Wastewater Treatment Process Improvement using Fate Modeling of Xenobiotic Organic Compounds

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Abstract

The presence of Xenobiotic Organic Compounds (XOCs) in municipal wastewater treatment plants' effluent raises a global concern due to the easy consumption of these micropollutants by organisms. The fate of XOCs removal mechanisms of these compounds remains a challenge in recent scientific research. This study aimed to create an uncalibrated mathematical fate model within the professional wastewater modeling simulation software in a first step that was able to address the fate of Sulfamethoxazole (SMX), its metabolite, and Nonylphenol ethoxylates (NPEOs) along with conventional compounds during an activated sludge process. For the calibration process as a next step, two different case studies were created with assigning related removal mechanisms to each group of compounds. In the calibration process, model parameters are tuned such that the model can best simulate the experimental data using optimization methods. The validation results showed that the proposed model successfully simulates the removal of XOCs. Results of sensitivity analysis showed that the fate model is more sensitive to biodegradation rate constant than Solid Retention Time (SRT).

Wastewater Treatment Process Improvement using Fate Modeling of Xenobiotic Organic Compounds

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Key Points:

- The developed fate model can be used to optimize the removal process of Xenobiotic Organic Compounds (XOCs)
- The removal efficiency of the SMX was found to be negative, because the conjugate was converted to SMX during the biotransformation process
- Sensitivity analysis of three different cases showed that the fate model was more sensitive to biodegradation rate than to sorption rate.

Abstract

The presence of Xenobiotic Organic Compounds (XOCs) in municipal wastewater treatment plants' effluent raises a global concern due to the easy consumption of these micropollutants by organisms. The fate of XOCs removal mechanisms of these compounds remains a challenge in recent scientific research. This study aimed to create an uncalibrated mathematical fate model within the professional wastewater modeling simulation software in a first step that was able to address the fate of Sulfamethoxazole (SMX), its metabolite, and Nonylphenol ethoxylates (NPEOs) along with conventional compounds during an activated sludge process. For the calibration process as a next step, two different case studies were created with assigning related removal mechanisms to each group of compounds. In the calibration process, model parameters are tuned such that the model can best simulate the experimental data using optimization methods. The validation results showed that the proposed model successfully simulates the removal of XOCs. Results of sensitivity analysis showed that the fate model is more sensitive to biodegradation rate constant than Solid Retention Time (SRT).

1 Introduction

Organic micropollutants have attracted significant concern from the scientific community because of their environmental fate and hazardous/ toxicological properties. These hazardous pollutants, which threaten human life and the environment, typically should have low concentrations of which range from ng/L to a few hundred µg/L in wastewater effluents. Many recent studies show the conventional wastewater treatment plants (WWTPs) are not able to remove these emerging compounds properly (Rathi, et al., 2021; Wang, et al., 2021; Jari, et al., 2022; Xiang, et al., 2022; Zhou, et al., 2022). Hence this study aims to address removal mechanisms of these compounds precisely and efficiently which in turn leads to improving the design and operational condition of WWTPs. With proper formulation of such innovative methods, the presence of hazardous materials in the environment can be assured within proper ranges. Thus, adverse effect on human/ aquatic life will be reduced significantly leading to a sustainable water cycle in an effort to promote means of human societies to reuse water.

Municipal wastewater contains a complex mixture of XOCs originating from personal care products, pharmaceuticals, secreted hormones, household, and industrial chemicals. These anthropogenic XOCs are of concern due to the increasing number of reports of reproductive disorders in aquatic wildlife residing below wastewater outfalls (Al Qarni et al., 2016; Maiti et al., 2016; Martin-Pascual et al., 2020; Quintelas et al., 2020). Several recent studies have estimated that wastewater could contain many types of XOCs. Particular XOCs, that are known to cause toxic effects in different recipients and species, are frequently reported in WWTP effluents in potentially toxic concentrations (Hamza et al., 2016; Wilson & Ashraf, 2018; Çeçen & Gül, 2020; Choudhary & Philip, 2021). In addition, these chemicals may cause long-term changes in aquatic ecosystems because of intrinsic properties such as high polarity and persistence (Baalbaki et al., 2017; Cheng et al., 2017). Feminization of male fish in different species is a well-known effect observed in recipients loaded with treated wastewater. Experiments with caged fish have confirmed that wastewater containing Endocrine Disrupting Compounds (EDC) can cause feminization. XOCs in freshwater has been observed and found to constitute a serious risk to human health and aquatic life (Contreras et al., 2019; Hai et al., 2016; Martin-Pascual et al., 2020; Wilson & Ashraf, 2018). Wastewater treatment plants (WWTPs) remove XOCs from the water mainly by sorption, biological and/or chemical

degradation, volatilization, and/or stripping. Conventional wastewater treatment is not directly designed for removing XOCs but nonetheless reduces the concentration of several key XOCs (Compagni et al., 2020; Contreras et al., 2019; van Bergen et al., 2020). Several studies have identified the biodegradation and sorption of XOCs as a vital elimination process in WWTPs (Baalbaki et al., 2017; Plósz & Ramin, 2019; van Bergen et al., 2020). However, the ability to utilize and control the parameters and processes governing the biodegradation of XOCs in activated sludge systems remains a challenge. Therefore, models developed and calibrated from experiments, with carefully selected model pollutants, should be constructed to support scientists efforts to discover and realize optimal treatment levels (Hatoum et al., 2019; Plósz & Ramin, 2019; Quintelas et al., 2020; Compagni et al., 2020).

Not all of the aforementioned processes are conducive for removing XOCs. For this reason, these compounds should be categorized regarding related mechanisms. For example, Nonylphenol Ethoxylates (NPEOs) are a class of compounds that are transformed by the abiotic cleavage process. In aerobic systems, the major pathway of biodegradation for NPEOs is stepwise oxidation and cleavage of the polyoxyethylene chain either by hydrolysis or an oxidative hydrolytic mechanism before biodegradation of this compound. Hence, these compounds are transformed by the abiotic cleavage process along with biodegradation and biotic hydrolysis (Karahan et al., 2010; Zonja et al., 2015; Aymerich et al., 2016). Another important class of compounds, used extensively in both human and veterinary medicine, is antibiotic sulfamethoxazole (SMX). The specific removal mechanisms for these compounds are aerobic and anoxic parent compound formation, co-metabolism, competitive inhibition along with normal aerobic and anoxic biodegradation and aerobic/anoxic sorption (Achermann et al., 2018; Plósz & Ramin, 2019; Brown et al., 2020; Çeçen & Gül, 2020; Compagni et al., 2020). In this work, the first step was recognition of removal mechanisms and compound categorization, which led to two influential case studies. The second step is fate modeling. In this step, the most recent models are investigated and compared. Most of the existing models describe the fate of XOC without including more complex mechanisms such as parent compound transformation, co-metabolism, etc. Only a few models have considered biodegradation in aerobic and anoxic conditions (Plósz et al., 2009; Suarez et al., 2010; Cheng et al., 2017; NELSON et al., 2018; Quintelas et al., 2020). In most fate models, the volatile fraction of total biomass has been employed in the biokinetic rate equations. This study's model will develop and separate a heterotrophic biomass, which will describe its role in the fate of XOCs more precisely that current models. Activated sludge model 1, ASM1, (by International Water Association (IWA)) was developed for the design and operation of biological wastewater treatment plants and removal of conventional contaminants; however, these models were not designed to predict the fate and transport of XOCs.

The objective of this work was to develop and critically evaluate an enhanced fate model for XOCs in wastewater treatment plants. Mechanisms that are responsible for the removal of XOCs in wastewater treatment were identified and integrated with an ASM1 model to create an uncalibrated fate model. Activated sludge models (ASM) can differentiate between viable and non-viable biomass, so it was expected that ASM-based integrated fate models should be able to provide more accurate predictions of XOC fate over a range of operating conditions. The newly created fate model will initially be incorporated into the GPS-X process simulator to create an uncalibrated fate model. Since only a small group of mechanisms is responsible for the removal of each compound, for the next step, mechanisms are categorized in two different case studies. Each case study will be individually calibrated and validated using corresponding data from the

literature. The combined enhanced model will be critically evaluated by conducting a sensitivity analysis that will evaluate the impact of operational and modeling parameters, such as Solid Retention Time (SRT), and biodegradation and partitioning coefficients, on the contaminant fate model (van Bergen et al., 2020; Wang et al., 2020). The proceeding section discusses the fate model structure which describes schematic modeling processes, case study descriptions including assigned specific removal mechanisms to each group of compounds, and model calibration processes that use optimization methods. Model parameters were 'tuned' such that the model could best follow the experimental data. Ultimately, results and analysis are provided to enhance modeling outputs and results discussions.

2 Fate Model Structure

The International Association on Water Pollution Research and Control (IAWPRC) task group realized that, due to the long solids retention times and low growth rates of bacteria, actual effluent substrate concentrations between different activated sludge treatment plants did not vary greatly. What significantly differed was the levels of MLSS and electron acceptor (oxygen or nitrate). Thus the focus of the Activated Sludge Model No.1 (ASM1) is the prediction of the solids generation and electron acceptor consumption (Plósz et al., 2009; Pomiès et al., 2013). This works model is employed to predict the viable biomass in the activated sludge process (heterotroph biomass). The main reason to use the ASM 1 model is the ability of this particular model to simulate biomass growth and differentiate between viable and non-viable biomass under aerobic and anoxic condition in WWTP studies, which is vital to accurate prediction of XOCs fate in WWTPs. It should be noted that instead of using Xss to describe the biomass concentration (as is traditionally employed in fate modeling) xbh was employed to take advantage of the integration of the fate model within the ASM based model.

The software GPS-X was used to carry out simulation results. This software is a multi-purpose modeling tool that can be employed for the simulation of municipal and industrial wastewater treatment plants. This software package provides conventional models such as ASM 1 as built-in libraries that can be used as a basis on which new models can be created. Within the GPS-X software, the Mantis model is used which is identical, with minor modifications, to ASM 1. A library within GPS-X details a list of wastewater process models using a set of basic wastewater components or state variables. The term state variable refers to the basic variables that are continuously integrated over time. The composite variables are those variables that are calculated from (or composed of) the state variables. The relationships between the state and composite variables are calculated at every connection point of the plant layout. For this research, the Industrial Pollutant Variables Library (CNIPLIB) was used. This library includes forty-six state variables: sixteen are predefined and thirty are user defined (15 soluble, 15 particulate). These state variables are used for fate model variables. For example, SMX in the solid phase, describes Xza while the soluble species describes Szf.

The integrated fate model employs an ASM-based (Mantis) model for prediction of viable biomass that is subsequently responsible for removal and transformation of trace compounds. Hence, the model is able to be employed for predicting the removal of conventional and trace compounds simultaneously. The “model developer”, which is a software tool developed by Hydromantis was used to generate the ASM based fate model. To create the new model in GPS-X, the model developerincluded the Mantis model matrix as the basis and the CNIPLIB library was used. CNIPLIB was selected as it has the capacity to employ a number of

pre-defined states for industrial customized components that in this article consisted of the target XOC's. The model developer contains several spreadsheets with the first spreadsheet containing the fate model matrix. The second sheet includes the composite variables vector for GPS-X. The third sheet contains the fate model parameters and coefficients, such as state variables, composite variables, and the stoichiometric and kinetic parameters, for both the conventional and the trace compounds. The last sheet contains the list of the GPS-X library state variables. The model developer converts the matrix components to a language that can be read by the GPS-X software.

Figure 1 depicts the workflow for the modeling process. Since specific groups of mechanisms were identified to be responsible for the removal of selected compounds, two different case studies were created for two different groups of compounds. Hence, two different submodels were created within the fate model. Each submodel was generated in the GPS-X software separately. To achieve this goal, compounds that were not included in a specific submodel, were omitted by inserting zero values in the corresponding rows and columns. For example, for Case Study 1, this was created for removal of SMX process rates and compounds that were not related to SMX fate were zeroed. The two different submodels were calibrated separately using relevant literature data for both the conventional and trace compounds, and the optimal parameters were obtained and inserted in the corresponding sheet of the model developer (third sheet). After this step, each submodel was generated in the GPS-X software by using the model developer tool, and the simulation results were reported.

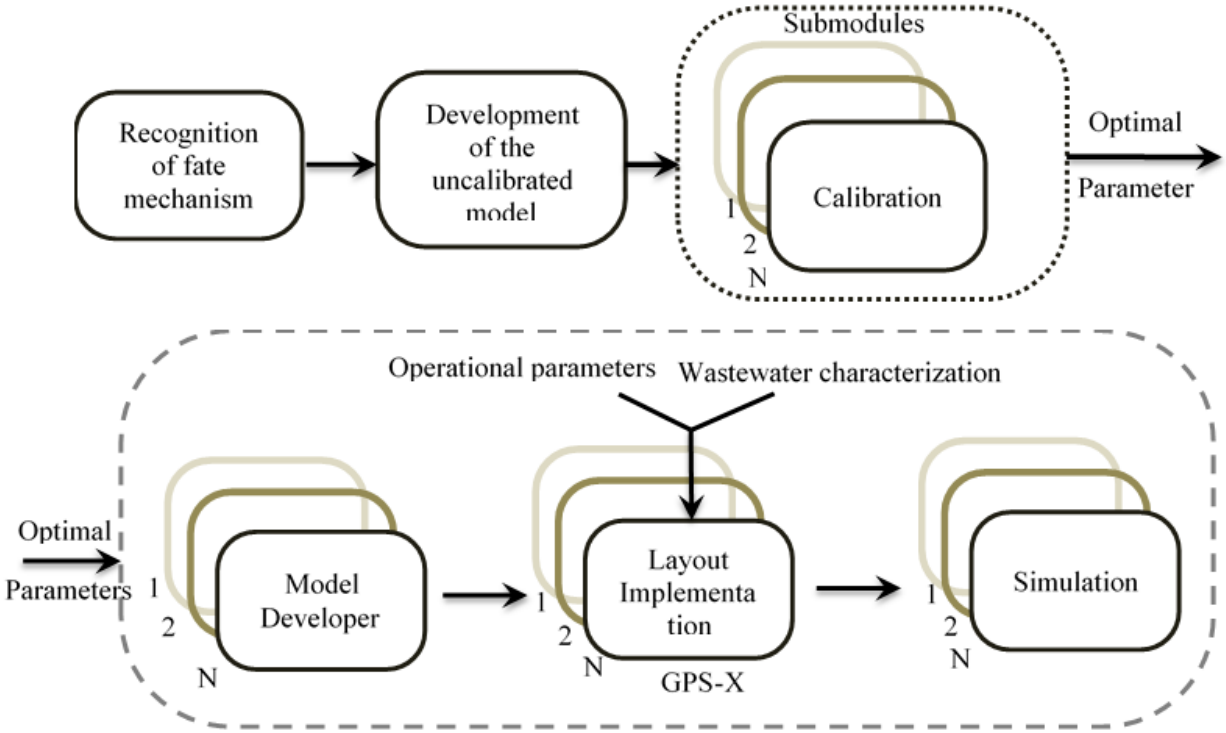


Figure 1. Schematic modeling process flow chart of this work

3 Case Studies Description

Since only selected mechanisms are responsible for the removal of a specific compound, two different case studies (two sub models) were developed for use in this study. Each case study addressed a specific group of compounds. First case study was created to address the

biodegradation and sorption of SMX along with biodegradation (conversion) of its metabolite to the parent compound (SMX). The removal mechanisms for these compounds are: aerobic and anoxic biodegradation, parent compound formation, co-metabolism and competitive inhibition and aerobic and anoxic sorption. In developing case study 1, all process rates and compound species that were not related to the SMX and its metabolite removal were omitted from the fate model matrix by inserting zeros in the relevant rows and columns. The submodel for this case was a Mantis based model that addressed the removal of SMX and its metabolite along with the conventional compounds. The Matrix for the SMX and its metabolite was presented in Table 1.

Table 1: process matrix of SMX and its metabolite

SMX and its metabolite components			Process rate	Process rate description
Szf	Szg	Xza		
-1	0	0	$k_{1BioOx} \cdot Szf \cdot \frac{(K_s \cdot \eta_{bio})}{(K_s \cdot \eta_{bio} + S_s)} \cdot \frac{S_o}{(K_o + S_o)} \cdot xbh$	Aerobic biotransformation of Szf
1	-1	0	$k_{1DecOx} \cdot Szg \cdot \frac{(K_s \cdot \eta_{1DEC})}{(K_s \cdot \eta_{1DEC} + S_s)} \cdot \frac{S_o}{(K_o + S_o)} \cdot xbh$	Aerobic parent compound transformation
-1	0	0	$k_{1BioAX} \cdot Szf \cdot \frac{(K_s \cdot \eta_{bio})}{(K_s \cdot \eta_{bio} + S_s)} \cdot \frac{S_o}{(K_o + S_o)} \cdot xbh$	Anoxic biotransformation of Szf
1	-1	0	$k_{1DecAx} \cdot Szg \cdot \frac{(K_s \cdot \eta_{1DEC})}{(K_s \cdot \eta_{1DEC} + S_s)} \cdot \frac{S_o}{(K_o + S_o)} \cdot xbh$	Anoxic parent compound transformation
1	0	-1	$K_{Des} \cdot Xza \cdot \frac{S_o}{(K_o + S_o)}$	Aerobic desorption of Szf
-1	0	1	$K_{Des} \cdot K_{1DOx}.Szf \cdot \frac{S_o}{(K_o + S_o)} \cdot X_{ss}$ $K_{Des} \cdot K_{1DAx}.Szf \cdot \frac{K_o}{(K_o + S_o)} \cdot X_{ss}$	Aerobic sorption of Szf
1	0	-1	$K_{Des} \cdot Xza \cdot \frac{K_o}{(K_o + S_o)}$	Anoxic desorption of Szf
-1	0	1	$K_{Des} \cdot K_{1DAx}.Szf \cdot \frac{K_o}{(K_o + S_o)} \cdot X_{ss}$	Anoxic sorption of Szf

Two major mechanisms are responsible for removal of SMX: biodegradation and sorption. For fate modeling of this compound, the impact of aerobic and anoxic conditions was considered for both biodegradation and sorption mechanisms. The biodegradation of its metabolite (daughter compound, Szg) was also considered in this model. The metabolite that was present in the raw wastewater during the biodegradation process was converted to the parent compound (SMX). The expressions for the process rates of aerobic/anoxic biodegradation, and aerobic/anoxic parent and daughter compounds transformation contain modifying terms, (1) and (2) respectively that reduce the rates in the presence of readily biodegradable COD. The uptake

of readily biodegradable COD (Ss) has been reported to cause competitive inhibition of micro pollutant biotransformation processes (Plósz et al., 2009).

$$\frac{(K_s \cdot \eta_{bio})}{(K_s \cdot \eta_{bio} + S_s)} \quad (1)$$

$$\frac{(K_s \cdot \eta_{1DEC})}{(K_s \cdot \eta_{1DEC} + S_s)} \quad (2)$$

(Plósz et al., 2009) observed an increase in the concentration of SMX, through wastewater treatment with negative or low removal efficiencies observed for this compound. Therefore it was concluded that other mechanisms should be taken into account during the removal of this compound (Plósz et al., 2009; Sipma et al., 2010). It is possible for certain pharmaceuticals that the conjugated form may be present in the raw wastewater at concentrations greater than of the parent. Thus a mechanism referred to as parent compound transformation was added. Equations 10 and 12 describe the process rates for the aforementioned phenomenon.

The model in this case study was calibrated using the data provided in (Plósz et al., 2009). The plant configuration for this study is shown in Figure 2. Since aerobic and anoxic biodegradation were included as removal mechanisms for SMX and its metabolite removal, aerobic and anoxic compartments were employed in the activated sludge process plant. For the sensitivity analysis of this case against SRT, only aerobic parent compound transformation, aerobic biodegradation, and aerobic sorption-desorption were considered to simplify the data interpretation.

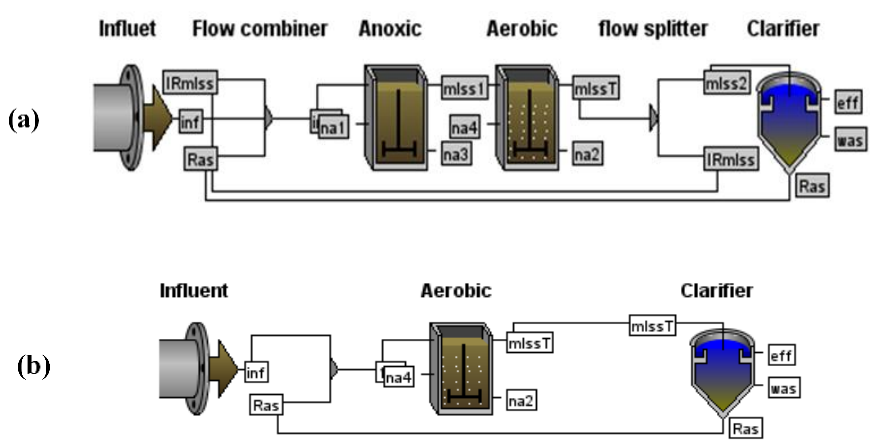


Figure 2. (a) Plant configuration for the removal of SMX; (b) Plant configuration for the removal of NPEOs

Second case study assessed the fate of nonylphenol ethoxylates (NPEOs) in an activated sludge process. The removal mechanisms for this compounds includes abiotic oxidative cleavage, biotic hydrolysis and aerobic biodegradation. A specific mechanism that has been reported to contribute to the removal of NPEO's is an abiotic oxidative cleavage process (Karahan et al., 2010). In this process, the NPEO's are converted to slowly biodegradable NPEOs, readily biodegradable NPEOs and non-biodegradable NPEOs. In addition, through a

hydrolysis process the slowly biodegradable portion of this compound is converted to the readily biodegradable form, and then this portion is biodegraded during the growth processes. This sub model was designed to predict the fate of NPEO's along with conventional compounds that was based on the Mantis model. The process rates are described in Table 2.

Table 2: process matrix of NPEO

NPEO Components				Process rate	Process rate Description
Sza	Szb	Szc	Szd		
-(1- f_{INPEO})	α	1- α	f_{INPEO}	$K_{OCL} \cdot Sza$	Abiotic cleavage
0	1	-1	0	$k_{hNPEO} \cdot [\frac{(Szc / xbh)}{K_{xNPEO} + (Szc / xbh)}] \cdot xbh$	Hydrolysis of NPEO
0	-1	0	0	$K_{bioNPEO} \cdot Szb \cdot \frac{K_s}{(K_s + S_s)} \cdot \frac{S_o}{(K_{oh} + S_o)} \cdot xbh$	Growth on SS_{NPEO}

The structure of the expression for the hydrolysis rate of NEPO's is similar to that of entrapped organics in Mantis model. The biodegradation structure of the SSNPEO is similar to that employed for the biodegradation of SMX and included a modifying term for readily biodegradable substrate [(Ks)/(Ks+Ss)] as the uptake of Ss can reduce the biodegradation of SSNPEO (Karahan et al., 2010). In this case study the model was calibrated using the experimental data provided in (Karahan et al., 2010). The plant configuration for this study is shown in Figure 2b. The WWTP physical and operational parameters are shown in Table 2. These parameters were also extracted from (Karahan et al., 2010).

In the calibration process, using optimization methods, model parameters can be 'tuned' such that the model can best follow the experimental data. A common error metric is Sum of Squared Errors (SSE) between the simulated results and measured data, optimal values of parameters of interest were found. Equation 1 shows the objective function for the calibration:

$$SSE = \sum_{i=1}^{n} SSE_i \quad \text{with} \quad SSE_i = \left(\frac{y_i^{sim} - y_i^{\exp}}{y_i^{\exp}}\right)^2 \tag{3}$$

Where y_i^{sim} and $y_i^{\exp}$ are the simulated and measured values of the response variable y (usually effluent substrate concentration), respectively. Index i refers to the ith data point where the total number of data points is n in the experimental process. Although using optimized parameter values, the model can best describe the system behaviour, in some cases, these parameter values are infeasible (Lindblom et al., 2009). Hence in the optimization problem, lower and upper bounds were added to the model parameters to avoid infeasible values for parameters. Therefore, the calibration process formulation was written as:

$$\begin{aligned} &\min \ SSE(t, P) \\ &LB_j \le P_j \le UB_j \end{aligned} \tag{4}$$

Where SSE is a function of time and vector of parameters P, LB and UB are the lower bounds and upper bounds on the parameter, and index j refers to the jth parameter. In this study, minimum and maximum values that were obtained from literature were adopted as LB and UB. For each calibration, parameters were obtained by solving the optimization problem using the Genetic Algorithm (GA) in MATLAB. To ensure the optimality of the parameter values, GA was run for two times, and then the parameters corresponding to the least objective function were put into the Pattern Search function as a Direct Search (DS) routine until the change in the objective function and constraint violation values were less than 1E-6. At this point the resulting values were accepted to provide the global optimum. The uncertainties involved in the calibration process are computed by means of a numerical method explained in (Draper & Smith, 1981). In a general case, the objective function J can be multi-objective, and defined as:

$$J = \sum_{i=1}^{n} J_i \quad \text{with} \quad J_i = \mu_1 \left(\frac{y_{i1}^{sim} - y_{i1}^{\exp}}{y_{i1}^{\exp}}\right)^2 + \mu_2 \left(\frac{y_{i2}^{sim} - y_{i2}^{\exp}}{y_{i2}^{\exp}}\right)^2 + \ldots \tag{5}$$

Where $\mu_1, \mu_2, \cdots$ are the weights of different terms in the objective function and are ith values of the multiple responses. Assuming a linear behavior for the response, this approach approximates the mean square error for each parameter from the sensitivity of the objective function to each parameter and a variance defined as follows:

$$\sigma^2 = \frac{\hat{J}}{n-p} \tag{6}$$

Where $\hat{J}$ is the objective function value at the optimal point, n is the number of observations, and p is the number of calibration parameters. Additionally, the sensitivity can be approximated in discrete form as follows:

$$\frac{\partial J_i}{\partial P_j} \simeq \frac{J_i(\hat{P}_j + \Delta P_j) - J_i(\hat{P}_j)}{\Delta P_j} \tag{7}$$

where $\hat{P}_j$ is the optimal estimate of parameter P, index i refers to the ith data point, index j refers to the jth parameter, $\hat{P}_j + \Delta P_j$ is the perturbed parameter, $J_i(\hat{P}_j + \Delta P_j)$ is the objective function at the perturbed parameter value, and $J_i(\hat{P}_j)$ is the objective function value at the optimal parameter estimate. Note that J_i is equal to the SSE_i in case the objective function is single objective, as defined in equation 1. Then the sensitivity matrix can be formed as follows:

$$S = \begin{bmatrix} S_{11} & S_{12} & \cdots & S_{1p} \\ S_{21} & S_{22} & \cdots & S_{2p} \\ \vdots & \vdots & S_{MN} & \vdots \\ S_{p1} & S_{p2} & \cdots & S_{pp} \end{bmatrix} \tag{8}$$

The sensitivity matrix is a symmetric square matrix (pxp) that includes the sensitivity of the objective function with respect to all calibration parameters. Each component is defined as:

$$S_{MN} = \sum_{i=1}^{n} \frac{\partial J_i}{\partial P_M} \frac{\partial J_i}{\partial P_N} \qquad \text{with } M, N \in \{1, 2, \ldots, p\} \tag{9}$$

Then the 95% confidence interval for each parameter is acquired as:

$$\hat{P}_j \pm 1.96\sqrt{V_{jj}} \quad \text{with} \quad V = \sigma^2 S^{-1} \tag{10}$$

Equation 10 calculates the interval for the jth estimated parameter with 95% confidence. By extracting data from the output of this calibration process, which was done for both conventional and trace compounds, the following results were found that are in the next section.

4 Results and Analysis

Fate modeling procedure in this work was done mainly by calibration and validation procedure, which required at least a primary and secondary experimental data set. Although measuring and obtaining these experimental data still remains a challenge especially for these micro pollutants, data for this work was extracted from proven scientific resources and fit correctly in the shape and operational condition of WWTPs.

The calibration of the model for case study 1 was performed for both conventional and fate model parameters. Since the estimation of biomass production is one of the key parameters for addressing the fate of trace compounds, matching of the biomass production in the steady state condition with the data set was employed for calibration. The experimental data presented in (Plósz et al., 2009) was used for the calibration of this model. The data set for the SMX was presented from continuous effluent flow of both the anoxic and aerobic reactor (Figure 3) in soluble form. Since the full data set was not available, the conventional parameters including total COD, inert inorganic suspended solids, particulate inert organic material, total suspended solids in the wastewater influent, plant configuration, and plant operational parameters, (SRT=16 days and HRT=5.33 hr) were set to those described by (Plósz et al., 2009). For other ASM1 parameters that were not reported in the related literature, the default values for municipal wastewater treatment plants were employed. By adjusting the inert organic suspended solids, influent VSS and the ratio of inert particulate COD to biodegradable COD in the wastewater influent by trial and error within the GPS-X software, and running simulations on the submodel of this case study, the biomass concentration in the bioreactor at steady state was matched with the corresponding experimental data presented in the literature. The relative error for this calibration was 0.5%. Active biomass is not measurable experimentally; thus, it is often assumed in fate models that the MLSS or MLVSS can represent the active biomass. However, in the new fate model that was developed in this research, the active heterotrophic biomass was used as the active fraction of the MLSS and was predicted by the conventional part of the model within GPS-X. Hence, the parameter values (kb, kd, etc) predicted in this research can be expected to be different from that reported in the literature. After conventional parameter calibration, according to the plant layout and submodel matrix, a corresponding set of differential equations were transferred to MATLAB where the fate model was calibrated with experimental data reported for the trace compound (SMX). To this goal, for each parameter of interest in the structure of the model matrix, the mean (μ) and standard deviation (σ) of the literature reported ranges were calculated. The mean and standard deviation were calculated over those reported in each reference, i.e., in most references, the reported values were in the form of uncertainty ranges (μ±σ). Then lower and upper bounds for the calibration parameters were set to μ-σ and μ+σ, respectively, see Table 3. For the anoxic bioreactor, as the work by (Plósz et al., 2009)

provided the only reported parameter values, the lower and upper bounds were set to 0.1 and 10 times the reported. For this case, the following objective function was considered:

$$SSE = 0.25\sum_{i=1}^{n}\left(\frac{Szf_{i,aerobic}^{sim} - Szf_{i,aerobic}^{ref}}{\max(Szf_{aerobic}^{ref})}\right)^2 + 0.25\sum_{i=1}^{n}\left(\frac{Szg_{i,aerobic}^{sim} - Szg_{i,aerobic}^{ref}}{\max(Szg_{aerobic}^{ref})}\right)^2 + 0.25\sum_{i=1}^{n}\left(\frac{Szf_{i,anoxic}^{sim} - Szf_{i,anoxic}^{ref}}{\max(Szf_{anoxic}^{ref})}\right)^2 + 0.25\sum_{i=1}^{n}\left(\frac{Szg_{i,anoxic}^{sim} - Szg_{i,anoxic}^{ref}}{\max(Szg_{anoxic}^{ref})}\right)^2 \quad (11)$$

where index i refers to the ith data point, $Szf_{aerobic}^{sim}$ is the simulated value for Szf (effluent concentration of SMX), Szf_{anoxic}^{sim}, is the simulated value for Szf (effluent of anoxic reactor), $Szf_{aerobic}^{ref}$ and Szf_{anoxic}^{ref} represent the experimental data for Szf in effluent of aeration and anoxic reactor, respectively from (Plósz et al., 2009), $Szg_{aerobic}^{sim}$ is the simulated Szg (the compound concentration biotransformed via the Szf in aerobic reactor effluent), Szg_{anoxic}^{sim} is the simulated Szg in effluent of anoxic reactor, and Szg_{i}^{ref} denotes the model results by (Plósz et al., 2009). Note that no experimental data was reported for Szg (Plósz et al., 2009). The objective function is written in a non-dimensionalized form to provide relatively similar effects of the two terms on the SSE; otherwise, the four terms could have such different values the optimizer would mostly reduce only the larger terms. A summary of the calibration results is presented in the following table:

Table 3: Calibration results for case study 1

Parameter	Lower Bound	Upper Bound	Optimal Value ± Standard Error
K_{1BioOx} (m^3/gbiomass/d)	6.937E-4	1.904E-3	1.529E-3±3.7E-4
K_{1BioAx} (m^3/gbiomass/d)	6.937E-4	1.904E-3	1.529E-3±3.7E-4
K_{1DecOx} (m^3/gbiomass/d)	6.8E-4	6.8E-2	3.312E-2±6.3E-3
K_{1DecAx} (m^3/gbiomass/d)	7.85E-4	7.85E-2	3.823E-2±5.8E-3
K_{1Dox} (m^3/gbiomass)	5.110E-5	3.893E-4	2.914E-4±3.4E-5
K_{1DAx} (m^3/gbiomass)	5.5E-5	5.5E-3	5.500E-4±4.1E-5
η_{bio}	1	3	2.886±0.46
η_{1Dec}	1	3	1.920±0.31

Following calibration, the fate model for case study 1 was validated with a different data than that used for calibration; therefore, in the validation phase, the experimental results of (Suarez et al., 2010) were used. To this goal, the wastewater characteristics and the plant operation conditions such as SRT, HRT, Mixed liquor suspended solid (MLSS) in steady state condition (g/m3) in the fate model were set to those presented in Suarez et al. 2010. The fate

model was run with those parameters at steady state condition. The removal efficiency of the SMX was predicted as -51%, which was somewhat different from that reported by Suarez et al. 2010. The removal efficiency was reported based on the parent compound that led to negative removal efficiency. The metabolite compound, which was called daughter compound, during the biotransformation process, was converted to the SMX. The main reason for the difference in removal efficiencies between Suarez et al. 2010 and the calibrated model could be because of the different ratio of the SMX and its metabolite, since in (Suarez et al., 2010) the concentration of metabolite was not reported. This ratio in the calibrated model was inserted from the wastewater characteristics provided by (Plósz et al., 2009). Temperature changes do not have influence on the removal of SMX (Suarez et al., 2010). Removal efficiencies reported in the literature varied in a wide range. For example, eliminations of 33±64, 0–84% and (-138)–60% can be found in (Castiglioni et al., 2005; GOBEL et al., 2007; Sipma et al., 2010) respectively. The reason for this wide range removal efficiency is due to the fact that real wastewaters, which have a more complex matrix, were used in these works. Negative elimination has also been found in the literature because of presence of conjugated metabolites in the complex wastewater (Plósz et al., 2009; Sipma et al., 2010; Suarez et al., 2010).

The submodel for case study 2 was calibrated for both conventional and fate model parameters before running simulations. In the conventional parameter calibration effort, wastewater characteristics, the biomass production at steady state conditions, SRT, and HRT in the system were adjusted to the plant data that were used for the calibration. The batch experimental data presented by (Karahan et al., 2010) was used for the calibration of this model. For the other ASM1 parameters that were not reported in the related literature, the default value for the municipal wastewater treatment plant was inserted into the GPS-X software. The SRT of 15 d and HRT of 24 hr were tuned with those of (Karahan et al., 2010). By adjusting the inert organic suspended solids, influent VSS and the ratio of inert particulate COD to biodegradable COD in wastewater influent by trial and error within the GPS-X software and running simulation on the submodel of this case study, the biomass concentration in the bioreactor at steady state was matched with the corresponding experimental data presented in that literature. This relative error for this calibration was 1.6% where the relative error (RE) for the calibration was calculated as 100*(experimental value -estimated value for TSS (gXssL-1)/ experimental value for TSS. In the structure of trace compound biodegradation process for recent fate models, the active biomass is not measurable experimentally; thus, it is often assumed that the MLSS or MLVSS can represent the active biomass. In the developed fate model here, the active heterotrophic biomass was used as an active fraction of MLSS and was predicted by the conventional part of the model (Mantis) within the GPS-X. After conventional parameter calibration, according to the plant layout and submodel matrix, the corresponding set of differential equations were transferred to MATLAB where the fate model was calibrated with experimental data reported for the trace compound (NPEO). The calibration for case study 2 is detailed here according to data presented for total COD and NPEO concentration in bulk liquid. The mean μ and standard deviation σ of the literature (Chang et al., 2005; Jahan et al., 2007; Karahan et al., 2010; Zhang et al., 2008) for the parameters of interest were calculated. It should be noted that the values in most references of the literature were reported as uncertainty intervals ($\mu\pm\sigma$), and there was no deterministic range for each parameter reported in the literature. Hence, a total mean and standard deviation over those reported means and standard deviations was calculated. Then lower and upper bounds of each parameter for the calibration were set to μ-σ and $\mu+\sigma$, respectively. For this case, the following objective function was considered:

$$SSE = 0.5\sum_{i=1}^{n}\left(\frac{Sza_i^{sim} - Sza_i^{\exp}}{\max(Sza^{\exp})}\right)^2 + 0.5\sum_{i=1}^{n}\left(\frac{COD_i^{sim} - COD_i^{\exp}}{\max(COD^{\exp})}\right)^2 \quad (12)$$

where i is the data point index, Sza is the effluent concentration of NPEO in bulk liquid, the superscripts "sim" and "exp" represent simulation (model) and experimental data from (Karahan et al., 2010), respectively. Note that the objective function is written in a non-dimensionalized form to provide relatively similar effects of the two terms on the SSE; otherwise, the two terms could have such different values that the optimizer would reduce only the larger term. A summary of the calibration results is presented in the following table:

Table 4. Calibration results for case study 2

Parameter	Lower Bound	Upper Bound	Optimal Value ± Standard Error
K_{OCL} (1/d)	0	-	250±13
K_{hNPEO} (1/d)	0	-	1.45±0.09
$K_{bioNPEO}$ (m3/gbiomass/d)	0.122	0.312	0.237±0.072

Table 5. Simulation results of case study 2

Sza_i (g/m^3)	Sza (g/m^3)	Szb (g/m^3)	Szc (g/m^3)	Szd (g/m^3)	SCOD (gCOD/m^3)	xbh (gCOD/m^3)	TSS in AR (g/m^3)	TSS in WAS (g/m^3)
114	0.300	0.570	0.997	35.910	26.530	760.70	1762	3286

As mentioned previously, the fate model parameters for NPEOs (case study 2) were calibrated using data by (Karahan et al., 2010). Following calibration, the fate model simulation results were validated with data reported by (Zhang et al., 2008). To this goal, the wastewater characteristics and the plant operation conditions of the fate model were set to those presented in (Zhang et al., 2008). The value of total COD influent was considered as 232 gCOD/m3 and the key parameters such as MLSS, SRT, HRT, etc was extracted from (Zhang et al., 2008). The fate model was run with those parameters at steady state condition. The removal efficiency of the NPEO was predicted as 98%. Since the SRT was not reported by (Zhang et al., 2008), that value was set to be 15 days. COD removal efficiency was estimated as 84%.

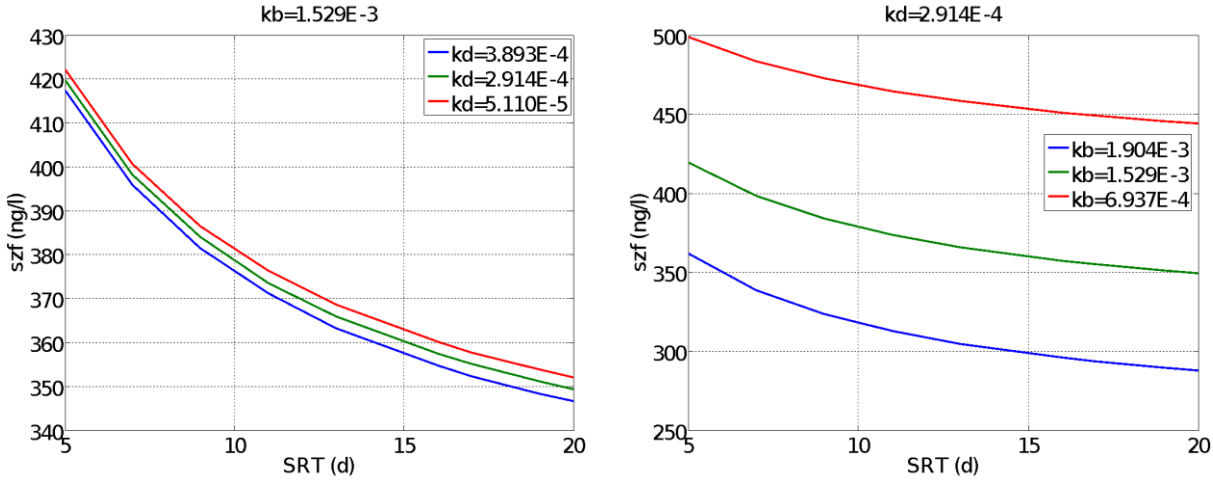
The estimated value was in good agreement with the results reported by (Zhang et al., 2008), even though the removal efficiency predicted by (Zhang et al., 2008) was 92%, the calibrated fate model higher estimation removal efficiency could be because of higher SRT than that of (Zhang et al., 2008). In wastewater treatment, certain design and operational parameters that affect the fate of micro-constituents can be controlled, while other parameters may be

determined by the facility design and/or geographic area. The crucial controllable operational parameter for relatively non-volatile compounds such as XOCs is the solid retention time (SRT), which has been identified in the literature as an important factor (van Bergen et al., 2020; Wang et al., 2020). The importance of this factor in removal of XOCs was investigated via a sensitivity analysis in the GPS-X software.

Other parameters in the proposed model, such as biodegradation and sorption rate coefficients (kb, kd) have been reported in the literature to span a range of values. Although values for these parameters were computed through a calibration process, to study the robustness of the simulation results, a sensitivity analysis was performed in this work. To this goal, different parameter values were collected from literature; the mean and standard deviation of these were calculated, and separate simulations using $\mu+\sigma$ (upper bound), and $\mu-\sigma$ (lower bound) and the calibrated parameter value for these parameters were run. The results of the various cases were plotted for analysis purposes. For case study 1 the anoxic compartment was excluded to simplify the sensitivity analysis interpretation. SRT has been identified earlier in the literature as an operational parameter that can be used to minimize the effluent concentrations of XOCs (Clara et al., 2005; GOBEL et al., 2007; Kreuzinger et al., 2004; Suarez et al., 2010). The effect of solid retention time on XOC fate over a range of approximately 5 to 20 days at 20°C was investigated in the first case study. The fate model addresses the fate of conventional compounds and xenobiotic organic compounds simultaneously. To explain the effect of SRT on the fate of xenobiotic organic compounds, the effect of SRT on heterotrophic biomass concentration and total suspended solid concentration in the aeration basin were as follows. By setting HRT equal to 10.8hr, the concentrations of active heterotrophic biomass (xbh) and total suspended solids (TSS) in the aeration basin increased as did SRT. Since xbh and TSS in the aeration basin are important parameters in the biodegradation and sorption of SMX, the effect of SRT on the fate of this compound could be explained by the variation of xbh and TSS concentration with respect to SRT. The influent concentration of the soluble (Szf) and particulate (Xza) forms of SMX were set at 210 ng/l and 0 ng/l respectively, and the influent concentration of the daughter compound (Szg) was set at 467 ng/l. Figure 5 presents the influence of SRT on the concentration of the soluble form of SMX (Szf) over a range of values of kd and kb. Figure 6 presents the corresponding solid phase concentration of SMX (Xza) in the waste stream while Figure 7 shows the effluent concentration and rate of biodegradation of Szg. From Figure 5 it can be see that there was a significant reduction in the effluent concentration of Szf (about 34% increase in removal efficiency of Szf between SRT=5 and SRT= 20 days) and Szg (about 15% increase in removal efficiency between SRT=5 and SRT= 20 days). During the biotransformation process, there was an interaction between metabolite compounds (Szg) and the parent compound (Szf). As a result of the biotransformation of Szg, these compounds were converted to the parent compounds and also the parent compound was biodegraded itself. The net result of these biotransformation processes was the production of the parent compound. As can be seen in Figure 5 at SRT= 16 days and kb and kd equal to the optimal values, with influent concentration of 210 ng/l, the effluent concentration of Szf was approximately 358 ng/l, so the removal efficiency of Szf was negative. The increase in concentration of active biomass (xbh) due to increase of SRT resulted in increases in the biodegradation rate of Szf (Figure 8) and Szg (Figure 7b) (about 27% increase in biodegradation of Szf and 3% increase in biodegradation of Szg).

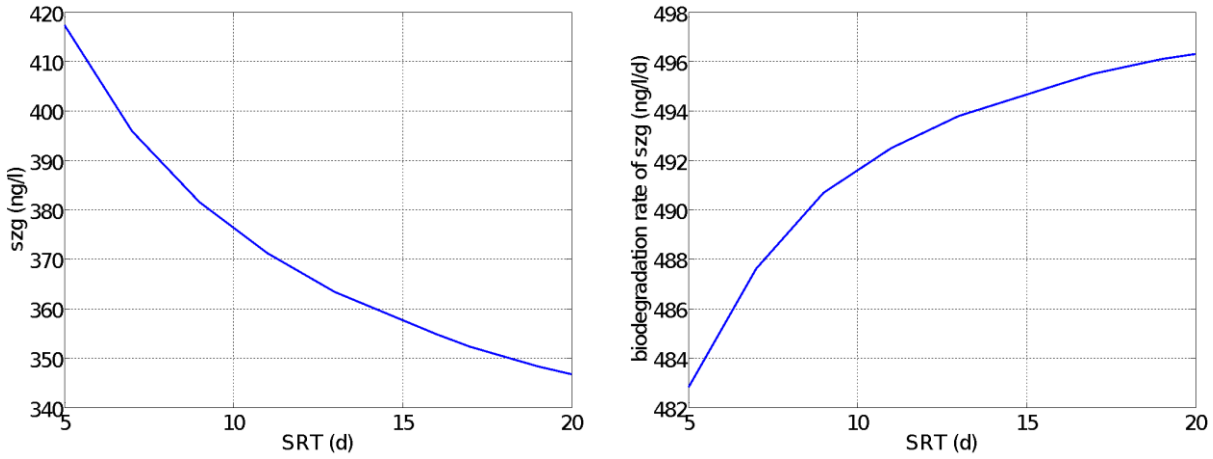
Figure 9 presents the sorption rate for SMX and represents the net effect of the sorption and desorption rates. The positive value shows that the rate of sorption was greater than the rate of desorption. The net sorption rate of SMX increased nearly 32% (Figure 9) over the range of

SRTs examined. With the increase of MLSS concentration, the amount of sorbed SMX to the sludge increases. This is because an increase of suspended solids in the system increases the number of reactive sites available to absorb SMX from solution. Following that the amount of SMX sorbed to the sludge was increased. Therefore, the increase of solid sludge in the solution enhanced the total sorption of SMX (Xza) (growth about 88%) by sludge and benefited the removal of SMX from water phase (Figures 6a and b). However the wastage rate of SMX decreased with increasing SRT, because for regulating SRT wastage flow rate was increased and this term was dominant in wastage flow of SMX.



(a) (b)

Figure 3. (a) Soluble SMX conc. in the effluent (*Szf*) with respect to *kd* in constant *kb* (b) Soluble SMX in effluent (*Szf*) with respect to *kb* in constant *kd*, Influent concentration of *Szf*= 210 ng/l, HRT=10.8hr



(a) (b)

Figure 4. (a) *Szg* conc. (b) and biodegradation rate for *Szg*, Influent concentration of *Szg*= 467 ng/l, HRT=10.8hr

To investigate the effect of biodegradation and solid liquid partitioning rate parameters on the removal of SMX, two different sets of plots (Figures 3,4) have been presented. The first

set shows the responses with three different solid liquid partitioning coefficient values (kd= μ+σ, calibrated value and μ-σ) at a fixed biodegradation rate coefficient (set to the calibrated value, kb=1.529E-3). The second set demonstrates the effects of varying the biodegradation rate coefficient (kb= μ+σ, calibrated value and μ-σ) at a fixed solid solid liquid partitioning coefficient (set to the calibrated value, kd=2.914E-4). The purpose of presenting these two sets of plots was to see the influence of these parameters on removal of XOCs.

Table 6 shows the percent of SMX removed, biotransformed and wasted at constant kb, SRT= 16 days, and HRT=10.8 hr. Increasing the value of kd resulted in a decrease of SMX in the soluble phase and an increase in the concentration of particulate SMX (Xza). Therefore, there was more removal in the liquid and solid phases. Furthermore, at constant kb, the higher kd has a higher net sorption rate, but a lower biodegradation rate, although, there was not a significant reduction of the biodegradation rate with higher kd values. The concentration of particulate SMX (Xza) contributed to the wasted mass. Since Xza increases in the wastage flow by the sorption process the wastage percentage was positive, but the removal and biotransformed percentage due to increasing soluble SMX in effluent were negative.

Table 6. Quantified effects of *kd* and *kb* on percentage of removed, biotransformed and wasted SMX

Rate Parameter		%removed*	%biotransformed*
Kb= 1.529E-3	Kd1=3.893E-4	-68.95	-78.35
	Kd2=2.914E-4	-70.19	-77.71
	Kd3=5.110E-5	-71.47	-77.06
Kd= 2.914E-4	Kb1=1.904E-3	-41	-47.21
	Kb2=1.529E-3	-70.19	-77.71
	Kb3=6.937E-4	-114.76	-124.23

* It should be noted that negative %removed and %biotransformed was because of biotransformation of metabolite to the SMX

Table 6 also presents the percentage of SMX removed, biotransformed and wasted at constant kd with SRT= 16 days, HRT=10.8 hr. With kd constant, at the higher values of kb, the biodegradation rate increases and effluent concentration becomes lower. Therefore, there is more removal in liquid phase; however, in this case, the sorption rate decreases and the particulate concentration in solid phase is lower. Generally, at higher SRTs, there was higher removal and biotransformation of SMX and a lower wasted percentage of SMX (Table 6). The wastage of SMX decreased with increasing SRT, because the wastage flow rate regulated for SRT control and this term was dominant in wastage of SMX (See Table 7). The negative removal efficiency and biotransformation were due to the conversion of the conjugate form to the parent compound (SMX) that compensated for the biodegradation of SMX. At higher SRT, more of SMX was biodegraded and at lower SRT, the conversion of the conjugated compound to parent compound dominated (Table 7).

Table 7. Variation of removed, biotransformed and wasted percentage of SMX at constant *kb* and *kd*, *kb*=1.529E-3, *kd*=2.914E-4, versus SRT, HRT=10.8hr

SRT (d)	%removed	%biotransformed	%wasted
5	-99.86	-121.86	22.00

9	-82.86	-94.89	12.03
13	-74.24	-83.03	8.79
16	-70.19	-77.71	7.52
20	-66.38	-72.86	6.48

It can be concluded that increases in SRT can enhance removal of SMX and its metabolite (daughter compound), since at higher SRT, there is higher removal efficiency and lower waste of SMX and also lower effluent concentration of metabolite. Due to conversion of metabolite to the parent compound, net biotransformation of the parent compound causes production of this compound. Therefore, the removal efficiency and also biotransformation rate of SMX were negative. Furthermore, at SRT higher than 16 days, the removal efficiency does not change significantly, so SRT=16 days can be reported as the optimal SRT for this case. The other interesting output of sensitivity analysis states that in the region of low SRT, the descending rate of effluent concentration of SMX is higher than that of higher region. Finally, results of Table 6 show the removal efficiency is more sensitive to biodegradation rate than sorption rate.

5 Conclusions

In this study, a fate model was developed that can be used to better understand and optimize the removal of Xenobiotic Organic Compounds (XOCs) in combination with the removal of traditional pollutants in wastewater treatment plants. Through modeling work, major mechanisms responsible for removal of XOCs in wastewater treatment were identified and integrated with an ASM1 model to create an uncalibrated model matrix. Since specific groups of mechanisms were responsible for the removal of selected compounds, two different case studies were created for two different groups of compounds. Therefore, two different sub models were created and categorized within the fate model. Each sub models calibrated and different data sets were used for the validation process. Sensitivity analysis was carried out against SRT and biodegradation and sorption coefficients. The major finding of this research can be summarized as follows: the removal efficiency of the SMX was found to be negative, because the conjugate was converted to SMX during the biotransformation process. This phenomenon compensates for biodegradation of SMX. The removal efficiency of XOCs was found to be sensitive to SRT, kb and kd. Although in most cases the fate model was more sensitive to kb and kd than to operational. Increases in SRT can enhance removal of all compounds that were studied in this research. Those compounds include SMX and its conjugate, NPEO. The optimal timeframe can be reported as 15 days. Sensitivity analysis of three different cases showed that the fate model was more sensitive to biodegradation rate than to sorption rate.

Although the integrated model of this thesis provides a novel framework for XOC fate simulation, there are still limitations that can be considered for further research on the fate of XOCs compounds as follows; various reliable sources of experimental data for both XOC and conventional compounds are important. The availability of this data for both conventional and trace compounds will lead to more robust and more accurate calibration and validation. Furthermore, there is a lack of information on XOCs transformation products in the aquatic systems that can impact the observed fate of the parent compounds in wastewater treatment. Since a co-metabolism mechanism is involved in the fate of most XOCs, the simultaneous measurement of primary substrate along with secondary substrate is required to better predict concentrations of trace organic compounds such as SMX and NPEO.

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