



# Adapting SimpleTreat for simulating behaviour of chemical substances during industrial sewage treatment



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## H I G H L I G H T S

- We present a model to predict the chemical fate in industrial wastewater treatment plants.
- The multimedia model SimpleTreat used for risk assessment was re-parameterized.
- The distribution and elimination of chemicals by sewage treatment was evaluated.
- The predicted removal rate of chemicals by industrial sewage treatment plants may be higher than in municipal installations.
- It is strongly recommended to validate the model in the context of environmental risk assessment.

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## A B S T R A C T

The multimedia model SimpleTreat, evaluates the distribution and elimination of chemicals by municipal sewage treatment plants (STP). It is applied in the framework of REACH (Registration, Evaluation, Authorization and Restriction of Chemicals). This article describes an adaptation of this model for application to industrial sewage treatment plants (I-STP). The intended use of this re-parametrized model is focused on risk assessment during manufacture and subsequent uses of chemicals, also in the framework of REACH. The results of an inquiry on the operational characteristics of industrial sewage treatment installations were used to re-parameterize the model. It appeared that one property of industrial sewage, i.e. Biological Oxygen Demand (BOD) in combination with one parameter of the activated sludge process, the hydraulic retention time (HRT) is satisfactory to define treatment of industrial wastewater by means of the activated sludge process. The adapted model was compared to the original municipal version, SimpleTreat 4.0, by means of a sensitivity analysis. The consistency of the model output was assessed by computing the emission to water from an I-STP of a set of fictitious chemicals. This set of chemicals exhibit a range of physico-chemical and biodegradability properties occurring in industrial wastewater. Predicted removal rates of a chemical from raw sewage are higher in industrial than in municipal STPs. The latter have typically shorter hydraulic retention times with diminished opportunity for elimination of the chemical due to volatilization and biodegradation.

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## 1. Introduction

SimpleTreat (Struijs et al., 1991) is a model to predict the fate of a chemical in a communal wastewater treatment plant. Currently,

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version 3.1 (Struijs, 1996) is in use to estimate chemical emission and exposure in the framework of risk assessment as described by the guidance on REACH (2006, European Chemicals Agency, <http://echa.europa.eu/>). The model is applied in the European Union (EU) substance regulation and legislation that exist beside REACH: for chemicals covered under the Biocidal Products Regulation, such as disinfectants, for active pharmaceutical ingredients regulated by the European Medicines Agency and for chemicals under the plant protection regulation. In Canada, SimpleTreat is one of 3 models used for risk assessment of substances under the Chemicals Management Plan.

One major feature of the model is that it only requires a few basic properties of the chemical for calculating relative emissions (percentage emission to air, to water and to soil). In combination with a simple emission scenario, these base set data are used as input for the computation of concentrations in treated wastewater flowing into the receiving water bodies, in produced sludge (applied to agricultural soil) and in the air above the STP.

Many chemical compounds under these regimes are organic acids or bases and are (partly) ionized in water. Although SimpleTreat 3.1 accounts for dissociation of organic acids and bases in chemical fate computation, the multi-equilibrium approach including an ionization equilibrium in water and partitioning between two adjacent media such as solids-water and air-water, is based on the assumption that the ionized chemical can exclusively exist in the water phase. Recent studies (Franco et al., 2013) showed that this approach erroneously ignores sorption of the ionized organic acid or base onto sludge particles.

A new version of the model (4.0) was launched recently (Struijs, 2014) with new rules for sorption of organic acids and bases according to Franco et al. (2013).

Without adaptation however, SimpleTreat 4.0 seems not suitable for the simulation of the behaviour of chemicals in industrial sewage treatment plants (I-STP). The wide variety in composition of industrial wastewater and specific operation characteristics of industrial activated sludge reactors is beyond the common range of municipal STPs. A limited examination of industrial activated sludge reactors indicated the wide variety with respect to the content of Biological Oxygen Demand (BOD) in industrial wastewater and the hydraulic retention time (HRT) of the aeration tank. Here we report the results of a project aimed to simulate the fate of chemicals in industrial wastewater treatment by parametrizing SimpleTreat 4.0. The adapted model was compared to the municipal version by means of a sensitivity analysis.

## 2. Methodology

### 2.1. Description of the SimpleTreat model

The structure of SimpleTreat for fate and emission predictions of chemicals in municipal wastewater treatment (Fig. 1a) is given by the box model scheme of Fig. 1b. The steady state non-equilibrium approach fits well with the aimed evaluation of chemical fate in wastewater treatment plants: 1) inter-compartment transport from water to sludge and from water to air and vice versa, 2) biodegradation and 3) transport through air, water, suspended solids and settled solids carrying the chemical. Steady state concentrations ( $dc_j/dt = 0$ ) are obtained from multiple mass balance calculation by solving nine linear equations according to:

$$V_j \cdot \frac{dc_j}{dt} = -k_j \cdot C_j \cdot V_j + \sum_i \text{ADV}_{ij} \cdot C_i + \sum_i \text{XCH}_{ij} \cdot C_i \quad (1)$$

with:

$\text{ADV}_{ij}$ : flow rate of media from box  $i$  to box  $j$ , advective, irreversible  
 $\text{XCH}_{ij}$ : flow rate of media from box  $i$  to box  $j$ , diffusive, reversible  
 $V_j$ : volume of box  $j$   
 $C_j$ : concentration in box  $j$   
 $C_{0j}$ : known chemical concentration in water ( $j = 2$ ) and suspended solids ( $j = 3$ ) in raw sewage entering the system  
 $C_i$ : concentration in medium  $i$  when the chemical is transported from medium  $i$  to medium  $j$  or flowing out of the system via air, water or (suspended) solids  
 $t$ : time  
 $k_j$ : first order biodegradation rate constant in box  $j$

For adaptation to industrial wastewater treatment there is no need to change the model structure of SimpleTreat as represented by Fig. 1b and Eq (1). Adapting the model requires a different choice of input parameters that define the activated sludge reactor formulated in terms of media flow rates and media retention times as they occur in an industrial STP. The composition of industrial wastewater causes different flows of water and solids compared to municipal wastewater. Moreover the high variability of the composition of industrial wastewater requires an alternative priority with respect to input parameters that define the sewage treatment installation. This has implications for the formulation of the parameters  $V_j$  and  $\text{ADV}_{ij}$  in Eq (1).

Input parameters with respect to a chemical require equilibrium partition coefficients between two adjacent media at each treatment step and first order degradation rate constants in each box. If partition coefficients are not available they are estimated from basic physical-chemical properties and a first order biodegradation rate constant in the aqueous phase of activated sludge which can be derived from results of standard biodegradability tests according to the OECD. SimpleTreat 4.0 suggests extrapolation methods for biodegradation according to REACH (2006).

The temperature input parameters are only used in the computation of the air-water partition coefficients and the equilibrium constant of  $\text{H}_2\text{O}$ . For municipal sewage treatment it was considered not necessary to include a temperature dependency of process rate parameters because the ambient temperature of municipal wastewater treatment installation is rather constant and close to standard conditions.

### 2.2. Simulating the activated sludge process treating municipal sewage

The volume of all basins (Fig. 1a) is proportional to the occupied area implying a constant depth. Volumes and flow rates of a municipal STP are proportional to the number of people connected to the sewer. Furthermore, the aeration tank which is also dependent on the sludge loading rate (SLR) of the activated sludge process. The SLR, also known as food to mass ratio, characterizes the mode of operation of the activated sludge process. The sludge loading rate represents the load of biological oxygen demand (BOD) in kg/d per amount of activated sludge ( $M_{\text{act,sl}}$  in kg dry weight activated sludge) present in aeration volume  $V$  ( $\text{m}^3$ ) available per unit of sewage flow rate  $\phi$  ( $\text{m}^3/\text{d}$ ). The available mass of activated sludge ( $M_{\text{act,sl}}$ ) equals the product of  $V$  and the concentration of activated sludge ( $C_{\text{act,sl}}$ ) which is between 2 and 8  $\text{kg}/\text{m}^3$  (Templeton and Butler, 2011). The concentrations are most often between 3 and 5  $\text{kg}/\text{m}^3$  and for modeling purposes it is satisfactory to assume that it is constant at 4  $\text{kg}/\text{m}^3$ . The BOD load equals the product of sewage flow rate  $\phi$  ( $\text{m}^3/\text{d}$ ) and BOD ( $\text{kg}/\text{m}^3$ ) in sewage entering the aeration tank. Furthermore, the ratio of  $V$  and  $\phi$  equals the hydraulic retention time of the aeration tank, HRT ( $d$ ). Eq (2) shows that for a constant BOD in (settled) sewage and a constant

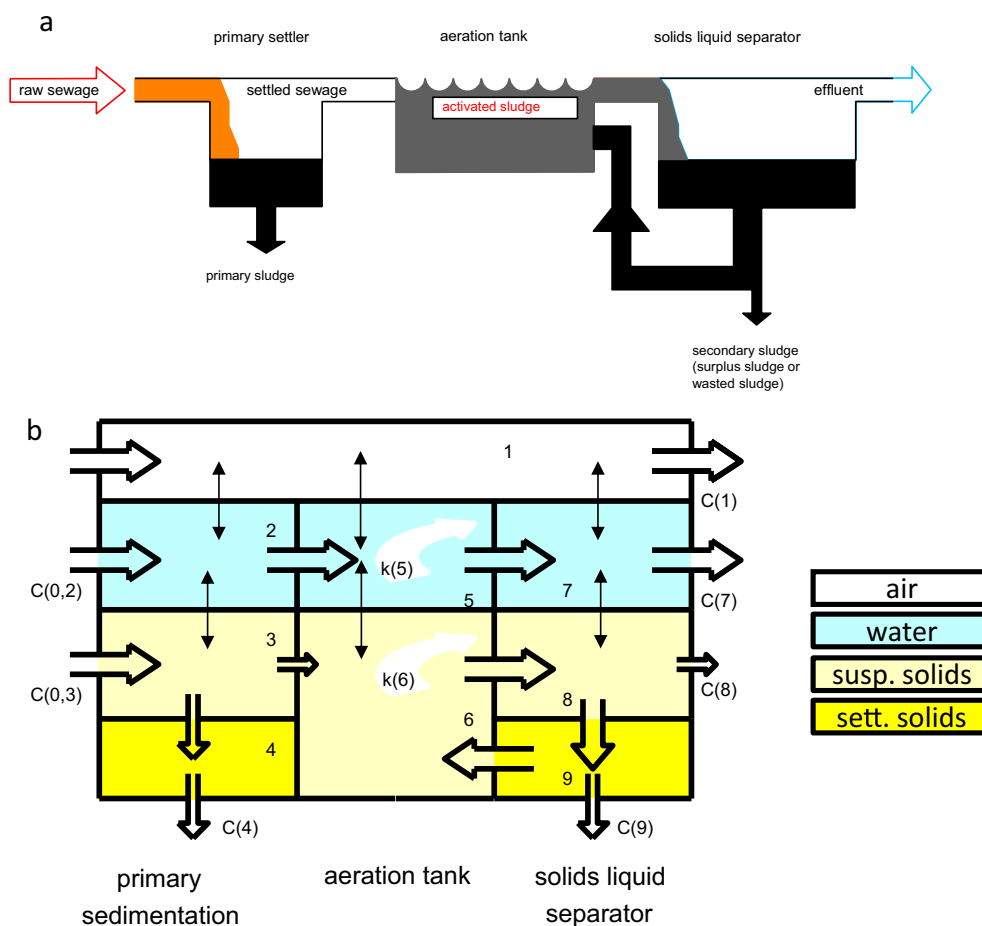


Fig. 1. Scheme of an STP equipped with a primary clarifier (a) and a box model presentation of the fate of a chemical in such a system (b).

activated sludge concentration in the aeration tank, the HRT is governed by the chosen SLR:

$$\text{SLR} = \frac{\text{BOD load (kg/d)}}{M_{\text{act.sl}} (\text{kg}_{\text{act.sl}})} = \frac{\text{BOD} \cdot \phi}{C_{\text{act.sl}} \cdot V} = \frac{\text{BOD}}{C_{\text{act.sl}} \cdot \text{HRT}} \quad (2)$$

For the purpose of environmental fate modeling, the flows of municipal BOD and sewage per capita can be considered constant in Europe. As a consequence, BOD in sewage that enters the aeration tank, is also constant provided that the primary clarifier functions in a constant manner with respect to BOD removal. In the framework of generic risk assessment this steady state scenario is a reasonable assumption. With constant BOD and  $C_{\text{act.sl}}$ , Eq (2) indicates that the SLR is inversely proportional to the HRT, implying that the mode of operation is defined by only one parameter, i.e. the SLR. This input parameter determines the retention times of water (HRT) and sludge (SRT) of the activated sludge process. Table 1 contains parameters for the operation of sewage works. SLR equal to 0.1 kg BOD/kg  $C_{\text{act.sl}}$ /d is a default setting reflecting the average operating mode of the European activated sludge reactor treating municipal sewage (Templeton and Butler, 2011). The model distinguishes two modes aeration, bubble and surface aeration (default).

The sludge flow (Fig. 2a) is a function of the sludge loading rate (SLR). Similarly, the sludge retention time (SRT) is a function of the SLR through a combination of empirical relationships (Struijs, 2014). The empirical equation for the sludge retention time includes the BOD removal rate and the yield of biomass per unit BOD

degraded by the activated sludge process. Both processes correlate (Fig. 2b) with the SLR (Mikkelsen, 1995).

### 2.3. Adaptation of SimpleTreat to industrial sewage treatment

#### 2.3.1. Modeling parameters

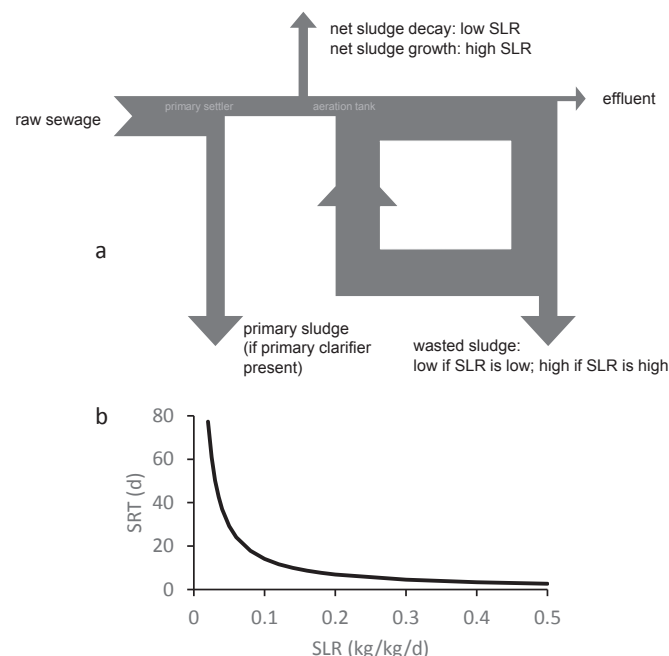
For modeling purposes it appears reasonable to neglect temporal variations of BOD. The same holds true for the assumption of a single value of BOD for all municipal wastewater. However, BOD can vary widely among different industrial sewage treatment installations with consequences for modeling the mode of operation of the activated sludge process. The concentration of activated sludge in industrial STPs ( $C_{\text{act.sl}}$ ) however can also be considered constant and similar to that in municipal STPs because it is characteristic of biological wastewater treatment (Templeton and Butler, 2011). Definition of the operation mode of an industrial sewage treatment plant is however different because the SLR is not suitable as a single input parameter to characterize the activated sludge process due to the high variability in BOD in raw (or settled) sewage among industrial wastewater treatment plants. The number of inhabitants to define the sewage flow rate and so the size of the STP is not convenient for industrial STPs while the sewage flow rate is a more suitable characteristic of an industrial STP (Table 1).

#### 2.3.2. Operation characteristics – industrial STPs

A survey among companies was performed to collect information about operation characteristics of their industrial sewage treatment plants such as BOD, HRT, sludge loading rate (SLR), and

**Table 1**  
Parameters defining biological treatment of sewage according to SimpleTreat.

Parameter	Municipal (SimpleTreat 4.0)		Industrial (I-SimpleTreat)	
	Value	Remarks	Value	Remarks
BOD	0.3 kg/m <sup>3</sup>	Dependent on per capita BOD input (kg/person/d) and sewage flow rate $\phi$ (m <sup>3</sup> /person/day)	Range 0.1–4 kg/m <sup>3</sup>	<b>Input parameter</b>
SLR	0.1 kg/kg/d	<b>Input parameter</b>	0.01–1 kg/kg/d	Dependent on BOD and HRT
HRT	12 h	Dependent on SLR	Range 12–240 h	<b>Input parameter</b>
SRT	15 d	Dependent on SLR	Range 2–80 d	Dependent on SLR
N	10,000 (default)	<b>Input parameter</b> (number people connected)	N/A	N/A
$\phi$	0.2 N m <sup>3</sup> /d	Dependent on N	m <sup>3</sup> /d	<b>Input parameter</b> , determines size of the STP



**Fig. 2.** Dependence of the sludge solids flow on sludge loading rate (a). The sludge retention time (SRT) is related to the sludge loading rate (b) according to empirical relationships (Struijs, 2014).

sludge retention time (SRT). These data are presented in Table 2. Four companies varying in production (oil, chemicals or personal care products) delivered information. Three companies reported data on more than one I-STP. The fourth company reported data that are representative for the whole of their I-STPs or what can be

considered as a mean.

### 2.3.3. Temperature dependency of processes

For industrial sewage treatment plants assuming a standard temperature is not satisfactory. The temperature in industrial wastewater may be as high as 35 °C (Schowanek et al., 2015). As a solution, the temperature dependence of the first order biodegradation rate constants ( $k_i$ ) is accounted for by Eq. (3). This is also known as the Q10 approach implying that the process rate (of biodegradation) has doubled if the temperature increases by 10° as is done in exposure modeling for REACH (2006):

$$k_j = k_{\text{biodeg}} \cdot 1.072^{(T_w - 288)} \quad (3)$$

where the actual temperature  $T_w$  is expressed in degrees Kelvin. In industrial SimpleTreat, the default temperature of water is 15 °C giving a value for  $k_j$  equal to  $k_{\text{biodeg}}$  which is the first order biodegradation rate constant applied in the SimpleTreat 4.0.

## 3. Results

### 3.1. Characterizing the activated sludge process in industrial treatment installations

Five companies have provided information on operation characteristics of their sewage treatment installations. One company however, failed to report hydraulic retention times leaving four companies of which useful information could be gathered. Company A reported sufficient information on three different plants while company B provided detailed information of two installations with a wide spread in operation characteristics. Company C averaged the parameters of ten sewage treatment plants with high BOD loads and long hydraulic retention times and another ten with lower BOD and HRT characteristics. Company D

**Table 2**  
Industrial sewage treatment data (BOD and HRT) provided by companies. Sludge loading rates (SLR) and sludge retention times (SRT) are calculated from BOD and HRT.

Installation	BOD (kg/m <sup>3</sup> )	HRT (hr)	SLR (kg/kg/d)	Reported	SRT (d)	Reported
A1	0.10	12	0.05		30.5	
A2	0.67	220	0.02		84.8	
A3	0.62	30	0.12		11.2	
B1	1.00	36	0.17	0.1	8.2	15 d
B2	3.50	24	0.88	0.4	1.5	7 d
C1 (10 I-STPs)	4.00	200	0.12	0.1	11.6	17 d
C2 (10 I-STPs)	2.00	120	0.10	0.1	14.1	17 d
D (several I-STPs)	0.97	36	0.16	<0.3	8.5	
SimpleTreat 4.0	0.3 <sup>a</sup>	18 <sup>b</sup>	0.1 <sup>c</sup>		14.1 <sup>d</sup>	

<sup>a</sup> Calculated from default parameters of raw sewage in the EU.

<sup>b</sup> Calculated by the SimpleTreat 4.0 based on default parameters.

<sup>c</sup> Default input parameter SLR (0.1 kg/kg/d).

<sup>d</sup> Calculated from SLR = 0.1 kg/kg/d.

provided sufficient data for this study, however only referring to the average of several sewage treatment plants which apparently have relatively low BOD loadings and short HRTs.

Table 2 summarizes reported BOD and HRT and shows how calculated and reported SLRs and SRTs of some plants may diverge. Fig. 3 indicates that the default operation mode of the municipal version of SimpleTreat is close to installation A1. The municipal model STP according to SimpleTreat 4.0 has a low BOD and regarding industrial plants, a short HRT, which is typical for a SLR of 0.1 kg/kg/d. Only installation A1 and D have been reported to be equipped with a primary clarifier. For the group of C2 we assume that the reported BOD pertains to settled sewage which implies that a primary clarifier was present.

Most industrial installations have BOD and HRT that are at least half an order of magnitude higher. If we would exclude A2 and B2 from this dataset, the points in Fig. 3, including the municipal STP, appear to be represented by the line  $HRT = 50.67 \cdot BOD$  ( $R^2 = 0.97$ ). The collected dataset seems however too small to consider A2 and B2 outliers.

There are deviations from the empirical relationship that determines the sludge retention time (SRT) which is a function of the sludge loading rate (SLR). In the model presented here, the SLR is determined by BOD and HRT according to Eqn (2). In municipal activated sludge reactors, a low sludge loading rate is usually associated with long hydraulic and sludge retention times and a high BOD removal rate. For example, the rather high SLR and low SRT calculated for plant B2 on the basis of reported BOD and HRT deviate from reported data (Table 2). This is not well understood unless the concentration of suspended solids in activated sludge is equal to 8 kg (dry weight) per  $m^3$  which is possible but unlikely. B2 deviates from the HRT/BOD ratio equal to 50 h/kg BOD (Fig. 3) which is constant for reactors with an activated sludge concentration of 4 kg/ $m^3$ . Installation B2 has a SLR of 0.88 kg BOD/kg activated sludge per day, calculated according eqn. (2) while the reported SLR was 0.4 kg BOD/kg activated sludge per day. A high SLR is empirically associated with a short sludge retention time (1.5 d calculated versus 7 d reported by company B). Installation A2 combines a low BOD load with a long HRT. Such a mode of operation resembles an oxidation ditch providing a high opportunity for chemicals to be eliminated through volatilization and biodegradation.

The temperature in installation A3 and some of company C and D was reported to be approximately 35 °C. It is assumed that this temperature in the activated process is constant. Therefore, a temperature adjustment factor was added to account for higher

biodegradation rates compared to the temperature of 15 °C as assumed for municipal STPs. For other biological processes like sludge decay or sludge growth in case of high BOD loads, temperature dependence could not be formulated because empirical relationships are only available for municipal STPs at temperatures around 15 °C.

### 3.2. Distinguishing archetypes of industrial activated sludge reactors

All installations of companies A and D and installation B1 treat low BOD sewage (0.1–1 kg/ $m^3$ ) whereas installation B2 and all of company C can be classified as reactors that treat sewage with high BOD (2–4 kg/ $m^3$ ). Similarly, we can distinguish activated sludge reactors with short HRTs in the range of 12–36 h (A1, A3, B and D) and with long HRTs between 120 and 220 h (A2 and C).

From this set of low/high ranges of BOD and HRT, a subdivision of I-STPs was made into four archetypes (Table 3):

1. Low BOD and low HRT
2. Low BOD and high HRT
3. High BOD and low HRT
4. High BOD and high HRT

Archetype 2) and 3) contain only one I-STP each, A2 and B2, respectively. Nevertheless, in order to cover all probable combinations we adhere to this set of four archetypes. Table 3 displays the sludge loading rate (SLR) calculated according to Eq (2) and sludge retention time (SRT) derived from empirical relationships as visualized by Fig. 2b.

### 3.3. Sensitivity analysis

The sensitivity of the chemical fraction emitted to surface water via effluent was analyzed by varying two partition coefficients that cover the majority of organic chemicals:

1. The Koc, the organic carbon referenced solids-water partition coefficient (L/kg) in the range between 10 and  $10^6$ ;
2. The Henry coefficient (H), reflecting the air-water partition coefficient in the range between 0.01 and  $10^3$  Pa  $m^3$  mol $^{-1}$

The dependent variable is the percentage emission to water predicted by the model. Emission to water is the sum of emission of purely dissolved and associated to suspended particles in the effluent. The calculations were carried out for several levels of biodegradability (Table 4) of which some are not distinguished by REACH (2006). With  $k_{biodeg}$  equal to 0.1 h $^{-1}$ , according to the label “Inherent biodegradability, fulfilling specific criteria” (Table 4), significant differences in emission to water are observed between industrial STPs with long hydraulic retention times and SimpleTreat 4.0 (Fig. 4).

According to REACH (2006), the biodegradation rate constant of substances which are inherently biodegradable but fail to fulfill specific criteria, should be set to zero. This can be the case if for example in the Zahn-Wellens test (OECD, 2006) the lag phase is 4 instead of 3 days (specific criterion) or the pass level was reached after 8 days instead of the period of 7 days (specific criterion). In such cases, REACH (2006) recommends to assign a biodegradation rate constant equal to zero in model calculations. Fig. 5 displays results of model simulations with a first order rate constant for biodegradation for a first order biodegradation rate constant equal to 0.03 h $^{-1}$ . The rationale was to see what the outcome would be if  $k$  is slightly above 0 h $^{-1}$ . For two archetypes of industrial STPs, both with high HRT, emission to water is less than 20% for all chemicals

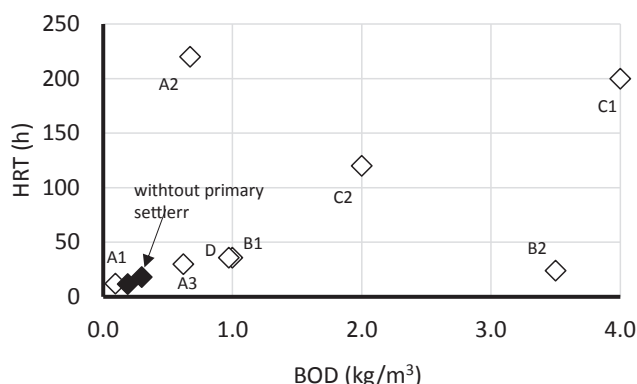


Fig. 3. Real world operation characteristic of industrial sewage treatment, black diamonds represent municipal plants (with and without primary clarifier) according to default settings of SimpleTreat 4.0. Installations A1 and C are known to be equipped with a primary clarifier. It is assumed that also the set of C2 have a primary clarifier.

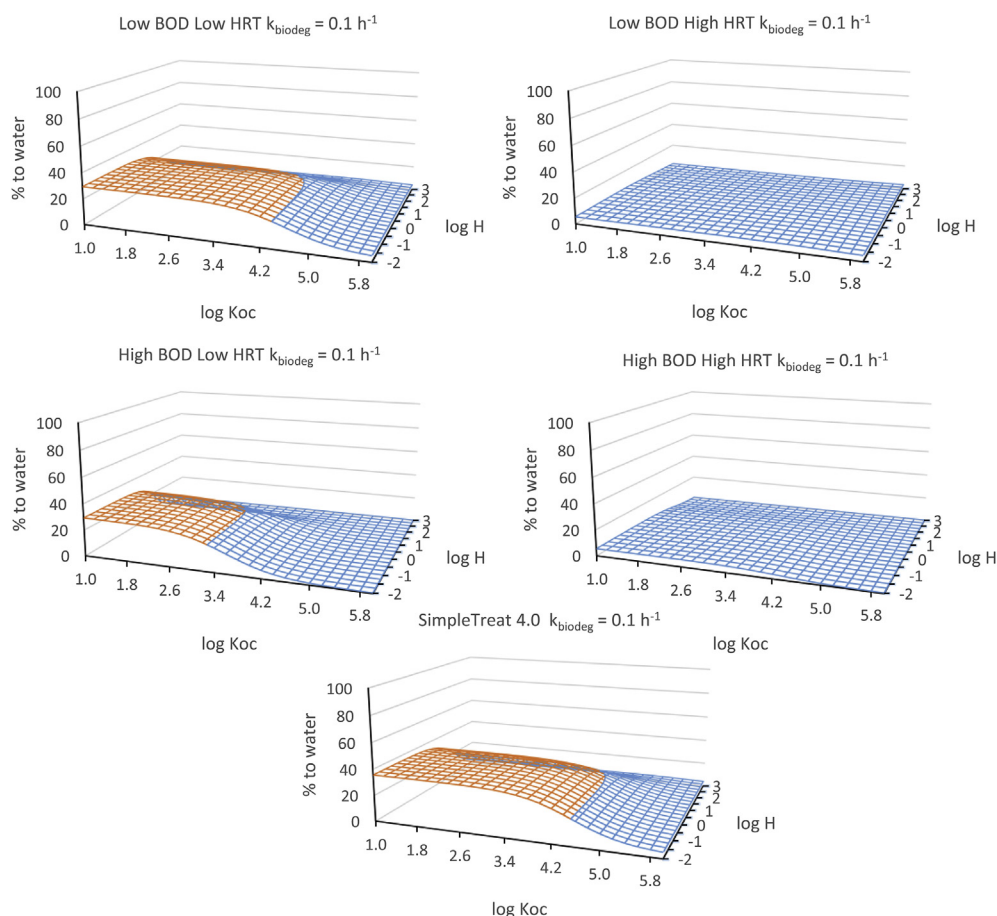


**Table 3**  
Archetype I-STPs derived from combinations of reported parameters that characterize industrial sewage and the activated sludge process of industrial installations. The SLR is calculated from BOD and HRT and the SRT is calculated from an empirical function of the SLT (Struijs, 2014).

Archetype	Installation	Archetype operating data			
		BOD (kg/m <sup>3</sup> )	HRT (hr)	SLR (kg/kg/d)	SRT (d)
1. Low BOD and low HRT	A1, A3, B1, D	0.3	24	0.075	19
2. Low BOD and high HRT	A2	0.3	170	0.011	153
3. High BOD and low HRT	B2	3	24	0.75	1.7
4. High BOD and high HRT	C1, C2	3	170	0.11	13
SimpleTreat 4.0		0.3	18	0.10	14

**Table 4**  
Biodegradability in activated sludge: extrapolation from test results to rate constants in SimpleTreat as recommended by REACH (2006).

Label	$k_{\text{biodeg}}$ (hr <sup>-1</sup> )	Remark
Ready biodegradable	1	Recommended by REACH
Ready biodegradable, not fulfilling 10-days window	0.3	Recommended by REACH
Inherently biodegradable, fulfilling specific criteria	0.1	Recommended by REACH
Inherently biodegradable	0.03	REACH: 0 hr <sup>-1</sup>
Inherently biodegradable	0.01	REACH: 0 hr <sup>-1</sup>
Inherently biodegradable	0.003	REACH: 0 hr <sup>-1</sup>
Not biodegradable	0	Recommended by REACH

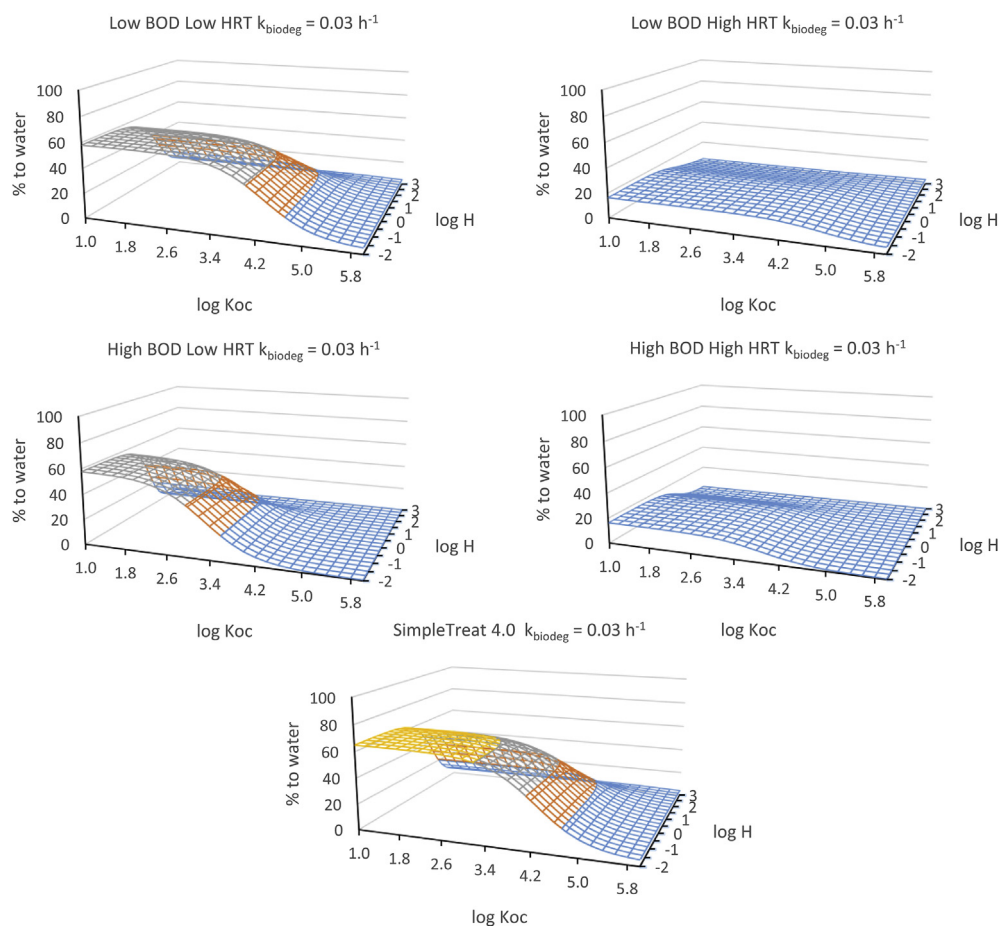


**Fig. 4.** Emission of chemicals to water from STPs for inherently biodegradable chemicals (fulfilling specific criteria):  $k_{\text{biodeg}}$  equal to 0.1 h<sup>-1</sup>. Emissions ranges to water are indicated as blue (0–20%) and red (20–40%).

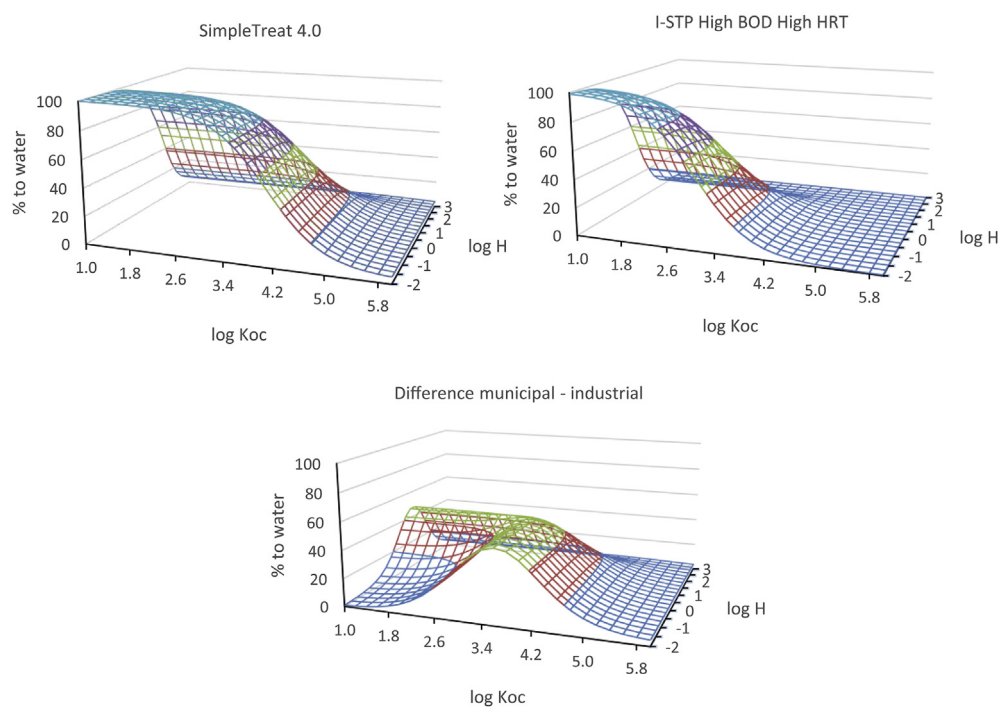
degrading with a first order rate constant as low as 0.03 h<sup>-1</sup> while emission to water would approach 100% if  $k = 0$  h<sup>-1</sup> (see Fig. 6) for non-sorptive, non-volatile chemicals.

Fig. 5 already showed that there is not much difference between

industrial STPs with a low BOD and HRT and SimpleTreat 4.0 if the first order rate constant for biodegradation approaches zero (0.03 h<sup>-1</sup>). With zero degradation the only possible removal pathway is through sorption and volatilization. For chemicals that



**Fig. 5.** Simulation of emission of chemicals to water with  $k_{\text{biodeg}}$  equal to  $0.03 \text{ h}^{-1}$ .



**Fig. 6.** Emission of persistent chemicals to water as predicted by SimpleTreat 4.0 and I-STP with high BOD and high HRT.

do not biodegrade, industrial STPs with a high BOD input and high HRT remove chemicals much better than an STP with low BOD and low HRT like SimpleTreat 4.0. Differences in emission of chemicals to water between SimpleTreat 4.0 and an industrial STP with high BOD and high HRT are observed in the upper plots of Fig. 6. If emission to water from an industrial STP with high BOD and high HRT is subtracted from emission to water from a municipal STP according to SimpleTreat 4.0, an interesting outcome is observed for chemicals with intermediate values of Koc and H. This is shown in the lower plot in Fig. 6. For very low Koc and H, all removal mechanisms are absent and both industrial and municipal emit 100% to water resulting in a difference equal to zero. For very high Koc and H, abiotic removal by both systems is high. As a result the difference in output between municipal and industrial approaches zero again. For moderate values of Koc and H, representing the majority of chemicals, emission to water from industrial STPs is significantly lower than from municipal STPs.

## 4. Discussion

### 4.1. Reflection on the results

A model that predicts the fate and emission of chemicals in an industrial STP would improve exposure and risk assessment of chemicals. It can be used to prioritize chemicals when emission to water is concerned. For that purpose, we have re-parametrized an existing model applicable to municipal wastewater treatment works. With respect to chemical fate processes however, the structure of the model has not been altered. Process formulations regarding intermedia transport of the modeled chemical remain unchanged. Only the equation for biodegradation of the chemical in activated sludge has become temperature dependent. Input parameters required to define the flow rates of water and particles are different. The existing model SimpleTreat 4.0 for municipal STPs is a special case of the re-parameterized model and can be typified as the variant low BOD in sewage in combination with a low hydraulic retention time (HRT). A limited survey on industrial STPs showed that several industrial installations are covered by this combination. The inquiry also showed that industrial STPs have rather different combinations of BOD in sewage and HRT.

As mentioned earlier, the temperature dependence of biological processes such as sludge decay (low BOD loading) or sludge growth (high BOD loading), is unknown. Empirical relationships are only available for municipal STPs at moderate temperatures. The relationship between sludge retention time and the sludge loading rate may be different in an activated sludge process at 35 °C compared to ambient levels of 15 °C.

The sensitivity analysis was carried out for 15 °C. According to Eq. (3), the first order rate constant for biodegradation in water in the aeration tank increase by a factor of four if the temperature is 35 °C instead of the municipal standard value of 15 °C. Percentages of emission to water would be significantly lower than given by Fig. 4 if the temperature were 35 °C. In other words, if the calculations were conducted for 35 °C a similar outcome would be obtained for a first order biodegradation rate constant as low as 0.025 h<sup>-1</sup>. Such a degradation rate constant is conceived to be zero by REACH (2006) for chemicals that are positive in the so-called inherent biodegradability tests (OECD, 2006) but do not fulfill the special criteria according to the OECD (2006). Chemicals are considered not-biodegradable if a first order biodegradation rate constant is below 0.1 h<sup>-1</sup>. Even if degradation is zero, the sensitivity analysis showed that compared to municipal STPs, for many chemicals the predicted emission to water is significantly lower in industrial STPs with high BOD in sewage and high HRT.

### 4.2. Methodological limitations

The industrial version of SimpleTreat is lacking a comparison between measured and predicted emissions of chemicals. The predicted emission of polycyclic musks to water has been compared to measured concentrations in effluent of municipal STPs by Artola-Garicano et al. (2003). They applied an older version of SimpleTreat. Recent validation results indicate that for low BOD and low HRT the model give fair predictions of emission of pharmaceuticals to water (Lautz et al., 2016). The mode of operation of the STP they modeled is essentially that of SimpleTreat 4.0 which resembles an industrial activated sludge reactor with low BOD and low HRT. Measured chemical concentrations in industrial installations have not been made available until now. Probably, data may have been collected by industrial companies for their own monitoring. It is strongly recommended however, to provide these data to allow validation of the adapted model presented in this article.

Volatilization and biodegradation are processes that genuinely eliminate the chemical from water. In conventional primary sedimentation the water retention time is only three or four hours which is sufficient for sedimentation of 50–65% of the suspended solids. Removal of sorptive chemicals via withdrawn primary sludge can be enhanced if the fraction of removed solids increases which can be simulated. Alternative degradation pathways of the chemical during or after secondary clarification (e.g. anaerobic digestion) is not included in the model.

## 5. Conclusions

The multi-media model SimpleTreat, applied in risk assessment of chemicals in the framework of REACH can be adapted for chemical fate modeling in industrial wastewater works.

An inquiry of industrial sewage treatment plants of several companies confirmed that changing the model structure of SimpleTreat was not necessary. The results of the inquiry showed a wide variation in concentration of BOD (biological oxygen demand) in industrial wastewater in contrast to municipal sewage which is constantly low in BOD content. It also indicated that the hydraulic retention times in industrial STPs may vary widely and are usually higher than in municipal STPs.

Equations for chemical intermedia transport remain similar with the exception of biodegradation of the modeled chemical for which a temperature adjustment factor was added. This is necessary because higher temperatures have been reported in industrial activated sludge installations. For other biological processes like sludge decay and growth (from BOD), temperature dependence could not be formulated because empirical relationships are lacking.

A comparison based on a sensitivity analysis on the adapted model regarding four archetypes of industrial STPs showed that elimination of chemicals is higher than in the municipal version of SimpleTreat.

It is strongly recommended to validate the adapted model SimpleTreat by comparing predicted concentrations in effluent and produced sludge and measured concentrations.

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The spreadsheet model of this study is available on request at [jaapstruijs@gmail.com](mailto:jaapstruijs@gmail.com).



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