Nitrate Contamination in Karst Aquifers in the Czech Republic

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0. Abstract

Surface waters in the Czech Republic as a whole reveal the mean nitrate concentration of 12.5 mg.l^{-1} (the set of 14,237 samples). The mean nitrate concentration in surface waters of the karst areas is 26 mg.l^{-1}, i.e. 2 times higher. However, many karst springs exceed the highest recommended values stipulated by legal standard for potable water in their nitrate concentration, i.e. 50 mg.l^{-1}. Springs draining forested catchments usually range between 10 and 20 mg.l^{-1} in their nitrate contents at present. Many karstic catchments include not only forests but also intensively agriculturally utilized land. The springs in such catchments were often proved contain 60–100 mg.l^{-1} nitrates. State-supported application of industrial and organic fertilizers led, mostly in the 1960s to 1980s, to gradual increase in groundwater concentrations of nitrates in karst springs. After cutting down financial support in agriculture in 1990, the amounts of industrial fertilizers used substantially decreased.

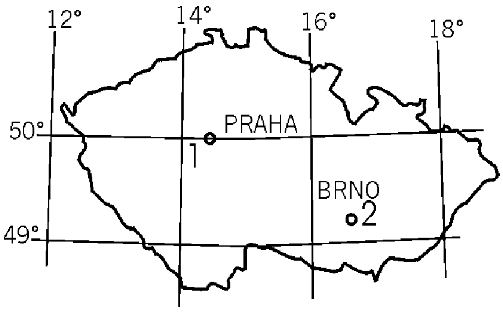

Fig.1 ***1- Bohemian Karst, 2 – Moravian Karst***

1. Introduction, geological settings of karst areas

Nitrates belong to the most common contaminants of the surface and ground waters. In the territory of the Czech Republic, an increase and evolution of nitrate contamination of waters has been documented on drinkable water sources. Since 1920, when nitrate contents in these waters were lower than 10 mg.l^{-1}, nitrate concentrations gradually increased by as much as 25 mg.l^{-1} to the year 1966 and by as much as 55 mg.l^{-1} to the year 1989. After 1989, a political change in the state caused a radical change in agriculture (significantly decreased volumes of nitrogenous fertilizers applied), resulted also in a decrease of nitrates in drinkable water sources in the period 1989-1993. Even though the amount of applied fertilizers continued to decrease (in 1995 it was about 50% of the 1998 value), nitrate concentrations in groundwater do not continue to decrease anymore after 1993. On the contrary, a continuing increase in nitrate concentrations in some drinkable water sources has been observed (PEKNY & SKOREPOVA, 1998). Yearly increase of nitrates in natural water of about 1 mg.l^{-1} on average was given in the 1990′ (SKOREPA & SKOREPOVA 1986, VOJTECH, 1988). Washing of nitrates into surface and ground waters is influenced by a number of factors, such as quantity and form of applied nitrogenous fertilizers, precipitations and temperature in given year, quality and quantity of the soil organic matter etc. Nitrate mobility has been influenced also by the increase of atmospheric deposition of nitrogen and soil acidification in the recent years. Nitrate washing into surface and groundwater is one of the indicators of destabilization of the ecosystem. Atmospheric deposition of nitrogen is manifested especially in natural and semi-natural ecosystems, whereas agricultural ecosystems receive a large part of nitrogen from fertilizers.

Karst areas formed by various types of limestones (Silurian to Triasic) occupy about 0.9% of the total area of the Czech Republic. The Bohemian Karst with the area of about 131 km^2, situated to south-west from the Czech capital Prague, and the Moravian Karst with the area of 85 km^2, located to north-east and north from Brno belong to the largest ones (Fig.1). A number of other smaller karst areas were formed in crystalline limestones of largely Palaeozoic age. Cretaceous limestones with some karst features furthermore occur in the Czech Cretaceous Basin in the northern and central part of the republic. In general, the karst areas represent rather islands with imperfectly developed karst morphology. Only the Moravian karst area, formed by Devonian and Lower Carboniferous limestones, includes a large spectrum of well-developed karst phenomena including groundwater streams. Due to the character of aquifers and a limited occurrence of the Neogene and Quaternary cover, carbonate rocks on the territory of the Czech Republic belong into a group of collectors with a high vulnerability as nitrogen washed from soils concerns.

2. Groundwater nitrate concentrations

Surface waters in the Czech Republic as a whole reveal the mean nitrate concentration of 12.5 mg.l^{-1} (the set of 14,237 samples) (VESELY et al., 1986, MAJER et al., 1992). The mean nitrate concentration in surface waters of the karst areas is

26 mg.l^{-1}, i.e. 2 times higher. However, many karst springs exceed the upper limit value stipulated by legal standard for potable water in their nitrate concentration, i.e. 50 mg.l^{-1}. Springs draining forested catchments usually range between 10 and 20 mg.l^{-1} in their nitrate contents at present. Many karst catchments include not only forests but also intensively agriculturally utilized land. The springs in such catchments were often proved to contain 60–100 mg.l^{-1} nitrates (KADLECOVA & ZAK, 1998).

Important relationships between the nitrogen concentrations in groundwater and agricultural activities revealed data acquired within the frame of the project Restriction of the areal contamination of surface and ground waters (PRCHALOVA et al., 2000). The Bohemian Karst area is mostly covered with arable and other soil - forests and permanent grass growths cover only 35% of the area. As a result, groundwater with nitrate contents lower than 25 mg.l^{-1} occur just on a small part of the area (5%). Nitrate concentrations between 25-45 mg.l^{-1} are typical for 25% and those higher than 45 mg.l^{-1} for 70% of the area. On the contrary, the situation as nitrate contamination of groundwater concerns is better in the area of the Moravian Karst, because the forest and permanent grass growths cover up to 55% of the total area. Groundwater with nitrate contents lower than 25 mg.l^{-1} occur on 51%, those with 25-45 mg.l^{-1} on 33% and those with nitrogen contents higher than 45 mg.l^{-1} on 16% of the area. The latter are encountered especially in the northern part of the Moravian Karst, where there is about 65% of the arable soil. In the karst aquifers of the smaller crystalline limestone occurrences and karst mountain areas (the Jeseniky Mts. and the eastern part of the Krkonose Mts.), nitrate contents in the groundwater are in general lower than 25 mg.l^{-1}. In the Bohemian Cretaceous Basin area, the fertile soils with higher contents of basic ions are more resistant, and there is no important nitrogen washing into groundwater.

3. Case study of the karst spring at Svatý Jan pod Skalou, Bohemian Karst

Karst environment is suitable for study of ground water nitrate contamination due to relatively thick undersaturated zone, to reducing conditions in soil, which enable denitrifying bacterial reactions only to a limited extent. Therefore nitrification - bacterial oxidation of organic nitrogen - predominates in soils. As soon as the infiltrated meteoric water penetrates the soil profile and gets into the rock environment of limestones, nitrates behave rather conservatively due to the prevailingly oxidation environment and rapid transport and their content neither the isotopic composition do not change considerably.

The groundwater pollution by nitrates in the karst aquifer was studied in detail in the Bohemian Karst area in the central part of the Barrandian, which is formed by a discontinuous mosaic of Silurian and Devonian limestones, isolated and interrupted by non-karst rocks (volcanic and volcaniclastic basaltic rocks, siltstones and shales) and folded into anticlines and synclines. These structures are affected by transverse faults with vertical and horizontal components of movement. The area of the Bohemian Karst is a 2nd-order hydrogeological structure (VCISLOVA, 1980) underlain by relatively impermeable Ordovician rocks. The Berounka River functions as a base level in its central and south-western parts. The principal base level on its north-eastern margin is the Vltava River.

The nitrogen evolution was monitored in the spring at Svatý Jan pod Skalou and its hydrogeological catchment area located in the NW part of the Bohemian Karst (BUZEK et al., 1998). Svatý Jan pod Skalou is located 25 km SE of Prague. This biggest karst spring lies near the bottom of a 140 m deep canyon of the Kačák Stream. Here, it drains the SW part of the Holyně-Hostim Syncline formed by volcanic rocks, limestones and siltstones of Silurian and Devonian age. The spring is located at the intersection of tectonic ruptures striking SW-NE and NW-SE to N-S, in the immediate proximity of the base level. An average yield of the spring is ca. 20 l.s^{-1} and the concentration of nitrates exceeds 50 mg.l^{-1} (Fig. 2). High nitrate concentrations in the Svatý Jan karst spring document its appurtenance to the group of springs dominated by agriculturally used land in a catchment of the area of ca. 8 - 10 km^2. The discharge, temperature, chemical and isotope ($\delta^{18}O$, $\delta^{15}N$ - NO_3^-, T) composition of the issued water were regularly monitored in 1994 - 1997 including the study of isotope composition of atmospheric precipitations. Monitoring was focused on the principal part of the Svatý Jan spring, called Ivanka and Ivan with Q_{min} of 14.1 l.s^{-1} and $Q_{max.}$ of 29 l.s^{-1} (Fig. 3). The correlation between maximal spring yield decrease and time has shown that the dominant circulation regimes of the Holyně-Hostim Syncline are those with laminar groundwater flow with different times of karst aquifer emptying. In these regimes, rocks are deformed mostly by a dense, largely equally spaced network of microfractures and small joints, and water-saturated tectonic zones play role of a buffer. Karst permeability becomes important only after heavy precipitation events, being associated particularly with shallow and rapid groundwater circulation with retardation times of several weeks to months.

Binary model according to HORTON (1935) was used for evaluation of the share of directly infiltrating precipitations due to a low variability of the $\delta^{18}O$ concentration in springs water and spring discharge. The ratio of the infiltration coefficient for the summer and winter season based on isotopic composition of oxygen from the precipitations and spring waters according to GRABCZAK et al. (1984) was used to calculate the average age of the water from tritium. It showed up that even though the amount of precipitations in the summer season is two times higher than in the winter one, the amount of water infiltrating in the deep aquifer is for both seasons approximately the same. Hydrological models according to YURTSEVERA (1983) and Flow model by MALOZSEWSKEHO (MALOSZEWSKI & ZUBER, 1996) were further used. On the basis of differences in hydrogen isotope concentrations (T) of the spring water and atmospheric precipitation, an average water retardation was determined with a 22-year circulation time in the structure, depending on the distance between precipitation infiltration and resurgence. The data on concentration of the individual nitrogen forms in soil and groundwater are not sufficient for the assessment of the importance of individual biogenic conversions in the nitrogen cycle, such as nitrification and denitrification. It is, therefore, necessary to combine data on concentration of the different

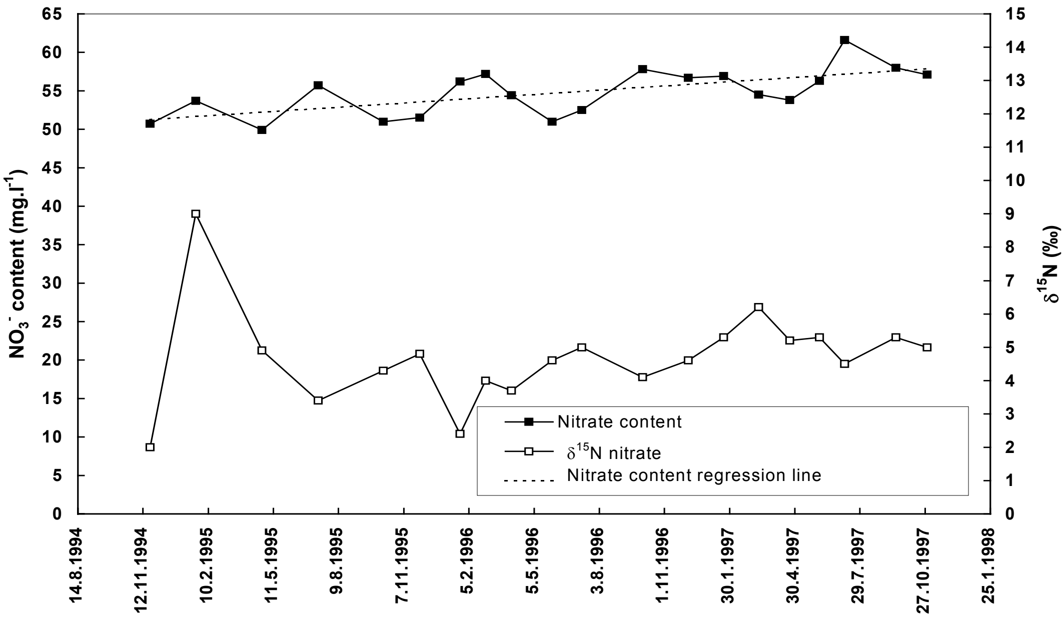

Fig. 2. Variations in nitrate concentration and nitrate isotope in the Svatý Jan spring in period 1994 – 1997

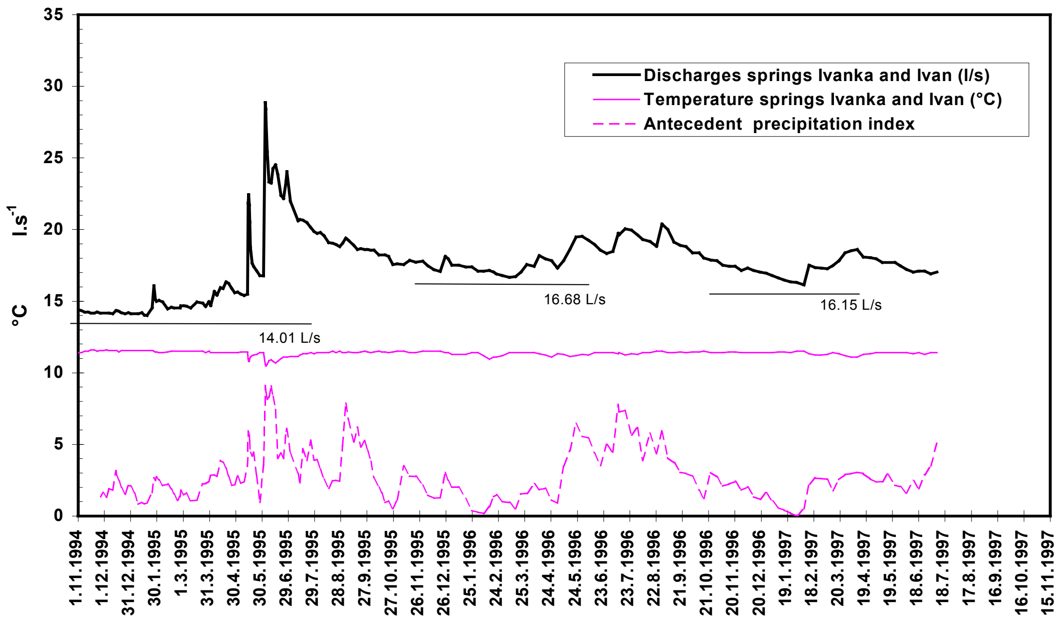

Fig. 3. ***Variations in yield and temperature of spring water and atmospheric precipitation in the studied period of 11/1994 - 10/1997.***

forms of nitrogen with the study of changes in its isotope composition. Most of the bacterial conversions in the nitrogen cycle is connected with large-scale isotope fractionation. To describe the nitrogen cycle in the catchment of the Svatý Jan spring, the chemical and isotope composition of nitrogen in nitrates was also regularly monitored in surface water and groundwater in the infiltration area of the spring and in other three hydrogeological objects: the Bubovický potok Stream, a well near the village of Kozolupy and a spring at Sedlec. The concentrations of nitrates and $\delta^{14}N$ isotopes of nitrates are shown in Fig. 4.

A geochemical model of the origin and history of nitrate contamination of the spring was elaborated on the basis of the above given data (spring yield, nitrate concentrations, and $\delta^{15}N$ $\delta^{18}O$ and T isotopes). Three components were modelled: 1. a component with slow groundwater circulation (avg. retardation of 22 years in rock environment) and agriculturally used catchment, representing 60-70% of the discharge water 2. a component with retardation time on the order of several months and agriculturally used catchment, representing 30% of the discharge water and 3. a component with rapid circulation (retardation time on the order of several days or weeks) and forested catchment, which characterizes geographical catchment of the spring with very low nitrate concentrations represent the remaining volume of less than 10%.

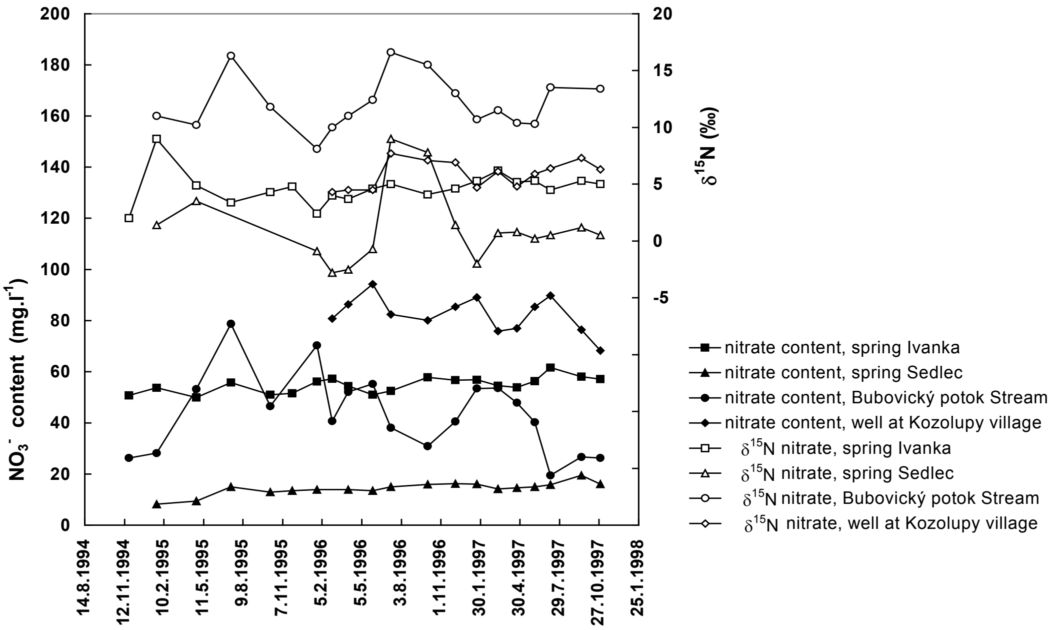

Fig. 4. ***Variations in concentrations of nitrates and isotopes of nitrates in the period 1994 - 1997***

The geochemical model revealed that nitrate concentrations in the Svatý Jan spring will increase due to the prevalence of the component of groundwater circulation with an average retardation period of 22 years, because water issued in late 1990s was recharged approximately in late 1970s, when nitrate concentrations in the recharging waters were still markedly increasing. Some increase in nitrate concentrations in spring water can be expected by 2005. The decrease in nitrate concentrations in spring waters in the future may be hindered by gradual washing of nitrates from a thick pile of weathering products, which fill the uneven karst surface in the infiltration area, as well as from the relatively thick unsaturated zone in limestones. The decrease in nitrate concentration in spring waters may be also hampered by diffusion of nitrates from immobile water in the karst aquifer into mobile water, or gravity water. Even though nitrogen input in agricultural soil from fertilizers decreased in the area Bohemian Karst, increase in nitrogen oxide concentrations (car traffic, gas introduction in local and central heating and gas introduction in large manufacturing plants) and even increase in ammonium concentration in local atmosphere has been registered recently. Current data on nitrate concentration in precipitations on free area range mostly around 4 mg.l^{-1} NO_3^-, in precipitations under the tree crown between 4 and 10 mg.l^{-1} NO_3^-, which probably represents one of the factors which influence present significant changes in plant assemblages in forest ecosystems (HOSEK & KAUFMAN, 1996, HOFFMAISTER, 1999). With respect to all these facts, the real decrease in nitrate concentrations in spring water will be probably much slower than expected by a model calculation considering mobile water only.

4. Conclusions

a. Karst aquifers on the territory of the Czech Republic belong into a group of collectors with a high vulnerability as nitrogen washed from soils concerns
b. Arable land of the karst area exhibit surplus of nitrogen, which is washed into groundwater. Fertile soils of the Bohemian Cretaceous Basin area with higher contents of basic ions are more resistant, and there is no important nitrogen washing into groundwater.
c. Some increase in nitrate concentrations in spring water Svaty Jan pod Skalou can be expected by 2005. Decreasing trend will be probably very slow due to the present higher atmospheric deposition.
d. Higher atmospheric deposition on the Bohemian Karst results in a small surplus of nitrogen in forest soil, which is reflected by a significant change in plant assemblages in forest ecosystems.

Acknowledgements

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