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Factors affecting the concentrations of pharmaceutical compounds in river and groundwaters: efficiency of riverbank filtration (Mosina-Krajkowo well field, Poland)

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Pharmaceutical compounds were investigated in river and riverbank filtration (RBF) water at the Mosina-Krajkowo site (Poland), in 6 sampling campaigns between November 2019 and June 2020. All of the ten pharmaceutical compounds tested for were detected in the water. Carbamazepine, fluconazole, tramadol, sulphamethoxazole and sulphapyridine were the most frequently found, the highest concentrations being observed in surface water. There was a reduction in their levels in the horizontal well (HW) with drains located below the river bottom, averaging 17%. Significantly higher reductions (53–71%) were observed in vertical wells (VWs). Mixing, sorption and biodegradation were distinguished as processes conditioning the reduction of pharmaceutical compounds along flow paths from the river to the wells. Their reduction in the HW occurs due to sorption onto fine sediments with high organic matter content and aerobic biodegradation, while in the VWs it is the effect of aerobic biodegradation and water mixing with unpolluted groundwater. Sorption on riverbed fine sediments can also occur, especially during low water levels in the river. Biodegradation develops in oxic conditions with aerobic bacteria. VWs located at similar distances from the river yielded different concentrations of pharmaceutical compounds, because of differences in geological structure, hydrogeological conditions and well operation parameters.

Key words: pharmaceutical compounds, riverbank filtration, sorption, biodegradation, water mixing

INTRODUCTION

The growing demand for water and the need to protect groundwater resources makes it necessary to search for alternative methods of obtaining drinking water. One of the methods used to enrich water resources is riverbank filtration (RBF). RBF is a cost-effective and sustainable natural water treatment process (Maeng et al., 2013). In RBF systems, surface water infiltrates through the river bank/riverbed and then flows through the aquifer media from the source (river) to the wells. As a result, processes occur that improve surface water quality, such as dilution, filtration, adsorption, biodegradation and redox reactions (Hiscock and Grischek 2002; Ray et al., 2002; Schubert, 2002; Weiss et al., 2005). This method is common in Europe and North America and is gaining popularity in India and Egypt (Sandhu et al., 2011; Ghodeif et al., 2016; Abdelrady et al., 2019). RBF systems significantly reduce concentrations of chemical and biological pollutants in the water and effectively reduce emerging contaminant concentrations such as pharmaceutical compounds (Benotti et al., 2012; D'Alessio et al., 2018; Nagy-Kovács et al., 2019).

River waters around the world are often contaminated with pharmaceutical compounds, such as human and veterinary antibiotics, endocrine disruptors, antiepileptic, antidepressant, antifungal, analgesic, antibacterial and analgesic drugs (Vieno et al., 2007; Kasprzyk-Hordern et al., 2009; Li, 2014; Sui et al., 2015; Styszko et al., 2021). These are increasingly frequently detected pollutants, and their sources in river water are municipal and hospital wastewater, landfills, farms and livestock farms (US EPA, 2006; Sui et al., 2015; Ślósarczyk et al., 2021). Pharmaceutical products are included (antibiotics, hormones) or are candidates to be included (sulphamethoxazole, fluconazole, carbamazepine and gabapentin) on the European Union Watch list (Gomez Cortes et al., 2020). Some, such as carbamazepine, diclofenac and sulphamethoxazole, have already been detected in tap water (Tauber, 2003; Kleywegt et al., 2011).

Most pharmaceutical products are persistent, chemically stable and degradation-resistant compounds. A common removal process of pharmaceutical compounds is by adsorption,

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which can occur on clay, fine-grained sediments or organic matter (Sui et al., 2015; Thiebault et al., 2015). Zuehlke et al. (2004) and Reddersen et al. (2002) described sorption as the primary removal process for some kind of pharmaceutical compounds (phenazone). Other studies indicate that pharmaceutical compounds are biodegradable or partially biodegradable, and their behaviour along flow paths depends on the hydrogeochemical conditions, e.g., redox conditions (Massmann et al., 2006; Burke et al., 2014). Many compounds are more quickly degraded under oxic conditions than in the absence of oxygen (Kovačević et al., 2017). Microbial degradation is attributed to aerobic bacteria (Sauber et al., 1977; Lingens et al., 1985; Zuehlke et al., 2004). A decrease in the concentration of pharmaceutical compounds may also be caused by mixing infiltrate water with unpolluted groundwater (Heberer et al., 2004).

Degradation of pharmaceutical compounds depends on their physical and chemical properties (Szymonik et al., 2017) and on hydrogeochemical conditions (Dillon et al., 2020). To reduce their concentrations, site-specific conditions should be considered (Nagy-Kovács et al., 2018). The degree of reduction may vary from site to site because of several factors influencing pharmaceutical compound behaviour (e.g., geological structure, hydrogeological and hydrochemical conditions, flow path lengths and travel times).

Previous studies conducted at the Mosina-Krajkowo site (west Poland) have detected organic micropollutants in the river and in RBF wells (Dragon et al., 2018, 2019; Kruć et al., 2019). A significant role of the RBF system in the removal of pharmaceutical compounds was documented, increasingly so with increasing distance from the river. The lowest reduction rate (~30%) was found in the horizontal well (HW) and observation wells located close to (11 and 38 m from) the river. A higher reduction rate of 70–80% was found in vertical wells (VWs) located at distances of not 60 m. At a distance of 250 m, only the most persistent compounds, such as carbamazepine, were detected. In the well located 680 m from the river, no pharmaceutical compounds were detected. A gradual decrease was noticed along the flow paths. However, identification of factors and processes that determine the behaviour of the pharmaceutical compounds was not made.

The main goals of the present study are the determination of:

- RBF water treatment efficiency in different types of wells (the HW and VWs);
- the factors and processes determining migration and attenuation of pharmaceutical compounds.

MATERIALS AND METHODS

STUDY AREA

The research was conducted at the Mosina-Krajkowo RBF well field abstracting water for the Poznań agglomeration (western Poland). The object is located on the left bank of the Warta River (272.5–274.5 km along the river's course). The well field consists of (1) Krajkowo Island: 29 RBF VWs, 1 RBF HW and 11 artificial recharge wells situated on the flood plain and (2) a group of 56 wells located on a higher terrace 400–1000 m from the river. The research was carried out on Krajkowo Island using the HW with drains located 5 m below the river bottom, 4 RBF VWs located at a distance of 55–80 m from the river (1AL, 19L, 24L and 34L) and two observation wells located at distances of 11 and 38 m from the river (168b/2 and 177b/1; Fig. 1 and Table 1). The well field on Krajkowo Island was operated at an average capacity of 50,000 m^3/d during the study period.

In the study area, there are very favourable hydrogeological conditions for water abstraction. The Quaternary aquifer succession is 40 m thick. The deeper part of the aquifer comprises

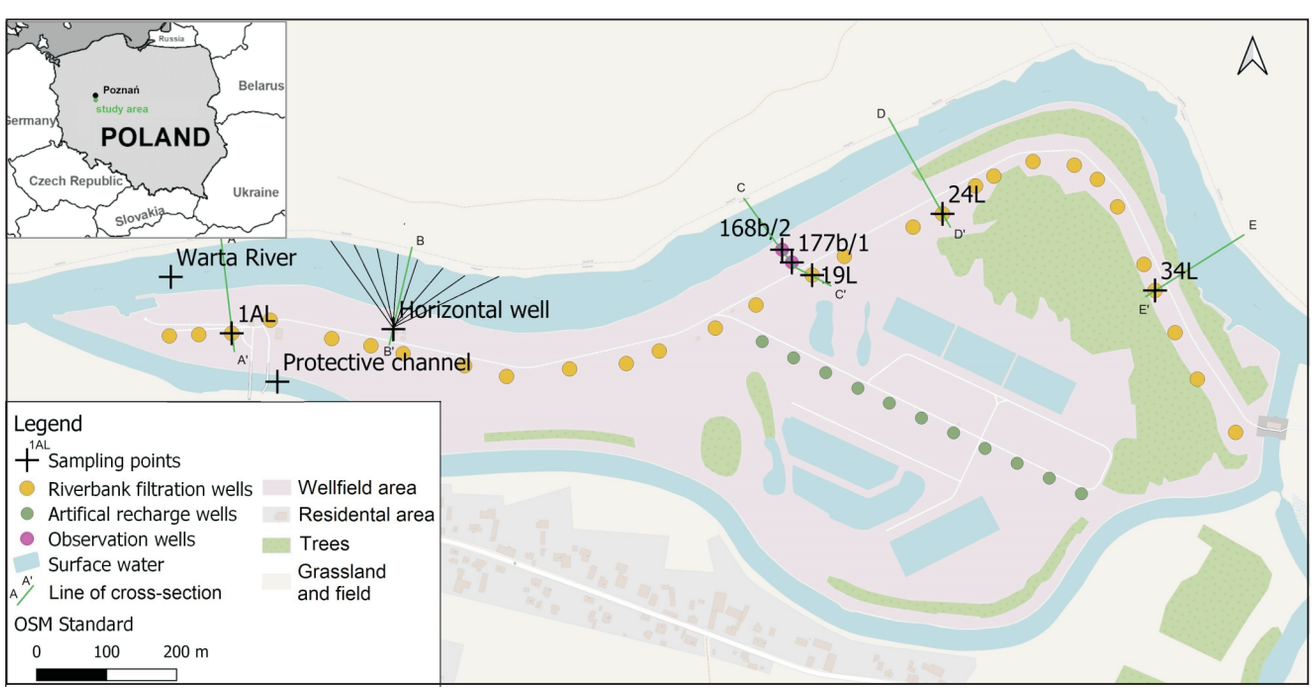

Fig. 1. Location map of the Mosina-Krajkowo well field

Table 1

Characterization of the VWs tested (Górski et al., 2018)

Wells	Ground level [m a.s.l.]	Groundwater level [m a.s.l.]			Mean hydraulic gradient	Hydraulic conductivity *k* [m/d]	Capacity [m^3/h]	Distance from the riverbank [m]	Travel time [months]	Screen [m b.g.l.]
		min	max	mean						
1AL	60.04	47.96	56.77	52.1	0.056	44.4	69	80	1–3	16.1–33.6
19L	58.93	53.47	55.62	54.09	0.038	93.6	102	65	1–3	16.0–21.0 & 24.0–32.0
24L	59.07	51.64	54.91	52.48	0.064	92.4	154	67	1–3	13.1–32.0
34L	59.58	–	–	–	–	26.2	87	55	1–3	23.0–35.0

deposits of the Wielkopolska Buried Valley (WBV), while its shallower part is composed of deposits of the Warsaw-Berlin Ice-Marginal Valley (WBIMV). The WBV deposits are Quaternary coarse-grained fluvioglacial sands and gravels and fluvial fine- and medium-grained sands. The WBIMV deposits are Quaternary fluvioglacial coarse-grained sands and fluvial fine- and medium-grained sands. Apart from lenses of clay, mud and peat, the WBV and WBIMV are locally separated by glacial tills (~10 m thick). Below the aquifer, there are Neogene clays. The geological structure and hydrogeological conditions in the area of the production wells (HW, 1AL, 19L, 24L, 34L) are shown in cross-sections (Fig. 2).

In the area of the HW drains, fine- and medium-grained sediments dominate. Among the VWs, the most complex geological structure is found in 19L and 1AL. In the case of 19L, it was necessary to separate the filter screens of the well, because of clays and mud. Coarse sands, gravel and sandy gravel occur in the aquifer in 24L and 34L, resulting in the most favourable conditions for infiltration. The river bottom shape, described by Przybyłek et al. (2017), differs between individual stretches. The greatest river depth occurs at the river bend, with shallower water in straight parts of the river (Fig. 2).

As regards the aquifer parameters, the hydraulic conductivity is highest in the area of 19L (93.6 m/d) and 24L (92.4 m/d) and lowest in 34L (26.2 m/d) and 1AL (44.4 m/d) (Table 1). The smallest hydraulic gradient value is 0.038 in 19L, and the highest is 0.064 in 24L. The VWs are filtered at different depths and their screens have different lengths (Fig. 2). The lowest depth of filtering and the longest screen are in the 24L well, and the highest depth and the shorter screen are in 34L. The four selected RBF VWs were operated at different capacities. The highest values were achieved by well 24L (154 m^3/h) and the lowest by 1AL (69 m^3/h) (Table 1).

In the well field area, continuously automatic measurements of the water level and temperature in the river and temperature in selected wells (including 24L and 34L) are carried out using loggers (Fig. 3A, B). Sudden temperature fluctuations in the wells result from interruptions in the operation of the well. The well's capacity is measured in each well. Precipitation was measured at the Ecological Station in Jeziory of the Adam Mickiewicz University (Poznań, Poland), located 10 km from the well field.

The research was carried out during relatively low water levels in the Warta River (Fig. 3A). The first four sampling campaigns took place at higher water levels (November and December 2019, January and February 2020), the next two at lower (April and June 2020). The highest precipitation levels were observed in November 2019, February 2019 and June 2020. The lowest was in December 2019 and April 2020.

River water temperature is the factor that determines the continuity of the RBF well field operation. A high temperature of the source water hinders the engineering water treatment process by causing bacterial growth on the granulated active carbon filters, so the well field does not operate during the summer months. At the turn of years 2019 and 2020, the well field was operating between November 2019 and June 2020, though not before and after this period.

SAMPLING

Surface and RBF water samples (8 sampling points) were taken in 6 sampling campaigns (November and December 2019, January, February, April and June 2020). The research period covered the annual work cycle of the well field. The samples were not collected in March and May 2020 as the well field area could not be entered because of the SARS-COV-2 pandemic.

The river water samples were taken using a scoop mounted on a 6 m long stick. The observation wells were pumped using a portable submersible pump 12V WaSP P3. The HW and VWs were pumped continuously during the sampling campaigns. The following parameters were measured directly in the field using multi-parameter water quality *Aquaread AP-800* equipment: temperature (T), pH, redox potential (ORP), dissolved oxygen (DO) and electric conductivity (EC). The alkalinity was measured in the field by fitration. The water samples were stored in HDPE bottles (standard water analysis) and dark glass bottles [Pharmaceutical active compound (PhAC) analysis]. Immediately after fieldwork, the refrigerated samples were delivered to the laboratory.

STANDARD WATER ANALYSIS

Standard water analyses were performed in the Adam Mickiewicz University Laboratory (Poznań, Poland) using a Metrohm ion chromatograph: the *881 Compact IC Pro* model (Metrohm, Switzerland). Anion (Cl^-, NO_3^-, NO_2^-, SO_4^{2-}) determination was made using a *Metrosep A Supp 4/5 Guard* (guard column) and *Metrosep A Supp 5* (separating column). The mobile phase employed was 3.2 mmol Na_2CO_3/1.0 mmol $NaHCO_3$, which flowed at 0.7 ml min^{-1}. Cation (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) determination was done using a *Metrosep C4 Guard* (guard column) and *Metrosep C4 150* (separating col-

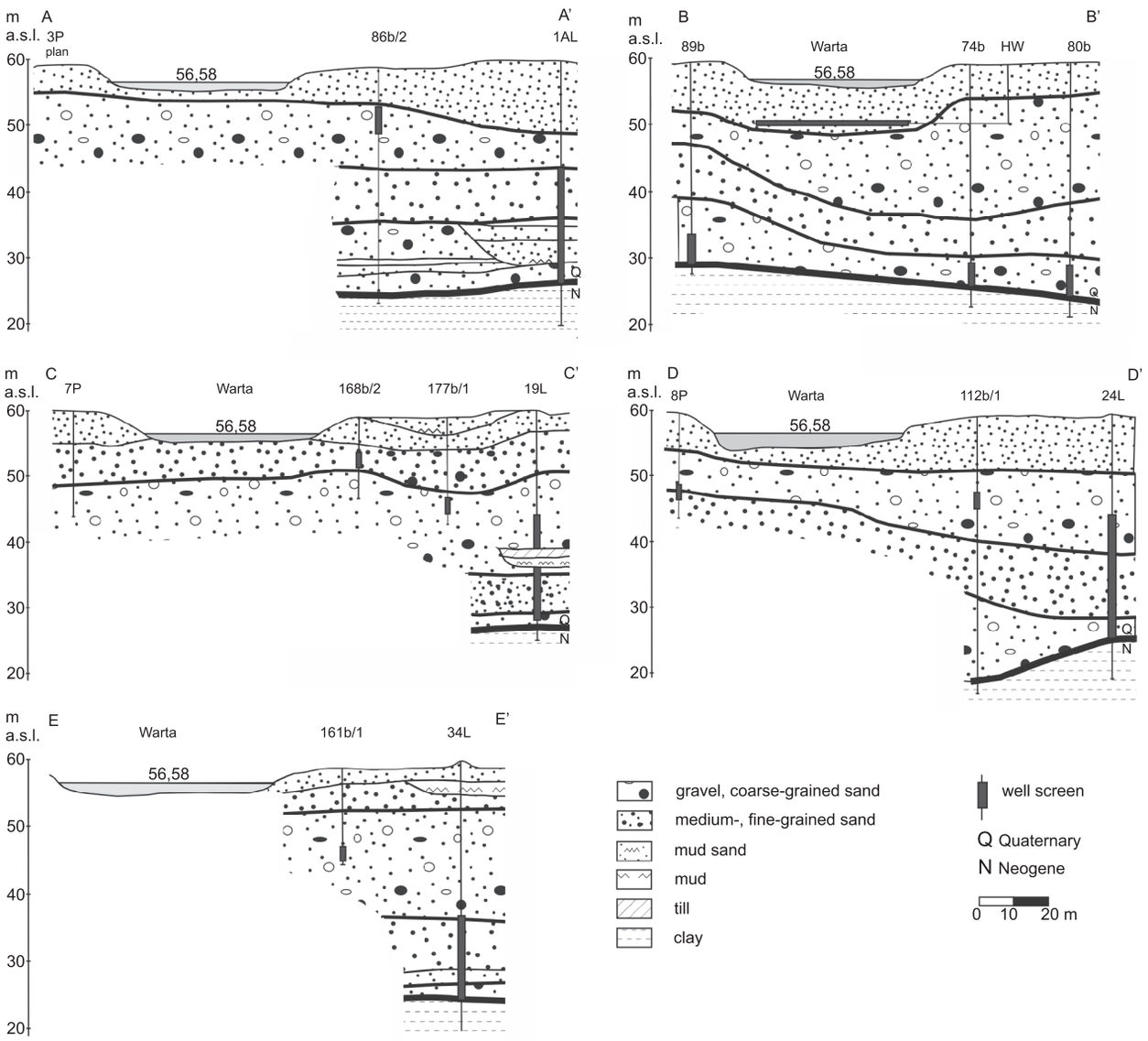

Fig. 2. Cross-sections (lines of cross-section according to Fig. 1)

umn). The mobile phase was 0.7 mmol $C_7H_5NO_4$/1.7 mmol HNO_3 flowing at 0.9 ml min^{-1} (Pełechaty et al., 2010).

PhACs ANALYSIS

Based on previous studies (Dragon et al., 2018; Kruć et al., 2019), ten of the most frequently detected pharmaceutical compounds that occur in the highest concentrations in this area were selected (Table 2) for analyses, performed in the Institute of Plant Protection – National Research Institute Laboratory (Poznań, Poland).

ANALYTICAL PROCEDURES

Sample preparation. The water samples collected were filtered through paper filters and then 250 mL water was extracted using the solid-phase extraction technique (SPE). Polypropylene tubes packed with the hydrophilic modified styrene polymer (*Supel*™*-Select* HLB SPE *Tube* 60 mg/3 mL, *Supelco*, USA) were used to extract and concentrate targeted compounds in the water samples. Methanol (Merck, Germany) was used to precondition SPE tubes and for elution of the compounds analysed. Extraction of water samples was performed by means of a 24-port SuperSeparator (Amersham, UK), equipped with a vacuum pump (Rocker, Taiwan). Evaporation of the final organic extract of pharmaceutical compounds was obtained after elution from extraction tubes in a gentle stream of nitrogen from a *Stuart* sample concentrator (Stuart, UK) was used. An ultrasonic bath *Sonorex* (Bandelin, Germany) was employed for dissolving the residues obtained after nitrogen drying in injection solvent. Syringe filters *PTFE*, 0.2 µm (Waters, USA) were applied for final sample processing, if necessary.

UPLC conditions. An ultra-performance liquid chromatograph *ACQUITY UPLC* system (Waters, USA) with column and autosampler thermostats, interfaced with a tandem quadrupole mass spectrometer *Quattro Premier* XE (Micromass, USA), was used for instrumental analysis. A NM30-LA (Peak Scientific, Scotland) nitrogen generator delivered the nebulizer and

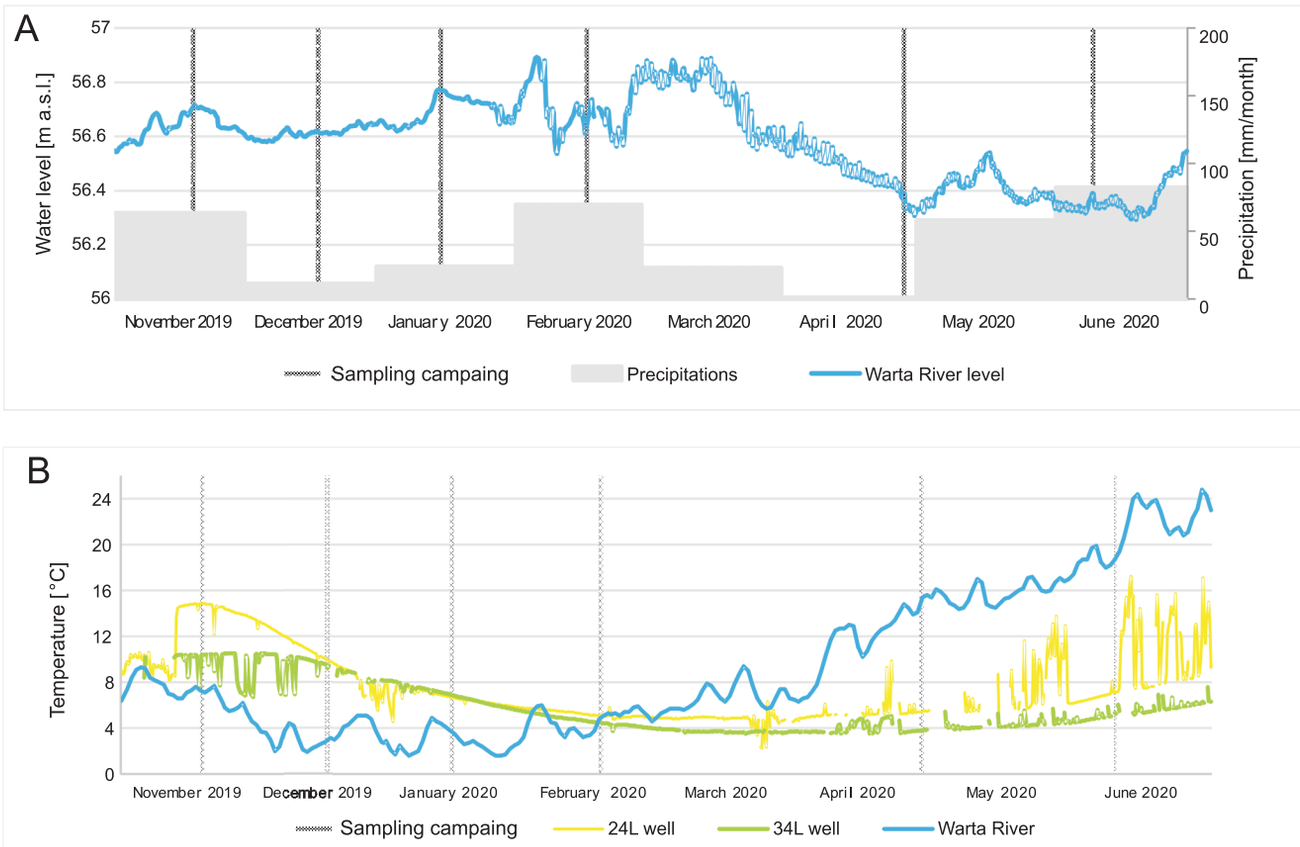

Fig. 3. Parameters through time: A – Warta River level and month sum of precipitation, B – temperature in the Warta River, 24L well and 34L well

Table 2

Pharmaceutical characterization

PhACs	Use	LOQ (µg/L)
Carbamazepine	antiepileptic	0.005
Diclofenac	nonsteroidal anti-inflammatory	0.01
Lamotrigine	antiepileptic, antidepressant	0.01
Fluconazole	antifungal	0.01
Gabapentin	antiepileptic	0.01
Paracetamol	analgesic	0.005
Sulphamethoxazole	human and veterinary antibiotic	0.005
Sulphapiridine	antibacterial	0.01
Telmisartan	treatment of high blood pressure	0.005
Tramadol	analgesic	0.005

LOQ – limit of Quantification

desolvation gas to the mass spectrometer. The instrument was controlled using *Waters MassLynx* software and data were evaluated using *Waters TargetLynx* software. Reverse-phase *UPLC* analysis was performed using a Waters *ACQUITY UPLC* column (BEH C_{18} 2.1 × 100 mm, 1.7 µm). The temperature of the column and autosampler was maintained by thermostat at 30°C. Sample extract volumes of 8 µL were injected into the system. The column was eluted with the mobile phase: water with 0.1% formic acid (A) and methanol with 0.1% ammonium acetate (B) at a flow rate of 0.3 mL min^{-1} using gradient mode. The gradient was programmed to increase the amount of B from an initial content of 0–100% in 6 min, 100% maintained 1 min (from 6 to 7 min) and returned to the initial conditions (0% B) in 2 min (from 7 to 9 min). The total duration of a single analytical run with system stabilization was 10 minutes.

MS/MS conditions. The interface conditions were optimized for maximum intensity of the precursor ions and were as follows: nebulizer and desolvation (drying gas) N_2 flows were set at 100 L h^{-1} and 700 L h^{-1}, respectively, source block and desolvation temperatures were 120 and 350°C, respectively. Argon was used as collision gas at the pressure of 6.9 × 10^{-3} mbar. Selection and tuning of multiple reaction monitoring (MRM) transitions were performed individually for each analyte on the instrument used in this work. All the compounds were analysed using positive electrospray ionization mode (ESI+). MS/MS scanning was performed only over 4.5 min, between 1.5 and 6 min. The conditions applied for the pharmaceutical compounds investigated are given in Table 3.

Method validation. All validation procedures were performed using control samples of distilled water (Millipore, USA) and certified reference materials of selected pharmaceutical compounds (Sigma-Aldrich, USA). Recoveries were determined for multiple replicates at two spiking concentrations. Precision was measured by relative standard deviation (RSD) for each spiking sample level. Linearity was assessed for the compounds analysed by multi-level standard calibration curves. Water sam-

Table 3

Mass spectrometry conditions of the PhACs studied

Name of compound	Retention time (min)	Dwell time (ms)	Cone voltage (V)	MRM transitions *m/z* (collision energy – eV)	
				Quantification	Identification
Paracetamol	1.92	100	30	152 >110 (15)	152>93 (25)
Sulphapiridyne	2.20	100	33	250 >92 (25)	250>156 (15)
Gabapentin	2.47	100	25	172 >154 (15)	172>137 (15)
Sulphamethoxazole	2.93	100	27	254 >92 (25)	254>156 (15)
Tramadol	3.21	100	23	264 >58 (15)	–
Fluconazole	3.37	100	25	307 >220 (20)	307>238 (15)
Lamotrigine	3.44	100	50	256 >211 (30)	256>159 (25)
Carbamazepine	4.64	100	32	237 >193 (35)	237>179 (35)
Diclofenac	5.61	100	22	296 >214 (30)	296>250 (15)
Telmisartan	5.65	100	70	515 >276 (50)	515>497 (35)

ples spiked with all the pharmaceutical compounds were extracted by applying the SPE method. The analytical signal was compared with a distilled water extract signal spiked with the target compounds after solid-phase extraction. Recoveries for water samples spiked with a mixture of compounds studied ranged from 80–105% and standard deviations varied between 4–11%. The limits of quantification for all target compounds were determined at levels between 0.005–0.01 μg/L (Table 2).

STATISTICAL DATA ANALYSIS

The percentage reduction (*R*%) of pharmaceutical compounds in RBF water in relation to river (source) water was calculated. The reduction was calculated for the sum of pharmaceutical compound concentrations in each series for each sampling point.

The frequency of detection (FoD) of pharmaceutical compounds in surface and RBF water was calculated for each substance detected. The number of sampling campaigns (6), frequency of occurrence of a given substance in the Warta River ($F_{Warta\ River}$) or wells (F_{well}) was assessed [eq. 1].

$$FoD = \frac{\Sigma F_{Warta\ River/well}}{6} \times 100\% \quad [1]$$

RESULTS

WATER CHEMISTRY DURING RBF

In Table 4, physical and chemical parameters of surface water, HW, observation well and VW water are compared. Generally, the RBF system stabilizes the water chemistry and physical properties. The temperature of surface water varies from 2.4 to 19.6°C, in the HW 4.3–16.8°C, in the observation well 5.7–20°C and the VWs 7.3–18.8°C. Total organic carbon (TOC) and dissolved organic carbon (DOC) decreased from averages of 6.0 mg/L and 5.3 mg/L, respectively, in surface water, to 4.3 and 4.2 mg/L in the HW, and 4.4 and 4.3 mg/L in the VWs (Table 4). The highest concentrations of TOC (9.9 mg/L) and DOC (6.2 mg/L) were detected in surface water. In the observation and VWs significant reduction of DO occurred along the flow paths. In the HW, the DO is 8.4 mg/L, while in the observation wells it is 1.0 mg/L and in the VWs it is 1.2 mg/L. The oxidation-reduction potential (ORP) changes behave similarly. In surface water and the HW, the ORP value is high (avg. 293 and 334 mV, respectively), while in the observation wells, the average value is 152 mV, and 145 mV in the VWs. Higher ORP in HW than in surface water is a result of the HW construction. Water collected through drains goes to a collecting well, where it can be oxygenated.

In the RBF water, a reduction in nitrates, nitrites, ammonium ions occurred in relation to surface water (Table 5). The average values of the nitrates, nitrites and ammonium ion in surface water are 1.58, 0.011 and 0.022 mg/L respectively, in the HW are 1.0, 0.011 and 0.013 mg/L and in the VWs are 0.66, 0.009 and 0.008 mg/L. The chloride concentrations (conservative tracer) achieved similar values in surface water (40.5–47.5 mg/L) and HW (42.3–46.1 mg/L), whereas the values decrease in the VWs (37.5–45.6 mg/L). Sodium and potassium concentrations decrease along flow paths from the river to the wells. The concentrations of calcium, magnesium, sulphates, hydrogen carbonate and total hardness of water increase in the RBF wells relative to surface water.

In surface and RBF water, all the pharmaceutical compounds tested for (10) were detected above the limit of quantification (LOQ) (Table 6). The most frequently detected substances were carbamazepine, fluconazole, tramadol, sulphamethoxazole and sulphapyridine. Diclofenac, lamotrigine, gabapentin and telmisartan occurred irregularly in each sampling series. Paracetamol was detected only in nine samples. In the river water, carbamazepine, telmisartan and tramadol reached the highest concentrations (0.092–0.209 μg/L, 0.124–0.233 μg/L, 0.071–0.282 μg/L, respectively), while gabapentin reached the lowest concentrations (0.006–0.007 μg/L). In production wells, carbamazepine and tramadol reached the highest concentrations (0.073–0.194 μg/L, 0.02–0.24 μg/L, respectively).

As regards the distribution of concentrations of pharmaceutical compounds at individual research points, the highest total concentrations were detected in the Warta River and protective

Table 4

On-site parameters, TOC and DOC in surface and RBF water

Parameter	Unit	Surface water (n = 12)			Riverbank filtration water								
					HW (n = 6)			Observation wells (n = 12)			VWs (n = 24)		
		min	max	**mean**	min	max	**mean**	min	max	**mean**	min	max	**mean**
Temperature	°C	2.4	19.6	**9.1**	4.3	16.8	**9.3**	5.7	20.0	**10.3**	7.3	18.8	**11.5**
EC	µS/cm	377	564	**503**	481	537	**517**	456	547	**514**	478	574	**530**
pH	–	8.1	9.4	**8.4**	7.3	8.6	**7.9**	6.5	9.0	**7.8**	6.5	8.2	**7.5**
Alkalinity	mval/L	3.0	4.3	**3.6**	3.3	3.7	**3.5**	2.8	3.8	**3.4**	3.0	4.4	**3.8**
ORP	mV	243	338	**293**	229	397	**334**	-48	310	**152**	75	295	**145**
DO	mg/L	–	–	**–**	5.7	10.5	**8.4**	0.0	3.7	**1.0**	0.0	8.5	**1.2**
TOC	mg/L	4.4	9.9	**6.0**	3.6	5.2	**4.3**	3.2	4.6	**3.9**	3.5	5.5	**4.4**
DOC	mg/L	4.3	6.2	**5.3**	3.4	5.1	**4.2**	3.0	4.6	**3.8**	3.5	5.2	**4.3**

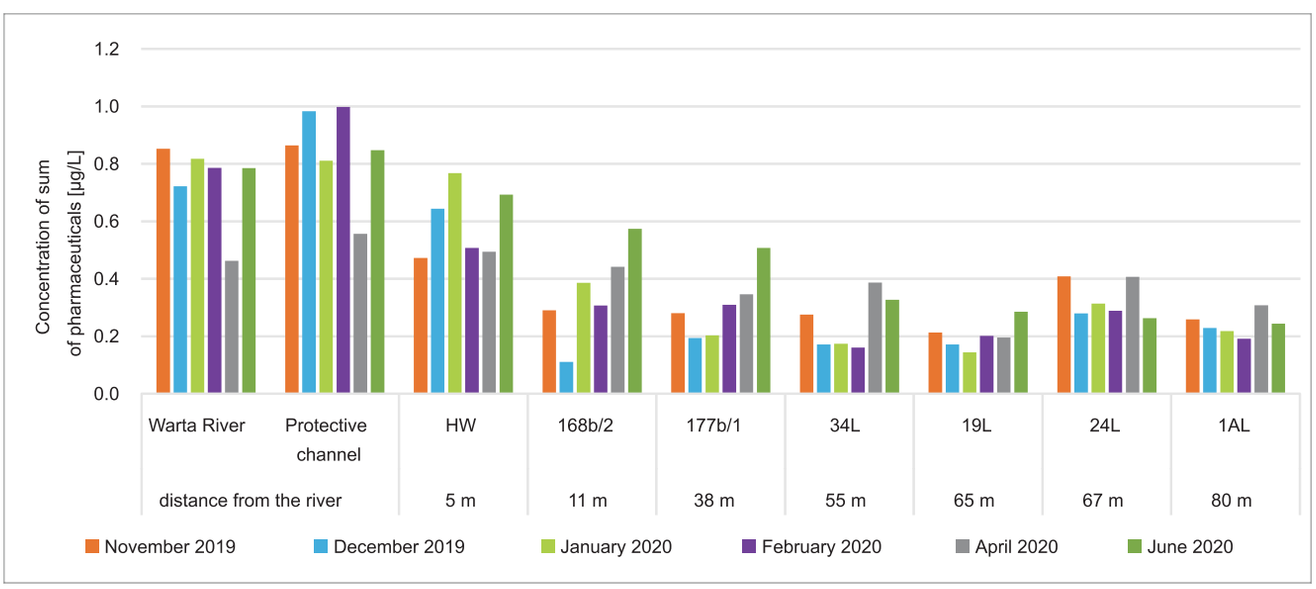

Fig. 4. Sum of pharmaceutical compound concentrations in each sampling point and campaign

channel (0.463–0.998 µg/L) (Fig. 4). Slightly lower concentrations occurred in the HW (0.473–0.768 µg/L), where the average reduction of the sum of pharmaceutical compounds in relation to the river was 17% (Table 7). In the observation wells, 27 m apart from each other, the concentrations varied slightly. The concentrations in observation wells were lower than those in surface water and the HW (0.111–0.574 µg/L). The reductions in concentrations were 49.3% in 168b/2 and 56.1% in 177b/1. The lowest concentrations were observed in the productive wells (0.144–0.409 µg/L), where higher concentrations were seen in wells 24L (0.263–0.409 µg/L) and 1AL (0.192–0.308 µg/L), and lower ones in 19L (0.144–0.286 µg/L) and 34L (0.161–0.387 µg/L). The reduction was lowest in 24L (52.8%) and was higher in 34L (62.8%), 1AL (64.9%) and 19L (71.5%).

Regarding variability in the sum of pharmaceutical compound concentrations in time, low concentrations in surface water and HW occurred in April 2020 and in observation and production wells in December 2019 and February 2020 (Fig. 4). High pharmaceutical concentrations occurred at all sampling points in June 2020.

VARIABILITY OF WATER CHEMISTRY AND PHYSICAL PROPERTIES IN THE PRODUCTIVE WELLS

During the research period, the water temperature decreases in surface water and the HW in November and December 2019 and increases in the remaining months (Fig. 5A). Water temperature in VWs decreases throughout the research period. The reverse tendency of temperature changes in time re-

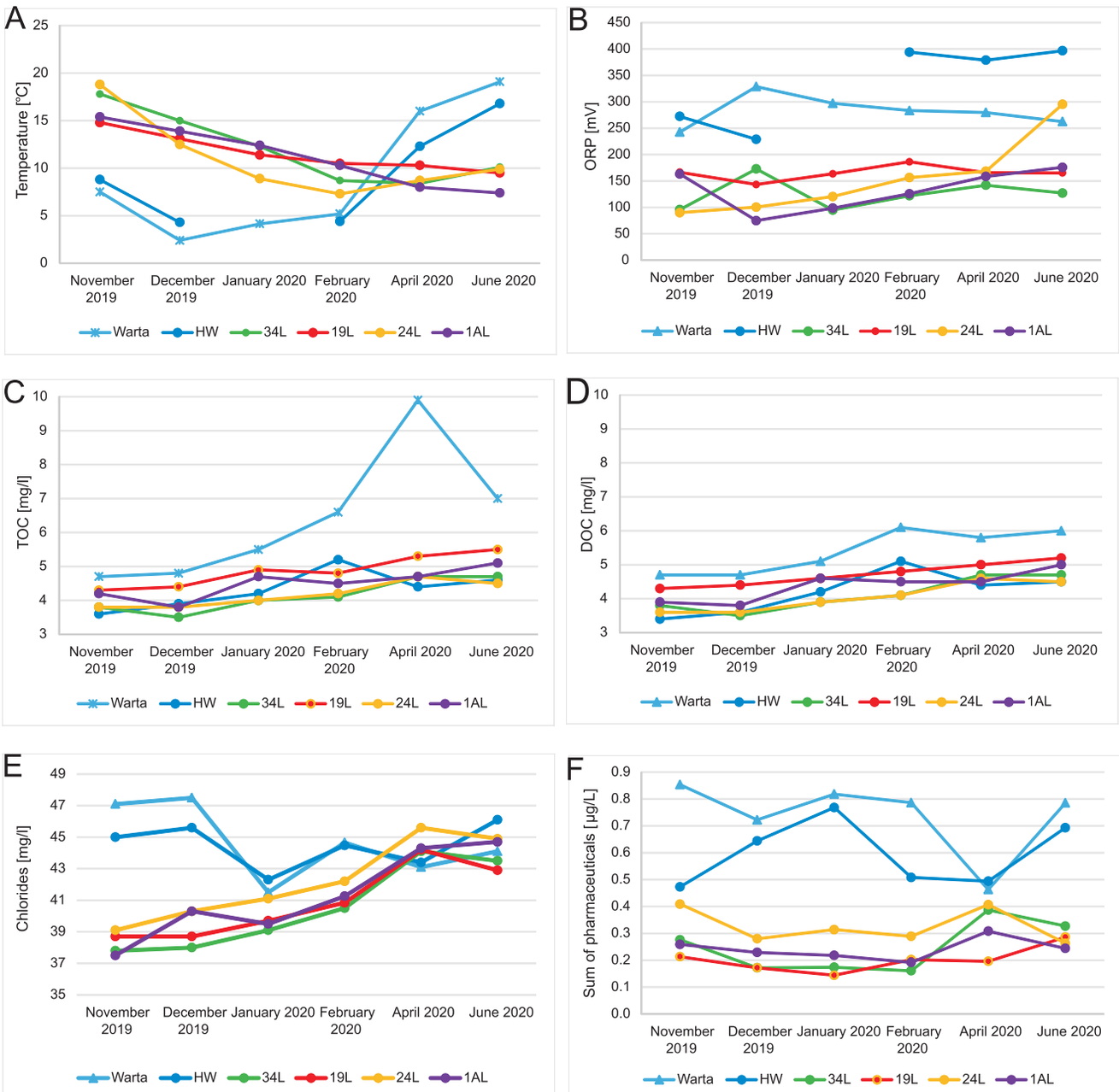

Fig. 5. Physical and chemical parameters of river water and bank filtrate at the Mosina-Krajkowo site, Nov. 2019–June 2020

sults from the 1–3 months travel time from the river to the wells (Table 1). The redox potential shows a similar but inverted tendency because it decreases in the Warta River and increases in VWs through time (Fig. 5A). The redox potential is higher at lower temperatures (Fig. 5B). High temperature amplitudes significantly influence the variability of redox conditions. The conditions change from more oxidizing in surface water to more reducing in the VWs. Among the VWs, 1AL and 34L have lower redox potential, and 19L and 24L have higher.

Like the temperature and ORP, TOC and DOC change at individual sampling points (Fig. 5C, D). Concentrations of TOC and DOC increase in time at each sampling point. The highest concentrations were detected in surface water, and the value decreased in the RBF wells. The highest concentrations were detected in well 19L among the wells, while the lowest concentrations characterize 24L and 34L. The reductions in TOC and DOC are very high in the HW (similar to the VWs). During the research period, chloride concentrations decreased in the Warta River and HW and increased in the VWs (Fig. 5E).

By contrast, the sum of pharmaceutical compound concentrations in the river and wells do not show any tendency (increase or decrease) over time (Fig. 5F). Concentrations are irregular, not showing seasonality. The lowest concentrations occurred in 19L well, which showed the highest TOC and DOC concentrations and the highest redox potential. Well 24L, which showed the lowest TOC and DOC concentrations and the high-

Table 5

Standard water parameters in surface and RBF water

Parameter	Unit	LOD	Surface water (n = 10)			Riverbank filtration water								
						HW (n = 5)			Observation wells (n = 10)			VWs (n = 20)		
			min	max	**mean**	min	max	**mean**	min	max	**mean**	min	max	**mean**
Total hardness $CaCO_3$	mg/l		210.3	235.9	**224.3**	216.5	248.6	**231.1**	187.8	246.0	**229.1**	205.2	285.5	**243.7**
HCO_3^-			183.0	231.8	**209.8**	201.3	225.7	**212.3**	170.8	231.8	**205.0**	183.0	268.4	**231.2**
Cl^-		0.011	40.5	47.5	**44.0**	42.3	46.1	**44.5**	39.1	45.5	**43.0**	37.5	45.6	**41.2**
NO_3^-		0.01	0.07	2.77	**1.58**	0.06	1.40	**1.00**	0.01	1.98	**0.59**	0.01	2.04	**0.66**
NO_2^-		0.002	0.005	0.022	**0.011**	0.007	0.015	**0.011**	0.004	0.014	**0.009**	0.002	0.019	**0.009**
NH_4^+		0.004	0.012	0.031	**0.022**	0.007	0.020	**0.013**	0.008	0.012	**0.009**	0.005	0.011	**0.008**
SO_4^{2-}		0.02	50.4	64.7	**58.4**	60.1	71.6	**65.2**	54.1	72.1	**65.2**	48.9	70.3	**60.0**
Ca^{2+}		0.007	73.2	79.9	**77.2**	73.1	85.9	**79.0**	63.5	85.5	**77.0**	69.5	94.8	**82.1**
Mg^{2+}		0.004	6.5	9.0	**7.7**	7.7	8.7	**8.3**	7.1	10.2	**9.0**	7.5	11.9	**9.5**
Na^+		0.003	22.3	31.9	**28.3**	28.1	30.9	**29.4**	23.5	29.9	**26.8**	23.8	29.9	**26.6**
K^+		0.006	3.7	7.2	**5.6**	3.9	6.9	**5.4**	4.2	6.5	**5.1**	3.1	5.9	**4.5**

LOD – limit of detection

Table 6

Pharmaceutical compounds in surface and RBF water

PhACs	Unit	LOQ	Surface water (n = 12)			Riverbank filtration water								
						HW (n = 6)			Observation wells (n = 12)			VWs (n = 24)		
			min	max	**mean**	min	max	**mean**	min	max	**mean**	min	max	**mean**
Carbamazepine	µg/L	0.005	0.092	0.209	**0.145**	0.088	0.194	**0.149**	0.038	0.152	**0.106**	0.068	0.140	**0.098**
Diclofenac		0.01	0.027	0.174	**0.105**	<LOQ	0.042	**0.020**	<LOQ	0.003	**0.001**	<LOQ	0.013	**0.003**
Lamotrigine		0.01	<LOQ	0.057	**0.031**	0.014	0.060	**0.031**	<LOQ	0.037	**0.015**	<LOQ	0.037	**0.015**
Fluconazole		0.01	0.04	0.064	**0.050**	0.043	0.068	**0.058**	0.016	0.069	**0.044**	<LOQ	0.068	**0.026**
Gabapentin		0.01	<LOQ	0.008	**0.004**	<LOQ	0.013	**0.006**	<LOQ	0.009	**0.004**	<LOQ	0.017	**0.005**
Paracetamol		0.005	<LOQ	0.035	**0.003**	<LOQ	0.024	**0.004**	<LOQ	0.022	**0.003**	<LOQ	0.035	**0.004**
Sulphametoxazol		0.005	<LOQ	0.062	**0.031**	<LOQ	0.099	**0.044**	<LOQ	0.095	**0.030**	<LOQ	0.110	**0.020**
Sulphapiridine		0.01	<LOQ	0.043	**0.025**	<LOQ	0.044	**0.020**	<LOQ	0.026	**0.013**	<LOQ	0.026	**0.012**
Telmisartan		0.005	0.124	0.257	**0.192**	0.066	0.166	**0.118**	<LOQ	0.075	**0.019**	<LOQ	0.033	**0.007**
Tramadol		0.005	0.071	0.381	**0.205**	0.080	0.240	**0.147**	0.020	0.328	**0.095**	0.020	0.162	**0.070**

LOQ – limit of quantification

est temperature amplitudes, showed the highest pharmaceutical concentrations. The redox potential is highly variable in 24L (lower or higher than in other VWs), while the sum of pharmaceutical compounds is always the highest of the VWs.

Figure 6 shows concentrations of individual pharmaceutical compounds in the Warta River and production wells (HW, 34L, 19L, 24L, and 1AL). Comparing the VWs, the concentrations are different in each well and the highest values of the most substances were found in 24L. Well 24L is 67 m away from the

Table 7

Percentage reductions in the sum of pharmaceutical compounds concentrations in each series and sampling point

	HW	168b/2	177b/1	34L	19L	24L	1AL
November 2019	44.5%	65.9%	67.1%	67.6%	75.0%	52.1%	69.6%
December 2019	10.8%	84.6%	73.1%	76.2%	76.2%	61.2%	68.3%
January 2020	6.1%	52.8%	75.2%	78.7%	82.4%	61.6%	73.3%
February 2020	35.4%	60.9%	60.6%	79.5%	74.3%	63.2%	75.6%
April 2020	–6.7%	4.5%	25.3%	16.4%	57.7%	12.1%	33.5%
June 2020	11.7%	26.9%	35.3%	58.3%	63.6%	66.5%	68.9%
Mean	**17.0%**	**49.3%**	**56.1%**	**62.8%**	**71.5%**	**52.8%**	**64.9%**

riverbank, which is a greater distance than 34L (55 m) and 19L (64 m). The significant difference between well 24L and the remaining VWs is visible in the case of carbamazepine, lamotrigine, fluconazole, sulphamethoxazole and telmisartan. Some of the pharmaceutical compounds was not detected in some series (lamotrigine, sulphapyridine, telmisartan). Most often, this lack was observed in well 19L.

The FoD of carbamazepine, fluconazole and tramadol were 100%, which means that they all were found in each sampling campaign at each sampling point (Table 8). High FoDs (min. 67%) were observed for sulphamethoxazole, sulphapyridine and telmisartan. These substances were detected at least four times. The least frequently detected pharmaceutical was paracetamol. The FoD does not decrease with increasing distance from the river bank.

DISCUSSION

It was documented that the RBF system stabilizes the physical and chemical parameters of surface water, with a decrease in concentrations of TOC, DOC, chlorides, nitrates, nitrites and ammonium being noted. Presented research is consistent with preliminary studies which showed that the Warta River and RBF water are contaminated by pharmaceutical compounds (Dragon et al., 2018; Kruć et al., 2019). Their concentrations do not show marked seasonal variability. However, the values were lower in surface water in April 2020. This may be related to low river water levels. In the dry periods an increased share of groundwater in river recharge takes place. The reason for the low concentrations in April is difficult to determine due to the lack of data from March and May 2020.

The most common occurrence and highest concentrations were found for carbamazepine, consistent with previous research conducted widely on the groundwater in Poland (Kuczyńska, 2019). The results obtained are comparable with data from Europe. The concentrations of the most common pharmaceutical compound, carbamazepine, are similar to concentrations recorded in winter in the catchment area of the Tegel waterworks (Berlin, Germany), and lower than concentrations in Berlin during the summer (Massmann et al., 2006). Carbamazepine concentrations are significantly higher in the Warta River and RBF water than in the Danube River and at RBF sites in Budapest (Nagy-Kovács et al., 2018). Sulphamethoxazole showed higher concentrations in surface and RBF water than at a RBF site in Serbia. In comparison, diclofenac concentrations were higher in the Warta River and comparable in RBF water (Kovačević et al., 2017). Sulphamethoxazole removal rates are similar to values achieved at a bank filtration site at Lake Tegel (50%) (Grünheid et al., 2005). Lamotrigine showed lower concentrations in Warta River and RBF water than in the Danube River and a bank filtration site in Hungary (Kondor et al., 2020). Generally, pharmaceutical compound concentrations show reductions along the flow paths from the river to the RBF well in the study area. Current research demonstrates that contaminant reduction increases with increasing distance from the river (Dragon et al., 2018; Kruć et al., 2019) and indicates ongoing processes affecting this reduction.

Mixing water is one of the processes occurring during RBF that can cause pharmaceutical compound concentrations to decrease in bank filtrate (Hiscock and Grischek, 2002). The RBF wells receive river water, though inflow of ambient groundwater is also possible. The unpolluted groundwater causes dilution of pollutants (Heberer et al., 2004; Kovačević et al., 2017). The results of groundwater flow modelling, conducted by Matusiak et al. (2021), established the average share of surface water in the VWs at 75.8%, with significant spatial differentiation along the well barrier in a wide range of 41.4–89.3%. The share of surface water in the total water balance in well 34L is 41%, 19L: 83%, 24L: 83%, and 1AL: 78%. The share of surface water in the HW is 100% (Górski et al., 2018). The ambient groundwater inflow and its differing share in the water balance are also shown by a chloride mass-balance conducted by Górski et al. (2021), in which the proportion of river water in the well varies from 22 to 85.3%. Conducted research supports the previous findings. Chloride concentration is higher in surface water and lower in the VWs, indicating mixing with ambient groundwater, characterized by lower chloride concentrations (Fig. 5E). The highest share of surface water is in VW 24L (with the highest chloride concentrations), and the lowest is in VW 34L (showing the lowest chloride concentrations), which is consistent with with groundwater flow modelling results (Fig. 5E and Appendix 1*). The analyses of temperature fluctuations during the research period also support this finding. The temperature fluctuations in well 24L are higher than in other wells and are most similar to the temperature in the river (Fig. 3B)

Another compound which indicates the process of water mixing is carbamazepine. Dvory et al. (2018) found that carbamazepine is a conservative pollutant. Other studies, performed

* Supplementary data associated with this article can be found, in the online version, at doi: 10.7306/gq.1635

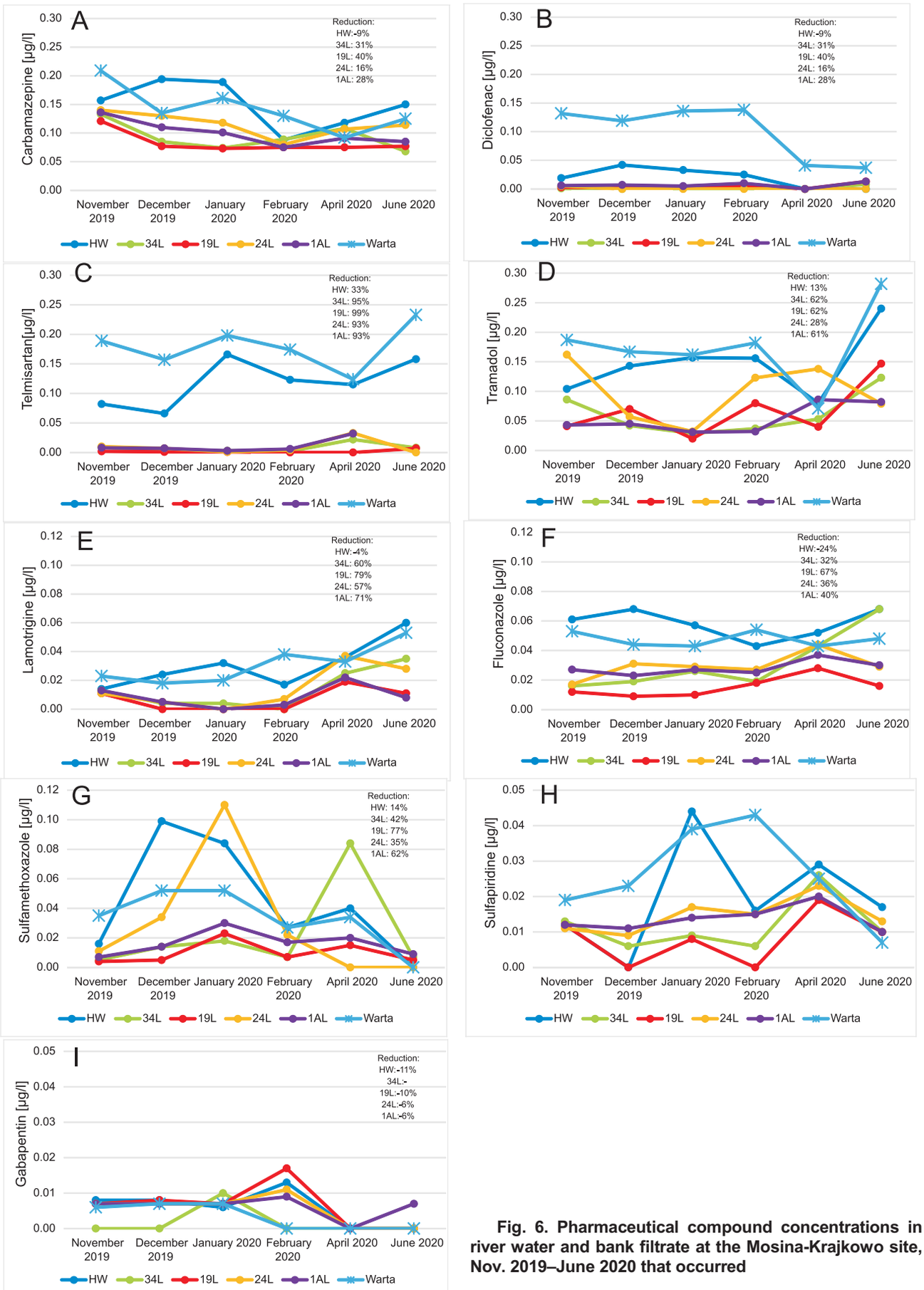

Fig. 6. Pharmaceutical compound concentrations in river water and bank filtrate at the Mosina-Krajkowo site, Nov. 2019–June 2020 that occurred

Table 8

Frequency of pharmaceutical compound detection (FoD %)

	Warta River	HW	168b/2	177b/1	34L	19L	24L	1AL
Carbamazepine	100	100	100	100	100	100	100	100
Diclofenac	100	67	0	50	67	83	33	83
Lamotrigine	100	100	83	100	83	50	83	83
Fluconazole	100	100	100	100	100	100	100	100
Gabapentin	50	67	33	67	17	67	67	83
Paracetamol	0	17	17	17	17	0	17	0
Sulphametoxazol	83	83	100	83	100	100	67	100
Sulphapiridine	100	83	100	83	100	67	100	100
Telmisartan	100	100	100	83	100	67	83	83
Tramadol	100	100	100	100	100	100	100	100

by Preuß et al. (2002), demonstrate the high stability of carbamazepine; under both under aerobic and anaerobic conditions reduction was <20% and was ascribed to biodegradation. Published data on the behaviour of carbamazepine is contradictory. However, in a similar pattern to that shown by Massmann et al. (2006) and Kondor et al. (2020), carbamazepine showed only modest reduction along flow paths from the river to the wells (HW: –9%, 34L: 31%, 19L: 40%, 24L: 16%, 1AL: 25%). Carbamazepine reductions were slightly higher than the share of groundwater in individual wells.

The pharmaceutical compounds in RBF water are diluted as a result of ambient inflow of unpolluted groundwater. However, the reduction in the sum of pharmaceutical compound concentrations in the HW is 17%, and in VWs this ranges between 52.8 and 71.5%, which significantly exceeds the share of groundwater, calculated based on groundwater flow modelling, chloride mass-balance, and the variability of carbamazepine concentrations. Therefore, this indicates that other processes have occurred along the flow paths from the river to the wells.

The pharmaceutical compounds investigated in the present study are characterized by low degradation and high chemical stability. As mentioned above, carbamazepine is a persistent and stable pollutant. However, as indicated by laboratory tests, other substances have similar features. High biological persistence and no biodegradability characterizes lamotrigine (Bollmann et al., 2016). Fluconazole is a persistent pharmaceutical compound, not adsorbed or biotransformed (Peng et al., 2012). Sulphamethoxazole is a persistent, poorly biodegradable pharmaceutical compound. It is adsorbed on activated carbon (Bizi, 2020). Diclofenac is slightly soluble in water, and does not biodegrade (Radjenovic et al., 2009; Vieno and Sillanpaa, 2014). Sulphapiridine can be removed from water through adsorption (on clay, activated carbon, or zeolite) (Avisar et al., 2010; Braschi et al., 2010; Caliskan and Gokturk, 2010). Tramadol tends to remain in the water phase (Gomez and Puttmann, 2012).

The HW has its filter screens in fine- and medium-grained sediments with high organic matter content. The abstraction of HW drains located directly below the river bed results from the filtration through the riverbed and fine- and medium-grained sediments, which favours the sorption processes. In the case of the VWs, infiltration is taking place mainly through the riverbank, particularly in the periods of clogging of the river bottom (Przybyłek et al., 2017). In this condition, the sorption processes are limited due to the lack of fine sediments and organic matter on the bank of the river, which is constantly washed out and locally eroded. The varied effects of water treatment resulting from riverbank/riverbed filtration were noted in the study by Górski et al. (2018). In that research, high reductions of TOC and COD were observed in the HW (riverbed filtration). By contrast, lower reductions of those parameters were seen in the vertical observation well (RBF) located 30 m from the riverbank. This is the effect of sorption, taking place during riverbed filtration, and its lack (or limitation) during RBF. In the current study, due to relatively low river water levels, which causes a lower infiltration zone on the riverbank (compared to the periods of higher surface water level), riverbed filtration may have been activated partially in the VWs. Flow of water through the fine bed sediments containing organic matter causes sorption of pharmaceutical compounds. In the present study, the TOC and DOC reductions were similar in the HW and VWs, despite the much greater distance in the case of the VWs.

The removal of pharmaceutical compounds from water is favoured by oxidising conditions (Kovačević et al., 2017). Published data indicate that degradation by aerobic bacteria is one of the main processes of removing pharmaceutical compounds at RBF sites (Massmann et al., 2006; Abdelrady et al., 2019). Generally more oxic infiltration is observed close to a surface water reservoir or river than further along the flow path (Heberer et al., 2008; Massmann et al., 2008a, b). The presence of dissolved oxygen and a relatively high redox potential allow aerobic biodegradation to take place. At the site studied, the ORP values decreased from 293 mV in surface water to 145 mV in the VWs (Table 3 and Fig. 5B). Biodegradation can be of primary importance in the VWs, in the section of water flow from the river to the wells, before the dissolved oxygen and redox potential decrease. In the HW dissolved oxygen is present and the redox potential is relatively high, however, due to the short travel time from the river to the wells (~1 day) and occurrence of organic-rich fine-grained sediments, the conditions are more favourable for sorption.

The VWs are located at similar distances from the river. However, the reduction in pharmaceutical compounds among individual wells varies (Table 6). A previous finding considered different infiltration conditions along the well barrier (Górski et al., 2021; Matusiak et al., 2021). Well 24L stands out, with the highest concentration of pharmaceutical compounds relative to the other wells. This may be caused by the particular nature of the geological structure, hydrogeological conditions, and well construction. The aquifer in the 24L area consists of coarse-

grained sediments with the highest hydraulic conductivity. The well is operated at the highest capacity, which leads to shorter travel times (Table 1). These conditions favour the rapid flow of water and a higher share of river water in the total water balance compared to the other wells, and so pharmaceutical compound concentrations in well 24L are higher than in the other wells.

SUMMARY AND CONCLUSIONS

1. Research showed the presence of pharmaceutical compounds in the Warta River and in riverbank filtration (RBF) water at the Mosina-Krajkowo site (West Poland). The highest concentrations of micropollutants occurred in surface water (Warta River, protective channel). The research also showed that pharmaceutical compound reduction increases as the sampling points' distance from the source water (river) increases.

2. The most frequently detected pharmaceutical compounds were: carbamazepine, fluconazole, tramadol, sulphamethoxazole and sulphapyridine. Among the ten compounds tested for carbamazepine concentrations were found to have the lowest reduction rates in the RBF water. The highest reduction rates were determined for diclofenac and telmisartan. The occurrence and concentrations of pharmaceutical compounds do not show marked seasonal variability.

3. In the horizontal well (HW), with drains located 5 m below the river bottom, the reduction in pharmaceutical compounds was lower than in the vertical wells (VWs). The HW abstracts surface water by riverbed filtration. Water infiltration through the fine bed sediments with a high content of organic matter causes sorption of the pharmaceutical compounds. Additionally, in the HW, conditions for biodegradation occur. The VWs abstract water mainly by riverbank filtration, due to more favourable conditions. The processes that reduce micropollutant concentrations in the VWs are: mixing with unpolluted ambient groundwater, aerobic biodegradation in the presence of dissolved oxygen and a relatively high redox potential in the water, and sorption on fine-grained sediments with high organic matter content.

4. Different degrees of reduction in pharmaceutical compounds, ranging from 53–71%, occurred in VWs located at similar distances from the river. This reflects different geological structures, hydrogeological conditions (e.g., hydraulic conductivity, hydraulic gradient) and operating parameters (e.g., capacity).

5. Research indicates the occurrence of pharmaceutical compounds listed on the European Union Watch list of substances of emerging concern, and shows the necessity of constant monitoring of both surface and RBF water as regards these compounds.

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