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Krzysztof Dragon (✉ smok@amu.edu.pl)

Adam Mickiewicz University in Poznań

Jozef Gorski

Adam Mickiewicz University in Poznań

Diana Burghardt

Technical University of Dresden

Research Article

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Posted Date: October 11th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-927050/v1>

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

Krzysztof Dragon^{1*}, Jozef Gorski¹ and Diana Burghardt²

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

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

Abstract: This article presents an examination of the influence of groundwater flow pattern and denitrification on nitrate migration in the regional recharge zone. For the investigation, both multicomponent chemical tracers and isotopic methods were used. The study revealed different denitrification intensities in regions with groundwater extraction and regions with natural gradients manifested by different levels of potable water contamination by nitrate. A contaminant plume was discovered in shallow parts of the aquifer which percolated into deeper parts of the flow system in the regions with a downward gradient induced by groundwater withdrawal, where the influence of denitrification was limited. The local conditions leading to intense of denitrification, i.e., local changes in geological conditions (low-permeability silt inserts), were also documented. The presented research proves that vertical changes in groundwater chemistry should be examined for effective groundwater resource management and protection, as they are extremely important in regional recharge zones with a downward gradient.

Keywords: 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 or stomach cancer in adults. Additionally, interactions between contaminated groundwater and surface water can impact surface water systems^{1, 2, 3}, leading to surface water eutrophication⁴. To protect the environment, the Nitrates Directive⁵ 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 high vulnerability to pollution from the surface^{6, 7, 8}. However, besides the fact that contamination is usually less effective in deep wells⁹, in some cases, nitrate contamination can also appear in deeper parts of the flow system¹⁰. The regional recharge zones are preferred for deep nitrate contamination due to the high downward gradient^{11, 12}.

The main mechanism of nitrate removal in groundwater is bacterial denitrification. The occurrence of denitrification has been documented in many groundwater systems^{e.g. 13, 14, 15, 16, 17}. 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 the reduced form of sulphur compounds) are available in sediments¹⁸. It has also been proven that denitrification is controlled by local (usually spatially and temporally variable) biogeochemical conditions.

A useful tool that can support the investigation of nitrate sources in groundwater is the isotope technique. The isotopic composition of nitrate, represented by $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ values, can be used to distinguish nitrate sources in groundwater^{7, 19, 20}. This technique is also used to document denitrification in the system^{8, 17, 21}. The traditional physical and chemical measurements (water level, major ion composition, geochemical investigation, etc.) can help to understand the relation of nitrate attenuation with groundwater flow pattern²².

During a previous study, groundwater flow pattern on nitrate migration was documented in the studied region¹². It was proven that nitrate contamination behaviour has different nature in the regions where groundwater exploitation is performed (easy nitrate deep percolation) than in the regions of natural gradients existence (lack of deep aquifer zones contamination).

The present study aimed to investigate denitrification processes in the regional recharge zone using a multicomponent chemical tracer approach, $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ isotopes and geochemical investigation. The specific objectives were: (1) identification of the denitrification in the system and its effectiveness in nitrate removal, (2) documentation of local denitrification variation caused by local geochemical sediments diversity and (3) identify the nitrate pollution plume in the shallow groundwater flow system zone and conditions for its downward migration.

The study area

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

The Quaternary sediments occur from the surface to a depth of more than 120 m. Glacial and fluvioglacial sediments dominate the lithology. Fluvioglacial sands and gravels form the aquifers (Fig. 2). The deepest aquifer (discovered in the studied region in 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 (Fig. 1 and 2) is formed by coarse sands and gravels in deeper parts and fine and medium sands in shallower parts. The thickness of the water-bearing sediments is variable, ranging between 20 and 40 m. The shallower aquifer units are composed of fine sands, and their thickness is usually less than 20 m.

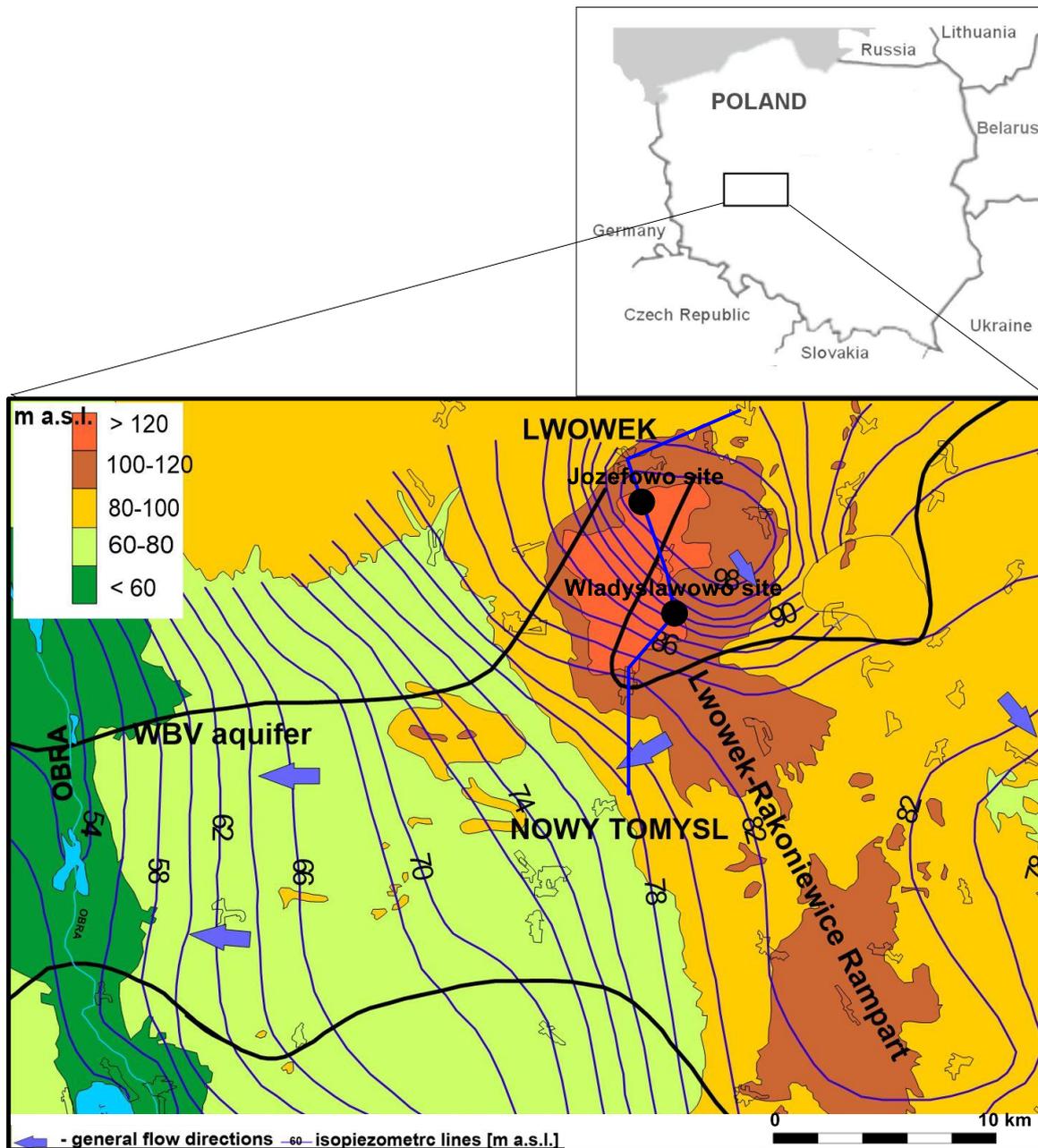


Figure 1. The study region on the background of hydroisohips contours and ground surface elevation. ——— - the line of cross-section presented on Fig. 2); ——— - the borders of the WBV aquifer

The confined aquifers are covered by an aquitard composed of glacial tills. The thickness of the aquitard is variable and ranges between 10 m in Wytomysl and more than 100 m in Chmielinko (Fig. 2). In the regions of Wladyslawowo and Jozefowo (the regions chosen for detailed investigation) the aquitard does not occur, and the sediments forming aquifers (sands and gravels) exist from the surface to a depth of more than 100 m (Fig. 2). In the regions

of hydrogeological windows occurrence, 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 chemistry of groundwater in aquifers nearby the regional recharge zone (including the main aquifer - WBV) is strongly influenced by the inflow of groundwater from the Lwówek-Rakoniewice Rampart²³.

The aquifers are recharged by direct water infiltration in the regions of hydrogeological windows occurrence and indirect vertical percolation of water through the glacial tills from the shallowest to the deepest aquifers²⁴.

In the study region the groundwater divide occurs (the central part of the regional recharge zone). From the groundwater divide, the water flows to the Warta River valley (eastward) and to the Obra River valley (westward) (Fig. 1). The downward gradient occurs in the central part of the recharge zone, what is manifested by the high difference of water level between shallow and deep aquifers (more than 14 m in Chmielinko – Fig. 2).

Notably, groundwater exploitation is performed in Jozefowo site, while in Wladyslawowo, groundwater exploitation is not performed. This difference allows documenting groundwater chemistry changes along a vertical profile in relation to water exploitation conditions.

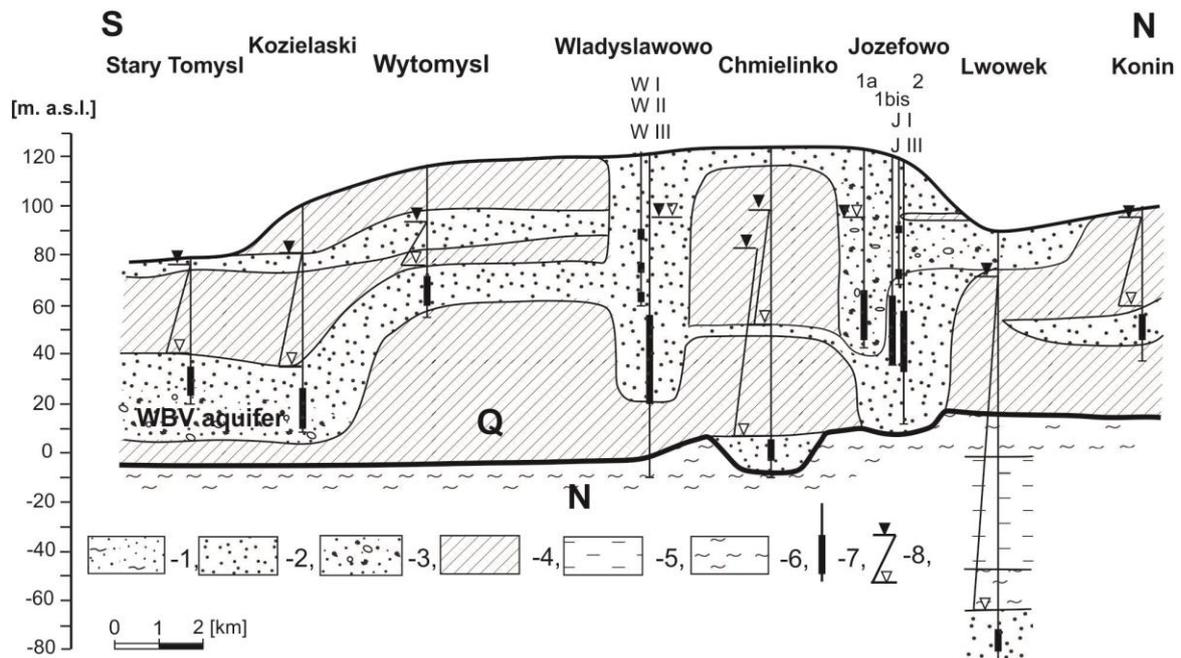


Figure 2. The hydrogeological cross-sections (after Dragon¹², modified). 1 - silty sand, 2 – fine and medium sand, 3 – coarse sand and gravel; 4 – till, 5- clay, 6 - silt, 7 - the well screens location, 7- groundwater level, Q- Quaternary, N – Neogene

Materials and methods

The unconfined parts of the flow system (in Wladyslawowo and Jozefowo – Fig. 2) were selected for the study of groundwater chemistry changes. The multilevel observation well was drilled at each site adjacent to the abstraction well what enabled us to use the abstraction well as the deepest sampling point. The multilevel system was attained using drilling of the net of observation wells in one location (several meters to each other), each equipped with a screen located in a different depth. The short screen interval (1 m) was used at each sampling point. Two multilevel screens were located close to (several metres) Jozefowo well 1bis at depths of 27-28 m (J I) and 46-47 m (J III). The three screens of the multilevel well in Wladyslawowo located around (at a distance of several metres) Wladyslawowo well 1 were positioned at 31-32 m (W I), 42-43 m (W II) and 54-55 m (W III). While production well's screen in Jozefowo

is positioned between 55 and 79.5 m and well in Wladyslawowo has a screen located at a depth between 64 and 100 m (Fig. 2).

Each multilevel observation well was created by dry drilling (without the use of drilling mud) to obtain representative sediment samples for geochemical analyses. During drilling, samples were collected every 1 m into plastic bags and then analysed in the laboratory to determine the grain size distribution, pH of water extracted from sediments (with the use of KCl), organic matter content determined by loss of mass upon ignition (temp. 110 0C and then 550 0C, expressed in g/kg) and calcium carbonate content obtained with the Scheibler volumetric method (expressed as % CO₃).

The sampling campaign performed in June 2018 comprised all multilevel observation wells, all exploitation wells in the Jozefowo site and an inactive well in Wladyslawowo (9 water samples). The MP1 Grundfos pump was used for water sampling in observation wells. The Grundfos SP17 pump powered by a power generator was used for pumping of inactive well in Wladyslawowo. 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 in Wladyslawowo.

The high-density polyethylene (HDPE) bottles were used to collect water samples. Chloroform was used to treat samples for nutrient analyses, while HNO₃ was used to treat samples for iron and manganese (and other metals) testing. The water samples during transport to the laboratory (the someday) were stored in a portable refrigerator at cold temperatures (~4-6°C). The parameters measured directly in the field with portable Aquaread AP-700 equipment includes: electrical conductivity, alkalinity, pH, redox potential, oxygen content and temperature. Chemical analyses were performed in the laboratory at Adam Mickiewicz University in Poznan (Institute of Geology, Poland) using an 881 Compact IC Pro ionic

chromatography. As a quality control measure, the ionic error balance was calculated. The calculated error did not exceed 3%.

Isotope ratio analysis of dissolved nitrate ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) 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 used, simplified denitrification method was published by (Stock et al.²⁵). After microbial sample preparation, simultaneous $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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‰ $\delta^{15}\text{N}$, +25.6‰ $\delta^{18}\text{O}$), USGS34 (-1.8‰ $\delta^{15}\text{N}$, -27.9‰ $\delta^{18}\text{O}$) and USGS32 (+18.0‰ $\delta^{15}\text{N}$, +25.7‰ $\delta^{18}\text{O}$). The uncertainty in $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ analyses resulting from sample preparation by denitrifying bacteria, the precision of triplicate analysis and calibration via IAEA standards was calculated according to Kragten²⁶ to $\leq \pm 1.5\text{‰}$ for both isotope ratios.

The isotope interpretation was performed on the background of stable isotopes of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurement as well as C^{14} and tritium measurements presented by Dragon¹². The results of previous isotope analyses presented by Dragon and Gorski²³ were used additionally for data interpretation.

Results

Geochemical characterization of the sediments

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 in Jozefowo and Wladyslawowo

sites (Figs. 3 and 4). This finding is related to soil type and lithology (tills occurrence in this zone). 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 visible at a depth of 39-40 m in Jozefowo (low-permeability silt inserts) and 45-46 m in Wladyslawowo (fine sands with visible crumbs of organic matter). In Wladyslawowo, a clear peak in organic matter content was also visible at a depth of 20 m. In a zone of high organic matter content a negative peak in pH usually occur. It is clear visible in both profiles (Fig. 3 i 4).

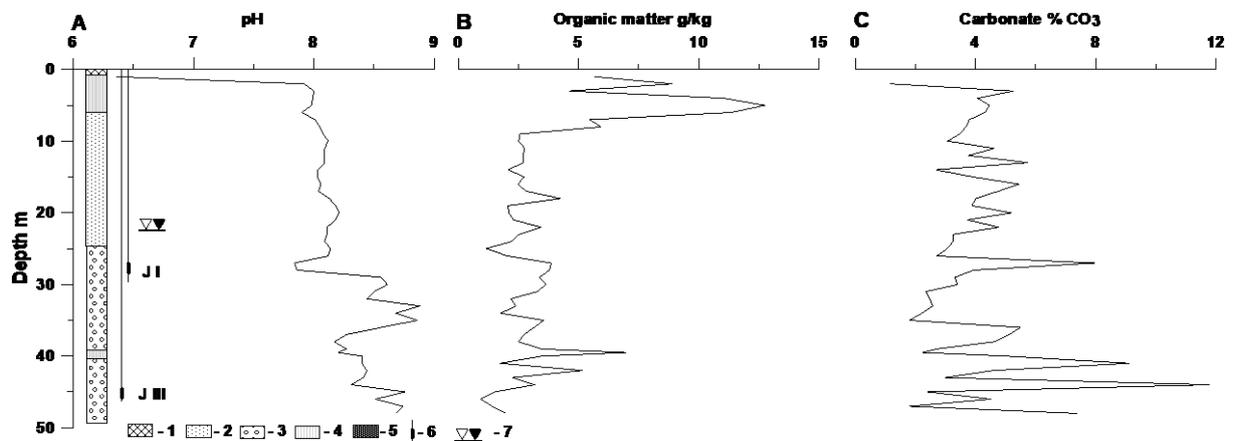


Figure 3. Changes of chosen geochemical parameters in vertical profile – Jozefowo site.

Explanations: 1 – soil, 2 – fine and medium sand, 3 – coarse sand and gravel, 4 – glacial till, 5 – fine sand with dispersed organic matter, 6 – well screen location, 7 – groundwater level

The pH values of extracted water were generally low in the shallow zone to a depth of 27 m in Jozefowo (pH close to 8.0) and to 30 m in Wladyslawowo (pH less than 8.5). 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 (Fig. 3 and 4), which is related to oxidation of organic matter.

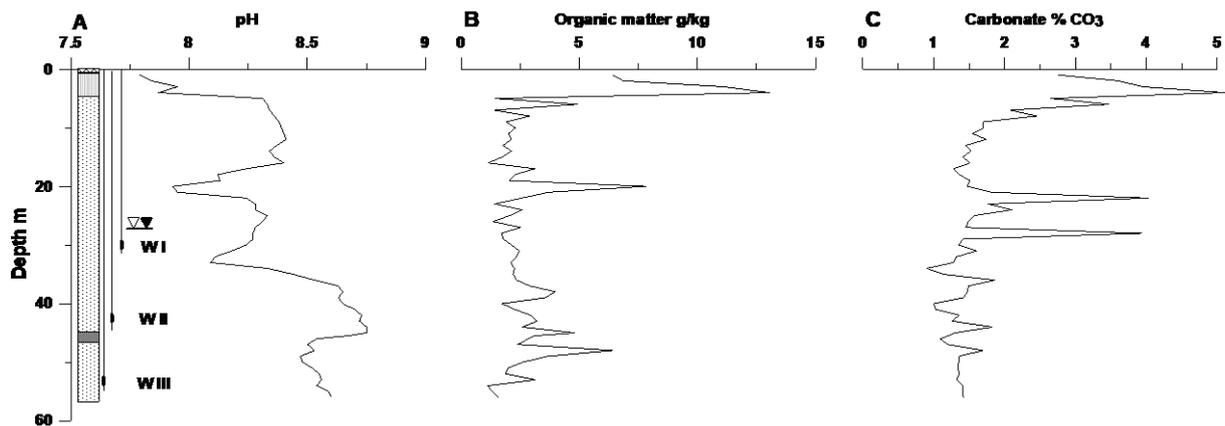


Figure 4. Changes of chosen geochemical parameters in vertical profile – Wladyslawowo site. Position of the well's screen is presented on left part of graph (see explanation on Fig. 3).

The carbonate concentration is clear related to granulometry of the sediments. Higher concentrations occur in zones of coarser deposits occur, especially coarse sands and gravels in Józefowo site. The high content of carbonate is also documented in shallow part in Wladyslawowo, where sandy tills occur in near surface of the profile.

Groundwater chemistry

The results of the hydrochemical investigation are summarized in Table 1. The nature of hydrochemical changes differed among the investigated sites. In Jozefowo, 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 mg/l 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 redox potential (297.7 mV 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 mg O₂/l and 2.5 mg O₂/l in the shallow and deep parts, respectively), with a significantly higher value in the middle part (4.5 mg O₂/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.

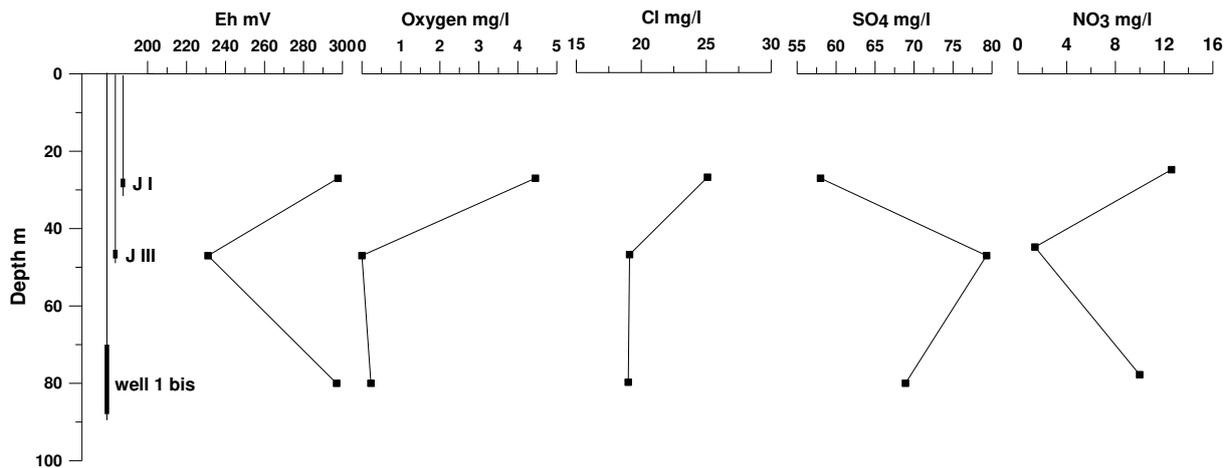


Figure. 5. Changes of chosen parameters with depth (Jozefowo site) (after: Dragon¹²). Position of the well's screen is presented on left part of graph (see explanation on Fig. 3).

Different trends of change in vertical groundwater chemistry were observable at the Wladyslawowo 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 shallowest part and less than 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.

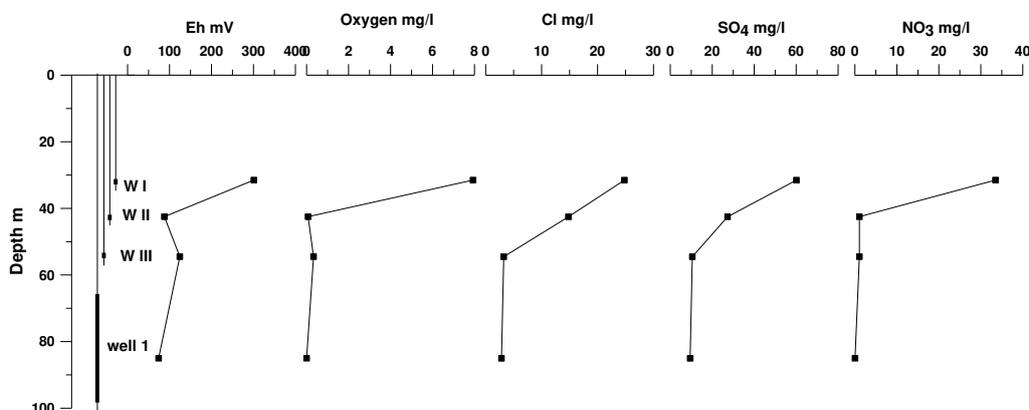


Figure. 6. Changes of chosen parameters in depth (Wladysawowo site) (after: Dragon¹²). Position of the well's screen is presented on left part of graph (see explanation on Fig. 3).

1

Table 1. Results of the chemical analyses, after Dagon¹²

	Unit	Jozefowo					Władysławowo			
		J I	J III	1bis	2	1a	W I	W II	W III	1
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
NO₃	mg/l	12.6	1.39	9.99	1.47	4.73	33.5	1.07	1.06	0.025
NO₂	mg/l	0.015	0.022	0.025	0.009	0.031	0.010	0.011	0.005	0.008
NH₄	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

2

Groundwater isotopic composition

The values of $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ dissolved in nitrate exhibited relatively wide ranges: between 2.1‰ and 37.1‰ for $\delta^{15}\text{N}$ and between 1.2 and 13.0‰ for $\delta^{18}\text{O}$. At the Wladyslawowo 1 sampling point, the concentration of nitrate was too low for these isotopes to be measured.

Table 2. Results of the isotopes investigation

No.	Sampling point	$\delta^{15}\text{N}$ ‰	$\delta^{18}\text{O}$ ‰	Groundwater calculated residence time [years]**
1	Józefowo J I	4.6	1.2	„recent” groundwater
2	Józefowo J III	37.1	12.4	-
3	Józefowo 1bis	12.7	4.8	„recent” groundwater
4	Józefowo 2	28.7	13.6	-
5	Józefowo 1a	11.5	7.1	-
6	Władysławowo W 1	2.1	1.4	„recent” groundwater
7	Władysławowo W II	24.9	13.0	-
8	Władysławowo W III	13.6	8.6	-
9	Władysławowo 1	n.m*	n.m*	2100 ± 350

n.m* - not measurable, nitrate amount too low.

** - groundwater age according to Dragon¹², „recent” groundwater – water infiltrating after 1960's

According to Dragon (2021)¹² the calculated based on ^{14}C isotopes groundwater residence time indicated occurrence of “recently” infiltrated water in Jozefowo (in both: deep and shallow parts of the aquifer) and in Wladyslawowo (only in shallow part of the aquifer). The residence time of groundwater occurring in deep part of the aquifer was 2100 years. Moreover, the tritium was detected in these samples representing “recent” groundwater, while in sample representing 2100 years old water tritium 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 the occurrence of denitrification processes. The presented research confirms the findings of a previous study¹¹ documenting a significant surplus of sulphate (a product of denitrification) in relation to chloride concentration¹⁸ 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 in Wladyslawowo 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 Jozefowo J III and well 2 sampling points. This finding suggests that the most intensive denitrification occurred at these locations.

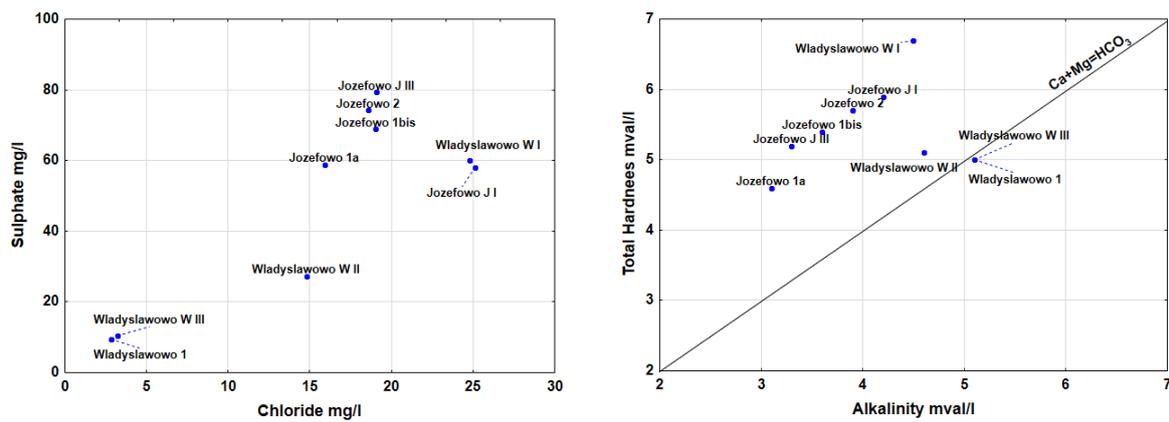


Figure 7. Scatter diagrams of chosen parameters

According to the isotope data ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ dissolved in nitrate), denitrification processes do not occur in the shallow zone (Fig. 8), where a relatively high oxygen content is available¹⁸, 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 Jozefowo site, where (according to Clark and Fritz¹⁵) almost 40 % of residual nitrate was documented (Fig. 8). Most intense denitrification occurred at the J III sampling point as well as in well Jozefowo 2, where less than 20% of residual nitrate was documented. This result is very consistent with the observations of groundwater chemistry presented above. Specifically, the highest $\delta^{15}\text{N}$ isotope values suggest that denitrification occurs at points 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 $\delta^{15}\text{N}$ values (Fig. 9).

The isotopic composition suggests that the main sources of nitrate are ammonium fertilizers²⁶ and manure spread over arable lands⁶. The influence of septic systems is negligible in the study region because agricultural land use prevails.

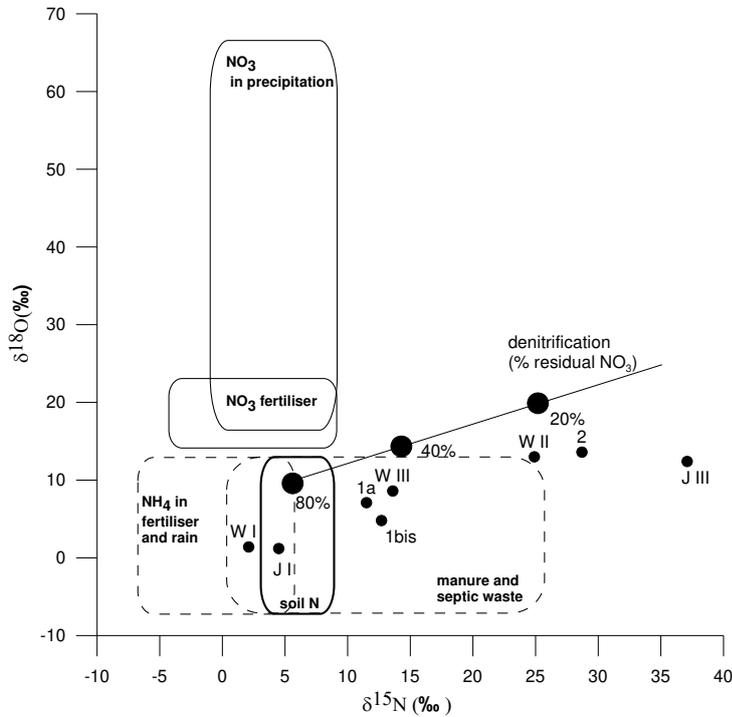


Figure 8. Cross plot of $\delta^{18}\text{O}$ versus $\delta^{15}\text{N}$ dissolved in nitrate. The isotopic composition characteristic for various NO_3 sources based on Cook and Herczeg²⁶, the percent of residual nitrate based on Clark and Fritz¹⁵

The investigation of denitrification revealed differences in this process among the investigated sites. At the Jozefowo 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 downward 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 of local low-permeability silts occurrence with a high organic matter content (Fig. 3). The lower pH and high organic matter in this zone can support heterotrophic denitrification considerably¹⁸, 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^{2, 27}. The products of denitrification in this zone are also transported downward, as shown by the relatively high sulphate concentration and $\delta^{15}\text{N}$ value, suggesting that denitrification also has an influence in the deep part of the flow system. This result was confirmed by the isotope data (Table 2), which showed similar tritium values throughout the entire profile, and ^{14}C dating data, which documented the occurrence of "recently" infiltrated water throughout the whole profile of the aquifer. Comparing the influences of denitrification among the productive wells at the Jozefowo site, it is clear that the most intense denitrification occurs in well 2 (Figs. 8 and 9), which also expressed the highest sulphate concentrations, confirming the occurrence of autotrophic denitrification.

Different denitrification mechanisms were observed at the Wladyslawowo site. 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 aquifer, denitrification does not occur because of a stagnation zone in this part of the flow system (as documented by Toth²⁸). According to the ^{14}C data, the groundwater residence time was 2100 years¹², and the difference between the water samples and other water samples was expressed by the more negative values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ stable isotopes for the former (Table 2).

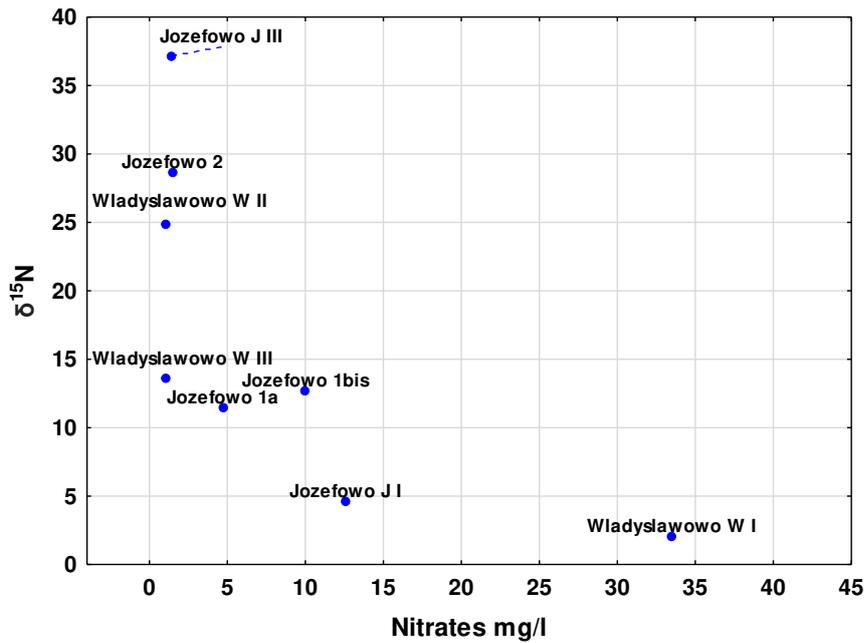


Figure 9. Scatter diagram of the nitrate concentrations versus $\delta^{15}\text{N}$

Conclusions

Denitrification processes influence the groundwater chemistry in the regional recharge zone (Lwowek region, Poland). A nitrate plume in the shallow part of the flow system was investigated. The downward migration of contaminants was highly dependent on local conditions. In the region with groundwater exploitation (the Jozefowo site), the induction of the downward 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 $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ isotope values). Local conditions favourable for denitrification due to the low-permeability silt inserts in geological profiles with high organic matter contents. In the region with a natural gradient (without groundwater exploitation, the Wladyslawowo site), denitrification was also documented in shallower parts of the aquifer profile (expressed by relatively high $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ 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.

The presented research shows that denitrification is effective in removing nitrate from groundwater. However, under some conditions (groundwater exploitation), the influence of denitrification is limited by a relative intensive inflow of contaminated groundwater from shallow parts of the aquifer. In the region with a natural gradient, it is expected that in the long term, if groundwater extraction will be initiated, the conditions favouring the seepage of contaminated groundwater from the shallow portion of the aquifer (hydrogeological windows) will occur and deep groundwater quality would deteriorate.

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

Acknowledgments: This work was made possible by financial support from the National Science Centre Poland (grant no. 2014/15/B/ST10/00119).

Author Contributions: K.D. prepared the manuscript; was responsible for the overall coordination of the research team. K.D. and J.G. interpreted the data and were involved in discussing the study; DB was responsible for laboratory measurements of the isotopes data and all authors read and approved the manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

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