Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.24108

159 (2019) 110–120
August

Removal of pharmaceutical residues from wastewater by woodchip-derived biochar

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Received 20 October 2018; Accepted 8 March 2019

ABSTRACT

The aim of this study was to evaluate the effectiveness of wood-derived biochar for the removal of 18 pharmaceutical compounds (PCs) from untreated municipal wastewater (WW). The WW samples were analyzed by an HPLC-Q-Orbitrap-HRMS method. Two aliquots of WWs were incubated with biochar sorbent for 2 h and 7 d. The highest absolute removal of PCs was achieved for ibuprofen and caffeine (2.6 and 13.2 mg L^{-1} after 7 d, respectively). The highest removal efficiency after 2 h incubation was detected for erythromycin (72.0% ± 12.7 %) while lower degree of removal was observed for other compounds with much higher initial concentrations. The results indicated that a 2 h sorption process on biochar may be insufficient and 7 d incubation is preferred for quantitative removal of xylazine, metoprolol, and azithromycin. However, the sorption of ketoprofen, diclofenac, ibuprofen, sulfamethoxazole, and simvastatin on biochar was more effective during the first 2 h than during the following 7 d. Regression analysis revealed a strong correlation (R^2~0.9) between the absolute amounts of the removed PCs and their initial concentrations. In this respect, the removal of the last traces of PCs from WW is expected to present technological challenges.

Keywords: Filtration media; Pharmaceutical residues; Wastewater; Woodchip-derived biochar

1. Introduction

The presence of pharmaceutical compounds (PCs) in water presents a public health concern and also a challenge to the analytical chemistry community. Effective removal of PCs from wastewaters (WWs) is an emerging objective for environmental technologies. The PCs present in WWs include a variety of polar organic molecules, which can undergo chemical transformations during the treatment process [1–3]. Reungoat et al. [4] described the removal of organic micropollutants from WWs in 6 stages, i.e., denitrification, pre-ozonation, coagulation/flocculation/dissolved air flotation and filtration (DAFF), main ozonation, activated carbon filtration, and final ozonation for disinfection. A combination of these stages can be used to sufficiently optimize the treatment process.

Porous materials, such as biochar, zeolites, metal-organic frameworks, covalent organic frameworks, polymers of intrinsic microporosity, zirconium-based porous materials, and conjugated microporous polymers have been recently tested in terms of their suitability for the removal of PCs from water [5]. Kah et al. [6] reviewed the use of such carbonaceous sorbents as carbon nanotubes, graphene, biochar, and activated carbon for the sorption of ionizable organic compounds, including PCs. The mechanisms relevant to the sorption of PCs include low-barrier, charge-assisted hydrogen bonds, van der Waals and cation-π interactions, with a key role attributed to pH and ionic strength [6,7]. The practical applicability of these sorbents may be limited by their

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Presented at the 6th International Conference on Sustainable Solid Waste Management (NAXOS 2018), 13-16 June 2018, Naxos Island, Greece.

sorption capacity for anions and poor mechanical properties [8]. Hybrid technologies have been recently used to develop modified biochars (BCs), e.g., by treatment of plant biomass with carbon nanotube suspensions prior to pyrolysis [9] or by adding iron for obtaining magnetically separable BCs [10–12].

The adsorption of PCs on BCs may be affected by the pH, contact time, temperature, sorbent particle size and amount, as well as by the properties of the particular PCs [13,14]. Experiments regarding the removal of triclosan from secondary WW effluent using wood-based BC in continuous flow-through columns indicated adsorption of triclosan by BC, but to a lesser extent than by activated carbon [15]. Naghdi et al. [16] studied the effect of pinewood BC-derived nanoparticles for the sorption of carbamazepine and showed a positive role of increasing pH values and benefits from the addition of surfactants [16].

One of the main factors influencing the sorption of PCs on biochars is the pH value, with a broad range of optimum values reported by different authors, e.g., pH = 3 [17,18]; pH = 4 [19,20], pH = 5.5 [21,22], pH = 12 [23]. The optimum pH value depended on the biochar feedstock and its pyrolysis conditions, as well as the characteristics of the PCs. In turn, the pH values had little effect on the removal of trichloroethylene, while the pyrolysis temperature influenced the sorption capacity of BCs due to differences in the surface areas, aromaticity, and the presence of non carbonized fraction [24]. The adsorption capacity of rice-straw-derived biochar for tetracycline depended on the pyrolysis temperature, as shown by Wang et al. [21]. Liu et al. [25] reported that high temperature biochars (≥500°C) exhibited higher sorption capacity for microcystin-LR toxin. In turn, Oh et al. [26] concluded that the removal of halogenated phenols, triclosan, and ibuprofen by biochars did not depend on the pyrolysis temperature. The authors compared BCs produced from fallen leaves, rice straw, corn stalk, coffee grounds, and other biological solids [27].

An additional key factor affecting the removal of PCs by BCs is the composition of WW. Comparing the sorption efficiency of BC for phenolic endocrine disrupting chemicals from different media showed the best performance in water, followed by sewage water treated in a membrane bioreactor and synthetic wastewater [18]. The adsorption of PCs may be inhibited by the presence of suspended solids, soluble organic compounds, colloids, and certain ions, as well as by the formation of precipitates on the sorbent surface [27,28].

Despite the large volume of scientific data available on the sorption of PCs from WW, there is still a lack of information regarding the removal of multiple contaminants, which occur in real WWs at nanomolar concentrations.

The aim of this study was to evaluate the effectiveness of wood-derived biochar for the removal of 18 PCs from untreated WW, sampled at the municipal WW treatment plant "Daugavgriva" near Riga, Latvia.

2. Materials and methods

2.1. Wastewater

The WW samples were collected in May 2016 from the untreated WW basin of the "Daugavgriva" WW treatment plant. All samples were collected in pre-cleaned 1 L amber glass bottles and kept at +4°C during the transportation and then at −20°C until the experiments. The WW samples had the following characteristics: pH 6.7–6.9; biological and chemical oxygen demand up to 200 and 350 mg L^{-1}, respectively.

2.2. Biochar sorbents

The feedstock for the preparation of BC sorbents consisted of shattered wooden boxes (10%) and disposable wooden pallets (90%). The BC was produced at the maximum pyrolysis temperature of 725°C with a residence time of 1 h, using continuous flow with constant heating. The generated producer gas had a temperature of 460°C. The bulk density of the BC was 0.16 g cm^{-3}; pH 7.39; BET surface area 3.72 m^2 g^{-1}; total pore volume 2.83 cm^3 g^{-1}; micropore volume 1.53 cm^3 g^{-1}; pore size 25.4 nm [29].

2.3. Sorption experiments

The removal of 18 PCs from WWs has been investigated under batch mode, taking into consideration the specific goal of this study, namely, behavior of multiple contaminants occurred in real WWs at nanomolar concentrations. The BC was sieved to obtain the particle fraction of >2 mm, weighed (4.00 ± 0.01 g) into 50 mL screw-cap conical polypropylene centrifuge tubes, rinsed with deionized water, and autoclaved at 1 bar pressure for 15 min. The WW samples prior to the incubation were filtered and aerated for 15 min. The experiment was performed in triplicate with WW samples (40 mL per tube) at 37°C. To avoid the photodegradation of PCs, the experiments were performed in the dark. The first stage of the experiment was run for 2 h and after this period the liquid phase was discarded. New portions of WW (40 mL) were added to the same tubes containing BC and the incubation was performed at 37°C for 7 days with agitation once per day. Two incubation periods characterized by the same initial concentrations of PCs were expected to reveal the both, sorption and biodegradation phenomena. The WWs treated in this way were sampled after 2 h and 7 d, and were immediately frozen until analysis.

2.4. HPLC analysis of WW samples

The WW samples were analyzed by applying the HPLC-Q-Orbitrap-HRMS method described in our previous study [30]. Detailed information on the analytical procedure is given in the Supplement 1. Instrumental limits of quantification (LOQ) and recovery for PCs used in this study are shown in Table S1. The formulas, molecular structures, and the therapeutic classes of the analyzed PCs are summarized in Table S2.

2.5. Statistical analysis

The experiments were performed in triplicate. Each data point presented in the figures is expressed as the mean value ± standard deviation. The differences between the treatments were assessed by the Student's t test and one-way analysis of variance (one-way ANOVA). The coefficient of determination R^2 of the linear regression model was estimated using Microsoft Excel.

3. Results

3.1. Removal of PCs from WWs using biochar

The concentrations of PCs in WWs were measured after incubation with BC for 2 h and 7 d. The highest absolute removal of PCs was achieved for ibuprofen and caffeine (2.6 and 13.2 mg L^{-1} after 7 d, respectively) (Fig. 1(a)). The removed amounts of other 16 PCs were considerably smaller due to their lower occurrence, with the lowest absolute amount observed in the case of erythromycin (18.6 and 17.7 ng L^{-1} after 2 h and 7 d, respectively). Moreover, the removal of naproxen after 2 h as well as ketoprofen and diclofenac after 7 d showed negative values (Fig. 1(b)).

The removal efficiency (RE) for each PC varied considerably among the tested compounds (Fig. 1(c)). The highest RE after 2 h incubation was detected for erythromycin, i.e., 72.0% ± 12.7%, while other compounds with much higher initial concentrations demonstrated lower RE values. In particular, the initial concentrations of diclofenac, ibuprofen, and caffeine were 50, 400, and 800 times higher on average, compared with erythromycin (Table S3), and the RE of those more abundant compounds after 2 h incubation reached only 22.7%, 37.3%, and 22.0%, respectively (Fig. 1(c)). Apparently, the sorption capacity of the BC was quite limited and all sorption sites for the particular PC molecules were occupied. The experiment used two aliquots of WWs for the incubation during 2 h and 7 d without changing the sorbent. The results of 7 d incubation of raw WWs with BC sorbent showed notable differences in the amounts of the removed PCs, compared with the previous 2 h incubation (Fig.1(c)). For example, xylazine, metoprolol, azithromycin, and trimethoprim after 7 d incubation were removed with moderate efficiency (RE ≥90%), while the previous 2 h incubation resulted in lower 60%–70% RE for these compounds.

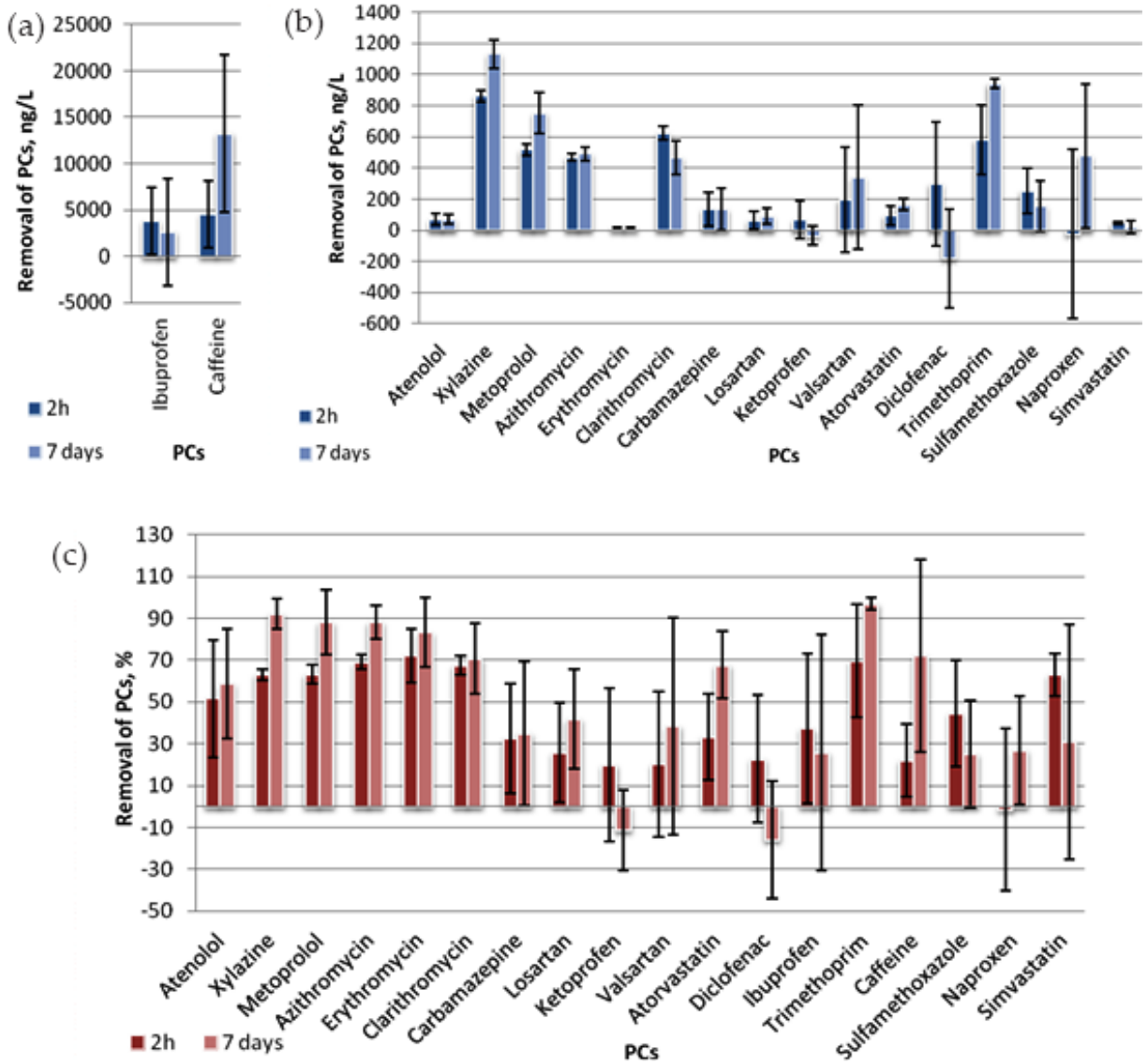

Fig. 1. Removal of PCs from municipal WWs by sorption on biochar during 2 h and 7 d incubation. (a) the removed amounts of ibuprofen and caffeine; (b) the removed amounts of 16 PCs with the removed amounts below 1,200 ng L^{-1}; (c) the RE of 18 PCs in %. The pH value after 7 d incubation was 8.2 ± 0.3.

The differences in RE during the two incubations for xylazine, metoprolol, and azithromycin were statistically significant ($p < 0.05$). The RE for caffeine increased from 22.0% in the first incubation to 72.2% in the second incubation, however, this difference was not statistically significant ($p > 0.05$) (Fig. 1(c)). The other tested compounds also differed in their RE among 2 h and 7 d incubations, but the high standard deviation of the measurements in three independent sorption batches negated the statistical significance of this observation ($p > 0.05$).

The obtained results indicated that sorption over a 2 h period may be insufficient for optimal removal of PCs under the tested conditions. Furthermore, additional removal of PCs during 7 d incubation was probably caused by biodegradation phenomena.

3.2. The coefficient of determination R^2 between the removal efficiency and physico-chemical characteristics of PCs

Our design of experiments involving simultaneous determination of 18 PCs in real WWs after incubation with BC for 2 h and 7 d provided large amount of data, which was subjected to statistical treatment by regression analysis. It was hypothesized that the sorption of PCs on woodchip-derived BC may depend on the molecular characteristics of PCs (Table S4). However, no strong correlation was found between the removal of PCs and their molecular characteristics. For the absolute amounts of the removed PCs, the highest R^2 (0.27) was attributed to the H donor bond count, which was expressed in nmol L^{-1} after 2 h incubation (Table 1). As for the removal efficiency after 2 h incubation, three parameters, i.e., the H acceptor bond count, the topological polar surface area, and the H donor bond count showed relatively high coefficients of determination, which reached 0.34, 0.30, and 0.27, respectively (Table 1). At the same time, the absolute removed amounts of PCs were found to depend on the initial concentration of these compounds in WW with the coefficient of determination $R^2 = 0.9$ (Table 1).

4. Discussion

This study showed notable differences in the behavior of 18 PCs in the presence of woodchip-derived BC, which may be affected by a range of factors, including the physicochemical characteristics of the sorbent and PCs, as well as the extraction medium.

Among the specific properties of BCs, a comparatively high pH is common. The role of pH for efficient removal of PCs has been discussed by many authors. Highly acidic conditions (pH 2) were reported to facilitate the sorption of 4-nitroaniline, salicylic acid, benzoic acid, and phthalic acid [31], as well as ibuprofen and ranitidine hydrochloride [32,33] by BCs. Conversely, the maximum adsorption capacity of three different BCs toward metronidazole was observed at pH 12, while the adsorption capacity varied slightly over the pH range from 4 to 10 [22]. In the case of cationic sulfonamides and chloramphenicol, Ahmed et al. [34] proposed two different sorption mechanisms at pH <2.0 and pH >7.0, namely, (i) π-π electron-donor-acceptor interactions and (ii) H-bond formation and proton exchange with water. In the present study, the average initial pH values of WW and BC were 6.8 and 7.4, respectively. The final pH values after 7 d incubation were 8.2 ± 0.3. Overall, the pH and other conditions for the sorption of specific PCs were not optimized.

Our experiments were designed to model the interactions of multi-compound pharmaceutical contamination at nanomolar concentrations with BC, using real municipal WW. For the reasons of technological practicality, the incubation time should be an important factor. The removal of PCs was compared after two applications of WW aliquots to the same portion of BC sorbent for the duration of 2 h and 7 d. The removal of five compounds (ketoprofen, diclofenac, ibuprofen, sulfamethoxazole, and simvastatin) among the tested 18 PCs was notably decreased during the second (7 d) stage of incubation (Fig. 1). This pointed to a more rapid sorption process and/or limited sorption sites on the BC for these compounds, as compared with the other 12 PCs tested.

Table 1
Coefficient of determination R^2 between the removed amounts of PCs and their physicochemical characteristics

	Removed PCs (ng L^{-1})		Removed PCs (nmol L^{-1})		Removal efficiency (%)	
	2 h	7 d	2 h	7 d	2 h	7 d
Molecular weight (g mol^{-1})	0.09	0.07	0.13	0.08	0.18	0.10
Heavy atom count	0.10	0.08	0.14	0.09	0.20	0.13
Solubility in water (mg L^{-1})	0.02	0.02	0.01	0.01	0.02	0.03
Dissociation constant (pKa)	0.01	0.00	0.02	0.02	**0.22**	**0.25**
Complexity	0.07	0.05	0.10	0.05	0.20	0.11
Topological polar surface area	0.08	0.04	0.11	0.05	**0.30**	**0.21**
H donor bond count	0.17	0.17	**0.27**	0.17	**0.27**	0.17
H acceptor bond count	0.06	0.04	0.09	0.05	**0.34**	**0.21**
Rotatable bond count	0.07	0.08	0.09	0.12	0.02	0.11
XlogP3	0.10	**0.23**	0.12	**0.23**	0.07	0.09
Melting point	**0.20**	0.17	**0.23**	**0.2**	0.07	0.11
log Kow	0.03	0.00	0.02	0.00	0.07	0.15
Initial concentration (ng L^{-1})	**0.91**	**0.89**	**0.93**	**0.89**	0.07	0.00
Initial concentration (nmol L^{-1})	**0.90**	**0.90**	**0.93**	**0.90**	0.07	0.00

Bold values represent the coefficient of determination $R^2 \geq 0.2$

A comparison of adsorption kinetics for some PCs on different BCs showed equilibration periods ranging from 2 min to 20 h [31–33,35,36]. A two-stage mechanism was proposed for the sorption of five acidic PCs (naproxen, ibuprofen, ketoprofen, aspirin, and salicylic acid) on rice straw BCs [7]. The predominant mechanism involved sorption on the external surface and diffusion of the adsorbed molecules into macro- and mesopores. The first stage was followed by diffusion of the adsorbed molecules into micropores. At relatively high initial pH values these PCs mainly exist as anionic species, while the surfaces of BC also gain negative charge, which may result in electrostatic repulsion between the sorbent and PC, reducing the possibility of hydrogen bonding [7].

Apart from the pH value, the composition and concentration of compounds to be adsorbed play an important role in sorption kinetics. The simultaneous presence of chemically diverse molecules in real WWs obviously results in competitive sorption processes. A competitive effect between caffeine and the background organic matter was shown for micro- and mesoporous activated carbons [37]. Ketoprofen and triclosan in a binary mixture competed for the adsorptive capacity of BCs, where π-π interactions were proposed as the main mechanism [38].

A special attention should be paid to the negative values of RE when the concentration of PCs increases after the treatment process. This phenomenon has been already described in previous studies [29,39–41]. We attribute it to the removal of naproxen from the pretreated BC after 2 h incubation, as well as ketoprofen and diclofenac after 7 d incubation (Figs. 1(b) and (c)). It is likely that physicochemical changes during the treatment, as well as microbial activity may be responsible for these phenomena.

One of the main objectives for our experiments was to study sorption processes at low concentrations of PCs. Wang et al. [42] reported about the sorption of 14 PCs at comparatively low concentrations on rice straw BC. It was shown that the sorption was promoted by the porosity of sorbent and suppressed by the electron-donating nature of PC molecules [41]. In this respect, the effects of 12 molecular characteristics on the removal of PCs were evaluated by performing regression analysis. As shown in Table 1, negligible R^2 values were generally obtained for the selected characteristics. Slightly increased correlation was found between the removed amounts of PCs and the number of H donor moieties in the molecule (R^2~0.3). In addition, the RE slightly correlated with the number of H acceptor moieties and the topological polar surface area of the PC molecules (R^2~0.3). Regarding the chemical properties of PCs, it should be noted that the solubility and polarity of these compounds could be affected even by small changes of chemical structure, thus resulting in a great variation in REs [43]. Our results indicated no correlation between the removal of PCs and their water solubility, while the topological polar surface area of PC molecules was shown to influence the RE (Table 1). Furthermore, the dissociation constant exhibited a comparatively strong effect on the RE (R^2~0.22–0.25) for both 2 h and 7 d incubation periods. Our data are in agreement with Wu et al. [38] who reported that the degree of molecular dissociation of PCs should be considered in the case of multicomponent systems.

At the same time, strong correlation was observed between the absolute amounts of the removed PCs and their initial concentrations (R^2~0.9). In this respect, the removal of the last traces of PCs from WW may present the most challenging technological problem. To date, none of the proposed processes can remove all the compounds of concern [4]. Further work is necessary for precisely predicting and tuning the properties of BC sorbents, as well as for evaluating the long-term effects of BC on the stabilization and bioavailability of contaminants [44].

5. Conclusions

The obtained results can be summarized in the following conclusions:

- The experimental setup chosen for this study has revealed some specific sorption behavior of individual PCs in complex mixtures, namely, real WW containing the 18 tested PCs. The incubation of two aliquots of WWs over 2 h and 7 d with the same sorbent showed a significantly enhanced (p <0.05) removal efficiency for xylazine, metoprolol, and azithromycin over 7 d, compared with the 2 h incubation. Otherwise, ketoprofen, diclofenac, ibuprofen, sulfamethoxazole, and simvastatin were better adsorbed on BC during the first 2 h, compared with the following 7 d. Thus, the optimal duration of sorption process should be compound-specific.
- Comparison of twelve molecular characteristics of the tested PCs indicated a slight correlation (R^2~0.3) of the amounts removed by treatment with BC and the number of H donor moieties in the molecule. The RE correlated (R^2~0.3) with the number of H donor moieties, H acceptor moieties, and the topological polar surface area. The utility of other molecular characteristics was not satisfactory.
- Regression analysis revealed a strong correlation (R^2~0.9) between the absolute amounts of the removed PCs and their initial concentrations. In this respect, the removal of the last traces of PCs from WW is expected to present technological challenges.

Acknowledgements

The study was financially supported by the ERDF project 1.1.1.1/16/A/113 "Development of new approaches for wasteless simultaneous production of bioethanol, furfural and other valuable products from local agricultural waste material". Authors are grateful to BlackCarbon, Denmark for supplying the biochar. Authors are grateful to Janis Jaunbergs, Ph.D. for suggested manuscript revisions.

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Supplementary information

1. Supplement 1

1.1. Analytical method for determination of PC residues in WW samples

1.1.1. Preparation of waste water samples

Prior to the solid phase extraction of wastewater samples, Strata X cartridges (Phenomenex, Torrance, CA, USA) were conditioned with methanol (3 mL) and deionized water (3 mL). Before extraction, the WW sample (20 mL) was supplemented with 0.5 M Na2EDTA solution (2 μL) and acetic acid (10 μL) in order to adjust the pH value to 3. The samples were loaded on columns at the approximate flow rate of 1 mL min^{-1} and then the cartridges were dried for 30 min under vacuum, followed by elution with methanol (6 mL). The eluted fractions were then evaporated to dryness under gentle nitrogen stream on a water bath at 40°C. The samples were reconstituted in 80:20 water/methanol (v/v) mixtures (100 μL).

1.1.2. Instrumental analysis

HPLC analysis of WW samples was performed using a Thermo Scientific Accela 1250 system (San Jose, CA, USA). Analytical standards of twenty-four most common multi-class PCs, as reported by the World Health Organization (WHO, 2016) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and Fluka (Buchs, Switzerland).

Chromatographic separation was achieved on a Phenomenex Kinetex C18 analytical column (100 × 2.1 mm, 2.6 μm). The mobile phase consisted of 0.1% formic acid in water (mobile phase A) and 100% MeOH (mobile phase B). A gradient program was used: 20% of mobile phase B was used from 0 to 1.0 min, 20% B to 95% B from 1.0 to 5.0 min, maintained at 95% B from 5.0 to 7.0 min, then decreased back to 20% B from 7.0 to 7.1 min, and finally the column was re-equilibrated with 20% B from 7.0 to 10 min. A 5 μL aliquot of the sample was injected. The column and autosampler temperatures were maintained at 40°C and 4°C, respectively.

Q Exactive™ Orbitrap-HRMS (Thermo Fisher Scientific, Waltham, MA, USA) detector was used to quantify the levels of PCs in the analyzed WW samples. The Q-Orbitrap-HRMS system was equipped with a heated electrospray (HESI II) ionization interface operated in the positive and negative ion modes at the ionization potential of 2.8 V. The heater and capillary temperatures were maintained at 300°C and 250°C, respectively. The following optimized parameters were applied for the gas flow: sheath gas (N_2) 40 arbitrary units (arb), auxiliary gas (N_2) 10 (arb), and S-Lens RF level at 50 (arb). The automatic gain control (AGC) target value was set to 3×10^6, the maximum injection time (IT) was set to 200 ms, and the scan rate was set at 1 scan s^{-1}. The Q-Orbitrap-HRMS system was operated in full scan mode (*m*/*z* 125 to 800) at a mass resolving power of 70,000 FWHM. The targeted MS/MS analysis was performed using a mass inclusion list containing the product ion mass values, collision energies, and the expected retention times of analytes. The Orbitrap spectrometer was operated both in the positive and negative ion modes at 17,500 FWHM. The AGC target value target was set to 2×10^5, the maximum IT was set to 50 ms. The isolation window of the quadrupole for precursors was set at *m*/*z* 2. Collision energies were optimized for each target compound by infusing the working mix standard solution at 10 ng μL^{-1} concentration. The mass tolerance window was set to 5 ppm. The instrument performance and data processing were controlled by Thermo Fisher Xcalibur™ and TraceFinder™ software (Thermo Fisher Scientific).

1.1.3. Performance of the method

The performance of the method was evaluated through the estimation of linearity, selectivity, and accuracy expressed as the percentage of recovery during the extraction, and the precision was expressed as relative standard deviation (RSD). The method was found to be selective by verifying the absence of an analytical signal at the retention time (RT) for the analyte in deionized water. The method showed good linearity with the determination coefficients higher than 0.99, evaluated at five matrix-matched calibration points over the 10–5,000 ng L^{-1} range for all compounds included in the study. The accuracy and precision were evaluated by spiking wastewater samples at 50, 400, and 800 ng L^{-1} levels for five replicates at each level over three days. The mean variation of coefficients for repeatability of the method ranged from 7.0% to 27%.

2. Supplement 2

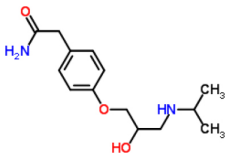
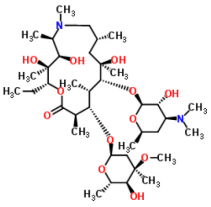
Table S1
Instrumental limits of quantification (LOQ) and recovery for PCs used in this study

Compound	LOQ, (ng L^{-1})	Recovery (%)		
		50 (ng L^{-1})	400 (ng L^{-1})	800 (ng L^{-1})
Atenolol	5	105	101	101
Atorvastatin	5	91	105	110
Azithromycin	10	132	127	118
Caffeine	1	138	128	130
Carbamazepine	0.1	106	99	102
Clarithromycin	0.1	88	92	82
Diclofenac	1	92	98	87
Erythromycin	1	90	93	89
Ibuprofen	5	105	86	93
Ketoprofen	1	87	92	102
Losartan	0.5	95	88	91
Metoprolol	0.5	121	107	110
Naproxen	0.1	84	85	90
Simvastatin	5	105	97	108
Sulfamethoxazole	0.5	104	92	87
Trimethoprim	0.1	132	138	130
Valsartan	1	101	97	94
Xylazine	0.1	110	106	111

3. Supplement 3

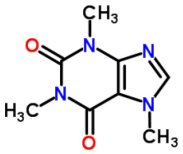
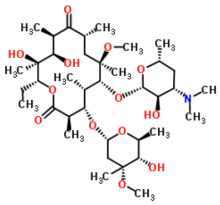
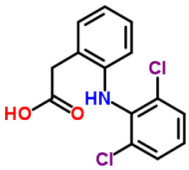
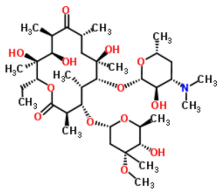
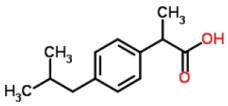
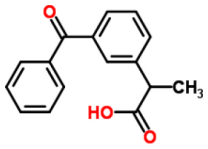
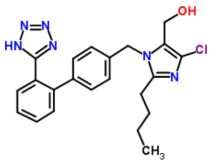
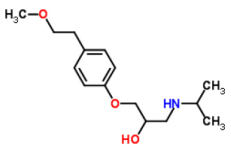
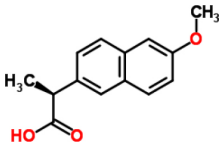
A total of 18 PCs were included in this study, based on the reported occurrence of PCs in municipal WWs in Europe and elsewhere. The compounds included in our study have been observed most frequently throughout Europe and their concentration levels were also higher in comparison with other PCs.

Table S2
Molecular structures and therapeutic classes of the PCs tested in WW during this study (http://www.chemspider.com/)

No.	Compound	Formula	Molecular structure	Therapeutic class
1	Atenolol	$C1_4H_{22}N_2O_3$		Antihypertensive agent
2	Atorvastatin	$C_{33}H_{35}FN_2O_5$		Cholesterol-lowering agent
3	Azithromycin	$C_{38}H_{72}N_2O_{12}$		Antibiotic (Macrolide)

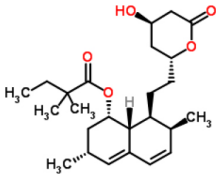
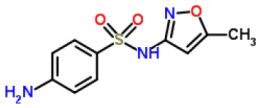
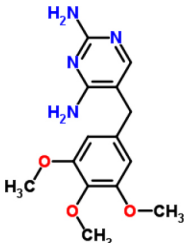
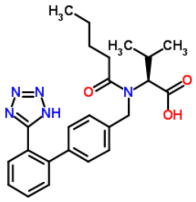
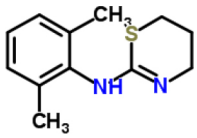
(Continued)

Table S2 (*Continued*)

No.	Compound	Formula	Molecular structure	Therapeutic class
4	Caffeine	$C_8H_{10}N_4O_2$		Central nervous system stimulant
5	Carbamazepine	$C_{15}H_{12}N_2O$		Anticonvulsant
6	Clarithromycin	$C_{38}H_{69}NO_{13}$		Antibiotic (Macrolide)
7	Diclofenac	$C_{14}H_{11}C_{l2}NO_2$		Nonsteroidal anti-inflammatory agent (NSAID)
8	Erythromycin	$C_{37}H_{67}NO_{13}$		Antibiotic (Macrolide)
9	Ibuprofen	$C_{13}H_{18}O_2$		NSAID
10	Ketoprofen	$C_{16}H_{14}O_3$		NSAID
11	Losartan	$C_{22}H_{23}ClN_6O$		Angiotensin-receptor blocker (ARB)
12	Metoprolol	$C_{15}H_{25}NO_3$		Cardioselective β1-adrenergic blocking agent
13	Naproxen	$C_{14}H_{14}O_3$		NSAID

(Continued)

Table S2 (*Continued*)

No.	Compound	Formula	Molecular structure	Therapeutic class
14	Simvastatin	$C_{25}H_{38}O_5$		Cholesterol-lowering agent
15	Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$		Antibacterial agent
16	Trimethoprim	$C_{14}H_{18}N_4O_3$		Antibacterial agent
17	Valsartan	$C_{24}H_{29}N_5O_3$		Angiotensin-receptor blocker (ARB)
18	Xylazine	$C_{12}H_{16}N_2S$		Alpha-adrenergic agonist (Veterinary drug)

4. Supplement 4

Table S3
Concentrations of PCs detected in untreated WWs of the WWTP ”Daugavgriva” near Riga, Latvia

Compound	Concentration (ng L^{-1})	Compound	Concentration (ng L^{-1})
Atenolol	133 ± 10	Clarithromycin	925 ± 35
Xylazine	1,366 ± 64	Carbamazepine	419 ± 20
Metoprolol	823 ± 44	Losartan	241 ± 20
Azithromycin	681 ± 19	Ketoprofen	336 ± 17
Erythromycin	26 ± 4	Valsartan	973 ± 44
Sulfamethoxazole	568 ± 27	Naproxen	1,405 ± 20
Atorvastatin	285 ± 2	Trimethoprim	834 ± 28
Diclofenac	1,312 ± 31	Caffeine	20,688 ± 719
Ibuprofen	10,234 ± 25	Simvastatin	76 ± 3

Table S4
Chemical and physical properties of PCs tested in WW in this study (https://pubchem.ncbi.nlm.nih.gov/)

	Atenolol	Xylazine	Meto prolol	Azithro mycin	Erythro mycin	Clarithro mycin	Carbama zepine	Losa rtan	Keto profen
Mol. weight (g mol^{-1})	266.3	220.3	167.4	748.0	733.9	748.0	236.3	422.9	254.3
Heavy atom count	19	15	19	52	51	52	18	30	19
Solubility in water (mg L^{-1})	13,300			2.37	2,000	0.33	18	0.82	51
pKa	9.6			8.74	8.88	8.99	13.9	5.5	4.45
Complexity	263	230	215	1,150	1,180	1,190	326	520	331
Topological polar surface area	84.6	49.7	50.7	180	194	183	46.3	92.5	54.4
H donor bond count	3	1	2	5	5	4	1	2	1
H acceptor bond count	4	2	4	14	14	14	1	5	3
Rotatable bond count	8	2	9	7	7	8		8	4
XlogP3	0.2	2.8	1.9	4	2.7	3.2	2.5	4.3	3.1
Melting point	147		120	114	191	220	190	184	94
log Kow	0.16	n.d.	1.88	4.02	3.06	3.16	2.45	4.01	3.12
Starting concentrations (ng L^{-1})	133.5	1,366.1	822.5	680.7	25.9	925.4	418.7	241.3	336.13
Starting concentrations (mol L^{-1})	0.5	6.2	3.1	0.9	0.03	1.2	1.8	0.6	1.3

	Valsartan	Atorvastatin	Diclo fenac	Ibuprofen	Trime thoprim	Caffeine	Sulfa metho xazole	Naproxen	Simva statin
Mol. weight (g mol^{-1})	435.5	558.7	296.1	206.3	290.3	194.2	253.3	230.3	418.6
Heavy atom count	32	41	19	15	21	14	17	17	30
Solubility in water (mg L^{-1})	1,406	1.23	2.37	21	400		610	15.9	0.765
pKa	3.6		4.15	4.91	7.12		1.6	4.15	
Complexity	608	822	304	203	307	293	346	277	706
Topological polar surface area	112	112	49.3	37.3	106	58.4	107	46.5	72.8
H donor bond count	2	4	2	1	2	0	2	1	1
H acceptor bond count	6	6	3	2	7	3	6	3	5
Rotatable bond count	10	12	4	4	5	0	3	3	7
XlogP3	4.4	5	4.4	3.5	0.9	–0.1	0.9	3.3	
Melting point	116	160	157	76	199		167	153	137
log Kow		n.d.	4.51	3.97	0.91	n.d.	0.89	3.18	4.68
Starting concentrations (ng L^{-1})	972.8	285.3	1,311.5	10,234.3	834.4	20,688.0	567.6	1,405.2	76.2
Starting concentrations (mol L^{-1})	2.2	0.5	4.4	49.6	2.9	106.5	2.2	6.1	0.2

n.d. – not determined