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Xenobiotic Removal Efficiencies in Wastewater Treatment Plants: Residence Time Distribution as a Guiding Principle for Sampling Strategies

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1. Introduction

Characterizing mixing regimes by residence time distribution (RTD) techniques in wastewater treatment plants (WWTPs) is well understood in hydraulic engineering (De Clercq et al., 1998). Nevertheless, it is often neglected in sampling campaigns of micropollutants. These campaigns usually aim at assessing xenobiotic removal efficiencies from full-scale mass balances. WWTP performances e.g. for chemical oxygen demand (COD) or NH_3-N are routinely evaluated by comparison of long-term influent-effluent data. However, the measurements and analyses of xenobiotics is cost- and work-intensive which is why often only a short sampling period (mostly 24 h in influent and effluent) is used as a tradeoff between cost and data density.

A number of investigations relying on 24-h composite samples use the mean hydraulic retention time (HRT) as time offset to match influent with effluent loads assuming a quantitative coverage of influent loads in the effluent or very stable influent concentrations over relevant periods. However, taking into consideration variable influent conditions and that residence time distributions (RTD) of perfect plug flow tanks do not apply to conventional WWTP reactors, mass balancing based on 24-h influent-effluent comparison may lead to biased or even negative removal efficiencies. It is therefore crucial to account for mixing characteristics in evaluating xenobiotic mass balances and to accordingly adapt sampling strategies.

The objective of the present study was to propose a method to reliably estimate xenobiotic removal efficiencies from monitoring data using hydraulic RTDs in WWTPs as a guiding principle. To this purpose, a completely mixed tanks-in-series approach was used to address the hydraulic mixing regime in a Luxembourg WWTP. It aims at bridging the gap between environmental chemistry and engineering practices in micropollutant sampling campaigns.

2. Materials and Methods

The plant layout of the Luxembourg WWTP Mamer was built in the wastewater modeling software GPS-X (Hydromantis, Canada) allowing dynamic simulation of WWTPs. Completely mixed tanks-in-series (n=4) with standard primary and secondary clarifiers were selected. Calibration was performed using wastewater conductivity measured in influents and effluents as well as hourly flow data during a three week period.The distribution of residence times of a xenobiotic within the plant was determined by model simulations. To this purpose, concentration pulses were created in the influent (duration: 24 h, following typical sampling periods of composite samples). The fraction of soluble inert COD S_i served as model substance for xenobiotics in the modeling software *GPS-X*.

Two model scenarios were set up to derive optimized sampling strategies taking WWTP Mamer as an example. Realistic measured influent concentrations of a xenobiotic (diclofenac) were introduced for four days on the basis of 2-h composite samples in dry weather scenario. Monte Carlo simulations were performed to assess the uncertainty introduced by discrete sampling on the load estimation.

3. Results and Discussion

Model calibration results show that modeled values matched measured effluent conductivity within i) the range of the effluent concentration and ii) the variation patterns of the effluent. The correlation coefficient was found to be R = 0.76 suggesting good tracking of the conductivity variation. Nevertheless, small differences between modeled and measured values are observable that may be caused by not considering short circuits, stagnant zones and non-ideal mixing in the model. Their influence might change with variable hydraulic loading.

The RTD of an inert soluble xenobiotic was determined using the calibrated model. During dry weather conditions, around 20 % of the influent water volume has been released within 24 hours while during a rainfall event already 60 % have been emitted during the same time. Shifting a 24-h sampling period by the HRT (17 h) as the temporal offset from the start of the influent sampling day would capture only around 30 % of the water volume that entered the WWTP 17 hours ago. Consequently, a 24-h effluent (composite) sample of WWTP Mamer would largely consist of wastewater originating from periods preceding the influent pulse during dry weather conditions. This shows that a daily water volume is distributed over more than one day when discharged in the effluent. Therefore, a daily influent load cannot be completely covered by (composite) samples taken over a period of only 24 h in the effluent. However, an optimum temporal offset can be identified, by which a 24-h effluent sampling period is shifted from the beginning of the influent period to cover the maximum percentage of the released load.

By sampling the concentrations and flow of 4 consecutive days in the influent, their fraction released during the chosen measurement period can be determined (Fig. 3.1.). The actual elimination efficiency can now be determined by estimating the reference load that actually corresponds to the effluent sample. This reference load is composed of load fractions of, in this case, four influent days:

$$L_{ref} = \sum f_n \cdot L_{inf,meas,n} \tag{1}$$

where L_{ref} = reference load [ng d^{-1}], f_n = fraction of the influent load of day n [-] on an effluent sampling period, $L_{inf,meas,n}$ = measured influent load of day n [ng d^{-1}].

This reference load is then used in the mass balance calculations and compared to the measured and potentially degraded effluent load. In the case that less than 100 % of the effluent load can be explained by the sampled influent days, the uncertainty of this non-sampled loading should be considered. For this reason, it was assumed that the loads of the non-covered period preceding the influent sampling days had the same daily average load and varied with the same standard deviation (± 27.2 %) as the measured loads. This would result in an uncertainty of ± 4 % on the total xenobiotic elimination efficiency. Monte Carlo analysis showed that the estimated load fraction in the outlet is additionally associated with an error of 6 % caused by discrete sampling and errors in flow measurement, resulting in a propagated error of 14.3% on the reference load.

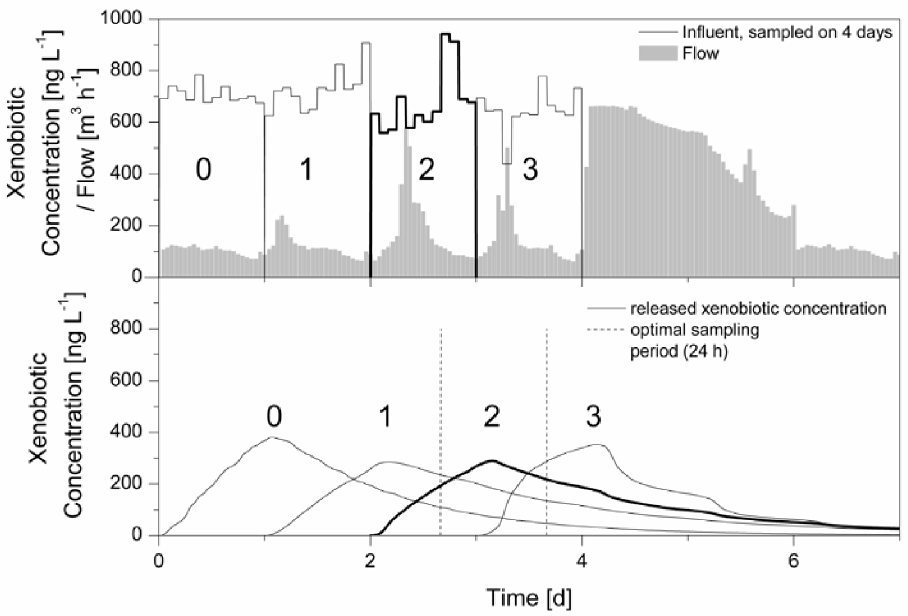

Figure 3.1. Contribution of influent loads on a 24 h effluent sampling period using realistic influent variation of xenobiotic concentrations (diclofenac, 2h composite samples) and flow (hourly values); temporal offset of the effluent sampling period from influent day 2: 18 h; water volume covered: 14.4 % of day 0, 22.4 % of day 1, 30.7 % of day 2 (optimum) and 16.0% of day 3.

4. Conclusions

Results showed that a 24-h effluent sampling period would cover only around a third of a corresponding 24-h influent load. Commonly reported negative elimination efficiencies of xenobiotics might therefore be also a consequence of biased sampling schemes. The optimal sampling setup for full-scale mass balancing at WWTP Mamer was determined to cover 4-5 consecutive days in the inlet and a single sampling day in the outlet. Due to influent variability and errors associated with discrete sampling (Ort et al., 2010), elimination efficiencies of less than 15-20 % are probably impossible to track in full-scale investigations.

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