WATER RESEARCH 45 (2011) 6152–6162

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# Xenobiotic removal efficiencies in wastewater treatment plants: Residence time distributions as a guiding principle for sampling strategies

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ARTICLE INFO

*Article history:*
Received 15 December 2010
Received in revised form
1 September 2011
Accepted 5 September 2011
Available online 22 September 2011

*Keywords:*
Hydraulic residence time
Sampling
Xenobiotics
Conductivity
Removal efficiency
Optimal experimental design

ABSTRACT

The effect of mixing regimes and residence time distribution (RTD) on solute transport in wastewater treatment plants (WWTPs) is well understood in environmental engineering. Nevertheless, it is frequently neglected in sampling design and data analysis for the investigation of polar xenobiotic removal efficiencies in WWTPs. Most studies on the latter use 24-h composite samples in influent and effluent. The effluent sampling period is often shifted by the mean hydraulic retention time assuming that this allows a total coverage of the influent load. However, this assumption disregards mixing regime characteristics as well as flow and concentration variability in evaluating xenobiotic removal performances and may consequently lead to biased estimates or even negative elimination efficiencies.

The present study aims at developing a modeling approach to estimate xenobiotic removal efficiencies from monitoring data taking the hydraulic RTD in WWTPs into consideration. For this purpose, completely mixed tanks-in-series were applied to address hydraulic mixing regimes in a Luxembourg WWTP. Hydraulic calibration for this WWTP was performed using wastewater conductivity as a tracer. The RTD mixing approach was coupled with first-order biodegradation kinetics for xenobiotics covering three classes of biodegradability during aerobic treatment.

Model simulations showed that a daily influent load is distributed over more than one day in the effluent. A 24-h sampling period with an optimal time offset between influent and effluent covers less than the half of the influent load in a dry weather scenario. According to RTD calculations, an optimized sampling strategy covering four consecutive measuring days in the influent would be necessary to estimate the full-scale elimination efficiencies with sufficient accuracy. Daily variations of influent flow and concentrations can substantially affect the reliability of these sampling results. Commonly reported negative removal efficiencies for xenobiotics might therefore be a consequence of biased sampling schemes. In this regard, the present study aims at contributing to bridge the gap between environmental chemistry and engineering practices.



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doi:10.1016/j.watres.2011.09.005

## 1. Introduction

The elimination of micropollutants in wastewater treatment plants (WWTPs) became a major concern during the last decade. A variety of polar micropollutants such as pharmaceuticals or personal care products pass biological wastewater treatment without being fully degraded (Bernhard et al., 2006; Reemtsma et al., 2006). In order to estimate micropollutant emissions to receiving waters, the removal performance of WWTPs is usually assessed by either full-scale balancing or by the determination of biodegradation rates at lab-scale (Vieno et al., 2007; Wick et al., 2009). Both estimation approaches rely essentially on the time that the water remains in the plant, normally referred to as the hydraulic retention time (HRT). The latter is an easily accessible parameter since it can be calculated from flow through and tank volumes. Most work carried out uses 24-h composite samples assuming quantitative coverage of influent loads in the effluent with a temporal shift proportional to the HRT 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 WWTPs reactors, mass balancing based on influent–effluent comparison may lead to biased or even negative removal efficiencies. Hence, an adequate description of the hydraulic characteristics is critical for designing sampling campaigns and predicting dynamic xenobiotic emission.

The characterization of mixing regimes in wastewater treatment plants with RTDs and pulse-response techniques is well explored and common practice (De Clercq et al., 1999; Gujer, 2008; Levenspiel, 1999). It was successfully applied to describe mixing regimes in a variety of tracer test studies (Fall and Loaiza-Navía, 2007; Capela et al., 2009). The RTD is hereby fitted by the number and size of tanks-in-series, the type of the mixing regime (completely mixed, plug-flow etc.) as well as the flow conditions. Artificial tracer tests with appropriate substances like e.g. lithium and bromide salts or fluorescent dyes are commonly used for hydraulic characterization of mixing regimes (Olivet et al., 2005). However, recent studies showed that the latter can also be realized with data from routine measurements of WWTPs such as temperature or conductivity (Ahnert et al., 2010).

The fact that the effluent concentration dynamics of hydrophilic micropollutants are largely governed by hydraulic mixing is often poorly considered and can lead to increased uncertainty and misinterpretation of the sampling results. Generally, WWTP performances are routinely evaluated by comparison of long-term influent–effluent data, e.g. for chemical oxygen demand (COD) or $NH_3$-N, and is therefore believed to be applicable to xenobiotics as well. However, the measurements and analyses of xenobiotics are 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. In such a case, the effect of influent variations on sampling results is naturally potentially much larger.

In this context, the present study aims to bridge the gap between hydrodynamic behavior and biodegradation in municipal WWTP to assess xenobiotic removal efficiencies and derive adequate sampling strategies. So far, the RTD concept has not been applied in combination with short-term xenobiotic mass balance calculations.

For this purpose, hydraulic mixing regimes were characterized by use of an RTD approach and coupled to first-order biodegradation kinetics. Biodegradation was modeled for three different levels of xenobiotic biodegradability which are representative for persistent as well as moderately and easily biodegradable compounds. Simulations were applied to derive optimal sampling strategies and to minimize sampling errors. Moreover, an RTD-based method is proposed for an adequate estimation of overall removal efficiencies as well as a guidance tool for designing measurement campaigns at full-scale WWTPs.

## 2. Material and methods

### 2.1. Sampling & WWTP data

Wastewater conductivity was measured in the influent (after sand trap) and the effluent (after secondary clarification) of the Luxembourg WWTP Mamer with YSI 600 OMS probes over a period of three weeks (sampling interval $\Delta t = 10$ min). Hourly inflow data and tank volumes were obtained from the plant operators (Water Syndicate SIDERO) (Fig. 1).

### 2.2. Modeling

#### 2.2.1. Plant layout & calibration

The plant layout of WWTP Mamer was reproduced in the wastewater modeling software GPS-X from Hydromantis (Hamilton, Canada) (Fig. 1). It is equipped with standard activated sludge models (Gujer et al., 1999; Henze et al., 1987) allowing dynamic simulation of WWTPs. Completely mixed tanks-in-series with rectangular primary clarifiers and circular secondary clarifiers were selected. For the latter, a 1-D model of settler mass balance equations is used for ten horizontal layers of equal depth. Volumes, sequence and tank operation were adjusted according to the data supplied by the plant managers (Table 1).

Measured wastewater conductivity was used as a tracer for model calibration at the given flow conditions of a three week period. Inlet conductivity was fed to the model as input and the predicted effluent conductivity was iteratively fit to the measured effluent data to determine the number of completely mixed tanks-in-series and to estimate the sludge recirculation flow used in the model. The difference between measured and predicted values was minimized by the chi square (Eq. (1)) within GPS-X.

$$x^2 = \sum_{i=1}^{N} \frac{1}{\sigma_i^2}(y_i - \hat{y}_i)^2 \quad (1)$$

where $x^2$ = chi square, $N$ = number of observations, $\sigma_i$ = standard deviation of the measurements, $y_i$ = measured values, $\hat{y}_i$ = predicted values.

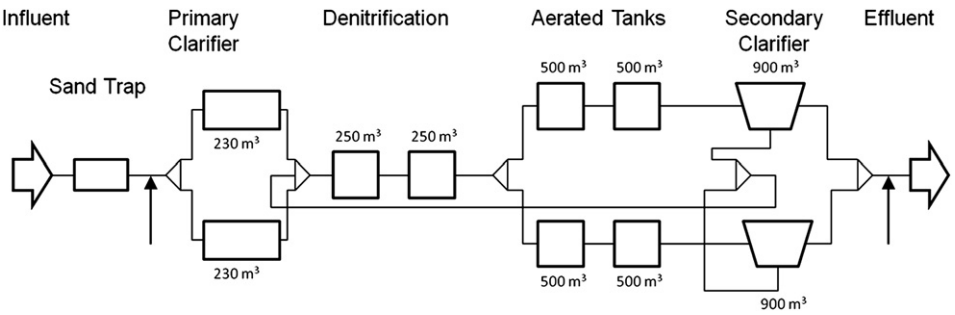


**Fig. 1 – Layout, tank volumes and tanks-in-series used in the model to describe the mixing regime of WWTP Mamer; arrows indicate point of sampling for conductivity.**

#### 2.2.2. *Residence time distribution (RTD)*

The distribution of residence times of a xenobiotic within the plant was determined by model simulations. To this purpose, concentrations 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 GPS-X. The COD $S_i$ fraction is neither degraded nor produced in the model and can therefore be used to determine RTDs.

Residence time distributions were obtained for various flow conditions including dry weather conditions and a storm event. They were exported to MatLab (MathWorks), fitted with a linear interpolant function ($r^2 = 1$) and integrated using the curve fitting toolbox. Stepwise integrals were determined for equal time steps which allow the calculation of the released fraction of $S_i$ on the total $S_i$ per step. Mass balances of $S_i$ were checked to assure that 100% of the $S_i$ influent signal has been released.

#### 2.2.3. *Biodegradation*

Organic micropollutant biodegradation in activated sludge is typically described with pseudo first-order or first-order reaction kinetics (Joss et al., 2006; Schwarzenbach et al., 2003). Here, first-order biodegradation rate constants $k_{biol}$ of 0.05, 0.5 and 5 $h^{-1}$ were chosen as representative values for three classes of biodegradability (persistent, moderately and easily biodegradable polar xenobiotics) to account for biological removal during the course of aerobic wastewater treatment. It was assumed that no significant degradation occurs during denitrification and in the clarifiers. To simulate xenobiotic biodegradation during aerobic conditions, first-order reaction kinetics was implemented into GPS-X:

$$r_{si} = -k_{biol} \cdot S_i \quad (2)$$

where $r_{si}$ = reaction rate [ng $L^{-1}$ $h^{-1}$], $k_{biol}$ = biodegradation rate constant [$h^{-1}$], $S_i$ = soluble xenobiotic concentration [ng $L^{-1}$].

To calculate the xenobiotic effluent loads as a function of the RTD, Eq. (2) is solved analytically for each residence time step $t_s$ of the RTD (temporal resolution = 1 min) and multiplied by the flow. The degraded effluent load for a given degradation rate constant is then the sum of all partial loads over the selected time span e.g. 24 h:

$$L_{eff} = \sum S_i \cdot e^{-k_{biol} \cdot t_s} \cdot Q \quad (3)$$

where $L_{eff}$ = total xenobiotic effluent load [g $d^{-1}$], $t_s$ = residence time step of the RTD and Q = flow [L $h^{-1}$].

The total elimination efficiency is then calculated by mass balancing the xenobiotic influent and effluent load:

$$E = \left(\frac{L_{inf} - L_{eff}}{L_{inf}}\right) \cdot 100 \quad (4)$$

where $E$ = elimination efficiency [%] and $L_{inf}$ = xenobiotic influent load [g $d^{-1}$].

#### 2.2.4. *Sampling scenarios*

Two model scenarios were set up to derive optimized sampling strategies taking WWTP Mamer as an example (Section 3.4). In scenario 1, a perfect steady-state xenobiotic influent loading was assumed on the basis of 8-h composite samples (total load: $2.96 \pm 0.8$ g $d^{-1}$; corresponding to

**Table 1 – Operational data of the investigated WWTP.**

| | WWTP Mamer |
|---|---|
| Population equivalents | 20,300 |
| Capacity utilization [%] | 100 |
| Average flow during dry weather [$m^3$ $h^{-1}$][a] | $136 \pm 54$ |
| Average flow during rainfall event [$m^3$ $h^{-1}$][a] | $503 \pm 44$ |
| *Hydraulic retention time*[b] *[h]* | |
| Mean HRT during dry weather | $16.7 \pm 3.7$ |
| Mean HRT on measured storm event | $4.6 \pm 1.4$ |
| Mean HRT in aerated tanks only; during dry weather | $7.3 \pm 3.5$ |
| Mean HRT in aerated tanks only; during measured rainfall event | $1.9 \pm 0.17$ |
| Recycled fraction of activated sludge [%][c] (flow proportional) | 0.8 |

a Flow conditions during the measurement campaign (3 weeks), daily mean during rainfall event.
b Calculated by the quotient of tank volume and flow through (single pass).
c Estimated from calibration.

measured loads of the pharmaceutical diclofenac; Table A.1; constant flow = 200 $m^3 h^{-1}$). In scenario 2, an example dataset for realistic influent variability was created from measured influent concentrations of two days on the basis of 2-h composite samples (see Appendix A). Since inlet concentration data was only available for two days, but a time series of four days was required, the scenario was completed by using generated concentration data for two additional days. Concentrations ($n = 12$ per day) were randomly generated from a normal distribution with mean and standard deviation of the measured concentrations ($703 \pm 35$ ng $L^{-1}$, $n = 24$). Corresponding measured hourly flow values of one week were used. The resulting average loads for these two days (day zero and three) were $2.1 \pm 0.6$ g $d^{-1}$ and $2.2 \pm 0.7$ g $d^{-1}$, respectively.

#### 2.2.5. *Uncertainty analysis*

Monte Carlo simulations were performed to assess the uncertainty introduced by discrete sampling on the load estimation. Following Ort and Gujer (2006), the error of a 2-h composite sample was assumed to be ±20% (minimum error for sampling intervals > 5 min). The flow error was estimated to be ±10%. The corresponding 2-h composite sample measurement values of day one and two were averaged for both flow and concentration in order to approximate a representative diurnal variation pattern ($n = 12$). Each concentration and flow value was varied by an error composed of the standard deviation of the 2-h composite sample measurement value as given before and a random error taken from a normal distribution assuming non-systematic error variability:

$$m^* = m_i + \sigma_i \cdot \varepsilon \quad (5)$$

where $m^*$ = varied value for flow and concentration, respectively, $i$ = number of the 2-h composite sample (1–12), $m_i$ = measured value of 2-h composite sample $i$, $\sigma$ = absolute standard deviation of 2-h composite sample $i$ and $\varepsilon$ = error taken from a Gaussian normal distribution (mean = 0, standard deviation = 1).

An array of 10,000 simulation runs assured to asymptotically approximate normal distributions. The resulting error associated with the determination of a load was evaluated by using the relative standard deviation and the 5 and 95% percentiles of the output distribution. Error propagation was calculated according to standard equations (Refsgaard et al., 2007).

## 3. Results and discussion

The investigated WWTP runs at full capacity with 20,300 population equivalents (PE). It operates with primary clarifiers, denitrification and two lanes with aerobic treatment followed by secondary clarifiers. The mean HRT, calculated by the quotient of average flow (hourly values over three weeks) and tank volumes was found to be $16.7 \pm 3.7$ h over the whole plant and $7.3 \pm 3.5$ h (single pass; ±one standard deviation) in the aerated tanks during dry weather conditions (Table 1). It decreased during a storm event (flow = $503 \pm 44$ $m^3 h^{-1}$) to $4.6 \pm 1.4$ h and $1.9 \pm 0.17$ h, respectively.

### 3.1. *Model calibration*

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 (Fig. 2). Artifacts in the effluent conductivity caused by measurement interferences were deleted resulting in gaps in the consecutive time series. Fig. 2 reveals that influent variations become dampened in the effluent but could be adequately reproduced by the model. The correlation coefficient was found to be $R = 0.76$ suggesting good tracking of the conductivity variation. Nonetheless, 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 number of completely mixed tanks-in-series was determined to be $n = 4$ (2 denitrification/2 aerobic treatment tanks as well as 2 clarifiers per lane, see Fig. 1) by minimizing chi square between modeled and measured effluent conductivity values.

WWTP Mamer operates with $FeCl_3$ addition for phosphate precipitation before activated sludge treatment which may influence the conductivity. Moreover, the latter can be affected by ionic compounds being produced or removed during biological treatment or changes in the pH. However, this is apparently of minor importance to the effluent conductivity since measured outlet patterns correlated well with modeled values using the measured influent conductivity as input. Also, the pH was found to be stable during the measurement period with $7.9 \pm 0.2$ ($n = 36$).

### 3.2. *Residence time distribution*

After having calibrated the model, the RTD of an inert soluble xenobiotic was determined by use of a $S_i$ injection pulse in the influent (duration: 24 h). Here, it should be kept in mind that the RTD is flow dependent. On that account, Fig. 3 shows modeled distributions at various given flow conditions in

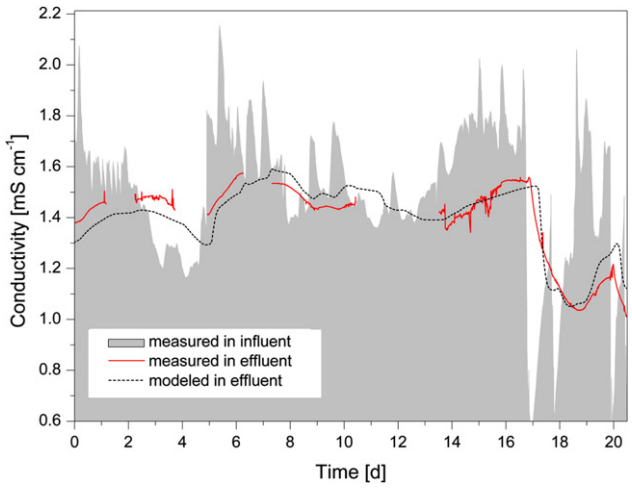


**Fig. 2 – Hydrodynamic calibration of WWTP Mamer using conductivity. Input data: influent conductivity (gray) and flow (hourly values, not shown).**

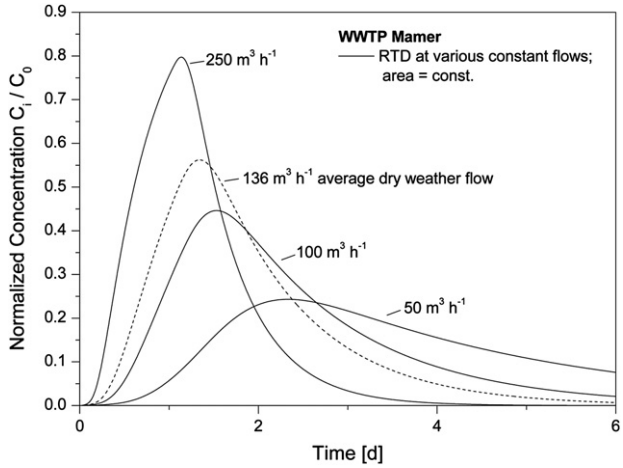


**Fig. 3 – Residence time distribution of xenobiotics at flows varying from 50 to 250 $m^3 h^{-1}$ as a result of an influent pulse in WWTP Mamer (duration: 24 h); areas of all curves are constant.**

order to illustrate the retention of different fractions of $S_i$ in the tanks. From this, percentiles can be determined giving the percentage of the released fraction of the influent water volume at a certain time t (Fig. 4). The RTD becomes more left-skewed with increased flow resulting in smaller percentiles. For instance, during dry weather conditions around 20% of the influent water volume have been released within 24 h while during a rainfall event already 60% have been emitted during the same time. When comparing those percentiles to the HRT from Table 1, the mismatch becomes apparent: at a mean HRT (16.7 h) only around 10% of the water volume that entered the WWTP 16.7 h ago has been released. A 24-h effluent (composite) sample shifted by a temporal offset of the HRT would contain only 30–40% of the influent pulse. Consequently, a large proportion of sampled wastewater would originate from periods preceding the influent pulse during dry weather conditions. This aspect is addressed in detail in Section 3.4.

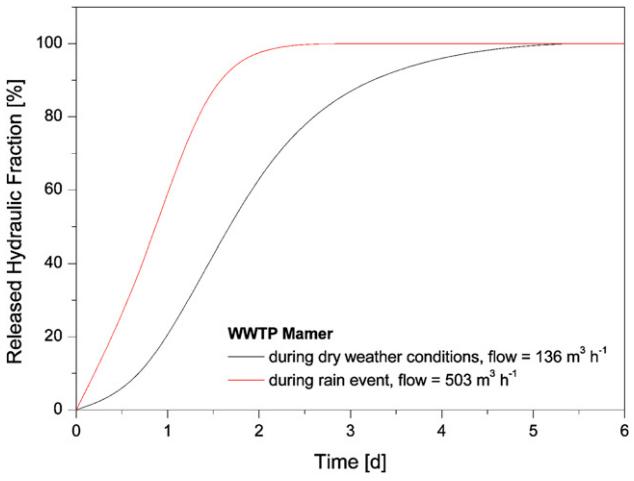


**Fig. 4 – Exit-age distributions as a result of $S_i$ influent pulse injections (duration: 24 h) showing the cumulative released water volume fractions in WWTP Mamer; flow was selected according to Table 1.**

### 3.3. *RTD effects on biodegradation*

For prediction of the overall removal efficiency, first-order kinetics is usually solved for the HRT. As can be seen from Fig. 3, a single mean HRT is not suited to describe the residence of wastewater volumes in reactor tanks, in particular for strongly skewed RTDs. The use of RTDs for removal calculations is therefore much more adequate. It allows depicting decreased removal efficiencies during rainfall events (Table 2). Under high flow conditions the RTD shifts toward a left-skewed distribution, i.e. that the RTD fractions of short retention in the plant increase. Hence, high flow leads to decreased retention times in the tanks and to a decreased removal assuming that degradation rates remain constant.

A visualization of flow influence on elimination efficiency is shown in Fig. 5, where the decrease of the elimination of a moderately biodegradable xenobiotic ($k_{biol} = 0.5\ h^{-1}$) with increasing flow through has been plotted. Using the model, elimination efficiencies can be described as a function of the flow. The dashed line indicates removal efficiencies calculated by use of the HRT. Compared to the solid line, which show the efficiencies based on the RTD, a clear mismatch of up to 45% is evident. There, the mixing regime has a significant impact causing lower degradation. As a consequence, the use of HRT and laboratory determined $k_{biol}$ may lead to an overestimation of the actual removal performance (Table 2).

The fact that a daily influent load is discharged in the effluent over a period longer than one day is a major concern for the determination of full-scale elimination efficiencies by influent–effluent mass balancing. To account for this hydraulic behavior and to derive more adequate sampling strategies, influent–effluent correspondence was investigated in the following scenarios.

### 3.4. *Sampling scenarios*

The adequate setting of sampling intervals to address mixing regimes is crucial for the determination of elimination rates at full-scale. For example, it is remarkable that negative removal efficiencies for several (biodegradable) pharmaceuticals have been reported in a variety of studies (Onesios et al., 2009). Although knowing that certain parent compounds can be formed by the cleavage of conjugates (Ternes, 1998), also inadequate sampling strategies can yield erroneous mass balances when the water volumes sampled in influent and effluent do not correspond. The importance of adapting sampling mode and frequency to influent variability and catchment structure as well as the errors being associated with discrete sampling have been shown before (Minkkinen, 2007; Minkkinen and Esbensen, 2009; Ort et al., 2010a).

Modeling simulations showed that a daily water volume is distributed over more than one day when discharged in the effluent. Consequently, a daily influent load cannot be completely covered by (composite) samples taken over a period of only 24 h at the outlet. However, an optimum temporal offset can be identified, by which a 24-h effluent

**Table 2 – Elimination efficiencies calculated on the basis of the RTD and the HRT in the aerated tanks for three different first-order degradation rate constants; dry weather: constant flow = 136 $m^3 h^{-1}$; storm event: constant flow = 503 $m^3 h^{-1}$.**

| Xenobiotic | Degradation rate constant, $k_{biol}$ [$h^{-1}$] | Total elimination efficiency | | | |
|---|---|---|---|---|---|
| | | Based on RTD [%] | | Based on HRT [%] | |
| | | Dry weather | Rain event | Dry weather | Rain event |
| Persistent | 0.05 | 10 | 4 | 31 | 10 |
| Moderately biodegradable | 0.5 | 55 | 21 | 98 | 63 |
| Easily biodegradable | 5 | 98 | 78 | 100 | 100 |

sampling period is shifted from the beginning of the influent period to cover the maximum percentage of the released load. Given these findings, the following model scenarios were set up to derive an optimized sampling strategy for reliable xenobiotic mass balances at full-scale:

• *Scenario 1*: In this scenario, the influent concentrations are assumed to be sampled on three consecutive days on a basis of 8-h composite samples, while the effluent is sampled on one day only. The effluent sampling period (24 h) was shifted by the optimum offset (here: 18 h) from the beginning of the second measurement day and is indicated as vertical dashed lines in Fig. 6. A perfect steady-state variation pattern was assumed with a constant flow (200 $m^3 h^{-1}$) and biodegradation was set to zero ($k_{biol} = 0\ h^{-1}$).

The water volume sampled on day two explains only 55.6% of the sampled effluent water volume. Consequently, the remaining 44.4% originate from preceding days and one following day, as can be seen from Fig. 6. Based on the RTD approach, the fractions of each (daily) influent water volume released at the time of the effluent sampling can be calculated (Table 3).

Subsequently, to obtain a reliable mass balance, it is preferable to explain the origin of 80–90% of the sampled effluent water volume. The number of influent sampling days needed to achieve this, can be derived from the cumulative proportions of each inlet measurement day on the effluent load. In this case, sampling influent days 1–3 would allow explaining 91.0% of the effluent sampled during a 24-h period. An additional fourth day would result in 99.2%. When sampling influent day 1–3, 9% of the effluent sample originates from unknown water volumes (day zero, non-covered period). The proportions of the influent load on the effluent sample match exactly the captured fractions, since an ideal steady-state was assumed (Table 3).

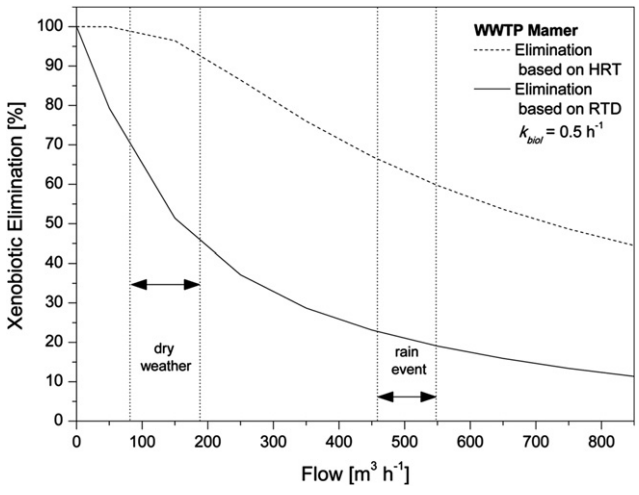


**Fig. 5 – Comparison of modeled elimination efficiencies for a moderately biodegradable xenobiotic ($k_{biol} = 0.5\ h^{-1}$) on the basis of HRT and RTD as residence times in aerated tanks at various constant flow conditions.**

A perfect diurnal concentration pattern at constant flow in the influent would result in periodic effluent concentrations (one effluent period may extend over more than 24 h). Under these simplifying conditions it would be sufficient to sample one in- and effluent periodical pattern with any time shift. Mass balance calculations would result in the same elimination efficiency. However, such stable conditions and constant periodic loads do not reflect reality. The concentrations of xenobiotics can vary largely during a diurnal cycle depending on their usage. Nelson et al. (2011) reported intense pulses that exceeded relative standard deviations of 100% of their daily means for selected pharmaceuticals in WWTP effluents. Further, strong diurnal variation was shown e.g. for benzotriazoles in influents (Ort et al., 2005). Hence, it can be expected that high variations in influent and effluent concentrations are very likely to occur. As a consequence, the variability of empirical data was used in Scenario 2 to adapt the sampling scheme to realistic conditions.

• *Scenario 2*: Here, realistic influent concentration patterns (2-h composite samples) during dry weather conditions were introduced as well as the corresponding measured flow (hourly values) during that period (Fig. 7). A diurnal variation can be observed in the flow as well as one rainfall event on day five. Again, biodegradation was set to zero ($k_{biol} = 0\ h^{-1}$).

The concentration variability of the influent load is propagated through the plant and can visibly be tracked in the released effluent concentrations. Applying the same sampling scheme as in scenario 1 (day 1–3), the origin of 71.1% of the effluent load could be explained with three consecutive inlet measurement days and added up to 84.9% when including day 0 (Table 4). Hence, 15.1% stem from loads of days preceding the influent sampling period and are therefore unknown.

Compared to scenario 1, scenario 2 shows a lower coverage during the effluent sampling time span. This is mainly due to the lower flow conditions that decelerate the xenobiotic release.

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

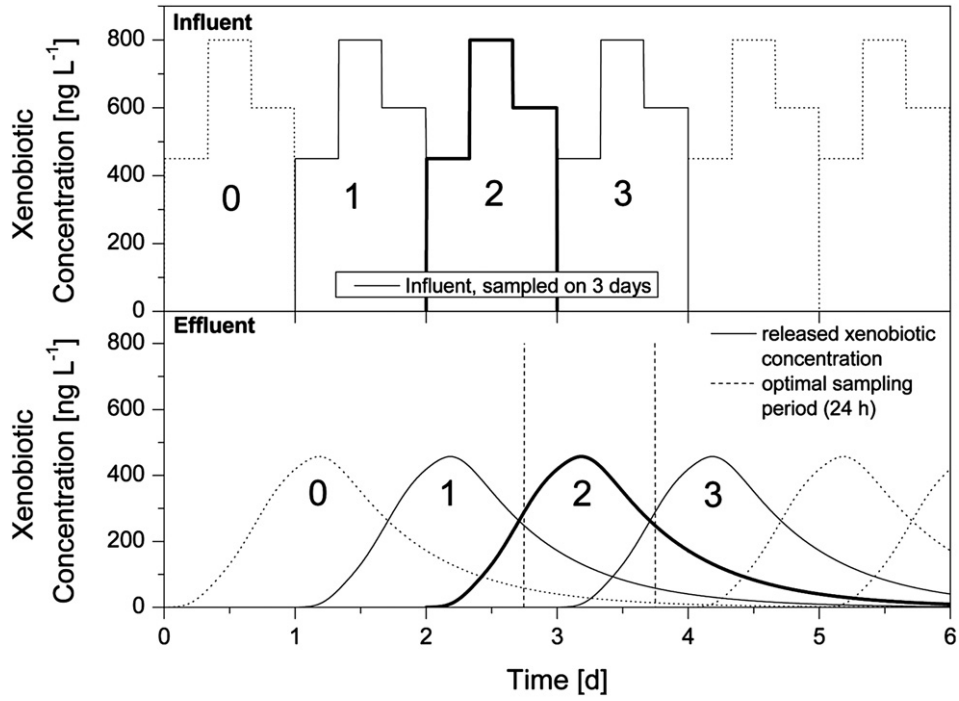


**Fig. 6 – Sampling scenario 1: xenobiotic concentrations assumed to be sampled on three consecutive days in the influent (8-h composite samples) and one sampling day in the effluent shifted by the optimum offset (18 h from the beginning of influent day 2); flow = 200 $m^3 h^{-1}$ (not shown); load fractions captured during the sampling period: 8.2% of day 0, 24.2% of day 1, 55.6% of day 2 and 11.2% of day 3.**

fractions of, in this case, four days (cf. Tables 3 and 4) and can thus be calculated as the sum of the latter (see Appendix B for a mathematical description). It 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 relevant influent loads have been covered, the uncertainty of this non-sampled loading needs to be considered. This uncertainty decreases with decreasing contribution to the sampled effluent load. Details of this aspect are addressed in Section 3.4.1.

Expanding the influent measurement period to 3 or 4 days may be no financial issue with four 24-h composite samples but can become decisive when a higher temporal resolution is required e.g. with 8-h or 2-h composite samples. There, the cost–benefit ratio with regard to the reliability of the results should be assessed in advance.

### 3.4.1. *Biodegradation scenarios*

In both scenarios, the elimination was set to 0% to calculate the fractions captured by effluent sampling. However, at full-scale, biodegradation takes place during biological treatment which reduces the influent load. Assuming that biodegradation is proportional to the concentration with a first-order rate constant $k_{biol}$, the relative fractions of the influent loads (and their ratios to each other) during the sampled effluent period remain constant, while only the absolute load changes. In this way, the calculation of the reference load is also valid for every biodegradation scenario.

In the following example, biodegradation was simulated in scenario 2 for the three xenobiotics of different persistence and a surrogate with $k_{biol} = 0\ h^{-1}$ (Table 5). The resulting elimination efficiencies are associated with an error because not the full 100% of the sampled load could be related to a sampled influent load. Therefore, 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 (day one and two). This would result in an uncertainty on the total elimination efficiency of ±4% for the surrogate, ±3% for a persistent, ±2% for a moderately biodegradable and ±0% for a readily biodegradable xenobiotic. The error decreases as the variation of the non-covered period has a comparatively lower impact on the mass balance for easily and moderately biodegradable xenobiotics.

Erroneous elimination efficiencies are obtained ranging from −14 to 16% for both the surrogate and the persistent xenobiotic when using the conventional 1–1 day influent–effluent mass balancing approach for each sampling day (day 0–3) with average loads. The uncertainty of these values can be expected to increase considerably under more variable influent conditions. However, the apparent elimination efficiencies of moderately and easily biodegradable substances are well approaching the true efficiency. This is due to the fact that, relative to the influent load, variations of largely degraded effluent loads affect the mass balance to a lesser extent, as it was the case before for the variations of the non-covered period. The conventional approach is thus more

**Table 3 – Load fractions of the consecutive influent measurement days captured during the effluent sampling period (24 h, from Fig. 6) and their proportion of the effluent load; the optimum outlet sampling period was calculated to start by an 18 h time shift from the beginning of day two.**

| Influent measurement day | Influent load fraction captured by effluent sampling[b] [%] | Proportion explained of the effluent load[c] [%] | |
|---|---|---|---|
| Day 0[a] | 8.2 | 8.2 | |
| Day 1 | 24.2 | 24.2 | |
| Day 2 (optimum offset) | 55.6 | 55.6 | 91.0 |
| Day 3 | 11.2 | 11.2 | 99.2 |
| Non-covered period | 0.8 | 0.8 | |

a Day 0 = day before the measuring period.
b Referred to the influent load of each measurement day.
c Referred to the calculated effluent load (2.96 g $d^{-1}$); in this case, the proportions of the effluent load are identical to the captured influent fractions since perfect steady-state conditions were assumed.

robust to influent variations of readily and biodegradable xenobiotics. Further, there was only a low variation of the loads during the four days in the influent. Nonetheless, disregarding the variation preceding and during a sampling campaign would make it virtually impossible to estimate how reliable the obtained elimination efficiency value actually is.

### 3.4.2. *Uncertainty analysis*

Besides the uncertainty of the non-covered period, elimination efficiencies estimated with the proposed approach are additionally associated with the error introduced by discrete (24-h) composite samples, depending on the mode and frequency. Influent short-term variations are usually not captured by most sampling schemes and are therefore an error source leading to non-representative results for average loads (Ort et al., 2010b). Flow measurement errors (here assumed to be ±10%) affect also the accuracy of the reference load determined by the RTD approach. Ort and Gujer (2006) showed for a middle-sized catchment that a sampling interval of at least five minutes (time-proportional) was required to obtain a representative influent composite sample (2-h) with standard deviations lower than ±20%. These errors must be considered in order to reliably estimate the reference load. To this purpose, Monte Carlo simulations were used to investigate the propagated error of flow and concentration sampling on the estimated reference load. Simulation results showed that fraction load estimates approximated a normal distribution with a relative standard deviation of ±6.4% and a range from −8.3 to 8.3% (5 and 95% percentiles). As the total reference load is composed of multiple load fractions (in this

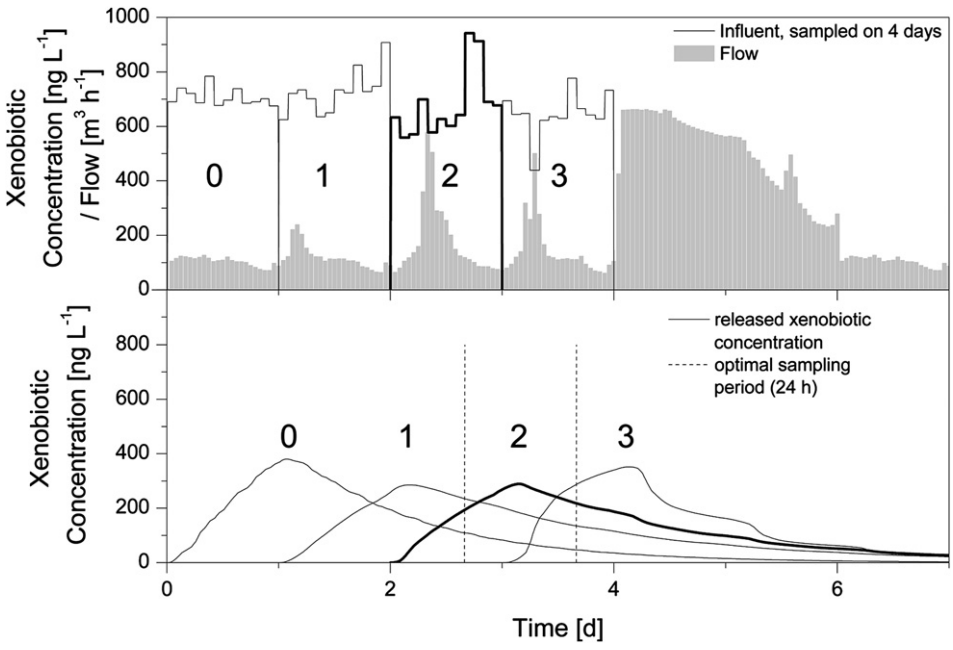


**Fig. 7 – Sampling scenario 2: xenobiotic concentrations assumed to be sampled on four consecutive days in the influent (2-h composite samples; realistic influent variability of xenobiotic concentrations (diclofenac)) and one sampling day in the effluent shifted by the optimum offset (18 h from the beginning of influent day 2); measured flow values were used (hourly values); load fractions captured during the sampling period: 14.4% of day 0, 22.4% of day 1, 30.7% of day 2 and 16.0% of day 3.**

**Table 4 – Load fractions of the consecutive influent measurement days captured during the effluent sampling period (24 h, from Fig. 7) and their proportion of the effluent load; the optimum outlet sampling period was calculated to start by an 18 h time shift from the beginning of day two.**

| Influent measurement day | Influent load fraction captured by effluent sampling[a] [%] | Proportion explained of the effluent load[b] [%] | |
|---|---|---|---|
| Day 0 | 14.4 | 13.8 | |
| Day 1 | 22.4 | 18.5 | |
| Day 2 (optimum offset) | 30.7 | 36.5 | 71.1 |
| Day 3 | 16.0 | 16.1 | |
| Non-covered period[c] | 14.8 | 15.1 | |
| | | | 84.9 |

a Referred to the influent load of each measurement day.
b Referred to the calculated effluent load (2.21 g $d^{-1}$).
c Comprises two days before day 0; loads were estimated as the average load of day 0–3.

**Table 5 – Elimination efficiencies estimated from four biodegradation scenarios based on mass balance calculations by i) using the fractionated reference load and ii) comparing daily average loads of each influent sampling day (0–3) to the sampled effluent load; average loads are given in Table A.1 and Section 2.2.4.**

| Xenobiotic | Degradation rate constant, $k_{biol}$ [$h^{-1}$] | Reference load [g $d^{-1}$] | Degraded load sampled in the effluent [g $d^{-1}$] | Elimination efficiency[a] [%] | Apparent elimination efficiency by conventional sampling scheme[b] [%] |
|---|---|---|---|---|---|
| Surrogate | 0 | 2.21 | 2.21 | 0 ± 4[c] | −3; −14; 10; 1 |
| Persistent | 0.05 | 2.21 | 2.01 | 9 ± 3[c] | 4; −6; 16; 9 |
| Moderately biodegradable | 0.5 | 2.21 | 1.09 | 51 ± 2[c] | 48; 43; 55; 50 |
| Easily biodegradable | 5 | 2.21 | 0.08 | 96 ± 0[c] | 96; 96; 97; 96 |

a Calculated using the reference load.
b Calculated by comparing the daily average load of each day (0–3) to the sampled effluent load.
c Error is caused by the assumed variation of the non-covered period preceding the influent sampling days (RSD = 27.2%).

case: the fractions of four days plus non-covered period), the total propagated error would be 14.3% based on the standard deviation. The length of the sampling time span (12 h, 24 h, 36 h) in the effluent has no effect on this error assuming the same sampling mode and frequency.

These sampling errors as well as the conditions of the unknown days preceding the sampling campaign, which may be highly variable, consequently affect mass balances. The latter can only be closed here for the WWTP Mamer since the non-sampled period is assumed to have similar average loads and variability as the measured days. It nonetheless demonstrates clearly how daily influent variation can lead to misinterpretation when the sampling intervals are not accurately set and short-term data is used, in particular based on 24-h composite samples.

**Table A.1 – Measured average concentrations and loads of diclofenac in the influent of WWTP Mamer on two independent measurement days for scenarios 1 and 2 (Figs. 6 and 7); loads calculated based on hourly flow and two hourly concentration data; stdev = one standard deviation.**

| Diclofenac | Day 1 [average ± stdev] | Day 2 [average ± stdev] |
|---|---|---|
| Concentration [ng $L^{-1}$] ($n = 12$) | 728 ± 39 | 678 ± 31 |
| Flow [$m^3$ $h^{-1}$] ($n = 24$) | 111 ± 14 | 160 ± 19 |
| Loads [g $d^{-1}$] | 1.9 ± 0.4 | 2.4 ± 0.8 |

## 4. Conclusions

This study demonstrates that hydrodynamic characteristics are crucial for elimination, emission prediction and sampling of xenobiotics in municipal WWTPs. The hydraulic retention time is only of limited use since it does not reveal any information about mixing and distribution behavior. In order to tackle this issue, a residence time distribution approach linked with biodegradation kinetics was applied. This approach illustrated the problems encountered when trying to match influent loads with effluent loads. Depending on the flow regime, a 24-h xenobiotic influent load can expand significantly over more than one day when released in the effluent. It shows that a 24-h sampling period can cover only a small percentage of the corresponding influent load.

The optimal sampling setup for full-scale mass balancing at the WWTP Mamer was determined to be a coverage of four consecutive days in the inlet and a single sampling day at the outlet with an offset of 66 h to the beginning of the inlet monitoring. The presented set-up would allow explaining the origin of 84.9% of the sampled effluent load under realistic

conditions. This coverage can be calculated for every WWTP that should be monitored and it is advisable to use simulations for the planning and evaluation of a monitoring campaign with regard to calculation of the total elimination efficiencies. However, the number of consecutive influent sampling days must be selected plant-specifically. It is related to the prevailing mixing regime and thus requires calibration via tracer tests. We demonstrated that calibrating hydraulic models by wastewater conductivity can offer a cost-effective option compared to artificial tracers and should therefore be implemented in full-scale measurement campaigns.

The uncertainty caused by non-covered periods preceding the sampling days can be estimated from the average loads and standard deviation of the measurement days assuming them to be representative for dry weather conditions. In the Mamer plant, an accurate full-scale mass balance is only possible by high inlet coverage with monitoring. The sampling mode and frequency but also analytical errors can cause additional uncertainty. Sewer network and catchment structure as well as rainfall events greatly determine the variability of flow and xenobiotic concentrations and can lead to short-term variations in the range of minutes (Ort et al., 2010a,b). With regard to these aspects and that the origin of a sampled effluent water volume could not be explained to 100%, this study reveals that elimination effciencies of less than 15–20% are probably impossible to track in full-scale investigations.

The present paper raises the issue of mass balancing influent and effluent loads on the basis of short-term WWTP measurement campaigns. We showed that apparent negative elimination efficiencies can be caused by inadequate sampling strategies. Results illustrate the need to cover influent loads over several days and to consider the hydraulic characteristics in treatment plants. Hence, the accuracy of reported full-scale elimination efficiencies should be revised under these aspects.

## Acknowledgments

This study was financed by the Luxembourg Research Fund (FNR) within AFR 07/017 and the DomesticPest project funded by the Ministry of the Interior and the Greater Region, Luxembourg. We would like to thank Julien Farlin for proofreading and Ulrich Leopold for his support in the uncertainty analysis. We thank the Water Syndicate SIDERO for their cooperation. Peter Vanrolleghem holds the Canada Research Chair in Water Quality Modelling.

## Appendix A. Example data

Example data introduced to scenario 2 consisted of i) the pharmaceutical diclofenac (time-proportional, 12 glass bottles, 2-h composite samples with 24 min aliquot sampling frequency in influents using ISCO 6700 autosampler units) analyzed on two independent days (28th May and 6th June 2009) as well as ii) hourly inflow data and tank volumes that were obtained from the plant operators (Water Syndicate SIDERO). The measurement error associated with the flow data is unknown and therefore assumed to be ±10%.

### A.1. *Xenobiotic analysis*

Samples were collected directly after a sampling cycle, stored at 4 °C and analyzed within 24 h. Diclofenac was analyzed by use of a LC–MS/MS system consisting of a Finnigan TSQ Quantum Discovery MAX from Thermo with a Surveyor MS Pump Plus (flow rate of 200 $\mu l\,min^{-1}$), a Surveyor LC-Pump Plus (flow rate of 2 $ml\,min^{-1}$) and an autosampler HTC PAL from CTC Analytics. A 1 ml online enrichment method was used with an extraction column Hypersil Gold (20 × 2.1 mm, particle size 12 μm) from Thermo. A polar endcapped $C_{18}$ column Gold aQ (100 × 2.1 mm, particle size 3 μm) served as chromatography column. The eluent was increased from 70:30% $H_2O$/MeOH to 0:100% within 22 min. Limits of quantification (LOQ) were found at 125 $ng\,L^{-1}$ in influent samples.

## Appendix B. Estimating the total elimination efficiency

The influent concentration and flow data of $n$ consecutive measurement days can be used for model simulations in order to calculate the actual inlet reference load that corresponds to the load proportions $f_n$ [–] captured by an effluent sampling period. This reference load can be determined as:

$$L_{ref} = \sum f_n \cdot L_{inf,meas,n} \quad (6)$$

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 $n$ [$ng\,d^{-1}$].

Subsequently, the measured (potentially degraded) effluent load can be related to $L_{ref}$ in order to calculate the actual elimination efficiency $E$ in [%]:

$$E = \left(\frac{L_{ref} - L_{eff,meas}}{L_{ref}}\right) \cdot 100 \quad (7)$$

where $L_{eff,meas}$ is the measured effluent load on a chosen sampling period.

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