

Influence of subsurface drainage systems on nitrate pollution of water supply aquifer (Tursko well-field, Poland)

Krzysztof Dragon¹ · Dariusz Kasztelan¹ · Jozef Gorski¹ · Joanna Najman²

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Abstract This study presents the behavior of nitrate in the recharge zone of Tursko well-field (south Wielkopolska, Poland). The presence of a contaminant plume derived from land drainage systems was documented. The contamination is reflected mainly by the high concentration of nitrate (>80 mg/l). It was documented that the contaminant plume migrates in the aquifer along a flow path from the contamination source to the well-field. The factor that retards nitrate migration is bacterial denitrification. As a result of the denitrification, the nitrate concentration decreases systematically along flow lines, but the concentration of other parameters—products of denitrification (sulfate and total hardness)—increases. The occurrence of denitrification was confirmed by measuring the gaseous excess of N₂ (the product of denitrification) and by using the isotopes of ¹⁵N and ¹⁸O dissolved in nitrate. These methods also enable the intensity of denitrification to be assessed.

Keywords Land drainage systems · Groundwater nitrate contamination · Gaseous nitrogen N₂ · Nitrogen and oxygen isotopes · Denitrification

Introduction

Subsurface tile land drainage systems play a significant role in agricultural production. Generally, tile drains also play a positive role in groundwater quality protection because they work as drainage elements of soil water and shallow groundwater, preventing recharge to groundwater below drains. Thus, tile drains reduce the amount of infiltration of this usually strongly contaminated by agricultural practices groundwater to deeper aquifers (Rodvang and Simpkins 2001).

Tile drains supply water to drainage ditches, which link drainage outlets from agricultural fields with natural occurring streams or rivers. Therefore, drainage ditches can transport contaminants from agricultural fields and affect water quality downstream (Kellers et al. 2000; Ahiablame et al. 2011). Moreover, drainage systems may systematically gather contaminants derived from dispersed sources or locations and aggregate them at cumulative concentrations downstream (Spaling 1995; Spaling and Smit 1995). Under specific conditions, the outlets of drainage pipes and drainage ditches being located in a recharge zone of a well-field can facilitate the migration of drainage water to deeper water supply aquifers. This is possible under natural flow conditions, but water extraction that causes the generation of a downward gradient accelerates downward migration considerably.

Correlation between agricultural land use and high nitrate concentrations in groundwater is a well-known phenomenon in many parts of the world (Bohlke 2002). Intensive agricultural crops often focus on increasing productivity with little attention to the environmental impact (Laronde et al. 1996). On the one hand, drainage systems improve top soil properties by leading to amelioration; on the other hand, they deteriorate the surface water quality by

✉ Krzysztof Dragon
smok@amu.edu.pl

¹ Department of Hydrogeology and Water Protection, Institute of Geology, Adam Mickiewicz University Poznan, Makow Polnych Street 16, 61-606 Poznan, Poland

² Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego Street 152, 31-342 Crakow, Poland

discharging drained water with a high nitrogen load (Mastrocicco et al. 2013). Nitrate contamination in groundwater underneath agricultural fields is observed in many parts of the world (e.g., Hudak 2000; Rodvang and Simpkins 2001; Chen et al. 2005). It has both environmental and health consequences (Chae et al. 2009). High nitrate concentrations in water used as a drinking water source are linked to health problems because it causes *methemoglobinemia* in infants or stomach cancer in adults. From this reason, the European Union, the World Health Organization, and the Polish legal system have determined the maximum acceptable concentration of nitrate in potable water to be 50 mg NO₃/l (11.3 mg N–NO₃/l) (Drinking Water Directive 98/83/EC 1998; World Health Organization 2004; Rozporządzenie 2007).

The natural mechanism for retardation of nitrate migration is bacterial denitrification. This process has been documented in a number of groundwater systems (Bennekom et al. 1993; Rivers et al. 1996; Aravena and Robertson 1998; Feast et al. 1998; Gorski and Kazmierczak-Wijura 2002; Einsiedel et al. 2005; Craig et al. 2010; Zurek et al. 2010; Dragon 2013). Denitrification in the subsurface is controlled by local biogeochemical conditions that are usually spatially and temporally variable (Rivett et al. 2008). In general, the denitrification process is effective under anaerobic conditions, in which electron donors (dissolved organic carbon, sedimentary organic matter or the reduced form of sulfur) are available.

The main objective of this study is to investigate the influence of tile drainage systems on groundwater chemistry deterioration. The specific targets are (1) the documentation of the contaminant plume moving along a flow path from drainage ditches to pumped wells and (2) the investigation of the denitrification processes and its effectiveness in nitrate plume retardation.

Study area

Hydrogeological setting

The study area covers the recharge zone of the Tursko well-field (supplying water for Pleszew town), which is located in the south part of the Wielkopolska region (Poland). The well-field is located in the Holocene fluvial terrace of Prosna River (Fig. 1). This region is characterized by sparse groundwater resources. The aquifer use as a water supply has limited spatial extent, and the various thickness ranges between several m to more than 60 m (Fig. 2). The lithology of the aquifer is dominated by fluvial and fluvio-glacial deposits. The deeper part of the aquifer is composed mainly of Pleistocene fluvio-glacial

sands and gravels (Fig. 2). The near surface zone is dominated by Holocene peats and silts with a thickness of approximately 3 m. Moreover, in the near surface zone, silty sands of fluvial origin dispersed with organic matter are observed, the thickness of which ranges between 5 and 10 m. The aquifer is characterized by unconfined conditions and high vulnerability to contamination from the surface.

The Tursko well-field consists of 3 continuously pumped wells. Wells II and III were built in 1976, and well IV was built in 2007. In the period between IV 2010 and XII 2013, well III was not operated. The well depth varies between 36 and 66 m (Fig. 2). The current wells yield is 200 m³/h, but well-field productivity (after the building of new wells) is intended to be increased to 410 m³/h. The well-field was intensively pumped from the spring of 2007. Before 2007, the wells were pumped only occasionally, usually during hot summers, in the periods of the greatest water requirements.

The principal source of the recharge is inflow of groundwater from upland region located south and west to the well-field (Fig. 1). The direct infiltration of rain water also occurs within the recharge area. Under natural groundwater flow conditions, the flow of water occurs from the upland area (from the south and west) to the Prosna River (regional discharge area). Under conditions of groundwater extraction when the cone of depression is created, the infiltration of surface water (from streams and drainage ditches) is more intensive.

Land use pattern and urbanization

The land use in the areas located south and west of the well-field as well as the well-field area is dominated by agricultural activity (Fig. 1). Both the use of chemical fertilizers and spreading of manure on the land are potential sources of groundwater contamination. Manure is often stored in large piles before being spread on the fields. Jedlec village is located west of the well-field. The main hazard to groundwater in that area is the lack of a central sewage system. Domestic sewage is stored in individual septic tanks, which are of not perfectly constructed and poorly maintained or used. This situation causes the leakage of untreated liquid waste into the ground and, in specific cases, directly into the groundwater.

The drainage systems are located on the upland region located south and west of the well-field. The outlets of the pipe drains serve as drainage water to the drainage ditch, which is located south of the well-field in the region between the recharge area and the wells (Figs. 1, 2). Below, at the bottom of this ditch, sandy rocks are observed. An unconfined water table is located below the

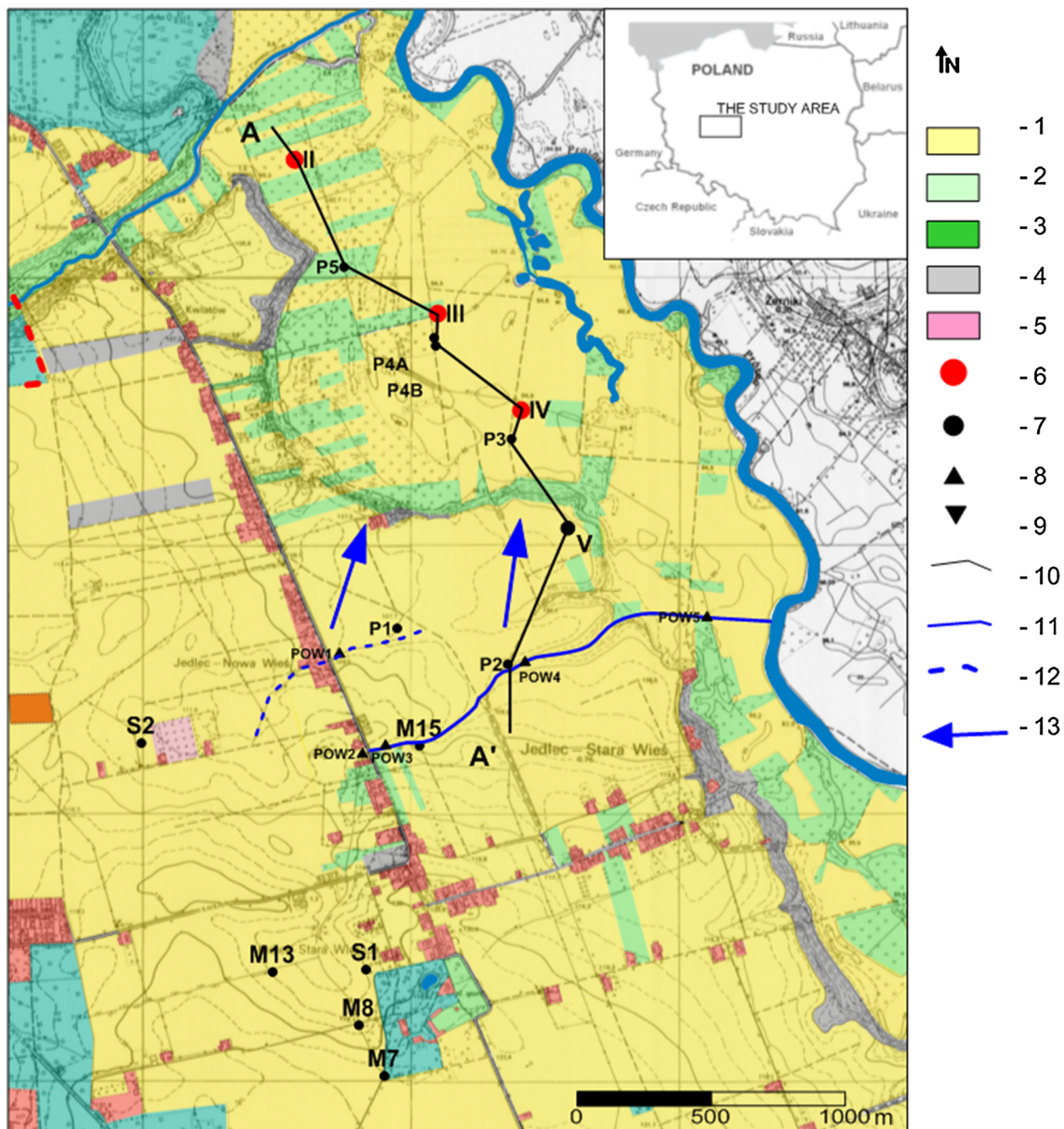


Fig. 1 The study area on land use types background. 1—Arable lands, 2—meadows and pastures, 3—forests, 4—wastelands, 5—household buildings, 6—wells, 7—piezometers, 8—surface water samples, 9—drainage water samples (*M*—outlets of the drainage

pipes, *S*—drainage settlers), 10—line of cross section—Fig. 2, 11—ameliorative channel, 12—periodic ameliorative channel, 13—groundwater flow direction

ditch bottom. These conditions enable infiltration of water from the ditch into the groundwater system. From 2007 this ditch received treated waste water from the sewage treatment plant in Goluchow. Another drainage channel that exists only periodically (usually after the winter-spring snow melt season and after long rainy seasons) is located 300 m north to the ditch (Fig. 2).

The specific attribute of the study area is a considerable fragmentation of arable land ownership, reflected by different levels of manure and fertilizers used by individual farmers.

Materials and methods

For the investigation of drainage water influence on the groundwater chemistry of drainage water, surface water as well as groundwater from piezometers and wells was sampled. The examination of groundwater chemistry was performed using data from groundwater sampling collected over 2012, 2013, and 2014. Each year, two sampling series was performed: first in the spring, after the winter-spring snow melt season (in the period when drainage systems transport significant amounts of water), and the second in

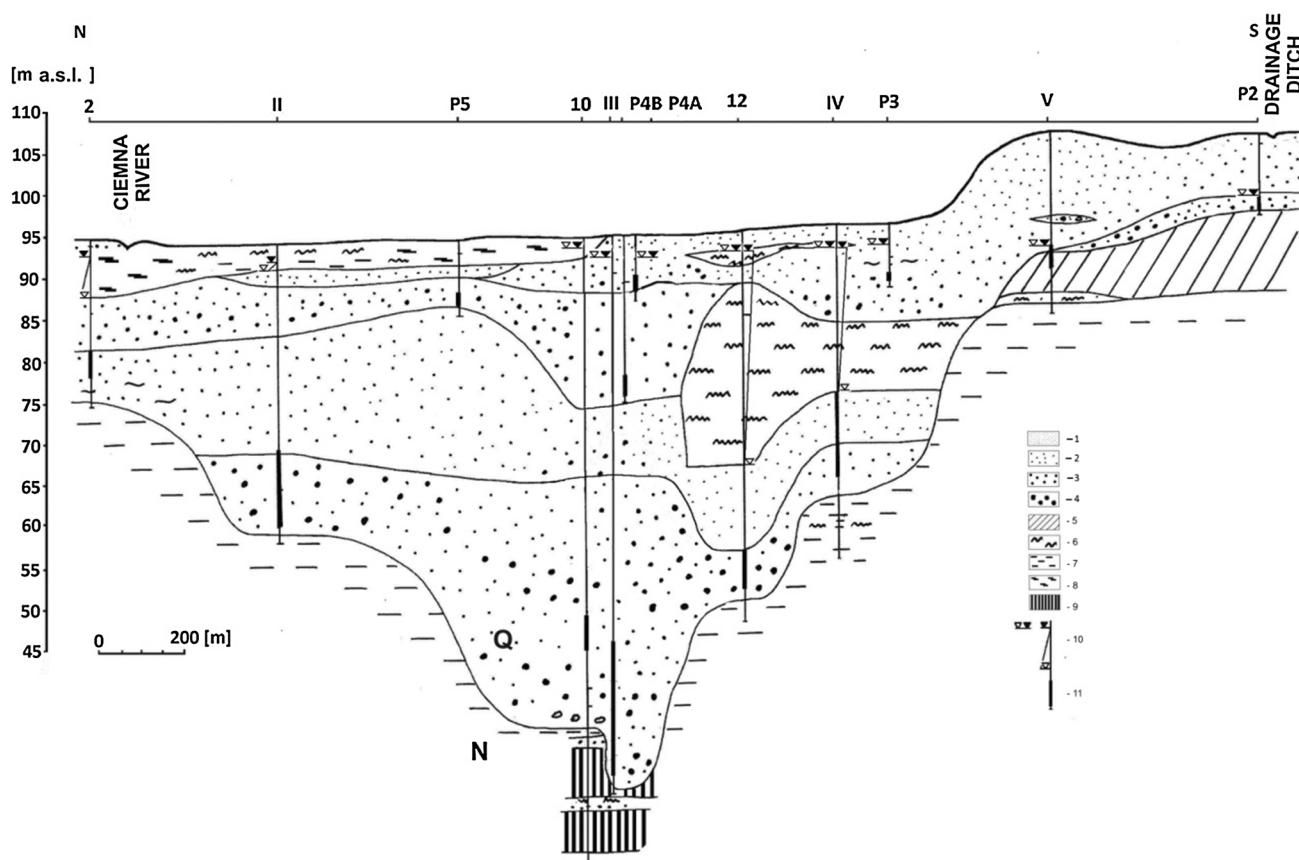


Fig. 2 Hydrogeological cross section. 1—Fine sand, 2—medium sand, 3—coarse sand, 4—gravel, 5—till, 6—silt, 7—clay, 8—peat, 9—brown coal, 10—ground water level, 11—location of the well screen, *Q* quaternary; *N* neogen

the autumn, after the dry season (this is when the drainage systems do not transport much water or sometimes do not work at all).

To identify the influence of the drainage systems on groundwater chemistry, the net of the piezometers was drilled. These piezometers were located in the recharge area of the well-field between the drainage ditches and the wells (Fig. 2). The location of these piezometers enables the identification of groundwater chemistry changes along the flow path. The piezometer P4 was installed as a multilevel system (the P4A piezometer screen is located in the shallow part of the aquifer, and the second P4B piezometer screen is located in the deeper part of the aquifer). Moreover, existing wells (screening the deepest parts of the aquifer) were used for groundwater sampling as well.

During the sampling procedure, the water was poured into 100-ml HDPE polyethylene bottles. Separate samples were taken for nutrient analyses (treated with chloroform) and for iron and manganese testing (treated with HNO_3). All bottles were rinsed three times and filled completely to prevent degassing. After sampling, water was stored in a transportable refrigerator. Water samples were immediately (on the same day) transported

to the laboratory. Water color, electrical conductivity, alkalinity, pH, and temperature were measured directly in the field. The field sampling was performed according to the ISO 5667-11 guidance (1993). The chemical analyses were performed at Adam Mickiewicz University in Poznan (Institute of Geology) using a CompactIC 881Pro ionic chromatograph. As a quality control measure, the ionic error balance was calculated. The calculated error did not exceed 3 %.

For identification of the denitrification processes, gaseous N_2 dissolved in the groundwater was measured. Excess N_2 (above equilibrium with respect to atmospheric N_2) was determined to be an indicator of denitrification. Groundwater usually contains elevated concentrations of nitrogen relative to those resulting from their contact with the atmosphere (Cook and Herczeg 2000). This “excess” is the result of accumulation of nitrogen from denitrification processes and the dissolution of air bubbles trapped during the process of infiltration (excess air):

$$C_m = C_{\text{atm}} + C_{\text{np}} + C_{\text{na}} \quad (1)$$

where, C_m is the gaseous nitrogen in groundwater; C_{atm} is the atmospheric component; C_{np} is the excess air

component; and C_{na} is the denitrification component (excess nitrogen).

Therefore, the correct identification of denitrification nitrogen requires the knowledge of the atmospheric component C_{atm} and the component of excess air C_{np} . These elements can be estimated using the temperature of the noble gases NGT (Noble Gas Temperature) and dissolved excess air, parameters reflecting the conditions at the water table during the infiltration process. Both parameters can be determined by the analysis of the noble gases—Ne and Ar dissolved in groundwater (Cook and Herczeg 2000). For the purposes of this study, the atmospheric component C_{atm} was calculated on the basis of NGT (Noble Gas Temperature) using the formula given by Weiss (1970). To determine the excess air component C_{np} , the Total Dissolution Model was applied (Aeschbach-Hertig et al. 1999, 2000). This model assumes the complete dissolution of trapped air bubbles and the subsequent total isolation of water from the atmosphere or soil air.

The samples used for dissolved gas analysis were collected in the field with the use of stainless steel vessels (doubled vessels for each water sample). The sealed connection between the vessels and the well creates an airtight condition to prevent degassing and contact between the water and the atmospheric air. Doubled samples were taken to indicate potential leaks (in case one sample leaked). The analyses were carried out in the laboratory of the Polish Academy of Science (Institute of Nuclear Physics) in Krakow. Gas extraction was carried out using the Head Space method (HS) (Sliwka and Lasa 2000). Analysis of N_2 , Ar, and Ne was performed using a ShimadzuGC-17A gas chromatograph equipped with two thermal-conductivity detectors TCD (TCD1 for the detection of neon and argon; TCD2 for the determination of nitrogen the thermal-conductivity) (Mochalski et al. 2006).

In five water samples, the isotopic composition of $\delta^{15}N$ and $\delta^{18}O$ dissolved in nitrate was determined. This measurement was possible only for samples with relatively high nitrate content (as 0.32 mmol of NO_3 is required for the analysis). The isotope analysis was performed in the laboratory of the AGH University of Science and Technology (Faculty of Physics and Applied Computer Science) in Cracow.

Results

Drainage water and surface water chemistry

Drainage water samples were collected at the outlets of the drainage pipes, at places where the drainage water recharge surface water. Moreover, water from two drainage settlers was collected (Fig. 1). The sampling of this water was

possible only in the spring of 2012 and 2013 after the snow melt season, because only in those periods were the drainage systems transporting water. During the remaining time period, the drains did not work. In the winter and spring of 2014, there was no snow cover and at the spring drainage systems transported only a small amount of water. In that case it was possible to collect water samples only from drainage settlers.

The specific attribute of drainage water is the very high concentrations of nitrate (Table 1). The nitrate concentration usually exceeds 70 mg/l (the maximum detected is 98.5 mg/l). The concentrations of nitrite and ammonia are low (below 0.01 and 0.1 mg/l, respectively). The concentration of chloride is variable (range between 27 and 112 mg/l). The sulfate concentration is also spatially changeable (between 40 and 137 mg/l). The drainage water is characterized by low alkalinity (usually below 4.0 meq/l) but relative high total hardness (TH) (usually more than 7.0 meq/l).

The exception to the present situation is water sampled in drainage settler S1, which is characterized by very high concentrations of almost all the water components (Table 1). This settler probably receives waste water from illegal septic tanks. The high boron and organic nitrogen concentrations confirm this condition (Table 1).

The distinct spatial differentiation of drainage water chemistry is caused by different uses of fertilizers and manure by individual farmers. The changeable concentration of chloride, sulfate and TH is probably caused by the spreading of domestic sewage directly on the land surface. The correlation of the boron concentration (an indicator of domestic sewage influence) with the above mentioned parameters confirms this interpretation.

The samples of surface water were taken from ditches that receive water from outlets of drainage pipes. One ditch functions all year (Fig. 1); this ditch also receives treated waste water from the treatment plant in Goluchow. The second ditch is located 300 m north of the first one (Fig. 1) and functions only periodically, during drainage system operations. This ditch receives water only from drainage outlets and the direct drainage of soil water after the snow melting season.

The chemistry of the surface water during the drainage system operations is very similar to that of the drainage water. It is reflected in water samples POW1 and POW2 (upstream to the waste water outlet). The nitrate concentration in the spring period is usually >70 mg/l (Table 2). The concentrations of nitrite and ammonia are low (below 0.04 and 0.2 mg/l, respectively). These indicators show that the surface water chemistry reflects the drainage water inflow. The surface water chemistry is completely different downstream of the outlet of waste water from the treatment plant. This situation is reflected in water samples POW3,

Table 1 The drainage water chemistry

Sample number	Date of sampling	pH	Alkalinity (meq/l)	Total hardness	Conductivity (µS/cm)	Fe (mg/l)	Mn (mg/l)	PO ₄ (mg/l)	F (mg/l)	Cl (mg/l)	NO ₃ (mg/l)	NO ₂ (mg/l)	NH ₄ (mg/l)	SO ₄ (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	B (µg/l)	N _{org} (mg/l)
S1	IV 2012	7.37	9.5	15.8	1671	1.53	0.63	<0.01	0.19	166.6	1.31	<0.001	0.590	262.1	263.2	32.1	74.2	38.5	-	0.8
S2		7.58	4.4	7.6	790	0.09	0.01	<0.01	0.24	27.9	69.9	<0.001	0.017	78.4	114.6	23.2	9.10	1.24	-	<0.2
M7		7.53	2.1	5.8	710	0.22	0.03	<0.01	0.22	47.6	89.9	<0.001	0.050	39.7	86.2	13.9	10.9	2.79	-	<0.2
M8		7.09	1.3	4.3	489	0.17	0.03	<0.01	0.13	19.8	66.9	<0.001	0.009	56.9	69.0	10.0	9.66	3.89	-	<0.2
MI3		7.11	3.6	8.0	871	0.08	0.01	<0.01	0.21	57.9	70.1	<0.001	0.002	105.8	134.2	16.2	19.5	3.01	-	<0.2
MI5		7.24	6.2	10.8	1254	0.34	0.22	<0.01	0.22	112.2	74.8	0.05	0.217	137.1	171.9	27.4	55.0	7.12	-	<0.2
S1	IV 2013	7.32	9.5	7.9	1876	1.73	0.691	0.19	0.24	170.9	0.197	0.015	0.643	260.1	269.9	25.9	70.6	37.2	99.2	-
S2		7.37	3.9	7.3	941	0.076	0.021	0.15	0.26	45.8	82.6	0.009	0.078	97.4	132.4	20.5	10.8	1.05	41.6	-
S2		7.24	3.5	7.0	942	0.04	0.033	0.11	0.25	32.3	79.1	0.011	0.078	98.6	128.2	20.3	9.82	0.99	33.1	-
M7		7.67	1.8	7.4	789	0.755	0.16	0.09	0.29	53.5	98.5	0.012	0.077	69.6	96.1	14.6	9.37	2.39	42.7	-
M8		7.36	1.9	7.5	590	0.445	0.091	0.15	0.18	29.1	74.9	0.008	0.079	56.9	76.5	10.1	9.06	5.71	33.6	-
MI3		7.3	3.5	6.5	972	0.248	0.042	0.09	0.32	79.3	76.9	0.007	0.025	108.2	136.3	18.5	19.1	5.45	44.3	-
S1	IV 2014	6.92	9.1	15.3	1730	1.98	0.67	<0.01	0.15	148.4	1.1	<0.001	1.132	280.8	246.1	36.5	60.9	33.0	54.4	-
S2		6.6	5.1	8.5	902	0.10	0.02	<0.01	0.20	38.9	47.4	<0.001	0.795	95.1	132.1	22.7	10.6	1.26	26.7	-

S samples taken from drainage settlers; M samples taken from ends of drainage pipes

POW4, and POW5. These water samples are characterized by high concentrations of almost all the components. The most notable concentration increases observed are those of ammonia, sodium, and potassium. Moreover, these waters have high concentrations of boron and organic nitrogen. The high nitrate content is diluted downstream. At the end of the ditch, the nitrate concentration is lower than 40 mg/l. Lower nitrate concentrations are also observed when the drainage systems are not operating (the autumn sampling series).

Groundwater chemistry

In the relatively small study area, distinct differences in the groundwater chemistry were documented (Tables 3, 4). In groundwater pumped from the net of the piezometers, the concentration of chloride ranged between 33 and 90 mg/l and the sulfate concentration between 130 and 325 mg/l (Table 3). The concentrations of sodium and potassium are very variable and range between 9 and 36 mg/l and between 1.8 and 12.4 mg/l, respectively. The most variable concentration is that of nitrate. The highest concentration of nitrate was documented near the drainage ditch (more than 110 mg/l). In the piezometers located at the greatest distance from the ditch, the concentration of nitrate was low (usually below 2 mg/l). The concentration of ammonia is relatively low (below 0.5 mg/l), with the exception of piezometer P4A (more than 1 mg/l). The concentrations of nitrite are relatively low, usually below 0.1 mg/l. The alkalinity of the groundwater varies between 2.1 and 5.6 meq/l, and the total hardness varies between 8.2 and 11.6 meq/l.

The distinct variations of the groundwater chemistry were also observed in the wells (Table 4). The chloride and sulfate concentrations varied between 37.7 and 47.7 mg/l and between 154 and 230 mg/l, respectively. The sodium and potassium concentrations were more stable in the wells and varied between 13 and 18 mg/l and between 2.6 and 4.5 mg/l, respectively. The concentration of nitrate was the highest in well IV, located closest to the drainage ditch (10.2 mg/l in spring of 2014). At the wells located further from the ditch, the nitrate concentration was low (below 2 mg/l). The total hardness ranged between 6.5 and 8.5 meq/l, and the alkalinity ranged between 3.8 and 4.2 meq/l. Relatively small concentrations of ammonia were observed (below 0.4 mg/l). Additionally, the nitrite concentrations were very low (below 0.001 mg/l).

Water isotope composition

The determination of both ¹⁵N and ¹⁸O isotopes in nitrate was feasible only for samples with relatively high nitrate content. The water samples for isotope analysis were taken

Table 2 Surface water chemistry

Sample number	Date of sampling	pH	Alkalinity (meq/l)	Total hardness	Conductivity (µS/cm)	Fe (mg/l)	Mn (mg/l)	PO ₄ (mg/l)	F (mg/l)	Cl (mg/l)	NO ₃ (mg/l)	NO ₂ (mg/l)	NH ₄ (mg/l)	SO ₄ (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	B (µg/l)	N _{org} (mg/l)
POW1	IV 2012	8.55	3.9	8.6	851	0.04	0.01	<0.01	0.25	45.5	82.8	0.05	0.005	122.4	140.5	19.5	12.2	2.65	-	<0.2
POW2		8.18	4.2	9.1	1051	0.09	0.02	<0.01	0.23	76.3	65.1	0.30	0.182	144.4	139.1	26.6	27.4	8.17	-	<0.2
POW3		7.90	8.0	8.1	1306	0.20	0.05	1.27	0.68	117.3	31.6	0.40	28.2	129.5	118.5	26.8	101.9	25.9	-	12.5
POW4		8.10	7.0	7.4	1292	0.24	0.08	0.94	0.54	116.1	44.3	0.46	20.8	131.8	105.4	26.0	97.2	21.9	-	7.4
POW3	X 2012	7.16	5.7	6.8	1352	0.34	0.06	2.53	0.82	157.7	39.7	1.83	0.407	114.7	94.8	24.8	134.1	31.5	199.9	-
POW4		7.67	5.6	6.6	1342	0.45	0.05	2.57	0.78	157.4	40.2	2.01	0.160	115.3	92.4	24.7	132.9	30.6	199.7	-
POW5		8.04	5.6	6.8	1324	0.27	0.03	2.45	0.85	158.6	40.2	2.50	0.157	115.4	95.5	24.9	133.2	30.3	196.9	-
POW1	IV 2013	7.87	3.7	4.8	1007	0.211	0.068	0.39	0.29	80.8	95.9	0.025	0.098	97.4	143.3	20.8	13.5	2.69	107.4	-
POW2		7.95	4.3	4.2	1179	0.227	0.055	0.35	0.32	92.1	85.2	0.031	0.106	142.2	159.7	21.9	27.6	9.99	104.5	-
POW3		7.49	7.3	7.1	1418	0.27	0.107	1.02	0.71	129.2	32.4	1.01	16.5	125.6	138.7	22.3	89.4	23.1	138.2	-
POW4		7.79	7.3	4.6	1403	0.272	0.122	1.25	0.64	132.4	38.5	1.22	15.5	120.3	136.2	25.6	88.1	22.2	137.4	-
POW5		8.1	7.5	4.5	1423	0.262	0.101	1.29	0.64	132.5	38.4	1.35	15.5	129.7	134.3	25.7	98.8	22.1	138.7	-
POW2	X 2013	7.71	5.4	6.4	909	0.24	0.07	0.88	0.35	150.5	42.6	0.023	0.094	95.8	93.4	21.4	121.9	24.55	197.4	-
POW3		7.42	6.1	6.5	1293	0.23	0.02	1.02	0.38	154.3	39.8	0.025	0.109	88.4	94.6	22.1	129.9	29.6	208.0	-
POW4		7.79	6.0	6.6	1287	0.29	0.04	0.90	0.37	151.2	38.5	0.036	0.104	90.3	95.9	22.6	121.8	28.8	205.5	-
POW5		8.08	6.0	6.7	1333	0.23	0.03	0.97	0.38	151.7	37.8	0.059	0.099	93.2	96.1	23.5	122.3	28.1	202.2	-
POW2	IV 2014	8.04	4.4	6.7	988	0.03	0.01	1.22	0.29	134.9	59.8	0.426	0.095	111.6	96.2	23.5	101.4	23.4	103.0	-
POW3		7.08	6.1	7.2	1226	0.03	0.02	1.54	0.31	132.3	34.5	1.121	0.121	107.8	106.5	23.1	104.8	25.2	111.5	-
POW4		7.57	5.7	7.3	1231	0.03	1.03	1.19	0.24	132.8	30.3	0.682	0.119	108.9	107.4	24.1	101.8	24.3	105.0	-
POW2	IX 2014	7.37	4.8	6.1	734	0.14	0.054	0.33	0.33	142.0	39.4	0.027	0.131	97.9	87.6	20.8	114.0	23.9	134.7	-
POW3		7.4	6.7	6.5	1160	0.10	0.062	0.39	0.39	139.3	32.7	0.031	0.122	81.5	92.4	22.9	119.4	29.2	150.9	-
POW4		7.79	6.4	6.5	1150	0.15	0.061	0.37	0.37	139.1	31.9	0.038	0.131	79.8	92.7	23.3	119.0	29.7	173.9	-

Table 3 Groundwater chemistry (piezometers)

Sample number	Date of sampling	pH (-)	Alkalinity (meq/l)	Total hardness	Conductivity (µS/cm)	Fe (mg/l)	Mn (mg/l)	PO ₄ (mg/l)	F (mg/l)	Cl (mg/l)	NO ₃ (mg/l)	NO ₂ (mg/l)	NH ₄ (mg/l)	SO ₄ (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	B (µg/l)	N _{org} (mg/l)
P1	IV 2012	6.60	2.1	8.2	990	0.70	0.07	<0.01	0.13	82.5	110.1	0.032	0.005	136	131	20.6	23.7	1.8	-	<0.2
P2		6.83	4.7	9.9	1155	1.13	0.13	<0.01	0.14	88.7	80.4	0.029	0.082	137	160	23.6	36.0	12.4	-	<0.2
P3		7.32	4.2	10.3	1052	0.18	0.72	<0.01	0.11	59.3	34.7	0.164	0.021	220	169	22.4	17.8	2.4	-	<0.2
P4A		7.29	4.1	11.6	1043	2.29	0.94	<0.01	0.11	35.1	11.9	0.050	0.433	325	192	24.1	8.9	4.2	-	0.2
P4B		7.30	5.6	10.4	1037	2.34	0.89	<0.01	0.25	38.6	0.022	<0.01	1.14	221	161	28.8	15.6	2.7	-	1.1
P5		6.67	3.9	10.6	1114	-	-	<0.01	0.42	33.7	0.95	<0.01	2.02	322	173	23.6	12.6	8.7	-	1.4
P1	X 2012	6.56	2.2	8.0	968	0.15	0.04	<0.01	0.09	69.3	112.7	0.021	0.013	139.9	124	21.4	24.4	2.0	35.6	-
P2		6.81	4.3	9.2	1113	0.22	0.11	<0.01	0.13	75.9	86.6	0.019	0.079	135.9	143	25.4	29.5	10.4	44.7	-
P3		7.06	4.4	9.8	998	0.23	0.74	<0.01	0.10	44.5	31.3	0.122	0.084	218.0	153.7	25.9	18.6	1.58	31.9	-
P4A		6.98	3.7	11.4	880	1.09	0.78	<0.01	0.10	32.2	12.6	0.020	0.472	305	189	23.3	7.9	4.3	30.8	-
P4B		7.20	4.6	9.9	1005	2.21	0.88	<0.01	0.28	59.6	0.019	<0.01	1.43	220	153	27.8	17.9	3.3	22.5	-
P5		6.70	4.2	9.2	1088	-	-	<0.01	0.47	42.0	1.22	<0.01	2.18	200	150	20.3	10.3	4.9	26.3	-
P1	IV 2013	6.76	2.4	7.9	1017	0.20	0.05	<0.01	0.08	67.8	113.5	0.019	0.009	137.3	125.6	20.3	23.7	2.10	31.8	-
P2		6.89	4.5	6.1	1135	0.194	0.115	<0.01	0.14	74.7	87.7	0.009	0.044	136.6	151.5	21.4	28.6	11.3	48.1	-
P3		7.16	4.9	6.4	1065	0.121	0.838	<0.01	0.14	45.4	29.9	0.085	0.032	225.8	169.7	24.9	18.2	2.31	30.3	-
4A		7.2	3.6	11.0	1102	1.24	0.86	<0.01	0.15	42.9	13.7	0.018	0.355	305.3	180.7	23.5	7.50	4.10	35.9	-
4B		7.22	4.6	10.1	1012	2.39	0.84	<0.01	0.25	55.9	2.30	0.028	1.02	225.2	158.1	26.3	16.4	3.00	26.3	-
P5		7.01	4.7	9.3	1290	-	-	0.08	0.49	40.7	3.30	0.008	2.25	198.1	154.5	19.2	11.2	4.55	34.4	-
P1	X 2013	6.94	3.2	8.6	1034	0.18	0.04	<0.01	0.11	60.3	125.2	0.011	0.007	126.0	138.2	21.2	19.6	2.38	39.3	-
P2		10.7	4.4	8.4	1043	0.32	0.14	<0.01	0.11	72.1	72.9	0.021	0.043	119.7	134.8	20.8	31.1	10.3	48.3	-
P3		7.12	4.2	9.6	980	0.26	0.64	<0.01	0.09	45.7	29.7	0.068	0.054	198.9	153.9	22.8	15.5	2.01	45.6	-
P4A		6.78	3.6	10.4	1028	0.90	0.68	<0.01	0.11	33.4	15.0	0.024	0.418	300.6	170.9	22.9	9.02	3.76	47.3	-
P4B		6.97	4.8	10.3	1006	1.91	0.78	0.02	0.20	41.9	0.036	<0.001	1.66	243.9	159.6	28.3	12.8	3.01	43.0	-
P5		6.84	4.4	8.8	858	-	-	<0.01	0.35	35.3	1.01	<0.001	1.85	199.9	145.1	19.1	10.9	5.39	45.6	-
P1	IV 2014	6.99	4.4	8.8	1047	0.13	0.03	<0.01	0.12	57.6	83.1	0.009	0.011	93.9	138.2	22.6	13.1	1.71	33.1	-
P2		6.96	4.4	8.1	918	0.21	0.06	<0.01	0.10	73.3	69.3	0.007	0.029	88.2	130.1	19.5	31.2	10.9	41.7	-
P3		7.04	44.2	9.3	951	0.27	0.59	<0.01	0.11	43.9	23.8	0.078	0.049	197.9	149.7	22.2	15.3	2.03	15.7	-
P4A		6.92	3.8	10.0	940	0.89	0.59	<0.01	0.15	32.6	8.95	0.028	0.503	271.4	164.8	21.1	8.55	3.54	24.8	-
P4B		6.95	5.3	9.2	875	0.96	0.76	<0.01	0.19	21.5	0.05	<0.001	1.77	191.2	139.6	27.1	11.0	2.94	24.5	-
P5		7.00	3.7	8.1	913	-	-	0.05	0.29	31.5	0.95	<0.001	1.96	202.1	133.7	17.9	11.3	5.41	26.0	-

Table 3 continued

Sample number	Date of sampling	pH (-)	Alkalinity (meq/l)	Total hardness	Conductivity (µS/cm)	Fe (mg/l)	Mn (mg/l)	PO ₄ (mg/l)	F (mg/l)	Cl (mg/l)	NO ₃ (mg/l)	NO ₂ (mg/l)	NH ₄ (mg/l)	SO ₄ (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	B (µg/l)	N _{org} (mg/l)
P1	IX 2014	6.88	4.3	8.8	829	0.16	0.05	<0.01	0.10	59.9	89.2	0.009	0.005	97.9	138.3	23.4	13.9	1.75	29.7	-
P2		6.79	4.5	8.5	1030	0.33	0.13	<0.01	0.12	70.6	77.2	0.015	0.031	120.3	135.5	21.7	32.3	11.1	37.4	-
P3		7.04	4.3	9.3	920	0.25	0.76	<0.01	0.08	46.1	30.7	0.061	0.038	193.9	149.8	22.5	16.1	2.06	35.4	-
P4A		7.19	3.8	10.8	997	1.30	0.71	<0.01	0.12	39.0	18.8	0.019	0.562	298.3	179.7	22.8	9.24	4.64	36.5	-
P4B		7.09	5.5	10.5	850	1.83	0.85	0.06	0.22	38.7	1.05	0.001	1.64	230.6	161.2	29.7	12.6	3.15	32.8	-
P5		6.79	3.7	8.5	790	-	-	<0.01	0.31	36.3	1.75	0.002	1.41	200.6	139.7	18.6	10.8	5.01	30.2	-

Table 4 Groundwater chemistry (wells)

Sample number	Date of sampling	pH (-)	Alkalinity (meq/l)	Total hardness	Conductivity (µS/cm)	Fe (mg/l)	Mn (mg/l)	PO ₄ (mg/l)	F (mg/l)	Cl (mg/l)	NO ₃ (mg/l)	NO ₂ (mg/l)	NH ₄ (mg/l)	SO ₄ (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	B (µg/l)	N _{org} (mg/l)
II	IV 2012	7.16	3.8	8.2	814	7.87	0.93	<0.01	0.32	43.9	0.959	<0.001	0.372	198	128.0	21.9	18.8	4.2	-	0.5
IV		7.26	4.9	8.5	816	0.82	0.85	<0.01	0.27	37.7	8.13	<0.001	0.316	154	130.0	24.7	15.8	2.6	-	0.2
II	X 2012	6.96	3.8	7.9	818	6.89	0.90	<0.01	0.30	45.5	1.90	<0.001	0.314	182.6	125.3	21.1	18.6	4.35	28.2	-
IV		7.08	3.9	8.2	832	1.49	0.87	<0.01	0.30	38.0	8.58	<0.001	0.275	182.3	124.9	24.2	15.8	2.71	27.9	-
II	IV 2013	7.04	3.8	2.6	826	6.657	0.943	<0.01	0.39	47.7	1.22	<0.001	0.37	180.4	125.5	21.2	18.6	4.54	24.8	-
IV		7.03	4.9	6.5	827	1.277	0.947	<0.01	0.35	39.1	8.69	<0.001	0.31	171.1	134.6	26.3	15.8	2.75	22.2	-
II	X 2013	7.18	3.8	7.7	790	6.35	0.79	<0.01	0.22	42.8	1.15	0.009	0.302	174.4	122.6	20.1	17.8	4.33	32.7	-
III		6.93	4.1	8.4	1058	4.07	0.87	<0.01	0.26	32.6	1.01	0.007	0.434	230.5	142.7	15.3	13.5	2.62	35.4	-
IV		6.83	4.2	8.4	855	1.39	0.87	<0.01	0.21	39.9	10.10	<0.001	0.223	180.5	128.1	24.6	14.5	2.57	33.8	-
II	IV 2014	7.17	3.7	7.6	776	4.50	0.66	<0.01	0.25	43.5	1.01	0.005	0.295	172.6	119.2	19.9	16.9	4.42	22.5	-
III		6.83	5.5	11.7	1064	3.05	0.68	<0.01	0.21	30.5	1.18	0.009	0.655	282.4	178.9	34.0	13.4	2.72	23.4	-
IV		7.17	5.5	8.5	880	0.75	0.66	<0.01	0.05	40.7	10.20	<0.001	0.321	156.9	129.9	24.7	13.9	2.54	20.7	-
II	IX 2014	7.48	3.6	7.6	758	4.38	0.70	<0.01	0.18	43.3	1.15	0.038	0.305	119.4	92.7	19.8	16.7	4.46	35.9	-
III		7.23	5.8	11.0	951	3.79	0.80	<0.01	0.21	32.3	1.00	0.007	0.459	172.2	119.4	29.5	14.1	2.79	33.1	-
IV		7.17	4.8	8.8	818	1.3	0.77	<0.01	0.20	39.4	10.00	0.008	0.305	134.9	172.2	25.1	15.3	2.64	31.2	-

Table 5 Result of the N₂ excess measurements and isotope analyses

Sample number	Nitrate concentration (mg/l)	Ne (g/cm ³)	Ar (g/cm ³)	NGT (°C)	Measured N ₂ (mg/l × 10 ⁻¹)	Excess N ₂ (mg/l)	δ ¹⁵ N _{air} (‰)	δ ¹⁸ O _{VSMOW} (‰)
P1	125.5	2.37 ± 0.12	7.72 ± 0.38	7.9	2.13 ± 0.1	<0.8 ± 0.8	–	–
P2	72.9	2.20 ± 0.12	7.90 ± 0.37	5.0	2.21 ± 0.11	<0.8 ± 0.8	10.4	7.9
P3	29.7	2.01 ± 0.11	7.75 ± 0.36	5.4	3.00 ± 0.14	9.5 ± 1.7	13.4	17.2
P4A	15.0	0.41 ± 0.02	4.07 ± 0.19	–	2.78 ± 0.14	Degassed water	–	–
P4B	0.036	1.69 ± 0.09	6.52 ± 0.31	10.6	3.34 ± 0.16	15.0 ± 2.1	–	–
P5	1.01	1.89 ± 0.10	6.88 ± 0.32	9.5	3.06 ± 0.16	11.9 ± 2.0	–	–
II	1.15	1.92 ± 0.10	7.43 ± 0.36	6.8	3.48 ± 0.21	15.1 ± 2.1	–	–
III	1.01	1.88 ± 0.10	7.25 ± 0.34	7.7	2.99 ± 0.16	10.8 ± 1.6	–	–
IV	10.1	1.98 ± 0.10	7.58 ± 0.36	5.6	3.03 ± 0.15	10.0 ± 1.9	23.5	12.5
S2	79.1	–	–	–	–	–	9.9	8.3
M13	76.9	–	–	–	–	–	11.4	8.7

“–” Not measured

from the drainage system (samples S2 and M13), from the piezometers (P2 and P3), and well IV.

The nitrogen isotope of dissolved nitrate (δ¹⁵N) had a wide range of values from 9.9 to 23.5 ‰ (Table 5). The isotope of δ¹⁸O in nitrate has a wide range of values between 7.9 and 17.2 ‰. The smallest value of these parameters was observed in the drainage water, and the greatest value was observed in well IV and piezometer P3. An increasing trend of isotope concentrations was observed along the flow path. Moreover, there was a discernible trend of increasing δ¹⁵N value with decreasing NO₃ concentrations.

Dissolved N₂

Gaseous N₂ was measured only in groundwater samples. Groundwater contains relatively high concentrations of excess N₂ (Table 5). The range of excess N₂ in the study area varied from <0.8 mg N₂/l in piezometers P1 and P2 to more than 15 mg N₂/l in piezometer P4B and well IV. In the sample taken from piezometer P4A, the water was degassed (the detected Ne and Ar concentrations are lower than the atmospheric component), which could explain why the solubility of gas in water was exceeded.

A very clear trend of increasing N₂ concentration was visible along the flow path. The smallest N₂ value was observed near the drainage ditch (P1 and P2) and increased in the piezometers along the flow path. The maximum value was observed in well II (furthest away from the drainage ditch). There was also a very clear trend of increasing N₂ with decreasing nitrate concentration. In the piezometers located furthest away from the drainage ditch, the nitrate concentrations were low, and the value of N₂ was the highest.

Discussion

Temporal groundwater chemistry variation

The most distinct groundwater chemistry changes with time were documented in the pumped wells. A distinct increase in the concentration of water components was observed (Fig. 3; Table 4). The chloride concentration increase was visible from 2007 (from the level of approximately 20 mg/l to more than 50 mg/l). Additionally, a distinct increase in nitrate was observed (from nearly 0 to 2 mg/l). The increase in total hardness, sulfate, iron and manganese concentrations were visible from 1976 (the beginning of the wells exploitation), but a distinct and sharp increase in 2007 was also observed. Only the changes in water chemistry in well IV did not follow this behavior. The ground water chemistry in that well was more stable; only a very distinct increase in the nitrate concentration was visible, from approximately 2 mg/l in 2007 (the start of well exploitation) to more than 10 mg/l in 2014 (explained further in the text).

The distinct increase in water component concentrations from 2007 is caused by the start of intensive water extraction and the creation of a stable cone of depression, which causes an increase in the hydraulic gradient. These conditions increase the groundwater flow velocity and enable the contaminants to move to deeper parts of the flow system. It is clear that the water component concentrations increase (mainly chloride, sulfate, and total hardness) in wells II and III that have an unconfined condition, and this condition is confirmed by the lack of its increase in well IV, with confined conditions. The concentration increase of iron, manganese, sulfate, and total hardness is caused by the oxidation of organic matter and sulfides in the vadose

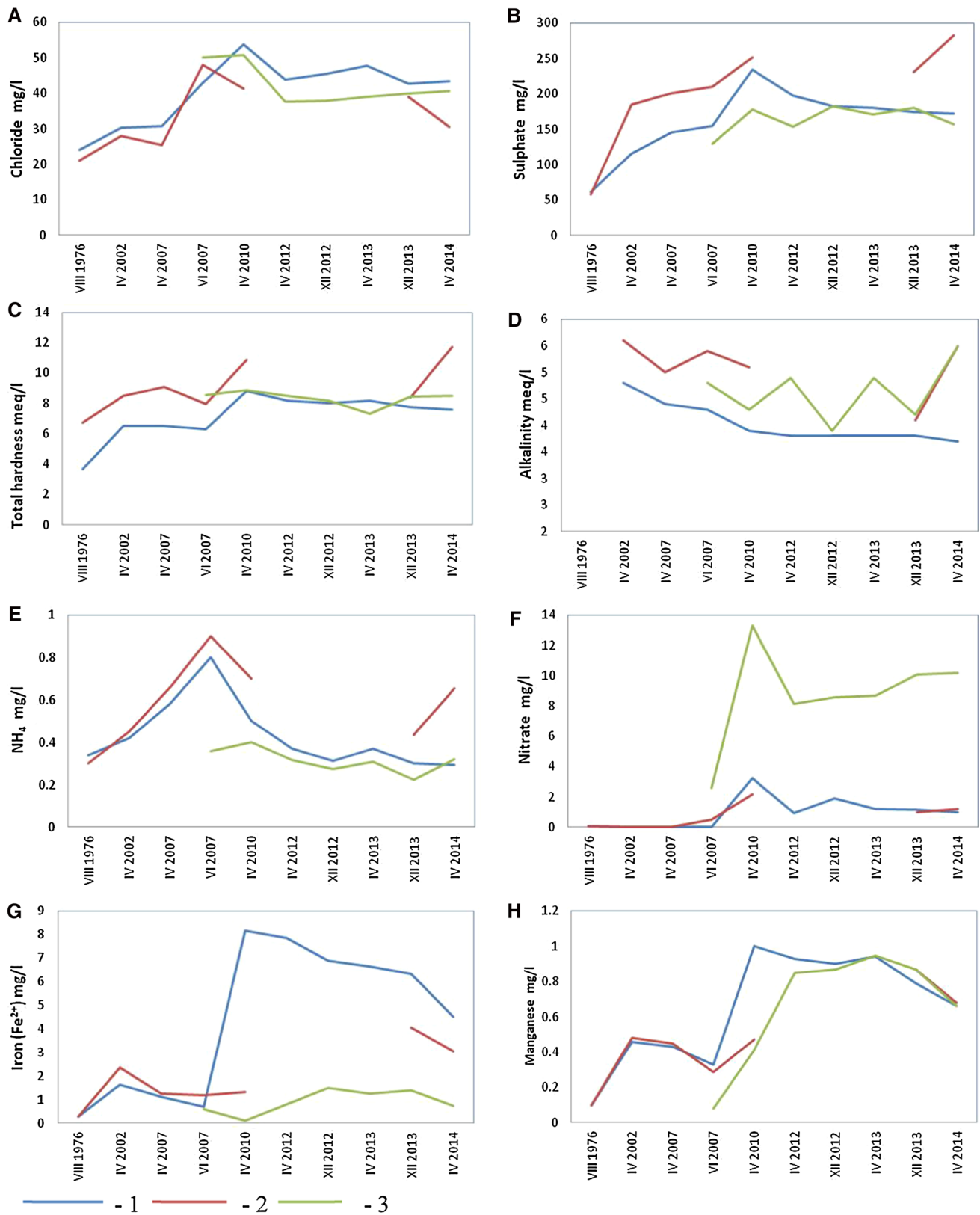


Fig. 3 Changes of groundwater chemistry during wells exploitation. 1—well II, 2—well III, 3—well IV. At the period between IV 2010 and XII 2013 well III was not operated

zone where the thickness increases during water extraction and in the upper parts of the aquifer. It is documented by a sharp concentration increase starting in 2007 (the beginning of intensive water extraction).

There is no apparent trend in water chemistry variation during 3 years of observation in the piezometers (Table 3). The chemical groundwater composition could be considered as relative stable, and there is no apparent trend of increase in the nutrient concentrations.

Spatial variation of groundwater chemistry

Meaningful groundwater chemistry differentiation was observed in the study area (Tables 3, 4). Figure 4 shows

the changes in groundwater chemistry along the flow lines. In the piezometers located nearest to the ameliorative ditch (P1 and P2), the concentrations of chloride and sodium were the highest (more than 60 and 20 mg/l, respectively). The concentration of nitrate is the highest at this location (more than 80 mg/l). In the direction of the groundwater flow, the concentrations of these parameters decrease considerably. In the piezometers P3 and P4A, the chloride concentrations decreased to <50 and 35 mg/l, respectively. The sodium concentration in piezometer P3 was <20 mg/l, and in piezometer P4A, it was <10 mg/l. In the remaining two piezometers (P4B and P5), the chloride concentration was <40 mg/l and that of sodium did not exceed 20 mg/l. The most distinct concentration decrease was observed for

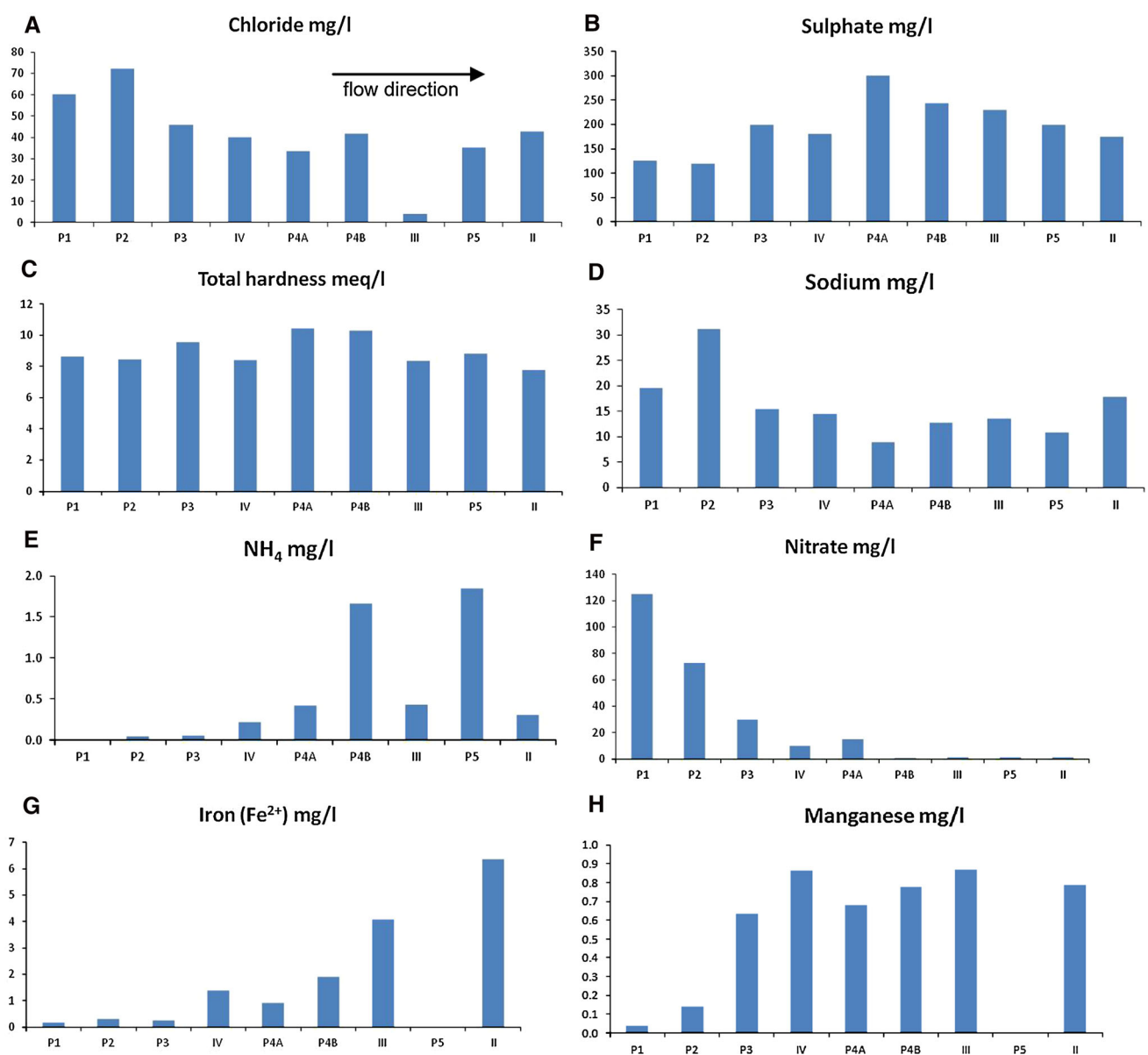


Fig. 4 Changes of groundwater chemistry along *flow lines* (based on data from sampling performed in autumn 2013)

nitrate. In piezometers P1 and P2, (located close to the drainage ditches) the concentration of nitrate exceeded 120 and 80 mg/l, respectively, but in piezometer P3, the nitrate concentration decreased to <35 mg/l and in P4A to <15 mg/l. In piezometer P4B (at this some location but screened in a deeper part of the aquifer), the nitrate concentration was very low (<1 mg/l). The concentration of nitrate in the deeper part of the aquifer in well IV (located close to piezometer P3—Fig. 2) was >10 mg/l. In the remaining wells, the concentration of nitrate was low (<2 mg/l).

Completely different types of groundwater chemistry changes were observed for the values of sulfate and total hardness. The concentration of these parameters was lowest near the ameliorative ditch and increased considerably along the flow lines. The concentration of sulfate in piezometers P1 and P2 was <140 mg/l, and the total hardness was <9 meq/l. Along the flow lines, the concentration of sulfate increased to more than 220 mg/l and more than 300 mg/l in piezometers P3 and P4A, respectively. The total hardness increased to more than 10 meq/l (in both piezometers). In piezometer P4B (the deeper part of the aquifer), the sulfate concentration and total hardness were lower in value (220 mg/l and <10 meq/l, respectively).

The concentrations of total iron, manganese and ammonia were the lowest in piezometers P1 and P2, with oxidation conditions. The highest concentrations were observed on the fluvial terrace with organic sediments (mainly silts, peats, and sands containing dispersed organic matter—Fig. 2—piezometers P4A, P4B, and P5).

Identification of the denitrification processes

The spatial groundwater chemistry differentiation observed in the shallow zone of the aquifer clearly indicated

denitrification processes. The decrease in chloride and sodium concentrations along the flow lines can be related to either dispersion or dilution processes. Nevertheless, the very clear tendency of a nitrate concentration decrease, with a concurrent total hardness and sulfate concentration increase, can be interpreted as result of denitrification.

The occurrence of denitrification confirms the measurement of gaseous N₂. The concentration of a gaseous excess of N₂ documented within the study area is characteristic of the denitrification influence (Table 5). A similar excess of N₂ due to denitrification has been previously documented elsewhere (Bennekomp et al. 1993; Blicher-Mathiesen et al. 1998; Craig et al. 2010; Welch et al. 2011). Importantly, the excess of N₂ is much lower in piezometers located close to ameliorative ditches (P1 and P2). Subsequently, there was a very clear increase in N₂ along the flow lines. At the same time, the concentration of nitrate decreased (Fig. 5a). The highest N₂ concentration occurred in wells II and III and piezometer P4B (the deeper part of the aquifer). The concentration of nitrate in these samples was the lowest (<2 mg/l).

The changes in gaseous N₂ concentration are consistent with the variability of isotopes ¹⁵N and ¹⁸O in nitrate. The change in the water isotope concentration along the flow lines is documented in Fig. 5b. The smallest ¹⁵N concentrations are documented in the drainage waters and in piezometer P2 located near the drainage ditch. The increase of ¹⁵N along the flow line is visible. The highest concentration was observed in well IV. It is consistent with the nitrate decrease (Fig. 5b). There is a discernible trend of increasing δ¹⁵N values with decreasing NO₃ concentrations, as would be expected from in situ denitrification (Fig. 6). In water samples enriched with nitrate (>80 mg/l) from the drainage systems (samples S2, M13, and P2), the value of ¹⁵N is the lowest. Along the flow lines in

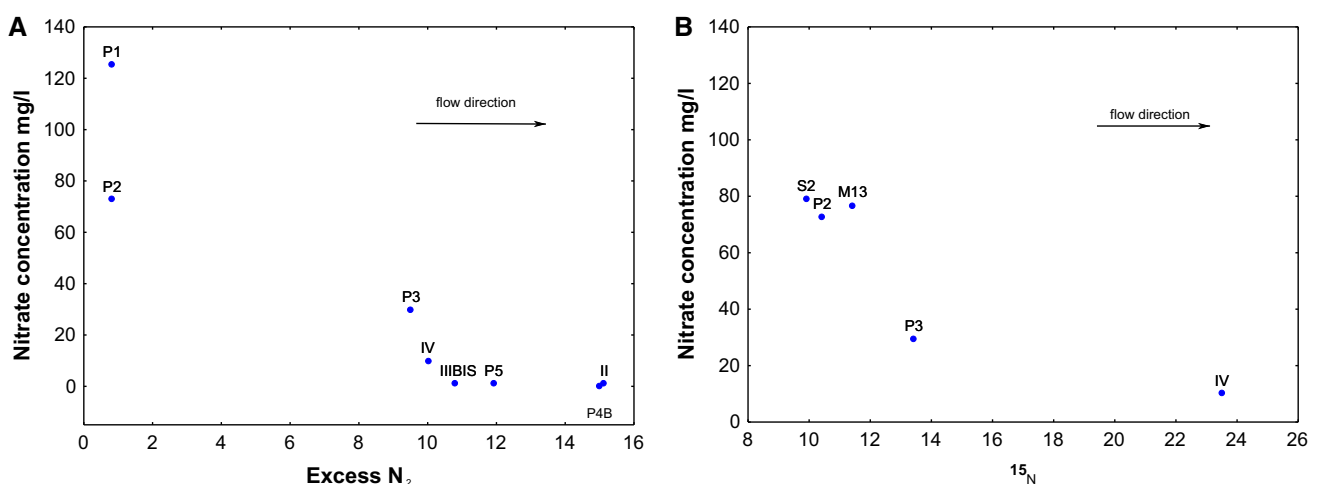
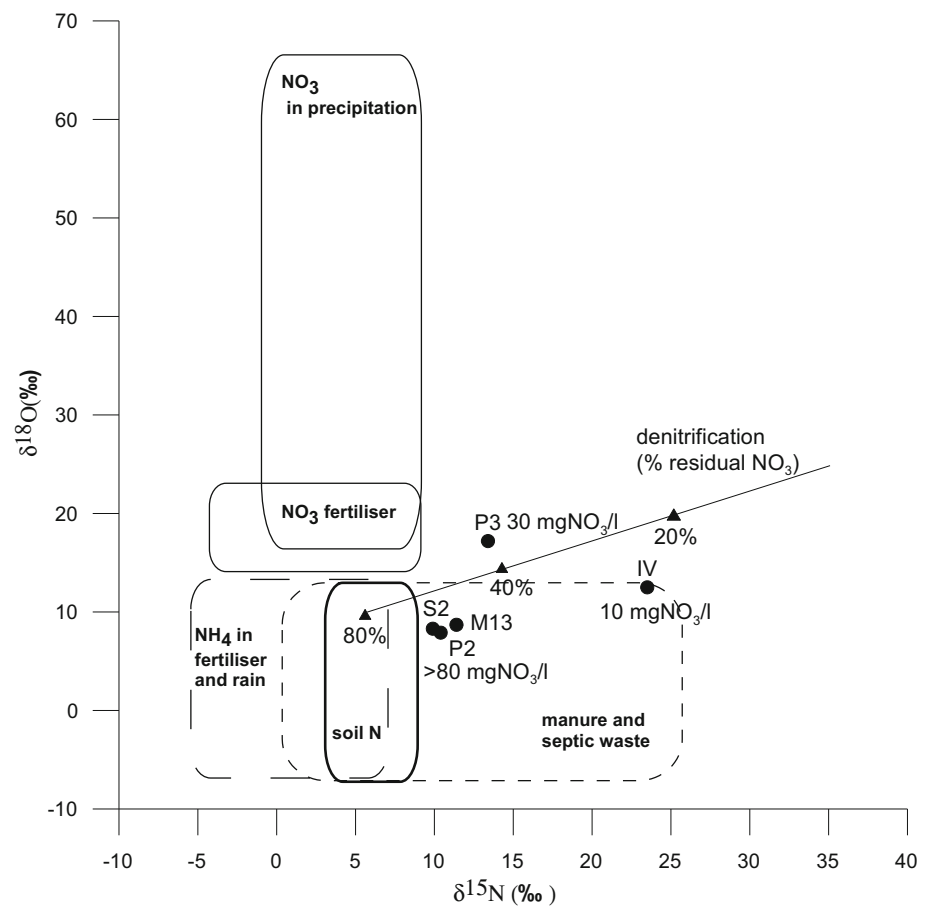


Fig. 5 Variability of nitrate concentrations in function of ¹⁵N in nitrate and excess of gaseous N₂

Fig. 6 Cross plot of $\delta^{18}\text{O}$ versus $\delta^{15}\text{N}$ in nitrate. The isotopic composition characteristic for various NO_3 sources based on Cook and Herczeg (2000), the percent of residual nitrate based on Clark and Fritz (1997)



piezometer P2—30 mg/l of nitrate responds to 40 % of residual nitrate. Downstream in well IV, the nitrate concentration of 10 mg/l responds to 20 % of residual nitrate (Clark and Fritz 1997).

The existence of a highly contaminated groundwater with a high content of nitrate in the shallow part of the flow system near pollution sources (drainage ditches) and a decrease of nitrate (in common with an increase of denitrification products: sulfate, total hardness and an excess of N_2) are consistent with the isotope composition changes (^{15}N and ^{18}O in nitrate) along the flow lines, documenting the occurrence of denitrification processes.

The sources of groundwater contamination in the study area are settlement and agricultural practices (mainly the application of fertilizers and manure to the land) along the whole surface water catchment. According to the isotopes of ^{15}N and ^{18}O in nitrate (Fig. 6), the main pollution source is manure application (Cook and Herczeg 2000). The main agricultural contamination indicator is nitrate, but the high concentration of chloride and the relatively high concentration of sulfate can indicate the spread of domestic waste water from septic tanks directly to the field surface. It has been documented that domestic sewage contamination adds to groundwater chloride, sulfate, and nitrate (Hudak

and Blanchard 1997). The relatively high concentration of boron documented in both the drainage water and the groundwater confirms this observation (Tables 1, 3).

The conceptual model of the groundwater flow is presented in Fig. 7. Subsequently, the contaminant spread on the land surface infiltrates the subsurface zone where nitrification processes occur under aerobic conditions (Clark and Fritz 1997). Drainage systems lower the water table, and subsequently, the thickness of the unsaturated zone increases. These conditions potentially increase the rate of nitrification (Bohlke 2002) because they increase the depth of oxygen penetration. These conditions are reflected by a high concentration of nitrate in both drainage and surface waters and low concentrations of nitrite and ammonia. Then, the contaminant plume moves from the drainage pipes to the surface water—collectors of drainage waters. The infiltrating nature of the ditches that receive the drainage water cause infiltration to the aquifer, and the nitrate plume is transported along the flow lines in the direction of the wells. The nitrate plume is observed mainly in the shallow zone (piezometers: P1, P2, P3, and P4A). In the deeper part of the flow system, the concentration of nitrate is low (<2 mg/l in wells II and III as well as in piezometer P4B). This is why a retardation of the nitrate

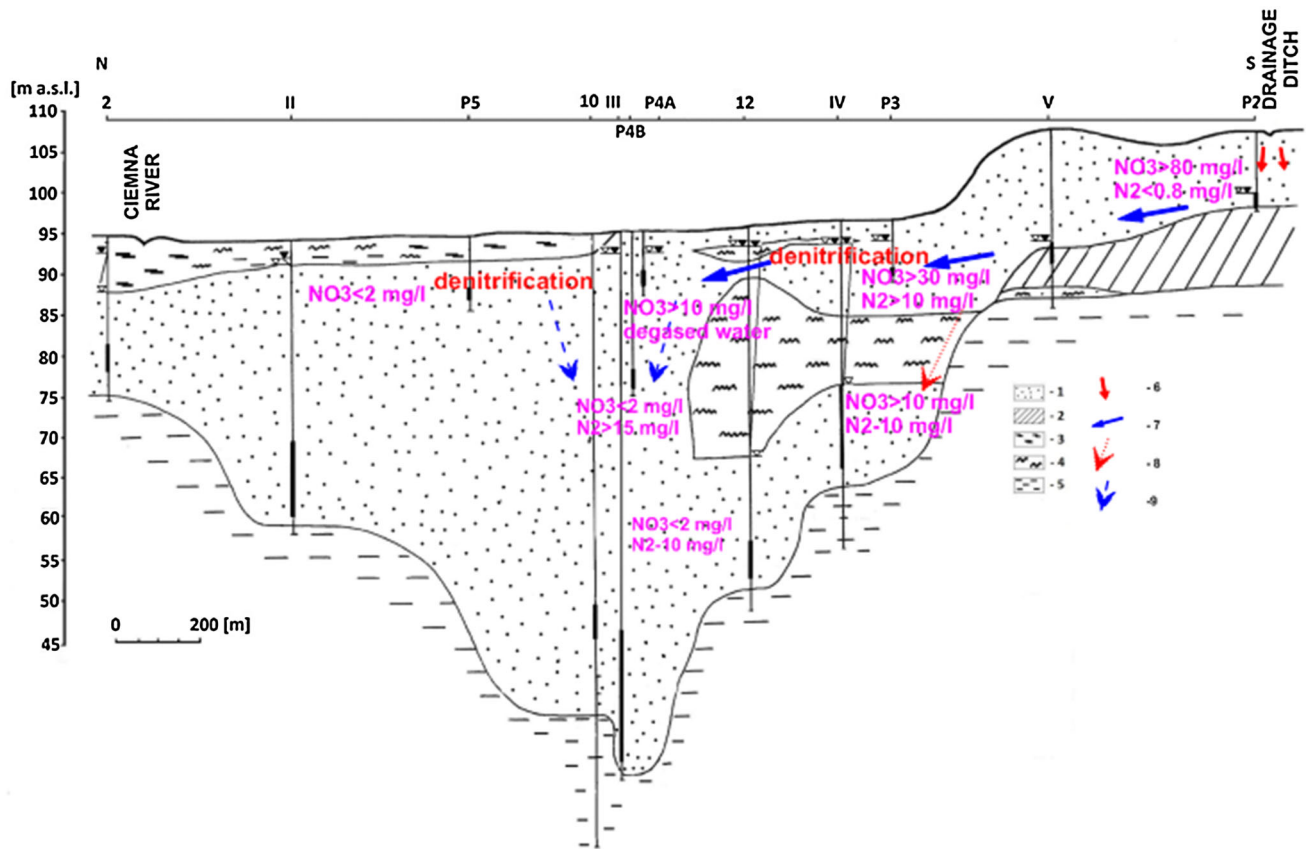


Fig. 7 The conceptual model of groundwater flow. 1—Aquifer rocks (sand and gravel), 2—till, 3—peat, 4—silt, 5—till, 6—direct water infiltration from drainage ditch; 7—groundwater flow in the aquifer;

8—percolation of groundwater through the aquitard; 9—downward migration in cone of depression zone. Remaining explanations on Fig. 2

plume by the denitrification process occurs mainly in the shallow zone on the valley area (<10 m deep), where there are sands containing dispersed organic matter; the exception is well IV (located at the closest distance from the pollution source). The increase in the nitrate concentration from approximately 2 mg/l in 2007 (the start of well exploitation) to more than 10 mg/l in 2014 indicates an influence of water extraction on the nitrate migration. The creation of the cone of depression causes a downward migration of nitrate and the penetration of the nitrate plume to the deeper parts of the aquifer. This well partially receives water that percolates through the silt aquitard most likely in the marginal part of the valley, where sandy lenses usually occur and partially receive water from the unconfined parts of the aquifer (Fig. 7). In wells II and III, the increase in the nitrate concentration is not significant. It is the result of nitrate removal by denitrification processes, confirmed by the highest observed concentration of N₂ in well II and piezometer P4B. In piezometer P4A, the N₂ is degassed completely, likely the result of the very high N₂ concentration consequently exceeding the hydrostatic pressure from the total pressure of the dissolved gases (Blicher-Mathiesen et al. 1998).

Conclusions

Groundwater in the recharge zone of the Tursko well-field (south Wielkopolska, Poland) is characterized by a high level of contamination. The main sources of groundwater contamination are application of fertilizers and manure to the field. These agricultural contaminants are then transported by drainage pipes to the surface water. The infiltrating character of the drainage ditches that receive strongly contaminated drainage water causes infiltration of contaminants to the water supply aquifer. Then, the contaminant plume is transported along the flow lines to the well-field.

The contamination is reflected mainly by a high concentration of nitrate. The nitrate concentration is highest near the contamination sources (drainage ditches). Along the flow lines, the concentration of nitrate decreases systematically, while at the same time, the total hardness and sulfate concentration increase. This is the result of denitrification that causes retardation of the nitrate migration significantly. The occurrence of denitrification was documented with the gaseous excess of N₂ as well as isotope analyses of ¹⁵N and ¹⁸O dissolved in the nitrate. The

systematic increase in the N_2 concentration was correlated with the nitrate concentration decrease along the flow lines. Additionally, the isotopes of ^{15}N and ^{18}O in nitrate increased along the flow lines, as would be expected from in situ denitrification. These data show that at the location of piezometer P3, 40 % of the residual nitrate occurs and that at well IV, only 20 % of the residual nitrate occurs. Further along the flow lines (piezometers P4A, P4B, wells II, and III), there is probably a reduction in nitrate to almost 100 %. Low nitrate concentrations occur there (<2 mg/l) and the high concentrations of denitrification products (sulfate, total hardness, and gaseous N_2).

The occurrence of denitrification processes is a protecting factor because it causes almost complete removal of nitrate from the groundwater. Unfortunately, at this same time the concentrations of other parameters (denitrification products) increase. As a result of denitrification, the concentrations of sulfate and total hardness are high (locally more than 300 mg/l and more than 11 meq/l, respectively). These values are higher than the upper permissible limits for drinking water. This condition can cause serious deterioration of groundwater chemistry on the Tursko well-field in the future, bearing in mind that the well-field will be expanded by constructing new wells and increasing the well-field productivity to 410 m^3/h in the future.

The research presented here confirms the cumulative effect of drainage systems. The contaminants are derived from dispersed sources localized at whole catchment areas and transported downstream by pipe drains system. The contaminated drainage water is then aggregated in drainage ditches that receive the water. Groundwater quality deteriorates under infiltrating conditions or if the ditches are located in the recharge area of the well-field.

We show that the drainage systems should be constructed taking into consideration conditions of groundwater quality protection. Not only the agricultural criterions but also conditions of groundwater protection should be considered, especially during the construction of new well-fields or during implementation of groundwater protection plans (development and implementation of well-field protection zones).

The data presented show that monitoring of groundwater chemistry at recharge zones of well-fields should be performed for both shallow and deep parts of the flow system, even if the shallow part is not used for water supply purposes. It is expected that in the long term, the quality of the deep groundwater will deteriorate if shallow contaminated groundwater penetrates the aquifer. It is also important to recognize geochemical factors that influence groundwater chemistry.

Our study demonstrates the effectiveness of the combined use of various methods (groundwater chemistry changes, isotopic methods, dissolved gaseous

measurements) for characterizing the behavior of nitrate, when it is possible to distinguish denitrification from dilution or dispersion processes.

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