NATURAL ATTENUATION OF PHARMACEUTICALS AND PERSONAL CARE PRODUCTS PERCOLATING THROUGH ROCKY SUBSTRATES – AN EXAMPLE BASED ON THE KÁRANÝ WATERWORKS

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ABSTRACT

This survey focused on a detailed analysis of the ability of fluvial Quaternary sediments to remove pharmaceuticals and personal care products (PPCPs) from drinking water. Thirty-eight PPCPs were detected in the Jizera River, which is used after infiltration to produce drinking water by the Káraný waterworks. Several PPCPs occurred in the water at concentrations exceeding 100 ng/l, some of which are not possible to remove (oxypurinol, acesulfame). The presence of PPCPs was monitored after infiltration and during passage through sandy gravels to the receiving well (total distance of 180 m) at monthly intervals in 2022–2023. PPCPs can be divided into different groups based on the results. Iohexol, iopromide, metoprolol, cetirizine, valsartan and clarithromycin were already below the established threshold after passing through 60 m of gravel. Other substances were gradually attenuated and a diverse group of PPCPs remained in the groundwater even after passing through 180 m of subsoil. Surprisingly, the PPCP with a high degree of attenuation, such as metformin, whose concentration drops from the original value of 677 ng/l to 16 ng/l, was in this group. The member of this group with lowest degree of attenuation was sulfamethoxazole with a value of 9%. Five substances (benzotriazole, propylparaben, bisphenol S, hydrochlorothiazide, ibuprofen-2-hydroxy) were identified as the most problematic since they passed through the quaternary fluvial aquifer practically unchanged and the process of qualitative treatment using artificial infiltration appears to be ineffective.

Keywords: artificial infiltration; natural attenuation; pharmaceuticals; personal care products

Introduction

Artificial recharge is a process by which various types of surface water (e.g. that from rivers, lakes, captured precipitation, but in extreme cases also treated wastewater) are transformed into groundwater. Primary aim is to slow down water runoff and retain water in the landscape, which can greatly benefit nature. This technology is becoming more and more popular globally. Artificial recharge is often used to revitalize and save wetlands or other water-bound ecosystems (Ruiz et al. 2023; Gómez-Escalonilla et al. 2024). Another common goal of artificial recharge is to create new water source for irrigation, especially in regions with a high level of groundwater overexploitation, such as India, Pakistan, USA, but also in Mediterranean countries in the EU (Maskey et al. 2022; Perdikaki et al. 2022). Artificial recharge is a very popular technology for producing high-quality sources of drinking water, e.g. via building artificial infiltration systems that use the natural attenuation properties of rocky substrates. Percolation through an unsaturated zone and aquifer, can result in a great improvement in the physical-chemical properties, removal of nitrogen and phosphorus compounds, as well as organic compounds, heavy metals and other undesirable components (Eisfeld et al. 2021; Sarfaraz et al. 2021; Hassan et al. 2023).

However, with advances in analytical techniques, such as, liquid or gas chromatography coupled with highly sensitive (tandem) mass spectrometry, a new qualitative problem has emerged in recent years. A wide range of previously unknown substances have been identified and quantified in the aquatic environment in ng/l to µg/l concentrations (Fawell and Ong 2012; Rivera-Utrilla et al. 2013; Yao et al. 2022) and in other parts of the ecosystem (Badani et al. 2023), pharmaceuticals and personal care products (PPCPs). Over 400 of them are recorded in surface and groundwater and constitute a large and diverse group of chemicals of mainly synthetic origin (e.g. drugs used to treat human and animal diseases, household chemicals and disinfectants, cleaning products, lotions, suncream agents, fragrances). Some of them are extremely persistent in the environment and have toxic and bio accumulative properties. Untreated and treated sewage, landfills, hospital waste, veterinary drugs and agricultural wastewaters are the main sources of PPCPs (Grasserová et al. 2020; Yao et al. 2022).

The most problematic drugs are the ones that are also the most representative in terms of numbers. Already more than a decade ago, global annual per capita use of pharmaceuticals was 15 g, which is three to ten times higher (50–150 g) in developed countries (Zhang et al. 2008). Moreover, the use of pharmaceuticals has

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continued to rise in recent years, driven by a growing need for drugs to treat age-related and chronic diseases (González Peña et al. 2021). Oncology is the other top therapeutic area driving drug sales globally and likely to show the largest growth in the see able future, followed by drugs for treating autoimmune diseases and diabetes. The COVID-19 pandemic also needs to be included, as vaccine Comirnaty was the world's top revenue generating pharmaceutical product during the height of the COVID-19 pandemic (Mikulic 2024). The total global pharmaceutical market was estimated at around 1.6 trillion U.S. dollars in 2023, which is an increase of over 100 billion dollars compared to 2022 (Mikulic 2024). The study of PPCPs in drinking water is even more complicated as the pharmaceutical industry currently produces more than 7,100 approved drugs for human or veterinary use. The total number of experimental or investigational drugs is also high, increasing by 38% from 3,394 to 6,231, between 2018 and 2023 (Knox et al. 2024). Not only do primary substances fall into this category, but also their by-products, which sometimes have much more negative properties. It is likely that these substances are present everywhere to varying extents and concentrations, and the awareness of their presence depends on which chemical substance laboratories focus on identifying in the water/environment.

The toxicity of drugs, especially endocrine disruptors, has recently become the subject of scientific debate and a global public health problem, primarily because of their individual or synergistic effects on humans and the ecosystem (Trapido et al. 2014; Barton-Maclaren et al. 2022; Wu et al. 2023; Dalamaga et al. 2024; He et al. 2024). These substances cause dysfunction of the endocrine system, manifesting in a variety of diseases, including developmental and metabolic disorders (Schneider et al. 2019; Robles-Matos et al. 2021; He et al. 2024). Another fundamental problem is that these pollutants occur in the environment almost exclusively as mixtures (Kolpin et al. 2002; Loos et al. 2009). The negative effects of PPCPs on animal species, especially those in the aquatic environment, are well documented (Hoeger et al. 2005; Lyssimachou and Arukwe 2007; Adeleye et al. 2022; Iturburu et al. 2024; Li et al. 2024). In contrast, there are very few studies on the negative effect on human health, especially clinical studies (Huang et al. 2020). Intensive and long-term studies of this issue are needed, especially of the drugs in drinking water, as this is one of the main sources of these substances for humans. The Káraný waterworks, where the occurrence and fate of PPCPs after percolating through a rocky environment is monitored, is the first to do this in the Czech Republic.

The Káraný waterworks, which is located in Central Bohemia (see Fig. 1), is a unique facility in the Czech Republic in using two different technologies. Between 1906 and 1913, a bank infiltration system was established and is still operating. It consists of 685 wells with a depth of 8–12 m, which are 20–40 m apart. The receiving wells are located mainly in gravel-sand fluvial sediments at about 250 m from the Jizera River. The total capacity of this system is 86 400 m^3/day.

Fig. 1 The location of the Káraný waterworks in the Czech Republic.

Since 1968, the waterworks has used an additional method to produce drinking water based on the principle of artificial recharge. The first step in this process is a simple mechanical treatment of the surface water from the river. The water is filtered through sand and pumped into infiltration basins, from where it seeps into sandy fluvial sediments with a thickness of 20 m. A system of large-diameter wells. with a total capacity of 77,760 m^3/day, is located about 200 m from the infiltration basins. The water from these wells is a mixture of infiltrated surface water and groundwater from the sand-gravel terrace in the east between the waterworks and the Jizera River.

The Káraný waterworks supplies approximately one third of the drinking water for the capital city of Prague, with more than 1.3 million inhabitants. In the last decade, monitoring the concentrations of PPCPs in drinking water has come to the fore. The source of this pollution is water from wastewater treatment plants (WWTP) the out flow from which goes into the Jizera River. The most important source of PPCPs is the city of Mladá Boleslav (45,000 inhabitants), in which is the Kosmonosy psychiatric hospital with a capacity of up to 600 patients.

Systematic monitoring of the water quality in the Jizera River between 2017 and 2021 in the section between Mladá Boleslav and Káraný (Hrkal et al. 2018; Hrkal 2022) revealed a wide range of PPCPs leaving the WWTP in Mladá Boleslav. Oxypurinol and telmisartan occurred in the treated wastewater at concentrations in the order of tens of μg/l; the other four drugs, namely diclofenac, tramadol, lamotrigine and hydrochlorothiazide, were present at concentrations in the order of units of mg/l. For the other 44 drugs analysed, concentrations systematically ranged from units to hundreds of ng/l. Even though treated wastewater is greatly diluted (the average flow of the Jizera River in Mladá Boleslav is 24 m^3/s), 38 PPCPs were recorded in the river water. Table 1 provides an overview of the most important substances

whose average concentrations in the water used to produce drinking water, at the Káraný waterworks, exceed 100 ng/l.

Table 1 Concentrations of PPCPs (ng/l) in the water of the Jizera river (monthly average for 2017–2018) (Hrkal et al. 2018).

PPCP substance	Concentration (ng/l)
Oxypurinol	379
Acesulfame	291
Telmisartan	210
Paraxanthine	209
Caffeine	172
Saccharin	156
Gabapentin	121
Iomeprol	110

Detailed monitoring revealed a significantly higher removal of PPCPs in the case of bank infiltration. The clogging zone of the riverbed was able to capture the vast majority of PPCPs thanks to the sorption properties of the clay minerals it contains. None of the PPCPs were regularly detected in the river during the monitoring, except very rarely in concentrations at the limit of detection.

A worse situation was revealed in the case of artificial recharge. In this case, the river water passes through the gravel in the infiltration basins and then through fluvial sediments of similar lithological composition. A thin clogging layer on the surface of the basins, which forms during the infiltration process, reduces the efficiency of infiltration. For this reason, it is mechanically removed approximately every two years. The sorption capacity of artificial infiltration is therefore less effective than bank infiltration. This was manifested in the presence of six substances, of which acesulfame and oxypurinol exceeded a concentration of 100 ng/l (Fig. 2).

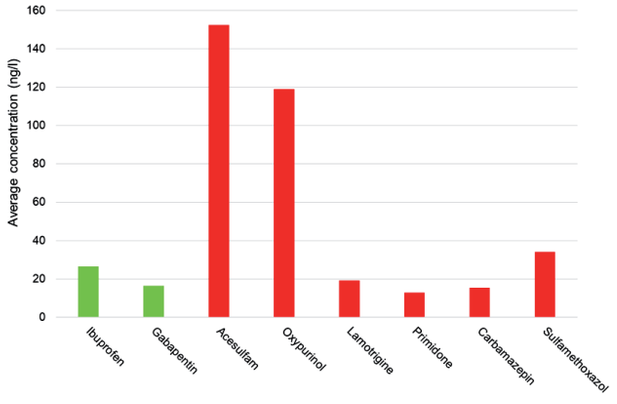

Fig. 2 Average concentrations (ng/l) of PPCPs in drinking water produced using artificial recharge (monthly averages from 2017–2018) (Hrkal et al. 2018) – unsystematic occurrences are in green, regularly occurring substances are in red.

Monitoring carried out between 2017 and 2018 revealed a problem. It assumed the process of artificial recharge was a "black box" and the chemistry was monitored in the input (raw river water) and output (drinking water produced). However, this monitoring did not reveal what happens to individual PPCPs when they pass through the infiltration basin and subsequently the rocky substrate. The new method of monitoring, the results of which are presented in this article, set out to answer this question. The main objective of this paper was to follow up and analytically extend the outputs of the previous monitoring system of PPCPs, which occur in the water used in the Káraný waterworks for producing potable water using an artificial filtration system. The objective was to describe what happens to PPCPs as they pass through this system, monitor changes in the concentrations of individual PPCPs, identify groups of PPCPs that are affected similarly and evaluate the effectiveness of natural attenuation for removing PPCPs from water. A secondary objective was to propose possible other solutions and identify technologies by which PPCPs can be destroyed or their concentrations can be further reduced .

Methodology

This two-year monitoring project focused on a detailed analysis of the behaviour of 43 PPCPs, the selection of which was based on the substances detected during previous monitoring between 2017 and 2018.

Monitoring and sampling

From May 2022 to April 2023, four samples of water were collected at the following locations at monthly intervals: river water entering the infiltration basin (i), monitoring well HV1 (ii), monitoring well HV2 (iii) and collection well R14 (iv). Locations monitored and schematic cross section of the site are presented in Fig. 3.

The wells HV1 and HV2 were located at a distance of 60 m and 120 m from the infiltration basin, respectively. They are 20 m deep with the following lithological profile: 0–2 m clayey sand (Quaternary), 2–19 m sandy gravel (Quaternary) and 19–20 m marl (Cretaceous). The diameter of both wells was between 2–19 m. Well, R14, is 145 m from the outer edge of the infiltration basin and has a diameter of 5 m. It is a Raney-type well with a depth of 20 m and the bottom of which is impermeable chalk clinker. Two drainage pipes 300 mm in diameter, located parallel to the axis of the infiltration basin, extended horizontally from both sides of the bottom of this well. The southern drain is 57 m long, the northern 45 m long. Thus, they can collect groundwater flowing from the infiltration basin, which includes that flowing from opposite sides of the Quaternary aquifer. The water in the R14 well is therefore a mixture of water from artificial recharge and groundwater, the quality of which is that of natural background water. Understanding the

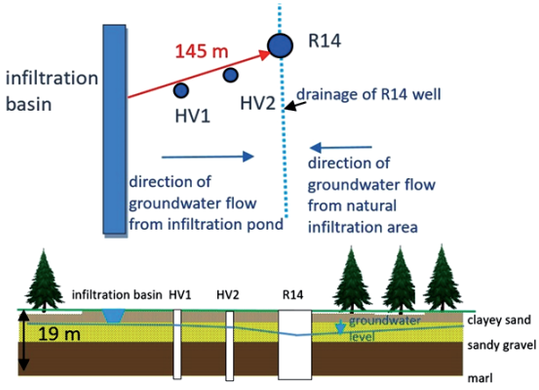

Fig. 3 Schematic presentation of the location and spatial distribution of sites monitored.

attenuation processes depends on a knowledge of the hydraulic properties of the Quaternary aquifer. Daily measurements of the levels in the observation wells 813, 814, 815, 817, 818 and 819, and in the infiltration basin and well R14 are available based on previous measurements (see Figs 4–6). The volumes of water flowing into the infiltration basin and withdrawn from well R14 were included in the data collected. Based on this data, the mean value of the saturated hydraulic conductivity of the aquifer k_f (4.2×10^{-4} m/s), the mean value of the effective porosity (27.5%) and range of the size of the hydraulic gradients I between the infiltration basin and R14 well in a situation corresponding to the sampling of groundwater (1×10^{-4} – 3×10^{-4}), were calculated. The actual rate of movement of groundwater between the infiltration basin and R14 well varied from 1×10^{-4} to 3×10^{-4} m/s (16.8 to 5.6 m/day). The retention time thus varied during the monitoring period, depending on the specific hydraulic situation, from 8.8 to 25.9 days.

Fig. 4 Location of wells and data on levels of groundwater.

Analytical methods

Sample preparation and analysis were done using the method of Dume et al. (2023). A reducing agent was added to the aqueous samples, the pH was adjusted to 3.5, the samples were placed in an ultrasonic bath (10 min,

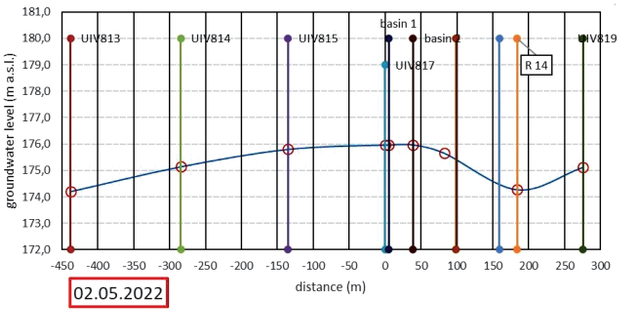

Fig. 5 Level of groundwater, basin infiltration = 0 l/s, R14 pumping = 19.88 l/s.

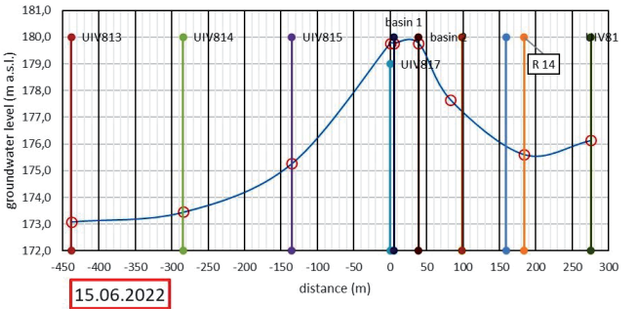

Fig. 6 Level of groundwater, basin infiltration = 22.12 l/s, R14 pumping = 20.47 l/s.

RT) and then centrifuged (10 min, 6,000 rpm). A 1.8 mL aliquot of supernatant from each sample was collected in a glass HPLC vial and analysed in triplicate.

The treated aqueous samples were analysed using an Agilent 6470 Triple Quadrupole LC-MS System liquid chromatograph with mass detection. The system was equipped with an Agilent Poroshell 120 EC-C18 column (100 × 3 mm; 2.7 µm) with an Agilent Poroshell 120 EC-C18 pre-column (5 × 3 mm; 2.7 µm) and an Agilent 6470 triple quadrupole. 0.5 mM ammonium fluoride in MiliQ water with addition of 0.01% formic acid (the mobile phase A) and 100% methanol (the mobile phase B) were used in the analyses. The gradient elution was as follows: (time [min], % phase B): 0, 5; 0.5, 5; 12.5, 100; 14.5, 100. The duration of an analysis was 16.5 minutes, the flow rate of the mobile phase was 0.6 ml/min. The chromatographic column was heated to a temperature of 40 °C, the temperature of the MS source was 210 °C, the gas flow in the source was 6 l/min, the capillary voltage was 2500 V. Substances were analysed in the dynamic MRM mode, when usually 2 MRMs were selected for each analyte transition. The standard addition method was used for quantification, when the concentration of the standards added to the sample was always 5, 25 or 125 ng/ml. Samples with a high concentration of analytes of interest outside the calibration range were diluted with water (MilliQ) and reanalysed. Data evaluation was done using the MassHunter Workstation Quantitative Analysis program (Version 10.0, Agilent).

Table 2 Changes recorded in the concentrations of different PPCPs in the infiltration basin and at the locations where samples were collected (after 60 m in well HV1, after 120 m in well HV2 and after 180 m in well R14), where effectiveness of natural attenuation of PPCPs passing through 180 m of fluvial deposit is expressed in %, (–) means concentration below the limit of quantification and N/A means "not applicable".

Median concentration (ng/l)							
			Monitoring location	**Infiltration pond**	**HV1**	**HV2**	**R14**	***Attenuation efficiency (%)***
	GROUP 1		Iohexol	39	–	–	–	N/A
			Iopromide	29	–	–	–	N/A
			Metoprolol	17	–	–	–	N/A
			Cetirizine	18	–	–	–	N/A
			Valsartan	16	–	–	–	N/A
			Clarithromycin	18	–	–	–	N/A
	GROUP 2		Iomeprol	180	38	–	–	N/A
			Tramadol	54	9	–	–	N/A
			Sulfapyridine	7	3	–	–	N/A
	GROUP 3A		Metformin	677	33	24	16	98
			Oxypurinol	623	340	148	83	87
			Paraxanthine	99	45	46	23	77
			Gabapentin	174	76	45	45	74
			Caffeine	130	74	79	43	67
			Sucralose	1,422	1,318	910	619	56
			Carbamazepine	24	22	15	11	55
			DEET	47	29	31	23	51
	GROUP 3B		Celiprolol	24	20	18	15	41
			Diclofenac	37	22	23	23	38
			Acesulfame	224	162	134	139	38
			Primidone	57	50	48	44	22
			Lamotrigine	47	44	29	37	20
			Sulfamethoxazole	35	55	40	32	9
	GROUP 4		Benzotriazole	230	277	217	265	N/A
			Propylparaben	4	5	4	5	N/A
			Bisphenol S	35	34	34	36	N/A
			Hydrochlorothiazide	13	24	14	14	N/A
			Ibuprofen-2-hydroxy	56	51	57	52	N/A

Results

The results of the two-year monitoring revealed that the PPCPs could be placed into different groups based on their presence in the rocky environment. The presence of a specific substance in at least 3 of the 14 samples analysed was chosen as an indication of systematic occurrence. The initial information indicates that a total of 38 substances meet this criterion in the inlet to the infiltration basin. Subsequently, 24 PPCPs were regularly detected in the outlet from well R14.

Changes in concentrations of PPCPs

Changes in concentrations of the important PPCPs detected during water treatment in the artificial recharge system are summarized in Table 2. For easier description and explanation of the presence of these substances they are divided into several groups in this table, the characteristics of which are described in the text below.

Group 1 includes pharmaceutical substances that were completely removed by the artificial recharge process, namely iohexol, iopromide, metoprolol, cetirizine, valsartan and clarithromycin. Concentrations of these substances fell below the limit of quantification as early as in the section between the infiltration basin and monitoring well HV1. They were either adsorbed directly by the clogging layer of infiltration basin, or natural attenuation occurred when they passed through the first 60 m of the sandy-gravel aquifer.

Group 2 includes three pharmaceuticals, namely iomeprol, tramadol and sulfapyridine, the concentration if which fell below the limit of quantification when passing through the long section of the 120 m fluvial aquifer. Their concentrations in well HV1 revealed a great decrease, but they were still systematically present (see Table 2). Saccharin, which was irregularly present in the infiltrated water and in very different concentrations from tens of ng/l to 250 ng/l. It was only very rarely detected at concentrations of around 20 ng/l in wells HV1 and HV2. Saccharin was not recorded in well R14 and is thus not included in Table 2.

PPCPs of Group 3 are those substances that passed unchanged in terms of concentration along the entire 180 m between the infiltration basin and well R14, but their concentrations decreased as they passed through the rocky substrate. These substances are divided in Table 2 according to their attenuation efficiency (percentage ratio between the initial and the final concentration) into two sub-groups (Group 3A, Group 3B), which emphasizes the differences in the effectiveness of natural attenuation in the decrease in the concentration of these substances in the samples. Group 3A consists of substances that are degraded very well or excellent with an efficiency above 50%. This group mainly includes metformin, a pharmaceutical for the treatment of diabetes, whose initial concentration decreased by 98%, and oxypurinol, an active metabolite of allopurinol, which is used to treat uric arthrosis, which was degraded by a similar amount. In contrast, the antibiotic sulfamethoxazole, the concentrations of which also decreased, but the attenuation efficiency was only 9%. The group of PPCPs for which the attenuation efficiency was evaluated at less than 50% also includes the sweetener acesulfame and five pharmaceuticals (see Group 3B in Table 2).

Finally, Group 4 includes five pharmaceutical substances that are the most problematic as they passed through the quaternary fluvial aquifer almost unchanged, which indicates that artificial recharge appears to be ineffective for eradicating them. This group includes the organic pollutant benzotriazole, preservative propylparaben, endocrine disruptor bisphenol S and pharmaceuticals hydrochlorothiazide and ibuprofen-2-hydroxy.

The relevant limits of quantification (LOQ) of the analytical methods used are summarized in Table 3.

Role of clogging layer

Until recently, the operators at the Káraný waterworks regarded the clogging layer on the surface of the infiltration basins as a nuisance. It gradually reduces the efficiency of infiltration. Therefore, approximately 10 cm of the uppermost layer was removed at more or less two-year intervals. However, the monitoring results indicated that the clogging layer might have a positive role in the elimination of some types of PPCPs. Since the clogging layer was present for two years, a sample of sediment from it was analysed for the presence of 43 PPCPs. The median content of these substance in the infiltrated water was used to calculate the amount of these substance trapped in the clogging layer during the two years. The results are summarized in Table 4.

The amount of PPCPs present in dry clogging layer, which accumulated over two years compared to the total amount of PPCPs in the infiltrated water over the same period is significantly lower than the sorption capacity of this layer. This indicates that it is highly likely that biodegradation of these PPCPs occurs in the clogging layer. This is also supported by the data reported in the EPI Suite database (US EPA 2012), which is based on using BioWin models.

Discussion

Monitoring PPCPs detected in surface water used to produce drinking water by means of artificial recharge at the Káraný waterworks showed very good attenuation of the substances detected. Concentration of most of them decreased after percolation through a 180 m gravel-sand aquifer and some PPCPs were even below the limit of quantification of the analytical method used. The artificial recharge process had no effect on only six pharmaceuticals. Artificial recharge and natural attenuation are not simple processes as they consist of a combination of many variables, which include the physicochemical parameters

Table 3 The relevant lower limits of quantification (LOQ) of the analytical methods used.

Substance	LOQ (ng/l)	Substance	LOQ (ng/l)	Substance	LOQ (ng/l)
Acesulfame	6.3	**Hydrochlorothiazide**	10.5	**Primidone**	2.5
Benzotriazole	12.5	**Ibuprofen-2-hydroxy**	12.5	**Propylparaben**	2.5
Bisphenol S	2.5	**Iohexol**	13.4	**Saccharine**	25.0
Caffeine	12.5	**Iomeprol**	23.9	**Sucralose**	123.0
Carbamazepine	8.5	**Iopromide**	35.1	**Sulfamethoxazole**	6.3
Celiprolol	10	**Lamotrigine**	2.5	**Telmisartan**	13.5
Cetirizine	32.7	**Metformin**	28.2	**Tramadol**	2.5
Clarithromycin	33.7	**Methylparaben**	32.2	**Valsartan**	6.3
DEET	10.0	**Metoprolol**	2.5	**Sulfapyridine**	2.5
Diclofenac	1.5	**Oxypurinol**	25.2		
Gabapentin	6.3	**Paraxanthine**	2.5		

Table 4 Estimated contents of PPCPs in the clogging layer on the surface of the infiltration basin.

Substance	Substance content (ng/g)	Substance content (kg/kg)	Estimated content in the entire volume of the clogging layer of the infiltration basin (kg)	Sorbed in the clogging layer over the 2 years (%)	Total amount of substance recorded over the 2 years in infiltrated water (kg)
Acesulfame	94.64	9.46E-08	0.188	11.6%	1.61
Caffeine	10.76	1.08E-08	0.021	2.3%	0.93
DEET	168.84	1.69E-07	0.335	99.2%	0.33
Gabapentin	1.87	1.87E-09	0.004	0.2%	2.46
Metformin	65.18	6.52E-08	0.129	8.0%	1.61
Methylparaben	19.42	1.94E-08	0.038	2.4%	1.61
Oxypurinol	187.63	1.88E-07	0.372	8.3%	4.50
Paraxanthine	6.89	6.89E-09	0.014	1.9%	0.72
Telmisartan	5.84	5.84E-09	0.012	v0.9%	1.33
Tramadol	3.83	3.83E-09	0.008	v2.1%	0.36

of the treated water and the geological-chemical composition of the given subsoil. The physical-chemical properties of PPCPs also affect their movement and transformation in aquifers (Wu et al. 2020). Thus, variability in the concentration of $PPCP_S$ is to be expected. Different frequencies of detection and rate of PPCPs removal are reported in other studies (Zou et al. 2011; Wu et al. 2020; Labad et al. 2023). For example, Wu et al. (2020) identified sulfamethoxazole and ibuprofen as the most frequently detected substances in groundwater passing through an artificial recharge system. This also corresponds with the current results, as sulfamethoxazole passed through the entire artificial recharge system at the Káraný waterworks and the efficiency of natural attenuation for it was only 9% and there was no change in the concentration in ibuprofen, which is a priority PPCPs as it belongs to a group of substances with middle or high ecological risk (Wu et al. 2020).

One of the simple measures to achieve an even greater reduction in the concentration of PPCPs, is to extend the clogging zone removal period. Although this will reduce the efficiency of infiltration, this is balanced by an increase in sorption capacity and longer duration of the action of biochemical processes that destroy PPCPs. The importance of biotransformation and sorption as the most important mechanisms for the natural attenuation of PPCPs is confirmed by several studies (Schaffer et al. 2012; Regnery et al. 2017). Muñoz-Vega et al. (2023) describe the influence of soil biofilms on hydraulic conductivity, reduction and fate of three pharmaceuticals with different physicochemical properties: carbamazepine, diclofenac, and metoprolol; PPCPs that were also recorded in the current study. They observed enhanced adsorption and biodegradation of all pharmaceuticals in the system, with high biological activity both in batch and column experiments. However, the measurable effectiveness of this process at Káraný needs to be tested in the future. The current results are not sufficient for a relevant evaluation and final conclusion.

Other options for greater or even complete elimination of PPCPs from drinking water include using activated carbon (AC) filters as an additional part of the treatment (Rao et al. 2021; Adegoke et al. 2022; Zhu et al. 2022) or an advanced oxidation processes (AOPs)

(Krishnan et al. 2021; Chen et al. 2023). Although these methods are very effective, they are relatively financially and technologically demanding, as well as time-consuming. Moreover, according to the EPI Suite database (US EPA 2012) some of PPCPs present in water are not subject to oxidative decomposition.

The question is whether this additional cleaning is really necessary. Natural attenuation, with few exceptions reduce the concentrations of PPCPs either below the limit of detection or to extremely low values in the tens of ng/l. Assessment of the risk posed by these substances at these concentrations to human health or the ecosystem, is practically non-existent, or is based on theoretical models and predictions. When using reference values for PPCPs in drinking water, several factors need to be considered because the level of exposure and sensitivity in humans is very variable. When there is more than one PPCP present in drinking water, which is almost always the case, it is difficult to predict the health risk of individual contaminants, as they may act independently or synergistically (Tijani et al. 2015).

Of the few studies on the effect of PPCPs on human health, there is one that reports that endocrine disruptors are responsible for low sperm count or reduced fertility (Andersson et al. 2007; Bolong et al. 2009; Benkhalifa et al. 2023; Mascarenhas et al. 2024). Probably the most serious problem is bacterial resistance to various antibiotics prescribed for humans and used in veterinary medicine, which may result in bacteria producing endocrine disruptors. PPCPs are known to be drivers of antibiotic resistance (Lu et al. 2018; Thiroux et al. 2023). A typical example is tetracycline, which often becomes a completely ineffective (Daghrir and Drogui 2013; Zhao et al. 2023).

Even if the concentrations of PPCPs are low in aquatic environments and even more so in drinking water, some older publications report that it is not a threat to human health (Houtman 2010; Stanford et al. 2010), but the concentration of PPCPs in drinking water has to be considered in a wider context. These substances are commonly ingested by people in other products, such as meat (veterinary medicines) or fruit and vegetables irrigated with water that contains PPCPs (Fromme et al. 2009; Zeng et al. 2022; Johnson and Bell 2023; Li et al. 2023), it is therefore necessary to consider the possibility of an additive negative effect when ingesting PPCPs from many sources. Moreover, since PPCPs are mainly man-made substances artificially introduced into an ecosystem that is vulnerable to them, it is incumbent on humanity to eliminate or reduce their concentration in the environment.

Conclusions

1) Artificial recharge appears to be an effective method for removing PPCPs, especially pharmaceuticals.
2) Of the 38 substances detected in infiltrated water, the concentration of six substances was reduced below the limit of quantification either by the clogging layer in the infiltration basin, or by percolating through the first 60 m of the gravel-sand aquifer.
3) Other substances were removed either by percolating through another 60 m of infiltration and were at extremely low concentrations in the water supply well.
4) Only five substances (benzotriazole, propylparaben, bisphenol S, hydrochlorothiazide and ibuprofen-2-hydroxy) passed through the Quaternary fluvial aquifer practically unchanged.
5) Residual concentrations in the order of tens of ng/1 of PPCPs remained in the drinking water, with the exception of benzotriazole and sucralose. Although these could be removed using an AC filter or the AOPs method, the question is whether these economically demanding cleaning methods are necessary. There is no clinical evidence that these substances negatively affect human health at such extremely low concentrations.
6) There is a need to consider utilizing the natural attenuation properties of the clogging layer in infiltration basin, which for certain pharmaceuticals is a very effective at destroying them or reducing their concentrations.

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