ATTENUATION OF SELECTED PHARMACEUTICALS DURING RIVERBANK FILTRATION IN DANUBE RIVER ALLUVION

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Abstract
The paper presents the results of the transport analysis for selected pharmaceuticals during riverbank filtration from the river Danube to the drainage wells at the specific site Kovin-Dubovac. In the Republic of Serbia the occurrence of pharmaceuticals in surface and groundwater was not sufficiently analyzed, so there is a need for research and testing of the occurrence and behavior of pharmaceuticals in order to better understand the flow of pharmaceuticals in the environment and transport of pharmaceuticals in groundwater during riverbank filtration. During the investigation period between 2009-2015, a total of 25 pharmaceuticals were analyzed in 52 samples, of which 13 samples of surface water and 39 samples of alluvial groundwater. A total of 7 pharmaceuticals in Danube River and 6 pharmaceuticals in alluvial groundwater were detected. Carbamazepine and metamizole metabolites N-acetyl-4-amino-antipyrine (4-AAA) and N-formyl-4-amino-antipyrine (4-FAA) have the highest frequency of occurrence in surface water and in groundwater samples, respectively. Results showed that riverbank filtration could significantly remove investigated pharmaceuticals. Percentage of removal during riverbank filtration was determined for carbamazepine (35%), trimethoprim (100%), 4-AAA (82%) and 4-FAA (43%). These results are extremely important for better understanding of self-purification potential of alluvial aquifers and protection from potential impacts of anthropogenic pollution to the groundwater sources in the Republic of Serbia.

Introduction
In the Republic of Serbia population growth is not present, but due to society urbanization and the increase of the average age of population [1], the use of pharmaceuticals is increasing in order to protect human health and improve the conditions and quality of life. In Serbia, the vast majority of cities and industrial systems directly discharge untreated water into natural or artificial recipients, leading to a cumulative occurrence of pharmaceuticals in surface and groundwaters. Also, there are many studies indicating that a large number of pharmaceuticals were not fully removed at the wastewater treatment plants [2,3,4,5]. As a result, pharmaceuticals occur in surface water and groundwater, according to several papers that present the results of studies conducted in Serbia [6,7,8,9]. Using the riverbank filtration (RBF), surface water is treated through filtration in the alluvial aquifer, which is a very important addition to the treatment of drinking water. Also, RBF can reduce the risk of accidental pollution. Due to these facts the knowledge of the processes that take place during the RBF in order to define the most optimal way of line treatment for drinking water and prevent possible occurrence of polluting substances in drinking water. The aim of our study was to obtain sufficient information about the occurrence of selected pharmaceuticals in surface water and groundwater, and to observe the removal of these pharmaceuticals through RBF, which is generally the method of choice for drinking water supply in Serbia.

Materials and methods

In the period 2009–2010 the water samples for pharmaceutical analysis were prepared applying the method of solid phase extraction (SPE) and extracts were analyzed using liquid chromatography tandem mass spectrometry method (LC-MS/MS). Detailed information about the used analytical procedure, instrumental parameters, SPE recoveries, calibration curves, accuracy, precision, detection limits, and quantification limits is described in the previously published study [10].

After the year 2010 samples were analyzed with the slightly modified methods previously published [10,11] in which 7 cardiovascular pharmaceuticals were added. The method was validated and the results are presented in the supplementary material of the published papers.

Out of 19 investigated pharmaceuticals, 12 were analyzed continuously between 2009 and 2015: sulfamethoxazole, trimethoprim, erythromycin, azithromycin, doxycycline, diazepam, bromazepam, lorazepam, carbamazepine, diclofenac and two metamizole metabolites, N-formyl-4-amino-antipyrine (4-FAA) and N-acetyl-4-amino-antipyrine (4-AAA). In the period 2010 – 2015, additional group of seven cardiovascular pharmaceuticals were included into analysis: enalapril, cilazapril, atorvastatin, simvastatin, amlodipine, metoprolol, bisprolol. Selected pharmaceuticals belong to different pharmaceutical classes and the selection was based on the application extent of pharmaceuticals in Serbia and the review of occurrence in surface water and groundwater [12]. Surface water and groundwater samples were sampled mainly in the spring and fall every year.

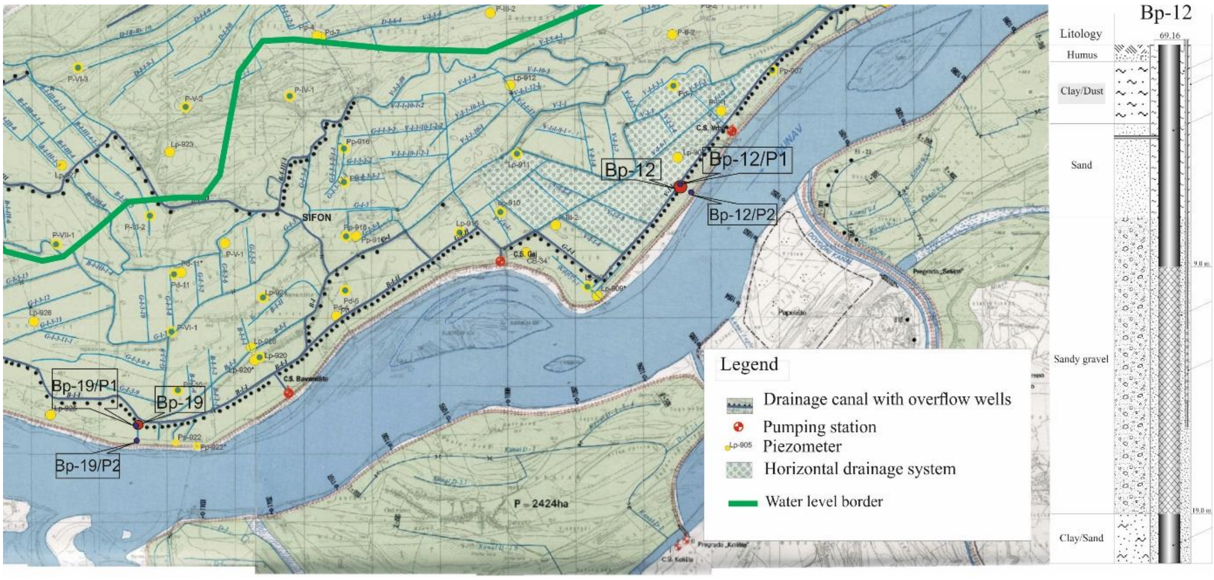

Figure 1. Research location and profile from one analysed drainage well Bp-12

Both, surface water and groundwater samples were taken at the same time during the investigation period. Surface water was sampled mid-stream, at a depth of about one meter. Groundwater samples (GW) were collected from wells in the immediate vicinity of the river Danube. In the case of free-flowing or pumped wells, measurements were conducted by submerging a peristaltic pump to the level of the well screen or horizontal collector, whereas in the case of observation wells the pump was submerged to the screen after removing a minimum of three water volumes from the observation wells with the use of a peristaltic pump.

Results and Discussion

Based on the results of analysis of the presence of selected pharmaceuticals into surface water and groundwater in the Danube River alluvion, it is evident that concentration in the groundwater was reduced as a result of the process of self-purification of groundwater during RBF. In Figure 2 there the average concentrations of detected pharmaceuticals in surface water and groundwater in the alluvium of the Danube River are shown.

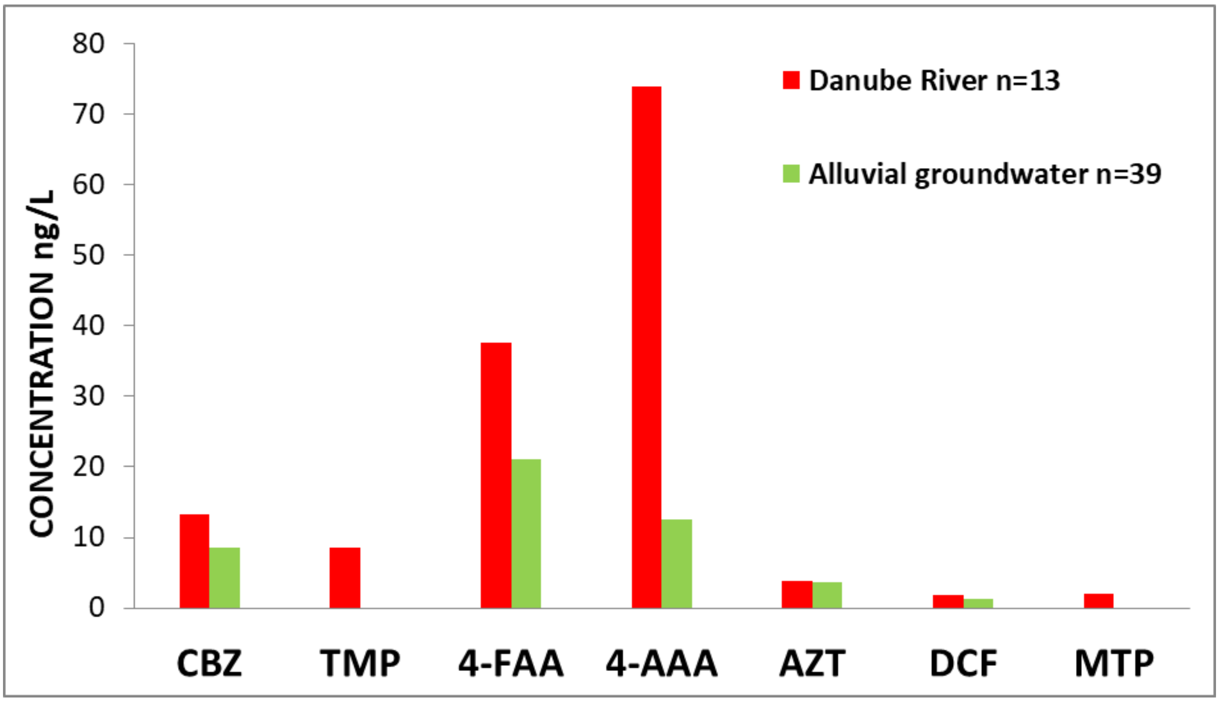

Figure 2. Average concentration of detected pharmaceuticals in the Danube River and corresponding wells of the drainage system Kovin-Dubovac (n - number of samples; ½ LOD - half of the value of the limit of detection was adopted, where the pharmaceuticals were not detected in the selected samples)

The average concentration of carbamazepine (CBZ) in the groundwater was reduced by 35% compared to the average concentration in the Danube River. Carbamazepine was detected in a total of 8 samples of the Danube River while it is registered with the concentration range between 12-32 ng/l. Trimethoprim (TMP) has been completely removed during RBF, and it was detected in one sample of the Danube River with a concentration of 110 ng/l. The average concentration of diclofenac (DCF) in the alluvial groundwater was decreased by 30% compared to the concentration in the Danube River. Diclofenac has been registered in the one sample of the Danube River with concentrations of 18 ng/l and in one sample of the alluvial groundwater with concentration of 13 ng/ l. At Kovin – Dubovac drainage system 4-FAA and 4-AAA were reduced by 43 % and by 82 % respectively. Metamizole metabolite 4-AAA was detected in 9 samples of the Danube River with concentration range of 31-260 ng/l, and in the alluvial groundwater 4-AAA was detected in a total of 14 samples with a concentration range of 12-105 ng/l. 4-FAA was detected in 9 samples of Danube River with concentration range between 28-144 ng/l, and in corresponding groundwater with the concentration range between 14-98 ng/l. Azithromycin (AZT) was detected in one sample of Danube River with concentration of 56 ng/l, and in two samples of corresponding groundwater 21-68 ng/l. Metoprolol (MTP) was detected in one sample in the Danube River with concentration of 35 ng/l, but it was not detected in alluvial groundwater. None of the other pharmaceuticals was detected in the surface water or groundwater samples. Because of the relatively small percentage of removal at a relatively long path from the river to the well (aproximatelly 400 meters) where carbamazepine was exposed to the process of self-purification can indicate that carbamazepine can be assessed as persistent pharmaceutical, as it was noted in previous studies [13,14]. Trimethoprim as readily degradable pharmaceutical was fully removed, because the degradation takes place relatively quickly [15]. Other pharmaceuticals were either not detected or the detection frequency was too low to quantify the rates of their removal through RBF.

Conclusion

Results clearly showed that concentration of selected pharmaceuticals could be reduced during RBF. In general, the concentrations detected in the Danube River were several times greater than those detected in the wells of Kovin – Dubovac drainage system. Removal of detected pharmaceuticals through RBF is evident in the area of the Kovin – Dubovac drainage system, with a relatively long path from the river to the well (approximately 400 meters). Carbamazepine was the most persistent pharmaceutical, and all other detected pharmaceutical were significantly attenuated or completely removed.

Acknowledgements

This research was supported by the Ministry of Education, Science and Technological Development, Republic of Serbia, under the Project No. TR 37014 and project III 46009.

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