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Occurrence and behaviour of 105 active pharmaceutical ingredients in sewage waters of a municipal sewer collection system

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ABSTRACT

The concentrations and behaviour of 105 different active pharmaceutical ingredients (APIs) in the aqueous phase of sewage water within a municipal sewer collection system have been investigated. Sewage water samples were gathered from seven pump stations (one of which was located within a university hospital) and from sewage water treatment influent and effluent. The targeted APIs were quantified using a multi-residue method based on online solid phase extraction liquid chromatography tandem mass spectrometry. The method was thoroughly validated and complies with EU regulations on sample handling, limits of quantification, quality control and selectivity. 51 APIs, including antibiotics, antidepressants, hypertension drugs, analgesics, NSAIDs and psycholeptics, were found frequently within the sewer collection system. API concentrations and mass flows were evaluated in terms of their frequency of detection, daily variation, median/minimum/maximum/average concentrations, demographic dissimilarities, removal efficiencies, and mass flow profiles relative to municipal sales data. Our results suggest that some APIs are removed from, or introduced to, the aqueous phase of sewage waters within the studied municipal collection system.

1. Introduction

In 1998, Halling-Sorensen published a highly cited review paper that identified active pharmaceuticals ingredients (APIs) as environmental micropollutants that were not being adequately monitored (Halling-Sørensen et al., 1998). This prompted several investigations into the distribution of APIs within the environment, and the number of papers published on this topic has increased from less than 100 per year during 1992–1995 to 900 in 2012 (Scifinder, 2013). It has been demonstrated that APIs are ubiquitous in untreated sewage water and that because many APIs are not readily removed in sewage treatment plants (STPs), they are also present in

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treated effluents and receiving waters (Gros et al., 2010; Hughes et al., 2013; Lindberg et al., 2005; Loos et al., 2013; Segura et al., 2009; Verlicchi et al., 2012). One reason for the increased interest in the environmental impact of APIs is that while their human toxicity has been investigated thoroughly, few have been studied in terms of their ecotoxicity (Boxall et al., 2012; Fent et al., 2006).

One of the most widely used technologies for the analysis of aqueous matrices is external solid phase extraction (SPE) in combination with liquid chromatography tandem mass spectrometry (LC-MS/MS). In general, APIs from a wide range of therapeutic classes are considered. However, it may be necessary to make compromises when selecting experimental conditions such that one cannot guarantee optimal performance for all APIs (Al-Odaini et al., 2010; Babic et al., 2010; Ferrer et al., 2010; Grabic et al., 2012; Schriks et al., 2010; Shao et al., 2009; Togola and Budzinski, 2008; Wu et al., 2008). However, multi-residue methods are rewarding since they can be applied in routine analyses and thereby provide a more comprehensive overview of the occurrence and fate of APIs in the environment (Buchberger, 2011; Petrovic et al., 2010). Multi-residue determination of environmental samples, in combination with online SPE LC-MS/MS, is an increasingly popular approach that can increase sample flow rate and minimize the labour involved in sampling and analysis (Farre et al., 2012). For example, López-Serna et al. (2010) reported the development of an online SPE LC-MS/MS method capable of determining 74 APIs in environmental and sewage waters within 67 min. Similarly, Khan et al. (2012) described a method that can determine 15 APIs (anti-

Table 1 – Descriptive data of the sampling locations.

Descriptive data	Hsd	Obb	T3	U9	U13	T5	NUS	Inf	Eff
Distance to STP (km)	14	13	2	1.7	0.4	0.5	2.3	–	–
Time to STP (min)[a]	467	433	67	57	15	18	77	–	–
Inhab. served[b]	5629	2193	12,200	57,219	16,609	24	6300[c]	94,334	94,334
Person equivalents (pe)	3304	1423	9860	62,409	17,027	9462	n.m.[d]	140,709	140,709
Sampling[e]	T	G	T	T	T	T	F	F	F
Sampling time day 1	10:10	10:25	09:15	09:30	09:45	10:50	n.m.	08:00	08:10
Sampling time day 2	10:10	10:35	11:15	09:20	09:50	11:05	n.m.	08:00	08:10
Sampling time day 3	10:30	10:50	09:25	09:45	10:05	09:05	08:00	08:00	08:10
Sampling time day 4	07:10	07:20	06:15	06:25	06:50	07:55	10:00	08:00	08:10
Sampling time day 5	09:50	10:20	09:15	09:25	09:35	10:35	n.m.	08:00	08:10
Sampling time day 6	09:10	09:15	08:25	08:35	08:50	09:35	n.m.	08:00	08:10
Sampling time day 7	08:45	09:00	10:00	10:15	10:30	09:40	n.m.	08:00	08:10
Flow measured	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes	Yes
Flow day 1 (m^3 day^{-1})	1542[f]	732	3251	14,380	3717	5218[g]	n.m.	28,840	28,840
Flow day 2 (m^3 day^{-1})	1542[f]	750	3377	15,710	3997	4434[g]	n.m.	29,810	29,810
Flow day 3 (m^3 day^{-1})	1542[f]	766	3451	16,180	4110	4731[g]	735	30,780	30,780
Flow day 4 (m^3 day^{-1})	1542[f]	773	3542	16,690	4209	9784[g]	704	36,540	36,540
Flow day 5 (m^3 day^{-1})	1542[f]	785	3520	16,440	4300	6113[g]	n.m.	32,700	32,700
Flow day 6 (m^3 day^{-1})	1542[f]	820	3488	15,740	4390	6430[g]	n.m.	32,410	32,410
Flow day 7 (m^3 day^{-1})	1542[f]	841	3601	16,100	4495	4691[g]	n.m.	31,270	31,270
Flow average (m^3 day^{-1})	1542[f]	781	3461	15,891	4174	5914[g]	720	31,764	31,764
Proportion flow (%)	4.7	2.4	10.7	48.9	12.8	18.2	2.2	–	–
Temp. day 1 (C°)	2.4	−3.2	−3.4	2.5	5.6	−5	−7	−6.1	−6.1
Temp. day 2 (C°)	3.5	−0.3	−1.3	3.6	4.7	−1.2	−4.8	−5.8	−5.8
Temp. day 3 (C°)	3.6	2.2	−2.1	1.5	3.4	3.4	−0.2	−1.9	−1.9
Temp. day 4 (C°)	2.5	−0.9	−0.1	3.7	4.1	−2.5	−4	−4.2	−4.2
Temp. day 5 (C°)	3.5	−2.3	−1.4	2.6	4.2	−4.9	−8.8	−9.5	−9.5
Temp. day 6 (C°)	−0.5	−1.1	−2.8	2.2	1	−1.6	−3.3	−3.1	−3.1
Temp. day 7 (C°)	−2.3	−2.6	−3.1	−2.1	−2.3	−4.1	−5.5	−7	−7
pH	7.3	7.7	7.4	7.4	7.5	7.8	n.m.	7.4	7.4
Conductivity (mS m^{-1})	51	59	65	100	59	100	n.m.	82	87
NH_4–N (mg L^{-1})	22	31	32	41	33	40	n.m.	36	34
BOD7 (mg L^{-1})	150	130	200	270	290	140	n.m.	320	7
Tot-N (mg L^{-1})	41	39	42	70	44	48	n.m.	59	45
Susp. matter (mg L^{-1})	170	110	200	350	180	140	n.m.	290	<8[h]
Susp. matter (kg day^{-1})	262	86	692	5562	751	828	n.m.	9212	<246[h]

[a] The time for the water flow of each sample location to reach the STP is based on a speed of 0.5 m s^{-1}.
[b] Inhabitants served, based on the register within the catchment area of each sample location.
[c] Estimated value, 5700 employees, 600 hospital beds.
[d] Not measured.
[e] T, Time proportional sampling; G, grab sampling (due to pump failure); F, Flow proportional sampling.
[f] Flowmeter malfunction, average flow during February 2013 used as representative approximation.
[g] Flowmeter not available, T5 daily flow calculated as follows: T5 = (Inf − (Hsd + Obb + T3 + U9 + U13)).
[h] Below detection limit.