

Article

Pharmaceuticals Load in the Svihov Water Reservoir (Czech Republic) and Impacts on Quality of Treated Drinking Water

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Abstract: An important component of micropollutants are PPCPs (pharmaceuticals and personal care products). This paper contains the results of the monitoring of surface water, groundwater and wastewater in the surrounding area of the Svihov drinking water reservoir. Over the period 2017–2019, over 21,000 water samples were taken and analyzed for 112 pharmaceuticals, their metabolites, and other chemicals. The results are discussed in detail for two streams with the highest observed concentration of PPCPs (Hnevkovice, Dolni Kralovice) and two streams with the highest water inflow into the reservoir, representing also the highest mass flow of PPCPs into the reservoir (Miletin, Kacerov). The overall analysis of the results shows that acesulfame, azithromycin, caffeine, gabapentin, hydrochlorothiazide, ibuprofen and its metabolites, oxypurinol, paraxanthine, and saccharin (on some profiles up to tens of thousands ng/dm^3) attain the highest concentration and occur most frequently. The evaluation of raw water and treated drinking water quality showed the significant positive effect of water retention in the reservoir (retention time of 413 days) and also of the treatment process, so that the treated drinking water is of high quality and contains only negligible residues of few PPCPs near the detection limit of the analytical method used.

Keywords: PPCP; pharmaceuticals; surface water; wastewater; groundwater; drinking water; water analyses; water-supply reservoir; micropollutants; personal care products

1. Introduction

1.1. Work Scope and Objectives

As the accuracy of analytical methods develops, it is possible to detect more and more substances belonging to the group of so-called micropollutants in natural water, occurring at very low concentration (usually in ng/dm^3 to $\mu\text{g}/\text{dm}^3$). A very important group of these substances are PPCPs (pharmaceuticals and personal care products)—medicines, hormones, antibiotics, cosmetics, drugs and other substances, including metabolites of the primary pollutants (Ferrer, Thurman [1], Richardson [2]). In the European Union, residues of a number of medicinal preparations have been detected in surface water and groundwater, soil, and in animal tissues at concentrations that vary depending on the medicinal preparation as well as on the nature and proximity of the source. Some painkillers, antimicrobials, antidepressants, contraceptives, and anti-parasitics are commonly found. Traces of some medical preparations may also penetrate drinking water and certain foods—European Commission [3].

The above findings led to the research on the Svihov reservoir on the Zelivka River used for drinking water supply to the population of the capital city of Prague and its surroundings, in order to observe the occurrence of PPCP substances in the largest water source in the Czech Republic. There have been long-term problems with the unsatisfactory level of municipal wastewater treatment

in the catchment of the reservoir, often manifested by increased residual content of basic nutrients (nitrogen, phosphorus) that contribute to eutrophic processes in the reservoir—Kvitek [4]. The objective of the research was to verify whether pharmaceuticals occur within the water flowing into the reservoir, and in the accumulated water in the Svihov reservoir, to determine the concentration and to examine how this is reflected in the quality of raw and treated drinking water. Nine surface inflows into the Svihov reservoir were selected and were sampled for PPCP substance content in the period February 2017–December 2018 at 2–4 week intervals. Samples of raw water from the reservoir and treated drinking water were also taken. All results are available in Supplementary Materials, Table S1. The paper deals with the selected four tributaries for capacity reasons. Subsequently, in 2019, additional sampling of discharged wastewater from the municipal wastewater treatment plant in Hnevkovice and analysis of groundwater from two municipal wells in Hnevkovice took place.

The research of Hrkal et al. [5] investigating the occurrence of pharmaceuticals in Karany, the second largest water source for Prague located north of the city with a capacity of up to 1 m³/s, was important for comparing with the results from the Svihov reservoir catchment area.

1.2. Current Situation

Because these substances do not yet have limits set for drinking water (in the Czech Republic or in other EU countries), their occurrence in natural raw water used for drinking water production attracts the attention of the professional and general public (Snyder [6]). From the perspective of drinking water production, the question is to what extent these substances can penetrate the entire water system (water accumulation, water treatment) up to the final product—drinking water (WHO [7,8]). The potential negative impact of PPCPs on human health at commonly observed concentrations in natural water has not yet been proved (Jones et al. [9], Stackelberg et al. [10]), therefore the term potential unquantified risk is used by Godoy et al. [11]. The World Health Organization (WHO) [7,8] states that, from the available data, medicinal preparations in drinking water at the identified low concentrations are unlikely to pose a threat to human health. However, WHO (World Health Organization) notes that the issue of residues of medicinal preparations cannot be ignored, as there may be potential effects of long-term exposure on vulnerable populations, implying the need to adopt a preventive approach, i.e., introducing a quality limit for drinking water. In addition, we do not yet sufficiently understand the potential ‘cocktail effects’ resulting from the combination of a wide range of medicinal preparations and other chemicals in the environment.

Surface and groundwater sources of drinking water receive these contaminants mainly from municipal wastewater, where they reflect the use of these chemicals by the population. Frequent occurrence of these substances is documented by many extensive studies, e.g., Bexfield et al. [12] summarizes the impact of pharmaceuticals on groundwater sources throughout the territory of the U.S.A. This study draws attention mainly to the impact on shallow water of agricultural areas, which is probably related to the decentralized disposal of wastewater containing residual concentrations of pharmaceuticals, both from human settlements and from livestock farms. These substances reach higher concentration especially in wastewater from hospitals, sanatoriums, senior homes, hospices and other places with high consumption of medicaments. Rozman et al. [13,14] report high medicaments concentration in “treated” wastewater discharged into the local stream from the Horni Berkovice Psychiatric Hospital, Czech Republic (gabapentin, hydrochlorothiazide, and carbamazepine reached the highest concentrations of up to several micrograms per liter). At the local level, sources of these substances from animal production and fish farms are important; here, various veterinary and nutritional products are commonly used [6]. However, as Battaglin et al. [15] point out, using the monitoring in Rocky Mountain National Park (U.S.A.) as an example, these substances are starting to be detected also in areas with little human activity; it is likely that these substances can be detected by today’s ultra-precise analytical methods.

Commonly used technologies of wastewater treatment (mechanical-biological treatment plants), especially in smaller municipalities, are usually not sufficiently effective and remove only part of

these substances, which reach the surface recipient and partially infiltrate into groundwater. The low efficiency of municipal wastewater treatment in terms of PPCP substances is reported both by sources from the Czech Republic (Chen [16], Vymazal et al. [17,18]) and from abroad. The low efficiency of pharmaceuticals removal in conventional municipal wastewater treatment plants is reported, for example, by data from the U.S.A.—Lubliner et al. [19], from Switzerland—Tauxe-Wuersch et al. [20], or from research conducted in Germany—Kasprzyk/Hordern et al. [21]. A significant increase in micropollutant removal efficiency can be achieved by incorporating another stage of wastewater treatment, e.g., by including sorption filters with activated carbon (Rodriguez et al. [22]).

The behavior of these substances in the environment and their impact on aquatic ecosystems have been the subject of many studies (Jobling et al. [23], Kostich et al. [24], Standley et al. [25], Yamamoto [26]), but there is still a lot of missing information on the transport properties, disintegration constants, sorption characteristics, accumulation in organisms, etc. (Kase [27]), because most of these substances have only recently been researched. Among them, we can name, e.g., Environmental risk limits for pharmaceuticals (RIVM) [28], who has been involved in The Netherlands in researching the risks and quality standards for four types of commonly occurring medicines in Dutch waters (carbamazepine, metformin, metoprolol, and amidotrizoic acid). The very broad spectrum of these substances, whose numbers are increasing with the rapid development of analytical procedures, is not beneficial for the early achievement of the research results needed to set quality limits. Today, tens to hundreds of individual substances are routinely analyzed in every sample.

In the Czech Republic, there are no legal limits for the content of pharmaceuticals in drinking water. In addition, the same situation applies at the European Union level, but a process to identify new potentially harmful substances exists. Article 8c of the Priority Substances Directive [29,30] requires the European Commission to propose a strategic approach to water pollution by pharmaceuticals (Marsland, Roy [31]). Under Article 8b of this Directive, the Commission is to update the list of monitored substances every two years. These substances may pose a significant risk to or via the aquatic environment and there is insufficient monitoring data on the actual risk they present. According to the current Commission Implementing Decision (EU) [32], a watch list has been set up for monitoring substances throughout the European Union in the field of water policy, updated every two years. The currently valid list contains the following PPCP substances or groups of substances: 17-alpha-ethinylestradiol (EE2), 17-beta-estradiol (E2), estrone (E1), macrolide antibiotics (erythromycin, clarithromycin, azithromycin), methiocarb, neonicotinoids (imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid), amoxicillin, and ciprofloxacin.

Other approaches include the International Memorandum (Wirtz [33]), which defined the so-called 'target value for pharmaceuticals in surface water for abstraction of drinking water', at 100 ng/dm³ for each individual chemical in the micro-pollutant group, including pharmaceuticals. It should be noted that this limit of 100 ng/dm³ already applies to drinking water in the Czech Republic [34] for the individual pesticides and their metabolites (with the exception of aldrin, dieldrin, heptachlor and heptachlorepoxyde with a limit of 30 ng/dm³), as well as for individual polyaromatic hydrocarbons. Based on the concentration of pharmaceuticals detected in our monitoring, it appears that the 100 ng/dm³ limit may also be the appropriate value for assessing the quality of water used for drinking water supply, regarding the presence of pharmaceuticals and their metabolites. This limit may be the target value at least until specific limit values are established for major occurring pharmaceuticals, based on long-term research and assessments of health and environmental risks.

2. Materials and Methods

2.1. Svihov Water Reservoir

The Svihov reservoir (Figure 1) on the Zelivka River is located in the central part of the Czech Republic, about 50 km south-west from the capital city of Prague, in the Czech-Moravian Highlands at an altitude of 392 m. It is the largest reservoir in Central Europe used for drinking water supply.

Completed in 1975, the backwater of the Zelivka-Svihov water reservoir reaches back 39.1 km, the total reservoir volume is 309.0 million m³, the flooded area is 1603 hectares, and the hydrological catchment area of the reservoir is 1178 km². The water supply has a capacity of 3.1 m³/s and covers about two thirds of the drinking water needs of the inhabitants of the capital city and its surroundings. The average long-term annual flow rate at the dam profile is 6.93 m³/s, and the 100-year-old flow rate attains 316.0 m³/s (www.pvl.cz [35]).

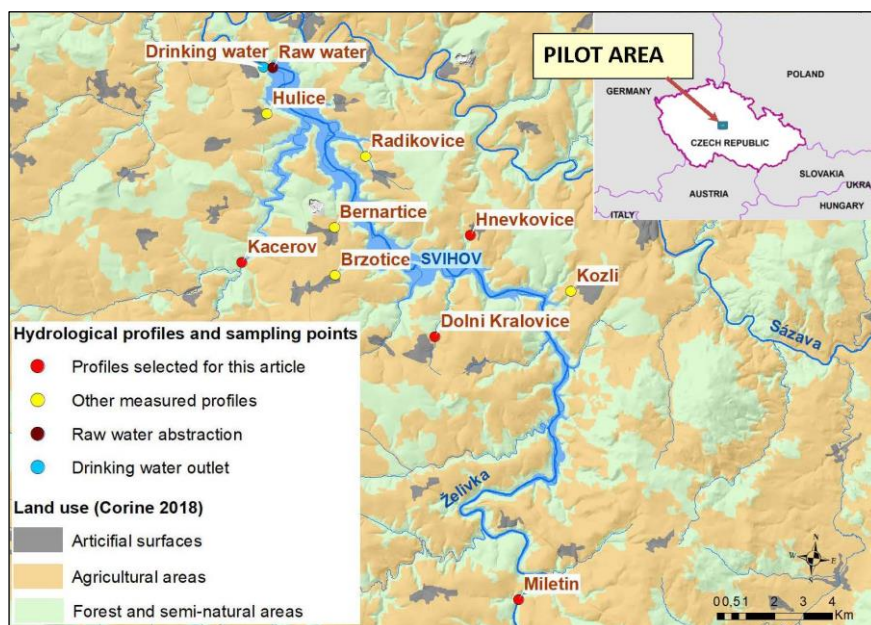


Figure 1. Svihov reservoir, location of hydrological profiles and sampling points. Topographical base map: geoportal.cuzk.cz.

2.2. Monitoring Methodology 2017–2018

A number of small local watercourses with a high proportion of wastewater, often poorly treated, from small municipalities around the reservoir flow into it and therefore PPCP type constituents were expected here (Morteani et al. [36], Swartz et al. [37], Kozisek et al. [38], Datel et al. [39]). The largest surface water inflows into the reservoir were identified in the project and nine main inflows with a significant proportion of wastewater from local municipalities were selected. Here, nine hydrological profiles were built (Figure 1) characterizing the source water for the Svihov reservoir. The profiles were used for flow rate measurement and water sampling. The largest inflow into the reservoir is the Zelivka River (Miletin profile).

The flow rates were measured using a Cipoletti or Thomson spillway (sharp edge trapezoidal or triangular spillway), and the overflow height was measured using the Solinst Levellogger Edge automatic probe [40] positioned at the spillway. Control measurements (always at the time of sampling) were carried out using a measuring vessel and a stopwatch. On the streams with higher flow rates (i.e., Miletin, Kacerov), CHMI (Czech Hydrometeorological Institute) [41] data were used.

The samples were taken in one-month intervals, yet in the summer period (July–August), when we expected a decrease in flow rates and thus an increase in the concentration of the monitored substances, the sampling period was shortened to a frequency of two to four times a month. The sampling points were located below the discharge point of treated wastewater from the WWTPs (wastewater treatment plants). Simultaneously with the sampling of nine selected hydrological profiles, a sample of raw water was also taken from the reservoir at the inlet of the raw water treatment plant, and a sample of the treated drinking water entering the water supply system. Sampling was carried out in accordance with the relevant technical standards of the ISO 5667 series. A volumetric sampler on a telescopic rod

was used to sample surface water, immersed in the water stream. Samples of raw and drinking water were taken from standard sampling taps in the raw water treatment plant. Within 32 sampling rounds, 21,174 water samples were taken from 20 February, 2017, to 12 November, 2018. Each sampling round was performed within one day.

At the start of the project in 2017, the laboratory offered to determine 46 different pharmaceuticals; however, their number was increasing very rapidly, and by the second half of 2018, the laboratory was already able to analyze 93 different pharmaceuticals and their metabolites. In the follow-up monitoring in 2019 (see below), 20 more substances were added to 113 substances (Tables 1 and 2). The negative aspect of this development is the varying length of monitoring series duration for the individual substances.

Table 1. List of analyzed pharmaceuticals and personal care products (PPCP) constituents monitored in 2017–2018. Marked in blue are the nine substances selected for water monitoring evaluation between 2017 and 2018, and in green the seven other substances deliberated additionally in the 2019 part of wastewater monitoring. Substances with concentration mostly below the detection limit (95–100% of samples) are marked in brown.

Analyzed Constituent	Detection Limit (ng/dm ³)	Analysis Uncertainty (%)	Use
17a-ethynilestradiol	2	35	hormone
17-alpha-estradiol	1	35	hormone
17-beta-estradiol	1	35	hormone
Acebutolol	10	35	beta blocker
Acesulfame	50	35	sweetener
Alfuzosin	10	35	beta blocker
Atenolol	10	30	beta blocker
Azithromycin	10	35	antibiotic
Bezafibrate	10	35	fibrate
Bisoprolol	10	35	beta blocker
Bisphenol A	50	35	plastics production
Bisphenol B	50	35	plastics production
Bisphenol S	50	35	plastics production
Caffeine	100	45	stimulant
Carbamazepine	10	30	antiepileptic
Carbamazepine-2-hydr.	10	35	carbamazepine metabolite
Carbamazepine-DH	10	40	carbamazepine metabolite
Carbamazepine-DHH	10	40	carbamazepine metabolite
Carbamazepine-E	10	40	carbamazepine metabolite
Celiprolol	10	35	beta blocker
Chloramphenicol	20	35	antibiotic
Ciprofloxacin	20	35	antibiotic
Citalopram	20	35	antidepressant
Clarithromycin	10	35	antibiotic
Clindamycin	10	35	antibiotic
Clofibric acid	10	35	clofibrate metabolite
Cotinine	20	35	stimulant
Cyclophosphamide	10	35	cancer chemotherapy
Diatrizoate	50	35	contrast medium
Diclofenac	20	30	NSAID (non-steroidal anti-inflammatory)

Table 1. Cont.

Analyzed Constituent	Detection Limit (ng/dm ³)	Analysis Uncertainty (%)	Use
Diclofenac-4-hydroxy	20	40	diclofenac metabolite
Diltiazem	10	35	vasodilator
Doxycycline	50	35	antibiotic
Enrofloxacin	20	35	antibiotic
Erythromycin	10	30	antibiotic
Estriol	10	35	hormone
Estrone	1	35	hormone
Fexofenadine	10	35	antihistaminic
Fluconazole	10	35	fungicide
Fluoxetine	10	35	antidepressant
Furosemide	50	35	diuretic
Gabapentin	10	35	sedative
Gemfibrozil	10	35	fibrate
Hydrochlorothiazide	50	35	diuretic
Ibuprofen	20	35	NSAID
Ibuprofen-2-hydroxy	30	40	ibuprofen metabolite
Ibuprofen-carboxy	20	40	ibuprofen metabolite
Iohexol	50	35	contrast medium
Iomeprol	50	35	contrast medium
Iopamidol	50	35	contrast medium
Iopromide	50	30	contrast medium
Irbesartan	10	35	treatment of hypertension
Ivermectin	50	35	antiparasitic
Ketoprofen	10	35	NSAID
Lamotrigine	10	35	anticonvulsant drug
Lovastatin	10	35	statin drug
Memantine	20	35	Alzheimer's disease medication
Metoprolol	10	30	beta blocker
Mirtazapine	10	35	antidepressant
Naproxen	50	30	NSAID
Naproxen-O-desmeth.	20	40	naproxen metabolite
Norfloxacin	20	35	antibiotic
Ofloxacin	20	35	antibiotic
Oxcarbazepine	10	40	anticonvulsant drug
Oxypurinol	50	35	treatment of hyperuricemia
Paracetamol	10	35	painkiller
Paraxanthine	100	35	psychoactive stimulator
Penicillin G	10	30	antibiotic
Phenazone	10	35	NSAID
Primidone	10	35	anticonvulsant drug
Progesterone	0.5	35	hormone
Propranolol	10	35	beta blocker
Propyphenazone	10	35	NSAID
Ranitidine	10	35	gastric acidity treatment
Roxithromycin	10	35	antibiotic

Table 1. Cont.

Analyzed Constituent	Detection Limit (ng/dm ³)	Analysis Uncertainty (%)	Use
Saccharin	50	35	sweetener
Sertraline	10	35	antidepressant
Simvastatin	10	35	statin drug
Sotalol	10	35	beta blocker
Sulfamerazine	10	35	antibiotic
Sulfamethazine	10	35	antibiotic
Sulfamethoxazole	10	30	antibiotic
Sulfanilamide	50	35	antibiotic
Sulfapyridine	10	35	antibiotic
Telmisartan	20	35	treatment of hypertension
Testosterone	0.5	35	hormone
Tiamulin	10	35	antibiotic
Tramadol	10	35	painkiller
Triclocarban	10	35	antimicrobial drug
Triclosan	20	30	antimicrobial drug
Trimethoprim	10	30	antibiotic
Valsartan	10	35	treatment of hypertension
Venlafaxine	10	35	antidepressant
Warfarin	10	30	blood anticoagulant

Table 2. List of analyzed PPCP constituents analyzed in 2019 in addition to 2017–2018 monitoring. Substances with concentration mostly below the detection limit (95–100% of samples) are marked in brown.

Analyzed Constituent	Detection Limit (ng/dm ³)	Analysis Uncertainty (%)	Use
4-formylaminoantipyrine	10	35	antibiotic
Atorvastatin	10	35	statin drug
Benzotriazole	20	35	anticorrosive and deicing products
Benzotriazole methyl	20	35	anticorrosive and deicing products
Bisoprolol	10	35	beta blocker
Butylparaben	10	35	antimicrobial drug
Climbazole	10	35	fungicide
Cyclamate	100	35	sweetener
DEET (diethyltoluamide)	10	30	insect repellent
Ethylparaben	10	35	antimicrobial drug
Metformin	20	40	diabetes medicine
Methylparaben	30	35	fungicide
Norverapamil	10	35	verapamil metabolite
OMC (ethylhexyl methoxycinnamate)	1000	35	cosmetics (hair spray, sunscreen)
Propylparaben	20	35	antimicrobial drug
Salbutamol	10	35	asthma treatment
Sucralose	1000	35	sweetener
Valsartan acid	10	35	valsartan metabolite
Verapamil	10	35	treatment of hypertension

2.3. Additional Monitoring in 2019

The monitoring results of 2017–2018 showed relatively high concentrations of PPCP substances in some local stream flow profiles. One of them was the Hnevkovice profile, which was selected for additional research. Samples from two wells in Hnevkovice were taken to compare the load in surface and groundwater, and in 2019 pre-treated wastewater from the municipal WWTP and water from the receiving stream (i.e., Hnevkovice Creek) were sampled (Figure 2). Point S1 was chosen at the Hnevkovice Creek 20 m above the water discharge from the WWTP, and point S2 on the Hnevkovice Creek 20 m below the water discharge from the WWTP (point S2 is identical to the Hnevkovice profile from monitoring in 2017–2018). Two accessible municipal wells W1 and W2 were used for groundwater sampling. Sampling was carried out according to relevant technical standards ISO 5667 series.



Figure 2. Hnevkovice—sampled wells (W1, W2), effluent from WWTP (wastewater treatment plant) and Hnevkovice stream upstream and downstream from the WWTP (S1, S2).

Wastewater is discharged from the WWTP at regular intervals of several minutes. The number and frequency of sampling was designed with respect to regular changes during the daily WWTP operation cycle. Two sampling cycles took place on 27–28 June and 21–22 October 2019. In one sampling cycle, one water sample was taken every three hours, i.e., eight samples per 24 h. Sampling of treated wastewater from the municipal wastewater treatment plant in the village of Hnevkovice was designed to determine the level and fluctuations of PPCP pollutant concentration in wastewater flowing to the Hnevkovice stream (and subsequently to the Svihov reservoir). One-off samples were also taken from the receiving stream (i.e., Hnevkovice Creek) above and below the discharge from the WWTP, in order to determine the impact of the discharged wastewater on water quality in the stream.

One-off sampling was carried out in accordance with the relevant technical standards of the ISO 5667 series. A volumetric zonal sampler on a rope was used to obtain the groundwater sample from the dug wells; water was sampled at about 0.5 m below the surface. A volumetric sampler on a telescopic rod was used to sample the wastewater and surface water and was immersed in the WWTP effluent or surface water flow.

2.4. Laboratory Work Methodology

The collected water samples were poured into glass sample bottles with ground neck/closure provided by the laboratory. The samples were stored in a refrigerated safety box according to the instruction of the laboratory and transported to an accredited laboratory, usually within a time between 6–10 h, where they were refrigerated, and the bottles were stored in an inclined position. The samples were analyzed by an accredited laboratory of the state-owned enterprise Povodi Vltavy (Vltava Watershed Authority) in Plzen, according to the internal standard operating procedures (SOP O-19-A) using the LC/MS (liquid chromatography/mass spectrometry) analytical method.

One multicomponent method was used for all analytes from the group of pharmaceuticals - direct injection of the water sample after centrifugation, pH adjustment (acidification) and an addition of a mixture of isotopically labeled standards. Micropollutants were measured with Agilent Technologies 1290 Infinity II UHPLC system coupled to an Agilent 6495 Triple Quadrupole MS system using a Waters Xbridge C18 column (4.6 × 100 mm, particle size 3.5 μm) supplemented with a pre-column, with an injection volume of 50 μL (manufacturer Agilent Technologies International Pte. Ltd., Yishun Ave 7, 768923 Singapore).

Within method validation, stability tests were performed to confirm the stability of all analytes in the sample for at least three weeks when refrigerated at an inclined position. The sample had to be cooled as soon as possible after collection and then frozen.

The quality of the analytical work was assured by adding isotopically labeled standards to each sample (internal standard method). The samples were evaluated on an eight-point linear calibration curve over a concentration range of 10–2000 ng/dm³. In each group of samples, two blank samples and two quality control samples of the entire procedure (independent mixture of all analytes added to water) were measured and evaluated. In addition, every fifth sample was measured in duplicate (once without addition and once with the addition of an independent mixture of all analytes) and the actual yields in the given matrix were calculated from the concentration difference and included in the final concentration calculation.

2.5. Processing of Chemical Analysis Results

The PPCP analytical data processing method encounters a problem caused by the fact that a significant part of the results lies below the detection limit. One solution could be that only results above the detection limit will be presented. This would, however, result in a significant distortion of the situation and underestimation of the results obtained.

Finally, a solution on the safe side, respecting the precautionary principle, was chosen as the basic approach to the risk analysis: samples with values below the detection limit are for the purposes of display in charts and the calculation of statistical parameters used at the detection limit concentration. Obviously, this approach has its drawbacks and presents the theoretically most unfavorable situation. However, given the importance of the research for the safety of the population, we consider this approach to be relatively the most correct one.

The evaluation of time series was based on the statistical parameter of median, and on the extreme values (MIN, MAX). The basic advantage of the median is that it is less affected by the extreme values. The time series of chemical analyses that we had display two problematic characteristics that disadvantage the use of the average: a significant proportion of samples has an unknown specific concentration value because they are below the detection limit of the analytical method, and additionally, from time to time extremely high concentrations occur, capable of greatly influencing the average value, but not the median value. The MAX values are essential for the safety of the population, as the assessment of drinking water is based on the requirement that the limits set are not exceeded.

For comparison, in the time series of concentrations in Section 3, the median, arithmetic mean, standard deviation and coefficient of variation are calculated. It can be seen that very high standard deviation values predominate, indicating a large statistical variability of the processed data sets.

The coefficient of variation (i.e., the ratio of the standard deviation to the arithmetic mean) reaches a minimum value of 33%, and in 28 out of 36 evaluated time series (sets of nine substances from four profiles) it exceeds 50%; nine sets have a coefficient of variation higher than 100%—these values make using the mean as a characteristic of the series very problematic.

3. Results

All results of chemical analyses are available in Table S1 in Supplementary Materials.

3.1. Monitoring 2017–2018

The monitoring results made it possible to separate the monitored streams into two basic groups: four streams with significantly higher concentrations and more frequent occurrence of PPCP substances (Hnevkovice, Kozli, Dolni Kralovice and Bernartice), and five profiles with relatively lower concentrations and less frequent occurrence of monitored substances (Radikovice, Hulice, Kacerov, Miletin and Brzotice). It has also been shown that some of the studied substances occur more frequently and in higher concentrations than others (see Discussion).

Furthermore, for the sake of clarity, we present in the charts nine PPCP substances, selected according to the highest concentration, highest frequency of occurrence in the monitoring period 2017–2018, and also according to occurrence in raw and treated drinking water. Four profiles were selected from the nine monitored profiles on local watercourses (Figure 1): two profiles at the largest tributaries to the Svihov reservoir (Miletin and Kacerov) and two profiles with the highest concentration and the highest incidence of monitored PPCP substances (Hnevkovice and Dolni Kralovice).

3.1.1. Hnevkovice Profile

The sampling profile on the Hnevkovice Creek is located at the end of the village of Hnevkovice, below the discharge point from the sewage treatment plant (point S2 in Figure 2). Further, under the profile, the stream continues through a forest, and after approximately 600 m it flows into the Svihov reservoir. Raw water intake at the reservoir dam is located about 11 km from the estuary of the stream into the reservoir. The catchment area is 0.543 km², rural settlement prevails (about 300 inhabitants in family houses with small farm animals), and intensively cultivated fields prevail around the village. The average rainfall is 681.8 mm, average temperature is 8.04 °C (data for the period 1961–2015), average altitude is 445.45 m above sea level, and average slope is 3.4% (TGM Water Research Institute internal database). The flow rate in the creek is strongly influenced by fluctuating effluent from the sewage water treatment plant and retention ponds, fluctuating between 0.0004–0.0056 m³/s (average 0.0016 m³/s); natural flow rate constitutes a lesser part of the total flow rate, especially under low flow conditions. The PPCP monitoring results are shown in Figure 3 and Tables 3 and 4.

Table 3. Hnevkovice Profile—number of samples.

Substance	Number of Samples	Detection Limit (ng/dm ³)	Number of Samples below Detection Limit
Acesulfame	16	50	0
Diclofenac	28	20	2
Gabapentin	28	10	2
Hydrochlorothiazide	28	50	0
Ibuprofen	28	20	2
Metoprolol	28	10	2
Oxypurinol	16	50	1
Paraxanthine	26	100	0
Tramadol	28	10	1

Table 4. Hnevkovice Profile—basic statistical parameters.

Substance	Min (ng/dm ³)	Max (ng/dm ³)	Median (ng/dm ³)	Average (ng/dm ³)	Standard Deviation (ng/dm ³)	Coefficient of Variation (%)
Acesulfame	443	15,000	1250	3846	4691	122
Diclofenac	<20	3400	816	908	651	72
Gabapentin	<10	33,000	1900	7701	9532	124
Hydrochlorothiazide	388	3440	1030	1291	744	58
Ibuprofen	<20	1200	274	413	350	85
Metoprolol	<10	1350	610	623	298	48
Oxypurinol	<50	34,700	20,250	16,946	11,167	66
Paraxanthine	306	32,000	1285	3464	6930	200
Tramadol	<10	1500	955	912	365	40

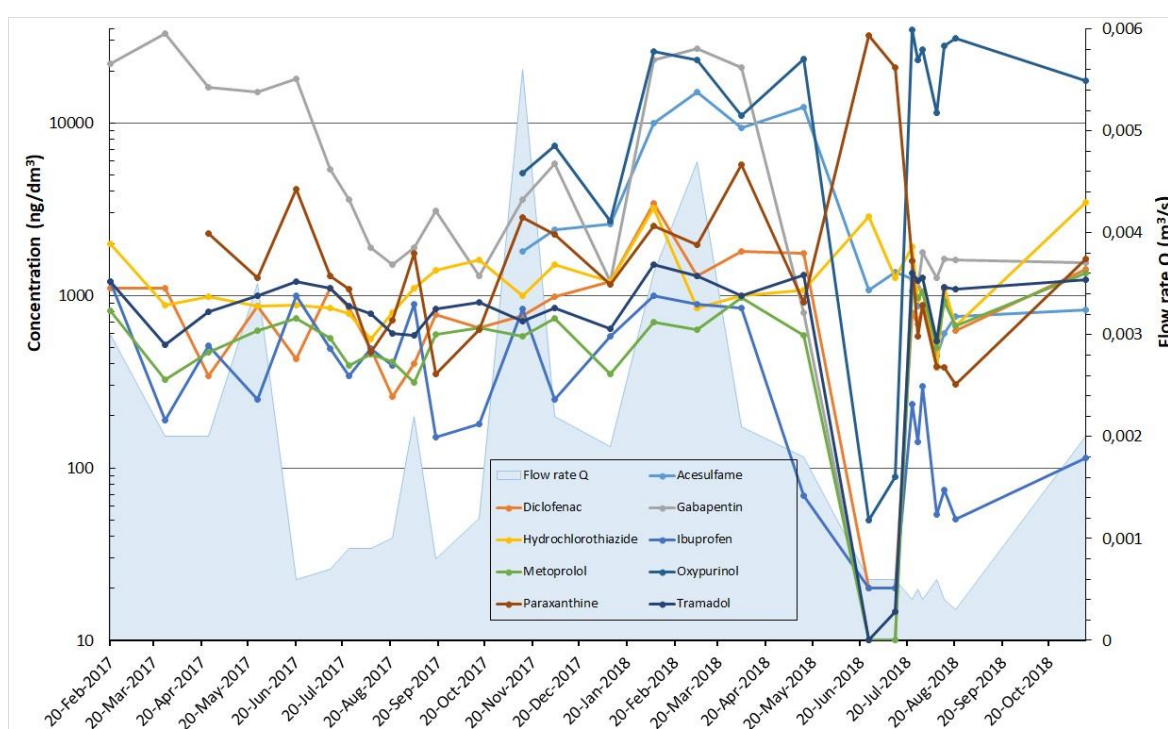


Figure 3. Monitoring results on Hnevkovice profile.

This is a profile with the unambiguously worst water quality values, with only a minimum number of values below the detection limit. All nine studied substances have maximum concentrations in thousands of ng/dm³, and four substances even in tens of thousands of ng/dm³ (acesulfame, gabapentin, oxypurinol, paraxanthine). Additionally, the median values are high, particularly with median value of 20,250 ng/dm³ found for oxypurinol. Furthermore, other substances not evaluated in this article had a maximum concentration over 1000 ng/dm³ (measured maximum concentration in brackets): azithromycin (1360 ng/dm³), cefiprolol (1690 ng/dm³), clarithromycin (2600 ng/dm³), furosemide (1800 ng/dm³), ibuprofen-2-hydroxy (700 ng/dm³), ibuprofen-carboxy (2200 ng/dm³), iopromide (34,400 ng/dm³, but rare occurrence), caffeine (3900 ng/dm³), lamotrigine (1310 ng/dm³), paracetamol (1800 ng/dm³), saccharin (10,000 ng/dm³). Values of over 1000 ng/dm³ were in most samples for cefiprolol (7 out of 8) and in a quarter to half of the samples of ibuprofen-2-hydroxy, caffeine and saccharin. For other substances, elevated concentrations are uncommon (1–5 out of 28). It is also worth noting that for iopromide 15 samples out of 28 were below the detection limit.

When assessing the nature of the settlement and land use, this pilot area is in no way different from the others in explaining the causes of the high concentrations of PPCP. Therefore, the Hnevkovice profile was chosen for additional monitoring in 2019 (Section 3.2).

3.1.2. Dolni Kralovice Profile

The measured profile is located at the end of the Dolni Kralovice village under the discharge from the WWTP (Figure 1). The creek flows into the Svihov reservoir after approximately 1600 m. Raw water intake from the reservoir at the dam is located about 11 km from the estuary of the stream into the reservoir. The catchment area is 1769 km², rural settlements predominate (approximately 700 inhabitants in family houses and small apartment houses, including shops, buildings with services and medical facilities). There is a large agricultural farm in the village including livestock and food industry buildings, and the surrounding land is dominated by fields with intensive crop production. The average rainfall is 670.8 mm, average temperature is 7.9 °C (data for the period 1961–2015), average altitude is 478.6 m above sea level, and the average slope is 3.4% (TGM Water Research Institute internal database). The flow in the stream is strongly influenced by fluctuating effluent from the wastewater treatment plant and retention basin fluctuating between 0.0012–0.0114 m³/s (average flow is 0.004 m³/s), natural flow constituting a minority of the total flow rate, especially under low flow conditions. The PPCP monitoring results are shown in Figure 4 and Tables 5 and 6.

Like Hnevkovice, the Dolni Kralovice profile belongs to those with the highest concentrations of PPCP substances. Oxypurinol, again, reaches the highest concentrations (maximum 20,000 ng/dm³, median 8205 ng/dm³), whereas all other selected substances except metoprolol and tramadol have peak values over 1000 ng/dm³; acesulfame, gabapentin, and hydrochlorothiazide even have median values above 1000 ng/dm³. Also, for some other substances (not selected for further evaluation in this article), peak concentrations of over 1000 ng/dm³ were found (measured maximum concentration in brackets): azithromycin (1600 ng/dm³), ibuprofen-2-hydroxy (12,900 ng/dm³), irbesartan (1530 ng/dm³), caffeine (4260 ng/dm³), naproxen (1050 ng/dm³), saccharin (6680 ng/dm³). Values above 1000 ng/dm³ were in the majority of samples for irbesartan (7 out of 8), but for other substances the increase in concentration is less common (1–6 out of 28).

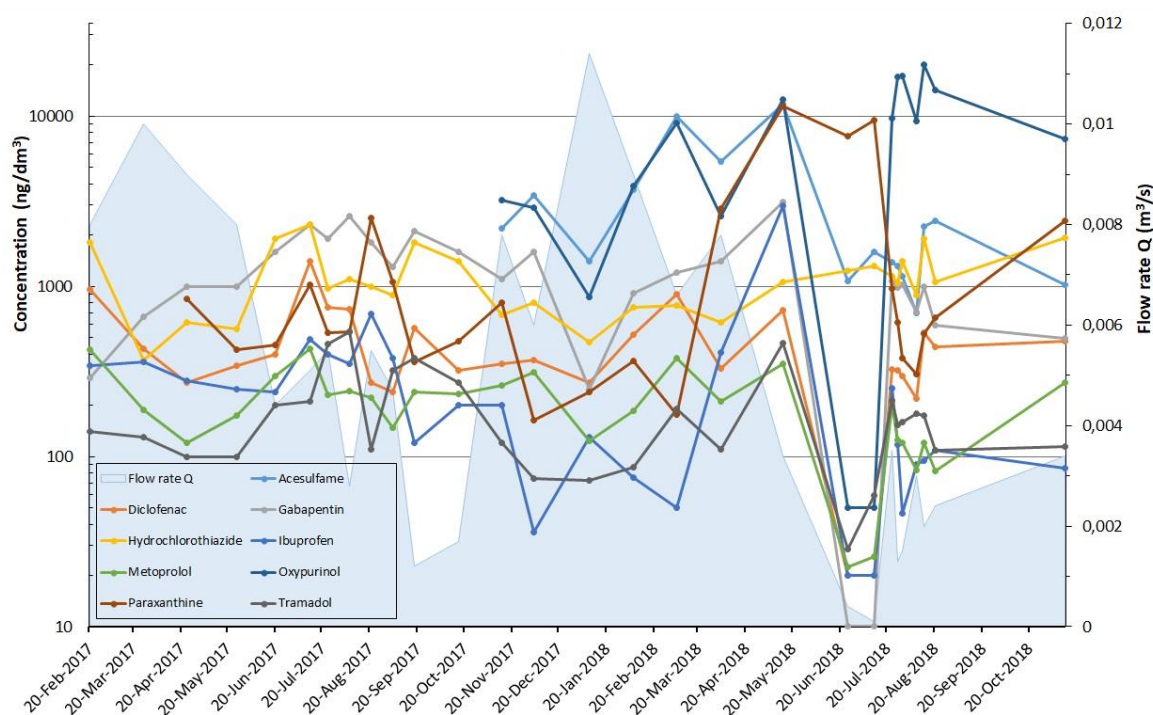


Figure 4. Monitoring results on Dolni Kralovice profile.

Table 5. Dolni Kralovice Profile—number of samples

Substance	Number of Samples	Detection Limit (ng/dm ³)	Number of Samples below Detection Limit
Acesulfame	16	50	0
Diclofenac	28	20	2
Gabapentin	28	10	2
Hydrochlorothiazide	28	50	0
Ibuprofen	28	20	2
Metoprolol	28	10	0
Oxypurinol	16	50	2
Paraxanthine	26	100	0
Tramadol	28	10	0

Table 6. Dolni Kralovice Profile—basic statistical parameters

Substance	Min (ng/dm ³)	Max (ng/dm ³)	Median (ng/dm ³)	Average (ng/dm ³)	Standard Deviation (ng/dm ³)	Coefficient of Variation (%)
Acesulfame	695	11,800	1900	3177	3164	100
Diclofenac	<20	1400	360	457	288	63
Gabapentin	<10	3120	1045	1200	740	62
Hydrochlorothiazide	370	2300	1055	1135	498	44
Ibuprofen	<20	2990	200	315	540	171
Metoprolol	22	429	205	208	106	51
Oxypurinol	<50	20,000	8205	8142	6378	78
Paraxanthine	163	11,400	577	1816	2907	160
Tramadol	29	540	147	188	129	69

The character of settlement and land use may explain the higher concentrations of PPCP in this catchment area. The community of Dolni Kralovice is one of the larger municipalities in the vicinity of the Svihov reservoir, and in addition the number of inhabitants is increased by employees in agricultural and food processing plants located in the catchment area. There are also service facilities, including medical facilities, where higher drug consumption is expected.

3.1.3. Miletin Profile

The measured profile is located on the Zelivka River, on which the Svihov reservoir is built, at the point of the Zelivka River inlet into the Svihov reservoir. It is the main inflow, providing about 70% of the total average inflow into the reservoir. The hydrological catchment belonging to the measured profile is extensive; the catchment area is 3020 km². The location of raw water intake from the reservoir at the dam is located about 20 km from the estuary of the river into the reservoir. The catchment area of the upper Zelivka River has many villages and towns, with approximately 40,000 inhabitants. Land use is mixed with intensive agricultural production, commercial forests, and settlements. Larger towns include Pelhrimov (16,000 inhabitants), Pacov (5000 inhabitants) and Cervena Recice (1000 inhabitants), while other inhabitants live in several rural municipalities with less than 1000 residents. In the catchment area there are several hospitals, other medical facilities, homes for the elderly and other facilities used by services. In the catchment, the average rainfall is 671.8 mm and average temperature 8.03 °C (data for the period 1961–2015), average altitude is 433.44 m above sea level and average slope is 3.3% (TGM Water Research Institute internal database). The flow rate in the river is influenced by several reservoirs and ponds, and by the discharge of wastewater throughout the

catchment. The flow rate fluctuated between 0.3–6.6 m³/s (long-term average flow rate of 2.8 m³/s according to the Czech Hydrometeorological Institute CHMI), and the share of wastewater represents a significant minority of the total flow rate (estimated at about 0.04 m³/s). The PPCP monitoring results are shown in Figure 5 and Tables 7 and 8.

Due to the high flow rates and large river catchment area, the water flow is diluted and delayed, resulting in lower PPCP concentration. The relatively low concentrations are offset by higher flow rates. Oxypurinol again shows the highest concentration (peak 1820 ng/dm³, median 483 ng/dm³), and paraxanthine exhibits maximums over 1000 ng/dm³. When other substances are assessed, no other has a maximum concentration above 1000 ng/dm³.

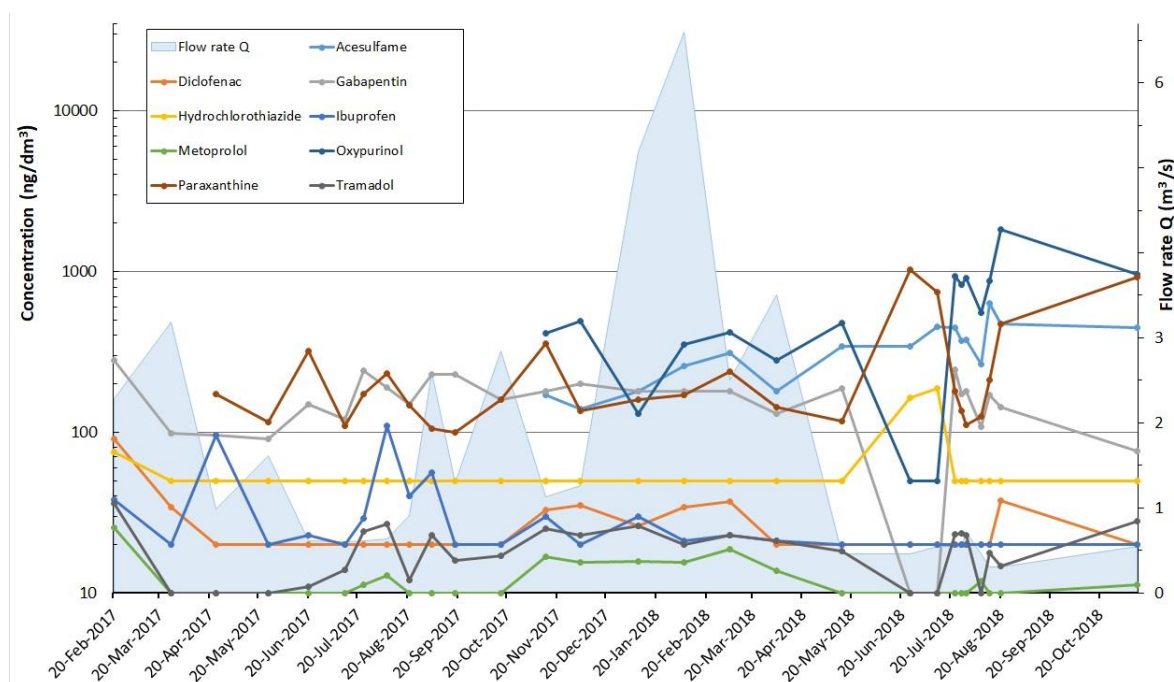


Figure 5. Monitoring results on Miletin profile (flow rates data [41]).

Table 7. Miletin Profile—number of samples.

Substance	Number of Samples	Detection Limit (ng/dm ³)	Number of Samples below Detection Limit
Acesulfame	16	50	0
Diclofenac	28	20	20
Gabapentin	28	10	2
Hydrochlorothiazide	28	50	25
Ibuprofen	28	20	16
Metoprolol	28	10	17
Oxypurinol	16	50	2
Paraxanthine	26	100	1
Tramadol	28	10	5

Table 8. Miletin Profile—basic statistical parameters

Substance	Min (ng/dm ³)	Max (ng/dm ³)	Median (ng/dm ³)	Average (ng/dm ³)	Standard Deviation (ng/dm ³)	Coefficient of Variation (%)
Acesulfame	140	631	343	337	131	39
Diclofenac	<20	91	<20	26	14	54
Gabapentin	<10	280	171	157	64	41
Hydrochlorothiazide	<50	188	<50	60	33	55
Ibuprofen	<20	110	<20	30	22	73
Metoprolol	<10	26	<10	12	4	33
Oxypurinol	<50	1820	483	597	436	73
Paraxanthine	<100	1020	165	264	246	93
Tramadol	<10	36	20	19	7	37

Although the PPCP concentrations are lower on the Miletin profile than on the previous two profiles, due to the high flow rate this stream brings the largest amount of PPCP into the Svihov reservoir (Section 4). Higher quantities of transported pharmaceuticals can be logically explained - there are many places in the large catchment area where significant mass flows of pharmaceuticals can be expected (larger cities, hospitals and other health and veterinary facilities, homes for the elderly, service facilities, etc.).

3.1.4. Kacerov Profile

The measured profile is located on Sedlicky Creek near the village of Kacerov at the point where the stream flows into the Svihov reservoir (edge of reservoir backwater). It is the largest tributary to the Svihov reservoir. The location of raw water intake from the reservoir at the dam is located about 6 km from the estuary of the stream into the reservoir. The monitored catchment is relatively extensive; Sedlicky Creek, with many tributaries, has a catchment area of 76 km². Within the catchment area, there are several municipalities with about 2300 inhabitants. Rural settlement prevails amid the villages; there are intensively cultivated fields and commercial forests. The main municipalities are Lhota Bubenec (village with intensive livestock farming), Krivsoudov (village), Ruzkovy Lhotice (village with a small farm), Cernici (smaller agricultural farm), Mala Paseka (village), Cechtice (larger village, two large agricultural farms, two industrial areas, medical facilities and service buildings) and Chrastovice (former village, now completely abandoned). The monitored catchment area has an average rainfall of 692.1 mm, and an average temperature of 7.87 °C (data for the period 1961–2015). The average altitude is 506.34 m above sea level, and the average slope is 3.6% (TGM Water Research Institute internal database). A number of ponds and the discharge of wastewater throughout the catchment area influence the creek flow rate. The flow rate fluctuated between 0.002–0.43 m³/s during the measurement period, and the proportion of wastewater does not constitute a major portion of the total flow rate, except in low flow conditions. The PPCP monitoring results are shown in Figure 6 and Tables 9 and 10.

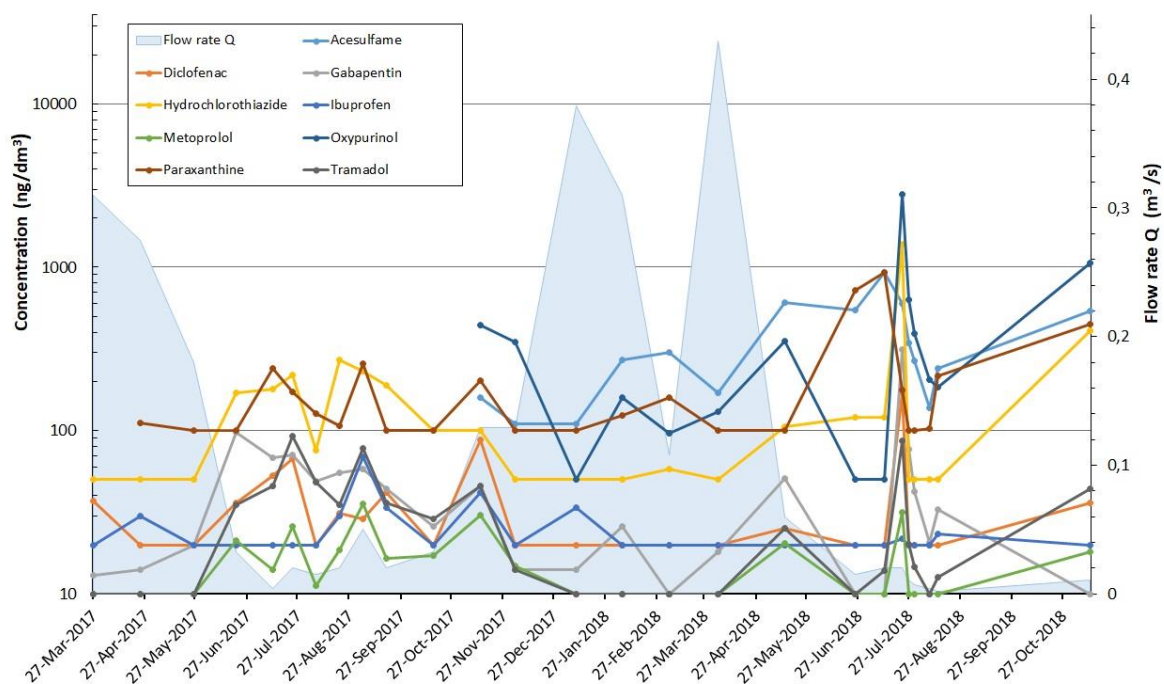


Figure 6. Monitoring results on Kacerov profile (flow rates data [41]).

Table 9. Kacerov Profile—number of samples

Substance	Number of Samples	Detection Limit (ng/dm ³)	Number of Samples below Detection Limit
Acesulfame	15	50	0
Diclofenac	26	20	15
Gabapentin	26	10	4
Hydrochlorothiazide	26	50	11
Ibuprofen	26	20	18
Metoprolol	26	10	13
Oxypurinol	15	50	3
Paraxanthine	25	100	10
Tramadol	26	10	9

Table 10. Kacerov Profile—basic statistical parameters

Substance	Min (ng/dm ³)	Max (ng/dm ³)	Median (ng/dm ³)	Average (ng/dm ³)	Standard Deviation (ng/dm ³)	Coefficient of Variation (%)
Acesulfame	110	931	270	356	231	50
Diclofenac	<20	170	<20	35	32	91
Gabapentin	<10	315	29	47	59	125
Hydrochlorothiazide	<50	1380	88	165	258	156
Ibuprofen	<20	69	<20	25	11	44
Metoprolol	<10	36	11	16	8	50
Oxypurinol	<50	2800	205	464	677	146
Paraxanthine	<100	933	112	204	202	99
Tramadol	<10	92	17	29	24	83

Of the selected substances, oxypurinol and hydrochlorothiazide reach the highest concentration with a maximum above 1000 ng/dm³, while acesulfame and paraxanthine peak just below 1000 ng/dm³. No other substances with concentrations above 1000 ng/dm³ were observed on the Kacerov profile; only one azithromycin analysis (931 ng/dm³) approached the 1000 ng/dm³ limit.

Although the PPCP concentrations are on average even lower on the Kacerov profile than on the Miletin profile, there is also a significant PPCP mass flow into the reservoir (Section 4). The sources of PPCP in the catchment area can be well identified - seven municipalities with agricultural and industrial sites, service facilities, medical facilities, in which the number of inhabitants is slightly increased by commuting employees).

3.1.5. Raw and Drinking Water Monitoring

The 2017–2018 water monitoring also included quality control of raw and drinking water. Raw water is taken from the intake tower building at the Svihov reservoir dam; the treated drinking water was sampled at the point where the water leaves the treatment plant to the water supply system. Detected substances above the detection limit are summarized in Table 11 (raw water) and Table 12 (drinking water). In contrast to the previous tables and graphs, all the analyzed substances were evaluated (93 items according to Table 1) because of their importance for the overall drinking water quality.

Table 11. Quality of raw water from the Svihov reservoir—all substances detected above the detection limit.

Substance	Number of Analyses Total	Number of Analyses above Detection Limit	Detection Limit (ng/dm ³)	Maximum Concentration (ng/dm ³)
Acesulfame	16	8	100	318
Azithromycin	28	2	10	274
Diclofenac	28	1	20	58
Estrone	6	2	1	5
Gabapentin	28	25	10	157
Hydrochlorothiazide	28	2	50	99
Chloramphenicol	28	1	20	48
Ibuprofen	28	3	20	56
Ibuprofen-2-hydroxy	28	2	30	91
Carbamazepine	28	7	10	13
Carbamazepine-E	28	2	10	12
Lamotrigine	8	5	10	15
Oxypurinol	16	7	50	868
Paraxanthine	26	13	100	424
Progesterone	6	2	0.5	2
Ranitidine	28	2	10	75
Sulfamerazine	28	2	10	22
Telmisartan	8	7	20	55
Tramadol	28	5	10	13
Trimethoprim	28	1	10	16

Table 12. Quality of drinking water produced—all substances detected above the detection limit.

Substance	Number of analyses Total	Number of Analyses above Detection Limit	Detection Limit (ng/dm ³)	Maximum Concentration (ng/dm ³)
Acesulfame	28	2	50	61
Azithromycin	28	2	10	28
Estrone	6	3	1	5
Gabapentin	28	1	10	18
Ibuprofen	28	3	20	52
Paraxanthine	28	1	100	187
Ranitidine	28	1	10	39
Sulfamerazine	28	1	10	24
Tramadol	28	1	10	85

Only 20 substances out of 93 in raw water had concentration values above the detection limit at least once during the 2-year monitoring period, whereas 73 substances were permanently below the detection limit.

3.2. Additional Monitoring Hnevkovice

In order to investigate the local situation more precisely, additional monitoring was carried out in the community of Hnevkovice (profile with the highest detected concentration of PPCP substances in 2017–2018 monitoring), consisting of detailed sampling of wastewater at the discharge from the WWTP, stream water above and below the WWTP, and groundwater from two selected wells. Samples of water at the discharge from the WWTP were taken in three-hour intervals on 27–28 June and on 21–22 October. The results of the selected pharmaceuticals are shown in charts in Figures 7–9. These are nine substances identical to the 2017–2018 monitoring, supplemented by another seven substances with high-recorded concentration. For the sake of clarity and due to a different scale of concentration, the substances are distributed into three charts.

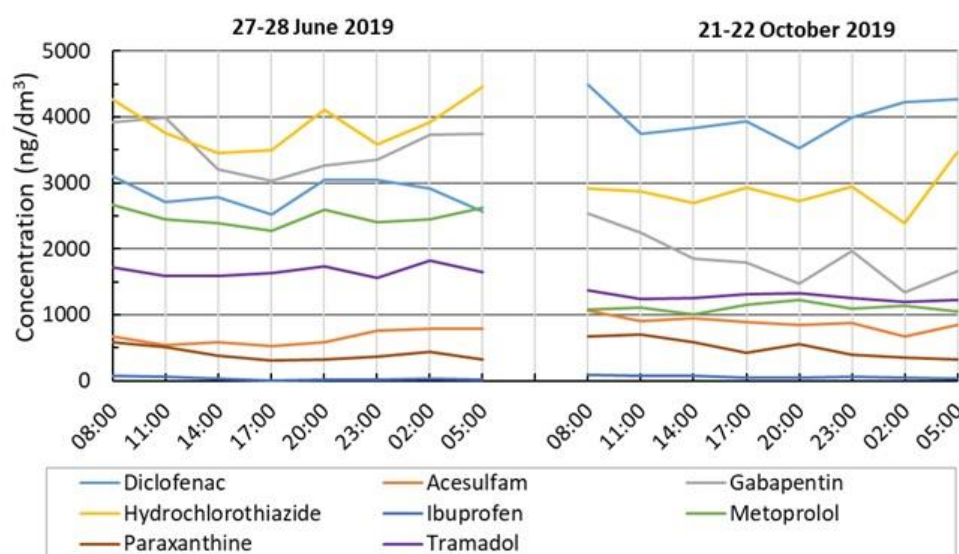


Figure 7. Water quality of the Hnevkovice WWTP (wastewater treatment plant) effluent: diclofenac, acesulfame, gabapentin, hydrochlorothiazide, ibuprofen, metoprolol, paraxanthine, tramadol.

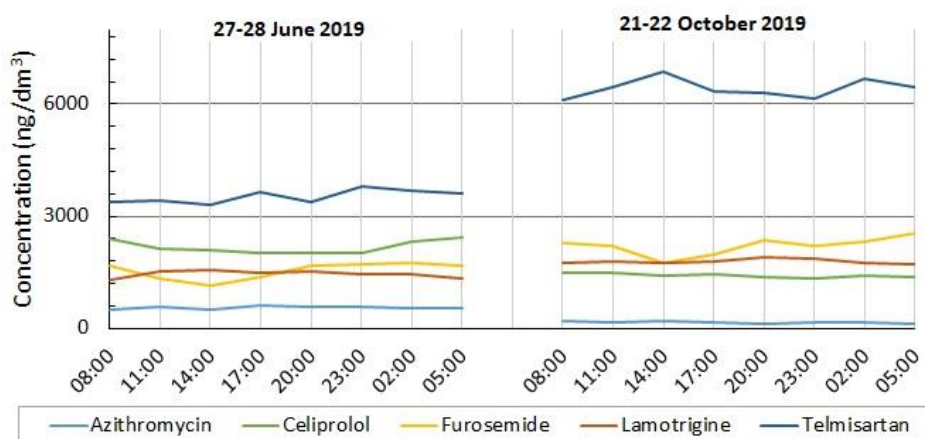


Figure 8. Water quality of the Hnevkovice WWTP effluent: azithromycin, furosemide, lamotrigine, telmisartan, celiprolol.

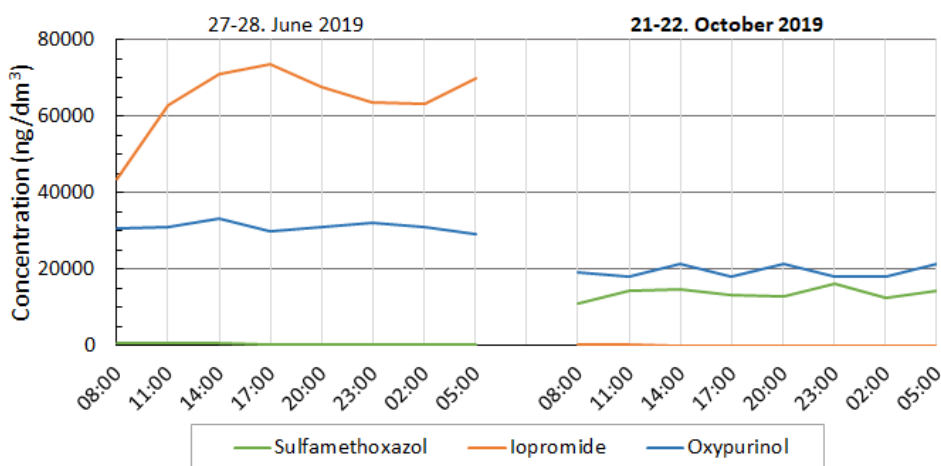


Figure 9. Water quality of the Hnevkovice WWTP effluent: iopromide, oxypurinol, and sulfamethoxazole.

The highest concentrations, observed in the spring period were found for iopromide (73,600 ng/dm³, spring) and oxypurinol (33,100 ng/dm³). In autumn, the concentrations were mostly lower, with oxypurinol (21,500 ng/dm³) and sulfamethoxazole (16,100 ng/dm³) being the highest. Surprisingly, the lowest concentration of monitored substances were also observed for iopromide (72 ng/dm³, autumn) and ibuprofen (below the detection limit). Iopromide is the substance with the largest, but well-explained, fluctuation in concentration. Because it is used as a contrast medium, e.g., in CT scans, its extremely high and short-term concentrations are related to the rapid excretion of this substance after the performed examination. Oxypurinol is a frequently used pharmaceutical for the treatment of increased uric acid content in blood, and the associated problems with joints and kidneys. Its high concentrations indicate the prevailing elderly population in the village.

For some other substances (over 16 mentioned above in charts) maximum concentrations were also found at over 1000 ng/dm³ (measured maximum values in brackets) detected in the effluent from the WWTP. June 2019: 4-formylamino antipyrine (1160 ng/dm³), benzotriazole (1060 ng/dm³), metformin (1730 ng/dm³), sucralose (5900 ng/dm³), valsartan acid (1060 ng/dm³). October 2019: 4 formylamino antipyrine (4800 ng/dm³), benzotriazole (1460 ng/dm³), diclofenac-4-hydroxy (2220 ng/dm³), sucralose (5200 ng/dm³), valsartan acid (1160 ng/dm³).

The charts in Figures 10 and 11 document the change of water quality in the Hnevkovice Creek due to the discharge of treated wastewater (16 selected substances according to Figures 7–9). In the stream profile above, the WWTP (S1 profile in Figure 2) were detected only slightly above the detection limit: in June 2019 gabapentin (77.1 ng/dm³), in October 2019 sulfamethoxazole (10.3 ng/dm³) and

telmisartan (32.2 ng/dm^3). Under the effluent discharge from the WWTP, concentrations of the monitored substances in the order of hundreds to thousands of ng/dm^3 were found, the highest concentration being that for oxypurinol ($13,700 \text{ ng/dm}^3$ in spring and $14,600 \text{ ng/dm}^3$ in autumn).

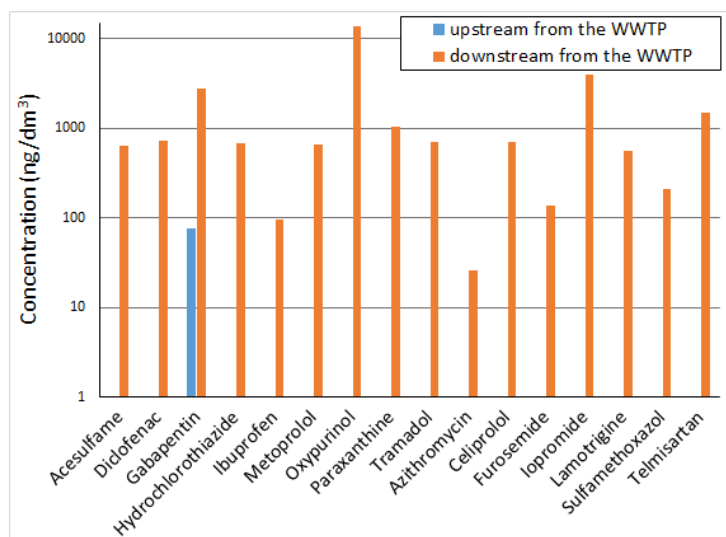


Figure 10. Concentration of 16 selected pharmaceuticals in the profiles upstream and downstream from the Hnevkovice WWTP on 28 June 2019 (only substances detected above the detection limit).

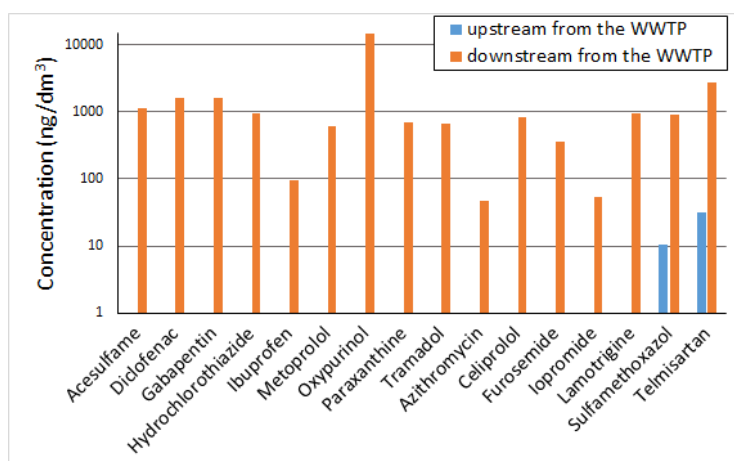


Figure 11. Concentration of 16 selected pharmaceuticals in profiles above and below Hnevkovice WWTP on 21 October 2019 (only substances detected above the detection limit).

On profile S2 Hnevkovice (Figure 2) (profile identical with the monitoring of 2017–2018), other substances with maximum concentrations of more than 1000 ng/dm^3 were detected that were not the subject of monitoring in 2017–2018 (measured maximum concentration provided in brackets): sucralose (2460 ng/dm^3), metformin (1340 ng/dm^3), 4-formylamino antipyrine (1320 ng/dm^3), and benzotriazole (1060 ng/dm^3).

High concentrations of some substances in surface and also in treated wastewater have raised the question of the extent to which these substances also occur in shallow groundwater, used by household wells to supply the population with drinking water. That groundwater is also drained into the Svihov reservoir and forms one—albeit small—water source for the reservoir (estimated inflow of $0.01\text{--}0.02 \text{ m}^3/\text{s}$ from the area immediately adjacent to the reservoir). Two municipal wells were selected in the center of Hnevkovice (W1, W2, Figure 2), and in October 2018 the water was analyzed for the

same range of substances as surface water (93 substances, Table 1). Groundwater is significantly less contaminated, with only four substances with low concentration (Table 13).

Table 13. Substances detected above the detection limit of two groundwater sources—Hnevkovice village wells (Figure 2).

Substance	Unit	Detection Limit	W1	W2
Acesulfame	ng/dm ³	50	212	
Bisphenol A	ng/dm ³	50		247
Estrone	ng/dm ³	1	3.6	2.5
Gabapentin	ng/dm ³	10	23.7	

The results indicate that the main problem of the Svihov reservoir catchment area in terms of occurrence of PPCP substances is the municipal wastewater and the level of its treatment in local WWTPs.

4. Discussion

4.1. Discussion of 2017–2018 Monitoring Results

The selected nine sampling profiles at the tributaries of the Svihov drinking water supply reservoir provided very different results. Regarding concentrations of the PPCP substances (93 analyzed substances in total), the Hnevkovice and Kozli profiles appear to be the worst, where the total sum of maximum concentrations of the analyzed substances is close to 200,000 ng/dm³. Next are the profiles Dolni Kralovice and Bernartice with a total sum of PPCP maximum concentration around 100,000 ng/dm³. The remaining five profiles have significantly lower concentrations of PPCP substances: Miletn, Kacerov and Radikovice with a sum of maximum concentrations around 8–10,000 ng/dm³, and the best quality profiles appear to be the profiles of Hulice a Brzotice with a sum of maximum concentrations of approximately 2000 ng/dm³.

The explanation is currently not entirely clear. The effect of dilution in higher flow rate streams (i.e., Miletn, Kacerov) is clear, but this does not apply to the cleanest profiles of Hulice and Brzotice, where there are also very low flow rates and comparable quantity of wastewater from other municipalities (Hnevkovice, Bernartice). Leaving aside the possibility of lower consumption of PPCP substances by the inhabitants of these municipalities (which does not seem very likely, as all municipalities are very similar in character), the only possible explanation may be the different efficiency of the municipal WWTPs in terms of PPCP removal.

Regarding the mass flow of PPCP substances into the Svihov reservoir, the situation is different; the monitored local streams usually have a flow rate fluctuating between 0.0002–0.005 m³/s (lower flow rates than long-term due to the drought since 2015). The flow rate on the Kacerov profile, however, is on the order of hundredth of m³/s (long-term average is 0.39 m³/s [35], and the average for the monitored period during the long-term drought is 0.08 m³/s). Additionally, the flow rate on the Miletn profile is in units of m³/s (long-term average 2.48 m³/s [35], average for the monitored period during the long-term drought is 1.300 m³/s). Thus, about 42% of the inflow was monitored in this project (long-term runoff average from the dam is 6.93 m³/s, inclusive of water-supply abstraction, [35]). Therefore, we consider the performed monitoring to be representative in terms of quality assessment of the inflowing water into the reservoir. The difference in flow rates is also reflected in the different mass flow of substances (Table 14). An accurate calculation is not possible due to large and frequent fluctuations in PPCP concentration and in WWTP effluent; therefore, the table contains only qualified parameter estimates and we are convinced that the estimates of the mass flow were accurate to the order of magnitude.

Table 14. Estimates of mass flow of PPCP substances into reservoir Svihov by concentration and flow rate.

Profile	Long-Term Average Flow Rate (L/s)	Estimate of Average PPCP Substance Concentration (ng/dm ³)	Mass Flow General Value (g/day)
Bernatice	0.2	11,000	1.0
Brzotice	0.8	400	0.02
Dolní Kralovice	5.0	18,000	7.8
Hněvkovice	1.7	36,000	5.3
Hulice	0.5	400	0.02
Kacarov	80	900	6.2
Kozlí	1.1	16,000	1.5
Miletín	1300	1400	157.3
Radkovice	1.3	800	0.9

In total, this represents a mass flow of approximately 180 g/day from 42% of total reservoir inflow. It can be estimated that around 400–500 g of PPCP substances flow into the Svihov reservoir per day on average (in the analyzed range, as shown in Tables 1 and 2).

Considering the frequency of occurrence of the individual PPCP substances analyzed, a group of substances that occur very often on most profiles and often at high concentration (thousands and even tens of thousands of ng/dm³) can be identified: acesulfame, azithromycin, caffeine, gabapentin, hydrochlorothiazide, ibuprofen and its metabolites, oxypurinol, paraxanthine, and saccharin. In addition to these constituents, we can identify other substances also occurring in the majority of analyses, but at a lower frequency and with lower concentrations (predominantly hundreds of ng/dm³): iopromide, metoprolol, paracetamol, and tramadol (Datel et al. [42,43]). Additionally, there is a group of 39 substances (out of the 112) that occur always, or usually, below the detection limit (see brown marked substances in Tables 1 and 2).

Interestingly, a good correlation between the flow rate and the concentration of PPCP substances cannot be established. This could be due to the high and fluctuating proportion of wastewater effluent from the WWTPs or the fluctuating quality of the effluent discharged (different residence time in the retention tank, different quality of sewage water entering the WWTP, probably different time of water treatment in the WWTP at peak loading and outside of it, etc.).

Other uncertainties during monitoring were the non-standard results from two sampling rounds 6–7 in 2018. For some substances, there is an inexplicable decline while for others there is an increase in the observed concentration without a clear link to the change in flow rates. If this is not an analysis error (which the laboratory has excluded), it would be possible to consider a change in the population composition in the area, e.g., due to summer holidays, which could also be reflected in the change in the way the various PPCP substances are used. It should be noted that the concentration of various pharmaceuticals measured might be related to only a few people who take these medicaments. Moreover, if these people leave temporarily and if other people taking completely different medicaments arrive for the summer holidays, this may have an impact on the changed wastewater quality. Verifying this hypothesis would, however, assume a socio-demographic study in the area.

4.2. Discussion of Additional 2019 Wastewater Monitoring—Hněvkovice

Additional monitoring of the WWTP Hněvkovice wastewater effluent in the year 2019 confirmed the most frequently occurring substances from the previous monitoring, and in addition other substances were found in high concentration in the WWTP effluent (thousands ng/dm³): celioprolol, diclofenac and diclofenac-4-hydroxy, furosemide, lamotrigine, metoprolol, sulfamethoxazole,

and telmisartan. In addition, wastewater analyses have also shown frequent and high concentrations of 4-formylaminoantipyrine, benzotriazole, and sucralose, which were not analyzed during the monitoring of 2017–2018.

The results show the insufficient functionality of WWTPs in terms of removal of PPCP (even in comparison with similar neighboring municipalities with comparable conditions (Bernartice, Brzotice, Hulice). Municipalities with poor quality of treated wastewater may have WWTPs with overloaded capacity. The low efficiency of local municipal wastewater treatment can be also related to the obsolete technology at some WWTPs; small municipalities often do not have professional staff for the correct operation of WWTPs, and in some cases they have insufficient capacity, especially at peak wastewater inflows to WWTPs.

Wastewater in Hnevkovice (and other municipalities around the Svihov water reservoir) is drained separately from storm water, so that only sewage water from the households and operations flows to the municipal wastewater treatment plants. Rainwater from streets and roofs is drained by the rainwater sewer to the nearest watercourse. The quantity of wastewater is the result of household water consumption, which is currently in small municipalities around 0.07–0.08 m³ per person per day [35]. In the Czech Republic, wastewater treatment plants are mostly two-stage mechanical-biological. The mechanical part separates larger objects and particles on the screens and separates the coarse sediment, fats and oils. Finally, the fine sediment is allowed to settle in a sedimentation tank. The biological part of the WWTP consists of activation tanks, where the wastewater is aerated, and aerobic biological treatment takes place in which bacteria and other organisms consume organic substances, nitrogen and phosphorus. Activated sludge from the bodies of microorganisms is separated in the consecutive settling tanks and the water flows for natural final treatment to the retention tank under the WWTP or directly into the stream. Most small municipal WWTPs operate in an automatic mode, but the optimum treatment efficiency depends on good maintenance and correct setup of the plant. The facility in Hnevkovice is under new construction and the community is experiencing population growth, and therefore the original capacity of the WWTP is probably also overloaded, thus reducing its efficiency [38,39].

It is not possible to directly compare the water samples at the effluent from the WWTP with the water samples in the stream below the WWTP. PPCP concentrations in wastewater are variable over time, the quantity of wastewater also changes over time, and the water flow rate in the stream is not constant, and further there is a retention tank between the WWTP and the stream. The retention tank retains water for several days for sedimentation and post-treatment processes before the water is released into the watercourse. The explanation for this phenomenon may be the considerable variation in the concentration of the analyzed substances in wastewater (depending on the intensity of use of various pharmaceuticals), including daily, weekly and seasonal cycles. The monitoring did not record these maximum concentrations (samples taken 1–2 times per month, on average). Substances can then accumulate in the retention tank and be gradually released, even in higher concentrations than represented by actual water quality coming directly from the WWTP.

4.3. Raw Water

Analysis of monitoring data from 2017–2018 shows that there is a significant difference in poorer water quality of tributaries to the reservoir and significantly better quality of water abstracted at the dam for treatment into drinking water. Therefore, there are favorable processes in the reservoir space that have a positive impact on the improvement of water quality, not only in PPCP parameters. According to the data of the water authority, the theoretical residence time of the water in the reservoir is 430 days, and the total long-term average inflow into the reservoir is 6.93 m³/s. The reservoir has a length of 39.1 km, and the volume of water in the reservoir is 309 million m³ [35].

The identification of the processes in the reservoir that have an impact on PPCP concentrations was not the subject of this project. However, it may be noted that the decrease in concentrations of some of the monitored substances may certainly be related to their degradation properties, whether on

the basis of biochemical or physical and chemical phenomena. The identified varying resistance to degradation is undoubtedly related to different resistance of the chemical molecules of the monitored organic substances to these processes. However, all of this is a matter of development in time, which is very rapid both in the development of knowledge about the behavior of these substances and in the development of analytical methods.

The subject of deposition of PPCP substances in sediments is also discussed in various archive sources. However, this accumulation does not seem to play a major role in the migration properties of most of the monitored substances. In addition, in this research several samples of sediments were taken for PPCP analysis in the Hnevkovice Creek estuary into the reservoir, but mostly with negative results (very small concentrations of PPCP in a solid phase).

A significant decrease in concentrations due to the retention in the reservoir occurred for the following substances: azithromycin, diclofenac, hydrochlorothiazide, ibuprofen-2-hydroxy, lamotrigine, metoprolol, telmisartan, and tramadol. On the other hand, there is a group of substances that have not displayed a significant decrease due to retention in the water reservoir: estrone, chloramphenicol, oxypurinol, progesterone, and sulfamerazine. A relatively minor effect of reservoir water retention is also shown for acesulfame, gabapentin, ibuprofen, carbamazepine, carbamazepine E, paraxanthine, ranitidine, and trimethoprim.

It can be concluded that a water reservoir with a sufficient retention time is much better for achieving a more favorable water quality, regarding the content of specific PPCP-type organic substances (and probably also pesticides, PAHs (polyaromatic hydrocarbons) and other organic degradable substances) than direct abstraction from the stream, but this influence differs for different substances.

4.4. Treated Drinking Water

For some PPCP substances, we have noticed a significant decrease during the water treatment process. The Zelivka Raw Water Treatment Plant is the largest water treatment plant for the capital city of Prague. The normal operating capacity of the treatment plant is 3 m³/s of drinking water, and at peak times it can produce up to 7 m³/s, making it one of the largest water treatment plants in Europe (www.pvl.cz [35], www.zelivska.cz [44]). The basic technology of raw water treatment is coagulation filtration with lowering of pH and dosage of aluminum sulphate. Water with precipitated impurities then undergoes one-stage filtration in open rapid sand filters (water passes through a layer of sand of the fraction 1.1–1.6 mm with a thickness of 1.6 m for about 1 h). Drinking water is finally treated with ozone and chlorine [45]. The basis of the currently developed treatment plant modernization is a new additional stage of treatment with granulated activated carbon filters to capture pesticides and other substances (e.g., medicines, hormones) in the future (Lepka [45]).

Analysis of monitoring data from 2017–2018 shows that the following substances respond well to the treatment process, mostly below the detection limit: acesulfame, hydrochlorothiazide, ibuprofen-2-hydroxy, carbamazepine, carbamazepine E, lamotrigine, oxypurinol, progesterone, telmisartan, and tramadol. It should be noted, however, that raw water already had mostly relatively low concentration (mostly in tens of ng/dm³; only acesulfame and oxypurinol often had input concentration about hundreds of ng/dm³), which the treatment plant handled well. On the contrary, there is a group of substances for which there was no significant decrease in water processing at the treatment plant, despite the fact that the input concentration was often very low (tens of ng/dm³): estrone, chloramphenicol, ibuprofen, paraxanthine, and sulfamerazine. There was also a relatively small decrease for azithromycin, gabapentin, ranitidine, and trimethoprim. Furthermore, it is alarming that the same substances tend to pass through the water reservoir (see above) over the water retention time (estrone, gabapentin, chloramphenicol, paraxanthine, ranitidine, sulfamerazine, and trimethoprim). The effect of the treatment plant cannot be commented on with regard to substances with concentrations in raw water already below the detection limit (from those discussed in the paper, e.g., diclofenac or metoprolol).

The overall quality of the produced drinking water regarding PPCP content can be assessed as high; if we do not consider substances with exceedance only in one analysis (out of 28 analyses), which is not conclusive, it can be stated that the following constituents occur with low frequency and in low concentration in the produced drinking water: ibuprofen (3 analyses out of 28, maximum 52 ng/dm³, detection limit 20 ng/dm³), estrone (3 analyses of 6, maximum 5 ng/dm³, detection limit 1 ng/dm³), acesulfame (2 analyses of 28, maximum 61 ng/dm³, detection limit of 50 ng/dm³) and azithromycin (2 analyses of 28, maximum 28 ng/dm³, detection limit 10 ng/dm³). There are no scientific sources that would challenge the safety of drinking water with such very low, and only occasional, concentration of PPCP substances (WHO [7,8], Godoy et al. [11], Bexfield et al. [12], Chen et al. [16], RIVM [28], Kozisek et al. [38]). The existing standard raw water treatment is therefore fully sufficient for the residual concentrations observed. However, it should be pointed out that if the substances that readily pass through the treatment process in higher concentration appear in raw water, there could be a problem with the quality of the drinking water, and the inclusion of an additional water treatment stage consisting of activated carbon filters may prove to be necessary.

5. Conclusions

The research has brought several valuable findings. In terms of frequency of occurrence of the individual PPCP substances analyzed, a group of substances occurring very frequently, on most profiles and often at high concentration (thousands and even tens of thousands of ng/dm³ on some profiles) can be identified: acesulfame, azithromycin, caffeine, gabapentin, hydrochlorothiazide, ibuprofen and its metabolites, oxypurinol, paraxanthine, and saccharin. Besides these, we can name other substances also occurring in the majority of analyses, but at a lower frequency and with lower concentrations (predominantly hundreds of ng/dm³): iopromide, metoprolol, paracetamol, and tramadol. Furthermore, there is a group of 39 substances (out of the 112) that are always or almost always (in 95–100% of cases) below the detection limit of the analytical method used.

According to the detected maximum concentration of PPCP substances, highly polluted local streams can be identified (Hnevkovice, Kozli, Dolni Kralovice, and Bernartice) with an average concentration of the sum of PPCP substances in thousands of ng/dm³ (and maximums for some substances up to tens of thousands ng/dm³—gabapentin, oxypurinol, paraxanthine). Of these, profiles Hnevkovice and Dolni Kralovice are discussed in detail in this paper. Moderately polluted are Miletin, Kacerov and Radikovice profiles with estimated average values around 1000 ng/dm³. The first two of these profiles are also discussed in detail in this paper. However, these are the profiles with the highest flow rates, so even though the concentration of PPCP substances does not reach the highest values, the PPCP mass flow from these profiles into the Svihov reservoir is the highest. Hulice and Brzotice profiles have the relatively lowest concentration of PPCP substances near the limit of detection in tens or exceptionally the first hundreds of ng/dm³.

The additional detailed monitoring of wastewater effluent from Hnevkovice WWTP on the one hand confirmed the results of the previous monitoring and also found high concentrations of some other substances present in the stream at much lower concentration (probably due to rapid disintegration), and on the other hand, provided indication of very high and rapid fluctuations in the quality of 'treated' wastewater (e.g., iopromide 73,600 ng/dm³ in spring and 72 only ng/dm³ in autumn, or sulfamethoxazole 505 ng/dm³ in spring and 16,100 ng/dm³ in autumn).

In the future, it is strongly recommended to ensure the optimal and not overloaded operation of all local WWTPs; in some cases, it may be necessary to consider their modernization or to supplement an additional treatment stage. Further research is needed on the migration parameters and degradation processes of PPCP substances, especially those that tend to remain in the natural aquatic environment for a long time and penetrate into the raw water, and in some rare cases, into drinking water (e.g., ibuprofen, estrone, acesulfame, azithromycin).

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4441/12/5/1387/s1>, Table S1: Chemical analyses.

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