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Obtaining process mass balances of pharmaceuticals and triclosan to determine their fate during wastewater treatment

Bruce Petrie, Ewan J. McAdam, John N. Lester, Elise Cartmell *

Cranfield Water Science Institute, Cranfield University, Bedfordshire, MK43 0AL, UK

HIGHLIGHTS

- Aqueous and particulate analysis of 10 pharmaceuticals and triclosan in wastewaters.
- Complete mass balance used to diagnose preferred fate pathways during ASP treatment.
- ASP removal directly compared to TF whilst receiving the same influent wastewater.
- Similar removals by ASP and TF which correlated to receiving concentration.
- Effluents contained significant particulate concentrations of some chemicals.

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ABSTRACT

To better understand pharmaceutical fate during wastewater treatment, analysis in both aqueous and particulate phases is needed. Reported herein is a multi-residue method for the determination of ten pharmaceutical drugs and the personal care product triclosan in wastewater matrices. Method quantitation limits ranged from 7.6 to 76.6 ng l^{-1} for aqueous phases and from 7.0 to 96.7 ng g^{-1} for particulate phases. The analytical method was applied to attain a complete process mass balance of a pilot-scale activated sludge plant (ASP) operated under controlled conditions. The mass balance (inclusive of aqueous and particulate concentrations at all sample points) was used to diagnose removal, revealing pharmaceuticals to be separable into three fate pathways: (a) biological degradation, (b) sorption onto activated sludge and (c) resistant to removal from the aqueous phase. These differences in fate behaviour explained a broad range of secondary removal observed (−8 to 99%). The ASP was also simultaneously compared to a full-scale trickling filter (TF) works whilst receiving the same influent wastewater. Performance of the ASP and TF was similar, achieving total pharmaceutical removals of 253 and 249 μg g^{-1} biochemical oxygen demand (BOD) removed, respectively. This corresponded with reductions in total pharmaceutical load of 91 and 90% (ANOVA, *p-value* > 0.05). Interestingly, despite low suspended solid concentrations final effluents of both the ASP and TF contained significant concentrations of some chemicals in the particulate phase. Individually, triclosan and the antibiotics ofloxacin and ciprofloxacin were within the particulate phase of effluents at concentrations ranging from 26 to 296 ng l^{-1}.

1. Introduction

Pharmaceuticals and personal care products of varying concentrations are observed in river waters (López-Serna et al., 2011; Fenech et al., 2013), posing potential threats to aquatic biota (Kidd et al., 2007). Their presence in surface waters is mainly attributed to their incomplete removal during wastewater treatment. Diagnosing wastewater treatment effectiveness for the removal of these contaminants relies on the application of analytical methodologies suitable for their determination within complex heterogeneous matrices. Recent analytical trends generally focus on the development of methods for the rapid determination of a high number of chemicals (≥47) within the aqueous phase of wastewaters (Gracia-Lor et al., 2011; López-Serna et al., 2011; Gros et al., 2012). However, to better understand their fate, determination within the particulate phase is also essential (Petrie et al., 2013a). Methods are available for particulate phase determinations (Radjenovic et al., 2009a; Baker and Kasprzyk-Hordern, 2011) but very little analysis is undertaken during routine monitoring due to the laborious sample collection and further extraction requirements. For example, 1 g of dried solids is often required for each analysis (Radjenovic et al., 2009a). Although this is relatively straightforward to obtain for sludge samples where high solid concentrations are observed, the solid content typical of final effluents (≤20 mg l^{-1}) underlines the time and effort requirement to collect suitable quantities of solids for replicate analysis. Consequently, there is a paucity of information on

* Corresponding author.
E-mail address: e.cartmell@cranfield.ac.uk (E. Cartmell).

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the distribution of pharmaceuticals within the particulate phase of various wastewater matrices. Therefore complete process mass balances have not been attained. However, these are essential to determine pathways of pharmaceutical removal during continuous flow processes.

Activated sludge plants and TFs are widely used biological wastewater treatment methods which, although never originally designed or operated to remove micropollutants, can remove pharmaceuticals and other trace contaminants to varying extents (Clara et al., 2005; Joss et al., 2005; Kasprzyk-Hordern et al., 2009; Radjenovic et al., 2009; Petrie et al., 2013a). Tertiary processes such as UV disinfection can also contribute to the removal of micropollutants (Salgado et al., 2012). Nevertheless, removal by biological processes is proposed to be achieved mainly by biomass sorption and biodegradation (Andersen et al., 2005; Langford et al., 2005; Radjenovic et al., 2009b). Differences in sorption and biodegradation behaviour between pharmaceuticals are considered to be influenced by their physicochemical properties. It has traditionally been assumed that hydrophobicity is a reasonable predictor of sorption. This assumption is applicable for some chemicals such as steroid estrogens (Gomes et al., 2011; Petrie et al., 2014a). However, it is inadequate to describe the behaviour of pharmaceuticals which exhibits a broad range of physicochemical properties (Table S1). For example, research has found that hydrophobicity alone was insufficient to describe sorption behaviour and other interactions are important, particularly for charged chemicals (Hyland et al., 2012). Pharmaceuticals also vary significantly in their biodegradability. For example, ibuprofen is considered susceptible to biodegradation whereas carbamazepine and diclofenac appear relatively resistant to biological attack (Petrie et al., 2013a). Only small losses are anticipated by volatilization during aeration (Jones et al., 2005). This study was aimed at improving the understanding of pharmaceutical removal during secondary wastewater treatment. To achieve this, an analytical method was developed and applied to monitor a pilot-scale ASP operated with municipal wastewater. Operation of a pilot-scale ASP ensured continuity in solid retention time (SRT) and hydraulic retention time (HRT) which is not often achieved at full-scale (Petrie et al., 2014a; Petrie et al., 2014b). This is essential to better understand pharmaceutical removal as these parameters can influence their removal (Clara et al., 2005; Petrie et al., 2014b). The determination of aqueous and particulate concentrations at all sampling points to complete the mass balance for all compounds enabled preferred fate pathways to be proposed. This also revealed the significance of pharmaceutical partitioning within the particulate phase of samples containing comparatively low suspended solid content (e.g., final effluents). Finally, removal performance of a full-scale TF was directly compared to the ASP whilst simultaneously receiving the same municipal wastewater.

2. Materials and methods

2.1. Chemicals

The analytical standards of acetaminophen, carbamazepine and fluoxetine hydrochloride were purchased from Sigma–Aldrich (Dorset, UK) and were of ≥95% purity. The standards bezafibrate, bezafibrate-d_6, carbamazepine-d_{10}, ciprofloxacin, ciprofloxacin-d_8, diclofenac, diclofenac-d_4, fluoxetine hydrochloride-d_5, ibuprofen, ibuprofen-d_3, naproxen, naproxen-d_3, ofloxacin, ofloxacin-d_3, propranolol, propranolol-d_7, triclosan and triclosan-d_3 were obtained from QMX laboratories (Thaxted, UK). These pharmaceuticals were selected to encompass a broad range of physicochemical compositions (hydrophobicity, molecular weight, etc.) (Table S1) and therefore a variety of expectant fate behaviours during wastewater treatment. The solvents methanol (MeOH), acetonitrile (ACN) and toluene were purchased from Rathburn Chemicals (Walkerburn, UK) and were high-performance liquid chromatography (HPLC) grade. Formic acid and ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) were obtained from Fisher Scientific (Loughborough, UK). Ultra-pure (UP) water of 18.2 MΩ quality (Elga, Marlow, UK) was utilised. Ammonium acetate and Sigmacote® (silanising reagent for glass surfaces) were also purchased from Sigma–Aldrich (Dorset, UK). Sigmacote® was used to de-activate all glassware before use. Both individual stock standard and deuterated standard solutions of 1 mg ml^{-1} were prepared in MeOH or a 50:50 mixture of MeOH and water and stored at 4 or −20 °C according to recommended storage conditions. For complete dissolution of ofloxacin and ciprofloxacin, sodium hydroxide was added to achieve a final concentration of 10 mM. These antibiotic stock solutions were replaced monthly. Ten mixed working standard solutions ranging from 0 to 1000 ng ml^{-1} (containing 200 ng ml^{-1} of each deuterated surrogate) were prepared daily in UP water:ACN:MeOH (90:8:2).

2.2. Wastewater treatment works

Samples for analysis were collected from a pilot-scale ASP and a full-scale TF work located on the same site. These received municipal wastewater of the same source containing indigenous concentrations of all chemicals. The pilot-scale ASP consisted of a primary sedimentation tank (0.18 m^3), an aerated basin (0.36 m^3) and a final clarifier (0.10 m^3). This was operated at an extended 30 day SRT whilst at a constant HRT of 24 h. Prior to monitoring for pharmaceuticals the ASP was operated at these conditions for 90 days (i.e., 3 × SRT) to achieve steady-state SRT conditions (Petrie et al., 2014a; Petrie et al., 2014b). Corresponding grab samples of crude wastewater, settled sewage (post primary treatment) and final effluent were collected over three consecutive days. Return activated sludge (RAS) (or waste activated sludge) was also collected daily. The TF serves a population equivalent of 3000 and has a dry weather flow of 650 m^3 d^{-1}. The works consisted of a roughing filter for bulk organic removal and two duplex filters for nitrification. Corresponding grab samples of settled sewage and final effluent were also collected daily over the same three consecutive days. The crude sewage sample was applicable for both the ASP and TF. All samples were collected in 2.5 l borosilicate glass bottles with Teflon lined caps.

2.3. Extraction procedure

Samples (200 ml) for aqueous phase extraction were filtered using 0.7 μm GF/F filters (Fisher Scientific, Loughborough, UK) to remove particulates within 15 min of collection. Samples had Na_2EDTA added to achieve a concentration of 0.1% (w/w) to improve extraction recoveries of the antibiotics (Hernandez et al., 2007). Each sample was then spiked with deuterated surrogates to achieve a concentration of 500 ng l^{-1}. To determine extraction efficiency, selected samples were spiked with an additional 500 ng l^{-1} of all reference standards. This was then subjected to solid phase extraction (SPE) using 200 mg:6 cc Oasis HLB cartridges (Waters, Elstree, UK). The extraction protocol was similar to that described by Gros et al. (2006). Cartridges were pre-conditioned with 5 ml MeOH followed by 5 ml UP water at a constant flow rate of 1 ml min^{-1}. Samples were then loaded at 5 ml min^{-1} and cartridges were rinsed with 5 ml UP water. These were then dried for 30 min under vacuum to remove excess water. Analytes were eluted on the same day using a 4 ml aliquot of MeOH at 1 ml min^{-1}. Extracts were then evaporated to dryness at 40 °C using a miVac Duo concentrator (Genevac, Ipswich, UK). These were then reconstituted in 0.5 ml UP water:ACN:MeOH (90:8:2) and transferred to auto-sampler vials. Extracts were stored at 4 °C and analysed within 24 h.

For particulate extractions, large volumes of sample (crude wastewater — 5 l, settled sewage — 10 l, final effluent — >50 l and RAS — 1 l) were centrifuged at 1500 ×g for 10 min and filtered to obtain the suspended solids. These were frozen immediately and then freeze-dried. Replicates of 0.3 to 0.5 g were spiked with a mixed solution of