Geological Quarterly, 2022, 66: 14
DOI: http://dx.doi.org/10.7306/gq.1646

The impact of treated wastewater effluent on contamination of a water supply aquifer during one decade of water exploitation (Tursko well field, Poland)

Krzysztof DRAGON[1, *], Roksana KRUĆ-FIJAŁKOWSKA[1], Magdalena MATUSIAK[1], Marcin SIEPAK[1],
Dariusz DROŻDŻYŃSKI[2] and Józef GÓRSKI[1]

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

[2] Institute of Plant Protection-National Research Institute, Department of Pesticide Residue Research, Władysława Węgorka 20, 60-318 Poznań, Poland

Dragon, K., Kruć-Fijałkowska, R., Matusiak, M., Siepak, M., Drożdżyński, D., Górski, J., 2022. The impact of treated wastewater effluent on contamination of a water supply aquifer during one decade of water exploitation (Tursko well field, Poland). Geological Quarterly, 2022, 66: 14, doi: 10.7306/gq.1646

Associated Editor: Beata Jaworska-Szulc

The recharge zone of an aquifer supplying the Tursko well-field (Poland), located in an area of sparse water resources, shows groundwater contamination manifested by high nitrate concentrations and pharmaceutical compounds. This study documents the steady deterioration of groundwater chemistry during one decade of groundwater exploitation, and analyses wastewater impact on the groundwater chemistry using pharmaceutical compounds as anthropogenic tracers, with focus on the influence of treated wastewater and drainage water. These waters infiltrate into groundwater from a drainage ditch located in the water supply aquifer's recharge zone. It is shown that strongly contaminated water can deliver organic matter and nutrients to the groundwater, activating or intensiying denitrification. As a result, the nitrate concentration has decreased in the groundwater, while concentrations of denitrification products have increased. Associated process of oxidation of organic matter causes periodic exceeding of limits allowed for drinking water. The ability of pharmaceutical compounds to act as anthropogenic tracers shows that infiltration of wastewater is a significant factor influencing drinking groundwater quality.

Key words: pharmaceuticals in groundwater, groundwater contamination by treated wastewater, denitrification, nitrate pollution.

INTRODUCTION

Increasing anthropogenic contamination can reduce groundwater quality as well as activate (or intensify) geochemical processes that modify its chemistry. One source of such contamination is wastewater (Asano and Cotruvo, 2004). Contamination by nitrates in groundwater beneath wastewater irrigation sites is a common problem (Obeidat et al., 2013; Fisher et al., 2016), though perceived as favourable for cultivation due to its nutrient content, and with advantages in rational water management, especially in dry regions (El Heloui et al., 2016). Regrettably, poor wastewater management practices can adversely impact local aquifers (Jampani et al., 2020). A common practice in wastewater management is the discharge of treated wastewater directly into surface water, which can lead to surface water contamination. The impact of wastewater on groundwater chemistry can appear especially in riverbank filtration systems, where due to their nature, the quality of extracted water is strongly dependent on the source (river) water quality (Dragon et al., 2018, 2019; Kruć et al., 2019). Impacts of wastewater on groundwater quality can also arise if treated wastewater is discharged into losing streams.

Treated wastewater effluent (TWE) can discharge, into the surface water, a range of persistent contaminants which are not removed in wastewater treatment (Kibuye et al., 2019). In recent years, attention has been focused on pharmaceutical products and drugs in water systems. Wastewater from sewage treatment plants is an important source of humans pharmaceutical compounds as these can pass through any stage of sewage treatment even if they are partially degraded or biotransformed (Strenn et al., 2004; Petrie et al., 2015; Su et al., 2020). The lack of regulations relating to pharmaceutical compound removal during sewage treatment means that any elimination is coincidental rather than deliberate. As a consequence, these substances reach the aquatic environment after TWE disposal, then are transported downstream in surface water and via rivers can reach groundwater and subsequently drinking water supply aquifers (Kondor et al., 2020). Because of anthropogenic origin of these substances there have been sev-

---

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

Received: January 7, 2022; accepted: April 14, 2022; first published online: August 19, 2022

eral approaches to use them to trace anthropogenic impact on the environment (Strenn et al., 2004; Massmann et al., 2008; Muller et al., 2012; Tran et al., 2014).

The Tursko well field's recharge area has been studied as regards the influence of drainage water on groundwater quality and the impact of denitrification on nitrate removal from groundwater (Dragon et al., 2016). In a 3-year study, a nitrate contamination plume was documented migrating from the contamination source to the well field. Oxidation of organic matter was found to be the geochemical process influencing groundwater chemistry. Natural nitrate removal resulting from denitrification occurring along flow paths was documented, while increase in the concentration of other constituents (e.g., sulphate and total hardness – products of denitrification) was also documented as a cause of groundwater quality deterioration. The drainage ditches that transfer surface water into the groundwater system were found to be the source of the contamination documented. These ditches receive strongly contaminated water from drainage pipes located upstream and since 2007 also effluent from a sewage treatment station. This situation causes a high risk of groundwater contamination. Based on the previous research, it was impossible to document TWE impact because both contamination sources (TWE and drainage water) have a similar effect on groundwater chemistry. It was inferred that to show the impact of TWE on groundwater chemistry an anthropogenic marker should be used. In the current work, pharmaceutical compounds were used as the tracer of wastewater influence.

The main objectives of this study are:
- investigation of the steady deterioration of groundwater chemistry during one decade of groundwater exploitation as the result of both drainage water and treated wastewater influence;
- analysing wastewater impact on groundwater using pharmaceutical compounds as an anthropogenic tracer.

STUDY AREA

HYDROGEOLOGICAL SETTINGS

The study area is located in the Prosna River valley, on the floodplain terrace in the southern part of the Wielkopolska region (Poland) (Fig. 1). Two rivers are located in the study area: the Prosna River flowing from south to north ~1 km east of the wells and the Ciemna River (Prosna tributary) flowing ~400 m north of well II.

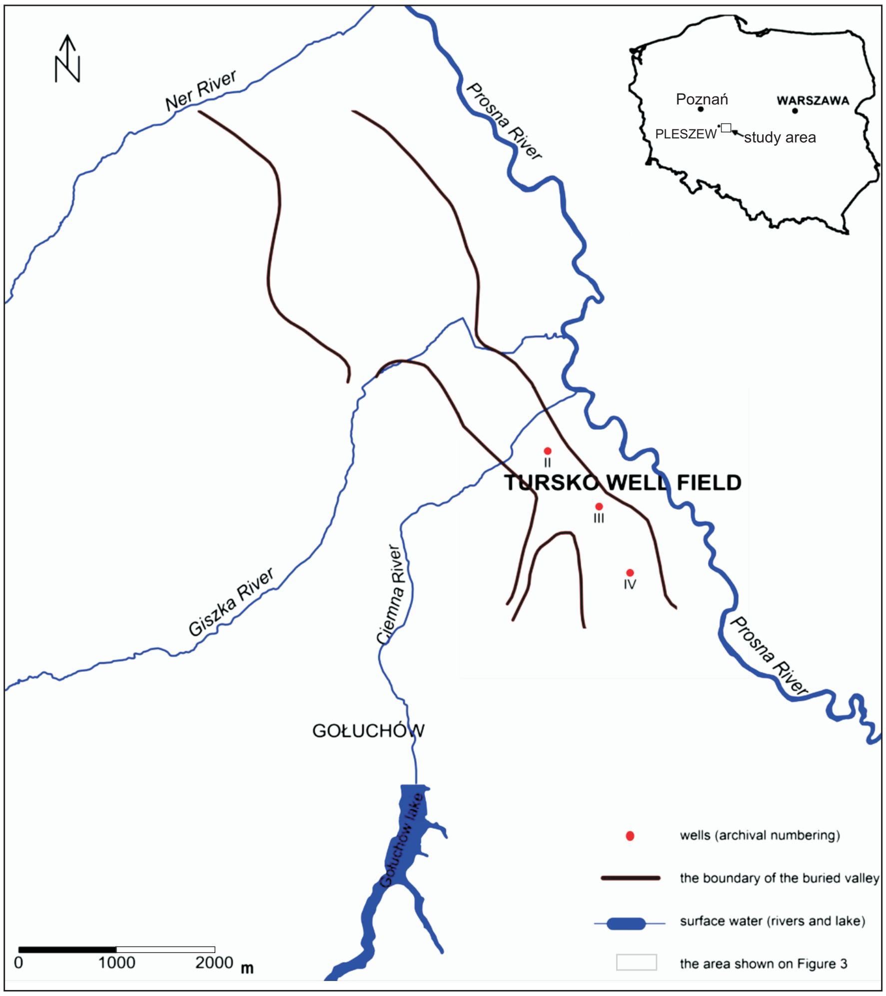

Fig. 1. The study area location

The study area covers the recharge zone of the water supply aquifer used to supply the town of Pleszew. This is a local aquifer in an area of sparse water resources. The aquifer's spatial spread is limited to a ~500–600 m wide strip located parallel the present Prosna riverbed, with a length of ~5 km. The thickness of the aquifer ranges from several to >60 m. There is a distinct increase in aquifer thickness in its central part, where the thickness of the aquifer deposits is >60 m (Fig. 2). Glacial and fluvioglacial deposits dominate the lithology. The deeper parts of the aquifer comprise fluvioglacial sands and gravels. In its upper parts fine and medium sands prevail. Holocene peats and silts occur in the near-surface zone, with a thickness of ~2–3 m. The aquifer is characterized by unconfined conditions with a relatively shallow (23 m below ground surface) water level. Locally, where peats and clays occur, confined conditions are present, leading to high vulnerability to pollution.

The Tursko well field comprises 3 continuously pumped wells. The well depths varies between 36 and 66 m (Fig. 2). The well field has been intensively pumped since 2007. The current yield of the wells is 200 m^3/h. Before 2007 the two wells then existing (nos. II and III) were pumped occasionally in the hot summers when there was the greatest need for water.

The principal source of recharge is inflow of groundwater infiltrating into the upland regions (Fig. 1). The groundwater flows, in natural conditions, from the upland area in the south and west to the Prosna River valley (Fig. 3). Direct rainwater and surface water infiltration also cause groundwater recharge in the valley area. Under groundwater exploitation conditions (with a cone of depression), the infiltration of surface water (especially from drainage ditches) is greater.

LAND USE AND URBANIZATION

Two villages are located close to the well field. Jedlec-Stara Wieś is located ~1.5 km south of well IV, and Jedlec-Nowa Wieś is located ~1 km west of the wells (Fig. 3). These villages are only partly connected to the central sewage system. In most cases, domestic sewage is stored in individual septic tanks, which are usually imperfectly constructed and used in poor condition.

The well field's recharge area is covered by arable lands located west and south of the floodplain terrace. Fertilizers and manure are frequently applied on arable lands and are potential sources of water contamination. The drainage systems here are constructed on such arable lands. The exits of the pipe drains provide drainage water to the drainage ditches located south of the well field (Fig. 3). From 2007 one ditch has also received TWE from the sewage treatment plant in Gołuchów. The TWE disposal site is located on the map (Fig. 3). Below the bottom of the ditch, permeable sediments occur (fine and medium sands). The unconfined water level occurs ~8 m below the ditch bottom (Fig. 2). These conditions enable infiltration of the contaminants from the ditch to the groundwater system. TWE is likely a more dangerous risk for groundwater contamination than drainage water because drainage pipes deliver water only periodically (during wet periods and spring thaws) while TWE is continually discharged and provides constant recharge of surface water. During a long period of the year, especially during hydrologic droughts, the drainage ditch in part located upstream of the TWE location is dry (Fig. 3).

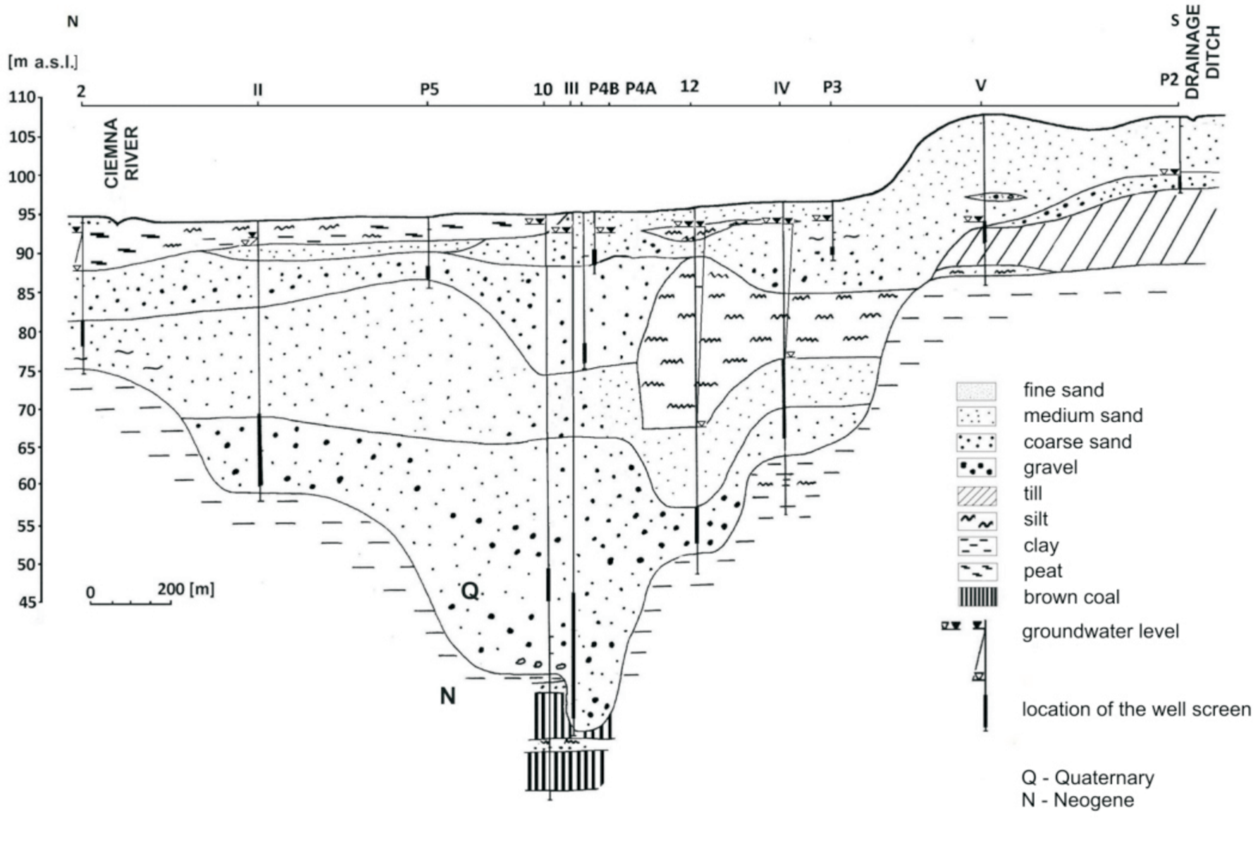

Fig. 2. Hydrogeological cross-section (after Dragon et al., 2016, modified; see Fig. 3 for location)

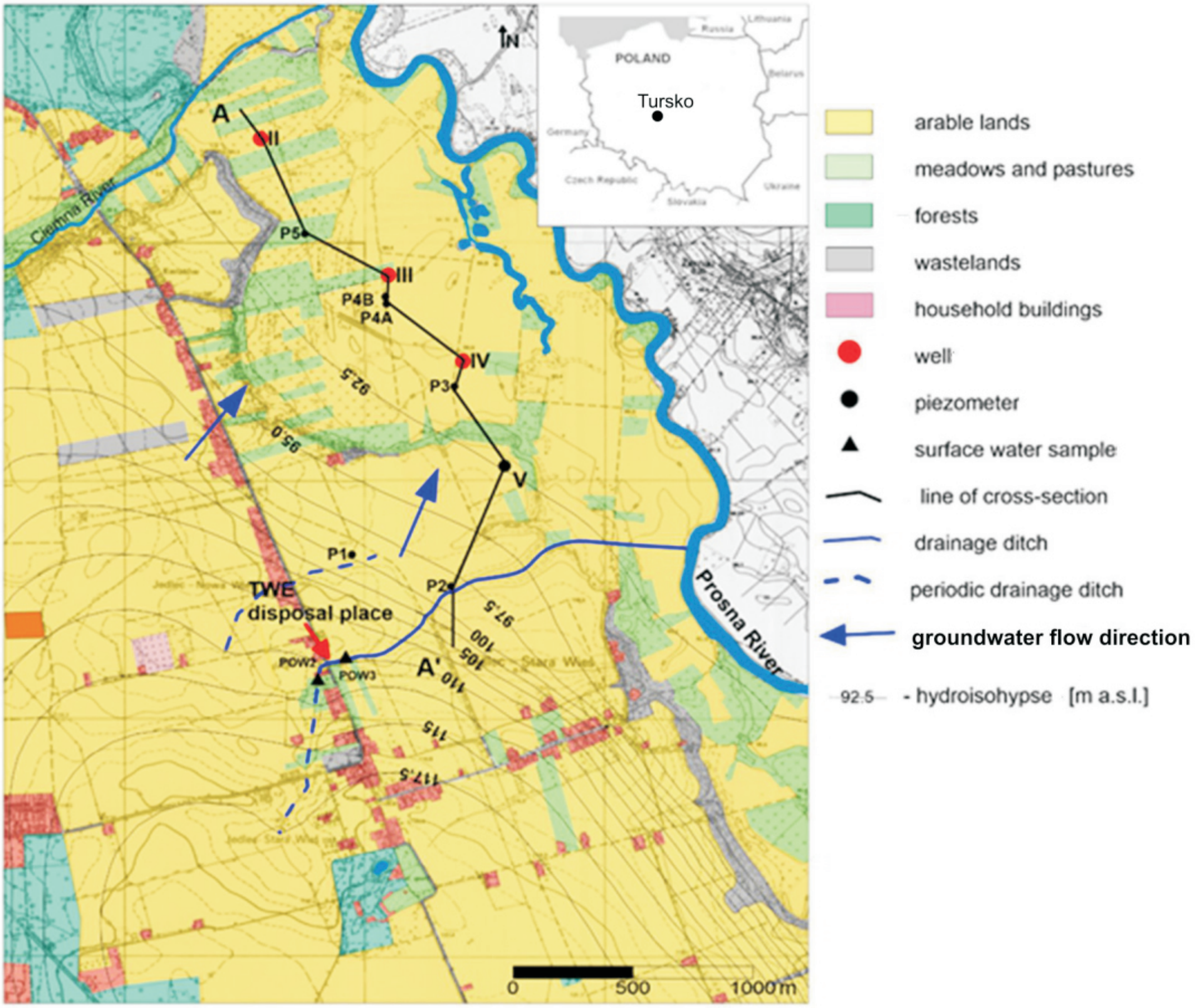

Fig. 3. The study area showing land use types

MATERIALS AND METHODS

In order to investigate the influence of TWE impact on groundwater quality, the surface water, as well as groundwater from piezometers and productive wells, were sampled in the spring of 2020. The sampling campaign included hydrochemical investigation at the following sampling points: TWE, surface water (2 sampling points), piezometers located on the flow lines between the drainage ditches and wells (3 sampling points) and the three productive wells (3 sampling points).

The production wells were pumped for a minimum of 24 h continuously before the sampling period. The piezometers were pumped using a portable pump powered by a battery (Gigant type). Water in the well columns was flushed a minimum of three times before sampling. Two piezometers (P1 and P2) among these sampled previously (Dragon et al., 2016) were not sampled because, during the dry period, water level decreased below the screen and sampling was not possible. The water was sampled into 100-ml HDPE polyethene bottles. The samples for nitrogen compound analyses were treated with chloroform and, for iron, manganese and boron testing were treated with HNO_3. All bottles were rinsed three times and emptied to prevent degassing. After sampling, water samples were immediately (on the same day) transported to the laboratory using a transportable refrigerator. Water alkalinity, electrical conductivity, pH, and temperature were measured directly in the field. The chemical analyses were performed at the Adam Mickiewicz University in Poznań, Poland (Institute of Geology).

The groundwater samples were analyzed for cations (Na^+, NH_4^+, K^+, Ca^{2+}, and Mg^{2+}) and anions (Cl^-, F^-, NO_3^-, NO_2^-, and SO_4^{2-}) using a *Metrohm 881 Compact IC Pro* ion chromatograph. The analytical procedure was described by Górski and Siepak (2014). As a quality control measure, the ionic error balance was calculated. The calculated error did not exceed 3%. Concentrations of Fe, Mn, and B were determined by inductively coupled plasma mass spectrometry (*ICP-QQQ 8800 Triple Quad*, Agilent Technologies). Instrument parameters and the analytical method parameters have been described separately (Siepak and Sojka, 2017). For ion chromatography (IC), *Merck* standard solutions (Merck, Darmstadt, Germany) and *CPAchem* (C.P.A. Ltd. Stara Zagora, Bulgaria) were used. The mobile phase for cations and anions was made from Fluka reagents (Sigma-Aldrich, Steinheim, Switzerland). Determination with the *ICP-QQQ* technique was done using calibration curves obtained from a diluted stock multi-element standard 100 µg/mL (VHG Labs, Manchester, USA). The reagents used were ultrapure, and the water was de-ionized to a resistivity of 18.2 MŮ cm in a *Direct-Q® 3 Ultrapure Water System apparatus* (Millipore, France). Analytical quality control was verified by analysing *SRM 1643f* (National Institute of Standards and Technology, Gaithersburg, USA) and *EnviroMAT™ Ground Water*, ES H1 (SCP SCIENCE, Canada) and high compliance with reference values was found.

The groundwater sampling for pharmaceutical compound measurement included 7 sampling points: TWE, piezometers located on the flow lines between a drainage ditch and the wells (3 sampling points), and the three productive wells. The water samples for pharmaceutical compound analysis were sampled into 100 ml brown glass bottles, stored frozen, and then transported to the analytical laboratory of Povodí Vltavy VHL Plzeň, Czech Republic. Extraction of the compounds investigated was performed using EPA analytical method No. 1694. A *1200 Infinity Ultra-High-Performance Liquid Chromatograph*, equipped with a binary solvent manager and sample manager (UHPLC) coupled with a *6495 Triple Quadrupole Mass Spectrometer* (MS/MS), operated by *MassHunter* software, all of Agilent Technologies (Agilent Technologies Inc. Santa Clara, CA, United States) was used for final determination of the pharmaceutical compounds. The separation was carried out on an *X-bridge C18* analytical column, 100 x 4.6 mm (i.d), 3.5 µm particle size (Waters Corp., Milford, MA, Unites States). The mobile phase consisted of methanol and water with acetic acid and ammonium fluoride as mobile phase additives in gradient mode. The flow rate was 0.5 ml/min. The injection volume was 50 µl.

The groundwater chemistry in a deep part of the aquifer was represented by data from wells. The wells' screen interval is located between the depths of 16.0–30.5 (well II), 42.0–46.0 (well III) and 20.0–31.0 (well IV). The groundwater chemistry in a shallow zone of the aquifer was represented by data from piezometers located between the drainage ditch and wells. These piezometers have screen intervals between 4.5 and 6 m (P3 and P4A) and between 16 and 19 m (P4B).

For the interpretation of temporal changes in groundwater chemistry, the well field monitoring data acquired annually in the spring by the water company were used. These data include the local well field monitoring results collected between 2016 and 2020 (five monitoring series). These data together with previous investigations allow recognition of the impact of TWE on groundwater chemistry during one decade (from 2007, when use of TWE was starting).

Meteorological data (precipitation) were obtained from the Kalisz meteorological gauging station (located ~15 km south), which is maintained by the Institute of Meteorology and Water Management – National Research Institute (IMGW-PIB).

RESULTS

TREATED WASTEWATER CHEMISTRY

The samples for investigation of wastewater chemistry were taken in place, where TWE is discharged into the ditch (Fig. 3). Temporal changes in the wastewater were analysed based on analysis of annually collected water samples (Table 1).

High electrical conductivity (>1000 µS/cm) was observed in the wastewater, while high concentrations of sodium (>125 mg/l), potassium (>26 mg/l) and chloride (usually >150 mg/l) were characteristic. The concentrations of nitrogen compounds were relatively high and very variable. The nitrate concentrations ranged from 5.89 to 83.8 mg/l. The most variable were concentrations of ammonia, usually 1–2 mg/l, but

Table 1

Changes in wastewater chemistry

Parameter	Unit	2012	2013	2014	2016	2017	2018	2019	2020
pH	–	7.04	7.33	7.03	7.80	7.60	7.14	7.40	–
Alkalinity	meq/l	5.6	8.0	7.0	5.5	6.7	6.6	6.3	–
Electrical conductivity	µS/cm	1341	1451	1290	1200	1070	1273	1272	1450
Iron	mg/l	0.34	0.25	0.06	–	0.13	0.18	0.15	0.13
Manganese	mg/l	0.06	0.15	0.03	–	0.05	0.07	0.07	0.04
Boron	µg/l	204.1	170.1	132.4	94.6	94.9	92.0	81.0	91.3
Fluoride	mg/l	0.79	0.66	0.29	0.90	1.00	0.98	0.80	1.20
Chloride	mg/l	159	142	148	47	181	178	190	417
Nitrite	mg/l	2.33	1.05	0.60	1.47	1.43	0.72	0.89	3.47
Nitrate	mg/l	41.6	5.89	17.2	83.8	17.6	14.4	36.8	33.7
Ammonia	mg/l	0.412	21.4	1.19	0.050	1.34	0.430	1.21	1.38
Sulphate	mg/l	121	107	11	83	71	72	63	58
Calcium	mg/l	96	94	96	88	100	100	89	91
Magnesium	mg/l	25	24	23	22	24	24	24	26
Total hardness	meq/l	6.8	8.0	6.7	6.4	4.3	7.1	11.1	6.6
Sodium	mg/l	134	125	135	130	140	150	160	160
Potassium	mg/l	31.3	29.1	29.7	31.0	26.0	26.0	89.0	32.0

concentrations >20 mg/l also appeared periodically. The nitrite concentrations were also relative high, usually >1 mg/l.

A specific attribute of the wastewater was a very high concentration of pharmaceutical compounds (see Table 4). In wastewater effluent of 2020 64 substances among 102 investigated were discovered at concentrations greater than the detection limit (LOQ). The total pharmaceutical compound concentrations were 106 μg/l. The following substances were discovered at concentrations >1.0 μg/l: carbamazepine, diclofenac, hydrochlorothiazide, saccharin, gabapentin, tramadol, carbamazepine-DHH, acesulfame, oxypurinol, fexofenadine, sotalol, telmisartan, metformin, benzotriazole, benzotriazole methyl and sucrose or valsartan acid.

SURFACE WATER CHEMISTRY

Surface water from the drainage ditch was sampled at two places (Fig. 3): one located upstream of the TWE (POW2) and one located downstream (POW3). The changes in surface water chemistry are shown in Table 2 (data based on well field monitoring). The surface water chemistry is characterized by high nitrate concentrations (usually >30 mg/l but in some periods >100 mg/l). High nitrite levels were also characteristic (at times >1 mg/l) and a significantly higher concentration downstream of the wastewater effluent is evident (Table 2). Ammonia concentrations are relatively low (<0.2 mg/l) but very high concentrations of ammonia appear downstream of the TWE periodically (16.5 and 28.2 mg/l). The concentrations of the remaining components (mainly chloride, sodium and potassium) are also significantly higher downstream of the TWE. Boron concentrations follow this behaviour also.

The Ciemna River that flows through the study area (Fig. 3) is located on an area of intensive agricultural production, a nitrate vulnerable zone (NVZ) and was also tested in 2010 and 2013 for pesticide residues (Drożdżyński, 2020). Sums of detected pesticides were, in spring and autumn season 2010, 2.64 and 0.28 μg/l, respectively. In spring and autumn 2013 the sums were similar, 3.22 and 0.24 μg/l, respectively. The results quoted indicate a significant anthropogenic impact on surface waters in the monitored area.

GROUNDWATER CHEMISTRY

Over a relatively small area, distinct differences in groundwater chemistry occur (Dragon et al., 2016). The concentration of chloride in piezometers (shallow aquifer zone) in the area between the drainage ditch and wells were at levels between 37 and 65 mg/l (Table 3). The sulphate concentrations were between 228 and 272 mg/l. The sodium and potassium concentrations were also variable and were between 11 and 23 mg/l and between 2.2 and 3.4 mg/l, respectively. The concentrations of nitrogen compounds were very variable. The nitrate concentrations were between <0.002 and 33.4 mg/l, and nitrite was at levels between <0.001 and 0.191 mg/l. The most variable was ammonia concentration, at between zero and 1.74 mg/l.

Distinct changes in groundwater chemistry were also observed in productive wells (deep aquifer zone). The chloride and sulphate concentrations varied between 38 and 54 mg/l and between 143 and 247 mg/l, respectively. The sodium and potassium concentrations were more stable in the wells and ranged between 19 and 22 mg/l (sodium) and 2.5 and 5 mg/l (potassium). The highest concentrations of nitrate were documented in well IV (16.8 mg/l). This is the well located closest to the drainage

Table 2

Changes in the surface water chemistry

Parameter	Unit	2012	2013	2014	2016	2018	2020					
		POW2	POW3	POW2	POW3	POW2	POW3	POW2	POW3	POW3	POW2	POW3
pH	–	8.18	7.90	7.87	7.95	8.04	7.08	8.00	7.94	7.31	7.61	7.58
Alkalilnity	meq/l	4.2	8.0	3.7	4.3	4.4	6.1	4.5	5.2	6.7	5.0	4.8
Electrical conductivity	S/cm	1051	1306	1007	1179	988	1226	969	1113	1287	1263	1281
Iron	mg/l	0.09	0.20	0.21	0.23	0.03	0.03	–	–	0.15	0.11	0.13
Manganese	mg/l	0.02	0.05	0.07	0.06	0.01	0.02	–	–	0.06	0.02	0.02
Boron	μg/l	–	–	104.5	138.2	103.0	111.5	46.1	77.9	92.0	22.1	47.8
Fluoride	mg/l	0.30	0.68	0.32	0.71	0.29	0.31	0.20	0.60	0.98	0.35	0.66
Chloride	mg/l	76.3	117.3	92.1	129.2	134.9	132.3	35.0	29.0	174.0	120.4	139.5
Nitrite	mg/l	0.230	0.400	0.031	1.01	0.43	1.21	0.542	0.996	0.704	0.027	0.031
Nitrate	mg/l	65.1	31.6	85.2	32.4	59.8	34.5	118.3	93.7	13.1	133.5	100.4
Ammonia	mg/l	0.182	28.2	0.106	16.5	0.095	0.121	0.050	0.030	0.430	0.109	0.118
Sulphate	mg/l	144.4	129.5	142.2	125.6	111.6	107.8	250.0	128.0	74.0	199.2	171.1
Calcium	mg/l	139.1	118.5	159.7	138.7	96.2	106.5	150.0	110.0	100.0	202.7	152.0
Magnesium	mg/l	26.6	26.8	21.9	22.3	23.5	23.1	19.0	21.0	23.0	32.6	31.4
Total hardness	meq/l	9.1	8.1	4.2	7.1	6.7	7.2	8.5	7.1	13.8	12.8	10.2
Sodium	mg/l	27.4	101.9	27.6	89.4	101.4	104.8	28.0	87.0	160.0	36.7	75.3
Potassium	mg/l	8.17	25.9	9.99	23.1	23.4	25.2	9.0	22.0	26.0	10.2	18.6

Table 3

The groundwater chemistry of the Tursko well field (groundwater sampling performed in 2020)

Parameter	Unit	P3	IV	P4A	P4B	III	II
Distance from the drainage ditch	m	820	920	1320	1340	1350	2020
pH	–	7.49	–	7.35	7.64	7.19	7.14
Electrical conductivity	µS/cm	1165	866	998	1050	1136	883
Iron	mg/l	<0.03	1.60	1.03	2.24	4.54	2.77
Manganese	mg/l	0.74	0.82	0.81	1.03	1.02	0.70
Boron	µg/l	–	–	–	–	–	–
Chloride	mg/l	65	39	37	53	38	54
Nitrite	mg/l	0.112	0.007	0.191	<0.001	0.049	0.028
Nitrate	mg/l	33.4	16.8	27.6	<0.002	0.080	0.510
Ammonia	mg/l	<0.001	0.430	0.610	1.74	0.560	0.330
Sulphate	mg/l	250	143	272	228	247	160
Calcium	mg/l	180	130	170	170	190	120
Magnesium	mg/l	27	24	22	26	33	20
Total hardness	meq/l	11.2	8.40	10.2	10.6	12.2	7.60
Sodium	mg/l	23	19	11	21	19	22
Potassium	mg/l	2.20	2.50	3.40	2.50	2.90	5.00

Table 4

Results of pharmaceutical compound investigation

Parameter	Unit	LOQ	Wastewater	P3	IV	P4A	P4B	III	II
Distance from the drainage ditch	m	–	–	820	920	1320	1340	1350	2020
Acesulfam	µg/l	<0.010	4.76	nd	nd	nd	nd	nd	0.067
Bisfenol A		<0.050	0.064	0.090	nd	nd	nd	nd	nd
Caffeine		<0.100	0.236	0.486	nd	0.108	nd	nd	nd
Gabapentin		<0.010	1.69	0.017	0.013	nd	nd	nd	nd
Paraxantine		<0.100	0.401	0.229	nd	nd	nd	nd	nd
Sotalol		<0.010	3.23	0.011	nd	nd	nd	nd	nd
Telmisaltan		<0.020	6.67	0.022	0.119	0.025	0.038	nd	0.022
Metformin		<0.050	9.82	nd	0.024	nd	nd	nd	nd
PFOS		<0.005		0.008	0.005	nd	nd	nd	0.007
Valsartan acid		<0.010	5.81	nd	0.014	nd	nd	nd	nd
Sum of the concentrations		–	32.7	0.863	0.175	0.133	0.038	nd	0.096

LOQ – limit of quantification; nd – not detected

ditch (Fig. 2). The lowest nitrate concentrations in well III were documented at a level of 0.08 mg/l. The total hardness ranged between 7.6 meq/l in well II and 12.2 meq/l in well III.

Pharmaceutical compounds were also determined in the groundwater (Table 4). In 2020 in piezometer P3 7 these substances were detected at a total concentration of 0.863 µg/l, while in well IV 5 substances at a total concentration of 0.175 µg/l were found. The lowest concentrations of pharmaceutical compounds were detected in sampling point P4A (2 substances at a total concentration of 0.133 µg/l), P4B (one substance at a concentration of 0.038 µg/l), and well II (3 substances at a concentration of 0.096 µg/l). In well III pharmaceutical compounds were not discovered.

DISCUSSION

SPATIAL VARIATION OF GROUNDWATER CHEMISTRY

The apparent spatial groundwater chemistry was documented in 2020, and was consistent with trends from a previous study (Dragon et al., 2016). The highest nitrate concentrations occurred closest to the drainage ditch (in sampling point P3 >30 mg/l). Along the flow paths, the concentrations decreased to 27.6 mg/l in piezometer P4A and <0.002 in the deeper piezometer P4B. In well IV (deeper aquifer zone) located between piezometer P3 and P4A the nitrate concentration was 16.8 mg/l (Table 3). This behaviour also followed the chloride concentrations: 65 mg/l in P3, 39 and 37 mg/l in well IV and sampling point P4A, respectively, as well as sodium. The sulphate concentrations show opposite trends: the smallest concentrations were observed in well IV (143 mg/l) and the largest in well III bis (247 mg/l). This trend also followed the total hardness: lowest in sampling points P3 and P4A and well IV (11.2, 10.2 and 8.4 meq/l, respectively) and significantly higher in well III (12.2 meq/l).

The concentrations of pharmaceutical compounds in general follow clear trends of nitrate changes (and also of chloride and sodium). The highest pharmaceutical compound concentrations occurred closest to the drainage ditch and clearly decreased along groundwater flow lines (Table 4). This trend is not represented by changes in well II (located farthest from the drainage ditch), where 2 substances were detected. This differentiation may be caused by infiltration of surface water from the Ciemna River but this question needs further research.

TEMPORAL CHANGES IN GROUNDWATER CHEMISTRY

Analysis of groundwater chemistry took place in the context described by Dragon et al. (2016) and complemented by further water analyses (between 2016–2020). Temporal changes in groundwater chemistry are illustrated in Figure 4 (wells) and Figure 5 (piezometers). A distinct increase in chloride, sulphate, total hardness, and iron and manganese is visible from 2007 in wells II and III (the operation of well IV was started in 2007). This situation was created by the start of constant well field operation since the spring of 2007 (previously, exploitation was sporadic). As the dynamic water level decreased (as the cone of depression formed), the contaminants moved from the shallow part of the aquifer to the deepest parts (well screen interval), especially in wells II and III, where unconfined conditions occur. From 2016 a sharp increase in sulphate concentration was observed, to levels of >450 mg/l. An increase of total hardness was also noted at this time, with a concentration of >12 meq/l. Concentrations of both compounds exceeded the parametric value for drinking water which is 10 meq/l (500 mg $CaCO_3$/l) (Rozporzadzenie, 2017). At the same time, concentrations of chloride increased by ~10–20 mg/l. Concentrations of iron and manganese (and also alkalinity) were relatively stable after the sharp increase in 2007. The concentration of ammonia after a clear sharp in 2007 was also relatively stable. In contrast, nitrate concentrations differed especially in well IV, where a stable concentration increase was visible first after starting well operation in 2007 and then from 2014. In wells II and III, after small increases in 2007 (at low concentrations), the nitrate level remained relatively low.

Groundwater chemistry in the shallow aquifer zone has been investigated in a piezometer network since 2012, and showed similar temporal changes to those observed in the wells. The most distinct is a clear sharp increase in sulphate concentrations observed from 2016 to 2018. Similar increases were observed in chloride and total hardness. A distinct increase in nitrate was observed in 2019 in shallow piezometers (P3 and P4A).

IDENTIFICATION OF TREATED WASTEWATER IMPACT ON GROUNDWATER CHEMISTRY

The main processes influencing groundwater chemistry in the recharge zone of the Tursko well field are the oxidation of organic matter and sulphides in the vadose zone and denitrification (Dragon et al., 2016). Both processes create quite similar groundwater chemistry changes, while their difficulty in interpretation stem from both processes (especially denitrification) being controlled by local biogeochemical conditions that are usually spatially and temporally variable (Rivett et al., 2008). In the case of oxidation of organic matter, there is an increase in sulphate and iron concentrations as well as in total hardness (Porowski et al., 2019), while denitrification causes increase in sulphate and total hardness (denitrification products – Bennekom et al., 1993). Autotrophic denitrification was indicated as a dominant process previously (Dragon et al., 2016). In general, the current study supports the earlier findings. Sulphate concentrations and total hardness (denitrification products) occurred in groundwater still at a very high level, especially in well III, where both parameters exceeded the parametric value for drinking water (Fig. 4), while very high levels were also found in the shallow zone in water sampled in piezometers. Sulphate concentrations persisted at concentrations higher than 200 mg/l, and total hardness at a level >10 meq/l. As a result of denitrification, nitrate concentrations are very low in the wells (Fig. 4 and Table 3).

The clear sharp increase in sulphate concentration and total hardness level is related to hydrological conditions. These increases are observable in relative wet (rainy) conditions that occur after a long hydrological drought. This was the case in 2016 when the rainy season occurred after the long dry season in 2011–2014 and the very dry year 2015 (Fig. 6). This caused a sharp increase in sulphate and total hardness levels (Figs. 4 and 5). An evident and sharp concentrations increase was also observed in 2020, especially in the shallow aquifer zone (Fig. 5), following wet weather conditions after dry seasons occurred in Poland in 2018 and 2019 (Fig. 6). This is the reason for the influence of both processes – denitrification and organic matter oxidation – during the dry season (lower water level). Both processes occur mainly in the shallow aquifer zone. The migration of the products of both processes after more intensive effective infiltration during the wet season to the deeper parts of the aquifer, especially during a wet season preceded by a long dry period (Figs. 4 and 5).

Both documented processes (organic matter oxidation and denitrification) are evident in wells II and III, while groundwater chemistry in well IV has a different origin. This is the well located closest to the drainage ditch, near to the floodplain boundary (Figs. 2 and 3). This well most probably receives shallow groundwater percolating through the aquitard in the marginal part of the floodplain (Dragon et al., 2016). The hydrogeochemical evidence suggests that an unrecognized “hydrogeological window” occurs there. This vertical percolation occurs before water reaches the floodplain terrace (Fig. 2). As a result, a high concentration of nitrate was documented there (and its increase during well operation), relatively low and stable concentrations of sulphate and of and total hardness (Fig. 4). This is because this water is only partially denitrified.

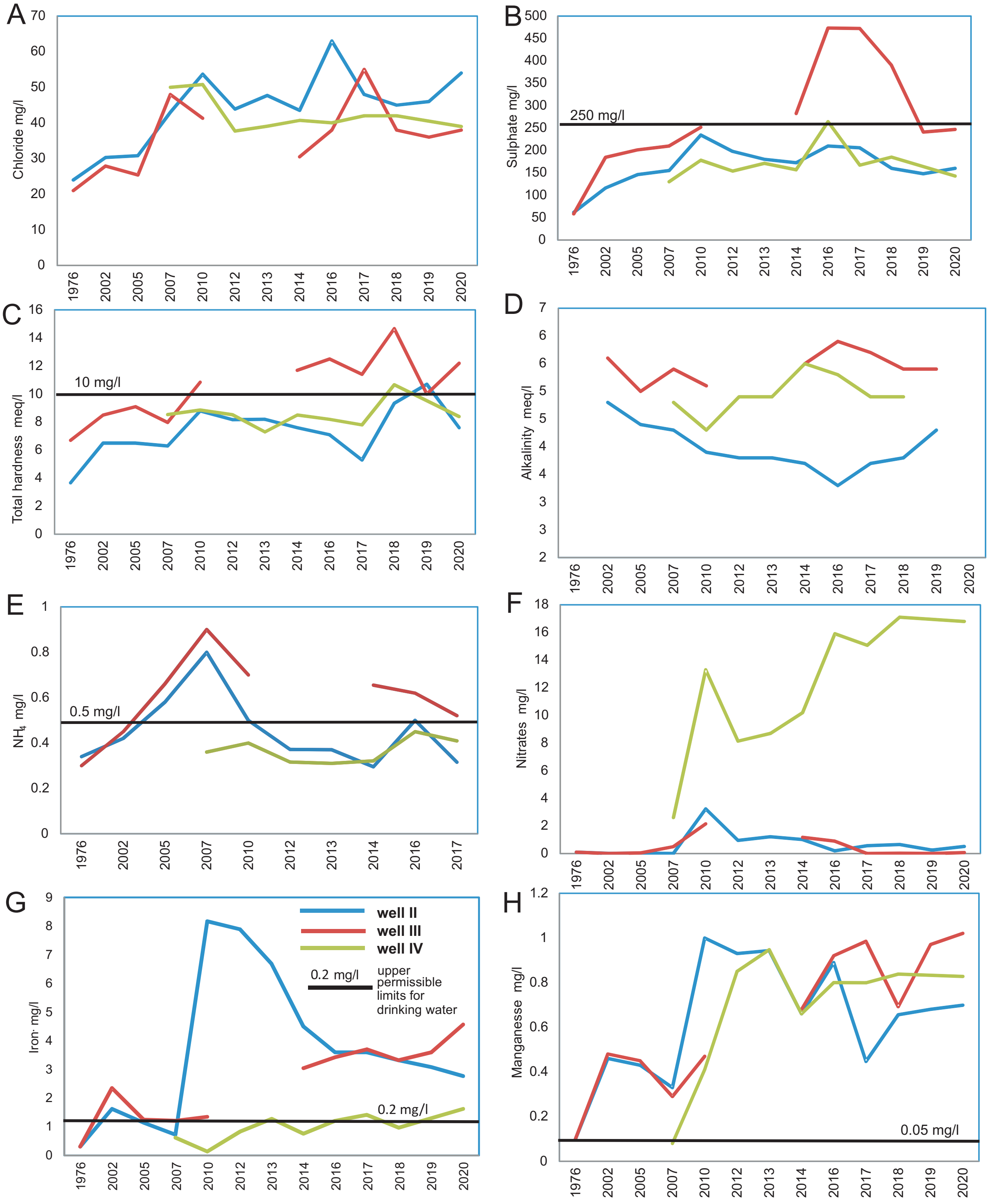

Fig. 4. Temporal changes of groundwater chemistry in the wells (deep aquifer zone)

In the period between IV 2010 and XII 2013 well III was not operated

The spatial differentiation of groundwater chemistry indicates that the primary source of groundwater pollution is the drainage ditch which carries polluted water from drainage pipes and TWE from the sewage treatment station. It is known that nitrogen compounds are supplied to groundwater by both TWE and drainage systems (DeSimone and Howes, 1998; Foster and Chilton, 2004; Dragon et al., 2016). The concentrations of nitrate are the highest close to the ditch and decrease along flow lines due to denitrification. As a consequence, the nitrate concentrations in wells II and III are very low (<2 mg/l), but

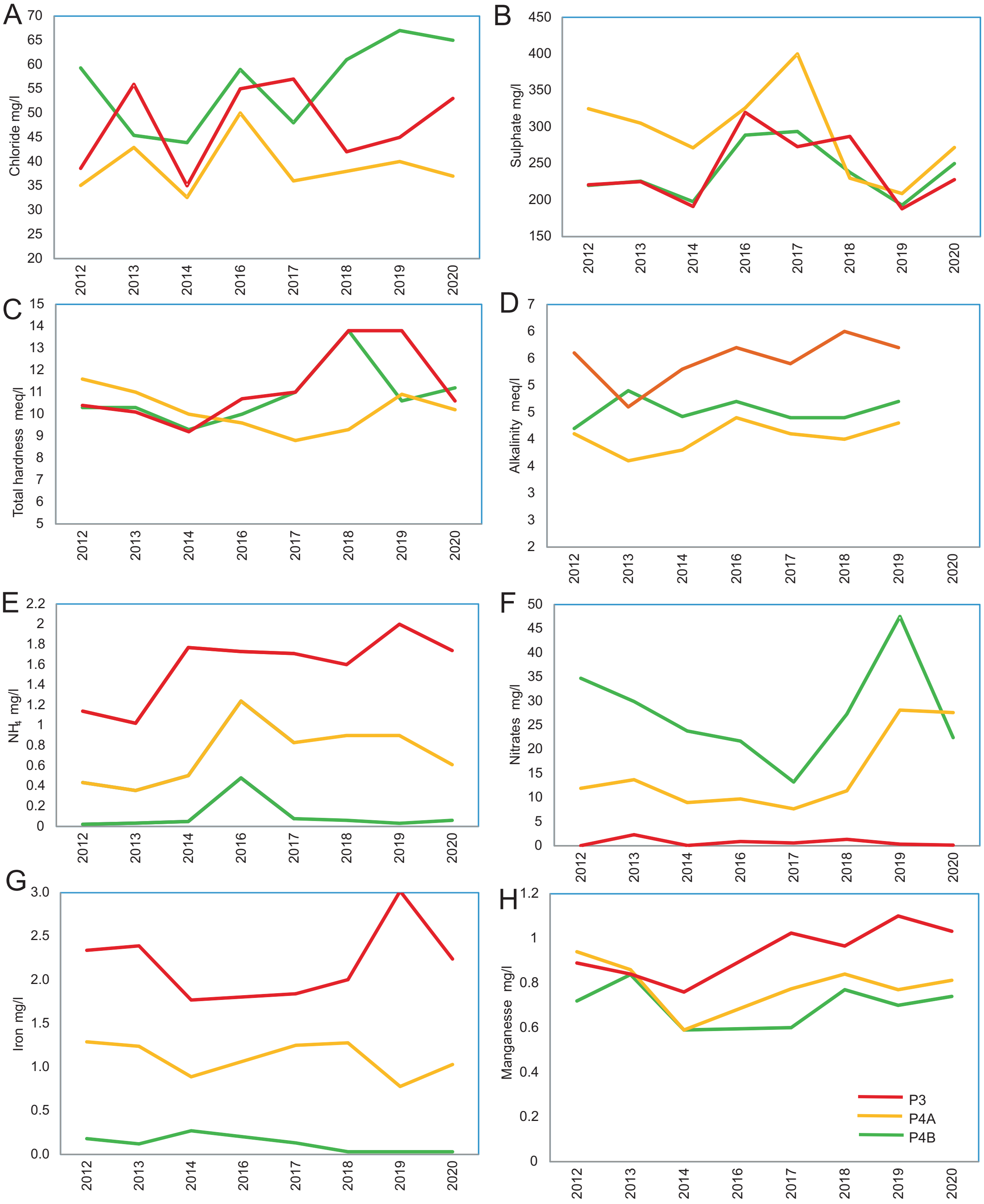

Fig. 5. Temporal changes in groundwater chemistry in observation wells (shallow aquifer zone)

denitrification products increase (total hardness and sulphate exceed the parametric value for drinking water in well III). The influence of drainage water is limited to the relative wet periods because during hydrological droughts (as in 2018 and 2019) the drainage pipes are not active. In these periods, the ditch received only TWE from the sewage treatment station because this recharge component is stagnant. In that case, during dry seasons the drainage ditch carries only wastewater. This causes a recharge by groundwater carrying a high content of organic matter. This matter activates or intensifies denitrification by enriching electron donors and nutrients for denitrifying bacterial growth (Feast et al., 1998; Rivett et al., 2008). The wastewater also supports the oxidation of organic matter in recharging the aquifer with additional, oxidisable organic matter.

The influence of TWE is shown by pharmaceutical compounds detected in both source surface water (at very high con-

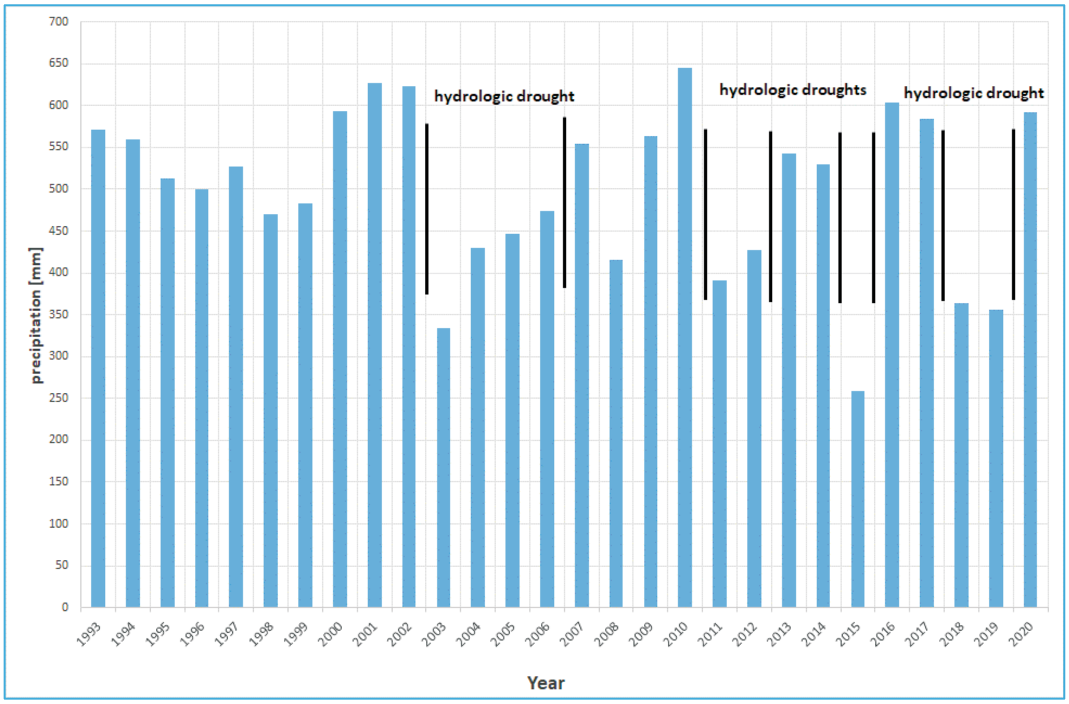

Fig. 6. Average annual precipitation in the Prosna River catchment (Kalisz meteorological gauging station)

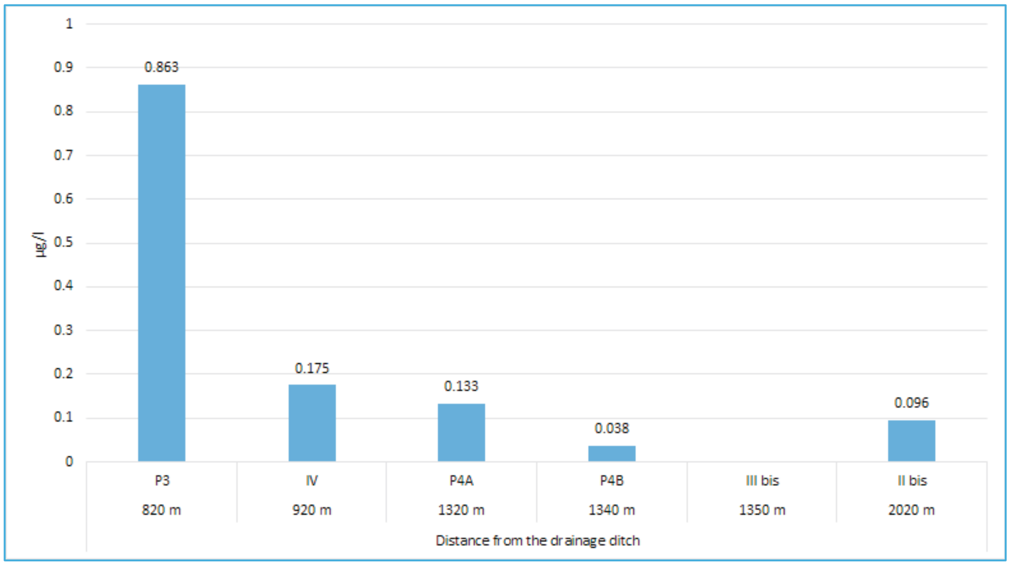

Fig. 7. The sum of pharmaceutical compound concentrations along flow path

centrations) and groundwater. These anthropogenic chemicals are used as a tracer of TWE influence (Van Stempvoort et al., 2013). The spatial differentiation of the pharmaceutical compounds in the groundwater expressly indicates the TWE influence (Fig. 7). A clear decrease in pharmaceutical compounds was observed especially in 2020. Close to the drainage ditch, the sum of pharmaceutical compound concentrations and the number of substances detected was the highest (in the P3 sampling point). Then the concentrations and numbers of detected substances decrease systematically along flow paths (Table 4). Pharmaceutical compounds were detected in productive well IV (located closest to the ditch and receiving shallow groundwater through “hydrogeological window” percolation). Along the flow path, the concentrations of the pharmaceutical compounds decreased systematically and in well III these substances was not detected. The spatial differentiation of these substances most probably is controlled by biodegradation (Maeng et al., 2010; Kruć et al., 2019). Additionally, drugs show a similar differentiation. Caffeine was detected in the P3 and P4A sampling points, decreasing along the flow path, while paraxanthine (a caffeine metabolite) was detected in the P3 sampling point (nearest to the contamination source).

The detection of pharmaceutical compounds in groundwater and their spatial differentiation means these substances can be used as anthropogenic tracers of TWE influence, and for the identification of contamination origin. Investigation of pharmaceutical compounds in TWE and groundwater indicates that infiltration of wastewater is a significant factor influencing groundwater drinking-water quality. This research shows a need for pharmaceutical compound monitoring in drinking water as well as monitoring of groundwater in the recharge zone of well fields. Understanding the environmental consequences of wastewater-derived contaminants is crucial for the adequate protection of water supply aquifers. The distinct increase of water components concentrations over time indicates a serious hazard as regards groundwater quality deterioration. This finding should be taken into consideration in thinking about water resources protection for the next generations (Dragon, 2012).

CONCLUSIONS

Anthropogenic impact on groundwater in the water supply aquifer was documented in the Tursko well field's recharge zone (South Wielkopolska, Poland). The infiltration of surface water causes groundwater contamination. The surface water is contaminated by both drainage systems and treated wastewater effluent. The drainage ditch, located in the well field's recharge area, receives drainage water from arable land and treated wastewater from the sewage treatment station. This causes the surface water to be strongly contaminated with a high content of organic matter, nutrients, and macrocomponents. In recent years also a high content of pharmaceutical compounds was investigated. The contaminated water from the ditch infiltrates into the groundwater system and then migrates along flow lines from the contamination source to productive wells.

In the context of a previous investigation, it was documented that the contaminated surface water impact is the main hydrogeochemical factor influencing groundwater chemistry. The infiltration of this water activates or intensifies hydrogeochemical processes in the aquifer (mainly denitrification) because a supply of groundwater with organic matter and nutrients for bacterial growth are indispensable for the development of denitrification. The primary source of contamination is treated wastewater effluent because the drainage water influence is limited to the wet periods when the drainage pipes are active. During the last dry period (in the years 2018 and 2019), the drainage systems were active only occasionally (after heavy rain). In contrast, the treated wastewater effluent is active all the time and provides constant recharge of surface water.

High levels of groundwater contamination were documented, reflected mainly by high nitrate concentrations. These concentrations are the highest close to the ditch and decrease systematically along the flow lines due to denitrification. At the same time, increasing concentrations of sulphate and total hardness occur (denitrification products), exceeding the parametric value for drinking water in the productive wells. However, the contamination level is significantly higher during wet periods following long hydrological droughts when sharp increases in sulphate and total hardness were observed due to oxidation of organic matter and sulphides. These processes have similar effects on groundwater chemistry and overlap with those from denitrification.

The occurrence of pharmaceutical compounds allows identification of the influence of treated wastewater on groundwater chemistry, by using these substances as anthropogenic tracers. The investigation shows a very high level of pharmaceutical compounds in the treated wastewater. These substances infiltrate into the groundwater system and then migrate along flow paths. As a result, the concentration of pharmaceutical compounds in groundwater is higher in sampling points located closest to the contamination source (the drainage ditch) and systematically decreases along the flow lines.

This research is an example of how an anthropogenic tracer (pharmaceutical substances) can be used for identification of wastewater impact as well as for the determination of contamination sources. It indicates a requirement for pharmaceutical compound monitoring in drinking water as well as monitoring of groundwater in the recharge zones of well fields. Understanding the environmental consequences of wastewater-derived contaminants is crucial for the effective protection of water supply aquifers.

Acknowledgements. The authors would like to thank the Municipal Company in Pleszew (Pleszew Waterworks operator) for its contribution. This work was financial supported by the Faculty of Geographical and Geological Sciences (Adam Mickiewicz University in Poznań, Poland) – internal grant: Subsidy for the maintenance and development of research potential.

REFERENCES

Asano, T., Cotruvo, J., 2004. Groundwater recharge with reclaimed municipal wastewater: health and regulatory considerations. Water Research, **38:** 1941–1951.

Bennekom, C.A., Kruithof, J.C., Krajenbrink, G.J.W., Koo, H.J., 1993. Effect of nutrient leaching on groundwater and drinking water. Water SRT Aqua, **42:** 77–87.

DeSimone, L., Howes, B., 1998. Nitrogen transport and transformations in a shallow aquifer receiving wastewater discharge: a mass balance approach. Water Resources Research, **34:** 271–285.

Dragon, K., 2012. The changes of groundwater chemistry of semi-confined buried valley aquifer during one decade of water exploitation. Environmental Earth Sciences, **65:** 1283–1290.

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

Dragon, K., Górski, J., Kruć, R., Drożdżynski, D., Grischek, T., 2018. Removal of natural organic matter and organic micropollutants during riverbank filtration in Krajkowo, Poland. Water, **10.**

Dragon, K., Drozdzynski, D., Gorski, J., Kruc, R., 2019. The migration of pesticide residues in groundwater at a bank filtration site (Krajkowo well field, Poland). Environmental Earth Sciences, **78.**

Drożdżynski, D., 2020. Pozostałości środków ochrony roślin w wodach powierzchniowych na terenach intensywnie użytkowanych rolniczo (in Polish). Scientific dissertations of Institute of Plant Protection – National Research Institute, **33**.

El Heloui, M., Mimouni, R., Hamadi, F., 2016. Impact of treated wastewater on groundwater quality in the region of Tiznit (Morocco). Journal of Water Reuse and Desalination, **6:** 454–463.

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

Fisher, I., Fisher, I.J., Phillips, P.J., Colella, K.M., Fisher, S.C., Tagliaferri, T., Foreman, W.T., Furlong, E.T., 2016. The impact of onsite wastewater disposal systems on groundwater in areas inundated by Hurricane Sandy in New York and New Jersey. Marine Pollution Bulletin, **107:** 509–517.

Foster, S., Chilton, P., 2004. Downstream of downtown: urban wastewater as groundwater recharge. Hydrogeology Journal, **12**: 115–120.

Górski, J., Siepak, M., 2014. Assessment of metal concentrations in tap-water – from source to the tap: a case study from Szczecin, Poland. Geologos, **20:** 25–33.

Jampani, M., Liedl, R., Hulsmann, S., Sonkamble, S., Amerasinghe, P., 2020. Hydrogeochemical and mixing processes controlling groundwater chemistry in a wastewater irrigated agricultural system of India. Chemosphere, **239.**

Kibuye, F.A., Gall, H.E., Elkin, K.R., Ayers, B., Veith, T.L., Miller, M., Janob, S., Hayden, K.R., Watson, J.E., Elliott, H.A., 2019. Fate of pharmaceuticals in a spray-irrigation system: from wastewater to groundwater. Science of the Total Environment, **654:** 197–208.

Kondor, A.C., Jakab, G., Vancsik, A., Filep, T., Szeberenyi, J., Szabo, L., Maasz, G., Ferinsz, A., Dobosy, P., Szalai, Z., 2020. Occurrence of pharmaceuticals in the Danube and drinking water wells: efficiency of riverbank filtration. Environmental Pollution, **265:** 114893.

Kruć, R., Dragon, K., Górski, J., 2019. Migration of pharmaceuticals from the Warta River to the aquifer at a riverbank filtration site in Krajkowo (Poland). Water, **11.**

Maeng, S.K., Ameda, E., Sharma, S.K., Grutzmacher, G., Amy, G.L., 2010. Organic micropollutant removal from wastewater effluent-impacted drinking water sources during bank filtration and artificial recharge. Water Research, **44:** 4003–4014.

Massmann, G., Nogeitzig, A., Taute, T., Pekdeger, A., 2008. Seasonal and spatial distribution of redox zones during lake bank filtration in Berlin, Germany. Environmental Geology, **54:** 53–65.

Muller, B., Scheytt, T., Asbrand, M., de Casas, A., 2012. Pharmaceuticals as indictors of sewage-influenced groundwater. Hydrogeology Journal, **20:** 1117–1129.

Obeidat, M., Awawdeh, M., Al-Mughaid, H., 2013. Impact of a domestic wastewater treatment plant on groundwater pollution, north Jordan. Revista Mexicana de Ciencias Geologicas, **30:** 371–384.

Petrie, B., Barden, R., Kasprzyk-Hordern, B., 2015. A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. Water Research, **72:** 3–27.

Porowski, A., Porowska, D., Halas, S., 2019. Identification of sulfate sources and biogeochemical processes in an aquifer affected by peatland: insights from monitoring the isotopic composition of groundwater sulfate in Kampinos National Park, Poland. Water, **11**: 1388.

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

Rozporządzenie Ministra Zdrowia z dnia 07 grudnia 2017 r. w sprawie jakości wody przeznaczonej do spożycia przez ludzi (Dz.U. 2017 nr 2294) (in Polish).

Siepak, M., Sojka, M., 2017. Application of multivariate statistical approach to identify trace elements sources in surface waters: a case study of Kowalskie and Stare Miasto reservoirs, Poland. Environmental Monitoring and Assessment, **189**.

Strenn, B., Clara, M., Gans, O., Kreuzinger, N., 2004. Carbamazepine, diclofenac, ibuprofen and bezafibrate – investigations on the behaviour of selected pharmaceuticals during wastewater treatment. Water Science and Technology, **50:** 269–276.

Su, D., Ben, W., Strobel, B., Qiang, Z., 2020. Occurrence, source estimation and risk assessment of pharmaceuticals in the Chaobai River characterized by adjacent land use. Science of the Total Environment, **712**.

Tran, N., Hu, J., Li, J., Ong, S., 2014. Suitability of artificial sweeteners as indicators of raw wastewater contamination in surface water and groundwater. Water Research, **48:** 443–456.

Van Stempvoort, D., Van Stempvoort, D.R., Roy, J.W., Grabuski, J., Brown, S.J., Bickerton, G., Sverko, E., 2013. An artificial sweetener and pharmaceutical compounds as co-tracers of urban wastewater in groundwater. Science of the Total Environment, **461:** 348–359.