UNIVERSITEIT
GENT

DEPARTMENT OF APPLIED MATHEMATICS,
BIOMETRICS AND PROCESS CONTROL

Intevation
GmbH

GREAT-ER II

Chemical Fate Models

Geo-referenced Regional Exposure Assessment Tool for European Rivers

Geert Boeije, Frank Koormann

November 01, 2005

Document History

Version	Author	Chapter	Description
October 2003	F. Koormann		Initial version, taken over from GREAT-ER 1.0
November 2005	F. Koormann	1,	GREAT-ER Sediment Extension description added: Sediment concentration and diffuse input

Table of Contents

1. Preface

GREAT-ER 1.0 (1996 – 1999, a research project funded by ERASM and the UK EA). Has proven the applicability of well-known exposure assessment models in a geo-referenced framework with a Monte-Carlo approach to derive frequency curves of chemicals over space and time.

GREAT-ER II is a software development project funded by CEFIC Long Range Research Initiative. The project can be seen as the successor of GREAT-ER 1.0 with the following aims:

- Independent GIS user interface
- Database
- Flexible modeling framework considering exchange and enhancement of models.

To demonstrate the functionality of the new modeling framework the models of GREAT-ER 1.0 have been reimplemented. To document these models the documentation of GREAT-ER 1.0 is used as a basis, with minor corrections of typos and naming changes.

The GREAT-ER II Sediment Extension enhances the GREAT-ER Model Suite with an equilibrium partitioning based model to consider substance concentrations in the sediment. In addition the model results for the water body can be displayed more detailed (dissolved, sorbed and total water column (the latter is the concentration originally displayed by GREAT-ER)).

Secondly a diffuse input has been added to the river models to link GREAT-ER with the TERRACE[1]

The work of Geert Boeije by writing this comprehensive documentation of the models covered by GREAT-ER is thankfully acknowledged.

Entry points to the work on the GREAT-ER Model system are:

- http://www.great-er.org
- http://great-er.intevation.org

---

[1] TERRACE: Terrestrial Runoff Modeling for RISK Assessment of Chemical Exposure, a CEFIC LRI project.

2. General Fate Pathway Structure

The general structure of the aquatic fate pathway within one segment which contains a waste water emission point is shown in Figure 1. For a segment without emission, it is given in Figure 2. This structure is identical for all complexity modes.
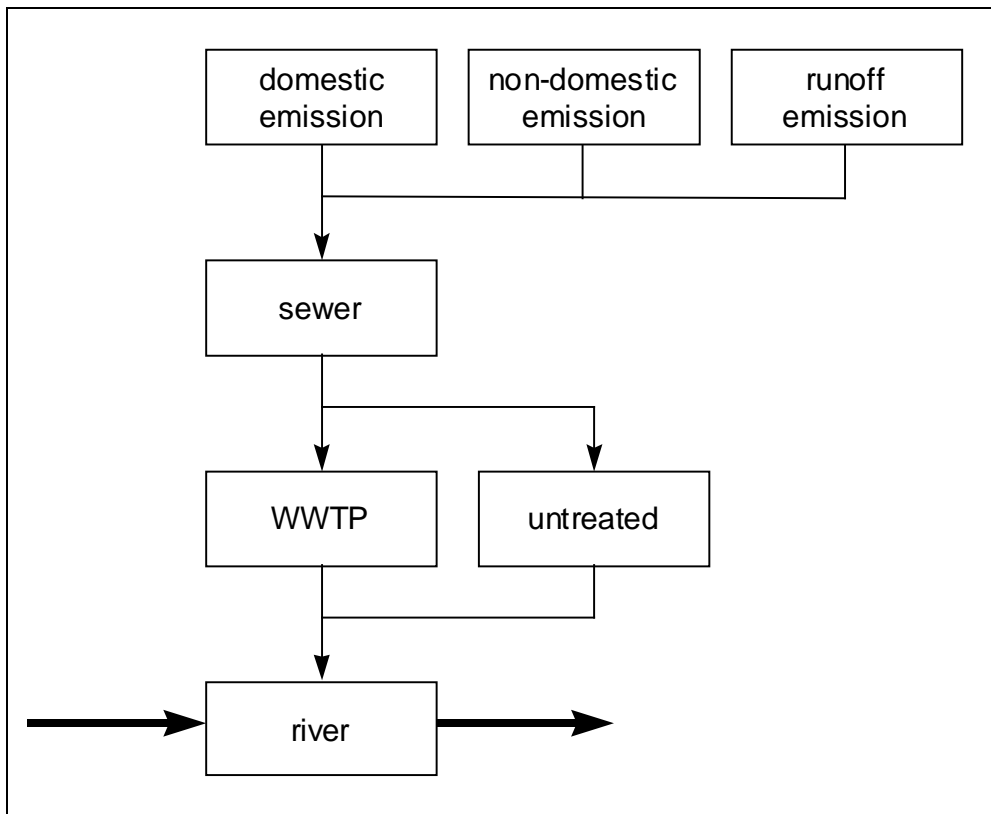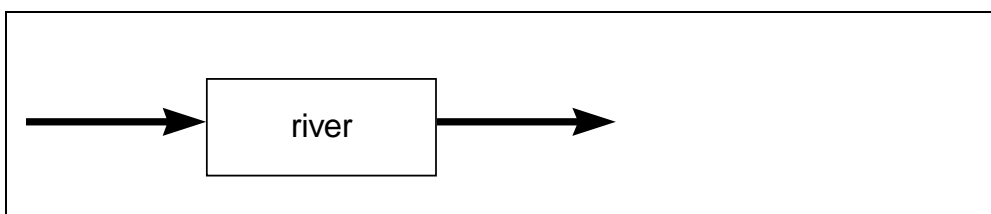

Figure 1. Fate pathway structure - with emission

Figure 2. Fate pathway structure - without emission

The sewer flow fraction entering the WWTP, f_{WWTP}, is given in the geo-reference parameter set for each waste water emission point.

3. Emission Models

3.1.1. Model

The emission models are identical in all complexity modes. For domestic emission:

$$\Phi = \left(M \cdot \frac{1000}{365 \cdot 24 \cdot 3600} \right) \cdot Pop$$

$$Q = \left(W \cdot \frac{1}{1000 \cdot 24 \cdot 3600} \right) \cdot Pop$$

For other emissions (non-domestic and runoff), the chemical mass fluxes are taken directly from the emission data. The flows are taken directly from the geo-referenced parameter set.

3.1.2. Required Parameters

M	chemical market (sales) data	*kg/(cap.year)*
Pop	population	*cap*
W	per capita water consumption	*L/(cap.d)*

4. Chemical Fate Models - Complexity Mode 1

Complexity Mode 1 allows GREAT-ER simulations with a minimal geographically referenced and chemical input data set.

4.1. Sewer

4.1.1. Model

No in-sewer removal is assumed to occur:

$R_{SEWER} = 0$

4.1.2. Required Parameters

4.2. WWTP

Chemical elimination in a WWTP is described by a fixed removal efficiency, which depends on the type of treatment:

4.2.1. Primary settler (= type 1)

Removal efficiency is taken directly from the chemical parameters set:

$R_{WWTP} = R1$

4.2.2. Activated sludge (= type 2)

If no primary settler is present, removal efficiency is taken directly from the chemical parameters set:

$R_{WWTP} = R2$

Otherwise, it is calculated from the combination (in series) of both primary and secondary treatment:

$R_{WWTP} = R1 + R2 - R1*R2$

4.2.3. Trickling filter (= type 3)

If no primary settler is present, removal efficiency is taken directly from the chemical parameters set.

$R_{WWTP} = R3$

Otherwise, it is calculated from the combination (in series) of both primary and secondary treatment:

$R_{WWTP} = R1 + R3 - R1*R3$

4.2.4. Required Parameters

Chemical

R1	chemical removal in a primary settler	-
R2	chemical removal in activated sludge	-
R3	chemical removal in a trickling filter	-

Geo-referenced

4.3. River

4.3.1. Model

Chemical elimination in rivers is described by first-order in-stream removal, assuming a fixed rate coefficient:

$$R_{RIVER} = 1 - e^{-HRT \cdot k}$$

Therewith follows

$$C_{RIVER} = C_0 e^{-HRT \cdot k}$$

For diffuse inputs (assuming a constant and continuous input over the stretch):

$$C_{RIVER} = C_0 e^{-HRT \cdot k} + \frac{I}{V \cdot k} \left(1 - e^{-HRT \cdot k}\right) \qquad \text{and with k = 0:} \qquad C_{RIVER} = C_0 + \frac{I}{V} \cdot HRT$$

The travel time *HRT* is calculated as:

HRT = V/(Q*3600)	for lakes
HRT = L/(v*3600)	for rivers

4.3.2. Required Parameters

Chemical

k	chemical in-stream removal rate	*h⁻¹*
I	diffuse input	*kg/d*

Geo-referenced

L	stretch length	*m*
v	flow velocity	*m/s*
V	lake volume (only in case of a lake)	*m³*

5. Chemical Fate Models - Complexity Mode 2

Complexity Mode 2 allows GREAT-ER simulations with a minimal geographically referenced input data set for rivers. However, for WWTPs a detailed data set is needed, as well as a detailed chemical parameters set.

5.1. Sewer

5.1.1. Model

In-sewer removal is assumed to be a fixed percentage, and is taken directly from the chemical parameter set

$R_{SEWER} = $ *from chemical parameters set*

5.1.2. Required Parameters

Chemical

R_{SEWER} chemical removal in the sewer   -

Geo-referenced

5.2. WWTP

Chemical elimination in a WWTP is described by mechanistic mathematical models for primary settling and for activated sludge. For trickling filter treatment, a simple percent removal model is used.

5.2.1. Primary settler (= type 1)

model identical to mode 3 - model and required parameters: see below

5.2.2. Activated sludge (= type 2)

model identical to mode 3 - model and required parameters: see below

5.2.3. Trickling filter (= type 3)

model identical to mode 3 - model and required parameters: see below

5.2.4. Required Parameters

see section on mode 3

5.3. River

5.3.1. Model

Chemical elimination in rivers (covering optional diffuse input) is described by first-order in-stream removal as already mentioned in 4.3.1 for mode 1:

$$C_{RIVER} = C_0 e^{-HRT \cdot k} + \frac{I}{V \cdot k} \left(1 - e^{-HRT \cdot k} \right)$$

The rate coefficient is calculated as follows:

$$k = k_{deg} + f_s \cdot k_{sed} + f_d \cdot k_{vol}$$

where
$$f_d = \frac{C_d}{C_t} = \frac{1}{1 + C_s/C_d} = \frac{1}{1 + 10^{-6} \cdot K_{d\_river} \cdot SS}$$
$$f_s = \frac{C_s}{C_t} = 1 - f_d$$

If K_{d_river} is not given, it is estimated as follows: $K_{d\_river} = f_{oc\_river} \cdot K_{oc}$

The travel time HRT is calculated as already mentioned in 4.3.1 for mode 1:

$HRT = V/(Q*3600)$ for lakes
$HRT = L/(v*3600)$ for rivers

Based on the above the dissolved and sorbed substance concentrations are derived:

$$C_{RIVER,dissolved} = f_d \cdot C_{RIVER} \qquad\qquad \text{and} \qquad C_{RIVER,sorbed} = f_s \cdot C_{RIVER}$$

5.3.2. Required Parameters

Chemical

$K_{d\_river}{}^{(1)}$	dissolved / sorbed partitioning coefficient	L/kg_{dwt}
K_{oc}	organic carbon / water partitioning coefficient	-
k_{deg}	river: 1st order chemical degradation rate, in the dissolved phase	h^{-1}
k_{sed}	river: 1st order net suspended solids settling rate	h^{-1}
k_{vol}	river: 1st order chemical volatilization rate	h^{-1}
I	diffuse input	kg/d

Geo-referenced

River Stretch

L	stretch length	m
v	flow velocity	m/s
V	lake volume (only in case of a lake)	m^3

River Class

| f_{oc_river} | river: suspended solids organic carbon fraction | - |
| SS | river suspended solids concentration | g_{dwt}/m^3 |

(1) to override estimation

5.4. Sediment

5.4.1. Model

The sediment concentration is derived from the river concentration based on equilibrium partitioning:

$$C_{SEDIMENT} = f_d \cdot C_{RIVER} \cdot K_{SW} = C_{RIVER,dissolved} \cdot \left(K_{d,RIVER} \cdot \frac{\rho_{SEDIMENT,dry}}{\rho_{WATER}} + \theta \right)$$

5.4.2. Required Parameters

Chemical

| K_{d_river} | dissolved / sorbed partitioning coefficient | L/kg_{dwt} |

Geo-referenced

None

Non Geo-referenced

$\rho_{SEDIMENT, dry}$	dry sediment density	kg_{dwt}/m^3
ρ_{WATER}	water density (1 kg_{dwt}/m^3)	kg_{dwt}/m^3
θ	volume fraction water in sediment	m^3/m^3

6. Chemical Fate Models - Complexity Mode 3

Complexity Mode 3 requires detailed parameters for rivers, for WWTPs and for the simulated chemical.

6.1. Sewer

6.1.1. Model

In-sewer removal is assumed to be a fixed percentage, and is taken directly from the chemical parameter set (identical to mode 2).

$R_{SEWER} = from\ chemical\ parameters\ set$

6.1.2. Required Parameters

Chemical

| R_{SEWER} | chemical removal in the sewer | - |

Geo-referenced

6.2. WWTP

Chemical elimination in primary and activated sludge WWTPs is described by models derived from *SimpleTreat* 3.0 (Struijs, 1996). For trickling filters, it is described by a fixed removal efficiency (identical to mode 1).

6.2.1. SIMPLEBOX Approach

Mass balancing in the primary settler model and the activated sludge model is performed according to the SIMPLEBOX method (van de Meent, 1993). For each box, a mass balance can be written as:

$$\text{mass change} = -\text{elimination} - \text{outflux to other boxes} - \text{outflux out of system}$$
$$+ \text{influx from other boxes} + \text{influx into system}$$

$$V_i \cdot \frac{dC_i}{dt} = -k_i \cdot C_i \cdot V_i - \sum_{j=1}^{6} \left(ADV_{i,j} + XCH_{i,j} \right) \cdot C_i - \Phi_{out}^i$$

or:

$$+ \sum_{j=1}^{6} \left(ADV_{j,i} + XCH_{j,i} \right) \cdot C_j + \Phi_{in}^i$$

At steady state, continuous and constant influxes into and outfluxes out of the system are assumed. The change in concentration dC_i/dt is zero. Hence, the mass balance equation for box *i* becomes:

$$k_i \cdot C_i \cdot V_i + \sum_{j=1}^{6} \left(ADV_{i,j} + XCH_{i,j} \right) \cdot C_i + \Phi_{out}^i - \sum_{j=1}^{6} \left(ADV_{j,i} + XCH_{j,i} \right) \cdot C_j = \Phi_{in}^i$$

The chemical fluxes Φ_{in} and Φ_{out} only relate to inputs and outputs at the entire WWTP level. Transport to or exchange with other boxes in the WWTP is described by the *ADV* and *XCH* terms. The latter are expressed as media volume flows (m^3/s). When the latter are multiplied by concentrations (g/m^3), the corresponding chemical mass fluxes are obtained (g/s).

The chemical fluxes out of the system (out of box *i*) can be expressed as: $\Phi_{out}^i = ADV_{i,0} \cdot C_i$

Hence, using matrix notation, the set of all 6 mass balances can be written as:

$$\begin{bmatrix} c_{1,1} & c_{1,2} & \Lambda & c_{1,6} \\ c_{2,1} & c_{2,2} & \Lambda & c_{2,6} \\ M & M & O & M \\ c_{6,1} & c_{6,2} & \Lambda & c_{6,6} \end{bmatrix} \cdot \begin{bmatrix} C_1 \\ C_2 \\ M \\ C_6 \end{bmatrix} = \begin{bmatrix} \Phi_{in}^1 \\ \Phi_{in}^2 \\ M \\ \Phi_{in}^6 \end{bmatrix} \quad \text{where} \quad \begin{cases} c_{i,i} = k_i \cdot V_i + \sum_{j=1}^{6} \left(ADV_{i,j} + XCH_{i,j} \right) + ADV_{i,0} \\ c_{i,j} = -\left(ADV_{j,i} + XCH_{j,i} \right) \end{cases}$$

or $\qquad \overline{COEF} \cdot \overline{C} = \overline{PHI}$

The concentrations in each box, C_i, can now be obtained by solving this set of equations, as follows:

$$\overline{C} = \left(\overline{COEF}\right)^{-1} \cdot \overline{PHI}$$

6.2.2. Primary settler (= type 1)

The Mode 2 Model is based on the settler model of *SimpleTreat* 3.0 (Struijs, 1996).

System Analysis

A '4-box model' was implemented (Figure 3). The system is divided into the different phases (air, dissolved, adsorbed to suspended solids, adsorbed to settled solids). In Figure 3, both the box names and numbers are given.
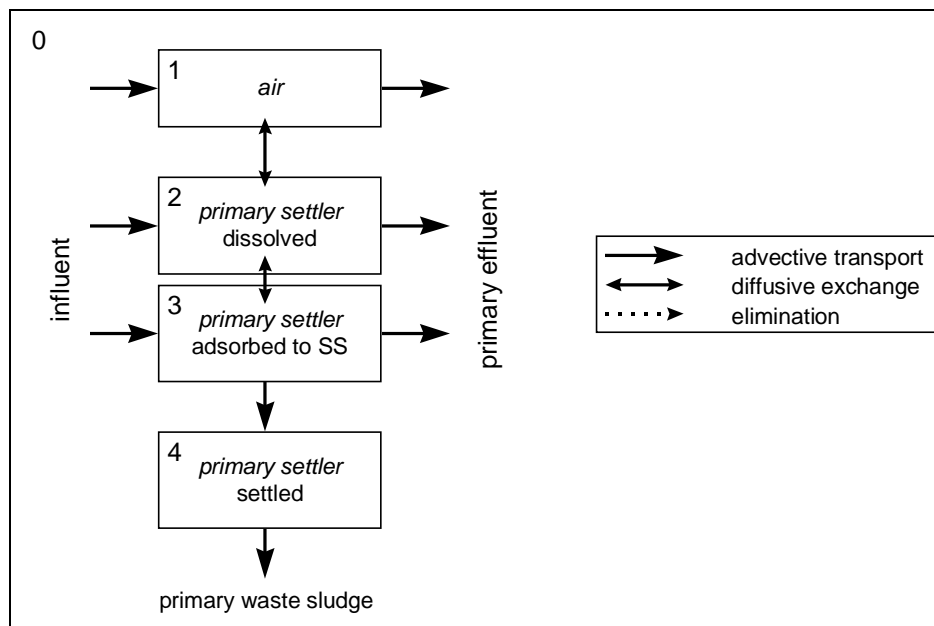

Figure 3. Primary Settler 4-box model

Influent

The influent consist of a dissolved and an adsorbed chemical fraction. A complete equilibrium between both phases is assumed. Note that this assumption may not be valid when sewer residence times are short. The influent enters the treatment system into box 2 (dissolved phase) and box 3 (adsorbed phase). The incoming mass fluxes are obtained as follows:

- into primary settler (dissolved):

$$\Phi_{in}^2 = \Phi_{in}^{primary} \cdot \frac{1}{1 + 10^{-6} \cdot SS_{sewage} \cdot K_d^{sewage}}$$

- into primary settler (sorbed):

$$\Phi_{in}^3 = \Phi_{in}^{primary} \cdot \frac{10^{-6} \cdot SS_{sewage} \cdot K_d^{sewage}}{1 + 10^{-6} \cdot SS_{sewage} \cdot K_d^{sewage}}$$

Advective Transport

Air advection

- into / out of area above settler:

$$ADV_{0,1} = ADV_{1,0} = h_{air} \cdot v_{wind} \cdot \sqrt{A_{prim}}$$

Water volume flow rate

- into / out of settler:

$$ADV_{0,2} = ADV_{2,0} = Q_{in}^{primary}$$

Solids <u>volume</u> flow rate

- into settler:

$$ADV_{0,3} = \frac{SS_{sewage}}{10^6 \cdot \rho_{solids}^{sewage}} \cdot Q_{in}^{primary}$$

- primary sedimentation + waste:

$$ADV_{3,4} = ADV_{4,0} = R_{prim}^{SS} \cdot ADV_{0,3}$$

- settler to primary effluent:

$$ADV_{3,0} = \left(1 - R_{prim}^{SS}\right) \cdot ADV_{0,3}$$

Diffusive Exchange

Derivation of partition coefficients

The sludge-water exchange coefficients for sewage is estimated from the chemical's octanol-water partitioning coefficient and the solids' organic contents.

$$K_d^{sewage} = f_{oc}^{sewage} \cdot K_{ow}$$

The air-water exchange coefficient (dimensionless Henry coefficient) is calculated as:

$$K_H = \frac{H}{\mathbf{R} \cdot (t_{air} + 273)}$$ with H estimated as: $H = \frac{P_{vapor}}{S_W}$

Calculation of fugacities and box volumes

<u>Fugacities</u>

Expressions for fugacities were obtained from Mackay and Paterson (1982).

- air:

$$Z_{air} = \frac{1}{\mathbf{R} \cdot (t_{air} + 273)}$$

- water:

$$Z_{water} = \frac{1}{H}$$

- primary sludge:

$$Z_{prim.sludge} = \frac{K_d^{sewage} \cdot \rho_{solids}^{sewage}}{H}$$

<u>Box Volumes</u>

- air above the settler:

$$V_1 = A_{prim} \cdot h_{air}$$

- primary settler (water):

$$V_2 = V_{prim}$$

- primary settler (solids):
$$V_3 = V_2 \cdot \frac{SS_{sewage}}{10^6 \cdot \rho_{solids}^{sewage}} = V_{prim} \cdot \frac{SS_{sewage}}{10^6 \cdot \rho_{solids}^{sewage}}$$

Note that the volume of compartment 4 (primary sludge thickening layers) need not be known by the model.

Media volume flow rates

The diffusion coefficient for chemical exchange between two boxes i and j is expressed in terms of first order kinetics, after Mackay and Paterson (1982).

<u>Sludge / Water exchange</u>

Between the dissolved and adsorbed phase in the primary settler, non-equilibrium partitioning is described in terms of (de-)sorption kinetics (first order), after Mackay and Paterson (1982). The applied kinetic rates are given in Table 1.

$$D_{2,3} = D_{3,2} = \frac{k_{prim}^{sorb}}{\dfrac{1}{V_2 \cdot Z_{water}} + \dfrac{1}{V_3 \cdot Z_{prim.sludge}}}$$

$$\rightarrow \qquad XCH_{2,3} = \frac{D_{2,3}}{Z_{water}} \qquad XCH_{3,2} = \frac{D_{2,3}}{Z_{prim.sludge}}$$

Table 1. Sorption/desorption kinetics in primary settler

		half-life (s)	1st order rate (s^-1)
primary settler	k_{prim}^{sorb}	3600	192.5 10^-6

<u>Air / Water exchange</u>

Surface volatilization is the only considered type of air-water exchange (Mackay et al., 1985).

$$D_{1,2} = D_{2,1} = \frac{A_{prim}}{\dfrac{1}{K_{air} \cdot Z_{air}} + \dfrac{1}{K_{water} \cdot Z_{water}}}$$

$$\rightarrow \qquad XCH_{1,2} = \frac{D_{1,2}}{Z_{air}} \qquad\qquad XCH_{2,1} = \frac{D_{1,2}}{Z_{water}}$$

Primary Settler Efficiency

The suspended solids removal efficiency of settlers generally decreases with increasing hydraulic load (e.g. Pflanz, 1969). Lessard and Beck (1993) used the following equation to relate the effluent suspended solids concentration (of a secondary clarifier) to the flow:

$$SS_{out} = \alpha_1 + \alpha_2 \cdot Q_{settler}$$

From this equation, the following was derived:

$$SS_{out} = SS_{in} \cdot \left(1 - R_{settler}^{SS}\right) = \alpha_1 + \alpha_2 \cdot Q_{settler}$$

$$\Rightarrow 1 - R_{settler}^{SS} = \frac{\alpha_1 + \alpha_2 \cdot Q_{settler}}{SS_{in}} \qquad \Rightarrow R_{settler}^{SS} = 1 - \frac{\alpha_1}{SS_{in}} - \frac{\alpha_2}{SS_{in}} \cdot Q_{settler}$$

$$\alpha_1 = \left|SS_{out}\right|_{Q_{settler}=0} = \left|SS_{out}\right|_{min} = SS_{in} \cdot \left(1 - \left|R_{settler}^{SS}\right|_{max}\right) \qquad \Rightarrow \frac{\alpha_1}{SS_{in}} = 1 - \left|R_{settler}^{SS}\right|_{max}$$

Hence:

$$R_{settler}^{SS} = 1 - \left(1 - \left|R_{settler}^{SS}\right|_{max}\right) - \frac{\alpha_2}{SS_{in}} \cdot Q_{settler}$$

$$\Rightarrow R_{settler}^{SS} = \left|R_{settler}^{SS}\right|_{max} - \alpha_{settler} \cdot \frac{Q_{settler}}{Q_{dwf}^{treated}} \qquad \text{with } \alpha_{settler} = \frac{\alpha_2 \cdot Q_{dwf}^{treated}}{SS_{in}}$$

For the primary settler, this becomes:

$$R_{prim}^{SS} = \left|R_{prim}^{SS}\right|_{max} - \alpha_{settler} \cdot \frac{Q_{out}^{primary}}{Q_{dwf}^{treated}}$$

Effluent - Removal Efficiency

The primary settler's effluent chemical mass flux and water flow are given by:

$$\Phi_{out}^{primary} = \left(C_2 + C_3 \cdot \frac{SS_{sewage} \cdot \left(1 - R_{prim}^{SS} \right)}{10^6 \cdot \rho_{solids}^{sewage}} \right) \cdot Q_{out}^{primary}$$

$$Q_{out}^{primary} = Q_{in}^{primary}$$

The primary settler's removal efficiency can be derived as:

$$R1^* = \frac{\Phi_{out}^{primary}}{\Phi_{in}^{primary}} = \frac{\left(C_2 + C_3 \cdot \dfrac{SS_{sewage} \cdot \left(1 - R_{prim}^{SS} \right)}{10^6 \cdot \rho_{solids}^{sewage}} \right) \cdot Q_{out}^{primary}}{\Phi_{in}^{primary}}$$

An additional output of the primary settler model is the fractionation between the dissolved and adsorbed chemical in the effluent:

$$f_d^{primary} = \frac{C_2}{\left(C_2 + C_3 \cdot \dfrac{SS_{sewage} \cdot \left(1 - R_{prim}^{SS} \right)}{10^6 \cdot \rho_{solids}^{sewage}} \right)} \qquad f_s^{primary} = 1 - f_d^{primary}$$

In case further (secondary) treatment follows the primary sedimentation, these dissolved and sorbed fractions are required for a correct calculation of the secondary influent.

6.2.3. Activated sludge (= type 2)

The Mode 2 Model is based on SimpleTreat 3.0. For a complete description of this model, reference is made to Struijs (1996). However, a number of modifications were made.

If no primary settler is present, removal efficiency is calculated as such:

$$R_{WWTP} = R2^*$$

Otherwise, it is calculated from the combination (in series) of both primary and secondary treatment:

$$R_{WWTP} = R1^* + R2^* - R1^* * R2^*$$

System Analysis

Only the '6-box model' (i.e. not including a primary settler) was implemented, with a number of modifications (Figure 4). The activated sludge system is divided into different compartments, based on the two sub-processes (aeration tank, secondary settler) and the different phases (air, dissolved, adsorbed to suspended solids, adsorbed to settled solids). In Figure 4, both the compartment ('box') names and numbers are given.

The following modifications were made, compared to Struijs (1996). The boxes were re-numbered, as only the 6-box model concept is used. Boxes 2 and 3 (representing the mixed liquor tank) were each subdivided into 3 redox zones (for nutrient removal plants). The chemical degradation rate is boxes 2 and 3, as well as the stripping rate in box 2, were modified to take this into account. An additional advective term from box 2 out of the system was included, to deal with chemical losses through aerosol formation. Sludge recycling was modified to take into account the dissolved phase of the recycle sludge (i.e. from box 4 to box 2).
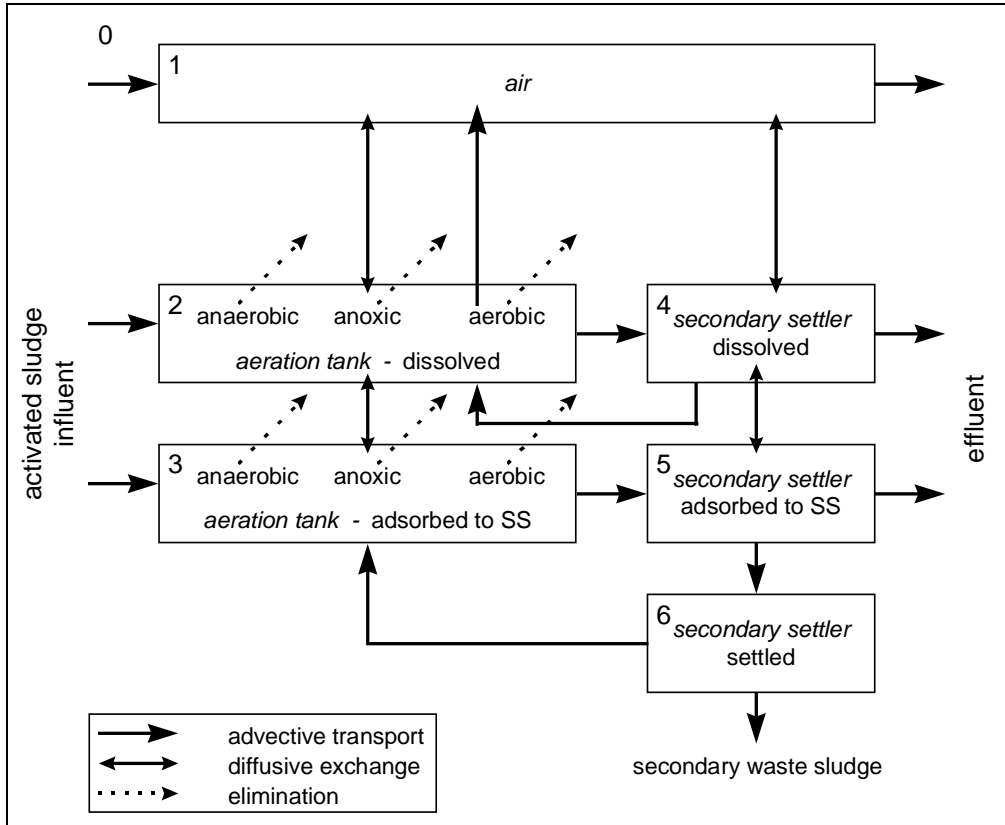
Figure 4. Modified 6-box model

Influent

The influent consist of a dissolved and an adsorbed chemical fraction. The influent enters the treatment system simultaneously into box 2 (aeration tank, dissolved phase) and box 3 (aeration tank, adsorbed phase). All other boxes receive no influent flux. The incoming mass fluxes are obtained as follows:

Without Primary Settler

If no primary settler is present, the dissolved and sorbed fraction of the influent are assumed to be in complete equilibrium. It has to be noted that this assumption may not be valid when residence times in the sewer system are short.

- into aeration tank (dissolved):

$$\Phi_{in}^2 = \Phi_{in}^{act.sludge} \cdot \frac{1}{1 + 10^{-6} \cdot SS_{sewage} \cdot K_d^{sewage}}$$

- into aeration tank (sorbed):

$$\Phi_{in}^3 = \Phi_{in}^{act.sludge} \cdot \frac{10^{-6} \cdot SS_{sewage} \cdot K_d^{sewage}}{1 + 10^{-6} \cdot SS_{sewage} \cdot K_d^{sewage}}$$

With Primary Settler

If the primary settler model is connected in front of the activated sludge model, the dissolved/sorbed fractionation of the settler model are used to calculate the secondary influent partitioning.

- into aeration tank(dissolved):

$$\Phi_{in}^2 = \Phi_{in}^{act.sludge} \cdot f_d^{primary}$$

- into aeration tank(sorbed):

$$\Phi_{in}^3 = \Phi_{in}^{act.sludge} \cdot f_s^{primary}$$

Advective Transport

Compared to SimpleTreat, the sludge recycling concept was modified. In SimpleTreat, only the solids phase of the sludge is recycled; the dissolved phase of the recycle sludge is not taken into account. In the GREAT-ER WWTP fate model, the terms $ADV_{4,2}$ and $ADV_{2,4}$ were modified, as well as $ADV_{3,5}$.

Air advection

- into / out of area above WWTP:

$$ADV_{0,1} = ADV_{1,0} = h_{air} \cdot v_{wind} \cdot \sqrt{A_{act.sludge} + A_{sec}}$$

Water volume flow rate

- into / out of WWTP:

$$ADV_{0,2} = ADV_{4,0} = Q_{in}^{act.sludge}$$

- sludge recycle flow:

$$ADV_{4,2} = R \cdot Q_{in}^{act.sludge}$$

- sludge propagation:

$$ADV_{2,4} = (1 + R) \cdot Q_{in}^{act.sludge}$$

An additional advective flow term was added. This term describes the transport of water droplets out of the activated sludge tank, through aerosol formation. There are indications that chemical elimination from the aeration tank may occur through the formation of aerosols (Carducci et al., 1995; Sawyer et al., 1996; Marcomini, 1997). However, thorough research on this topic has not yet been conducted, the process is not yet well understood. Hence, a conservative approach was selected, and this chemical elimination route was not included in the model:

- aerosol formation:

$$ADV_{2,1} = 0$$

Solids <u>volume</u> flow rate

- influent to aeration tank:

$$ADV_{0,3} = \frac{SS_{sewage}}{10^6 \cdot \rho_{solids}^{sewage}} \cdot Q_{in}^{act.sludge}$$

- aeration tank to secondary settler:

$$ADV_{3,5} = \frac{SS_{ML}}{10^6 \cdot \rho_{solids}^{ML}} \cdot Q_{in}^{act.sludge} \cdot (1 + R)$$

- secondary sedimentation:

$$ADV_{5,6} = R_{sec}^{SS} \cdot ADV_{3,5}$$

- secondary settler to effluent:

$$ADV_{5,0} = (1 - R_{sec}^{SS}) \cdot ADV_{3,5}$$

- secondary waste sludge:

$$ADV_{6,0} = \frac{\Phi^{SS}_{surplus}}{10^6 \cdot \rho^{ML}_{solids}}$$

- recycle sludge:

$$ADV_{6,3} = ADV_{5,6} - ADV_{6,0}$$

Diffusive Exchange

Derivation of partition coefficients

A pH correction (as used in SimpleTreat 3.0) is not implemented, as information on pH control in WWTPs will generally not be available on a regional level. Hence, pH control to a neutral set-point (pH 7) was assumed.

The sludge-water exchange coefficients (for sewage and for mixed liquor) are estimated from the chemical's octanol-water partitioning coefficient and the considered solids' organic contents.

$$K^{ML}_d = f^{ML}_{oc} \cdot K_{ow}$$

The air-water exchange coefficient (dimensionless Henry coefficient) is calculated as:

$$K_H = \frac{H}{R \cdot (t_{air} + 273)}$$ with H estimated as: $H = \frac{P_{vapor}}{S_W}$

Calculation of fugacities and box volumes

For the calculation of the diffusive exchanges, the fugacity approach is applied. The fugacities of the different media have to be known, as well as the volumes of the different compartments. Expressions for fugacities were obtained from Mackay and Paterson (1982).

Fugacities

- air:

$$Z_{air} = \frac{1}{\mathbf{R} \cdot (t_{air} + 273)}$$

- water:

$$Z_{water} = \frac{1}{H}$$

- mixed liquor (aeration tank sludge):

$$Z_{ML} = \frac{K^{ML}_d \cdot \rho^{ML}_{solids}}{H}$$

Box Volumes

- air above the WWTP:

$$V_1 = (A_{act.sludge} + A_{sec}) \cdot h_{air}$$

- aeration tank (water):

$$V_2 = V_{act.sludge}$$

- aeration tank (solids):
$$V_3 = V_2 \cdot \frac{SS_{ML}}{10^6 \cdot \rho_{solids}^{ML}} = V_{act.sludge} \cdot \frac{SS_{ML}}{10^6 \cdot \rho_{solids}^{ML}}$$

- secondary settler (water):
$$V_4 = V_{sec}$$

- secondary settler (solids):
$$V_5 = V_4 \cdot \frac{\left(1 - R_{sec}^{SS}\right) \cdot SS_{ML}}{10^6 \cdot \rho_{solids}^{ML}} = V_{sec} \cdot \frac{\left(1 - R_{sec}^{SS}\right) \cdot SS_{ML}}{10^6 \cdot \rho_{solids}^{ML}}$$

Note that the volume of compartment 6 (secondary sludge thickening layer) need not be known by the model.

Media volume flow rates

The diffusion coefficient for chemical exchange between two boxes i and j is expressed in terms of first order kinetics, after Mackay and Paterson (1982):

$$D_{i,j} = D_{j,i} = \frac{k_{diff}}{\dfrac{1}{V_i \cdot Z_i} + \dfrac{1}{V_j \cdot Z_j}}$$

Then, the exchange from box i to j is calculated as:

$$XCH_{i,j} = \frac{D_{i,j}}{Z_i}$$

Sludge / Water exchange

Between the dissolved and adsorbed phase in the primary settler, the aeration tank and the secondary settler, non-equilibrium partitioning is described. Chemical exchange between both phases is expressed in terms of (de-)sorption kinetics (first order), after Mackay and Paterson (1982).

- aeration tank (mixed liquor):

$$D_{2,3} = D_{3,2} = \frac{k_{act.sludge}^{sorb}}{\dfrac{1}{V_2 \cdot Z_{water}} + \dfrac{1}{V_3 \cdot Z_{ML}}}$$

$$\rightarrow \qquad XCH_{2,3} = \frac{D_{2,3}}{Z_{water}} \qquad XCH_{3,2} = \frac{D_{2,3}}{Z_{ML}}$$

- secondary settler:

$$D_{4,5} = D_{5,4} = \frac{k_{sec}^{sorb}}{\dfrac{1}{V_4 \cdot Z_{water}} + \dfrac{1}{V_5 \cdot Z_{ML}}}$$

$$\rightarrow \qquad XCH_{4,5} = \frac{D_{4,5}}{Z_{water}} \qquad XCH_{5,4} = \frac{D_{4,5}}{Z_{ML}}$$

The applied kinetic rates for sorption / desorption are given in Table 2 (from Struijs, 1996).

Table 2. Sorption/desorption kinetic rates

		half-life (s)	1st order rate (s-1)
aeration tank	$k_{act.sludge}^{sorb}$	360	1.925 10-3
secondary settler	k_{sec}^{sorb}	3600	192.5 10-6

Air / Water exchange

Two types of air-water exchange are considered: surface volatilization (without impact of aeration) and stripping (due to aeration). Stripping can be either by surface aeration or by of (submerged) bubble aeration. The modeling approach is based on a two-layer model (Liss and Slater, 1974; Mackay and Leinonen, 1975).

For the secondary settler, only surface volatilization was taken into account - stripping at the weir was not considered. The expressions for the transfer coefficients $D_{i,j}$ are taken from Mackay et al. (1985). It can be shown that these expressions are equivalent to the standard diffusive exchange equations, which are applied for the sludge-water exchange, and for volatilization and stripping from the aerator.

- secondary settler:

$$D_{1,4} = D_{4,1} = \frac{A_{sec}}{\dfrac{1}{K_{air} \cdot Z_{air}} + \dfrac{1}{K_{water} \cdot Z_{water}}}$$

$$\rightarrow \qquad XCH_{1,4} = \frac{D_{1,4}}{Z_{air}} \qquad XCH_{4,1} = \frac{D_{1,4}}{Z_{water}}$$

- aeration tank:

> For the aeration tank, stripping due to aeration is an additional fate process, next to surface volatilization. In this case, the standard exchange equation of Mackay and Paterson (1982) is applied. In nutrient removal plants (with anoxic and anaerobic zones) only the aerobic fraction of the activated sludge tank is aerated. Hence a correction factor for the tank volume which undergoes stripping is taken into account.

$$D_{1,2} = D_{2,1} = \frac{k_{str}}{\dfrac{1}{V_1 \cdot \dfrac{A_{act.sludge}}{A_{act.sludge} + A_{sec}} \cdot Z_{air}} + \dfrac{1}{\left(f_{aerobic}^{act.sludge} \cdot V_2 \right) \cdot Z_{water}}}$$

$$+ \frac{k_v}{\dfrac{1}{V_1 \cdot \dfrac{A_{act.sludge}}{A_{act.sludge} + A_{sec}} \cdot Z_{air}} + \dfrac{1}{V_2 \cdot Z_{water}}}$$

$\rightarrow \qquad XCH_{1,2} = \dfrac{D_{1,2}}{Z_{air}} \qquad\qquad XCH_{2,1} = \dfrac{D_{2,1}}{Z_{water}}$

* <u>volatilization</u>:

k_v is derived as: $k_v = \dfrac{\dfrac{1}{h_{air}} + \dfrac{K_H}{h_{act.sludge}}}{\dfrac{1}{K_{air}} + \dfrac{K_H}{K_{water}}}$

* <u>stripping</u>:

k_{str} depends on the type of aeration: surface aeration versus bubble aeration. Note that in the calculations below, activated sludge tank *HRT*s / volumes were replaced by the corresponding aerobic values. Also note that the oxygen requirement (*OxReq*) estimation was modified compared to SimpleTreat 3.0 (see below).

- surface aeration (after Roberts et al., 1984; Munz and Roberts, 1989):

$$k_{str}^{surface} = \Psi \cdot GPC \cdot \frac{OxReq}{3600 \cdot \left(f_{aerobic}^{act.sludge} \cdot HRT_{act.sludge} \right) \cdot \left(DO_{sat} - DO \right)}$$

$$\begin{cases} H \geq 250 \dfrac{Pa}{m^3 mol} \Rightarrow GPC = 1 \\[2em] H < 250 \dfrac{Pa}{m^3 mol} \Rightarrow GPC = \dfrac{\dfrac{k_G a}{k_L a} \cdot K_H}{\dfrac{k_G a}{k_L a} \cdot K_H + 1} \cong \dfrac{40 \cdot K_H}{40 \cdot K_H + 1} \end{cases}$$

- bubble aeration (after Hsieh et al., 1993):

$$k_{str}^{bubble} = 0.89 \cdot 10^{-3} \cdot \frac{OxReq}{f_{aerobic}^{act.sludge} \cdot V_{act.sludge}} \cdot H^{1.04}$$

Note that the Oxygen Requirement (*OxReq*) concept (as for surface aeration) is used, rather than the per capita aeration rate (G^{cap}) which is used in SimpleTreat.

* aerosol formation:

Chemical elimination through the formation of aerosols is not described as a diffusive exchange, but as an advective transport of water droplets out of the activated sludge tank. Note that this term is currently set to zero, as the link between chemical fate and aersol formation is not yet well understood.

Degradation in the Activated Sludge Tank

An approach similar to Cowan et al. (1993a) is used as the default within GREAT-ER. However, a double first-order approach is used, both to concentration and to biomass. The 'standard' SimpleTreat approach which only considers dissolved phase degradation, is merely a specific case of this more general method. Alternatively, Monod kinetics can be used.

The presence of anoxic and / or anaerobic tanks / zones in nutrient removal plants is taken into account by means of an oxygen correction factor.

Pseudo First-Order

A standard degradation rate is to be supplied, valid for the combined biological and non-biological degradation in the dissolved phase. Together with this, a sorbed phase correction factor is to be used. The effect of temperature can be taken into account by means of a Q10 factor, which is equivalent to but more transparent than the method used in SimpleTreat 3.0.

- aeration tank (dissolved): $\qquad k_2 = \left(k_{biodeg}^{WWTP} \cdot \alpha_{redox} + k_{nonbiodeg}^{WWTP} \right) \cdot \alpha_{temp}$

- aeration tank (sorbed): $\qquad k_3 = \left(k_{biodeg}^{WWTP} \cdot \alpha_{redox} + k_{nonbiodeg}^{WWTP} \right) \cdot \alpha_{temp} \cdot \alpha_s$

The 1st order biodegradation rate is derived from a double first order rate, taking into account the biomass level in the reactor. Note that a correction factor is applied to convert mixed liquor suspended solids to active biomass.

$$k_{biodeg}^{WWTP} = k_{biodeg}^{standard} \cdot SS_{ML} \cdot \alpha_{act.sludge}$$

Monod

As non-biological degradation or other non-biological processes can not be described using this approach, it should only be used with chemicals that are mainly removed by biodegradation way.

$$k_2 = k_3 = k_{monod}$$

The pseudo 1st order biodegradation rate is derived from Monod kinetics as follows:

$$k_{monod} = \ln\left(\frac{C_{influent}}{C_{st.st.}} \right) \cdot \frac{1}{HRT_{act.sludge}} = \ln\left(C_{influent} \middle/ \frac{\left(1 + b \cdot SRT\right) \cdot K_s}{SRT \cdot \left(Y \cdot k_{max} - b\right) - 1} \right) \cdot \frac{1}{HRT_{act.sludge}}$$

$$C_{influent} = \frac{\Phi_{in}^{act.sludge}}{Q_{in}^{act.sludge}}$$

This is corrected for short sludge retention times as follows (after Birch,1991):

$$SRT < \left(\frac{(Y \cdot k_{max}) \cdot C_{influent}}{K_s + C_{influent}} - b \right)^{-1} \Rightarrow k_{monod} = 0$$

The maximal degradation rate, k_{max}, is derived from a standard value after correction for temperature and oxygen:

$$k_{max} = k_{max}^{standard} \cdot \alpha_{temp} \cdot \alpha_{redox}$$

Corrections for Temperature and Oxygen

- temperature effect:
$$\alpha_{temp} = Q_{10}^{\frac{t_{ML}-20}{10}}$$

- oxygen:
$$\alpha_{redox} = f_{aerobic}^{act.sludge} \cdot 1 + f_{anoxic}^{act.sludge} \cdot \alpha_{anoxic} + f_{anaerobic}^{act.sludge} \cdot \alpha_{anaerobic}$$

Secondary Settler Efficiency

The suspended solids removal efficiency of settlers generally decreases with increasing hydraulic load (e.g. Pflanz, 1969). Lessard and Beck (1993) used the following equation to relate the effluent suspended solids concentration (of a secondary clarifier) to the flow:

$$SS_{out} = \alpha_1 + \alpha_2 \cdot Q_{settler}$$

From this equation, the following was derived:

$$SS_{out} = SS_{in} \cdot \left(1 - R_{settler}^{SS}\right) = \alpha_1 + \alpha_2 \cdot Q_{settler}$$

$$\Rightarrow 1 - R_{settler}^{SS} = \frac{\alpha_1 + \alpha_2 \cdot Q_{settler}}{SS_{in}} \qquad \Rightarrow R_{settler}^{SS} = 1 - \frac{\alpha_1}{SS_{in}} - \frac{\alpha_2}{SS_{in}} \cdot Q_{settler}$$

$$\alpha_1 = \left|SS_{out}\right|_{Q_{settler}=0} = \left|SS_{out}\right|_{min} = SS_{in} \cdot \left(1 - \left|R_{settler}^{SS}\right|_{max}\right) \qquad \Rightarrow \frac{\alpha_1}{SS_{in}} = 1 - \left|R_{settler}^{SS}\right|_{max}$$

Hence:

$$R_{settler}^{SS} = 1 - \left(1 - \left|R_{settler}^{SS}\right|_{max}\right) - \frac{\alpha_2}{SS_{in}} \cdot Q_{settler}$$

$$\Rightarrow R_{settler}^{SS} = \left|R_{settler}^{SS}\right|_{max} - \alpha_{settler} \cdot \frac{Q_{settler}}{Q_{dwf}^{treated}} \qquad \text{with } \alpha_{settler} = \frac{\alpha_2 \cdot Q_{dwf}^{treated}}{SS_{in}}$$

For the secondary settler, this becomes:

$$R_{sec}^{SS} = \left| R_{sec}^{SS} \right|_{max} - \alpha_{settler} \cdot \frac{Q_{out}^{act.sludge}}{Q_{dwf}^{treated}}$$

Estimation of Operation Parameters

Oxygen Requirement

In SimpleTreat, it is assumed that the requirement for oxygen input into the activated sludge tank is equal to the biological oxygen demand in the influent. This does not take into account oxygen requirement for endogenous respiration of the biomass, the oxygen needed for nitrification, and the oxygen which can be recuperated by denitrification. Hence, an alternative calculation of *OxReq* is used in GREAT-ER:

$$OxReq = \frac{\Phi_{BOD} \cdot (1 - 1.33 \cdot Y)}{Q_{in}^{act.sludge}} \qquad \text{(organics oxydation)}$$

$$+ \frac{V_{act.sludge} \cdot SS_{ML} \cdot \left(r_{end} \cdot \frac{1}{3600 \cdot 24} \right)}{Q_{in}^{act.sludge}} \qquad \text{(endogenous respiration)}$$

$$+ \frac{(\Phi_N - Y \cdot \Phi_{BOD} \cdot 5\%) \cdot (4.33 \cdot \varepsilon_N - 2.86 \cdot \varepsilon_N \cdot \varepsilon_{DN})}{Q_{in}^{act.sludge}} \qquad \text{(nitrification / denitrification)}$$

no primary settler: $\qquad \Phi_{BOD} = \dfrac{\Phi_{BOD}^{cap}}{3600 \cdot 24} \cdot N \qquad\qquad \Phi_N = \dfrac{\Phi_N^{cap}}{3600 \cdot 24} \cdot N$

with primary settler: $\qquad \Phi_{BOD} = \dfrac{\Phi_{BOD}^{cap}}{3600 \cdot 24} \cdot N \cdot \left(1 - R_{prim}^{BOD} \right) \qquad \Phi_N = \dfrac{\Phi_N^{cap}}{3600 \cdot 24} \cdot N \cdot \left(1 - R_{prim}^{N} \right)$

Saturation Oxygen Concentration

The saturation dissolved O_2 concentration can be calculated as a function of temperature (Verstraete, 1992), taking into account a correction for salinity:

$$DO_{sat} = \left(14.65 - 0.41 \cdot t_{ML} + 7.99 \cdot 10^{-3} \cdot t_{ML}^2 - 7.78 \cdot 10^{-5} \cdot t_{ML}^3 \right) \cdot \left(1 - 9 \cdot 10^{-6} \cdot sal_{ML} \right)$$

Surplus sludge production

$$\Phi_{surplus}^{SS} = Q_{in}^{act.sludge} \cdot \left(BOD \cdot R_{act.sludge}^{BOD} \cdot Y - SS_{effluent} \right) = \Phi_{BOD} \cdot R_{act.sludge}^{BOD} \cdot Y - Q_{in}^{act.sludge} \cdot SS_{effluent}$$

$$SS_{effluent} = SS_{ML} \cdot \left(1 - R_{sec}^{SS} \right)$$

$$R_{act.sludge}^{BOD} = 0.818 - 0.0422 \cdot \ln B_X \qquad \text{(Mikkelsen, 1995)}$$
$$Y = 0.947 + 0.0739 \cdot \ln B_X \qquad \text{(Mikkelsen, 1995)}$$

Effluent - Removal Efficiency

The plant's effluent chemical mass flux and water flow are given by:

$$\Phi_{out}^{act.sludge} = \left(C_4 + C_5 \cdot \frac{SS_{ML} \cdot \left(1 - R_{sec}^{SS}\right)}{10^6 \cdot \rho_{solids}^{ML}} \right) \cdot Q_{out}^{act.sludge}$$

$$Q_{out}^{act.sludge} = Q_{in}^{act.sludge}$$

The plant's removal efficiency can be derived as:

$$R_{act.sludge} = 1 - \frac{\Phi_{out}^{act.sludge}}{\Phi_{in}^{act.sludge}} = \frac{\left(C_4 + C_5 \cdot \dfrac{SS_{ML} \cdot \left(1 - R_{sec}^{SS}\right)}{10^6 \cdot \rho_{solids}^{ML}} \right) \cdot Q_{out}^{act.sludge}}{\Phi_{in}^{act.sludge}}$$

6.2.4. Trickling filter (= type 3)

If no primary settler is present, removal efficiency is taken directly from the chemical parameters set.

$R_{WWTP} = R3$

Otherwise, it is calculated from the combination (in series) of both primary and secondary treatment. Note that the <u>mode 1 primary settler model</u> is used, NOT its mode 3 equivalent. This is to ensure that the entire trickling filter treatment plant (including primary and secondary settling) is modeled using a consistent model complexity. Hence, $R1$ is taken directly from the chemical parameter set.

$R_{WWTP} = R1 + R3 - R1*R3$

6.2.5. Required Parameters

Chemical

b	competent biomass cell decay rate	s^{-1}
H [1]	Henry's law coefficient	$Pa.m^3.mol^{-1}$
$k_{biodeg}^{standard}$	double 1st order biodegradation rate (standard conditions)	$(g_{dwt}/m^3)^{-1}s^{-1}$
$k_{max}^{standard}$	maximal biodegradation rate (Monod kinetics - standard conditions)	s^{-1}
$k_{nonbiodeg}^{WWTP}$	1st order rate for non-biological degradation in the WWTP	s^{-1}
K_d^{sewage} [1]	solids/liquid partitioning coefficient for sewage	L/kg_{dwt}
K_d^{ML} [1]	solids / liquid partitioning coefficient for mixed liquor	L/kg_{dwt}
K_s	Monod kinetics half-saturation constant	$g/m3$
K_{ow}	octanol / water partitioning coefficient	-
P_{vapor}	chemical vapor pressure	Pa
Q_{10}	degradation rate change per 10 °C	-
$R1$	chemical removal in a primary settler	-
$R3$	chemical removal in a trickling filter	-
S_W	chemical water solubility	mol/m^3

Y	competent biomass yield coefficient	-
α_s	correction factor for sorbed phase degradation	-
α_{anoxic}	correction factor for anoxic degradation	-
$\alpha_{anaerobic}$	correction factor for anaerobic degradation	-

Geo-referenced

aeration type	type of aeration in the aeration tank	*bubble / surface*
B_X	sludge loading rate	$g_{BOD}.g_{dwt}^{-1}.d^{-1}$
DO	actual dissolved oxygen concentration in the aeration tank	g_{O2}/m^3
$f_{aerobic}^{act.sludge}$	aerated (aerobic) fraction of the activated sludge tank	-
$f_{anoxic}^{act.sludge}$	anoxic fraction of the activated sludge tank	-
$f_{anaerobic}^{act.sludge}$	anaerobic fraction of the activated sludge tank	-
$h_{act.sludge}$	activated sludge tank depth	m
h_{prim}	primary settler depth	m
h_{sec}	secondary settler depth	m
N	number of people connected to the WWTP	cap
r_{end}	endogenous respiration rate	$kg_{O2}.kg_{dwt}^{-1}.d^{-1}$
R	sludge recycle ratio	-
$\left|R_{prim}^{SS}\right|_{max}$	maximal primary settler suspended solids removal efficiency	-
$\left|R_{sec}^{SS}\right|_{max}$	maximal secondary settler suspended solids removal efficiency	-
sal_{ML}	mixed liquor salinity	kg_{Cl}/m^3
SS_{ML}	mixed liquor (act. sludge) suspended solids concentration	g_{dwt}/m^3
Y	biomass yield coefficient	-
$\alpha_{settler}$	empirical parameter (effect of flow / DWF on solids removal)	-
$\alpha_{biomass}$	correction factor for biomass activity	-
ε_{DN}	efficiency of denitrification	-
ε_N	efficiency of nitrification	-

Non Geo-referenced

f_{oc}^{sewage}	sewage solids organic carbon fraction	-
f_{oc}^{ML}	mixed liquor solids organic carbon fraction	-
h_{air}	air mixing height	m
$k_{act.sludge}^{sorb}$	first-order (de)sorption rate in the activated sludge tank	s^{-1}
k_{prim}^{sorb}	first-order (de)sorption rate in the primary settler	s^{-1}
k_{sec}^{sorb}	first-order (de)sorption rate in the secondary settler	s^{-1}
$k_G a/k_L a$	ratio of chemical mass transfer rates in air and water (40)	-
K_{air}	mass transfer coefficient in air (2.78 10^{-3})	m/s
K_{water}	mass transfer coefficient in water (2.78 10^{-5})	m/s
v_{wind}	wind speed above the WWTP	m/s
R_{prim}^{BOD}	BOD removal efficiency in the primary settler	-
R_{prim}^{N}	N removal efficiency in the primary settler	-
SS_{sewage}	influent suspended solids concentration	g_{dwt}/m^3
t_{air}	air temperature	$^{\circ}C$

t_{ML}	mixed liquor temperature	$°C$
ρ_{solids}^{sewage}	density of sewage (influent) solids	kg_{dwt}/L
Φ_{BOD}^{cap}	daily per capita BOD emission flux	$g_{BOD}.cap^{-1}.d$
Φ_{N}^{cap}	daily per capita N emission flux	$g_{N}.cap^{-1}.d$
SS_{sewage}	influent suspended solids concentration	g_{dwt}/m^3
ρ_{solids}^{sewage}	density of sewage (influent) solids	kg_{dwt}/L
ρ_{solids}^{ML}	density of mixed liquor (act. sludge) solids	kg_{dwt}/L
ψ	surface aeration empirical constant (0.6)	-

$^{(1)}$ to override estimation

6.3. River

6.3.1. Model

Mode 3 is a further expansion of Mode 2. The separated individual fate processes, which are considered as black boxes in Mode 2, are described by means of mechanistic models. A hybrid approach is possible: depending on the available data or on chemical properties, some processes can be described in Mode 2, while others can be described in the more detailed Mode 3.

Degradation is further split up into three sub-processes. The chemical's water solubility is also taken into account. It is assumed that sedimentation only occurs with sorbed chemical. Only the dissolved chemical can volatilize. The non-soluble chemical fraction is not taken into account for further reactions or processes.

Chemical elimination in rivers is described by first-order in-stream removal. In addition to 4.3.1 for mode 1, a correction is made for solubility:

$$\begin{cases} C_0 < S_W \cdot MM & \Rightarrow & C_{initial} = C_0 \\ C_0 \geq S_W \cdot MM & \Rightarrow & C_{initial} = S_W \cdot MM \end{cases}$$

The travel time HRT is calculated as already mentioned in 4.3.1 for mode 1:

$HRT = V/(Q*3600)$ for lakes
$HRT = L/(v*3600)$ for rivers

The rate coefficient is calculated as follows:

$$k = k_{deg} + f_s \cdot k_{sed} + f_d \cdot k_{vol}$$

where

$$f_d = \frac{C_d}{C_t} = \frac{1}{1 + C_s/C_d} = \frac{1}{1 + 10^{-6} \cdot K_{d\_river} \cdot SS}$$

$$f_s = \frac{C_s}{C_t} = 1 - f_d$$

If K_{d_river} is not given, it is estimated as follows: $K_{d\_river} = f_{oc\_river} \cdot K_{oc}$

The rate coefficients of the different sub-processes are calculated in individual sub-models.

Degradation

$$k_{deg} = k_{hydrolysis} + k_{photolysis} + k_{biodeg}$$

hydrolysis

The hydrolysis model was taken from SMPTOX4 mode 3 (EPA, 1995). This model makes a differentiation between neutral, acid and basic hydrolysis.

$$k_{hydrolysis} = K_b \cdot [OH^-] + K_n + K_a \cdot [H^+] = K_b \cdot 10^{pH-14} + K_n + K_a \cdot 10^{-pH}$$

photolysis

The model for photolysis was taken from SMPTOX4 mode 3 (EPA, 1995). The model takes into account the light extinction in the water column, using a 1st order extinction rate and the river depth.

$$k_{photolysis} = k_{ph,0} \cdot \frac{1 - e^{-k_z \cdot d}}{k_z \cdot d}$$

biodegradation

For biodegradation, the following aspects are taken into account: different degradation rates in the sorbed and dissolved phase (as in ROUT, Cowan et al., 1993b); influence of dissolved oxygen on biodegradation; temperature correction of the biodegradation rate; 1st order kinetics to both concentration and biomass, river's self-purification potential.

Kinetics are assumed to be first-order to both chemical concentration and biomass concentration. From the standard 'double first-order' rate, a pseudo-first-order rate is derived by multiplying the former with the biomass level. Also, the specific river's self-purification potential (biodegradation potential) can be taken into account, by means of a correction factor. This factor allows the model to deal with different river types in a pan-European framework. How this river-class dependent factor should be determined is still an open question. It could e.g. be derived from BOD removal rates in the river (fast BOD removal correlated with fast chemical removal), or from river geometry (higher rates in small natural rivers with a lot of biofilm material). It could also be derived from BOD levels in the river, assuming that high BOD levels will result in a higher biomass activity.

$$k_{biodeg} = k_{biodeg}^{standard} \cdot X \cdot \left(f_d + f_s \cdot \alpha_s \right) \cdot \alpha_{DO} \cdot \alpha_{temp} \cdot \alpha_{river}$$

$$\alpha_{DO} = \frac{DO}{K_{DO} + DO} + \frac{K_{DO}}{K_{DO} + DO} \cdot \alpha_{anaerobic}$$

$$\alpha_{temp} = Q_{10}^{\frac{t_{water} - 20}{10}}$$

Sedimentation

Chemical elimination through sedimentation is directly related to suspended solids settling. A suspended solids settling rate can be given as such, as a river-specific property, or it can be derived from a settling velocity and the river's depth. In its turn, the settling velocity is estimated from annual sediment growth and sediment porosity and density (cf. CemoS, Trapp and Matthies, 1996).

$$k_{sed} = \frac{v_{sed}}{d}$$

$$v_{sed} = \frac{\left(v_{growth}^{sed} \cdot 3.171 \cdot 10^{-11} \right) \cdot \left(10^6 \cdot \rho_{SS} \right) \cdot \left(1 - \varepsilon_{sed} \right)}{SS}$$

Volatilization

Volatilization is modeled using the approach followed in CemoS (Trapp and Matthies, 1996). This method is based on the two film theory (Whitman, 1923). A complete mixing, due to turbulence, of both the river water column and the atmospheric compartment is assumed. On the other hand, the two boundary layers are considered to be laminar, and are assumed to control the exchange rate between water and air. This exchange rate is calculated from the chemical's Henry's law constant (i.e. the air / water partitioning constant), the conductance of the gaseous and liquid films, and the river's depth. For the estimation of these conductances, two distinct approaches are applied. For lakes, the method described by Mackay and Yeun (1983) is used. For rivers, the approach of Southworth (1979) is applied. Both approaches are also described and compared in Trapp and Harland (1995). A similar volatilization modeling approach is followed in SAMS (Matthies et al., 1992), RIVMODEL (ECETOC, 1994), as well as SMPTOX4 (EPA, 1995).

$$k_{vol} = \frac{1}{d} \cdot \frac{1}{\left(\frac{1}{k_l} + \frac{1}{K_H^* \cdot k_g} \right)}$$

if pH and pKa are known, the following correction is applied:

$$K_H^* = K_H \cdot \frac{1}{1 + 10^{a \cdot (pH - pKa)}}$$

for acidic dissociation: a = 1

for basic dissociation: a = -1

Note that K_H can be estimated as $\qquad K_H = \frac{H}{R \cdot (t_{air} + 273)}$

and H can be estimated as $\qquad H = \frac{P_{vapor}}{S_W}$

for rivers: after Southworth (1979)

$$k_g = 3.16 \cdot 10^{-3} \cdot (v + v_{fr}) \cdot \sqrt{\frac{18}{MM}}$$

$$k_l = 65.31 \cdot 10^{-6} \cdot F \cdot \frac{v^{0.969}}{d^{0.673}} \cdot \sqrt{\frac{32}{MM}} \qquad F = \begin{cases} v_{fr} < 1.9 \ m/s : F = 1 \\ 5 > v_{fr} \geq 1.9 \ m/s : F = e^{0.526\left(v_{wind,0.1}-1.9\right)} \end{cases}$$

$$v_{fr} = v_{wind,10} \cdot \left(\log\frac{0.1}{z_0} \Big/ \log\frac{10}{z_0} \right) \qquad z_0 = 10^{-3} m \text{ above rivers}$$

for lakes: after Mackay & Yeun (1983)

$$k_g = 10^{-3} + 46.2 \cdot 10^{-3} \cdot v_{shear} \cdot \frac{1}{\sqrt[3]{SC_g^{\,2}}}$$

$$k_l = 10^{-6} + \alpha \cdot v_{shear}^{\,\beta} \cdot \frac{1}{\sqrt{SC_l}} \quad \begin{cases} v_{shear} < 0.3 \; m/s \\ 0.3 \; m/s \le v_{shear} \le 1 \; m/s \end{cases} \quad \begin{array}{ll} \Rightarrow \alpha = 14.4 \cdot 10^{-3} & \beta = 2.2 \\ \Rightarrow \alpha = 3.4 \cdot 10^{-3} & \beta = 1 \end{array}$$

$$v_{shear} = 0.0359 \cdot v_{wind,10}^{\,0.93}$$

$$SC_g = \frac{\eta_g}{D_g} = \frac{1.4 \cdot 10^{-6}}{2.22 \cdot \sqrt{\dfrac{18}{MM}}} \qquad\qquad SC_l = \frac{\eta_l}{D_l} = \frac{1.0 \cdot 10^{-6}}{172.8 \cdot 10^{-6} \cdot \sqrt{\dfrac{32}{MM}}}$$

6.3.2. Required Parameters

Chemical

H [1]	Henry's law constant	$Pa.m^3.mol^{-1}$
K_a	acid hydrolysis rate	$(mol/L^3)^{-1}t^{-1}$
K_b	base hydrolysis rate	$(mol/L^3)^{-1}t^{-1}$
K_{d_river} [1]	dissolved / sorbed partitioning coefficient	L/kg_{dwt}
K_{DO}	oxygen saturation constant for aerobic biodegradation	g_{O2}/m^3
K_n	neutral hydrolysis rate	$(mol/L^3)^{-1}t^{-1}$
K_{oc}	organic carbon / water partitioning coefficient	-
$k_{ph,0}$	near-surface photolysis rate	s^{-1}
$k_{biodeg}^{standard}$	double 1st order biodegradation rate (standard conditions)	$(g_{dwt}/m^3)^{-1}s^{-1}$
MM	chemical molar mass	g/mol
P_{vapor}	chemical vapor pressure	Pa
pKa	chemical acid / base dissociation constant	-
Q_{10}	biodegradation Q10 factor (rate change factor per 10ºC)	-
S_W	chemical solubility in water	mol/m^3
$\alpha_{anaerobic}$	rate correction for anaerobic biodegradation	-
α_{DO}	biodegradation rate correction for dissolved oxygen	-
α_{river}	rate correction for biodegradation in the specific river type	-
α_s	rate correction for biodegradation in the sorbed phase	-

Geo-referenced

River Stretch

d	river depth	m
L	stretch length	m
v	river flow velocity	m/s
V	lake volume (only in case of a lake)	m^3

River Class

DO	dissolved oxygen concentration	g_{O2}/m^3
f_{oc}	suspended solids organic carbon fraction	-
k_z	light extinction coefficient	m^{-1}
lake/river	is the stretch a lake or a river ?	-
pH	acidity	-
SS	suspended solids concentration	g_{dwt}/m^3
v_{growth}^{sed}	sediment growth velocity	$mm/year$
X	lumped river biomass level (suspended and in biofilms)	g_{dwt}/m^3
α_{river}	rate correction for biodegradation in the specific river type	-
ε_{sed}	sediment porosity	-
ρ_{SS}	sediment solids particle density	kg_{dwt}/L

Non Geo-referenced

t_{water}	water temperature	^oC
$v_{wind,10}$	wind speed (at 10 m height)	m/s

6.4. Sediment

6.4.1. Model

The sediment concentration is derived from the river concentration based on equilibrium partitioning:

$$C_{SEDIMENT} = f_d \cdot C_{RIVER} \cdot K_{SW} = C_{RIVER,dissolved} \cdot \left(K_{d,RIVER} \cdot \frac{\rho_{SEDIMENT,dry}}{\rho_{WATER}} + \theta \right)$$

6.4.2. Required Parameters

Chemical

K_{d_river}	dissolved / sorbed partitioning coefficient	L/kg_{dwt}

Geo-referenced

None

Non Geo-referenced

$\rho_{SEDIMENT, dry}$	dry sediment density	kg_{dwt}/m^3
ρ_{WATER}	water density (1000 kg/m^3)	kg/m^3
θ	volume fraction water in sediment	m^3/m^3

7. References

Birch, R.R. (1991). Prediction of the fate of detergent chemicals during sewage treatment. J. Chem. Tech. Biotechnol., 50, 411-422.

Carducci, A., Arrighi, S & Ruschi, A. (1995). Detection of coliphages and enteroviruses in sewage and aerosol from an activated sludge wastewater treatment plant. Letters in Applied Microbiology, 21(3), 207-209.

Cowan, C.E., Larson, R.J., Feijtel, T.C.J. & Rapaport, R.A. (1993a). An improved model for prediciting the fate of consumer product chemicals in wastewater treatment plants. Water Research, 27(4), 561-573.

Cowan, C.E., Caprara, R.J., White, C.E., Merves, M.L. & Gullotti, M.J. (1993b). A model for predicting the fate of 'down-the-drain' consumer product ingredients in United States rivers. Water Environment Federation - 66th annual conference & exposition, Anaheim, Ca., Oct. 3-7, 1993, 351-358.

ECETOC (1994). HAZCHEM. A mathematical model for use in risk assessment of substances. Special Report No. 8. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, 107p.

EPA (1995). SMPTOX version 4.0 (SMPTOX4). User's Manual. United States Environmental Protection Agency. Athens, Georgia, 46p.

Lessard, P. & Beck, M.B. (1993). Dynamic modelling of the activated sludge process: a case study. Wat. Res., 27(6), 963-978.

Mackay, D. & Paterson, S. (1982). Fugacity revisited. Environ. Sci. Technol., 16, 654A-660A.

Mackay, D. & Yeun, A.T.K. (1983). Mass transfer coefficient correlations for organic solutes from water. Environmental Science and Technology 17, 211.

Mackay, D., Paterson, S., Cheung, B. & Brock Neely, W. (1985). Evaluating the environmental behavior of chemicals with a level III fugacity model. Chemosphere, 14, 445-474.

Marcomini, A. (1997). Personal Communication.

Matthies, M., Brüggemann, R. & Münzer, B. (1992). Screening assessment model system SAMS. Version 1.1. Handbook. User's guide and description. Prepared for: OECD Environmental Directorate, Paris. 71p.

Meent, van de, D. (1993). SIMPLEBOX: a generic multimedia fate evaluation model. Report nr. 672720001. National Institute of Public Health and Environmental Protection (RIVM), Bilthoven, The Netherlands.

Mikkelsen, J. (1995). Fate model for organic chemicals in an activated sludge wastewater treatment plant - modification of SimpleTreat. National Environment Research Institute, Denmark. Prepared for the Danish EPA.

Pflanz, P. (1969). Performance of secondary sedimentation basins. In: Advances in Water Pollution Research. Jenkins, S.H. (Ed.). pp. 569-581. Pergamon Press, London.

Sawyer, B, Rao, K.C., O'Brien, P., Elenbogen, G., Zenz, D.R. & Lue-Hing, C. (1996). Changes in bacteial aerosols with height above aeration tanks. Journal of Environmental Engineering New York, 122(5), 368-373.

Southworth, G.R. (1979). The role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments. Bull. Environ. Contam. Toxicol. 21, 507.

Struijs, J. (1996). SimpleTreat 3.0: a model to predict the distribution and elimination of chemicals by sewage treatment plants. Report nr. 719101025. National Institute of Public Health and Environmental Protection (RIVM), Bilthoven, The Netherlands.

Trapp, S. & Harland, B. (1995). Field test of volatilization models. Environmental Science and Pollution Research 2(3), 164-169.

Trapp, S. & Matthies, M. (1996). Dynamik von Schadstoffen - Umweltmodellierung mit CemoS. Eine Einführung. Springer-Verlag, Berlin, 276 p.

Verstraete, W. (1992). Biotechnological Processes in Environmental Technology. Course. Laboratory General and Applied Microbial Ecology, University of Gent.

Whitman, W.G. (1923). A preliminary experimental confirmation of the two-film theory of gas-adsorption. Chem. Metall. Eng. 29, 146.

8. Notation

$ADV_{i,j}$	advective flow rate from compartment i to compartment j	m^3/s
$A_{act.sludge}$	surface area of the activated sludge tank	m^2
A_{prim}	primary settler surface area	m^2
A_{sec}	secondary settler surface area	m^2
b	competent biomass cell decay rate	s^{-1}
B_X	sludge loading rate	$g_{BOD} \cdot g_{dwt}^{-1} \cdot d^{-1}$
$c_{i,j}$	advection / exchange / conversion coefficient	m^3/s
C_d	dissolved chemical concentration	g/m^3
C_i	chemical concentration in compartment i	g/m^3
$C_{initial}$	true concentration at the start of the river stretch	g/m^3
$C_{influent}$	chemical concentration (total, in influent)	$g/m3$
C_0	theoretical concentration at the start of the river stretch	g/m^3
C_s	sorbed chemical concentration	g/m^3
$C_{st.st.}$	chemical concentration (total, at steady-state in mixed liquor)	$g/m3$
C_t	total chemical concentration	g/m^3
C_x	concentration at the end of the river stretch	g/m^3
$\overline{C}$	concentrations vector	-
$\overline{COEF}$	coefficients matrix	-
C_d	dissolved chemical concentration	g/m^3
C_s	sorbed chemical concentration	g/m^3
C_t	total chemical concentration	g/m^3
d	river depth	m
$D_{i,j}$	interphase transfer (diffusion) coefficient from box i to box j	$mol.s^{-1}.Pa^{-1}$
D_g	diffusion coefficient in air	m^2/s
D_l	diffusion coefficient in water	m^2/s
DO_{sat}	saturation dissolved oxygen concentration	g_{O2}/m^3
DO	dissolved oxygen concentration	g_{O2}/m^3
$f_{aerobic}^{act.sludge}$	aerated (aerobic) fraction of the activated sludge tank	-
$f_{anoxic}^{act.sludge}$	anoxic fraction of the activated sludge tank	-
$f_{anaerobic}^{act.sludge}$	anaerobic fraction of the activated sludge tank	-
f_d	dissolved chemical fraction	-
$f_d^{primary}$	primary settler's effluent - dissolved fraction	-
$f_s^{primary}$	primary settler's effluent - sorbed fraction	-
f_{oc}, f_{oc_river}	river: suspended solids organic carbon fraction	-
f_{oc}^{ML}	mixed liquor solids organic carbon fraction	-
f_{oc}^{sewage}	sewage solids organic carbon fraction	-
f_s	sorbed chemical fraction	-
F	correction factor for high wind speeds	-
GPC	surface aeration gas phase correction	-
$h_{act.sludge}$	activated sludge tank depth	m
h_{air}	air mixing height	m
h_{prim}	primary settler depth	m
H	Henry's law coefficient	$Pa.m^3.mol^{-1}$
HRT	hydraulic residence (travel) time	h
$HRT_{act.sludge}$	hydraulic residence time in the activated sludge tank	s
k	chemical in-stream removal rate	h^{-1}

k_{diff}	first-order diffusive transfer kinetics rate	s^{-1}
k_i	first-order chemical elimination rate in compartment i	s^{-1}
k_{deg}	river: 1st order chemical degradation rate, in the dissolved phase	h^{-1}
k_{sed}	river: 1st order net suspended solids settling rate	h^{-1}
k_{vol}	river: 1st order chemical volatilization rate	h^{-1}
k_{str}	first-order rate constant for stripping in the activated sludge tank	s^{-1}
$k_{str}^{surface}$	first-order rate stripping rate - surface aeration	s^{-1}
k_{str}^{bubble}	first-order rate stripping rate - bubble aeration	s^{-1}
k_v	first-order rate constant for volatilization in the activated sludge tank	s^{-1}
k_Ga/k_La	ratio of chemical mass transfer rates in air and water (40)	-
$k_{act.sludge}^{sorb}$	first-order (de)sorption rate in the activated sludge tank	s^{-1}
k_{prim}^{sorb}	first-order (de)sorption rate in the primary settler	s^{-1}
k_{sec}^{sorb}	first-order (de)sorption rate in the secondary settler	s^{-1}
k_{biodeg}	1st order chemical biodegradation rate	s^{-1}
$k_{biodeg}^{standard}$	double 1st order biodegradation rate (standard conditions)	$(g_{dwt}/m^3)^{-1}s^{-1}$
k_{biodeg}^{WWTP}	1st order rate for biological degradation in the WWTP	s^{-1}
$k_{nonbiodeg}^{WWTP}$	1st order rate for non-biological degradation in the WWTP	s^{-1}
k_{deg}	1st order chemical degradation rate	s^{-1}
k_{deg}^{WWTP}	first-order degradation rate in activated sludge	s^{-1}
k_g	conductance of gaseous film	m/s
$k_{hydrolysis}$	1st order chemical hydrolysis rate	s^{-1}
k_l	conductance of liquid film	m/s
k_{max}	maximal biodegradation rate (Monod kinetics)	s^{-1}
$k_{photolysis}$	1st order chemical photolysis rate	s^{-1}
$k_{ph,0}$	near-surface photolysis rate	s^{-1}
$k_{max}^{standard}$	maximal biodegradation rate (Monod kinetics - standard conditions)	s^{-1}
k_{monod}	pseudo-first-order biodegradation rate based on Monod kinetics	s^{-1}
k_{sed}	1st order net suspended solids settling rate	s^{-1}
k_{vol}	1st order chemical volatilization rate	s^{-1}
k_z	light extinction coefficient	m^{-1}
K_a	acid hydrolysis rate	$(mol/L^3)^{-1}t^{-1}$
K_b	base hydrolysis rate	$(mol/L^3)^{-1}t^{-1}$
K_n	neutral hydrolysis rate	$(mol/L^3)^{-1}t^{-1}$
K_{air}	mass transfer coefficient in air (2.78 10^{-3})	m/s
K_{water}	mass transfer coefficient in water (2.78 10^{-5})	m/s
K_d	solids / liquid partitioning coefficient	L/kg
K_d^{ML}	solids / liquid partitioning coefficient for mixed liquor	L/kg_{dwt}
K_d^{sewage}	solids/liquid partitioning coefficient for sewage	L/kg_{dwt}
K_{DO}	oxygen saturation constant for aerobic biodegradation	g_{O2}/m^3
K_H	air / water partitioning coefficient (dimensionless Henry coefficient)	-
K_{oc}	organic carbon / water partitioning coefficient	-
K_{ow}	octanol / water partitioning coefficient	-
K_s	Monod kinetics half-saturation constant	g/m^3
L	stretch length	m
M	chemical market (sales) data	$kg/(cap.year)$
MM	chemical molar mass	g/mol

N	number of people connected to the WWTP	cap
$OxReq$	oxygen requirement in the activated sludge tank	g_{O2}/m^3
pH	acidity	-
pKa	chemical acid / base dissociation constant	-
P_{vapor}	chemical vapor pressure	Pa
$\overline{PHI}$	system in-/outflux vector	-
Pop	population	cap
P_{vapor}	chemical vapor pressure	Pa
Q	flow	m^3/s
Q_{10}	biodegradation Q10 factor (rate change factor per 10ºC)	-
$Q_{in}^{act.sludge}$	influent flow	m^3/s
$Q_{out}^{act.sludge}$	WWTP effluent flow	m^3/s
$Q_{in}^{primary}$	primary settler influent flow	m^3/s
$Q_{out}^{primary}$	primary settler effluent flow	m^3/s
$Q_{dwf}^{treated}$	treated flow, under dry weather conditions	m^3/s
$Q_{settler}$	flow through settler	m^3/s
$\mathbf{R}$	universal gas constant (8.314)	$J.K^{-1}.mol^{-1-}$
R	sludge recycle ratio	-
r_{end}	endogenous respiration rate	$kg_{O2}.kg_{dwt}^{-1}.d^{-1}$
R_{SEWER}	chemical removal in the sewer	-
R_{RIVER}	chemical removal in the river	-
R_{WWTP}	chemical removal in the WWTP	-
$R1$	chemical removal in a primary settler	-
$R1^*$	predicted chemical removal in a primary settler	-
$R2$	chemical removal in activated sludge	-
$R2^*$	predicted chemical removal in activated sludge	-
$R3$	chemical removal in a trickling filter	-
R_{prim}^{SS}	primary settler suspended solids removal efficiency	-
$\left|R_{prim}^{SS}\right|_{max}$	maximal primary settler suspended solids removal efficiency	-
R_{sec}^{SS}	secondary settler suspended solids removal efficiency	-
$\left|R_{sec}^{SS}\right|_{max}$	maximal secondary settler suspended solids removal efficiency	-
$R_{settler}^{SS}$	settler suspended solids removal efficiency	-
$R_{act.sludge}^{BOD}$	BOD removal efficiency in the activated sludge tank	-
R_{prim}^{BOD}	BOD removal efficiency in the primary settler	-
R_{prim}^{N}	N removal efficiency in the primary settler	-
sal_{ML}	mixed liquor salinity	kg_{Cl}/m^3
SC_g	Schmidt number in air	-
SC_l	Schmidt number in liquid	-
S_W	chemical solubility in water	mol/m^3
SRT	sludge residence time	s
SS	suspended solids concentration	g_{dwt}/m^3
SS_{out}	settler effluent suspended solids concentration	g_{dwt}/m^3
SS_{ML}	mixed liquor (act. sludge) suspended solids concentration	g_{dwt}/m^3
SS_{sewage}	influent suspended solids concentration	g_{dwt}/m^3
S_W	chemical water solubility	mol/m^3

t_{air}	air temperature	$°C$
t_{ML}	mixed liquor temperature	$°C$
t_{water}	water temperature	$°C$
v	flow velocity	m/s
v_{fr}	friction velocity (wind speed at 10 cm height)	m/s
v_{growth}^{sed}	sediment growth velocity	$mm/year$
v_{sed}	suspended solids settling velocity	m/s
v_{shear}	shear wind velocity (lakes)	m/s
v_{wind}	wind speed above the WWTP	m/s
$v_{wind,10}$	wind speed (at 10 m height)	m/s
V	lake volume	m^3
V_i	volume of compartment i	m^3
$V_{act.sludge}$	volume of the activated sludge tank	m^3
V_{prim}	primary settler volume	m^3
V_{sec}	secondary settler volume	m^3
w	river width	m
W	per capita water consumption	$L/(cap.d)$
x	river stretch length	m
X	lumped river biomass level (suspended and in biofilms)	g_{dwt}/m^3
$XCH_{i,j}$	diffusive exchange flow rate from compartment i to compartment j	m^3/s
Y	competent biomass yield coefficient	-
z_0	roughness height	m
Z_i	fugacity capacity of box i	$mol.m^{-3}.Pa^{-1}$
Z_x	fugacity capacity of medium x	$mol.m^{-3}.Pa^{-1}$
α_1	empirical parameter (minimal SS level in effluent)	g_{dwt}/m^3
α_2	empirical parameter (effect of flow on effluent solids level)	$g_{dwt}.m^{-3}.s.\ m^{-3}$
$\alpha_{act.sludge}$	correction factor for biomass activity in activated sludge	-
α_{anoxic}	correction factor for anoxic degradation	-
$\alpha_{anaerobic}$	correction factor for anaerobic degradation	-
α_{redox}	degradation correction factor for different redox zones	-
α_{river}	rate correction for biodegradation in the specific river type	-
α_s	correction factor for sorbed phase degradation	-
$\alpha_{settler}$	empirical parameter (effect of flow/DWF on solids removal)	-
α_{temp}	degradation correction factor for temperature	-
α_{DO}	biodegradation rate correction for dissolved oxygen	-
ε_{sed}	sediment porosity	-
ε_N	efficiency of nitrification	-
ε_{DN}	efficiency of denitrification	-
η_g	kinematic viscosity coefficient for air	m^2/s
η_l	kinematic viscosity coefficient for water	m^2/s
Φ	chemical mass flux	g/s
Φ_{in}^i	chemical mass flux into the system (into box i)	g/s
Φ_{out}^i	chemical mass flux from box i out of the system	g/s
$\Phi_{in}^{act.sludge}$	influent chemical mass flux	g/s
$\Phi_{out}^{act.sludge}$	WWTP effluent chemical mass flux	g/s
$\Phi_{in}^{primary}$	primary settler influent chemical mass flux	g/s
$\Phi_{out}^{primary}$	primary settler effluent chemical mass flux	g/s

Great-er_model_equations.doc

$\Phi_{surplus}^{SS}$	surplus mixed liquor (waste sludge) suspended solids flux	g_{dwt}/s
Φ_{BOD}	influent BOD flux	g_{BOD}/s
Φ_{BOD}^{cap}	daily per capita BOD emission flux	$g_{BOD}.cap^{-1}.d$
Φ_N	influent N flux	g_N/s
Φ_N^{cap}	daily per capita N emission flux	$g_N.cap^{-1}.d$
ρ_{SS}	sediment solids particle density	kg_{dwt}/L
ρ_{solids}^{sewage}	density of sewage (influent) solids	kg_{dwt}/L
ρ_{solids}^{ML}	density of mixed liquor (act. sludge) solids	kg_{dwt}/L
ψ	surface aeration empirical constant	-