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Comprehensive evaluation of pharmaceuticals and personal care products (PPCPs) in urban sewers: Degradation, intermediate products and environmental risk

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ABSTRACT

The release of pharmaceuticals and personal care products (PPCPs) is one of the most concern issues which affect the stability of environment. In this study, the transformation, typical metabolites and risk evaluation of five dominating PPCPs (acetaminophen, triclosan, caffeine, N,N-diethyl-m-toluamide and sulfamethoxazole) were investigated in a pilot sewer. Firstly, the mass balance analysis indicated, although the PPCPs have the peculiarity of degradation-resistant, the biodegradation of PPCPs still plays a more important role in sewers, and then, liquid chromatography coupled to mass spectrometry (UHPLC-Q Exactive MS) methods were utilized to reveal their fate during pipeline transportation. In total, six transformation products (TPs) were detected and identified. The transformation occurring in sewers involved rearrangement of the aminobenzene moiety, ether bond breaking, hydrolysis of hydroxy compounds and dealkylation. Finally, risk(s) were estimated by calculating risk quotients (RQs). TCS is "high risk" (RQ $>$ 200), SMX is "minimal risk" (RQ $<$ 0.3), and the other compounds examined are "low or medium risk" and vary widely (RQ $\approx$ 3.75–98.19). Thus, based on this investigation, insights into PPCPs bioconversions in sewers were revealed, which could improve the understanding of subsequent treatment process of the wastewater treatment plant (WWTP) and reduced environmental risks caused by micropollutants.

1. Introduction

Over the past ten years, PPCPs have received increasing attention due to their ever increasing use and emissions into the environment, as well as the characteristics of "pseudo persistent" contaminants [1]. In urban wastewater systems (UWS), the actual and main source of PPCPs is households in the upper reaches of catchments, where medicines are consumed and eventually released into sewer systems [2]. Sewer systems of drains, pipes and pumping stations that transport wastewater to a wastewater treatment plant (WWTP). Complex processes are involved, and material exchange occurs at the interfaces of the five major phases (e.g., the water phase, biofilm, sediment, atmosphere and walls). Due to exchange effects, active chemical and biological reactions are promoted in sewer systems, which are hot-spots for microbial diversity and activity [3].

Thai et al. (2014) [4] found that the biofilms in the lab-scale sewer (compared to wastewater only) significantly improved the degradation efficiency of the compounds. In the past ten years, the development of analytical technology and instruments has improved detection and analysis capabilities for trace-level compounds in different environments. Although a few studies have reported the concentrations of PPCPs in sewage, their concentrations range from ng/L to μg/L [5], they can exist in various environmental media and have potential adverse effects on the ecosystem and human health.

After human consumption of PPCPs, compounds are extensively metabolized in the human body and usually only metabolites are excreted in urine and/or faeces and eventually enter the sewage system. However, the presence of biofilms in sewers, results in the occurrence of

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unpredictable transformation products (TPs) in the effluent [6]. Most TPs are due to biodegradation, such as hydroxyl derivatives and glucuronide conjugates [7]. Because these TPs are usually unknown compounds, research on wastewater is currently viewed as a boring and challenging research field [8]. To our knowledge, little research has paid attention to the study of TPs generated from target pollutants in sewers. Nevertheless, these TPs may have a more important role in the environment because they may be more stable and/or toxic than their parent compounds [9]. Therefore, it is necessary to identify TPs which from during sewer transportation. Although conventional WWTPs can partly degrade PPCPs [10]. However, the removal efficiency of PPCPs was not considered in the design, resulting in a large quantity of PPCPs from being released into the environment [11], which may cause potential ecological impacts. The lack of chemical constituents and relevant toxicity data in wastewater environmental media has led to imperfections in environmental risk assessment systems. The Swiss Federal Office for the Environment has adopted relevant regulatory recommendations to monitor and evaluate of the risk of environmental effects from PPCPs. The environmental impact of PPCPs is assessed using environmental risk assessment (ERA) approaches [12]. Usually, risk estimation is performed by calculating risk quotient(s) (RQ), which includes measured environmental concentrations (MEC) and predicted no-effect concentrations (PNEC) of pollutants [13]. The RQs values are used as indicators in this paper to indicate the level of environmental risk posed by acetaminophen (APAP), triclosan (TCS), caffeine (CAF), N,N-diethyl-m-toluamide (DEET) and sulfamethoxazole (SMX) in sewers [14].

The purpose of this study is to determine the degradation and transformation of PPCPs in sewer systems and their environmental risks. Studies conducted to investigate TPs formation in sewer systems were performed by spiking high levels of the PPCPs of interest individually in a 1,200 m pilot sewer system over a period of 90 days. In the experiment, changes of chemical oxygen demand (COD), ammonia nitrogen (NH_4^+-N), total nitrogen (TN), and total phosphorus (TP) were monitored and the degradation of PPCPs was identified by Soxhlet extraction (SE) - solid phase extraction (SPE) combined with high-performance liquid chromatography (HPLC) technology. To detect TPs, which are used for the evaluation of removal efficiencies in WWTPs, the intermediate products of microbial biotransformation were further explored by using mass spectrometry (MS). Therefore, based on the valuable information of the selected PPCPs, the environmental risks in sewer systems can be better assessed. In addition, this study can improve and update understanding of the biotic processes involved in micropollutants removal in sewer systems and enhance the theoretical basis for future development of urban sewer systems.

2. Materials and methods

2.1. Sewer system setup and operation

We constructed a pilot test device to simulate an urban sewer system at the Xi'an No. 5 WWTP in China (Fig. S1). The total length of the system was 1,200 m and the main body was made of PVC pipe with a diameter of 40 mm. In this study, the temperature inside the piping system was stabilized by control the inlet water temperature and covered with sponge material. There were 35 layers from top to bottom. To fully simulate the flow in actual sewers, the inner wall of the pipe was properly polished to achieve the appropriate roughness, using a small-diameter pipe inner wall grinding machine. The force driving the sewage flow was gravity. The slope of the pipeline was 5‰, and a flow of 0.6 m/s could be maintained under these conditions [15]. The synthetic sewage in this study was refreshed periodically for one day.

2.2. Sample collection and pretreatment

For the wastewater sampling, the samples were collected from inspection well of the pilot sewer system to detect the water quality. The sampling times were at 7th day, 14th day, 21th day, 28th day, 35th day, 42th day, 49th day, 56th day, 63th day, 70th day, 77th day, 84th day and 90th day of the experimental process.

For the sediment samples at the bottom of the sewer are collected and processed by SE - SPE method [16]. Weigh 10.0 g of the sediment sample and mix it with 10.0 g of anhydrous sodium sulfate, add 100 mL of extraction solvent and extract for 4 h in a Soxhlet extractor, collect the extract, dry it with weak nitrogen at room temperature, and add 5 mL of n-hexane dissolve by shaking. Then 5 mL of methanol was used to condition the Oasis HLB SPE cartridges and 5 mL of the sample was loaded into the cartridge followed by washing off the impurities with 5 mL of distilled water. The traces of water from the sorbent were removed under vacuum for 10 min and 5 mL of methanol was passed through the cartridge to elute the adsorbed analytes. The eluent was concentrated to 1 mL by blowing it with nitrogen gas and analyzed by UHPLC. The sampling times were at 30th day, 60th day and 90th day of the experimental process.

2.3. Synthetic wastewater and PPCPs

We set up two different systems to simulate the influent water quality system of urban sewers; one had added PPCPs (group A), and the other had no added PPCPs (group B). The other wastewater quality characteristics of the two groups were the same, but the PPCPs compositions were different (Tables S1 and S2).

2.4. The properties of target compounds

A wide range of PPCPs with different properties and uses are present in urban sewers. To obtain a comprehensive view in this study, the selection of compounds was based on a variety of criteria. Antibiotic pharmaceuticals (SMX), nonantibiotic pharmaceuticals (CAF and APAP), broad-spectrum antibacterial (TCS), and pesticides (DEET) were included. Furthermore, consumption of chemicals and the occurrence of PPCPs in world-wide monitoring studies were considered. Five different PPCPs were investigated in this study. Their molecular information and basic physical and chemical properties are shown in Table S3. A complete list of monitored chemical substances can be found in the Supplementary information (Table S4), including P_{Ka}, K_{ow}, and k_{oc}.

2.5. Chemical analysis

An Ultimate 3000 UHPLC-Q Exactive Mass was employed for the detection and quantification of the target trace-level PPCPs (Thermo Scientific, US). Chromatographic separation was performed using an Agilent ZORBAX Eclipse Plus C-18 column (250 mm × 4.6 mm, 5 μm particle size).

Mobile phase compositions consisted of 0.1% formic acid water (A) and acetonitrile (B) and had the following gradient: 0 min, 5% B; 3 min, 5% B; 20 min, 90% B; 25 min, 95% B; 30 min, 95% B; 31 min, 5% B; and 38 min, 5% B. The injection volume was 5 μL and the flow rate was 0.6 mL/min. The MS system was operated by a Thermo Scientific Q Exactive instrument and an HESI ion source. COD, NH_4^+-N, TN, and TP were measured according to standard methods [17].

2.6. PPCPs mass balance

Throughout the wastewater treatment process, the mass balance of PPCPs can be described as follows:

$$M_w = Q_w \times C_w \quad (1)$$

$$M_s = Q_s \times C_s \quad (2)$$

where M_w and M_s represent the average mass of PPCPs in sewage and sediment (μg/d), respectively, Q_w and Q_s represent the average flux of

sewage and sediment (L/d and kg/d), respectively, and C_w and C_s represent the average concentration of PPCPs in sewage and sediment, respectively.

In this experiment, the removal of PPCPs is mainly accomplished by adsorption and biodegradation so the mass balance formula is as follows:

$$M_{in} = M_{ef} + M_{bio} + M_{sor} \quad (3)$$

where M_{in} and M_{ef} represent the mass of each PPCPs in the influent and effluent (μg/d), respectively, M_{bio} represents the mass of PPCPs removed by biodegradation (μg/d), and M_{sor} indicates the mass of PPCPs removed by adsorption (μg/d). In this experiment, M_{in}, M_{ef} and M_{sor} were all measured experimentally, while M_{bio} was calculated by formula (3).

In addition, the biodegradation rate (R_{bio}, %) and adsorption removal rate (R_{sor}, %) are calculated as follows:

$$R_{bio} = M_{bio}/M_{in} \times 100 \quad (4)$$

$$R_{sor} = M_{sor}/M_{in} \times 100 \quad (5)$$

2.7. Environmental risk assessment

PNEC values are mainly derived from the EC-European Commission technical guidance document on risk [18] (EC, 2003), the WikiPharma database (https://www.mistrapharma.se/), and related values reported in the scientific literature [19]. PNEC is the ratio of the no observed effect concentration (NOEC) to the assessment factor (AF) and is expressed as:

$$PNEC = NOEC/AF \quad (6)$$

If NOEC is missing, EC_{50} or LC_{50} values are use in the equation instead and AF is usually 1,000. The NOEC, LC_{50} and EC_{50} values for the different investigated compounds are shown in Table S5. MEC_{Inf} and MEC_{Enf} correspond to the concentration of influent drugs on the first day (1 d) and the concentration of effluent on the last day (90 d), respectively.

According to EU technical guidelines on environmental risk assessment, the RQ method is used to assess the environmental risk level of micropollutants in the water environment. RQ is expressed as:

$$RQ = MEC/PNEC \quad (7)$$

Based on to the RQ value, there are four environmental risk levels. The RQ value is between 0.01 and 1 for minimal risk, between 1 and 10 for low risk, between 10 and 100 for medium risk, and greater than 100 for high risk.

3. Results and discussion

3.1. Degradation of PPCPs in the sewer system

In this study, COD, NH_4^+-N, TN, and TP were detected by the 0-90th day (Fig. S2) which prove that the presence of PPCPs will affect the conversion of wastewater quality in sewers. Therefore, it is urgent to comprehensively evaluate the degradation of PPCPs in sewers. The concentrations of the target PPCPs in the simulated wastewater varied from 40 to 50 μg/L. Removal of PPCPs in sewers is mainly achieved by physical adsorption and biodegradation. Considering that the circulation of organics between urban sewage and sediment can facilitate their biodegradation, it is essential to examine their fates in each pathway separately [20]. Shi et al. (2018) [21] proposed three integrated approaches of physical pollutant deposition (PPD), biological transformation adsorption (BTA), and biological transformation release (BTR), based on the physical and biological pollutant exchange phenomenon between sewage and sediment. Studies have shown that part of the PPCPs was adsorbed in the sediment [22]. However, the PPCPs in the sewage removed by adsorption did not change their molecular structures but instead transferred from the sewage to the sediment. Therefore, this study focused on the biodegradation of PPCPs in sewage.

There are two main aspects of biodegradation in sewage. The biological metabolism of rich microbial communities in the biofilm and the sediment. The concentrations of five specific PPCPs were monitored weekly throughout the experiment (Fig. 1). Compared with other micropollutants, SMX and CAF had higher degradation efficiencies. This is because of their hydrophilicity and low log K_{ow} nature, which leads to ready biodegradation. In addition, the degradation rates of APAP, TCS, and DEET were relatively low and these compounds were characterized as being relatively persistent and water soluble. There was a biological treatment process during the operation of the sewer system [23]. The main removal mechanism for most PPCPs in activated sludge reactors under aerobic, nitrifying and anoxic conditions is biodegradation [10]. This is mainly because the biofilm on the pipe walls has been acclimated for a long period of time and the biodegradability of the system has improved.

Due to design requirements and changes in water quantity, particulate matter deposition occurs and causes formation of sewer sediment in sewers, which has a certain adsorption effect for carbon, nitrogen and phosphorus pollutants [24]. Fig. 1f summarizes the concentration levels of target PPCPs detected in the sediment. The adsorption capacity of TCS and CAF reached 7 ng/g or higher and, in particular, the CAF adsorption capacity was as high as 9 ng/g or greater after 60 d (Table S6); this was the highest adsorption capacity detected in this research. This is because CAF is a hydrophilic basic compound. Water flowing in sewers is deprotonated and adsorbed with the sediment particles through ion exchange and electrochemical reactions [25]. TCS also has a high adsorption capacity (>7.85 ng/g) because the molecular structure of TCS includes one –OH and multiple CL groups and exhibits weak acidity. In addition, the pH of this system is approximately 7 and more than 80% of TCS molecules are positively charged, so the adsorption capacity was strong [26]. Therefore, we believe that both TCS and CAF are easily adsorbed organic substances. For a few PPCPs (e.g., DEET, APAP, and SMX), lower sediment concentrations indicate that the decreased concentration of these substances mainly may be due to biodegradation [27,28].

However, it is worth noting that previous studies have not attempted to assess the interrelationship of PPCPs between physical adsorption and biodegradation in sewers. Table S7 and Fig. 2 show that DEET, APAP, TCS, CAF and SMX are mainly present in sewage and that their proportions in sediment are relatively small. According to the mass balance analysis, it is known that DEET, APAP, TCS, CAF and SMX pollution in sewage can be reduced to a certain extent through biodegradation. This is sufficient to prove the key role of biodegradation in sewers. In addition, the coexistence of sediment and biofilm in sewer systems promotes biotransformation of some hydrophobic compounds (such as TCS) [29]. By considering the relationships between sediment characteristics, microbial populations, and anaerobic biological processes (e.g., hydrolysis, acid production, acetic acid production, and methanogenesis), it is necessary to study further the effects of intermediates produced by biological degradation on the system.

3.2. Identification of PPCPs intermediate products

Microbial biotransformation occurs when pollutants travel over a long distance and due to the existence of biofilms in sewer systems. PPCPs were added at high concentrations of 40–50 μg/L to also allow detection of the main TPs [30,31]. The metabolites were initially identified via interpretation of the MS/MS information and retention times of the parent compounds. The six most important TPs from five PPCPs were detected and are listed in Table 1.

PPCPs standard solutions TCS, DEET, SMX, CAF and APAP, were gradually accumulated and configured to the sewer system. This pattern facilitated the characterization of unknown compounds and was used to determine the fragmentation pattern for each substance. Screening and

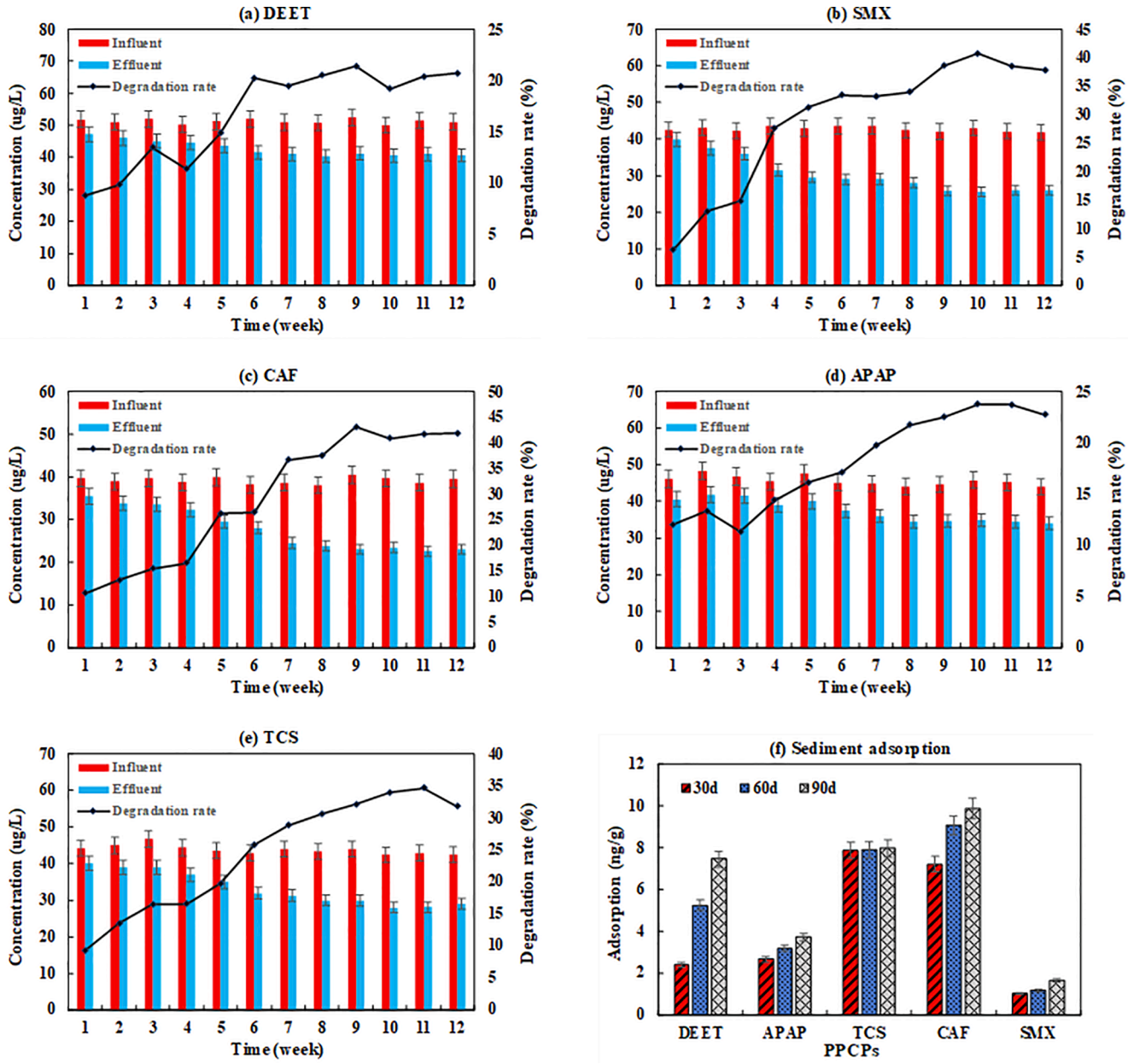

Fig. 1. Weekly concentration changes of five PPCPs ((a) DEET, (b) SMX, (c) CAF, (d) APAP, and (e) TCS), the accumulated adsorption capacity of sediment after 30 days, 60 days and 90 days of operation in sewers (f).

analysis of the degradation and conversion of micropollutants (PPCPs) were conducted by UHPLC-Q Exactive MS during simulated urban sewer network transportation using the chromatographic conditions indicated in Section 2.5. This was achieved in full scan mode and selected ion monitoring (SIM) in negative and positive ionization modes (Figs. S3 and S4). Subsequently, MS/MS fragmentation experiments were performed to initially identify TPs.

3.2.1. Pattern I

In mixed standard negative ion mode, SMX and TCS were detected at retention times of 14.09 and 20.93 min (Fig. 3a) but two TPs (e.g., TP-156 and TP-141) with *m/z* of 156.01 and 141.98 were detected in the wastewater samples (Fig. 4a and b, Table S8). Among them, TP-141 (4-chlorocatechol $[M–H]^-$ = 141.98 amu) came from the parent compound TCS (*m/z* = 286.9439 for MH–) due to C–O cleavage [32]. The known microbial TPs of triclosan are methyl-triclosan, 2,4-dichlorophenol, 4-chlorocatechol, monohydroxy-triclosan and dihydroxy-triclosan showing agreement with our findings [33]. In addition, TP-156 will be discussed in pattern II.

3.2.2. Pattern II

In addition, in mixed standard positive ion mode, five TPs with *m/z* of 110.06, 138.07, 108.04, 156.01 and 119.05 (e.g., TP-110, TP-138, TP-108, TP-156 and TP-119, respectively) were detected at t_R 9.88, 11.52, 14.09, and 17.05 min, respectively (Fig. 3b, Table S9). Among them, the characteristic product ions *m/z* 156.01 and 108.04 are consistent with related research on SMX TPs. The parent compound SMX (*m/z* = 252.0448 for MH^- and *m/z* = 254.0594 for MH^+) mainly undergoes rearrangement of the aminobenzene moiety, cleavage of the S-N bond and isoxazole ring, and loss of the SO_2 group, which produces TP-156 and TP-108 [34] (Fig. 4e). The parent compound APAP (*m/z* = 152.0706 for MH^+) undergoes a cleavage reaction to produce TP-110 (hydroquinone $[M+H]^+$ = 110.06 amu). Zhang et al. (2017) [35] found that the main degradation mechanism of APAP is hydroxylation,

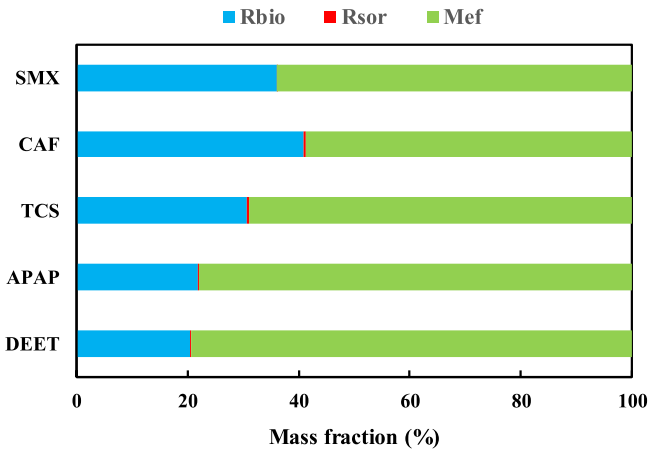

Fig. 2. Mass balance for DEET, SMX, CAF, APAP, and TCS.

which can be attributed to the generation of hydroxylated aromatics such as hydroquinone and catechol. This is consistent with the peak observed at m/z 152.0706 (TP-110) in our study (Fig. 4c). TP-138 (m/z 138.07) (Fig. 4d) immediately formed after adding CAF to sewers. Accurate mass measurements recorded for the protonated CAF molecule (m/z195.0875, $C_8H_{11}N_4O_2$) showed excellent agreement between the experimental and calculated m/z values. TP-119 ($[M+H]^+ = 119.05$ amu) (Fig. 4f) came from the parent compound DEET ($m/z = 192.1383$ for MH^+). In general, the hydroxylation and oxidation processes are the main conversion pathways for DEET in wastewater samples.

3.3. Proposed transformation pathways and environmental implications

A possible transformation pathway of TCS in sewer systems is shown in Fig. 5a. The oxidation of TCS to monohydroxy- and dihydroxy-triclosan results in the formation of 4-chlorocatechol through breakage of the ether bond [36]. Fig. 5b shows an ion fragment at m/z 156.0120 [$C_6H_6NO_2S$], which corresponds to the sulfonamide bond cleavage. In addition, the initial degradation of SMX is due to the erosion of ·OH radicals on the isoxazole ring, which eventually formed m/z 108.04 [C_6H_6NO] [37]. The main metabolite of APAP in this study was hydroquinone ($m/z = 110.06$) (Fig. 5c). According to earlier reports, hydroquinone is produced by nitrogen elimination and hydrolysis of the hydroxy compounds of APAP [35]. The formation of hydroquinone ($m/z = 110.06$) is due to the hydrolysis reaction of APAP in sewer system, from which nitrogen elimination is followed by hydroxylation [38]. As shown in Fig. 5d, TP-138 ($m/z = 138.07$) may be the result of the opening of the imidazole ring after breaking caffeine's N_9C_8 double bond [39]. DEET biodegradation in sewers may be related to dealkylation and mono- and poly- hydroxylation followed by oxidation of the hydroxyl groups and cleavage of the alkyl chains in the water environment [40] (Fig. 5e).

The parent compounds of PPCPs and their TPs can not be completely removed when entering a WWTP after long-distance transportation in urban sewers. They will eventually enter the surface water with the WWTP wastewater discharge and endanger the environment [41]. Heavy rains will cause sewer overflows, and at this time, the mixture of rain and sewage enters the environment [42]. However, there are few studies on the degradation behaviour of PPCPs in sewers but this situation clearly may have negative impacts on the environment. Except for the inlet and outlet waters of sewers, different wastewater treatment processes may cause different conversions of parent compounds. WWTPs have shown good removal of traditional organic compounds (such as BOD, COD, TP and TN) and can degrade a small number of PPCPs [43]. When WWTP sewage is discharged into surface water, it eventually enters the groundwater through a series of natural phenomena. At present, there are few studies on TPs in either surface water or groundwater environments. Peng et al. (2014) found TCS and SMX in groundwater and surface water in the vicinity of Chinese municipal landfills [44]. In general, pollution by PPCPs and the subsequent environmental risks must be of concern. It is necessary to study the impact of PPCPs pollution in various wastewater treatment processes including urban sewer systems.

3.4. Environmental risk assessment

Risk assessment needs to identify potential adverse consequences along with their severity and likelihood. It includes four key steps: hazard identification, dose-response analysis, exposure assessment and risk characterization [45]. At present, risk assessment of PPCPs is mainly focused on the parent compounds [46] and there is little research on their metabolism and degradation products. The degradation products themselves or interactions with the parent substances may produce greater toxic effects and cause greater environmental risks [41]. It is necessary to establish an environmental risk assessment model for PPCPs in sewer systems and calculate RQs to assess the current environmental risks of PPCPs in sewers. Based on the PNEC and MEC results reported in Section 2.7, RQ calculations were performed to estimate the

Table 1
Main TPs identified for SMX, CAF, APAP, TCS and DEET.

Compound	Abbreviation	Molecular formula	$^{a}t_R$ (min)	Measured m/z [M+H]	Measured m/z [M−H]	Most important fragment ions (m/z)
Triclosan	TCS	$C_{12}H_7C_{l3}O_2$	20.93		286.9439	TP-141.98
N,N-diethyl-m-toluamide	DEET	$C_{12}H_{17}NO$	17.08	192.1383		TP-119.05
Sulfamethoxazole	SMX	$C_{10}H_{11}N_3O_3S$	14.09	254.0594	252.0448	TP-108.04, TP-156.01
Caffeine	CAF	$C_8H_{10}N_4O_2$	11.53	195.0877		TP-138.07
Acetaminophen	APAP	$C_8H_9NO_2$	9.91	152.0706		TP-110.06

Table 2
Summary of the calculated RQ values and their fraction for risk (high/medium/low/minimal) for China.

Compound	Surface water			Sediment		
	Concentration range (μg/L)	RQ value (range)	Fraction (%) for risks (high/medium/low/minimal)	Concentration range (ng/g dw)	RQ value (range)	Fraction (%) for risks (high/medium/low/minimal)
DEET	0.55–1.29	0.03–0.12	0/6/89/5	0.97–4.10	0.01–2.29	6/59/35/0
TCS	0.04–0.54	0.54–20.5	89/11/0/0	0.18–1.63	0.71–10.1	71/29/0/0
APAP	22.46–8588.04	0.03–0.07	0/0/32/68	1.35–118.02	0.15–0.96	0/5/53/42
CAF	8868.70–456992.79	0.32–8.27	40/53/7/0	2.43–518.86	0.17–2.41	15/70/15/0
SMX	1.01–145.29	0.01–0.02	0/0/5/95	1.42–55.30	0.00–0.05	0/0/44/56

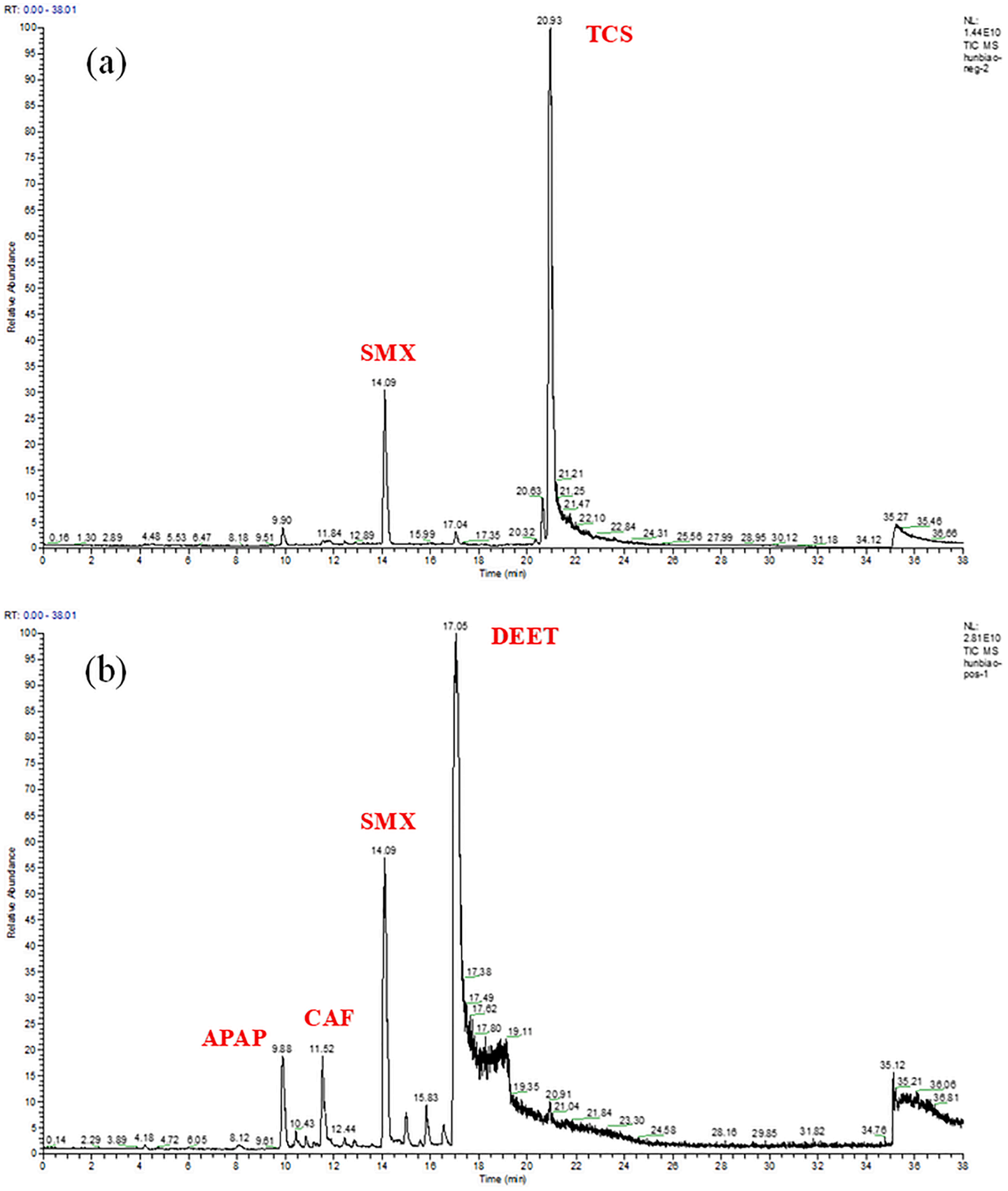

Fig. 3. Total ion currents of mixed standard samples. (a) Negative ion mode and (b) positive ion mode.

risks of TCS, SMX, CAF, APAP, and DEET to sewer systems. To comprehensive evaluation of PPCPs during sewer transportation, the simulated PPCPs influent concentrations (40–50 μg/L) were relatively high in actual concentrations range [10,11,47], so the environmental risk values were also in actual range. However, the purpose of this study is to explore the environmental risk differences of PPCPs before and after the 1,200 m transfer distance within the sewer. As shown in Fig. 6, the RQ values for the influent and effluent concentrations were calculated.

The RQs were rated from highest to lowest in the following order: TCS > CAF > DEET > APAP > SMX (Fig. 6). The RQ value of TCS is as high as 212–333. Although it exhibits a good degradation effect in sewers, it still presents a high risk to the environment. The RQ value of SMX is less than 0.3 which is a minimal risk. Lucy et al. (2018) [48] calculated the receptor-specific risk quotient based on the average

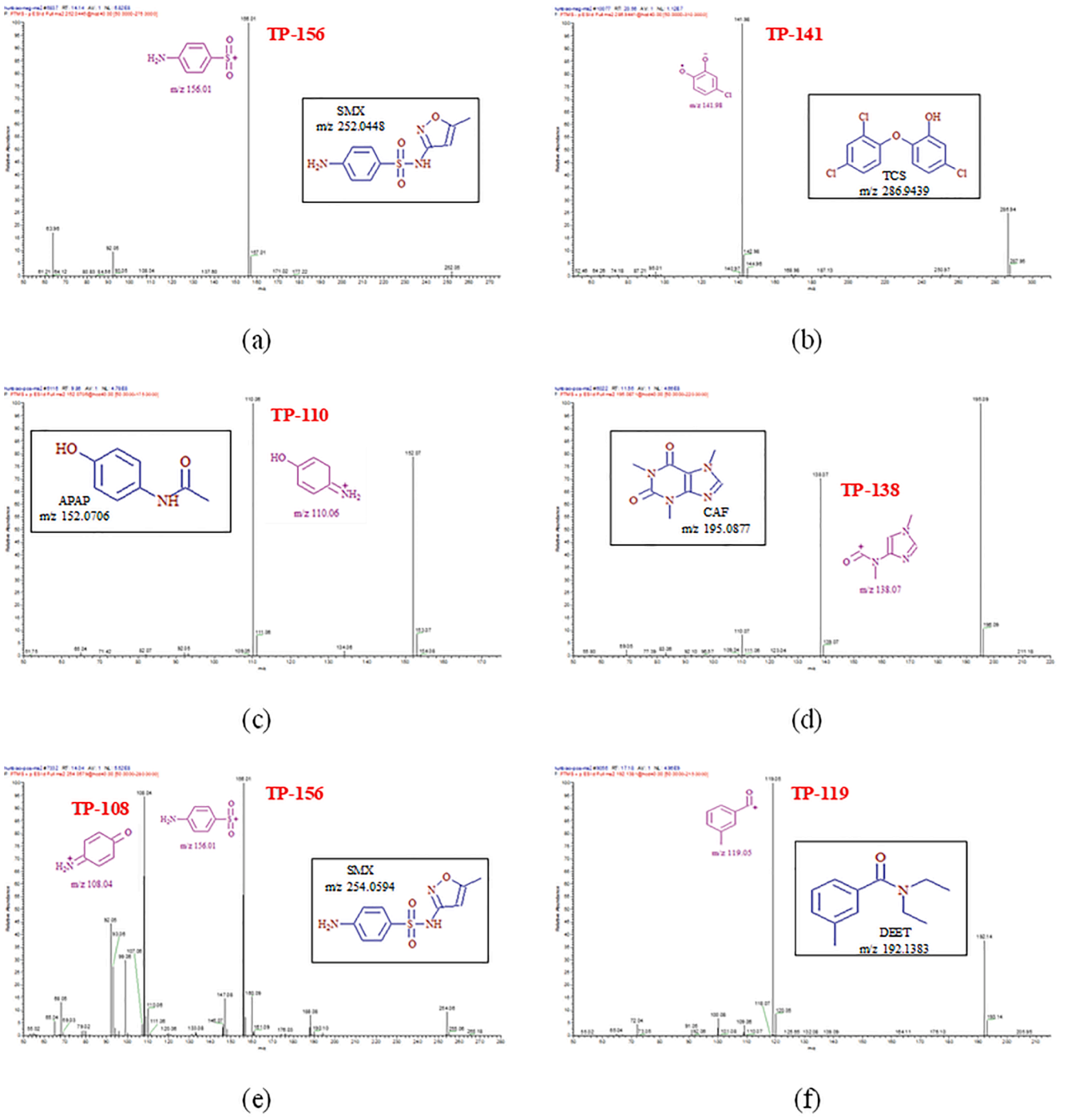

Fig. 4. MS/MS spectra of parent compounds. (a) SMX$[M-H]^-$, (b) TCS$[M-H]^-$, (c) APAP$[M+H]^+$, (d) CAF$[M+H]^+$, (e) SMX$[M+H]^+$ and (f) DEET$[M+H]^{+\cdot}$.

concentration of SMX in the wastewater of a WWTP and found that the RQ indicated safe exposure (RQ < 1). Even though CAF exists in sewers at a relatively high concentrations in this study, it showed medium risk, which indicates that concentrations are not consistent with environmental risks [46]. Table 2 summarizes the RQ values of selected PPCPs in the surface water and sediments of rivers in China [49]. It can be found that the proportion of "high risk" of TCS in surface water and sediment is higher than for other compounds, which is consistent with the results of this study. TCS adsorption onto sediments will convert TCS to methyl triclosan, which may pose more serious environmental risks [50]. In addition, the back-estimated usage of DEET in China is more than 70 t/y and the estimated emissions are more than 45 t/y [49]. Large emission will inevitably cause potential environmental risks, especially in sediments; 59% of the relevant studies consider DEET as "medium risk" (Table 2). CAF is widely used in today's society and has high water solubility and difficult volatility. Humans directly or indirectly discard CAF into the water environment and it will exist in the water environment for an extended period. As shown in Table 2, the total amount of CAF in surface water and sediments is the greatest and should receive more attention. In contrast, the remaining compounds (e.g., SMX and APAP) pose low or minimal risk to the environment. However, given the large environmental load of these substances, their potential negative effects should not be ignored due to the limited ecotoxicological data currently available.

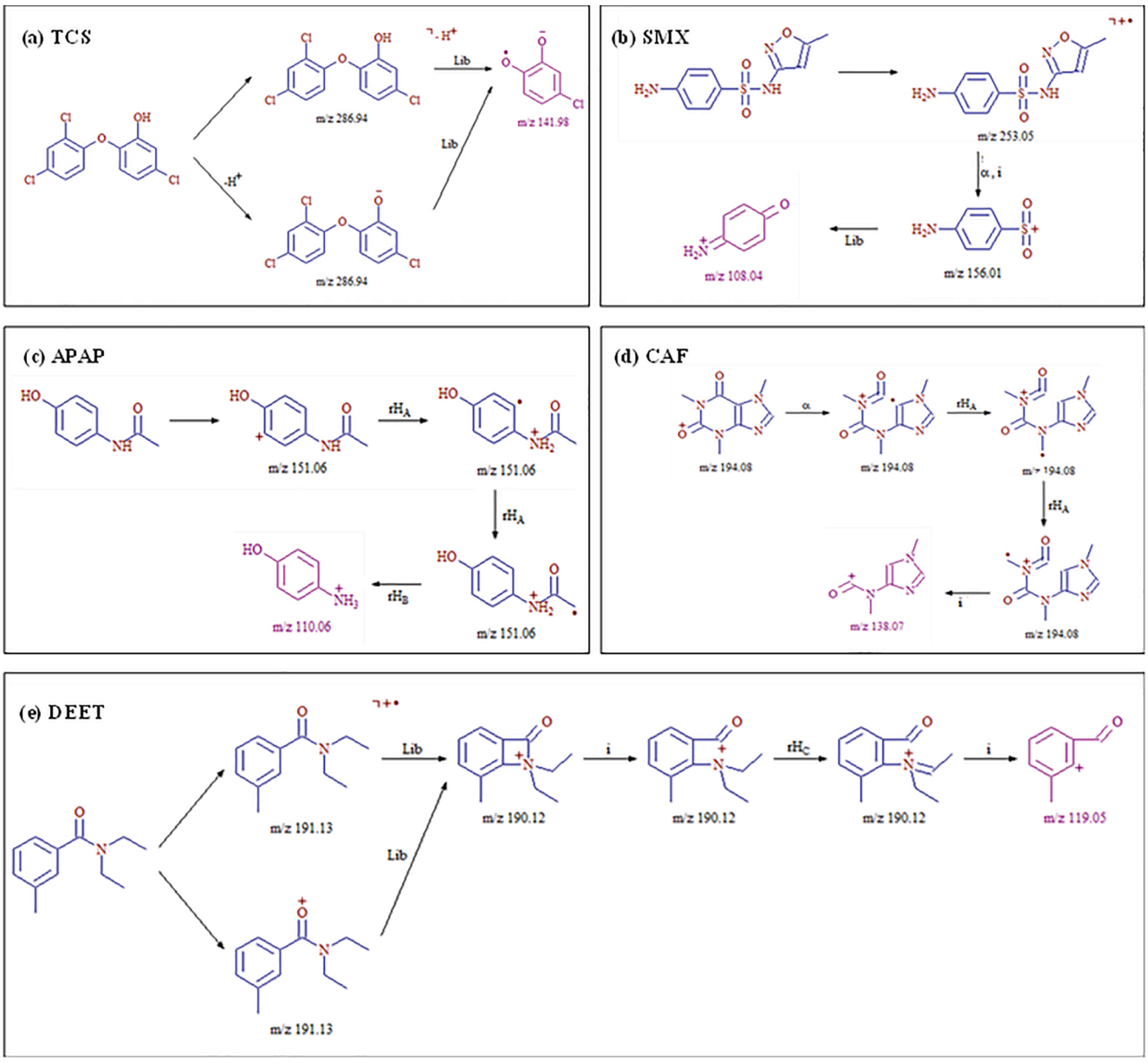

Fig. 5. Proposed in-sewer biotransformation pathways of TCS (a), SMX (b), APAP (c), CAF (d), and DEET (e).

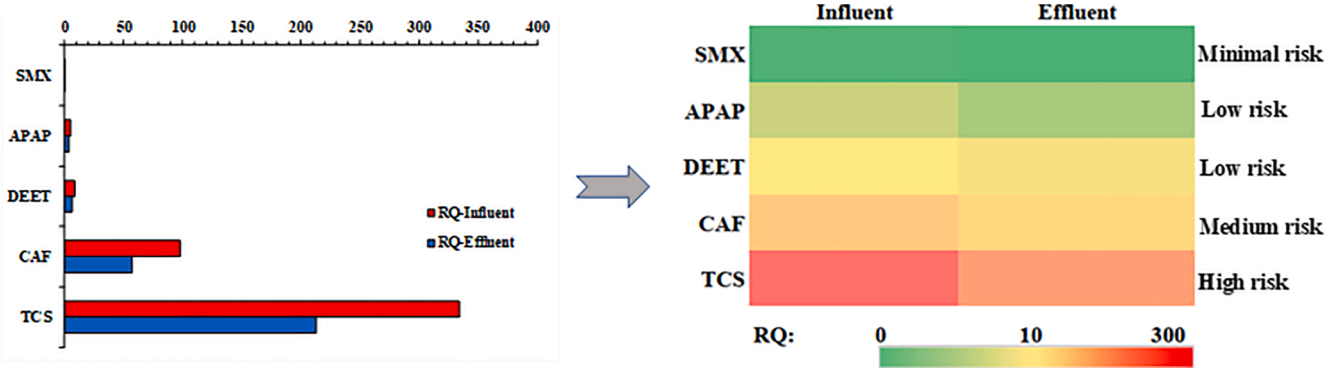

Fig. 6. Risk assessment of five PPCPs in the sewer of the influent and effluent.

At present, little is known about the basic data of PPCPs such as the toxicity of TPs or metabolites in the environment. Therefore, no environmental risk assessment was performed for metabolites in this study but the concentrations of TPs and metabolites in the environment were even higher than those of their parent compounds. Therefore, the significance of this study is to reiterate the concern that metabolites produced by biological effects during sewer transportation may bring more serious environmental risks. At the same time, higher requirements are imposed on the processes of WWTPs or other sewage treatment facilities. In addition, the PNEC used in environmental risk assessment is not consistent, and there will be some differences in RQ results in each study. Therefore, there is an urgent need to strengthen research on sewers and bioaccumulation of PPCPs and establish a unified benchmark for risk assessment of PPCPs based on human health and ecological environmental safety [14]. Combined sewer systems transport wastewater to sewage treatment plants. After long-distance transportation, the wastewater quality is transformed to some extent due to the biofilm present [51]. This also proves that urban sewer systems can effectively reduce the burden of micropollutants in the sewage treatment plant and can also bring additional benefits to the downstream processes of WWTPs.

4. Conclusions

Based on a 1,200-m pilot experimental sewer system, the biotransformation of PPCPs in sewers was revealed in this study. The main findings are as follows:

(1) The combined action of biodegradation and physical adsorption played an important role in the degradation of PPCPs and based on the HPLC results, the degradation rate of CAF (41.39%) was highest in water while the adsorption capacity for CAF (9.87 ng/g) was highest in sediment.
(2) MS analysis revealed the types of key TPs involved in the biotransformation of PPCPs. It indicated that, due to the different characteristics of the compounds involved, TP-156 and TP-141 were resolved in negative ion mode while TP-110, TP-138, TP-108, TP-156 and TP-119.05 were resolved in positive ion mode.
(3) By analysing the information of the TPs, the key biotransformation pathways of CAF, APAP, DEET, TCS and SMX can be deduced, which has guiding significance for future research on the field of PPCP biodegradation.
(4) Using the RQ method, the environmental risks in the sewer system were revealed. The results indicated that the biotransformation function of PPCPs should not be overlooked in sewers, which has important reference significance for the study of wastewater quality changes in WWTPs.

Author contributions

The manuscript was written by contributions of all authors. All authors have approved the final version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2020.127024.

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