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Occurrence and fate of antibiotic, analgesic/anti-inflammatory, and antifungal compounds in five wastewater treatment processes

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HIGHLIGHTS

- Concentration of 62 PPCPs in 72 liquid and 24 biosolid samples from 6 WWTPs
- Different PPCP removal patterns by WWTP and season were observed.
- Factors affecting PPCP removals included temperature, HRT, and nitrification.
- PPCP removals were highest in facultative lagoon and lowest in primary treatment.
- Anti-inflammatories were biodegraded while antibiotics were highly persistent.

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ABSTRACT

The presence of pharmaceuticals and personal care products (PPCPs) in the aquatic environment as a result of wastewater effluent discharge is a concern in many countries. In order to expand our understanding on the occurrence and fate of PPCPs during wastewater treatment processes, 62 antibiotic, analgesic/anti-inflammatory, and antifungal compounds were analyzed in 72 liquid and 24 biosolid samples from six wastewater treatment plants (WWTPs) during the summer and winter seasons of 2010–2012. This is the first scientific study to compare five different wastewater treatment processes: facultative and aerated lagoons, chemically-enhanced primary treatment, secondary activated sludge, and advanced biological nutrient removal. PPCPs were detected in all WWTP influents at median concentrations of 1.5 to 92,000 ng/L, with no seasonal differences. PPCPs were also found in all final effluents at median levels ranging from 3.6 to 4200 ng/L with higher values during winter ($p < 0.05$). Removal efficiencies ranged between −450% and 120%, depending on the compound, WWTP type, and season. Mass balance showed that the fate of analgesic/anti-inflammatory compounds was predominantly biodegradation during biological treatment, while antibiotics and antifungal compounds were more likely to sorb to sludge. However, some PPCPs remained soluble and were detected in effluent samples. Overall, this study highlighted the occurrence and behavior of a large set of PPCPs and determined how their removal is affected by environmental/operational factors in different WWTPs.

1. Introduction

The use of pharmaceuticals has increased greatly in recent years. For example, Canadian sales of prescription drugs grew by almost US$8 billion between 2006 and 2011 (IMS Health Canada, 2012). Currently, there are more than 3000 compounds used as pharmaceuticals; these are divided into 24 different therapeutic classes, among which analgesic/anti-inflammatory compounds and antibiotics are the most commonly consumed (Richardson and Ternes, 2011).

Due to the increased consumption of pharmaceuticals and personal care products (PPCPs) more PPCPs are being released into wastewater via wash-off, urine, and feces, as parent compounds, conjugates or metabolites (Langford and Thomas, 2009). This has triggered concern because in the environment, certain PPCPs are persistent and bioaccumulative, potentially producing health and ecological impacts (Brausch et al., 2012; Brausch and Rand, 2011). Adverse effects from the presence of PPCPs in the aquatic environment have been reported for bacterial, invertebrate, aquatic vertebrates, and algal populations in the receiving waters of wastewater treatment systems, which include wastewater treatment plants (WWTPs) and on-site wastewater treatment systems (Du et al., 2014; Brodin et al., 2013; Fatta-Kassinos et al., 2011). Therefore, it is crucial to determine PPCP occurrence and fate during wastewater treatment. WWTPs are designed to remove oxygen demand, suspended solids, pathogens, and nutrients from wastewater, but not to remove PPCPs. Studies have reported that PPCPs are not completely removed during wastewater treatment since

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they are detected in effluents (Daughton and Ternes, 1999). In addition, certain PPCP tends to sorb to biosolids, which may be ultimately discharged to soil through the land application of biosolids.

Considering that PPCPs enter the environment via WWTP effluents or land application of biosolids, their levels in these matrices have become an increasing area of concern. Several analytical procedures have been developed to accurately quantify PPCPs, mainly based on liquid chromatography (LC) coupled with mass spectrometry (MS) in combination with modern extraction and clean-up procedures (Richardson and Ternes, 2011). Using these analytical procedures, PPCPs are measured at low ng/L levels in influent and effluent, and ng/g levels in biosolids. Diverse studies have analyzed PPCPs, many of them belonging to the antibiotic, analgesic/anti-inflammatory, and antifungal groups in these matrices (Gao et al., 2012; Jia et al., 2012; Behera et al., 2011; Ziylan and Ince, 2011; Li and Zhang, 2010; Gobel et al., 2007). However, the effect of environmental and treatment process operational factors on the fate and removal of PPCPs from wastewater has not been previously studied. This knowledge is essential to help scientists and WWTP managers optimize the removal of PPCPs during wastewater treatment; consequently reducing their discharge to the environment.

This study evaluated the occurrence and fate of sixty-two commonly consumed PPCPs: antibiotic, analgesic/anti-inflammatory, and antifungal compounds. PPCPs were analyzed in 72 liquid and 24 biosolid samples collected during the summer and winter of 2010–2012 from six Canadian WWTPs. Participating WWTPs employed five different treatment processes: facultative lagoon, aerated lagoon, chemically-assisted primary treatment, secondary activated sludge, and advanced biological nutrient removal. The main objective of this investigation was to delineate the effect of different wastewater treatment processes on PPCP removal efficiencies and to calculate mass balances in order to understand the fate of PPCPs after wastewater treatment. A unique feature of this research is that it included the occurrence and fate of PPCPs in chemically-assisted primary treatment and lagoons in addition to secondary activated sludge and advanced biological nutrient removal processes.

2. Materials and methods

2.1. Sample collection and preparation

A total of 96 samples of raw influent, final effluent, and biosolids were collected from 6 WWTPs. Plant J is a facultative lagoon, plant U employs chemically-assisted primary treatment, plants Q and MH use secondary activated sludge, plant E has advanced biological nutrient removal, and plant TB is an aerated lagoon. Liquid and solid streams of each plant were sampled twice a year (summer and winter) with the exceptions of plants J and TB, which were sampled only for liquid stream. Additional information on treatment processes at these WWTPs is provided in Table S1. Influent and effluent samples were collected for 3 consecutive days (i.e. 3 samples) using Hach Sigma 900 refrigerated autosamplers (Hach Company, Loveland CO, USA) to obtain 24-h equal volume composite samples at 400 mL every 30 min. Treated biosolids were grab sampled (i.e. 3 samples) after solid treatment and dewatering where applicable. In the case of biosolids, the use of grab samples is adequate because digester retention times at WWTPs decrease variability in sludge characteristics, generating a more homogeneous mixture. Consequently, for short-term period sampling, a grab sample can be comparable to a composite (US EPA, 1988). Wastewater and biosolid samples were subsampled into 1000 mL high-density polyethylene bottles and shipped to the laboratory on ice by overnight courier. This sampling protocol provides information about variability in wastewater composition over three days and per season, as discussed by Ort et al. (2010b).

2.2. Chemical analysis

Sixty-two pharmaceuticals belonging to three different families: antibiotic, analgesic/anti-inflammatory, and antifungal compounds were analyzed by AXYS Analytical Services (Sidney, BC, Canada) based on EPA method 1694 (US EPA, 2007). Seven compounds were added to the analytical protocol: betamethasone, fluocinonide, methylprednisolone, prednisolone, 2-hydroxy-ibuprofen, hydrocodone, and oxycodone (Table 1). Briefly, filtered wastewater samples were adjusted for acidic and basic conditions at pH ~4.0 and 10, respectively, and then extracted by solid phase extraction (SPE). Dry biosolids were ultrasonically extracted with a phosphate buffer/acetonitrile solution, and then pH was adjusted for acidic (pH ~4.0) and basic (pH 10) conditions. Acidic and basic biosolid extracts were cleaned using SPE. The obtained wastewater and biosolid extracts were analyzed by liquid chromatography tandem mass spectrometry (LC–MS/MS) in multiple reaction monitoring (MRM) mode. Target compounds were quantified by comparing the area of the quantification ion to that of the ^{13}C-labeled standards and correcting for response factors. Procedural blanks were analyzed, together with duplicates and spiked reference samples. In the case of procedural blanks, less than 0.25 ng/sample was found. Sample duplicates had RSD lower than 16% in wastewater and 22% in biosolids while spiked blanks showed recoveries between 50 and 130%. The recoveries of surrogate standards were calculated and monitored to ensure overall data quality which ranged from 20% to 140% and from 20% to 150% in wastewater and biosolids, respectively where 80% of recoveries ranged between 50 and 120%. The recovery values were in agreement with the quality control range provided by AXYS Analytical services for these challenging matrices. Additional information on PPCPs' chemical analysis is detailed in the Supplementary material.

2.3. Conventional parameters

Total Kjeldahl nitrogen (TKN), ammonia nitrogen, total suspended solids (TSS) and chemical oxygen demand (COD) were analyzed according to the standard methods (APHA, 2005). TKN is the overall concentration of organic nitrogen and ammonia nitrogen. TKN and ammonia nitrogen concentrations were used to estimate nitrification efficiency (Eq. (1)). Nitrification is the microbial oxidation of ammonia via nitrite to nitrate and its efficiency can be estimated by the loss of ammonia nitrogen between influent and final effluent. However, TKN in influent was used in the calculation because ammonia nitrogen can be produced through breakdown of organic nitrogen. This calculation assumed that all organic nitrogen in influent was changed to ammonia nitrogen, and the elimination of ammonia nitrogen was due to its oxidation only without considering its use for biomass generation. Although the estimated nitrification efficiency is less precise due to assumptions, it provides an indication of the degree of nitrification.

$$\text{Nitrification}(\%) = \frac{(\text{TKN}_{\text{influent}}, \text{mg/L} - \text{Ammonia nitrogen}_{\text{final effluent}}, \text{mg/L}) \times 100}{(\text{TKN}_{\text{influent}}, \text{mg/L})} \quad (1)$$

2.4. Calculation of mass balance

The removal of PPCPs during wastewater treatment processes can occur through degradation, sorption to solids, and volatilization. In the present study, since the target compounds are considered relatively non-volatile (Monteiro and Boxall, 2010), the volatilization process was assumed to be negligible. Thus, degradation and sorption are assumed to be the primary mechanisms for the removal of these substances, where degradation included photodegradation and biodegradation. The mass balance calculation was based on the following equations:

$$m_{inf} = m_{eff} + m_{degr} + m_{sorp} \quad (2)$$

where,

$$m_{inf}\,(\text{kg/d}) = \text{mean flow rate}\,(\text{m}^3/\text{d}) \times \text{median influent PPCP concentration}\,(\text{ng/L}) \times 10^{-9}$$