



National Institute for Public Health  
and the Environment  
*Ministry of Health, Welfare and Sport*

**SimpleTreat 4.0: a model to predict  
fate and emission of chemicals in  
wastewater treatment plants**

*Background report describing the equations*

RIVM report 601353005/2014

J. Struijs



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## Colophon

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Jaap Struijs, RIVM

Contact:

Dr T.P. Traas

M&V/VSP/ICH

theo.traas@rivm.nl

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P.O. Box 1 | 3720 BA Bilthoven

The Netherlands

[www.rivm.nl/en](http://www.rivm.nl/en)

## Publiekssamenvatting

### **SimpleTreat 4.0, een model dat gedrag en uitstoot van chemicaliën in rioolwaterzuiveringen voorspelt**

Chemische stoffen kunnen via het afvalwater dat bedrijven en huishoudens in het riool lozen in het milieu terechtkomen. Het RIVM heeft in 1992 het zogeheten SimpleTreat-model ontwikkeld, waarmee kan worden geschat in welke mate de milieucompartimenten (bodem, water of lucht) via afvalwater aan dergelijke stoffen blootstaan. Het RIVM geeft nu een overzicht van alle technische details van de nieuwste versie van het model (4.0), dat in 2013 is herzien. De bedoeling hiervan is om alle wiskundige vergelijkingen en rekenmethodieken die in het model worden gebruikt, vast te leggen en overzichtelijk weer te geven.

De beoordelingssystematiek voor chemische stoffen, inclusief het SimpleTreat-model, was oorspronkelijk bedoeld om de Nederlandse Wet Milieugevaarlijke Stoffen te ondersteunen. Sinds 2003 is het door de Europese Unie overgenomen en vanaf 2007 maakt het deel uit van de Europese regelgeving voor chemische stoffen REACH (Registratie, Evaluatie, Autorisatie van Chemische stoffen). Ook buiten Europa bestaat er veel belangstelling voor SimpleTreat.

#### **Redenen herziening model**

Het model is om twee redenen herzien. Als eerste waren aanpassingen nodig om het model bruikbaar te maken voor de Europese wetgevingen voor chemische stoffen die naast REACH bestaan: de biocidenrichtlijn (ontsmettingsmiddelen), de regulering van de toelating van medicijnen, en de regulering voor het gebruik van gewasbeschermingsmiddelen. Aparte wetgevende kaders zijn ingevoerd vanwege het specifieke gebruik van deze stoffen. Daarnaast komen er meer geneesmiddelen en biociden in het milieu terecht door het toegenomen gebruik ervan. Een apart beoordelingssysteem is nodig omdat deze categorieën chemicaliën een ander gedrag vertonen. In de tweede plaats is er in toenemende mate behoefte aan een model voor de emissie van chemische stoffen door installaties die industrieel afvalwater zuiveren. Dat was er eerder nog niet. De aard van dit afvalwater wijkt af van het huishoudelijke afvalwater.

#### Trefwoorden:

lotgevallen model voor chemicaliën, emissiemodel, rioolwaterzuiveringen, behandeling voor huishoudelijk/industrieel afvalwater



## Abstract

### **SimpleTreat 4.0, a model to predict the fate and emission of chemicals in wastewater treatment plants**

Chemical substances in wastewater discharged into the sewer by companies and households may reach the environment. In 1992, the National Institute of Public Health and the Environment (RIVM) developed the so-called SimpleTreat model to estimate exposure of the receiving compartments (soil, water and air) to these chemicals present in wastewater. The RIVM presents an overview here of all technical details of the model revised in 2013 (version 4.0). The purpose of this report is to conveniently arrange a document containing all mathematical equations and computation methods applied in the model.

The assessment system for chemicals, including the SimpleTreat model, was originally meant to support the Netherlands Chemical Substances Act. In 2003 the European Union adopted this methodology and since 2007 it has been a part of the European legislation for chemicals REACH (Registration, Evaluation and Authorization of Chemicals). The SimpleTreat model is also receiving considerable attention outside the European Union.

### **Reasons for the revision**

The revision was necessary for two reasons. First, the modifications were required to make the model suitable for European substance regulation and legislation that exist beside REACH: for chemicals covered under the Biocidal Products Directive, such as disinfectants, for active pharmaceutical ingredients regulated by the European Medicines Agency and for chemicals under the plant protection regulation. These regulations came separately into force because of their specific use. Furthermore, the emission of pharmaceuticals and biocides is higher because of increased use. An independent assessment methodology is required because these categories of chemicals show a different behaviour. Second, there is an increasing need for a model that predicts the emission of chemicals from plants that treat industrial wastewater. This type of wastewater is different from communal wastewater.

### **Keywords:**

chemical fate model, emission model, sewage treatment plant, treatment of domestic wastewater/industrial wastewater



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## Summary

Chemical substances in wastewater emitted by companies and households into the sewer may find their way into the environment. The emission of new substances is regulated by chemical legislation, for which a system was required to assess the human and environmental risks. In the framework of this risk assessment system, the National Institute for Public Health and the Environment (RIVM) in the Netherlands developed the SimpleTreat model. The model estimates the extent to which environmental compartments (soil, water and air) are exposed to chemicals discharged into the sewer. Since 2003, the EU has adopted the risk assessment methodology implemented in EUSES. In 2007, the European REACH legislation (Registration, Evaluation, Authorization and restriction of Chemicals) came into force, relying on EUSES with regard to environmental risk assessment.

This report describes the model SimpleTreat 4.0, a model to predict the fate and emission of chemicals in wastewater treatment plants. SimpleTreat 4.0 is an improved version of SimpleTreat 3.1., applied in the European REACH legislation (Registration, Evaluation, Authorization and restriction of Chemicals). Version 3.1 has become accepted as a useful tool for generic exposure assessment. It is now recognized that the accuracy of exposure assessment, particularly with respect to the water compartment in urban regions, is strongly influenced by the accuracy with which the chemical fate in sewage treatment plants (STP) can be predicted.

Chemicals covered not only under REACH but also those covered under the Biocidal Products Regulation (BPR) and active pharmaceutical ingredients regulated by the European Medicines Agency (EMA) are being evaluated using SimpleTreat 3.1. In the Netherlands, it is even applied to substances that are assessed according to the regulation on plant protection products (PPP) 1107/2009 because drainage water from greenhouses in which PPPs are applied is collected and discharged into sewer systems.

This extended application has led to reservations with respect to the ability of the model to predict complicated substances. Most chemicals under BPR, EMA and PPP may exist in the ionic state or have surface-active properties, while the SimpleTreat model was designed to compute the fate of hydrophobic (neutral) chemicals. In the year of 2012, the German Federal Environment Agency asked for an evaluation of SimpleTreat, with special emphasis on its predicting behaviour regarding biocides and pharmaceuticals. The study revealed that the assumption that only the neutral chemical is available for sorption into sludge and that the ionized species can only exist in the true dissolved phase may lead to erroneous results.

The operation mode of sewage treatment plants (STP) in the EU has changed somewhat in the last two decades. Moreover, there is an increasing demand to simulate the fate of chemicals in installations treating industrial wastewater. These developments required some modifications of the model. With respect to SimpleTreat 3.1, these adaptations can be grouped into three categories.

1. Wider choice to define wastewater. In SimpleTreat 3.1, a fixed part (2/3) of the solids in domestic sewage is assumed to settle in the primary clarifier and a fixed part of the total BOD (biological oxygen demand) in raw sewage is dissolved. The remaining (also fixed) part resides in the solids. In version 4.0, these partitions can be chosen.

This modification makes it possible to simulate the fate of chemicals in industrial wastewater.

2. Improved formulation of the partitioning of chemicals. The partitioning of organic acids and bases over (suspended) solids and the water phase has improved in line with recent insights.
3. Revision of fixed and default parameters. Some parameters no longer reflected the technological state of the art. For example, the average concentration of suspended solids in the effluent is now four times lower than was calculated by SimpleTreat 3.1. This has a significant effect on the emission of strongly adsorbing chemicals into the receiving bodies of water.

## 1 Introduction

Discharged chemicals in the industrial world reach the environment most often through wastewater that has been treated. Although industrial wastewater is a relevant source, emission via residential wastewater treatment plants (STP) is the major route to the environment. This is why the risk assessment of chemicals has focussed on this pathway. A major proportion of communal wastewater (sewage) in the industrial world is treated by residential STPs. These systems were initially designed to remove BOD (biochemical oxygen demand) from communal sewage. More recently, STPs also eliminate other nutrients such as phosphorus and nitrogen. During this process, chemicals may be biodegraded or distributed over the receiving environmental compartments of water, agricultural soil or air (Figure 1). Assessing the exposure to the chemicals in wastewater requires evaluation of the chemical fate in wastewater treatment installations. The pathway from the sewer system to the receiving environmental compartments runs via an STP.

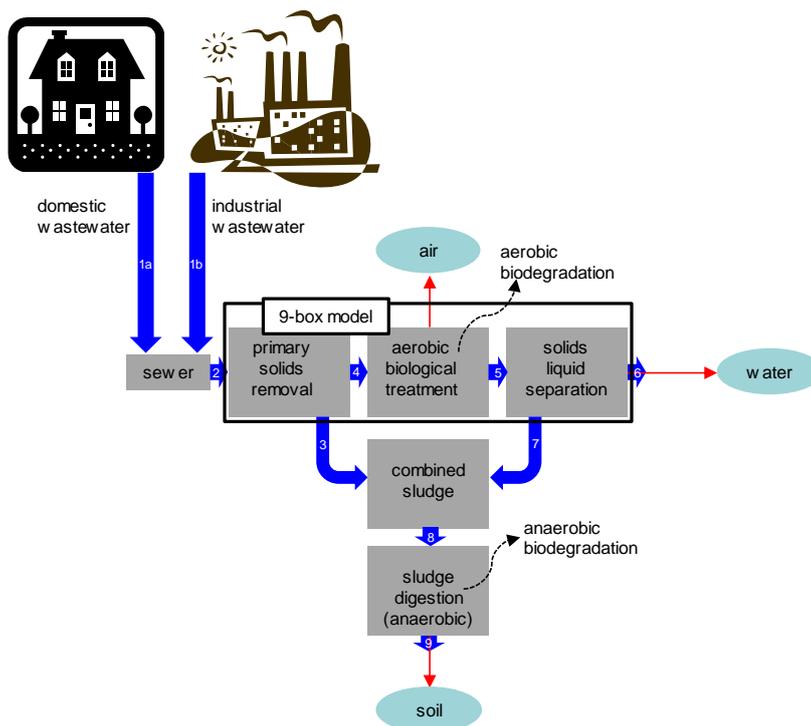


Figure 1 The emission scenario of SimpleTreat, a fate model of a chemical in wastewater discharged into the sewer. Emission routes are air, water and soil. Thick arrows indicate flows of raw residential sewage (1a, 2) and/or industrial wastewater (1b, 2), primary sludge (3), settled sewage (4), activated sludge (5), effluent (6), surplus sludge, also known as secondary or wasted sludge (7) and combined sludge (8). Red arrows indicate emission routes to air, water and soil. Aerobic biodegradation in the aeration tank is the only elimination process.

Figure 1 is a diagram of the SimpleTreat model in its environment. The core of the model is a multimedia box computation of the chemical fate in the technosphere of an STP. The 9-box model includes a primary clarifier, an activated sludge reactor (aerobic treatment) and secondary sedimentation (solids-liquid separation). The model computes the fluxes of the chemical via air, water and solids and the chemical concentrations in the media flowing out of the system, describing the local environment of a communal STP. Originally developed by Struijs et al. (1991), the program has been revised (Struijs, 1996) and adapted to be generically applicable for the European Union. It functions as a central emission and exposure assessment device in the EUSES system (TGD, 2003).

One major feature of the model is that it only requires a few basic properties in the base-set data of the chemical to calculate 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 that flows into the receiving water bodies, in sludge produced (applied to agricultural soil) and in the air above the STP. The emission scenario requires only two input data: the emission rate of the chemical into the sewage system and the size of an average STP in terms of the number of inhabitants connected to it. SimpleTreat allows a choice of various operation modes such as absence/presence of a primary clarifier, aeration regime and sludge loading rate.

SimpleTreat 3.1 is the recommended STP model in Europe for environmental risk assessment of industrial chemicals (REACH<sup>1</sup>), chemicals covered under the Biocidal Products Regulation (BPR) and active pharmaceutical ingredients regulated by the European Medicines Agency (EMA). In the Netherlands, it is applied to substances that are assessed according to the regulation on plant protection products (PPP) 1107/2009 because drainage water from greenhouses in which PPPs are applied is collected and discharged into sewer systems.

Multi-media models, also known as box models, have been found suitable for estimating fate and environmental concentrations of neutral organic chemicals that are typified by a degree of hydrophobicity, air-water partition coefficient and microbial degradability. The Federal Environment Agency (UBA) of Germany decided to investigate the validity domain of SimpleTreat 3.1 with respect to more complex chemicals (Struijs, 2013). This evaluation was the motive for extending the applicability of SimpleTreat beyond neutral substances, particularly with respect to organic chemicals that are ionized. Franco et al. (2011) have indicated that almost half of the notified chemicals under REACH are ionizable. In a recent study, Franco and Trapp (2010) suggested that a significant fraction of industrial chemicals that have been pre-registered in Europe likely consist of ionizable organic chemicals, whereas the majority of active pharmaceutical ingredients are ionizable (ECETOC, 2013). Neutral chemicals under BPR and EMA are even a minor proportion. The conclusions of these recent studies prompted the revision of SimpleTreat 3.1. Studies mentioned above have also identified some parameters with respect to the operation mode of STPs that are considered to be out of date. In addition, the OECD recently launched a joint project to compile the current methodologies, tools and models used for estimating removal/emissions of micro-pollutants from/by wastewater treatment systems. A questionnaire indicated that there is interest in extending its applicability to treatment of industrial wastewaters (OECD, 2013).

<sup>1</sup> Registration, Evaluation, Authorization and restriction of Chemical

This report describes in detail the technical aspects of a new version: SimpleTreat 4.0. The structure of the model has not changed; it is still a steady state non-equilibrium 9-box model. It differs from version 3.1 with respect to:

- having parameter settings which better reflect the current technology of sewage treatment;
- affording greater flexibility to define wastewater and treatment in the primary clarifier, which makes modelling the fate and emission of chemicals in industrial wastewater possible;
- being scientifically state of the art for estimating the solids-water partition constants of ionized chemicals.

The chemical route to the STP begins with discharge of wastewater into the sewer, where it may remain for hours or days. Sewage in this system consists of two media, i.e. water and solids. In this a binary phase system, the chemical is in equilibrium. Consequently, the chemical enters the STP through two phases, the water phase and the solids phase. SimpleTreat 4.0 offers greater flexibility in defining characteristics of the particulate and aqueous phases and treatment in the primary clarifier. This makes it possible to simulate the fate of a chemical during the treatment of industrial wastewater. New rules for the equilibrium partitioning of ionized chemicals (organic acids and bases) are applied to sewage and activated sludge.



## 2 Characterization of the sewage treatment process

### 2.1 Raw sewage and its treatment

Describing the process of sewage treatment starts with the parameterization of inflowing wastewater. Communal sewage can be characterized in terms of flows per capita: volume sewage, mass of solids or BOD (biochemical oxygen demand) per person equivalent per day. The inflow of raw sewage, solids (dry weight) and BOD is expressed per person equivalent (PE) in Table 1.

*Table 1 Flow characteristics of raw sewage. Values in the last column are default settings typical for communal wastewater produced daily by one inhabitant (PE)*

symbol	meaning	Units	default
Q	Sewage flow	$\text{m}^3 \cdot \text{d}^{-1} \cdot \text{PE}^{-1}$	0.2
SO	Mass of sewage solids	$\text{kg} \cdot \text{d}^{-1} \cdot \text{PE}^{-1}$	0.09
BOD	Mass of O <sub>2</sub> binding material in sewage	$\text{kg BOD} \cdot \text{d}^{-1} \cdot \text{PE}^{-1}$	0.06

BOD is associated with large organic molecules that are easily decomposed by bacteria. However, oxygen is required for this process whereby these molecules are broken down into smaller molecules and eventually into carbon dioxide and water. The amount of oxygen required for this process is known as BOD. An STP is primarily a BOD elimination installation. STPs are often equipped with a primary clarifier that eliminates part of the solids in sewage and a fair share of the BOD content of raw sewage because BOD in sewage is distributed over the aqueous and particulate phases (Table 2). After primary sedimentation, the so-called settled sewage enters the activated sludge process. This technique consists of the aeration of slurry with a high, but stationary content of micro-organisms and a second tank where separation of suspended solids through sedimentation takes place (Figure 2). This tank is also known as the solids liquid separator. Typical for the activated sludge technique is the fact that the settled solids are tracked back to the aerator. The supernatant leaves effluent (treated wastewater) with low concentrations of solids and oxygen-consuming substances.

BOD that is not removed by the primary clarifier enters the aeration tank. The BOD load of the aerator has influence on the reactor volume and so on the aeration time (hydraulic retention time). It also has an impact on the fate of the solids in the activated sludge process (sludge retention time). The solid phase of raw sewage has the attributes of the density and fraction of organic carbon. The fraction of sewage solids removed due to sedimentation in the primary clarifier (FS) as well as the fraction of BOD in raw sewage that is located in the solids phase of sewage are considered "properties" of raw sewage in the primary sedimentation tank (Table 2). In multimedia models of the real world, FS would be derived from process parameters characterized by the settling velocity of suspended solids.

All parameters in Tables 1 and 2 were fixed in SimpleTreat 3.1, except the sewage flow (Q), which varies between 0.45 (North America) and 0.15 in some countries in Europe. The revised version offers the modeller the option to choose all parameters in Tables 1 and 2. This enables the evaluation of the fate of chemicals during treatment of industrial wastewater.

Table 2 Properties of raw sewage. Values in the last column are default settings representing communal wastewater

symbol	Meaning	units	default
FB	Fraction BOD in sewage solids	-	0.5417
FS	Fraction sewage solids removed by primary settler	-	0.667
foc <sub>S</sub>	Fraction organic carbon in sewage solids	-	0.3
d <sub>S</sub>	Density of sewage solids	kg·L <sup>-1</sup>	1.5

Table 3 Derived parameters with respect to raw sewage

symbol	Meaning	units	equation	default
C <sub>SO,S</sub>	Conc. solids in raw sewage	kg·m <sup>-3</sup>	$\frac{SO}{Q}$	0.45
C <sub>BOD,S</sub>	Conc. BOD in raw sewage	kg BOD·m <sup>-3</sup>	$\frac{BOD}{Q}$	0.3

## 2.2 Defining the primary clarifier

With respect to the primary sedimentation tank, two parameters required to describe the functioning of the primary sedimentation tank are fixed (Table 4). The geometry of the primary sedimentation tank and other relevant characteristics are given in Table 5.

Table 4 Fixed properties of the primary sedimentation (PS) tank

symbol	meaning	units	value
h <sub>PS</sub>	Depth of the PS tank	M	4
HRT <sub>PS</sub>	Hydraulic retention time	hr	2

Table 5 Derived parameters with respect to the primary sedimentation tank (PS)

symbol	Meaning	units	equation	default
VOL <sub>PS</sub>	Volume PS per person	m <sup>3</sup> ·PE <sup>-1</sup>	$\frac{Q \cdot \text{HRT}_{PS}}{24}$	1.67·10 <sup>-2</sup>
AREA <sub>PS</sub>	Area PS per person	m <sup>2</sup> ·PE <sup>-1</sup>	$\frac{Q \cdot \text{HRT}_{PS}}{24 \cdot h_{PS}}$	4.167·10 <sup>-3</sup>
C <sub>SO,PS</sub>	Conc. suspended solids in PS	kg·m <sup>-3</sup>	(1 – FS) · C <sub>SO,S</sub>	0.15
FP	Fraction BOD removed by PS	-	FS · FB	0.36

The fraction of BOD removed in the primary clarifier of a communal STP is typically in the range of 0.3 and 0.4. C<sub>SO,PS</sub> is the steady state concentration of solids in the liquid (also known as “settled sewage”) that enters the aeration tank. If the fraction of solids removed by the primary clarifier (FS) is zero, then the fraction of BOD removed (FP) is also zero. This approaches the scenario of an STP without a primary clarifier when raw sewage enters the activated sludge process directly. Nevertheless, a separate box model is employed (“6-box”) to conduct the computation for this scenario to avoid numerical problems in chemical fate computations. In Appendix B, the equations for an STP without primary clarifier are given.

### 2.3 Defining the activated sludge process

The activated sludge process combines aeration of activated sludge and sedimentation in a separate basin where the particles settle. The settled sludge is tracked back to the aeration tank (aerator). The aeration tank contains slurry ("mixed liquor") with a high concentration of suspended solids, a significant portion of which is of microbial origin. In the secondary sedimentation tank the sludge solids are separated from liquid that has a low concentration of suspended solids (effluent). This tank is also called the solids-liquid separator (SLS). Properties of the solids such as  $f_{oc}$  and  $d$  (see Table 6) in the solids-liquid separator and recycled sludge are identical to those of activated sludge. Again, the steady state concentration of suspended solids is not determined by a process parameter such as the settling velocity. It is a fixed value that reflects the practice of treating communal wastewater using modern biological methods. Note that the concentration of suspended solids in the SLS and in effluent is a factor of 4 lower than in SimpleTreat 3.1.

Table 6 Fixed properties of the aeration tank and the activated sludge process (aeration tank, solids-liquid-separation and recycled sludge)

symbol	Meaning	units	value
$h_{AS} = h_{SLS}$	Depth of aeration tank and SLS	m	3
$HRT_{SLS}$	Hydraulic retention time SLS	hr	6
$C_{SO,AS}$	Conc. suspended solids in activated sludge	$kg \cdot m^{-3}$	4
$C_{SO,SLS}$	Conc. suspended solids in effluent	$kg \cdot m^{-3}$	0.0075
$d_{AS}$	Density of activated sludge solids	$kg \cdot L^{-1}$	1.3
$f_{oc,AS}$	Fraction organic carbon activated sludge	-	0.37

The modeller has several possibilities to define the mode of operation of the STP. The sludge loading rate parameter,  $k_{SLR}$  in  $kg O_2 \cdot kg \text{ dry weight}^{-1} \cdot d^{-1}$ , typifies the BOD loading of the installation (Table 7). This parameter is also known as the food to mass ratio (F/M).

Table 7 Input parameters characterizing the mode of operation of the activated sludge reactor

symbol	Meaning	Units	default
$k_{SLR}$	Sludge loading rate	$kg O_2 \cdot kg^{-1} \cdot d^{-1}$	0.1
M	Aeration mode: surface (s) or bubble (b)	-	s

The total BOD input to the aerator depends on the performance of the primary sedimentation tank. The concentration of oxygen-binding substances flowing into the aerator, for which the term "oxygen requirement" is used, depends on  $Q$  and the BOD input from the primary clarifier. Table 8 shows that the equation for the aeration volume available for one person follows from the  $k_{SLR}$  and characteristics of (settled) sewage and activated sludge.

Table 8 Derived parameters with respect to the activated sludge process

symbol	Meaning	units	equation	default
OxReq	Oxygen requirement	kg O <sub>2</sub> ·m <sup>-3</sup>	$(1 - FP) \cdot \frac{BOD}{Q}$	0.192
VOL <sub>AS</sub>	Volume aerator per person	m <sup>3</sup> ·PE <sup>-1</sup>	$\frac{Q \cdot OxReq}{k_{SLR} \cdot C_{SO,AS}}$	9.6·10 <sup>-2</sup>
AREA <sub>AS</sub>	Area aerator per person	m <sup>2</sup> ·PE <sup>-1</sup>	$\frac{VOL_{AS}}{h_{AS}}$	3.2·10 <sup>-2</sup>
HRT <sub>AS</sub>	Hydraulic retention time aerator	hr	$\frac{VOL_{AS}}{Q} \cdot 24$	11.5
VOL <sub>SLS</sub>	Volume SLS per person	m <sup>3</sup> ·PE <sup>-1</sup>	$\frac{Q \cdot HRT_{SLS}}{24}$	5.0·10 <sup>-2</sup>
AREA <sub>SLS</sub>	Area SLS per person	m <sup>2</sup> ·PE <sup>-1</sup>	$\frac{VOL_{SLS}}{h_{SLS}}$	1.67·10 <sup>-2</sup>

From the input parameter  $k_{SLR}$  (Table 7), also known as the food to mass ratio (F/M), several parameters are derived that are typical for the operation of the plant. Mikkelsen (1995) reported the fraction BOD removal to correlate with  $\ln k_{SLR}$  according to:

$$F_{BODrem} = 0.818 - 0.0422 \cdot \ln k_{SLR} \quad 1$$

with

$F_{BODrem}$  : fraction of BOD removed by the activated sludge process [-]

The yield of biomass per unit BOD degraded in the aeration tank also correlates (Mikkelsen, 1995) with the sludge loading rate:

$$Y_{BOD} = 0.947 + 0.0739 \cdot \ln k_{SLR} \quad 2$$

with

$Y_{BOD}$  : yield of biomass (sludge growth) per BOD [kg dwt·kg BOD<sup>-1</sup>]

Mikkelsen (1995) derived equations 1 and 2 using data from Henze (1992). The amount of surplus sludge produced daily, also known as wasted sludge, depends on the presence of primary sedimentation. The net production per capita is obtained after subtraction of the emitted solids via the effluent:

$$SU = Q \cdot (OxReq \cdot F_{BODrem} \cdot Y_{BOD} - C_{SO,SLS}) \quad 3$$

with

$SU$  : wasted (surplus) sludge [kg dwt·PE<sup>-1</sup>·d<sup>-1</sup>]

If equations 1 - 3 are combined with parameters of Tables 6 to 8, the dependence on the characteristics of raw sewage and the performance of primary sedimentation disappear when deriving an expression for the sludge retention time, because the oxygen requirement cancels:

$$SRT = \frac{VOL_{AS} \cdot C_{SO,AS}}{SU + C_{SO,SLS} \cdot Q} = \frac{1}{k_{SLR} \cdot F_{BODrem} \cdot Y_{BOD}} \quad 4$$

with

SRT : sludge retention time [d]

Using the previous default settings, the STP has a mode of operation as characterized in Table 9. This mode of operation is typical for an average STP in Western Europe that predominantly treats communal wastewater. Such an STP has concentrations of suspended solids in settled sewage (sewage after primary sedimentation), activated sludge and effluent as visualized in Figure 2. The corresponding flows of solids per capita per day are given in Figure 3.

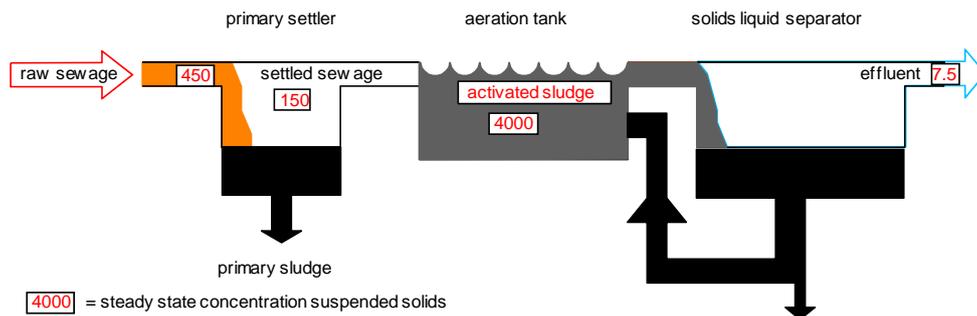


Figure 2 Solids concentration (mg/L) in the distinguished basins of an STP equipped with a primary clarifier

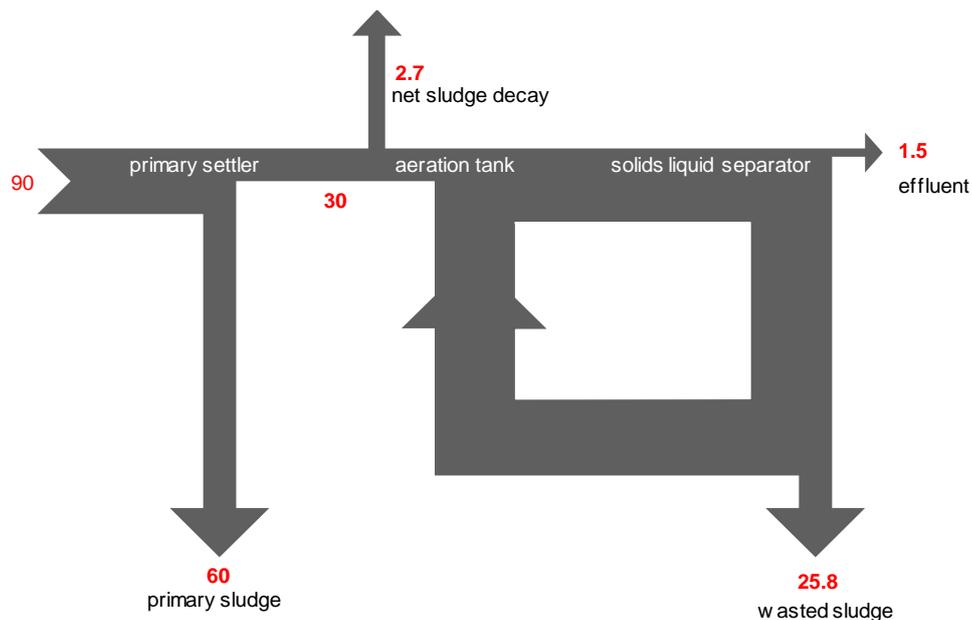


Figure 3 Solids flow (gram dry weight per inhabitant per day) in an STP equipped with a primary clarifier

Table 9 Characterization of the activated sludge process with  $k_{SLR} = 0.1 \text{ kg O}_2 \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$  and default values according to Tables 1 and 2

<b>symbol</b>	<b>Meaning</b>	<b>units</b>	<b>default</b>
$F_{\text{BODrem}}$	Fraction BOD removed in activated sludge process	-	0.915
$Y_{\text{BOD}}$	Sludge growth	$\text{kg} \cdot \text{kg BOD}^{-1}$	0.777
SU	Wasted sludge (surplus sludge)	$\text{kg} \cdot \text{d}^{-1} \cdot \text{PE}^{-1}$	0.026
SRT	sludge retention time	d	14.1

### 3 Definition of the modelled chemical

A set of inter-media equilibrium partition coefficients is a part of the required input parameters of the modelled chemical. Measured inter-media equilibrium partition coefficients are preferred over data estimated using methods based on compound properties. In most cases, however, measured data are not available. The equilibrium partition coefficient, which is the ratio of equilibrium concentrations, is a parameter that is indispensable to the derivation of intermedia transport rates. This net transport occurs across the boundary of adjacent media if concentrations are not in equilibrium. SimpleTreat is a non-equilibrium, steady state box-model.

In a second paragraph, the so-called base-set properties are given. An explanation is given on how to use them as input parameters for the model. The set contains basic physico-chemical properties, as well as the outcome of a standardized biodegradability test. This paragraph elucidates how these base-set data are processed in the model calculation to derive surrogate equilibrium partitioning coefficients if measured partition data for the chemical are not available.

#### 3.1 Equilibrium partitioning constants

Variables involved in the definition of relevant equilibrium partitioning coefficients or constants are given in Table 10. Equilibrium partitioning constants that are used for the calculation of inter-media transport rates of the chemical in an STP environment are given in Table 11.

Table 10 Concentrations in the distinguished media in an STP

Symbol	Meaning	units
SO <sub>S</sub>	Chemical concentration in sewage solids (raw and settled)	mg·kg <sup>-1</sup>
SO <sub>AS</sub>	Chemical concentration in activated sludge solids	mg·kg <sup>-1</sup>
W	Chemical concentration in water	mg·L <sup>-1</sup>
A	Chemical concentration in air	mg·L <sup>-1</sup>

Table 11 Equilibrium partition coefficients

Symbol	Meaning	Equation	units
K <sub>AW</sub>	Air-water equilibrium partition constant	$\frac{A}{W}$	-
K <sub>PS</sub>	Sewage solids-water equilibrium partition constant	$\frac{SO_S}{W}$	L·kg <sup>-1</sup>
K <sub>PAS</sub>	Activated sludge solids-water equilibrium partition constant	$\frac{SO_{SA}}{W}$	L·kg <sup>-1</sup>

An alternative partition parameter for air-water is Henry's law constant (H), which is the equilibrium ratio of the vapour pressure of a chemical and the concentration in the water phase:

$$H = \frac{P \cdot MW}{W} = R \cdot T \cdot K_{AW}$$

5

Henry's law constant,  $H$ , has dimensions of  $\text{Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ .  $P$  is the vapour pressure in Pascal (Pa) of the chemical in equilibrium with the aqueous concentration  $W$ ,  $MW$  is the molecular weight of the chemical in  $\text{g}\cdot\text{mol}^{-1}$ ,  $R$  is the gas constant ( $8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ) and  $T$  is the absolute temperature (K).  $K_{AW}$  is also known as the dimensionless Henry constant.

## 3.2 Estimation methods for equilibrium partitioning constants

### 3.2.1 Neutral organic chemicals

From base-set data (Table 12) the air-water equilibrium partition coefficients of organic chemicals is estimated according to:

$$K_{AW} = \frac{H}{R \cdot T} = \frac{VP \cdot \frac{MW}{SOL}}{R \cdot T} \quad 6$$

Table 12 Base-set data of a chemical

symbol	Meaning	Units
MW	Molecular weight	$\text{g}\cdot\text{mol}^{-1}$
SOL	Water solubility	$\text{mg}\cdot\text{L}^{-1}$
VP	Vapour pressure	Pa
Kow	Octanol-water partition coefficient	-

For the partitioning of the chemical between solids and the aqueous phase, a simple relationship is applied:

$$K_p = \text{foc} \cdot K_{oc} \quad 7$$

with

$K_p$  : partition coefficients [ $\text{L}\cdot\text{kg}^{-1}$ ] for sewage ( $K_{pS}$ ) or activated sludge ( $K_{pAS}$ )

$K_{oc}$  : partition coefficient for organic [ $\text{L}\cdot\text{kg}^{-1}$ ]

$\text{foc}$  : fraction organic carbon solids,  $\text{foc}_S$  or  $\text{foc}_{AS}$  [-]

This relationship reflects that  $K_p$  depends on 1) a property of the environment, i.e. the organic carbon fraction ( $\text{foc}$ ) of the particles in raw sewage and activated sludge and 2) a property of the chemical, the organic carbon partition coefficient ( $K_{oc}$ ), also known as the "organic carbon normalized partition coefficient",  $K_p/\text{foc}$ . The value of the  $\text{foc}$  of the solids in raw sewage (0.3) and activated sludge (0.37) is considerably higher than is assumed in the real world, where the fraction  $\text{foc}$  in soil is 0.02, in sediment 0.05 and in suspended solids equals 0.1 (TGD, 2003).

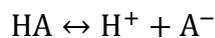
$K_{oc}$  was initially estimated through a simple proportionality relationship with a substance property  $K_{ow}$ , the octanol-water partition coefficient.  $K_{ow}$  is equal to  $C^O/C^W$ , being the concentration of the *neutral* chemical in octanol ( $C^O$ ) divided by the concentration of the *neutral* chemical in water ( $C^W$ ). The  $K_{ow}$  is part of the base-set data of a chemical used as input in SimpleTreat (Struijs et al., 1991; Struijs, 1996). In the last revision of SimpleTreat in 2003, the equation of Sablic and Güsten (1995) was introduced for chemicals that are predominantly hydrophobic:

$$K_{oc} = 1.26 \cdot K_{ow}^{0.81} \quad 8$$

Unlike rules for estimating the bio-concentration potential from  $K_{ow}$ , which is limited by the molecular weight of 700 (TGD, 2003), the applicability range of the relationship between  $K_p$  and  $K_{ow}$  is wide. Nevertheless, special structural properties related to, for example, amphiphilic substances (surfactants) or dissociating substances (organic acids, bases) may lead to multiple equilibrium processes.

### 3.2.2 Organic acids and bases

For an acid HA, dissociation results in two species, the neutral HA and the negatively charged  $A^-$ :



The acid dissociation constant ( $K_a$ ) is defined as:

$$K_a = \frac{[H^+] \cdot [A^-]}{[HA]} \quad 9$$

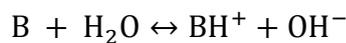
The neutral fraction of the chemical ( $F_{n_a}$ ) depends on the pH and pKa (negative logarithm of  $K_a$ ) and is calculated according to:

$$F_{n_a} = \frac{[HA]}{[HA] + [A^-]} = \frac{1}{1 + 10^{(pH-pK_a)}} \quad 10$$

The ionized fraction of an acid ( $F_{i_a}$ ) is equal to  $1 - F_{n_a}$ .

The neutral fraction of an organic acid ( $F_{n_a}$ ) is calculated from property pKa according to equation 10. In all STP basins, the pH is assumed to be equal to 7.

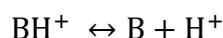
An organic base (B) dissociates according to:



with base dissociation constant:

$$K_b = \frac{[BH^+] \cdot [OH^-]}{[B]} \quad 11$$

The *conjugated* acid of an organic base (B) dissociates according to:



with a dissociation constant ( $K_a$ ) of the conjugated acid which now looks like:

$$K_a = \frac{[B] \cdot [H^+]}{[BH^+]} \quad 12$$

The pKb (negative logarithm of Kb) of base B can be calculated from the pKa of its conjugated acid (BH<sup>+</sup>) and pKw. The latter is the negative logarithm of the ion product of water, Kw (Henderson 1908):



The pKw is dependent on the water temperature according to:

$$\text{pKw} = 25.35757 - 0.03818 \cdot T_{\text{water}} \quad 14$$

with the water temperature,  $T_{\text{water}}$ , in K. At ambient temperature (20 °C), pKw is approximately 14. The sum of pKb and pKa equals pKw. The fraction of neutral species for an organic base  $F_{n_b}$  is:

$$F_{n_b} = \frac{[\text{B}]}{[\text{B}] + [\text{BH}^+]} = \frac{1}{1 + 10^{(\text{pKa}-\text{pH})}} \quad 15$$

The ionized fraction of a base ( $F_{i_b}$ ) equals  $1-F_{n_b}$ .

For monovalent organic acids or bases, the fraction of neutral species is determined on the basis of *one input parameter*, i.e. the acid dissociation constant Ka. It is the dissociation constant of either an acid which is neutral or the dissociation constant of the ionized *conjugated* acid of a base:

$$F_n = \frac{1}{1 + 10^{\gamma \cdot (\text{pH}-\text{pKa})}} \quad 16$$

In the case of acids,  $\gamma$  equals 1 and, in the case of bases,  $\gamma$  is -1. This equation is known as the Henderson-Hasselbach equation (Henderson 1908). Ionizable organics are present as neutral and charged species in fraction according to input substance parameters  $\gamma$  and pKa and an environmental characteristic pH.

Only the neutral molecule of acid HA or base B is available for transport across the water-air interface. The equation for Kaw (eqn 17) can be applied for the neutral fraction (eqn 16) at pH equal to 7 for the aqueous phase in an STP. Only the neutral chemical can cross the boundary between air and water, implying that the ionized fraction is not available for volatilization. This seems a valid assumption and the only fate process for ions would be advective transport through water and biodegradation in water and possibly sorption to suspended particles. For estimating the equilibrium partitioning of an organic acid or base between air and water, this may be correct. For an organic acid and an organic base, this would give an equilibrium partition coefficient KAW that depends on the fraction neutral (Fn) of the acid or of the base:

$$K_{AW} = \frac{H}{R \cdot T} \cdot F_n = \frac{VP \cdot \frac{MW}{SOL}}{R \cdot T} \cdot F_n \quad 17$$

Sorption to sludge, however, is complicated by the fact that ions may also adsorb to sludge solids due to, for example, electrostatic interactions. Therefore, it is unlikely that the solids-water partition coefficient for the ionic fraction is equal to zero.

For acids and bases, Franco et al. (2013<sup>a</sup>) recently proposed an alternative calculation of Koc. For organic acids, they derived an equation for Koc as a function of Kow and Ka applicable to soil and sediments. They concluded that this equation is also applicable to sludge solids:

$$Koc_a = F_n \cdot 10^{0.54 \cdot \log(Kow) + 1.11} + (1 - F_n) \cdot 10^{0.11 \cdot \log(Kow) + 1.54} \quad 18$$

where  $F_n$  is the fraction of neutral species, calculated at  $pH_{opt} = pH_{actual} - 0.6$  (Franco et al. 2009). Kow is the octanol-water partition coefficient of the neutral species. Default  $pH_{actual}$  is 7.

For organic bases, Franco et al. (2013<sup>a</sup>) were aware of the fact that the equation for Koc for soils and sediments would not necessarily prove satisfactory for sewage and activated sludge solids. The generally high Koc values observed for cations and the statistically significant correlation with Kow resulted in a simple regression based on  $Dow$ . The Dow of an organic compound is the apparent octanol-water partition coefficient at the actual pH and includes concentrations in octanol and water (superscript o and w, respectively) of both the neutral (subscript n) and ionized (subscript ion) of the chemical:

$$\begin{aligned} Dow &= \frac{C_n^o + C_{ion}^o}{C_n^w + C_{ion}^w} = \\ &= F_n \cdot \frac{C_n^o}{C_n^w} + (1 - F_n) \cdot \frac{C_{ion}^o}{C_{ion}^w} = \\ &= F_n \cdot Kow + (1 - F_n) \cdot Kow(\text{ionized}) \cong F_n \cdot Kow \end{aligned} \quad 19$$

In equation 19, the approximation is made that the concentration of an ionized organic compound in the octanol phase is virtually zero and that  $Kow(\text{ionized})$  is negligible. ECETOC (2013) and Franco et al. (2013<sup>a</sup>) proposed a regression for Koc of monovalent bases with  $pKa \geq 4$ :

$$Koc_b = 10^{0.31 \cdot \log(Dow) + 2.78} \quad 20$$

This equation is the preferred default in SimpleTreat 4.0. If, however, Dow is not given but only Kow is known, i.e. the octanol-water partition coefficient experimentally determined at a pH at which the chemical is predominantly in its neutral form, then Dow is estimated as  $F_n \cdot Kow$  (see eqn 19).



## 4 Description of the model

The model structure of SimpleTreat has not changed with respect to version 3.1. It is a multimedia model of the fate of a chemical (Figure 4) submitted to the following processes: advection, depicted as open arrows which represent media flows, intermedia transport (two-headed arrows) and degradation (curved arrows).

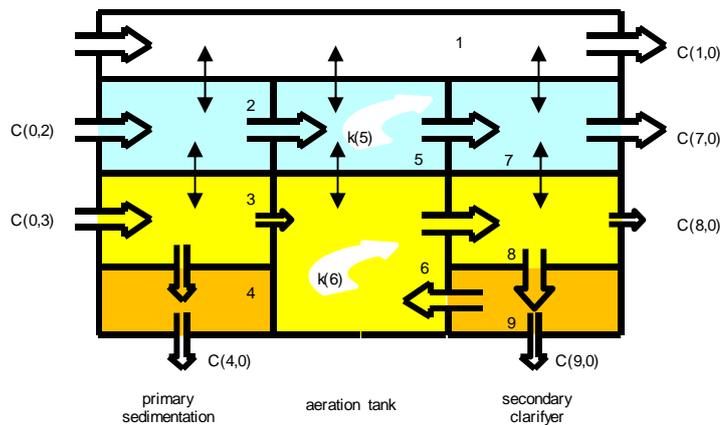


Figure 4 Box representation ("9-box") of the chemical fate in a sewage treatment plant which combines primary sedimentation and the activated sludge process (Struijs, 1996)

Nine of the fifteen media flows are flows of particles, suspended or settled, carrying the adsorbed chemical from outside the system (0,j), from box i to box j or out of the system (i,0). The product of the media volume flow and the concentration of the source box is the irreversible *media mass flow* ( $\text{g}\cdot\text{s}^{-1}$ ). The two-headed arrows represent reversible or diffusive transport between adjacent media, such as air-water and solids-water. Rate and direction of the net *diffusive mass flow* ( $XCH_{i,j}\cdot C_i$  in  $\text{g}\cdot\text{s}^{-1}$ ) is driven by non-equilibrium concentrations. Curved arrows stand for the disappearance of the chemical in boxes 5 and 6 (the aqueous and the suspended solids phase in the aeration tank), implying that a chemical is solely biodegraded in activated sludge.

Steady state concentrations ( $\text{d}C_j/\text{d}t = 0$ ) are obtained from multiple mass balance calculation by solving nine linear equations according to:

$$V_j \cdot \frac{\text{d}C_j}{\text{d}t} = -k_j \cdot C_j \cdot V_j + \sum_i \text{ADV}_{i,j} \cdot C_i + \sum_i \text{XCH}_{i,j} \cdot C_i \quad 21$$

with

- $\text{ADV}_{i,j}$  : flow rate of media [ $\text{m}^3\cdot\text{s}^{-1}$ ] from box i to box j, advective, irreversible
- $\text{XCH}_{i,j}$  : flow rate of media [ $\text{m}^3\cdot\text{s}^{-1}$ ] from box i to box j, diffusive, reversible
- $V_j$  : volume of box j [ $\text{m}^3$ ]
- $C_i$  : concentrations in box i [ $\text{g}\cdot\text{m}^{-3}$ ]
- $C_{0,j}$  : concentration in medium j outside the system
- $C_{i,0}$  : concentration in medium i flowing out of the system (air, water or solids)
- $t$  : time [s]
- $k_i$  : first-order biodegradation rate constant in box i [ $\text{s}^{-1}$ ]

In the next chapters, expressions for the media flow rates ADV and XCH are derived. In Appendix A, expressions for all  $V_i$ ,  $ADV_{i,j}$  and  $XCH_{i,j}$  are given. In Appendix B, figures, equations and default values are given for an STP without primary clarifier, the so-called "6-box" scenario.

## 5 Chemical fate processes

A subdivision is made into three categories of processes. First, there is advective transport of a medium carrying the chemical with it. This chemical fate process is irreversible. Second, there is diffusive (reversible) intermedia transport which is driven by non-equilibrium concentrations in adjacent media, tending to the direction of equilibrium. The third type is first-order degradation. This process occurs inside a medium. Processes related to water and solids occur in three separate basins which are interconnected in a special way. Transport of solids is rather complex due to sludge recycling, sludge growth or sludge decay in the activated sludge process. Depending on the mode of operation of an STP, the volume of the suspended solid phase in the aerator may increase due to microbial growth or decrease due to sludge decay. Solids are withdrawn from different basins. There are two types of solids, each with their specific properties – such as specific density and the fraction of organic carbon: 1) sewage (raw or settled) and primary sludge and 2) activated sludge suspended in the aerator – in the solids-liquid separator and in effluent and in wasted or surplus sludge.

### 5.1 Advective transport

Three types of media flows ( $\text{m}^3 \cdot \text{s}^{-1}$ ) are distinguished. An air column moves across the sewage treatment plant, carrying the chemicals in the gas phase away. A volume of water enters the primary clarifier of an STP. This volume passes the three basins connected in a series. Water leaves the installation via the secondary clarifier (solids-liquid separator). The flow of water causes transport of the dissolved chemical through the three basins. The flow of solids, also in  $\text{m}^3 \cdot \text{s}^{-1}$ , causes import, transport inside the system and export of the chemical in the adsorbed state. Advective transport coefficients (ADV) are not dependent on the chemical. For all media (air, water and solids), volume flow rates are formulated from which "media mass flow rates" ( $\text{g} \cdot \text{s}^{-1}$ ) are derived by multiplying the volume flow rate with the concentration in the source medium ( $\text{g} \cdot \text{m}^3$ ). The area of a basin (AREA) is proportional to the number of inhabitants (N). According to Tables 5 and 8, the areas for the three basins PS, AS and SLS are expressed in area per person ( $\text{m}^2 \cdot \text{he}^{-1}$ ).

#### 5.1.1

##### *Air*

Air advection depends on the wind speed (WS), the air mixing height (h) and the sum of areas of the three basins. In Table 13, default values are given. The advective volume flow rate for the air compartment,  $\text{ADV}_{\text{air}}$ , is proportional to:

$$\text{ADV}_{\text{air}} = h \cdot \text{WS} \cdot \sqrt{(\text{AREA}_{\text{PS}} + \text{AREA}_{\text{AS}} + \text{AREA}_{\text{SLS}})} \quad 22$$

with

$$\text{ADV}_{\text{air}} : \text{air flow rate into or out of the area of an STP } [\text{m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1/2}]$$

The advective volume flow rate for air depends on the plant's mode of operation. This choice determines the area of the active sludge reactor (Table 7), which depends on the oxygen requirement determining the volume and thus the area of the aerator. The areas of the primary sedimentation tank and the solids-liquid separator depend only on the sewage flow per inhabitant Q as  $\text{HRT}_{\text{PS}}$  and  $h_{\text{PS}}$  and respectively,  $\text{HRT}_{\text{SLS}}$  and  $h_{\text{SLS}}$  are fixed (Tables 5 and 7). The values for

advective flow rates are given per person (PE). The actual flow rates have to be multiplied by the number of personal equivalents connected to the STP, N, except for air, which should be multiplied by  $\sqrt{N}$ .

Table 13 Default parameters that define the air compartment of an STP

Symbol	Meaning	Units	Value
WS	Wind speed	$\text{m}\cdot\text{s}^{-1}$	3
h	Air mixing height	m	10

### 5.1.2 Water

The water volume flow rate ( $\text{m}^3\cdot\text{s}^{-1}\cdot\text{PE}^{-1}$ ) into, inside and out of the installation is considered proportional to the sewage flow, Q, according to:

$$\text{ADV}_{\text{water}} = \frac{Q}{24 \cdot 3600} \quad 23$$

All water volume flow rates in the system are equal (box 2, 5 and 7 in Figure 4).

### 5.1.3 Sewage solids

The volume flow rate of solids into, inside and out of the primary settler is shown by the following three equations:

$$\text{ADV}_{\text{raw sewage solids}} = \frac{SO}{1000 \cdot d_s \cdot 24 \cdot 3600} \quad 24$$

$$\text{ADV}_{\text{primary sludge solids}} = \frac{FS \cdot SO}{1000 \cdot d_s \cdot 24 \cdot 3600} \quad 25$$

$$\text{ADV}_{\text{settled sewage solids}} = \frac{(1 - FS) \cdot SO}{1000 \cdot d_s \cdot 24 \cdot 3600} \quad 26$$

with  $\text{ADV}_{\text{solids}}$  in  $\text{m}^3\cdot\text{i}^{-1}$ , SO in  $\text{kg}\cdot\text{d}^{-1}\cdot 1\text{S}^{-1}$ ,  $d_s$  in  $\text{kg}\cdot\text{L}^{-1}$  and dimensionless FS shown in Tables 1 and 2. The volume flow rate of primary sludge solids results from primary sedimentation, which is equal to the fraction FS of volume flow rate related to the inflow of raw sewage. The remaining fraction of solids (1-FS) flowing into the aerator, is related to suspended solids in settled sewage.

### 5.1.4 Activated sludge solids

The fixed values for the volume flow rate of activated sludge solids from the aerator into the solids liquid separator is equal to:

$$\text{ADV}_{\text{activated sludge solids}} = \frac{Q \cdot C_{\text{SO,AS}}}{1000 \cdot d_{\text{AS}} \cdot 24 \cdot 3600} \quad 27$$

with  $C_{\text{SO,AS}}$  ( $\text{kg}\cdot\text{m}^{-3}$ ) and  $d_{\text{AS}}$  ( $\text{kg}\cdot\text{L}^{-1}$ ) as shown in Table 6. For the solids leaving the STP via effluent, the volume flow rate equals:

$$ADV_{\text{effluent solids}} = \frac{Q \cdot C_{\text{SO,SLS}}}{1000 \cdot d_{\text{AS}} \cdot 24 \cdot 3600} \quad 28$$

with  $C_{\text{SO,SLS}}$  ( $\text{kg} \cdot \text{m}^{-3}$ ) shown in Table 6. The volume flow rate of surplus sludge or wasted sludge solids is:

$$ADV_{\text{surplus solids}} = \frac{\text{SU}}{1000 \cdot d_{\text{AS}} \cdot 24 \cdot 3600} \quad 29$$

with SU in  $\text{kg} \cdot \text{PE}^{-1} \cdot \text{d}^{-1}$  as calculated according to Table 9. Both  $ADV_{\text{effluent solids}}$  and  $ADV_{\text{surplus solids}}$  reflect the solids emission, expressed as volume flow rates, by the activated sludge process. The equation for  $ADV_{\text{activated sludge solids}}$  is part of the internal sludge recycling. There are two other flows of activated sludge solids. The difference in solids volume flow rates between the activated sludge inflow (eqn 27) and the effluent solids outflow (eqn 28) is equal to the sedimentation rate in the solids liquid separator expressed as solids volume flow rate:

$$ADV_{\text{sedimentation SLS}} = ADV_{\text{activated sludge solids}} - ADV_{\text{effluent solids}} \quad 30$$

Recycling of the sludge solids (return sludge) is the difference between sedimentation and the production of wasted (surplus) sludge (see Figure 4):

$$ADV_{\text{return sludge solids}} = ADV_{\text{sedimentation SLS}} - ADV_{\text{surplus solids}} \quad 31$$

## 5.2 Diffusive transport

Diffusive transport processes are driven by non-equilibrium concentrations in adjacent phases. In the model, these are the solids-water and air-water interphases. Partition coefficients for solids-water ( $K_p$ ) and air-water ( $K_{\text{AW}}$ ) are input parameters necessary to quantify the extent to which the actual concentrations deviate from the equilibrium concentration. Diffusive transport across the interphase is proportional to the departure from the equilibrium concentration. Also, for diffusive transport, volume flow rates (symbol XCH) are derived in  $\text{m}^3 \cdot \text{v}^{-1}$ . XCH is called the mass transfer coefficient, which has to be multiplied by the concentration in the source phase (in  $\text{g} \cdot \text{m}^{-3}$ ) to obtain the mass flow ( $\text{g} \cdot \text{s}^{-1}$ ). Diffusive mass flows should be evaluated for both directions, i.e. both  $XCH_{i,j}$  for transport from  $i$  to  $j$  and  $XCH_{j,i}$  for transport from medium  $j$  to medium  $i$ .

Table 14 Fixed parameters for deriving diffusive volume flow rates (Mackay et al., 1985)

symbol	Meaning	Units	Value
$k_{PS}$	First-order rate constant for (de)sorption in PS	$s^{-1}$	$1.925 \cdot 10^{-4}$
$k_{SLS}$	First-order rate constant for (de)sorption in SLS	$s^{-1}$	$1.925 \cdot 10^{-4}$
$k_{AS}$	First-order rate constant for (de)sorption in AS	$s^{-1}$	$1.925 \cdot 10^{-3}$
$K_{air}$	Mass transfer coefficient in air	$m \cdot s^{-1}$	$2.78 \cdot 10^{-3}$
$K_{water}$	Mass transfer coefficient in water	$m \cdot s^{-1}$	$2.78 \cdot 10^{-5}$

Table 14 contains fixed rate constants required for deriving diffusive volume flow rates. The first-order rate constants for sorption and desorption in this table are derived from a half-life of one hour for uptake by suspended particles (sorption) or clearance (desorption) in the primary settler and the solids-liquid separator. This figure was applied by Mackay et al. (1985) for (de)sorption processes in suspended particles in natural freshwater systems. The primary clarifier and the solids-liquid separator considered here are lakes or lagoons. The activated sludge reactor, however, is a heavily aerated system and therefore (de)sorption is assumed to be significantly faster. It is assumed that the half-life is a factor of ten lower, i.e. 0.1 hour. This half-life is fairly well in agreement with the data obtained by Dobbs et al. (1989) through experiment. They observed equilibrium in approximately one hour.

Table 15 Dependent parameters for deriving diffusive volume flow rates

Symbol	Meaning	Units	Equation	Value
$V_{PS}$	Volume of suspended solids in PS	$m^3 \cdot PE^{-1}$	$\frac{VOL_{PS} \cdot C_{SO,PS}}{1000 \cdot d_S}$	$1.67 \cdot 10^{-6}$
$V_{AS}$	Volume of suspended solids in AS	$m^3 \cdot PE^{-1}$	$\frac{VOL_{AS} \cdot C_{SO,AS}}{1000 \cdot d_{AS}}$	$2.95 \cdot 10^{-4}$
$V_{SLS}$	Volume of solids in SLS	$m^3 \cdot PE^{-1}$	$\frac{VOL_{SLS} \cdot C_{SO,SLS}}{1000 \cdot d_{AS}}$	$2.88 \cdot 10^{-7}$

The volumes of the suspended solids phases in Table 15 are calculated according to (default) values in Tables 1 to 9.

#### 5.2.1 Non-equilibrium at the suspended solids-water interphase

Interphase transport is reversible and the volume flow rates have to be evaluated for both directions across the interphase. In Table 16, the diffusive volume flow rates (XCH) are listed. XCH is a *reversible* diffusive volume flow rate and, in the equations for XCH partition, coefficients of the chemical ( $K_{PS}$  and  $K_{AS}$ ) appear which are related to a chemical property.

#### 5.2.2 Reversible air-water transfer without aeration

Diffusive transport to air is thought to occur exclusively from the water phase. The NEUTRAL chemical is available for volatilization processes only if it is purely dissolved. The rate of these processes depends on how far the actual

concentrations deviate from the equilibrium concentrations in air and water. Both in the primary clarifier and in the solids liquid separator, air-water transport is simulated using a two-layer model. A gas phase resistance in series with a water phase resistance was applied by Liss & Slater (1974) and extended by Mackay & Leinonen (1975). According to Mackay et al. (1985), expressions for XCH are formulated in Table 17 for volatilization/gas absorption in basins without engineered aeration. For the aerator, the mass transport coefficients in Table 17 are considered baseline transport coefficients, reflecting (reversible) mass transfer as if the aeration basin is a lake or lagoon.

Table 16 Mass transfer coefficients at the solids water interphase ( $m^3 \cdot s^{-1} \cdot PE^{-1}$ )

Symbol	Equation
$XCH_{\text{water-solids PS}}$	$\frac{k_{PS}}{\frac{1}{VOL_{PS}} + \frac{1}{V_{PS} \cdot K_{PS} \cdot d_S}}$
$XCH_{\text{solids-water PS}}$	$\frac{k_{PS}}{\frac{K_{PS} \cdot d_S}{VOL_{PS}} + \frac{1}{V_{PS}}}$
$XCH_{\text{water-solids AS}}$	$\frac{k_{AS}}{\frac{1}{VOL_{AS}} + \frac{1}{V_{AS} \cdot K_{PAS} \cdot d_{AS}}}$
$XCH_{\text{solids-water AS}}$	$\frac{k_{AS}}{\frac{K_{PAS} \cdot d_{AS}}{VOL_{AS}} + \frac{1}{V_{AS}}}$
$XCH_{\text{water-solids SLS}}$	$\frac{k_{SLS}}{\frac{1}{VOL_{SLS}} + \frac{1}{V_{SLS} \cdot K_{PAS} \cdot d_{AS}}}$
$XCH_{\text{solids-water SLS}}$	$\frac{k_{SLS}}{\frac{K_{PAS} \cdot d_{AS}}{VOL_{SLS}} + \frac{1}{V_{SLS}}}$

### 5.2.3

#### *Reversible air-water transfer due to aeration*

In addition to baseline mass transfer in the aeration tank, shown in Table 17, air-water exchange of chemicals in the aerator is enhanced by engineered aeration. The expressions for the aerator in Table 17 may be regarded as the minimal mass transport coefficient for air-water exchange. At least for chemicals with a volatility higher than  $H = 50 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ , aeration causes increased removal rates due to stripping. The two types of stripping processes distinguished in SimpleTreat are surface aeration and bubble aeration. Several expressions for first-order rate constants have been reported.

Surface aeration. Roberts et al. (1984) derived an expression for the first-order rate constant for surface aeration. They ignored the correction for the gas phase resistance and instead considered a proportionality constant equal to 0.6 to be satisfactory. This is, however, appropriate for volatile chemicals. This approximation has been shown adequate only if  $H$  exceeds  $250 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$  ( $K_{AW} = 0.1$ ). This means that liquid layer resistance controls the rate of interphase mass transfer. The equation of Roberts et al. (1984), modified by a

factor accounting for the gas phase resistance (GPC) for chemicals with  $H < 250 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ , would have the following form:

$$k_s = \text{GPC} \frac{\text{OxReq}}{3600 \cdot \text{HRT}_{\text{AS}} \cdot \Delta\text{O}_2} \quad 32$$

with

$k_s$  : first-order transfer rate constant for surface aeration [ $\text{s}^{-1}$ ]

*Table 17 Mass transfer coefficients at the air-water interphase without aeration ( $\text{m}^3\cdot\text{s}^{-1}\cdot\text{PE}^{-1}$ ). Subscript NA (no aeration) is used here to refer to the activated sludge reactor without engineered aeration.*

Symbol	Equation
$\text{XCH}_{\text{water-air PS}}$	$\frac{\text{AREA}_{\text{PS}}}{\frac{1}{K_{\text{air}} \cdot K_{\text{AW}}} + \frac{1}{K_{\text{water}}}}$
$\text{XCH}_{\text{air-water PS}}$	$\frac{\text{AREA}_{\text{PS}}}{\frac{1}{K_{\text{air}}} + \frac{K_{\text{AW}}}{K_{\text{water}}}}$
$\text{XCH}_{\text{water-air NA}}$	$\frac{\text{AREA}_{\text{AS}}}{\frac{1}{K_{\text{air}} \cdot K_{\text{AW}}} + \frac{1}{K_{\text{water}}}}$
$\text{XCH}_{\text{air-water NA}}$	$\frac{\text{AREA}_{\text{AS}}}{\frac{1}{K_{\text{air}}} + \frac{K_{\text{AW}}}{K_{\text{water}}}}$
$\text{XCH}_{\text{water-air SLS}}$	$\frac{\text{AREA}_{\text{SLS}}}{\frac{1}{K_{\text{air}} \cdot K_{\text{AW}}} + \frac{1}{K_{\text{water}}}}$
$\text{XCH}_{\text{air-water SLS}}$	$\frac{\text{AREA}_{\text{SLS}}}{\frac{1}{K_{\text{air}}} + \frac{K_{\text{AW}}}{K_{\text{water}}}}$

In Table 18, values are given according to the aeration regime. The parameters  $\text{HRT}_{\text{AS}}$  and  $\text{OxReq}$  are dependent on the operation mode of the STP and are shown in Table 7. The gas phase resistance correction, recommended by Munz & Roberts (1989), depends on the air-water partition coefficient  $K_{\text{AW}}$  of the chemical:

$$\text{GPC} = \frac{\frac{k_{\text{Ga}}}{k_{\text{La}}} \cdot K_{\text{AW}}}{\frac{k_{\text{Ga}}}{k_{\text{La}}} \cdot K_{\text{AW}} + 1} \quad 33$$

The mass transfer rate constants  $k_{\text{Ga}}$  and  $k_{\text{La}}$  are given in Table 18. They are calculated as the quotient of the mass transfer rate coefficients,  $K_{\text{air}}$  (Table 14),

and the air mixing height (Table 13) and as the quotient of  $K_{\text{water}}$  (Table 14) and the depth of the aeration basin (Table 6), respectively.

*Table 18 Default parameters required to compute water-air exchange in an aerated system*

Symbol	Meaning	units	Value
$\Delta O_2$	$Co_{x_{\text{sat}}} - Co_{x_{\text{AS}}}$	$\text{kg O}_2 \cdot \text{m}^{-3}$	0.007
$Co_{x_{\text{sat}}}$	Saturation $O_2$ concentration	$\text{kg O}_2 \cdot \text{m}^{-3}$	0.009
$Co_{x_{\text{AS}}}$	Actual $O_2$ concentration in activated sludge	$\text{kg O}_2 \cdot \text{m}^{-3}$	0.002
$k_{\text{Ga}}$	Gas phase mass transfer rate constant	$\text{s}^{-1}$	$2.78 \cdot 10^{-4}$
$k_{\text{La}}$	Liquid phase mass transfer rate constant	$\text{s}^{-1}$	$9.27 \cdot 10^{-6}$
G	Aeration rate bubble aeration	$\text{m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$	$1.31 \cdot 10^{-5}$

Applying the equation for GPC, instead of the factor of 0.6, extends the validity  $k_s$  to chemicals with  $H < 250 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$  ( $K_{\text{AW}} < 0.1$ ) when the gas phase resistance has to be taken into account.

Bubble aeration. If oxygen is supplied by bubble or diffuse aeration, the first-order rate constant of air-water exchange proposed by Hsieh et al. (1993) is applied in the SimpleTreat model:

$$k_b = 8.9 \cdot 10^{-4} \frac{G}{\text{VOL}_{\text{AS}}} H^{1.04} \quad 34$$

with

$k_b$  : first-order transfer rate constant for bubble aeration [ $\text{s}^{-1}$ ]

This expression is almost similar to the relationship given by Blackburn et al. (1984), used in an earlier version of SimpleTreat. Note that through  $\text{VOL}_{\text{AS}}$  (Table 8) the rate constant  $k_b$  is not only dependent on the sludge loading rate but also on the presence (or not) and mode of operation of the primary clarifier.

*Table 19 Mass transfer coefficients at the air water interphase of an aerated activated sludge reactor ( $\text{m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$ ), either by surface aeration ( $k_s$ ) or by bubble aeration ( $k_b$ )*

Symbol	Equation
$\text{XCH}_{\text{water-air aeration}}$	$\frac{k_{s,b}}{\frac{1}{\text{VOL}_{\text{AS}}} + \frac{1}{\text{AREA}_{\text{AS}} \cdot h \cdot K_{\text{AW}}}}$
$\text{XCH}_{\text{air-water aeration}}$	$\frac{k_{s,b}}{\frac{K_{\text{AW}}}{\text{VOL}_{\text{AS}}} + \frac{1}{\text{AREA}_{\text{AS}} \cdot h}}$

Engineered aeration combined with baseline volatilization and gas absorption

Mass transfer coefficients for mechanical or bubble aeration are given in Table 19. These are added to mass transfer coefficients for baseline volatilization and gas absorption (Table 17) to obtain the overall mass transfer coefficient for volatilization of the chemical:

$$XCH_{\text{water-air}}(\text{overall}) = XCH_{\text{water-air NA}} + XCH_{\text{water-air aeration}} \quad 35$$

and for gas absorption:

$$XCH_{\text{air-water}}(\text{overall}) = XCH_{\text{air-water NA}} + XCH_{\text{air-water aeration}} \quad 36$$

Mikkelsen (1995) also proposed calculating the overall interphase transfer rate constant as the sum of surface volatilization/gas absorption and stripping. For a given sludge loading rate, the air-water interphase mass transfer coefficient (XCH) is plotted versus  $K_{AW}$  in Fig 5. Mass transfer coefficients for volatilization and gas absorption without aeration are higher than for surface or bubble aeration for  $K_{AW} < 0.025$ .

With inserted parameters that are typical for an activated sludge reactor ( $G$ ,  $\Delta O_2$  etc.), surface aeration is more efficient than bubble aeration up to  $K_{AW} = 1$ .

Figure 5 shows interphase transfer coefficients applied in SimpleTreat 4.0. This figure shows that combined transfer coefficients with surface aeration (black) are higher than for bubble aeration (blue) if  $K_{AW}$  is below 1.

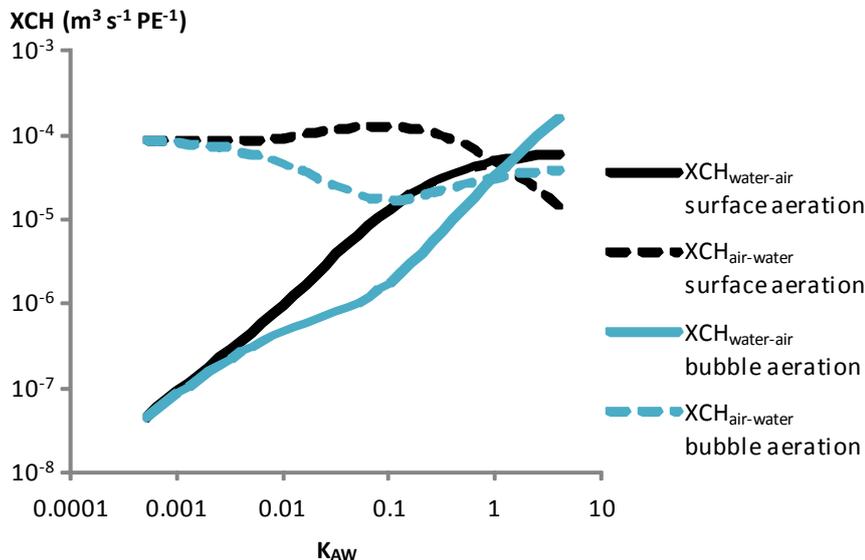


Figure 5 Surface aeration compared with bubble aeration in the activated sludge reactor. The overall mass transfer coefficients are plotted versus  $K_{AW}$

### 5.3 Degradation processes

In activated sludge. Although, before the chemical enters an STP, it can be degraded and this process can also occur in the primary clarifier, it is assumed that elimination through degradation can only occur in the aeration tank. In the

activated sludge reactor, the degradation process can occur in the water phase only or in both the water and solids phases according first-order kinetics. If the half-life of a chemical in activated sludge ( $t_{1/2a}$ ) is measured, for example, by means of a test guideline OECD 314, the first-order rate constant ( $k_{AS}$ ) is calculated according to:

$$k_{AS\ water} = k_{AS\ solids} = \frac{\ln 2}{t_{1/2a}} \quad 37$$

By converting the units of  $k_{AS\ water}$  and  $k_{AS\ solids}$  from reciprocal hours or days into reciprocal seconds, the first-order degradation rate constants in box 5 (water) and box 6 (activated sludge solids),  $k_5$  and  $k_6$  respectively, are derived (see equation 21). If measured half-lives are not available, the first rate constant of the chemical in the aqueous phase of activated sludge,  $k_{AS\ water}$ , is estimated on the bases of test results according to the OECD 301 series as described in a guidance report (Struijs, 2014). In SimpleTreat 4.0, rate constants by the TGD (2003) are suggested (Appendix E).

The anaerobic digester. Nowadays, most STPs are equipped with an anaerobic digesting installation. Combined sludge is transferred to anaerobic digesters (flow indicated as number 8 in Figure 2) which most often operate as batch or plug-flow systems with a rather long residence time (RT) of 30 to 60 days. Anaerobic biodegradation is particularly relevant for chemicals with a high solids-water partition coefficient. A first-order rate constant for anaerobic biodegradation cannot be entered into the box-modelling system directly. Instead, the half-life for elimination of the chemical in the anaerobic digester is applied to calculate an attenuation factor for the concentration of the chemical in combined sludge. The chemical concentration in combined sludge multiplied by this factor yields the chemical flux via solids that reaches the soil. This attenuation factor is the anaerobic reduction factor (ARF) due to anaerobic biodegradation processes in the digesting tank. It depends on the measured residence time (ResdT) and is a function of the measured half-life ( $t_{1/2an}$ ):

$$ARF = 2^{-\frac{ResdT}{t_{1/2an}}} \quad 38$$

The model does not perform this calculation. The user has to evaluate ARF from ResdT and  $t_{1/2an}$ .

#### 5.4 Chemical loading via the sewer

A chemical with property  $Kp_s$  enters an STP of size N person equivalents (PE) through both the aqueous phase and the solids phase. If the discharge rate of the chemical is E kg per day, the nominal concentration, distributed over the aqueous phase and the particle phase is given in Table 20.

Table 20 Chemical loading and concentrations in water and solids entering an STP serving  $N$  inhabitants.

Symbol	Meaning	Units	Equation
$E$	Emission rate of the chemical	$\text{kg}\cdot\text{d}^{-1}$	-
$C_0$	Nominal concentration of the chemical in raw sewage	$\text{g}\cdot\text{m}^{-3}$	$\frac{E \cdot 1000}{Q \cdot N}$
$W_s$	Concentration in sewage in aqueous medium	$\text{g}\cdot\text{m}^{-3}$	$\frac{C_0}{1 + K_{p_s} \cdot \frac{SO}{Q} \cdot \frac{1}{1000}}$
$S_s$	Concentration in sewage associated with solids	$\text{g}\cdot\text{m}^{-3}$	$C_0 - W_s$
$SO_s$	Concentration in sewage solids (dry weight)	$\text{mg}\cdot\text{kg}^{-1}$	$\frac{C_0 \cdot K_{p_s}}{1 + K_{p_s} \cdot \frac{SO}{Q} \cdot \frac{1}{1000}}$
$SO_{s \text{ VOL}}$	Concentration in sewage solids medium (dry weight)	$\text{g}\cdot\text{m}^{-3}$	$\frac{C_0 \cdot K_{p_s} \cdot d_s}{1 + K_{p_s} \cdot \frac{SO}{Q} \cdot \frac{1}{1000}}$

In the model, concentrations in only two media in sewage are defined, i.e. the aqueous phase and the solids phase of raw sewage (Figure 4):

$$C(0,2) = W_s \quad 39$$

$$C(0,3) = SO_{s \text{ VOL}} \quad 40$$

The concentrations in media flowing out of the system are given as  $C(i,0)$  in Figure 3. However, these concentrations are equal to the steady state concentrations in box  $i$ .

## 6 Model output

The concentration (in units of g per m<sup>3</sup> medium) in medium i flowing out of the system ( $C_{i,0}$ ) is the primary output of the box model computation. There are 5 concentrations which are used as follows:

1. Directly:
  - a. the concentration in air can be used to assess occupational,
  - b. primary sludge and secondary sludge in g per m<sup>3</sup> dry weight (is equal to mg per L dry weight). Most often these concentrations are converted into units of mg chemical per kg dry matter by multiplying with the density of dry matter ( $d_S$  or  $d_{AS}$  in kg per L).
2. To obtain derived concentrations
  - a. Concentration in combined sludge: primary and secondary (wasted) sludge;
  - b. Concentration in digested sludge;
  - c. Concentration in activated sludge (mixed liquor);
  - d. Concentration in effluent (combined dissolved and sorbed to particles).
3. Multiplied by the appropriate advective flow rates ( $ADV_{i,0}$ ) to obtain
  - a. Absolute chemical mass fluxes to air, water and soil in appropriate units;
  - b. Relative chemical mass fluxes (%).

### 6.1 Emission to air

The fraction of the chemical emitted to air ( $E_{air}$ ) by an STP of the size of N inhabitants is:

$$E_{air} = 3600 \cdot 24 \cdot \frac{C_1 \cdot ADV_{1,0} \cdot \sqrt{N}}{1000 \cdot E} \quad 41$$

### 6.2 Emission to water

The total concentration ( $C_T$  in mg·L<sup>-1</sup>) in effluent discharged into the receiving water body is:

$$C_T = C_7 + C_8 \cdot \frac{C_{SO,SLS}}{1000 \cdot d_{AS}} \quad 42$$

The concentration in effluent suspended solids is  $C_8/d_{AS}$  (mg·kg<sup>-1</sup>). The fraction ( $E_{eff}$ ) of the chemical input that leaves an STP serving N inhabitants via effluent is:

$$E_{eff} = \frac{C_T \cdot Q \cdot N}{1000 \cdot E} \quad 43$$

### 6.3 Emission via combined sludge

Without anaerobic treatment of the combined sludge, the fraction ( $E_{\text{sludge}}$ ) of the chemical leaving an STP of  $N$  people equals

The concentration in combined sludge ( $C_{\text{CS}}$  in mg/kg dry weight) equals

$$E_{\text{sludge}} = \frac{C_4 \cdot \text{ADV}_{4,0} + C_9 \cdot \text{ADV}_{9,0}}{1000 \cdot E} \cdot N$$

$$= \frac{\frac{\text{FS} \cdot \text{SO}}{1000 \cdot d_{\text{RS}}} \cdot C_4 + \frac{\text{SU}}{1000 \cdot d_{\text{AS}}} \cdot C_9}{1000 \cdot E} \cdot N$$
44

### 6.4 Emission via digested sludge

With anaerobic treatment of combined sludge, the anaerobic reduction factor (ARF) has to be taken into account for the fraction of the chemical emitted by digested sludge:

$$E_{\text{dig sludge}} = \text{ARF} \cdot E_{\text{sludge}}$$
46

The user has to calculate  $E_{\text{dig sludge}}$  from model output  $E_{\text{sludge}}$  and the manually computed ARF.

The concentration of the chemical in digested sludge ( $C_{\text{DS}}$  in mg/kg dry weight) is determined by the concentration in combined sludge ( $C_{\text{CS}}$ ), the anaerobic reduction factor (ARF) and the reduction of the dry weight volume of the combined sludge due to conversion into  $\text{CO}_2$  and methane. It is assumed that that this volume is reduced by 50 %:

$$C_{\text{DS}} = \frac{\text{ARF} \cdot C_{\text{CS}}}{0.5}$$
47

The user has to calculate  $C_{\text{DS}}$  from model output  $C_{\text{CS}}$  and ARF, the latter is manually computed.

### 6.5 Concentration in activated sludge

The total concentration ( $C_{\text{T act sl}}$  in  $\text{mg} \cdot \text{L}^{-1}$ ) in activated sludge, i.e. the slurry also known as mixed liquor, equals

## 7 Discussion

Verification of the revised model was conducted as follows. Parameters that can be chosen in SimpleTreat 4.0 were set at fixed values applied in SimpleTreat 3.1. Also some parameters that cannot be selected by the model user, such as the concentration of suspended solids in effluent, were set equal to those in the old version. Both models were tested against a set of chemicals in Table E1 of Appendix D to compare relative and absolute emissions. The results were identical.

### 7.1 BOD removal characterized by the sludge loading rate

Both in version 3.1 and version 4.0, the engineered environment in which SimpleTreat models the fate of a chemical may be conceived as an aqueous system that removes BOD. It is an aerated slurry (activated sludge or mixed liquor) that degrades BOD to an extent determined by the sludge loading rate (SLR), a characteristic that defines the operating mode of the activated sludge process. The hydraulic retention time and sludge retention time are both dependent on the chosen value of SLR (see Table 8 and equation 4). A low value for SLR, for example 0.1 kg BOD per kg dry weight activated sludge per day, is typical for a high BOD removal. A relatively high SLR (for example 0.3) is associated with relatively short retention times of water and sludge and lower BOD removal.

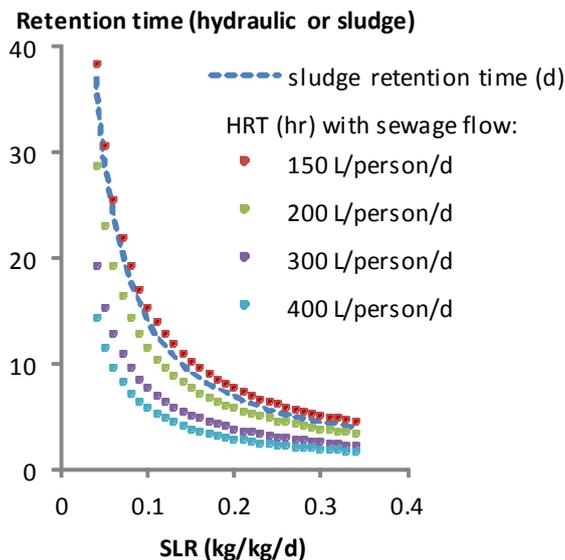


Figure 6 Hydraulic retention time depends on the SLR and the daily volume per person if BOD per person per day stays constant

Default settings (hydraulic retention time and sludge retention time for varying SLR) with respect to the composition of wastewater are shown in Table C1 in Appendix C. Domestic sewage in the EU has a default composition of 0.3 g/L BOD and 0.45 g/L solids. Note that, for a similar value of SLR, the hydraulic retention time for an STP without primary sedimentation is longer than the hydraulic retention time for a system equipped with a primary clarifier. This is explained from the consideration that the primary clarifier removes 36 % of the

BOD of raw sewage. Without primary sedimentation, the activated reactor receives significantly more BOD per volume of sewage per capita than it does after primary sedimentation. For a similar SLR, the hydraulic retention time must be longer if the BOD input is higher. This may be understood from the dimensions of the sludge loading rate, i.e. amount of BOD per amount of activated sludge (mass solids) per time. Here "time" should be interpreted as the hydraulic retention time. As a consequence, a non-sorptive chemical that is partly eliminated because it is volatile and/or biodegradable is removed at a higher rate in a system without primary clarifier. Table C1 shows that, for a fixed SLR, the associated hydraulic retention time is longer. This will cause a higher rate of volatilization and biodegradation. In the past, such a counter-intuitive outcome has evoked questions such as "if the primary clarifier removes nothing at all, the rest of the system should function similarly". Different BOD inputs per volume of sewage is associated with different volumes of the aeration tank and so also different hydraulic retention times.

## 7.2 Applicability of SimpleTreat to North America

In SimpleTreat 3.1 and 4.0, the amount of BOD produced per capita (60 g) can be chosen. With respect to domestic wastewater, the modeller would rarely overrule this default value because it is typical for domestic sewage. Apparently this is also the case in North America (Swerdfeger, 2014). The daily amount of BOD per person that is discharged into a Canadian sewer seems to be around this value. The BOD concentration in sewage, however, may vary. In North America, the volume of water discharged per capita (Q) is 400 L/d, compared with the European sewage flow rate of 200 L/d. Communal wastewater in North America differs from the European scenario only with respect to the volume of sewage produced per person per day. As the BOD load per person per day is more or less equal to Europe, according to Table 8 the available aeration volume per person on both continents would be equal. As a consequence, the hydraulic retention time in North America is shorter. The SRT, however, depends only on the SLR (see equation 4). In Figure 6 several scenarios are displayed with respect to Q, keeping other properties constant (solids and BOD per person per day).

This raises questions as to the applicability of SimpleTreat in scenarios that reflect a high volume for the same load of BOD per day. For non-sorptive chemicals that are biodegradable and/or volatile, the removal due to biodegradation and volatilization may be underestimated in the North American scenario due to a hydraulic retention time that is significantly shorter (Figure 6). For sorptive chemicals, the difference is less because the sludge retention time is affected only by the SLR and not by the HRT. The values in Table C1 are apparently typical for the European situation (60 g BOD in 200 L sewage produced by one European). Therefore, Table C1 also shows the HRTs that SimpleTreat (3.1 and 4.0) would calculate for North America (Q = 400 L/p/day). To adjust the model so that it is also suitable for North America, the calculated hydraulic retention time (Table 8) may be multiplied by a factor of two. This factor has not yet been implemented in the model and therefore SimpleTreat should be used with care for a scenario with sewage flow in the range of 400 to 450 L/p/d.

## 7.3 Applicability of SimpleTreat to industrial wastewater

It is expected that the adjustment through a certain factor, as is done for STPs in North America, is also needed here to simulate biological treatment of

industrial wastewater. In the range of plausible sludge loading rates, the hydraulic retention times of the activated sludge process are apparently confined within a certain range quotient of the amount of BOD and the volume of sewage.

Both in version 3.1 and 4.0, the BOD input to the aerator only varies due to a choice with respect to the mode of operation. This can be the scenario with or without primary sedimentation (in both 3.1 and 4.0). A new feature is that with primary sedimentation, the parameters FS (fraction solids removed by the primary clarifier) and FB (fraction of BOD in solids) allows a wider variation of settled wastewater that flows into the aerator and therefore also the BOD input to the aerator. This affects the hydraulic retention time of the activated sludge process.

By varying the fraction of sewage solids that is removed by the primary sedimentation (FS), the BOD input to the aeration tank is affected. This is because part of the BOD in raw sewage is present in the solids, a default fraction of 2/3 of which is settled. In SimpleTreat 3.1, that fraction was fixed (Figure 7a). The distribution of BOD in raw sewage over the solids and aqueous phases (FB) was also fixed at 0.54 in SimpleTreat 3.1. In the revised version, FB can be varied (Figure 7b). The default is 0.54, which is typical for domestic sewage. As a consequence, the fraction of BOD eliminated by the primary clarifier ( $FP = FS \cdot FB$ ) was fixed in SimpleTreat 3.1, but is now variable in version 4.0 through choosing other values for FS and FB (Figure 7c).

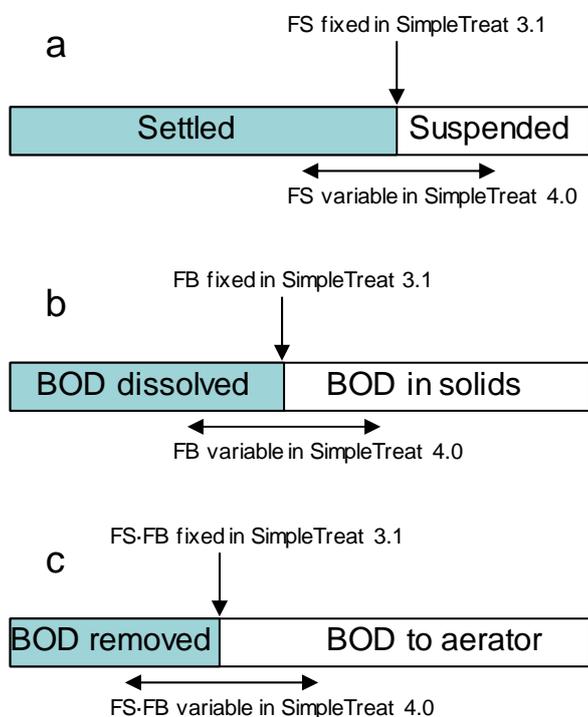


Figure 7 Properties of raw and settled sewage. FS and FB indicate default values in SimpleTreat 4.0

Choosing the parameters in Table 1 and Table 2 enables the simulation of industrial wastewater for at least the food sector and so also the fate of a chemical in an industrial treatment installation.

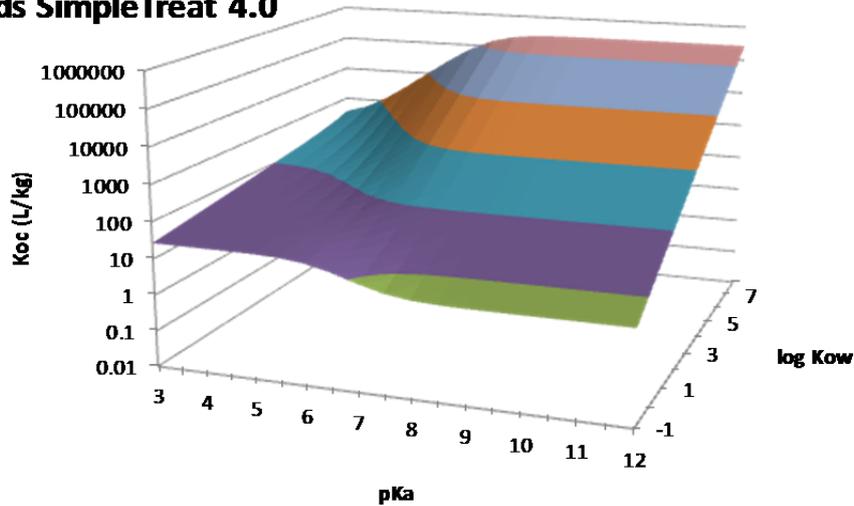
## 7.4 Estimation of Koc

If measured sludge-water partition coefficients or organic carbon-water partition constants (Koc) are not available, somehow an estimate has to be made. Equation 18 gives an expression for monovalent organic acids. Figure 8 illustrates how Koc estimated by version 4.0 deviates from SimpleTreat 3.1.

Note that, in ranges pKa 3 to 7 and log Kow -1 to 3, covering a fair share of organic acids, estimated Koc values may be underestimated by version 3.1 up to a factor 3,000.

For organic bases, the difference is even bigger (Figure 9).

### Acids SimpleTreat 4.0



### Acids SimpleTreat 3.1

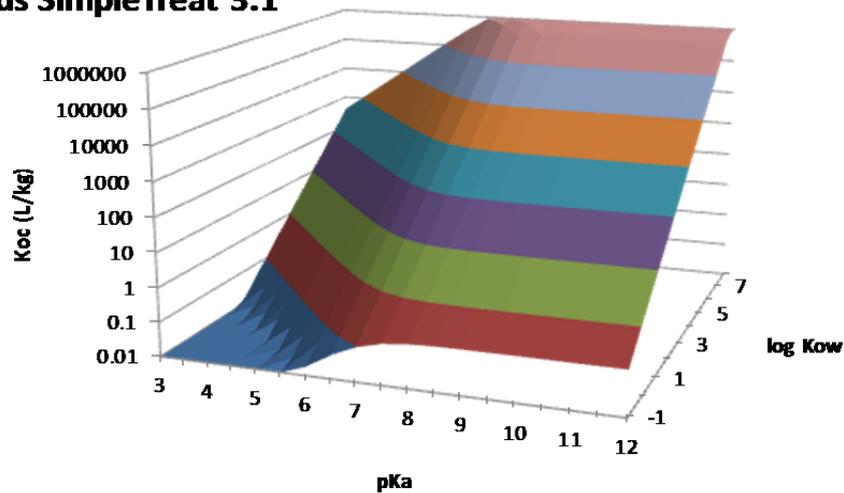


Figure 8 Koc of organic acids estimated by SimpleTreat 4.0 compared with version 3.1

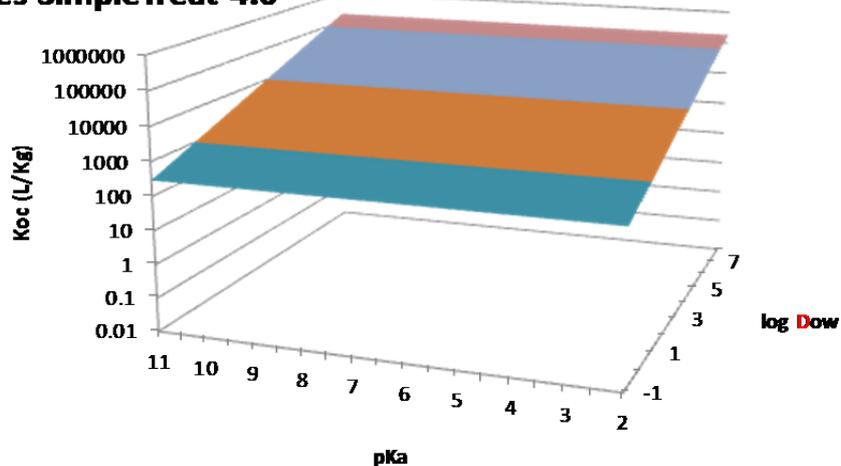
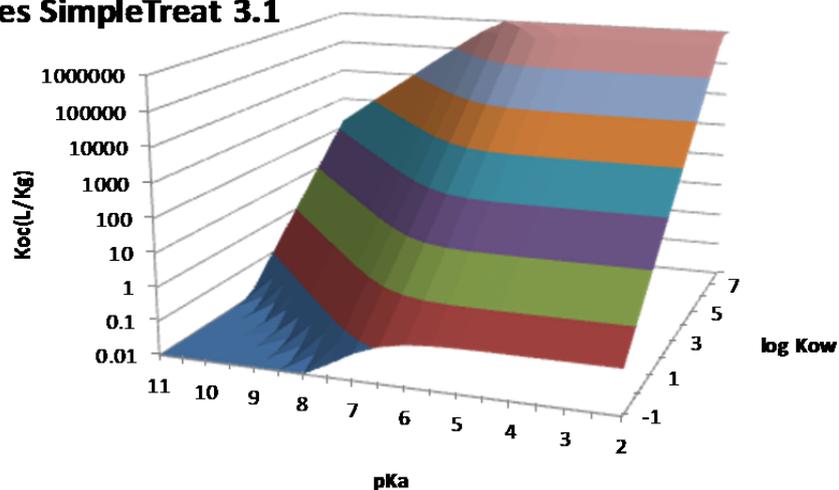
**Bases SimpleTreat 4.0****Bases SimpleTreat 3.1**

Figure 9  $K_{oc}$  of organic bases estimated by SimpleTreat 4.0 compared with version 3.1

### 7.5 Default SLR and fixed suspended solids in effluent

The fixed parameter with respect to the concentration of suspended solids has been adjusted by a factor of 4. The concentration in SimpleTreat 3.1 was set at 30 mg dry weight/L and could be varied by the modeller. In version 4.0, it is set at 7.5 mg dry weight/L, which better reflects modern installations that treat domestic wastewater.

The default value for the sludge loading rate (SLR) is now 0.1, instead of 0.15 kg/kg/d. The increase of the treatment rate in the EU and therefore also the average loading of STPs justifies this new default.



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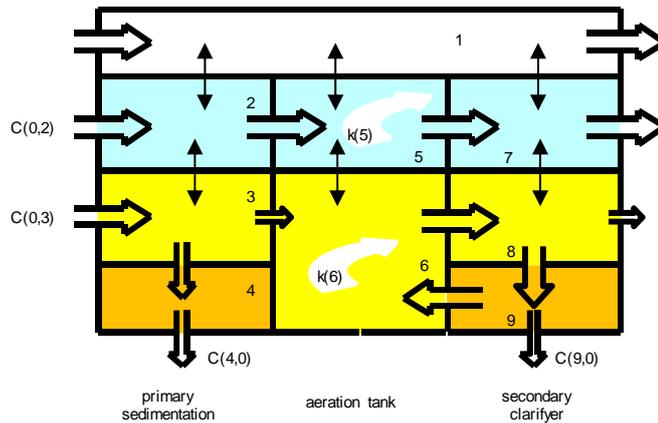
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9 *Appendix A Parameters and mass balance equations*



*Figure A1 Box representation of an STP with a primary clarifier. Advection (irreversible transport) is depicted as open arrows representing media flows, intermedia transport (reversible transport) as two-headed arrows and degradation in compartment  $i$  by curved arrows*

The volumes of the nine boxes of Figure A1 are given per person equivalent (PE) for default settings in Table A1. In the second column, symbols are displayed as given in the main text of the report. Note that the sediment volumes in the primary and secondary clarifiers are equivalent to the solids production per inhabitant per day, i.e. sewage solids and surplus sludge, respectively.

Table A1 Volumes of the nine boxes per inhabitant

$V_i$	Equation	default value ( $m^3 \cdot PE^{-1}$ )
$V_1$	$h \cdot (AREA_{PS} + AREA_{AS} + AREA_{SLS})$	0.53
$V_2$	$\frac{Q \cdot HRT_{PS}}{24}$	$1.67 \cdot 10^{-2}$
$V_3$	$\frac{V_2 \cdot (1 - FS) \cdot C_{SO,S}}{1000 \cdot d_S}$	$1.67 \cdot 10^{-6}$
$V_4$	$\frac{SO \cdot FS \cdot 1(d)}{1000 \cdot d_S}$	$4.17 \cdot 10^{-5}$
$V_5$	$\frac{Q \cdot OxReq}{k_{SLR} \cdot C_{SO,AS}}$	$9.58 \cdot 10^{-2}$
$V_6$	$\frac{V_5 \cdot C_{SO,AS}}{1000 \cdot d_{AS}}$	$2.95 \cdot 10^{-4}$
$V_7$	$\frac{Q \cdot HRT_{SLS}}{24}$	$5.0 \cdot 10^{-2}$
$V_8$	$\frac{V_7 \cdot C_{SO,SLS}}{1000 \cdot d_{AS}}$	$2.88 \cdot 10^{-7}$
$V_9$	$\frac{SU \cdot 1(d)}{1000 \cdot d_{AS}}$	$1.67 \cdot 10^{-5}$

Table A2 Irreversible advective transport: volume flow rates for an STP serving  $N$  inhabitants

<b>ADV<sub>i,j</sub></b>	<b>Equation</b>	<b>default value</b>
ADV <sub>0,1</sub>	$\frac{h \cdot WS}{\sqrt{(AREA_{PS} + AREA_{AS} + AREA_{SLS})}}$	$6.9 \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1/2}$
ADV <sub>1,0</sub>	$\frac{h \cdot WS}{\sqrt{(AREA_{PS} + AREA_{AS} + AREA_{SLS})}}$	$6.9 \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1/2}$
ADV <sub>0,2</sub>	$\frac{Q}{24 \cdot 3600}$	$2.31 \cdot 10^{-6} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>2,5</sub>	$\frac{Q}{24 \cdot 3600}$	$2.31 \cdot 10^{-6} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>5,7</sub>	$\frac{Q}{24 \cdot 3600}$	$2.31 \cdot 10^{-6} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>7,0</sub>	$\frac{Q}{24 \cdot 3600}$	$2.31 \cdot 10^{-6} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>0,3</sub>	$\frac{SO}{1000 \cdot d_{RS} \cdot 24 \cdot 3600}$	$6.94 \cdot 10^{-10} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>3,4</sub>	$\frac{FS \cdot SO}{1000 \cdot d_{RS} \cdot 24 \cdot 3600}$	$4.63 \cdot 10^{-10} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>3,6</sub>	$\frac{(1 - FS) \cdot SO}{1000 \cdot d_{RS} \cdot 24 \cdot 3600}$	$2.31 \cdot 10^{-10} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>4,0</sub>	$\frac{FS \cdot SO}{1000 \cdot d_{RS} \cdot 24 \cdot 3600}$	$4.63 \cdot 10^{-10} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>6,8</sub>	$\frac{Q \cdot C_{SO,AS}}{1000 \cdot d_{AS} \cdot 24 \cdot 3600}$	$7.12 \cdot 10^{-9} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>8,0</sub>	$\frac{Q \cdot C_{SO,SLS}}{1000 \cdot d_{AS} \cdot 24 \cdot 3600}$	$1.34 \cdot 10^{-11} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>8,9</sub>	$\frac{Q \cdot (C_{SO,AS} - C_{SO,SLS})}{1000 \cdot d_{AS} \cdot 24 \cdot 3600}$	$7.11 \cdot 10^{-9} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>9,0</sub>	$\frac{SU}{1000 \cdot d_{AS} \cdot 24 \cdot 3600}$	$2.29 \cdot 10^{-10} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>9,6</sub>	$\frac{Q \cdot (C_{SO,AS} - C_{SO,SLS}) - SU}{1000 \cdot d_{AS} \cdot 24 \cdot 3600}$	$6.88 \cdot 10^{-9} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
Sludge decay	$ADV_{3,6} \cdot \frac{d_s}{d_{AS}} + ADV_{9,6} - ADV_{6,8}$	$2.44 \cdot 10^{-11} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$

Table A3 Reversible inter-media transport coefficients ( $m^3 \cdot s^{-1} \cdot PE^{-1}$ )

<b>XCH<sub>i,j</sub></b>	<b>Equation</b>
XCH <sub>1,2</sub>	$\frac{AREA_{PS}}{\frac{1}{K_{air}} + \frac{K_{AW}}{K_{water}}}$
XCH <sub>2,1</sub>	$\frac{AREA_{PS}}{\frac{1}{K_{air} \cdot K_{AW}} + \frac{1}{K_{water}}}$
XCH <sub>2,3</sub>	$\frac{k_{PS}}{\frac{1}{V_2} + \frac{1}{V_3 \cdot K_{PS} \cdot d_S}}$
XCH <sub>3,2</sub>	$\frac{k_{PS}}{\frac{K_{PS} \cdot d_S}{V_2} + \frac{1}{V_3}}$
XCH <sub>1,5</sub>	$\frac{k_{s,b}}{\frac{K_{AW}}{V_5} + \frac{1}{AREA_{AS} \cdot h}}$
XCH <sub>5,1</sub>	$\frac{k_{s,b}}{\frac{1}{V_5} + \frac{1}{AREA_{AS} \cdot h \cdot K_{AW}}}$
XCH <sub>5,6</sub>	$\frac{k_{AS}}{\frac{1}{V_5} + \frac{1}{V_6 \cdot K_{PAS} \cdot d_{AS}}}$
XCH <sub>6,5</sub>	$\frac{k_{AS}}{\frac{K_{PAS} \cdot d_{AS}}{V_5} + \frac{1}{V_6}}$
XCH <sub>1,7</sub>	$\frac{AREA_{SLS}}{\frac{1}{K_{air}} + \frac{K_{AW}}{K_{water}}}$
XCH <sub>7,1</sub>	$\frac{AREA_{SLS}}{\frac{1}{K_{air} \cdot K_{AW}} + \frac{1}{K_{water}}}$
XCH <sub>7,8</sub>	$\frac{k_{SLS}}{\frac{1}{V_7} + \frac{1}{V_8 \cdot K_{PAS} \cdot d_{AS}}}$
XCH <sub>8,7</sub>	$\frac{k_{SLS}}{\frac{K_{PAS} \cdot d_{AS}}{V_7} + \frac{1}{V_8}}$

In Table A2, all media flow rates are listed. Owing to flow balance considerations, in the last column the default sludge decay rate is given in similar units as those for all solids flow rates. Although the sludge decay rate, expressed as “volume flow rate”, does not occur in the nine mass balance equations that are necessary to compute the nine concentrations in the boxes 1 to 9, it is given in Table A2 to illustrate that, for default settings, sludge decay exceeds solids emission via effluent ( $ADV_{8,0}$ ). Furthermore, sludge decay constitutes more than 10 % of the waste sludge production ( $ADV_{9,0}$ ). Table A3 displays the equations for diffusive interphase transport. No default values are given because mass transfer coefficients ( $XCH_{i,j}$ ) are a function of the equilibrium partition constants.

### Mass balance equations

$$\text{box 1: } C_1 \cdot (XCH_{1,2} + XCH_{1,5} + XCH_{1,7} + ADV_{1,0}) - C_2 \cdot XCH_{2,1} - C_5 \cdot XCH_{5,1} - C_7 \cdot XCH_{7,1} = 0$$

$$\text{box 2: } C_1 \cdot XCH_{1,2} - C_2 \cdot (XCH_{2,1} + XCH_{2,3} + ADV_{2,5}) + C_3 \cdot XCH_{3,2} = -C(0,2) \cdot ADV_{0,2}$$

$$\text{box 3: } C_2 \cdot XCH_{2,3} - C_3 \cdot (XCH_{3,2} + ADV_{3,6} + ADV_{3,4}) = -C(0,3) \cdot ADV_{0,3}$$

$$\text{box 4: } C_3 \cdot ADV_{3,4} - C_4 \cdot ADV_{4,0} = 0$$

$$\text{box 5: } C_1 \cdot XCH_{1,5} + C_2 \cdot ADV_{2,5} - C_5 \cdot (XCH_{5,1} + XCH_{5,6} + ADV_{5,7} + k_5 \cdot V_5) + C_6 \cdot XCH_{6,5} = 0$$

$$\text{box 6: } C_3 \cdot ADV_{3,6} + C_5 \cdot XCH_{5,6} - C_6 \cdot (XCH_{6,5} + ADV_{6,8} + k_6 \cdot V_6) + C_9 \cdot ADV_{9,6} = 0$$

$$\text{box 7: } C_1 \cdot XCH_{1,7} + C_5 \cdot ADV_{5,7} - C_7 \cdot (XCH_{7,1} + XCH_{7,8} + ADV_{7,0}) + C_8 \cdot XCH_{8,7} = 0$$

$$\text{box 8: } C_6 \cdot ADV_{6,8} + C_7 \cdot XCH_{7,8} - C_8 \cdot (XCH_{8,7} + ADV_{8,0} + ADV_{8,9}) = 0$$

$$\text{box 9: } C_8 \cdot ADV_{8,9} - C_9 \cdot (ADV_{9,6} + ADV_{9,0}) = 0$$



10 *Appendix B Mass balance equations for the 6-box model*

This type of communal wastewater treatment plant is visualized by Figure B1. The solids flow is given by Figure B2.

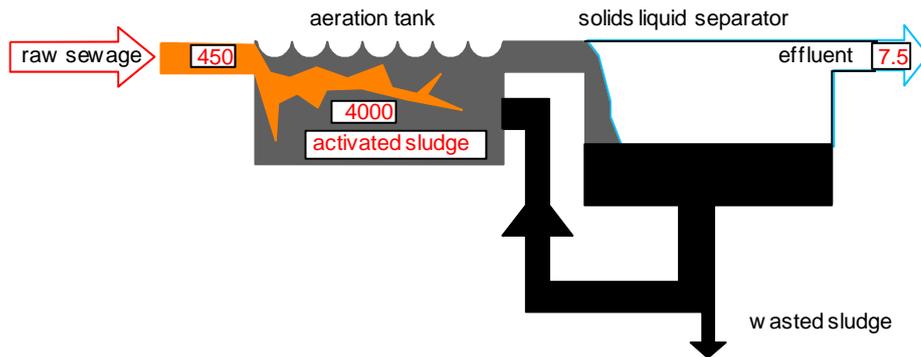


Figure B1 Solids concentration (mg/L) in the distinguished basins of an STP equipped with a primary clarifier

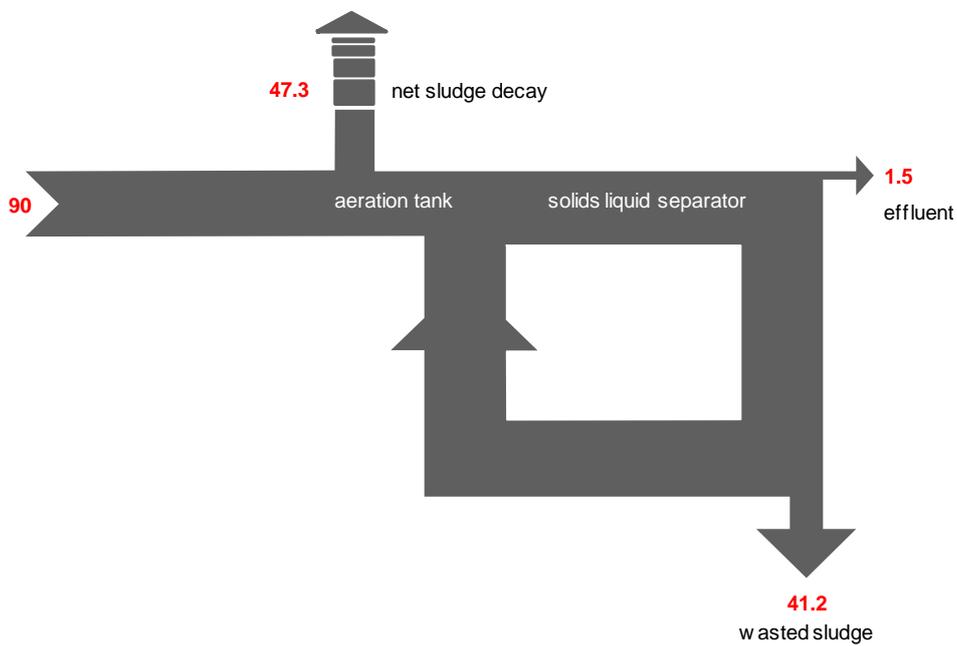


Figure B2 Solids flow in grams per inhabitant per day in an STP without a primary clarifier

The volumes of the six boxes of Figure B3 are given per person equivalent (PE) for default settings in Table B1. In the first column, symbols are displayed as given in the main text of the report. For OxReq the equation given by Table 7 can be used, provided that the parameter FP is set to zero. Derived parameters with respect to the activated sludge process are shown in Table B1. Note that without primary sedimentation, the volume and the area of the aerator are larger as OxReq increases. Also, the wasted sludge production (SU) is higher because OxReq is higher (eqn 3). Note also that the total area of the STP

without primary clarifier, is larger than the total area of an STP with primary clarifier. The reason is that the volume (and area) of an activated sludge reactor treating raw sewage directly is significantly higher due to the fact that OxReq is higher. Therefore, parameters such as  $AREA_{AS}$ ,  $VOL_{AS}$ ,  $HRT_{AS}$  and the production of surplus sludge (SU), which are dependent on OxReq, have subscript 6 to indicate that they pertain to the 6-box model. The parameters related to the secondary clarifier,  $VOL_{SLS}$  and  $AREA_{SLS}$ , do not have the subscript 6 as they are identical to the 9-box scenario.

Table B1 Derived parameters with respect to the activated sludge process.  
 $VOL_{SLS}$  and  $AREA_{SLS}$  are equal to values given in Table 7.

symbol	Meaning	units	equation	default value
$OxReq^6$	Oxygen requirement	$kg \cdot m^{-3}$	$\frac{BOD}{Q}$	0.300
$VOL_{AS}^6$	Volume aerator per person	$m^3 \cdot PE^{-1}$	$\frac{Q \cdot OxReq^6}{k_{SLR} \cdot C_{SO,AS}}$	$1.5 \cdot 10^{-1}$
$AREA_{AS}^6$	Area aerator per person	$m^2 \cdot PE^{-1}$	$\frac{VOL_{AS}^6}{h_{AS}}$	$5.0 \cdot 10^{-2}$
$HRT_{AS}^6$	Hydraulic retention time aerator	hr	$\frac{VOL_{AS}^6}{Q}$	18.0
$SU^6$	Wasted (surplus) sludge	$kg \text{ dwt} \cdot PE^{-1} \cdot d^{-1}$	$Q \cdot (OxReq^6 \cdot F_{BODrem} \cdot Y_{BOD} - C_{SO,SLS})$	$4.1 \cdot 10^{-2}$

Table B2 Volumes of the six boxes per inhabitant. Note that  $V_7$  and  $V_8$  are equal to values in Table A1.

$V_i$	Equation	default value ( $m^3 \cdot PE^{-1}$ )
$V_1$	$h \cdot (AREA_{AS}^6 + AREA_{SLS})$	0.67
$V_5$	$\frac{Q \cdot OxReq^6}{k_{SLR} \cdot C_{SO,AS}}$	$1.5 \cdot 10^{-1}$
$V_6$	$\frac{V_5 \cdot C_{SO,AS}}{1000 \cdot d_{AS}}$	$4.62 \cdot 10^{-4}$
$V_7$	$\frac{Q \cdot HRT_{SLS}}{24}$	$5.0 \cdot 10^{-2}$
$V_8$	$\frac{V_7 \cdot C_{SO,SLS}}{1000 \cdot d_{AS}}$	$2.88 \cdot 10^{-7}$
$V_9$	$\frac{SU^6 \cdot 1(d)}{1000 \cdot d_{AS}}$	$3.17 \cdot 10^{-5}$

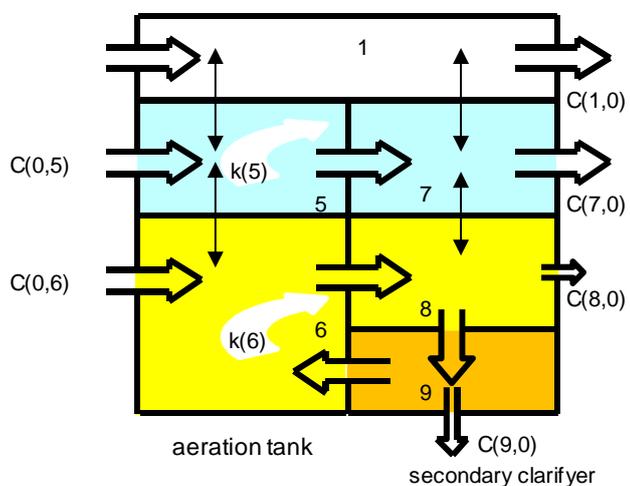


Figure B3 Box representation of an STP without primary clarifier. Advection (irreversible transport) is depicted as open arrows representing media flows, intermedia transport (reversible transport) as two-headed arrows and degradation in compartment  $i$  by curved arrows

Table B3 Irreversible advective transport: volume flow rates for an STP without a primary clarifier

<b>ADV<sub>i,j</sub></b>	<b>Equation</b>	<b>default</b>
ADV <sub>0,1</sub>	$h \cdot WS \cdot \sqrt{(AREA_{AS}^6 + AREA_{SLS})}$	$7.75 \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1/2}$
ADV <sub>1,0</sub>	$h \cdot WS \cdot \sqrt{(AREA_{AS}^6 + AREA_{SLS})}$	$7.75 \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1/2}$
ADV <sub>0,5</sub>	$\frac{Q}{24 \cdot 3600}$	$2.31 \cdot 10^{-6} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>0,6</sub>	$\frac{SO}{1000 \cdot d_{RS} \cdot 24 \cdot 3600}$	$6.94 \cdot 10^{-10} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>5,7</sub>	$\frac{Q}{24 \cdot 3600}$	$2.31 \cdot 10^{-6} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>7,0</sub>	$\frac{Q}{24 \cdot 3600}$	$2.31 \cdot 10^{-6} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>6,8</sub>	$\frac{Q \cdot C_{SO,AS}}{1000 \cdot d_{AS} \cdot 24 \cdot 3600}$	$7.12 \cdot 10^{-9} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>8,0</sub>	$\frac{Q \cdot C_{SO,SLS}}{1000 \cdot d_{AS} \cdot 24 \cdot 3600}$	$1.34 \cdot 10^{-11} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>8,9</sub>	$\frac{Q \cdot (C_{SO,AS} - C_{SO,SLS})}{1000 \cdot d_{AS} \cdot 24 \cdot 3600}$	$7.11 \cdot 10^{-9} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>9,0</sub>	$\frac{SU^6}{1000 \cdot d_{AS} \cdot 24 \cdot 3600}$	$3.66 \cdot 10^{-10} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
ADV <sub>9,6</sub>	$\frac{Q \cdot (C_{SO,AS} - C_{SO,SLS}) - SU^6}{1000 \cdot d_{AS} \cdot 24 \cdot 3600}$	$6.74 \cdot 10^{-9} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$
Sludge decay	$ADV_{0,6} \cdot \frac{d_s}{d_{AS}} + ADV_{9,6} - ADV_{6,8}$	$4.35 \cdot 10^{-10} \text{ m}^3 \cdot \text{s}^{-1} \cdot \text{PE}^{-1}$

Note that, in this scenario, sludge decay exceeds not only the emission of sludge via effluent (by far) but even the wasted sludge production.

Table B4 Reversible intermedia transport coefficients ( $m^3 \cdot s^{-1} \cdot PE^{-1}$ )

$XCH_{i,j}$	Equation
$XCH_{1,5}$	$\frac{k_{s,b}}{\frac{K_{AW}}{V_5} + \frac{1}{AREA_{AS}^6 \cdot h}}$
$XCH_{5,1}$	$\frac{k_{s,b}}{\frac{1}{V_5} + \frac{1}{AREA_{AS}^6 \cdot h \cdot K_{AW}}}$
$XCH_{5,6}$	$\frac{k_{AS}}{\frac{1}{V_5} + \frac{1}{V_6 \cdot K_{PAS} \cdot d_{AS}}}$
$XCH_{6,5}$	$\frac{k_{AS}}{\frac{K_{PAS} \cdot d_{AS}}{V_5} + \frac{1}{V_6}}$
$XCH_{1,7}$	$\frac{AREA_{SLS}}{\frac{1}{K_{air}} + \frac{K_{AW}}{K_{water}}}$
$XCH_{7,1}$	$\frac{AREA_{SLS}}{\frac{1}{K_{air} \cdot K_{AW}} + \frac{1}{K_{water}}}$
$XCH_{7,8}$	$\frac{k_{SLS}}{\frac{1}{V_7} + \frac{1}{V_8 \cdot K_{PAS} \cdot d_{AS}}}$
$XCH_{8,7}$	$\frac{k_{SLS}}{\frac{K_{PAS} \cdot d_{AS}}{V_7} + \frac{1}{V_8}}$

**Mass balance equations**

$$\text{box 1: } C_1 \cdot (XCH_{1,5} + XCH_{1,7} + ADV_{1,0}) - C_5 \cdot XCH_{5,1} - C_7 \cdot XCH_{7,1} = 0$$

$$\text{box 5: } C_1 \cdot XCH_{1,5} - C_5 \cdot (XCH_{5,1} + XCH_{5,6} + ADV_{5,7} + k_5 \cdot V_5) + C_6 \cdot XCH_{6,5} = -C(0,5) \cdot ADV_{0,5}$$

$$\text{box 6: } C_5 \cdot XCH_{5,6} - C_6 \cdot (XCH_{6,5} + ADV_{6,8} + k_6 \cdot V_6) + C_9 \cdot ADV_{9,6} = -C(0,6) \cdot ADV_{0,6}$$

$$\text{box 7: } C_1 \cdot XCH_{1,7} + C_5 \cdot ADV_{5,7} - C_7 \cdot (XCH_{7,1} + XCH_{7,8} + ADV_{7,0}) + C_8 \cdot XCH_{8,7} = 0$$

$$\text{box 8: } C_6 \cdot ADV_{6,8} + C_7 \cdot XCH_{7,8} - C_8 \cdot (XCH_{8,7} + ADV_{8,9} + ADV_{8,0}) = 0$$

$$\text{box 9: } C_8 \cdot ADV_{8,9} - C_9 \cdot (ADV_{9,6} + ADV_{9,0}) = 0$$



## 11 Appendix C Sludge loading rate and related parameters

Table C1 displays HRT (with and without primary clarifier) and SRT for the default emission scenario in SimpleTreat 4.0:

- sewage flow rate = 200 L/PE/d,
- BOD input = 60 g/PE/d,
- SO and FP as in Table 1 and 5, respectively.

The values between brackets indicate HRTs only if the sewage flow rate increases to 400 L/PE/d. Note that the sludge retention time does not change with the sewage flow rate.

*Table C1 Hydraulic retention times (HRT) and sludge retention times (SRT) related to different values of the sludge loading rate.*

<b>SLR (kg O<sub>2</sub> kg·dwt<sup>-1</sup>·d<sup>-1</sup>)</b>	<b>HRT (hr) <i>primary clarifier</i></b>	<b>HRT (hr) <i>no primary clarifier</i></b>	<b>SRT (d)</b>	<b>nitrification</b>
0.04 (low)	28.7 (14.4)	45 (22.5)	37.0	yes
0.06 (low)	19.2 (9.6)	30 (15)	24.1	yes
0.1 (low)	11.5 (5.7)	18 (9)	14.1	yes
0.15 (medium)	7.7 (3.8)	12 (6)	9.2	yes
0.2 (medium)	5.7 (2.9)	9 (4.5)	6.8	no
0.3 (high)	3.8 (1.9)	6 (3)	4.5	no
0.6 high)	1.9 (1.0)	3 (1.5)	2.2	no



## 12 Appendix D Air-water diffusive transport coefficients

Diffusive air-water transport coefficients are analyzed for the aerator. In Figure D1, the first order rate constants for surface aeration ( $k_s$ ) and bubble aeration ( $k_b$ ) are compared to the analogue related to the two layer model applied by Liss & Slater (1974) and Mackay & Leinonen (1975). This analogue first-order rate constant for volatilization and gas absorption without forced aeration,  $k_{va}$  ( $s^{-1}$ ) is derived by equating the expression for XCH in Table 19, but with  $k_{s,b}$  replaced with  $k_{va}$ , to the corresponding equation in Table 17:

$$k_{va} = \frac{\frac{1}{h} + \frac{K_{AW}}{h_{AS}}}{\frac{1}{K_{air}} + \frac{K_{AW}}{K_{water}}}$$

Figure D1 shows that, for chemicals with  $K_{AW} < 0.01$ , the first-order rate constant for exchange between air and water ( $k_{NA}$ ), according to the two film models (Liss & Slater, 1974; Mackay & Leinonen, 1975), is higher than  $k_s$  and  $k_b$ .

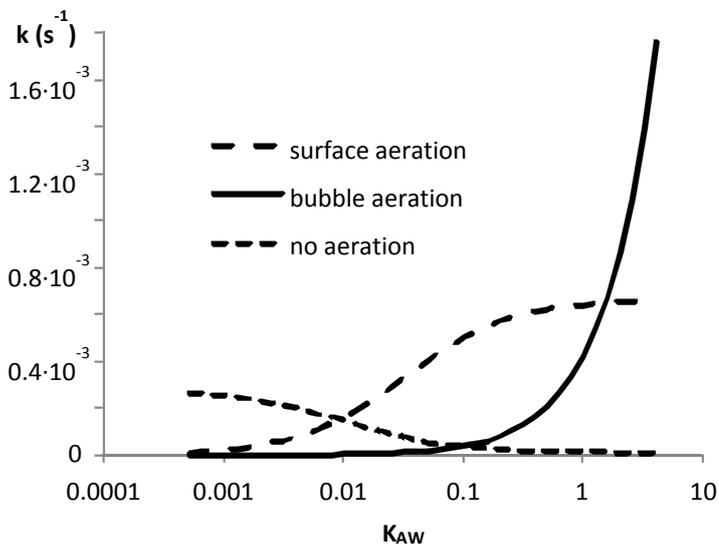


Figure D1 First-order interphase transfer rate constants for chemicals with air-water equilibrium partition coefficients ( $K_{AW}$ ) between 0.0001 and 10

With surface or bubble aeration (Table 19) and without aeration (NA, see Table 17), as well as the combination, (NA + SA or NA + BA) are plotted as a function of  $K_{AW}$  in Figures D2.

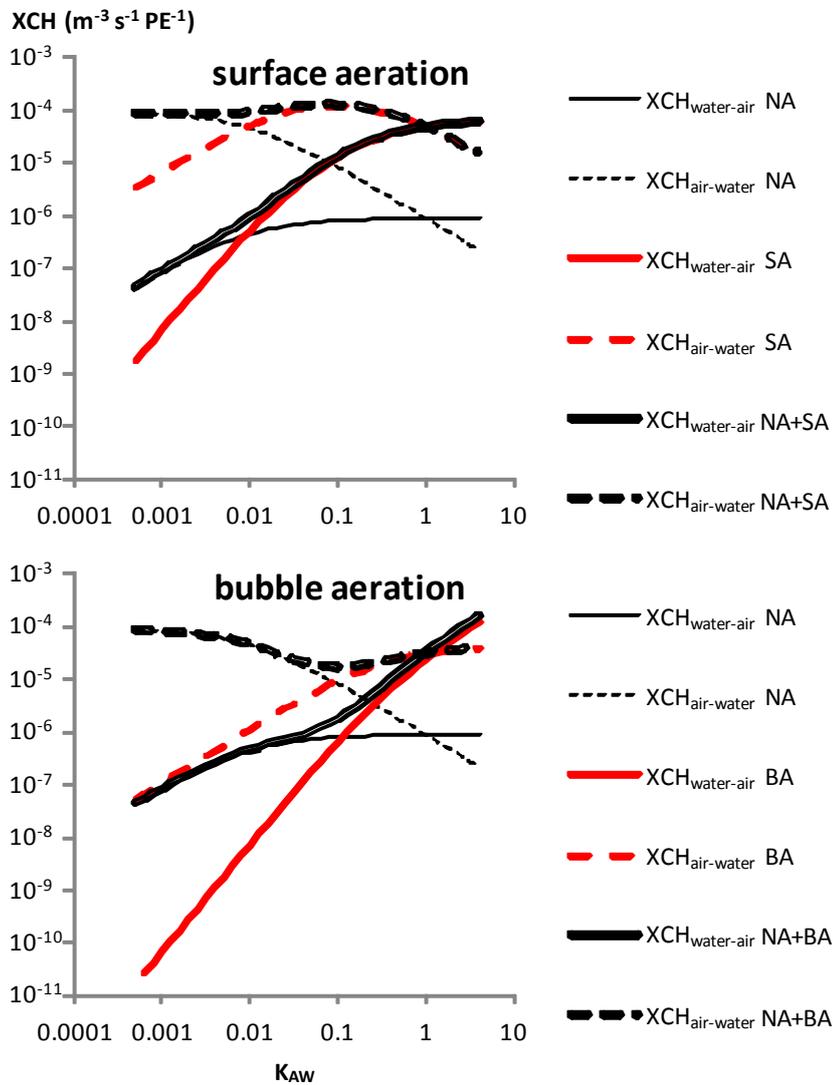


Figure D2 Mass transfer coefficients with respect to the air-water interphase for chemicals with varying air-water equilibrium partition coefficients ( $K_{AW}$ )

With the inserted parameters that are typical for an activated sludge reactor ( $G$ ,  $\Delta O_2$  etc.), surface aeration is more efficient than bubble aeration up to  $K_{AW}$  equal to 1. Figure 5 shows that combined transfer coefficients with surface aeration (black) are higher than those for bubble aeration (blue) if  $K_{aw}$  is below 1. The curves in Figure 5 represent the interphase transfer coefficients applied in SimpleTreat 4.0.

## 13 Appendix E Model Verification: version 4.0 compared with 3.1

SimpleTreat 4.0 was parameterized in such a fashion that the output of calculations with respect to a set of hypothetical chemicals (Table E1) was expected to give identical results as SimpleTreat 3.1. Results differed less than 0.01 %.

*Table E1 Physico-chemical properties of hypothetical chemicals selected for model verifications. The evaluations were conducted for four levels of biodegradability.*

<b>chemical (non-)persistent</b>	<b>Kow (-)</b>	<b>Vapour pressure (Pa)</b>	<b>Solubility (mg/L)</b>
1	0.01	1	0.001
2	1	1	0.001
3	100	1	0.001
4	3000	1	0.001
5	30000	1	0.001
6	100000	1	0.001
7	1	1	1
8	100	1	1
9	3000	1	1
10	30000	0.1	1

The levels of biodegradability are "ready biodegradability" (OECD 301 series), with or without fulfilment of the 10-d time window (first order biodegradation rate constant 1 and 0.3 d<sup>-1</sup>, respectively) and "inherent biodegradability" (OECD 302 series), with or without fulfilling specific criteria (first-order biodegradation rate constant 0.1 and 0 d<sup>-1</sup>, respectively).

**RIVM**

*Committed to health and sustainability*