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The occurrence of contaminants of emerging concern in Slovenian and Croatian wastewaters and receiving Sava river☆

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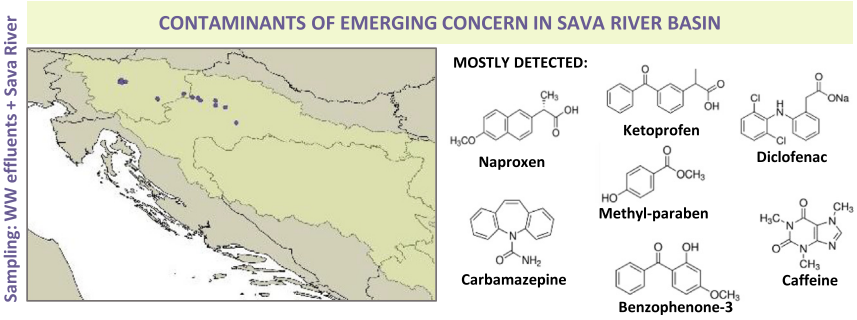
HIGHLIGHTS

- Bisphenols E and B were detected >LOQ in European SW for the first time.
- Bisphenols AP, CL2, P and Z were detected >LOQ in European WW for the first time.
- Correlation between CEC mass loads in Sava River and corresponding WWs was observed.
- Overall CEC contamination downstream the Sava River was confirmed.
- All SWs with detected HM-BP, IB or BePB posed at least a medium environmental risk.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the occurrence of 48 contaminants of emerging concern (CECs) in wastewater effluents from three Slovenian and three Croatian waste water treatment plants (WWTPs) representing the major inputs into the upper and middle course of the Sava River and simultaneously in the Sava River itself. Two sampling campaigns were carried out (May and July 2017). Samples were extracted using solid-phase extraction and analysed by gas chromatography - mass spectrometry. In effluents, 23 CECs were >LOQ with caffeine and the UV-filter 4-hydroxybenzophenone (H-BP) present in the highest concentrations (<49,600 ng L^{-1} and <28,900 ng L^{-1}, respectively) and most frequently detected (detection frequency; DFr > 83.3%). Bisphenol B and E were detected for the first time in WW from Velika Gorica (May) and Zaprešić (July), respectively. In surface water (SW), 19 CECs were detected >LOQ with CAF again being the most abundant and most frequently detected (DFr = 92.9%). Bisphenols AP, CL2, P and Z were detected >LOQ for the first time in European SW. Active pharmaceutical ingredients naproxen, ketoprofen, carbamazepine and diclofenac; the preservative methyl paraben; CAF and UV-filter HM-BP were the

☆ Bisphenol A (BPA), 2-ethylhexyl 4-methoxycinnamate (CNM), 2-hydroxy-4-methoxybenzophenone (HM-BP), 2,2′-methylenediphenol (BIS2), 4,4′-biphenol (BP4,4), 4,4′-dihydroxydiphenyl ether (DHDPE), bisphenol AF (BPAF), bisphenol AP (BPAP), bisphenol C (BPC), bisphenol E (BPE), bisphenol F (BPF), bisphenol FL (BPFL), bisphenol M (BPM), bisphenol BP (BPBP), bisphenol P (BPP), bisphenol S (BPS), bisphenol Z (BPZ), 4-cumylphenol (HPP), 2,4-dihydroxybenzophenone (DH-BP), estrone (E1), 17β-estradiol (E2), 17α-ethynyl estradiol (EE2), CAF, 4-hydroxybenzophenone (H-BP), 2,2′-dihydroxy-4-methoxybenzophenone (DHM-BP), clofibric acid (CLA), ibuprofen (IB), naproxen (NP), ketoprofen (KP), diclofenac (DF) and its three transformation products (TPs), diazepam (DZP), methyl paraben (MePB), ethyl paraben (EtPB), propyl paraben (PrPB), butyl paraben (BuPB), isobutyl paraben (iBuPB), benzyl paraben (BePB), nonylphenol (NONPH) and triclosan (TCS), carbamazepine (CBZ), iso-propyl paraben (iPrPB), bisphenol B (BPB), mecoprop (MEC), bisphenol Cl (BPCL2), bisphenol PH (BPPH), wastewater (WW), wastewater treatment plant (WWTP), surface water (SW), contaminant of emerging concern (CEC), active pharmaceutical ingredients (APIs), personal care products (PCPs), risk quotient (RQ), environmental risk assessment (ERA), transformation products (TPs), solid-phase extraction (SPE), N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA), N-(tert-butyldimethylsilyl)-N-methyltrifluoroacetamide with 1% tert-butyldimethylchlorosilane (MTBSTFA with 1% TBDMCS), Predicted No-Effect Concentration (PNEC), assessment factor (AF), which is 1000 in the case of acute toxicity. When using the data for chronic toxicity, PNEC derives from the ratio between the No-Effect Concentration (NOEC), detection frequency (DFr), limit of quantification (LOQ).

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Mass loads
Risk assessment

most abundant CECs in SW and WW. An increasing trend in the total CEC load downstream was observed, indicating the cumulative effects of individual sources along the river. The Croatian Zaprešić, Zagreb and Velika Gorica WWTP effluents contributed the most towards the enhanced loads of the CECs studied probably due to their size or insufficient treatment. HM-BP was the only compound found at a levels exhibiting high environmental risk (RQ = 1.13) downstream from Ljubljana and Domžale-Kamnik WWTPs. Other SW samples that contained HM-BP, ibuprofen (API) and/or benzyl paraben (preservative) posed a medium risk to the environment. The results suggest the need for further monitoring of CECs in the Sava River Basin.

1. Introduction

Contaminants of emerging concern (CEC) occur in the environment on a global scale and encompass active pharmaceutical ingredients (APIs), personal care products (PCPs), life-style compounds like caffeine (CAF) and other substances, that appear in the environment due to human activities and have the potential to harm biota and humans (Sauvé and Desrosiers, 2014). Their widespread occurrence in wastewaters (WWs) and surface waters (SWs) has been continuously reported. In addition, some CECs with known effects on aqueous biota remain recalcitrant during WW treatment and under environmental conditions and new CECs with unknown effects are continually being reported (Bueno et al., 2012; Petrie et al., 2016).

It is hard if not impossible to monitor the presence of all potentially harmful compounds in the environment and even harder to control their release into the aquatic environment, e.g. with appropriate treatment technologies in wastewater treatment plants (WWTPs). Therefore, providing data on CEC occurrence is essential and serves as a basis for prioritizing candidates that must be monitored and consequently regulated in-terms of emissions. This has already been done for certain CECs in the EU by establishing the WFD Watch list (CECs that are to be monitored) and Priority list (CECs for which Environmental Quality Standards in SWs have been set) (EU Decision 495, 2015; Tousova et al., 2017; Sousa et al., 2018). However, many areas within Europe remain to be investigated in terms of environmental CEC occurrence. An example is Central and South Europe, where the Sava River, the largest tributary (by flow) of the Danube River flows. The Sava River springs in the Slovenian mountains and travels a distance of 945 km passing through Croatia, Bosnia and Herzegovina eventually to join the Danube in Serbia. Since the river supplies the groundwater aquifers, which are an important source of potable water for inhabitants living in this area, it is important to monitor its quality especially on account of surrounding agricultural and industrial activities (Milačič et al., 2017). So far, there have been several attempts to perform a comprehensive region-specific prioritization of contaminants in the Sava River, which covers a wide spectrum of important compounds like polyaromatic hydrocarbons (PAH) and CECs such as APIs (Smital et al., 2013; Tousova et al., 2017). However, given the growing number of CECs, gaps in the data are inevitable, for example data for benzyl paraben, BPA and its alternatives are missing. The aim of this study was to collect and analyse SW and WW from WWTPs at locations in Slovenia and Croatia along the Sava River and analyse them for 48 CECs including APIs and their selected transformation products (TPs), preservatives, bisphenol compounds, and estrogenic hormones. In addition, an environmental risk assessment based on the concentrations of CECs detected in Sava River was performed for the first time in the Sava River catchment.

2. Experimental

2.1. Materials for organic analysis

Information on reagents, solvents and analytical standards of CECs and surrogate standards used for the chemical analysis is given in detail in the Supplementary Information (SI-I).

2.2. Sampling

Samples of WW effluent from three Slovenian and three Croatian WWTPs were collected during a dry period on two occasions (23rd May and 12th July 2017). The WWTPs differ in size (population equivalents; P.E.), treatment technology, receiving WW and daily flow rates (Table 1). Additional information on each WWTP is given in SI-II.

With the exception of grab WW samples from WWTP-DK (in May), WWTP-ZG (in July) and Zaprešić (May and July), all samples were collected as 24 h time-proportional samples.

The Sava River *prior* to or after WW discharges was sampled at seven locations (three in Slovenia and four in Croatia) on the same day as the equivalent WW samples (Table 1, Fig. 1). The Slovenian samples were collected *prior* to the WWTP-LJ discharge (Ljubljana), after WWTP-LJ and WWTP-DK discharge (Jevnica) and *prior* to the Krka River tributary, into which the WWTP-NM discharges its effluent (Brežice). The First Croatian sample was collected after the Krka River tributary (Otok Samoborski), the second after the discharge point of the WWTP-Zaprešić and the Krapina River tributary (Jankomir), the third after WWTPs ZG and Velika Gorica discharge points (Oborovo) and the fourth after the city of Sisak and the tributary of the Kolpa River (Crnac). All SWs were collected as a grab samples. The daily flows of Sava River used for mass load calculations are given in SI-II. Clearly, dilution is an important process contributing to the reduction of contaminant levels in the surface waters. The hydraulic dilution factors of wastewaters after the discharge into the Sava river varied considerably from 35 to >1000, depending on the location. As expected, the lowest factors in in the studied period were found downstream of the largest cities Zagreb and Ljubljana (35 to 55 and 92 to 110, respectively).

All samples were filtered through glass-microfiber (Machery Nagel, Düeren, Germany) and then cellulose nitrate membrane filters (0.45 μm; Sartorius Stedim Biotech GmbH, Göttingen, Germany) and stored at −20 °C *prior* to analysis.

2.3. Sample preparation and analysis

Table 2 shows the procedure for solid-phase extraction (SPE). Each SW and WW sample was pre-concentrated using an Oasis HLB Prime cartridge (3 cc, 60 mg, Waters, Massachusetts, USA). After loading, the sorbent was washed and/or dried under vacuum (−10 mmHg, 20 min) and eluted with the optimal solution (Table 2). The solvent was evaporated under nitrogen *prior* to derivatization.

The dried extracts were then halved (Group A: CAF, HPP, NONPH, BIS2, BPAF, DFtp3, H-BP, HM-BP, DHDPE, DH-BP, BP4,4, BPF, BPE, BPA, DHM-BP, BPC, BPB, CNM, BPCL2, BPZ, E1, BPS, E2, BPAP, EE2, BPM, BPP, BPBP, BPPH, BPFL; Group B: MePB, CLA, EtPB, iPrPB, IB, MEC, PrPB, iBuPB, BuPB, DFtp1, NP, TCS, KP, BePB, DZP, CBZ, DF, DFtp2). Group A was derivatized with 50 μL *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) in 50 μL pyridine at 60 °C for 1 h, whereas Group B was silylated with 30 μL *N*-(*tert*-butyldimethylsilyl)-*N*-methyltrifluoroacetamide with 1% *tert*-butyldimethylchlorosilane (MTBSTFA with 1% TBDMCS) in 70 μL ethyl acetate at 60 °C for 16 h. Samples were analysed using GC–MS (Agilent 7890B/5977A, USA). Chromatographic separation was achieved on a DB-5 MS capillary column (30 m × 0.25 mm × 0.25 μm; Agilent, USA) with helium as the