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

Evaluation of the model SimpleTreat

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Colophon

**Umwelt
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Amt**

For our Environment

Abstract

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Chemical substances in wastewater emitted by companies and households into the sewer may find their way to the environment. Since 1986, the emission of new substances is regulated by chemical legislation. To this end, a system was required to assess human and environmental risk. 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. This model estimates to which extent environmental compartments (soil, water and air) are exposed to these new chemicals. Since 2003, the EU has adopted this risk assessment methodology.

At the initiative of the German Federal Environment Agency (UBA), the RIVM has examined if the SimpleTreat model is still satisfactory. The reason was that characteristics of the chemicals discharged into the sewer system have changed in the last decades. The evaluation has shown that the model suffices for chemicals that are soluble in water or fat or that are biodegradable. Most industrial chemicals fall into these categories. Moreover, in the last decades emissions have been more strictly regulated or have been reduced because technology of wastewater treatment has improved. The model however appears less suitable for chemicals that are biologically active, such as medicines, disinfectants (biocides) and substances that are surface active (soap). Most of these agents have been designed to affect living organisms and therefore have different chemical characteristics. The amount of biologically active agents reaching the environment via municipal wastewater treatment facilities has increased in the last few years.

To make the model appropriate for these 'difficult' chemicals, some modifications are necessary, for which this evaluation provides starting points. The RIVM will collaborate on a revision of the model.

Keywords: wastewater treatment plant, emission, industrial chemicals, biocides, pharmaceuticals, REACH

Rapport in het kort

Evaluatie van het model SimpleTreat

Chemische stoffen in het afvalwater dat bedrijven en huishoudens in het riool lozen, kunnen in het milieu terechtkomen. Sinds 1986 was er wetgeving die de uitstoot van nieuwe stoffen reguleert. Hierbij was een beoordelingssysteem nodig om eventuele schadelijke effecten voor mens en milieu te kunnen aangeven. Voor dit beoordelingssysteem heeft het RIVM indertijd het zogeheten SimpleTreat-model ontwikkeld. Hiermee kan worden geschat welk deel van het milieu aan dergelijke stoffen blootstaat (bodem, water of lucht) en in welke mate dat gebeurt. De EU heeft deze beoordelingssystematiek sinds 2003 overgenomen.

Op initiatief van het Duitse ministerie van milieu (UBA) heeft het RIVM in 2012 verkend of het SimpleTreat-model nog steeds voldoet. Aanleiding is dat de aard van de chemicaliën in afvalwater de laatste decennia is veranderd. Uit de verkenning blijkt dat het model voldoet voor middelen die oplosbaar zijn in water of in vet en voor stoffen die biologisch afbreekbaar zijn. Dit betreft vooral industriële stoffen, waarvan de uitstoot de afgelopen decennia sterk is gereguleerd als gevolg van aangescherpte regelgeving en verbeterde technologie van de afvalwaterzuivering. Het model blijkt minder geschikt te zijn voor biologisch actieve stoffen, zoals geneesmiddelen en ontsmettingsmiddelen (biociden), of stoffen die oppervlakteactief zijn (zeep). Deze stoffen zijn ontwikkeld om dat wat leeft te beïnvloeden, en hebben andere eigenschappen. De hoeveelheid van biologisch actieve stoffen die via afvalwater in ons leefmilieu terechtkomt, is de laatste jaren juist toegenomen.

Om het model ook te laten voldoen voor de nieuwe typen 'moeilijke' stoffen zijn enkele aanpassingen nodig, waarvoor de evaluatie handvatten biedt. Het RIVM zal in 2013 meewerken aan deze revisie.

Trefwoorden: rioolwaterzuiveringen, emissies, industriële chemicaliën, biociden, geneesmiddelen, REACH

Kurzfassung

**Beurteilung des Modells SimpleTreat für die
Umweltexpositionsbewertung von Chemikalien**

Chemikalien inklusive Wirkstoffe aus Bioziden und Arzneimitteln gelangen über
Hersteller, Formulierer und Verwender in das Abwassersystem und werden über
Kläranlagen indirekt in die Umwelt eingetragen. Seit 1986 werden Emissionen
von neuen chemischen Substanzen durch das Chemikaliengesetz geregelt. Zu
diesem Zweck war ein System erforderlich mit dem das Risiko für Mensch und
Umwelt ausgehend von diesen Chemikalien bewertet werden kann. Im Rahmen
dieser Risikobewertung hat das National Institute for Public Health and the
Environment (RIVM) der Niederlande das Modell SimpleTreat entwickelt. Das
Modell schätzt die Verteilung von Chemikalien in einer Standard-Kläranlage ab
(Verbleib in Luft, Wasser oder an Klärschlamm durch Adsorption und Elimination
durch Abbau). Seit 2003 hat die Europäische Union das Modell in die
Risikobewertung übernommen.

Auf Initiative des Umweltbundesamtes (UBA) hat RIVM überprüft, ob die
berechneten Vorhersagen von SimpleTreat auch für Wirkstoffe aus Bioziden und
Arzneimitteln zutreffend sind. Hintergrund ist, dass sich die stoffinhärenten
Eigenschaften neuer Substanzen, die ins Abwassersystem gelangen können, in
den letzten Jahrzehnten verändert haben.
Die Beurteilung des Modells zeigt, dass es für die Risikobewertung von wasser-
und fettlöslichen sowie biologisch abbaubaren Chemikalien weiterhin anwendbar
ist. Der größte Teil an Industriechemikalien fällt unter diese Kategorie.
Außerdem werden Emissionen von Chemikalien inklusive Wirkstoffen aus
Bioziden und Arzneimitteln der letzten Jahrzehnte immer strenger reguliert oder
sind reduziert worden, weil sich die Technologie der Abwasserbehandlung
verbessert hat. Die Abschätzungen von SimpleTreat sind jedoch weniger
geeignet für Substanzen, die biologisch aktive Eigenschaften aufweisen
(Wirkstoffe aus Bioziden und Arzneimitteln) oder oberflächenaktiv sind (Seifen).
Die meisten dieser Substanzen wurden entwickelt, um auf lebende Organismen
zu wirken und weisen deshalb verschiedene Eigenschaften auf. Die Menge an
diversen stoffinhärenten Eigenschaften von Chemikalien, die über eine
kommunale Kläranlage in die Umwelt gelangen können, hat sich in den letzten
Jahren vergrößert.

Das Modell SimpleTreat muss für diese „problematischen" Chemikalien bzw.
Wirkstoffe angepasst werden. Die dafür notwendigen Modifizierungen sind in
dieser Evaluierung beschrieben und begründet. In naher Zukunft wird RIVM das
Modell in Zusammenarbeit mit verschiedenen Interessengemeinschaften
überarbeiten.

Schlüsselwörter: Kläranlage, Umwelteintrag, Industriechemikalien, Biozide,
Arzneimittel, REACH

Contents

Summary

SimpleTreat 3.1 has become accepted as a useful tool for generic exposure assessment. It is used as the default calculation in European Union System for the Evaluation and Evaluation of Substances (EUSES). Behaviour in sewage treatment plants (STP) is critical because it mainly determines the concentration of chemicals in freshwater at downstream sites after emission (e.g. by households). Hence, there are doubts on the reliability with respect to organic chemicals having other characteristics than only being hydrophobic. There are doubts as to the ability of the model to predict more complicated substances that may exist in the ionic state or have surface active properties. The German Federal Environment Agency asked for an evaluation of SimpleTreat, with special emphasis on its predicting behaviour regarding biocides and pharmaceuticals.

Field and laboratory data were collected to conduct a comparison. In the low range of measured or estimated sludge water sorption constants (partition coefficients), there is a negligible discrepancy in model output of emission to water between predicted with measured and estimated sorption constants, even if they differ a factor of 30 because only removal due to volatilization or biodegradation is determining the fate of the chemical. If the range of sorption constants and biodegradability rates is wider, predictions based on measured partition coefficients are in better agreement with observations in the real world. Unfortunately, measured relevant sorption constants are often absent. The current estimation procedure of those constants by SimpleTreat 3.1 may lead to erroneous results. Although the model has been adapted to describe ionisation, the fate of organic ions is limited to the unbound aqueous phase. This may seriously restrict the applicability domain.

This study reviews the implemented default values regarding operational parameters of sewage treatment plants, reflecting the current sewage technology (for example the sludge loading rate) since the SimpleTreat model describes sewage treatment technology of 25 years ago. In addition, refinement options are discussed allowing the user to have a greater flexibility to estimate the distribution of chemicals from sewage treatment plants.

Revision of the SimpleTreat model is encouraged and as such this report may serve as a preamble of a project aiming at a new version of the model which is better applicable to compute the fate and emission of the so-called 'difficult chemicals' such as biocides and pharmaceuticals.

Abbreviation/symbol	Meaning
BOD	Biological Oxygen Demand
BPD	Biocidal Products Directive
dwt	dry weight
ECETOC	European Centre for Ecotoxicology and Toxicology of Chemicals
ECHA	European Chemical Agency
EMA	European Medicines Agency
EUSES	European Union System for the Evaluation and Evaluation of Substances
Fn	fraction of the neutral chemical in water
foc	organic carbon fraction of suspended or settled solids
H	Henry's Law constant ($Pa \cdot m^3 \cdot mol^{-1}$)
Ka (Kb)	acidic (base) dissociation constant
Kaw	dimensionless Henry's Law constant (=H/(RT))
Koc	partition coefficient organic carbon-water (L/kg)
Kow	octanol-water partition coefficient (L/L)
Kp	solids-water partition coefficient (L/kg)
LCA	Life Cycle Assessment
MOLW	molecular weight ($g \cdot mol^{-1}$)
N	number inhabitants
OECD	Organisation for Economic Cooperation and Development
PE	person equivalent
pH	negative logarithm of the hydrogen ion concentration
pKa (pKb)	negative logarithm of Ka (Kb)
PPP	plant protection products
Q	sewage flow ($m^3 \cdot PE^{-1} \cdot d^{-1}$)
R	the universal gas constant ($J \cdot K^{-1} \cdot mol^{-1}$)
RA	risk assessment
REACH	**R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emical substances
RIVM	National Institute for Public Health and the Environment
SLR	sludge loading rate ($kg_{BOD} \ kg_{dwt}^{-1} \ d^{-1}$)
SOL	water solubility ($g \cdot m^{-3}$)
STP	sewage treatment plant
T	absolute temperature (K)
TGD	Technical Guidance Document
UBA	Umwelt Bundesambt (UBA) German Federal Environment Agency
VP	vapour pressure (Pa)

1   Introduction

SimpleTreat is a software program to estimate the fate of chemicals in a conventional activated sludge process. It was designed to compute the emission of chemicals from a communal wastewater treatment plant. Originally developed by the Netherlands National Institute for Public Health and the Environment (RIVM) as a spreadsheet model (Struijs et al., 1991), the program has been revised (Struijs, 1996) and adapted to be generically applicable for countries in the EU. It functions as a central exposure assessment device in the EUSES system (TGD, 2003). SimpleTreat version 3.1 is now the recommended model in the EU for the environmental risk assessment of industrial chemicals (REACH), for chemicals covered under the Biocidal Products Directive (BPD), for active pharmaceutical ingredients regulated by the European Medicines Agency (EMA) and even substances assessed according to the regulation on plant protection products (PPP) 1107/2009. In the Netherlands, drainage water from greenhouses where PPPs are applied, is collected and discharged into sewer systems.

SimpleTreat requires for the calculations only few chemical properties, available in the so-called base set according to EUSES (TGD, 2003):
*   molecular weight;
*   vapour pressure;
*   water solubility;
*   octanol-water partition coefficient;
*   result of a standard biodegradability test.

Unfortunately, base set properties are not solids-water partition coefficients (Kp) for raw sewage or activated sludge or the air-water partition coefficient. These partition coefficients, indispensable in quantitative environmental exposure assessment, are estimated from the base set properties Kow and vapour pressure/water solubility, respectively.
For neutral hydrophobic chemicals, this input is satisfactory. Recently, it appeared that only half of 1500 pre-registered chemicals under REACH belong to this category (Franco, 2010) and the other half consists of acids, bases or both, i.e. zwitterions which include amphoteric chemicals. Most active pharmaceutical ingredients have acidic and/or basic functionalities, their ionisation state is controlled by both solution pH and acidic dissociation constants (i.e. Ka values) (Babic et al., 2007). Although SimpleTreat includes a computation routine considered appropriate for chemicals that are both ionisable and hydrophobic in the neutral state, there are doubts about the accuracy of the multi-equilibrium description sludge-water partitioning of these complex compounds.

The German Federal Environment Agency (UBA) initiated a study to evaluate this model with emphasis on the correctness of predictions for this difficult category of chemicals. The UBA commissioned RIVM to conduct a study on the validity and the applicability domain of SimpleTreat with special emphasis on pharmaceuticals and biocides. This study also suggests alternative application modes in case, due to their specific properties, these substances fall beyond the applicability domain of the model. Proposals are made to modify and improve SimpleTreat to enable the evaluation of 'difficult chemicals'.

This report describes an evaluation, starting with a survey of the model to identify possible weaknesses. In the third chapter results are presented of

testing SimpleTreat against field and laboratory observations. Results are interpreted leading to tentative conclusions and recommendation as to an alternative application of the current model. The latter includes a modification of default values that can be chosen by the user. Model parameters that cannot be changed by the user are proposed in an outline on a revision of SimpleTreat.

2 Basic principles of SimpleTreat: are rules for equilibrium partitioning valid?

Current environmental fate models, applied in risk assessment (RA) and Life Cycle Assessment (LCA), have limitations regarding spatial and temporal specificity. For their intended use, i.e. generic exposure assessment in some sort of archetype environment, these limitations are usually acceptable. More problematic is the applicability domain regarding the diverse chemical classes. The REACH chemical space (Franco, 2010) is rather complex as it includes inorganic salts, metals, organometallic substances, salts of ionisable organic chemicals and ionisable organic groups such as carboxylic acids, phenols or anilines. The latter category also includes ionic surfactants (detergents, dyes and adhesives). Only slightly more than 50% of the REACH chemicals consist of neutral hydrophobic organic chemicals for which these multimedia chemical fate models were developed. Most active pharmaceutical ingredients have acidic and/or basic functionalities, their ionisation state is controlled by both solution pH and acidic dissociation constants (i.e. K_a values) (Babic, et al, 2007).

2.1 Basic principles

Multimedia models evaluate exposure concentrations in a standard world whereas SimpleTreat calculates the fate of chemicals in a more engineered environment, which results in emission rates of a modelled chemical from a communal sewage treatment plant (STP). Like most multimedia models, it is based on the fugacity concept as introduced by Mackay (1979) for the computation of diffusive transport of the chemical between two adjacent media. Fugacity is the escaping tendency of a chemical from one medium to another. Diffusive transport can occur in both directions and represents the exchange of a chemical. Direction is in the direction of thermodynamic equilibrium and the extent of net diffusive transport is determined by the measure of deviation from the chemical equilibrium condition. Equilibrium between adjacent boxes implies that fugacities are equal and net transport across the interface is zero. The boxes are considered homogeneous but the concentrations in the boxes do not necessarily fulfil equilibrium conditions. Concentrations in each box are considered constant in time. SimpleTreat is a steady state non-equilibrium multimedia model in which all transport and degradation processes are linear with respect to concentrations.

Figure 1 a) is a scheme of an STP, b) shows the flow of solids in such a system and c) is a box representation of fate processes of a chemical in this engineered environment. The performance of the box model, Figure 1 c), has been shown to be strongly influenced by the parameterisation of all media flows, i.e. water, air, solids represented as open arrows in Figure 1 c). The media flows of the different media through an STP are based on the availability of accurate flow data. They reflect the functioning of an STP as Biological Oxygen Demand (BOD) and sludge removing system and govern the fate of BOD and sludge. The removal of sludge and BOD are closely linked, in that BOD is partly eliminated due to sedimentation of primary sludge and is partly biodegraded in the aeration tank where it also causes the formation of (surplus) sludge. The sludge regime is given by Figure 1 b). Typical STP operating characteristics, such as sludge age and hydraulic retention time are converted into media flow rates.

a)

600 primary settler

settled sewage
200

aeration tank
activated sludge
3300

solids liquid separator

effluent 30

raw sewage

primary sludge

wasted sludge

| 3300 | = steady state concentration suspended solids (mg dry matter /L) |

b)

3 net sludge growth or degradation, dependent on sludge loading rate

90 primary settler 30 aeration tank solids liquid separator 6 effluent

60 primary sludge

21 wasted sludge, dependent on sludge loading rate

c)

1 C(1,0)

C(0,2) 2 k(5) 5 7 C(7,0)

C(0,3) 3 6 8 C(8,0)

4 9

C(4,0) C(9,0)

primary sedimentation
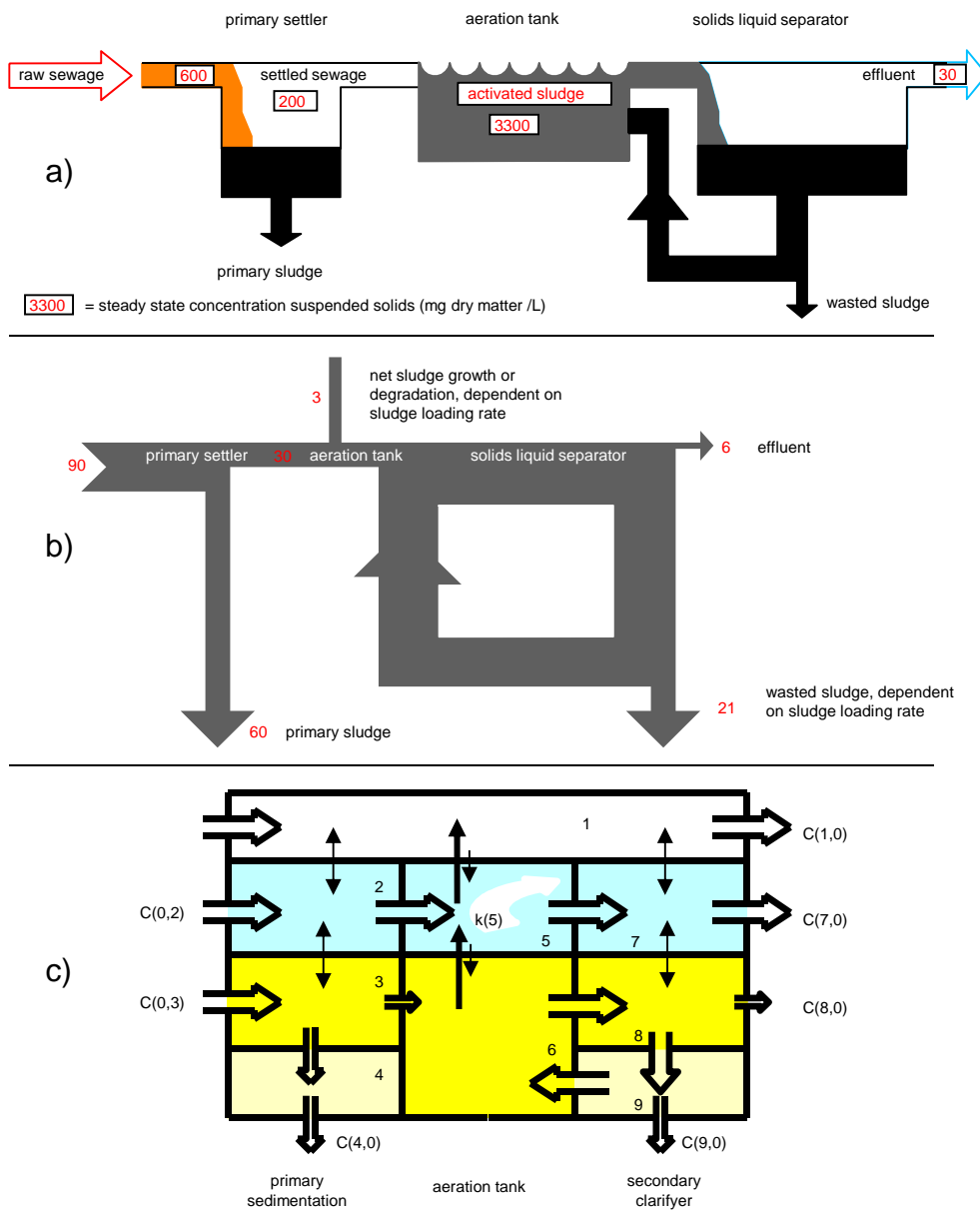
aeration tank

secondary clarifyer

Figure 1 Characteristics of an average sewage treatment plant in the EU (a); the sludge flows in grams per inhabitant, partly recycled (b) and the box representation of the chemical fate in such a system (c). See text for explanation.

In Figure 1 c) nine out of fifteen media flows are related to solids flows carrying the adsorbed chemical from outside the system (0) or box i to box j (or outside the system). The solid arrows in Figure 1 c) represent diffusive transport between some adjacent media, such as air-water and solids-water, driven by non-equilibrium concentrations.

The only curved arrow stands for disappearing of the chemical in box 5 (water in the aeration tank) implying that a chemical is only subject to biodegradation in the aqueous phase of activated sludge which is represented by box 5 (water).

Steady state concentrations (dC/dt = 0) are obtained from multiple mass balance calculation by solving nine linear equations according to:

$$V_j \cdot \frac{dC_j}{dt} = -k_j \cdot C_j \cdot V_j + \sum_i MED_{i,j} \cdot C_i + \sum_i DIFF_{i,j}$$

with

$MED_{i,j}$	:	media volume flow [m^3·s^{-1}] from source i to destination box j,
$DIFF_{i,j}$	:	diffusive mass flow [g·s^{-1}] from source i to destination box j,
V_j	:	volume of box j [m^3]
C_j	:	concentration in box j [g·m^{-3}]
t	:	time [s]
k_j	:	first order biodegradation rate constant in box j [s^{-1}]

The group $MED_{i,j} \cdot C_i$ represents an advective mass flows from box i to box j carrying the chemical with concentration C_i with it. Direction and velocity of the diffuse mass flow $DIFF_{i,j}$ are determined by the extent with which the concentrations in i and j deviate from equilibrium conditions. More information on the technical-scientific background of the model is given by Struijs (1996). The validity of model predictions is substantially influenced by how the ratio of equilibrium concentrations for each pair of adjacent media (for example air and water) is calculated. These equilibrium constants play a dominant role in multimedia models and are required input for the model. Unfortunately, most of these equilibrium partition constants are often not available. In the same way as multimedia chemical fate models designed for generic risk assessment, SimpleTreat is also usually run on a basic input set of chemical properties mandatory for notification and regulation of chemicals, on which equilibrium partition coefficients are assessed.

2.2 How equilibrium partitioning is calculated

If the chemical is neutral and hydrophobic, SimpleTreat derives partition coefficients for air-water and solids-water from base set properties of the chemical such as the water solubility, vapour pressure and octanol-water partition coefficient. Necessary characteristics of relevant environmental media such as temperature and the organic carbon fraction of the particles are known. Moreover, the assumption that they are constant in time is acceptable for generic risk assessment. These so-called base set data of a chemical to be notified or regulated are used to *estimate* equilibrium partition coefficients. For

this reason, multimedia chemical fate evaluation based on the fugacity principle is only applicable to neutral hydrophobic chemicals.

The estimation of transfer of a chemical from the aqueous phase to the air is based on the equilibrium partitioning between air and water. It is a simple function of the temperature (T, in º Kelvin) and Henry's Law constant (H, in $Pa \cdot m^3 \cdot mol^{-1}$) which is estimated from three base-set data:

$$H = \frac{VP \cdot MOLW}{SOL}$$

with:

MOLW	:	molecular weight ($g \cdot mol^{-1}$)
VP	:	the vapour pressure (Pa)
SOL	:	water solubility ($g \cdot m^{-3}$)

The air-water equilibrium partition coefficient (Kaw) also known as the 'dimensionless Henry's Law constant' is equal to:

$$Kaw = \frac{H}{R \cdot T}$$

with:

R	:	the universal gas constant ($8.314\ J \cdot K^{-1} \cdot mol^{-1}$)
T	:	absolute temperature (K)

For partitioning between settled or suspended solids and the aqueous phase a simple relationship is applied:

$$Kp = foc \cdot Koc$$

with:

Kp	:	equilibrium partition coefficient sludge-water (L/kg)
Koc	:	partition coefficient organic carbon-water (L/kg)
foc	:	organic carbon fraction of suspended/settled solids (-)

Also, this relationship reflects that Kp depends on 1) the organic carbon fraction of the particles in raw sewage and activated sludge (foc) which is a property of the environment, and 2) on a property of the chemical, the organic carbon-water partition coefficient (Koc). The latter is also known as the 'organic carbon normalised partition coefficient', Kp/foc. The value of foc of the solids in raw sewage (0.3) and activated sludge (0.37) is considerably higher than is assumed in the real world due to the concentration of microorganisms. To compare, according to the TGD (2003), the fraction foc in soil is 0.02, in sediment 0.05 and in suspended solids in the water compartment it equals 0.1. Koc was initially estimated through simple proportionality relationships with a substance property (Kow) which is part of the base set data of a chemical (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:

$$Koc = 1.26 \cdot Kow^{0.81}$$

with:

Kow : octanol-water partition coefficient (L/L)

Unlike rules for estimating the bioconcentration potential from Kow, which is limited by the molecular weight of 700 (TGD, 2003), the applicability range of the relationship between Kp and Kow is wide. Nevertheless, special structural properties, related to for example amphiphilic substances (surfactants) or dissociating substances, may lead to multiple equilibrium processes.

2.3 The applicability of estimated partition constants for organic acids and bases

SimpleTreat (Struijs et al., 1981; Struijs, 1996) always had a calculation routine to account for dissociation of organic acids and bases in combination of partitioning between water and other phases. The input sheet (Appendix A) of the spreadsheet version contains additional cells for the acid (Ka) and base (Kb) dissociation constant to define the chemical. If Ka or Kb is not declared, the model assumes the chemical to be neutral by assigning a default value of 10^{-20} to Ka. If a higher value than 10^{-20} is given, the chemical is assumed an acid. If a value higher than 10^{-20} is inserted for Kb, a base is assumed. For an acid HA, dissociation results in two species, HA and A⁻:

$$\underbrace{HA}_{Kaw(H,T)} \leftrightarrow H^+ + \underbrace{A}_{Kaw=0}{}^-$$
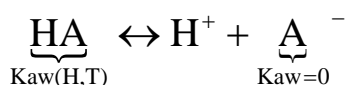
$$Ka = \frac{[H^+][A^-]}{[HA]}$$

For air-water partitioning the above equation implies that only the neutral species can volatilise, depending on the dimensionless Henry's Law constant Kaw. The equation also shows an air-water partitioning equal to zero for the ionised species. As usually ionised organic chemical will not volatilise, this is a fair premise. If the fraction of the neutral or ionised form can be calculated, the mass balance equation for a water compartment includes the total aqueous concentration of this organic acid, [HA] + [A⁻] which is accounted for in formulating the advective mass flow for the aqueous phase. This is based on the fraction of the neutral chemical (Fn), calculated according to pKa (negative logarithm of Ka):

$$Fn = \frac{[HA]}{[HA]+[A^-]} = \frac{1}{1+10^{(pH-pKa)}}$$

Because in all basins of a STP the pH is assumed equal to 7, the neutral fraction can be calculated if the substance property Ka is known.

An organic base dissociates according to:

$$\underbrace{B}_{Kaw(H,T)} + H_2O \leftrightarrow \underbrace{BH^+}_{Kaw=0} + OH^-$$
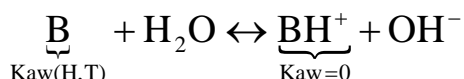
Similar reasoning hold for the calculation of the neutral fraction of B:

$$Kb = \frac{\left[BH^+\right]\left[OH^-\right]}{\left[B\right]}$$

$$Fn = \frac{\left[B\right]}{\left[B\right]+\left[BH^+\right]} = \frac{1}{1+10^{(pKw-pKb-pH)}}$$

In this equation, pKb and pKw are the negative logarithms of Kb and Kw (water dissociation constant), respectively.

Only the neutral molecule of the acid (HA) or base (B) is available for interface transport from water to air. The equation for Kaw (SOL, VP, T) can be used for this neutral fraction. Because only the neutral chemical can cross the boundary between air and water, this implies that the ionised fraction is <u>not</u> 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 exchange of an acid or base between air and water this may be correct. Sorption to sludge however is complicated by the fact that ions may also adsorb to sediment and sludge solids due to, for example, electrostatic interactions. It is unlikely that the solids-water partition coefficient for the ionic fraction is zero:

$$\underbrace{HA}_{Kp(foc,Kow)} \leftrightarrow H^+ + \underbrace{A}_{Kp=0?}{}^-$$

$$\underbrace{B}_{Kp(foc,Kow)} + H_2O \leftrightarrow \underbrace{BH^+}_{Kp=0?} + OH^-$$
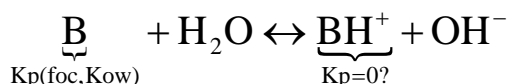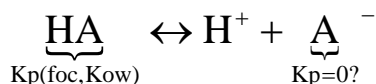
Adsorption of ionised chemicals onto sludge is probably underestimated in SimpleTreat because it set to zero. It implies that transport of ionised species through sludge, carrying (part of) the ionised chemical with it, is neglected. In an engineered environment like a STP, media flows (water and solids) are much faster than in a natural environment and play a dominant role in the fate of chemicals. Therefore, erroneous estimations of solids-water partitioning of an organic acid or base may adversely affect fate predictions in an STP.

Unless a chemical is readily biodegradable when fast removal due to biodegradation dominates other fate processes, SimpleTreat is probably not suitable to correctly predict the fate and emission of chemicals that are acids or bases and that are partly dissociated at pH equal to 7.

This seriously puts limits on the applicability domain of the model. It is estimated that of the pre-registered REACH chemicals (143,000 in 2010), about one-third is mostly ionised at pH 7 (Franco, 2010). Examples of widely used ionising chemicals can be found among detergents, pesticides and pharmaceuticals. According to Babic et al. (2007), 80% of biocides are ionised. For ionising chemicals, electrical interaction and sorption to particles is to a high degree dependent on pKa and the pH of the environment (Franco and Trapp, 2008; Franco, 2010) and these processes need therefore to be taken into account.

Recently, progress has been made in modelling the partitioning behaviour for acids and bases. Franco and Trapp (2008) implemented newly derived rules for partitioning of ionic species in multimedia models. For suspended particles and sediment in natural systems these new rules may provide better methods for calculating exposure concentrations of organic acids and bases. It is questionable however, if this approach for partitioning of ionisable chemicals is also applicable to activated sludge. There is a difference between natural water-solids (sediment) systems – which may vary in pH considerably – and activated sludge which is high in organic carbon and low in clay minerals and has a constant pH. Given the different composition and electrical interactions in sewage sludge water-solids systems compared to soil pore water-solids systems, the partitioning behaviour within a wastewater treatment plant may differ from sorption to soils. As discussed above, improved estimates for Koc of sludge are probably even more important for bases.

3 Testing SimpleTreat on 'difficult substances' (work package 1)

Working package 1 (WP1) focuses on the following questions:
- What is the validity and application domain of SimpleTreat: how realistic is the model?
- How does it predict fate in and emission from STPs of so-called 'difficult chemicals' (surfactants, ionised compounds etc.)?
- Is it applicable to biocides and pharmaceuticals in its current form?
- How do model predictions compare to measured data?

Ideally, chemicals in a comparison study span a wide range of chemical properties. We anticipated that it is difficult to collect data that are appropriate for this purpose. Chemicals with known properties should be measurable in several media, especially in raw sewage, in sludge and in effluent.

3.1 Validation by Environment Canada (2005)

Environment Canada conducted a study in 2005 with the aim to identify suitable models of the chemical fate in STP's for use in exposure assessment (Crechem Technologies Inc., 2005). Environment Canada had the following questions:

1. What predictions do we need and how accurate should they be?
2. How simple should it be:
   - with respect to trade-offs between accuracy and complexity?
   - is there an interface between multiple users and expert users?
3. Which inputs are available? Which are necessary?

The selected chemicals, measured and predicted emissions are given in Table 1.

Among the polycyclic aromatic hydrocarbons and brominated flame retardants, only one compound of the selected chemicals is an active pharmaceutical ingredient regulated by the European Medicines Agency (EMA), i.e. triclosan. However, this compound is also a biocide.
The study indicated that SimpleTreat yielded the most accurate results of the four models and the predicted total removal was within 5% of the measurement for the majority of the substances measured. The difference with Toxchem+ though was small (Figure 2) and therefore the two models are recommended for use in exposure assessment to provide estimates for total removal by sewage treatment plants.

Conclusions:
1. For the set of test chemicals chosen in this validation program SimpleTreat 3.1 produced fair prediction in the framework of generic risk assessment.
2. The set of test chemicals contains only one substance, i.e. the pharmaceutical and at the same time biocidal active substance triclosan, that falls in the domain of interest for this evaluation.
3. The predicted elimination of triclosan was close to measured data and closer than prediction of the other models.

Table 1: Model predictions versus measurement for total removal.

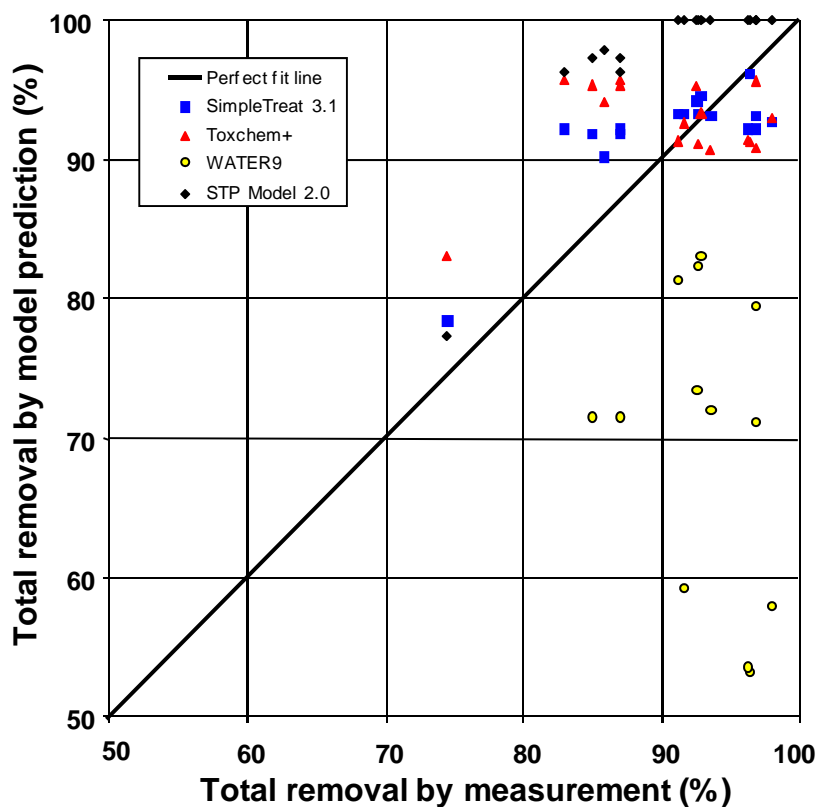| Substance	Total removal (%)				
	Meas.	SimpleTr.	Toxchem+	WATER9	STP model
Acenaphthylene	91.3	93.2	91.3	81.2	100.0
Acenaphthene	92.7	93.2	91.1	82.3	100.0
Fluorene	92.9	94.6	93.3	83.0	100.0
Phenanthrene	96.8	93.1	90.8	71.1	100.0
Anthracene	93.6	93.1	90.7	71.9	100.0
Fluoranthene	96.4	96.2	91.2	53.2	100.0
Pyrene	91.7	93.2	92.6	59.1	100.0
Benzo(a)anthracene	98.1	92.7	93.0	57.8	100.0
Chrysene/triphenylene	96.3	92.2	91.0-91.8	52.9-53.8	100.0
Benzo(k)fluoranthene	96.9	92.2	95.7	79.3	100.0
BDE47[1]	85.9	90.2	94.2	48.4	97.9
BDE99[2]	87.0	91.8	95.4	71.4	97.3
BDE100[3]	85.0	91.8	95.4	71.4	97.3
BDE153[4]	87.0	92.2	95.8	Error	96.3
BDE154[5]	82.9	92.2	95.8	Error	96.3
TBBPA[6]	74.5	78.4	83.1	19.3	77.3
Triclosan[7]	92.6	94.3	95.3	73.3	100.0

[1] 2,2',4,4'-tetrabromodiphenyl ether   [5] 2,2',4,4',5,6'-hexabromodiphenyl ether

[2] 2,2',4,4',5-pentabromodiphenyl ether   [6] tetrabromobisphenol A

[3] 2,2',4,4',6-pentabromodiphenyl ether   [7] 5-chloro-2-(2,4-dichlorophenoxy) phenol

[4] 2,2',4,4',5,5'-hexabromodiphenyl ether

Figure 2 Model prediction versus measurement for total removal (Table 1).

3.2 Five anonymous biocides: estimated and measured Koc

The selected substances that were selected here, were submitted for evaluation under the Biocidal Products Directive (BPD). Physico-chemical and biodegradability properties of five anonymous biocides were obtained (UBA, 2012), denoted as 1 to 5 (Table 2). Data on hydrophobicity span more than four orders of magnitude, but are rather low. All biocides are readily biodegradable, although number 5 without fulfilling the ten day window criterion. At the moment, there is less information on monitoring data which exclusively focuses on biocidal usage. For the here selected biocidal active substances, no measured concentrations are available, neither in sewage sludge nor in the corresponding effluent of the STP. Therefore only estimated and measured partition coefficients and the consequences for model output can be compared.

Table 2 Chemical properties of five biocides.

property	biocide	1	2	3	4	5
MOLW	$g \cdot mol^{-1}$	100	200	30	60.1	90.1
Kow		0.5	$1.6 \cdot 10^5$	2.2	1.1	0.2
VP	Pa	44	$4.0 \cdot 10^4$	74.5	$5.8 \cdot 10^3$	0.23
SOL	$mg \cdot L^{-1}$	$5.1 \cdot 10^5$	16	$3.3 \cdot 10^5$	10^6	10^6
Biodeg	hr^{-1}	1	1	1	1	0.3

Table 3 Estimated and measured partition coefficients.

biocide	pKa	Koc estimated	Koc measured	H estimated	H measured
1		0.68	**326**	0.0	0.0
2	5.3	325	**300**[*]	0.0	0.0
3		2.42	**15.9**	0.0	**0.034**
4		1.38	**3.3**	0.3	**0.82**
5	3.9	0.005	**20.0**	0.0	0.0

[*] Koc was determined by QSAR implemented in the ACD software and ranges from 10.1 L/kg, ionised form at pH 8 (anion) to 4,878 L/kg, non-ionised form at pH 5 (free acid). Measured log Kow was 5.2 (pH = 3), 4.98 (pH = 5) and 2.35 (pH = 7)
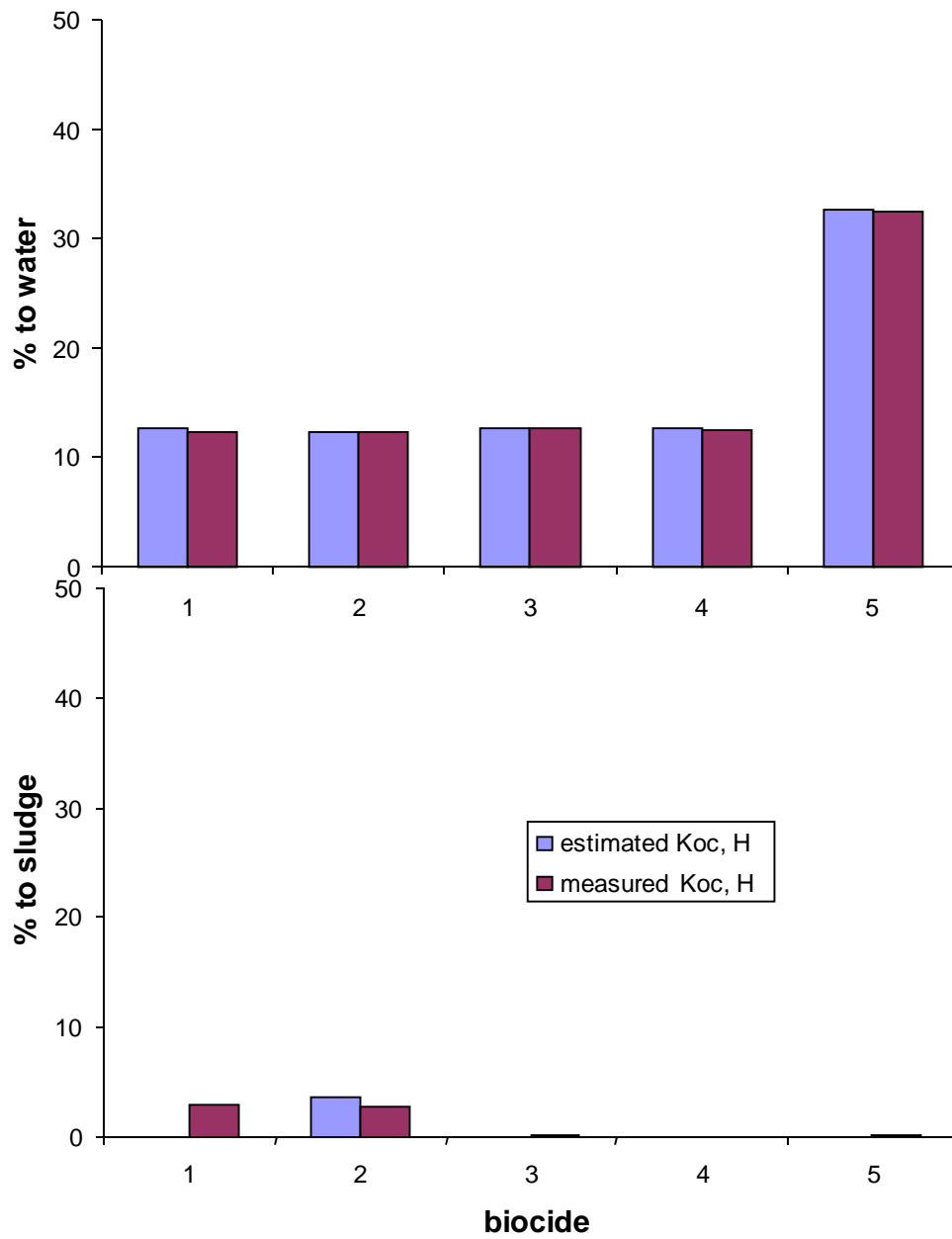
Figure 3 Influence of quality of partition coefficients on the predictions of the five biocides in Table 2 by SimpleTreat.
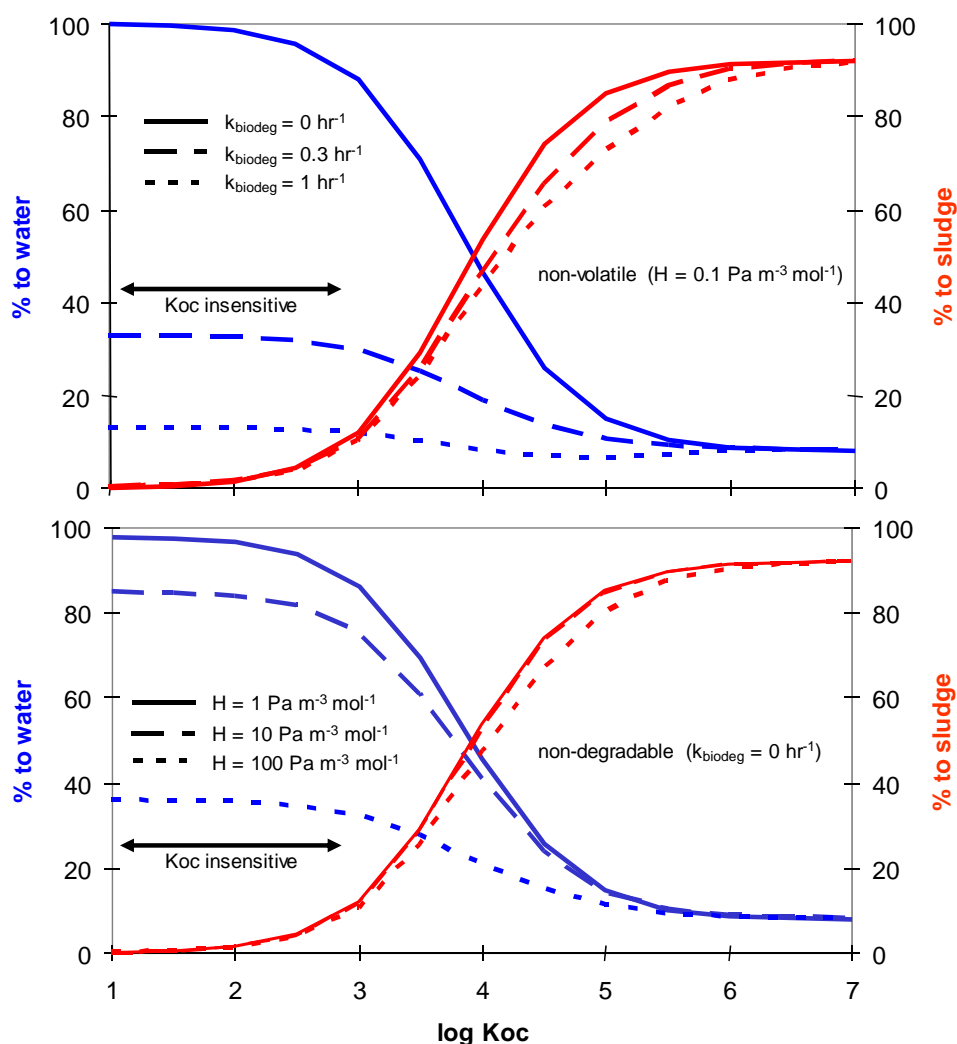
Figure 4 Sensitivity of the model for the organic carbon sorption coefficient for various biodegradation rates (upper panel): 0 hr^{-1} (persistent), 0.3 hr^{-1} (readily biodegradable, no 10 d window), 1 hr^{-1}(readily biodegradable) and for varying volatility (lower panel): H = 1 to 100 Pa m^{-3} mol^{-1} (higher H indicates higher volatility). The two-headed arrow indicates where model predictions are not sensitive for Koc.

Conclusions:
1. With this set of input parameters emissions to water and sludge display little sensitivity for Koc. In this range of Koc and H there is little difference between estimated Koc from Kow (or Henry coefficient, H) and measured Koc (or H).
2. Biocide 2 shows a good agreement between estimated and experimentally derived Koc. From the combination of the base set input data Kow (Kow = 1.6 10^5) and additional pKa equal to 5.3 a value for Koc equal to 325 is estimated, which is very close to 300.
3. Large discrepancies between estimated and measured Koc for biocide 1 and 5 do not cause significant differences in emission to water and sludge. This can be understood from the observation of the low sensitivity of the model in the Koc range between 10 and 300 which corresponds to 1 and 2.5 on the log Koc axis (Fig 4). In this Koc range, biodegradation is the dominant removal mechanism. In the Koc range up to 300, emission to water is

determined by the disappearance rate from water in the aeration tank by degradation if volatilization can be neglected (H < 0.1 Pa m^3·mol^{-1}).
4. Figure 4 also indicates that if Kow or Koc are in the range between 1,000 and 100,000, the model is rather sensitive for Koc. In this range, elimination of a persistent and non-volatile chemical changes from 10% to almost 90%, solely due to sorption onto sludge and subsequent sludge withdrawal.

3.3 Biocides (A to E): measured elimination rates

Physico-chemical and biodegradability properties of five anonymous biocides were obtained from UBA (2012), denoted as A to E (Table 4). Besides the measured partitioning data with respect to Koc and H, also measured concentrations or percentages removal are given. Biocides A and B were measured in real STP's whereas C, D and E were tested in laboratory simulation studies (OECD 303 biodegradability test). The base set properties are given in Table 4. D and E are readily biodegradable (E without fulfilling the ten day window), A, B and C are persistent (negative result in a ready biodegradability test) which is concluded as no other biodegradation data is present.

Table 4 Chemical properties of biocides A to E.

Biocide	A	B	C	D	E
MOLW (g/mol)	151	229	115	150	206
Kow (-)	5.0	129	0.5	2.5	398
VP (Pa)	6.3·10^{-5}	3.4·10^{-2}	0.6	1.2	6.1·10^{-6}
SOL (mg/L)	1.3·10^3	8.6·10^3	1·10^6	2.8·10^6	52
k biodeg (hr^{-1})	0	0	0	1	0.3

Results depicted in Figure 6 indicate that in real-world STP's (A and B), biodegradation is underestimated. A negative result in a ready biodegradability test has a low predictive value with respect to persistency. Biocide A is certainly not readily biodegradable as it emitted to water at higher rates, 16% and 26%, than is expected from compounds that fulfil the ten day window criterion in those tests. With a conservative rate constant (1 hr^{-1}) SimpleTreat would predict 12.7% emission to water if biodegradation is the only elimination mechanism. If this criterion is not fulfilled, SimpleTreat would predict 33% emission to water due to a first order degradation rate constant equal to 0.3 hr^{-1} which is considered as rather conservative by most experts. The conclusion can be drawn that given these considerations, prediction and observation are not necessarily in disagreement, because a higher tier biodegradability test result is absent. Biocide B is completely biodegraded, but due to the stringent character of the OECD 301 series for ready biodegradability, SimpleTreat predicts no degradation. Also for this compound the absence of a higher tier biodegradation test result causes an overestimation of emission to water.
A similar pattern is observed with biocide C of which the biodegradation process is tested in the laboratory. A result like this is rather common: a negative result in a 'ready' test combines well with biodegradation to a high extent in the OECD 303 test.
Biocide D displays good agreement between modelled and observed in the laboratory as is expected from a positive result in 'ready' test and more than 80% degradation in the OECD 303 test.
Biocide E appeared readily biodegradable although without fulfilling the ten day window criterion. Unexpectedly, this compound appeared not degradable in the OECD 303 test. This combination of test outcomes is very rare as ready biodegradability tests are very stringent. This means that a positive test result

(the chemical is mineralised in 28 days also if the ten day window criterion is not fulfilled) has a high predictive value to the real world like an STP or surface water (the chemical degrades rapidly in all aerobic environments like a STP). The OECD 303 test mimics the real world of a STP. This test is less stringent than the ready biodegradability series which means that a 'ready' chemical is expected to degrade in an OECD 303 test. Biocide E however, does not follow this pattern.
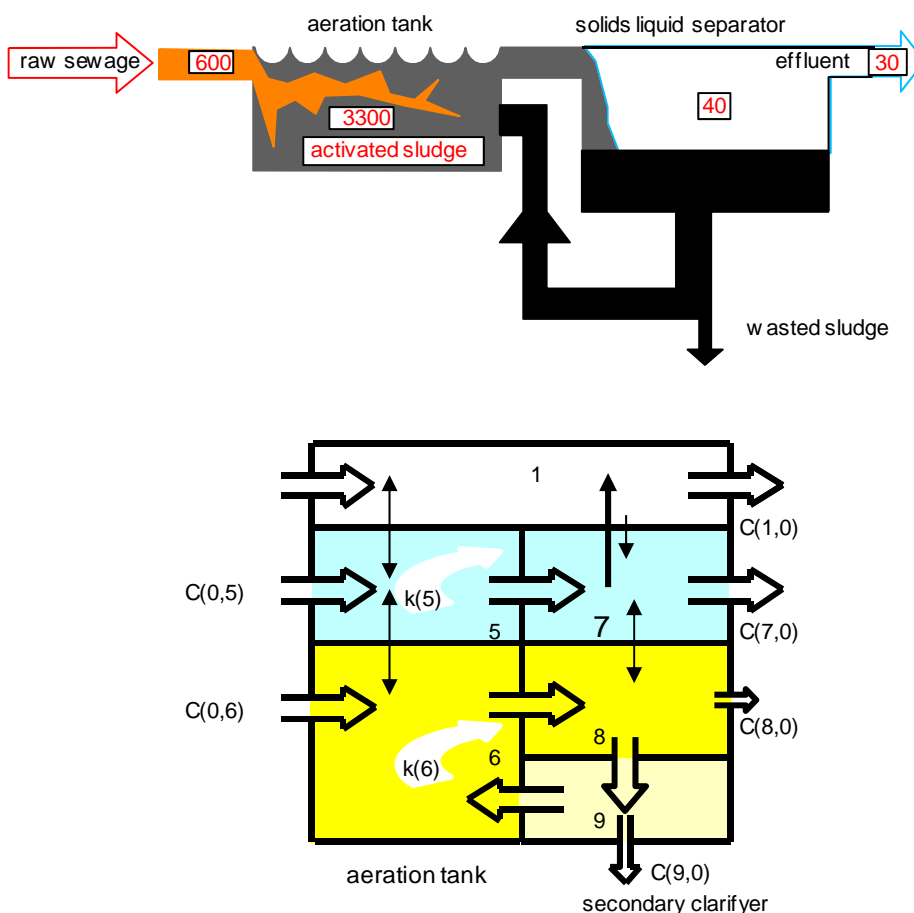
Figure 5 The OECD 303 simulation test is an STP without a primary clarification tank. In SimpleTreat the calculations for biocides C, D and E are conducted in the six box mode.

Conclusions:
1. Results for biocides A and B are <u>not</u> conflicting. This conclusion must be drawn because higher tier biodegradation tests are not present.
2. From base set physico-chemical properties removal due to sorption and volatilization is not expected.
3. Only biodegradation is a dominant elimination mechanism and only biocide E displays the very rare combination of being readily biodegradable, but also being persistent in the OECD 303 test. SimpleTreat derives default biodegradation rate constants from standardised test methods at the screening level, i.e. at the 'ready' or 'inherent' level. A positive 'ready' result predicts degradation in an STP while a negative 'inherent' result predicts persistence. Biocide E seems to display a false positive result (positive in a 'ready' test while negative in an OECD 303 test).

% compound
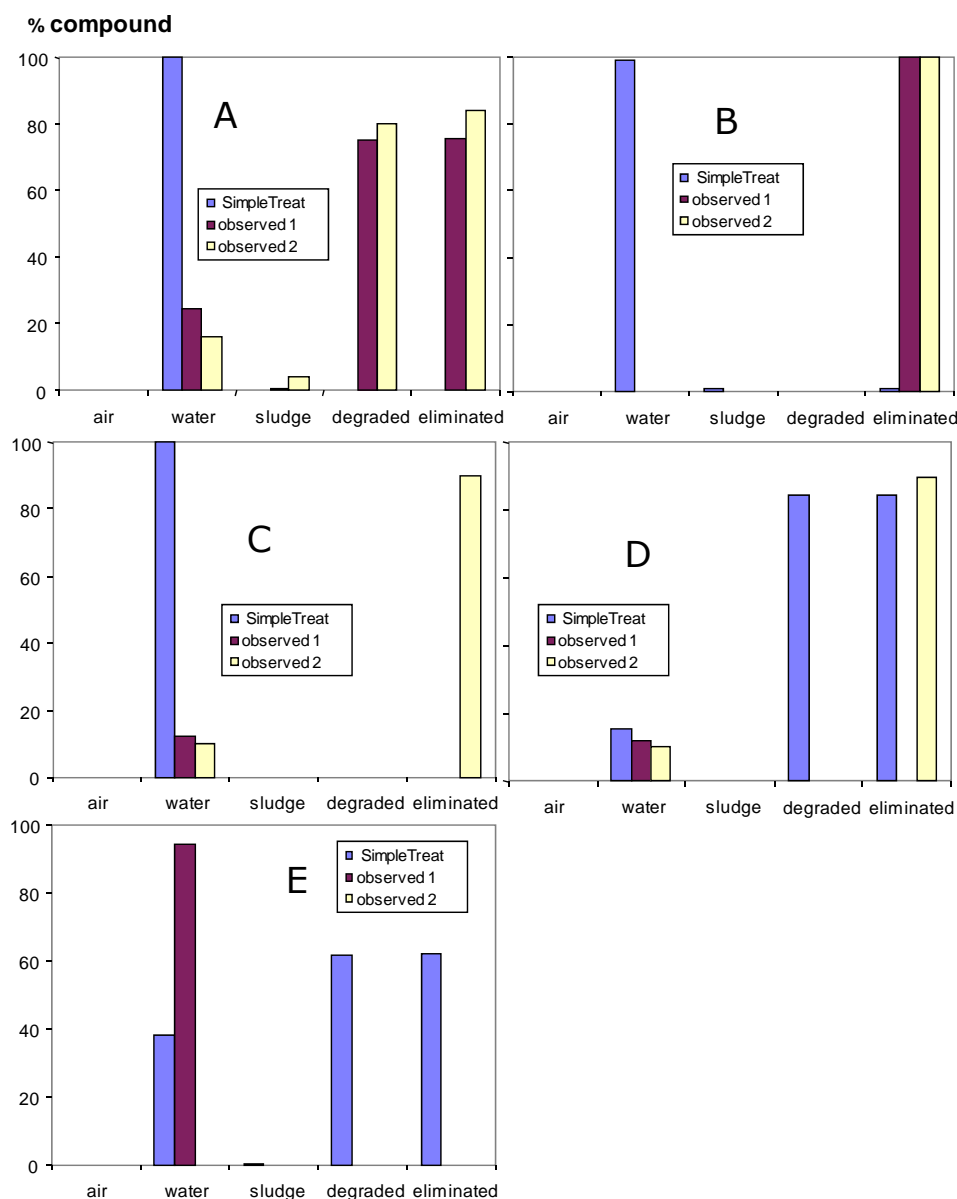
Figure 6 Elimination rates (%) of five anonymous biocides (A to E).

3.4   Diverse chemicals collected from literature

Franco et al. (2012) collected from literature field data of a diverse group of 10 chemicals (Table 5) for calculating the median and the 5th and 95th percentile emission data. Compound properties for this set of compounds are given in Table 6.

Modeled and measured relative emission rates to water are given in Figure 7 showing that when measured Koc data are used as input, predictions improve. This increasing agreement becomes clearer when the results are presented in an alternative way. Figure 8 shows that this tendency to a better agreement can be expressed quantitatively as R^2 increases from 0.530 to 0.775.

Table 5 Chemicals collected from literature.

Chemical	short name	nature	function
Tonalide[a]	AHTN	neutral	
Permethrin[b]	PMT	neutral	pharm., biocide
Decamethylcyclopentasiloxane[c]	D5	neutral	
Triclosan[d]	TCS	acid	pharm., biocide
Ibuprofen[e]	IBU	acid	pharm.
Trimethoprim[f]	TMP	base	pharm.
Linear alkylbenzene sulfonate[g]	LAS	acid, mixture	surfactant
Benzalkonium chloride[h]	BAC	base, mixture	surfactant
Ethylenediaminetetraacetic acid[i]	EDTA	ligand	
Zinc pyrithione[j]	ZPT	ligand	biocide

[a] Artola-Garicano et al. (2003); Horii et al. (2007); Kupper et al. (2006); Clara et al. (2005); Lee et al. (2010)
[b] Gomez et al. (2007); Kupper et al. (2006)
[c] Kazuyuki et al. (2007), ECHA (2012)
[d] MacAvoy et al. (2002), ECHA (2012)
[e] Gomez et al. (2007), ECHA (2012)
[f] Paxeus (2004)
[f,h] Clara et al. (2007)
[g,i,j] ECHA (2012)

Table 6 Basic properties of chemicals collected from literature. EDTA is a polyvalent acid. See for literature references Franco et al. 2012.

	pKa	pKb	H	Log Kow	Log Koc	biodegrad. Screen. test
AHTN			37.1	5.40	3.85	no
PMT			0.19	6.10	4.14	read. biod. no 10 d window
D5			$3.34 \cdot 10^6$	8.02	5.17	no
TCS	8.00		$5.1 \cdot 10^{-4}$	4.90	4.67	inherently biod.
IBU	4.91		0.056	3.87	2.33	readily biod.
TMP		7.12	n.a.	0.91	3.02	no
LAS	n.a.		n.a.	3.32	3.70	read. biod. no 10 d window
BAC		n.a.	n.a.	1.35	4.12	read. biod. no 10 d window
EDTA	-0.1; 1.4; 2.2; 2.5; 6.1; 10.4		n.a.	-3.86	<1.00	inherently biod.
ZPT		4.67	n.a.	0.90	3.64	no
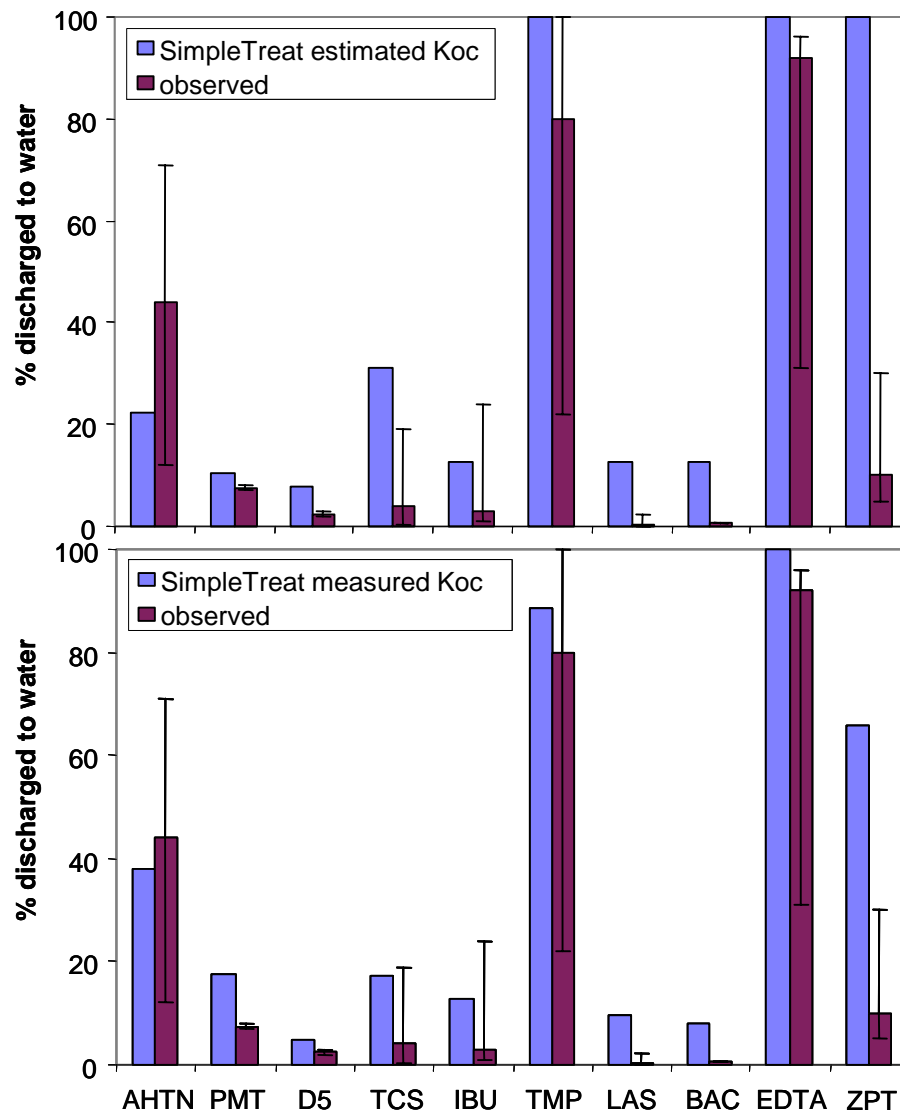
Figure 7 Predicted versus measured emission to water. Koc is either estimated from Kow (upper panel) according to the equation of Sablic and Güsten (1995) or measured and used as input (lower panel) in the input sheet (see Appendix A). This is done by calculating Kp (activated sludge) from by multiplication of Koc (measured) with 0.37 (fraction organic carbon in activated sludge).

Conclusions:
1. When biodegradation is a relevant removal mechanism, SimpleTreat overestimates emission to water. This is due to the conservative rate constants in the TGD (2003) according to the precautionary principle. Especially for test results falling in the category ready biodegradability without fulfilling ten day window and inherent biodegradability, SimpleTreat overestimates emission to water.
2. Input of measured Koc data improves the prediction as they are in a better agreement to measured data. With default estimated Koc, SimpleTreat underestimates the emission of AHTN to water is regarded alarming. When a measured Koc is used as input, there is a fair agreement between prediction and measured data, although the variation in observed data is large.
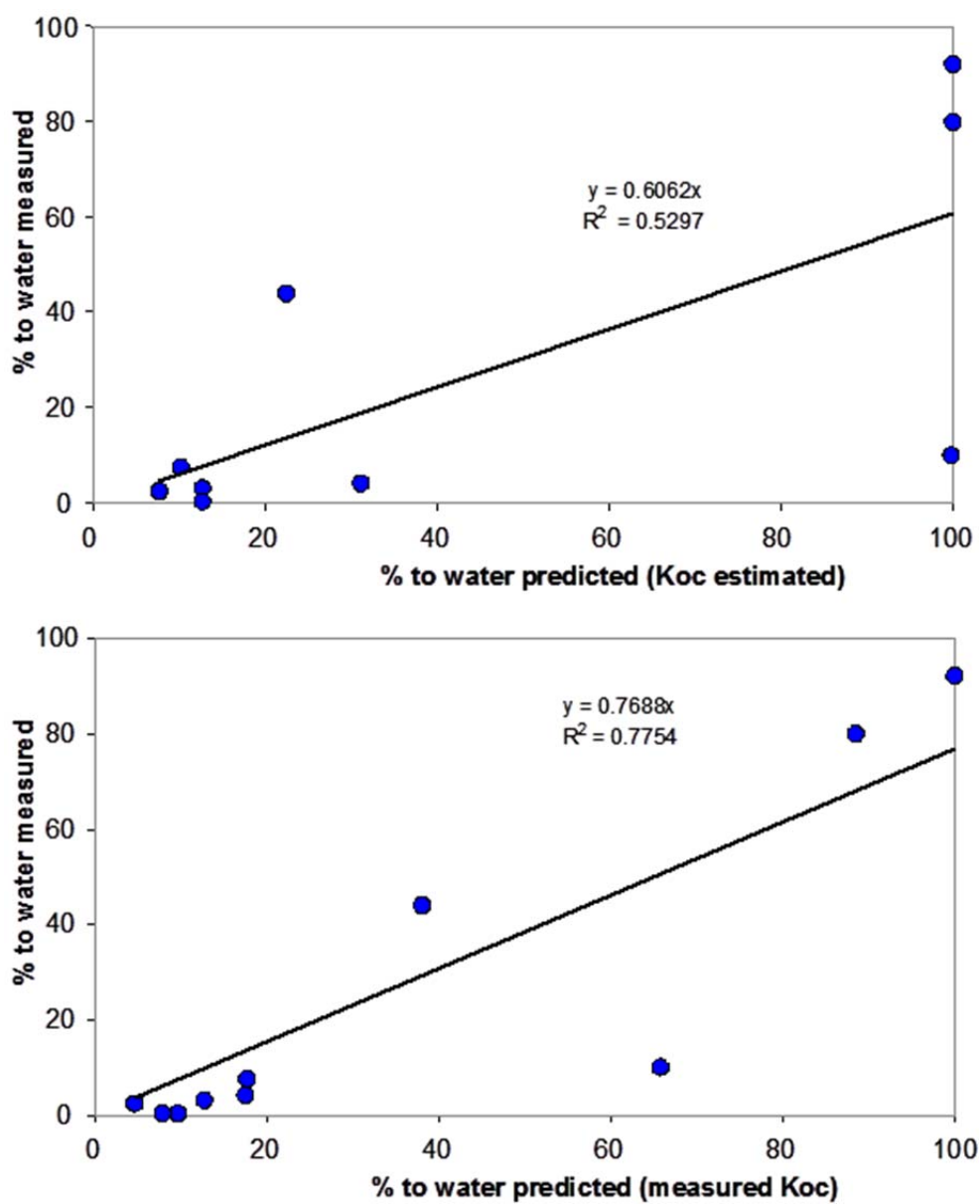
Figure 8 Predicted versus measured emission to water. Koc is estimated from Kow (upper panel) or measured and used as input (lower panel).

4 Do default values in the model reflect the current technology? (work package 2) and what are the refinement options? (work package 3)

Generally, the model is not very sensitive for the choice of default operation parameters compared to its sensitivity to partition coefficients unless unrealistic values are chosen. Nevertheless, some default parameters in the model may be reconsidered. This is wise to avoid discussions that are not really relevant for the use of the model. Some of these parameters are so-called fixed default parameters. This means that some choices can be made with respect to the operation of an STP that cannot be changed by the model user. Examples are the sewage or solids inflow per person per day (200 L and 90 g, respectively) or concentrations of suspended solids in raw sewage, activated sludge and in the effluent (600, 3300 and 30 mg/L, respectively). Fixed default parameters are visualised in Figure 9.
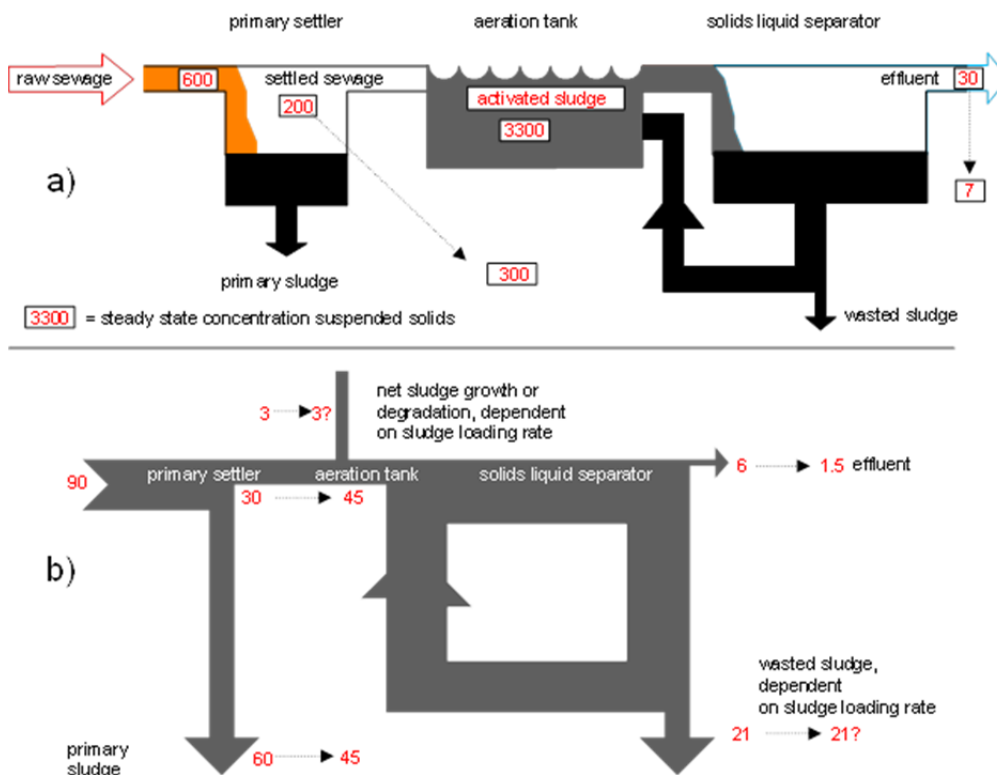
Figure 9 Proposed modifications of default parameters in specific for an STP with a primary sedimentation tank (a) and the solids mass balance in dry weight solids per capita per day (b).

4.1   Fraction solids removed by the primary clarifier

The fraction of solids in raw sewage removed from the primary sedimentation tank is not included in Table 8. In the current version of SimpleTreat this fraction is two-thirds. Figure 8 a) implies that when the steady state concentration solids concentration in raw sewage is 600 mg/Land in the primary settler is 200 mg dry weight solids per litre, two-thirds of the solids leaves the system as primary sludge. Now there seems to be agreement that a fraction of one half better reflects the reality (Franco et al., 2012). This would affect the model output more significantly. Changing the fraction of solids from raw sewage removed by the primary clarifier from 0.67 to 0.50 would give a scenario somewhere in between the current 9-box version of SimpleTreat, i.e. with primary sedimentation, and the 6-box version (without primary sedimentation). In the latter version, all BOD is discharged into the activated sludge reactor because 0% of the inflow of the sewage solids having a high BOD content is removed by the primary clarifier. In SimpleTreat the total amount BOD (both dissolved and in solids) per weight unit activated sludge per person per day is an important operation parameter. It affects the hydraulic and sludge retention time and has influence on the elimination rate due to volatilization (if the chemical has a relatively high H value) or biodegradation (if the chemical is biodegradable). The sludge and BOD regimes in the 9-box and 6-box versions are in principle different. In fact both systems are different models which are not always understood. It frequently evokes questions which are not very relevant. For example, if a chemical has a very low Koc so that that elimination due to sludge withdrawal is zero and the chemical is biodegradable (or volatile) the 6-box version gives slightly higher removal rates. This can be explained if we consider that a longer time the chemical remains in the aerator because more BOD has to be processed. As a result, with similar rate constants for biodegradation (or volatilization), there is more time for biodegradation (or volatilization) to occur.

4.2   Default parameters that can be changed

Default parameters that can be changed by the user can be seen as a refinement option as it allows changing the scenario. In the TGD (2003) numbers are given as defaults. In EUSES it is difficult to recognise that these are variable input parameters. For example, for the volume of waste water per person per day (Q) the value of 0.2 m^3 is taken (Table 7). In North America Q is as high as 0.5 m^3 whereas in many countries in Europe Q is approximately 0.15 m^3. The product of Q and N (number of inhabitants connected) determines the emission scenario in terms of volume sewage, inflow of solids. If the emission rate of the chemical is known, the chemical concentration in raw sewage is calculated by the model.
The depth of the tanks is constant but their volume is proportional to N which means that in SimpleTreat the areas of all tanks are scaled to N. For the aeration tank this area is not only scaled to N but is also dependent on the mode of operation which is expressed as sludge loading rate (or the choice between with or without primary sedimentation).

Readily biodegradable substances fulfilling the ten day window criterion are discharged to surface water through the effluent at the relatively high level of 12.7% and even at 32.6% if the ten day criterion is not fulfilled. In earlier versions of SimpleTreat, this percentage would be less than 5% for all readily biodegradable chemicals (with or without the ten day criterion) when the SLR is

equal to 0.15 kg BOD/kg dry weight activated sludge per day. This lower emission rate is caused by a first order rate degradation constant equal to 3/hr. The current recommended choice of SLR should be reconsidered. It has been suggested that due to increasing treatment facilities the default value for SLR (0.15 kg BOD per kg solids per day) may be lowered to 0.1 (Price, 2011). However it has to be confirmed that the average SLR in the EU is better represented by 0.1 than by 0.15 kg_{BOD} per kg_{dwt} per day.

Table 7 Input parameters characterizing size and the operation mode of a treatment plant. PE is person equivalent, k_{dwt} is kg dry weight.

parameter	units	meaning	default
Q	m^3 PE^{-1} d^{-1}	sewage flow	0.2
N	PE	number inhabitants	10,000
SLR	kg_{BOD} kg_{dwt}^{-1} d^{-1}	sludge loading rate	0.15
M	-	aeration: surface (s) bubble (b)	s

In Appendix A the input sheet of the spreadsheet version of SimpleTreat displays a table with several sludge loading rates (SLR) and the consequences for retention times. The hydraulic retention time is dependent on the loading of an STP, expressed as sludge loading rate (SLR). A high SLR, for example 0.6 kg BOD per kg activated sludge (dry weight) per day, is typically coupled with a relatively short hydraulic retention time of 1.7 hr. From a simple mass balance calculation, removal is as high as 85.6% if the degradation rate constant is 3/hr, even during this short period. When the EU adopted the revised version of SimpleTreat 3.0 (1996), the first order biodegradation rate constant for readily biodegradable compounds reduced from 3/hr to 1/hr. This value was considered a compromise as well as a precautionary measure. In Figure 9 the minimum elimination percentage (if biodegradation is the sole removal mechanism) is plotted against the sludge loading of the activated sludge process for first order degradation rate constants that fall in the range of ready biodegradability:

- k = 3/hr as in the first version of SimpleTreat (Struijs et al., 1991). This degradation rate constant gives the best agreement with observations in the field and in laboratory experiments that simulate the fate of a chemical in the STP;
- k = 1/hr as in EUSES (TGD, 2003) however, for readily biodegradable compounds that fulfil the ten day window;
- k = 0.3/hr if a chemical passes the ready biodegradability test without fulfilling the ten day criterion. For SLR equal to 0.1 instead of 0.15 kg BOD/kg sludge/d, the emission of readily biodegradable (fulfilling the ten day window criterion) compounds to water would decrease from 12.7% to 9% (see Figure 10).

4.3 Fixed default parameters

Fixed default parameters are given Table 8. The hydraulic retention time in the aerator is not present in this table because it is a rather complex function of the sludge retention time, see for detailed information Struijs (1996). This dependency results in values that are given in the table in the input sheet (Appendix A).

Table 8 Fixed parameters for raw sewage and the operation of domestic waste water treatment. PE is person equivalent, d_{dwt} means density on dry weight basis.

| parameter	units	meaning	value
raw sewage			
BOD	g O_2 PE^{-1} d^{-1}	Mass of O_2 binding material per person per day	54
SOLIDS	kg_{dwt} PE^{-1} d^{-1}	Dry weight solids produced per person per day	0.09
d_{RS}	kg_{dwt} L^{-1}	Density solids	1.500
foc_{RS}	-	Fraction organic carbon	0.3
primary settler			
h_{PS}	m	Depth	4
HRT_{PS}	hr	Hydraulic retention time	2
d_{PS}	kg_{dwt} L^{-1}	Density solids	1.500
foc_{PS}	-	Fraction organic carbon solids	0.3
activated sludge tank			
h_A	m	Depth	3
d_A	kg_{dwt} L^{-1}	Density solids activated sludge	1.300
foc_A	-	Fraction organic carbon solids	0.37
CAS	kg_{dwt} m^{-3}	Conc. solids of activated sludge	4
Cox	kg m^{-3}	Steady state O_2 conc. in activated sludge	0.002
G	m^3 s^{-1} PE^{-1}	Aeration rate bubble aeration	$1.3 \cdot 10^{-5}$
solids liquid separator			
h_{SLS}	m	Depth	3
d_{SLS}	kg_{dwt} L^{-1}	Density susp. and settled solids	1.300
foc_{SLS}	-	Fraction organic carbon solids	0.37
CEF	kg_{dwt} m^{-3}	Conc. solids in effluent	0.03
HRT_{SLS}	hr	Hydraulic retention time	6
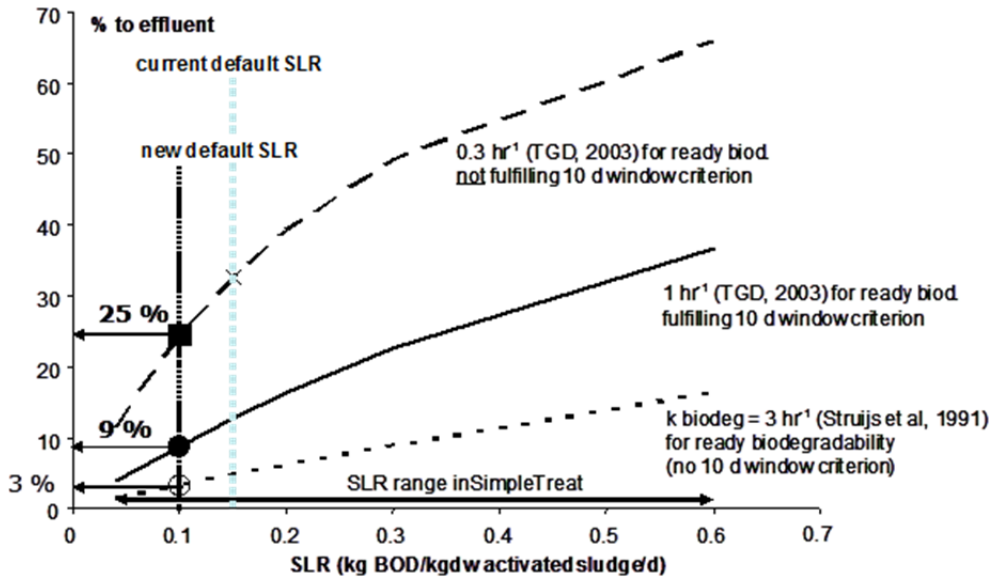
Figure 10 Emission to water if the recommended sludge loading rate decreases from 0.15 to 0.1 kg BOD per kg dry weight activated sludge per day.

5 Proposals to adapt the model: outlook to a revision of SimpleTreat (work package 4)

There are no reasons to reject the box model concept of this model, neither are there indications that the process formulations for degradation, media flows and inter compartment transport ('diffuse mass flows') need to be altered. This evaluation points to the paramount influence of adequate input of equilibrium partition constants, especially for sludge water. What need to be changed is the multiple equilibrium computations for ionised chemicals. For acids and bases an alternative calculation of the organic carbon-water partition coefficient is needed.

5.1 Incorporating new equations for Koc

New equations for Koc as a function of Kow and Ka (or Kb) have been presented recently (Franco et al., 2012). For organic acids they have derived:

$$Koc = Fn \cdot 10^{0.54 \cdot \log Kow + 1.11} + Fa \cdot 10^{0.11 \cdot \log Kow + 1.54}$$

with Fn and Fa the fractions of neutral and anionic species, respectively calculated at optional which pH is the ambient pH minus 0.6. Also in this equation Kow has been determined for the chemical in the neutral state. This equation is identical to what has been found earlier for soils (Franco and Trapp, 2008). This can be seen as an alternative for the multiple equilibrium calculations as carried out by SimpleTreat from the Kow of the compound in the neutral state and the fraction of the ionised species at pH 7 calculated from the acid or base dissociation constants.

Tentatively, the equations by Franco and Trapp (2008) for natural solids-water systems may be applied. As the equation derived by Franco and Trapp (2008) for organic bases is not satisfactory for activated sludge at a later stage the results of an ECETOC task force (ECETOC, 2012) may be employed. The ECETOC task force gathered partition coefficients of chemicals that can exist as ionised species in activated sludge. Recently, Franco et al. (2012) applied the ECETOC results for deriving Koc of organic bases in SimpleTreat.

The alternative equations for organic carbon referenced sludge-water partition coefficients (Koc) can be incorporated in the model. This can be done as either as an alternative for the multiple equilibrium calculation in SimpleTreat 3.1.

5.2 Use new equations for Koc without altering the model

The equations for Koc acids (Franco and Trapp, 2008) and bases (ECETOC, 2012) can also be applied to calculate a Koc value *as input* in case a measured Koc is not available. SimpleTreat allows input of sludge water partition coefficients (Kp) *directly*. If this option is used all estimation methods based on substance properties such as Kow, Ka and Kb are overruled. If a value of Kp is given (in L/kg dry weight) it is considered an input parameter while air-water partitioning is still assessed from the vapour pressure and the water solubility (of the neutral chemical). For a specified acid or base, Kp values are evaluated by multiplying the calculated Koc value with foc fractions 0.30 and 0.37 for raw sewage and activated sludge, respectively. For pharmaceuticals, surfactants and

biocides the air-water partition coefficient is usually very low because the vapour pressure is negligible. The fate of these chemicals is determined by sludge water partitioning, biodegradation and advective transport via water and sludge.
With a more user-friendly input sheet which has a provision for both input of Kp and Koc, the new Koc rules do not necessarily have to be included in the model. The modeller self can calculate the Koc and use it as input so that all default estimations are overruled. This requires the support of a good guidance document or an easily accessible user manual.

5.3 Additional fate processes: anaerobic digestion

The dimensions and operation parameters of an anaerobic digester are formulated in terms of the number of inhabitants. Accordingly, an algorithm is developed for elimination of the chemical under methane producing conditions in the sludge digesting tank. This algorithm can be made compatible to the model SimpleTreat. It simply computes the reduction of the chemical concentration in the sludge produced by an STP by means of this algorithm.
For this extension the input sheet needs to have an input cell for input of the first order degradation rate constant that characterises the anaerobic biodegradability of a chemical.

6   Discussion

6.1   Sludge water partitioning

We have investigated the applicability of SimpleTreat for a broader range of organic chemicals than only hydrophobic. This was done without changing the model structure but making use of some special options of this model regarding the input of special parameters:

- Acid and base dissociation constants (Ka, Kb) in combination of the Kow of the compound in the neutral state. This implies that Kow is measured at some extreme pH at which the chemical is predominantly in the neutral state,
- Measured data for Kp (raw sewage and activated sludge) or Koc which overrule estimated Kp or Koc based on Kow according to the equation of Sablic and Güsten (1995).

The applicability of SimpleTreat 3.1 for inorganic chemicals (e.g. metals) and nano-materials was however not evaluated because that was beyond the scope of the study.

From the data set consisting of biocides 1 to 5 (Table 2), it was demonstrated that the estimation of the Koc for one biocide, which was based on a Kow value as high as 160,000 and which was determined at a low pH (at least lower than pH 4) in combination with a pKa of 5.3 as input parameter, yielded a Koc value of 300 L/kg. This appeared very close to the measured Koc at pH 7 (325 L/kg). Other results of WP 1 however, showed that overruling default estimation of partition coefficients by direct input of measured Koc data results in better predictions of emission via water or sludge.

Both soil-pore water and sludge-water partition coefficients of registered biocides are most often available as well as the organic carbon fraction of the soil and sludge. Of a set of 22 anonymous pharmaceuticals obtained from the UBA, soil and sludge water partition coefficients were determined according to a standardised method (OECD 106). There is some scientific/technical debate on the apparent difference between Koc soil and Koc sludge which should not occur ideally. It is beyond the framework of this research and therefore only the sludge-water partition coefficients (Kp) were investigated.

Figure 10 compares modelled log Kp data (log Kp SimpleTreat) with measured data. Kp SimpleTreat is calculated with the equation Kp = 0.37 Koc in which 0.37 is equal to the organic carbon fraction of activated sludge as applied in SimpleTreat. Koc is calculated according to the equation Koc = 1.26 Kow$^{0.81}$ (Sablic and Güsten, 1995) as applied in the model. Two-third of this dataset shows that the measured Kp is higher than Kp estimated by SimpleTreat. The difference may be a factor up to 30. In the higher region (Kp > 3,000 L/kg) there seems to be better agreement.

These results lead to a tentative conclusion that the input sheet may be maintained but should be designed in a more user-friendly way. More importantly, a revision of the model should be accompanied by a good guidance report.

Sometimes however, measured Koc (or Kp) date are not available or not suitable to use as input. In that case, we cannot always rely on the multiple equilibrium calculations based on hydrophobic sorption and ionisation of acids and bases. The new rules for Koc (Franco et al., 2012) may be applied as an alternative.
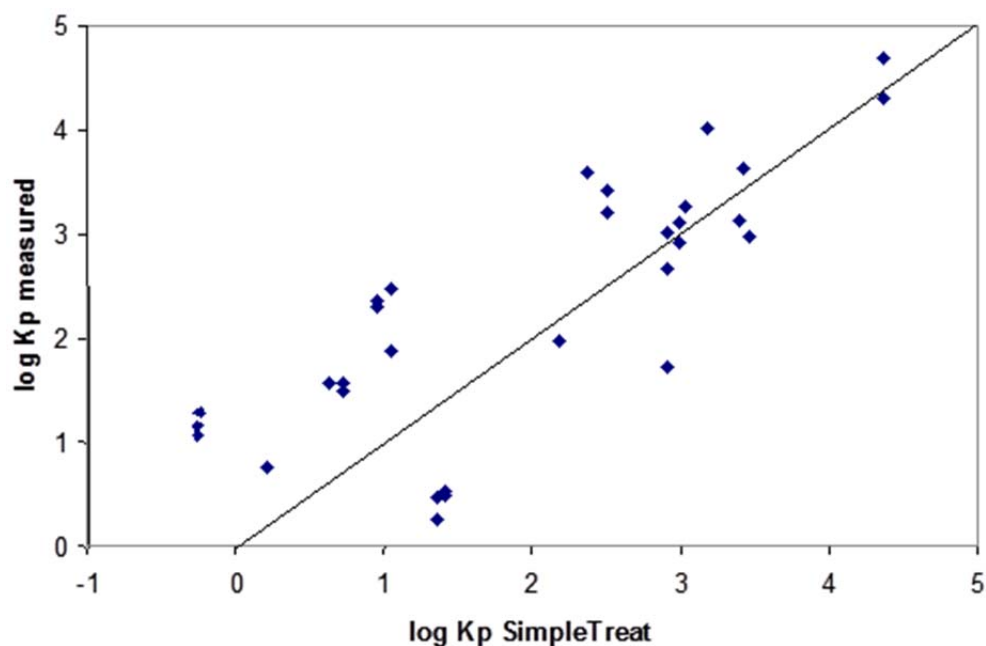
Figure 11 A set of measured and estimated sludge water partition coefficients of 22 anonymous pharmaceuticals provided by UBA.

6.2 Fate processes in the current model

The technical modifications in the spreadsheet version of SimpleTreat, as proposed in previous sections, focus on improved rules for solids water partitioning. However, the kinetic description of biodegradation may be improved or at least brought into agreement with developments on testing methods as proposed by the OECD, the EU and the ISO.
In the current version of SimpleTreat, biodegradation of the modelled chemical is considered to occur exclusively in the aqueous phase of activated sludge in the aeration tank (TGD, 2003, p 61). The feasibility and applicability for generic substance evaluation is matter of discussion. The OECD 314 (OECD, 2008) test is an example of new methods of assessing biodegradation in activated sludge.

6.3 Conclusion and outlook

This report is both an evaluation and a discussion document aiming at a revision of SimpleTreat 3.1. It may be regarded a preamble of an update of the model. Parties involved are UBA, RIVM, ECHA, academia (Radboud University of Nijmegen in the Netherlands) and the industry.

This evaluation indicated that the default computation of sludge-water partition coefficients for 'difficult' compounds may deviate considerably from measured sorption constants. This report and other on-going scientific activities with

respect to SimpleTreat 3.1 support a revision of the model (e.g. a recently published study by Franco et al., 2012). A scoping report on the need of a revision of the model by the REACH bureau of the RIVM is in preparation. The REACH/RIVM report describes the scope of a revision of SimpleTreat. Deliverables are a new model in spreadsheet format, a user manual, a scientific article – if appropriate – and presentations during workshops and conferences.

Revision of the model would include:
1) making it compatible to input data which are mandatory under the different substance regulations;
2) improving default calculations to estimate partition coefficients for complicated substances that may exist in the ionic state;
3) adjusting default values regarding operational parameters of sewage treatment plants as the current default values do not reflect the current sewage technology.

The project aiming at a revision of SimpleTreat 3.1 may be carried out in coordination with ECHA.

7   References

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Appendix A Input sheet of SimpleTreat 3.1

SimpleTreat 3.1 (version, 14 Mar 03)								
input								
Characterization of the chemical								
Name compound = hypotheticum					s			
Physico-chemical properties				table 1:				
Molecular weight =	[	1E+02	] g mol^{-1}	0.1 kg mol^{-1}	Sludge loading rate (SLR) related to hydraulic retentiontime			
K_{ow} =	[	1E+03	] (-)	1000 (-)	(HRT) and sludge retention time (SRT). HRT with primary			
Vapour pressure =	[	1E+00	] Pa	1 Pa	sedimentation (PS) and without; PS has no influence on SRT.			
Solubility =	[	1E+02	] mg L^{-1}	1 mol m^{-3}	SLR	HRT (PS)	HRT	SRT	nitrification
K_a =	[	1E-20	] (-)	1E-20 (-)	(kg$_{BOD}$ kg$_{dwt}^{-1}$ d^{-1})	(hr)	(hr)	(d)	(-)
K_b =	[	1E-20	] (-)	1E-20 (-)	0.04 (low)	25.9	40.5	37.0	yes
Henry constant (H) =	[	**1E+00**	] Pa m^3 mol^{-1}	1 Pa m^3 mol^{-1}	0.06 (low)	17.3	27	24.1	yes
K_p (raw sewage) =	[	**1E+02**	] L kg$_{dwt}^{-1}$	101.7 L kg$_{dwt}^{-1}$	0.1 (low)	10.4	16.2	14.1	yes
K_p (activated sludge) =	[	**1E+02**	] L kg$_{dwt}^{-1}$	125.4 L kg$_{dwt}^{-1}$	0.15 (medium)	6.9	10.8	9.2	yes
					0.2 (medium)	5.2	8.1	6.8	no
Emission scenario					0.3 (high)	3.5	5.4	4.5	no
T air =	[	15	] centigrade	288 Kelvin	0.6 high)	1.7	2.7	2.2	no
T water =	[	15	] centigrade	288 Kelvin					
Windspeed =	[	3	] m s^{-1}	3 m s^{-1}					
Sewage flow =	[	200	] L person^{-1}d^{-1}	0.2 m^3 person^{-1}d^{-1}					
Number inhabitants =	[	1E+04	] person	10000 person					
sludge loading rate (table 1) =	[	0.15	] kg$_{BOD}$ kg$_{dwt}^{-1}$ d^{-1}	0.15 kg$_{BOD}$ kg$_{dwt}^{-1}$ d^{-1}					
Bubble or surface aeration: b/s	[	s	] (-)	s (-)					
Emission rate chemical =	[	1	] kg d^{-1}	1 kg d^{-1}					

table 2: chosen operation parameters				table 3:	
Sludge loading rate =	0.15 kg$_{BOD}$ kg$_{dwt}^{-1}$ d^{-1}			Concentration in raw sewage calculated from	
with primary sedimentation				the default emission rate of the chemical	
HRT =	6.9 hr			C total raw sewage=	5.0E-01 mg l^{-1}
SRT =	9.2 d			Dissolved =	96 %
without primary sedimentation				C dissolved =	4.8E-01 mg l^{-1}
HRT =	10.8 hr			C in solids =	4.9E+01 mg kg^{-1}
SRT =	9.2 d				

Biodegradation in activated sludge

Temperature dependence (y/n)	[	n	] (-)	n

Method 1: estimated from OECD/EU standardized biodegradability tests (USES 2.0)
Assumption: degradation according to first order kinetics with respect to the concentration in the aqueous
phase of activated sludge, implying that the chemical adsorbed to solids is not available for biodegradation.
The following values are recommended:
Readily biodegradable, fulfilling 10 d window criterion: range is 1 to 3 hr^{-1} (TGD-EU: 1 hr^{-1})
Readily biodegradable, not fulfilling 10 d window criterion: range is 0.3 to 1 hr^{-1} (TGD-EU: 0.3 hr^{-1})
Inherently biodegradable in MITI II and within 10 d in the Zahn-Wellens (window = 3 d): range is 0.1 to 0.3 hr^{-1}
Inherently biodegradable: range is 0 .01 to 0.1 hr^{-1} (TGD-EU: 0.1 hr^{-1})

k biodeg1 =	[	0	] hr^{-1}	0 s^{-1} ,T water = 15 C

Method 2: chemical is biodegradable in activated sludge batch test (draft ISO test)
Assumption: degradation according to first order kinetics with respect to the concentration in the slurry phase,
implying that biodegradation occurs both in the aqueous and the solids phase of activated sludge.

k biodeg2 =	[	0	] hr^{-1}	0 s^{-1} ,T water = 15 C

Method 3: chemical is biodegradable in activated sludge, Monod Kinetics
Assumption: biodegradation in the aqueous phase of activated sludge, however, the rate constant is
a function of the influent concentration, μ_{max} and K_s and the sludge retention time. Default values
for μ_{max} and K_s pertain to readily biodegradable chemicals.

μ_{max} =	[	2	] d^{-1}	2 d^{-1}
K_s =	[	0.5	] mg L^{-1}	0.5 mg L^{-1}

Appendix B Output sheet of SimpleTreat 3.1

output of SimpleTreat 3.1 (14 Mar 03)							
report of	hypotheticum						
including primary sedimentation							
Elimination in the primary settler							
volatilization	0.2						
via primary sludge	2.9						
total	3.1 %						
				without primary sedimentation			
Elimination in the aerator				Elimination in the aerator			
stripping	0.9			stripping	1.4		
biodegradation	0.0			biodegradation	0.0		
total	0.9 %			total	1.4 %		
Elimination in the solids liquid separator				Elimination in the solids liquid separator			
volatilization	0.8			volatilization	0.8		
via surplus sludge	1.1			via surplus sludge	2.0		
total	1.9 %			total	2.8 %		
Total elimination from waste water	5.9 %			Total elimination from waste water	4.2 %		
Total emission via effluent	94.1 %------V			Total emission via effluent	95.8 %------V		
		93.76 % dissolved				95.44 % dissolved	
		0.36 % associated				0.36 % associated	
balance	100.0 %			balance	100.0 %		
Summary of distribution				Summary of distribution			
to air	1.8			to air	2.2		
to water	94.1			to water	95.8		
via primary sludge	2.9			via surplus sludge	2.0		
via surplus sludge	1.1			degraded	0.0		
degraded	0.0			total	100.0 %		
total	100.0 %						
Concentrations				Concentrations			
in air	3.56E-07 g m^{-3}			in air	3.93E-07 g m^{-3}		
in combined sludge	5.11E+01 mg kg^{-1}			in surplus sludge	6.03E+01 mg kg^{-1}		
|_____	in primary sludge: 4.86E+01 mg kg^{-1}			in effluent (total)	4.79E-01 mg l^{-1}		
|_____	in surplus sludge: 5.92E+01 mg kg^{-1}			|_____	dissolved 4.77E-01 mg l^{-1}		
in effluent (total)	0.47058 mg l^{-1}			|_____	associated 1.81E-03 mg l^{-1}		
|_____	dissolved 4.69E-01 mg l^{-1}			in solids effluent	6.03E+01 mg kg^{-1}		
|_____	associated 1.78E-03 mg l^{-1}						
in solids effluent	5.92E+01 mg kg^{-1}						
Operation of the plant equipped with a primary settler				Operation of the plant without primary settler			
Sludge loading rate =	0.15 kg BOD (kg dw)$^{-1}$ d^{-1}			Sludge loading rate =	0.15 kg BOD (kg dw)$^{-1}$ d^{-1}		
HRT =	6.9 h			HRT =	10.8 h		
SRT =	9.20 d			SRT =	9.20 d		
Aeration mode =	surface aeration			Aeration mode =	surface aeration		
Primary sludge =	6.00E+02 kg dry weight d^{-1}			Surplus sludge =	3.31E+02 kg dry weight d^{-1}		
Surplus sludge =	1.90E+02 kg dry weight d^{-1}			Total wastewater =	2.00E+03 m^3 d^{-1}		
Total sludge =	7.90E+02 kg dry weight d^{-1}						
Total wastewater =	2.00E+03 m^3 d^{-1}						