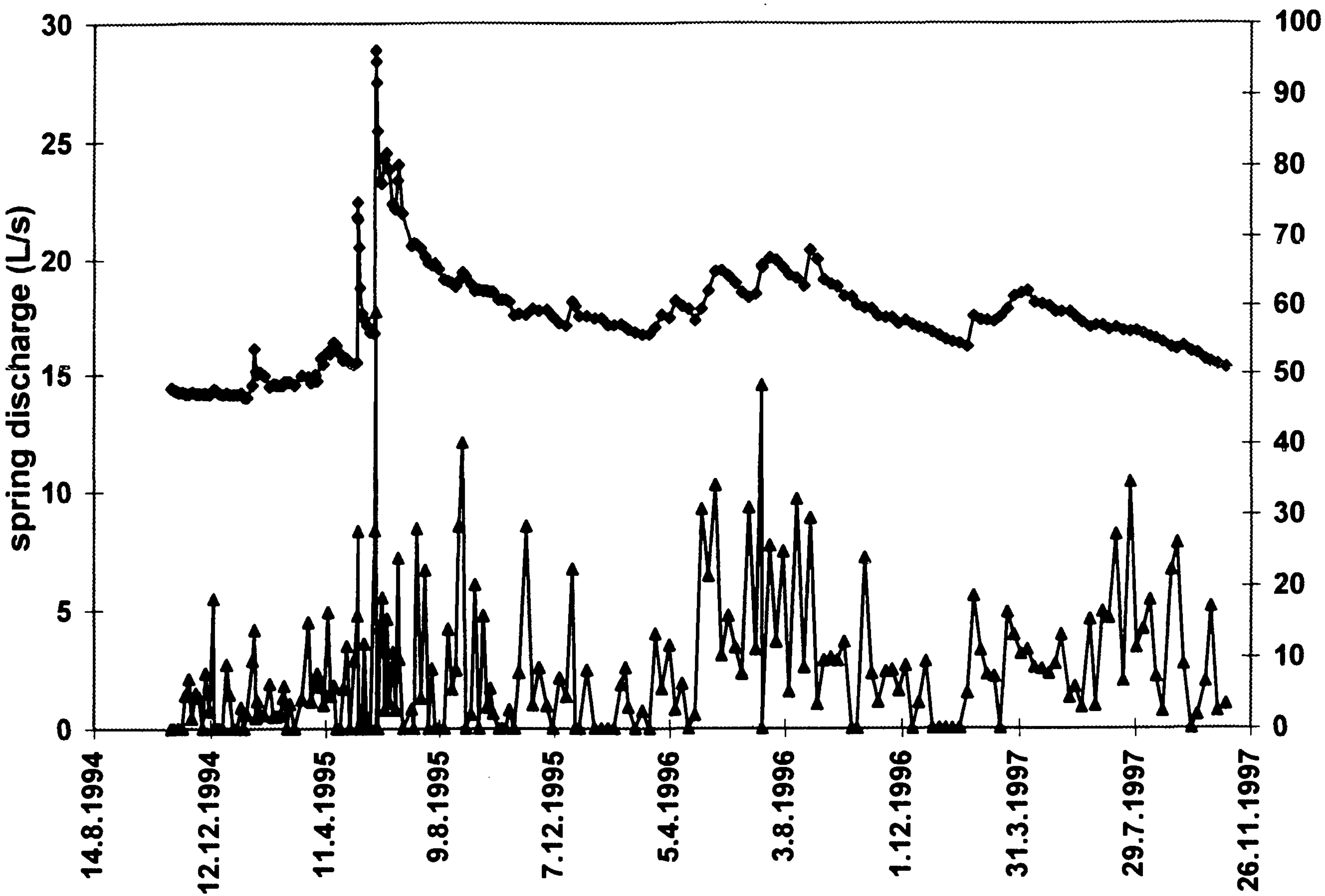

Fig. 2. Spring discharge and precipitation in the recharge area.

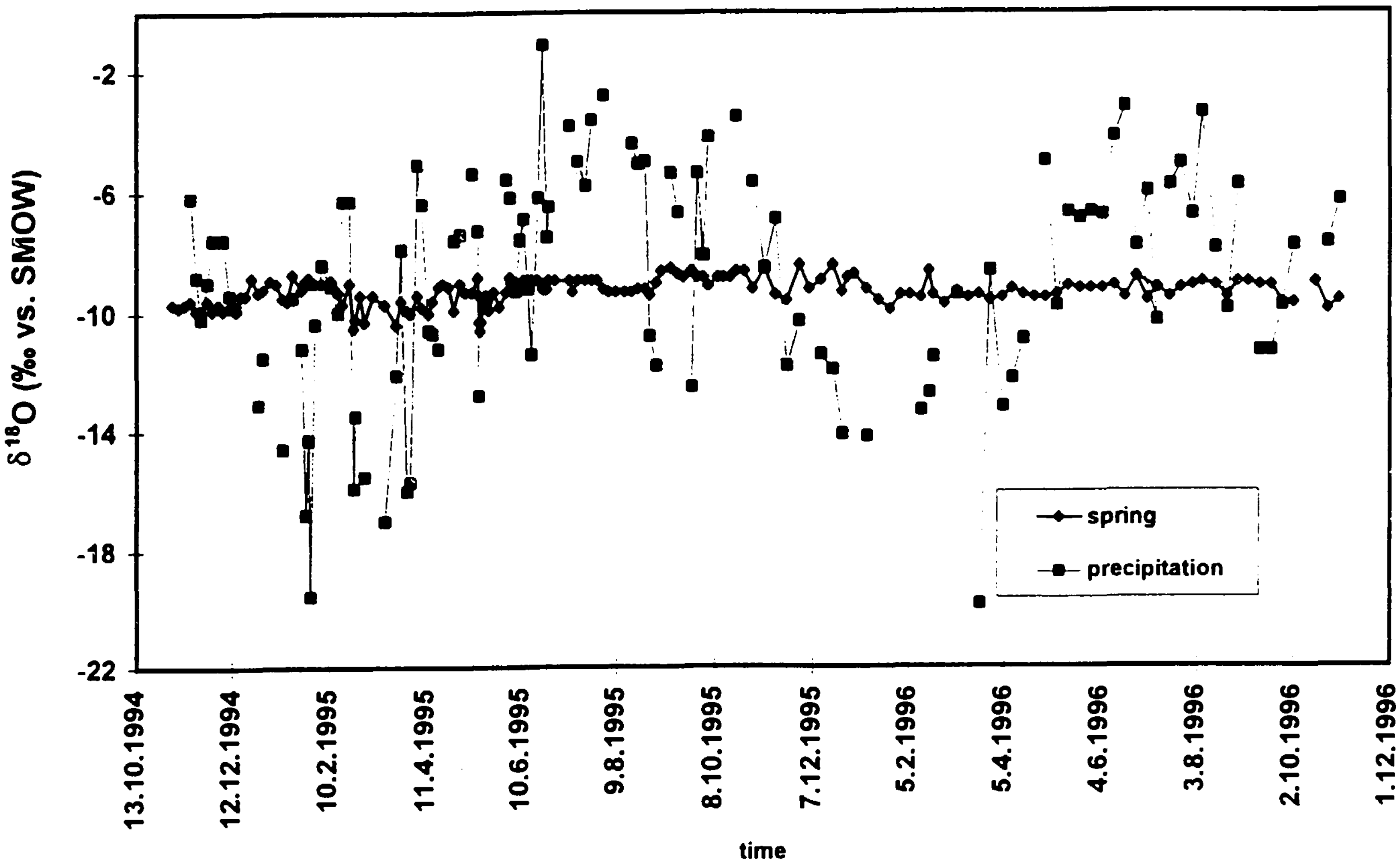

Fig. 3. d[18]O of discharge and precipitation.

(measured at IAEA laboratories in Vienna). In the past 46 TU was measured in 1986. These data together with recently measured discharge values were used for model age calculation [5].

4.2. $\delta^{18}O$ data

The $\delta^{18}O$ records of spring discharge and precipitation are represented on Fig. 3. Direct contribution of rapidly infiltrated precipitation is low, the variation of discharge $\delta^{18}O$ values corresponds to a dumping effect of the karst volume. The primary (seasonal) variation of $\delta^{18}O$ in precipitation appears in discharge $\delta^{18}O$ values with delay from two to about eight weeks. The complete two year record enables us to evaluate some spring characteristics such as direct component of discharge, infiltration coefficient (necessary for age model calculation) or to estimate an average residence time in the system. The direct or short time component of discharge p was calculated from seasonal weighted values of precipitation and discharge using Eqs.1 and 2:

$$\delta^{18}O_{tot} = p^* \delta^{18}O_{prec} + (1-p)^* \delta^{18}O_{gw}, \qquad \delta^{18}O_{gw} = \delta^{18}O_{average} \tag{1}$$

$$\delta = (\delta^{18}O_{tot} - \delta^{18}O_{gw})/(\delta^{18}O_{prec} - \delta^{18}O_{gw}) \tag{2}$$

Measured values are summarized in Table I, calculated p values are presented in Table II.

The proportion of direct (short time) component of the total discharge of karstic system is low as it corresponds to the relatively low importance of direct inflow on the total karst recharge. The estimation of $\delta^{18}O_{gw}$ for all year period was calculated to be related to the seasonal p values. The value -9.35 ‰ is far from the $\delta^{18}O$ values for base flow conditions (autumn and winter 1994 ~ -9.1‰) and it reflects unusually high precipitation input in spring 1995. In the year 1995 the average discharge is mostly formed by the volume component rather than old groundwater.

The proportion of volume and the old component of the total karst discharge cannot be estimated as easily as the direct precipitation component. We do not know the infiltration in winter and summer period (so we cannot calculate the input $\delta^{18}O$ values of volume reservoir) and a roughly estimated size does not allow to precise estimate of the resulting time shift in $\delta^{18}O$ without modelling of mixing inside the reservoir. The infiltration coefficient a defined as the ratio of summer and winter infiltration $a = a_s/a_w$ can be calculated from the weighted $\delta^{18}O$ of precipitation in winter and summer period (w and s, i and j indices) and $\delta^{18}O_{gw}$ (Eq.3) [6]:

$$a = (S_w P_i d_i - d_{gw} S_w P_i)/(d_{gw} S_s P_j - S_s P_j d_j) \tag{3}$$

The a value is a relative number i.e. a value 0.5 means twice more infiltration in winter than in summer. With values from Table 1 we can calculate a for 1995 as 0.4 and for 1996 0.3 i.e. $\delta^{18}O_{gw}$ corresponds to ratio of summer and winter precipitation 1:2.5 in 1995 and 1:3.3 in 1996. These values are quite close to the reciprocal ratio of precipitation sums in summer and winter period (see Table I), which means that the infiltrated amounts are roughly the same in winter and summer periods.

Table I: Measured $\delta^{18}O$, precipitation and discharge values and calculated weighted averages

Period	winter 95	summer 95	all 95	winter 96	s ummer 96	all 96
$\delta^{18}O_{prec}$ w.avg.(‰)	-11.34	-7.36	-8.54	-12.25	-7.52	-8.67
$\delta^{18}O_{tot}$ w.avg. (‰)	-9.51	-9.11	-9.27	-9.23	-8.95	-9.08
SP_id_i	-2345	-3593.3	-5938.3	-1785.3	-3298.8	-5084.1
SP_i	206.7	488.3	695	145.7	438.7	584.4
$SQ_id_i^*$	-1144.2	-1650.6	-2794.8	-1367	-1495.2	-2862.2
SQi^*	120.2	181.2	301.4	148	167	315

* Qi are in mm, recalculated from 19l/s average discharge and 7.6 km^2 of recharge area

Table II: Calculated proportions of precipitation on total discharge

Period	winter 95	summer 95	all 1995	winter 96	summer 95	all 1996
p	0.11	0.08	0.1*	0.05	0.08	0.07*

* all year values calculated with the following estimation of $\delta^{18}O_{gw}$: (1995) -9.35‰ and (1996) -9.11‰

The $\delta^{18}O$ of precipitation plotted against time (Fig. 3), can be approximated by a simple sine function $\delta^{18}O_{prec} = D + A \sin wt$. Supposing that such precipitation infiltrates to „well mixed" groundwater system (an exponential model) with volume V which is discharged with a steady flow rate Q, the average residence time of infiltrated precipitation in groundwater system is T = V/Q. T can be calculated from the attenuation of the sine amplitude A of input to B of output

$$\delta^{18}O_{gw} = D + B \sin(wt+f) \qquad (4)$$

where f is a phase shift, which is usually without any physical meaning because it is from the function definition limited to 3 months maximum. The attenuation is B/A and corresponding residence time T is calculated as [7]:

$$T = 1/2p\ [(B/A)^{-2} - 1]^{1/2} \text{, by definition T is in years} \qquad (5)$$

T values calculated from winter and all year periods are summarized in Table III. This varies between 16 (1995) and 21 months (1996). As the direct component of the total discharge has only a minor effect (about 10% in average conditions, up to 20% in the flood events), the residence time estimate represents the karst volume component and deep groundwater component together and can be used for futher estimation of component volumes as related to the total karst volume in model calculations.

Table III. Calculated karstic residence time from attentuation of $\delta^{18}O$

Period	winter95	all 1995	winter96	all 1996
Tx12 (in months)	15.3	16.7	16.4	21.2

4.3. $\delta^{15}N$ of spring nitrates

The nitrate content of the discharge varies with time within a range of about 10% (see Fig. 4). Decrease of nitrate content corresponds with abundant precipitation and can be explained as a dilution effect of direct (or short time) component of total discharge. Direct inflow of precipitation brings low nitrate content from atmospheric nitrate and infiltrated

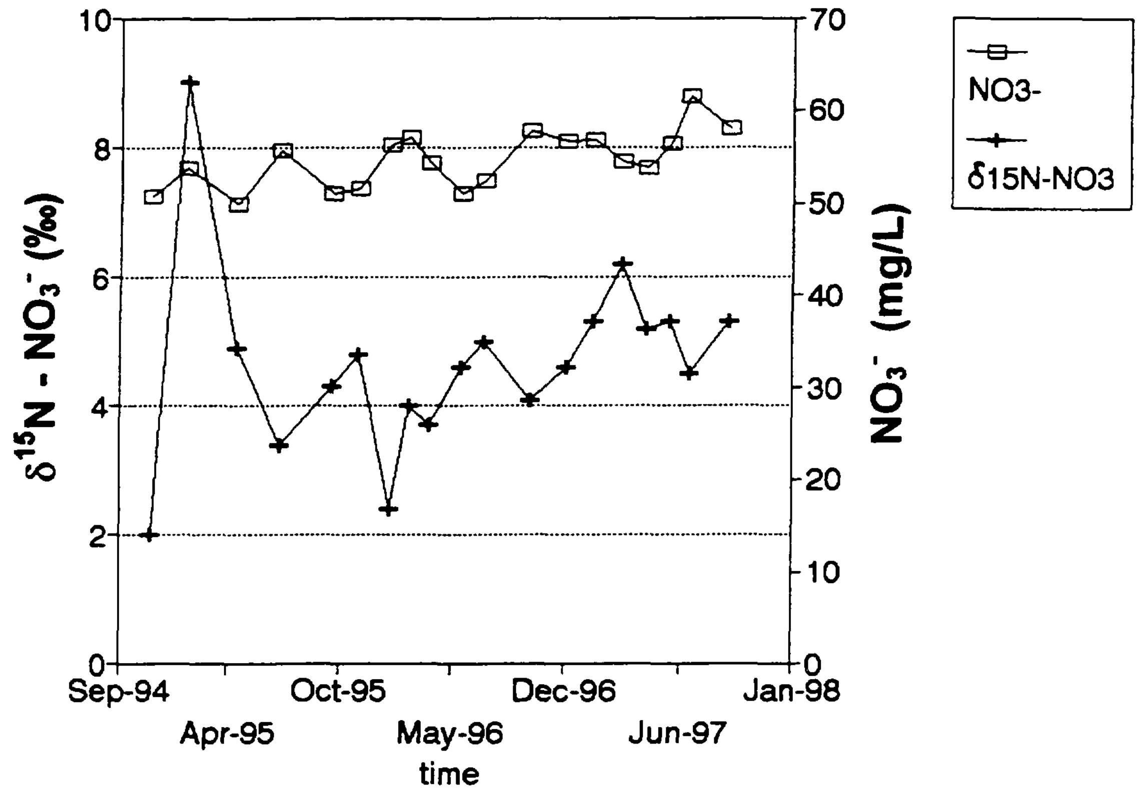

Fig. 4. Nitrate content and $\delta^{15}N$ of nitrate in spring discharge.

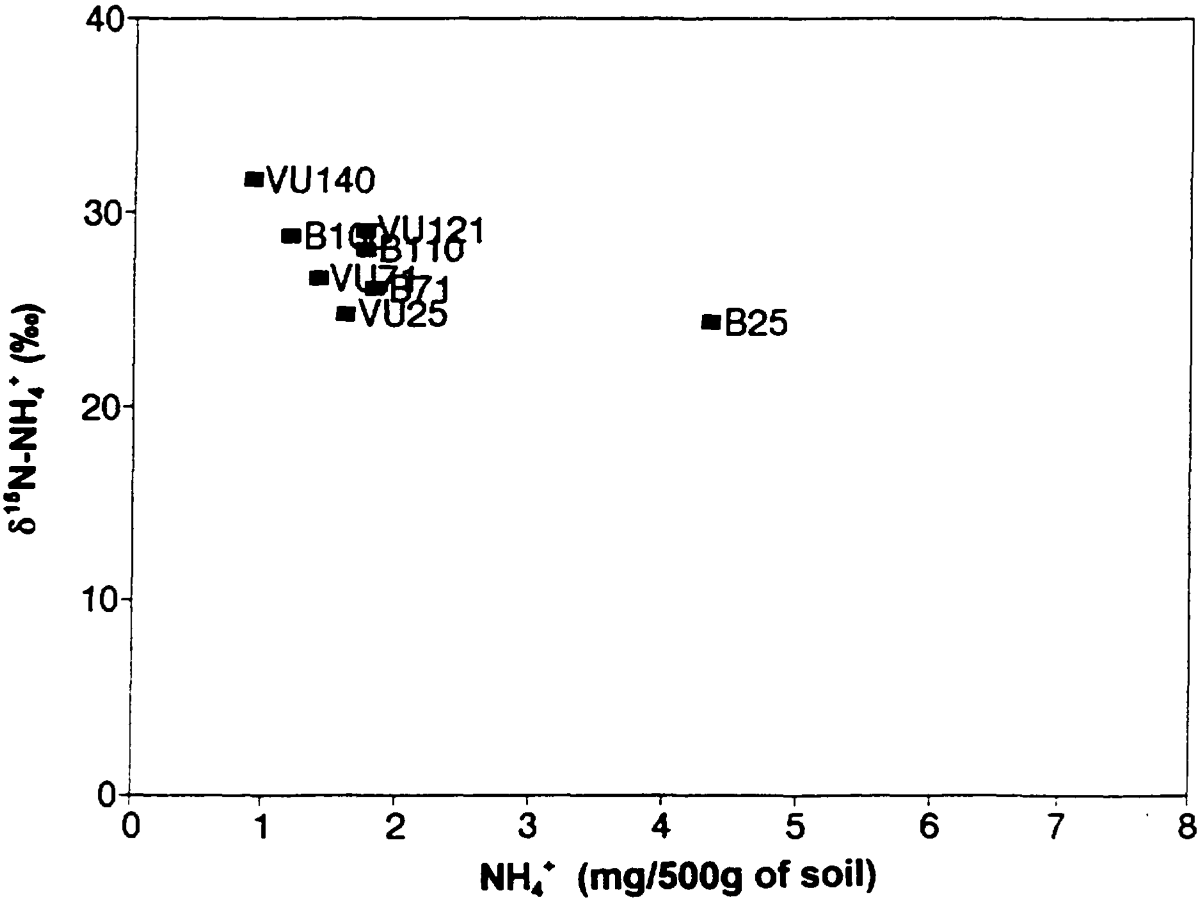

Fig. 5. $\delta^{15}N$ of exchangeable ammonium in soil extract (B - Bubovice, VU - Vysoký Újezd, numbers correspond to sample depth in cm).

forest soil water which are both in the range of 1-2 mg of nitrate per liter. Most of the nitrate is coming from the karst volume or deep groundwater with nitrate content increasing with time. In contrast to nitrate content, the $\delta^{15}N$ of nitrates varies with time periodically (Fig. 4) from about 5 to 2‰ with one exceptional value around 10‰ in the beginning of study. Two hypotheses have been developed for explanation of $\delta^{15}N$ variation: (i) nitrate from the karst volume and deep groundwater participate with different contributions to overall discharge and both the reservoirs have different $\delta^{15}N$ (karst close to zero and deep groundwater more positive because of denitrification reactions in the aquifer), (ii) nitrate infiltrating to the karstic system has a different $\delta^{15}N$, according with applied fertilizers in the past. The areas of fertilizer application have different distances from the discharge site i.e. infiltrated waters have different travel times in the karstic system and the resulting nitrate mixture varies in $\delta^{15}N$. A deep reservoir with stable nitrate content and $\delta^{15}N$ buffers variation of the karst volume content. Both hypotheses have a weak point in the rather low variation of nitrate content i.e. we have to suppose that sources have similar nitrate content but different $\delta^{15}N$. The very positive $\delta^{15}N$ of discharged nitrate at the beginning of the study has not been completely explained. Probably it resulted from the unusually dry season 1994, with highly nitrified ammonium nitrogen accumulated in the soil and drained with the first heavy storm to the karst volume to be discharged and with delay corresponding to its travel time.

4.4. $\delta^{15}N$ in soil and other sources

To identify infiltrating nitrates soil profiles at two sites were investigated for $\delta^{15}N$ of exchangeable ammonium and nitrate in soil solutes. Profiles are located at about 2 km (site Bubovice=B) and 3.5 km (site Vysoký Újezd=VU) distance from the discharge site. Samples were taken from the Ap horizon (0-25cm), Bv1 and Bv2 horizons (25-71cm, 71-121cm) and C horizon (121-140cm). The $\delta^{15}N$ of ammonium ions is positive, in the range from 25 to 32‰, resulting from extensive fractionation by ammonia loss and following nitrification (see Fig. 5). $\delta^{15}N$ of nitrate produced from these ammonium ions is in the range from 10 to 14‰ (see Fig. 6). Such nitrate is typical for most of the horizons at the Bubovice site. Nitrate of inorganic origin with $\delta^{15}N$ around 0‰ are typical for the Vysoký Újezd site (and 110cm horizon at Bubovice) [8].

Two types of nitrates with different $\delta^{15}N$ were localized in the soils of the probable recharge area of the karst system. One type of nitrate is produced by nitrification of ammonium ions of organic origin and their $\delta^{15}N$ varies around 10‰. Other type of nitrate is the rest of the extensive application of inorganic nitrate fertilizer with $\delta^{15}N$ around 0‰. This nitrate is not changed by any denitrification. According to the agronomic record, we expect that all of the recharge area consists of parts with these two types of nitrate corresponding to fertilizer application in the past. It means that infiltrating precipitation transfer both type of nitrates into the karst volume and the resulting $\delta^{15}N$ of nitrate in discharge varies according to predominance of one of them in the volume component of the karst dicharge.

Infiltrated nitrate was also monitored in small water sources located in or close to the recharge area of the karstic system. Two of them should be mentioned because they represent nitrate infiltrating to shallow groundwater. One is a spring at Sedlec, another a well at Kozolupy (Fig. 6). The $\delta^{15}N$ of spring nitrate varies from 2 to 9 ‰ with more positive values during summer and less positive values in winter. The seasonal effect results both from the source and water mixing. At base flow conditions spring nitrate has $\delta^{15}N$ close to 2‰ which changes to negative or positive values according to inorganic or organic nitrate as they

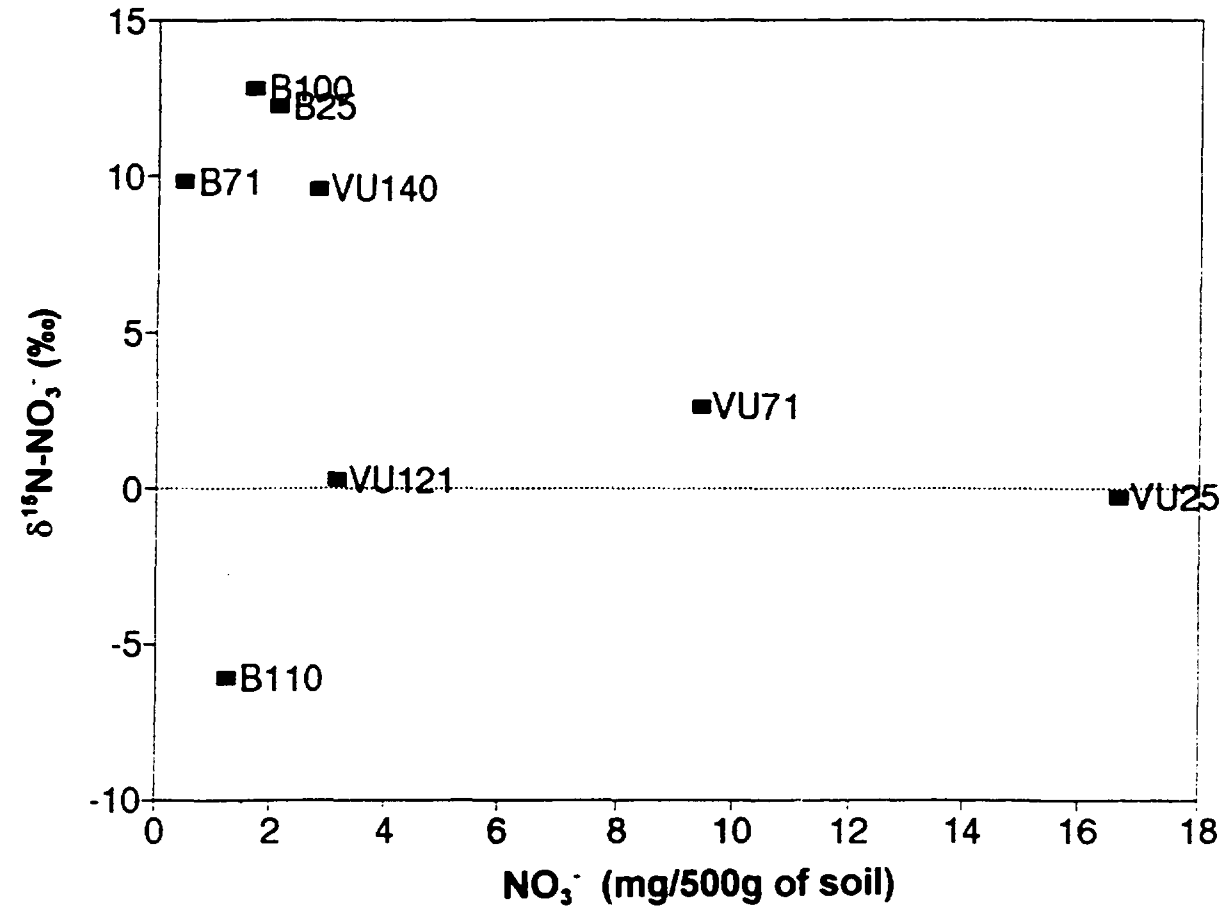

Fig. 6. $\delta^{15}N$ of nitrate in soil extract (B - Bubovice, VU - Vysoký Újezd, numbers correspond to sample depth in cm).

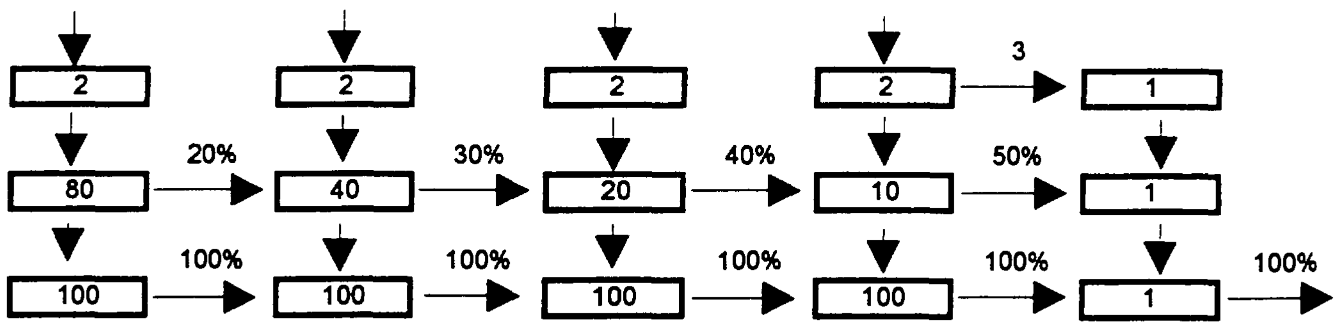

Fig.7. Cell combination used in model calculation. Numbers are volumes of cells (two units correspond to one day average discharge).

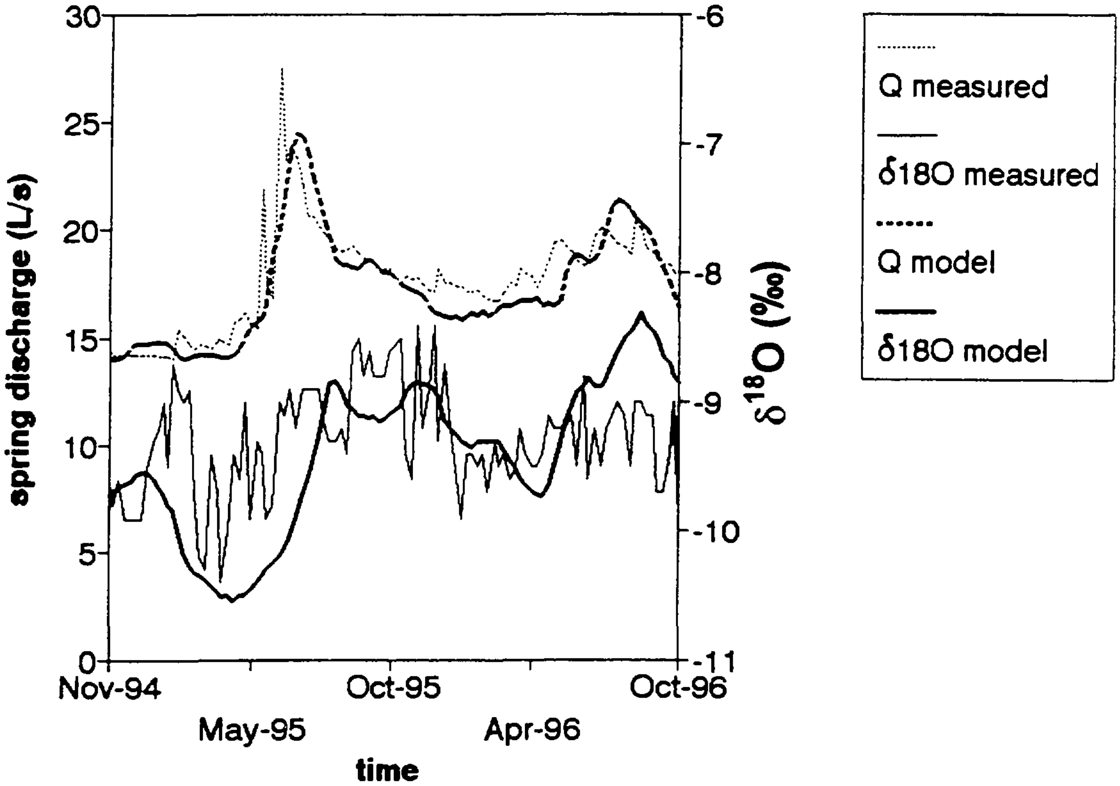

Fig.8. Observed and calculated discharge and $\delta^{18}O$ of the spring.

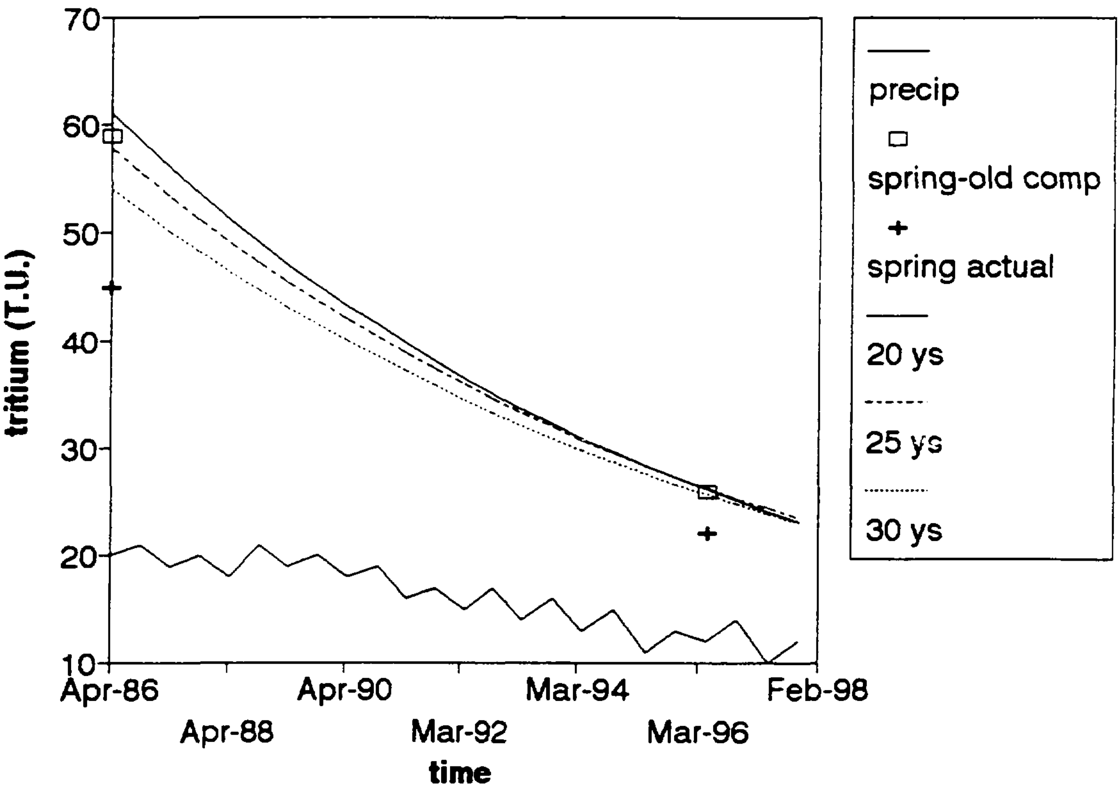

Fig.9. Observed and fitted tritium concentrations for old discharge component.

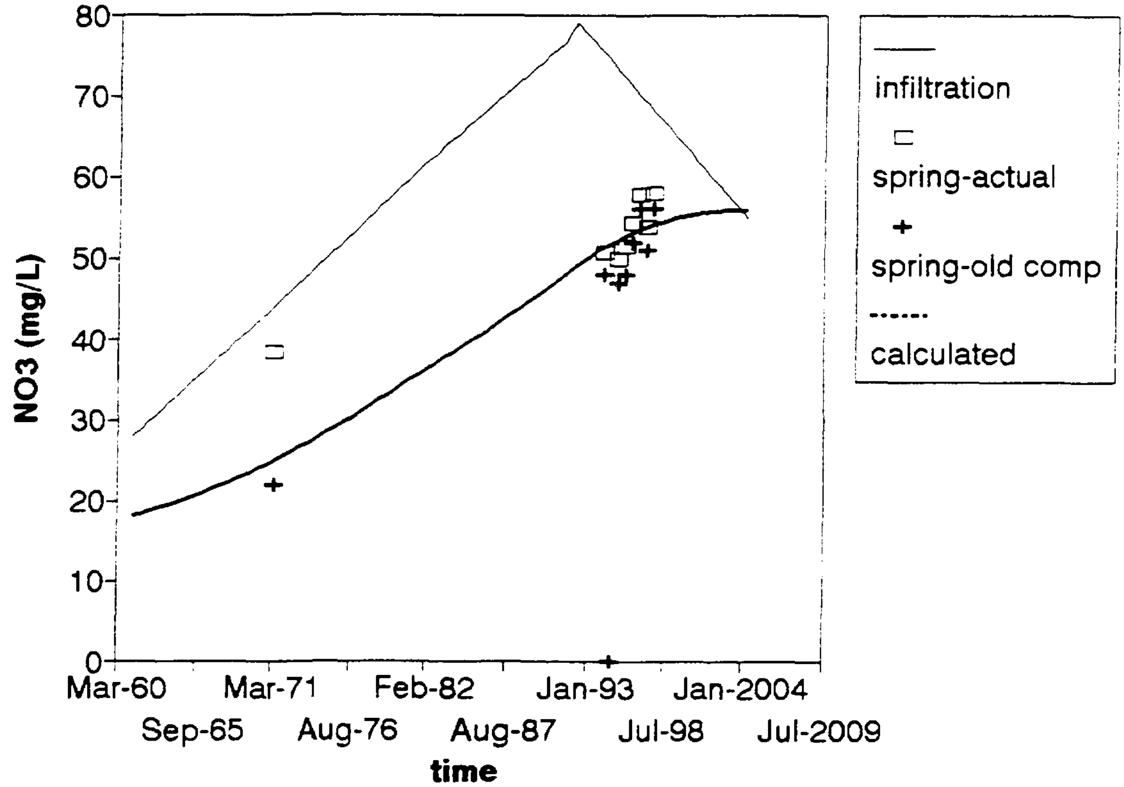

Fig.10. Calculated nitrate content of infiltrated water and old discharge component.

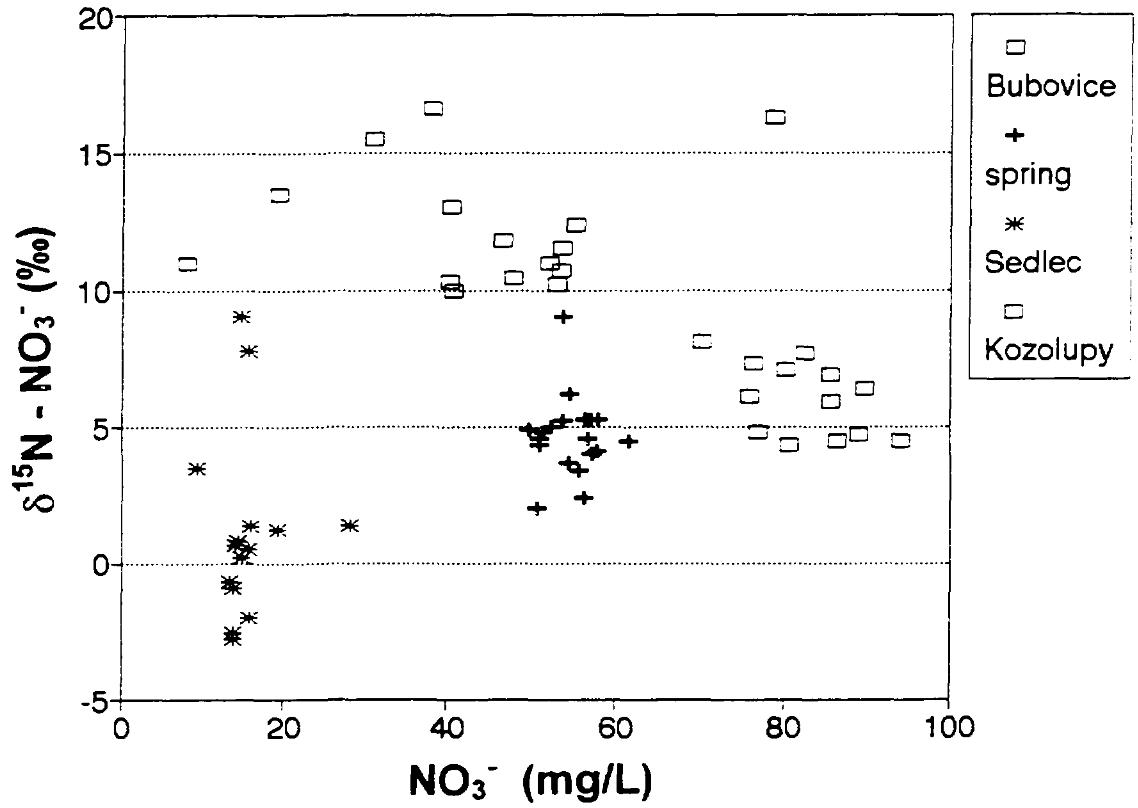

Fig.11. Plot of $\delta^{15}N$ versus nitrate content for all monitored water sources.

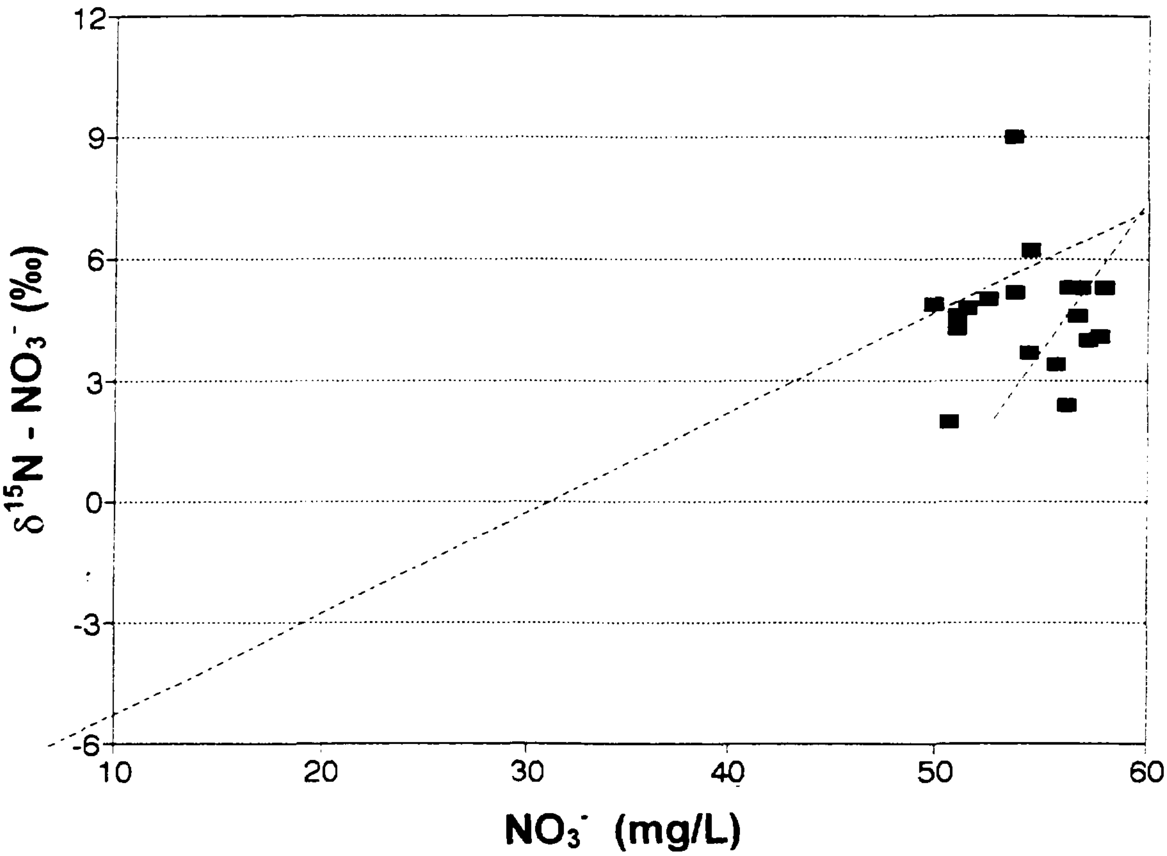

Fig.12. Plot of $\delta^{15}N$ versus nitrate content for the spring.

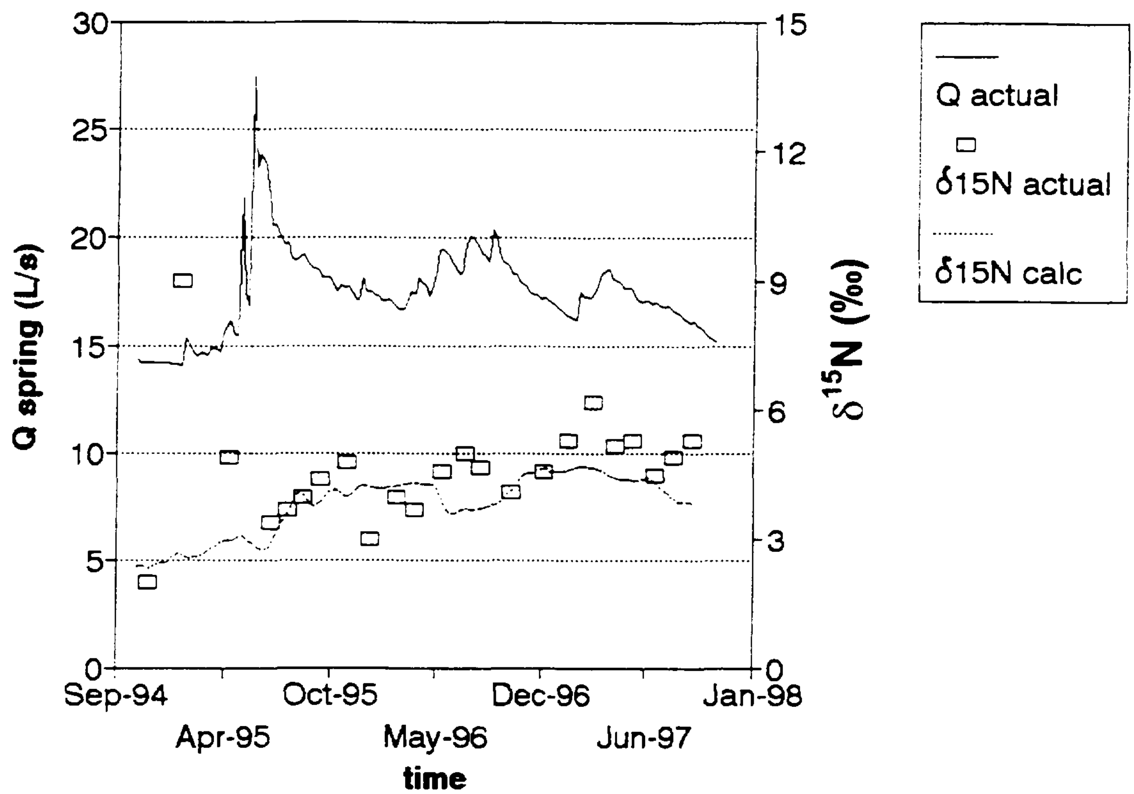

Fig.13. Observed and calculated $\delta^{15}N$ of nitrate in the spring. The same model parameters were used as for $\delta^{18}O$ calculation.

participate in discharge. Average nitrate content is about 15 mg/L with low contamination from agriculture activities (the spring is located outside the fields). The Kozolupy well collects shallow infiltrated water from an agricultural area close to the Bubovice soil profile. Nitrate of organic origin dominates in runoff and the nitrate content is even higher than in the karstic spring.

4.5. System modelling

A compartmental (mixing cell) model [5] was used for discharge and ^{18}O modelling. Cell mixing models proved to be usefull in the modelling of karstic systems [5, 10]. Their advantage is optimalization of both variables, i.e., discharge flow and ^{18}O using a single parameter of cell size (transit time). The program MODEL written by Y.Yurtsever [11] was used. An estimate of cell sizes is based on observed values recalculated for the average discharge of the spring (Fig.7). In the first row, the cell combination represents shallow soil layer keeping recharge water for one day only. The last member contributes as a direct contribution to discharge. In the second row, the horizontal cell combination can be considered as a relatively fast flow through well-connected karstified fractures which partially supply spring discharge and partially infiltrate to the deeper reservoir. In the third row, the horizontal cell combination resembles slow flow from a deeper structure. The total volume of the cells is close to the volume estimated from an attenuation of ^{18}O variation (Eqs. 4 and 5). Calculated values fit the observed variations in discharge and ^{18}O with exception of fast changes within one or two sampling time intervals (Fig.8).

4.6. Turnover time of the deep ground water component

The conceptual model developed for spring discharge and ^{18}O variations cannot be easily used for estimation of turnover time (mean residence time) of the groundwater reservoir. Only a few tritium data from a relatively short period are available and model volume size is too small to give a reasonable estimation of an old component of spring discharge. From the mass balance of discharge, it is estimated that the contribution of old water component is about 60 or 70 % of total discharge. The rest is recent precipitation (direct and fast components). Assuming 60% contribution of an old component, we can estimate its tritium concentration from the measured tritium content of precipitation and discharge. These values together with the value measured ten years ago were used for groundwater age estimation. The input tritium function was calculated from the Vienna record (which is nearly identical with the tritium record measured abou 60 km from the studied area [12]). The same infiltrated amount was assumed during winter and summer periods. The tritium distribution was calculated for groundwater reservoir sizes corresponding to residence time variation of from twenty to thirty years (Fig.9). About twenty two years residence time gives the best fit.

4.7. Nitrate content prediction

A substantial decrease of the applied fertilizers during the most recent years (down to about 35% of dose applied before 1990) enables the prediction of changes in nitrate content of the spring water. With an estimation of groundwater residence time, we can calculate the predicted nitrate content in ground water. For this an input function of infiltrated nitrate was constructed based on both historical and recent data (Fig.10). Using the same type calculation as for tritium we can construct a future development of nitrate content of ground water component. According to this model the nitrate content of the spring will be stabilized in the next six or seven years and will start to decrease in about ten years. As expected, any remediation of the quality of the groundwater is quite slow even after such a dramatic decrease in applied fertilizers.

4.8. Modelling of ^{15}N in spring

The conceptual model of system flow may be further used for calculation of $\delta^{15}N$ in discharge. Inputs are not so well defined as in the case of ^{18}O in precipitation (more heterogenic) and the time interval is longer. To be sure about the $\delta^{15}N$ range of possible infiltrating inputs into the karstic system, we compared the nitrate content and $\delta^{15}N$ of the spring and all other water sources in the area (Fig.11). From the plot of $\delta^{15}N$ versus concentration we can identify possible sources (if measured) contributing to spring discharge. Theoretically the $\delta^{15}N$ of the spring should be combined from water monitored at Sedlec and Kozolupy. A dilution effect of direct atmospheric input can be estimated from measured precipitation samples, in which $\delta^{15}N$ varies in the range from -2 to -10‰ and nitrate content from 5 to 10 mg/L, or from the extrapolation of $\delta^{15}N$ versus concentration plot of the spring (Fig.12). From the latter, two types of „mixing“ lines were identified with end members (marginal points) corresponding to: -6‰ and 8 mg/L for an average atmospheric input, 2‰ and 52 mg/L for ground water component, and 7‰ and 60 mg/L for recently infiltrating water. It is difficult to reconstruct their time variation. It seems to be a crucial problem in the case of modelling of $\delta^{15}N$ in the spring discharge. Using Sedlec and Kozolupy data together with an average atmospheric input as the actual input functions for the model we obtain $\delta^{15}N$ variation which is in the range of observed values but the calculated period is nearly twice as long as the actual period (Fig.13).

5. DISCUSSION

The parameters of the conceptual model of flow and ^{18}O in discharge were derived under simplified assumptions (constant volume of the system, limited number of inputs and mixing cells) and may serve as a starting point for further study. The actual system obviously changed its volume during the study as can be seen from different values of base flow at the beginning and after the first and second years of observation. Including volume changes into the model is not possible and can be substituted by modification of input function only, which would mean an a posteriori change of actual data. Calculated discharge and its $\delta^{18}O$ are assumed to be continually mixed before output from the system. Actual discharge is mixed in large horizontal channels close to the output and discharged water is inhomogenic in composition and flow dynamics. Moreover, the unsaturated zone is formed by large fissures in the vertical direction which are discontinous in flow according to infiltration. Following an abundant precipitation event fissures are filled with fast infiltration because of shallow soil zone and develop a hydrostatic pressure against groundwater flow to supress it. This is obvious from the $\delta^{18}O$ record of discharge which varies within the measured interval from the actual value to some „bias“ value which is nearly constant. The process is repeated regularly after sufficiently high precipitation. In the model this was approximated by a „threshhold“ value, but the flow is not pulsing as an actual discharge would.

An estimate of ground water turnover time is an important parameter for any type of calculation of future nitrate content in the spring. The calculated value is very probably an overestimation because of existence of stagnant zones which contribute to tritium concentration by diffusion but do not contribute to mobile water. Nitrate calculation will not be affected if nitrate is distributed similarly to tritium.

The conceptual model used which was acceptable for flow and $\delta^{18}O$ modelling fails in the case of $\delta^{15}N$ of dissolved nitrate. It may result from unknown inhomogenities either of isotopic composition of the infiltrated nitrate, or from different mobility of water and dissolved component. Any adsorption effects can be excluded in the case of nitrate, as well as additional reactions changing the isotope composition (denitrification) which is highly unlikely in the aerated unsaturated zone. Different mobility of dissolved nitrate and water can occur by delay of dissolved tracer in a microporous structure when mobile water is transported through fractures or karstic channels, or during partial saturation of the soil zone. The surface of karstic rocks below the soil layer is deeply weathered and very complex morphologically. Some sites are covered by a rather shallow soil layer, some sites develop deep pockets with high storage capacity for dissolved tracers which are mobilized only with infiltrating water. Abundant precipitation events which saturated even deep pockets transport substantially more nitrate than small events. Considering a short period of $\delta^{15}N$ variation in discharge water, such „flush" of nitrate inputs in the karstic system seem to be more probable than delayed diffusive transport.

6. SUMMARY

Data from flow dynamics, ^{18}O and tritium were sufficient for estimation of volume of the karstic system and residence times of three contributions (direct infiltration, fast and old component) of spring discharge. Estimated turnover time of the old component (about twenty two years) could be used for calculation of spring nitrate content in future. Sources of nitrate pollution were identified from $\delta^{15}N$ in soil solutes at sites with different agronomic records (sequential use of organic and inorganic fertilizers). Spring discharge nitrate is formed from an atmospheric source (an average nitrate content of 8mg/L and $\delta^{15}N$ -6‰) and two groundwater components with nitrate content from 50 to 60 mg/L and $\delta^{15}N$ values from 2 to 7‰. Atmospheric nitrate has a diluting effect only in the range of 10% maximum. The contribution of groundwater components varies in time more frequently than can be described by the model developed for flow dynamics and ^{18}O. It may result from different mechanism of water and nitrate transport within the unsaturated zone.

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