Modelling biotransformation of drug biomarkers by sewer biofilms

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ABSTRACT
Due to the presence of biofilms in sewer systems, conventional and trace organic chemicals may undergo significant biological transformation during wastewater drainage. Modelling in-sewer conversion processes of organic chemicals is thus crucial in view of predicting their occurrence in sewers, especially for wastewater-based epidemiology. In this study, biotransformation of two illicit drugs, methadone (METD) and its human metabolite EDDP, was assessed in aerobic and anaerobic biofilms in two lab-scale annular rotating reactors, simulating typical conditions in sewers. Two models were tested to describe biofilm-mediated transformation, namely (i) a model based on the Activated Sludge Model for Xenobiotics (ASM-X) framework, and (ii) an extension of ASM-X with description of primary metabolic processes based on existing Activated Sludge Models (e.g., ASM1). Results indicate that transformation of the selected drugs can only be modelled using the second approach, as biotransformation is enhanced in the presence of bioavailable organic carbon.

INTRODUCTION
Transformation of organic chemicals present in untreated sewage can be significantly influenced by sewer biofilms. While pressurized sewers are predominantly anaerobic and favor the growth, among others, of sulfate reducing bacteria (SRB), gravity sewers are mostly aerobic due to reaeration and heterotrophic biomass prevails in biofilms with comparably high activity (Hvitved-Jacobsen et al. 2002). Understanding the role of sewer biofilms on the transformation of pollutants can help predicting pollutant loadings to downstream wastewater treatment plants. This is even more relevant to the emerging field of wastewater-based epidemiology, in which estimation of illicit drug consumption at community level relies on the quantification of urinary drug biomarkers in untreated wastewater. Recent research has been focusing on illicit drug transformation in sewers (Ramin et al., 2016; McCall et al., 2016). To the best of our knowledge, there has been no comprehensive study correlating the functionality of in-sewer biofilm on transformation of primary pollutants (e.g., organic substrates) and trace organic chemicals (e.g., illicit drugs) under different redox conditions. Thus, the aim of this study was to investigate the removal of illicit drugs and primary pollutants (COD, sulfate) in well-controlled biofilm systems under aerobic and anaerobic conditions.

MATERIALS AND METHODS
Experimental assessment
Two annular rotating biofilm reactors were used to simulate shear conditions prevailing in the sewers (see Fig. 1). The reactors were run for 14 months under continuous-flow operation, fed with pre-clarified wastewater (4 L d⁻¹), to establish stable biofilms (thickness: 0.75 mm, aerobic; 1 mm, anaerobic). Batch experiments were then performed by connecting each biofilm reactor to an external tank (recirculation flow=4 L h⁻¹). Experiments were started by spiking a mixture of 16
illicit drugs and metabolites (final concentration=10 µg L⁻¹) in methanol (MeOH) to the external tanks. During the experiments, temperature (aerobic T\text{mean}=17.0°C; anaerobic T\text{mean}=17.8°C) and pH (aerobic pH\text{mean}=8.7; anaerobic pH\text{mean}=9.2) were monitored. Samples were collected to measure illicit drug concentrations at regular intervals. Biological activity in the reactors was also monitored by measuring soluble COD, nitrate, ammonium and sulfate using colorimetric methods. Batch experiments (volume=4 L) to assess sorption to biofilms were carried out by suspending the biofilm on two removable slides in tap water and used and adding sodium azide (0.05%) to inhibit biological activity. Sample preparation and analysis for drug biomarkers were carried out according to Bijlsma et al. (2013). Further details can be also found in Ramin et al. (2016).

Modelling framework
To simulate biofilm-mediated transformation of drug biomarkers, two 1-D models were tested:

a) transformation-sorption model based on the Activated Sludge Model for Xenobiotics (ASM-X) (Plósz et al., 2013), in which biofilm was considered as a homogeneous medium and negligible biomass growth was assumed. Biotransformation was described using pseudo-first-order kinetics (constant biomass).

b) an extension of the above-mentioned ASM-X, with the description of primary metabolic processes as in the Activated Sludge Model no. 1 (ASM1; Henze et al., 2000) for heterotrophic and autotrophic biomass and as in Jiang et al. (2009) for anaerobic processes. In the latter model, the biofilm was considered as heterogeneous medium, in which biofilm growth and detachment were explicitly described. Biotransformation in model was formulated using second-order kinetics with active biomass as a state variable and a switching function for bioavailable organic carbon (i.e., biotransformation enhancement in presence of substrate).

Model parameters for abiotic transformation, sorption and biotransformation by suspended solids were adopted from Ramin et al., 2016. Chemical fluxes between bulk phase and biofilm were described according to the two-film theory, with no reaction occurring in the boundary layer (Wanner et al., 2006). The spatial discretization of the biofilm was done according to Vangsgaard et al. (2012). The models were implemented in Matlab R2014a (MathWorks, US).

RESULTS AND DISCUSSION
Biological activity of reactor
Concentrations of soluble COD, sulfate, ammonium and nitrate during biofilm experiments are presented in Fig. 2. We assumed that methanol (MeOH), introduced with the spiking solution, is not utilized as growth substrate, similarly to what found for suspended biomass (Ramin et al., 2016). The final soluble COD data reflect the concentration of inert COD and residual (not evaporated) MeOH. Sulfate was significantly removed in the anaerobic reactor during the first day of the experiment, (likely due to SRB activity), while remaining constant during the second day (possibly in the absence of readily biodegradable organic substrate). In the aerobic biofilm, sulfate was formed likely due to hydrogen sulfide oxidation. Ammonium removal was shown under both redox conditions. In the aerobic reactor, this could have resulted from ammonia assimilation for growth, considering that nitrifiers are usually outcompeted by heterotrophs in sewer biofilms (Jiang et al., 2009). Nevertheless, ammonia stripping may not be excluded at high pH in both reactors.

Sorption and transformation of drug biomarkers
Fig. 3 illustrates the concentration profiles of two drug biomarkers, methadone (METD) and its main human metabolite (EDDP) during batch experiments with active biofilm. It was observed that METD is sorbed in both aerobic and anaerobic biofilms whilst EDDP was only sorbed in the anaerobic biofilm (data not shown). METD removal was much higher in the aerobic biofilm than in
the anaerobic one. The opposite was observed for EDDP, i.e., higher removal in the anaerobic biofilm. It was assumed that these chemicals have independent transformation pathways in biofilms, similar to raw wastewater (Ramin et al., 2016). The simplified biofilm model (a) was used to simulate the transformations. It was observed that there is a systematic deviation between model predictions and measurements (Fig. 3). It can be hypothesized that these chemicals undergo a co-metabolic transformation with enhancement effect in which the drug transformation rate is reduced significantly during the second day of the experiment where readily biodegradable substrate was possibly limiting. The preliminary results of model (b) – describing co-metabolic processes in a heterogeneous biofilm model – can more precisely predict the removal of the selected drug biomarkers (data not shown).

This study demonstrates the capability of sewer biosolids to transform drug biomarkers. Furthermore, the study shows the importance of identifying the right model structure (i.e., co-metabolic model) to properly predict biofilm mediated drug transformation. The model identified and calibrated in this study will contribute to increase the accuracy of drug consumption estimates in wastewater based epidemiology.

Figure 1. Configuration of annular rotating biofilm reactor connected to an external jacketed tank with recirculating flow during a batch experiment. Samples were taken from the outlet of the biofilm reactor. To maintain aerobic and anaerobic conditions inside the reactors, the external tank was sparged with dried atmospheric air or nitrogen, respectively. The profile inside the reactor illustrates a typical concentration profile of substrates inside the biofilm.

Figure 2. Concentrations of soluble COD, sulfate, ammonium and nitrate during biofilm experiments in batch mode under aerobic and anaerobic conditions.
Figure 3. Concentration profiles of METD and EDDP during batch experiments with aerobic and anaerobic biofilms. The shaded areas reflect the 95% confidence interval of the model (a) predictions.

REFERENCES


