

Environmental exposure of pharmaceuticals and musk fragrances in the Somes River before and after upgrading the municipal wastewater treatment plant Cluj-Napoca, Romania

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Abstract

Background, aim, and scope Pharmaceutically active substances are a class of emerging contaminants, which has led to increasing concern about potential environmental risks. After excretion, substantial amounts of unchanged pharmaceuticals and their metabolites are discharged into domestic wastewaters. The absence of data on the environmental exposure in Eastern Europe is significant, since use patterns and volumes differ from country to country. In Romania, 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 behavior of pharmaceuticals and personal care products (PPCPs) in wastewaters and surface waters. The objective of the present study was to

investigate the occurrence of selected PPCPs during the transport in the Somes River by mass flow analysis before and after upgrading a municipal wastewater treatment plant (WWTP) in Cluj-Napoca, which serves 350,000 inhabitants and is the largest plant discharging into the Somes River. The concentrations of PPCPs at Cluj-Napoca can be correlated with the high population and a high number of hospitals located in the catchment area leading to higher mass flows. The results of this study are expected to provide information, with respect to the Romanian conditions, for environmental scientists, WWTP operators, and legal authorities. The data should support the improvement of existing WWTPs and implementation of new ones where necessary and, therefore, minimize the input of contaminants into ambient waters.

Materials and methods The PPCPs were selected on the basis of consumption at the regional scale, reported aquatic toxicity, and the suitability of the gas chromatography/mass spectrometry (GC/MS) method for the determination of the compounds at trace levels. The studied PPCPs, caffeine (stimulant), carbamazepine (antiepileptic), pentoxifylline (anticoagulant), cyclophosphamide (cytostatic), ibuprofen (analgesic), and galaxolide (musk fragrance), were determined in samples of the Somes River. The analytes were enriched by solid-phase extraction and subsequently determined by GC/MS. Caffeine, pentoxifylline, and galaxolide were determined underivatized, whereas the acidic pharmaceuticals carbamazepine, cyclophosphamide, and ibuprofen were determined after derivatization with *N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide.

Results and discussion The concentrations in the Somes River varied from below 10 ng/L up to 10 µg/L. A substantial decrease of the exposure in the Somes River could be observed due to the upgrade of the municipal WWTP in Cluj-Napoca. The loads in the river stretch between Cluj-Napoca and Dej (Somes Mic) varied strongly:

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caffeine (400–2,000 g/day), carbamazepine (78–213 g/day), galaxolide (140–684 g/day), ibuprofen (84–108 g/day). After the upgrade of the WWTP Cluj-Napoca, the concentrations in the Somes of caffeine, pentoxifylline, cyclophosphamide, galaxolide, and tonalide were significantly reduced (over 75%). One might be cautious comparing both studies because the relative efficiency of the WWTP's removal of PPCP was not evaluated. However, the significantly lower concentrations of most compounds after the upgrade of the WWTP Cluj-Napoca allow one to infer that the technical measures at the source substantially reduced inputs of contaminants to the receiving river. DeJ loads of the poorly biodegradable substance carbamazepine increased by a factor of 2–3 as a result of wastewater discharges into the river. The disproportionate increase in caffeine loads by a factor of 4 below Cluj-Napoca indicates inputs of untreated wastewater from the Somes Mare due to the discharge of untreated wastewater derived from Bistrita, Nasaud, and Beclean (115,000 inhabitants).

Conclusions The relative contribution of treated and untreated wastewater in surface water might be assessed by measuring chemical markers. Recalcitrant pharmaceuticals like carbamazepine are suitable as chemical markers for estimating the relative contribution of wastewater in surface water. The easily degradable caffeine might be a good indicator for raw sewage and hardly treated wastewaters.

Recommendations and perspectives Municipal WWTPs have the potential of a significant contribution in reducing the load of contaminants to ambient waters. The efficiency of the wastewater treatment in Cluj-Napoca improved considerably after the upgrade of the WWTP. Therefore, it is crucial that several WWTPs must be implemented or improved in the Somes Valley Watershed in order to reduce the discharge of contaminants in the Somes River from these point sources.

Keywords Cluj-Napoca · ESTROM · Mass flows · Musk fragrances · Personal care products (PPCP) · Pharmaceuticals · Somes River · Wastewater treatment plant

1 Background, aim, and scope

Pharmaceutically active substances are a class of new, so-called emerging contaminants, which has led to increasing concern about potential environmental risks. After excretion, substantial amounts of unchanged pharmaceuticals and their metabolites are discharged into domestic wastewaters. If they are not removed during wastewater treatment, these substances will be discharged into ambient waters. Therefore, at least in highly developed countries where more than 90% of the dry weather wastewater flow is treated in municipal wastewater treatment plants

(WWTPs), the sewer system represents the major point source of pharmaceuticals and personal care products (PPCPs). Additionally, direct inputs into ambient waters are also possible through storm water overflow and leaks in the sewer system. Discharge of the effluents from WWTPs into the receiving waters results in a further dilution of the pharmacological active substances which occur at concentrations up to the high nanograms per liter range in contaminated surface water.

Over the last 10 years, the occurrence of PPCPs and natural estrogens in wastewater and surface water has been widely reported and extensively reviewed (e.g., Halling-Sorensen et al. 1998; Daughton and Ternes 1999; Heberer 2002; Jones et al. 2005; Alder et al. 2006; Lishman et al. 2006; Khetan and Collins 2007). Most of the studies showing the ubiquitous occurrence of PPCPs in the environment have been conducted in Western Europe and in North America, but very little is known about the situation in Eastern Europe. Environmental concentrations of PPCPs in North America may be different from Europe as a consequence of differing PPCP use patterns, water consumption, and operation conditions of municipal WWTPs. Sorption onto particles and biotransformation are the most significant processes determining the fate of PPCPs in municipal WWTP. The elimination rate of PPCPs is dependent of the physicochemical properties of the substance, on the treatment process applied, and on further factors, like the age of the activated sludge (solid retention time [SRT]), the hydraulic retention time (HRT), temperature of the wastewater, the microbial population, etc. SRT is a major factor influencing microbial transformation and maximum transformation was determined at an SRT >10–12 days for several PPCPs (Ternes et al. 2004; Joss et al. 2005). Once pharmaceuticals reach surface waters, they can be transformed mainly via biodegradation and photodegradation or they can sorb onto the suspended particles in the water. The concentrations in surface waters are very much dependent on the contribution of the wastewater flow to the receiving water flow and, therefore, of the dilution of the wastewater that occurs.

Data regarding the WWTP efficiency in Romania are not available. The absence of data for Eastern Europe is significant since the technology used and the WWTP efficiency differ from region to region. Generally, the WWTPs consist of a primary and a secondary treatment (grit, primary settler, and activated sludge treatment with secondary clarifier), although wastewaters are often discharged into surface waters without proper treatment.

The objective of our study was (1) to obtain systematic and comprehensive, analytically measured data on the occurrence and environmental behavior of PPCPs in surface water in the Somes Valley Watershed and (2) to evaluate the contribution of WWTP effluents before and after upgrading the municipal WWTP in Cluj-Napoca in the year 2003. The

concentrations of PPCPs at Cluj-Napoca can be correlated with the high population and a high number of hospitals located in the catchment area leading to higher mass flows. The presented results and discussion are based on two earlier performed studies (Moldovan 2006; Moldovan et al. 2007). The pharmaceuticals and musk fragrances were selected on the basis of consumption at the regional scale, reported aquatic toxicity, and the suitability of the gas chromatography/mass spectrometry (GC/MS) method for the determination of the compounds at trace levels. The results of this study are expected to provide information for environmental scientists, WWTP operators, and legal authorities with respect to the Romanian circumstances. The data should support the improvement of existing WWTPs and implementation of new ones where necessary and, therefore, minimize the discharge of contaminants into ambient waters.

2 Materials and methods

2.1 WWTP Cluj-Napoca

The WWTP Cluj-Napoca is the largest WWTP in Transylvania, Romania and serves a residential population of around of 350,000 inhabitants. The average raw inflow was 86,000 m³/day (2 m³/s) during dry weather conditions.

After an upgrade in the year 2003, the WWTP was operated with a solid retention time of approximately 12 days. Primary treatment consists of a screen, grit removal, and a primary clarifier. The primary effluent is transferred into the activated sludge reactor and, subsequently, to the secondary clarifier. The combined hydraulic residence time in the primary clarifier, the aerobic reactor, and the secondary clarifier was approximately 24 h. The secondary effluent is discharged into the Somes River. Before the upgrade, the aerobic treatment was one third of the present size, the total hydraulic residence time was 12–14 h, and the solid retention time was approximately 2–4 days. The average chemical oxygen demand (COD measured as BOD₅) was 11 mg/L before the upgrade (2001) and 5.5 mg/L after the upgrade (2006).

2.2 Description of the sampling site and sampling collection

The Somes River Watershed is populated by 1,800,000 inhabitants in the northwest of Romania. The Somes Mic originates south of Cluj-Napoca and merges at Dej with the Somes Mare to the Somes which flows into the Tiza in Hungary and later into the Danube. The Somes receives a variety of organic wastes from urban areas, factories, and individual households as well as treated and nearly untreated wastewater effluents from several municipal

WWTPs. The most important WWTPs in the Somes Mic are Cluj-Napoca, Gherla, and Dej.

The map of Somes River catchment and collection sites is shown in Fig. 1. The samples were taken at three sites along the 60-km river stretch between Cluj-Napoca and Dej: site 1, downstream of Cluj-Napoca (350,000 inhabitants); site 2, downstream of Gherla (30,000 inhabitants); and site 3, upstream of Dej, after confluence of Somesul Mic (20 m³/s) with Somesul Mare (40 m³/s). The watershed of Somesul Mare before merging with the Somesul Mic is inhabited by approximately 115,000 residents.

Two sampling campaigns were conducted: the first river sampling occurred in April 2001 before the upgrade of the WWTP Cluj-Napoca and the second occurred in September 2006 after the upgrade. Grab samples were collected at the three sites, at least 1 km downstream of WWTPs effluents and the tributary Somes Mare. The river water samples were taken from 0.5 m under the surface. To have complete mixing between WWTP effluent and tributaries at the sampling location, samples were taken over the whole width (on a bridge) and combined to one sample. Grab samples of WWTP effluents were collected at the same time. The average flow of the river does not fluctuate very much, with a maximum flow during spring time demonstrating a 20% higher flow than in winter. The flow and the temperature of the Somes during both campaigns were comparable.

2.3 Chemical analyses

The detailed analytical method has been published elsewhere (Moldovan 2006; Moldovan et al. 2007). Briefly,



Fig. 1 Map of the Somes River catchment indicating the sampling sites 1–3 in the Somes River

river water samples (500 mL) were enriched by solid-phase extraction (Oasis HLB cartridges of 60 mg, Waters; enrichment factor, 1,000-fold), followed by GC/MS. In the first campaign, separation and detection were performed on a GC/MS system (Fisons MD 800 mass spectrometer) operated in EI mode at 70 eV and in the second campaign on a GC–ITMS system (Thermo Electron Polaris Q Mass Spectrometer) operated in EI mode at 70 eV. The gas chromatographs were equipped with a capillary column HP-5MS (30×0.25 mm) with 0.25 μm film thickness. Caffeine, pentoxifylline, and galaxolide were determined underivatized, whereas the acidic pharmaceuticals, carbamazepine, cyclophosphamide, and ibuprofen, were determined after derivatization with *N*-methyl-*N*-(trimethylsilyl)-trifluoroacetamide (MSTFA, Sigma) at 70°C for 15 min).

For validation, two replicates were performed using river water spiked with 500 ng/L of each compound. For recoveries over the entire procedure, river water samples were spiked prior to extraction with 10–500 ng/L of analytes. The calculated amount of PPCPs minus the amount already present before spiking was then divided by the spiked concentration. The recoveries ranged from 55% to 110%. The results were corrected with the corresponding recovery rates. Calibration curves ranged from 10 to 500 ng/L (and up to 2,000 ng/L for caffeine). The response signals showed a linear range from 10 to 500 ng/L with a correlation coefficient better than 0.9940. The overall precision was below 15%. The limits of quantification (LOQ) were around 30 ng/L at the first campaign and around 10 ng/L at the second campaign. The quantifications were performed using diphenylamine (in the first campaign) and ibuprofen-¹³C₃, caffeine-¹³C₃, and tonalide-D₃ (in the second campaign) as an internal standard.

3 Results and discussions

The selected compounds are presented in Table 1. The chromatographic separation obtained by diagnostic ions of caffeine, galaxolide, and tonalide, as well as the labeled compounds caffeine-¹³C₃ and tonalide-D₃, used as an internal standard, are shown in Fig. 2. For quantification and identification of target compounds, the mass spectra in the full scan mode were used. The concentrations of the target compounds (in nanograms per liter) at sites 1–3 before and after the upgrade of the WWTP in Cluj-Napoca are given in Table 2. The loads (in grams per day) for both sampling campaigns are shown in Fig. 3.

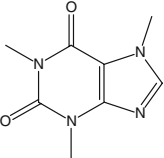
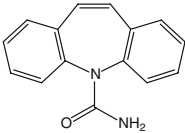
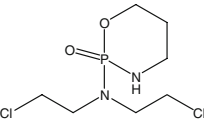
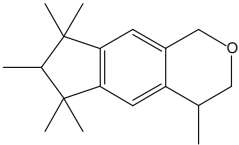
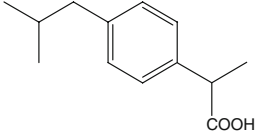
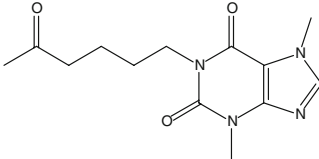
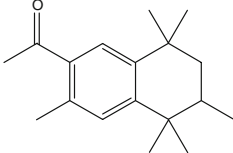
Before the WWTP upgrade, the concentrations of pentoxifylline, a haemorrhagic and vasodilator agent, were around 300 ng/L at sites 1 and 2 (corresponding to a load of 500 g/day) and below the LOQ at site 3. After the upgrade of the WWTP, the concentrations were below the LOQ at all sites. This behavior is consistent with the

working hypothesis that the main source of pentoxifylline is the University Hospital of Cluj-Napoca, Department of Cardiovascular Diseases and that it is efficiently eliminated in the upgraded WWTP with a SRT of approximately 12 days. In a German survey, the concentrations of pentoxifylline were also below the LOQ and only a few nanograms per liter were detected in some effluents of Canadian WWTPs (BLAC 2003; Metcalfe et al. 2003).

Another compound with a similar behavior was cyclophosphamide, an important cytostatic drug used in the chemotherapy of cancer and in the treatment of autoimmune diseases. Thus, residues of cytostatic drugs almost exclusively originate from hospital applications. Cyclophosphamide was not detected above the LOQ (10 ng/L) in any sample during the second campaign. However, in the first campaign before the upgrade, cyclophosphamide was detected at concentrations of 65 and 45 ng/L at sites 1 and 2, respectively. At site 3, the concentrations were <LOQ presumably due to the confluence of Somesul Mic with Somesul Mare. These concentrations translate to loads of 112 and 89 g/day at sites 1 and 2, respectively. These concentrations are surprisingly high compared to literature data and one reason could be that the Oncological University Hospital is the sole hospital for cancer treatment in Transylvania and, therefore, the main source for cytostatic drugs. In a German study, cyclophosphamide was determined at maximum concentrations of 20 ng/L in four out of 16 effluent samples (Ternes 1998). In Switzerland, cyclophosphamide was detected in untreated and treated wastewater at concentrations of 2–11 ng/L and high persistence in WWTPs was suggested (Buerge et al. 2006a). In a German survey, the concentrations of cyclophosphamide in grab samples of wastewaters and surface waters were mostly below the LOQ with few exceptions with levels in wastewaters up to 150 ng/L and one detected in surface waters at 100 ng/L (BLAC 2003).

Ibuprofen (an analgesic drug) was frequently detected in effluents and surface waters in Europe due to its high prescription rates and wide usage. In our study, the concentrations at site 1 varied between 85 and 63 ng/L and at site 2 between 115 and 59 ng/L. In WWTPs, the biological transformation of a compound depends on the age of the activated sludge. Ibuprofen requires an SRT of 2–4 days for a significant (>90%) degradation (Ternes et al. 2004; Joss et al. 2005). Assuming a SRT of 2–4 days before the upgrade of the WWTP Cluj-Napoca, a relatively efficient removal of ibuprofen could already be expected. Therefore, an additional increase up to 10–12 days would not show a dramatic improvement of the elimination. The ibuprofen concentrations in the Somes River in both sampling campaigns were probably within the range of daily and weekly variations. The concentrations in the Somes are significantly lower compared to values of

Table 1 Selected compounds, molecular structures, and quantification ions

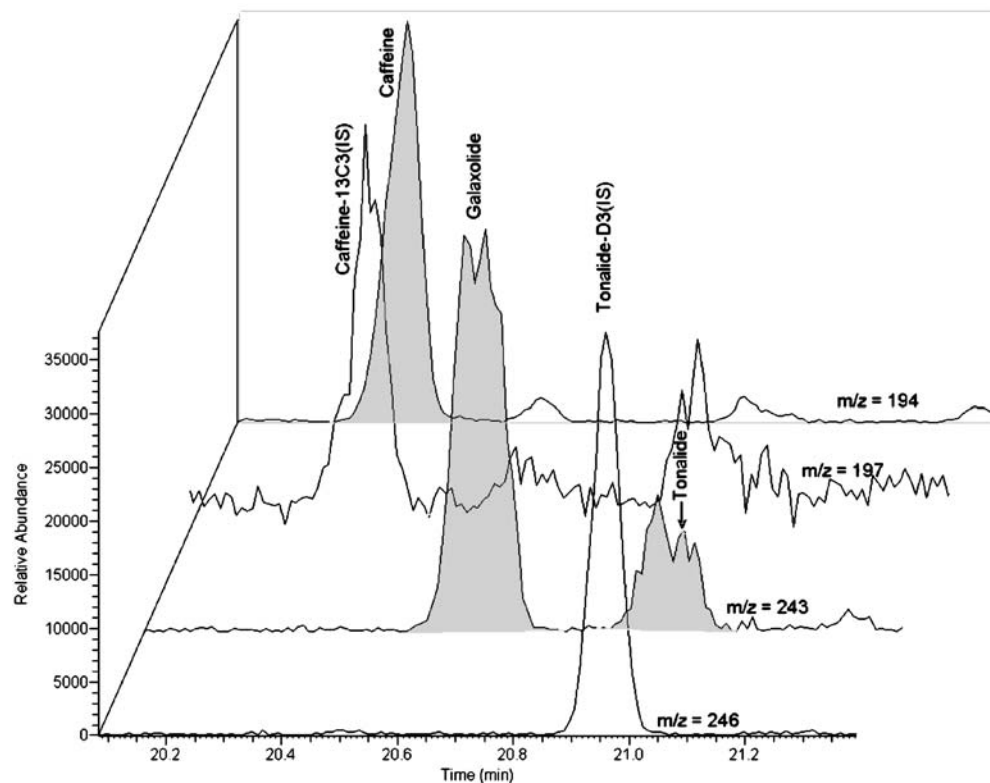
Compound	Chemical structure	Chemical formulae molecular mass	Quantification ion
Caffeine (1,3,7-trimethyl xanthine)		$C_8H_{10}N_4O_2$ M=194	194
(*) $^{13}C_3$ -Caffeine		$^{13}C_3C_5N_4O_2$ M=197	197
Carbamazepine (5H-dibenz[b,f]azepine-5-carboxamide)		$C_{15}H_{12}N_2O$ M=308	193
(*) D_{10} -Carbamazepine		$C_{15}H_2D_{10}N_2O$, TMS, M=318	203
Cyclophosphamide		$C_7H_{15}Cl_2N_2O_2P$ M=260	211
Galaxolide (1,3,4,6,7,8-hexa hydro-4,6,6,7,8,8-hexamethyl-cyclo penta-(g)-2-benzopyran) (HHCB)		$C_{18}H_{26}O$ M=258	243
Ibuprofen (a-methyl-4(2-methylpropyl)-benzeneacetic acid)		$C_{13}H_{18}O_2$ M=278	160
(*) $^{13}C_3$ -Ibuprofen		$^{13}C_3C_{10}H_{18}O_2$ M=236	162
Pentoxifylline (3,7-dimethyl-1-(5-oxohexyl) xanthine)		$C_{13}H_{18}N_4O_3$ M=278	221
Tonalide (7-acetyl-1,1,3,4,4,6-hexa methyltetralin) (AHTN)		$C_{18}H_{26}O$ M=258	243
(*) D_3 -Tonalide		$C_{18}H_{23}D_3O$ M=261	246

The internal standards are marked with an asterisk

200 ng/L as reported for the USA (Kolpin et al. 2002) and UK (Ashton et al. 2004), but comparable to concentrations in Spanish rivers (Gros et al. 2007). In the first campaign the loads at sites 1, 2 and 3 were 130, 220 g/d, respectively. In the second campaign the loads at sites 1, 2, and 3 were 108, 103, 73 g/d, respectively.

The concentrations and loads of carbamazepine (an antiepileptic and antidepressant) were similar in both sampling campaigns and were relatively constant at the three sampling sites. In the first campaign, the concentrations at sites 1, 2, and 3 were 65 ng/L, 72 ng/L, and below the LOQ, respectively, and the LOQ of carbamazepine

Fig. 2 Chromatograms of the diagnostic ions m/z 194, 197, 243, and 246 for water samples



pine was 30 ng/L. The loads at sites 1 and 2 were 113 and 140 g/day, respectively. In the second campaign (LOQ <10 ng/L), the concentrations at sites 1, 2, and 3 were 45, 56, and 35 ng/L, respectively. These concentrations are comparable to other Western European rivers (Gros et al. 2007) or up to one order of magnitude lower compared to rivers with a high share of wastewater effluents with concentrations up to 1,800 ng/L (BLAC 2003). The corresponding loads at the three sites were 78, 96, and 181 g/day, respectively. The increase of the load at site 3 is due to the input of the Somesul Mare River where wastewater effluents from relatively important cities (Bis- trita, Nasaud, and Beclean) are being discharged. Because

carbamazepine is not significantly removed in WWTPs (Jones et al. 2002; Strenn et al. 2004; Wiegel et al. 2004; Joss et al. 2005) it can be a good indicator for evaluating whether surface water is impacted by contamination from municipal sewage effluent or whether contamination asso- ciated with sewage effluent can be transported into ground water at ground water recharge sites (Clara et al. 2004; Heberer et al. 2004).

Caffeine has a widespread usage in beverages, food, and pharmaceuticals. Despite the efficient removal in most WWTPs (>90%), caffeine is ubiquitously found in rivers and lakes. Caffeine is efficiently eliminated in WWTPs and is, therefore, a suitable indicator for surface water pollution

Table 2 Average concentrations (in nanograms per liter) of the PPCPs before and after the upgrade of the WWTP Cluj-Napoca

No.	Compound	Site 1 (Cluj-Napoca)		Site 2 (Gherla)		Site 3 (Dej)	
		Before	After	Before	After	Before	After
1	Caffeine	2,772	228	9,700	333	428	333
2	Carbamazepine	65	45	72	56	<LOQ	38
3	Cyclophosphamide	65	<LOQ	46	<LOQ	<LOQ	<LOQ
4	Galaxolide	300	81	314	155	172	13
5	Ibuprofen	85	63	115	59	<LOQ	16
6	Pentoxifylline	291	<LOQ	299	<LOQ	<LOQ	<LOQ
7	Tonalide	106	<LOQ	101	<LOQ	81	<LOQ

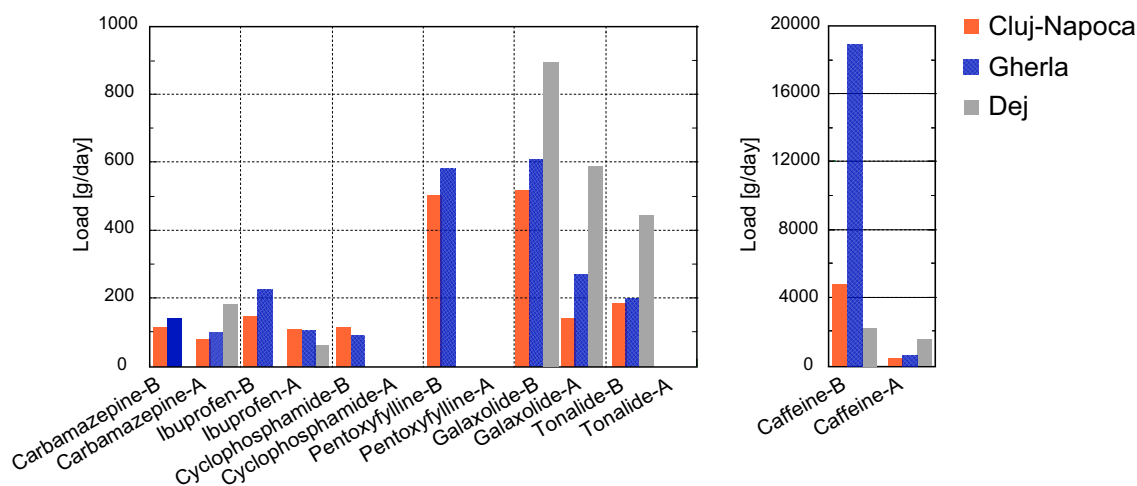


Fig. 3 Mass flows of the studied compounds in the Somes River Watershed before (*B*) and after (*A*) the upgrade of the WWTP Cluj-Napoca

by untreated municipal wastewater (from combined sewer overflow, direct discharges) (Buerge et al. 2003, 2006b). According to a recent study, caffeine should pose negligible risk for most aquatic vertebrate and invertebrate organisms (Moore et al. 2008). In our first sampling campaign, caffeine was detected at very high concentrations at sites 1 and 2. The average concentrations were up to 2,800 ng/L at site 1, over 9,700 ng/L at site 2, and 430 ng/L at site 3 (because of the dilution with the Somesul Mare River with a two times higher water discharge than Somesul Mic River). The corresponding loads were 4,790, 18,850 and 2,229 g/day, respectively. In the second sampling campaign, the measured concentrations at sites 1, 2, and 3 were 228, 332, and 312 ng/L, respectively. The corresponding loads were 394, 576, and 1,617 g/day, respectively. Caffeine concentrations and loads found at sites 1 and 2 during the first campaign could not be explained by the discharge of treated wastewater; hence, inputs of untreated wastewater were assumed to be responsible for the comparatively high concentrations. Concentrations of caffeine in untreated wastewater are, in fact, orders of magnitude higher than in treated wastewater (Moldovan 2006), reflecting the improvement of the WWTP Cluj-Napoca.

Polycyclic musks have been recognized as important contaminants in wastewater effluents and surface waters and have been described to occur as ubiquitous contaminants. They are not readily biodegradable in WWTPs, and an elimination of 50% is expected to mainly be due to sorption onto sludge (Herren and Berset 2000; Joss et al. 2005). The musk fragrance galaxolide was detected in the first campaign at sites 1 and 2 at concentrations above 300 ng/L and at site 3 at 170 ng/L. The corresponding loads were above 520 g/day at sites 1 and 2 and above 890 g/day at site 3. In the second campaign, the concentrations were

81, 155, and 113 ng/L at sites 1–3, respectively. The corresponding loads were 140, 268, and 586 g/day. The reduction of the load between both campaigns of 73% (site 1) and 51% (site 2) may refer to a more efficient elimination through sorption onto sewage sludge after upgrading the WWTP Cluj-Napoca, although the collected grab samples cannot account for temporal variations. Before the WWTP upgrade, the concentrations of tonalide, were around 100 ng/L (corresponding to a load of 180, 200 444 g/d at sites 1–3, respectively. After the upgrade, the concentrations were below the LOQ at all sites

One should be cautious in comparing both sampling campaigns because the relative efficiency of the WWTP's removal of PPCP was not evaluated. However, the significant lower concentrations of most compounds after the upgrade of the WWTP Cluj-Napoca allow inferring that the technical measures at the WWTP substantially reduced inputs of contaminants to the receiving river. At Dej, loads of the poorly biodegradable substance carbamazepine increased by a factor of 2–3 as a result of wastewater discharges into the river. The disproportionate increase in caffeine loads by a factor of 4 below Cluj-Napoca indicates inputs of untreated wastewater from the Somes Mare.

The relative contribution of treated and untreated wastewater in surface water may be assessed by measuring chemical markers. Suitable indicators for wastewater could also help to detect and locate sources of water pollution. Appropriate compounds are, on the one hand, those which are persistent in sewage treatment and mobile in surface waters and groundwater like carbamazepine or compounds that are easily degraded during wastewater treatment and, thus, good indicators for raw sewage. Caffeine is efficiently eliminated in WWTPs and is, therefore, a suitable indicator for surface water pollution by untreated municipal wastewater (from combined sewer overflow, direct discharges)

(Buerge et al. 2003, 2006b). During the second campaign, the loads at Dej (site 3) of the recalcitrant carbamazepine increased by a factor of 2 compared to site 1. The concurrent increase of the caffeine load by a factor of nearly 5 refers to a discharge of untreated wastewater into the Somes. Because the increase of the load occurred after the confluence of the Somes Mic and the Somes Mare, this increase must be due to the discharge of untreated wastewater deriving from Bistrita, Nasaud, and Beclean (115,000 inhabitants).

4 Conclusions

We investigated the environmental exposure of PPCPs before and after an upgrade of the main WWTP discharging into the Somes River. The main conclusions are:

1. The concentrations in the Somes River of the studied PPCPs varied from below 10 ng/L up to 10 µg/L.
2. A substantial decrease of the PPCPs concentrations in the Somes River could be observed due to the upgrade of the municipal WWTP in Cluj-Napoca:
 - (a) Pentoxifylline and cyclophosphamide were not detected anymore in the Somes River after the WWTP upgrade.
 - (b) The concentrations and loads of galaxolide decreased significantly at the measuring site 1 after the upgrade.
 - (c) The contribution of the easily degradable caffeine from the WWTP decreased by one order of magnitude after the upgrade. The load increased after the merger of the Somesul Mare and Somesul Mic can be explained by the discharge of untreated wastewater into Somesul Mare.
 - (d) The concentrations and loads of carbamazepine remained similar within the expected temporal variations.
3. The relative contribution of treated and untreated wastewater in surface water may be assessed by measuring chemical markers. Recalcitrant pharmaceuticals like carbamazepine are suitable as chemical markers for estimating the relative contribution of wastewater in surface water. The easily degradable caffeine could be a good indicator for untreated wastewaters.

5 Recommendations and perspectives

Municipal WWTPs have the potential to make a significant contribution in reducing the loads of pharmaceuticals and other organic contaminants to ambient waters (Joss et al. 2006). Technically and economically feasible options are available for upgrading WWTPs and reducing contaminant

load in the effluent. The efficiency of the wastewater treatment in Cluj-Napoca improved considerably after the upgrade of the WWTP. Therefore, it is crucial that, in the Somes Valley Watershed, several WWTPs must be implemented or improved in order to reduce the discharge of contaminants in the Somes from these point sources.

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