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Predicting the fate of micropollutants during wastewater treatment: Calibration and sensitivity analysis

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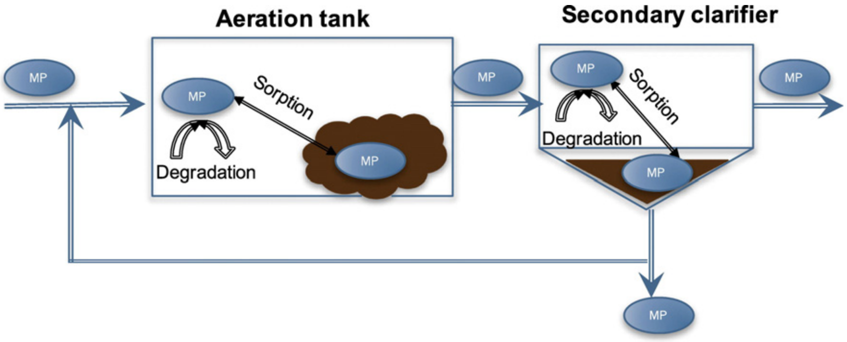
HIGHLIGHTS

- A MP fate model was implemented and calibrated with full-scale measurements.
- Considering biodegradation in the secondary clarifier was important for modelling some MPs.
- The most influential parameters of the model depended on the dominant fate process
- Sensitivity analysis suggests suitable measurement conditions for improved calibration.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence of micropollutants in the environment and their toxic impacts on the aquatic environment have raised concern about their inefficient removal in wastewater treatment plants. In this study, the fate of micropollutants of four different classes was simulated in a conventional activated sludge plant using a bioreactor micropollutant fate model coupled to a settler model. The latter was based on the Bürger-Diehl model extended for the first time to include micropollutant fate processes. Calibration of model parameters was completed by matching modelling results with full-scale measurements (i.e. including aqueous and particulate phase concentrations of micropollutants) obtained from a 4-day sampling campaign. Modelling results showed that further biodegradation takes place in the sludge blanket of the settler for the highly biodegradable caffeine, underlining the need for a reactive settler model. The adopted Monte Carlo based calibration approach also provided an overview of the model's global sensitivity to the parameters. This analysis showed that for each micropollutant and according to the dominant fate process, a different set of one or more parameters had a significant impact on the model fit, justifying the selection of parameter subsets for model calibration. A dynamic local sensitivity analysis was also performed with the calibrated parameters. This analysis supported the conclusions from the global sensitivity and provided guidance for future sampling campaigns. This study expands the understanding of micropollutant fate models when applied to different micropollutants, in terms of global and local sensitivity to model parameters, as well as the identifiability of the parameters.

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1. Introduction

The presence of pharmaceuticals and personal care products (PPCPs), as well as hormones, in the environment was proven to have adverse effects on aquatic life, raising concern about their insufficient removal from wastewater (Gay et al., 2016; Kidd et al., 2007; Purdom et al., 1994). The two major processes influencing the fate of micropollutants (MPs) during activated sludge treatment are biodegradation and sorption that act at different degrees on MPs with different characteristics (Joss et al., 2006; Radjenović et al., 2009; Ternes et al., 2004). Hence, although most of the emphasis in activated sludge mathematical modelling has been placed on conventional pollutants, some mathematical models were also developed to describe the fate and discharge of MPs in activated sludge systems and proposed as a cost-effective tool for risk assessment (Cowan et al., 1993; Plósz et al., 2012; Urase and Kikuta, 2005; Vezzaro et al., 2014).

Since the fate of MPs is influenced by the fate of conventional pollutants (e.g. solids that affect the sorption and biodegradation of micropollutants), simultaneous modelling of conventional and micropollutants was made possible by extending the well-known Activated Sludge Models (ASMs) developed many years ago (Henze et al., 1987; Henze et al., 1999). The most notable examples of models tackling both conventional pollutants and MPs are the ASM-X model (Plósz et al., 2012; Plósz et al., 2010) and another more recent model based on the ASM2d model (Vezzaro et al., 2014). The majority of MP fate studies in activated sludge focused their efforts on the modelling of the removal in bioreactors and considered the MP fate processes taking place in the secondary clarifier as insignificant (Cloutier et al., 2008; Plósz et al., 2010). However, it is well-known that biological degradation of conventional pollutants can occur in the settler, especially under conditions of long residence times and incomplete denitrification (Siegrist et al., 1995; Koch et al., 1999). Although no specific experimental evidence for the removal of micropollutants in secondary settling tanks has been presented in the literature, MPs are known to co-metabolise with other biodegradable compounds (Clouzot et al., 2013). Hence, the removal of micropollutants in secondary settling tanks should, likely, not be disregarded. So far, only one study by Vezzaro et al. (2014) considered MP fate processes in the clarifier through an extension of the Takács settling model (Takács et al., 1991).

Several constitutive relations to model the different MP fate processes have been proposed in the literature (Plósz et al., 2013; Clouzot et al., 2013). For environmental applications, mostly non-compound specific relations have been used to describe the kinetics of biodegradation, as well as the kinetics and equilibrium of sorption of micropollutants in activated sludge units (Joss et al., 2006; Pomiès et al., 2013). Previous efforts were made to calibrate the model parameters to describe the fate of specific types of MPs (Cloutier et al., 2008; Cowan et al., 1993; Pomiès et al., 2013), with only few studies focusing on PPCPs and hormones (Plósz et al., 2012; Plósz et al., 2010; Urase and Kikuta, 2005). However, a large uncertainty on the calibrated parameters was identified as a major gap in the field of micropollutant modelling in WWTPs, a factor that is aggravated by the lack of knowledge on the sensitivity of the MP fate models to their parameters (Pomiès et al., 2013). This leaves the model users unsure about the degree of confidence in the parameters values reported in the literature.

Measurements of the MP loads sorbed onto sludge for model parameter calibration are limited in the literature to lab scale measurements (Joss et al., 2004; Plósz et al., 2012; Xue et al., 2010), which often cannot be simply extrapolated to the fate of MPs in the complex environment of full-scale WWTP systems. On the other hand, full-scale sampling campaigns are often limited in resources and time preventing very dedicated experiments (Clouzot et al., 2013).

In the present study, a MP fate model based on ASM2d (bioreactor) was further modified and coupled to a reactive settler model extended for the first time from the Bürger-Diehl settler model, which itself incorporates the latest important advancements in the field of secondary settler modelling (Bürger et al., 2012). The scope of the current paper was to obtain reasonable predictions of the removal efficiencies of different types of micropollutants during activated sludge treatment through the calibration of the most influential model parameters for each compound. This was performed using full-scale MP concentration measurements collected from a sampling campaign that was meant to be feasible in terms of efforts and resources supplied by the utility running the plant.

Given the chronic nature of the impacts of the studied CECs, sub-daily variations were not deemed of importance for this study, and only the 24-h average load was considered for sampling. Samples were collected under dry weather conditions, since that is when surface water bodies are expected to be the most sensitive to wastewater discharges as a result of the limited dilution. A model that was previously calibrated with respect to conventional pollutants using one-year data was used as a starting point for the current MP calibration. The MPs investigated in the present study included a hormone (i.e. androstenedione), a pharmaceutical (i.e. ibuprofen), an antibacterial agent (i.e. triclosan) and a nervous stimulant (i.e. caffeine). Ibuprofen, triclosan and caffeine were selected based on their high detection frequency in wastewater effluents (Dickenson et al., 2011), while little data is available regarding the levels and fate of androstenedione (Baalbaki et al., 2016; Esperanza et al., 2007). The target MPs were also previously observed to be influenced by sorption and biodegradation fate processes to variable extents in WWTPs (Baalbaki et al., 2016), while volatilization is not considered as significant (Struijs et al., 1991; Virkutyte et al., 2010). For sorption, both the kinetics and the equilibrium equations were considered in the bioreactor and settler models. Sensitivity analysis was performed to explore the impact of the MP fate model parameters on each of the fitted variables, in relation to the input dynamics. Prior to calibrating the model for micropollutant fate, the hydraulic model of the WWTP was identified and the activated sludge unit was calibrated with respect to conventional pollutants, as described in our previous studies (Baalbaki et al., 2016; Baalbaki et al., 2017).

2. Materials and methods

2.1. Full-scale activated sludge

Concentrations of the target MPs were measured in samples collected over four dry days at the full-scale activated sludge unit of the Guelph WWTP (Guelph, Ontario, Canada). The WWTP contains four activated sludge lines, followed by tertiary treatment by rotating biological contactors (RBCs) and sand filtration, as well as disinfection by chlorine. It serves a population of 135,000 inhabitants and receives an average flow of 50,750 m^3/day. The final de-chlorinated effluent is discharged into a nearby river. The first of the four lines of activated sludge (line 1) was selected for this study. This line contains two aeration tanks in parallel, and the output of both tanks is combined and sent to a single secondary clarifier. Ferric chloride is added for phosphorus removal to the input to the primary clarifier (i.e. 1 L/min) and at a lower dosage to the return sludge of line 1 (i.e. 0.55 L/min). The main characteristics of line 1, including average hydraulic and solids retention time (HRT and SRT, respectively), as well as the average mixed liquor suspended solids concentration (MLSS), average mixed liquor volatile suspended solids concentration (MLVSS) and average temperature measurements over the sampling period are summarized in Table 1.

2.2. Sampling

Sampling was performed over four days in the period of July 21–25, 2014 in dry conditions. The number of sampling days was selected based on a hydraulic model for this WWTP (Baalbaki et al., 2016). As shown in Fig. 1, samples were collected from the effluent of the primary clarifier or primary effluent (PE), the effluent of the aeration tanks (AE), the effluent of the secondary clarifier (SE), as well as from the secondary waste sludge at the underflow of the secondary clarifier (WAS) and from the sludge of the primary clarifier (not shown in Fig. 1). Samples from the PE and SE were collected as 24-h composite flow-proportional samples using onsite Hach Sigma samplers, where the samples were refrigerated at 4 °C until retrieved (daily). Due to the absence of an onsite sampler in the AE location, 24-h composite time-proportional samples from this stream were obtained using ISCO 6712 samplers (Avensys, St-Laurent, QC, Canada) equipped with 24 bottles and packed with ice (replaced daily). Waste activated Sludge samples were collected as grab samples on each of the four days. All collected samples were transferred into 1-L Nalgene certified pre-cleaned amber bottles (Fisher Scientific) at the end of each day of sampling, stored at −20 °C and kept frozen until extracted.

2.3. Sample preparation

The four target micropollutants extracted from the wastewater and biosolids samples, as well as information on their respective internal standards and suppliers, are listed in Table 2. The aqueous samples from the PE, AE and SE locations were filtered using 1-μm glass-fiber filters (Fisher Scientific). The filtered samples (100 mL for PE and 200 mL for AE and SE) were spiked with internal standards to account for the extraction recovery and matrix effects and then subjected to solid-phase extraction (SPE). The cartridges used for extraction were the Oasis MAX anion exchange cartridges (Waters, MA, USA), following the method described by Metcalfe et al. (2014) and summarized in the supplementary material (Table S1). The SPE extraction recoveries of target MPs in procedural blanks ranged from 90% to 130%, as reported earlier (Li et al., 2010). Extraction of sludge samples was conducted using a Dionex ASE 350 accelerated solvent extraction (ASE) system (Thermo Fisher Scientific, Waltham, MA, USA) followed by solid-phase extraction. Approximately 1 g of freeze-dried sludge was placed in ASE stainless steel cells and spiked with internal surrogates (Table 2, 100 ng/g). The ASE and SPE methods used for the analysis of the biosolids were previously described in the literature (Edwards et al., 2009) and are summarized in Table S1 of the supplementary material. The extraction recoveries of target analytes from biosolids was >70%. All aqueous and sludge samples were extracted in triplicates.

2.4. Chemical analysis

Chemical analysis was performed by liquid chromatography with tandem mass spectrometry (LC-MS/MS) using an Agilent 1100 HPLC (Mississauga, ON, Canada) coupled to a Q-Trap 5500 instrument (AB Sciex, Concord, ON, Canada) operated with a turbospray ionization source. The method used for chromatographic separation was described by Metcalfe et al. (2014). Ibuprofen and triclosan were measured in negative ionization mode, while caffeine and androstenedione were measured in positive ionization model. Acquisition was performed in multiple-reaction-monitoring (MRM) mode. The parameters used for MRM are listed elsewhere (Metcalfe et al., 2014; Thompson et al., 2011). Results of the recovery of the spiked internal standards were used to determine the concentration of the target MPs.

Table 1
Main characteristics of the Guelph WWTP, including average hydraulic and solids retention times (HRT and SRT), average temperature, mixed liquor suspended solids and volatile suspended solids concentrations (MLSS and MLVSS) during the sampling campaign (i.e. July 2014).

Characteristic		Value
HRT (h)	Primary clarifier (line 1)	3.72
	Aeration tanks (line 1)	6.30
	Secondary clarifier (line 1)	2.90
SRT of line 1 (day)		7.76
Average water T (°C)		20
Average MLSS (mg/L)		3560
Average MLVSS (mg/L)		2790

2.5. Modelling and simulations

The residence time and consequent removal of micropollutants in the WWTP is impacted by the hydrodynamics of treatment units (Majewsky et al., 2011; Ort et al., 2010). Hence, prior to modelling the fate of MPs, a hydraulic model of the activated sludge process under study was created using measurements of the wastewater's electrical conductivity as a tracer to investigate the residence time distribution. A tanks-in-series model was fitted to the tracer data, and the optimum hydraulic model was found to consist of three aeration tanks in series and one secondary clarifier. More details on the methodology and the results of the hydraulic calibration can be found elsewhere (Baalbaki et al., 2016).

After setting up the hydraulic model, a detailed calibration of the biokinetic and settler model parameters, as well as characterization of input chemical oxygen demand and suspended solids were performed using one-year measurements of dissolved oxygen, solids and nutrient concentrations at different locations of the studied activated sludge unit (Baalbaki et al., 2017). Briefly, with the goal of modelling the fate of micropollutants in mind, specific attention was paid to predicting the concentration of biomass in the bioreactor, as well as the solids retention time (i.e. by predicting the solids concentrations in the waste stream), since the latter is known to affect the diversity of the biomass (Saikaly and Oerther, 2004). The concentration and the diversity of biomass are both expected to have an important influence on the rate of biodegradation of MPs (Kreuzinger et al., 2004; Suarez et al., 2010). The MP concentration in the waste stream also influences the extent of MP removal through adsorption. Compared to the Takács model, the Bürger-Diehl settling model was found to provide a better description of the suspended solids balance of the system and was, thus, selected for the further modelling steps (Baalbaki et al., 2017; Bürger et al., 2012; Takács et al., 1991). High concentrations of dissolved oxygen were observed in the aeration tanks at all times, indicating a relatively high oxygen transfer rate parameter, k_La. The high oxygen concentration prevents the occurrence of denitrification in the WWTP, a feature that was further confirmed by high nitrate concentrations in the effluent. Following proper calibration with respect to solids and oxygen concentrations, simulations with the standard ASM kinetic parameters provided satisfactory predictions of the effluent pollutant concentrations (i.e. Chemical oxygen demand or COD, nitrate and ammonium), resulting in a fully calibrated model for conventional pollutants. Further details on the calibration procedure with respect to solids, nutrients and dissolved oxygen are described elsewhere (Baalbaki et al., 2017), since the current study focuses on the application and extension of this model to predict the fate of micropollutants.

All model simulations were performed in the software WEST (MIKE by DHI, Denmark). The variable-coefficient ODE (i.e. VODE) integrator available in WEST was used with a tolerance of 10^{-8} for its efficient run time. Processes describing the fate of MPs were included in the bioreactor model based on the extended bioreactor model library that was first developed by Vezzaro et al. (2014). The Bürger-Diehl settling model (Bürger et al., 2012) was extended to include the processes determining the fate of micropollutants (i.e. biodegradation and sorption). The specific modifications are further elaborated upon in Section 3.2 of the discussion. The modified bioreactor and extended settler models were coupled.

All dynamic simulations were preceded by steady-state simulations over 23 days (i.e. 3 × SRT) in order to obtain a good estimate of the initial conditions of solids concentration in different locations of the activated sludge unit. Also, to obtain realistic initial conditions of micropollutant concentrations, dynamic simulations were performed over a period of time starting a few days before the first day of sampling and assuming that the micropollutant concentrations were similar to

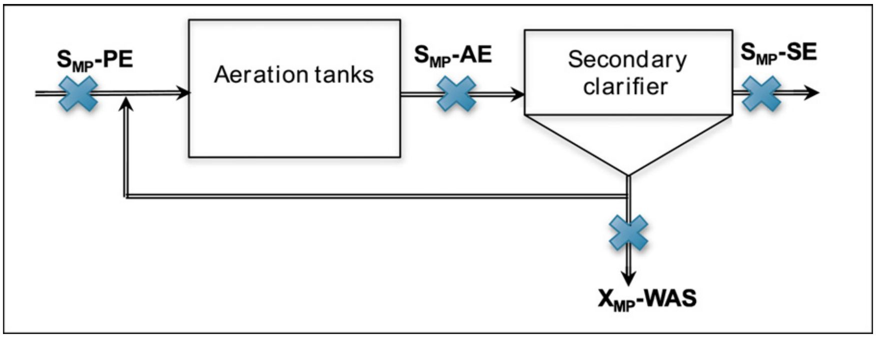

Fig. 1. Schematic of the investigated full-scale activated sludge unit. Sampling locations are indicated with a cross sign (PE: primary effluent, AE: aeration effluent, SE: secondary effluent, WAS: waste activated sludge) and the corresponding measurements taken (S_{MP} and X_{MP} indicate measurement of the micropollutant concentration in aqueous and particulate phases, respectively).

the measured ones. The input to the model (i.e. primary effluent) consisted of the following measured time series: flow rates, measurements of conventional pollutants, such as TSS, ammonia and COD, as well as the incoming concentration of the micropollutants in dissolved and particulate phases. The latter was obtained from analysis of the collected primary sludge.

2.6. Model results analysis

The model output variables considered are the soluble micropolutant concentration in the effluent from the aeration tank and secondary clarifier (i.e. S_{MP}-AE and S_{MP}-SE, respectively), as well as the particulate micropollutant concentration in the waste sludge (i.e. X_{MP}-WAS), as shown in Fig. 1. Calibration of model parameters was carried out using a Monte Carlo based approach with the scenario analysis tool available in WEST, similar to the approach suggested by Sin et al. (2008). For each parameter, a number of discrete values were defined over a broad range of parameter values that were based on literature findings, and simulations were performed for all possible parameter combinations. Subsequently, the goodness of fit for each simulation was determined by the chi-square (χ^2) criterion, as proposed by Dochain and Vanrolleghem (2001) and expressed in Eq. 1, where $\widehat{y}_i$ and y_i represent the predicted and the measured variable value, respectively at time point i and σ_i is the standard deviation of the measurements at time point i.

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

All measurement values (i.e. soluble and particulate micropollutant concentrations) with their corresponding simulated values were considered for the calculation of χ^2 in Eq. 1. The chi-square error was used to quantify the degree of mismatch between the results from simulations and measurements, since it accounts for measurement uncertainty through the standard deviations obtained from lab replicates for each of the four days. In order to compare the simulated profiles with the measured ones for error calculations, the simulated profiles were converted into a similar time scale by calculating the average daily values (flow-average or time-average), since measurements were based on time-proportional and flow-proportional samples at the AE and SE locations, respectively. The optimal parameter set was determined from the simulation with the lowest χ^2 value. Moreover, by studying the evolution of χ^2 values over the tested parameter intervals, conclusions could be drawn on the model fit's global sensitivity to the parameters, as well as the identifiability of each parameter (i.e. the existence of a unique small range of parameter values that minimize the χ^2). In addition to the χ^2 criterion, the two-sample t-test with a confidence level of 95% was performed to verify the capability of the best-fit model to well predict the average micropollutant concentration in the particulate phase in the waste sludge.

Local sensitivity analysis around the optimal parameter values was carried out in the WEST software in order to understand the dynamic effect of small variations in the model parameters on the three model output variables. In theory, the relative sensitivity is determined by Eq. 2 in discrete form, where t represents the time, y the variable and θ the input parameter, which is varied systematically by $\Delta\theta$ (perturbation). Therefore, the output of the sensitivity analysis conveys a message about the percentage change in the output variable resulting from a theoretical 100% change in the parameter, even though the actual perturbation is significantly lower than 100%.

$$\text{Relative sensitivity} = \frac{y(t, \theta + \Delta\theta) - y(t, \theta)}{\Delta\theta} \frac{\theta}{y} \quad (2)$$

3. Results and discussion

3.1. Observed concentrations and removals

Measurements collected from the sampling campaign and used in the present study for the calibration of the micropollutant fate model

Table 2
Target MPs along with their types, subtypes, internal standards, limits of detection (LODs) and limits of quantification (LOQs) in aqueous and biosolids samples, as well as suppliers.

Type	Subtype	Compound	Internal standard (Labelled surrogate)	Aqueous samples LOD, LOQ (ng/L)[a]	Biosolids LOD, LOQ (ng/L)[a]	Supplier[b] Compound, surrogate
Pharmaceuticals	Analgesics	Ibuprofen	Ibuprofen-13C3	6, 21	10, 32	S, I
Personal Care Product	Antibacterial	Triclosan	Triclosan-13C12	6, 19	6, 19	K, M
Steroid hormone		Androstenedione	Androstene-3,17-dione-2,3,4-13C3	2, 5	7, 25	S, C
Nervous stimulant		Caffeine	Caffeine-13C3	4, 14	5, 16	S, I

[a] LODs and LOQs were obtained based on standard deviation of y-intercept of line obtained from measured concentrations of serial dilutions.
[b] Supplier (compound, surrogate): **S:** Sigma-Aldrich Canada (Oakville, ON, Canada), **I:** C/D/N Isotopes (Pointe-Claire, QC, Canada), **C:** Cerilliant Corporation (Round Rock, Tex, USA), **M:** Cambridge isotope Laboratories (Tewksbury, MA, USA), **K:** KICTeam (Langley, BC, Canada).

were previously reported in a study focusing on a mass balance analysis identifying the extent of biodegradation and sorption in wastewater treatment steps (Baalbaki et al., 2016). This previous study provided evidence that both biodegradation and sorption of the four target MPs occur in the activated sludge unit under study at the prevalent conditions (Baalbaki et al., 2016). In the influent to the activated sludge process, triclosan and androstenedione were observed at average concentrations of 132 and 65 ng/L, respectively. The widespread analgesic ibuprofen and the stimulant caffeine present in many beverages entered at higher average concentrations of 1.68 μg/L and 25.3 μg/L, respectively. As reported in the previous work (Baalbaki et al., 2016), the removal of ibuprofen and caffeine by the activated sludge unit under study was 99% and 94%, respectively. This high removal efficiency is in good agreement with previous literature (Behera et al., 2011; Clara et al., 2005; Radjenović et al., 2009). Triclosan had a removal of 72%, also consistent with previous observations (Behera et al., 2011), while androstenedione was removed at a lower efficiency of 33%. Ibuprofen and androstenedione had an average particulate concentration in the secondary waste sludge of 39 ng/g and 38 ng/g, respectively. On the other hand, due to its higher input concentration, caffeine was observed at a high concentration (i.e. 776 ng/g) in secondary waste sludge. For triclosan, the measured particulate concentration in waste sludge was 1334 ng/g, which can be attributed to its known hydrophobicity (Petrie et al., 2014). These four MPs were thus selected for the modelling study based on the diversity observed in their biodegradation and sorption tendency, as reported in the literature and indicated by the experimental results of the current study (Baalbaki et al., 2016). This variability in MP fate allows for a more comprehensive exploration of MP fate model calibration and sensitivity analysis for variable combinations of parameter values. Although samples from the aeration effluent were collected as time-proportional ones, simulations indicated that the difference in concentration between time-proportional and flow-proportional micropollutant concentrations in the aeration tank effluent remains below 5%, indicating a small bias caused by collecting time-proportional samples, not limiting the value of the calibration performed.

3.2. Model structure

The processes accounted for in the model are biological degradation and sorption, since these were suggested to be the most significant processes for the target MPs (Andersen et al., 2005; Joss et al., 2006; Ternes et al., 2004). For a completely mixed unit with constant volume, the micropollutant soluble concentration dynamics are expressed by Eq. 3 taking into account the incoming and outgoing MP load, as well as sorption and biodegradation processes. Due to the effect of the variation in the active biomass concentration on the aerobic biodegradation rate (Pomiès et al., 2013), the biodegradation pseudo first-order kinetic equation in the model by Vezzaro et al. (2014) where the biomass is assumed to be constant was modified to include the effect of temporal variations in the active biomass concentration, as shown in Eq. 4. In a literature review, Pomiès et al. (2013) showed that this relation is suitable to represent the aerobic biodegradation of pharmaceuticals and hormones. Its parameters were calibrated using experimental data in several studies from literature.

Since the MP model was based on the model developed by Vezzaro et al. (2014) that used ASM2d as a basis, the denitrifcation process under anoxic conditions is accounted for in the model. Thus, in this study, equations representing both aerobic biodegradation and anoxic biodegradation are included in the model separately (Eq. 4 and Eq. 5, respectively). However, given the presence of ample oxygen (i.e. constantly >2.5 mg/L) in the activated sludge system under study (i.e. above the limit that ensures the absence of anoxia), only aerobic biodegradation is expected to occur. For the same reason, the monod-kinetics term in Eq. 4 approaches a value of one. The active biomass concentration in Eq. 4 is calculated by the model as the sum of the concentrations of the following particulate ASM2d model components: heterotrophic (X_{OHO}), autotrophic (X_{AOO}) and phosphate accumulating organisms (X_{PAO}). The concentrations of these components composing the biomass are predicted by the previously calibrated conventional pollutant model (Baalbaki et al., 2017) that is used in the present study. A Monod-type substrate saturation kinetics was not deemed necessary due to the generally low concentrations of micropollutants, as well as the fact that the first-order kinetic equation was proven to yield satisfactory predictions for micropollutants (Namkung and Rittmann, 1987; Vezzaro et al., 2014). Instantaneous sorption leading to equilibrium was assumed in the majority of studies on the fate of MPs (Parker et al., 1994; Plósz et al., 2012; Pomiès et al., 2013). However, in the present study, a more realistic approach was considered by accounting for the kinetics of both sorption and desorption in addition to the equilibrium, as shown in Eq. 6 and Eq. 7, respectively (Urase and Kikuta, 2005). It is important to note that the equations representing MP biodegradation and sorption are not limited to specific MPs, but are general for all MPs (Pomiès et al., 2013). The model becomes specific to a given MP only when values of the compound-specific parameters are substituted into the equations.

$$\frac{dS_{MP}}{dt} = \frac{F_{MP,in}}{V} - \frac{F_{MP,out}}{V} + r_{aer,bio} + r_{anox,bio} + r_{sor} \tag{3}$$

$$r_{aer,bio} = -k_{bio}{}^{*}\frac{S_O}{K_O + S_O}{}^{*}S_{MP}{}^{*}X_{active} \tag{4}$$

$$r_{anox,bio} = -k_{anox,bio}{}^{*}S_{MP}{}^{*}X_{active}{}^{*}\frac{K_O}{K_O + S_O}{}^{*}\frac{S_{NO}}{K_{NO} + S_{NO}} \tag{5}$$

$$r_{sor} = -k_{sor}{}^{*}S_{MP}{}^{*}X_{TSS} + k_{des}{}^{*}X_{MP} \tag{6}$$

$$K_{d'} = \frac{1}{K_d} = \frac{k_{des}}{k_{sor}{}^{*}1000\left(\frac{g}{kg}\right)} = \frac{S_{MP}{}^{*}X_{SS}}{X_{MP}{}^{*}1000\left(\frac{g}{kg}\right)} \tag{7}$$

Where:

- S_{MP} & X_{MP}: Concentration of micropollutant in dissolved and particulate phases (ng/L)
- $F_{MP,in}$ & $F_{MP,out}$: Input and output micropollutant load, respectively (ng/day)
- V: Volume of the treatment unit (bioreactor or secondary clarifier) (L, input)
- $r_{aer,bio}$, $r_{anox,bio}$ & r_{sor}: Rate of micropollutant aerobic biodegradation, anoxic biodegradation and sorption/desorption, respectively (ng/(L . day), calculated)
- X_{active} & X_{TSS}: Concentration of active biomass and suspended solids, respectively (gSS/L, predicted by the conventional pollutant model)
- k_{bio}&$k_{anox,bio}$: Aerobic and anoxic biodegradation 1st order rate constant (L/(gSS . day), input)
- k_{sor}: Sorption first order rate constant (L/(gSS . day), input)
- S_O and S_{NO}: Concentration of oxygen and nitrate, respectively (mg/L)
- K_O & K_{NO}: Oxygen half saturation/inhibition coefficient and nitrate half saturation coefficient, respectively (mg/L, input). These have values of 0.2 mg O_2/L and 0.5 mg NO_3/L, respectively in the standard ASM2d model.
- k_{des}: Desorption first order rate constant (1/day, calculated)
- $K_{d'}$: Inverse of the partition coefficient at equilibrium (kgSS/L, input)

To model the behaviour of MPs in the secondary settling tank, two adjustments were made to the Bürger-Diehl secondary settler model: First, instead of tracking only the transport of a single lumped solids component throughout the clarifier as formulated in the standard Bürger-Diehl model, in this study, the transport of each model component (i.e. soluble and particulate components), including micropollutants, was tracked separately. This allowed accounting for the propagation of micropollutants in the clarifier under the effects of gravity settling (for particulate components), as well as flow rate (for particulate and soluble components). This is important since inaccurate representation of the propagation of the soluble and particulate organics within the clarifier was proven to cause a bias in their concentration in the output sludge that is partially recycled back (Jeppsson and Diehl, 1996).

The second adjustment was the inclusion of the fate processes (i.e. biodegradation and sorption) acting on micropollutants in the secondary clarifier. Almost all of the previous studies on MP fate modelling in activated sludge assumed that removal of micropollutants in the secondary clarifier is negligible. Fig. 2 demonstrates that removal processes in the secondary clarifier can potentially be of importance. Although ignoring biodegradation in the settler does not impact the MP concentration in the clarifier's supernatant, it increases the average soluble concentration of micropollutants in the waste sludge by >100% (Fig. 2(a)). The target micropollutant caffeine, represented in Fig. 2, is known to biodegrade extensively, as discussed earlier, indicating that the high biomass concentration at the bottom of the settler allows for significant biodegradation to take place (Eq. 4). This result is particularly relevant since, for the system under study, the model predicted only 4% of the total solids mass to be present in the secondary clarifier which can be explained by the good settling characteristics of the sludge (i.e. low sludge volume index with an average of 58 mL/g). Consequently, for other activated sludge systems operating at high sludge blanket and thus containing a higher percentage of solids in the secondary clarifier, the micropollutant biodegradation process in the secondary clarifier could be even more significant. Accurate prediction of the micropollutant load in the underflow of the settler by accounting for the MP biodegradation is particularly important when modelling the overall fate of MPs in the entire WWTP as the underflow is often partially recycled back to the head works after treatment, increasing the load of the MP to the WWTP. In contrast, in the upper region of the settler, the biomass is present at low concentration, which explains the observation that the simulated concentration of caffeine in the supernatant was unaffected by the inclusion or exclusion of the biodegradation reactions (Fig. 2(b)). This difference in the extent of biodegradation throughout the settler results in spatial variation in the soluble and particulate micropollutant concentrations across the settler that is overlooked in non-reactive settler models.

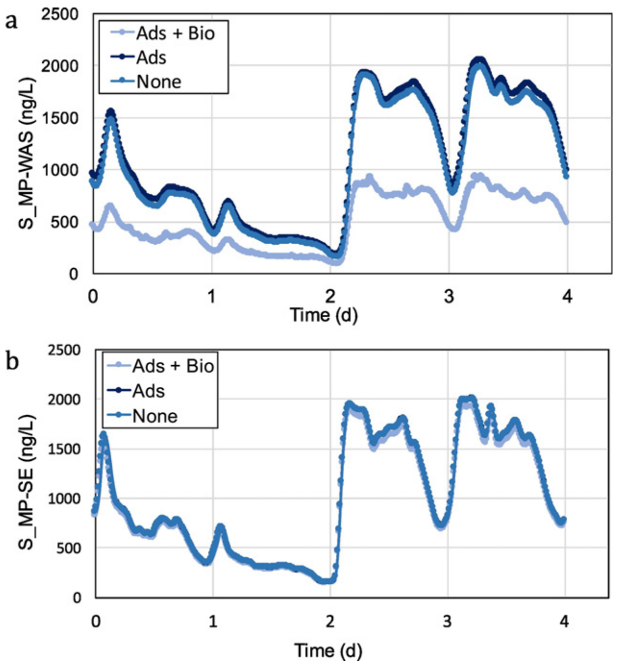

Fig. 2. Predicted profiles of soluble caffeine concentration in the two outputs of the secondary clarifier: a) secondary waste sludge and b) secondary effluent, accounting for both sorption and biodegradation (Ads + bio), only sorption (Ads) or none of the fate processes (None) in the secondary clarifier.

3.3. Impact of individual model parameters

The behaviour of the model and the interaction between the different processes (i.e. aerobic biodegradation Eq. 4 and adsorption Eq. 6) are illustrated in Fig. 3 by changing process parameters for caffeine, used here as an example. It is important to note that a logarithmic scale was selected for the particulate micropollutant concentration (ng/g) given the high variability in the model output resulting from a change in k_{bio}. The influence of the parameter k_{bio} (present in the aerobic biodegradation rate equation (Eq. 3)) is evident, as with faster biodegradation, both the soluble and particulate micropollutant concentrations decline notably (i.e. increasing k_{bio} from 5 to 10 L/(gSS.d) decreases the S_{MP} and X_{MP} by 75% and 85% on average, respectively). Although the adsorbed portion of the micropollutant is not considered to be biodegraded in this model, the decrease in S_{MP} at higher k_{bio} disturbs the equilibrium and causes subsequent desorption leading to a decrease in X_{MP}.

The influence of $K_{d'}$ that pertains to the equilibrium of adsorption on the micropollutant concentration is less straightforward. As shown in Eq. 6, a higher $K_{d'}$ increases the desorption kinetics thus moving the micropollutant sorption equilibrium to the soluble phase. This effect of increasing $K_{d'}$ can be clearly seen in Fig. 3 through an increase in the S_{MP}, accompanied by a decrease in X_{MP} for slow biodegradation kinetics (defined by low k_{bio} values). When the biodegradation kinetics are fast (i.e. $k_{bio} > 10$ L/(gSS. day)), increasing $K_{d'}$ still decreases X_{MP} significantly but the influence on S_{MP} is less pronounced (Fig. 3(b)). Indeed, when the biodegradation kinetics are much faster than those for desorption, any desorbed MP load will undergo almost instantaneous biodegradation, and hence a change in the desorption rate constant is less effective on the soluble MP concentration. In fact, it was observed that at k_{bio} value that is as high as 50 L/(gSS.d), increasing the $K_{d'}$ (and desorption) induces a slight decrease only in the soluble MP concentration in the

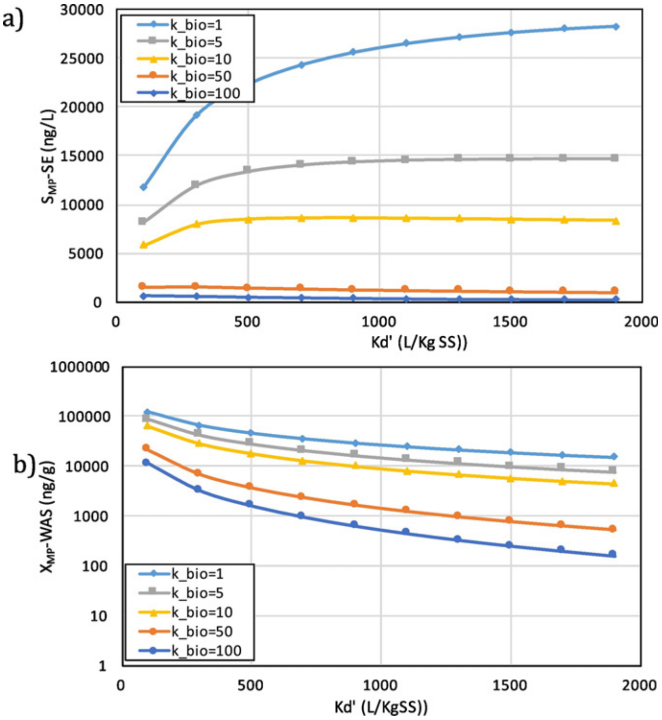

Fig. 3. Impact of changing $K_{d'}$ on the concentration of caffeine in a) secondary effluent (soluble) and b) WAS (particulate) at different k_{bio} values (L/(gSS . day)) and at fixed $k_{sor} = 5$ L/(gSS . day). XMP-WAS was plotted on a logarithmic axis due to the sharp variations induced by changing k_{bio} and $K_{d'}$.

secondary effluent. This can be directly associated with the reduced particulate MP concentration due to the high desorption rate, as well as the subsequent immediate biodegradation, resulting in a lower MP load available for desorption and thus lower soluble MP concentrations. Hence, the effects of parameters on the model output are not independent, that is, the effect of one parameter depends on the value of the other parameters. It is thus necessary to evaluate the different combinations of parameters at different ranges for calibration, as explained in the following section. The effect of varying k_{sor} that is linked to $K_{d'}$ by Eq. 6 is not shown here, but it is discussed in the following section.

3.4. Calibration

A scenario analysis was performed by simulating the model for all possible combinations of parameters over pre-defined intervals based on literature values. For each simulation, the χ^2 was calculated based on both the model outputs and the observations. In each dot plot in Fig. 4, the evolution of the normalized χ^2 (i.e. expressed as χ^2 of each simulation divided by the minimum χ^2) is shown as a function of changes in a specific parameter but taking into consideration all combinations of numeric values of the other parameters. These plots allow to assess the global sensitivity of the micropollutant model to changes in each parameter, as well as to analyze the identifiability of the parameter. A clear minimum in the χ^2 value at a specific parameter value indicates that the parameter is identifiable. Large changes in χ^2 over a parameter interval correspond to a high sensitivity of the model output to this parameter. It is important to note that the χ^2 takes into consideration the errors (i.e. standard deviations) in measurements during χ^2 calculation. A logarithmic axis was used for the normalized χ^2, since it was observed to vary greatly at different combinations of the parameters.

3.4.1. Caffeine

For caffeine, it was observed that changing k_{bio} value (i.e. from around 20 to 30 L/gSS.day) decreases the minimum χ^2 by more than one third, demonstrating the high impact of this parameter on the model fit. Low χ^2 values are clearly found at high biodegradation rates. The optimum fit was observed at $k_{bio} = 33$ L/gSS.day, which is within the wide range of parameter values encountered in the literature 1–240 L/gSS.day (Bertolini, 2011; Xue et al., 2010). The large variability in the observed k_{bio} values in the literature could be attributed to the variable properties of the biomass and the suspended solids in the systems used for calibration (Ternes and Joss, 2006).

The optimal model fit was observed at $K_{d'} > 0.001$ kgSS/L which is consistent with previous literature (Stevens-Garmon et al., 2011; Xue et al., 2010). Contrary to k_{bio}, varying the value of k_{sor} did not have a pronounced influence on the minimum χ^2, as low χ^2 values can be found over the entire parameter range. This indicates the lack of identifiabiltiy of k_{sor} and $K_{d'}$ and can be explained by the extensive biodegradation of caffeine at the investigated range of k_{bio}, which reduces the model's sensitivity to the other fate processes. It is also observed that increasing k_{bio} beyond 40 L/gSS.day, decreases the degree of variability of the χ^2 value (i.e. the length of the dotted lines in Fig. 4), indicating a lower sensitivity of the model to the other parameters when biodegradation is more significant. This is reasonably interpreted by the fact that when biodegradation is faster, resulting in a rapid decline in the MP concentration, the effect of changing sorption parameters is less influential.

The best-fit model yielded a predicted profile of caffeine's concentration in the secondary effluent that was in agreement with the measured profile, as shown in Fig. 5(a) by comparing the simulated and measured MP concentration profiles. In addition, the predicted output concentration time series with a 15-min time step was used to obtain a daily flow-average of the simulated micropollutant's concentration represented by triangles in Fig. 5. This allows comparison with the measured concentrations obtained from 24-h composite samples (i.e. represented by squares). Similar to the secondary effluent, the best-fit model yielded a good fit between the simulated and the measured caffeine concentrations in the aeration tank outlet (results not shown). In addition, the average (i.e. over the 4 measurement days) simulated concentrations of MPs in the solids of the waste sludge from the best-fit model are visually compared to the measurements in Fig. 6. The p-value representing a measure of the match between the average measurements and simulations are shown to be >0.05, indicating that the model well predicts the underflow particulate concentration of caffeine, as the difference between these is statistically insignificant. Average particulate MP concentrations were used for assessing the model fit in Eq. 1, unlike soluble MP concentrations, since the particulate MP concentrations are less temporally variable throughout the four days of sampling, due to the SRT of almost eight days.

3.4.2. Ibuprofen

The plots for ibuprofen are similar to those for caffeine, which could be explained by the fact that both are highly biodegradable, with no significant adsorption taking place. The best fit was observed at $k_{bio} = 77$ L/gSS.day. This value is higher than the previously observed values in the literature 1.3–38 L/gSS.day (Abegglen et al., 2009; Fernandez-Fontaina et al., 2012; Suarez et al., 2010). The high k_{bio} values obtained in the present study relative to the literature for ibuprofen could be associated with the higher dissolved oxygen concentration in the aeration tanks of the system under study (i.e. 4–6 mg/L during the majority of the sampling period compared to <4 mg/L in the literature). Xue et al. (2010) demonstrated that at higher dissolved oxygen concentration, the biodegradation of micropollutants is enhanced, which is represented by a higher k_{bio}. Fig. 4 shows that both $K_{d'}$ and k_{sor} are non-identifiable. The best-fit model provided good predictions of the soluble micropollutant concentration in secondary effluent and particulate phase in the settler's underflow, as shown in Fig. 5(b) and Fig. 6, respectively.

3.4.3. Androstenedione

As shown in Fig. 4, androstenedione exhibits an evident minimum in χ^2 at an optimum value of k_{bio} 2.2 L/gSS.day. Higher k_{bio} values lead to higher errors (i.e. increasing k_{bio} from 2 to 4 L/(gSS.day) was shown to triple the minimum χ^2). The clear minimum in the χ^2 values for the partially biodegradable androstenedione also indicates that varying k_{bio} has a profound influence on the model fit. Hence, the biodegradation rate constant for androstenedione can be estimated with high confidence since the model is highly sensitive to this parameter. From the available literature, no data were found to model the fate of androstenedione in the activated sludge process, and only one previous explored its removal in activated sludge treatment (Esperanza et al., 2007). Similar to caffeine and ibuprofen, $K_{d'}$ and k_{sor} did not have a notable influence on the model fit.

3.4.4. Triclosan

For triclosan, a clear optimum in χ^2 values can be found for both k_{sor} and $K_{d'}$. The minimum χ^2 was observed at $k_{sor} = 4.4$L/gSS.day and $K_{d'} = 7\text{x}10^{-6}$ kgSS/L or lower. The $K_{d'}$ value that leads to the best-fit model is within the ranges observed in the literature (Nakada et al., 2010), although other literature reported higher values (Hyland et al., 2012). One explanation for the observed $K_{d'}$ being at the lower end of the literature values is the addition of ferric chloride in the unit under study, which alters the properties of the sludge, potentially increasing the sorption potential of MPs onto it. In fact, it was previously observed that chemical additions to activated sludge decreases the value of $K_{d'}$ for triclosan (Zhu, 2014). Using the optimum $K_{d'}$ and k_{sor} resulted in predicted particulate underflow concentrations that correspond to the measurements with p-value > 0.05, and the concentration in the secondary effluent also showed a fairly good match with measurements (Fig. 6 and Fig. 5, respectively). Unlike sorption parameters, wide variations in the k_{bio} value did not lead to changes in the model fit, indicating low sensitivity of the model to this parameter.

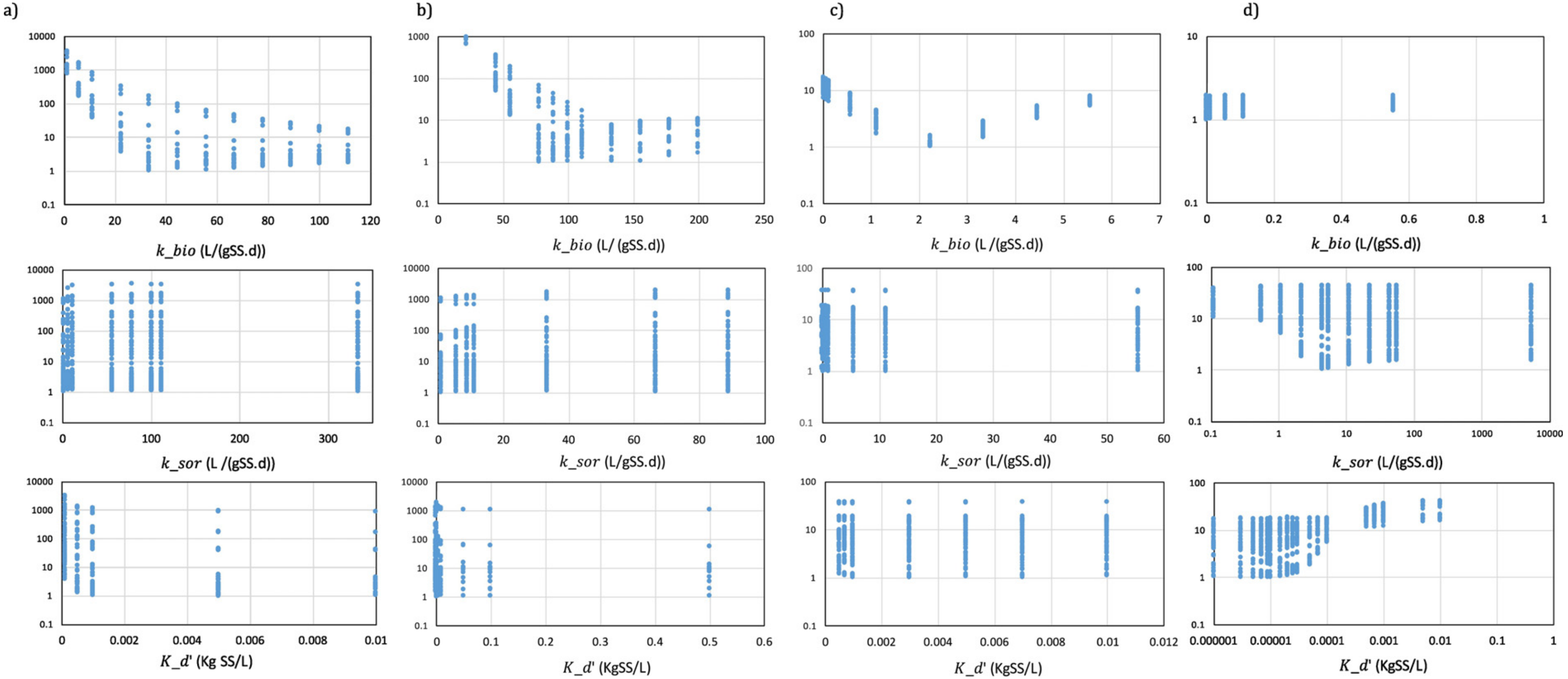

Fig. 4. Normalized χ^2 represented as a ratio of the minimum χ^2 for a) caffeine, b) ibuprofen, c) androstenedione, d) triclosan as a result of varying each model parameter: k_{bio} (first row), k_{sor} (second row) and $K_{d'}$ (third row).

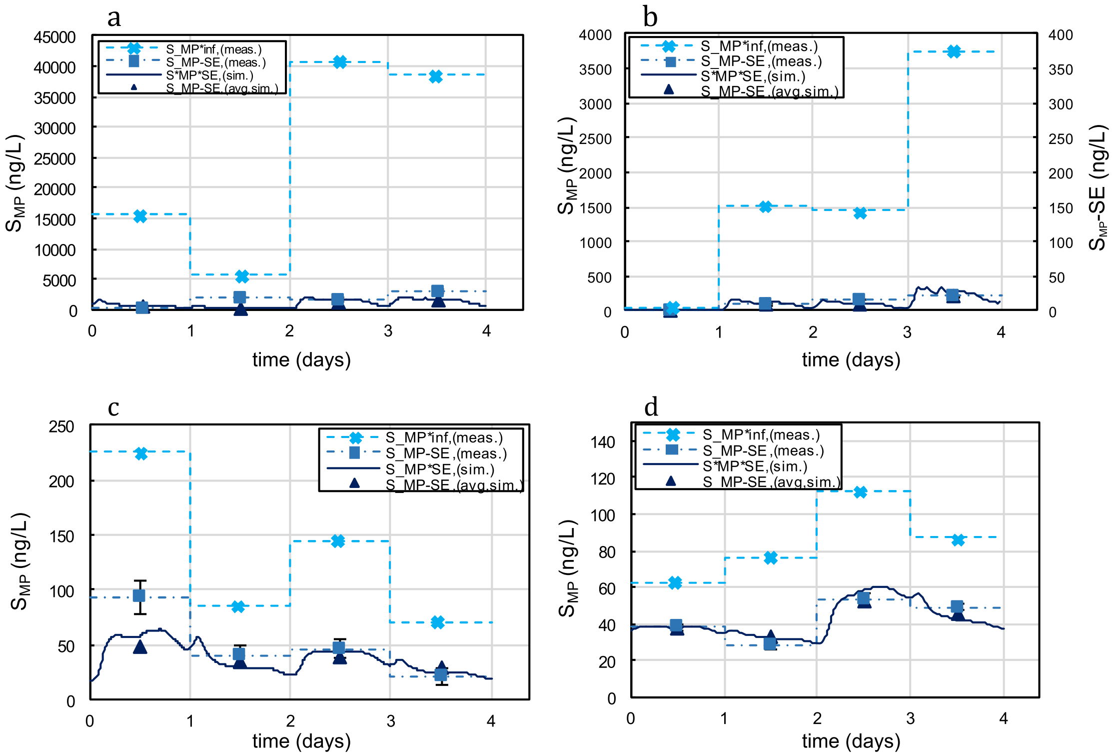

Fig. 5. Measured (meas.) influent concentrations as well as measured and simulated (sim.) soluble secondary effluent concentrations for a) caffeine, b) ibuprofen, c) triclosan, d) androstenedione. The flow-average of simulated values are shown as (avg sim.). For ibuprofen only, the soluble effluent concentrations are displayed on a separate secondary axis since values are much lower than in the input.

3.4.5. General

In summary, it is observed that the sensitivity of the model fit to biodegradation and sorption parameters, as well as the identifiability of the parameters is variable, depending on the micropollutant considered. Differences in the chemical properties of micropollutants cause them to be more or less susceptible to certain fate pathways, which influences the model's sensitivity to the parameter, as well as the identifiability of the parameter. In general, model parameters of dominant processes (i.e. biodegradation for caffeine, ibuprofen and androstenedione and sorption/desorption for Triclosan) were the most influential and had good identifiability, whereas parameters of less dominant processes showed poor identifiability.

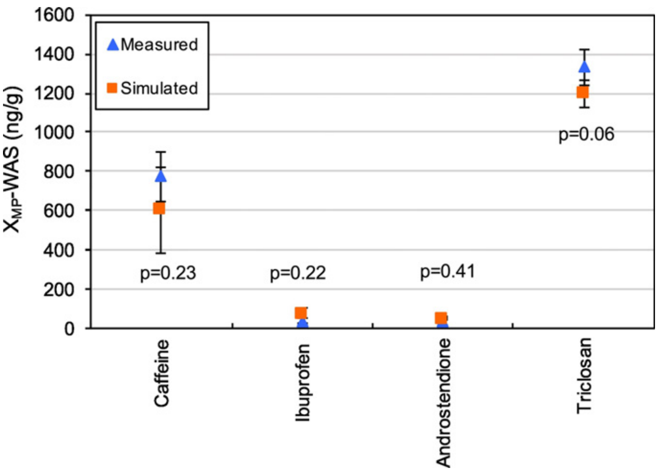

Fig. 6. Measured and simulated concentrations of each micropollutant in secondary waste sludge (ng/g). The error bars represent the standard deviations obtained from measurements on the four days of sampling for both simulations and measurements. P-values from the two-sample t-test represent the match between the measured and simulated concentration of the micropollutant.

Identifiability of parameters is not only dependent upon the measurements but also upon the process conditions and the model structure. In order to improve the identifiability of less influential parameters, dedicated experiments could be conducted to obtain more detailed information under specific process conditions. However, one should always consider whether it is worth it to invest time and resources for the determination of the kinetics of processes whose contribution to the overall removal under prevailing conditions is limited. For the current study, this was not deemed necessary since the model provided satisfactory predictions of the overall removal efficiencies of the compound under study (Fig. 5).

3.5. Dynamic local sensitivity analysis

After obtaining the optimal values of the most effective parameters for each of the four micropollutants, a local sensitivity analysis was performed to investigate the dynamic sensitivity of the different model variables throughout the four-day simulations, as shown in Fig. 7. This analysis provides information to link the model's sensitivity to parameters with the dynamics of input MP concentration and process conditions. Such analysis can provide valuable information for the design of future measurement campaigns based on expected influent dynamic conditions. For illustration, this analysis was performed for caffeine and triclosan only, since their behaviour in activated sludge treatment was shown to be influenced by different fate processes and their concentration in the influent is highly dynamic. Using WEST's default perturbation factor (i.e. the factor change in the parameter) of 10^{-6}, inconclusive sensitivity profiles were obtained, due to interference of numerical errors with the small effects on output variable caused by the applied perturbations, due to the very low MP concentrations (De Pauw and Vanrolleghem, 2006). Hence, the perturbation factor was set to a higher value of 10^{-2}, and the assumption of linearity of the sensitivity was verified to be still valid by the equality of the backward and forward relative sensitivities (i.e. by both increasing and decreasing the parameter with the same perturbation) (De Pauw and Vanrolleghem, 2006).

As shown in Fig. 7, for caffeine at the best-fit parameters, the most influential parameter on the soluble micropollutant concentrations is k_{bio}, which is in agreement with the observations made in the previous section. This is supported by numerical sensitivity values indicating that a 100% theoretical change in the parameter results in >100% change in soluble micropollutant concentrations at all monitored locations. On the contrary, the sensitivity to k_{sor} was low (<50% change in X_{MP} and S_{MP} due to 100% change in parameter), while the sensitivity to $K_{d'}$ that describes sorption equilibrium was high for the micropollutant concentration in the waste sludge only. A notable reduction in the sensitivity of S_{MP} to k_{bio} is observed to take place on the third day. The specific time where the sensitivity to k_{bio} is lowest corresponds to a drastic increase in the concentration of caffeine at the input to the activated sludge unit (i.e. from, 5,920 ng/L to 40,700 ng/L) and also at the headworks (i.e. from 4,813 ng/L to 50,800 ng/L). The effect of the increase in input concentration on the sensitivity of S_{MP} to k_{bio} is mathematically reasonable, since the expression of the time-dependent S_{MP} obtained from the numerical solution of Eq. 3 contains all the following: the parameter k_{bio}, the incoming MP concentration and the initial MP concentration (affected by previous incoming concentrations). A lower sensitivity to k_{bio}, as observed on the third day, indicates that parameter k_{bio} value is not significantly affecting the simulation due to other influences on the system. This is expected to increase the uncertainty of the calibrated k_{bio} value if data were only available in such circumstances. Hence, avoiding sampling during expected sharp dynamics in input caffeine (i.e. such as over weekdays and weekends or around peak periods during the day for high-frequency samples) improves the calibration of k_{bio} by eliminating data in low sensitivity conditions.

For triclosan, hypothetically increasing $K_{d'}$ by 100% increased the soluble MP concentration by 10–40% and decreased the particulate concentration (in ng/L) by <5%, which is reasonably explained by the higher calculated k_{des} associated with the larger value of input $K_{d'}$. Increasing k_{sor} by 100% was continuously shown to decrease the soluble MP concentration by 40–100% at all locations of the activated sludge. Considering that in the input, the soluble to particulate MP fraction (i.e. average of 3×10^{-4} kgSS/L) is higher than that for secondary sludge at equilibrium determined by $K_{d'}$ (1×10^{-5} kgSS/L), faster kinetics towards equilibrium will continuously reduce the soluble MP concentration to achieve $K_{d'}$. The amount of reduction in the soluble MP concentration due to perturbations in k_{sor} exhibited a time-dependent profile with higher reductions in S_{MP} (i.e. higher sensitivity to k_{sor}) observed on the first and the third days where the soluble load is the highest. This further emphasizes the impact of the input MP concentration profile on the model's sensitivity. The sensitivity of the particulate MP concentration to all model parameters was lower than that of the soluble MP concentration (i.e. <20% change in X_{MP} for 100% theoretical change in parameter). This indicates that in the case of triclosan, measuring the micropollutant concentration in the aqueous phase might be sufficient for calibration, due to the higher sensitivity of the aqueous phase to the model parameters compared to the particulate phase.

4. Conclusion

In this study, a model calibrated for conventional pollutants was extended to include MP fate processes and was subsequently calibrated for a number of specific MPs of different classes using full-scale measurements. The micropollutants' fate processes were included in the bioreactor model through an available extension of the ASM2d model and in the secondary clarifier model by extending the Bürger-Diehl settler model for the first time to include the propagation and the fate processes of MPs. Comparing results from the reactive and non-reactive settler models indicated that a mismatch of 100% in the simulated micropollutant soluble concentration at the underflow of the settler would occur as a result of ignoring biodegradation taking place in the settler for the case of the highly biodegradable caffeine. A Monte Carlo based scenario analysis was used to find optimal parameter values, as well as to provide information on parameter's identifiability and the model's global sensitivity. Depending on the process that plays the major role in the fate of a specific micropollutant, different model parameters could affect the fit of the model to different extents, which

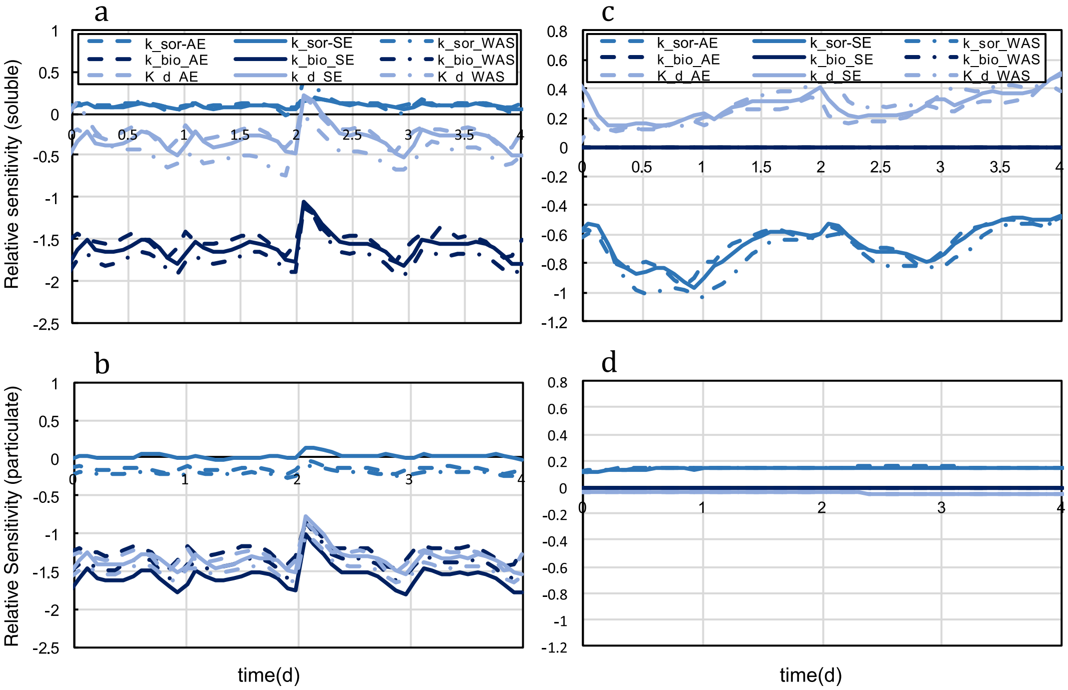

Fig. 7. Dynamic local sensitivity of the MP soluble concentrations (upper graphs) and particulate concentrations (lower graphs) to small perturbations in the three parameters for caffeine (a & b) and triclosan (c & d) in different locations (AE: effluent of aeration tank, SE: effluent of secondary clarifier, WAS: waste activated sludge).

eventually determines the identifiability of the calibrated parameters. While for the highly biodegradable caffeine and ibuprofen, k_{bio} was found to be the most significant parameter influencing the fit of the model, for triclosan, both sorption parameters k_{sor} and $K_{d'}$ were more significant. For androstenedione, which is mildly degradable, the k_{bio} showed a clearer optimum compared to caffeine and ibuprofen. Dynamic local sensitivity analysis was performed and proposed to serve as a tool in the design of sampling campaigns for improved calibration of model parameters, since it provides insights on preferable input dynamics during sampling, as well as on necessary types of measurements (i.e. particulate or soluble MP concentrations). These analyses provided novel insights on the sensitivity of a micropollutant activated sludge model to the different model parameters, as well as on the temporal variability in the sensitivity in relation to input dynamics. The sampling campaign used, limited in resource and time requirements, indicated a potential for future applications of this fate model by WWTP operators for the purpose of developing risk assessment tools to evaluate the discharge of micropollutants into the environment.

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