Research Paper

Occurrence and removal efficiency of pharmaceuticals in an urban wastewater treatment plant: Mass balance, fate and consumption assessment

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ABSTRACT

The occurrence of 15 pharmaceutically active compounds (PACs) in an urban wastewater treatment plant (WWTP) was assessed in both influent and effluent samples. PACs were quantified by gas chromatography coupled to mass spectrometry. The sampling campaign was carried out during summer (n = 13) to assess the variation in both the influent concentrations and the removal efficiencies in similar climatic conditions. Among the selected PACs, all were quantified in influent samples but two of them were not systematically detected mainly due to the high quantification limit. PACs were detected at $\mu g\,L^{-1}$ levels with a maximum concentration of 96.7 $\mu g\,L^{-1}$ for Acetaminophen. The mean mass balance of the whole PAC pool during tracking was 448.5 and 26.3 g day^{-1} in influents and effluents respectively. However, the removal efficiency varied depending on the sample (e.g. between −20 and 50% for Diclofenac). The fate of PACs during water treatment therefore depends on the removal quality in general, highlighted by the removal of nitrogen or BOD$_5$. As a result, effluent concentrations were variable, unlike influent concentrations which were used to correctly assess the consumption behaviour of the population around the sampled WWTP. Although the daily mass loads were comparable with those found in other studies in Europe for the same type of WWTP, the estimated consumption sometimes exhibited significant differences with the theoretical one. These differences depend on the mode of consumption, i.e. whether the therapeutic class treats chronic or episodic diseases, and on the scale gap between estimated and theoretical concentrations.

1. Introduction

In recent decades Pharmaceutically Active Compounds (PACs) have been extensively investigated as they represent a common and persistent form of pollution in numerous water compartments, from wastewaters to drinking water [1,2]. Due to their high frequency of detection [3–5] and their significant concentrations in natural waters (i.e. from ng L^{-1} to µg L^{-1}), they are now considered as a potential hazard for numerous living beings, including humans [6,7]. A study has recently demonstrated at field-relevant concentration (i.e. tested at 1.8 µg L^{-1}, for a field concentration of 0.58 µg L^{-1}) the impact of a benzodiazepine on the behaviour of the European Perch [8].

The main origin of these contaminants is human and cattle therapies which lead to variable rates of excretion via urine and faeces, depending on the PACs characteristics [9]. Due to the continuous increase in drug consumption during the XXth century, the levels of contamination raise serious questions about the amounts of PACs prescribed [10].

Activated sludge treatment plants are the most common and

therefore the most widely studied type of Wastewater Treatment Plant (WWTP) around the world [11–13]. This type of plant allows a significant removal of classical chemical parameters such as BOD$_5$ or TP [14]. However, the removal of PACs remains insufficient [15,16]. The discrepancy between this insufficient removal and the increase in drug consumption means that contamination by PACs will remain a problem for the foreseeable future.

Several studies propose innovative tertiary treatments in order to improve the removal of PACs [17–20]. Their use is nevertheless expensive and it seems important to better understand the origin of this lack of efficiency in activated sludge treatment.

Estimating the link between the consumption of a drug and the contamination level in effluent is important for field managers in order to assess the level of pollution in real time. Tracking the concentration of PACs in influents can also provide information on the consumption behaviour of the population concerned in order to determine some site-specific features [21]. To address this issue, influents and effluents were sampled within the same season. Several studies have demonstrated that the removal efficiency is not constant throughout the year, due to a

seasonal effect [22,23]. It also appeared important to assess the variability in removal efficiency within a single season, in our case summer, in order to determine whether removal remains constant during the same climatic event and what the origin of these variations is, such as for example variation in the efficiency of treatment step.

The analytical method selected in the present work was GC–MS. Previous studies have demonstrated that, although not widely used, this technique is suitable for the analysis of pharmaceutical residues at field-relevant concentrations [14,24]. While GC–MS presents some disadvantages compared to HPLC–MS[2] (analytical duration and sample preparation), the equipment is widely available and the method has certain advantages (weak matrix effect, low analytical cost) that offset its drawbacks [25].

The aim of this study was therefore to optimize this technique for the analysis of PACs generated by human consumption in both influents and effluents in order to assess the fate of PACs during activated sludge treatment within the same season. The results obtained should suggest new tools for a better prediction of removal assessment and consequently of environmental contamination.

2. Materials and methods

2.1. Site settings

The WWTP investigated is one of the three main plants that serve the town of Orléans. The purification capacity of the installation is 93,933 population equivalent (PE). Influents arrive at the WWTP by two routes: the first collects the industrial effluents of a paper mill and the second collects domestic waste. Since 1989, the effluents have been discharged into the Loire river.

The treatment chain of domestic effluents consists in a conventional activated sludge treatment (Fig. S1) with a hydraulic retention time of 2 days and a solid retention time between 10 and 20 days.

2.2. Sample collection

Influents and effluents were collected by an automatic sampler indexed to the flow between April and August 2015 ($n = 13$). Each sample was a 24h-composite and was collected in 5-l glass jars. After collection, samples were filtered with glass fiber filters (GF/A and GF/F, Whatman) and 0.45 μm filters (Millipore) within 2 h. The filters were previously heated at 105 °C during 24 h to eliminate any residual water. Residues were stored in the fridge before solid-phase extraction, carried out within the following 2 days.

The physico-chemical parameters (BOD$_5$, COD, etc.) of the collected samples were also analyzed and are summarized in Table S1.

2.3. Chemical reagents

The 15 PAC standards (purity grade > 98%; see Table 1 for details) were obtained from Sigma-Aldrich for Acetaminophen (ACM), Atenolol (ATE), Carbamazepine (CBZ), Codeine (COD), Diazepam (DIA), Doxepin (DOX), Gemfibrozil (GEM), Ketoprofen (KET), Metoprolol (MET), Naproxen (NAP), Oxazepam (OXA), Salicylic acid (SCA), Tramadol (TRA), and from Acros Organics for Diclofenac (DIC) and Ibuprofen (IBU). The PAC standards were selected from various therapeutic classes: analgesics (ACM and SCA), anti-inflammatory drugs (DIC, IBU, KET and NAP), psychotropic drugs (CBZ, DIA, DOX and OXA), β-blockers (ATE and MET) and lipid regulators (GEM). The internal standards Tramadol-d6 and 5α-cholestane were purchased from Sigma-Aldrich.

Chemical reagents of analytical grade, methanol (MeOH) and pyridine were purchased from Fisher Scientific. *N-tert*-Butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA, 95%) was supplied by Sigma-Aldrich.

2.4. Residues concentration and analysis

Leachate solutions were concentrated by Solid-Phase Extraction (SPE) and analyzed by Gas Chromatography coupled to Mass Spectrometry (GC–MS). This methodology was already used in previous studies [20,33] but was optimized here for low concentrations.

PAC concentration was carried out on a 6 mL glass cartridge filled with HR-X phase (Macherey-Nagel). Cartridges were conditioned with 5 mL of MeOH followed by 5 mL of ultra-pure water. Columns were filled with 100 mL of sample, previously spiked with the appropriate amount of the first internal standard (i.e. Tramadol-d6), and then rinsed with 5 mL of ultra-pure water before drying for 30 min under vacuum. Finally, elution was performed with 3 × 5 mL of MeOH. Thereafter, the second internal standard (i.e. 5α-cholestane) was added to organic layers in order to control the conservation and the injection of the samples. Then, organic layers were evaporated under reduced pressure. Residues were finally derivatized in a pyridine-MTBSTFA mix (60:40) at 60 °C during 60 min.

Analyses were performed on a Trace GC Ultra gas chromatograph (GC) coupled to a TSQ Quantum XLS mass spectrometer equipped with an AS 3000 autosampler (both from Thermo Scientific). The GC was fitted with a Thermo Trace Gold TG-5 MS capillary column (60 m, 0.25 mm i.d., 0.25 μm film thickness).

The temperature of the column was held at 50 °C for 3 min, increased from 50 to 120 °C at 30 °C min^{-1}, and from 120 to 310 °C at 3 °C min^{-1} with a final isothermal hold at 310 °C for 21 min. 2 μL of sample was injected in splitless mode at 280 °C. Helium was the carrier gas (1 mL min^{-1}). The mass spectrometer was operated in EI mode at 70 eV, from m/z 50 to 500.

Calibration curves were realized following the same preparation procedure as for the samples. The Method Quantification Limit (MQL) was estimated by using a signal to noise ratio of up to 10 [31].

2.5. Processing of results

The use of raw concentrations is not a consistent way to assess the removal efficiency of WWTPs and the daily variation in the amount of PACs. The irregularity of the flow of both influents and effluents impacts the assessment of the removal efficiency based on concentrations. It is therefore necessary to calculate both influent and effluent load. In the present study, they were two reasons for this irregularity: (i) the flow generated by the industrial installation is not regular over the week since the factory closes during the weekend; (ii) influents are contaminated by rainwater despite the splitter network. By taking into account the flow, it is possible to calculate the load of PACs that passed through the WWTP for each sampling campaign.

$$load = CxF$$

with load, the mass load of PACs in mg day^{-1}, C, the concentration in μg L^{-1}, and F, the flow in m^3 day^{-1}

The removal efficiencies were hereafter calculated based on loads.

$$Removal = 100 - \frac{(load_{eff} x100)}{load_{inf}}$$

with *Removal* the removal efficiency in%

Another mandatory back-calculation is to normalize the load by the number of PE.

$$DML = \frac{load}{n_{PE}}$$

with DML, the daily mass load in mg day^{-1} PE^{-1} and n_{PE}, the population-equivalent number around the WWTP.

Lastly, to calculate the consumption of each PAC, a correction factor must be applied by taking into account the sorption on suspended particles and the molar ratio between the parent and the targeted residue [27,34]. In the present study, two PACs are concerned by this