Modelling Illicit Drug Fate in Sewers for Wastewater-Based Epidemiology

With increasing consumption of illicit drugs, in particular cocaine and cannabis, in recent decades, the negative social and public health impact has also propagated. Following drug consumption and human metabolism, fractions of unchanged parent drugs and metabolites are excreted into toilets. After transport in sewers, these chemicals enter wastewater treatment plants (WWTPs). Monitoring campaigns are normally performed at WWTP influent to collect representative samples for subsequent quantitative chemical analysis, measured drug loads are used to estimate population-normalized parent drug consumption based on a candidate biomarker (the parent drug itself or one of the human metabolites). This approach has gained increasing attention in the past decade and is termed wastewater-based epidemiology. It has been shown that this emerging approach can improve and complement survey-based methods.

Sewer systems can be considered as biological reactors, in which the concentration of organic chemicals present in wastewater can be impacted by in-sewer processes during hydraulic residence time. Illicit drug biomarkers, as trace organic chemicals in the range of nanograms to micrograms per liter, are subject to physical, chemical or biological processes in sewers (fate processes). The occurrence of these processes may lead to significant change of drug loads at WWTP influent compared to source release points. Therefore, not accounting for these variations may negatively affect drug use estimates. However, due to a lack of sufficient evidence on potential in-sewer sorption and transformation of drug biomarkers, these processes are often neglected by wastewater-based epidemiologists. The motivation of this thesis was to overcome this substantial knowledge gap by: (i) providing new evidence on sorption and transformation of drug biomarkers in raw wastewater and sewer biofilms; and (ii) developing modelling tools – by combining and extending existing modelling frameworks – to predict such processes. To achieve this goal, a substantial part of this thesis was dedicated to the experimental assessment and modelling of in-sewer processes by means of laboratory scale studies under the conditions representative to sewer systems. Eventually, the prediction of in-sewer processes at the catchment level was carried out and back-calculation of drug consumption was performed using measured data from a monitoring campaign.

Overall, the methodology used in this thesis combined different aspects, namely: (i) optimal experimental design; (ii) mathematical formulation of processes; (iii) model calibration; (iv) uncertainty analysis and model parameters identifiability; (v) model validation; and (vi) model application for back-calculation at catchment level. In this thesis, 16 drug biomarkers were selected based on their ubiquitous occurrence in wastewater, and include cocaine, methamphetamine, methadone, heroin, codeine and tetrahydrocannabinol (THC) and their respective major human metabolites.

In-sewer processes, namely, sorption and transformation of these chemicals were assessed in raw wastewater (suspended biomass) and sewer biofilms in targeted batch experiments. These experiments were conducted under aerobic and anaerobic conditions. Annular rotating biofilm reactors were used to simulate shear conditions prevailing in sewers and were operated over 14 months. Abiotic transformation (e.g., hydrolysis) was also evaluated using mineral water and sorption to suspended solids and biofilms were additionally assessed. Overall, two sets of experiments were performed and used for model calibration and model validation purposes.

To predict the fate of drug biomarkers in raw wastewater, simultaneous evaluation and modelling of substrate utilization and microbial growth processes was performed. It was hypothesized that active biomass dynamics during batch experiments (due to high substrate availability and significant microbial growth) can significantly impact the prediction of biotransformation rates. For this purpose, the Wastewater Aerobic/anaerobic Transformations in Sewers (WATS) model was combined with the Activated Sludge Model for Xenobiotics (ASM-X) to predict the fate of drug biomarkers together with the primary metabolic processes. Two new processes were considered, namely sorption-desorption to reactor wall and abiotic transformation. As for sewer biofilms, the extended ASM-X model was further modified by accounting for diffusive mass transfer limitations of biomarkers from the bulk phase into the biofilm and within the biofilm matrix. Selected model parameters were estimated with the Bayesian optimization method DREAM(ZS). A calibration methodology was developed with focus on uncertainty propagation among model parameters, e.g. from abiotic transformation rates to biotransformation rates. Subsequently, uncertainty analysis was performed to assess the impact of variability of model parameters on model output. Moreover, different transformation pathways were tested for the selected biomarkers and new pathways were identified based on mass balance, uncertainty analysis, and feasibility of transformations (according to an existing pathway database). Results from the experimental and modelling assessment indicated that by ignoring primary metabolic processes in raw wastewater would impose significant overestimation (up to 385%) of transformation rates under aerobic conditions, whereas no difference was found under anaerobic conditions. Abiotic transformation processes were the dominant removal mechanism for many of the selected chemicals (e.g., cocaine: 80-100%, batch experiments with raw wastewater) under both aerobic and anaerobic conditions. Several biomarkers underwent substantial biotransformation e.g., almost complete removal of heroin and morphine-3-glucuronide after 12 h in batch experiments with raw wastewater. It was further observed that sewer biofilms can enhance biotransformation of a number of selected chemicals, such as benzoylcegonine and 6-monoacetylmorphine. Overall, redox conditions were found to have an influence on biotransformation rates (especially for methadone) and, to a lesser extent, on abiotic transformation rates. Only a few chemicals, such as 11-hydroxy-THC, were found to sorb onto suspended solids and sewer biofilms. Validation of calibrated models with an independent dataset was successful for most compounds, the main exception being methadone under aerobic conditions.

To demonstrate the impact of in-sewer processes on estimation of daily drug use at catchment level, a generic scenario analysis was performed to assess the uncertainties associated with in-sewer processes and sampling. It was found that ignoring in-sewer processes for cocaine and its metabolite benzoylcegonine can add up to 11% (median value for a large catchment) error in daily cocaine consumption estimates. This error was 43% and 11% for estimates of daily heroin use with 6-monoacetylmorphine and morphine as candidate biomarkers, respectively. In contrary, sampling error (flow-proportional sampling mode) was the highest in the smallest catchment – up to 17% for cocaine.
Subsequently, measured cocaine and benzoylecgonine loads from a 2-week monitoring campaign at the Lynetten WWTP influent (Copenhagen, Denmark) was used to estimate cocaine consumption in two upstream catchments by accounting for in-sewer fate processes. Significant differences in consumption trends were observed between weekdays, weekends, holidays and a street music festival. On average, twice as high cocaine consumption was found during festival period as compared to normal weekdays. Wastewater-based epidemiology is a truly interdisciplinary approach in which engineering tools, including models developed and tested in this thesis, can be beneficial for the accurate estimation of drug consumption in urban areas.