Vertical nitrate migration and denitrification zones in a regional recharge area (Lwówek region, Poland)

Krzysztof DRAGON[1, *], Józef GÓRSKI[1] and Diana BURGHARDT[2]

[1] Adam Mickiewicz University in Poznań, Institute of Geology, Department of Hydrogeology and Water Protection, Bogumiła Krygowskiego 12, 61-680 Poznań, Poland

[2] Technical University of Dresden, Institute of Groundwater Management, Department of Environmental Sciences, Bergstraße 66, 01069 Dresden, Germany

We examine the influence of groundwater flow patterns and denitrification on nitrate migration in a regional recharge zone. It has been shown that nitrate contamination has a different behaviour in regions where groundwater is exploited (where deep percolation of nitrate takes place) than where natural gradients exist (with no deep aquifer zone contamination). Multicomponent chemical tracers and isotopic methods were used in the investigation. A contaminant plume was discovered in shallow parts of the aquifer which percolated into deeper parts of the flow system in those regions with a downwards gradient induced by groundwater withdrawal, where the influence of denitrification was limited. Local conditions leading to intense denitrification, i.e., local changes in geological conditions (low-permeability silt intercalations), were also documented. Therefore, vertical changes in groundwater chemistry should be examined to ensure groundwater resource management and protection, as these are extremely important in regional recharge zones with a downwards gradient.

Key words: nitrate contamination, denitrification, groundwater flow pattern, nitrogen isotopes, sediment geochemistry.

INTRODUCTION

Groundwater pollution by nitrates is currently one of the most critical environmental problems recognized in European Union (EU) countries. High nitrate concentrations in potable water can cause health problems such as methemoglobinemia in infants and stomach cancer in adults. Additionally, interactions between contaminated groundwater and surface water can impact aquatic ecosystems (Hu et al., 2016; Lasagna et al., 2016; Górski et al., 2019), leading to surface water eutrophication (Hutchins, 2012; Capell et al., 2021). Human activities and associated nitrate pollution lead to high risk of marine ecosystem contamination (Malagó et al., 2019). It is an important issue also in the Baltic Sea Basin (Højberg et al., 2017). To protect the environment, the Nitrates Directive (91/676/EEC) was implemented, and EU countries identified nitrate vulnerable zones (NVZs) and established action programmes for the management of agricultural practices. However, for effective management and protection of water, an investigation of the processes that control nitrate migration is crucial.

Groundwater in shallow unconfined groundwater systems is easily contaminated by nitrate because of its high vulnerability to pollution from the surface (Wassenaar, 1995; Feast et al., 1998; Kaown et al., 2018; Karlovic et al., 2022). While contamination is usually less prevalent in deep wells (Nishikiori, 2012), in some instances nitrate contamination can also appear in deeper parts of the flow system (Chen et al., 2005). Regional recharge zones are more vulnerable to deep nitrate contamination due to the high downwards gradient that facilitates nitrate movement into deeper aquifers before it can be denitrified (Dragon, 2013, 2021).

The main mechanism of nitrate removal in groundwater is bacterial denitrification, which has been documented in many groundwater systems (e.g., Aravena and Robertson, 1998; Einsiedl et al., 2005; Craig et al., 2010; Żurek et al., 2010; Dragon et al., 2016). In general, denitrification involves the reduction of nitrate via a series of biologically controlled reactions under anaerobic conditions if electron donors (e.g., organic matter, dissolved organic carbon, or reduced sulphur compounds) are available in sediments (Rivett et al., 2008). It has also been shown that denitrification is controlled by local (usually spatially and temporally variable) biogeochemical conditions.

Isotopic methods can support the investigation of nitrate sources in groundwater. The isotopic composition of nitrate, represented by ^{15}N-NO_3 and ^{18}O-NO_3 values, can be used to

* Corresponding author, e-mail: smok@amu.edu.pl

distinguish nitrate sources in groundwater (Feast et al., 1998; Zhang et al., 2013; Lasagna and De Luca, 2019). This technique is also used to document denitrification in the system (Feast et al., 1998; Craig et al., 2010; Dragon et al., 2016; Kaown et al., 2018). Traditional physical and chemical measurements (water level, major ion composition, geochemical investigation, etc.) can also help investigate the relation of nitrate attenuation to groundwater flow patterns (Pfeiffer et al., 2006). Groundwater chemistry can give information regarding conditions of contaminant migration (Fryar et al., 2000).

In a previous study (Dragon, 2021), groundwater flow pattern in relation to nitrate migration was documented in the study region (Lwówek region, Poland). It was shown that nitrate contamination behaves differently in those areas where groundwater is exploited (that facilitates nitrate deep percolation) compared to regions of natural groundwater gradients (with no deep aquifer zone contamination).

The present study investigates denitrification processes in the regional recharge zone using a multicomponent chemical tracer approach, ^{15}N-NO_3 and ^{18}O-NO_3 isotopes and geochemical investigation. The specific objectives were: (1) identification of denitrification in the system and its effectiveness in nitrate removal, (2) documentation of local denitrification variation caused by local geological conditions or lithology (geochemical sedimentary diversity) and (3) identify the nitrate pollution plume in the shallow groundwater flow system zone and conditions for its downward migration.

THE STUDY REGION

The study region is located in the middle part of Wielkopolska upland area (Poland) on the Lwówek–Rakoniewice Rampart and the pilot sites are located in the highest part of the region where the regional recharge zone of Quaternary aquifers is present. In this region, the ground elevation reaches 138 m a.s.l., decreasing in all directions from the peak elevation to less than 100 m a.s.l. (Fig. 1).

Quaternary deposits occur from the surface to a depth of >120 m. Glacial and fluvioglacial deposits dominate the lithology. Fluvioglacial sands and gravels form the aquifers (Fig. 2). The deepest aquifer discovered in the study region, at Chmielinko (Fig. 2) is composed of fine sands and is relatively thin, usually less than 20 m thick. The Wielkopolska Buried Valley aquifer (WBV), located south of the study region (Figs. 1 and 2) is composed of coarse sands and gravels in the deeper parts and fine and medium sands in shallower parts. The thickness of the water-bearing deposits is variable, ranging between 20 and 40 m. The shallower aquifer units are composed of fine sands, and their thickness is usually <20 m.

The confined aquifers are covered by an aquitard composed of glacial till. The thickness of the aquitard is variable and ranges between 10 m in Wytomyśl and >100 m in Chmielinko (Fig. 2). In the regions of Władysławowo and Józefowo (the regions chosen for detailed investigation) this aquitard is not present, and the aquifer deposits (sands and gravels) extend from the surface to a depth of >100 m (Fig. 2). Where hydrogeological windows occur, the aquifers stay connected hydraulically, while in the regions where aquitards occur, glacial tills cause the aquifers to be vertically isolated. It was documented previously that the groundwater chemistry in aquifers near the regional recharge zone (including the main aquifer – WBV) is strongly influenced by the inflow of groundwater from the Lwówek–Rakoniewice Rampart (Dragon and Górski, 2015).

The aquifers are recharged by direct water infiltration where hydrogeological windows are present and by indirect vertical percolation of water through the glacial tills from the shallowest to the deepest aquifers (Dragon and Górski, 2009).

In the study region the groundwater divide is present (the central part of the regional recharge zone). From the groundwater divide, the water flows to the Warta River valley (eastwards) and to the Obra River valley (westwards; Fig. 1). The downwards gradient occurs in the central part of the recharge zone, being manifested by the large water level difference between the shallow and deep aquifers (>14 m in Chmielinko; Fig. 2).

Notably, groundwater is exploited at the Józefowo site, though not at Władysławowo. This difference allows documentation of groundwater chemistry changes along a vertical profile with respect to water exploitation.

MATERIALS AND METHODS

The unconfined parts of the flow system (at Władysławowo and Józefowo; Fig. 2) were selected for the study of groundwater chemistry changes. A multilevel observation well was drilled at each site adjacent to the abstraction well, enabling us to use the abstraction well as the deepest sampling point. The multilevel system was effected by drilling a net of observation wells at one location (several metres away from each other), each equipped with a screen located at a different depth. A short screen interval (1 m) was used at each sampling point. Two multilevel screens were located close to (several metres from) the Józefowo well 1 bis at depths of 27–28 m (J I) and 46–47 m (J III). The three screens of the multilevel well at Władysławowo located several metres from Władysławowo well 1 were positioned at 31–32 m (W I), 42–43 m (W II) and 54–55 m (W III). The production well screen at Józefowo was positioned at between 55 and 79.5 m, while the well at Władysławowo had a screen located between 64 and 100 m depth (Fig. 2).

Each multilevel observation well was formed by dry drilling (without the use of drilling mud) to obtain representative sediment samples for geochemical analysis. During drilling, samples were collected every 1 m into plastic bags and then analysed in the laboratory to determine the grain size distribution, the pH of water extracted from the deposits (with the use of KCl), the organic matter content determined by loss of mass upon ignition (temp. 110°C and then 550°C, expressed in g/kg) and the calcium carbonate content obtained by the Scheibler volumetric method (expressed as %CO_3).

The sampling campaign performed in June 2018 comprised all multilevel observation wells, all exploitation wells at the Józefowo site and an inactive well at Władysławowo (9 water samples). An *MP1 Grundfos* pump was used for water sampling in the observation wells. A *Grundfos SP17* pump powered by a generator was used for pumping the inactive well at Władysławowo. The observation wells were pumped for a minimum of 2 h before sampling to ensure at least three water exchanges in the well pipes, while 12 h of pumping cleaning was performed before sampling in the inactive well at Władysławowo.

High-density polyethene (HDPE) bottles were used to collect the water samples. Chloroform was used to preserve samples for nutrient analyses, while HNO_3 was used to treat samples for iron and manganese (and other metals) testing. The water samples during transport to the laboratory were stored in a portable refrigerator at low temperatures (~4–6°C). The parameters measured directly in the field with portable Aquaread AP-700 equipment included electrical conductivity, alkalinity, pH, redox potential, oxygen content and temperature. Chemical analyses were performed in the laboratory at the Adam Mickiewicz University in Poznań (Institute of Geology, Poland)
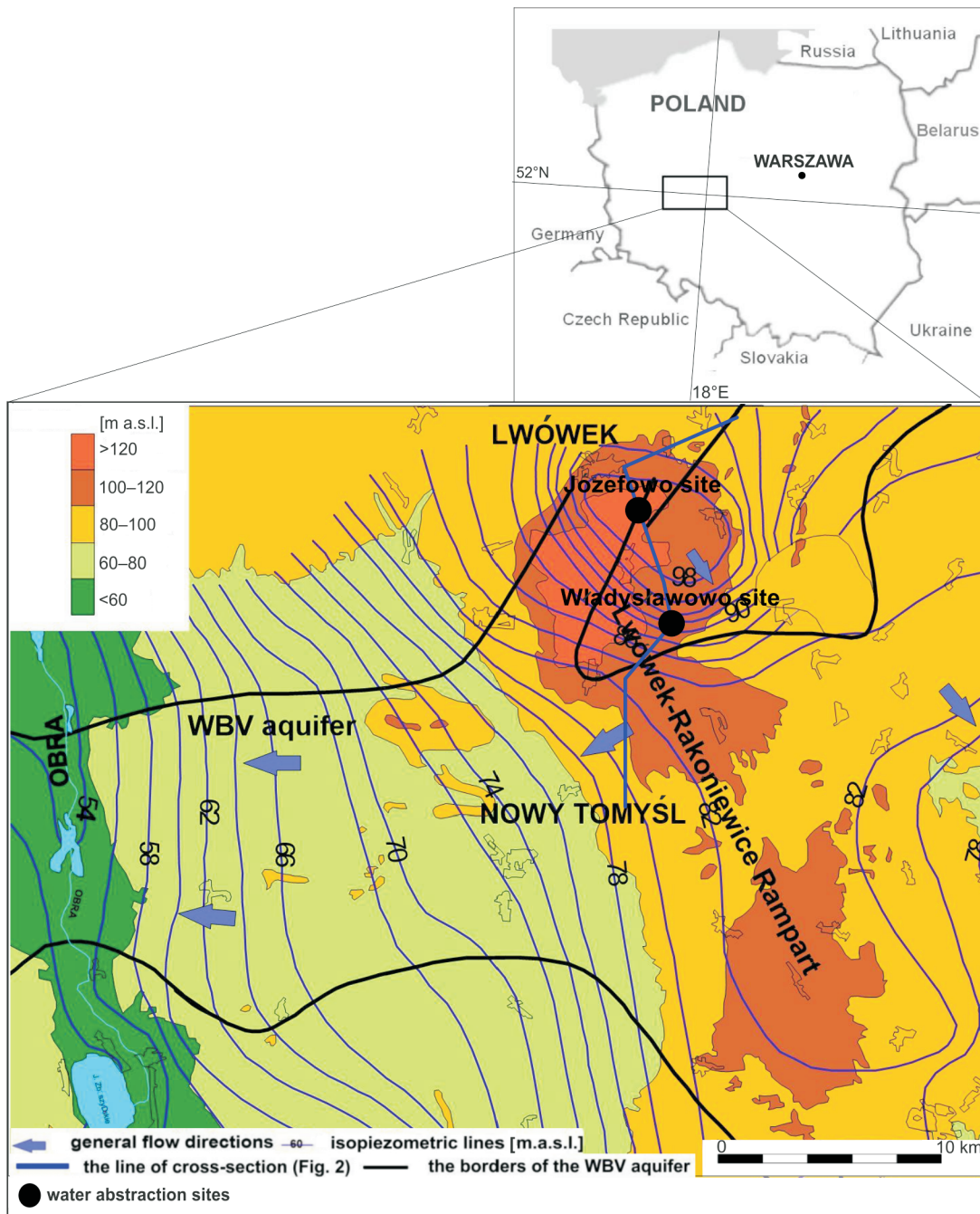
Fig. 1. The study region showing hydroisohip contours and ground surface elevation

WBV aquifers – Wielkopolska Buried Valley aquifer

using an *881 Compact IC Pro ionic* chromatograph. As a quality control measure, the ionic error balance was calculated. The calculated error did not exceed 3%.

Isotope ratio analysis of dissolved nitrate (^{15}N and ^{18}O) was performed at the Technical University of Dresden (Germany), Institute of Groundwater Management. Groundwater samples with volumes of 50 to 100 ml were collected, membrane-filtered (0.2 µm pore size) and stored frozen until analysis. The minimum concentration for technically feasible sample preparation in the laboratory was 0.25 mg NO_3/l. Dissolved nitrate was transformed completely into gaseous N_2O by a culture of the denitrifying bacterium *Pseudomonas aureofaciens*. The simplified denitrification method used has been published by

Stock et al. (2021). After microbial sample preparation, simultaneous ^{15}N and ^{18}O analyses of N_2O sample gases were performed by a *GasBench II* device with a denitrification kit and a *Delta V Plus* isotope mass spectrometer (both Thermo Fisher Scientific). Calibration was performed with the IAEA isotope standards NO_3 (+4.7‰ ^{15}N, +25.6‰ ^{18}O), USGS34 (–1.8‰ ^{15}N, –27.9‰ ^{18}O) and USGS32 (+18.0‰ ^{15}N, +25.7‰ ^{18}O). The uncertainty in ^{15}N and ^{18}O analyses resulting from sample preparation by denitrifying bacteria, the precision of triplicate analysis and calibration via IAEA standards were calculated according to Kragten (Dunn and Carter, 2018) to ±1.5‰ for both isotope ratios.
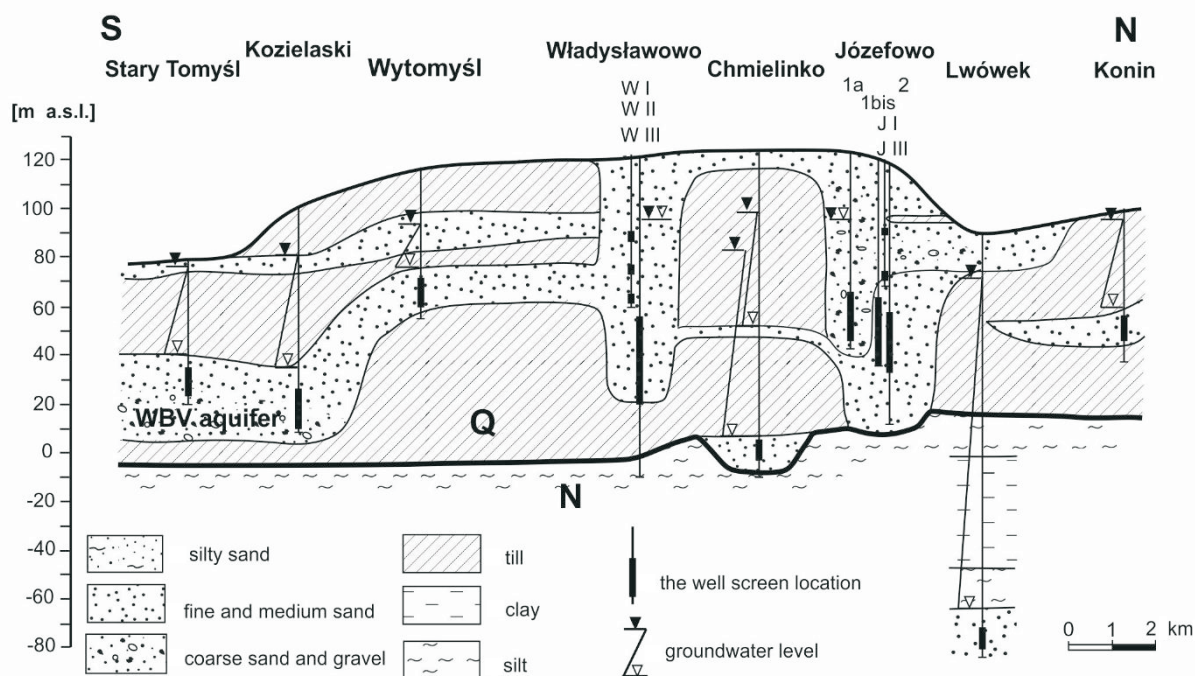
Fig. 2. Hydrogeological cross-section (after Dragon, 2021, modified)

The isotopic interpretation was made in the context of stable isotope measurements of ^{18}O and ^{2}H as well as C^{14} and tritium measurements published by Dragon (2021). The results of previous isotope analyses described by Dragon and Górski (2015) were used additionally for data interpretation.

RESULTS

GEOCHEMICAL CHARACTERIZATION OF THE DEPOSITS

The geochemical features revealed a low pH and high organic matter content in the shallow zone to a depth of several metres below the surface at the Józefowo and Władysławowo sites (Figs. 3 and 4). This finding is related to a soil type that usually has a higher organic matter content and lithology (carbonate-poor tills). Below a depth of ~10 m, the organic matter content was much lower, but clear peaks (at a level of 5 to 7 g/kg) were detectable at a depth of 39–40 m at Józefowo (low-permeability silt intercalations) and 45–46 m at Władysławowo (fine sands with visible patches of organic matter). At Władysławowo, a clear peak in organic matter content was also noted at a depth of 20 m. Zone with high organic matter usually coincide with decreased pH, as is clearly visible in both profiles (Figs. 3 and 4).

The pH values of extracted water were generally lower in the shallow zone to a depth of 27 m at Józefowo (pH close to 8.0) and to 30 m at Władysławowo (pH less than 8.5) than in the deep zone. Below these zones, the pH increased to a value of 9.0, but peaks with lower pH were visible in zones with higher organic matter contents (Figs. 3 and 4), related to oxidation of organic matter.

The carbonate concentration is clearly related to sedimentary grain size. Higher concentrations occur in zones of coarser deposits, especially coarse sands and gravels at the Józefowo site. A high carbonate was also documented at shallow levels at Władysławowo, where sandy tills occur near surface.

GROUNDWATER CHEMISTRY

The hydrochemical results are summarized in Table 1. The nature of hydrochemical changes differed among the sites investigated. At Józefowo, the water chemistry was very similar between the shallowest and deepest parts of the aquifer, with evident deviation in the middle of the profile (Fig. 5). This deviation was related mainly to nitrate concentration (12.6 and 9.99 mg/l in the shallow and deep parts of the aquifer, respectively) and sulphate concentration (58.0 and 68.0 mg/l, respectively). In the middle part of the profile, the nitrate concentration was much lower (1.39 mg/l), but the sulphate concentration was higher (79.3 mg/l). Similar changes were observed for the redox potential (297.7 and 297.0 mV in the shallow and deep parts, respectively), with a considerably smaller value in the middle part of the profile (231.0 mV), and oxidisability (3.0 and 2.5 mg O_2/l in the shallow and deep parts, respectively), with a significantly higher value in the middle part (4.5 mg O_2/l). The oxygen concentration was high only in the shallowest part of the aquifer (4.45 mg/l) and was very low (0.23 mg/l) in the deepest part of the aquifer.

Different vertical groundwater chemistry trends were observed at the Władysławowo site (Fig. 6). The concentrations of almost all constituents were highest in the shallow part of the aquifer, with decreasing trends in the deepest parts. The nitrate concentration in the shallow part of the aquifer was relatively high (33.5 mg/l), decreasing to 1 mg/l in the deepest parts. The sulphate concentration was 27.3 mg/l in the shallow part and decreased to less than 10 mg/l in the deepest part. A similar trend was observed for redox potential (>300 mV in the shallow-
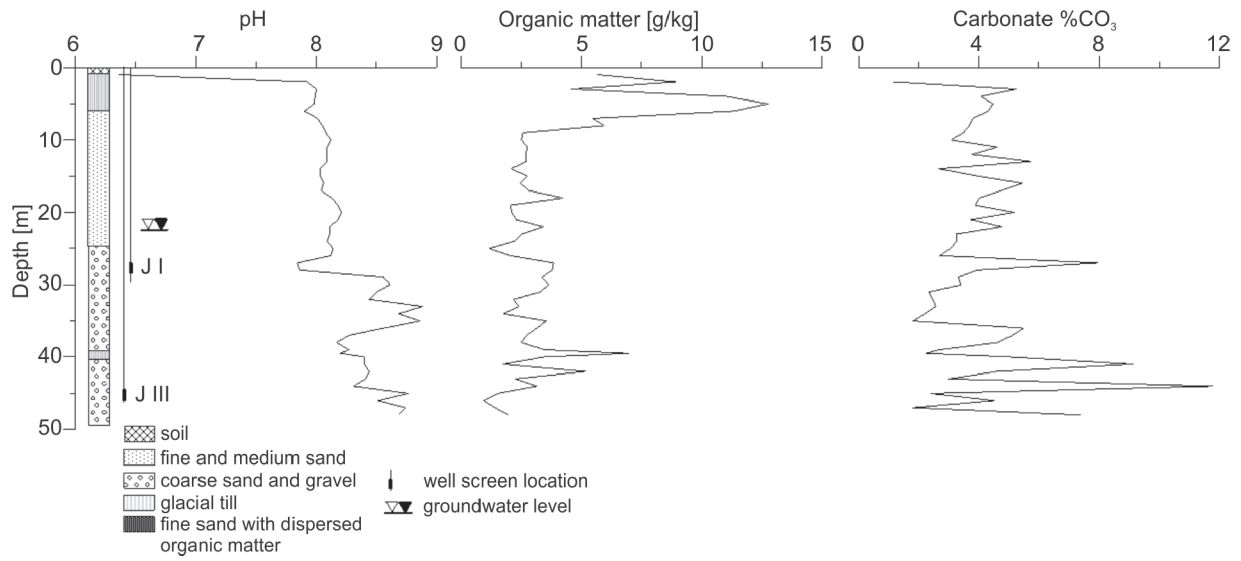
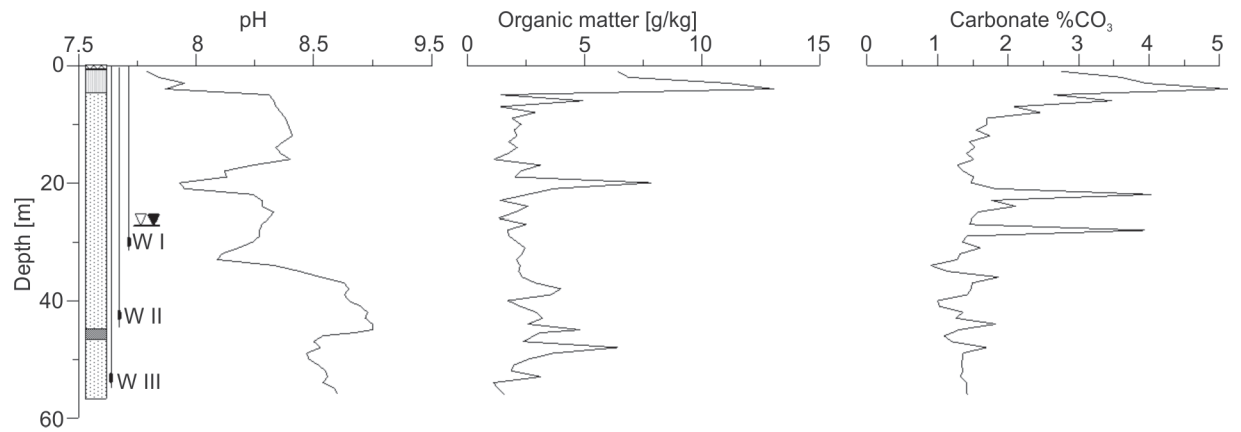**Fig. 3. Vertical changes in geochemical parameters at Józefowo**

Fig. 4. Vertical changes in selected geochemical parameters, Władysławowo site

The position of the well screen is shown on the left part of the graph (see explanation on Fig. 3)
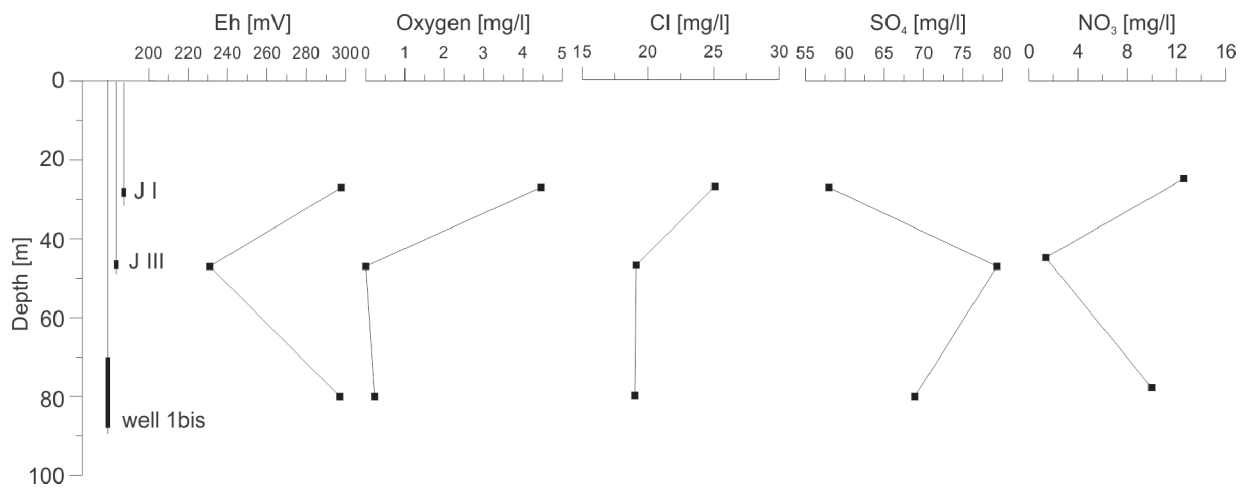

Fig. 5. Changes of selected parameters with depth, Józefowo site (after Dragon, 2021)

The position of the well screen is shown on the left part of the graph (see explanation on Fig. 3)

T a b l e 1

Results of the chemical analyses (after Dragon, 2021)

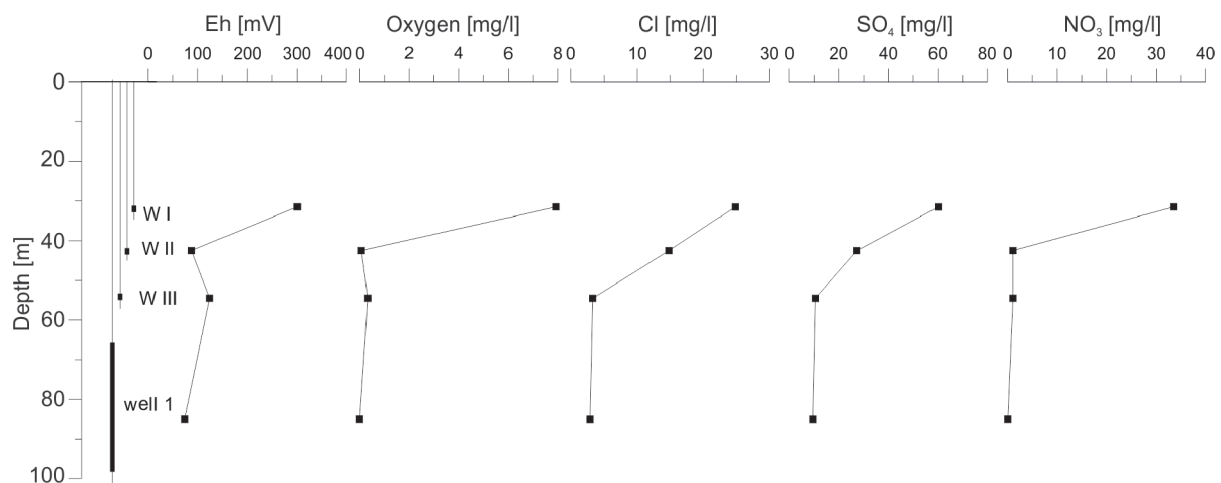|	Unit	Józefowo					Władysławowo			
		J I	J III	1bis	2	1a	W I	W II	W III	1
Screen interval	m below ground surface	27.0–28.0	46.5–47.5	55.5–79.5	62.0–87.0	59.6–77.0	31.0–32.5	42.0–43.0	54.0–55.0	64.0–100.0
pH	[-]	7.76	7.81	7.33	7.67	7.59	7.33	7.43	7.15	7.71
Temperature	°C	11.2	11.7	10.7	11.4	11.3	11.5	12	11.4	10.7
Total organic carbon	mg/l	0.80	0.78	0.77	0.85	0.68	0.83	1.2	1.1	1.1
Eh	mV	297.7	231.0	297.0	164.3	157.0	301.0	87.7	124.6	74.0
Oxygen	mg/l	4.45	0.00	0.23	0.00	0.02	7.93	0.07	0.33	0.00
Oxidisability	mgO_2/l	3.0	4.5	2.5	2.5	2.7	3.5	5.5	5.3	4.0
Electrical conductivity	µS/cm	698	575	625	605.0	502	757	534	509	491
Alkalinity	meq/l	4.2	3.3	3.6	3.9	3.1	4.5	4.6	5.1	5.1
Chloride	mg/l	25.1	19.1	19.0	18.6	15.9	24.8	14.8	3.23	2.83
Sulphate	mg/l	58.0	79.3	68.9	74.2	58.8	60.1	27.3	10.5	9.46
Calcium	mg/l	99.6	88.3	92.0	98.7	77.0	116.8	87.4	84.5	85.9
Magnesium	mg/l	11.1	9.22	9.98	9.0	8.62	10.0	8.43	9.27	8.95
Sodium	mg/l	6.58	4.99	4.96	5.12	4.16	6.32	5.25	5.60	5.83
Potassium	mg/l	1.34	1.48	1.24	1.30	0.92	1.22	2.71	2.89	2.24
Nitrate	mg/l	12.6	1.39	9.99	1.47	4.73	33.5	1.07	1.06	0.025
Nitrite	mg/l	0.015	0.022	0.025	0.009	0.031	0.010	0.011	0.005	0.008
Ammonia	mg/l	0.221	0.121	0.532	0.240	0.108	0.795	0.635	0.595	0.661
Fluorite	mg/l	0.21	0.21	0.23	0.14	0.19	0.18	0.14	0.12	0.12
Iron	mg/l	0.07	0.08	0.09	0.35	0.25	0.14	0.42	1.54	1.82
Manganese	mg/l	0.03	0.05	0.04	0.06	0.06	0.04	0.07	0.10	0.09
Boron	µg/l	5.81	2.63	9.38	6.05	3.92	6.20	17.3	32.7	29.9
Total hardness	meq/l	5.9	5.2	5.4	5.7	4.6	6.7	5.1	5.0	5.0

Fig. 6. Changes in selected parameters with depth Władysławowo site (after Dragon 2021

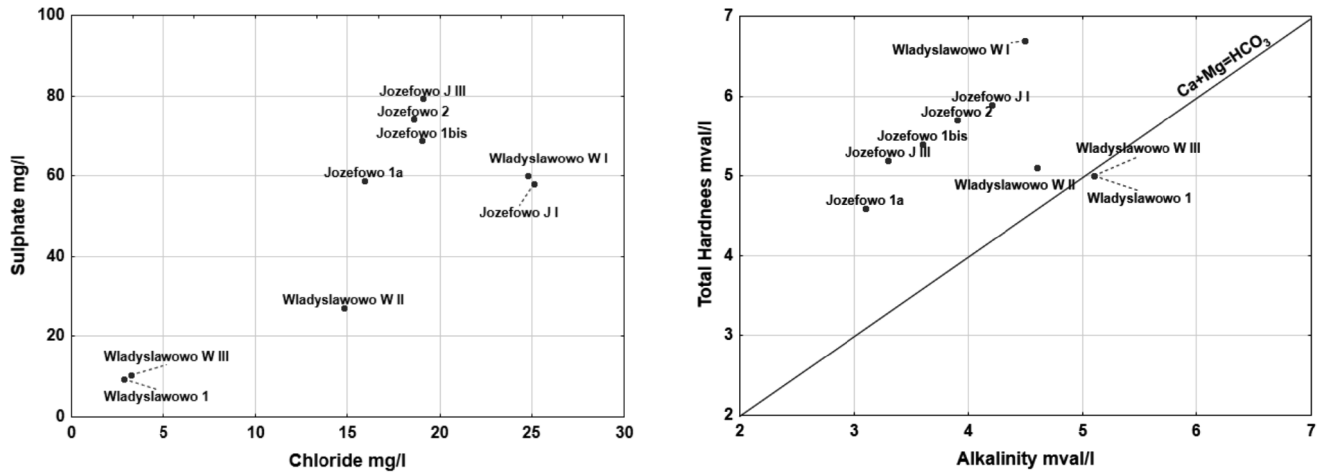The position of the well screen is shown on the left part of the graph (see explanation on Fig. 3)

Fig. 7. Scatter diagrams of selected parameters

est part and <100 mV in the deepest part). The oxygen concentration decreased clearly from 7.93 mg/l in the shallowest part to 0.33 at the W III sampling point, while in the deepest part, oxygen was not detected.

DISCUSSION

The nature of the vertical changes in groundwater chemistry, especially the decrease in nitrate concentration with an increase in sulphate concentration, suggests that denitrification

took place. Our research supports the findings of a previous study (Dragon, 2013) documenting a significant surplus of sulphate (a product of denitrification) in relation to chloride concentration (Rivett et al., 2008) as well as excessive total hardness (i.e., Ca and Mg) in relation to alkalinity (i.e., HCO_3), which explains the permanent hardness (non-carbonate hardness balanced by a high sulphate concentration). This was evident in all water samples except for that collected at Władysławowo from the deep part of the aquifer (Fig. 7) and explains the influence of denitrification products. The largest surplus of sulphate versus chloride was evident at the Józefowo J III and well 2 sampling
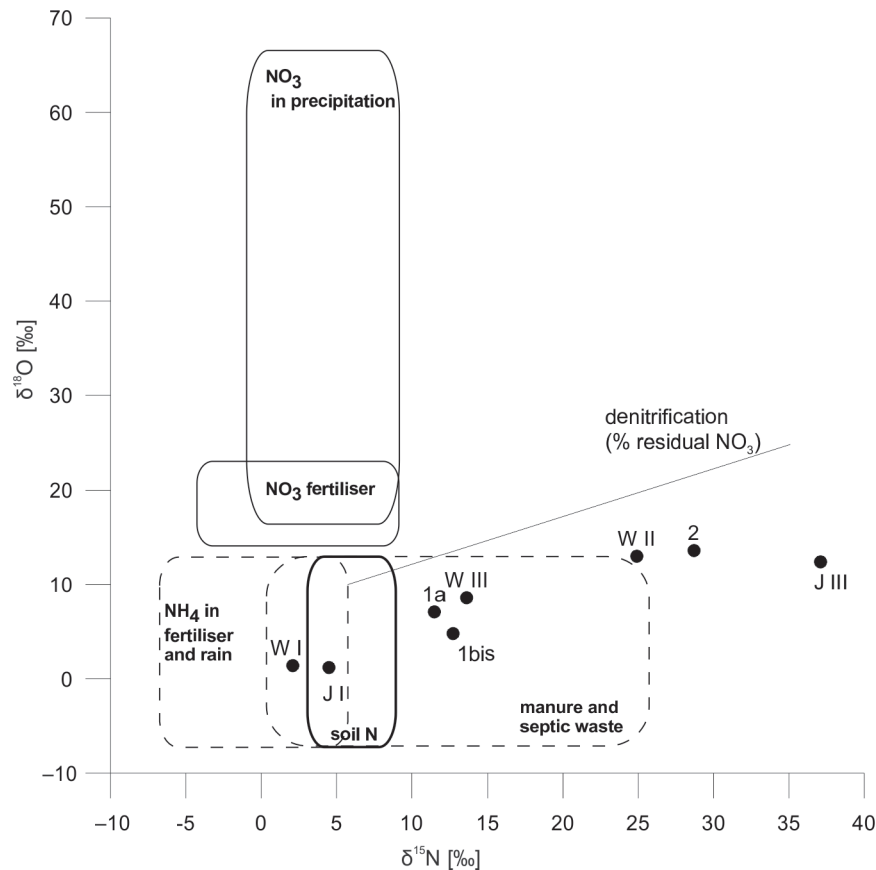

Fig. 8. Cross-plot of ^{18}O *versus* ^{15}N in nitrate

The isotopic composition characteristic for various NO_3 sources is based on
Cook and Herczeg (2000)

points. This finding suggests that the most intensive denitrification occurred at these locations.

According to the isotope data (^{15}N and ^{18}O in nitrate), denitrification processes do not occur in the shallow zone (Fig. 8), where there is a relatively high oxygen content (Rivett et al., 2008), as demonstrated by the most negative isotope values at sampling points representing the shallowest parts of the flow system (J I, W I). In the deepest zone, denitrification is relatively intense in all wells at the Józefowo site. The most intense denitrification occurred at the J III sampling point as well as in the Józefowo 2 well (Fig. 8). This result is consistent with the observations of groundwater chemistry presented above. Specifically, the highest ^{15}N isotope values suggest that denitrification occurs at levels with the lowest nitrate concentrations, while the shallowest part of the flow system (where denitrification does not occur and nitrate concentrations are high) is characterized by the smallest ^{15}N values (Fig. 9).

The isotopic composition suggests that the main sources of nitrate are ammonium fertilizers (Cook and Herczeg, 2000) and manure spread over arable lands (Wassenaar, 1995). The influence of septic systems is negligible in the study region because agricultural land use prevails.

The investigation of denitrification revealed differences in this process among the sites investigated. At the Józefowo site, denitrification was most intense in the middle part of the profile (J III), while in the deepest part, the denitrification intensity was lower, as shown by the relatively high nitrate concentrations at a great depth (well 1 bis). The creation of a downwards gradient by water exploitation caused relatively easy deep penetration of groundwater with high nitrate and oxygen contents from the shallow part of the aquifer. In the middle part of the aquifer, local conditions favourable for denitrification developed because local low-permeability silts with a high organic matter content are present (Fig. 3). The lower pH and high organic matter in this zone can support heterotrophic denitrification (Rivett et al., 2008), but the relatively high sulphate concentration suggests that autotrophic denitrification also occurs. Zones of lower permeability can support denitrification because microbial community-driven denitrification is greater in such zones (Sanchez-Perez et al., 2003; Lasagna et al., 2016). The products of denitrification in this zone are also transported downwards, as shown by the relatively high sulphate concentration and ^{15}N value, suggesting that denitrification also has an influence in the deep part of the flow system. This result was consistent with the isotope data (Dragon, 2021), which showed similar tritium values throughout the entire profile, and the ^{14}C dating data, which documented the occurrence of "recently" infiltrated water throughout the whole profile of the aquifer. In the light of all the data it is concluded that the well 1 bis is recharged by a mixture of downwards flux and some component bypassing the denitrification zone. Comparing the influences of denitrification among the productive wells at the Józefowo site, it is clear that the most intense denitrification occurs in well 2 (Figs. 8 and 9), which also showed the highest sulphate concentrations, indicating the occurrence of autotrophic denitrification.

Different denitrification mechanisms were observed at the Władysławowo site (that is currently not used for water abstraction). The denitrification at this site occurred at relatively shallow depths (W II and W III sampling points), but heterotrophic denitrification most likely prevails there, as shown by the lack of a sulphate surplus in relation to chloride and total hardness versus alkalinity (Fig. 7). In contrast, in the deepest parts of the
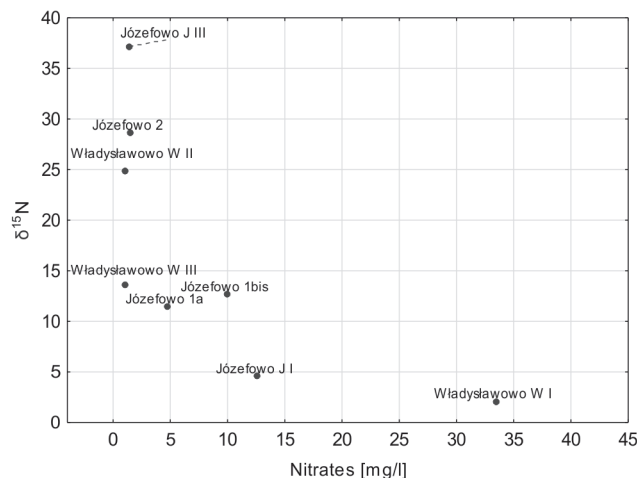

Fig. 9. Scatter diagram of nitrate concentrations *versus* ^{15}N

aquifer, denitrification does not occur because of a stagnation zone in this part of the flow system. A similar stagnation zone was documented by Toth (1963). According to the ^{14}C data, the groundwater residence time was 2100 years and the difference between the water samples and other water samples was expressed by the more negative values of ^{18}O and ^{2}H stable isotopes for the former (Dragon, 2021).

CONCLUSIONS

Denitrification processes influence the groundwater chemistry in a regional recharge zone (Lwówek region, Poland). A nitrate plume in the shallow part of the flow system was investigated. The downwards migration of contaminants was highly dependent on local conditions. In the region with groundwater exploitation (the Józefowo site), the downwards gradient enables migration of the contaminants to a deep part of the aquifer, as documented by the occurrence of "recently" infiltrated groundwater (according to radiocarbon dating) with a tritium content similar to that observed in shallow groundwater. In the middle parts of the aquifer profile, intense denitrification was documented (as shown by high ^{15}N and ^{18}O isotope values). Local conditions favourable for denitrification due to low-permeability silt inserscalations with high organic matter contents in the geological profiles. In the region with a natural gradient (without groundwater exploitation, the Władysławowo site), denitrification was also documented in the shallower parts of the aquifer profile (expressed by relatively high ^{15}N and ^{18}O isotope values), while in the deepest part, a stagnation zone was discovered. In this zone, 2100-year-old groundwater was detected (according to radiocarbon dating) without tritium.

This study shows that denitrification is effective in removing nitrate from groundwater. However, under some conditions (groundwater exploitation), the influence of denitrification is limited by enhanced inflow of contaminated groundwater from shallow parts of the aquifer. In that region the nitrate concentration in the deep zone is similar to that observed in the shallow zone. In the region with a natural gradient, it is expected that in the long term, if groundwater extraction will be initiated, conditions favouring the seepage of contaminated groundwater from

the shallow portion of the aquifer (hydrogeological windows) will arise and deep groundwater quality would deteriorate.

It was shown that for effective groundwater resource management and protection, investigation of vertical groundwater chemistry changes is crucial, even if shallow groundwater is not used for water supply purposes. Such investigations are particularly significant for regional recharge zones with downward gradients.

REFERENCES

Aravena, R., Robertson, W., 1998. Use of multiple isotope tracers to evaluate denitrification in ground water: study of nitrate from a large-flux septic system plume. Ground Water, **36**: 975–982.

Capell, R., Bartosova, A., Tonderski, K., Arheimer, B., Pedersen, S.M., Zilans, A., 2021. From local measures to regional impacts: Modelling changes in nutrient loads to the Baltic Sea. Journal of Hydrology: Regional Studies, **36**: 100867.

Chen, J., Tang, C., Sakura, Y., Yu, J., Fukushima, Y., 2005. Nitrate pollution from agriculture in different hydrogeological zones of the regional groundwater flow system in the North China Plain. Hydrogeology Journal, **13**: 481–492.

Cook, P.G., Herczeg, A.L., 2000. Environmental Tracers in Subsurface Hydrology. Kluwer Academic Publishers, Boston/Dordrecht/London Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources.

Craig, L., Bahr, J., Roden, E., 2010. Localized zones of denitrification in a floodplain aquifer in southern Wisconsin, USA. Hydrogeology Journal, **18**: 1867–1879.

Dragon, K., 2013. Grounwater nitrate pollution in the recharge zone of a regional Quaternary flow system (Wielkopolska region, Poland). Environmental Earth Sciences, **68**: 2099–2109.

Dragon, K., 2021. Identification of groundwater conditions in the recharge zone of regionally extended aquifer system with use of water chemistry and isotopes (Lwowek region, Poland). Journal of Hydrology: Regional Studies, **34**: 100787.

Dragon, K., Górski, J., 2009. Identification of hydrogeochemical zones in postglacial buried valley aquifer (Wielkopolska Buried Valley aquifer, Poland). Environmental Geology, **58**: 859–866.

Dragon, K., Górski, J., 2015. Identification of groundwater chemistry origins in a regional aquifer system (Wielkopolska region, Poland). Environmental Earth Sciences, **73**: 2153–2167.

Dragon, K., Kasztelan, D., Górski, J., Najman, J., 2016. Influence of subsurface drainage systems on nitrate pollution of water supply aquifer (Tursko well-field, Poland). Environmental Earth Sciences, **75**.

Dunn, P., Carter, J., 2018. Publication of the second edition of the FIRMS Good Practice Guide for Isotope Ratio Mass Spectrometry. Science & Justice, **58**: 467–468.

Einsiedl, F., Maloszewski, P., Stichler, W., 2005. Estimation of denitrification potential in a karst aquifer using the ^{15}N and ^{18}O isotopes of NO$_3^-$. Biogeochemistry, **72**: 67–86.

Feast, N., Hiscock, K., Dennis, P., Andrews, J., 1998. Nitrogen isotope hydrochemistry and denitrification within the Chalk aquifer system of north Norfolk, UK. Journal of Hydrology, **211**: 233–252.

Fryar, A.E., Macko, S.A., Mullican III, W.F., Romanak, K.D., Bennet P.C., 2000. Nitrate reduction during groundwater recharge, Southern High Plains, Texas. Journal of Contaminant Hydrology, **40**: 335–363.

Górski, J., Dragon, K., Kaczmarek, P., 2019. Nitrate pollution in the Warta River (Poland) between 1958 and 2016: trends and causes. Environmental Science and Pollution Research, **26**: 2038–2046.

Højberga, A.L., Hansena, A.L., Wachniew, P., Żurek, A., Virtanenc, S., Arustiened, J., Strömqviste, J., Rankinenf, K., Refsgaard, J.C., 2017. Review and assessment of nitrate reduction in groundwater in the Baltic Sea Basin. Journal of Hydrology: Regional Studies, **12**: 50–68.

Hu, L., Xu, Z., Huang, W., 2016. Development of a river-groundwater interaction model and its application to a catchment in Northwestern China. Journal of Hydrology, **543**: 483–500.

Hutchins, M., 2012. What impact might mitigation of diffuse nitrate pollution have on river water quality in a rural catchment? Journal of Environmental Management, **109**: 19–26.

Kaown, D., Kaown, D., Koh, E.H., Mayer, B., Kim, H., Park, D.K., Park, B.H., Lee, K.K., 2018. Application of multiple-isotope and groundwater-age data to identify factors affecting the extent of denitrification in a shallow aquifer near a river in South Korea. Hydrogeology Journal, **26**: 2009–2020.

Karlovic, I., Posavec, K., Larva, O., Markovic, T., 2022. Numerical groundwater flow and nitrate transport assessment in alluvial aquifer of Varazdin region, NW Croatia. Journal of Hydrology: Regional Studies, **41**: 101084.

Lasagna, M., De Luca, D.A., 2019. Evaluation of sources and fate of nitrates in the western Po plain groundwater (Italy) using nitrogen and boron isotopes. Environmental Science and Pollution Research, **26**: 2089–2104.

Lasagna, M., De Luca, D.A., Franchino, E., 2016. The role of physical and biological processes in aquifers and their importance on groundwater vulnerability to nitrate pollution. Environmental Earth Sciences, **75**.

Malagó, A., Bouraoui, F., Grizzetti, B., Roo, A.D., 2019. Modelling nutrient fluxes into the Mediterranean Sea. Hydrology: Regional Studies, **22**: 100592.

Nishikiori, T., 2012. Distribution of nitrate in groundwater affected by the presence of an aquitard at an agricultural area in Chiba, Japan. Environmental Earth Sciences **67**: 1531–1545.

Pfeiffer, S., Bahr, J., Beilfuss, R., 2006. Identification of groundwater flowpaths and denitrification zones in a dynamic floodpain aquifer. Journal of Hydrology, **325**: 262–272.

Rivett, M., Buss, S., Morgan, P., Smith, J., Bemment, C., 2008. Nitrate attenuation in groundwater: A review of biogeochemical controlling processes. Water Research, **42**: 4215–4232.

Sanchez-Perez, J., Bouey, C., Sauvage, S., Teissier, S., Antiguedad, I., Vervier, P., 2003. A standardised method for measuring in situ denitrification in shallow aquifers: numerical validation and measurements in riparian wetlands. Hydrology and Earth System Sciences, **7**: 87–96.

Stock, P., Roder, S., Burghardt, D., 2021. Further optimisation of the denitrifier method for the rapid N-15 and O-18 analysis of nitrate in natural water samples. Rapid Communications in Mass Spectrometry, **35**.

Toth, J., 1963. A theoretical analysis of groundwater flow in small drainage basins. Journal of Geophysical Research, **68**: 4795.

Wassenaar, L., 1995. Evaluation of the origin and fate of nitrate in the Abbotsford aquifer using the isotopes of N-15 and O-18 in NO$_3^-$. Applied Geochemistry, **10**: 391–405.

Zhang, C.Y., Zhang, S., Yin, M.Y., Ma, L.N., He, Z., Ning, Z., 2013. Nitrogen isotope studies of nitrate contamination of the thick vadose zones in the wastewater-irrigated area. Environmental Earth Sciences, **68**: 1475–1483.

Żurek, A., Różański, K., Mochalski, P., Kuc, T., 2010. Assessment of denitrification rate in fissured-karstic aquifer near Opole (South-West Poland): combined use of gaseous and isotope tracers. Biuletyn Państwowego Instytutu Geologicznego, **441**: 209–216.