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Evaluating the degradation, sorption, and negative mass balances of pharmaceuticals and personal care products during wastewater treatment ☆

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HIGHLIGHTS

- Fate of 57 *in situ* PPCPs were assessed in activated sludge process.
- Forty-eight PPCPs were detected in soluble and twenty-nine were detected in solids.
- Negative mass balances observed for a subset of PPCPs.
- Some biodegradable PPCPs stop being degraded at low, yet notable, concentrations.

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ABSTRACT

Conventional activated sludge (CAS) wastewater treatment processes are insufficient at removing many pharmaceutical and personal care products (PPCPs) from wastewater. In addition, negative mass balances, where the effluent concentration is greater than the influent concentration, have been observed in wastewater treatment studies and a further understanding of these results is needed. In this study, the fate and occurrence of 57 PPCPs and hormones were evaluated in an activated sludge process and the mass balances were determined. The goal of the project was to understand the PPCPs biological degradation and the extent of sorption to solids. The samples containing *in situ* PPCPs (i.e. samples were not spiked with additional PPCPs) were evaluated. Forty-eight of the PPCPs were detected in the soluble form and 29 were detected sorbed to solids. Two notable results were found. First, the results of this study indicate a subset of the highly biodegradable PPCPs stop being degraded at low, yet notable, concentrations. Second, the results revealed that negative mass balances were present for a subset of the PPCPs when evaluating both the soluble and sorbed concentration, for example carbamazepine and ofloxacin. Desorption from solids was not found to attribute to negative mass balances. Overall, the results from this study provide new insights into the fate of PPCPs during CAS wastewater treatment by evaluating the degradation kinetics and sorption and the results may explain the consistent levels of highly degradable PPCPs being emitted from WWTPs worldwide.

1. Introduction

Risk analyses and exposure studies have led to the concern that the levels of pharmaceuticals and personal care products (PPCPs) and hormones discharged into the environment from wastewater treatment plants (WWTPs) may have a negative impact on the ecosystem (Al Aukidy et al., 2012; Blair et al., 2013a; Brodin et al., 2013; Niemuth and Klaper, 2015). Furthermore, influent concentrations and the removal of PPCPs from wastewater has been found to vary widely (Miege et al., 2009; Oulton et al., 2010; Verlicchi et al., 2012). Information regarding the fate of PPCPs in wastewater is limited; in particular, the understanding of the fate of PPCPs in an aerobic wastewater treatment process is incomplete.

WWTPs that utilize conventional activated sludge (CAS) systems have been found to present a wide range of removal efficiencies for different PPCPs (Verlicchi et al., 2012). During a CAS process, three mechanisms can be used to determine the fate of

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PPCPs: biological degradation, sorption, and volatilization (Joss et al., 2006). Sorption to solids is expected to be significant for PPCPs with a log octanol–water partitioning coefficient (K_{ow}) greater than 4.0 (Thompson et al., 2011). Few PPCPs have a logK_{ow} greater than 4.0 and removal by sorption was concluded to be a minor removal mechanism for most PPCPs (Gulde et al., 2014; Khan and Ongerth, 2002; Radjenović et al., 2009). Volatilization can be considered negligible for the majority of PPCPs (Joss et al., 2006). The disparity commonly observed in PPCPs removal during aerobic wastewater treatment is likely due to the varying operating parameters that can impact the fate such as the solids retention time, hydraulic retention time, concentration of suspended solids, fraction of heterotrophic and autotrophic biomass, pH, and other operating and influent conditions (Alvarino et al., 2014; Fernandez-Fontaina et al., 2012; Gulde et al., 2014; Majewsky et al., 2011a,b; Tran et al., 2013; Verlicchi et al., 2012).

Some studies assessing the fate of PPCPs in wastewater have encountered issues with negative mass balances, where lower concentrations were seen in the influent than the effluent. Reasons for this can include improperly addressing the fluid dynamics of a WWTP (Majewsky et al., 2011b; Ort et al., 2010; Rodayan et al., 2014), conjugate compounds that are not detected at the influent could be retransformed into the original compound due to biological processes (Kumar et al., 2012; Monteiro and Boxall, 2010; Salgado et al., 2012; Verlicchi et al., 2012), desorption from the return activated sludge may occur during the secondary treatment process (Salgado et al., 2012), and PPCPs may be released from fecal particles as the feces are being broken down by microbes (Göbel et al., 2007).

While many studies have investigated PPCPs during an aerobic wastewater treatment process, numerous questions remain regarding the fate of PPCPs within conventional activated sludge treatment processes. Therefore, the goals of this study will be to: (1) further examine the occurrence and fate of 57 commonly used PPCPs in an aeration basin; (2) determine the degradation rate constants and sorption coefficients; and (3) assess the negative mass balances observed in previous studies. These goals were evaluated by determining the fate and kinetics of 57 PPCPs in mixed liquor activated sludge from a wastewater treatment plant in Milwaukee, Wisconsin, USA. This paper presents a substantial PPCP data set by evaluating the hourly soluble and sorbed levels within an aerated batch reactor using *in situ* PPCPs.

2. Materials and methods

2.1. Sampling site

Mixed liquor activated sludge was used from South Shore Water Reclamation Facility (SSWRF) in Oak Creek, WI, which is a facility that services the greater Milwaukee, WI area. SSWRF uses preliminary treatment (7 bar screens/grit channels), primary treatment (16 primary clarifiers), conventional activated sludge treatment (28 plug flow aeration basins and 24 secondary clarifiers) and chlorine disinfection (2 5-pass contact channels). SSWRF has a treatment capacity of 1,135,000 m^3 day^{-1} with an average flow of approximately 379,000 m^3 day^{-1}. The base flow is 227,000–284,000 m^3 - day^{-1} in dry conditions. Average flow rates on the sampling dates, November 5, 6, and 7, 2013, were 246,000 m^3 day^{-1}, 238,000 m^3 - day^{-1}, and 291,000 m^3 day^{-1}, respectively. The mean hydraulic retention time in the aeration basin at SSWRF is approximately 10 h.

2.2. Batch reactor

One hundred ninety liters of mixed liquor activated sludge from SSWRF was transferred to a batch reactor from the head of a plug flow aeration basin on three separate dates (November 5, 6, and 7, 2013). Eleven samples were collected per day for the mixed liquor suspended solids (MLSS) and PPCPs analyses, where the samples were collected initially and then hourly for the next 10 h. For the liquid PPCPs analysis, the hourly samples were allowed to settle for 5 min and the supernatant was decanted with a target volume of 500 mL for each extraction method (acidic, basic, and hormone). Two 500 mL samples of mixed liquor activated sludge samples were collected for the solids PPCPs and MLSS analyses. The 10 h duration was selected because under normal operating conditions, a CAS aerobic basin has a hydraulic retention time of 6–12 h (Metcalf and Eddy Inc., 2003). The mixed liquor was not spiked with PPCPs; only the *in situ* PPCPs in the mixed liquor were evaluated. Aeration was completed using a Hakko 60 L Air Pump and a submerged Matala 22.9 cm membrane disk diffuser. Dissolved oxygen levels were kept between 6 and 9 mg L^{-1} (average of 7.5 mg L^{-1}) as to not limit the amount of oxygen available to the microbes.

2.3. PPCPs analysis

PPCPs were extracted and analyzed based upon US EPA Method 1694 (USEPA, 2007a) for pharmaceuticals and US EPA Method 1698 (USEPA, 2007b) for steroids and hormones by using high performance liquid chromatography combined with tandem mass spectrometry (HPLC/MS/MS) with modifications as published by Blair et al. (2013b). The PPCPs were selected for this study based on the EPA methods. The same 57 PPCPs were assessed for both the soluble and solid levels.

2.4. K_{biol} calculation

To evaluate the degradation of soluble PPCPs, pseudo first-order kinetics (Joss et al., 2006) was used to determine the biological rate constant:

$$\frac{dS_t}{dt} = -K_{biol}\text{MLSS}\ S_0 \quad (1)$$

where S_t is the soluble compound concentration at time t (ng L^{-1}), t is hydraulic retention time (h), K_{biol} is the intrinsic biological rate constant (L g^{-1} h^{-1}), MLSS is the concentration of suspended solids (average daily g L^{-1}), and S_0 is the initial soluble compound concentration (ng L^{-1}). Pseudo-first-order kinetics is used to describe exponential degradation with the mixed liquor suspended solids concentration proportionally influencing the rate.

The K_{biol} values were found by regression using the negative of the slope of the natural log of the concentration divided by the initial concentration over time, with the intercept set at zero. The K_{biol} values are based on the loss of the parent compound. In this study, no attempt was made to evaluate the reaction products. If a compound approached a degradation plateau (where degradation appears to stop) or the MDL, the values preceding and ending at the plateau or MDL values were used. PPCPs with a starting soluble concentration of less than 3 times the MDL were omitted from the K_{biol} calculations.

2.5. K_d calculation

To evaluate the extent of sorption, the sorption coefficient (K_d) is typically defined for equilibrium conditions in a batch reactor (Joss et al., 2006):

$$K_d = \frac{X}{\text{MLSS} * S} \quad (2)$$

where K_d is the sorption coefficient of activated sludge (L kg^{-1}), X is the sorbed compound concentration expressed per unit of volume