

The occurrence of microorganic contaminants (pharmaceuticals and pesticides) in a river bank filtration site recharged by an agriculturally- and wastewater-impacted small lowland river (Oborniki site, Poland)

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A high contamination level by microorganic pollutants (contaminants of emerging concern – CECs and pesticides) was documented at the Oborniki River bank filtration site (Poland) recharged by surface water from the Wełna River. The highest concentration of CECs and pesticides was found in surface water samples. The documented contamination level of Wełna River water (the river draining a small lowland catchment) is higher than that documented in bigger rivers like the Warta, Iżera and Elbe. High contamination levels were documented also in wells that are recharged by water from the Wełna River via bank filtration. The removal rate observed in wells (compared with source river water) was estimated as 57% for CECs and 74% for pesticides while the removal rate calculated for carbamazepine (a conservative pharmaceutical substance) was 26%. In one well the nicosulfuron concentration was higher than the upper permissible limit. Among the substances detected were also 2 banned constituents: chlorotoluron and izoproturon.

Key words: pharmaceuticals and pesticides in groundwater and surface water, river bank filtration, small lowland river.

INTRODUCTION

Contaminants of emerging concern (CECs) and pesticides are increasingly detected in aquatic systems due to the rapid development of analytical methods enabling the detection of substances that occur in the environment at relatively low concentrations, at the level of $\mu\text{g/l}$ or ng/l (Munro et al., 2019; Fonseca et al., 2020). Agricultural activity is undoubtedly the primary source of pesticides in surface waters (Guzzella et al., 2006; Loos et al., 2010; Köck-Schulmeyer et al., 2014). The use of pesticides during cultivation significantly improves harvest quality and yield. But, pesticides and their degradation products can contaminate different environmental components, including surface water and groundwater (Dragon et al., 2019; Lee et al., 2019; Khezami et al., 2024). The CECs (mainly pharmaceuticals, personal care

products, sweeteners, etc.) appear in aquatic systems by entering surface water primarily through discharge effluent from wastewater treatment plants (WTP; Maeng et al., 2010; Hollender et al., 2018; van Driezum et al., 2019; Dragon et al., 2022). It is known that conventional WTPs do not eliminate CECs during the treatment process (Kibuye et al., 2019). Scientific publications have documented the occurrence of organic micropollutants in surface water worldwide. This relates to both pesticides (e.g., Loos et al., 2010; Reh et al., 2013; Kock-Schulmeyer et al., 2014) and pharmaceuticals (e.g., Li, 2014; Hamann et al., 2016). Some studies document that micropollutants' migration in groundwater systems is highly dependent on surface water quality, for example, at riverbank filtration sites (Massmann et al., 2008; Kovačević et al., 2017; Hollender et al., 2018; van Driezum et al., 2019; Kruc et al., 2019).

The associated negative environmental and public health impacts have caused considerable social and scientific concern worldwide. Additionally, groundwater contamination by synthetic organic chemicals is attracting growing attention because it can potentially negatively affect human health (Postigo and Barceló, 2015; Kruc-Fijałkowska et al., 2022). Due to the nega-

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tive impact of pesticides on human health, the Drinking Water Directive 98/83/EC (EC, 1998) defines a maximum concentration of 0.1 mg/l for individual pesticides and their degradation products and 0.5 mg/l for total pesticides present in a sample. These values are identical to the groundwater quality standards used in Poland (Regulation..., 2017). Moreover, in the EU directive 2020/2184 (EC, 2020) on the quality of water intended for human consumption, risk-based pesticide monitoring is requested (only pesticides that are likely present in a given environment need to be monitored). However, there are still no permissible limits for pharmaceuticals in drinking water. Only some substances are included in Watch Lists which are forcing Member States of the European Union to measure these constituents in aquatic systems (EC, 2022).

The lack of the formal requirements as regards CEC investigation discourages waterworks operators from including these substances during operational well-field monitoring. However, in the light of future changes in water monitoring, there is a need to investigate CECs to recognize their occurrence and behaviour in aquatic systems.

The objectives of the present study are: (1) the investigation of CEC and pesticide contamination levels in a river bank filtration system; (2) assessment of the removal rates of CECs and pesticides during underground flow from surface water to wells; (3) comparison of the CEC and pesticide contamination levels in the Wełna, a small lowland river, with large rivers in Poland, Czech Republic and Germany (based on published data).

SITE DESCRIPTION

The Oborniki well-field is located in the Wełna River valley, ~2 km from the town centre. The well-field is situated at the end of the Wełna River catchment area, ~3 km from the Wełna River confluence with the Warta River. The Wełna River is a small lowland river 118 km long with a catchment area of 2621 km² (Fig. 1). Many lakes are present in the catchment area, and the river flows through 9 of them. The catchment area is characterized by intensive agricultural activity. There are 13 towns and villages with >1000 inhabitants located in the catchment area upstream of the Oborniki well-field, each connected to a sewage system (WTP; Fig. 1A). The WTPs are usually located near surface water, and the outlets of the treated wastewater are connected to a river or lake.

The average Wełna River flow rate is 10.1 m³/s, and the mean low flow is 2.31 m³/s. The river is between 16 and 38 m wide, and the depth is 0.4–1.4 m. The river level is regulated in the well-field area by a weir located on the Młynówka channel (Fig. 1B).

The Oborniki well-field is composed of 13 productive wells (Fig. 1B). Four wells are located on the right side of the river on an artificial Island situated between the Wełna River and Młynówka channel, while nine wells are located on the left side of the river on two well barriers located between the infiltration pond and the river (Fig. 1B and Table 2). The wells are recharged by both river bank filtration from the Wełna River and artificial infiltration from the pond (~60 m²), which is recharged by water taken from the Wełna River. In the well-field vicinity to the west and north sides, there are forests, while on the south side, there is an industrial area and a main road as well as a railway line (Fig. 1B). Close (~300 m away) to the east side of the well-field, there is the residential area of Kowanówko village. There is a relatively new central sewage system connected to the WTP, but there are still buildings not connected to the central system.

The unconfined aquifer used for water supply has a relatively small thickness of 10–20 m (Fig. 2). In the shallow part of the aquifer, fine sands are dominant, while in deeper parts coarse sands and gravels occur. The aquifer is underlain by clays or muds, and locally tills. The average yield of each well is between 40 and 50 m³/h. The average yield of the well-field is between 187 m³/h and 292 m³/h. The well-field has been operating since 1983.

There has been no assessment of the main components in the water balance of the wells investigated, but taking into consideration data from other sites located in similar settings, it can be inferred that in the Oborniki well-field, due to the relatively close distance of the wells to the river, the share of river water in the wells is large (>70%), especially in wells located close to the river channel.

MATERIALS AND METHODS

Two sampling campaigns have been conducted to assess the level of groundwater contamination by microorganic pollutants, in October 2022 and in June 2023. The first sampling campaign included hydrochemical investigation in all productive wells and surface water (source water) taken from the Wełna River and infiltration pond. The first sampling series included material for investigating basic surface water and groundwater chemistry, pesticides, and the screening sampling of pharmaceuticals. This screening investigation aimed to select sampling points for a more detailed investigation of CECs in the second sampling series. The second sampling series included material for an investigation of pesticides and comprehensive analyses of CECs, and was performed in 6 selected productive wells and surface water at two points along the Wełna River. The infiltration pond was excluded from the analyses in the second sampling series due to clogging of its bottom, which was documented also by hydrochemical investigation.

The production wells were pumped continuously for at least one day before the sampling period. The surface water was sampled using a telescopic basket 5 m long. The basic groundwater chemistry investigation samples were sampled into three 100-ml high-density HPDE polythene bottles. The Fe and Mn testing samples were treated with HNO₃, while samples for nitrogen compounds were treated with chloroform. The water samples for pesticide investigation were sampled into 300 ml brown glass bottles with PTFE caps. The samples for the comprehensive investigation of pharmaceuticals were sampled in 100 ml brown glass bottles. All bottles were rinsed three times and emptied to prevent degassing. Directly in the field, electrical conductivity, pH, temperature, oxygen, and ORP (Oxidation-Reduction Potential) measurements were performed using an Elmetron CX-461 multidevice (Elmetron, Zabrze, Poland). After sampling, the water samples were transported to the laboratory on the same day using a transportable refrigerator. The samples for comprehensive investigation of pharmaceuticals were frozen directly in the field using a Meteor type transportable freezer and stored at –18°C during transportation to the laboratory.

The chemical analyses were performed at the Institute of Geology, Adam Mickiewicz University in Poznań, Poland. The groundwater samples were analyzed for cations (Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) and anions (Cl⁻, NO₃⁻, NO₂⁻ and SO₄²⁻) using a Metrohm 881 Compact IC Pro ion chromatograph (Metrohm AG, Herisau, Switzerland). To ensure data quality, the ionic error balance was calculated and found to be within 3%. Furthermore, concentrations of Al, Cr, Ni, Cu, Zn, As, Cd, Pb, Fe and

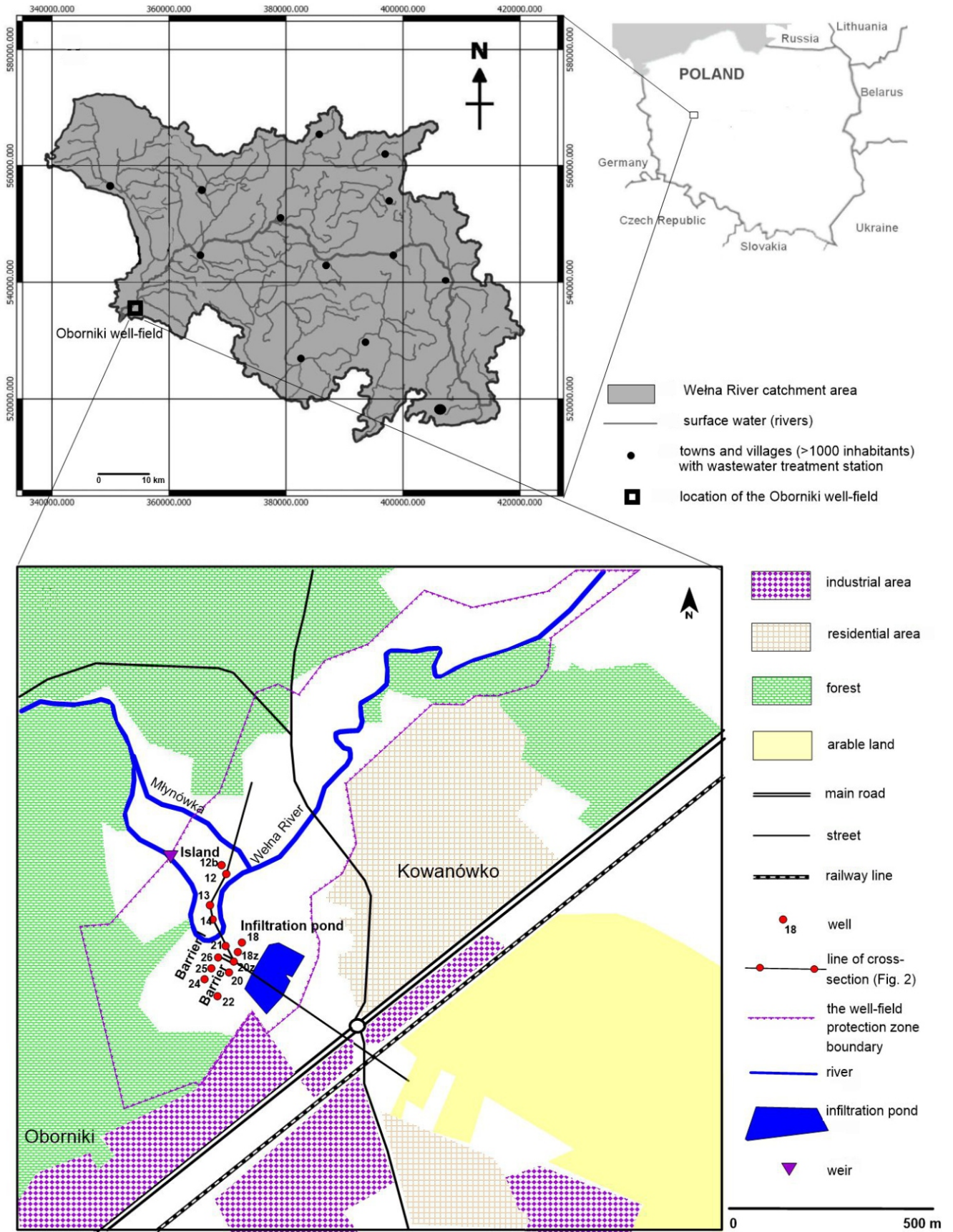


Fig. 1. Location map

A – map of the Wełna River catchment; B – location map of the Oborniki well-field

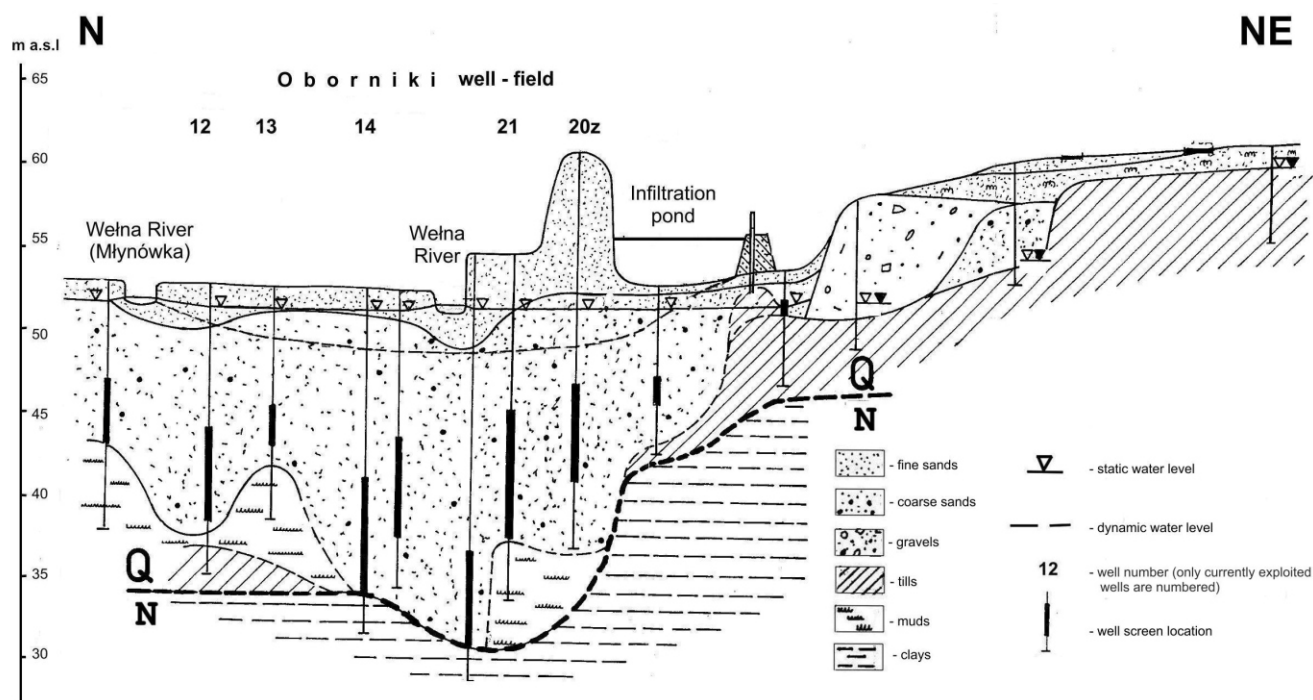


Fig. 2. Cross-section

Mn were determined using inductively coupled plasma mass spectrometry (ICP-QQQ 8800 Triple Quad, Agilent Technologies Inc. Santa Clara, CA, United States). The analytical procedures, instrumental operating parameters, and chemical reagents used are described in detail in the studies of [Górski and Siepak \(2014\)](#) and [Siepak and Sojka \(2017\)](#).

The measurement of pesticides and the screening of pharmaceuticals were performed in the Institute of Plant Protection – National Research Institute in Poznań, Poland. The study covered over 327 active substances including plant protection products and 14 pharmaceutical substances ([Appendix 1](#)). These substances were extracted from water samples using solid-phase extraction (SPE) with graphite carbon black. The final determination of the compounds was performed using reverse-phase ultra-performance liquid chromatography with a quadrupole mass spectrometer (RP-UPLC-MS/MS), following the methods of [Di Corcia et al. \(2000\)](#) and [Jeannot et al. \(2000\)](#).

The comprehensive analyses of pharmaceuticals (including 120 substances) were performed at the Povodí Vltavy VHL Plzeň, Czech Republic laboratory. Extraction of the compounds investigated was performed using EPA analytical method No. 1694 ([EPA, 2007](#)). 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 pharmaceuticals. The separation was achieved on an X-Bridge C18 analytical column (100 mm 4.6 mm i.d., 3.5 µm particle size) from Waters Corp. (Milford, MA, United States). The mobile phase, consisting of methanol and water with acetic acid and ammonium fluoride additives, was applied in gradient mode. The flow rate was set at 0.5 ml/min, with an injection volume of 50 µl.

Surface water chemistry data from the period 2014–2023, investigated annually by the waterworks operator, were used in this study. These data included the following water components: Cl^- , NH_4^+ , NO_2^- , NO_3^- , Fe and Mn as well as Cr, Zn and Pb.

RESULTS

SURFACE WATER CHEMISTRY

Relatively high levels of Cl^- and NO_3^- were present in the surface water. The Cl^- concentrations in the period between 2014 and 2020 were in the range 53–62 mg/l, and then in the period between 2021–2023 increased to a level of 71–76 mg/l ([Fig. 3](#)). The concentrations of nitrate varied across a wide range of 2.6–8.4 mg/l, relating to meteorological conditions. The increase in chloride concentrations is associated with increased treated wastewater effluent discharge to surface water due to an extension of the sewage systems in many towns and villages in recent years in Poland. The chloride ion is identified as the most sensitive tracer of anthropogenic impact ([Dragon, 2012](#)). The remaining water components, i.e. NH_4^+ , NO_2^- as well as Cr, Zn and Pb, occurred at low concentrations (close to the detection limit). The Fe and Mn occurred also at a low range of concentrations (usually 0.2–0.9 mg/l and 0.1–0.9 mg/l, respectively).

GROUNDWATER CHEMISTRY

The groundwater chemistry characterization is shown in [Table 1](#). Analysis of groundwater chemistry was performed in 2022 in all wells as well as in the Wełna River and infiltration pond. The water in the Wełna River and infiltration pond was

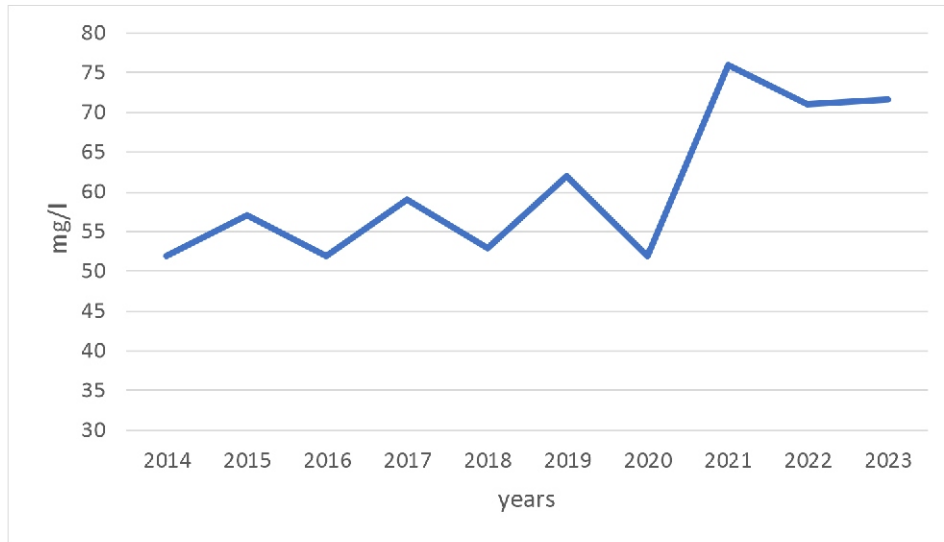


Fig. 3. Changes in chloride concentrations in the Wełna River

Table 1

Statistical characterization of the groundwater chemistry

Parameter	Unit	Average	Median	Min	Max	Range	Standard deviation	
pH	-	7.51	7.52	7.40	7.70	0.30	0.09	
ORP	mV	208.4	200.1	83.6	284.6	201.0	63.6	
Electrical conductivity	μS/cm	819.8	808.9	618.9	1095.8	476.9	106.9	
Alkalinity	mval/l	4.5	4.6	4.3	4.7	0.4	0.1	
Total hardness		6.4	6.4	6.2	6.7	0.5	0.2	
NH ₄ ⁺	mg/l	0.14	0.10	0.01	0.45	0.45	0.15	
NO ₂ ⁻		0.008	0.008	0.003	0.012	0.009	0.002	
NO ₃ ⁻		1.4	1.0	0.8	4.3	3.5	1.2	
Cl ⁻		78.3	73.2	67.3	118.3	51.0	12.9	
SO ₄ ²⁻		82.3	81.5	67.7	108.8	41.1	9.7	
Na ⁺		41.4	35.9	33.6	86.1	52.5	14.1	
K ⁺		8.1	8.2	6.5	10.1	3.6	1.0	
Fe		μg/l	438.4	161.1	112.9	2329.4	2216.5	621.5
Mn			619.5	748.5	57.2	1212.7	1155.5	425.7
Al	0.68		0.26	0.06	4.42	4.36	1.16	
Cr	0.15		0.07	0.01	0.93	0.93	0.25	
Ni	4.71		3.88	0.10	9.82	9.73	3.41	
Cu	1.63		1.52	0.33	2.88	2.55	0.73	
Zn	3.22		2.47	0.81	12.8	12.0	3.10	
As	1.91		1.39	0.50	5.67	5.17	1.46	
Cd	0.046		0.051	0.009	0.082	0.074	0.024	
Pb	0.26		0.21	0.11	0.67	0.56	0.16	

characterized by relatively high concentrations of Cl^- (68 and 72 mg/l, respectively) and SO_4^{2-} (91.7 and 94.1 mg/l, respectively), as well as NO_3^- (1.89 and 5.03 mg/l, respectively). The concentrations of Cl^- and SO_4^{2-} in the wells were very similar to that observed in surface water. During water flow through the aquifer, the concentration of NO_3^- decreases (mostly below 1 mg/l). The total hardness increased from 5.6–5.9 meq/l in surface water to 6.2–6.7 meq/l in wells. In groundwater the concentrations of NH_4^+ occurred at low levels (usually below 0.1 mg/l). In some wells, the concentrations of NH_4^+ were higher due to local hydrogeochemical conditions (occurrence of organic matter in the sediments). In these wells, the potential ORP also occurs at a lower level. This is characteristic of wells 12, 13 and 20, where the concentrations of NH_4^+ (mg/l) and ORP were observed at levels of: 0.44 mV and 83.6 mV; 0.451 mV and 171.4 mV; and 0.259 mV and 115.8 mV, respectively. The ORP was higher than 200 mV in most of the remaining wells. The impact of pollution sources was observed in some wells. The influence of industrial areas as well as of communications routes (the main road and railway line) was also indicated. This is connected mainly to well no. 22, where increased concentrations of Cl^- (118.3 mg/l), SO_4^{2-} (108.8 mg/l), and NO_3^- (4.28 mg/l) were observed. This is also evident in wells 25, 20, and 20z recharged mainly by the infiltration pond. However, in the period of this study, infiltration was limited because the infiltration pond was not de-clogged during the last five years. The influence of residential areas was indicated in well no. 18z (located nearest to the residential area of Kowanówko village; Fig. 1), where a concentration of NO_3^- at a level of 3.78 mg/l was indicated (most probably derived from leaky sewage systems).

CONTAMINANTS OF EMERGING CONCERN (CECS) AND PESTICIDES (SCREENING SAMPLING – OCTOBER 2022)

CECs

Analysis for 14 substances indicated 5 of them in the water sampled. The sum of CEC concentrations and the number of substances detected is shown in Table 2. The sum of pharmaceutical concentrations in the surface water is 442 ng/l and 465 ng/l (in the Wełna River and infiltration pond, respectively). The sum of pharmaceutical concentration was in a range of 216–343 ng/l in most wells. The exceptions characterized by lower concentrations are wells no. 20z and 22. Moreover, CECs were not detected in well no. 26 (Table 2). The lower concentration of CECs in these wells is caused by more intensive recharge by ambient groundwater flowing from the south in conditions of limited infiltration from the clogged infiltration pond. This is also reflected by the highest concentrations of Cl^- and NO_3^-

in these wells. Among the CECs investigated, carbamazepine showed the highest concentration (in both surface water and groundwater in all wells, except for well 26).

PESTICIDES

Similarly to the CECs, the highest pesticide concentrations and the highest number of detected substances were found in the surface water. 12 substances were detected in the Wełna River and 17 in the infiltration pond. The sum of pesticide concentrations was highest in the infiltration pond (1122 ng/l), while it was 319 ng/l in the Wełna River. In groundwater in most of the wells, the sum of pesticide concentrations was found to be in a range between 290–566 ng/l. Similarly to the CECs, the sum of pesticide concentrations was significantly lower in well no 26, while in well 22 pesticides were not detected. This corroborates more intensive recharge by ambient groundwater in these wells. In all water samples, herbicides dominated (mainly nicosulfuron and metsulfuron-methyl). The fungicide fluopicolide was found as well. Banned pesticides (chloridazon and isoproturon) were found in almost all samples analysed. These pesticides have been banned in Polish and the EU since 2020 (chloridazon) and 2016 (isoproturon). The pesticide concentrations are shown in Table 3.

CONTAMINANTS OF EMERGING CONCERN (CECs) AND PESTICIDES (JUNE 2023 SAMPLING)

CECs

The Wełna River and the six wells characterized by water chemistry reflecting the infiltration of water from the river were selected for a more precise investigation performed in June 2023 (Table 3). The results of the CEC investigation are shown in Table 4. Among 120 substances investigated, 28 CECs were detected in the water samples. The highest number of substances (23) was detected in surface water of the Wełna River. The highest sum of CEC concentrations (Fig. 4) was also found in the Wełna River (6661.8 ng/l). The sum of CEC concentrations in the wells was between 2443.7 and 4864.3 ng/l. The exception is the water sample taken from well no. 25 with significantly lower concentrations (735.5 ng/l). The lower concentration of CECs in this well indicates a higher ambient groundwater inflow compared to the remaining wells.

The research shows the occurrence of painkillers, antibiotics, anti-inflammatory and antidiabetic drugs, antiepileptics, antidepressants, and their metabolites. Moreover, corrosion inhibitors, drugs and cosmetic preservatives as well as bisphenol S were detected. The highest concentrations of the substances sucralose (3280 ng/l) and oxypurinol (1980 ng/l) were found in

Table 2

Variations in pharmaceutical concentrations (Oborniki well-field) – screening sampling (October 2022)

	Sampling points													
	Wełna River	Infiltration pond	Wells											
			Island			Barrier I				Barrier II				
			12	13	14	21	26	25	24	18	18z	20	20z	22
ng/l														
The sum of detected pharmaceuticals	442	465	267	225	265	343	0	216	290	312	223	222	99	36
Number of detected substances	4	5	3	3	4	4	0	3	3	4	3	4	2	1
Carbamazepine	243	229	229	173	184	225	0	174	229	224	173	173	88	36

Table 3

Variations in pesticide concentrations (Oborniki well-field) – screening sampling (October 2022)

	Sampling points													
	Wełna River	Infiltration pond	Wells											
			Island			Barrier I				Barrier II				
			12	13	14	21	26	25	24	18	18z	20	20z	22
ng/l														
The sum of detected pesticides	319	1122	343	290	332	329	39	617	339	342	357	566	403	0
Number of detected substances	12	17	8	7	7	9	2	10	8	11	9	10	8	0

the Wełna River, these forming 79 % the sum of all substances detected. A similar situation was observed in all wells; sucralose was detected in the range of 1050–1680 ng/l, and oxypurinol was detected in the range of 175–541 ng/l. In all wells investigated, relatively high concentrations of acesulfame, benzotriazole-1-H, carbamazepine, and valsartan acid were observed. In wells no. 12 and 18z, relatively high concentrations of caffeine, methylparaben, and paraxanthine were detected. Moreover, in well no. 18z bisphenol S occurred. These substances were not detected in surface water in either the Wełna River or the infiltration pond or in the remaining wells. Taking

into consideration the highest sum of pharmaceutical concentrations in well 18z, inflow of contaminated groundwater from the built-up area can be inferred, where leaking septic tanks may be located. Comparing the CEC concentrations in the Wełna River and wells 12, 14, 21, and 20, the value of the CEC reduction rate during underground contaminants migration is estimated at ~57%.

Carbamazepine (known as the most conservative substance; [Dragon et al., 2018](#)) occurs in the Wełna River at a concentration of 122 ng/l. By comparison, in the wells the observed concentrations occur in the range of 84.6–101.0 ng/l ([Fig. 5](#)).

Table 4

Variations in pharmaceutical concentrations (Oborniki well-field) – June 2023

	Unit	Limit of quantification (LOQ)	Sampling points						
			Wełna River	Wells					
				Island		Barrier I		Barrier II	
				12	14	21	25	18z	20
The sum of detected pharmaceuticals	ng/l	-	6661.8	3582.9	2437.4	2443.7	735.5	4864.3	2717.7
Number of detected substances		-	23	19	16	16	11	20	15
4-acetamidoantipyrine	ng/l	10	72.5	<LOQ	13.0	22.9	<LOQ	13.7	23.6
4-formylaminoantipyrine		10	107	49.7	55.7	59.1	23.1	39.9	98.5
Acesulfame		50	98.1	107	112	137	126	102	185
Benzotriazole-1-H		50	65.9	59.7	59.9	71.8	<LOQ	<LOQ	52.1
Benzotriazole-5-methyl-1-H		20	63.4	47.3	50.9	46.0	23.3	30.5	41.8
Bisphenol S		20	<LOQ	31.7	<LOQ	<LOQ	<LOQ	671	<LOQ
Caffeine		100	<LOQ	604	<LOQ	<LOQ	<LOQ	878	<LOQ
Carbamazepine		10	122	84.6	85.0	89.1	59.8	72.9	101
Cetirizine		10	19.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
DEET (Diethyltoluamide)		30	41.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Diclofenac		10	28.3	20.8	23.0	21.6	<LOQ	12.5	17.8
Fexofenadine		10	33.5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Fluconazole		10	14.9	<LOQ	<LOQ	10.2	<LOQ	<LOQ	12.4
Gabapentin		10	52.1	18.6	21.8	25.4	13.1	13.8	13.6
Lamotrigine		10	55.8	32.3	39.2	49.3	21.4	34.4	31.3
Metformin		50	71.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Methylparaben		30	<LOQ	395	<LOQ	<LOQ	<LOQ	815	<LOQ
Oxypurinol		10	1980	483	541	436	358	481	175
Paraxanthine		100	<LOQ	349	<LOQ	<LOQ	<LOQ	407	<LOQ
Saccharin		50	<LOQ	64.1	<LOQ	<LOQ	<LOQ	85.7	<LOQ
Sucralose		1000	3280	1070	1220	1230	<LOQ	1050	1680
Sulfamethoxazole		3	6.4	<LOQ	3.0	<LOQ	7.0	3.2	<LOQ
Telmisartan		20	135	22.7	22.1	34.9	<LOQ	<LOQ	22.3
Tramadol		10	51.4	19.8	35.8	41.1	19.6	29.8	22.3
Valsartan		10	19.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Valsartan acid		10	302	99.6	135	147	39.0	70.9	241
Venlafaxine		5	7.6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Venlafaxine O-desmethyl		5	34.1	24.0	20.0	22.3	<LOQ	6.1	<LOQ

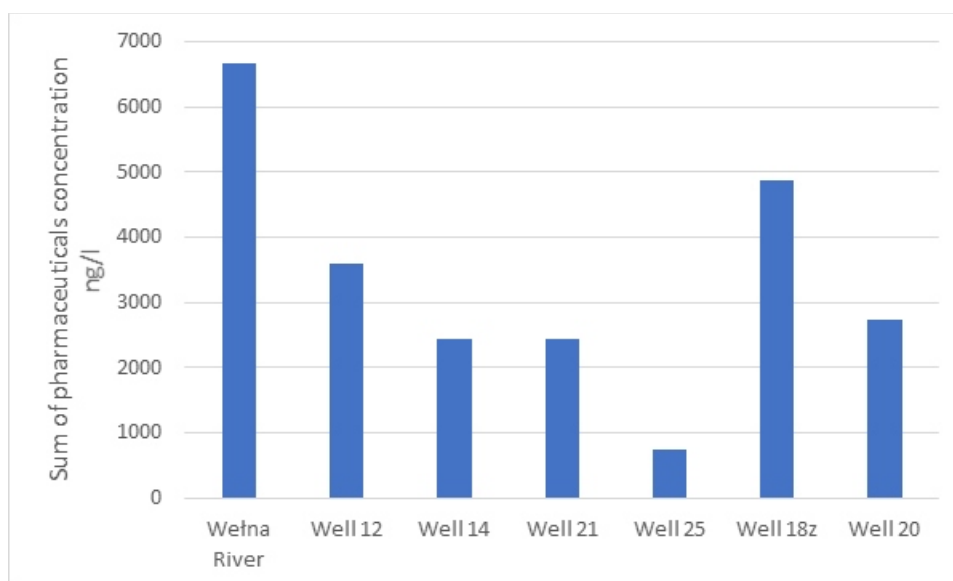


Fig. 4. Sums of pharmaceutical concentrations (sampling date: June of 2023)

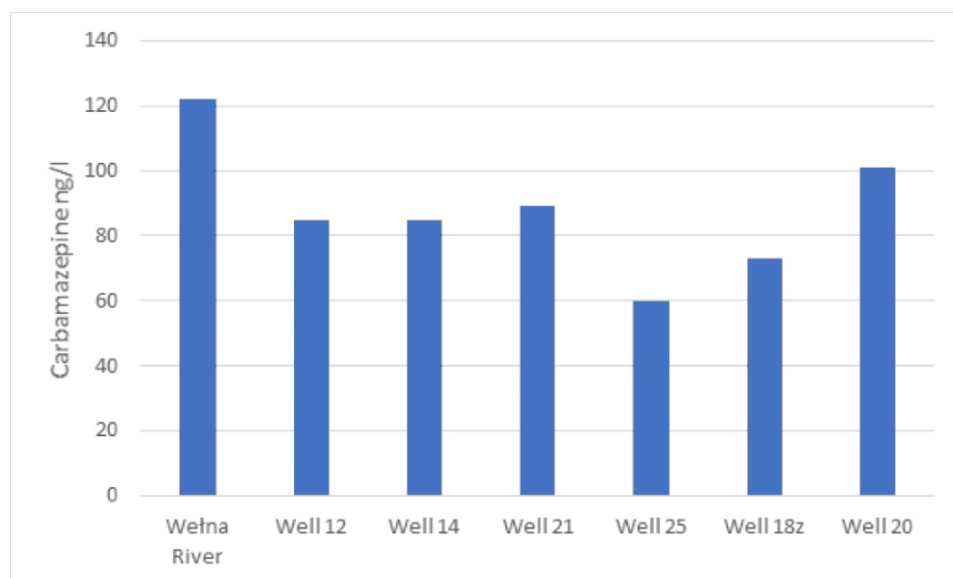


Fig. 5. Variations in carbamazepine concentrations

The calculated reduction rate (compared to the source water of the Wefna River and wells) is lower than for other compounds (at a level of 26 %).

PESTICIDES

The results of the pesticide investigation are shown in Table 5, and the sum of pesticide concentrations in Figure 6. Of the 327 substances analysed for, 24 were detected. The highest number of detected substances was in the Wefna River (18). In the wells investigated, the number of detected substances varied from 11 to 14. Among the substances detected, herbicides dominated (13 substances), fungicides represented 7, and insecticides 3. Among the banned herbicides detected,

chloridazon and isoproturon were analysed for. Both substances were banned in EU countries, in 2020 and 2016 (respectively).

The sum of pesticide concentrations is the highest in the Wefna River (1331 ng/l). In the wells, the sum of pesticide concentrations in the range of 282–443 was recorded. The highest concentration represents chlorotoluron (402.8 ng/l), terbutylazine (337.1 ng/l), and nicosulfuron (121.8 ng/l). Relatively high concentrations of nicosulfuron (30.3–104.9 ng/l), flupyradifurone (44.2–78.3 ng/l) and fluopicolid (34.0–43.2 ng/l) were also detected in the wells. Notably, the banned substance chloridazon was detected in the wells (no. 20, 18z, 25, and 12), though was absent from the river. The second banned substance, isoproturon, was detected in the Wefna River (22.9 ng/l)

Table 5

Variations in pesticide concentrations (Oborniki well-field) – June 2023

	Unit	Limit of qualification (LOQ)	Sampling points						
			Wełna River	Wells					
				Island		Barrier I		Barrier II	
			12	14	21	25	18z	20	
The sum of detected pesticides	ng/l		1 331	302	330	337	383	282	443
Number of detected substances			18	12	13	14	14	11	12
2,6-ichlorobenzamide	ng/l	8	8.8	<LOQ	<LOQ	8.5	<LOQ	10.5	<LOQ
Acetamiprid		8	14.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Azoxystrobin		10	33.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Chloridazon		10	<LOQ	14.1	<LOQ	<LOQ	13.7	13.3	48.6
Chlortoluron		10	402.8	46.2	40.3	58.0	26.9	24.0	32.3
Cyantraniliprole		10	26.7	<LOQ	37.1	45.5	38.7	21.2	11.0
Diflufenican		8	23.9	<LOQ	<LOQ	8.3	<LOQ	<LOQ	<LOQ
Fluconazole		10	50.4	22.7	36.3	<LOQ	20.5	<LOQ	27.3
Flufenacet		8	<LOQ	<LOQ	<LOQ	<LOQ	8.0	<LOQ	<LOQ
Fluopicolide		10	76.7	37.2	39.3	43.2	34.0	37.0	38.1
Fluopyram		8	11.2	8.9	8.7	<LOQ	<LOQ	<LOQ	<LOQ
Fluoxastrobin		8	20.6	<LOQ	8.5	8.9	<LOQ	<LOQ	<LOQ
Flupyradifurone		10	24.2	66.9	50.1	44.2	78.3	71.5	74.5
Isoproturon		8	22.9	10.9	8.5	<LOQ	8.2	<LOQ	15.0
Metamitron		8	<LOQ	11.2	9.3	8.6	<LOQ	<LOQ	<LOQ
Metazachlor		10	11.2	<LOQ	<LOQ	<LOQ	13.4	<LOQ	<LOQ
Metolachlor-S		10	51.2	<LOQ	<LOQ	16.3	10.6	22.1	<LOQ
Metsulfuron-methyl		10	<LOQ	<LOQ	<LOQ	<LOQ	24.9	<LOQ	30.7
Nicosulfuron		10	121.8	21.0	33.4	30.4	77.8	40.2	104.9
Tebuconazole		8	62.8	28.8	28.3	18.9	9.0	13.1	27.3
Terbuthylazine	10	337.1	21.4	19.0	24.6	19.3	20.6	21.6	
Bentazone	8	30.9	13.1	11.0	12.7	<LOQ	8.2	11.7	

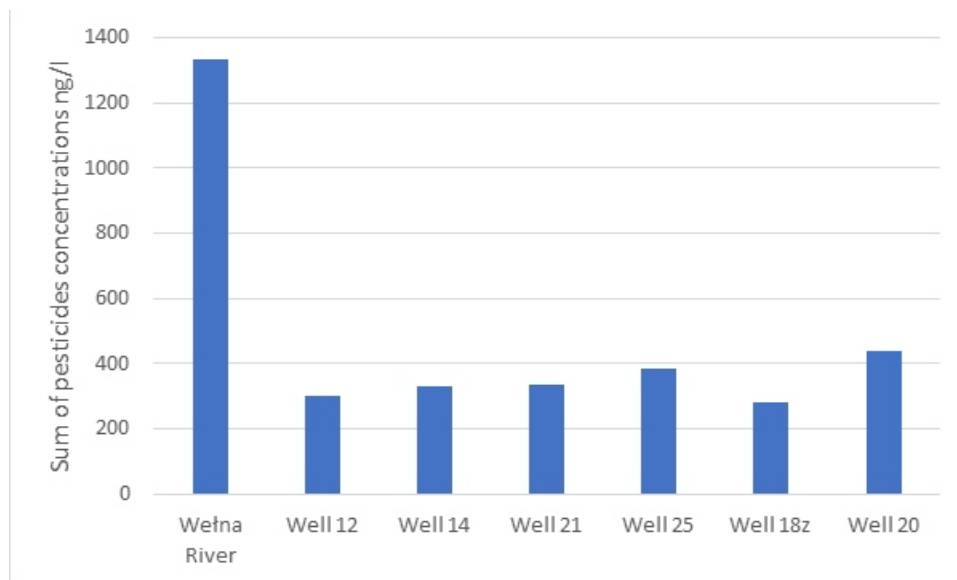


Fig. 6. The sum of pesticide concentrations

and in the wells (8.2–15.0 ng/l). Comparing the sum of pesticide concentrations in the Wełna River and the average concentration in the wells (346.2 ng/l), the reduction rate is calculated at 74%.

DISCUSSION

The analysis of the Oborniki site described shows a relatively high level of water contamination by CECs. The results indicated in the Wełna River can be compared to rivers located in

regions characterized by similar land use. Comparing our results to those found in one of the largest rivers in Poland, the Warta River (Kruć et al., 2019; Kruć-Fijałkowska et al., 2022), significantly higher concentrations of sucralose (3280 ng/l) and oxypurinol (1980 ng/l) were detected. The remaining substances detected were characterized by slightly higher or similar concentrations compared to the Warta River. In the Wełna River, the concentrations of sucralose and oxypurinol were also higher than in the Jizera River (Czech Republic) and the Elbe River (Germany; Hrkal et al., 2023). Comparing the CEC levels in the Wełna River to other small rivers, even higher concentra-

tions were detected in the Kłodnica and Drama rivers (Upper Silesia, Poland), where oxypurinol at the level of 32100 ng/l was detected (Ślósarczyk, 2022). In these rivers, jopromid also has a high concentration (23700 ng/l), and diclofenac is also high (5060 ng/l). The Kłodnica and Drama rivers are located in industrial and built-up areas with many sources of pharmaceutical pollution (including sewage treatment stations and hospitals).

A different situation was found for pesticide contamination. In the Wełna River, very high concentrations of chlorotoluron (402.8 ng/l), terbuthylazine (337.1 ng/l), and nicosulfuron (121.8 ng/l) were found. These herbicides are used mainly on spring crops and appeared in surface water after the rainy season in the late spring of 2023. These observed very high concentrations of pesticides in the spring period were similar to those recorded in the Warta River previously in 2018 (Kruć-Fijałkowska et al., 2022).

The comparison of the pesticide concentrations in the Wełna River and the Warta River (Dragon et al., 2019) shows a lower level of pesticide contamination in the Warta River. This relates to chlorotoluron, terbuthylazine and nicosulfuron (detected in the Warta River at the level of 47 ng/l, 12 ng/l, and 23 ng/l, respectively) and also the remaining substances investigated, except for metazachlor present in the Warta River at a level of 30 ng/l, while in the Wełna River, the concentration is 11.2 ng/l. It is clear that the pesticide concentrations are lower in the larger Warta River due to the dilution of these contaminants in large volumes of river water. The recharge of the river by groundwater unpolluted by pesticides from deeper parts of the flow system contributes to this phenomenon. There is a lack of drainage from deep parts of the flow system in the case of small river valleys (like the Wełna River valley) and there is no inflow of unpolluted groundwater to the surface water in this case. The high concentration of pesticides is mainly caused by surface runoff and the influence of land drainage systems, especially during long wet periods that occur after hydrological droughts (Dragon et al., 2019). The problem of pesticide contamination of small river systems is observed in many parts of the world (Halbach et al., 2021; Mac Loughlin et al., 2022).

There is a reduction in concentrations of both pesticides and CECs investigated in the Oborniki well-field. The reduction rate of the sum of pharmaceuticals is 57%, while that for pesticides is 74%. These values are similar to that in the Krajkowo site located in the Warta River valley, where a reduction rate of pesticides of 53–71.5% was observed, while the reduction rate of pharmaceuticals was 80% (Kruć-Fijałkowska et al., 2022). The main factor responsible for the reduction of these substances is aerobic biodegradation in the presence of dissolved

oxygen and a relatively high ORP in the water (Kruć-Fijałkowska et al., 2022). The influence of other processes, like mixing with ambient groundwater (Górski et al., 2018) is limited due to the relative proximity of the wells to the river.

CONCLUSIONS

The research described documents the state of water pollution by contaminants of emerging concern (CECs) and pesticides in a small lowland river (the Wełna River) characterized by extensive agricultural activity in the catchment area and receiving treated wastewater from many wastewater treatment plants. A relatively high pollution level was documented also in wells of the Oborniki bank filtration site, recharged by the surface water from the Wełna River.

High levels of CECs were detected in the Wełna River water as well as in wells. The high concentration of sucralose (3289 ng/l) and oxypurinol (1780 ng/l) in the Wełna River water were also detected in the wells (sucralose up to 1680 ng/l, oxypurinol up to 541 ng/l). These concentrations are significantly higher than in the Warta River (one of the biggest rivers in Poland). The concentrations of remaining substances were similar to the level observed in the Warta River as well as in the Iżera and Elbe rivers. The reduction rate for the CECs observed in the wells was assessed at 57% (compared to the source river water).

A high level of Wełna River pesticide contamination was indicated, significantly higher than that observed in the Warta River. This is related mainly to 3 herbicides: chlorotoluron, terbuthylazine and nicosulfuron. The remaining substances also occur in the Wełna River at higher concentrations. The reduction rate for the pesticides observed in wells was assessed at 74% (compared to the source river water). In one well the nicosulfuron concentration was higher than the upper permissible limit. Among the substances detected were also 2 banned constituents: chlorotoluron and izoproturon.

The high level of CEC and pesticide contamination documented at the bank filtration site shows the need for river (source) water monitoring to investigate the contamination sources and implement water protection procedures. There is also a need for CECs and pesticides to be investigated in treated the water used for water supply purposes after treatment and disinfection.

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REFERENCES

- Di Corcia, A., Nazzari, M., Rao, R., Samperi, R., Sebastiani, E., 2000. Simultaneous determination of acidic and non-acidic pesticides in natural waters by liquid chromatography-mass spectrometry. *Journal of Chromatography A*, **878**: 87–98; [https://doi.org/10.1016/S0021-9673\(00\)00263-6](https://doi.org/10.1016/S0021-9673(00)00263-6)
- Dragon, K., 2012. The changes of ground water chemistry of semi-con fined buried valley aquifer during one decade of water exploitation. *Environmental Earth Sciences*, **65**: 1283–1290; <https://doi.org/10.1007/s12665-011-1376-2>
- Dragon, K., Górski, J., Kruć, R., Drożdżyński, D., Grischek, T., 2018. Removal of natural organic matter and organic micro-pollutants during river bank filtration in Krajkowo, Poland. *Water*, **10**, 593; <https://doi.org/10.3390/w10101457>
- Dragon, K., Drożdżyński, D., Górski, J., Kruć, R., 2019. The migration of pesticide residues in groundwater at a bank filtration site (Krajkowo well field, Poland). *Environmental Earth Sciences*, **78**; <https://doi.org/10.1007/s12665-019-8598-0>
- 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*, **66**, 14; <https://doi.org/10.7306/gq.1646>

- EPA, 2027.** Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS. U.S. Environmental Protection Agency, Washington.
- European Commission (EC), 1998** Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Off. J. Europ. Union L327/1. 22/12/2000.
- European Commission (EC), 2020/2184** of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption.
- European Commission (EC), 2022/1307** of 22 July 2022 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council.
- Fonseca, E., Hernández, F., Ibáñez, M., Rico, A., Pitarch, E., Bijlsma, L., 2020.** Occurrence and ecological risks of pharmaceuticals in a Mediterranean river in Eastern Spain. *Environment International*, **144**, 106004; <https://doi.org/10.1016/j.envint.2020.106004>
- 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; <https://doi.org/10.2478/logos-2014-0004>
- Górski, J., Dragon, K., Kruć, R., 2018.** A comparison of the efficiency of river bank filtration treatments in different types of wells. *Geologos*, **24**: 245–251; <https://doi.org/10.2478/logos-2018-0025>
- Guzzella, L., Pozzoni, F., Giuliano, G., 2006.** Herbicide contamination of surficial groundwater in Northern Italy. *Environmental Pollution*, **142**: 344–353; <https://doi.org/10.1016/j.envpol.2005.10.037>
- Halbach, K., Möder, M., Schrader, S., Liebmann, L., Schäfer, R.B., Schneeweiss, A., Schreiner, V.C., Vormeier, P., Weisner, O., Liess, M., Reemtsma, T., 2021.** Small streams-large concentrations? Pesticide monitoring in small agricultural streams in Germany during dry weather and rainfall. *Water Research*, **203**, 117535; <https://doi.org/10.1016/j.watres.2021.117535>
- Hamann, E., Stuyfzand, P.J., Greskowiak, J., Timmer, H., Massmann, G., 2016.** The fate of organic micropollutants during long-term/long-distance river bank filtration. *Science of The Total Environment*, **545–546**: 629–640; <https://doi.org/10.1016/j.scitotenv.2015.12.057>
- Hollender, J., Rothardt, J., Radny, D., Loos, M., Epting, J., Huggenberger, P., Borer, P., Singer, H., 2018.** Comprehensive micropollutant screening using LC-HRMS/MS at three riverbank filtration sites to assess natural attenuation and potential implications for human health. *Water Research X*, **1**, 100007; <https://doi.org/10.1016/j.wroa.2018.100007>
- Hrkal, Z., Adomat, Y., Rozman, D., Grischek, T., 2023.** Efficiency of micropollutant removal through artificial recharge and riverbank filtration: case studies of Káraný, Czech Republic and Dresden-Hosterwitz, Germany. *Environmental Earth Sciences*, **82**, 155; <https://doi.org/10.1007/s12665-023-10785-7>
- Jeannot, R., Sabik, H., Sauvard, E., Genin, E., 2000.** Application of liquid chromatography with mass spectrometry combined with photodiode array detection and tandem mass spectrometry for monitoring pesticides in surface waters. *Journal of Chromatography A*, **879**: 51–71; [https://doi.org/10.1016/S0021-9673\(00\)00098-4](https://doi.org/10.1016/S0021-9673(00)00098-4)
- Khezami, F., Gómez-Navarro, O., Barbieri, M.V., Khiari, N., Chkirbene, A., Chiron, S., Khadhar, S., Pérez, S., 2024.** Occurrence of contaminants of emerging concern and pesticides and relative risk assessment in Tunisian groundwater. *Science of The Total Environment*, **906**, 167319; <https://doi.org/10.1016/j.scitotenv.2023.167319>
- Kibuye, F.A., Gall, H.E., Elkin, K.R., Ayers, B., Veith, T.L., Miller, M., Jacob, 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; <https://doi.org/10.1016/j.scitotenv.2018.10.442>
- Köck-Schulmeyer, M., Ginebreda, A., Postigo, C., Garrido, T., Fraile, J., López de Alda, M., Barceló, D., 2014.** Four-year advanced monitoring program of polar pesticides in groundwater of Catalonia (NE-Spain). *Science of The Total Environment*, **470–471**: 1087–1098; <https://doi.org/10.1016/j.scitotenv.2013.10.079>
- Kovačević, S., Radišić, M., Laušević, M., Dimkić, M., 2017.** Occurrence and behavior of selected pharmaceuticals during riverbank filtration in The Republic of Serbia. *Environmental Science and Pollution Research*, **24**: 2075–2088; <https://doi.org/10.1007/s11356-016-7959-4>
- Kruć, R., Dragon, K., Górski, J., 2019.** Migration of pharmaceuticals from the Warta River to the aquifer at a river bank filtration site in Krajkowo (Poland). *Water*, **11**, 2238; <https://doi.org/10.3390/w11112238>
- Kruć-Fijałkowska, R., Dragon, K., Drożdżyński, D., Górski, J., 2022.** Seasonal variation of pesticides in surface water and drinking water wells in the annual cycle in western Poland, and potential health risk assessment. *Scientific Reports*, **12**, 3317; <https://doi.org/10.1038/s41598-022-07385-z>
- Lee, H.J., Kim, K.Y., Hamm, S.Y., Kim, M., Kim, H.K., Oh, J.E., 2019.** Occurrence and distribution of pharmaceutical and personal care products, artificial sweeteners, and pesticides in groundwater from an agricultural area in Korea. *Science of The Total Environment*, **659**: 168–176; <https://doi.org/10.1016/j.scitotenv.2018.12.258>
- Li, W.C., 2014.** Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil. *Environmental Pollution*, **187**: 193–201; <https://doi.org/10.1016/j.envpol.2014.01.015>
- Loos, R., Locoro, G., Comero, S., Contini, S., Schwesig, D., Werres, F., Balsaa, P., Gans, O., Weiss, S., Blaha, L., Bolchi M., Gawlik B.M., 2010.** Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. *Water Research* **44**: 4115–4126; <https://doi.org/10.1016/j.watres.2010.05.032>
- Mac Loughlin, T.M., Peluso, M.L., Marino, D.J.G., 2022.** Multiple pesticides occurrence, fate, and environmental risk assessment in a small horticultural stream of Argentina. *Science of The Total Environment*, **802**, 149893; <https://doi.org/10.1016/j.scitotenv.2021.149893>
- Maeng, S.K., Ameda, E., Sharma, S.K., Grützmacher, 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; <https://doi.org/10.1016/j.watres.2010.03.035>
- 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; <https://doi.org/10.1007/s00254-007-0792-9>
- Munro, K., Martins, C.P.B., Loewenthal, M., Comber, S., Cowan, D.A., Pereira, L., Barron, L.P., 2019.** Evaluation of combined sewer overflow impacts on short-term pharmaceutical and illicit drug occurrence in a heavily urbanised tidal river catchment (London, UK). *Science of The Total Environment*, **657**: 1099–1111; <https://doi.org/10.1016/j.scitotenv.2018.12.108>
- Postigo, C., Barceló, D., 2015.** Synthetic organic compounds and their transformation products in groundwater: occurrence, fate and mitigation. *Science of The Total Environment*, **503–504**: 32–47; <https://doi.org/10.1016/j.scitotenv.2014.06.019>
- Regulation of Minister of Health concerning quality of water for consumption** from 07 December of 2017 (Dz.U. 2017 nr 2294) (in Polish) Rozporządzenie Ministra Zdrowia z dnia 07 grudnia 2017 r. w sprawie jakości wody przeznaczonej do spożycia przez ludzi.
- Reh, R., Licha, T., Geyer, T., Nödler, K., Sauter, M., 2013.** Occurrence and spatial distribution of organic micro-pollutants in a complex hydrogeological karst system during low flow and high flow periods, results of a two-year study. *Science of The Total Environment*, **443**: 438–445; <https://doi.org/10.1016/j.scitotenv.2012.11.005>
- 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**, 364; <https://doi.org/10.1007/s10661-017-6089-x>
- Ślósarczyk, K., 2022.** Występowanie farmaceutyków i środków higieny osobistej w środowisku wodnym w wybranych obszarach południowej Polski. Ph.D. Thesis, Silesian University.
- Van Driezum, I.H., Derx, J., Oudega, T.J., Zessner, M., Naus, F.L., Saracevic, E., Kirschner, A.K.T., Sommer, R., Farnleitner, A.H., Blaschke, A.P., 2019.** Spatiotemporal resolved sampling for the interpretation of micropollutant removal during riverbank filtration. *Science of The Total Environment*, **649**: 212–223; <https://doi.org/10.1016/j.scitotenv.2018.08.300>

APPENDIX 1

List of analysed substances

First and second sampling campaign – pesticides

No.	Pesticide residue	Pesticide type
1	2,6-Dichlorobenzamide	Fun
2	6-Chlor-3-phenylpyridazin-4-ol	Herb
3	Acetamiprid	Ins
4	Acetochlor	Herb
5	Alachlor	Herb
6	Aldicarb-sulfone	Ins
7	Ametocradin	Fun
8	Ametryn	Herb
9	Amidosulfuron	Herb
10	Amisulbrom	Fun
11	Atrazine	Herb
12	Atrazine desethyl	Herb
13	Azaconazole	Fun
14	Azinophos-ethyl	Ins
15	Azinophos-methyl	Ins
16	Azoxystrobin	Fun
17	Beflubutamid	Herb
18	Benalaxyl / Benalaxyl-M	Fun
19	Bendiocarb	Ins
20	Bensulfuron-methyl	Herb
21	Bentazone	Herb
22	Benthiavalicarb-isopropyl	Fun
23	Benzovindiflupyr	Fun
24	Benzoximate	Fun
25	Bifenthrin	Ins
26	Bitertanol	Fun
27	Bixafen	Fun
28	Boscalid	Fun
29	Bromacil	Herb
30	Bromoxynil	Herb
31	Bupirimate	Fun
32	Buprofezin	Ins
33	Butafenacil	Herb
34	Butoxycarboxim	Ins
35	Buturon	Herb
36	Cadusafos	Ins
37	Carbaryl	Ins
38	Carbendazim	Fun
39	Carbetamide	Herb
40	Carbofuran	Ins
41	Carbofuran-3-hydroxy	Ins
42	Carboxin	Fun
43	Carfentrazone-ethyl	Herb
44	Chlorbromuron	Herb
45	Chlorfenvinphos	Ins
46	Chloridazon	Herb
47	Chlorantraniliprole	Ins

No.	Pesticide residue	Pesticide type
48	Chloroxuron	Herb
49	Chlorsulfuron	Herb
50	Chlortoluron	Herb
51	Chromafenozide	Ins
52	Cinosulfuron	Herb
53	Clodinafop-propargyl	Herb
54	Clofentezine	Ins
55	Clomazone	Herb
56	Clothianidin	Ins
57	Coumaphos	Ins
58	Cyanazine	Herb
59	Cyantraniliprole	Ins
60	Cycloxydim	Herb
61	Cycluron	Herb
62	Cyflufenamid	Fun
63	Cyhalothrin-lambda-gamma	Ins
64	Cymoxanil	Fun
65	Cypermethrin Alfa-Zeta	Ins
66	Cyprazine	Herb
67	Cyproconazole	Fun
68	Cyprodinil	Fun
69	Demeton-S	Ins
70	Demeton-S-methyl-sulfone	Ins
71	Desmedipham	Herb
72	Diazinon	Ins
73	Dichlorprop	Herb
74	Diclofop	Herb
75	Dicrotophos	Ins
76	Diethofencarb	Fun
77	Difenoconazole	Fun
78	Difenoxyuron	Herb
79	Diflubenzuron	Ins
80	Diflufenican	Herb
81	Dimefuron	Herb
82	Dimethachlor	Herb
83	Dimethenamide	Herb
84	Dimethoate	Ins
85	Dimethomorph	Fun
86	Dimoxystrobin	Fun
87	Disulfoton-sulfon	Ins
88	Disulfoton-sufoxide	Ins
89	Diuron	Herb
90	DMSA	Meta
91	DMST	Meta
92	EPN	Ins
93	Epoxiconazole	Fun
94	Etaconazole	Fun
95	Ethiofencarb	Ins
96	Ethiofencarb-sulfone	Meta
97	Ethiofencarb-sulfoxide	Meta
98	Ethion	Ins

No.	Pesticide residue	Pesticide type
99	Ethiprole	Ins
100	Ethirimol	Fun
101	Ethofumesate	Herb
102	Ethoprophos	Ins
103	Etofenprox	Ins
104	Etoxazole	Ins
105	Famoxadon	Fun
106	Fenamidone	Fun
107	Fenamiphos	Ins
108	Fenamiphos-sulfone	Meta
109	Fenamiphos-sulfoxide	Meta
110	Fenazaquin	Ins
111	Fenbuconazole	Fun
112	Fenchlorazol-ethyl	Herb
113	Fenfuram	Fun
114	Fenhexamid	Fun
115	Fenobucarb	Ins
116	Fenoxaprop-ethyl	Herb
117	Fenoxycarb	Ins
118	Fenpropidin	Fun
119	Fenpropimorph	Fun
120	Fenpyrazamine	Fun
121	Fenpyroximate	Ins
122	Fensulfothion-sulfone	Ins
123	Fenuron	Herb
124	Fipronil	Ins
125	Fipronil-sulfon	Meta
126	Flazasulfuron	Herb
127	Flonicamid	Ins
128	Florasulam	Herb
129	Fluazifop-P	Herb
130	Fluazifop-P-butyl	Herb
131	Fluazinam	Fun
132	Fluazuron	Ins
133	Fluconazole	Fun
134	Fludioxonil	Fun
135	Flufenacet	Herb
136	Flufenoxuron	Ins
137	Fluometuron	Herb
138	Fluopicolid	Fun
139	Fluopyram	Fun
140	Fluoroglycofene-ethyl	Herb
141	Fluoxastrobin	Fun
142	Fluridone	Herb
143	Fluroxypyr-meptyl	Herb
144	Flurtamone	Herb
145	Flusilazole	Fun
146	Fluthiacet-methyl	Herb
147	Flutolanil	Fun
148	Fluxapyroxad	Fun
149	Foramsulfuron	Herb

No.	Pesticide residue	Pesticide type
150	Forchlorfenuron	PGR
151	Formothion	Ins
152	Fosthiazate	Ins
153	Fuberidazole	Fun
154	Furalaxyl	Fun
155	Furathiocarb	Ins
156	Halofenozide	Ins
157	Haloxyfop-ethoxyetyl	Herb
158	Haloxyfop-metyl	Herb
159	Heptenophos	Ins
160	Hexaflumuron	Ins
161	Hexazinone	Herb
162	Hexythiazox	Ins
163	Imazalil	Fun
164	Imazamox	Herb
165	Imidacloprid	Ins
166	Indoxacarb	Ins
167	Iodosulfuron-methyl	Herb
168	Ipconazole	Fun
169	Iprovalicarb	Fun
170	Isofetamid	Fun
171	Isoprocarb	Ins
172	Isoprothiolane	Fun/Ins
173	Isoproturon	Herb
174	Isoxaben	Herb
175	Isxadifen-ethyl	Herb
176	Isoxaflutole	Herb
177	Isopyrazam	Fun
178	Lenacil	Herb
179	Linuron	Herb
180	Malaoxon	Meta
181	Malathion	Ins
182	Mandipropamid	Fun
183	MCPA	Herb
184	MCPB	Herb
185	Mecarbam	Ins
186	Mefenacet	Herb
187	Mefenpyr-diethyl	Herb
188	Mepanipirim	Fun
189	Mepronil	Fun
190	Mesosulfuron-methyl	Herb
191	Metalaxyl / Metalaksyl-M	Fun
192	Metazachlor	Herb
193	Metconazole	Fun
194	Methabenzthiazuron	Herb
195	Methfuroxam	Fun
196	Methidathion	Ins
197	Methiocarb	Ins
198	Methiocarb-sulfon	Meta
199	Methiocarb-sulfoxid	Meta
200	Methomyl	Ins

No.	Pesticide residue	Pesticide type
201	Methoprotryne	Herb
202	Methoxyfenozide	Ins
203	Metobromuron	Herb
204	Metolachlor-S / Metolachlor	Herb
205	Metosulam	Herb
206	Metoxuron	Herb
207	Metrafenone	Fun
208	Metsulfuron-methyl	Herb
209	Mexacarbate	Ins
210	Monocrotophos	Ins
211	Monolinuron	Herb
212	Monuron	Herb
213	Myclobutanil	Fun
214	Napropamide	Herb
215	Neburon	Herb
216	Nicosulfuron	Herb
217	Nitenpyram	Ins
218	Norflurazon	Herb
219	Novaluron	Ins
220	Omethoate	Ins
221	Oxadixyl	Fun
222	Oxamyl	Ins
223	Oxycarboxin	Fun
224	Oxydemeton-methyl	Ins
225	Paclobutrazol	PGR/Fun
226	Paraoxon-methyl	Meta
227	Penconazole	Fun
228	Pencycuron	Fun
229	Penflufen	Fun
230	Penoxsulam	Herb
231	Penthiopyrad	Fun
232	Pethoxamid	Herb
233	Phenmedipham	Herb
234	Phenthoate	Ins
235	Phorate-sulfon	Meta
236	Phorate-sulfoxid	Meta
237	Phosalone	Ins
238	Phosmet	Ins
239	Picolinafen	Herb
240	Picoxystrobin	Fun
241	Pinoxaden	Herb
242	Pirimicarb	Ins
243	Pirimicarb-desmethyl	Meta
244	Pirimiphos-ethyl	Ins
245	Pirimiphos-methyl	Ins
246	Prochloraz	Fun
247	Procyazine	Herb
248	Profenofos	Ins
249	Promecarb	Ins
250	Prometon	Herb
251	Prometryn	Herb

No.	Pesticide residue	Pesticide type
252	Propaquizafop	Herb
253	Propargite	Ins
254	Propazine	Herb
255	Propiconazole	Fun
256	Propoxur	Ins
257	Propoxycarbazone-sodium	Herb
258	Propyzamide	Herb
259	Proquinazid	Fun
260	Prosulfuron	Herb
261	Prothioconazole desthio	Fun
262	Pyraclostrobin	Fun
263	Pyraflufen-ethyl	Herb
264	Pyrazophos	Fun
265	Pyridaben	Ins
266	Pyrimethanil	Fun
267	Pyriproxyfen	Ins
268	Pyroxsulam	Herb
269	Quinoxifen	Fun
270	Quinmerac	Herb
271	Quizalofop-P-ethyl	Herb
272	Rimsulfuron	Herb
273	Rotenone	Ins
274	Secbumeton	Herb
275	Siduron	Herb
276	Siltiofam	Fun
277	Simazine	Herb
278	Simetryn	Herb
279	Spinosyn A	Ins
280	Spinosyn D	Ins
281	Spirodiclofen	Ins
282	Spiromesifen	Ins
283	Spirotetramat	Ins
284	Spirotetramat-enol	Meta
285	Spirotetramat-ketohydroxy	Meta
286	Spirotetramat-monohydroxy	Meta
287	Spiroxamine	Fun
288	Sulfentrazone	Herb
289	Sulfometuron-methyl	Herb
290	Sulfosulfuron	Herb
291	Sulfoxaflor	Ins
292	Tebuconazol	Fun
293	Tebufenozide	Ins
294	Tebufenpyrad	Ins
295	Tebuthiuron	Herb
296	Teflubenzuron	Ins
297	Tepraloxydim	Herb
298	Terbumeton	Herb
299	Terbuthylazine	Herb
300	Terbutryne	Herb
301	Tetrachlorvinphos	Ins
302	Tetraconazole	Fun

No.	Pesticide residue	Pesticide type
303	Thiabendazol	Fun
304	Thiacloprid	Ins
305	Thiamethoxam	Ins
306	Thifensulfuron-methyl	Herb
307	Thiobencarb	Herb
308	Thiodicarb	Ins
309	Thiofanox-sulfone	Meta
310	Thiophanate-ethyl	Fun
311	Thiophanate-methyl	Fun
312	Tralkoxydim	Herb
313	Triadimefon	Fun
314	Triasulfuron	Herb
315	Triazophos	Ins
316	Triazoxide	Fun
317	Tribenuron-methyl	Herb
318	Tricyclazole	Fun
319	Trifloxystrobin	Fun
320	Triflumizole	Fun
321	Triflumuron	Ins
322	Triflusulfuron-methyl	Herb
323	Triticonazole	Fun
324	Tritosulfuron	Herb
325	Valifenalate	Fun
326	Vamidotion	Ins
327	Zoxamide	Fun

Ins – insecticide, Herb – herbicide, Fun – fungicide, Meta – metabolite, PGR – plant growth regulator

First sampling campaign – pharmaceuticals

No.	Pharmaceutical	Description
1	Acesulfame	Sugar substitute
2	Carbamazepine	Psychotropic, anticonvulsant and mood stabilising
3	Diclofenac	NSAID, analgesic and antipyretic
4	Fluconazole	Antifungal
5	Gabapentin	Anticonvulsant
6	Ibuprofen	NSAID
7	Lamotrigine	Antiepileptic and mood stabilising
8	Metformin	Anti-diabetic drug
9	Oxipurinol	Inhibitor of xanthine oxidase
10	Paracetamol	Analgesic and antipyretic
11	Sulfamethoxazole	Antibiotic
12	Sulfanilamide	Antibiotic
13	Sulfapyridine	Antibiotic
14	Telmisartan	Antihypertensive
15	Tramadol	Opioid

Second sampling campaign – pharmaceuticals

No.	Pharmaceuticals and personal care products	Description
1	4-acetamidoantipyrine	Metabolite of dipyron (analgetic)
2	4-formylaminoantipyrine	Metabolite of dipyron (analgetic)
3	Acebutulol	Beta blocker
4	Acesulfam	Sugar substitute
5	Alfuzosin	Alpha-1 blocker
6	Amitriptiline	Antidepressant
7	Atenolol	Beta blocker
8	Atorvastatin	Lipid-modifying agent
9	Avobenzon	Uv filter
10	Azithromycin	Antibiotic
11	Benzotriazole	Benzotriazole
12	Benzotriazole 1-methyl	Benzotriazole
13	Benzotriazole 4-methyl	Benzotriazole
14	Bezafibrate	Fibrate
15	Bisoprolol	Beta blocker
16	Bisphenol A	Alkylphenol
17	Bisphenol B	Alkylphenol
18	Bisphenol S	Alkylphenol
19	Butylparaben	Cosmetic and pharmaceutical preservatives
20	Caffeine	Stimulant
21	Carbamazepine	Psychotropic, anticonvulsant and mood stabilising
22	Carbamazepine 10,11-dihydro-10-hydroxy	Metabolite
23	Carbamazepine 10,11-dihydroxy	Metabolite
24	Carbamazepine 10,11-epoxide	Metabolite
25	Carbamazepine 2-hydroxy	Metabolite
26	Celiprolol	Beta blocker
27	Cetirizine	Antihistamine
28	Citalopram	Antidepressant
29	Clarithromycin	Antibiotic
30	Climbazole	Antifungal
31	Clindamycin	Antibiotic
32	Clofibrac acid	Fibrate
33	Cotinine	Metabolite of nicotine
34	Cyclamate	Sugar substitute
35	Cyclophosphamide	Chemotherapeutic agent
36	Deet	Repellent
37	Diatrizoate	Contrast agent
38	Diclofenac	NSAID, analgesic and antipyretic
39	Diclofenac-4'-hydroxy	Metabolite
40	Diltiazem	Antiarrhythmic
41	Disopyramide	Antiarrhythmic

No.	Pharmaceuticals and personal care products	Description
42	Eprosartan	Antihypertensive
43	Erythromycin	Antibiotic
44	Ethylparaben	Cosmetic and pharmaceutical preservatives
45	Fexofenadine	Antihistamine
46	Fluconazole	Antifungal
47	Fluoxetine	Antidepressant
48	Furosemide	Diuretic
49	Gabapentin	Anticonvulsant
50	Gemfibrozil	Fibrate
51	Hydrochlorothiazide	Diuretic
52	Chloramphenicol	Antibiotic
53	Ibuprofen	NSAID
54	Ibuprofen-2-hydroxy	Metabolite
55	Ibuprofen-carboxy	Metabolite
56	Iohexol	Contrast agent
57	Iomeprol	Contrast agent
58	Iopamidol	Contrast agent
59	Iopromid	Contrast agent
60	Irbesartan	Antihypertensive
61	Ivermectin	Antiparasitic, antihelmintics
62	Ketoprofen	NSAID
63	Lamotrigine	Antiepileptic and mood stabilising
64	Lansoprazole sulphone	A medication which reduces stomach acid
65	Lincomycin	Antibiotic
66	Losartan	Antihypertensive
67	Lovastatin	Lipid-modifying agent
68	Mebendazole	Antiparasitics
69	Memantine	Psychoanaleptic (anti-dementia agent)
70	Metformin	Anti-diabetic drug
71	Methylparaben	Cosmetic and pharmaceutical preservatives
72	Metoprolol	Beta blocker
73	Mirtazapine	Antidepressant
74	Naproxene	NSAID
75	Naproxene-o-desmethyl	Metabolite
76	Norverapamil	Metabolite of verapamil (antiarytmic)
77	Octocrylene	Ingredient in sunscreens and cosmetics
78	Octyl methoxycinnamate (OMC)	UV filter
79	Oxcarbazepine	Metabolite
80	Oxybenzone	Uv filter
81	Oxypurinol	Inhibitor of xanthine oxidase
82	Paracetamol	Analgesic and antipyretic
83	Paraxanthine	Metabolite of caffeine
84	Peniciline G	Antibiotic
85	Phenazone	NSAID

No.	Pharmaceuticals and personal care products	Description
86	Primidone	Antiepileptic
87	Propranolol	Beta blocker
88	Propylparaben	Cosmetic and pharmaceutical preservatives
89	Propyphenazone	NSAID
90	Ranitidin	Histamine receptor modulator
91	Rosuvastatin	Lipid-modifying agent
92	Roxithromycin	Antibiotic
93	Saccharin	Sugar substitute
94	Salbutamol	Antiasthmatics
95	Sertraline	Antidepressant
96	Simvastatin	Lipid-modifying agent
97	Sitagliptin	Anti-diabetic drug
98	Sotalol	Beta blocker
99	Sucralose	Sugar substitute
100	Sulfadiazine	Antibiotic
101	Sulfamerazine	Antibiotic
102	Sulfamethazine	Antibiotic
103	Sulfamethoxazole	Antibiotic
104	Sulfanilamide	Antibiotic
105	Sulfapyridine	Antibiotic
106	Telmisartan	Antihypertensive
107	Theophylline	Antiasthmatics
108	Tiamulin	Veterinary antibiotic
109	Torasemide	Diuretic
110	Tramadol	Opioid
111	Trazodone	Antidepressant
112	Triclocarban	Antibacterial agent
113	Triclosan	Antibacterial agent
114	Trimetoprim	Antibiotic
115	Valsartan	Antihypertensive
116	Valsartan acid	Metabolite of valsartan (antihypertens)
117	Venlafaxine	Antidepressant
118	Venlafaxine O-desmethyl	Antidepressant
119	Verapamil	Antiarrhythmic
120	Warfarin	Anticoagulant