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Presence of pharmaceutical compounds in groundwater with respect to land use in the vicinity of sampling sites

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Abstract

The present paper discusses the results of an analysis of the impact of land use on the distribution of pharmaceuticals in groundwater samples collected during a pilot study of the contents of pharmaceuticals and hormones in groundwater taken from the national groundwater monitoring network of the Polish Geological Institute - National Research Institute. Samples were collected during monitoring campaigns from 160 groundwater monitoring sites in various land use types in 2016 and 2017. Samples were analysed for a total of 34 active substances, including natural and synthetic oestrogen hormones, cardiovascular and respiratory medications, analgesics and anti-inflammatories, antidepressants, antimicrobial drugs and anti-epileptics. Our study confirmed the presence of pharmaceuticals in 53 per cent of groundwater samples taken. Data show variations in the distribution of pharmaceuticals depending on land use type, which can thus be employed in pressure analysis and identification of sources of pollution.

Key words: water quality, groundwater pollution, pharmaceuticals, Poland

1. Introduction

The presence of pharmaceuticals in groundwater has been widely studied and discussed over the past few years (Seiler et al., 1999; Sacher et al., 2001; Kolpin et al., 2002; Cordy et al., 2004; Verstraeten et al., 2005; Barnes et al., 2008; Zuccato et al., 2008; Loos et al., 2010; Vulliet & Cren-Olive, 2011; Lapworth et al., 2012; Stuart et al., 2012; Gaffney et al., 2015; Lopez et al., 2015; Lapworth et al., 2019). Their presence is most commonly associated with pollution from communal wastewater (Seiler et al., 1999; Verstraeten et al., 2005) as well as with agriculture because veterinary medicines can often be found in manure, used as a natural fertiliser (Lapworth et al., 2012; Stuart et al., 2012). Pharmaceuticals are one of many substances known as anthropogenic organic compounds that have only recently been recognised as a growing threat to groundwater resources. Their occurrence and fate in the environment are not well understood and mostly not regulated; however, increasingly more studies confirm the growing problem of their presence in both groundwater and surface water. For that reason, pharmaceuticals were one of the first groups of emerging contaminants that have been considered for detailed analysis when developing a methodology for a groundwater watch list for substances of emerging concerns (Lapworth et al., 2019). Such watch list is a consequence of the 2014 review of the EU Groundwater Directive Annexes (Commission Directive 2014/80/EU) during which the need to

obtain and respond to new information on other substances that pose a potential risk was officially acknowledged. As such the Commission delegated the task of developing such a watch list to expert groups who work under the Common Implementation Strategy for Directive 2000/60/EC.

In Poland, studies of pharmaceutical content in groundwater are not widespread. However, the few research results available have confirmed the validity of their implementation (Caban et al., 2015; Kmiecik et al., 2017a, 2017b; Kuczyńska, 2017; Kuczyńska & Janica, 2017). In 2016-2017, the Polish Geological Institute - National Research Institute conducted a pilot study of the content of pharmaceuticals in groundwater throughout the country. The first part of the research was carried out on the occasion of implementation of surveillance monitoring in 2016, at the request of the Chief Inspectorate of the Environment (Kuczyńska, 2017). This proved the presence of active pharmaceutical substances in > 60 per cent of 93 samples selected for analytical studies. The study was continued in 2017, albeit to a smaller extent due to budget cuts. In 2017 sampling was carried out during operational and research monitoring at the request of the Chief Inspectorate of the Environment and the National Water Management Board. In both years, sampling was funded by the National Fund for Water Management and Environmental Protection. The costs of laboratory analyses were paid for as part of the PGI-NRI's statutory research scheme that is funded by the Ministry of Science and Higher Education. For the present paper data from the 2-year pilot were analysed together and are presented in the light of land use, together with a comparison with results of other monitoring data.

2. Methodology

2.1. Sampling

The pilot study on pharmaceutical content in groundwater was undertaken during two sampling campaigns in the years 2016-2017. In 2016 sampling was carried out on the occasion of surveillance monitoring across the entire country, in all groundwater bodies (172). The total number of monitoring boreholes covered during the surveillance campaign was 1,266. Of these, 105 monitoring boreholes were selected for determination of pharmaceuticals. Locations of sampling points were carefully studied to reflect potential pollution sources associated with the proximity to urban agglomerations or rural areas (poor sewage networks, spread of manure), or close to documented outbreaks of pollution, e.g., a cemetery, a hospital, sewage treatment plants, or a short distance from surface water courses. The depth to the water-bearing zone and borehole logs were analysed to ensure that sampling locations could have been exposed particularly to the impact of municipal anthropogenic pressure due to the shallow occurrence of water-bearing horizons, devoid of isolation. During the initial selection, 105 wells were selected to meet the above assumptions, while sampling attempts were made in 98 boreholes. For technical reasons (no possibility of sampling) and random (damage to samples during transport), samples collected in 93 selected locations were analysed. These points were located within an area of 60 groundwater bodies, 98 per cent of which are within porous Quaternary formations. Sixteen out of 60 groundwater bodies covered by this studywere defined at the risk of not achieving environmental goals in river basin management plans for 2016-2021 (Regulation of the Council of Ministers, Dz. U. 2016 poz. 1818, poz. 1911, poz. 1914, poz. 1915, poz. 1917, poz. 1918, poz. 1919, poz. 1929, poz. 1959, poz. 1967).

In 2017 sampling was carried out within the framework of operational and research monitoring. The operational monitoring was done in 392 monitoring boreholes located within 66 groundwater bodies, including 39 GWBs that were defined at the risk of not achieving environmental goals in river basin management plans for 2016-2021 and 27 GWBs were included in the monitoring of nitrate-vulnerable zones 2012-2015. In total 50 sampling points were selected and samples collected from 46 of these. An additional set of 21 samples was collected from a network serving research monitoring that is destined to monitor water quality in areas of potential environmental problems linked with industrial activities or large accumulation of pollution sources such as agglomerations. Again, depth to the water-bearing zone and borehole logs were analysed to ensure that sampling locations could have been particularly exposed to the impact of municipal anthropogenic pressure due to the shallow occurrence of water-bearing horizons, devoid of isolation. In total 67 samples were collected for the 2017 study. There were no duplicate sampling locations over those two years and in both years collections were made between April and October. The total number of samples analysed was 160.

Water samples were collected in accordance with accreditation rules for the collection of groundwater samples held by the Polish Geological Institute-National Research,and in line with the PN-EN ISO 5667-11:2004P standard. To collect representative

groundwater samples, monitoring boreholes were cleaned and pumped out using suction pumps prior to water sampling. Temperature stability, pH and conductivity were monitored in order to confirm the inflow of fresh water from an aquifer to the sampling wells. Depending on the stability of the parameters monitored, the volume of water pumped from wells varied from 3 to 5 volumes of stagnant water. Water samples were collected into three 1-litre bottles of pharmaceutical glass. Bottles and cups were rinsed with water before a water sample was taken. Water was kept under a cork, under which an aluminium foil was placed to protect against sorption of more non-polar analytes. Bottles with water samples were transported to the laboratory in thermal containers equipped with cooling cartridges. Samples were delivered to the laboratory within 24 hours of sampling.

2.2. Chemical analysis

The scope of analytical tests included 34 active substances of the following groups of drugs:

- Oestrogenic hormones: estrone, estriol, 17α-ethinylestradiol (EE2), 17β-estradiol (E2), testosterone;
- β-blockers (drugs against cardiovascular disease): nadolol (2016), atenolol (2017), metoprolol, pindolol, propranolol;
- β-agonists (medicines against respiratory diseases): terbutaline, salbutamol;
- Analgesics and anti-inflammatory drugs: diclofenac, ibuprofen, ketoprofen, naproxen, paracetamol, flurbiprofen;
- Antidepressants: imipramine, clomipramine, doxepine (2016 only), amitriptyline (2017 only);
- Antimicrobial agents (sulfonamides and antibiotics): sulfadiazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfamethoxazole, sulfapyridine and sulfathiazole, sulfachloropiridazine and trimethoprim, enrofloxacin;
- Anti-epileptics: carbamazepine;
- Caffeine (2017 only).

Chemical analyses were done at the Faculty of Chemistry of the University of Gdańsk in the Laboratory of Analytical and Environmental Monitoring using gas and liquid chromatography (Caban et al., 2012; Borecka et al., 2015; Caban et al., 2015). The sample preparation step included a high-volume solid phase extraction using accelerated extraction discs and derivatisation (GC/MS method only). The final determinations were made using two techniques, depending on the group of drugs. Oestrogenic hormones, β-blockers, β-agonists, analgesics and tricyclic antidepressants were determined by gas chromatography coupled with mass spectrometry (GC/MS) in the mode of selected ion monitoring (SIM). Antimicrobial drugs, carbamazepine and caffeine were determined using high-performance liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) in the MRM recording mode. Quality of results was achieved by instrumental and methodological validation, which

Table 1. Metrological parameters of analytical methods of compounds using GC /MS (SIM) and LC-MS/MS (MRM).

Pharmaceuticals	Year	Range of linearity[1] (ng/dm^3)	MQL[2] (ng/dm^3)	R[3]	RSD[4]	Recovery[5] (%)
17alfa-etynyloestradiol (EE2)	2016	10–100	10	0.9998	3.64–3.45	95.8–109.5
	2017	5–100	5	0.9996	2.1–7.3	65.3–110.0
17beta-estradiol (E2)	2016	5–100	5	0.9997	0.81–1.62	82.6–109.1
	2017	5–100	5	0.9998	5.3–7.7	93.6–113.8
Amitryptyline	2017	10–100	10	0.9999	5.0–8.5	95.1–111.5
Atenolol	2017	1–100	1	0.9988	1.2–6.4	94.7–102.16
Diclofenac	2016	5–100	5	0.9997	0.32–3.23	82.9–100.1
	2017	5–100	5	0.9999	5.0–6.9	88.3–111.6
Doxepine	2016	5–100	5	1.0000	0.65–1.98	91.6–104.4
Enrofloxacin	2016	5–100	5	0.9997	0.82–1.80	83.3–108.9
	2017	5–100	5	0.9998	2.47–6.18	95.1–101.7
Estriol	2016	5–100	5	0.9996	1.55–3.70	70.6–101.6
	2017	5–100	5	0.9999	7.1–13.1	84.8–108.6
Estrone	2016	5–100	5	0.9998	2.92–7.37	84.9–110.5
	2017	5–100	5	0.9993	2.0–8.0	87.7–113.9
Flurbiprofen	2016	5–100	5	0.9999	1.71–2.97	79.1–115.3
	2017	5–100	5	0.9998	1.4–5.0	89.6–115.6
Ibuprofen	2016	5–100	5	0.9991	1.60–1.83	81.2–116.6
	2017	5–100	5	0.9998	4.4–5.2	93.8–112.6

Pharmaceuticals	Year	Range of linearity[1] (ng/dm^3)	MQL[2] (ng/dm^3)	R[3]	RSD[4]	Recovery[5] (%)
Imipramine	2016	5–100	5	0.9998	1.73–6.64	88.1–109.9
	2017	5–100	5	0.9993	1.8–7.8	80.7–111.9
Carbamazepine	2016	1–100	1	0.9997	1.65–6.21	81.8–108.9
	2017	1–100	1	0.9993	0.96–5.68	92.3–103.8
Ketoprofen	2016	5–100	5	0.9999	1.86–4.42	85.1–102.0
	2017	5–100	5	1.0000	3.0–8.1	88.0–109.9
Clomipramine	2016	10–100	10	0.9998	1.69–8.01	88.1–106.4
	2017	10–100	10	0.9990	5.8–10.6	95.6–113.9
Caffeine	2017	5–100	5	1.0000	5.12–8.97	80.3–104.6
Metoprolol	2016	1–100	1	0.9998	0.23–6.81	90.9–115.3
	2017	10–100	10	0.9890	3.9–4.3	96.9–118.1
Nadolol	2016	1–100	1	1.0000	0.54–4.74	93.6–101.7
Naproxen	2016	5–100	5	0.9996	0.17–3.58	72.9–105.3
	2017	5–100	5	0.9999	2.4–7.5	89.0–103.4
Paracetamol	2016	5–100	5	1.0000	4.56–8.68	98.4–109.6
	2017	5–100	5	0.9999	1.6–7.9	86.3–115.2
Pindolol	2016	10–100	10	0.9998	3.26–8.01	83.0–11.1.
	2017	10–100	10	0.9850	4.0–6.8	89.2–137.3
Propranolol	2016	5–100	5	1.0000	0.10–3.52	97.7–102.7
	2017	5–100	5	0.9990	0.9–7.5	96.5–112.0
Salbutamol	2016	5–100	5	0.9975	1.39–4.77	97.9–121.1
	2017	5–100	5	0.9979	5.2–6.6	68.3–102.4
Sulfachloropiridazine	2016	1–100	1	0.9999	0.43–5.22	96.7–117.9
	2017	1–100	1	0.9999	2.70–7.94	95.5–114.8
Sulfadiazine	2016	1–100	1	0.9999	1.99–5.38	95.6–108.5
	2017	1–100	1	0.9998	1.74–5.73	84.8–117.0
Sulfadimethoxine	2016	1–100	1	0.9998	3.66–7.90	91.7–102.2
	2017	1–100	1	1.0000	1.45–5.91	97.7–116.5
Sulfamerazine	2016	1–100	1	0.9998	4.08–8.97	89.9–101.9
	2017	1–100	1	0.9999	2.62–6.45	95.2–112.0
Sulfamethazine	2016	1–100	1	1.0000	3.30–6.76	95.6–100.4
	2017	1–100	1	0.9998	1.40–4.26	92.6–102.0
Sulfamethoxazole	2016	1–100	1	1.0000	0.85–8.11	99.1–111.8
	2017	1–100	1	0.9997	2.32–5.72	91.4–102.5
Sulfapiridine	2016	1–100	1	1.0000	2.71–8.56	98.8–103.7
	2017	1–100	1	0.9994	1.47–4.29	84.3–100.2
Sulfathiazole	2016	1–100	1	0.9997	2.36–6.09	92.7–128.4
	2017	1–100	1	0.9999	1.96–6.50	98.9–103.9
Terbutaline	2016	5–100	5	1.0000	1.00–2.18	98.4–100.0
	2017	5–100	5	0.9998	4.0–8.7	87.0–113.8
Testosterone	2016	30–100	30	0.9999	1.82–6.74	94.0–99.6
	2017	50–100	50	0.9999	4.0–7.8	60.7–105.2
Trimetoprim	2016	1–100	1	0.9998	0.94–9.10	93.9–111.5
	2017	1–100	1	0.9990	2.19–7.29	86.0–116.7

[1]Range of linearity – range of the analytical method in which the output signal is proportional to the analyte being determined.

[2]MQL – method quantification limit; the lowest concentration of the substance possible to quantify by a given analytical method with assumed precision and accuracy.

[3]R – correlation coefficient; a statistical measure that characterises linearity and defines the relationship between test results and concentrations of the substance.

[4]RSD – relative standard deviation; a statistical measure that defines the dispersion of a data set relative to its mean.

[5]Recovery – part of the substance recovered from the sample tested, determined on the basis of measurements of the substance in enriched and non-enriched samples.

was done in the same way for both analytical methods. A known amount of the analyte mixture at concentrations of 1-100 ng/dm^3 was added to tap water samples with a conductivity similar to the samples tested, then subjected to extraction and instrumental analysis similar to the analysis of groundwater samples. Based on the results, metrological parameters of analytical methods were calculated (Table 1). Method quantification limits (MQL) differed from 1 to 50 ng/dm^3, and were lower for the high-performance liquid chromatography technique coupled with tandem mass spectrometry (LC-MS/MS). The highest MQL limits concerned testosterone in GC/MS (SIM) technology and amounted to 30–50 ng/dm^3, and enrofloxacin and caffeine in LC-MS/MS (MRM) technology to 5 ng/dm^3.

3. Results

3.1. Detection of pharmaceuticals

Pharmaceuticals were detected at 85 locations, which amounts to 53 per cent of all sampling points. In total, 24 out of 34 analytes that were included in the 2-year study were detected in water samples. The following ten substances were not detected in any sample: nadolol, atenolol, pindolol, terbutaline, doxepine, imipramine, clomipramine, amitriptyline, sulfachloropiridazine and trimethoprim (Table 2, Fig. 1). The most commonly seen substance was carbamazepine, which was found in a total of 33 monitored locations (21 per cent of all boreholes samples). Carbamazepine is an anti-

Table 2. Number of positive detections and maximum concentrations of specific pharmaceuticals analysed in the present study

No.	Pharmaceuticals	No. of sites with detection	No. of sites with detection below MQL	No. of sites with detection above MQL	Maximum concentration (ng/dm^3)
1	Estrone	3	0	3	69
2	Estriol	1	0	1	5
3	17α-etynyloestradiol (EE2)	2	0	2	61
4	17α-etynyloestradiol (EE2)	1	0	1	10
5	Testosterone	2	2	0	
6	Nadolol	0			
7	Atenolol	0			
8	Metoprolol	1	0	1	5
9	Pindolol	0			
10	Propranolol	3	1	2	28
11	Terbutaline	0			
12	Salbutamol	1	1	0	
13	Diclofenac	9	3	6	42
14	Ibuprofen	19	10	9	599
15	Ketoprofen	5	0	5	27
16	Naproxen	4	2	2	40
17	Paracetamol	4	2	2	52
18	Flurbiprofen	7	5	2	22
19	Doxepine	0			
20	Imipramine	0			
21	Clomipramine	0			
22	Amitryptyline	0			
23	Caffeine	1	0	1	641
24	Carbamazepine	33	0	33	869
25	Sulfadiazine	5	0	5	28
26	Sulfadimethoxine	10	4	6	6
27	Sulfachloropiridazine	0			
28	Sulfamerazine	4	0	4	105
29	Sulfamethazine	5	3	2	31
30	Sulfamethoxazole	20	0	20	66
31	Sulfapyridine	7	2	5	23
32	Sulfathiazole	1	0	1	2
33	Enrofloxacin	14	10	4	7
34	Trimethoprim	0			

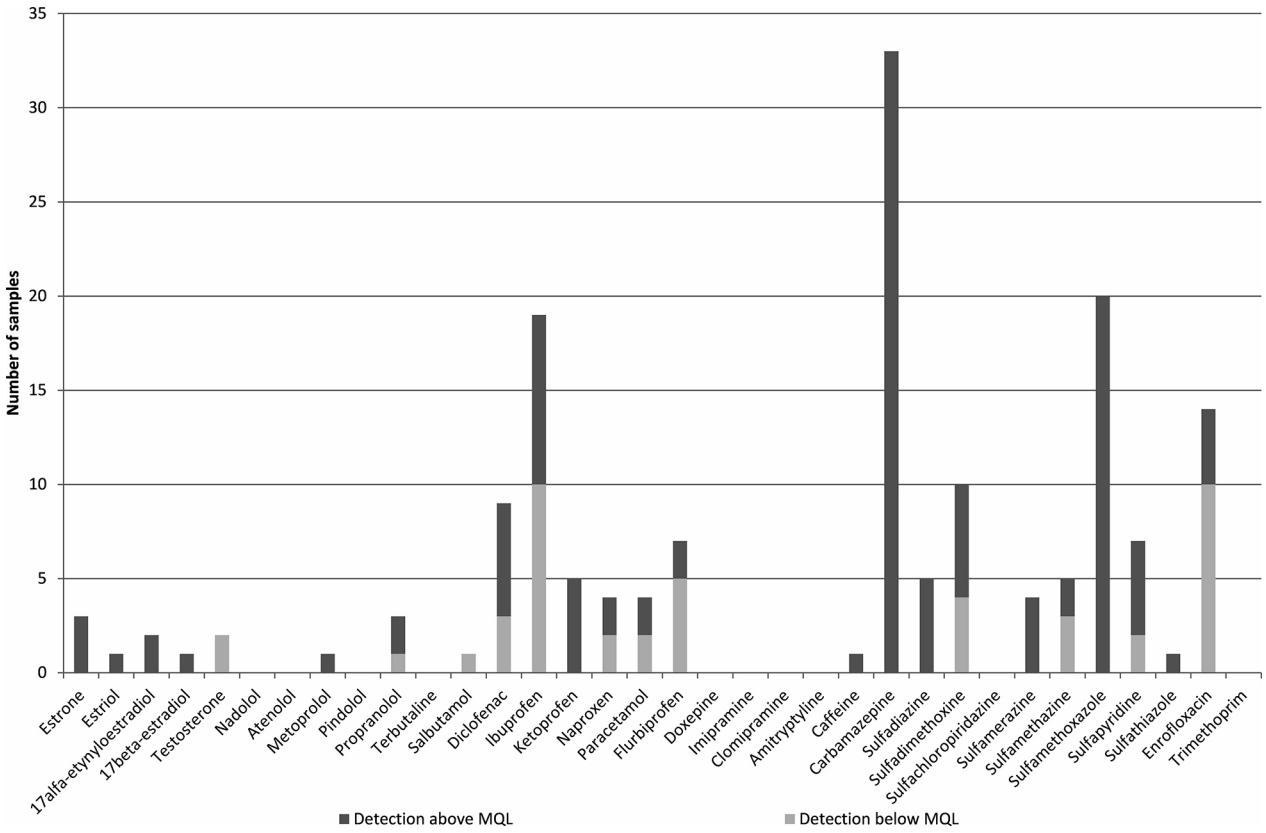

Fig. 1. Distribution of pharmaceuticals in water samples collected for the present study in 2016 and 2017

convulsant medication used primarily in the treatment of epilepsy and neuropathic pain. It is also used to treat schizophrenia and bipolar disorder. It is very mobile and persistent and therefore often found in groundwater (Lapworth et al., 2012; Lopez et al., 2015; Lapworth et al., 2019). All concentrations detected during the present study were quantified and varied from 1 to 869 ng/dm^3. The highest value was found in a shallow borehole drilled in Quaternary sands in a small town east of Warsaw. Other studies have reported maximum concentrations in groundwater varying from *c*. 99 to 900 ng/dm^3 (Sacher et al., 2001; Focazio et al., 2008; Lapworth et al., 2012). The second most commonly found substance was the human and veterinary antibiotic sulfamethoxazole. Sulfamethoxazole results in high concentrations in urine, hence is a good indicator of sewage. The substance was found in 20 sampling locations (13 per cent) with concentrations varying between 1 and 66 ng/dm^3. The highest concentration was found in a shallow borehole screened in sands in a touristic/rural area in northern Poland. Sulfamethoxazole was also the second most commonly found pharmaceutical reported in Lapworth's review of 2012 (Lapworth et al., 2012), where it was reported at a maximum of 1,100 ng/dm^3. Lopez et al. (2015) noted sulfamethoxazole to be the most frequently quantified antibiotic in France. The pain relief and anti-inflammatory drug ibuprofen was the third most commonly found drug that was detected in 19 locations (12 per cent); however, in 10 of these concentrations were found to be too low to quantify (i.e., marked as below method quantification limit). Quantifiable concentrations varied between 5 and 599 ng/dm^3. Ibuprofen was also the third most commonly found pharmaceutical reported by Lapworth et al. (2012), who noted maximum concentrations of 12,000 ng/dm^3. In the USA maximum concentrations were reported at 3,110 ng/dm^3 (Barnes et al., 2008). Sacher et al. (2001) also looked for ibuprofen in Germany, but did not report any positive findings. The veterinary antibiotic enrofloxacin was found in 14 sampling locations, which accounts for nine per cent of all sampling locations; however, at only 4 locations concentrations were found at quantitative levels and these varied between 5 and 7 ng/dm^3. This antibiotic was also studied by Barnes et al. (2008) in the USA, but not detected. Another veterinary antibiotic, sulfadimethoxine, was found in 10 locations (6 per cent). Quantified concentrations were detected in 6 of these, varying between 1 and 6 ng/dm^3. Sulfadimethoxine was also studied in the USA by Barnes et al. (2008), but not detected. Di-

clofenac was the second most common drug, after ibuprofen, of the group of analgesics and anti-inflammatory drugs. It was detected in nine sampled locations; in three samples concentrations were at levels below MQL. Concentrations varied from 5 to 42 ng/dm^3. Lapworth et al. (2012, 2019) reported maximum concentrations of 590 ng/dm^3 and also found diclofenac to be the second most commonly analysedpharmaceutical in groundwater across Europe, albeit with low detection rates. Flurbiprofen and sulfapyridine are the last pharmaceuticals among the drugs that were found at more than five sampling points. Flurbiprofen is a non-steroid, anti-inflammatory drug commonly used for treatment of rheumatoid problems. It was detected at seven sampling locations (4 per cent) and concentrations were quantified in two of them ranging between 5 and 22 ng/dm^3. Sulfapyridine is a human antibiotic. It was detected at seven sites, at five of which it was quantified at concentrations ranging from 1 to 23 ng/dm^3. All other drugs were found at a maximum of five locations.

3.2. Distribution of pharmaceuticals in relation to land use

All sampling locations were categorised with respect to land use based on the most recent information from CORINE Land Cover system (2018) and information provided by field technicians. To simplify categorisation of land use types, sampling points were assigned to five land use classes, namely: forests, meadows, industrial and dense urban areas, agricultural areas (villages and crop fields) and urban areas with scattered buildings. Sampling locations located in meadows and forests were usually associated with foresters' buildings or other touristic premises of occasional usageand agro-tourism. This study was aimed at sites with high potential for documentation of pharmaceuticals due to land use and construction of sampling boreholes. Statistics demonstrated a high potential for the presence of pharmaceuticals at all types of land use (Table 3). However, the land use type that proved to be the most prone to pollution with pharmaceuticals are agricultural areas. This is the type of use that was also most extensively covered by the present study. Fifty-two per cent of all sampling sites were located in rural areas and 55 per cent of them showed positive detection of pharmaceuticals. This is due mainly to poor sewage management in rural areas, often based on septic tanks and use of trickled systems, as well as manure distribution as part of agricultural practice. A similar situation was found in urban areas with scattered buildings. Fifty-nine per cent of all sites located in this land use type were proved to be polluted with pharmaceuticals. Sampling locations in meadows and forests were separated from agricultural use and are located in places where pressure from agriculture is considered low; yet, results showed that they are also subjected to pollution from anthropogenic sources.

The distribution of specific types of drugs at different land use type is presented in Table 4. The highest number of different drugs (21 substances) was found in agricultural areas. The most commonly detected drugs here were sulfametoxazole (an antibiotic for human and veterinary use alike), ibuprofen and carbamazepine. They were found at 17, 16 and 13 per cent of sites, respectively. Other, less common drugs found are sulfadimetoxine (10 per cent of sites) and enrofloxacin (8 per cent of sites), which are both veterinary antibiotics. In urban areas with scattered buildings a total of 20 different substances were found, which is similar to what was found in samples from agricultural lands. However, the distribution of specific pharmaceuticals is different. The pharmaceutical of the highest occurrence in urban areas is carbamazepine, which was found in 34 per cent of samples. In agricultural areas carbamazepine was found in only 13 per cent of samples. The second most common drug in urban areas is diclofenac, which was found in 10 per cent of sites. In agricultural areas the most common pain killer and anti-inflammatory drug was ibuprofen, which was found in 16 per cent of sampling points

Table 3. Distribution of sites with positive detection of pharmaceuticals among different land use types at monitoring sites

Land use type at the sampling site	Number of sites		Sites with pharmaceuticals among the same land use type	Sites with pharmaceuticals among all land use types
	–	%	%	%
Forests	23	14	30	4
Meadows	7	4	57	3
Industrial and urban areas (dense)	6	4	67	3
Agricultural areas	83	52	55	29
Urban areas with scattered buildings	41	26	59	15

Table 4. Distribution of pharmaceuticals with respect to land use types at monitoring sites (number of positive detection, percentage of sites with positive detection within a given land use type)

Pharmaceuticals	Forests		Meadows		Industrial and urban areas (dense)		Agricultural areas		Urban areas with scattered buildings	
	–	%	–	%	–	%	–	%	–	%
Estrone							1	1	2	5
Estriol									1	2
17alfa-etynyloestradiol							1	1	1	2
17beta-estradiol							1	1		
Testosterone							1	1	1	2
Metoprolol									1	2
Propranolol							1	1	2	5
Salbutamol							1	1		
Diclofenac			1	14			4	5	4	10
Ibuprofen			1	14	2	33	13	16	3	7
Ketoprofen			1	14			3	4	1	2
Naproxen							3	4	1	2
Paracetamol							4	5		
Flurbiprofen	1	4	1	14			3	4	2	5
Caffeine									1	2
Carbamazepine	4	17	3	43	1	17	11	13	14	34
Sulfadiazine							4	5	1	2
Sulfadimethoxine							8	10	2	5
Sulfamerazine							2	2	2	5
Sulfamethazine							4	5	1	2
Sulfamethoxazole	2	9	1	14			14	17	3	7
Sulfapyridine							5	6	2	5
Sulfathiazole							1	1		
Enrofloxacin	2	9	1	14	1	17	7	8	3	7

of that sampling group. Diclofenac was found only in 5 per cent of samples in agricultural areas.With respect to hormones, these were found at onefold sites and occurred in both agricultural and urban areas. There was definitely a higher detection of sulfonamides and antibiotics in agricultural areas than in urban areas. After summarising the number of positive detections of all antimicrobial agents, these were found at 57 per cent of sites in agricultural areas *vs* 34 per cent of urban areas and this probably reflects the wider use of veterinary drugs in rural areas.

Carbamazepine, the most commonly found drug during this study, was also found at sites located near meadows, which are also associated with agricultural areas and in forests, which most likely reflects poor sewage management at these sites. At sites classified as meadows there were also single detections of various anti-inflammatory drugs such as diclofenac, ibuprofen, ketoprofen and flurbiprofen and also the veterinary antibiotics sulfametoxazole and enrofloxacin. The two last-named were more often found at sites associated with forests.

4. Conclusions

The main aim of the present study was to determine whether active substances of pharmaceuticals do indeed pose a risk to groundwater resources in Poland, as suggested by studies in western Europe and the USA. Results of this study confirm the hypothesis that the risk of pollution with pharmaceuticals does exist also in Poland and needs further assessment and perhaps regulations at national level for the sake of future protection of groundwater resources. It needs to be noted; however, that samples were collected only once in each monitoring sites and as such represent temporary concentrations. Their long-term presence, as well as the level of concentrations, need to be confirmed by repetitive, systematic sampling. The problem seems to be most relevant in rural areas, but urban planning with scattered building is nearly equally threatened by the problem. The distribution of active substances found during the present study with respect to land use at sampling locations indicates communal waste water sources to be the most probable sources of pollution with pharmaceuticals.

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