Environmental Pollution 242 (2018) 143–154

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Seasonal and spatial variations in the occurrence, mass loadings and removal of compounds of emerging concern in the Slovene aqueous environment and environmental risk assessment☆

Marjeta Česen [a, b, *], David Heath [a, b], Marko Krivec [c], Janez Košmrlj [c], Tina Kosjek [a, b], Ester Heath [a, b]

[a] Department of Environmental Sciences, Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
[b] Jožef Stefan International Postgraduate School, Jamova cesta 39, 1000 Ljubljana, Slovenia
[c] Department of Chemistry and Biochemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, 1000 Ljubljana, Slovenia

A R T I C L E I N F O

Article history:
Received 2 February 2018
Received in revised form
4 June 2018
Available online 26 June 2018

Keywords:
Compound of emerging concern
Transformation product
Occurrence
Removal
Risk assessment

A B S T R A C T

This study reports the development of a multi-residue method for determining 48 compounds of emerging concern (CEC) including three diclofenac transformation products (TP) in Slovenian wastewater (WW) and surface water (SW). For solid-phase extraction (SPE), Oasis™ Prime cartridges were favoured over Oasis HLB™. The validated method was then applied to 43 SW and 52 WW samples collected at nine locations. Ten bisphenols in WW and 14 bisphenols in SW were traced in Europe for the first time. Among all of the 48 targeted CEC, 21 were >LOQ in the influents and 20 in the effluents. One diclofenac TP was also quantified in WWs (3.04–78.1 ng L^{-1}) for the first time. As expected, based on mass loads in the wastewater treatment plant influents, caffeine is consumed in high amounts (105,000 mg day^{-1} 1000 $inhab.^{-1}$) in Slovenia, while active pharmaceutical ingredients (APIs) are consumed in lower amounts compared to other European countries. Removal was lower in winter in the case of four bisphenols (17–78%), one preservative (36%) and four APIs (-14–91%), but remained constant for caffeine, one API, two UV-filters and three preservatives (all >85.5%). Overall, a constructed wetland showed the lowest (0–80%) and most inconsistent removal efficiencies (SD > 40% for some CECs) of CECs including caffeine, two UV-filters, two preservatives and two APIs compared to other treatment technologies. The method was also able to quantify Bisphenol S in SW (<36.2 ng L^{-1}). Environmental risk was assessed *via* risk quotients (RQs) based on WW and SW data. Two UV-filters (oxybenzone and dioxybenzone), estrone and triclosan, despite their low abundance posed a medium to high environmental risk with RQs between 0.282 (for HM-BP) and 15.5 (for E1).

1. Introduction

Half of the world's population will be living in water-stressed areas by 2025 due to increasing population and limited water resources. This means that careful management of water resources, including control over chemical pollution, is urgently required (World Health Organisation, 2017). Compounds of emerging concern (CEC), which are released into the aquatic environment continuously, pose a threat to aquatic organisms (Baalbaki et al., 2016). These compounds include active pharmaceutical ingredients (APIs), personal care products (PCPs), "life-style" products such as caffeine (CAF), food additives and industrial chemicals like bisphenol A (BPA), which have been extensively studied in surface waters (SW) and wastewaters (WW) globally (Reemtsma et al., 2006; Terzić et al., 2008; Bueno et al., 2012; Verlicchi et al., 2012; Loos et al., 2013; Meffe and de Bustamante, 2014; Robles-Molina et al., 2014; Birch et al., 2015; Baalbaki et al., 2016; Fairbairn et al., 2016; Meador et al., 2016; Petrie et al., 2016; Archer et al., 2017; Stipaničev et al., 2017). Their main source is WW from wastewater treatment plants (WWTPs) and animal elimination of veterinary APIs and hormones (Boxall, 2012; Bueno et al., 2012). So far, studies have focused mainly on the parent compounds, while metabolites and transformation products (TPs) are rarely

☆ This paper has been recommended for acceptance by Klaus Kummerer.

* Corresponding author. Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia.
E-mail address: marjeta.cesen@ijs.si (M. Česen).

https://doi.org/10.1016/j.envpol.2018.06.052
0269-7491/

investigated (Soares et al., 2008; Petrie et al., 2015; Hamza et al., 2016; Naidu et al., 2016).

The occurrence of CEC in the environment cannot be generalised over Europe and regional case studies, evaluating the temporal and spatial occurrence of CEC, are essential to assess pollution sources. This lack of data can be correlated to current EU regulation regarding SWs and WWs. The EU Water Framework Directive (WFD) establishes a list of 45 priority compounds for which Environmental Quality standards (EQS) in SWs have been set with an additional 17 compounds included on Watch list that are to be monitored within the EU region (Stipaničev et al., 2017; EU Decision 495/2015). At the moment, only certain CEC appear on these two lists, including nonylphenols (Priority list) and APIs and hormones (Watch list) although other contaminants also have the potential to affect aqueous biota (EU Decision 495/2015; Meffe and de Bustamante, 2014; Robles-Molina et al., 2014; Loos et al., 2013).

To determine large numbers of CEC in SW and WW samples, validated, rapid, robust, cheap, and greener analytical methods, which typically include solid-phase extraction (SPE) followed by either liquid or gas chromatography coupled to mass spectrometry (LC-MS or GC-MS) are needed (Robles-Molina et al., 2014; Petrie et al., 2016). Such methods will, along with risk assessment, enable the identification of the most potent contaminants and their inclusion on the WFD Watch list and/or Priority list.

The aim of this study was to develop an analytical method for determining the following groups of CEC in WW and SW (Table 1): Endocrine disrupting compounds (hormones and industrial chemicals - bisphenols); UV-filters used in personal care products (benzophenones and others); APIs (analgetic, antiepileptic and anti-anxiety drugs along with their selected metabolites/TPs); Preservatives used in food and/or cosmetics (parabens and triclosan; TCS) and Others (CAF and the herbicide mecoprop; MEC). Individual compounds were chosen based on a review of the available literature, which revealed CEC of high use/consumption (e.g. analgetics, BPA, certain parabens and UV-filters) or low, in certain cases even not invetigated, presence in the aquatic environment (e.g. other bisphenols, UV-filters and banned parabens, the selected TPs of APIs). The developed and validated method was then used to analyse Slovene SW and WW samples to fill the existing data gaps for Central Europe region and to assess the temporal and spatial variations in CEC mass loads. Our final aim was to determine the removal efficiency of WWTP technologies and to use the occurrence data to perform an environmental risk assessment (ERA).

2. Experimental

2.1. Reagents, standards and materials

Information on reagents, solvents and analytical standards (Table 1) are available in the Supplementary Information (SI-I). The standards of DF transformation products (DFtp1-3) were custom synthesised and are also described in details in SI-I along with surrogate standards. These compounds have been shown to be formed during wastewater treatment, e.g. biodegradation (Osorio et al., 2014), advanced catalytic dechlorination (Gusseme et al., 2012) and under sunlight (Agüera et al., 2005; Gusseme et al., 2012), respectively. The cartridges for SPE were Oasis HLB Prime and Oasis HLB both obtained from Waters (Massachusetts, USA).

2.2. Sampling

Samples of WW from nine Slovene WWTPs and receiving SWs (rivers) were collected (Table 2). The WWTPs differed in size (population equivalents; P.E.) and treatment technology and in the received WW, which varied in organic loadings (COD: 155–1044 mg O_2/L; SI-II). Additional sampling information is given in SI-II. To assess seasonal variations in CEC mass loading and treatment removal efficiency, samples of WW were collected in Summer, Autumn and Winter (August 2016 to February 2017; SI-II). At the WWTP Rakitna, samples were collected only twice (Summer, 2016 and Winter, 2017). With the exception of the WWTP Rakitna (2-h time-proportional samples), all 52 samples of influents and effluents (V = 1) were collected during a dry period (24-h time-proportional samples). In addition, 43 grab SW samples (V = 1 L) were collected downstream from each WWTP outflow in Summer (Table 2). In Autumn and Winter, SW was sampled also upstream of the WWTP discharges. All samples were filtered through a glass-microfiber (Machery Nagel, Düeren, Germany) and a 0.45 μm

Table 1
Commercial names and abbreviations of the studied CEC.

Commercial name	Abbreviation	Commercial name	Abbreviation
Bisphenol A	BPA	4-hydroxybenzophenone	H-BP
Bisphenol AF	BPAF	Oxybenzone	HM-BP (BP3)
Bisphenol AP	BPAP	Dioxybenzone	DHM-BP (BP8)
Bisphenol B	BPB	2-ethylhexyl 4-methoxycinnamate	CNM
Bisphenol BP	BPBP	Carbamazepine	CBZ
Bisphenol C	BPC	Clofibric acid	CLA
Bisphenol Cl	BPCL2	Diazepam	DZP
Bisphenol E	BPE	Diclofenac as sodium salt	DF
Bisphenol F	BPF	{2-[(2,6-Dichlorophenyl)amino]-5-nitrophenyl}acetic acid	DFtp1
Bisphenol FL	BPFL	2-anilinophenylacetic acid	DFtp2
Bisphenol M	BPM	2-[(2-Chlorophenyl)amino]-benzaldehyde	DFtp3
Bisphenol P	BPP	Ibuprofen	IB
Bisphenol PH	BPPH	Ketoprofen	KP
Bisphenol S	BPS	Naproxen	NP
Bisphenol Z	BPZ	Methyl paraben	MePB
4,4′-bisphenol	BP4,4	Ethyl paraben	EtPB
2,2′-methylenediphenol	BIS2	Propyl paraben	PrPB
4,4′-dihydroxydiphenyl ether	DHDPE	Iso-Propyl paraben	IPrPB
4-cumylphenol	HPP	Butyl paraben	BuPB
4-nonyl-phenol	NONPH	Iso-Butyl paraben	IBuPB
Estrone	E1	Benzyl-paraben	BePB
17β-estradiol	E2	Irgasan, triclosan	TCS
17α-ethynyl estradiol	EE2	Caffeine	CAF
2,4-dihydroxybenzophenone	DH-BP (BP1)	Mecoprop	MEC