ZAP, K. V. (1860): Benediktinští klášterové sv. Jana Křtitele na Ostrově a ve Skalách. – Památky archeologické, 4, 108–117, 154–173. Praha.

ZAPLETAL, J. (1989): Podtraťová jeskyně – vertikální rozpětí přes 100 m. Zpráva o průzkumné činnosti za období 1981–1989. – Čes. Kras, 15, 81–85. Beroun.

ZEMAN, O. (1996): Hydrogeologie karbonátových hornin siluru a devonu Barrandienu. Bakalářská práce. – MS Přírodověd. fak. Univ. Karl. Praha.

ŽÁK, K. (1999): Vztah hydrotermálních a krasových procesů v Českém krasu; diskuse. – Čes. Kras, 25, 53–63. Beroun.

ŽÁK, K. – KADLECOVÁ, R. – KADLEC, J. – KOLČAVA, M. (1996): Chování krasových pramenů ve Svatém Janu pod Skalou během mimořádných srážkových událostí v květnu a červnu 1995 a nový občasný ponor v údolí Propadlé vody. – Čes. Kras, 22, 41–47. Beroun.

sine (1962): Dictionary of geological terms. – American Geological Institute, Dolphin Books. New York.

– (1982): Mapa CHKO Český kras 1 : 25 000. – Správa CHKO Český kras. Karlštejn.

– (1994): Svatý Jan pod Skalou, dějiny místa a bývalého kláštera benediktinů „Ve skalách". – Nákladem Svatojanské nadace. Svatý Jan pod Skalou.

– (1996): Vyšší geomorfologické jednotky České republiky. – Čes. úst. zeměměřický a katastrální. Praha.

Holocene calcareous tufa accumulation and karstic spring in Svatý Jan pod Skalou (Bohemian Karst)

English Summary

This extended English summary refers to Figures, Tables and Appendices included in the Czech-written text. Figure and Table captions are given both in Czech and English. Authors of individual parts of this English summary are identical to the authors of corresponding Czech-written sections.

1. Introduction

In the Bohemian Karst, a NE-SW elongated karstic area located in the central part of the Czech Republic between Praha and Zdice, numerous Holocene deposits of calcareous tufa occur. The tufa accumulations, deposited by karstic springs and several surface streams, were studied in detail by lithological and especially biostratigraphical methods (mostly assemblages of *Mollusca*) over the past decades. Regional reviews were published by KOVANDA (1971) and LOŽEK (1992). Today, numerous karstic springs and several small surface streams still deposit calcareous tufa in this area.

Among Holocene tufa accumulations of the Bohemian Karst the deposit in Svatý Jan pod Skalou is of prime importance. Svatý Jan pod Skalou is a small village located 25 km SW of Prague in a deep valley of the Kačák stream cutting across Silurian and Devonian sequences of the Barrandian Palaeozoic. At the bottom of the valley the largest karstic spring of the entire area (mean discharge of about 20 L/s) has formed a 17 m thick tufa deposit. The sedimentary sequence of the tufa accumulation records climatic changes and nature development of the area during most of the Holocene. The site has been thoroughly investigated using lithological and biostratigraphical methods, and ^{14}C dating of carbonate was performed on several calcareous tufa layers in the upper part of the sedimentary sequence. Various aspects of the calcareous tufa accumulation in Svatý Jan pod Skalou have been studied by (chronologically): KREJČÍ 1877, BABOR 1901, POČTA 1917, PETRBOK 1923a, 1923b, 1925, NĚMEJC 1927, 1928, SLAVÍK 1930, PETRBOK 1933–1934, 1936, 1940, 1941, Němejc 1942, PETRBOK 1956a, LOŽEK 1955, 1959, 1960, KOTLABA 1962, LOŽEK 1964, JÄGER – LOŽEK 1968, JÄGER 1969, KOVANDA in ŠIBRAVA et al. 1969, LOŽEK 1967a, KOVANDA 1971, ŠVASTAL 1972, LOŽEK 1973a, 1973b, KRÁLÍK 1974, LOŽEK 1974, ŠILAR 1976, CÍLEK 1988, HORVATINČIĆ et al. 1989, BOUZEK 1990, ŠILAR et al. 1990, BOUZEK 1993, LOŽEK – CÍLEK 1994, LOŽEK – CÍLEK 1995a, BENKOVÁ – ČTVERÁK 1998.

The extraordinary beauty of the deep canyon with steep limestone walls and the existence of a permanent source of drinking water attracted man's attention very early. Several caves were populated as early as in Late Palaeolithic and a large fortified settlement existed on a hill adjacent to the spring during the Late Bronze Age. According to a legend, St. Ivan lived in a cave inside the tufa accumulation as a hermit in the 9th century AD. Later in the Middle Ages the site became an important place of pilgrimage. A large Baroque monastery and church were built near the cave. Human activity brought serious damage to the tufa accumulation, leaving several artificial cuts, caves and vaults accessible for study. Thus, the internal structure of the tufa accumulation can be studied in a great detail.

During the earlier research of calcareous tufa accumulations of the Bohemian Karst radiogenic dating in combination with biostratigraphic and geochemical tools have never been used. Therefore, we performed a detailed study of the climatic record at Svatý Jan pod Skalou using several different dating methods, molluscan assemblages and geochemical data. In addition, long-term monitoring of the karstic spring was carried out and a hydrological model was developed. This paper presents the results of research into two different yet genetically linked objects – the tufa deposit and the karstic spring.

Present-day geographical, environmental and climatic conditions

The bottom of the deep valley of the Kačák stream is in the village of Svatý Jan pod Skalou located at ~230 m a. s. l. This Quaternary, up to 160 m deep valley is surrounded, especially in the east, by a relatively flat countryside with altitudes between ~420 and ~380 m a. s. l., representing old peneplanated Cretaceous and Tertiary surfaces. Natural and/or semi-natural plant assemblages of the valley are highly variable, dominated by oak, beech and ironwood forests, while the flat countryside is dominated by agriculturally cultivated fields. The valley is part of the State National Reserve Karlštejn, the whole area belongs to the "Protected Landscape Area Český kras" (Bohemian Karst).

The study site belongs climatically to a relatively warm and dry area of central Bohemia. Present-day mean annual temperatures are between 8 and 9 °C and mean annual precipitation totals are slightly above 500 mm.

Morphology of the valley is controlled by rock lithology and by folding and faulting of a Palaeozoic unmetamorphosed sedimentary sequence. Silurian rocks are represented mostly by altered submarine basalts (diabases) and tuffs, and occasionally by shales and limestones. The volcanic rocks locally emerged from the sea during Silurian, forming volcanic islands. The Devonian rocks are represented mostly by a sequence of lithologically variable limestones, while the uppermost part of the sequence (Late Eifelian to Givetian) is formed by flysh-like siltstones and claystones. The principal fold structure of the studied area is the NE-SW trending Holyně-Hostim Syncline, affected by both longitudinal and transverse faults. These two systems of faults are important for both the circulation of groundwater and development of caves. Details on Palaeozoic rocks can be found in Chlupáč et al. (1998).

Since the karstic rocks are in places overlain by Cretaceous marine sediments and fluvial sands and gravels of a complex system of Tertiary and Quaternary river terraces, the evolution of karstic features (caves, groundwater flowpaths, etc.) is extremely difficult to understand and opinions often vary. There is, however, an agreement in that the cave systems evolved in several steps over long periods of time, often deep below the local erosion base.

History of human impact on the calcareous tufa deposit

The first important period of human activity relates to construction of two fortified settlements on hills adjacent to the spring and tufa accumulation during the Late Bronze Age. The area was intensively populated until the Early Iron Age (Benková – Čtverák 1998). The construction of fortifications consumed much timber and extensive deforestation of the slopes overlooking the tufa deposit could have been, along with climatic change, the reasons for the formation of a gully in the tufa accumulation.

The so called Ivan's cave, formed probably by subrosion and/or erosion of the Kačák stream in the frontal part of the tufa accumulation, was artificially enlarged several times. The existence of the cave and a chapel in it was mentioned for the first time in 1205, when the Bohemian king Přemysl Otakar I confirmed donation of the cave to the Ostrov monastery. Both the cave and the frontal cascade of the tufa accumulation were artificially modified on many occasions. The largest changes were related to the construction of a new monastery and especially the new church (1657–1661). Probably in this period two extensive vaults inside the tufa deposit were also excavated.

2. Geological, morphological, lithological, paleopedological and mineralogical description of the tufa accumulation

The location and extent of the calcareous tufa accumulation in Svatý Jan pod Skalou are, together with a geological map of the adjacent area and with location of geologically and hydrogeologically important objects, shown in Fig. 2. The internal structure of the accumulation is best seen in an artificial longitudinal cut through the tufa body, about 70 m long. The outcrop starts at the steep frontal part of the deposit close to the church in the W, continues as an about 8 m high, ca. 30 m long artificial cut to the E (see Fig. 3), then changes its direction to NE and continues for another about 50 m along the shallow gully. At the place where this longitudinal section changes its direction, an excavated 6 m deep test pit is located, with a research drilling at its bottom. The overall thickness of Holocene sediments (mainly calcareous tufa) accessible for sampling is nearly 17 m. This vertical profile through the whole accumulation was selected for an integrated study (see Fig. 7 for detailed profile description and location of samples).

East of the tufa accumulation, there is a dry karstic valley called Propadlé vody (Sunken Waters) with just an ephemeral surface stream that appears for several hours or days during/after large precipitation events. From this valley clastic material was transported on the surface of the tufa accumulation by floods, especially during the sedimentation of the upper part of the tufa accumulation. An increasing proportion of clastic material in the tufa profiles located closer to the outlet of the Propadlé vody valley was recorded in three excavated cuts (see Figs. 4 and 5). Today, the spring discharges at the base of the tufa accumulation. The position of original spring is unknown, but it is generally believed that it was located either somewhere in the upper part of the tufa body or nearby in the valley of Propadlé vody. It follows that the resurgence point was moving during the tufa accumulation.

The SW part of the tufa accumulation has been removed both by erosion and quarrying of hard tufa for construction. The original extent of the deposit in this direction can be estimated from small remnants of tufa on limestone walls of the Kačák canyon (see Fig. 8).

As evidenced by drillings below the church and at the bottom of the test pit, the whole tufa accumulation is underlain by a relatively flat fluvial terrace of the Kačák stream. The terrace is of Late Pleistocene/Early Holocene age and is dominated by rounded pebbles of Upper Proterozoic graywackes, shales and silicites. Near the outlet of the Propadlé vody valley, angular fragments of limestones and Silurian diabases are more abundant, but the rounded material of the fluvial terrace is also present.

Today, the spring discharges between the tufa accumulation and the underlying gravel terrace. Several drillings verified an existence of cavities and hydraulically connected channels at this level. Subrosion of fine-grained portion of the clastic sediments resulted in gravitational movements and cracking of both the tufa deposit and the adjacent church (Fig. 1).

Lithology of the tufa deposit

Lithology of the deposit is highly variable both laterally and vertically. The frontal cascade is formed by hard porous (phytohermal) tufa across the whole thickness of the deposit. Behind the frontal cascade, where individual sedimentary layers are horizontal or sub-horizontal, two lithologically different complexes can be defined, with the boundary roughly equivalent to surface level at the site of the research pit, i. e., level of 0 m in Fig. 7:

i) the lower lithologically uniform sequence of hard porous tufa with only a few intercalations of disaggregating loose tufa containing a very limited amount of exotic clastic material, and

ii) the upper lithologically varied complex of layers of porous phytohermal tufa, oncoidal tufa and even lacustrine-like tufa intercalated with several horizons of buried soils and detrital horizons of coarse limestone scree. The scree horizons of the upper sequence become more frequent toward the dry valley of Propadlé vody.

The uppermost part of the upper sequence contains numerous fragments of pottery (especially in layers 3 to 9 in Fig. 7) which were dated to the Late Bronze and Early Iron Ages, as the so called Knovíz Culture (Štítary stage, HB1) and Bylany Culture (H C–D), which existed in this territory between ~8th and 5th centuries BC (Benková – Čtverák 1998).

Based on micromorphological study, the fossil soils occurring in the upper part of the sedimentary sequence are autochthonous (or semi-autochthonous) buried brown rendzina-type soils (rendzic leptosols), with minor admixture of quartz, mica and feldspar grains indicating transport of clastic material on the surface of the tufa accumulation during soil evolution.

The clastic horizons of the upper sequence are dominated by angular limestone fragments but contain also rounded quartz pebbles, indicating transport of clastic material from relics of Tertiary sediments from the upper segments of the Propadlé vody catchment.

Mineralogy and diagenesis of calcareous tufa

Mineralogy of tufa is very simple, dominated by low-Mg calcite and minor clay minerals and quartz grains present in the upper part of the sequence. In the upper one third of the thickness yellow, red and black layers of tufa coloured by Fe-hydroxides and Mn-hydroxides occur, precipitated on geochemical barriers of buried soils.

Some authors (e.g., Kovanda 1964, Ložek 1963a) have suggested diagenetic changes of calcareous tufa resulting in significant solidification of the tufa by filling of open spaces and recrystallization of calcite ("travertinization of tufa"). Detailed study of hard tufa from the lower sequence has shown that even small cavities after decomposed wood and leaves remain unfilled. The diagenetic processes were therefore of minor importance. Minor recrystallization of calcite which took place probably soon after deposition should have no significant effect on the geochemical record of climatic changes.

3. Mollusca from Svatý Jan pod Skalou and their comparison with those from the Švarcava valley

Molluscan shells occur in all layers of the tufa deposit in Svatý Jan pod Skalou. They are much more abundant in loose layers than in solid tufa. The malacofauna from this site was already described by Petrbok (1923) in his paper on molluscs from travertines in the Beroun area. This first list of species was repeatedly supplemented (Petrbok 1925, 1936, 1940, 1956a, 1956b).

J. Petrbok attributed all molluscan records from Svatý Jan to the "Atlantic Littorinian", a moist phase in which a great majority of tufa deposits of the Bohemian karst were formed. The malacofauna described by Petrbok (l. c.) consists predominantly of demanding woodland species and includes no elements of Early Holocene *Discus ruderatus*-fauna, because the Early Holocene layers were not exposed at that time. Of particular interest is a rather high number of aquatic species reported by Petrbok, for instance the presence of *Bathyomphalus contortus* (L.); among terrestrial species even the alpine element *Neostyriaca corynodes* (Held) is cited, but its occurrence in the Holocene of the Bohemian Karst is unlikely.

New investigations were initiated in 1960 when K.-D. Jäger and V. Ložek cleaned and documented a profile which was later connected with the excavation S1 (see Fig. 2 for location, Fig. 6 for a profile drawing). The main results were published in a short preliminary report (Ložek 1960).

Analysis of malacofauna, chronology and paleoenvironmental reconstruction

Samples were taken from all layers exposed in the profile (layers 1 to 24, sampled 2/11/1960), from the excavated pit S1 at the foot of the tufa wall (layers 25 to 27, 10/10/1966 and 28 to 30, 12/7/1994), and from the research drilling (layers 31 to 36, 15/10/1996). Typical sample volume was 5 to 10 L. The tufa and earth material was air-dried, wet-sieved and the molluscan shells were separated. The techniques of sampling and shell separation were described by Ložek (1964). The results are given in Table 4 including information on ecology and biostratigraphy of each species. The layer numbers in the text and in Table 4 refer to Fig. 7.

The whole profile is dominated by well-developed woodland malacofauna which includes a number of species with high temperature and moisture requirements, i.e., an assemblage corresponding to the climatic optimum. The number of shells transported from various habitats surrounding the tufa deposit, particularly from xerothermic rock cliffs, remains very low throughout the sequence. Changes in the occurrence of several species as well as in the presence of particular ecological groups enable the tufa sequence to be subdivided into several units characterised by the presence/absence of certain elements.

The number of species and specimens obtained from the lowermost section of the accumulation using the research drilling (layers 31 to 36) was very small. The occurrence of individual species did not differ significantly from the overlying complex of solid tufa studied in more detail.

The basal complex of solid tufa in the excavated test pit (layers 30 to 28) is characterised by high numbers of two open-country species – *Truncatellina cylindrica* and *Vallonia costata* – which suddenly disappear in horizon 28. This layer is characterised by abrupt decrease in species richness. *Carychium tridentatum* is abundant. *Trichia sericea*, characteristic of the older half of Holocene, occurs in layers 30 to 28. Already the horizon 30 provided the demanding thermophilous element *Truncatellina claustralis* associated with Early Holocene elements, such as *Discus ruderatus* and *Perpolita petronella* occurring in very small numbers. Interesting is the occurrence of *Laciniaria plicata* and the appearance of neoendemic *Bulgarica nitidosa* in the loose interlayer 29. Some species characteristic of the younger half of the Holocene, particularly *Helicodonta obvoluta*, still lack. Aquatic species are absent.

Loose layers between the lower scree horizon (25) and the complex of solid tufa (28 to 30) include very rich malacofauna characterised by the appearance of sensitive woodland species, such as *Platyla polita*, *Bulgarica cana* and *Cochlodina orthosoma*. Early Holocene elements are represented by *Clausilia cruciata*, whereas *Trichia sericea*, *Vallonia costata* and *Truncatellina cylindrica* disappear. Of interest is the find of one specimen of *Chondrina avenacea*, a rupestral epilithic species, and the strong occurrence of aquatic species *Radix ovata* and *Pisidium spp*. The woodland species show a marked increase in the assemblage. Early Holocene elements, for example *Discus ruderatus* and *Perpolita petronella*, are declining and disappear in the overlying loose strata 26 and 27. All these data suggest a rather open forest with denser parklands in some places under very favourable soil and moisture conditions, which corresponds to the late Atlantic phase.

The lower scree horizon (25) is characterised by a maximum species richness (46 species), high numbers of aquatic and wetland elements, as well as by the appearance of *Isognomostoma isognomostomos*. The genus *Aegopinella* is here probably represented even by the hygrophilous species *Ae. nitens*, only this horizon provided *Vertigo alpestris* and the last occurrence of *Discus ruderatus*. Even though scree indicates transport of clastic material from broader surroundings, the horizon includes no rupestral species coming from the cliffs situated in the immediate neighbourhood of the tufa deposit.

The thick complex (layers 24 to 10) between lower and upper scree horizons is characterised by a wide variety of lithofacies reflecting the alternation of tufa wetlands, small pools and short dry periods, but its assemblages are less diverse. Aquatic and wetland species remain important and their representation attains its maximum in the intercalation of fine limnic tufa (layers 20 and 21), largely dominated by *Radix ovata* with subordinate *Pisidium casertanum*. Only this horizon provided the wetland element *Oxyloma elegans*. In layer 17 *Arianta arbustorum* and *Helicigona lapicida* appear, whereas the first record of a species characteristic of the younger part of Holocene, *Helicodonta obvoluta*, comes from the layer 12. The richest woodland assemblages was recorded in layer 15 (32 species). The appearance of *Arianta* has a local character, at present this species is again extinct in the area. Such situation, as well as the stratigraphic position, are characteristic of the Epiatlantic phase (sensu JÄGER 1969).

The upper scree complex with humic rendzina matrix and prehistoric pottery (layers 9 to 7), archaeologically dated to the declining Bronze Age and Early Iron Age at about 800–500 BC, includes again species-rich (34 and 38 species) assemblages, in which woodland snails remain dominant. Even here thermophilous *Truncatellina claustralis* appears in association with *Ena obscura*. *Cochlicopa lubricella* and *Vallonia costata* in high amounts as well as the appearance of *Granaria frumentum* (7) reflect partial clearance of forests. This corresponds to Subboreal (sensu JÄGER 1969) and partly to the start of the moister and cooler Subatlantic. Importantly, the woodland character of the malacofauna remains preserved, although higher numbers of such species as *Cochlicopa lubricella*, *Vallonia costata* and the admixture of *Granaria frumentum* reflect a clearance of the adjacent forest complex.

In the uppermost, predominantly clastic layers (6 to 2) the woodland character of malacofauna continues, the species richness slightly decreases and several elements indicating further clearance in the surroundings appear (*Vallonia pulchella*, *Pupilla muscorum*, *Cecilioides*). However, *Platyla polita*, a sensitive woodland species is still present, *Laciniaria plicata* re-appears (at present extinct in the Bohemian Karst) and even in the subsurface layer 2 *Helicodonta obvoluta* remains important. By contrast, modern immigrants are represented only by the terricolous *Cecilioides acicula* which penetrates into deeper soil horizons. The assemblages of the youngest layers are increasingly consistent with present-day conditions. Today's environment is characterised by fully developed woodland biocenoses including rich forest snail communities. It is obvious that neither prehistoric nor historic human activities were enough intensive to lead to depaouperization of woodland ecosystems and expansion of species characteristic of cultivated areas.

Malacostratigraphy of the tufa deposit in the Švarcava Valley

Since the tufa accumulation in Svatý Jan pod Skalou does not extend to Early Holocene and the Pleistocene/Holocene boundary, another profile was selected to prolong the sedimentary record. This tufa deposit is situated in the valley of the Švarcava Brook at the western margin of the town Černošice. The upper part of the deposit exposed by an erosional cut of the Švarcava Brook was cleaned in 1966 and 1967 and samples were taken from selected horizons. These samples provided rich malacofauna (Ložek 1968). The morphology of the deposit was described by Ložek (1967b). In 1982, the whole tufa sequence including the upper part of the underlying alluvial complex of strata was excavated. The profile is documented in Fig. 13. All layers provided a rich molluscan fauna whose semi-quantitative analysis is given in Table 5.

Malacostratigraphic analysis and stratigraphic interpretation of the Švarcava profile

Several stratigraphically significant assemblage zones can be distinguished in the profile which correspond to individual phases of Postglacial development.

In basal gravelly and muddy sediments (layers 20 and 19) open-country and indifferent species predominate, whereas climatically demanding elements are absent. Woodland fauna is represented only by 3 rather tolerant species.

Of prime importance are the records of 3 glacial elements – *Columella columella*, *Vallonia tenuilabris* and *Vertigo parcedentata*, represented, however, only by 3 specimens. It should be stressed that shells from layer 20 were extracted only from a small core sample and do not represent a complete assemblage. The composition of sediments and fauna indicate Late Glacial.

Layers 18 and 17 are characterised by appearance of a number of woodland elements, however, the open-ground species remain dominant. Index species of the *Discus ruderatus*-fauna, i.e., *Perpolita petronella*, *Clausilia cruciata* and *Vertigo substriata* associated with *Vallonia costata* in very high numbers are of importance for the stratigraphic placement of the beginning tufa formation. This faunal change reflects gradual warming and expansion of light woodland which probably corresponds to Preboreal.

The thick overlying tufa complex (layers 16 to 7) is characterised by the expansion of further woodland elements, such as *Ena montana*, *Monachoides doliolum*, *Helix pomatia* and *Aegopinella minor*. *Clausilia cruciata* declines in layer 15, *Perpolita petronella* in layer 12, the numbers of *Discus ruderatus* decrease gradually. The occurrence of steppe elements *Helicopsis striata* and *Chondrula tridens* in layer 13 indicates the existence of steppe patches in the catchment of the Švarcava Brook. *Discus rotundatus* appears in layer 11 and rises to significant values in the whole overlying complex, the neoendemite *Bulgarica nitidosa* appears in layer 8.

Layers 6 and 5 are characterised by a striking change in sedimentation: tufa precipitation declines and is replaced by loamy sediments of alluvial or colluvial character, more or less affected by pedogenic processes (layer 6). *Carychium tridentatum* culminates, aquatic and wetland species disappear, *Cepaea hortensis* first occurrs in layer 5a.

This development of molluscan fauna as well as the decline of tufa precipitation at the boundary of layers 7/6 indicate that the complex of layers 8 to 5a may be of Atlantic age. The sedimentation break is related to the downcutting of the Švarcava Brook during a very moist phase in the early Atlantic, when the surface of the tufa deposit, formerly a patchwork of marshy ground with pools and occasional streams separated by higher drier ridges, dried out. This process was supported by abrupt decrease in rainfall in early Neolithic times, i.e., in Middle Atlantic (Ložek 1997). Consequently, tufa precipitation was largely replaced by clastic terrigenous sediments and/or pedogenesis.

This is equally true of the overlying strata where the terrestrial component became quite dominant. *Discus ruderatus* and *Trichia serices* disappear in layer 4, *Vitrea crystallina* and *Macrogastra plicatula* in layer 3; from layer 3 comes the only record of *Platyla polita*. Layer 3 is also characterised by the first appearance of *Alinda biplicata* and *Vertigo pygmaea*. Only in the rendzina soil layers 2 and 1 *Aegopinella nitens*, *Cecilioides acicula*, *Oxychilus cellarius*, *Trichia hispida* and important numbers of *Vallonia pulchella* were recorded. Of particular interest is the presence of *Truncatellina claustralis* in layer 2, a thermophilous element characteristic of the younger half of the Holocene.

In summary, it is likely that layer 4 represents Epiatlantic and layers 3 to 1 Late Holocene. A more detailed stratification of layers 3 to 1 is impossible because of an intensive bioturbation of the soil material including shells that accompanied the rendzina soil forming process (Ložek 1964).

Comparison of the Svatý Jan pod Skalou and Švarcava profiles

In contrast to Svatý Jan pod Skalou, where the tufa was deposited close to the spring situated in the outlet of a dry valley without floodplain into the much larger Kačák Valley, the tufa deposit on Švarcava forms part of a well developed floodplain of a perennial stream. The tufa deposit is developed as a distinct, flat, 3 m high terrace in the valley bottom, affected by downcutting of the Švarcava Brook whose present-day floodplain is thus inserted in the tufa body. The bedrock in the surroundings of the Švarcava site consists of Upper Ordovician and Silurian shales and diabases which grade into Upper Silurian and Devonian limestones more than 1 km upstream in the area of Solopysky. The major part of the Švarcava catchment thus consists of limestones. Consequently, the molluscan assemblages incorporated in the investigated tufa deposit represent mostly the floodplain fauna.

Despite this environmental difference, the sequence of molluscan assemblages enables a correlation with the tufa deposit at Svatý Jan pod Skalou. This is particularly true of the zone in which index species of the older half of the Holocene (i. e., *Discus ruderatus*, *Perpolia petronella*, *Trichia sericea*, *Vertigo substriata*, *V. alpestris*) are replaced by Middle to Late Holocene elements, for example *Alinda biplicata* or *Bulgarica nitidosa*. This zone corresponds to the complex of layers 12 to 5 at Švarcava and layers 30 to

25 in Svatý Jan pod Skalou. In comparison with Svatý Jan pod Skalou, Švarcava is characterised by a considerably lower number of woodland elements (ecological group 1), since it is situated in the NE part of the Bohemian Karst which was never colonised by a number of otherwise widespread mid-European woodland snails (*Helicodonta, Isognomostoma, Petasina, Helicigona, Ruthenica*) during Postglacial (Ložek 1973).

Erosion which occurred near the boundary of layers 7 and 6 at Švarcava is known from numerous sites. The sedimentary sequence corresponding to the younger half of Holocene is poorly developed and differentiated at Švarcava. This contrasts with Svatý Jan where the younger half of Holocene is represented by a thick tufa complex of Epiatlantic age capped by a Subboreal rendzina soil with scree and Late Bronze Age pottery.

4. Geochronological and geochemical study of the calcareous tufa

Dating of calcareous tufa

For dating of individual layers of the calcareous tufa accumulation in Svatý Jan pod Skalou a combination of several methods was used. The only method for which a sample can be collected anywhere in the studied profile is ^{14}C dating of carbonate. By this method 11 samples covering 14.3 m of the thickness have been dated by conventional counting method (see Tab. 6). Since ^{14}C dating of carbonate is plagued by a number of uncertainties (unknown initial activity because of mixing of organic matter-derived carbon and limestone carbon, possibility of post-depositional changes because of tufa diagenesis, infilling of pores, etc.), small pieces of charcoal or sedimentary organic matter from selected horizons were dated also by ^{14}C using AMS (see Tab. 6). Several samples of tufa were dated also by $^{230}Th/^{234}U$ (see Tab. 7).

The ^{14}C data on organic matter have been calibrated for variable initial concentration of ^{14}C using published calibration curves. In the intervals between dated samples, ages of individual depth levels were calculated assuming constant accumulation rate. In the interval between the deepest sample of organic matter dated by AMS ^{14}C (–2.95 to –3.05 m) and the base of tufa accumulation (i.e., –9.9 m) the age difference was estimated based on carbonate ^{14}C data, which indicate age difference of about 1000 years between these two horizons. Fig. 14 shows ^{14}C ages based on calibrated data of organic matter and also the ^{14}C carbonate ages, calculated assuming identical initial activity of carbonate carbon of 80 pmc.

The carbonate ^{14}C data differ from the organic matter ^{14}C data indicating that either the carbonate initial activity changed over time, or the carbonate was influenced by recrystallization and post-depositional changes (see Fig. 14). Therefore, only the organic matter ^{14}C data were used for the interpretation of paleoclimatic record.

For $^{230}Th/^{234}U$ dating five horizons of hard porous tufa were selected (analysed in CERAK, Belgium, by Y. Qunif, Tab. 7). All samples had suitable U contents (0.263 to 0.761 ppm U). Unfortunately, the admixture of clastic Th component adsorbed on clay minerals was too high and the $^{230}Th/^{232}Th$ was lower then 10. Moreover, variable $^{234}U/^{238}U$ ratio indicated disturbed isotopic systems. Even the sample with the highest $^{230}Th/^{232}Th$ ratio (–5.40 to –5.50 m, 0.761 ppm U) indicated unrealistically high age of 10.6 ± 0.4 ka. After finishing the research drilling into the deepest part of the accumulation, $^{230}Th/^{234}U$ dating was applied once more (analysed in Geological Institute of Polish Academy of Sciences by H. Hercman) on a selected sample of solid tufa with limited number of pores (sample location: –8.30 m). The sample contained 0.50 ± 0.01 ppm U and the $^{230}Th/^{232}Th$ ratio was again low. The sample yielded uncorrected age of 10.39 ± 0.24 ka. Since this sample was the most suitable for the $^{230}Th/^{234}U$ dating, a rough correction to subtract the detritic thorium was applied on the raw data. The corrected age of 8 ± 1 ka is in agreement with other dating methods.

Sample collection for the study of geochemical record of climatic changes

Samples for geochemical study were collected by the channel method, each sample representing an average of a profile segment about 0.2 m thick. Altogether 83 samples were collected in two sampling campaigns. After drying coarse clastic material was removed by combination of sieving and hand-picking, with special care given to the removal of any clasts of Palaeozoic limestones. Samples were then homogenised and the carbonate content, organic matter content, carbonate $\delta^{13}C$ and $\delta^{18}O$ and organic matter $\delta^{13}C$ values were determined (Appendix 1).

Since the results of dating and of malacostratigraphic analysis indicated that the Svatý Jan profile does not extent to the early part of Holocene, another calcareous tufa profile in the area was selected to prolong the geochemical record. Based on available biostratigraphic data, a profile in fluvial (valley-bottom) calcareous tufa accumulation in the valley of the Švarcava Brook, located about 12 km E of Svatý Jan close to town of Černošice was selected. In this additional profile only carbonate $\delta^{13}C$ and $\delta^{18}O$ analyses (Appendix 3) and ^{14}C dating of organic matter were performed.

Interpretation of the geochemical record

Based on calibrated organic matter ^{14}C data and based on the assumption of a constant accumulation rate between each pair of dated profile levels, a model age was attributed to each sample of the Svatý Jan profile. Carbonate content and carbonate $\delta^{13}C$ and $\delta^{18}O$ data were then plotted against the age (Figs. 15, 16, 17).

The highest carbonate contents were recorded in the profile section dated between 8800 and 8600 years BP. Near the level with model ages of around 8500 years BP, there are several distinct horizons enriched in clastic material (mostly clay minerals, organic matter, quartz and feldspar grains). The most stable climatic conditions (so-called climatic optimum of Holocene) with very limited transport of any clastic material and with deposition of relatively pure calcareous tufa occurred between –3.00 and +0.07 m (corresponding model ages of 8400 and 6700 years BP). In the second part of Atlantic (since about 6700 years BP) the carbonate content decreased and the proportion of clastic material increased irregularly. The first maximum of clastic material transport into the studied profile occurred around 6200 years BP.

The overlying lithologically variable sequence contains numerous horizons very rich in clastic material and also horizons of buried soils. The lowest carbonate content was recorded in a buried soil horizon at +3.50 to +3.75 m (layer 15 in Fig. 7). The upper scree horizon at +5.05 to +5.20 m corresponds roughly to 3100 years BP and above it the deposition of calcareous tufa was discontinued.

The oxygen isotopic composition of freshwater carbonates is influenced by several partly interdependent factors, the two most important being temperature-controlled oxygen isotope fractionation calcite-water and temperature-controlled variability of oxygen isotopic composition of meteoric waters (Gascoyne 1992, Dorale et al. 1992). These two factors have an opposite influence on the carbonate $\delta^{18}O$ data, with the effect of temperature-controlled variability of oxygen isotopic composition of meteoric waters being usually the more important factor in the mild climatic zones (cf. Pazdur and Pazdur 1988).

The present-day spring discharging in Svatý Jan pod Skalou shows a stable temperature slightly higher than the mean annual temperature in this area. This can be viewed as evidence for a relatively deep circulation of karstic water. Based on measured tritium (^3H) activities in spring water, the average residence time of the water in the aquifer was calculated at 22 years (see below in the hydrological section of this paper). With respect to the large discharge of the spring (~20 L/s) and with respect to the location of the tufa accumulation near the spring, any significant water temperature changes and/or isotopic effects connected with water evaporation at the site of deposition probably can be neglected. With respect to these facts, we suggest that changes in the $\delta^{18}O$ values of meteoric waters were the most important factor controlling changes in $\delta^{18}O$ of the deposited carbonate. Under these conditions higher carbonate $\delta^{18}O$ values should indicate higher temperatures and *vice versa*.

The carbonate $\delta^{18}O$ record obtained from the Svatý Jan profile (Fig. 16) was compared with ice $\delta^{18}O$ in the Greenland GISP 2 profile (Grootes et al. 1993, Stuiver et al. 1995, profile dating after Sowers et al., 1993, Meese et al. 1994). With respect to dating uncertainty at Svatý Jan, oscillations of both curves in Fig. 16 can be viewed as similar. A significant temperature increase marking the onset of Holocene is clearly not recorded at Svatý Jan. This is in good agreement with both the results of dating of the profile and with the biostratigraphic analysis of molluscan assemblages.

Carbonate $\delta^{13}C$ valus at Svatý Jan show higher variability than $\delta^{18}O$ values. Moreover, it was found that the carbonate $\delta^{13}C$ data are probably controlled by different mechanisms in the lower series of hard pure tufa with high carbonate content and in the upper varied sedimentary series. While in the lower profile section the $\delta^{13}C$ and $\delta^{18}O$ of carbonate change independently, in the upper part of the profile there is significant correlation (Fig. 18). With respect to the fact the differences between the $\delta^{13}C$ values of carbonate and organic matter are almost constant throughout the profile, the kinetic effect of CO_2 escape from the water at the site of deposition had probably only minor influence on the carbonate $\delta^{13}C$ systematics. Climatically-induced changes in soil processes in the recharge area were probably more important.

Results from the auxiliary profile in the Švarcava valley

Based on malacostratigraphic analysis, Ložek (1967, 1968) suggested that the profile in the valley of Švarcava represents one of rare examples in the Bohemian Karst, where the transition between Late Glacial and Early Holocene is recorded, and where the Early Holocene is already represented by carbonate-bearing sediments.

The AMS ^{14}C dating of residual sedimentary organic matter separated from a sample collected near the lower limit of carbonate-rich sediments (–3.40 m, upper part of layer 19, Fig. 13) yielded radiocarbon content equivalent to $37.05 \pm 0{,}41$ pmc, which yields corrected age between 8954 and 8554 years BP (68 % confidence interval). Based on this dating we concluded that the onset of intensive carbonate deposition is roughly synchronous with Svatý Jan pod Skalou. The $\delta^{18}O$ profile is shown in Fig. 19. The data are not significantly lower than in the Svatý Jan profile, except for the deepest sample, which possibly records the terminal part of a temperature increase in Early Holocene.

One possible explanation of the difference in ^{14}C dating and the biostratigraphical interpretation based on molluscan assemblages at Švarcava is that some shells of Late Glacial and/or Early Holocene molluscs present in the lowermost sandy-clayey loam with numerous stony fragments and occasional carbonate oncoliths were redeposited by fluvial activity of the Švarcava Brook. This feature is quite common at calcareous tufa deposits formed in surface streams (Pazdur et al. 1988). Another explanation is that the deep narrow NW–SE oriented valley of Švarcava Brook was at the studied site colonised by sensitive woodland elements later than the Svatý Jan pod Skalou site, which is located below W and SW oriented slopes.

Interpretation of lithological, biostratigraphical and geochemical record of Holocene climatic changes in the Bohemian Karst

The climate changes and flora & fauna evolution during the course of Holocene in the Central European region have been reviewed several times (e. g., based on the karst record, by Ložek – Cílek 1995). These studies concluded that the temporal evolution of calcareous tufa bodies has numerous similar features in a large territory limited by the Danube river in the S, by German and Polish lowlands in the N, by Slovak Karst in the E, and by Thuringia in the W. These similarities indicate that regional climatic factors were the main control of calcareous tufa formation while the local factors were of only minor importance. The same is true about Late Holocene erosion and destruction of the accumulated tufa bodies (Jäger – Ložek 1968, Ložek 1973, Pazdur 1988, Hennig et al. 1983, Goudie et al. 1993, Ložek 1997, Ložek – Cílek 1995, Cílek 1997).

The studied accumulation in Svatý Jan pod Skalou in the Bohemian Karst fits well within this general regional frame. Based on the performed lithological, paleopedological, biostratigraphic, geochemical and geochronological studies of this locality, in combination with the knowledge obtained from other localities in the area, four distinct phases important for the formation/destruction of calcareous tufa accumulations can be distinguished:

- transition from Late Glacial to Holocene
- a phase of humid stable climate in the Atlantic
- a phase of oscillation between dry and wet climate
- termination of tufa deposition and destruction of the bodies in Late Holocene.

Transition from Late Glacial to Holocene

In this paper we accept as a boundary of Holocene 11 500 years BP (Gulliksen et al. 1998, Roberts 1998). All ages mentioned in this discussion are calibrated (calendar) ages BP.

During the periods of high fluvial activity in Allerød (about 14 000 years BP) any deposits of calcareous tufa (if formed) were destroyed by erosion. The rock bottom of the valley was at this time up to 8 to 9 m deeper than is the surface level of the recent floodplain.

The accumulation in Svatý Jan pod Skalou is underlain by a Late Glacial/Early Holocene gravel terrace, containing in its uppermost part fragments of calcareous tufa. For the onset of calcareous tufa formation two controlling factors were of prime importance:

- decrease in fluvial activity of the Kačák stream, and
- an increase in dissolved load of spring water connected with expansion of plant communities and evolution of soil profiles in the recharge area.

Both geochronological dating and assemblages of *Mollusca* indicate that the basal tufa layer in Svatý Jan pod Skalou is around 9500 years BP old, i. e., the transition Late Glacial/Holocene is not represented by carbonate-rich sediments.

The supplementary profile in the valley of the Švarcava Brook near Černošice yielded a similar ^{14}C date of the beginning of intensive carbonate deposition, in spite of the presence of Late Glacial/Early Holocene molluscan elements in the underlying clay-dominated sediments and in the lowermost part of the carbonate-rich sediments.

These results are in a good agreement with studies of fluvial sediments of the largest Bohemian river Labe (Růžičková – Zeman 1994), where the formation of the Early Holocene flood plain was dated also around 9500 years BP.

Phase of humid stable climate in the Atlantic

During this phase of humid and stable climate an intensive growth of calcareous tufa accumulations is evidenced at most localities. Massive accumulations of structural tufa with very limited quantity of clastic material were formed during this period. Based on the study of the Svatý Jan pod Skalou profile, the maximal growth of massive structural calcareous tufa occurred between 8400 and 6500 years BP. In the surrounding areas brown decalcified rendzina-type soils were formed with some residual corroded clasts of limestone. Slope transport of scree was at its minimum. Based on the $\delta^{18}O$ record, the temperature reached its maximum around 7500 years BP. Generally, the mean annual temperatures of this period were only about 1 to 2 °C higher than during the later period. More importantly, annual precipitation totals were higher and oceanic-type climate prevailed with smaller temperature differences between winters and summers. Almost continuous cover of the country by forests resulted in increased evapotranspiration and in steady flow conditions in perennial streams.

Phase of oscillation between dry and wet climate

This next phase is limited approximately by a datum of 6500 years BP in the Bohemian Karst and corresponds to the beginning of Epiatlantic (sensu Jäger 1969) or to the boundary between Atlantic 1 and Atlantic 2 in the classical Blytt-Sernander scheme. This phase is characterised by rapid oscillations of dry and wet periods which resulted in alternation of structural tufa and disagreggating loose tufa with intercalations of fossil soils and scree. In well developed profiles up to 5 dry oscillations can be recorded. The duration of these dry oscillations is not precisely known. Based on paleopedological analysis, the buried soils in the Svatý Jan pod Skalou profile were classified as autochthonous or pseudo-autochthonous. The duration of the whole phase was about 4000 years. The lithological characteristics of the studied profile with more than 6 m of calcareous tufa indicate that dry periods were not longer than several hundreds years.

Based on the study of peat profiles in Denmark, Aaby (1976) concluded that climatic oscillations occurred each 260 or, less frequently, each 520 years. A 800-year periodicity was found as dominant for peat profiles in northern England (Barber et al. 1994). Similar periodicities with several hundred-years order were recorded also by study of glacier movements (Grove 1979).

The $\delta^{18}O$ record from Svatý Jan pod Skalou shows that for these climatic oscillations changes in precipitation quantity were more important than changes in temperature. In addition to dry periods, this phase is characterised also by floods which transported clastic material through now dry karstic valleys over long distances.

Local clearance of forests, related both to climate changes and expanding pasture, can be documented biostratigraphically during the younger part of this phase. This feature, together with irregular precipitation during the year produced a distinct flood event around 3100 years BP. Higher in the sedimentary record it there is another horizon of calcareous tufa dated both archaeologically and by ^{14}C to ~2700 years BP. This corresponds roughly to the beginning of Subatlantic, characterised by wetter and slightly cooler climate.

Wet and cooler climate with frequent temperature oscillations around 0 °C is generally more suitable for the formation of slope scree. In the sedimentary profiles located below the slopes or below rock overhangs, horizons of scree are quite common during this phase (Ložek – Cílek 1995). At the same time, a significant increase in precipitation was recorded biostratigraphically in sediments of lakes in the Šumava Mountains (Veselý 1998) or by expansion of wetlands in low-elevation areas (e.g., around 2650 BP in the Netherlands, Geel et al. 1996).

Termination of tufa deposition and destruction of the tufa bodies in Late Holocene

The formation of calcareous tufa bodies was terminated at numerous localities in the Central European territory between 2500 and 2200 years BP. This stage is characterised by several short dry periods, evidenced by human settlement on river floodplains (Bouzek 1993). During Subatlantic the deposition of calcareous tufa almost ceased in the Bohemian Karst. The Late Holocene decline of calcareous tufa formation in Central Europe was probably connected with a decrease in the quantity of infiltrating precipitation and/or with changes in soil processes. These changes could have been also connected with different temperature variability throughout the year.

Holocene calcareous tufa accumulations of the Bohemian Karst were later affected by erosion, which, in places, downcut the tufa bodies to the underlying rocks. Precise dating of these erosional events is not available, some could have occurred as late as in the Middle Ages, when enormous floods were recorded on Bohemian rivers. The karstic springs often moved and started to discharge at the base of individual tufa bodies.

5. Karstic spring in Svatý Jan pod pod Skalou

Introduction

The karstic spring in Svatý Jan pod Skalou represents the largest spring of the entire Bohemian Karst (mean discharge ~20 L/s). With respect to the importance of Svatý Jan pod Skalou as a place of pilgrimage in the past, to its present-day popularity as a tourist sight, and its location close to Prague, the spring became quite famous.

The use of its water can be traced back to the Late Bronze Age, as indicated by numerous finds of artifacts in the upper part of the accumulation of calcareous tufa deposited by the spring. During the younger period recorded in the St. Ivan legend and after the foundation of the monastery the spring played a key role again. The monastery was abolished in 1785 by the Austrian emperor Joseph II. Later the spring water was used by industries (Fig. 20). In the late 19th and early 20th century attempts were being made to open a spa at Svatý Jan pod Skalou (Fig. 21). At the same period the spring water started to be bottled under the trade mark "Ivanka" (Fig. 21). Today, the use of the water is limited by its high nitrate content (above 50 mg NO_3^-/L).

In contrast to the intensive studies of the calcareous tufa accumulation, the spring was rarely studied in the past. During a regional hydrogeological survey of Devonian and Silurian rocks of the Prague basin, discharge, chemistry and bacteriologic quality of the water were monitored for several years. Two radionuclide tracer experiments aimed at understanding of groundwater pathways were performed (Včíslová 1980, Skořepa – Včíslová 1973, 1975). Discharge and temperature of one of the spring discharges has been monitored since 1974 by the Czech Hydrometeorological Institute (CHMI).

The new research program

The new research program was launched in autumn of 1994 by construction of a new notch weir for measurement of discharge below the confluence of the two largest spring outflows. The existing measurement weir of CHMI and the new weir enabled monitoring of discharge of the two spring outflows separately. Monitoring of precipitation, discharge and temperature with a period of 3.5 and later 7 days continued for three hydrological years from November 1994 until October 1997. For two years precipitation and spring water $\delta^{18}O$ values and tritium (^3H) activities were also measured. Spring water chemistry, water chemistry of several hydrogeologically important objects in the recharge area, nitrate $\delta^{15}N$, bicarbonate $\delta^{13}C$, and sulfate $\delta^{34}S$ were monitored as well. In addition, groundwater levels in selected objects in the recharge area (wells, caves) were monitored. During floods in May and June 1995 a tracer experiment was performed between a sink hole in the recharge area and the spring. All data were used in modeling of the hydrological system of the spring and in modeling of temporal evolution of nitrate contamination of the deep karstic-type aquifer.

Hydrogeological description of the spring

The spring drains the SW part of the Holyně-Hostim Syncline. It discharges at a place where the limestone sequence of the syncline's NW flank is crosscut by a deep valley of the Kačák stream. The discharge site is, moreover, controlled by crosscutting longitudinal and transversal faults (Fig. 23).

The spring discharges at the base of a large accumulation of calcareous tufa in several places. The location of the most important outflows is given in Fig. 2. The largest outflow called Ivanka (10 to 14 L/s) is tapped by an earth cut collecting water into a small walled well. This outflow, located at the place of former factory building on privately owned land, is generally not known to the public. Such is not the case with respect to the second largest outflow called Ivan (~4 L/s), discharging directly in the church in a separate vaulted chamber constructed close to the famous St. Ivan's cave. The weir of the Czech Hydrometeorological Institute is located in this outflow in front of the church. Discharge relations between these two largest outflows were changed by both natural and artificial influences several times in the past, making the long-term record of the discharge of Ivan outflow difficult to interpret.

In addition to these two largest spring discharges several smaller outflows can be found in the monastery and its surroundings. Discharge and temperature of another outflow (~1 L/s) pumped out from a well in the boiler room of the monastery were also monitored. Numerous smaller outflows of the spring water mix directly with the Kačák stream.

In autumn 1998, after the project termination, the new notch weir was blinded and the spring waters were redirected into a system of old underground corridors in the basement of the former factory. The enthalpy of this water is used for heating of a private house using a thermal pump.

Based on the knowledge obtained from the drillings, the base of the tufa accumulation is located about 1 m deeper than is the present-day water level in the adjacent Kačák stream. The tufa accumulation is underlain by a coarse-grained gravel terrace. The spring water discharges into this highly porous environment, where it partly mixes with groundwater of alluvial sediments of the present-day flood plain of Kačák. It follows that a good estimate of total discharge of the spring is difficult.

Geographical catchment and hydrogeological recharge area and the tracer experiment

The geographical catchment of the spring has an area around 1 sq. km, not sufficient to produce such high discharge as observed (it would require at least 8 sq. km recharge area). It is, therefore, clear that the hydrogeological recharge area is not identical to the geographical catchment. Judging by geological conditions, the hydrogeological recharge area of the spring probably extends several km in the NE direction along the limestone belt in the NW flank of the Holyně-Hostim syncline. Geographically, this territory belongs to the upper segments of the catchments of Studený (Karlický) Brook and of Břesnice (Bubovice) Brooks. Communication with limestones in the syncline's SE flank is less obvious, since the central part of the syncline is filled with non-karstic siltstones and shales of the Srbsko Formation.

In the small geographical catchment of the Svatý Jan pod Skalou spring (i. e., the dry valley of Propadlé vody) limestones represent about 2/3 while the rest in the upper SE section of the catchment is formed by non-karstic rocks of the Srbsko Formation. At the boundary between these two lithologically different sections several periodic swallow holes exist which are active during large precipitation events. The limestone-dominated part contains some cave systems and abandoned quarries. The entire geographical catchment is forested and the limestones are covered with only small layers of weathering products and soils.

In contrast, the dominant part of the hydrogeological catchment is characterized by locally very thick layers of Cretaceous and Tertiary clastic sediments (sandstones, sands, gravels, etc.) covering deeply corroded surface of limestones. This peneplanated countryside is intensively cultivated (arable land represents about 1/2 of the suggested hydrogeological catchment). Schematic geographical and geological maps with location of hydrogeologically important objects are in Fig. 23 and a geological profile across the syncline is shown in Fig. 24.

A possibility of hydrogeological communication of the limestone belt in the syncline NW flank with limestone belt of the SE flank is supported by very high correlation coefficient (0.96) between the discharge of the spring in Svatý Jan pod Skalou (NW flank) and groundwater level in the Arnoldka Cave (SE flank, Fig. 26).

One possibility how to improve our understanding of karstic underground drainage are tracer experiments. After the flood event in June 1995 a tracer experiment was performed between the periodic swallow hole called Arnika, located in the upper part of the Propadlé vody valley, and the spring in Svatý Jan, using NaCl as a tracer. The two main outflows of the spring had an overall discharge of 24.5 L/s and the periodic stream disappearing in the swallow hole around 0.3 L/s. The traced section of the underground system was about 1 km long with denivellation of 127 m. With respect to delayed arrival of the signal and thus very high tracer dilution Na^+ concentrations had to be determined instead of the originally planed Cl^-, which had too high background in the spring water. The results are shown in Fig. 27. A signal occurred 19 to 20 hours after injection, culminated 26 hours and ceased 37 hours after injection. The outflows Ivan and Ivanka had identical response and contained thus water from the same system, while the discharge in boiler room contained a significant proportion of some other water type.

Assuming good mixing and no tracer loss in the system, total discharge of the spring can be calculated (e. g., Florkowski 1991) at 36.9 L/s. Since some loss of the tracer is probable by sorption of Na^+ on clay minerals, the true total discharge was between the value measured on the new notch weir (i. e., Ivanka and Ivan outflows together, 24.5 L/s) and the calculated value. Similarly, the volume of conduits between the injection and discharge point can be calculated (between 1680 and 2530 m^3).

Hydrograph analysis and temperature changes in the Svatý Jan pod Skalou spring

Several years prior to the project were characterized by very low annual precipitation totals. The long-term average of annual precipitation equals 530 mm in Karlštejn and 570 mm in Chrustenice. Both stations are located within a few km of the study area. Annual precipitation totals for several years before the project launch are shown in Fig. 28. Most precipitation typically occurs between May and August while winter months are relatively dry with usually limited quantity of snow and/or rain (Fig. 29).

In contrast to several dry years before the project beginning, the 1995 precipitation total was high (in Chrustenice 666 mm, 126 % of the long-term average), and directly in Svatý Jan pod Skalou the annual total equaled 695 mm. In 1995, the largest precipitation event occurred on June 1–June 2 (59.1 mm of precipitation in Svatý Jan) resulting in local floods. Years 1996 and 1997 were closer to average.

The hydrograph of the Svatý Jan pod Skalou spring is shown in Fig. 31. Apparently, the discharge variability is very small (ratio of minimum and maximum observed discharge 1 : 2, in years without flood events 4 : 5). This feature is not typical of most karstic hydrological systems in classical karst areas, where springs usually exhibit much larger variability.

Typically, the discharge of karstic springs can be described as composed of three components with different residence times (modified after Ford – Williams 1989, Shevenel 1996):

- a short residence time component, using preferential hydrogeological systems of caves, more extensive karstified fissures and karstified bedding planes (residence time hours to days),
- a medium residence time component, using a system of small interconnected fissures (residence time weeks to months), and
- a long residence time component, using microfissures and structural micropores in the limestone (residence time years).

In the case of the Svatý Jan pod Skalou spring medium and long residence time components clearly dominate. The existence of several regimes can be seen also from the groundwater discharge decrease diagrams after Kullman (1990), Figs. 32, 33.

The temperature of the spring water oscillated between 10.5 and 11.6 °C with an average of 11.4 °C. This temperature is significantly higher than the annual mean temperature of the area (~8.5 °C) indicating rather deep and slow groundwater circulation. The observed small temperature minima of the spring water are related to floods or snowmelt events (i.e., penetration of short residence time component), while during the low discharge periods, when the water from the deepest circulation pathways dominates, the spring temperature is at its maximum. The higher temperature of the spring was used for thermal modeling of the depth of groundwater circulation (see below).

The thermal pattern of the Ivanka and Ivan outflows is identical while the smaller discharge in the boiler room of the monastery exhibits a different pattern (Fig. 34). This is another piece of evidence that this particular discharge involves a significant proportion of water from another source, probably partly phreatic waters of fluvial sediments of the Kačák floodplain.

Oxygen stable isotopes and tritium concentrations in precipitation and the spring

These geochemical parameter were used to estimate the actual residence time of groundwater in the aquifer and to further constrain parameters for modeling.

The oxygen isotope study comprised more than 160 pairs of $\delta^{18}O$ determinations in precipitation and the spring water. The sampling interval was 3.5 days during the first year and 7 days during the second year of the project. The data are shown in Fig. 36. In contrast to the highly variable precipitation record, the spring shows only small changes in $\delta^{18}O$. This clearly shows that long residence time waters dominate in the spring.

Excursions from the long-term averaged spring value can be used to estimate a proportion of the short residence time karstic component during flood events, supposing only two components form the discharge (Horton 1935). Such calculation has shown that the short residence time component has generally a minor importance in the case of the Svatý Jan pod Skalou spring, making up usually between 8 and 11 % of the discharge (including the proportion of phreatic waters from floodplain sediments of the Kačák stream which partly mix with the discharging karstic waters below the base of the tufa accumulation). During the largest recorded flood, the calculated proportion of these short residence time waters entering the groundwater system mostly below the Propadlé vody valley (i. e., close to the spring) was 37 %.

Tritium (^3H) concentrations were determined on 8 pairs of precipitation samples and averaged spring discharge samples (half year and two months volume weighted averages). The data are shown in Fig. 37, together with older determinations by Šilar et al. (1990) and Horvatinčić et al. (1989).

For the calculation of mean residence time from the ^3H data, the proportion of summer and winter precipitation (which have different ^3H concentrations) in the infiltration waters must be estimated. We used an estimate based on the oxygen isotopic composition of average summer precipitation and average winter precipitation and average $\delta^{18}O$ of the discharge (Grabczak et al. 1984). The calculations have shown that even if the quantity of summer precipitation is at least twice higher than that of winter precipitation, the infiltrating quantity of water is approximately the same during winter and summer. Data by International Atomic Energy Agency in Vienna were used as long-term ^3H precipitation record . These long-term data do not differ significantly from short-time records from the territory of the Czech Republic. For the calculation an exponential model (mixed reservoir) was used. As one of parameters of the model, the proportion of water with short and medium residence time must be estimated. Using the results of $\delta^{18}O$ and volume modeling (see below) the proportion of these waters was estimated at 30 %. A mean residence time of 22 years can be then calculated for the dominant (70 %) long-residence time component of the spring (Fig. 38).

Hydrological models of the karstic groundwater system

Several models were used to describe the behavior of the studied karstic groundwater system. One potential problem in applying hydrological models to long-residence time karstic system, is the fact that the stored groundwater volume of these systems varies with time, while most published models consider constant aquifer volume. In the recharge area of the system under study the groundwater level oscillates significantly. As seen from monitoring of groundwater level in some caves (e.g., Fig. 26), oscillations with amplitude of up to 20 m occur, reflecting not only short-time irregularities in the precipitation quantity but also long-term precipitation history. After recharging a higher aquifer level by a large precipitation event (like the flood in June 1995) it takes months to years to reach again the original level.

Compartment (mixing cell) models were shown to be useful in the modeling of karstic systems. The model by YURTSEVER (1983) was applied for discharge and $\delta^{18}O$. An estimate of cell volume (transit time) was based on values calculated from the hydrograph. The arrangement and volume of individual cells is shown in Fig. 39.

Comparison of modeled and actual discharge and $\delta^{18}O$ data is shown on Fig. 40. While the actual discharge dynamics fits the modeled data relatively well, the variations of modeled $\delta^{18}O$ are less frequent than those of the measured data. One possible cause of this phenomenon is partial blocking of the discharge pathways of the long residence time component by increased hydraulic head of the medium residence time component in the periods when the groundwater level in the recharge area is high. This can produce the observed medium-time (weeks to months) pulses of the $\delta^{18}O$ value.

Variability of the $\delta^{18}O$ value in the precipitation and discharge can be also modeled alone, by a separation of discharge $\delta^{18}O$ variability from the precipitation $\delta^{18}O$ variability (deconvolution). For such modeling, the FLOW model by MALOSZEWSKI and ZUBER (1996) was used. This model does no consider discharge variability and considers only natural (or artificial) tracer concentration in the input and output of the system.

With respect to a large difference in precipitation quantity in 1995 and 1966, each year was treated separately. Our aim was to estimate the proportion of the long residence time and medium + short residence time components in the spring discharge. The best agreement between modeled and measured $\delta^{18}O$ was obtained for 70 % of the long residence time component (Fig. 41).

Thermal modeling of the circulation depth of the groundwater

The simplest calculation of the circulation depth of groundwater is based on the difference between spring temperature and mean temperature of the near-surface environment, and on the geothermal gradient measured in drillings. This calculation does not take into account an obvious fact that the descending groundwater adsorbs some proportion of the Earth's heat flow. This process can be of importance especially in karstic areas where the groundwater flow can be very quick and spatially concentrated. Based on reasoning by BÖGLI (1971) a formula incorporating this fact was created by BRUTHANS (1999), see Appendix 12.

A conventional calculation estimates the circulation depth of 160 m below the surface in the recharge area, i.e., roughly into the level of discharge. A more realistic calculation taking into account the fact that a proportion of the heat flow is adsorbed by the circulating water yields mean circulation depth of 300 m below the recharge area surface, i. e., more than 100 m below the spring level.

Summary of model calculations

When the results of all observations and modeling are considered together, the following conclusions can be drawn.

Except for a small proportion of phreatic water from fluvial sands of the Kačák flood plain which mixes with the spring water close to the discharge site, the spring can be characterized as composed of three components with different underground residence times:

- groundwater of a short residence time (hours to days) which typically forms only a very small proportion of the discharging water (0 to 10 %), can reach up to 40 % during large precipitation events. Most of this water infiltrates through open karstic-type inputs like periodic swallow holes located mostly in the dry valley of Propadlé vody.
- groundwater of a medium residence time (weeks to months) represents much slower drainage of an interconnected system of small karstified cracks, bedding planes and fault zones, and locally also larger but isolated caves in the much larger main recharge area of the spring. The groundwater level in this area is very deep below the surface (several tens to one hundred meters) and the infiltration is further retarded by locally thick layers of Cretaceous and Tertiary sediments and soils. This component is responsible for the medium-time oscillations of the $\delta^{18}O$ value. It typically forms up to 30 % of the discharging water.
- groundwater with a long residence time, which generally dominates the discharge (typically 60 to 70 %, in long dry periods even > 90 % of the discharge). This component probably represents drainage of small non-karstified cracks, limestone pores and discharge of waters which circulate in the deep part of the Holyně-Hostim syncline below the level of discharge. Based on the ^{3}H modeling, this component has mean residence time around 22 years. Its $\delta^{18}O$ value and chemical composition are relatively stable, representing long-term average of infiltrating waters.

6. Chemical composition of the spring water and its contamination by nitrates

Introduction

Most springs of the Bohemian Karst which have significant proportion of cultivated land in their recharge areas are contaminated by nitrates as a result of intensive farming. At present, water from numerous springs (60 to 100 mg NO_3^-/L) exceeds the nitrate limit of the Czech drinking water standard (50 mg NO_3^-/L). The springs with forested catchments of the Bohemian Karst also exhibit slightly increasing nitrate contents as a result of increased atmospheric deposition of nitrogen compounds (HOŠEK – KAUFMAN 1996, LOCHMAN et al. 1996, HOŠEK 1997, MARTÍNEK 1999, HOFMEISTER 1999) and reach currently 10 to 20 mg NO_3^-/L.

The spring in Svatý Jan pod Skalou clearly belongs to the group of nitrate-contaminated springs. Historical farming (starting in some areas several thousands years ago) based on extensive use of organic fertilizers (manure, etc.) did not produced significant problems in groundwater quality until approximately 1965. Starting from this date, application of industrial fertilizers and increased quantity of organic fertilizers from intensive animal breeding led to gradual nitrate increase in the groundwater. Typical nitrogen dose applied on fields in the recharge area between 1968 and 1989 was 90 to 100 kg N/ha/year. After 1989, as a result of political changes and diminishing governmental support of agriculture, this dose was reduced on average to 1/3.

New research program

Changes in chemical composition of discharging water were monitored for three years between November 1, 1994 and October 31, 1997 (22 sampling dates). For better understanding of possible nitrate sources in the recharge area, several other objects were sampled – the Bubovice Brook, representing a small surface stream in the countryside with intensive farming, a well near Kozolupy, characterizing shallow groundwater in the area of intensive farming, and a karstic spring near Sedlec, representing carbonate-precipitating springs in the forested catchments.

For understanding of importance of individual biologic conversions in the nitrogen cycling, data on contents of nitrogen compound are not sufficient, since they do not allow to quantify the importance of individual biologic conversions. Therefore, stable isotope ratios of nitrate nitrogen were also monitored in the spring and selected hydrogeological objects in the recharge area. In addition, nitrogen compound concentration and isotopic composition in soil profiles were studied at two sites. The first site was characterized by non-karstic rocks and application of predominantly organic fertilizers, the second by limestone bedrock and intensive application of industrial fertilizers. The obtained data are in Appendix 13 (chemistry of waters), 14 (trace elements and some other contaminants in waters), 15 (nitrogen isotope data), 16 (description of soil profiles) and 17 (analytical data in soil profiles).

Characteristics of water chemistry of the studied objects

The karstic spring in Svatý Jan pod Skalou is characterized by a small variability of groundwater chemistry. The discharging water of the HCO_3-Ca-SO_4 type with TDS usually in the range of 680 to 690 mg/L is occasionally diluted by the short residence time component during large precipitation events. Short residence time waters from the forested geographic catchment of the spring have, when compared to long-residence time component infiltrating in the cultivated areas, much lower contents of nitrates and chlorides, but significantly higher content of sulfate as a result of pyrite oxidation in sedimentary rocks.

The slowly increasing nitrate content of the spring averages at present slightly above 50 mg/L. Contents of ammonium ions and nitrites were below the detection limits in the spring water. Carbon isotopic composition of HCO_3^- shows minor oscillations which correlate with oscillations of $\delta^{15}N$ nitrate, both reflecting mainly soil processes in the infiltration area (Fig. 42).

The small spring located near Sedlec (see Fig. 23), with a discharge usually below 0.1 L/s, was selected as a carbonate precipitating spring with a forested catchment. The spring water has low, during the time only slightly increasing nitrate contents in the rage 9 to 19 mg/L. Low contents (up to 0.4 mg NH_4^+/L) of ammonium ions were detected during the winter season.

The well near Kozolupy is located in an intensively cultivated area and represents a shallow groundwater aquifer in the central part of Holyně-Hostim Syncline. The nitrate contents oscillated slightly between 75 and 90 mg/L with slightly decreasing trend as a result of reduced dose of fertilizers during the last decade. A single summer sampling of waters in an amelioration drainage system yielded 145 mg NO_3^-/L.

The Bubovický Brook, a small perennial surface stream in an intensively cultivated area, had the most variable nitrate contents (22 to 78 mg/L) and during the winter season increased contents of ammonium ions (2.3 mg/L).

Interpretation of the nitrogen isotope data

Typical isotopic composition of nitrogen of potential nitrate sources as determined by Buzek et al. (1998a) is given in Table 10. Even if the nitrogen isotopic compositions of potential sources are contrasting, an estimate of their importance for contamination of the deep karstic aquifer is not easy, since numerous biologic fractionations are involved in the nitrogen cycle.

Samples from the soil profiles have shown different nitrogen isotope systematics of the site Vysoký Újezd (VU), characterized by application of exclusively organic fertilizer and of the site Bubovice (B) dominated by industrial nitrate fertilizers. Results are given in Figs. 43 and 44. Ammonium ions of both sites are of predominantly organic origin and their isotopic composition is more or less influenced by nitrification. The highest content of ammonium ions was found in the uppermost horizon of the B site. The estimate of nitrate origin is more complex. As expected, the VU site had $\delta^{15}N$ values in the range of industrial nitrate fertilizers with only minor influence of bacterial processes, while the B site is characterized by nitrates derived by oxidation of organic ammonium nitrogen. Surprising was a low $\delta^{15}N$ value of the deepest horizon at the B site, reflecting probably industrial fertilizers applied some longer time before. Based on the study of both sites it is probable that the infiltrating waters of the period of high doses of industrial nitrate fertilizers in the past were characterized by nitrates with $\delta^{15}N$ values in the range typical of this source (i.e., $\delta^{15}N$ –3 to +2 ‰), with only minor influence of isotopic shifts related to biological processes.

The spring in Svatý Jan pod Skalou had relatively small variability of nitrate content, and, except of one positive excursion at the beginning of the monitoring period, relatively small variability of the $\delta^{15}N$ values (Fig. 45, 46).

When all monitored hydrogeological objects in the recharge area are plotted together with the spring data in a $\delta^{15}N$ vs. nitrate concentration plot (Fig. 47), the nitrate concentration and isotopic composition of the spring can be theoretically produced by mixing of two endmembers, the low nitrate content – low $\delta^{15}N$ waters infiltrating in the forested part of the catchment, and high nitrate content – medium $\delta^{15}N$ values infiltrating in the cultivated areas. Unfortunately, this concept does not describe spatial and temporal variability in possible nitrate sources. Moreover, the Bubovice Brook, which represents the surface drainage of the recharge area, had higher $\delta^{15}N$ values. This is why we focused on analysis and modeling of the data obtained from the spring itself.

Modeling of the origin and future evolution of nitrate contamination of the deep karstic aquifer

Scatter in diagrams of nitrate concentration vs. $\delta^{15}N$ values (Fig. 48) and chloride concentration vs. $\delta^{15}N$ values (Fig. 49) for the Svatý Jan pod Skalou spring indicates mixing of several components. The three most important components are:

- low nitrate (~10 mg/L) and chloride concentration and low $\delta^{15}N$ value short residence time component entering the system during large precipitation events. With respect to low nitrate content, this component cannot produce the observed oscillations of the spring $\delta^{15}N$ values,
- high nitrate (~ 60 mg/L) and chloride content and high $\delta^{15}N$ values (~ +7 ‰) component, which corresponds to medium residence time waters of the hydrological model (see above). This component represents washing out of free (mobile) nitrates from cultivated soils in the main recharge area. This component is responsible for the observed variability of nitrate $\delta^{15}N$ values and was responsible for a significant increase in $\delta^{15}N$ values observed after a snowmelt in winter 1995, when, after a long dry period, nitrates with high $\delta^{15}N$ values were washed out from cultivated soils, and
- high nitrate (~52 mg/L) and chloride, medium $\delta^{15}N$ (~ +2 ‰) component, representing long-residence time waters (average residence time ~22 years), contaminated by nitrates in the past, during application of high doses of mostly industrial nitrate fertilizers.

When the nitrate concentrations and $\delta^{15}N$ values of these end-members are incorporated into the hydrological model of Yurtsever (1983, see above), the agreement of modeled and measured $\delta^{15}N$ values of the spring is poor (Fig 50). The principal reasons of this discrepancy are temporal (and spatial, within the recharge area) variability of nitrate content and nitrate $\delta^{15}N$ of the medium residence time component, and errors in estimation of proportion of individual components. Therefore, for each sampling date the proportions of components were estimated based on discharge dynamics and variability in $\delta^{18}O$ of the discharging water. Using calculated proportions of individual components, a corresponding nitrate concentration and $\delta^{15}N$ values of the medium residence time component were calculated, to produce model system output in agreement with the observed spring discharge data (Fig. 53). The calculated data for the medium residence time component agree well with experimental data. The calculated medium residence time component shows three local maxima (during winter) and minima (during summer) of $\delta^{15}N$ values, corresponding to seasonal variability of biologic processes in soils.

Nitrate contamination – an outlook

Monitoring of nitrate concentrations and $\delta^{15}N$ values in the Svatý Jan pod Skalou spring and several hydrogeological objects in the recharge area enables to make prediction of the evolution of nitrate contamination in the future (Fig. 52). While nitrate contents in surface streams and shallow groundwater of the cultivated land already slightly decrease, reflecting the reduced doses of applied fertilizers, the nitrate content of the spring in Svatý Jan pod Skalou continues to increase.

There are several reasons for this increase:

- with respect to long average residence time of the spring main component, a decrease can occur only following a corresponding lag. Most groundwater discharging today infiltrated during late 1970ties, when nitrate contents of infiltration still increased,
- a future nitrate concentration decrease in the discharge can be retarded by sequential washing out of nitrates from thick weathering products and Cretaceous and Tertiary sediments, which cover most of the recharge area, and
- the decrease can be further retarded by diffusion of nitrates from immobile water in micro-pores into mobile water of macro-pores.

Translated by K. Žák and M. Novák