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Assessment of denitrification rates in fissured-karstic aquifer near Opole (SW Poland): combined use of gaseous and isotope tracers

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INTRODUCTION

Unconfined groundwater systems, particularly fissured-karstic aquifers, are vulnerable to anthropogenic pollution and the resulting deterioration of groundwater quality. Dissolved nitrate is among the most common pollutants occurring in shallow groundwater systems in Europe. Under natural conditions, denitrification is the only process leading to reduction of nitrate content in groundwater. The end-product of this process is gaseous nitrogen. The intensity of denitrification process is controlled by redox potential, availability of labile organic matter and presence of denitrifying bacteria in the system.

Here we discuss nitrate pollution in a groundwater system situated near Opole, south-west Poland (Kryza, Staśko, 2000). The investigated aquifer is of high economic value as a source of drinking water for the Opole region. Since more than three decades a substantial deterioration of water quality is observed in the southern, unconfined part of the system, resulting mainly from elevated concentrations of nitrates, often exceeding the maximum permissible concentration allowed by Polish law (50 $mgNO_3/dm^3$). However, it was observed that the nitrate concentrations drop abruptly in the northern, confined part of the system, which needed to be explained. From several possibilities, the authors suggested denitrification process as being the main reason for those observations. This possibility has been examined in the framework of the presented study by combined use of two independent tracers of the denitrification process: (i) the nitrogen and oxygen isotope composition of the dissolved nitrate, and (ii) the excess of dissolved nitrogen in groundwater. Assessment of denitrification rates in various parts of the studied system is of importance for effective management of available groundwater resources and for planning of new production boreholes.

DENITRIFICATION IN GROUNDWATER SYSTEMS

There are several ways of identifying the denitrification processes in groundwater systems: (i) microbiological identification of specific strains of denitrifying bacteria in groundwater (Barabasz, 1985), (ii) exploring the links between redox potential of groundwater and occurrence of denitrification process (Mariotti, 1986), (iii) identifying specific proteins in groundwater characteristic for the denitrification process (Santoro, 2009), (iv) measuring the excess concentration of nitrogen gas in groundwater (Heaton et al., 1983), and (v) analysing nitrogen and oxygen isotope composition of the dissolved nitrate (Böttcher et al., 1990). The last two methods were employed in the framework of the present study and are discussed below in some detail.

Tracing the denitrification process using excess nitrogen concentration in groundwater

The measured concentration of gaseous nitrogen dissolved in groundwater (C_m) can be separated into three components (e.g. Heaton et al, 1983; Cook, Herczeg, 2000; Żurek, Mochalski, 2010):

$$C_m = C_{atm} + C_{exa} + C_{den} \tag{1}$$

The atmospheric component (C_{atm}) represents equilibrium concentration of atmospheric N_2 dissolved in the infiltrating water under pressure and temperature conditions characteristic for the recharge area of the given groundwater system. The excess air component (C_{exa}) stems from the fact that the infiltration process usually leads to dissolution of some additional air in groundwater, when compared to the equilibrium amount dissolved under given pressure and temperature conditions. The denitrification component (C_{den}) represents gaseous N_2 produced during the denitrification process. In order to derive the denitrification component from the measured concentration of N_2 in groundwater, the remaining two components have to be measured or assessed.

Isotopic composition of nitrate as an indicator of denitrification process

Physical, biological and chemical processes associated with nitrogen cycling in nature lead to isotope differentiation of substrates and products in the course of various chemical reactions and transformations of nitrogen compounds. They may influence stable isotope ratios of nitrogen ($^{15}N/^{14}N$) or oxygen ($^{18}O/^{16}O$) or isotopic composition of other elements (such as hydrogen) present in some of those compounds.

During denitrification processes isotopically light molecules of NO_3^- are favoured. Isotopic fractionation can be expressed by the following approximate formula:

$$\varepsilon_{product\text{-}substrate} = \varepsilon_{p\text{-}s} \approx \delta^{15}N_{product} - {}^{15}N_{substrate} \qquad (2)$$

where $\varepsilon_{p\text{-}s}$ stands for effective isotope depletion in ^{15}N of the product, when compared to the substrate. Similar expression can be formulated for ^{18}O although in this case there are two substrates (NO_3^- and H_2O) and two products (HCO_3^-, CO_2) containing oxygen atoms, associated with the denitrification process.

Isotopic evolution of the product(s) and substrate(s) during the denitrification process can be described by the so-called Rayleigh model. The following approximate formula applies for calculating the nitrogen isotope composition of nitrate remaining in groundwater, when the initial isotopic composition ($\delta^{15}N_{si}$) and the isotope depletion $\varepsilon_{p\text{-}s}$ is known (e.g. Mariotti et al., 1988):

$$\delta^{15}N_{sf} = \delta^{15}N_{si} + \varepsilon_{p\text{-}s} \cdot \ln(F) \qquad (3)$$

where F is the fraction of nitrate left in the system from the beginning of the process. Similar equation can be written for ^{18}O.

Denitrification processes observed in the field usually reveal a linear relationship between ^{18}O and ^{15}N isotope enrichments in the remaining nitrate pool, the ratio being between 0.5 and 0.7 (Aravena, Robertson, 1998; Kendall et al., 2007). However, in the laboratory denitrification experiments with isolated strains of denitrifying bacteria Ganger et al. (2004, 2008) found the ratio of ^{18}O to ^{15}N enrichment close to one. The denitrification process in groundwater can be then identified by the characteristic shift towards more positive $\delta^{15}N$ and $\delta^{18}O$ values measured in the dissolved nitrate, associated with the reduction of NO_3 content (e.g. Leibundgut et al., 2009).

STUDY AREA

The studied aquifer (Major Groundwater Basin No. 333) is located in south-west Poland, in the vicinity of Opole (Fig. 1). This is a fissured-karstic system filled with Muschelkalk sediments consisting of carbonate and dolomite rocks with presence of fissures, cracks and karstic voids which control the flow of water. Water-bearing Permian-Triasic complex is composed of horizons of Bunter Sandstone and sediments of Roethian formation (Staśko, 1992; Kryza, Staśko, 2000) Hydrological conditions on the investigated area are determined by monoclinal structure of geological layers (Fig. 2). Outcrops of the water–bearing layers are located south of Opole, in the Strzelce Opolskie region (Fig. 1).

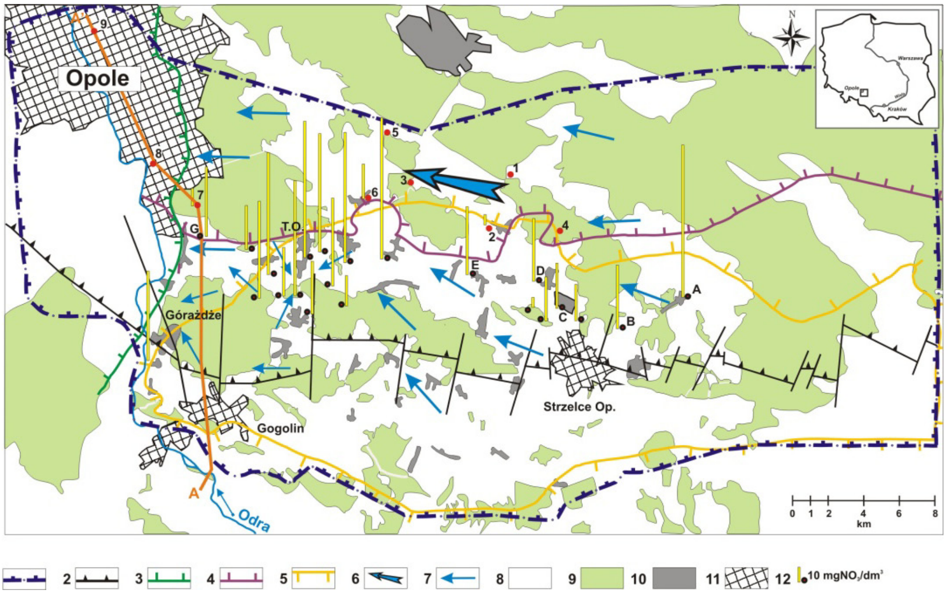

Figure 1. Hydrogeological and land-use map of the study area. The wells discussed in the text are labeled by letters (A to G) and numbers (1 to 9). Explanations: 1 — boundaries of the aquifer; 2 — range of Muschelkalk formation; 3 — range of Cretaceous formation; 4 — range of impermeable Keuper deposits; 5 — range of Quaternary cover; 6 — regional direction of groundwater flow; 7 — local directions of groundwater flow; 8 — agricultural areas; 9 — forests; 10 — rural areas without sewage system; 11 — towns with central sewage system; 12 — monitoring points with nitrate concentration in mgNO3/dm³; T.O. — Tarnów Opolski.

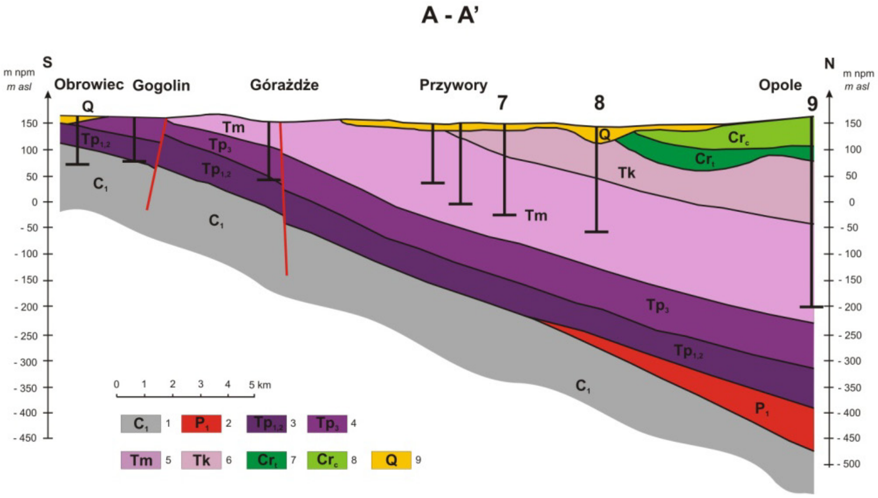

Figure 2. Geological cross-section A-A' (Poprawski, 1987; Staśko, 1992 — modified). Explanations: 1 — Lower Carboniferous: grauwackes, schists, conglomerates; 2 — Lower Permian: conglomerates and sandstones; Triassic (3-7): 3 — Lower and Middle Bunter Sandstones: sandstones, mundstones, conglomerates; 4 — Roethian: dolomites, marls, limestones with evaporite; 5 — Muschelkalk: limestones, marls and dolomites; 6 — Keuper: claystones, mundstones, marls and sandstones; Cretaceous (7-8): 7 — Turonian: marls and mundstones; 8 — Cenomanian: sands, sandstones; 9 — Quaternary: sands, gravels, glacial till.

Natural conditions of water circulation in the aquifer are varying spatially, reflecting diverse geological structure and changing permeability of the main water-bearing layer. In southern part of the system, where well-permeable zone of Muschelkalk outcrops is located, only partly covered with thin Quaternary sediments, preferable conditions for recharge and groundwater flow occur. Under natural conditions, the main groundwater flow direction was to the west, towards Odra river (Fig. 1). Recharge in northern part of the aquifer is very limited due to sick cover of loamy sediments of Keuper. Present-day flow conditions in the system are heavily modified due to intensive abstraction (municipal pumping stations) and dewatering of local quarries supplying raw material for cement industry. Large depression cones have developed particularly in the area of Opole, Strzelce Opolskie, Tarnów Opolski, and Górażdże.

METHODS

In the framework of the present study nine wells located in the confined part of the system were selected for combined measurements of excess gaseous nitrogen and analysis of ^{18}O and ^{15}N isotope composition of dissolved nitrate (wells 1 to 9 in Fig. 1). Those analyses were supplemented by measurements of dissolved nitrate and tritium content. For those wells also basic physico-chemical characteristics measured in-situ (temperature, pH, Eh, electrical conductivity, dissolved oxygen) are available (Żurek, Mochalski, 2010). For comparison, seven wells located in the unconfined part of the system, on the general direction of groundwater flow, were selected (wells A to G in Fig. 1). Oxygen and nitrogen isotope composition of dissolved nitrate, supplemented by nitrate and tritium content, are available for those wells from former studies (Kleczkowski et al., 1987, Różański et al., 2007).

Isotopic composition of nitrogen and oxygen in dissolved nitrate was measured in mass spectrometry laboratory of the Environmental Physics Group, Faculty of Physics and Applied Computer Science, AGH University of Science and Technology. Details of sample preparation technique are described in Chmura et al. (2009). The results of isotope analyses are reported as relative deviations of the measured isotope ratios (^{15}N/^{14}N and ^{18}O/^{16}O) from generally excepted standards, expressed in per mill. The standards used are atmospheric nitrogen (Mariotti, 1983) and the international reference material VSMOW (Coplen, 1996) for δ^{15}N and δ^{18}O, respectively. Measurement uncertainties of δ^{15}N and δ^{18}O (1 sigma) were in the order of 0.3 ‰ and 0.6 ‰, respectively (Chmura et al., 2009).

Nitrogen gas associated with the denitrification process was measured in the laboratory of the Department of Physicochemistry of Ecosystems, Institute of Nuclear Physics PAN, using gas chromatographic method. Details of sample preparation and measurement technique are presented elsewhere (Mochalski et al., 2006; Żurek, Mochalski, 2010).

Measurements of nitrate concentration in the investigated samples were performed by spectrophotometry with the standard uncertainty in the order of 0.1 mgNO$_3^-$/dm^3. Tritium content in water samples was measured in the tritium laboratory of the Environmental Physics Group, Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, using electrolytic enrichment followed by low-level liquid scintillation spectrometry (Florkowski, 1981; Kuc, Grabczak, 2005). Tritium results are reported in tritium units (TU). One TU corresponds to the isotopic ratio ^{3}H/^{1}H=10^{-18} (1TU = 0.1192 Bg/kg of water). Measurement uncertainties are in the order of 0.3 TU.

RESULTS AND DISCUSSION

The data discussed in the present work are summarized in Table 1.

Table 1. Nitrate content, $\delta^{15}N$ and $\delta^{18}O$ of nitrate, tritium, nitrogen from denitrification, equivalent nitrate concentration and oxygen content in sampled wells.

Well symbol	**NO_3^- [mg/dm^3]**	**$\delta^{15}N$ (NO_3) [‰]**	**$\delta^{18}O$ (NO_3) [‰]**	**^3H [TU]**	**$N_{2\,den}$ x10^{-3} [cm$^3_{STP}$/cm^3]**	**$NO_3^-{}_{den}$ [mg/dm^3]**	**O_2 [mg/dm^3]**
			Uncovered S part of aquifer				
A	100.5	5.4	14.3	10.3 (02.11.2005)*	n. m.	n. m.	n. m.
B	42.0	4.5	14.3	10.5 (02.11.2005)*	n. m.	n. m.	n. m.
C	30.0	8.9	4.4	11.4 (02.11.2006)*	n. m.	n. m.	n. m.
D	50.2	5.4	14.5	11.3 (02.11.2005)*	n. m.	n. m.	n. m.
E	45.0	7.1	17.0	11.7 (02.11.2005)*	n. m.	n. m.	n. m.
F	93.0	4.9	15.1	13.0 (08.11.2005)*	n. m.	n. m.	n. m.
G	45.4	5.5	15.5	12.5 (08.11.2005)*	n. m.	n. m.	n. m.
			N part of aquifer covered with Keuper sediments				
1	2.4	18.9	16.2	0.0	0.74±0.53	4.1±3.1	0.00
2	2.7	18.5	10.3	0.6	<0.6	<3.5	0.35
3	0.6	21.1	6.0	0.4	<0.6	<3.5	0.30
4	0.5	23.5	20.2	0.0	<0.6	<3.5	0.26
5	0.3	23.5	35.5	0.3	n. m.	n. m.	n. m.
6	22.3	6.1	15.5	3.7 (08.11.2005)*	<0.6	<3.5	9.0
7	12.5	6.0	16.6	6.9 (08.11.2005)*	3.23±0.61	17.0±3.5	6.4
8	<0.1	n. m.	n. m.	0.0**	<0.6	<3.5	0.09
9	<0.1	n. m.	n. m.	0.0**	<0.6	<3.5	4.5

* - Różański et al. 2007; ** - Kleczkowski et al. 1987.

$\delta^{18}O$ of dissolved nitrate is plotted as a function of $\delta^{15}N$ in Fig. 3, on the background of typical ranges of these values observed in different compartments of nitrogen cycle (Kendall et al., 2007).

The group of wells (A to G) representing unconfined part of the system reveals high nitrate content (between ca. 30 and 100 mg NO_3/dm^3) accompanied by high tritium content (between 10.3 and 13 TU), comparable to tritium concentration in present-day precipitation in southern Poland. This confirms relatively fast infiltration and presence of fresh water in this part of the aquifer supporting high pumping yields of the production wells, in agreement with the fissured-karstic character of the system.

The isotopic composition of dissolved nitrate in this group of wells forms a tight cluster bordering the area typical for NO_3 from fertilizer input. This strongly suggest that major input of nitrate to groundwater in this area is most probably from agriculture. The only exception is the well C which reveals distinctly lower $\delta^{18}O$ and higher $\delta^{15}N$ values, associated with lowest nitrate content (30 mg/dm^{-3}) when compared to the remaining wells in this group. In contrast to other wells, nitrate in this case may originate from point source (persistent application of manure or leaking septic wastes in the vicinity of the well).

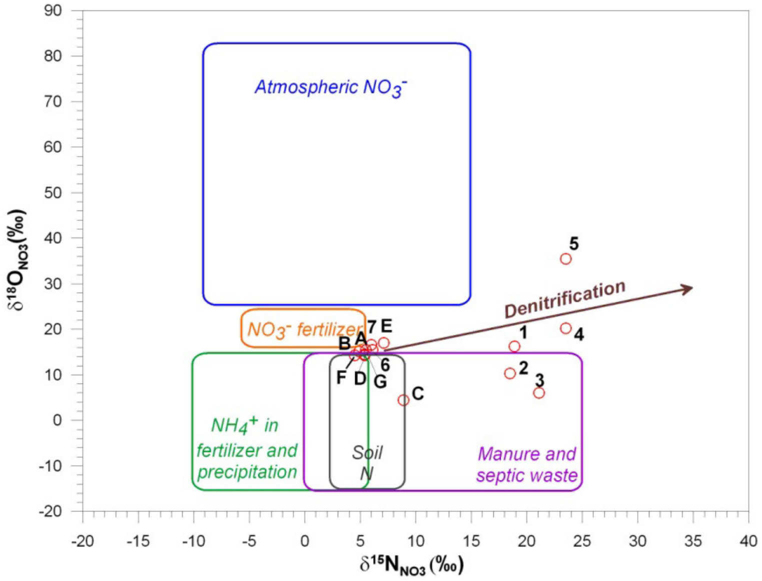

Figure 3. $\delta^{15}N(NO_3)$ - $^{18}O(NO_3)$ relationship for the data presented in Table 1. Ranges of ^{15}N and ^{18}O isotope signatures of different sources of nitrate are shown after Kendall et al. (2007).

The wells located in the confined part of the system, with the exception of well no.6 and no.7, reveal greatly reduced nitrate content, between ca. 0.3 and 2.7 mg NO_3/dm^3 (wells 1 to 5). Such decrease of nitrate content together with $\delta^{18}O$ and $\delta^{15}N$ data for those wells suggest well-advanced denitrification process. They are shifted on the $\delta^{18}O$-$\delta^{15}N$ plot to the right-hand side with respect to the data representing unconfined part of the system, clustering along the denitrification line with the slope of ca. 0.5. The enrichment in ^{15}N varies between ca. 15‰ (wells nos. 1, 2 and 3) and 20‰ (wells nos. 4 and 5) which corresponds to ca. 3 to 5-fold reduction of the initial nitrate content (Ganger et al., 2008), suggesting that the initial nitrate content varied between ca. 1.5 and 3 mg NO_3/dm^3 for wells nos. 3, 4 and 5 and between ca. 7 and 12 mg NO_3/dm^3 for wells nos. 1 and 2. Water in those wells does not contain any significant amounts of tritium, strongly suggesting its pre-bomb age, in agreement with natural ranges of initial nitrate content assessed above. It is apparent from Table 1 that the detection limit of the nitrogen excess method is in the order of 3.5 mg/dm^3 of decomposed NO_3^-. It is, therefore, not surprising that in case of wells nos. 3 and 4 no nitrogen associated with denitrification could be detected (well no.5 was not measured). Well no.1 falls just at the border of the sensitivity of the method. The assessed initial concentration of NO_3^- in this well derived from excess of nitrogen (ca. 3.4 to 9.6 mg NO_3/dm^3) falls within the range suggested by the isotopic composition of nitrate (7 and 12 mg NO_3/dm^3) possibly indicating some (if any) input of anthropogenic nitrate. Traces of tritium in well no.2 (0.6 TU) might indicate small admixture of fresh water.

Well no.6 is located just at the border of the confined part of the system (cf. Fig. 1). It reveals elevated nitrate content (22.3 mg NO_3/dm^3) with its ^{15}N and ^{18}O isotopic composition lacking any sign of denitrification (cf. Fig. 3). Also the excess of nitrogen is below the detection limit. These indicators, combined with significant tritium content (3.7 TU) clearly demonstrate that although the well is located already within the confined part of the system, the travel time of water to this well from the recharge area is apparently too short for the denitrification process to leave significant imprint either in the isotopic composition of nitrate or in the excess of nitrogen.

Well no.7 is located in the western part of the system, close to Opole municipal area. Water from this well contains significant amount of nitrate (12.5 mg NO_3/dm^3). Isotopic signature of nitrate does not reveal any signs of the denitrification process. Tritium content is relatively high (6.9 TU), pointing to recent recharge. Surprisingly enough, this water reveals high N_2 excess, equivalent to ca 17 mg NO_3/dm^3 of decomposed nitrate. Such high value cannot be reconciled with significant tritium content in this water and with the isotopic signature of nitrate nor revealing any signs of the denitrification process. High concentration of dissolved oxygen equal 6.4 mg/dm^3 (Table 1) and high redox potential (344 mV) reported by Żurek and Mochalski (2010) for this well essentially exclude any significant denitrification in this case. Therefore, other reasons for high N_2 excess detected in this water must be thought.

Wells no. 8 and 9 are located within Opole municipal area, in the north-west corner of the study area. Nitrate content in these wells is below the detection limit of the method used (<0.1 mg NO_3/dm^3). Water is tritium-free and no traces of N_2 excess could be detected. All these indicators suggest significant age of groundwater and (almost) complete denitrification of the natural nitrate. Interestingly enough, well no.9 revealed noble gas temperature equal ca. 3.6°C (Żurek, Mochalski, 2010), pointing to glacial origin of this water. Glacial origin of water in this part of the system is also suggested by significantly reduced ^2H and ^{18}O content in this water when compared to recent recharge (Kleczkowski et al., 1988), providing independent proof of its great age.

CONCLUDING REMARKS

The investigated groundwater system located in south-west Poland revealed a broad range of nitrate concentration. The measured nitrate content varied from below detection limit (<0.1) to ca. 100 mg/dm^3. A dominant role of diffuse source of nitrate (fertilizers) was confirmed, based on oxygen and nitrogen isotopic composition of nitrate. The measured concentration of tritium in the analyzed groundwater samples also varied in relatively broad range, from 0 to ca. 13 TU.

Two contrasting groups of wells (one group located in the unconfined part of the system, representing presumable recharge area, and the second one located in the confined part) analyzed in the present study allowed a deeper insight into the fate of nitrate in the system. Isotope fingerprint of the denitrification process was clearly identified in several wells located in the confined part. Water from these wells was generally tritium-free and revealed very low nitrate contents which isotopic signature pointed to well-advanced denitrification process.

The measured ^{18}O and ^{15}N isotope enrichments in the remaining nitrate in the wells located in confined part of the investigated system indicate that initial nitrate concentrations were generally within the natural range or close to it (< 10 mg/dm^3) suggesting that water being pumped by those wells was recharged before significant input of nitrate from fertilizers occurred in this area. This is consistent with absence of tritium in these wells. In turn, this would mean that the plume of anthropogenic nitrate did not yet penetrate substantially into confined part of the system and with time the wells located in this part may also experience elevated nitrate contents.

Wells nos.6 and 7 which are located already within the confined part of the system, at the distance of ca. 0.5 and 2 km to the unconfined part, respectively, allowed an interesting glimpse into the dynamics of the denitrification process. Isotopic composition of nitrate from these wells did not revealed any signs of denitrification, despite the fact that tritium content was reduced to ca. 40-50% of the values recorded in the unconfined part, suggesting not negligible travel time of water to those wells within the confined part. Also other indicators (Eh, dissolved oxygen) clearly showed that appropriate conditions for denitrification were not yet reached in these two cases.

The method of identifying denitrification process in groundwater via excess of gaseous nitrogen turned out to be not sufficiently sensitive to detect denitrification of natural nitrate which concentrations in groundwater in the study area are thought to be generally well below 10 $mgNO_3/dm^3$. Nevertheless, this method remains an attractive tool for quantification of the denitrification processes in systems where denitrification of anthropogenic nitrate is already underway.

The presented study demonstrated that combining isotope analyses of nitrates with tritium or other transient tracers may provide additional insights into the dynamics of water and nitrate movement and transformation in groundwater systems.

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