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Concentration evolution of pharmaceutically active compounds in raw urban and industrial wastewater

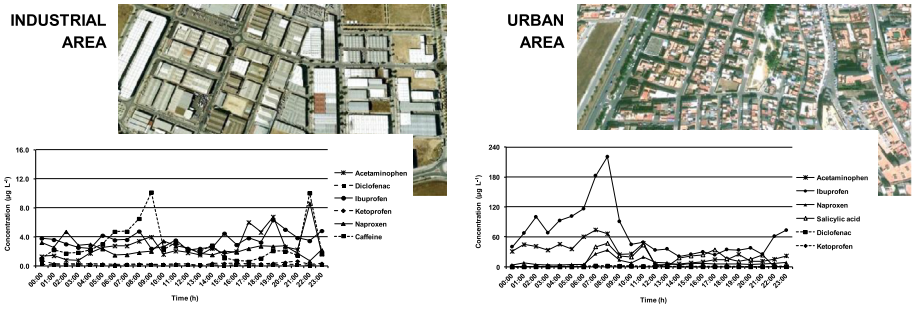
Dolores Camacho-Muñoz, Julia Martín, Juan Luis Santos, Irene Aparicio, Esteban Alonso *

Department of Analytical Chemistry, Escuela Politécnica Superior, University of Seville, C/Virgen de África 7, E-41011 Seville, Spain

HIGHLIGHTS

- Seasonal and hourly discharge patterns of pharmaceuticals were characterized.
- Relation between consumption/excretion patterns and hourly variability was found.
- Industrial discharge was the main source of salicylic acid.

GRAPHICAL ABSTRACT



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ABSTRACT

The distribution of pharmaceutically active compounds in the environment has been reported in several works in which wastewater treatment plants have been identified as the main source of these compounds to the environment. The concentrations of these compounds in influent wastewater can vary widely not only during the day but also along the year, because of the seasonal-consumption patterns of some pharmaceuticals. However, only few studies have attempted to assess the hourly variability of the concentrations of pharmaceutically active compounds in wastewater. In this work, the distribution and seasonal and hourly variability of twenty-one pharmaceuticals, belonging to seven therapeutic groups, have been investigated in urban and industrial wastewater. The highest concentrations of pharmaceutically active compounds, except salicylic acid, were found in urban wastewater, especially in the case of anti-inflammatory drugs and caffeine. The highest concentrations of salicylic acid were measured in industrial wastewater, reaching concentration levels up to 3295 μg L^{-1}. The studied pharmaceutically active compounds showed different distribution patterns during winter and summer periods. Temporal variability of pharmaceutically active compounds during a 24-h period showed a distribution in concordance with their consumption and excretion patterns, in the case of urban wastewater, and with the schedule of industrial activities, in the case of industrial wastewater.

1. Introduction

The presence of a broad spectrum of organic pollutants in the environment has been widely recognized as a potential environmental threat (Bolong et al., 2009; Santos et al., 2010). The compounds usually reported in the aquatic environment are not only priority organic pollutants but also emerging pollutants. Among emerging pollutants, pharmaceutically active compounds have attracted worldwide interest because of their pseudo-persistence, their continuous discharge to the environment and their potential ecotoxicological effects (Camacho-Muñoz et al., 2012a; Rodil et al., 2012). After their consumption, pharmaceutically active compounds usually end up in sewer systems reaching

* Corresponding author. Tel.: +34 9 5455 2858; fax: +34 9 5428 2777.
E-mail address: ealonso@us.es (E. Alonso).

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Table 1
Range, mean and RSD values of urban and industrial wastewater characterization parameters.

Parameter	Urban wastewater			Industrial wastewater		
	Range	Mean	RSD (%)	Range	Mean	RSD (%)
Cl^- (mg L^{-1})*	53–92	79.6	11	201–943	426	50
F^- (mg L^{-1})	–	–	–	0–0.67	0.14	121
TK (mg L^{-1})*	14–23	20.5	10	24–329	60.5	103
D-Fe (mg L^{-1})	0.01–0.15	0.08	33	0.04–0.57	0.27	51
T-Fe (mg L^{-1})	0.16–1.10	0.49	49	0.20–1.80	0.83	51
D-Al (mg L^{-1})	<0.05–0.29	0.07	95	0–0.21	0.09	75
T-Al (mg L^{-1})	0.20–2.40	1.08	59	0.07–0.80	0.30	63
D-Mn (mg L^{-1})	0.03–0.04	0.03	10	<0.01–0.20	0.08	63
T-Mn (mg L^{-1})	0.03–0.06	0.05	15	<0.01–0.24	0.10	59
T-Cu (mg L^{-1})	<0.01–0.05	0.03	41	<0.01–0.02	0.01	47
D-Zn (mg L^{-1})	<0.01–0.13	0.05	60	<0.01–0.09	0.03	61
T-Zn (mg L^{-1})	0.03–0.20	0.10	38	0.04–0.23	0.12	44
T-Co (mg L^{-1})	<0.01–0.05	0.003	359	<0.01–1.00	0.04	484
D-Cr (mg L^{-1})	–	–	–	<0.005–0.01	0.005	93
T-Cr (mg L^{-1})	–	–	–	<0.005–0.03	0.01	77
D-Ni (mg L^{-1})	–	–	–	<0.005–0.07	0.01	131
T-Ni (mg L^{-1})	<0.005–0.02	0.003	207	<0.005–0.43	0.03	282
T-Pb (mg L^{-1})	<0.005–0.02	0.003	167	–	–	–
TSS (mg L^{-1})	40–320	170	45	33–308	78.5	76
COD (mg L^{-1})*	83–784	519	37	359–1760	963	49
BOD_5 (mg L^{-1} O_2)*	46–436	267	37	151–1236	646	57
pH*	7.7–8.1	7.84	1	7.6–8.8	8.32	4
Conductivity (μs cm^{-1} 25 °C)*	754–1227	1031	12	1927–4810	3188	26
TP (mg L^{-1})	2.0–6.1	4.46	23	2.2–8.1	3.81	32
PO_4^{-3} (mg L^{-1})	5.1–18.0	12.3	24	5.8–24.0	10.2	36
TN (mg L^{-1})	20–81	53.0	28	21–178	48.9	88
$N–NH_4^+$ (mg L^{-1})	15–59	38.0	28	15–153	42.3	95

D-: Dissolved.
T-: Total.
* Concentrations statistically different in urban and industrial wastewater.

wastewater treatment plants (WWTPs), where they are not completely removed, being discharged with effluent wastewater into receiving streams (Jelic et al., 2011; Bueno et al., 2012; Camacho-Muñoz et al., 2012b).

Concentrations of pharmaceutically active compounds in influent wastewater can exhibit seasonal, weekly and even diurnal variations (Plósz et al., 2010). However, only a few studies have paid attention to temporal evolution of these compounds in influent loads. Göbel et al. (2005) evaluated concentrations of pharmaceutically active compounds in influent wastewater from a municipal WWTP and Joss et al. (2005) assessed a similar study in effluent wastewater. In both studies, samples were taken in 8-h intervals during one sampling day and diurnal variation patterns were reported for several compounds such as carbamazepine and iopromide. Gerrity et al. (2011) collected 30-min composite samples over 12-h periods during a massive sport event to study the occurrence of prescription pharmaceuticals and illicit drugs. In this study, temporal variations were observed for several compounds such as atenolol and benzoylecgonine (cocaine metabolite). Salgado et al. (2011) carried out an intensive campaign in a municipal WWTP to assess the dynamics of pharmaceutically active compounds and musks in influent wastewater. Samples were collected every 2 h during two consecutive 48-h periods over two successive weeks. They observed that the concentrations of pharmaceutically active compounds in influent wastewater were subject to a wider variability than the concentrations of musks. The typical diurnal pattern of pollutants, higher concentrations during the day than during the night, was observed for musks (cashmeran, celestolide, galaxolide, tonalide and traseolide) and some of pharmaceutically active compounds, while some of the other pharmaceutically active compounds frequently detected (clofibric acid, diclofenac, enalapril, fluoxetine, indapamide, ketoprofen and paroxetine) showed the opposite trend or no trend.

Most of the studies reported in the literature about the temporal evolution of pharmaceutically active compounds in influent loads (Göbel et al., 2005; Joss et al., 2005; Martinovic et al., 2008; Takao et al., 2008; Ort et al., 2010; Plósz et al., 2010; Nelson et al., 2011; Postigo et al., 2011) have been carried out with sample collection in 8-h intervals, or even longer intervals. Moreover, to the best of our knowledge, until now there are not studies in the literature reporting the discharge patterns these compounds from different sources. The knowledge of these discharge patterns could be of great interest for the design and operation of WWTPs.

In this study, twenty-one pharmaceutically active compounds belonging to seven therapeutic groups, including six non-steroidal anti-inflammatory drugs (acetaminophen, diclofenac, ibuprofen, ketoprofen, naproxen and salicylic acid), five antibiotics (ciprofloxacin, norfloxacin, ofloxacin, sulfamethoxazole and trimethoprim), a β-blocker (propranolol), three lipid regulators (bezafibrate, clofibric acid, and gemfibrozil), an antiepileptic drug (carbamazepine), four estrogens (17α-ethinylestradiol, 17β-estradiol, estriol and estrone) and a nervous stimulant (caffeine), were analyzed in urban and industrial wastewater collected every hour during 24-h periods. Temporal evolution of the studied compounds, their domestic and industrial sources and their seasonal variations were evaluated.

2. Experimental

2.1. Chemical and reagents

HPLC-grade acetonitrile, methanol and water were supplied by Romil Ltd. (Barcelona, Spain). HPLC-grade acetone, analytical grade sulfuric acid and formic acid 98% were obtained from Panreac (Barcelona, Spain). Ammonium formate was purchased from Sigma–Aldrich (Steinheim, USA). Acetaminophen (>99%), carbamazepine (>99%), clofibric acid (>97%), diclofenac sodium salt, ketoprofen