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Temporal dynamics of human-excreted pollutants in wastewater treatment plant influents: Toward a better knowledge of mass load fluctuations

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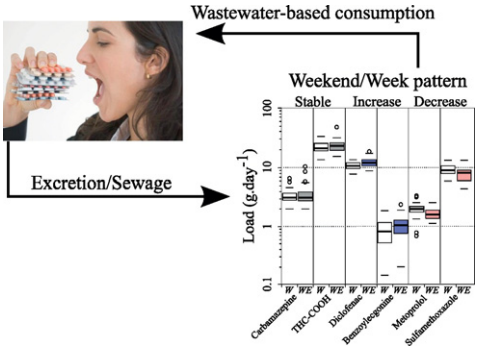
HIGHLIGHTS

- Loads of 25 human-excreted contaminants were investigated during 85 consecutive days.
- Both pharmaceuticals and illicit drugs could exhibit weekly patterns.
- Weekly patterns come from both variations in excretion rate and population amount.
- Wastewater-based consumption allows to assess site-specific features.

GRAPHICAL ABSTRACT



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ABSTRACT

The occurrence of 25 drug target residues (illicit drugs or pharmaceutically active compounds) was investigated during 85 consecutive days in the influents of a wastewater treatment plant in the Region Centre-Val de Loire, France. This long tracking period allowed a better understanding of the patterns affecting the occurrence of this type of contaminants. Among them, 2 were never detected (i.e. heroin and amphetamine). Concerning illicit drugs two patterns were found. Cocaine and ecstasy median loads varied considerably between weekdays and weekend days (i.e. 18.3 and 35.9% respectively) whereas cannabis and heroin (based on 6-mono-acetylmorphine loads) loads were within the same order of magnitude with a significant statistical correlation with pharmaceuticals such as acetaminophen or ketoprofen.

The consumption of selected drugs was back-calculated from the loads. Among illicit drugs the highest consumption was found for cannabis with a median consumption of 51 $mg \cdot day^{-1} \cdot inhabitant^{-1}$ (inh) whereas the median consumption for cocaine (based on benzoylecgonine loads) and ecstasy was 32 and 6 $mg \cdot day^{-1} \cdot 10^{3} \cdot inh^{-1}$ respectively.

The highest consumption values of pharmaceutically active compounds (PACs) were found for acetaminophen and acetylsalicylic acid with 108.8 and 34.1 $mg \cdot day^{-1} \cdot inh^{-1}$ respectively, in good agreement with national sales data. A statistically significant weekly pattern was found for several PACs such as metoprolol and trimethoprim, but with the opposite pattern to that of illicit drugs. The variations in daily PAC loads could provide information about the mobility of people in the catchment, especially on the basis of daily taken PACs (i.e. to treat chronicle diseases).

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1. Introduction

Emerging pollutants constitute a major, common, and persistent form of pollution in numerous environmental compartments (Bueno et al., 2012; Deblonde et al., 2011). Among them, pharmaceutically active compounds (PACs) present significant concentrations in natural waters, from $ng \cdot L^{-1}$ to $\mu g \cdot L^{-1}$ (Loos et al., 2009; Lopez et al., 2015; Mompelat et al., 2009). These contaminants originate from human and animal therapies and are excreted at a significant rate via urine and feces, depending on the compound characteristics (Lienert et al., 2007). Similarly, illicit drugs (IDs) are human-excreted contaminants, for which the level of contamination and the route leading to the natural environment are the same as those of PACs (Kasprzyk-Hordern et al., 2008; Postigo et al., 2010). After excretion, these compounds are mainly transferred to wastewater treatment plants (WTPs) where their incomplete removal constitutes a potential hazard for numerous living organisms, including humans (Brodin et al., 2014; de Jongh et al., 2012).

Most studies on PACs and IDs concern the assessment of their removal in classical WTPs (e.g. Fatta-Kassinos et al., 2011; Petrovic et al., 2009; Subedi and Kannan, 2014; Verlicchi et al., 2012) or focus on innovative techniques aiming at optimizing removal in order to protect natural environments (e.g. Rattier et al., 2014; Thiebault et al., 2016).

Yet, it appears crucial to better understand the temporal dynamics of PACs and IDs in order to both adjust the removal capacity of WTPs and predict contamination levels in natural waters. Consumption of PACs is known to vary with time mainly due to the medication rate of each therapeutic class. For example, antibiotics are occasional medications strongly impacted by seasonality (Golovko et al., 2014). Conversely, β-blockers and anti-diabetics are consumed on a more regular basis, because they treat chronic diseases (Sui et al., 2011). It can therefore be assumed that PAC concentrations exhibit different temporal dynamics depending on their therapeutic targets. The temporal dynamics of IDs are less understood although a relationship has been established between an increase in loads of certain IDs (i.e. recreational drugs) following several patterns such as special events (Gerrity et al., 2011) and weekends (Gatidou et al., 2016; van Nuijs et al., 2011). According to recent studies, the level of contamination of a wide range of PACs and IDs in the influent of WTPs can be correlated to the consumption rate of the population (Baker et al., 2014; Baz-Lomba et al., 2016; Celle-Jeanton et al., 2014; Krizman et al., 2016), to the amount of inhabitants in the catchment (Lai et al., 2015) and to the level of contamination within natural environments (Klaminder et al., 2015). The calculation of consumption based on loads of drug target residue (DTR) in wastewater treatment plant influents (influents) requires the use of several parameters: (i) the concentrations of DTR in influents, (ii) the flow rate of influents, (iii) the number of inhabitants in the catchment of the WTP and (iv) the percentage of parent compound excreted as DTR, the molar ratio, the stability and the sorption onto suspended particles, data that are available in the literature, albeit with some variations (Gracia-Lor et al., 2016).

Numerous studies directly compare the loads of DTR in influents with consumption levels (Besse et al., 2008; Chiffre et al., 2016; Yan et al., 2014). Few consider that the transit from excretion to arrival at the WTP can affect the form and the amount of both PACs and IDs, depending on their chemical reactivity, their sensitivity to degradation and to the physico-chemical conditions that prevail in the medium during transport. Changes in the physico-chemical conditions could therefore constitute an additional parameter that should be taken into account to explain the temporal variability of DTR loads in influents. A large dataset is also helpful to assess the temporal variability of contaminant loads in influents as it could highlight certain temporal patterns in DTR loads, making it possible to assess their regularity over time. In this study, we present for the first time the daily evolution of PACs and IDs based on 25 DTR loads during 85 consecutive days. The large dataset enabled us to (i) determine the temporal trends of various PACs and IDs on a season scale; (ii) compare the results with predicted loads and consumption in order to detect some site-specific features; (iii) use the statistical correlations between DTR in order to better understand parameters that impacting their excretion/consumption.

2. Material and methods

2.1. Sample collection and general setting

Influents were collected each day during 85 consecutive days, between March 21st and June 13th 2016 except on March 31st, providing a set of 84 samples. Sampling consisted of a volume-proportional composite with a sampling of 50 mL every 30 m^3 of influents between 0 h00 and 23 h59. For the mean influent volume value, this corresponds to a mix of 167 samples per day. The chemical parameters of influents during the study are given in Table S1. The selected WTP has a capacity of 94,000 population-equivalents corrected to 70,000 inhabitants (inh) considering the number of inhabitants on the catchment. Because IDs are not innocuous pollutants from a political and epidemiological point of view, the exact emplacement of the WTP investigated in this study is not disclosed, in accordance with ethical guidelines (Hall et al., 2012; Prichard et al., 2014).

2.2. Chemical reagents

Standards for acetaminophen (ACM), atenolol (ATE), bezafibrate (BZB), carbamazepine (CBZ), codeine (COD), diclofenac (DCF), ibuprofen (IBP), ketoprofen (KET), metoprolol (MET), oxazepam (OXA), salicylic acid (SCA), sulfamethoxazole (SUL), tramadol (TRA) and trimethoprim (TMP) were purchased from Sigma-Aldrich with a purity >98%. The standards for 6-mono-acetylmorphine (6MAM), amphetamine (AMP), benzoylecgonine (BZE), buprenorphine (BUP), cocaethylene (CET), cocaine (COC), heroin (HER), 3,4-methylenedioxy-*N*-methylamphetamine (MDMA), methadone (METD), morphine (MOR) and 11-nor-delta-9-hydroxytetrahydrocannabinol (THC-COOH) were purchased from LGC Standards. Extraction and separation solvents, methanol (MeOH) and acetonitrile (AcN) were purchased from Fisher-Scientific, assuming an analytical grade (purity up to 99.95%).

2.3. Sample preparation

After collection, influents were filtered with glass-fiber filters (GF/F, Whatman) prior to solid-phase extraction (SPE). SPE was carried out by using Chromabond HR-X cartridges (6 mL × 500 mg, Macherey-Nagel). Cartridges were conditioned with 6 mL of MeOH followed by 6 mL of ultra-pure water. Then, the cartridges were filled with 250 mL of influent prior to flushing with 6 mL of ultra-pure water before drying for 30 min under vacuum. Finally, elution of DTR was performed with 6 mL of MeOH before drying under nitrogen flow and storage at −10 °C. Samples were recovered in ultra-pure water acidified with 0.1% of formic acid before injection.

2.4. Quantification and validation

Chromatographic separation was achieved with an Ultimate 3000 RSLC (Thermo Fisher Scientific Inc., CA, USA) liquid chromatography system equipped with a binary pump and a Nucleodur C_{18} Gravity column (150 mm × 3 μm, Macherey-Nagel) supplemented by a guard column. Separation was performed at a flow rate of 1 $mL \cdot min^{-1}$ and the temperature was maintained at 30 °C. Two solvents were used as mobile phase: ultrapure water (solvent A) and AcN (solvent B) both acidified with 0.1% of formic acid. The elution gradient was a transition from 95% to 5% of A in 50 min followed by 10 min of 100% of B and then a return to the initial conditions (95% of A) during 10 min for a total analysis time of 71 min. The chromatography system was coupled to a TSQ Endura triple quadrupole mass spectrometer equipped with a heated