

Article

Migration of Pharmaceuticals from the Warta River to the Aquifer at a Riverbank Filtration Site in Krajkowo (Poland)

Roksana Kruc ^{*}, Krzysztof Dragon  and Józef Górski

Institute of Geology, Department of Hydrogeology and Water Protection, Adam Mickiewicz University, ul. Bogumiła Krygowskiego 12, 61-680 Poznań; Poland; smok@amu.edu.pl (K.D.); gorski@amu.edu.pl (J.G.)

^{*} Correspondence: roksana.kruc@amu.edu.pl

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Abstract: Studies on the presence of pharmaceuticals in water were carried out on the riverbank filtration site, Krajkowo–Poznań (Poland). A preliminary investigation conducted in 3 sampling points showed the presence of pharmaceuticals in both surface water and bank filtrate. Based on the above, an extended analysis was made in July, August and October 2018 and included surface water and wells located at a different distance (5–250 m) and travel time (1–150 days) from source water (Warta River). Firstly, 75 compounds (antibiotics, anti-inflammatory and analgesic drugs, psychotropic drugs, x-ray agents and β -blockers) were tested and 25 of them were detected in the river or bank filtrate. The highest concentrations were observed in source water and then were reduced along the flow path. The sampling points located close to the river (<38 m) are characterized by low removal. Higher removal is visible in wells located 64–82 m away from the river, while 250 m from the river most compounds are completely attenuated. Carbamazepine, gabapentin, tramadol, oxypurinol, fluconazole, and lamotrigine are the most common compounds. Some of the tested parameters occur only in the river water, e.g., iopromide, diclofenac, iohexol, clindamycin, fexofenadine and valsartan. The research shows that at the site, a significant attenuation of pharmaceuticals can be achieved at travel times of 40–50 days and distances of 60–80 m, although higher values are ensured when the well is located more than 250 m away.

Keywords: riverbank filtration; pharmaceuticals in groundwater; removal of pharmaceuticals

1. Introduction

Riverbank filtration (RBF) systems are widely used for drinking water supplies. RBF, by forcing the infiltration of surface water into the groundwater systems, allows relatively large amounts of water to be obtained, especially in the alluvial aquifers located in the European lowland areas in river valleys and ice-marginal valleys [1,2]. The infiltration of surface water to groundwater systems and water passage through the aquifer media causes improvements in water quality by a set of processes including: sorption, redox processes and biodegradation [3,4]. The mixing of bank filtrates with ambient, usually unpolluted groundwater, also takes place [5,6]. Nevertheless, the quality of bank filtrate is strongly dependent on surface water quality. Currently, this dependency is extremely important due to the detection of contaminants (e.g., pharmaceuticals) in the river (source) water. The occurrence of pharmaceuticals (such as antibiotics, analgesics, blood lipid regulators, contrast agents) has been studied all over the world in surface and also in groundwater [7–9]. The occurrence of micropollutants was documented in Chinese rivers [10,11], Japanese rivers [11], Korean rivers [11], Kenyan rivers [12] USA rivers [13,14] and also European rivers [1,15,16] and has also been previously documented in the Warta River [17]. In cases of heavily polluted surface water or temporary occurrences of peak

constituent concentrations in rivers (e.g., during extreme weather conditions [18]), the contaminants can migrate to production wells in reduced concentration [4,19]. These remaining residues necessitate removal by the use of engineering techniques in treatment plants. However, a properly constructed RBF system can also be used as a natural water treatment method [16]. This can be achieved if the travel time (i.e., time of water passage from surface water to wells) is long enough to remove or considerably reduce the contaminants from the bank filtrate [1,4,16].

The goals of the research presented here are (i) to report the occurrence of a large number of pharmaceuticals in both river and bank filtrate and (ii) the investigation of their attenuation during bank filtrations. The data was analysed at points at different distances (and likewise travel times) from the river, as well as in various types of wells (vertical and horizontal), as according to the literature [4,7] the removal of pharmaceuticals increases with increasing distance (as well as travel time) from the source water.

2. Materials and Methods

2.1. Site Description

For the investigation of pharmaceuticals in river and bank filtrate water, the Krajkowo well field was selected. This well field is located 30 km from Poznań City. The well field is composed of the following (Figure 1): (1) a well group located on the floodplain along the Warta River (RBF-c) at a distance of 60–80 m from the riverbank; (2) a group of 56 wells situated on a higher terrace located 400–1000 m from the river (RBF-f); (3) one horizontal well (HW) with 8 radial drains situated 5 m below the river bottom. In the Krajkowo well field, one additional well group is recharged from artificial ponds. This part of the well field was not considered in this study. A detailed description of the well fields is presented in previous work [20].

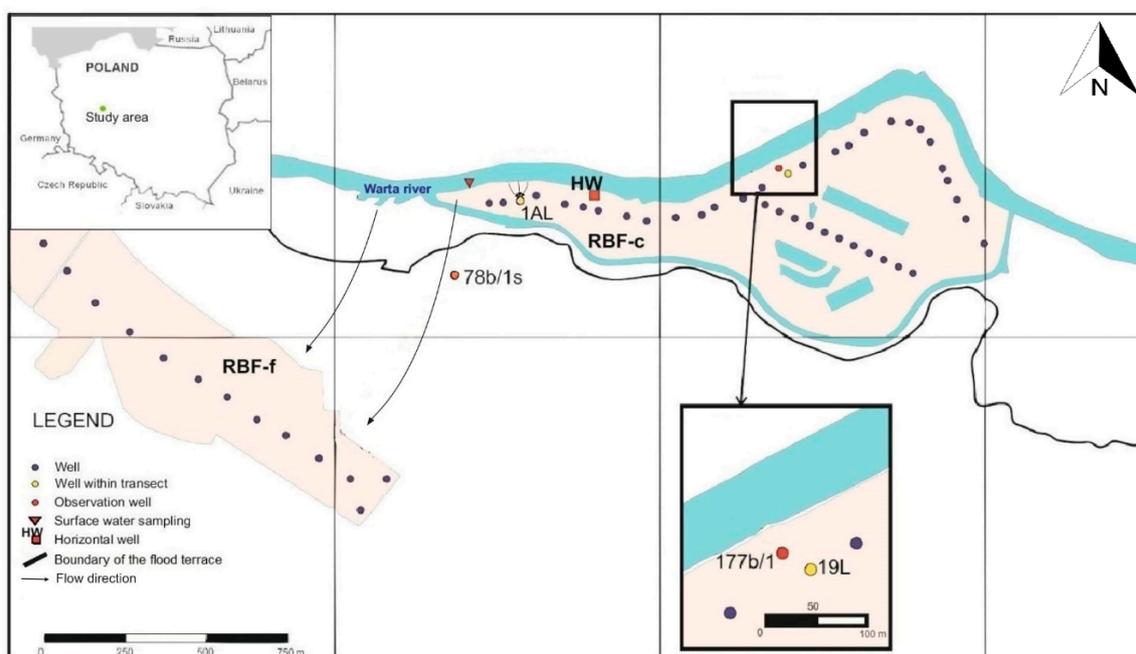


Figure 1. Situation map of the study area. RBF: riverbank filtration; RBF-c: wells on the flood terrace; RBF-f: wells on the higher terrace; and HW: horizontal well. [2] modified.

The Krajkowo well field is located in a region of favourable hydrogeological conditions. The total thickness of the aquifer is up to 40 m. In the upper part of the aquifer, there are sediments of the Warsaw-Berlin ice-marginal valley. Deeper sediments of the Wielkopolska Buried Valley are present.

In the profile of aquifer sediments, there are fluvial fine and medium-grained sands and fluvio-glacial coarse-grained sands with gravels. The total well field production is approximately 70,000–120,000 m³/day.

2.2. Methods

For the investigation of pharmaceutical behaviour along flow paths from the river to the wells, 6 sampling points were selected, source water (the Warta River) and the wells located at different distances from the river (Table 1). Three production wells were selected for the research: HW, 19L, and 1AL. The closest sampling point is HW. Observation well 177b/1 is located between the river and well 19L. Observation well 78b/1s is the furthest away sampling point. The RBF-f wells shown in Figure 1 were in continuous operation during 2 years, including the period of our investigations. This situation enabled the observation of bank filtrate in well 78b/1s (Figure 1). The water balance and residence time were estimated based on the analyses of the hydrochemical data and the results of the mathematical modelling of groundwater flow. The well field monitoring data performed by the water company were also used for the interpretation.

Table 1. Characterization of sampling points.

Sampling Points	Location	Distance from the River Bank (m)	Depth of the Well Screen (m)	Contribution of River Water to Total Water Balance in Well (%)	Residence Time (days)
Warta River	-	-	-	-	-
Horizontal well-HW	Drains under river bottom	-	5 m below river bottom	100	1
Observation well 177b/1	Floodplain	38	12.5–14.5	100	24
Vertical well 19L	Floodplain	64	24.0–32.0	65–85	40
Vertical well 1AL	Floodplain	82	16.5–32.5	65–85	50
Observation well 78b/1s	Higher terrace	250	18.0–28.0	60	150

For the preliminary investigation of pharmaceuticals, 3 sampling points were selected (surface water, 1AL, and 78b/1s). Three sampling sessions were performed on September 2017, May 2018 and June 2018. The laboratory measurements addressing 13 constituents were performed in the ALS Laboratory in Prague. Based on this investigation, consecutive sampling campaigns were planned. The next investigations were performed in July, August and October 2018 and included six sampling points (surface water, HW, 177b/1, 1AL, 19L, and 78b/1s). The measurements of 75 constituents were performed in the Laboratory of Povodí Vltavy VHL Plzeň. (Table 2).

Table 2. List of substances tested in extended investigation (July, August, October 2018).

Parameters	LOQ	Parameters	LOQ	Parameters	LOQ
Carbamazepine	<10	Saccharin	<50	Alfuzosin	<10
Erythromycin	<10	Gabapentin	<10	Bisoprolol	<10
Sulfamethoxazol	<10	Tramadol	<10	Celiprolol	<10
Iopromide	<50	Clarithromycin	<10	Citalopram	<20
Ibuprofen	<20	Roxithromycin	<10	Clindamycin	<10
Diclofenac	<20	Azithromycin	<10	Cyclophosphamide	<10
Iopamidol	<50	Carbamazepine-DH	<10	Diltiazem	<10
Atenolol	<10	Oxcarbazepine	<10	Fexofenadine	<10
Caffein	<100	Ibuprofen-2-hydroxy	<30	Fluconazole	<10
Ketoprofen	<10	Ibuprofen-carboxy	<20	Fluoxetine	<10
Metoprolol	<10	Diclofenac-4-hydroxy	<20	Iomeprol	<50
Peniciline G	<10	Naproxene-O-desmeth	<20	Irbesartan	<10
Sulfamerazine	<10	Venlafaxine	<10	Ivermectin	<10
Sulfamethazin	<10	Sertraline	<10	Lamotrigine	<10
Sulfapyridin	<10	Ranitidine	<10	Lovastatin	<10
Trimetoprim	<10	Iohexol	<50	Memantine	<20
Furosemide	<10	Carbamazepine-2-hydr	<10	Mirtazapine	<10
Gemfibrozil	<50	Clofibric acid	<10	Phenazone	<10
Hydrochlorothiazide	<10	Cotinine	<20	Primidone	<10

Table 2. Cont.

Parameters	LOQ	Parameters	LOQ	Parameters	LOQ
Naproxene	<50	Paraxanthine	<100	Propranolol	<10
Triclocarban	<10	Bisfenol B	<50	Propyphenazone	<10
Triclosan	<20	Bisfenol S	<50	Simvastatin	<10
Chloramphenicol	<20	Oxypurinol	<50	Sotalol	<10
Bezafibrate	<10	Tiamulin	<10	Telmisartan	<20
Warfarin	<10	Acebutolol	<10	Valsartan	<10

The sampling collection took one day. The samples were taken from surface water, observation and production wells. The observation wells were pumped using a portable pump (MP-1, Grundfos, Bjerringbro, Denmark). The production wells were pumped continuously before and during the sampling periods. The water samples were stored in glass bottles and transported in a refrigerated container and frozen. After 5 days of storage at $-18\text{ }^{\circ}\text{C}$ temperature, the samples were delivered to the laboratory. The investigation of pharmaceuticals in the ALS Laboratory in Prague was performed using liquid chromatography (LC-MS/MS). The extended investigations in the laboratory of Povodí Vltavy VHL Plzeň were carried out using liquid chromatography (LC-MS/MS) and ultra-high-performance liquid chromatography (UHPLC MS/MS). A 1200 Ultra-High-Performance Liquid Chromatograph (UHPLC) tandem with 6495 Triple Quad Mass Spectrophotometer (MS/MS) of Agilent Technologies was used in ESI mode. The separation was carried out on an X-bridge C18 analytical column ($100 \times 4.6\text{ mm}$, $3.5\text{ }\mu\text{m}$ particle size). The mobile phase consisted of (A) methanol and (B) water with 0.02% acetic acid and 5 mM ammonium fluoride as mobile phase additives. The flow rate was 0.5 mL min^{-1} . The injection volume was 0.050 mL.

3. Results

Preliminary investigations performed in September 2017 and, May and June 2018 at three sampling points allowed the determination of occurrences of pharmaceuticals in the surface and bank filtrate water (Table 3). Among the 13 measured parameters, antibiotics, anti-inflammatory and analgesic drugs, psychotropic drugs, X-ray agents and β -blockers were detected. The highest pharmaceutical concentrations and the largest variety of substances were detected in the Warta River (max. 485 ng/L). The investigation showed that the concentrations in bank filtration wells were considerably lower (max. 184 ng/L). Some of the pharmaceuticals were detected only in the river water (iomeprol (max. 156 ng/L), iopromide (max. 413 ng/L), metoprolol (max. 26 ng/L), metformin (max. 88 ng/L) and 1H-Benzotriazole (140 ng/L)). In well 1AL, located 82 m away from the river, 5 substances were detected (carbamazepine (max. 145 ng/L), sulfamethoxazole (max. 20 ng/L), diclofenac (max. 99 ng/L), naproxen (max. 21 ng/L) and iohexol (max. 146 ng/L)). In observation well 78b/1s that is located 250 m from the river, only 2 constituents were detected (carbamazepine (max. 81 ng/L), iohexol (max. 184 ng/L)). The results documented the occurrence of pharmaceuticals in both surface water and bank filtrates.

In July, August and October 2018, the analyses involving 75 different compounds at 6 sampling points were conducted. The analyses included antibiotics, anti-inflammatory and analgesic drugs, psychotropic drugs, X-ray agents, β -blockers, sweeteners and drugs, such as caffeine. A total of 25 of the 75 tested pharmaceuticals were detected (Table 4).

Table 3. Concentrations of pharmaceuticals in ng/L: The preliminary investigation. <LOQ - below limit of quantification. (Measurements performed in ALS Laboratory in Prague).

		September 2017				May 2018			June 2018		
		LOQ	Warta 1AL 78b/1s			Warta 1AL 78b/1s			Warta 1AL 78b/1s		
Antibiotics	Sulfamethoxazole	<10	43	15	<LOQ	306	20	<LOQ	24	16	<LOQ
	Iopromide	<30	<LOQ	<LOQ	<LOQ	413	<LOQ	<LOQ	79	<LOQ	<LOQ
X-ray agents	Iohecol	<10	120	<LOQ	<LOQ	217	<LOQ	<LOQ	485	146	184
	Iomeprol	<39	<LOQ	<LOQ	<LOQ	156	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Psychotropic	Carbamazepine	<10	110	145	81	208	73	9	91	77	75
Beta-blockers	Metoprolol	<100	<LOQ	<LOQ	<LOQ	26	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Anti-inflammatory	Diclofenac	<10	43	99	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Naproxene	<10	39	<LOQ	<LOQ	31	21	<LOQ	<LOQ	<LOQ	<LOQ
Antidiabetic	Metmorfina	<50	88	<LOQ	<LOQ	79	<LOQ	<LOQ	55	<LOQ	<LOQ
Benzotriazole	1H-Benzotriazole	<80	140	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Ketoprofen, iopamidol, and ibuprofen were never detected.

In general, the highest concentration of pharmaceuticals was detected in the river water (Table 4). However, the concentrations decrease along the flow path from the river to the wells (Figure 2). The distance and travel time have an impact on the decrease in concentrations. Some of the substances occurred only in the river water (iopromide (max. 149 ng/L), diclofenac (max. 37.4 ng/L), metoprolol (max. 19.6 ng/L), penicillin G (max. 17.1 ng/L), saccharine (max. 360 ng/L), iohecol (max. 120 ng/L), cotinine (max. 50.8 ng/L), clindamycin (max. 12.7 ng/L), fexofenadine (max. 40.7 ng/L), valsartan) others also in the closest wells, HW and 177b/1 (caffeine, paraxanthine, sulfapyridine, sotalol, telmisartan) or just there (primidone). Carbamazepine, sulfamethoxazole, gabapentin, tramadol, oxypurinol, fluconazole and lamotrigine, are the most common compounds from all sampling sessions and sampling points, being episodically detected also in the farthest production wells: 19L and 1AL.

The concentration of some pharmaceuticals in the Warta River and the nearest well, HW, are similar (e.g., carbamazepine, sulfamethoxazole, tramadol, fluconazole, lamotrigine (Table 4)). This result is due to the short distance (5 m) and short travel time (1 day) between the river and this well. Most of the substances found in the HW well were also observed in well 177b/1, but at lower concentrations. The significant decreases in concentrations occurred in production wells 19L and 1AL, where most of the parameters were below LOQ. This finding is due to the longer distances (64–82 m) and travel times (40–50 days) for these wells. In well 78b/1s, which is located 250 m away from the Warta River with a travel time of 150 days, only two parameters, carbamazepine and gabapentin, were detected and were at relatively low concentrations. This is the result of water mixing (Figure 2 and Table 4).

The detected parameter concentrations in the river water range from 10.8 ng/L (sulfapyridine) to 1470 ng/L (paraxanthine). The highest concentrations in river water occurred in the August 2018 sampling session. Oxypurinol presented high concentrations in river water that persisted (even at higher values) in nearby wells (HW) and also in more distant ones (1AL). Carbamazepine also persisted at high concentrations (135 ng/L in river water and 179 ng/L in HW).

Figure 3 shows the concentration of individuals groups of parameters. The groups were established based on the use of the substances. Nine groups were separated: antibiotics; X-ray agents; psychotropics, anticonvulsants, and antiepileptics; beta-blockers and cardiac drugs; drugs like caffeine; analgesics and anti-inflammatories; antifungals and antibacterials; antihistamines; and xanthine oxidase inhibitors. The highest concentrations show xanthine oxidase inhibitors, although there is only one substance in this group (oxypurinol). Psychotropics, anticonvulsant and antiepileptic drugs and drugs like caffeine also reach high concentrations. On the lower level antibiotics were detected: X-ray agents; beta-blockers and cardiac drugs; analgesic and anti-inflammatory; as well as antifungal and antibacterial.

Table 4. Concentrations of pharmaceuticals in ng/L: Extended investigations. HW - Horizontal well, <LOQ - below limit of quantification. Measurements performed in VHL Plzeň.

		LOQ	July 2018						August 2018						October 2018					
			Warta	HW	177b/1	19L	1AL	78b/1s	Warta	HW	177b/1	19L	1AL	78b/1s	Warta	HW	177b/1	19L	1AL	78b/1s
Antibiotics	Clindamycin	<10	12.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	12.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Penicillin G	<10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	13	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	17.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Sulfamethoxazole	<10	29.3	27.1	15.9	<LOQ	15	<LOQ	18.8	17.1	12.4	<LOQ	<LOQ	<LOQ	37.7	21.8	10.1	<LOQ	10.5	<LOQ
X-ray Agents	Iohexol	<50	120	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	90	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Iopromide	<50	149	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	59.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	105	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Psychotropic, Anticonvulsant, Antiepileptic	Carbamazepine	<10	130	179	161	112	110	83.1	132	131	131	88.6	99	63.6	135	134	148	135	123	80.3
	Gabapentin	<10	97	53.3	18.7	13	14	21.3	55.6	27	25.2	12.6	13.8	15.6	81.5	61.7	13.5	<LOQ	10.2	24
	Lamotrigine	<10	35.8	54	29.1	15	21	<LOQ	36.1	44.9	26.7	15.6	16.6	<LOQ	45.1	42.6	38.3	24.6	25.2	<LOQ
	Primidone	<10	<LOQ	12.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	10.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	10.2	11.6	<LOQ	<LOQ	<LOQ
Beta-blockers, Cardiac Drugs	Metoprolol	<10	11.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	19.6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Sotalol	<10	23.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	14.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	50.3	14.1	<LOQ	<LOQ	<LOQ	<LOQ
	Telmisartan	<20	140	62.5	<LOQ	<LOQ	<LOQ	<LOQ	132	52	<LOQ	<LOQ	<LOQ	<LOQ	136	60.5	<LOQ	<LOQ	<LOQ	<LOQ
	Valsartan	<10	61.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	23	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	28.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Drugs, e.g., Caffeine	Caffeine	<100	154	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1350	<LOQ	140	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Continine	<20	30.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	50.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Saccharin	<50	111	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	360	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Paraxanthine	<100	163	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1470	<LOQ	104	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Analgesics, anti-Inflammatory	Diclofenac	<20	24.5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	37.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Tramadol	<10	76.1	73.7	35.9	19	22	<LOQ	52	38.1	27.4	17	20.5	<LOQ	83.8	64.4	35.3	24.4	27.9	<LOQ
Antifungal and Antibacterial	Fluconazole	<10	35.6	48.4	21.5	12	21	<LOQ	32.5	42.1	20.2	10.4	19.6	<LOQ	51.7	51.6	29.2	15	21.5	<LOQ
	Sulfapyridine	<10	<LOQ	10.7	14.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	11.7	<LOQ	<LOQ	<LOQ	10.8	11.2	13	<LOQ	<LOQ	<LOQ
Antihistamine	Fexofenadine	<10	40.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	28.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	33.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Xanthine Oxidase Inhibit	Oxypurinol	<50	388	1350	503	237	345	<LOQ	610	1100	486	130	228	<LOQ	1050	1010	652	260	317	<LOQ

Iomeprol (94.7 ng/L) and venlafaxine (12.1 ng/L), were detected once and only in the Warta River.

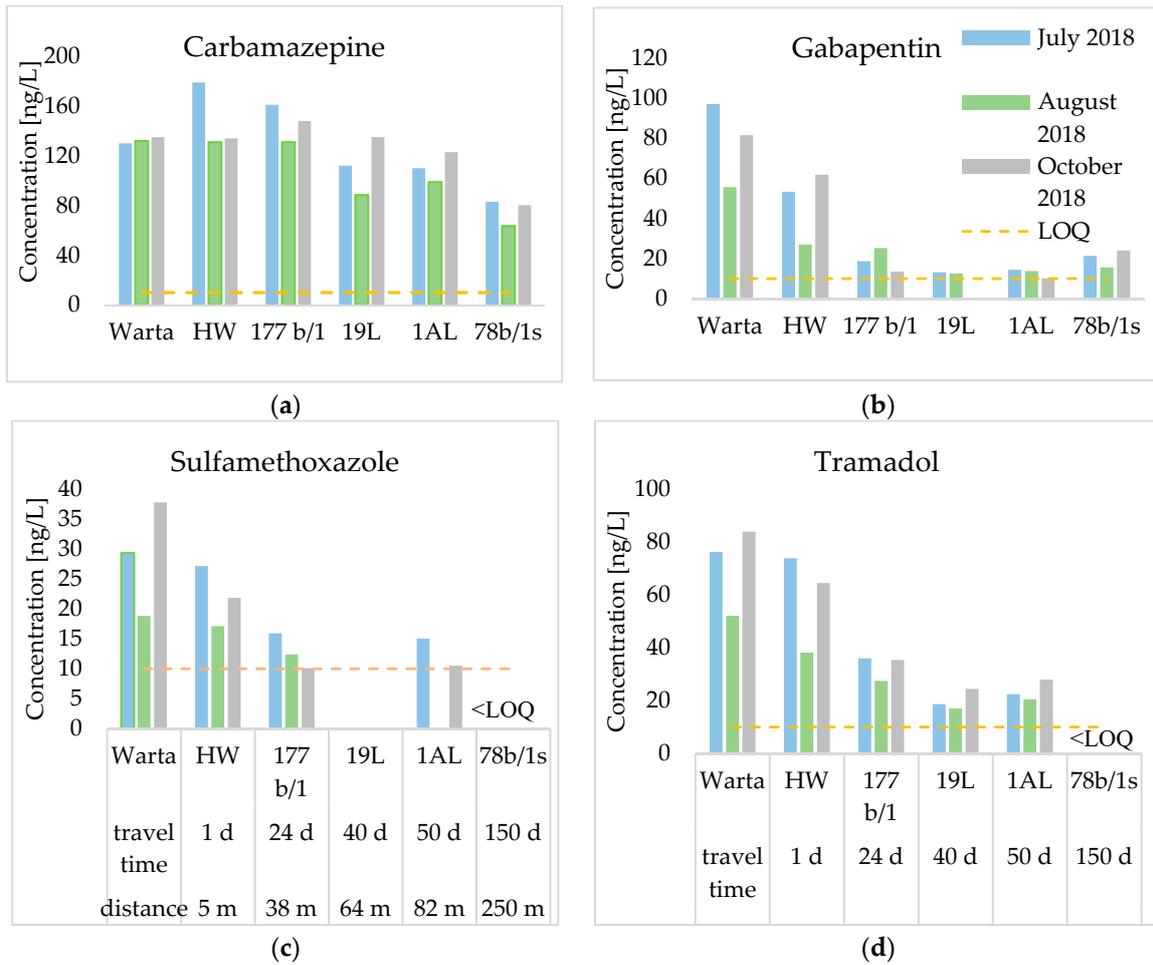


Figure 2. Concentrations of carbamazepine (a), gabapentin (b), sulfamethoxazole (c), and tramadol (d) for 3 sampling sessions.

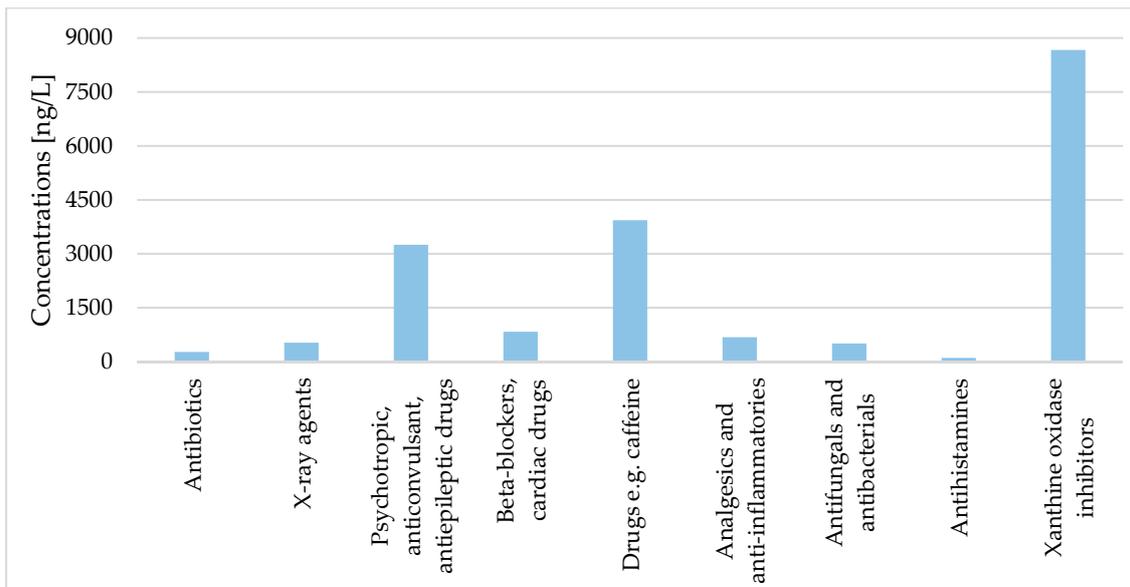


Figure 3. Sum of concentrations of all pharmaceuticals in each series in categories of pharmaceutical according to the application.

Table 5 shows the percentage of removal for pharmaceuticals at sampling points located at different distances from the river. The removal was calculated using the formula:

$$\text{Removal (\%)} = \frac{\text{concentration in river} - \text{concentration in well}}{\text{concentration in river}} \times 100\% \quad (1)$$

Table 5. Removal of pharmaceuticals in %. HW—Horizontal well.

	HW			177b/1			19L			1AL			78b/1s		
	VII	VIII	X	VII	VIII	X	VII	VIII	X	VII	VIII	X	VII	VIII	X
	2018			2018			2018			2018			2018		
Carbamazepine	−37.7	0.8	0.7	−23.8	0.8	−9.6	13.8	32.9	0	15.4	25.0	26.7	36.1	51.8	40.5
Sulfamethoxazole	7.5	9.0	42.2	45.7	34.0	73.2	100	100	100	48.8	100	100	100	100	100
Gabapentin	45.1	51.4	24.3	80.7	54.7	83.4	86.5	77.3	100	85.2	75.2	83.1	78.0	71.9	70.6
Tramadol	3.2	26.7	23.2	52.8	47.3	57.9	75.6	67.3	70.9	70.6	60.6	75.5	100	100	100
Oxypurinol	−247.9	−80.3	3.8	−29.6	20.3	37.9	38.9	78.7	75.2	11.1	62.6	78.3	100	100	100
Fluconazole	−36.0	−29.5	0.2	39.6	37.8	43.5	65.7	68.0	71.0	40.7	39.7	62.1	100	100	100
Lamotrigine	−50.8	−24.4	5.5	18.7	26.0	15.1	58.1	56.8	45.5	40.5	54.0	63.2	100	100	100

The removal is calculated on detected values only and mixing was not accounted for.

The lowest removal was observed in the HW. In the HW, some of the parameters increase, which probably occurs because there were higher concentrations in the Warta River before the sampling periods. In observation well 177b/1, removal varies over a range of −29.6–100% depending of the compound. The removal in two production wells, 19L and 1AL, show similar values. At the furthest sampling point, 78b/1s, most parameters reduced by 100%. The removal probably depends on the location of the sampling point (distance and travel time from the river) but is also different for specific compounds. The evaluation of the lowest removal shows that carbamazepine (a psychotropic drug) is found at the farthest points (78b/1s – 250 m from the river) and decreases by 36.1–51.8%, whereas sulfamethoxazole (an antibiotic), gabapentin (an anti-epileptic drug) and tramadol (an analgesic drug) reach similar values at a distance of 38 m (177b/1s). Carbamazepine is a difficult compound to remove in spite of long distances and travel times. Gabapentin attains the highest removal but is not completely removed, even at the farthest point.

The total reductions of some (Table 5) pharmaceuticals (sulfamethoxazole, tramadol, oxypurinol, fluconazole, lamotrigine) are achieved in wells 19L, 1AL and an observation well 78b/1s, while this did not occur in HW and 177b/1. The results indicate that at the given conditions, significant reductions in pharmaceutical concentrations can be achieved at travel times of 40–50 days and distances of 60–80 m, although higher values of the reduction can be achieved when the well is located more than 250 m away.

The degree of removal of pharmaceuticals at sampling points depends not only on the travel time in the subsurface, but also on the diverse impact of sorption and biodegradation, and the influence of temperature and redox conditions on those processes [21]. The assessment of the impact of these factors was not analyzed in detail in this study. However, based on well field monitoring data, it can be assumed that in wells located close to the river (HW, 177b/1, 19L, 1AL), the biodegradation and oxidation occur because of oxic conditions. The following data confirmed this: oxygen 1–6.2 mg/L, nitrate 0.5–18 mg/L and a lack of hydrogen sulfide. In the well located further away from the river (78b/s), there are trace concentrations of nitrates (0.08–0.26 mg/L) and a lack of oxygen, however, the presence of hydrogen sulfide (0.024–0.066 mg/L) is noted. It can also be added that the redox processes and biodegradation in wells located close to the river are also favored by higher temperatures in summer (15–17 °C). Whereas, further away from the river (78b/s well), the temperatures are leveled in the range of (8–12 °C), similar to ambient groundwater.

4. Discussion

The concentrations of pharmaceuticals in the Warta River were found at levels previously documented in European rivers and lakes [1,7,22]. Carbamazepine concentrations in the Warta River

(130–135 ng/L) are at a similar level as in the Nairobi River (Kenya) [23] 100 ng/L and in the Leine River (Germany) 144 ng/L [24]. However, carbamazepine concentrations in the Warta River are much lower than in Lake Tegel (510 ng/L) and Lake Wennsee (310 ng/L) [19]. Similar concentrations also show Sulfamethoxazole in the Warta River is 18.8–37.7 ng/L and in the Lake Maggiore (Italy) 10ng/L [25], in the Douro River (Portugal) 53.3 ng/L [26]. Among 75 substances, 25 were detected in the river. Nonsteroidal anti-inflammatory drugs (diclofenac) previously measured in the Warta River were documented at lower concentrations in the current research than in 2007 [15], while ibuprofen and benzaifibrate documented earlier were not detected in the current research [2,15].

The research presented confirms high percentages of removal for organic micropollutants at the RBF sites [2,7,8,19,22,27–30]. Among 25 substances measured in the Warta River, 12 were not detected in the RBF site in Krajkowo (valsartan, fexofenadine, clindamycin, saccharin, iopromide, diclofenac, cotinine, iohexol, metoprolol, penicillin G, iomeprol and venlafaxine). In the case of the organic micropollutants research at two sites in Budapest, out of the 36 analyzed micropollutants, 12 were present in almost all the samples [22]. It is documented in the literature [3,4,27] that the transport and removal of organic micropollutants during subsurface movement from rivers to wells depends highly on the prevailing hydrochemical conditions along the flow path. As a result, different degradation behaviour can be seen for individual sites. The percentage of removal of carbamazepine varied between 37.7 and 51.8%, which was relatively persistent during subsurface flow as was observed previously at other sites [4,22,27,28]. Carbamazepine was also detected in well 78b/1s, where the travel time is 5 months. The result is comparable to findings from Berlin, where carbamazepine occurs in the well where the travel time is 2.8–4.3 months [19]. In the 78b/1s well, Gabapentin was also detected but was characterized by a relatively high percentage of removal (>70%). Oxypurinol was not removed along short distances (relatively high concentrations were seen in HW and 177b/1), but in production wells (distance 64–82 m), the percentage of the removal increased to a range of 11–78% and at distances of 250 m (78b/1s), and the complete removal was achieved. These analyses confirm earlier findings, documenting carbamazepine as a persistent constituent, while gabapentin and oxypurinol are subjects to primary degradation during filtration [27].

The high percentages of removal are achieved for the remaining substances that occur in bank filtrates (Figure 2, Table 5). The remaining substances detected in bank filtrates show a relatively high percentage of removal (typically more than 70%) in production wells located 64–82 m from the river. A similar reduction was observed in the Rhine River in wells located at 70 m, where the removal was >51% [8] and Lake Tegel in Berlin where the wells, located at 90 m distance from a lake, were removed >51% (Table 5) [29]. A total of 12 substances were detected in the Warta River that did not occur in bank filtrates, showing the complete removal even at short distances.

The negative removal observed in the case of HW and 177b/1 (the sampling points located at the nearest distance to the river) inaccurately suggest an increase in concentrations during subsurface flow and is probably due to unrecognized fluctuations in concentrations in the source water before sampling (carbamazepine, oxypurinol, lamotrigine, fluconazole). A similar situation was encountered at the RBF site in Austria. The higher concentrations of some substances appear in the wells at higher distances [24]. The same effect is responsible for fluctuations in the removal during the investigation periods (e.g., 11.1–78.3% for the case of oxypurinol in well 1AL). It is also possible due to the transformation from other compounds.

5. Conclusions

The research carried out on the Krajkowo riverbank filtration site (Poland) contained 75 different compounds, including antibiotics, anti-inflammatory and analgesic drugs, psychotropic drugs, X-ray agents, β -blockers and sweeteners. A total of 25 of these have been detected. The highest concentrations were found in the Warta River.

In the bank filtrates, 13 compounds were detected. Their concentrations declined along the flow path. The number of detected pharmaceuticals at each sampling point decreased with increasing

distances. The lowest removal was noticed in the horizontal well. In wells 1AL and 19L (distances from the river of 64 to 82 m, respectively), the removal of most parameters was approximately 70–80%. For the observation well 78b/1s (at a distance of 250 m from the river), only 2 compounds were detected.

This research shows the significant role of bank filtration in the removal of pharmaceuticals. Under similar hydrogeological conditions, wells should be located at least 60 m from the river. Higher removal can be achieved at distances of 250 m from the source water. However, the results obtained emphasize the need for further monitoring studies to recognize the factors that determine the variability of micropollutants in the river, as well as in the production wells (hydrological conditions and seasons of the year). It is also necessary to identify processes that condition the migration and removal of micropollutants. Future research should focus on fewer compounds and their metabolites.

Author Contributions: R.K. prepared the manuscript and all authors read and approved the manuscript, R.K. took part in fieldwork and performed graphical and statistical interpretations; K.D., J.G. and R.K. interpreted the data and were involved in discussing the study; J.G., K.D. and R.K., were responsible for the overall coordination of the research team.

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Abbreviations

The following abbreviations are used in this manuscript:

BF bank filtrate
HW horizontal well

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