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ENVIRONMENTAL EXPOSURE OF PHARMACEUTICALS IN THE SOMES VALLEY WATERSHED IN ROMANIA

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Abstract

The selected PPCPs, carbamazepine, pentoxyfylline, ibuprofen, diazepam, galaxolide, tonalide and triclosan were determined in wastewater effluents with individual concentrations ranging from 15 to 800 ng/L. Caffeine was measured at concentrations up to 42'000 ng/L. Due to the high contamination of WWTP effluents, the receiving river was also polluted. The most abundant PPCPs measured in the Somes were caffeine, galaxolide, carbamazepine and triclosan.

The concentrations in the effluents of the different wastewater treatment plants (WWTPs) varied considerably and the differences are due to different elimination efficiencies of the studied PPCPs during sewage treatment. This study is a first overview of PPCPs along on Romanian part of river Somes.

Keywords: PPCPs; Pharmaceuticals; Musk fragrances; surface water.

Introduction

The widespread presence of pharmaceuticals in the aquatic environment[2-5] is due of their extensive use in medical practices[6] and incomplete removal in Wastewater Treatment Plants (WWTP). Pharmaceuticals are designed to target specific metabolic pathways in humans and animals but there is also concern that they may pose a potential risk to aquatic organisms[7-9] at the low ng/L level. It is also assumed that PPCPs could act as pseudo-persistent compounds, because of their continual discharge into aquatic media via WWTP effluents[8-10]. .

The PPCPs concentrations in the river water are dependent on the percentage of wastewater entering the river and therefore of the dilution of the wastewater that occurs. For most European countries wastewater may be expected to be diluted between 10 and 100 times by the receiving waters. The absence of data for Eastern Europe is significant since use patterns and volumes differ from country to country. Occurrence data are therefore required for human pharmaceuticals in aquatic systems in Romania. In this part of Europe the majority of wastewater, from highly-populated cities and industrial complex zones, is still discharged into surface waters without proper treatment or after inefficient treatment. In respect to this, it is important to determine the environmental occurrence and fate of PPCPs in wastewaters and surface waters.

The objective of the present study was to investigate the behaviour of selected PPCPs during the transport in the river Somes by mass flow analysis. The results should provide support for the improvement of the existing WWTPs and therefore minimise their loads into the aquatic einvironment.

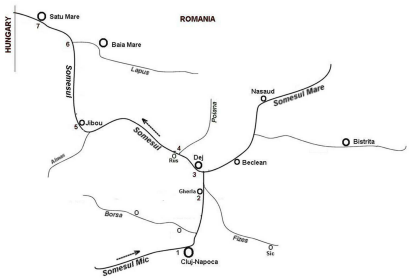

Figure 1. Sample location on Somes River: 1) Cluj-Napoca, 2) Gherla, 3) Dej, 4) Rus, 5) Jibou, 6, Baia Mare and 7) Satu Mare

Experimental

Description of the sampling site area and sampling

The map of the Somes River Basin and the sampling locations are shown in the Figure 1. The average flow of the river is: 20-25 m^3/s at the sampling sites 1-3, 65-70 m^3/s at the sites 3-5 (after confluence of the river Somesul Mic with the river Somesul Mare) and 80-90 m^3/s at the sites 6-7 (after confluence with Lapus River).

Grab samples from the river were taken at least 1 km up- and downstream of tributaries and effluents of WWTPs entering into the Somes. In order to have complete mixing between WWTP effluent or tributaries and the sampling point, samples were taken over the whole width (usually situated on a bridge connecting the shores) and combined to one sample. The samples were collected at 15 sites along the 250 km river stretch between Cluj-Napoca and Satu Mare in September 2006. Samples were collected in glass bottles and kept at 7°C until analysis (maximum 8 days) and were analysed for neutral and acidic PPCPs.
[2].

Sample preparation, analytical methods and quality control

The samples were acidified with 2N HCL to pH 2 and filtered on a glass fibre filter of 0.45 µm (Whatman, Maidstone, England). Briefly, analytes were concentrated by solid-phase extraction performed on Oasis HLB cartridges (60 mg, Waters) and subsequently analysed on a GC/ITMS system,.The TMS derivatives were obtained by reaction with N-Methyl-N-(trimethylsilyl)-trifluoracetamide (MSTFA, Sigma) at 70^0 C for 15 min. The limit of quantification (LOQ) ranged between 2.5 and 37 ng/l (ratio signal/noise 10) depending on the compound. Quantification was performed using the corresponding labelled internal standards ($^{13}C_3$-Ibuprofen, $^{13}C_3$-Caffeine, D_3-Tonalide, $^{13}C_{12}$-Triclosan, D_{10}-Carbamazepine, D_5-Diazepam) added prior to enrichment (except galaxolide which was measured relative to the tonalide-D_{10} and pentoxyfylline measured relative to D_5-Diazepam).

Results and discussions

The concentration of target compounds were calculated from chromatograms based on diagnostic ions. The concentrations and loads calculated for every site, upstream (denoted by B) and downstream (denoted by A) are shown in the Fig 2 and Fig 3. The concentrations of compounds measured in different municipal WWTP effluents are shown in Table 1.

Table 1. Average concentration of compounds in effluent of WWTP from Cluj-Napoca (1). Gherla (2), Dej (3), Baia Mare (4) and Satu Mare (5).

Substance	Concentration (ng/l)				
	WWTP 1	WWTP 2	WWTP 3	WWTP 4	WWTP 5
Ibuprofen	14.1	302.8	340.4	209.98	416.0
Caffeine	27.1	23918.1	42560.1	23337.1	25506.8
Galaxolide	680.4	609.9	774.1	530.4	1597.2
Tonalide	71.3	135.6	38.4	60.4	281.5
Triclosan	209.5	284.2	352.9	299.5	758.1
Carbamazepine	728.7	367.8	774.1	192.8	641.3
Pentoxifylline	30.2	212.1	360.13	153.2	242.3
Diazepam	10.6	29.2	23.9	22.4	17.8

Carbamazepine. The concentrations in grab samples of the effluents from the WWTPs in Cluj-Napoca, Gherla, Dej, Baia Mare and Satu Mare varied between 248 and 774 ng/L. The highest concentration was measured in the effluents of the WWTP in Clul-Napoca reflecting the higher number of inhabitants in the catchments area of this WWTP.

In the Somes the concentrations were relatively constant, varying between 23 and 44 ng/L over the whole river stretch. The loads in the Somes varied between 77.6 g/day in Cluj-Napoca and increased to around 210-230 g/day after Somesul Mic and Somesul Mare merged.

Caffeine .The concentrations of caffeine in the effluents from most WWTPs along the Somes River (Table 4) ranged between 24'000 and 42'000 ng/l except in the effluent of the WWTP in Cluj-Napoca where it was around 30 ng/l. The low concentrations in the effluent refer to the efficient removal in this WWTP in contrast to the other WWTPs located at the Somes. The caffeine concentration along the Somes after Cluj-Napoca was relatively constant, varying between 230 and 330 ng/L

The calculated load of caffeine along Somes (Table 2) was below 600 g/day in the river stretch 1-3 (Somesul Mic) and increased up to 2400 g/day after the confluence with Somesul Mare (location 3 to Dej).

The distribution of load along of Somes River shows that: a) the loads of caffeine are proportional to the number of inhabitants living in the respective catchments; b) the caffeine is biodegraded in-situ in the segment of slow flow conditions, between sites 5 and 6 along 50 km, and c) only the WWTP at site 1, in Cluj-Napoca, is working efficiently, the load of caffeine being small close to Cluj considering the high population (above of 350 000).

After site 3 (Dej) the caffeine load is high due to the discharge of only mechanically treated wastewater or due to poor biological treatment from localities situated at Somesul Mare as: Bistrita (75 000 inhabitants), Nasaud (50 000) and Beclean (15 000). A high caffeine load was observed at site 6 (Baia Mare) due to the relatively high number of inhabitants (200'000) and this implies that the WWTP at Baia Mare is working inefficiently. The contribution of wastewater from Baia Mare to the caffeine load was 1000 g/day.

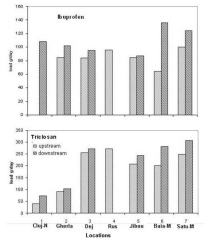

Figure 4. Distribution of Ibuprofen and Triclosan load (g/day) along of Somes River.

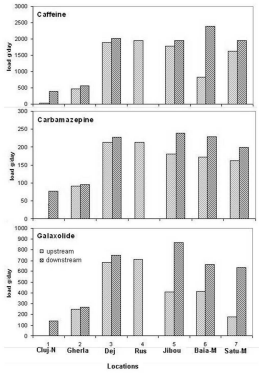

Figure 3. Distribution of Caffeine, Carbamazepine and Galaxolide load (g/day) along of Somes River. The number 1-7 correspond to the sites from Fig. 1.

Pentoxyphylline. The concentration of pentoxyphylline in the effluent of Cluj Napoca WWTP (efficient working) is low (under 30 ng/l) but in others (see Table 4) is in the concentration range 150-360 ng/l. This behaviour leads to conclusion that this compound is efficiently removed in WWTPs and therefore it can be a good marker for untreated wastewater. The small concentrations measured for pentoxyphylline along the Somes River (below LOQ) can be explained by the efficient removal during wastewater treatment in the WWTP of Cluj-Napoca

The concentrations of **ibuprofen** in the effluent of the WWTP in Cluj-Napoca was 14 ng/l where in the effluents of the other WWTPs the concentrations ranged between 150 and 350 ng/L These significantly higher concentrations reflect again the poor efficiency of these WWTPs, in contrast to the WWTP in Cluj-Napoca.

The load of **galaxolide** measured in the river stretch between location 1 and 3 (Somesul Mic) was around 250g/day and went up to 700g/day at site 3 (Dej) after Somesul Mic and Somesul Mare merge into the Somesul. At locations 3 and 7 the difference of the loads between down- and upstream of the cities is significant, leading to the conclusion that this compound is strongly removed, probably mainly due to sorption (favoured by a slow flowing conditions of the Somes).

The transport in the Somes caused a decrease of **triclosan** in river stretches downstream of a WWTP and upstream of the next WWTP (e.g. stretches 4A-5B, 5A-6B) probably mainly due to direct photo-transformation although sorption to the sediment may also play a significant role.

Conclusions: In this study the loads along of river Somes can be classified in three groups:a) The loads of caffeine and galaxolide ranged between 500-2000 g/day and 200-800 g/day respectively, and significantly different loads were calculated between up- and downstream of WWTPs; b) The loads group of carbamazepine and triclosan were relatively constant along the river and the loads varied between 100-200 and 100-250 g/day, respectively.;c) The load of ibuprofen was below 100 g/day and very constant along the river.

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