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PPCP Monitoring in Drinking Water Supply Systems: The Example of Káraný Waterworks in Central Bohemia

Zbyněk Hrkal [1,2,*], Pavel Eckhardt [1], Anna Hrabánková [1], Eva Novotná [1] and David Rozman [1,2]

[1] T.G. Masaryk Water Research Institute, p.r.i, 160 00 Praha 6-Dejvice, Czech Republic; eckhardt@vuv.cz (P.E.); hrabankova@vuv.cz (A.H.); novotna@vuv.cz (E.N.); rozman@vuv.cz (D.R.)

[2] Institute of Hydrogeology, Engineering Geology and Applied Geophysics, Faculty of Sciences, Charles University, Albertov 6, 12 843 Prague 2, Czech Republic

* Correspondence: hrkal@vuv.cz; Tel.: +420-606-079-144

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Abstract: The Káraný waterworks supplies drinking water to about one-third of Prague, the capital city of the Czech Republic with a population of more than 1 million. The combination of two technologies—bank infiltration and artificial recharge—are used for production of drinking water. The two-year monitoring of PPCPs (pharmaceuticals and personal care products) at monthly intervals observed temporal changes in 81 substances in the source river and groundwater, and the efficacy of contamination removal depended on the treatment technology used. The results showed a very wide range of PPCPs discharged from the waste water treatment plant at Mladá Boleslav into the Jizera River at concentrations ranging from ng/L to µg/L. Acesulfame and oxypurinol in concentrations exceeding 100 ng/L systematically occurred, and then a few tens of ng/L of carbamazepine, sulfamethoxazole, primidone, and lamotrigine were regularly detected at the water outlet using the artificial recharge for production of drinking water. Bank infiltration was found more efficient in removing PPCP substances at the Káraný locality where none of the monitored substances was systematically detected in the mixed sample.

Keywords: emerging pollutants; wastewater; drinking water; bank infiltration; artificial recharge

1. Introduction

Only a few years ago, most experts in water management had only very vague ideas about the occurrence and amount of the so-called micropollutants, that are substances contained in water at extremely low concentrations in the order of nanograms per liter. Also, for this reason until now, these substances are not dealt with in the Czech or European legislation for drinking water. However, very fast development of sophisticated analytical laboratory methods disclosed a number of pharmaceuticals in water. The abbreviation PPCP (pharmaceuticals and personal care products) for this very diverse group of substances is now used [1–4].

PPCPs include, for example, pharmaceuticals that enter waste waters from sewers. Current purification technologies are mostly inefficient, and in the extreme case, some substances are not removed at all during the water purification process. During the monitoring Czech-Norwegian Research Programme project AQUARIUS (Assessing water quality improvement options concerning nutrient and pharmaceutical contaminants in rural watersheds) undertaken at the pilot site of Horní Beřkovice in Central Bohemia, PPCPs such as hydrochlorothiazide, sulfamethoxazole, sulphapyridine, sulphanilamide, carbamazepine, including its metabolite carbamazepine-10,11-epoxide, were systematically detected downgradient from the mechanical and biological waste water treatment plant between the years 2015 and 2016 [5,6]. These substances were also recorded at very low concentrations in the order of tens to hundreds of nanograms per liter (only carbamazepine, gabapentin, and hydrochlorothiazide were detected at concentrations in the order of micrograms per liter). Similar results were observed in constructed wetlands in the catchment of the Želivka water reservoir [7–9].

Similar studies carried out in the USA [10], Great Britain [11], Germany [12], and Switzerland [13] showed identical problems with the low efficiency of traditional wastewater treatment plants. The technological solution of eliminating the majority of forms of PPCPs from wastewater exists and comprises the use of activated carbon. The high efficacy of this technology was demonstrated in a number of experiments by Rodrigues et al. [14] and Rivera-Utrilla et al. [15] but it is a relatively high cost method.

Considering the extremely low detected concentrations, the negative impact of PPCPs on human health is still speculative [16,17]. No long-term clinical studies have shown any negative effects of PPCPs contained in drinking water on the human organism. For this reason, we are still working with the term potential or unquantified risk [18,19].

Since 2013, the European Commission has implemented PPCPs to legislation by establishing a watch list of substances for EU-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council. The document was amended in 2015 (EU 2015/495) [20] and currently includes anti-inflammatory pharmaceutical diclofenac, hormones 17-beta-estradiol (E2), 17-alpha-ethinylestradiol (EE2), estrone (E1), antibiotics erythromycin, clarithromycin, azithromycin, and several other substances like selected insecticides and herbicides.

In the Czech Republic, PPCPs in drinking water have not been adequately addressed. For this reason, the present study is focused particularly on the detection of PPCPs in the process of drinking water treatment in the Káraný waterworks. The monitoring system is designed to clarify the behavior of micropollutants on their way from the source to the waterworks.

2. Materials and Methods

2.1. Characteristics of the Káraný Pilot Site

The above-mentioned findings led to the initiation of the detailed monitoring of the quality of drinking water at the Káraný waterworks supplying the capital city of Prague. The selected pilot area is a unique locality. Along a 32 km long stretch of the Jizera River from Mladá Boleslav to the Sojovice weir, as shown in Figure 1, the behavior of pharmaceuticals was studied. Finally, the efficacy of removing PPCPs during bank infiltration and artificial recharge was assessed.

The waterworks at Káraný operates on the principle of combining two independent drinking water treatment technologies. The first one is now historic, but still a perfectly functioning project of bank infiltration built between 1906 and 1913. It consists of 685 wells of a depth ranging from 8 to 12 m, spaced 20 to 40 m apart, situated in the sand-gravel fluvial terraces ca. 250 m from the bank of the Jizera River, as shown in Figure 1. The total capacity of this system is up to 1000 L/s.

Another section of the waterworks started in 1968 and relies on artificial recharge [21] during which the surface water from the Jizera River is, after a simple mechanical treatment, pumped into infiltration ponds, as shown in Figure 2, from where it moves into about 20 m thick sandy fluvial sediments. The water table is at an average level of 10 to 14 m below ground so that there is, in the unsaturated zone, sufficient storage space for seepage water. At a distance of approximately 200 m from the infiltration ponds, there is a system of large-diameter wells with a total capacity of up to 900 L/s. The tapped water is a mixture of infiltrated water and original groundwater in a sandy-gravel terrace inflowing from the east towards the Jizera River. Water balance model studies [22] assume that 20% to 30% of groundwater participates in the resulting mixture, while the remaining 70% to 80%

consists of water from the artificial recharge. However, these proportions may vary depending on the operating conditions of the waterworks.

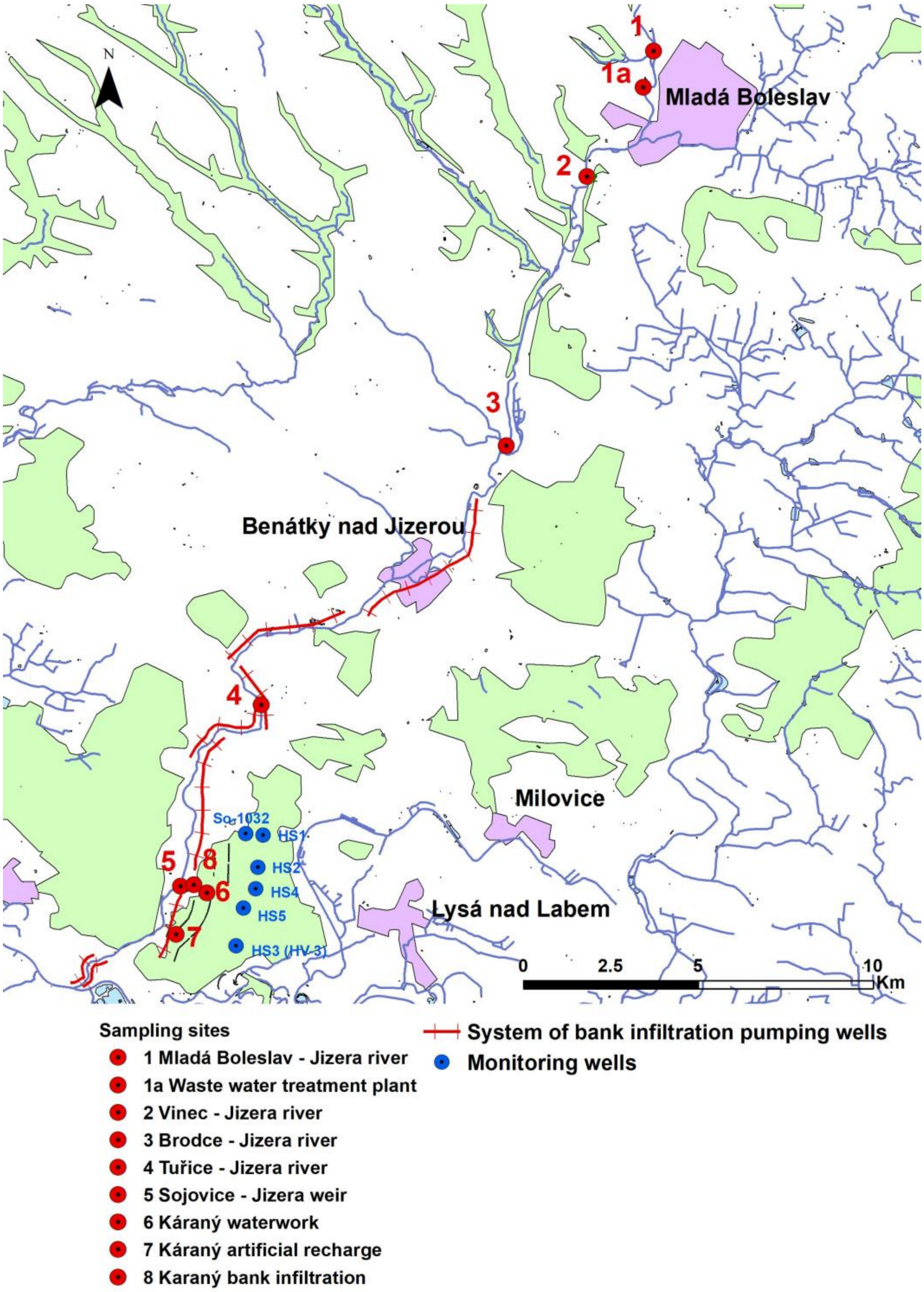

Figure 1. Sampling sites on the Jizera River.

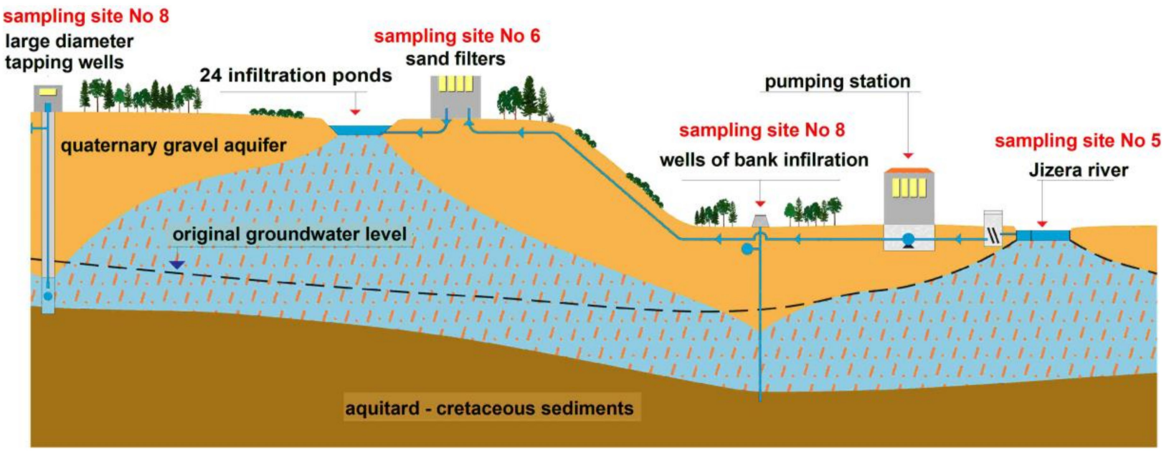

Figure 2. Scheme of Káraný waterworks (modified from Skalický [22]).

A total of 94 PPCPs or their metabolites were monitored on a monthly basis during two consecutive years. During July and August 2017, when the water discharge of the Jizera River was expected to decrease, and therefore the concentrations of the monitored substances increased, the frequency of sampling was shortened to once a week. In addition, changes in PPCP concentrations in river water over a period of 24 h were monitored by sampling at 2-h intervals one time in August 2017.

Sampling was carried out at nine sites, as shown in Figure 1. Profiles No. 1–No. 5 represent sampling sites on the Jizera River. Profile No. 1 upstream of the Mladá Boleslav town characterizes the quality of water flowing from the upper reaches of the river above the municipal wastewater treatment plant. Analyses from profile No. 1a define the quality of the purified urban wastewater (including a psychiatric hospital) discharged in the Jizera River. The results from profiles No. 2, No. 3, No. 4, and No. 5 show changes in water quality during its flow in the watercourse. Profile No. 5 is a key point for the Káraný waterworks, because it is a sampling site for the subsequent artificial recharge process.

The sixth sampling site represents the water quality after its mechanical treatment and prior to infiltration into the Quaternary aquifer. The analysis at monitoring site No. 7 characterizes the water mixture from all currently operating wells downgradient from the artificial recharge. It actually defines the qualitative changes that take place in the process of artificial recharge. However, the analyses do not always take into account the mixing from all infiltration ponds. For operational reasons, there may occur a situation when some of the wells can be temporarily shut down.

Analyses from the eighth sampling site represent a mixture of water from bank infiltration wells. However, these are not all used permanently, depending on the input parameters of the tapped water, and the desired yield, so that some parts of the water system are cut off.

To clarify the quality of groundwater in the Quaternary aquifer inflowing from the east, a group of water monitoring boreholes marked 9, 10, 11, and 12, as shown in Figure 1, were also sampled in October 2018.

2.2. Analytical Methods

The analyses of the collected wastewater, surface and groundwater, mud and soil samples were carried out according to a validated procedure in the Vltava catchment laboratory.

Samples were taken in a 60 mL amber glass vial (filling only half of the volume). Samples were stored in a freezer (in an inclined position). On the day of analysis, samples were defrosted at a maximum of 30 °C. It was necessary to continue the analysis procedure immediately after defrosting.

Two methods were developed for analysis of PPCPs—Method A (ESI+ (Electrospray ionization) mode)) and Method B (ESI− mode). The samples were centrifuged in headspace vials for 5 min at about 3500 rpm. Then, 1.50 grams of the samples were weighed in a 2 mL vial on the analytical balance. Then, 1.5 μL of formic acid (Method A) or 1.5 μL of acetic acid (Method B) was added into the sample. An isotope dilution was performed in the next step. Deuterized internal standards of d10-carbamazepine, d6-sulfamethoxazole, d3-iopromide, and 13C2-erythomycin (Method A), or d3-ibuprofen, d4-diclofenac, d3-naproxen, d5-chloramphenicol, and d3-iopamidol (Method B) were used.

PPCPs were separated and detected by LC-MS/MS (Liquide Chromatography-Mass Spectrometry/ Mass Spectrometry) methods based on direct injection of the sample into a chromatograph. A 1200 Ultra High-Performance Liquid Chromatograph (UHPLC, Agilent Technologies, Santa Clara, CA, USA) tandem with 6410 Triple Quad Mass Spectrophotometer (MS/MS, Agilent Technologies, Santa Clara, CA, USA) from Agilent Technologies were used in ESI+ or ESI− mode.

Method A (ESI+)—the separation was carried out on a Zorbax Eclipse XDB-C18 analytical column (100 × 4.6 mm, 3.5 μm particle size, Agilent Technologies, Santa Clara, CA, USA). The mobile phase consisted of methanol and water with 0.1% formic acid and 5 mM ammonium formate as the mobile phase additives. The flow rate was 0.25 mL min^{-1}. Injection volume was 0.50 mL.

Method B (ESI−)The separation was carried out on a Zorbax Eclipse XDB-C18 analytical column (150 × 4.6 mm, 3.5 μm particle size). The mobile phase consisted of methanol and water with 0.05% acetic acid as the mobile phase additive. The flow rate was 0.25 mL min^{-1}. Injection volume was 1 mL.

The samples for non-steroidal anti-inflammatory drugs were first acidified by acetic acid, filtered through a 0.45 μm cellulose filter, and mixed with an internal standard solution. The internal standard solution was prepared of deuterized solids (98% purity) and water from a UHQ (Ultra High Quality) system. The SPE (Solid Phase Extraction) was performed on a high-performance liquid chromatography column.

The samples for the estrogen group analysis were first acidified by hydrochloric acid to pH 2. Then, acetonitrile solutions of particular substances were added as internal standards, the pH was raised to 7.8, and samples were filtered through a 1 μm glass-fiber filter. The SPE was performed on a conditioned solid phase extraction disc. The analytes were eluted by acetonitrile, dried, dissolved in hexane and dichloromethane, cleaned on a florisil column, and transferred to the solution for LC/MS (Liquide Chromatography-Mass Spectrometry/ Mass Spectrometry) detection.

3. Results

3.1. Source Area of PPCPs in the River Water

All smaller cities in the upper reaches of the Jizera River are a source of PPCPs contained in the river water. However, absolutely crucial is the city of Mladá Boleslav with a population of more than 44,000; especially the psychiatric hospital at Kosmonosy that is connected to the local sewage treatment plant. Its importance is documented in Figure 3, which demonstrates the varied composition of PPCPs that are at concentrations exceeding thousands of nanograms per liter and being discharged into the Jizera River. Only substances that appeared in analyses over the reference period of two years and being above the detection limit in more than 25% of cases were included in the survey. Therefore, accidental or sporadic occurrences were excluded from the statistics.

The results clearly show the impact of the Mladá Boleslav wastewater treatment plant on the quality of water in the Jizera River. Oxypurinol and telmisartan occur systematically in purified waste water at concentrations of tens of micrograms per liter, and the other four drugs, namely diclofenac, tramadol, lamotrigine, and hydrochlorothiazide, enter the stream at concentrations at the micrograms per liter level. As for analyses of the other 44 pharmaceuticals, their concentrations are systematically ranging from a single nanogram to hundreds of nanograms per liter.

Outflow from the wastewater treatment plant usually is in tens of L/s, while the Jizera River discharge at Mladá Boleslav is in m^3 per second range for most of the year. Nevertheless, as follows from the comparison of long-term concentrations of micropollutants on the profile above the treatment plant (profile No. 1), and at the sampling site below it (profile No. 2), there is a distinct impact on the quality of surface water. Figure 4 shows the qualitative changes that occur in the long term (2-year average) on a relatively short stretch of 8 km of the Jizera River between profiles No. 1 and No. 2. Of the 44 substances systematically detected in the river water below the wastewater treatment plant on profile No. 2, 18 substances showed elevated content, while only three of them decreased slightly, and concentrations of the remaining substances were found more or less stable. The impact of discharging treated wastewater in the case of oxypurinol, telmisartan, and iomeprol is quite conclusive. These substances were either absent on profile No. 1 (iomeprol) or only detected at low concentrations (oxypurinol, telmisartan).

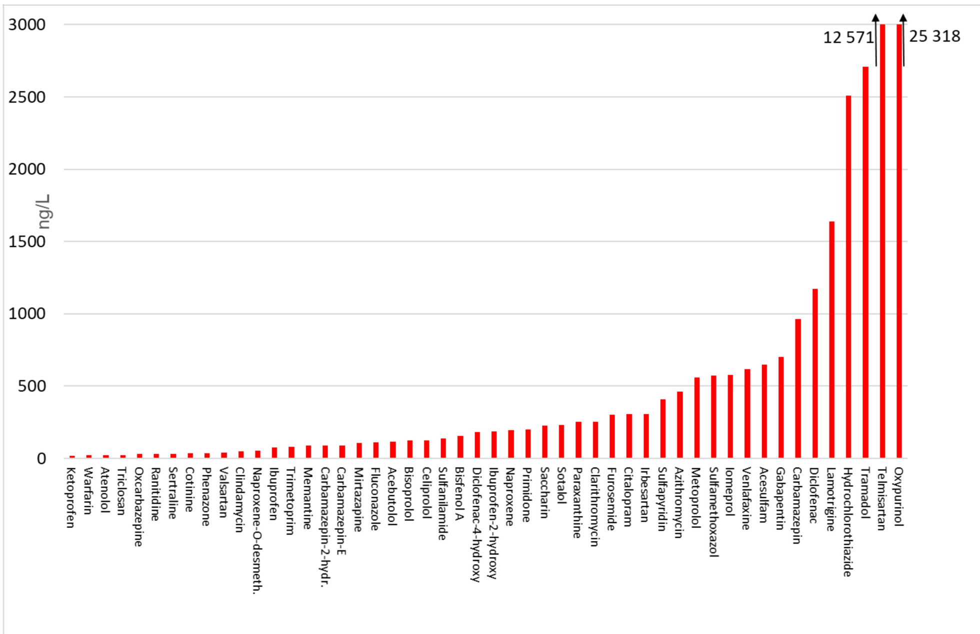

Figure 3. Average content of pharmaceuticals and personal care products (PPCPs) that are systematically discharged from the wastewater treatment plant in Mladá Boleslav.

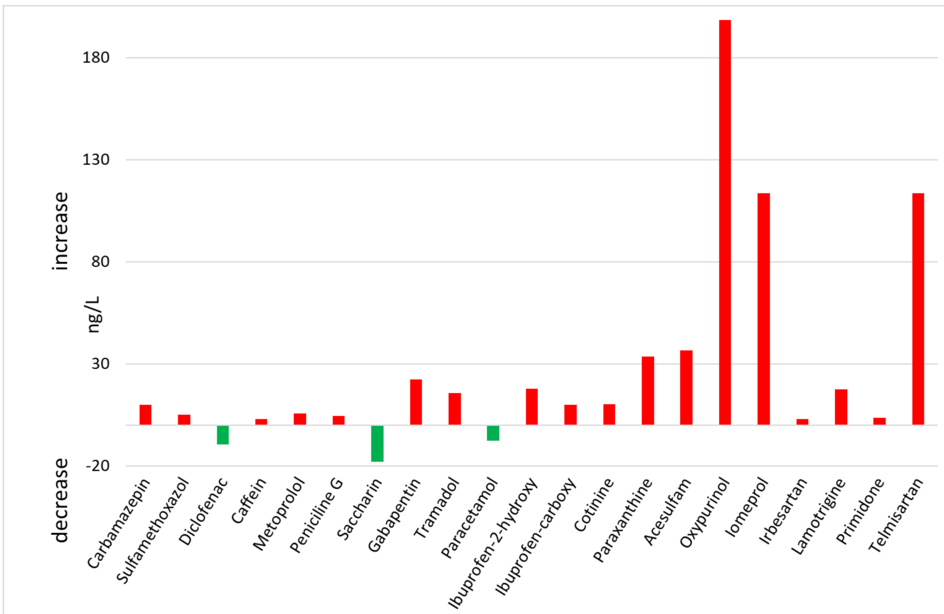

Figure 4. Changes in long-term concentrations of monitored PPCPs on the profiles above and below the wastewater treatment plant at Mladá Boleslav (in red are substances whose concentrations have increased in this section of the watercourse, the green ones have fallen).

3.2. Changes in PPCP Concentrations in River Water between Mladá Boleslav and the Weir in Sojovice

The monitored profiles on the Jizera River in the section between Mladá Boleslav and the weir in Sojovice—where the water is collected for artificial recharge—document the processes resulting in natural attenuation of pharmaceuticals in the river water. Only small tributaries with very limited water discharge join this stretch of the Jizera River, so they do not significantly affect the water balance of the Jizera River. The municipal wastewater treatment plant of the city of Benátky nad Jizerou, with a population of 7400, appears to be the only new source of pharmaceuticals. This fact is very clear in comparison to the two-year monitoring of average river water quality on profiles No. 2 Vinec and No. 5 Sojovice weir. While the concentrations of most substances were found to be decreasing downstream of Mladá Boleslav in a stretch about 32 km long, as shown in Figure 5, their content between the profiles No. 1 and No. 2 were observed to be increasing in general.

The section of the Jizera River around the Sojovice weir plays a key role for part of the Káraný waterworks, which uses artificial recharge for the production of drinking water. This water is the source for further treatment, more or less using natural purification processes. Despite the predominant decreasing trend of most pollutants in the Jizera River downstream of Mladá Boleslav, their detected number and concentrations in absolute values remain at relatively high levels (Figure 6). The waterworks in Káraný infiltrates a very varied mixture of 26 micropollutants whose average concentration in four cases exceeds 200 ng/L.

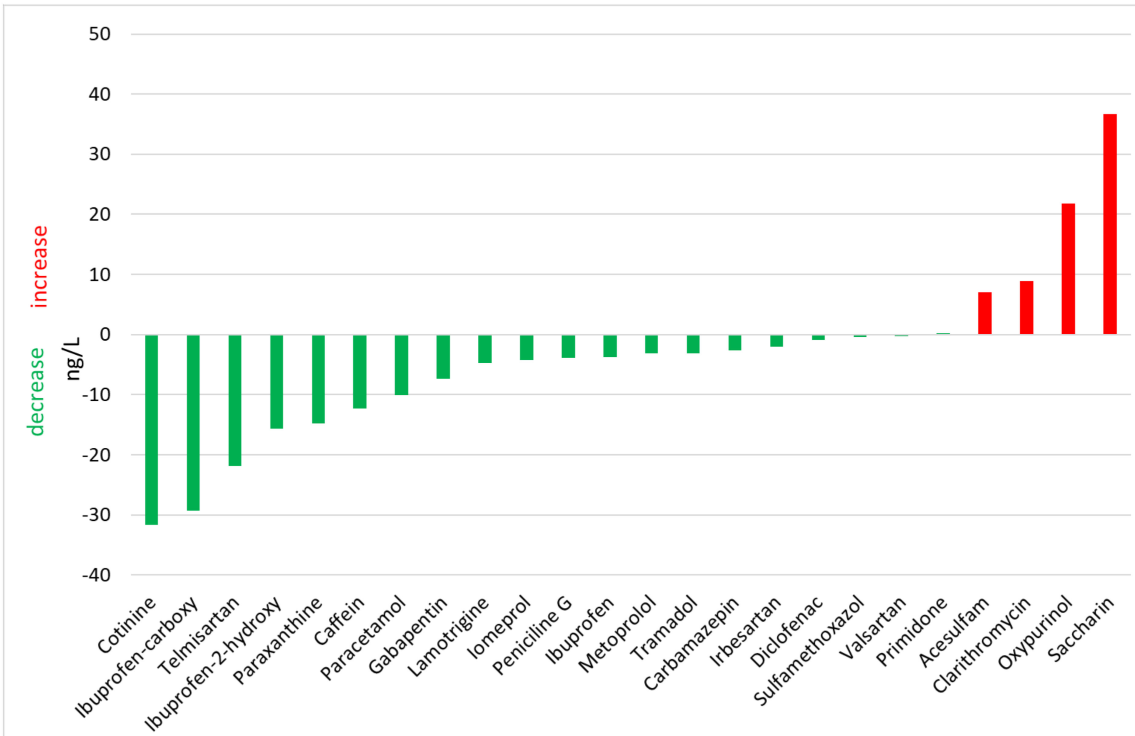

Figure 5. Changes in long-term concentrations of monitored PPCPs between profiles No. 2 and No. 5 Sojovice weir.

Interesting results were obtained along profile No. 5 during 8 August 2017. The data acquired in two-hour consecutive intervals showed a large variability in concentrations of some groups of micropollutants over a short period of one single day, as shown in Figure 7. The monitored substances can be divided into several groups. The first group consisted of carbamazepine, sulfamethoxazole, metoprolol, gabapentin, or tramadol; the concentrations of which did not change over the last 24 h, and whose contents are subject only to longer-term changes.

Conversely, ibuprofen, ibuprofen-2-hydroxy, or diclofenac concentrations in surface water changed even during a few hours. Ibuprofen showed a relatively obvious trend with gradual onset from night-time concentration values of about 40 ng/L, which doubled shortly after midday, and was followed by a slight decline. Ibuprofen-2-hydroxy had a maximum at 140 ng/L at 06:00, followed by a systematic drop until night-time. Diclofenac fluctuated during the day without any clear trend.

There was a very specific behavior of saccharin and caffeine. Both micropollutants reflect the habits and lifestyle of the common population, first appearing in surface water as late as at around 10:00, and the last caffeine was detected in surface water at 20:00. Saccharin was detected two hours later. Thus, it is evident that the residence time of these two substances in water was very short, and their occurrence was closely linked to the local source.

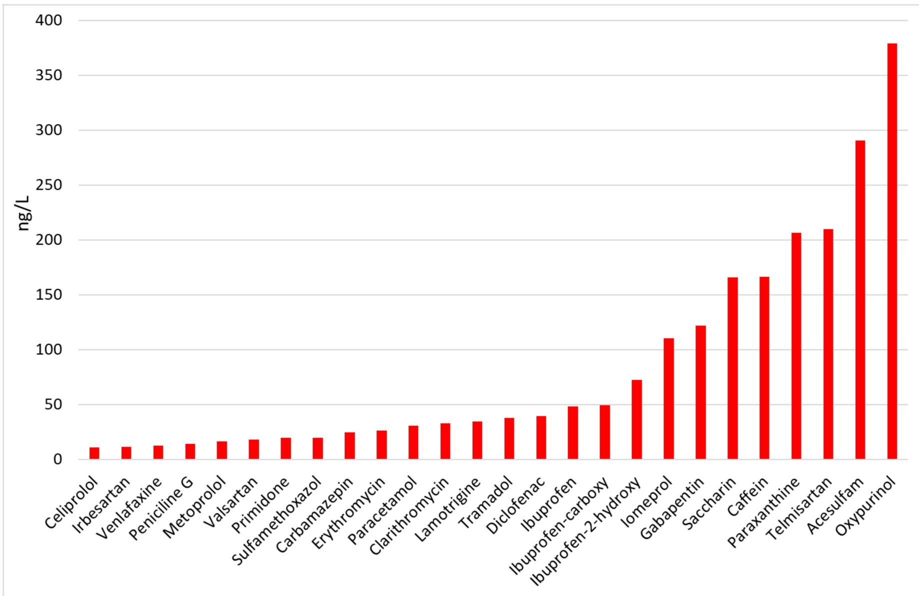

Figure 6. Long-term average concentrations of PPCPs on profile No. 5 Sojovice weir.

The data suggest that to achieve a reliable comparability of input data for subsequent statistical processing, it is necessary to adhere to a uniform sampling time.

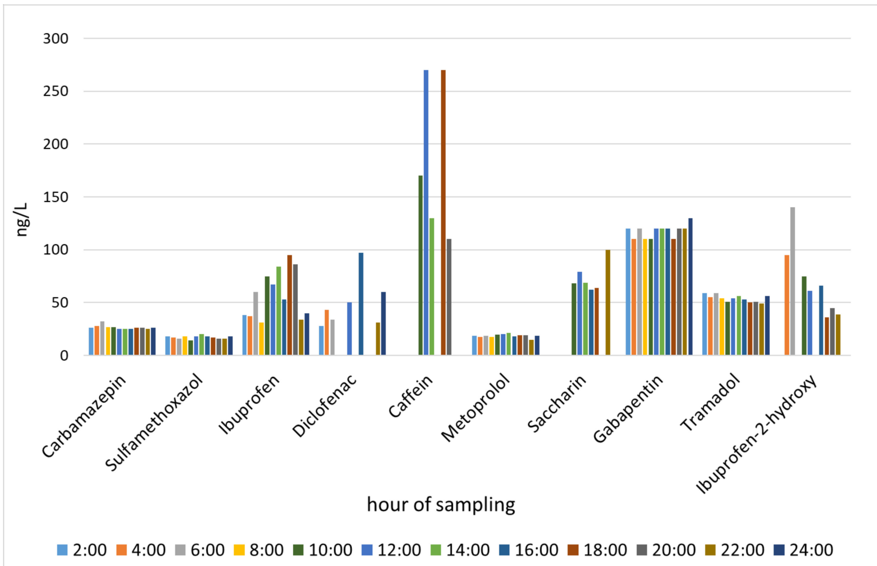

Figure 7. Time-related changes in concentrations of selected PPCPs on profile No. 5 during August 2017.

The quality of source water for artificial recharge and bank infiltration is subject to relatively considerable time-related changes in water discharge. Figure 8 clearly demonstrates the dilution ability of the selected three pharmaceuticals that systematically occur in the stream on profile No. 5. The content of metoprolol, carbamazepine, and tramadol at elevated water discharges (10 m^3/s) were always below the detection limit of the analytical method used.

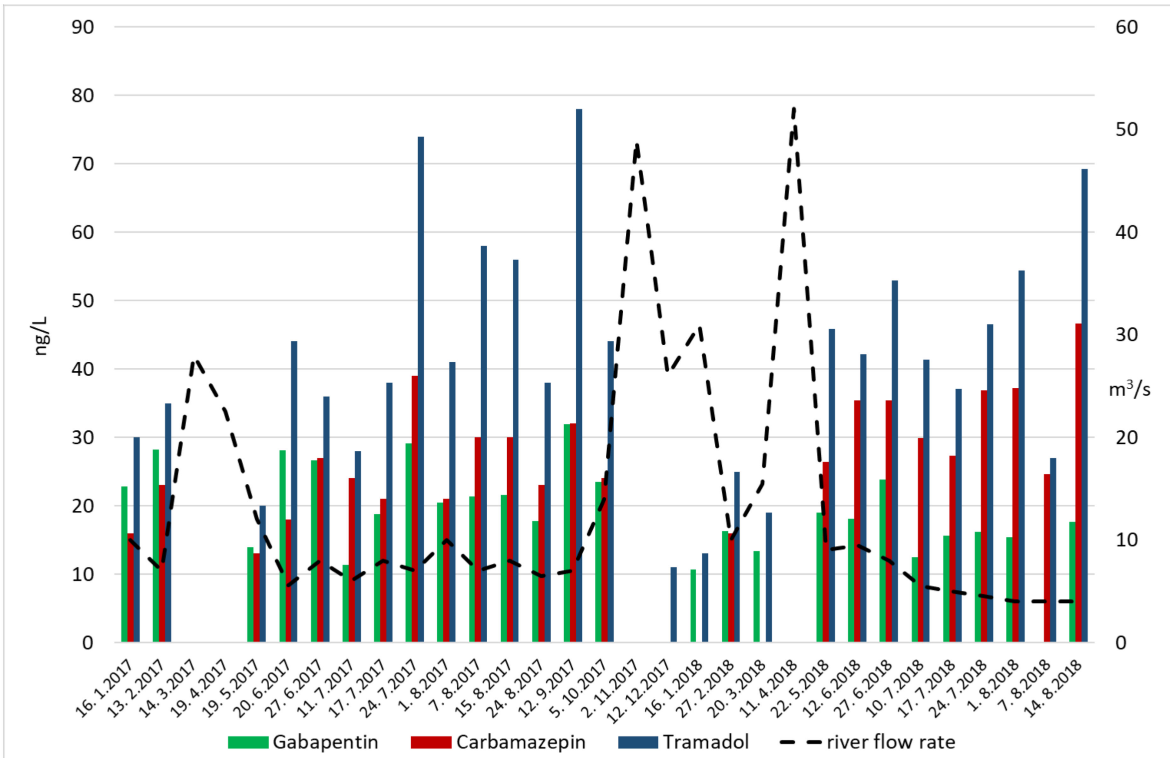

Figure 8. Changes in concentrations of selected PPCPs on profile No. 5 in relation to water discharge.

3.3. Removal of PPCP Substances during the Production of Drinking Water Using Artificial Recharge

The results of artificial recharge clearly show that the efficacy of PPCP removal is relatively high. A total of 26 substances were detected on the No. 5 profile Sojovice weir and 16 of them completely disappeared after treatment. This process does not involve mechanical treatment, which does not affect the monitored substances. Therefore, their removal takes place only when the surface water has passed and been infiltrated through the unconsolidated rock.

Only six substances occur systematically in groundwater tapped from the system of large-diameter wells in the vicinity of infiltration ponds. They include, in particular, acesulfame and oxypurinol at concentrations exceeding 100 ng/L that were evidently associated with the wastewater treatment plant in Mladá Boleslav. Other substances, which systematically occur in the produced water, were only at concentrations of the first tens of ng/L. These include carbamazepine, sulfamethoxazole, primidone, and lamotrigine.

Figure 9 gives the average values of ibuprofen and paraxanthine. These substances, however, occur rather rarely in water from artificial recharge (ibuprofen two times and gabapentin five times) obviously without exhibiting any systematic trend.

Water tapped along the infiltration ponds is a mixture of Quaternary groundwater and water from infiltration technology. The model study by Milický [23] assumes the dominant proportion (70–80%) of the component comes from artificial recharge. In September 2018, in order to verify the influence of groundwater inflow, the "natural background" was checked on a one-time basis in monitoring boreholes of the Káraný waterworks east of the artificial recharge objects. The results showed that PPCPs that systematically occurred in a mixed sample of collected water did not appear in any of the boreholes, as shown in Table 1. Consequently, these micropollutants must have originated from the river water. On the contrary, ibuprofen—only randomly occurring in the mixed sample—was detected in the boreholes. These results indicate the existence of another source of contamination independent of the river water that that spreads in the quaternary aquifer from the east.

Drinking water production in the Káraný waterworks varies depending on the demand. When the infiltration is reduced, then the influence of river water on total chemistry is reduced. The resulting concentrations of PPCPs can therefore be affected by the Quaternary aquifer. However, to prove this assumption, it would be necessary to monitor boreholes, and to have a longer series of analyses available.

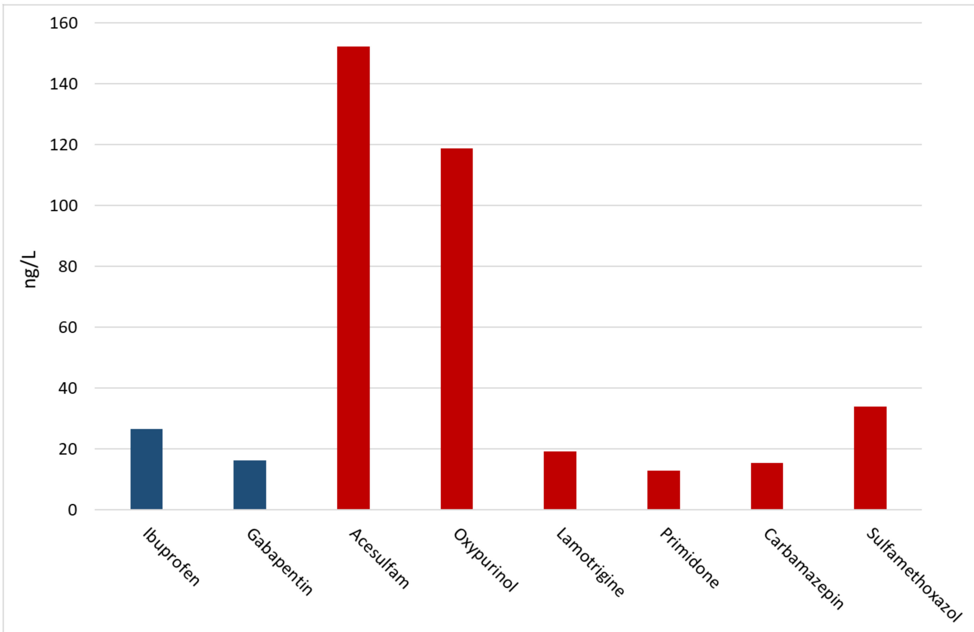

Figure 9. Long-term average values of PPCPs detected in water after artificial recharge (blue are mean values of random occurrences, red are mean values of systematically occurring substances).

Table 1. Contents of PPCP substances in monitoring wells SO 1032, HS1, HS2, HS3, HS4 and HS5 of the Káraný waterworks (position of well depicted in Figure 1, data in bold are higher than detection limit).

		Well					
Name of Monitoring Well		**SO 1032**	**HS1**	**HS2**	**HS3**	**HS4**	**HS5**
PPCP	**Unit**						
Bisfenol A	**ng/L**	**63.4**	<50.0	**217**	<50.0	<50.0	**85.3**
Ibuprofen	**ng/L**	<20.0	<20.0	**34.8**	**25.9**	<20.0	<20.0
Caffein	**ng/L**	<100	<100	**186**	**128**	<100	<100
Ketoprofen	**ng/L**	<10.0	<10.0	**24.5**	**53.1**	**20.2**	<10.0
Saccharin	**ng/L**	<50.0	<50.0	**51.5**	<50.0	<50.0	**81.9**
Paracetamol	**ng/L**	**10.4**	<10.0	<10.0	<10.0	<10.0	**138**
Paraxanthine	**ng/L**	<100	<100	**114**	**172**	<100	<100
Bisfenol S	**ng/L**	<50.0	<50.0	**4570**	**565**	<50.0	**62.8**

3.4. Removal of PPCPs during Drinking Water Production Using Bank Infiltration Technology

The water quality of bank infiltration was studied at the Káraný waterworks on a mixed sample from 685 wells. Not all wells for bank infiltration were always contributing to the resulting mixed sample, as some were often disconnected. The analyses from No. 3 and No. 4 profiles represent point data, whereas the chemical composition of the water from the bank infiltration characterizes the average concentrations over the entire length of the bank profile. An overview of PPCPs that occurred in a mixture of bank infiltration is given in Table 2. The results show that no substances systematically occurring in this water were found.

Acesulfame occurred most frequently (in 6 cases of the 31 analyzed samples), while other substances were detected at most three times. Caffeine showed the highest values in the first hundreds of ng/L, while paraxanthine was found in only one case. The amounts of all other substances were in tens of ng/L. All micropollutants were found to behave independently. There is no pair that shows a common trend.

Table 2. An overview of PPCPs in a mixed sample of bank infiltration (the table shows only the observed time periods when at least one substance was found above the detection limit).

PPCP	Unit	Sampling Data													
		16.1.2017	**19.5.2017**	**20.6.2017**	**27.6.2017**	**11.7.2017**	**24.8.2017**	**5.10.2017**	**2.11.2017**	**12.12.2017**	**11.4.2017**	**22.5.2017**	**27.6.2017**	**10.7.2017**	**14.8.2017**
Ibuprofen	ng/L	54					31								
Diclofenac	ng/L			31											
Caffein	ng/L					140			230					148	
Chloramphenicol	ng/L										32				
Saccharin	ng/L		65												
Gabapentin	ng/L				11										
Paracetamol	ng/L				10	16									
Clarithromycin	ng/L														
Roxithromycin	ng/L														
Paraxanthine	ng/L					141									
Acesulfam	ng/L							57	64			58	60	60	59
Oxypurinol	ng/L									72				50	61
Primidone	ng/L														11

4. Discussion

Two-year monitoring results demonstrated a wide range of PPCPs in the Jizera River basin. The main cause of their spread is the low efficiency of sewage treatment plants and the presence of a significant source of PPCPs—A psychiatric hospital at Kosmonosy.

When comparing the two purification technologies used in the Káraný waterworks, the bank infiltration as a process eliminating the pharmaceuticals from the original river water was found more efficient relative to artificial recharge technology. The reason for this may be the higher content of clay minerals in the bottom and sides of the river bed, while artificial recharge takes place in clean sands and gravel.

The issues of the occurrence of PPCPs in drinking water in the Káraný waterworks is more or less associated only with artificial recharge. The problem can be solved in several ways. The cheapest is the optimization of drinking water production. The waterworks would limit the artificial recharge operation in low flow periods, when PPCPs in the Jizera River water are high. The second option is to equip the wastewater treatment plant in Mladá Boleslav with an active carbon filter. The same filter in the pretreatment technology in Káraný waterworks should solve the problem.

5. Conclusions

- Raw water from the Jizera River contains a range of PPCPs in concentrations ranging from nanograms to micrograms per liter.
- The wastewater treatment plant at Mladá Boleslav significantly affects the quality of water used for production of drinking water in the Káraný waterworks. Of the 44 substances systematically detected in the river water below the wastewater treatment plant, 18 substances showed elevated content. The increase of telmisartan and iomeprol concentrations was approximately 100 ng/L, and in the case of oxypurinol, nearly 200 ng/L.
- The water discharge during flood periods significantly affects the time-related variability in PPCP content in river water. At elevated water discharges (10 m^3/s), PPCP concentrations were always below the detection limit of the analytical method used.
- The time-related variability of some PPCPs in river water during 24 h demonstrates the need for a uniform time schedule for sampling.
- Acesulfame and oxypurinol were detected in concentrations exceeding 100 ng/L in purified water using artificial recharge technology. Both these substances originate from a wastewater treatment plant comprising waste water from the psychiatric hospital at Kosmonosy. Systematic occurrence of carbamazepine, sulfamethoxazole, primidone, and lamotrigine in amounts of the first tens of ng/L originated from the river water used for artificial recharge.
- Ibuprofen and gabapentin were detected at irregular time intervals in drinking water produced through artificial recharge. Ibuprofen may come from the environment of the Quaternary aquifer when the share of artificial recharge on the total balance of mixed sample is lower.
- Bank infiltration is a technology that removes PPCPs in a more effective way than artificial recharge. None of the monitored substances occurred systematically in the mixed sample. Acesulfame occurred most frequently (in 6 cases of the 31 samples analyzed), while other substances were detected three times in maximum in concentrations of only the first tens of ng/L. The occurrences of individual detected substances were not correlated.

Author Contributions: Z.H. and A.H. conceived and designed the experiments; P.E., D.R., and E.N. performed the monitoring; Z.H. analyzed the data; P.E., D.R., and E.N. contributed materials/analysis tools; Z.H. wrote the paper.

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