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# Changes in the groundwater quality of the main useful aquifer as a result of the hazard of nitrates from agricultural sources

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Abstract. The article presents the results of research, conducted in central Poland, where agriculture is the dominant type of land use. This activity is considered as a common potential hazard to groundwater quality because of the use of nitrate fertilizers, especially for small groundwater intakes used for the purpose of rural water supply. For this kind of intake seven scenarios of groundwater quality hazard were elaborated based on the results of the hydrodynamic modelling research in this area including the following: calculation of volume and time of leakage through the aquitard formations to the main useful aquifer, verification of the indirect protection zone and definition of the size of the well capture zone. The scenarios considered the current groundwater quality hazard as well as changes in agricultural land use or changes in fertilizer doses needed to decrease groundwater hazard by nitrates in the intake.

Key words: groundwater quality, nitrogen loads, nitrates, agricultural land use, main useful aquifer

# Introduction

The aim of the prognosis of the groundwater quality hazard is to define ways to protect the groundwater exploited from intakes. These tasks should be realized as a result of sustainable space management, especially in the area of well capture zones. There is a necessity of forecasting groundwater quality due to the assumptions of the Water Framework Directive (2000/60/EC) and the Nitrate Directive (91/676/EEC; Council... 1991), which both state that the reduction of pollution from agricultural sources is a part of the sustainable management of water resources. In the presented assessment of the groundwater hazard, the important role of the hydrodynamic model should be underlined. The results of modelling allowed the size of the well capture zone, the volume of water and time of groundwater residence in this zone to be determined. These necessary data were used to compute the average nitrogen load transferred to groundwater from an agricultural land use area, considered as a potential hazard to groundwater quality.

# Location of the Research Area

The study area is located in central Poland, approx. 60 km east of Warsaw, in the area of a geomorphological unit called Kałuszynska Upland (Kondracki 2002), within the upper part of the Osownica catchment – 5th order river in the Liwiec basin (Czarnecka 2005).

Hazards and ways to protect the groundwater quality of the main useful aquifer against pollution caused by nitrates from agricultural sources



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were discussed based on the example of the intake of the main useful aquifer (Meszczyński, Szydeł 1998), used for the purpose of rural water supply in Czarnogłów village, located in the central part of the Osownica catchment, shown in Figure 1. The intake consists of two wells: no. 1 – emergency well (Szymańska 2002); 2 – active well (Wdowiak 1985). Agricultural land use in the well capture zone, and higher nitrate concentrations than in the groundwater exploited from the other wells located in the research area, imposed an indirect protection zone designation. The indirect protection zone was established as a circle of 30 m from the well (Wdowiak 1985), and in 1998 was extended to 100 m (Popowski 1998).



Fig. 1. Location of the research area

## Hydrodynamic Modelling

The boundary of the indirect protection zone was verified by hydrodynamic modelling performed in

the Visual Modflow ver. 4.2 (McDonald, Harbaugh 1988). The model covered the area of 76.8 km<sup>2</sup> (Fig. 1) and consisted of 3 layers: shallow aquifer (I), aquitard formation (tills, clays) and main useful aquifer (II), all presented in the discretized way in

 $25\times25$  m cells. The main objective was to estimate the recharge rate of the shallow aquifer (Zabłocki 2012), but also the recharge of the deeper aquifer (main useful aquifer) was taken into account in the model calculations. Value of leakage from the subsurface aquifer (I) to the main useful aquifer (II) was computed as one of the components of the water balance for a steady state defined as the average annual state, shown in Table 1.

In the vicinity of Czarnogłów village leakage has higher values due to 12-metre sandy and weathered tills (Fig. 2) and breccia documented also in Jaworek intake (south east, see Fig. 1). Sandy tills have formed a hydrogeological window in this region which is the primary recharge area for the main useful aquifer.

second (II) aquifer		
	Value of leakage	

Table 1. Direction and value of leakage between the first (I) and the

	value of leakage				
Area	I ↓ II	 ↑ 	 ↓ 	I ↑ II	
-	[m³/d/km²]		[l/s/km <sup>2</sup> ]		
Intake area	58.1	0.0	0.7	0.0	
Modelled research area	33.2	3.2	0.4	< 0.1	



Fig. 2. Hydrogeological cross section in the research area (location in Fig. 1)



Fig. 3. Scenario no. 1 - the current groundwater hazard by nitrates calculated from nitrogen loads delivered with infiltration water in the well capture zone

The boundary of the well capture zone and that of the indirect protection zone were set using the MODPATH module. Flow lines were drawn on the basis of previously selected points in Modflow, representing the beginning or end of the particle pathway in the hydrogeological system (forward or backward particles). Forward particles were set in the model boundary (to the south of the intake), and backward particles were set as a circle in the cell representing the intake. Calculations of flow line courses were made after the model calibration process was conducted, which included hydraulic conductivity corrections in the aquitard formation between the first (I) and second (II) aquifer. Every single flow line was marked by points representing the travel time of a particle. For this study markers were set every 1 year. The well capture zone of around 0.57 km<sup>2</sup> and its boundary were set according to the external pathways of particles reaching the intake (Fig. 3). The designated indirect protection zone of 0.37 km<sup>2</sup>, identical to the 25-year duration of groundwater residence in the hydrogeological system, is wider than in previously proposed variants (0.0028-0.0314 km<sup>2</sup>). A 25-year isochrone was delineated after taking into account particle travel time containing leakage through sandy and weathered tills (vertical flow) which takes 13 years, and 12 year of groundwater flow in the main aquifer (lateral flow). The mean residence time for the well capture zone was calculated for 27 years, but the first response in groundwater chemistry depends on the time of vertical flow, so it can be observed after 13 years.

# Nitrogen Loads Transferred to Groundwater

Nitrogen loads transferred to the main useful aquifer from agricultural areas were determined according to the doses of organic and mineral fertilizers calculated as a pure component (nitrogen) with assessment as to which part of the dose was washed out beyond the root zone. For further study, nitrogen fertilizer usage in the Dobre municipality, where the intake is located, was used, based on the results of the Agricultural Census of 2010 (www. gus.gov.pl, 12.2012) (Table 2).

Table 2. Organic and mineral fertilizer usage in the municipalities in the research area (average usage from the period 2002-2010)

Municipality	Fertilizer usage [kgN/ha·year]			
	Organic	Mineral	Total usage	
Wierzbno	44.6	49.5	94.1	
Dobre	21.1	33.0	54.1	
Jakubów	29.7	46.2	75.9	
Kałuszyn	23.4	41.9	65.3	

The leaching rate is the second necessary component for determining the nitrogen loads transferred to groundwater from agricultural areas. According to the Decree of the Minister of the Environment of 23<sup>rd</sup> December 2002 (Dz.U. nr. 241, poz. 2093) the leaching rate is assumed to be a constant value of 0.15 used to estimate the nitrogen loads in the infiltration waters. Direct studies have shown considerable variability of the nitrogen leaching rate from agricultural areas, in the range of 2-3% in areas with extensive farming (Żurek 2009) to 20-25% in the large river basins with a much higher usage of nitrogenous fertilizers (Żurek 2008) than in the research area.

The nitrogen leaching rate was assessed by performing factor analysis (Zabłocki 2013). This analysis had the aim of identifying statistically significant processes forming groundwater chemistry. The analysis was conducted on the basis of the results of 289 chemistry analyses, recognition of hydrogeological conditions and land use forms. The interpretation of the factors allowed the selection, inter alia, of the process identified as nitrogen leaching from the soils as factor 1 (F1), responsible for 22% of data variation for groundwater chemistry forming. The assumption was made that the impact factor, computed as the factor score (spatial variability of factor strength), was proportional to the value of the leaching rate (Table 3).

Table 3. Values of leaching rate adopted on the basis of factor analysis results (Zabłocki 2013)

Strength of the factor influence	F1 factor score	Leaching rate	Percentage of well capture zone area
Very strong	> 2.25	0.15	_
	2.25-2.00	0.14	3.0
	2.00-1.75	0.13	10.4
	1.75-1.50	0.12	17.0
	1.50-1.25	0.11	24.3
	1.25-1.00	0.10	20.6
Strong	1.00-0.50	0.07	23.5
Average	0.500.50	0.05	1.2
No influence	< -0.50	0.02	_

The assessment of the current hazard of groundwater quality by nitrate was obtained by overlaying layers concerning the recharge rate and the value of the nitrogen loads transferred with infiltration waters. The piston model was assumed for the migration of the pollutants within leaching water to the main useful aquifer. Expected nitrate concentrations in groundwater were calculated according to the formula (Żurek et al. 2004):

$$C_{NO3} = L_N \cdot 443/R_2$$

where:

- L<sub>N</sub> nitrogen loads transferred with infiltration waters [kgN/ha·year];
- C<sub>NO3</sub> expected nitrate concentration in groundwater [mg/L];
- R recharge rate [mm/year] taken from the results of the hydrodynamic modelling (Zabłocki 2012).

Spatial precision of calculations was limited by the modelling accuracy, where the recharge rate was computed in every  $25 \times 25$  m cell.

### Results

Seven scenarios of groundwater quality hazard by nitrates were identified as the results of the research.

The current hazard of groundwater quality by nitrates is presented in scenario no. 1. Presented

in Figure 3 nitrate distribution represents nitrate concentration in the infiltration waters in the well capture zone area and it is the result of the spatial variability of the recharge rate and nitrogen load (refers to land use forms). The lowest concentrations refer to the forest area with the nitrogen load set at 1.5 kgN/ha-year. Expected nitrate concentrations in groundwater in the active well were calculated as the mean value (weighted by the area) of nitrogen loads and the recharge rate in the well capture zone. After comparing the results with the concentration of nitrate in the groundwater sample taken from the intake in 2009, high compliance of the observed and predicted concentrations of nitrate was achieved (Table 4). Nitrate concentration measured in 2009 is close to the average concentration from the years 2002-2005 (data from the Sanitary -Epidemiological Station in Mińsk Mazowiecki; Sanitary-Epidemiological... 2005).

Table 4. Scenarios of groundwater hazard of the main useful aquifer	
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No.	Scenarios no. 1-7 of groundwater hazard	Average fertilizer	Average nitro-	Nitrate concentration in groundwater in the active well	
		uoses	gen loaus	Calculated	Observed
		[kgN/ha·	year]	[mg/l]	
1	Current groundwater hazard	54.1	4.9	21.9	22.58 (25.09.2009)ª
2	Hazard after land reuse for agricultural activity	54.1	5.2	23.0	_
3	Hazard after limitation of agricultural area	54.1	2.6	11.6	—
4	Hazard after limitation in fertilizer doses for un- changed land use structure	22.4 (41.5% currently used dose)	2.2	10	-
5	Hazard in 1980s and 1990s	71.9 (133% currently used dose)	6.9	30.4	30.53 (average in years 1993-2002) <sup>b</sup>
6	Hazard where groundwater is classified as endan- gered by nitrate pollution	95.2 (176% currently used dose)	9.0	40	44.28 (10.05.2000) <sup>b</sup>
7	Hazard where groundwater is classified as polluted by nitrates	119.5 (221% currently used dose)	11.3	50	_

a - groundwater sample taken from the active well (own studies);

b – data from Sanitary-Epidemiological Station in Mińsk Mazowiecki (Sanitary-Epidemiological... 2005)

The changes in land use in the well capture zone are presented in scenario no. 2 and no. 3. Reuse of land for agricultural activity was considered in scenario no. 2. A slight increase in the average nitrogen loads and in nitrate concentrations in the groundwater from 21.9 to 23.0 mg/l NO<sub>3</sub> were observed due to the small size of these areas.

Effects of the limitation of the area of agricultural activity were elaborated in scenario no. 3. The limitation was considered in order to decrease nitrate concentrations in the groundwater to the value close to the upper limit of the background value (10 mg/l NO<sub>3</sub>) for the main useful aquifer in Kałuszyńska Upland (Meszczyński, Szydeł 1998). Due to the unfavourable conditions of nitrate reduction in the main useful aquifer (no direct redox measurement, but average oxygen content in the groundwater in the years 1993-2005 is 1.90 mg/l  $O_2$ , and average ammonia ion concentration is < 0.01 mg/l NH<sub>4</sub>), scenarios with decreased nitrogen loads transferred to the groundwater should be considered as the only form of effective protection of water quality in this aquifer.

Areas with the highest nitrogen leaching rate (> 0.11), and with predicted nitrate concentrations exceeding 40 mg/l NO<sub>3</sub> were excluded from agricultural activity in this scenario. Doses of fertilizers used on the remaining agricultural land were unchanged.

The results show the need to exclude from the agricultural activity an area of  $0.32 \text{ km}^2$  (56% of the area of the well capture zone) to obtain the nitrate concentration at the level of 12 mg/l NO<sub>3</sub>. The share of the agricultural area, which it is necessary to convert in this type of scenarios, is usually high and frequently exceeds 40% of the analysed area, which indicates the need for a strong transformation of the agricultural structure (Wendland et al. 2007).

The scenario concerning the changes in fertilizer doses for unchanged land use structure was also considered. Calculations in scenario no. 4 show the necessity of decreasing fertilizer doses to 22.4 kgN/ ha·year (45% of currently used doses) to achieve nitrate concentration in the active well around the upper limit of the background value in the region.

In scenario no. 5 information on long term groundwater quality changes was used to determine the hazard by nitrates in the 1980s and 1990s. The average nitrate concentration observed in the period 1993-2002 corresponds to the amount of fertilizer application 71.9 kgN/ha·year (133% of the currently used doses, Table 4). The decrease in nitrate concentrations from 30-40 to 20-25 mg/l NO<sub>2</sub> from 2002 is related to the changes in agricultural land use intensity in the early 1990s. The results of this transformation are noticeable in the groundwater chemistry after 12-13 years, which refers to the time of vertical flow to the main useful aquifer in this region estimated during groundwater flow modelling. This period can be interpreted as the time of the first groundwater response to land use transformation in the well capture zone. Almost identical ranges of changes in concentrations of nitrate (from 50 to 25 mg/l NO<sub>3</sub>) were observed in agricultural areas in Switzerland after the introduction of extensive farming (Baillieux et al. 2010).

A correctly functioning model, representing the current hazard by nitrates, was used in scenario no. 6 and in scenario no. 7 to prepare predictions of possible groundwater chemistry changes in the intake. Scenario no. 6 assumed groundwater to be classified as endangered by pollution (the nitrate concentration limit was set at 40 mg/l according to the Decree of the Minister of the Environment of 23<sup>rd</sup> December 2002). Allowable nitrogen loads transferred to the groundwater, which do not cause the endangering of groundwater, were determined on the basis of increased fertilizer doses without changing land use structure. With the dose of fertilizers at an amount of 95.2 kgN/ha·year (176% of the currently used doses), the mean nitrogen load is 6.86 kgN/ha·year and the nitrate concentration does not exceed 40 mg/l.

Scenario no. 7 assumed groundwater to be classified as polluted (the nitrate concentration limit was set at 50 mg/l NO<sub>3</sub> according to the Decree of the Minister of the Environment of  $23^{rd}$  December 2002). Hypothetical nitrate pollution was found when the nitrogen loads reached 11.3 kgN/ha·year, which refers to fertilization at an amount of 119.5 kgN/ha·year (221% of the currently used dose). It should be noted that groundwater contamination by nitrates will occur when fertilizer usage is significantly lower than the maximum allowable dose of nitrogen in livestock manures constituted in the Nitrate Directive (91/676/EEC; Council... 1991) – 170 kgN/ha·year.

#### Conclusions

- 1. The presented scenarios concerned forecasting of the groundwater quality hazard of the main useful aquifer by nitrates from agricultural activity.
- 2. The results of the research showed that despite theoretically significant isolation of the main useful aquifer, built by 12-metre tills, groundwater hazard by nitrates leaking from soils is high.
- The size of indirect protection zones should be verified by the hydrogeological modelling studies for the possibility of their location within an

area of strong anthropogenic influence from agricultural activity.

- 4. Acceptable fertilizer doses, not causing groundwater pollution by nitrates, should be determined in the previously verified areas. There is a possibility of contamination when applying fertilizer doses at an amount of 119.5 kgN/ha·year. It is a significantly lower dose than specified in the Nitrate Directive (91/676/EEC; Council... 1991) for livestock manures at an amount of 170 kgN/ ha·year.
- 5. A decrease in nitrate concentration in the groundwater can be achieved by a decrease in nitrogen loads transferred to the groundwater which can be achieved by limitation of fertilizer doses in the well capture zone or by significant exclusion of some crops from agricultural use.
- 6. A decrease in nitrogen loads is the simplest way of space management. This solution needs only transformation from intensive to extensive farming, which can be achieved by fertilizer usage in lower doses. In the research area a decrease in fertilizer doses to around 40% is needed to decrease nitrate concentration in the groundwater to  $10 \text{ mg/l NO}_3$ .
- 7. The exclusion of over 50% of crops from agricultural activity in the well capture zone is needed to reach the same goal.
- 8. The decrease in nitrogen loads in some crops to the values representing natural areas (i.e. forests 0.5-1.9 kgN/ha·year) in both examples (scenario no. 3 and 4) can be observed in groundwater with a delay of minimum 13 years, and directly after land use change a significant increase in nitrogen loads can be observed.

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