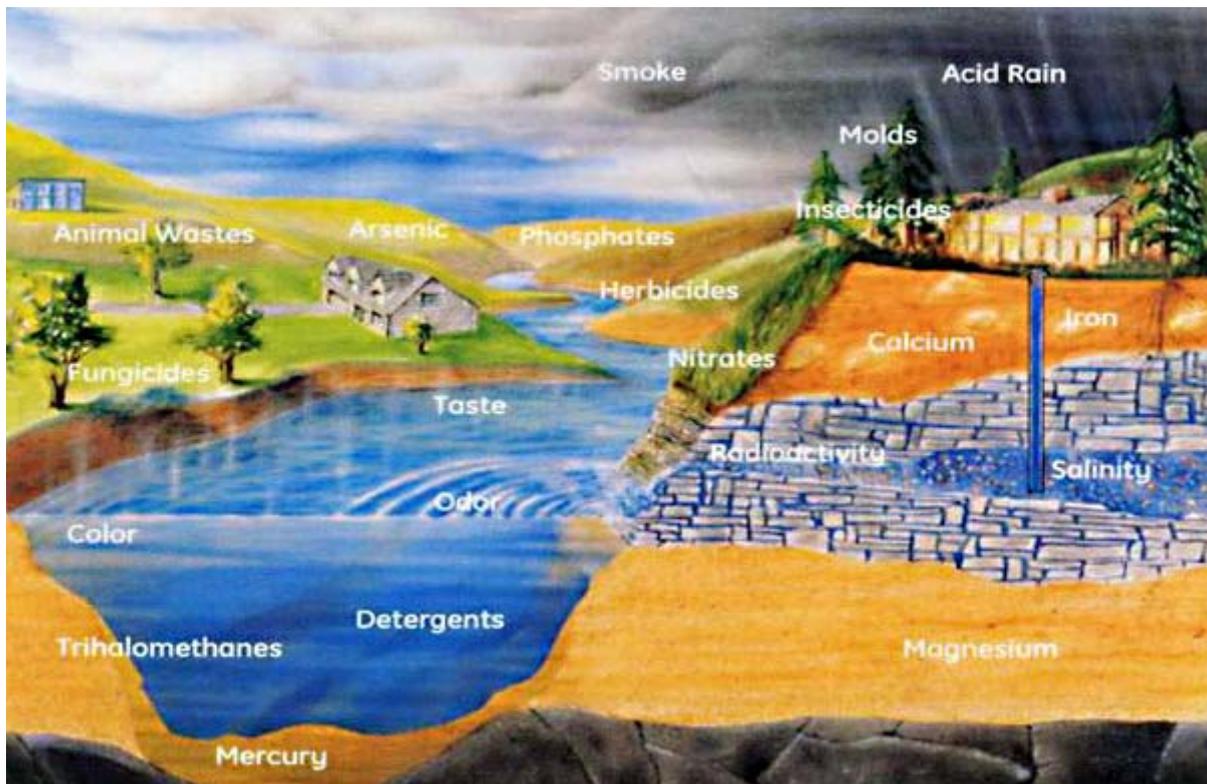




ScorePP is a Specific Targeted Research Project (STREP) funded by the European Commission under the Sixth Framework Programme

ScorePP



Multimedia model at river basin scale

Deliverable No: D7.3, Date: 24 December 2008

Dissemination level: PU

Webbey De Keyser¹, Frederik Verdonck¹, Veerle Gevaert¹, Lorenzo Benedetti¹, Peter A. Vanrolleghem²

¹ Department of Applied Mathematics, Biometrics and Process Control, Ghent University

² Département de génie civil, modelEAU

Source Control Options for Reducing Emissions of Priority Pollutants (ScorePP)

Sixth Framework Programme, Sub-Priority 1.1.6.3, Global Change and Ecosystems

Project no. 037036, www.scorepp.eu, Duration: 1 October 2006 – 30 September 2009

Deliverable number:	D7.3
Deliverable title:	Multimedia model at river basin scale
Authors:	Webbey De Keyser Frederik Verdonck Veerle Gevaert Lorenzo Benedetti Peter A. Vanrolleghem
Review and Assessment	Natasa Atanasova
Date submitted to project coordinator:	2008-12-24
Approved by (Work package leader) :	2008-12-24
Approved by (Project Coordinator) :	2009-01-09

Abstract

A multimedia model at river basin scale was developed and implemented in the WEST modeling and simulation environment. The multimedia model is complementary to the integrated urban scale model of Task 7.4, providing model-based boundary conditions and allowing a chemical's fate assessment to be performed on larger scales, both in time and space.

The multimedia modeling framework based on a chemical's fugacity (often called "Mackay models"), was compared with the SimpleBox models, which are a hands-on adaptation of the fugacity-based models implemented in Excel, also providing equations for the estimation of parameter values on the basis of well-known properties. A multimedia model analogous to the SimpleBox models was implemented in WEST in order to provide full compatibility with the urban scale model of Task 7.4. The WEST implementation provides full flexibility in terms of addition or removal of environmental compartments and mass transfer processes.

Steady state partitioning (comparable to Mackay level III) as well as dynamic simulations (level IV) can be run with the multimedia model, either as a stand alone model or in connection with a dynamic integrated model.

The model implementation was verified through benchmarking exercises with both SimpleBox and fugacity-based models. The results were satisfactory, as comparable environmental distributions were obtained.

Acknowledgement

The presented results have been obtained within the framework of the project ScorePP - "Source Control Options for Reducing Emissions of Priority Pollutants", contract no. 037036, a project coordinated by Department of Environmental Engineering, Technical University of Denmark within the Energy, Environment and Sustainable Development section of the European Community's Sixth Framework Programme for Research, Technological Development and Demonstration.

Table of Contents

1	Introduction	3
1.1	Multimedia models	3
1.2	Aim	3
2	Model selection	4
2.1	Mackay versus SimpleBox	4
2.2	Fundamental changes	11
3	Model implementation	12
3.1	Configuration	12
3.2	Model building	13
3.3	Remark	14
3.4	Air compartment model	14
	3.4.1 Model inputs	14
	3.4.2 Initial calculations	15
	3.4.3 Dynamic equations	15
3.5	Soil compartment model	16
	3.5.1 Model inputs	16
	3.5.2 Initial calculations	17
	3.5.3 Dynamic equations	17
3.6	Water compartment model	19
	3.6.1 Model inputs	19
	3.6.2 Initial calculations	20
	3.6.3 Dynamic equations	20
3.7	Sediment compartment model	21
	3.7.1 Model inputs	21
	3.7.2 Initial calculations	22
	3.7.3 Dynamic equations	22
3.8	Groundwater compartment model	24
	3.8.1 Model inputs	24
	3.8.2 Dynamic equations	24
3.9	Dataserver	24
4	Model verification by comparison with SimpleBox	31
4.1	Setup	31
4.2	Results	31
4.3	Mass balance	34

5	Verification by comparison with another multimedia fate model	34
5.1	Benzene partitioning in a simple evaluative environment	34
5.2	Hexachlorobiphenyl partitioning in a “real” environment	36
6	Conclusions	39
	References	40

1 Introduction

1.1 Multimedia models

Since their introduction in the late 1970s, multimedia models have gained growing use as tools to assess current and future human and ecological exposure to pollutants released to the environment. The first models, e.g. Mackay's unit world model (Mackay and Paterson, 1981; Mackay *et al.*, 1983), were relatively simple in structure and detail, but during the last decades, more complex and sophisticated models were developed by adding different types of compartments to the models, e.g. vegetation compartments (Severinsen and Jager, 1998; Cousins and Mackay, 2001), and organic film-compartments coating impervious surfaces (Diamond *et al.*, 2001). Nested, dynamic and GIS-based models were developed (Brandes *et al.*, 1996; Woodfine *et al.*, 2001; Suzuki *et al.*, 2004), models with layered air and soil compartments arose (Toose *et al.*, 2004), and models for multi-species chemicals were introduced (Fenner *et al.*, 2000; Cahill and Mackay, 2003).

The simple models typically contain a set of equations estimating the transport and breakdown rates of chemical pollutants in different environmental compartments. Often, these are based on empirical relationships representing equilibrium concentrations of a pollutant in different media. The compartments' mass balances can be written as differential equations which can be solved either dynamically or to obtain steady state pollutant concentrations.

1.2 Aim

The integrated dynamic model to be established in Task 7.4 allows to study the fate of emitted priority pollutants in the urban environment. The aim of Task 7.3 is two-fold. The first aim is to frame these urban scale results in a regional scale context, e.g. the river basin, to assess the main sinks and source to sink flows. Like this, the effect of applying emission control strategies within the urban scale model on other parts of the environment outside the urban scale can be estimated and assessed. For example, a certain emission barrier might cause a shift of the pollutant's major sink from the surface water to the groundwater. As the groundwater is not included in the urban scale model, these PP-caused risks outside the urban scale environment might not be noticed in case no multimedia model is wrapped around the integrated urban scale model.

The second aim is to provide boundary conditions for the urban scale model, like for example pollutant (anthropogenic) background concentrations in an upstream river part.

A multimedia modeling approach was selected (see next section) and was implemented in the WEST® modeling and simulation software (Vanhooren *et al.*, 2003). This was preferred above the use of an existing implementation in e.g. Excel or Matlab for compatibility reasons with the urban integrated model already available in WEST. Like this, the integrated dynamic model of Task 7.4 can interact directly with the multimedia model instead of using input and output files.

Additionally, WEST easily deals with dynamic simulations, while most multimedia models consider dynamic equation solving as being the "fourth level", after three levels of steady state solutions.

2 Model selection

2.1 Mackay versus SimpleBox

In the “classical” Mackay models (Mackay, 2001), the pollutant’s fugacity is calculated as a state variable in each compartment. A chemical’s fugacity f is its tendency to escape from the environmental compartment to reach a concentration in equilibrium with the concentrations in other media. The dynamic equations are basically mass balances, in which the pollutant’s mass m can be written as $C \cdot V$ and its concentration C as $Z \cdot f$ with Z a constant for each pollutant in each environmental compartment.

The difficulty is to determine all Z values (by means of equilibrium distribution constants K), mass transfer coefficients and first order rate constants k . For some of those parameters default values are reported in Mackay (2001), others depend on the pollutant, and yet others are not discussed. As this data collection is a tremendous task, another but similar modeling approach was explored: SimpleBox.

SimpleBox is a nested multimedia environmental fate model which was developed at the Netherlands’ National Institute of Public Health and Environment in the framework of EUSES (Brandes *et al.*, 1996). The model is basically a Mackay-type model, with the major difference that no fugacities are calculated, but the pollutant concentrations are directly used as state variables and the equilibrium distribution constants are directly used to express phase equilibrium. Like this, the more abstract Z and f values are avoided.

To point out other differences, the equations of the SimpleBox model were compared with the equations used in the “classical” fugacity approach described by Mackay (2001). Table 1 gives an overview of the equations used to calculate process rates in both models. The used parameters and variables are explained in Table 2.

Table 1. Gujer matrix comparing the Mackay model with the SimpleBox model. The environmental sink and source compartments are A (air), W (water), E (soil) and S (sediment).

Process description causing the pollutant flux	Compartment				Rate (mol pollutant · d ⁻¹)	
	A	W	E	S	Mackay level III/IV	SimpleBox
Deposition of PM in water bodies		-1		+1	$A_{SW} \cdot U_{DP} \cdot Z_P \cdot f_W$	$A_{SW} \cdot v_{\text{settling}} \cdot F_W \cdot C_W$
Resuspension of sediment particles		+1		-1	$A_{SW} \cdot U_{RS} \cdot Z_S \cdot f_S$	$A_{SW} \cdot U_{RS} \cdot C_S$
Diffusion from water to sediment		-1		+1	$\frac{f_W \cdot A_{SW}}{\frac{1}{k_{SW} \cdot Z_W} + \frac{1}{k_{WS} \cdot Z_S}}$	$\frac{(1-F_W) \cdot A_{SW} \cdot C_W}{\frac{1}{k_{SW}} + \frac{1}{k_{WS}}} (*)$
Diffusion from sediment to water		+1		-1	$\frac{f_S \cdot A_{SW}}{\frac{1}{k_{SW} \cdot Z_W} + \frac{1}{k_{WS} \cdot Z_S}}$	$\frac{A_{SW} \cdot C_S}{K_{SW} \cdot \left(\frac{1}{k_{SW}} + \frac{1}{k_{WS}} \right)} (*)$
Soil runoff to water		+1	-1		$U_{EW} \cdot A_{EA} \cdot Z_E \cdot f_E$	$U_{EW} \cdot A_{EA} \cdot C_E$
Water runoff to water		+1	-1		$U_{WW} \cdot A_{EA} \cdot Z_W \cdot f_E$	$U_{WW} \cdot A_{EA} \cdot C_E / K_{EW}$
Diffusion from air to soil (absorption)	-1		+1		$\frac{f_A \cdot A_{EA}}{\frac{1}{k_{EA} \cdot Z_A} + \frac{Y_E}{B_{EA} \cdot Z_A + B_{EW} \cdot Z_W}}$	$\frac{(1-F_A) \cdot A_{EA} \cdot C_A}{\frac{1}{k_{VA}} + \frac{K_{AW}}{K_{EW} \cdot k_{VE}}}$
Diffusion from soil to air (volatilization)	+1		-1		$\frac{f_E \cdot A_{EA}}{\frac{1}{k_{EA} \cdot Z_A} + \frac{Y_E}{B_{EA} \cdot Z_A + B_{EW} \cdot Z_W}}$	$\frac{A_{EA} \cdot C_E}{\frac{1}{k_{VE}} + \frac{K_{EW}}{K_{AW} \cdot k_{VA}}}$
Wet deposition on soil (incl rain dissolution)	-1		+1		$A_{EA} \cdot U_R \cdot v_Q \cdot f_A \cdot (Q \cdot Z_Q + Z_W)$	$A_{EA} \cdot U_R \cdot \left(Q \cdot F_A + \frac{1-F_A}{K_{AW}} \right) \cdot C_A$
Dry deposition on soil	-1		+1		$A_{EA} \cdot U_Q \cdot v_Q \cdot Z_Q \cdot f_A$	$A_{EA} \cdot U_Q \cdot F_A \cdot C_A$
Diffusion from air to water (absorption)	-1	+1			$\frac{f_A \cdot A_{AW}}{\frac{1}{k_{VA} \cdot Z_A} + \frac{1}{k_{VW} \cdot Z_W}}$	$\frac{(1-F_A) \cdot A_{AW} \cdot C_A}{\frac{K_{AW}}{k_{VW}} + \frac{1}{k_{VA}}}$
Diffusion from water to air (volatilization)	+1	-1			$\frac{f_W \cdot A_{AW}}{\frac{1}{k_{VA} \cdot Z_A} + \frac{1}{k_{VW} \cdot Z_W}}$	$\frac{(1-F_W) \cdot A_{AW} \cdot C_W}{\frac{1}{k_{VW}} + \frac{1}{K_{AW} \cdot k_{VA}}}$
Wet deposition on water (incl rain dissolution)	-1	+1			$A_{AW} \cdot U_R \cdot v_Q \cdot f_A \cdot (Q \cdot Z_Q + Z_W)$	$A_{AW} \cdot U_R \cdot \left(Q \cdot F_A + \frac{1-F_A}{K_{AW}} \right) \cdot C_A$
Dry deposition on water	-1	+1			$A_{AW} \cdot U_Q \cdot v_Q \cdot Z_Q \cdot f_A$	$A_{AW} \cdot U_Q \cdot F_A \cdot C_A$
Advective input into air	+1				$G_A \cdot C_{BA}$	$G_A \cdot C_{BA}$
Advective input into water		+1			$G_W \cdot C_{BW}$	$G_W \cdot C_{BW}$
Advective output from air	-1				$G_A \cdot Z_A \cdot f_A$	$G_A \cdot C_A$
Advective output from water		-1			$G_W \cdot Z_W \cdot f_W$	$G_W \cdot C_W$
Direct emission into air	+1				E_A	E_A
Direct emission into water		+1			E_W	E_W
Direct emission into soil			+1		E_E	E_E
Direct emission into sediment				+1	E_S	/
Removal from air by reaction	-1				$k_A \cdot V_A \cdot Z_A \cdot f_A$	$k_A \cdot V_A \cdot (1-F_A) \cdot C_A$
Removal from water by reaction		-1			$k_W \cdot V_W \cdot Z_W \cdot f_W$	$k_W \cdot V_W \cdot (1-F_W) \cdot C_W$
Removal from soil by reaction			-1		$k_E \cdot V_E \cdot Z_E \cdot f_E$	$k_E \cdot V_E \cdot C_E$
Removal from sediment by reaction				-1	$k_S \cdot V_S \cdot Z_S \cdot f_S$	$k_S \cdot V_S \cdot C_S$
Removal from sediment by burial				-1	/	$A_{SW} \cdot U_{DPnet} \cdot C_S$
Leaching from soil to groundwater			-1		/	$U_R \cdot F_{RE} \cdot A_{EA} \cdot C_E / K_{EW}$

*: these are the equations actually used in SimpleBox, although they are incorrect. For explanation: see below in equations (25) and (35).

Table 2. Parameters and variables used in the equations in Table 1.

Name	Meaning	Units *	Remarks **
A_{AW}	interface air - water	L^2	user input
A_{EA}	interface soil - air	L^2	user input
A_{SW}	interface water - sediment	L^2	user input $= A_{AW}$
B_{EA}	effective diffusivity in air phase of the soil	$L^2.T^{-1}$	default value Mackay: 0.04 m ² /h Millington-Quirk equation: $B_A \cdot F_{AE}^{10/3} / (F_{AE} + F_{WE})^2$ with: B_A : molecular diffusivity in air (typical: 0.43 m ² .d ⁻¹ (for pesticides, see Jury <i>et al.</i> , 1983)) F_{AE} : volume fraction of air in soil (e.g. 0.2) F_{WE} : volume fraction of water in soil (e.g. 0.2)
B_{EW}	effective diffusivity in water phase of the soil	$L^2.T^{-1}$	default value Mackay: 4E-6 m ² /h Millington-Quirk equation: $B_W \cdot F_{WE}^{10/3} / (F_{AE} + F_{WE})^2$ with: B_W : molecular diffusivity in water (typical: 4.3E-5 m ² .d ⁻¹ (for pesticides, see Jury <i>et al.</i> , 1983)) F_{AE} : volume fraction of air in soil (e.g. 0.2) F_{WE} : volume fraction of water in soil (e.g. 0.2)
C_A	overall concentration in air	mole.L ⁻³	dynamic variable, includes aerosol and gas phase
C_E	overall concentration in soil	mole.L ⁻³	dynamic variable, includes gas, water and solid phase
C_S	overall concentration in sediment	mole.L ⁻³	dynamic variable, includes water and solid phase
C_W	pollutant concentration in water	mole.L ⁻³	dynamic variable, includes water and solid phase
C_{BA}	pollutant background concentration in inflowing air	mole.L ⁻³	user input
C_{BW}	pollutant background concentration in inflowing water	mole/L ³	user input
E_A	emission rate to air	mole.T ⁻¹	user input
E_E	emission rate to soil	mole.T ⁻¹	user input
E_W	emission rate to water	mole.T ⁻¹	user input
E_S	emission rate to sediment	mole.T ⁻¹	user input
f_A	fugacity of the pollutant in air	P	dynamic variable
f_E	fugacity of the pollutant in soil	P	dynamic variable
f_S	fugacity of the pollutant in sediment	P	dynamic variable
f_W	fugacity of the pollutant in water	P	dynamic variable
F_A	fraction of the pollutant in air which is attached to aerosols	-	estimation in SimpleBox: $\approx \frac{10^{-4}}{P_{vap} + 10^{-4}}$ for liquids

			$\approx \frac{10^{-4}}{P_{\text{vap}} \cdot e^{6.79 \cdot \left(1 - \frac{T_M}{T}\right)} + 10^{-4}}$ for solids with: P_{vap} = pollutant's vapour pressure (Pa) T_M = pollutant's melting point (K) T = absolute temperature (K)
F_{RE}	fraction of rainwater that infiltrates the soil	-	default value in SimpleBox: 0.25 default value in CHEMFRANCE: 0.40 (Devillers and Bintein, 1995)
F_{W}	fraction of the pollutant in water which is attached to particulates	-	estimation in SimpleBox: $\frac{K_p \cdot \text{SUSP}}{1000 + K_p \cdot \text{SUSP}}$ with: SUSP : concentration of suspended matter in the water (default in SimpleBox: 15 g.m ⁻³) K_p : solid-water partition coefficient $= 1.26 \cdot K_{\text{OW}}^{0.81} \cdot C_{\text{org}}$ with: C_{org} = organic carbon content of the solid K_{OW} = octanol-water partition coefficient (estimation only valid for non-ionic organic chemicals)
G_{A}	advective air flow rate	L ³ .T ⁻¹	estimation in SimpleBox: $\frac{(A_{\text{AW}} + A_{\text{EA}}) \cdot H_{\text{A}} \cdot U_{10}}{\sqrt{(A_{\text{AW}} + A_{\text{EA}}) \cdot \pi / 4}}$ with: H_{A} : height of the air compartment U_{10} : wind velocity 10m above the earth's surface (default in SimpleBox: 3 m.s ⁻¹)
G_{W}	advective water flow rate	L ³ .T ⁻¹	user input
K_{AW}	air-water equilibrium distribution constant	-	estimation in SimpleBox: $\frac{H}{R \cdot T} = \frac{P_{\text{vap}}}{\text{Sol} \cdot R \cdot T}$ with: H : Henry coefficient (Pa.m ³ .mol ⁻¹) R : Gas constant (8.314 Pa.m ³ .mol ⁻¹ .K ⁻¹) T : ambient temperature (K) P_{vap} = pollutant's vapour pressure at temperature T (Pa) Sol : solubility in water at temperature T (mole.m ⁻³)
K_{EW}	soil-water equilibrium distribution constant	-	estimation in SimpleBox: $F_{\text{AE}} \cdot K_{\text{AW}} + F_{\text{WE}} + F_{\text{E}} \cdot K_p \cdot \rho / 1000$ with: F_{AE} : volume fraction of air in soil (e.g. 0.2) F_{WE} : volume fraction of water in soil (e.g. 0.2) F_{E} : volume fraction of solids in soil (e.g. 0.6) ρ : density of the solid phase (e.g. 2500 kg.m ⁻³) 1000: conversion factor (g.kg ⁻¹) K_p : solid-water partition coefficient $= 1.26 \cdot K_{\text{OW}}^{0.81} \cdot C_{\text{org}}$ with: C_{org} : organic carbon content of the solid (default in SimpleBox 0.02 for soil)

			<p>K_{OW}: octanol-water partition coefficient (estimation only valid for non-ionic organic chemicals)</p>
K_{SW}	sediment-water equilibrium distribution constant	-	<p>estimation in SimpleBox: $F_{WS} + (1-F_{WS}) \cdot K_p \cdot \rho / 1000$ with: F_{WS}: volume fraction of water in sediment (e.g. 0.8) ρ: density of the solid phase (e.g. 2500 kg.m⁻³) 1000: conversion factor (g.kg⁻¹) K_p: solid-water partition coefficient $= 1.26 \cdot K_{OW}^{0.81} \cdot C_{org}$ with: C_{org}: organic carbon content of the solid (default in SimpleBox 0.05 for sediment) K_{OW}: octanol-water partition coefficient (estimation only valid for non-ionic organic chemicals)</p>
k_A	pseudo first order degradation rate constant in air	T ⁻¹	<p>estimation in SimpleBox: $\ln 2 / 160 = 0.693 / 160$ with: 160 days: maximum half life for organic chemicals due to pseudo first order reaction with OH radicals</p>
k_E	pseudo first order degradation rate constant in soil	T ⁻¹	<p>estimation in SimpleBox: $\frac{\ln(2)}{t_{1/2}} \cdot 2^{\frac{T-298}{10}} \cdot \frac{F_{WE}}{K_{EW}} \cdot \frac{BACT_{soilwater}}{BACT_{test}}$ with : $t_{1/2}$: half life determined in test vessel F_{WE}: volume fraction of water in soil (e.g. 0.2) $BACT_{soilwater}$: bacteria concentration in the soil, expressed per water phase volume (default 1.4E6/F_{WE} cfu.ml⁻¹ in SimpleBox 3.0) $BACT_{test}$: bacteria concentration in the test vessel (default 4E4 cfu.ml⁻¹)</p>
k_S	pseudo first order degradation rate constant in sediment	T ⁻¹	<p>estimation in SimpleBox: $\frac{\ln(2)}{t_{1/2}} \cdot 2^{\frac{T-298}{10}} \cdot \frac{F_{WS}}{K_{SW}} \cdot \frac{BACT_{sediment}}{BACT_{test}}$ with : $t_{1/2}$: half life determined in test vessel F_{WS}: volume fraction of water in sediment (e.g. 0.8) $BACT_{soilwater}$: bacteria concentration in the sediment, expressed per water phase volume (default 1.8E9/F_{WS} cfu.ml⁻¹) $BACT_{test}$: bacteria concentration in the test vessel (default 4E4 cfu.ml⁻¹)</p>
k_W	pseudo first order degradation rate constant in water	T ⁻¹	<p>estimation in SimpleBox: $\frac{\ln(2)}{t_{1/2}} \cdot 2^{\frac{T-298}{10}} \cdot \frac{BACT_{water}}{BACT_{test}}$ with : $t_{1/2}$: half life determined in test vessel $BACT_{water}$: bacteria concentration in water (default 4E4 cfu.ml⁻¹) $BACT_{test}$: bacteria concentration in the test vessel (default 4E4 cfu.ml⁻¹)</p>

k_{EA}	air side mass transfer coefficient for soil-air diffusion	$L \cdot T^{-1}$	<p>default value in Mackay: $1 \text{ m} \cdot \text{h}^{-1}$ (or $3.77 \text{ m} \cdot \text{h}^{-1}$ used in an example after Jury <i>et al.</i>, 1983)</p> <p>In SimpleBox, it is assumed that there is only one air side mass transfer coefficient for both soil-air and water-air diffusion processes: $k_{EA} = k_{VA}$</p>
k_{SW}	water side mass transfer coefficient for sediment-water diffusion	$L \cdot T^{-1}$	<p>default value in Mackay and SimpleBox: $0.01 \text{ m} \cdot \text{h}^{-1}$</p>
k_{VA}	air side mass transfer coefficient for water-air diffusion	$L \cdot T^{-1}$	<p>estimation in MacKay: $3.6 + 5 \cdot U_{10}^{1.2} \text{ (m} \cdot \text{h}^{-1}\text{)}$</p> <p>estimation in SimpleBox: $36 \cdot (0.3 + 0.2 \cdot U_{10}) \cdot (18 / \text{MM})^{0.355} \text{ (m} \cdot \text{h}^{-1}\text{)}$ (after Schwarzenbach <i>et al.</i>, 1993) with: U_{10}: wind velocity 10m above the earth's surface ($\text{m} \cdot \text{s}^{-1}$) (default in SimpleBox: $3 \text{ m} \cdot \text{s}^{-1}$) MM: molecular mass of the pollutant ($\text{g} \cdot \text{mole}^{-1}$)</p>
k_{VE}	soil side mass transfer coefficient for soil-air diffusion	$L \cdot T^{-1}$	<p>estimation in SimpleBox: $v_{\text{eff}} + \frac{D_{\text{eff}}}{H_{\text{Epen}}}$ with: H_{Epen}: chemical dependent penetration depth $= \frac{v_{\text{eff}} + \sqrt{v_{\text{eff}}^2 + 4 \cdot D_{\text{eff}} \cdot k_E}}{2 \cdot k_E}$</p> <p>$v_{\text{eff}}$: effective advective transport in soil $= U_R \cdot F_{RE} / K_{EW}$</p> <p>$D_{\text{eff}}$: effective diffusion coefficient in soil $= \frac{D_W \cdot F_{WE}^{1.5} + D_A \cdot F_{AE}^{1.5} \cdot K_{AW}}{K_{EW}}$</p> <p>with: D_W: diffusion coefficient in water $= 2E-9 \cdot \sqrt{\frac{32}{\text{MM}}} \text{ (m}^2 \cdot \text{s}^{-1}\text{)}$</p> <p>$D_A$: diffusion coefficient in air $= 2.57E-5 \cdot \sqrt{\frac{18}{\text{MM}}} \text{ (m}^2 \cdot \text{s}^{-1}\text{)}$</p> <p>$\text{MM}$: molecular mass of the pollutant ($\text{g} \cdot \text{mole}^{-1}$) F_{AE}: volume fraction of air in soil (e.g. 0.2) F_{WE}: volume fraction of water in soil (e.g. 0.2)</p>
k_{VW}	water side mass transfer coefficient for water-air diffusion	$L \cdot T^{-1}$	<p>default value in Mackay: $0.03 \text{ m} \cdot \text{h}^{-1}$</p> <p>estimation in MacKay: $0.0036 + 0.01 \cdot U_{10}^{1.2} \text{ (m} \cdot \text{h}^{-1}\text{)}$</p> <p>estimation in SimpleBox 3.0: $36 \cdot (4E-4 + 4E-5 \cdot U_{10}^2) \cdot \left(\frac{32}{\text{MM}}\right)^{0.25} \text{ (m} \cdot \text{h}^{-1}\text{)}$ (after Schwarzenbach <i>et al.</i>, 1993)</p> <p>with: U_{10}: wind velocity 10m above the earth's surface ($\text{m} \cdot \text{s}^{-1}$) (default in SimpleBox: $3 \text{ m} \cdot \text{s}^{-1}$) MM: molecular mass of the pollutant ($\text{g} \cdot \text{mole}^{-1}$)</p>

k_{WS}	sediment side mass transfer coefficient for sediment-water diffusion	$L \cdot T^{-1}$	estimation in SimpleBox and MacKay: B/Y with: B: molecular diffusivity in sediment (default in SimpleBox: $2E-6 \text{ m}^2 \cdot \text{h}^{-1}$) Y: layer thickness (default in MacKay: 5 mm) (default in SimpleBox: 2 cm)
Q	scavenging ratio	-	default value in SimpleBox and Mackay: 2E5
U_{DP}	sediment deposition rate	$L \cdot T^{-1}$	default value in Mackay: $4.6E-8 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ estimation in SimpleBox: $= \frac{v_{\text{settling}} \cdot \text{SUSP}}{(1 - F_{WS}) \cdot \rho}$ with: v_{settling} : settling velocity of suspended particles in the water (default $2.5 \text{ m} \cdot \text{d}^{-1}$) SUSP: suspended matter concentration in the water (default: $15 \text{ g} \cdot \text{m}^{-3}$) F_{WS} : volume fraction of water in sediment (e.g. 0.8) ρ : density of the solid phase (e.g. $2500 \text{ kg} \cdot \text{m}^{-3}$)
U_{DPnet}	net sedimentation rate	$L \cdot T^{-1}$	estimation in SimpleBox: $\frac{\text{PROD} \cdot A_{AW} + (C_{BW} - C_W) \cdot G_W + U_{EW} \cdot A_{EA} \cdot F_E \cdot \rho}{(1 - F_{WS}) \cdot \rho \cdot A_{AW}}$ with: PROD = production rate of suspended matter (default $10 \text{ g} \cdot \text{m}^{-2} \cdot \text{year}^{-1}$) F_E : volume fraction of solids in soil (e.g. 0.6) ρ : density of the solid phase (e.g. $2500 \text{ kg} \cdot \text{m}^{-3}$) F_{WS} : volume fraction of water in sediment (e.g. 0.8)
U_{EW}	solids runoff rate from soil	$L \cdot T^{-1}$	default value in Mackay: $2.3E-8 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ default value in SimpleBox: $0.03 \text{ mm} \cdot \text{year}^{-1}$
U_Q	dry deposition velocity	$L \cdot T^{-1}$	default value in Mackay: $10.8 \text{ m} \cdot \text{h}^{-1}$ default value in SimpleBox: $1 \text{ mm} \cdot \text{s}^{-1}$
U_R	rain intensity	$L \cdot T^{-1}$	default value in Mackay: $9.7E-5 \text{ m} \cdot \text{h}^{-1}$ default value in SimpleBox: $700 \text{ mm} \cdot \text{year}^{-1}$
U_{RS}	sediment resuspension rate	$L \cdot T^{-1}$	default value in Mackay: $1.1E-8 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ estimation in SimpleBox: IF $U_{DP} > U_{DPnet}$ THEN $U_{DP} - U_{DPnet}$ ELSE 0
U_{WW}	water runoff rate from soil	$L \cdot T^{-1}$	default value in Mackay: $3.9E-5 \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ estimation in SimpleBox: $U_R \cdot \text{FRAC}$ with: FRAC: fraction of rain water that runs off (default 0.25)
V_A	air volume	L^3	user input
V_E	soil volume	L^3	user input
V_S	sediment volume	L^3	user input
V_W	water volume	L^3	user input
Z_A	Z value for air	$\text{mole} \cdot L^{-3} \cdot P^{-1}$	estimation in MacKay: $1/RT$ with: R: gas constant ($8.314 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)

			T: absolute temperature (K)
Z _E	Z value for soil	mole.L ⁻³ .P ⁻¹	estimation in MacKay: K _{EW} ·Z _W
Z _P	Z value for particles in water	mole.L ⁻³ .P ⁻¹	estimation in MacKay: K _{PW} ·Z _W with: K _{PW} : particles-water equilibrium distribution constant, estimated in SimpleBox as: K _p · SUSP with: SUSP: suspended matter concentration in the water (default: 15 g.m ⁻³) K _p : solid-water partition coefficient = 1.26 · K _{OW} ^{0.81} · C _{org} with: C _{org} : organic carbon content of the solid (default for suspended solids: 0.1) K _{OW} : octanol-water partition coefficient (estimation only valid for non-ionic organic chemicals)
Z _Q	Z value for aerosols	mole.L ⁻³ .P ⁻¹	estimation in MacKay: K _{QA} ·Z _A with: K _{QA} : aerosol-air equilibrium distribution constant
Z _S	Z value for sediment	mole.L ⁻³ .P ⁻¹	estimation in MacKay: K _{SW} ·Z _W
Z _W	Z value for water	mole.L ⁻³ .P ⁻¹	estimation in MacKay: 1/H = Z _A /K _{AW} with: H: Henry coefficient

*: L = length, T = time, P = pressure.

** : parameters used in estimation equations are explained unless they occur as an entry in the table.

From the equations in the above tables it is clear that the Mackay approach focuses on a solid theoretical framework, while in SimpleBox it was tried to provide parameter estimation equations for almost any not readily available parameter. Some of the assumptions in SimpleBox might be rather rough, but as the model is used at a European level for chemical risk assessment, as described in the EU Technical Guidance Documents, and the model has been developed in a stakeholder process including both regulatory and industry parties, it was assumed that the obtained results are sufficiently satisfying for the purpose of the ScorePP project. In case the fugacity based approach was used in ScorePP, a number of parameters would have to be estimated according to equations suggested in literature, which is exactly what the authors of SimpleBox already did. Therefore, it seems more consistent to use the SimpleBox approach for the whole model and not only for the purpose of parameter estimation, although the SimpleBox documentation and Excel implementation are less transparent than the more theoretical Mackay approach.

The multimedia model implemented for this Task was therefore based on SimpleBox 2.0 and 3.0 (Brandes *et al.*, 1996, den Hollander *et al.*, 2003). In the next sections, the implemented equations and the functioning of the multimedia model is described.

Brandes *et al.* (1996) stressed that some of the partition models are only valid for non-ionic organic chemicals. As a result, these equations and **the complete multimedia model should not be used for strong acids and bases occurring in ionic form, anionic and cationic surfactants and metals.**

2.2 Fundamental changes

In SimpleBox, four different scales are included: local, regional, continental and global. Each scale consists of several environmental compartments, with mass flows from one compartment to another and from one scale to another. For the purpose of ScorePP, only a river basin scale is needed. Therefore it was decided to work with the regional scale and to omit the others.

Also the sewage treatment plants, which are in SimpleBox treated as a special kind of pollutant source, were implemented in the ScorePP multimedia model as a separate model block providing emission inputs to water, air and soil compartment models. Like this, the user can decide to include or omit sewage treatment plants as a pollutant source, or to use more sophisticated models when available.

A groundwater compartment is not included in SimpleBox, although a leaching rate from the soil compartment is calculated as a removal process from the modeled system. Because pollutant concentrations in the groundwater might be relevant within the ScorePP project, a groundwater compartment was added.

On the other hand it was decided not to include biomass compartments as ScorePP focuses on the (urban) water compartments, although it will be clear from section 3.1 that extending the model with an additional compartment can easily be done if needed (e.g. biota in the water compartments, vegetation in contact with soil and air).

3 Model implementation

3.1 Configuration

The multimedia model implementation in WEST was based on a modular concept: each environmental compartment is visualized as a node with links representing mass flows from one compartment to the other. Figure 1 shows a basic multimedia model configuration containing five compartments: air, soil, groundwater, surface water and sediment. The modular approach allows multiple occurrences of each environmental compartment, e.g. a second water compartment (with an additional sediment compartment linked to it) could be added to this configuration for example to represent sea water. Another example is the use of multiple soil nodes to model the different behaviour of agricultural soil versus natural or urban soil.

The numbers indicated in Figure 1 refer to the following mass transfer processes:

1. diffusion from water to air (volatilization)
2. diffusion from air to water (gas absorption)
3. diffusion from soil to air (volatilization)
4. diffusion from air to soil (gas absorption)
5. wet and dry deposition from air, split up towards soil and water by a splitter
6. water runoff and soil runoff (erosion)
7. leaching from soil to groundwater
8. diffusion from water to sediment and sedimentation of suspended particles
9. diffusion from sediment to water and resuspension of sediment particles

Besides the environmental compartments, the model also contains a dataserver node which is connected to all compartment nodes – the connection lines were omitted to keep the figure clear. This dataserver model block has two objectives:

- a. Providing a number of calculated or estimated parameter values to multiple blocks needing these values.
- b. Providing the user with a set of default values for pollutant-dependent parameters.

By shifting these parameters and equations from the environmental compartment models to a central calculation unit, redundant calculations are avoided and the risk of using different values for the same parameter in different compartment models is strongly reduced. The user is still able to

override the parameter values directly in the compartment blocks. This can be useful e.g. in case the dataserver node provides an estimated parameter value, while the user knows the exact value. Like this, the estimation can easily be overruled.

Each of the environmental compartments can have one or more inputs by direct emission, e.g. values transferred from a tab delimited text file via an input block or mass flows originating from other model components like a sewage treatment plant, CSO (combined sewer overflow) events, ... In the basic configuration of Figure 1, no such emissions into the environmental compartments are considered. Like this, the shown compartments form a closed system (apart from inputs and outputs due to convection of air and water). In other words, a simulation performed with this configuration shows how the system evolves to a steady state based on dynamic equilibrium partitioning of the chemical present at the initial time (determined by the initial pollutant concentrations in the different compartments).

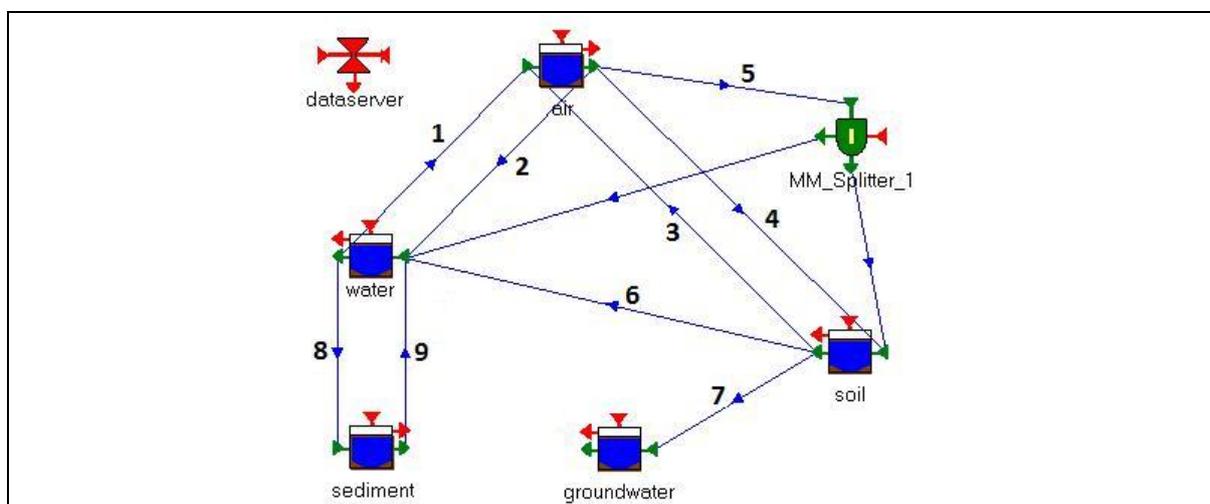


Figure 1. WEST configuration of a basic multimedia model setup (without direct emissions to the environmental compartments); the dataserver related connection lines were omitted to keep the figure clear.

3.2 Model building

In each of the environmental compartment models, a mass balance is made over the pollutant mass fluxes entering the compartment and the fluxes leaving the compartment. It was assumed that all compartments are completely mixed (CSTR) and chemical equilibrium is established instantaneously between the phases within each compartment. Only the magnitude of the mass flows leaving the compartment is calculated. The magnitude of the entering mass flows is obtained from the other compartments or from input files. This procedure is illustrated in the next paragraphs.

In WEST, models are built up in a hierarchical structure, as shown in Figure 2. A generic environmental compartment model contains some parameter and variable definitions common to all environmental compartments to avoid redundancy. All parameter definitions, variable declarations and equations which are not common to all compartments, are contained in the specific submodels.

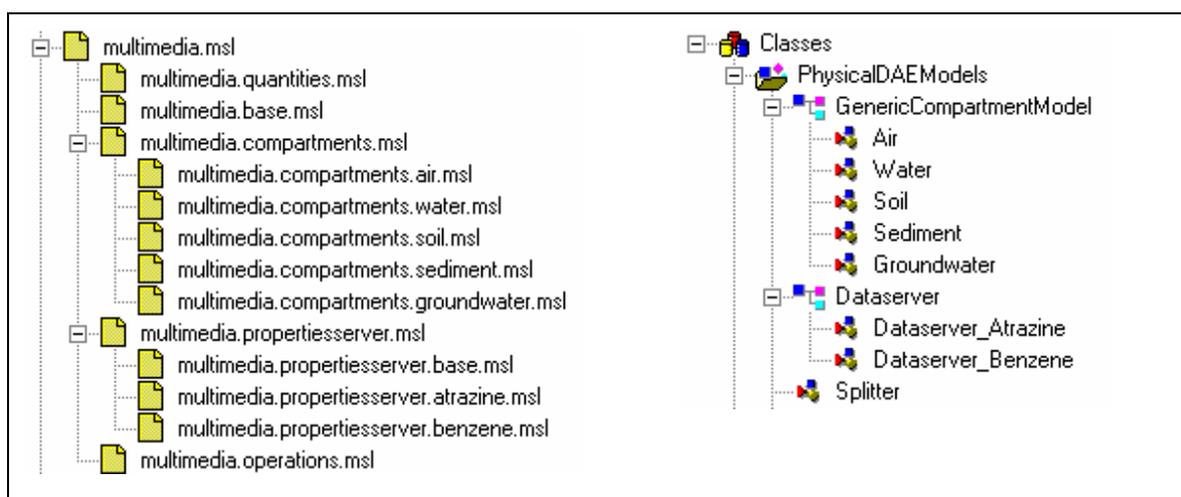


Figure 2. Hierarchical structure of the multimedia model implementation in WEST.

3.3 Remark

In the following model descriptions, parameter names are in italics, variable names and constants are in plain text. The mentioned units are in accordance with the default units in WEST: e.g. days for time and grams for mass. As SimpleBox makes use of the SI unit system (s for time, kg for mass), this explains the use of conversion factors.

3.4 Air compartment model

3.4.1 Model inputs

The air compartment model needs several input parameters as listed in Table 3. No default parameter values are specified for *AdvectiveAirFlow* and *InflowConcentration* as these parameters are fully dependent on the modeled region. For a lot of other parameters, no default values are specified here because they can be retrieved from the dataserver model block – either because they are needed in more than one compartment model or because a calculation/estimation based on other parameters is needed to obtain the (default) value.

Table 3. Model inputs for the air compartment model.

Name	Meaning	Default value	Units
A_{AW}	Total surface area of the water-air interface	(from dataserver)	m ²
A_{EA}	Total surface area of the soil-air interface	(from dataserver)	m ²
<i>AdvectiveAirFlow</i>	Advective flow rate of this compartment (put to -1 for automatic estimation)		m ³ .d ⁻¹
F_A	Fraction of pollutant in air which is attached to aerosols	(from dataserver)	-
H_A	Height of the air compartment	1 000	m
<i>InflowConcentration</i>	Pollutant concentration in inflowing air		g.m ⁻³
k_A	Pseudo first order degradation rate constant in air	(from dataserver)	d ⁻¹
K_{AW}	Air-water equilibrium distribution constant	(from dataserver)	-
K_{EW}	Soil-water equilibrium distribution constant	(from dataserver)	-
<i>masstransfer k_{VA}</i>	Air side mass transfer coefficient, for	(from dataserver)	m.d ⁻¹

	volatilization and gas absorption		
$masstransfer_k_VE$	Soil side mass transfer coefficient, for volatilization and gas absorption	(from dataserver)	$m.d^{-1}$
$masstransfer_k_VW$	Water side mass transfer coefficient, for volatilization and gas absorption	(from dataserver)	$m.d^{-1}$
Q	Scavenging ratio	200 000	-
U_{10}	Wind velocity at a height of 10m	(from dataserver)	$m.d^{-1}$
U_Q	Dry deposition velocity	86.4	$m.d^{-1}$
U_R	Rain intensity	(from dataserver)	$m.d^{-1}$

3.4.2 Initial calculations

The “initial” section contains calculations that are performed only once at the beginning of a simulation. Therefore only equations which are not time dependent are formulated here.

If the advective air flowrate is not explicitly specified, it is estimated assuming the modeled area is circular and the wind speed is homogenous at all heights:

$$\begin{aligned}
 \text{AdvectiveAirFlowrate [m}^3\text{.d}^{-1}] &= \text{IF (AdvectiveAirFlow} == -1) & (1) \\
 &\text{THEN } \frac{(A_{AW} + A_{EA}) \cdot H_A \cdot U_{10}}{\sqrt{(A_{AW} + A_{EA}) \cdot 3.14 / 4}} \\
 &\text{ELSE AdvectiveAirFlow}
 \end{aligned}$$

Mass fluxes of incoming pollutant flows are calculated in the next section as they are time dependent, except for import due to advective air flow:

$$\text{ImportAdv [g.d}^{-1}] = \text{AdvectiveAirFlowrate} \cdot \text{InflowConcentration} \quad (2)$$

3.4.3 Dynamic equations

First, the pollutant mass fluxes due to intermedia mass transfer are calculated. Import of the substance to the air compartment is calculated by summing all mass fluxes connected to the “in” terminal (the import due to advection as calculated in equation (2) is not included herein):

$$\text{Import [g.d}^{-1}] = \sum [\text{all interface links connected to the in terminal}] \quad (3)$$

This principle is used in all compartment models, so equation (3) is common in all models and is therefore part of the GenericCompartmentModel. Every compartment model has several specific interface link variables. For the air compartment, these specific interface links are In_DiffusionFromWater and In_DiffusionFromSoil. Next to these specific interface variables, a number of dummy input variables (called Extra_input_1 to Extra_input_8) is available in the GenericCompartmentModel. These dummy input variables can be used to receive emission data from a text file via an input node or for instance in case a configuration with two soil compartments is modeled. In this example, there will be two incoming mass flows due to diffusion from soil, while there is only one interface variable In_DiffusionFromSoil.

Next, all outgoing mass fluxes are calculated.

Export of the pollutant by advection is calculated assuming the compartment is homogenous (CSTR):

$$\text{ExportAdv [g.d}^{-1}] = \text{AdvectiveAirFlowrate} \cdot \text{PollutantConc} \quad (4)$$

Diffusion mass fluxes to soil and water are calculated by assuming that the overall mass transfer coefficient can be written as a combination of an air side mass transfer coefficient and a soil / water side mass transfer coefficient:

$$\text{DiffusionToSoil [g.d}^{-1}] = \frac{(1 - F_A) \cdot A_{EA} \cdot \text{PollutantConc}}{\frac{1}{\text{masstransfer_k_VA}} + \frac{K_{AW}}{\text{masstransfer_k_VE}}} \quad (5)$$

$$\text{DiffusionToWater [g.d}^{-1}] = \frac{(1 - F_A) \cdot A_{AW} \cdot \text{PollutantConc}}{\frac{1}{\text{masstransfer_k_VA}} + \frac{K_{AW}}{\text{masstransfer_k_VW}}} \quad (6)$$

Note that there is only one air side mass transfer coefficient *masstransfer_k_VA* for both diffusion processes, as is the case in SimpleBox.

Dry and wet deposition rates are calculated separately:

$$\text{DryDeposition [g.d}^{-1}] = (A_{EA} + A_{AW}) \cdot U_Q \cdot F_A \cdot \text{PollutantConc} \quad (7)$$

$$\text{WetDeposition [g.d}^{-1}] = (A_{EA} + A_{AW}) \cdot U_R \cdot \text{PollutantConc} \cdot \left(Q \cdot F_A + \frac{I - F_A}{K_{AW}} \right) \quad (8)$$

The last term in the wet deposition equation takes into account both scavenging and rain dissolution phenomena.

Due to reaction with OH radicals, the pollutant can be removed from the air:

$$\text{RemovalByReaction [g.d}^{-1}] = k_A \cdot ((A_{AW} + A_{EA}) \cdot H_A) \cdot (I - F_A) \cdot \text{PollutantConc} \quad (9)$$

Finally, the mass balance equation becomes:

$$\frac{d \text{PollutantMass}}{d t} \text{ [g.d}^{-1}] = \text{Import} + \text{ImportAdv} - \text{ExportAdv} - \text{DryDeposition} \\ - \text{WetDeposition} - \text{RemovalByReaction} \\ - \text{DiffusionToSoil} - \text{DiffusionToWater} \quad (10)$$

The pollutant concentration is calculated from the pollutant mass:

$$\text{PollutantConc [g.m}^{-3}] = \frac{\text{PollutantMass}}{(A_{AW} + A_{EA}) \cdot H_A} \quad (11)$$

3.5 Soil compartment model

3.5.1 Model inputs

Table 4 lists the needed model inputs and default values in case they cannot be obtained from the dataserer node.

Table 4. Model inputs for the soil compartment model.

Name	Meaning	Default value	Units
A_{EA}	Surface area of the soil-air interface	(from dataserver)	m ²
F_{RE}	Fraction of rainwater that infiltrates the soil	(from dataserver)	-
F_{RW}	Fraction of rain water that runs off	0.25	-
H_E	Height (depth) of the soil compartment. Default 0.05 for industrial and urban soil, 0.20 for agricultural soil. Or obtain a chemical dependent soil depth from the properties server.	(from dataserver)	m
K_{AW}	Air-water equilibrium distribution constant	(from dataserver)	-
k_E	Pseudo first order degradation rate constant in soil	(from dataserver)	d ⁻¹
K_{EW}	Soil-water equilibrium distribution constant	(from dataserver)	-
$masstransfer_k_VA$	Air side mass transfer coefficient, for volatilisation and gas absorption	(from dataserver)	m.d ⁻¹
$masstransfer_k_VE$	Soil side mass transfer coefficient, for volatilisation and gas absorption	(from dataserver)	m.d ⁻¹
U_{EW}	Solids runoff rate from soil	8.22E-8 (*)	m.d ⁻¹
U_R	Rain intensity	(from dataserver)	m.d ⁻¹

3.5.2 Initial calculations

The water runoff rate from soil to water can be calculated time independently as a fraction of the rain intensity:

$$U_{WW} [\text{m.d}^{-1}] = U_R \cdot F_{RW} \quad (12)$$

3.5.3 Dynamic equations

The diffusion mass flux from soil to air is calculated as function of the soil side and air side mass transfer coefficients, similar to equation (5):

$$\text{DiffusionToAir} [\text{g.d}^{-1}] = \frac{A_{EA} \cdot \text{PollutantConc}}{\frac{1}{\text{masstransfer_k_VE}} + \frac{K_{EW}}{K_{AW} \cdot \text{masstransfer_k_VA}}} \quad (13)$$

The default value for U_{EW} corresponding with 0.03 mm per year was copied from SimpleBox, but for some European regions this is probably an underestimation of the actual erosion rate. **Fout! Verwijzingsbron niet gevonden.** Figure 3 shows the estimated soil erosion risk for the largest part of Europe (Kirkby et al., 2004). The legend is in t.ha⁻¹.yr⁻¹, which can be converted to the desired units of m.d⁻¹ by multiplication with the conversion factor proposed in equation (14).

$$U_{EW} [\text{m.d}^{-1}] = \frac{1\text{E6} [\text{g.t}^{-1}]}{\rho [\text{g.m}^{-3}] \cdot F_{EE} [-] \cdot 1\text{E4} [\text{m}^2.\text{ha}^{-1}] \cdot 365 [\text{d.yr}^{-1}]} \cdot U_{EW} [\text{t.ha}^{-1}.\text{yr}^{-1}] \quad (14)$$

with F_{EE} the volume fraction of solids in the soil, as will be calculated further in Table 8. Using the default values for ρ and F_{EE} yields a conversion factor of 1.83E-7. This equation was not implemented in the model: it is only presented here as a help for the user to determine a more applicable parameter value for U_{EW} than the default value.

Leaching from soil to groundwater is expressed as an amount of soil water that leaves the soil compartment with a flow rate equal to the fraction of rain water that infiltrates the soil:

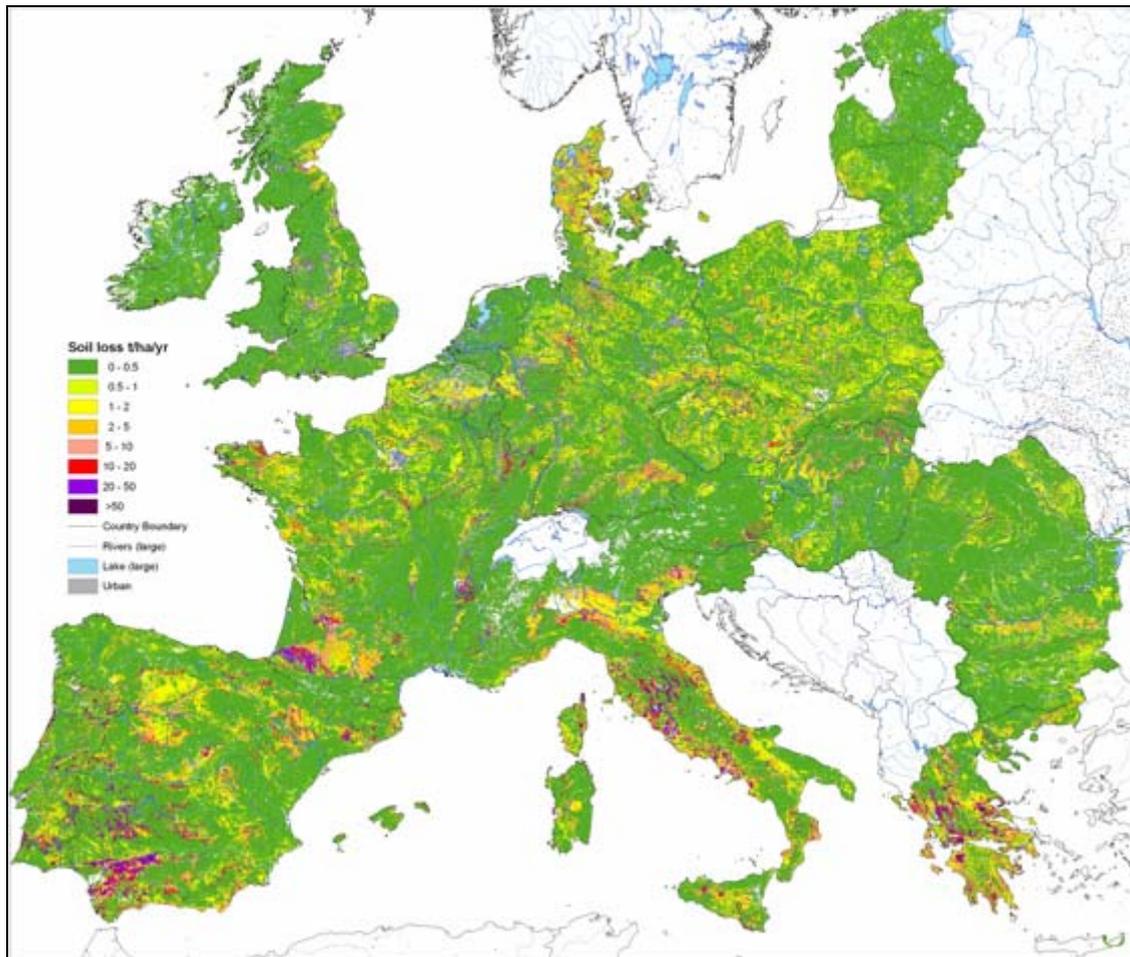


Figure 3. Soil erosion risk in Europe. Pan-European Soil Erosion Risk Assessment (PESERA) model estimations in $t \cdot ha^{-1} \cdot yr^{-1}$.

$$\text{LeachingToGroundwater} [g \cdot d^{-1}] = U_R \cdot F_RE \cdot A_EA \cdot \frac{\text{PollutantConc}}{K_EW} \quad (15)$$

Runoff has two components: runoff of rainwater from soil to surface water and runoff of soil particles (erosion):

$$\text{SoilRunoffToWater} [g \cdot d^{-1}] = U_EW \cdot A_EA \cdot \text{PollutantConc} \quad (16)$$

$$\text{WaterRunoffToWater} [g \cdot d^{-1}] = U_WW \cdot A_EA \cdot \frac{\text{PollutantConc}}{K_EW} \quad (17)$$

The pollutant can also be removed from the soil compartment by bacterial breakdown, modeled as a first order process:

$$\text{RemovalByReaction} [g \cdot d^{-1}] = k_E \cdot (A_EA \cdot H_E) \cdot \text{PollutantConc} \quad (18)$$

The mass balance unites all these processes:

$$\frac{d \text{PollutantMass}}{d t} [\text{g.d}^{-1}] = \text{Import} - \text{DiffusionToAir} - \text{RemovalByReaction} \\ - \text{LeachingToGroundwater} - \text{WaterRunoffToWater} \\ - \text{SoilRunoffToWater} \quad (19)$$

Note that the Import term is calculated as in equation (3), as a part of the GenericCompartmentModel. Next to the eight generic input variables, compartment specific interface variables are In_DiffusionFromAir, In_DryDepositionFromAir and In_WetDepositionFromAir.

The pollutant concentration is calculated from the pollutant mass analogous to equation (11):

$$\text{PollutantConc} [\text{g.m}^{-3}] = \frac{\text{PollutantMass}}{A_{EA} \cdot H_E} \quad (20)$$

3.6 Water compartment model

3.6.1 Model inputs

Table 5 lists the needed model inputs and default values in case they cannot be obtained from the dataserver node.

Table 5. Model inputs for the water compartment model.

Name	Meaning	Default value	Units
<i>A_{AW}</i>	Surface area of the air-water interface	(from dataserver)	m ²
<i>A_{SW}</i>	Surface area of the water-sediment interface	(from dataserver)	m ²
<i>AdvectiveWaterFlowrate</i>	Advective flow rate of this compartment. Can be constant or dynamic input from an upstream river model.	(from dataserver)	m ³ .d ⁻¹
<i>C_{org_sediment}</i>	Organic carbon content of the sediment top layer (kg OC / kg solids)	(from dataserver)	-
<i>C_{org_susp}</i>	Organic carbon content of the suspended particles (kg OC / kg solids)	0.1	-
<i>C_{susp}</i>	Suspended matter concentration. Default 15 for fresh water, 5 for seawater.	15	g.m ⁻³
<i>H_W</i>	Height (depth) of the water compartment. Default 3 for fresh water, 25 for sea water	3	m
<i>InflowConcentration</i>	Pollutant concentration in inflowing water. Can be constant or dynamic input from an upstream river model.		g.m ⁻³
<i>K_{AW}</i>	Air-water equilibrium distribution constant	(from dataserver)	-
<i>K_{SW}</i>	Sediment-water equilibrium distribution constant	(from dataserver)	-
<i>k_W</i>	Pseudo first order degradation constant in water	(from dataserver)	d ⁻¹
<i>KOC</i>	Organic carbon - Water partition coefficient of the pollutant	(from dataserver)	-
<i>masstransfer_k_SW</i>	Water side mass transfer coefficient	(from dataserver)	m.d ⁻¹

<i>masstransfer_k_VA</i>	Air side mass transfer coefficient, for volatilisation and gas absorption	(from dataserer)	m.d ⁻¹
<i>masstransfer_k_VW</i>	Water side mass transfer coefficient, for volatilisation and gas absorption	(from dataserer)	m.d ⁻¹
<i>masstransfer_k_WS</i>	Sediment side mass transfer coefficient	(from dataserer)	m.d ⁻¹
<i>v_settling</i>	Settling velocity of suspended particles in the water	(from dataserer)	m.d ⁻¹

3.6.2 Initial calculations

The solid-water partition coefficients for suspended matter in the water compartment can be estimated by multiplying the organic carbon - water partition coefficient with the organic carbon content of the solids:

$$K_P_susp [l.kg^{-1}] = C_org_susp \cdot KOC \quad (21)$$

Note that this equation is not valid for metals. For metals, it is recommended to enter directly solid-water partition coefficients. This requests a small change in the model, replacing the state variable *K_P_susp* by a parameter *K_P_susp*.

The fraction of the pollutant in the water compartment which is attached to suspended particles can be estimated with equation (22), in which 1 000 000 is a conversion term with units [g.l.kg⁻¹.m⁻³]:

$$F_W [-] = \frac{\frac{K_P_susp \cdot C_susp}{1\,000\,000}}{1 + \frac{K_P_susp \cdot C_susp}{1\,000\,000}} = \frac{K_P_susp \cdot C_susp}{1\,000\,000 + K_P_susp \cdot C_susp} \quad (22)$$

The pollutant mass flux entering the water compartment by advective transport is calculated from the water flow rate and the pollutant's background concentration, similar to equation (2):

$$ImportAdv [g.d^{-1}] = AdvectiveWaterFlowrate \cdot InflowConcentration \quad (23)$$

3.6.3 Dynamic equations

The diffusion mass transfer coefficient for water-air diffusion is again a combination of the water side and air side mass transfer coefficients in series:

$$DiffusionToAir [g.d^{-1}] = \frac{(1 - F_W) \cdot A_AW \cdot PollutantConc}{\frac{1}{masstransfer_k_VW} + \frac{1}{K_AW \cdot masstransfer_k_VA}} \quad (24)$$

Analogous for the water-sediment diffusion process:

$$DiffusionToSediment [g.d^{-1}] = \frac{(1 - F_W) \cdot A_SW \cdot PollutantConc}{\frac{1}{masstransfer_k_WS} + \frac{1}{K_SW \cdot masstransfer_k_SW}} \quad (25)$$

Note that this last equation differs from the equation used in SimpleBox (see Table 1). The factor *K_SW* is needed to convert the denominator's last term's units from (m³ sediment·m⁻²·d⁻¹)⁻¹ to (m³ water·m⁻²·d⁻¹)⁻¹, but was omitted (forgotten?) in SimpleBox.

The export process rate is obtained similar to equation (4):

$$ExportAdv [g.d^{-1}] = AdvectiveWaterFlowrate \cdot PollutantConc \quad (26)$$

Deposition of suspended particles onto the sediment is calculated as:

$$\text{DepositionToSediment [g.d}^{-1}] = A_{SW} \cdot v_{\text{settling}} \cdot F_W \cdot \text{PollutantConc} \quad (27)$$

Removal of the pollutant by bacterial breakdown is assumed to happen according to a (pseudo) first order degradation rate constant:

$$\text{RemovalByReaction [g.d}^{-1}] = k_W \cdot (A_{AW} \cdot H_W) \cdot (1 - F_W) \cdot \text{PollutantConc} \quad (28)$$

Finally, the mass balance becomes:

$$\begin{aligned} \frac{d \text{PollutantMass}}{d t} \text{ [g.d}^{-1}] &= \text{Import} + \text{ImportAdv} - \text{ExportAdv} \\ &\quad - \text{DiffusionToAir} - \text{DiffusionToSediment} \\ &\quad - \text{RemovalByReaction} - \text{DepositionToSediment} \end{aligned} \quad (29)$$

The Import term is calculated as in equation (3), as a part of the GenericCompartmentModel. Next to the eight generic input variables, compartment specific interface variables are In_DiffusionFromAir, In_DiffusionFromSediment, In_DryDepositionFromAir, In_WetDepositionFromAir, In_ResuspensionFromSediment, In_WaterRunoffFromSoil, In_SoilRunoffFromSoil and In_LeachingFromGroundwater.

The calculation of the pollutant concentration is based on the pollutant mass, the surface area of the water compartment and its height:

$$\text{PollutantConc [g.m}^{-3}] = \frac{\text{PollutantMass}}{A_{AW} \cdot H_W} \quad (30)$$

3.7 Sediment compartment model

3.7.1 Model inputs

Table 6 lists the needed model inputs and default values in case they cannot be obtained from the dataserer node.

Table 6. Model inputs for the sediment compartment model.

Name	Meaning	Default value	Units
A_{EA}	Surface area of the soil-air interface	(from dataserer)	m ²
A_{SW}	Surface area of the water-sediment interface	(from dataserer)	m ²
<i>AdvectiveWaterFlowrate</i>	Advective flow rate of this compartment. Can be constant or dynamic input from an upstream river model.	(from dataserer)	m ³ .d ⁻¹
C_{susp}	Suspended matter concentration in the water compartment above the sediment. Default 15 for fresh water, 5 for seawater.	15	g.m ⁻³
$C_{\text{org_sediment}}$	Organic carbon content of the sediment top layer (kg OC / kg solids)	(from dataserer)	-
$C_{\text{susp_in}}$	Suspended matter 'background concentration' in the water entering the water compartment above the sediment. Default value 25 or dynamic input from an upstream river model.		g.m ⁻³

<i>F_EE</i>	Volume fraction of the solid phase in the soil compartment	(from dataserver)	-
<i>F_WS</i>	Volume fraction of the water phase in the sediment compartment	(from dataserver)	-
<i>Gross_Sedimentation_Rate</i>	Gross sedimentation rate. Put to -1 for automatic estimation.	-1	m.d ⁻¹
<i>H_S</i>	Height (depth) of the sediment compartment.	0.03	m
<i>In_Susp_WWTP</i>	Suspended matter (TSS) input massflux into the water compartment above the sediment. Can be constant (default 30-40 g/m ³ x discharge flow rate) or dynamic input from a treatment plant model.		g.d ⁻¹
<i>k_S</i>	Pseudo first order degradation constant in sediment	(from dataserver)	d ⁻¹
<i>K_SW</i>	Sediment-water equilibrium distribution constant	(from dataserver)	-
<i>masstransfer k_SW</i>	Water side mass transfer coefficient	(from dataserver)	m.d ⁻¹
<i>masstransfer k_WS</i>	Sediment side mass transfer coefficient	(from dataserver)	m.d ⁻¹
<i>Net_Sedimentation_Rate</i>	Net sedimentation rate. (gross sedimentation minus resuspension) Put to -1 for automatic estimation.	-1	m.d ⁻¹
<i>Prod_Susp</i>	Production rate of suspended matter in the water compartment above the sediment	0.0274	g.m ⁻² .d ⁻¹
<i>rho</i>	Density of the solid phase of the sediment compartment	(from dataserver)	g.m ⁻³
<i>U_EW</i>	Solids runoff rate from soil	8.22E-8	m.d ⁻¹
<i>v_settling</i>	Settling velocity of suspended particles in the water	(from dataserver)	m.d ⁻¹

3.7.2 Initial calculations

Sedimentation is calculated in two different ways: a gross and net sedimentation rate. Both estimations can be overruled by user defined constants if the parameters *Gross_Sedimentation_Rate* and *Net_Sedimentation_Rate* are defined.

First, the gross sedimentation rate is determined by a settling velocity parameter, from which the mass flux of the settling particles and of the pollutant attached to it is calculated:

$$\begin{aligned}
 \text{GrossSedimentationRate [g.d}^{-1}] &= \text{IF } (Gross_Sedimentation_Rate == -1) \\
 &\quad \text{THEN } \frac{v_settling \cdot C_susp}{(1 - F_WS) \cdot rho} \\
 &\quad \text{ELSE } Gross_Sedimentation_Rate
 \end{aligned} \tag{31}$$

3.7.3 Dynamic equations

The net sedimentation rate is dynamically calculated from a suspended solids mass balance. The difference between particles entering and particles leaving the water compartment is supposed to settle, as the suspended solids concentration in the water compartment is supposed to be constant.

$$\begin{aligned}
 \text{NetSedimentationRate [m.d}^{-1}] &= \\
 &\text{IF (Net_Sedimentation_Rate == -1)} \\
 &\quad \left(\frac{\text{Prod_Susp} \cdot A_SW + C_susp_in \cdot \text{AdvectiveWaterFlowrate} \right. \\
 &\quad \quad \left. + \text{In_Susp_WWTP} + U_EW \cdot A_EA \cdot \rho \cdot F_EE \right. \\
 &\quad \quad \left. - C_susp \cdot \text{AdvectiveWaterFlowrate} \right) \\
 &\text{THEN} \frac{\hspace{10em}}{(1 - F_WS) \cdot \rho \cdot A_SW} \quad (32) \\
 &\text{ELSE Net_Sedimentation_Rate}
 \end{aligned}$$

The suspended solids released from wastewater treatment plants are included in the mass balance although apparently they were omitted from SimpleBox version 3.0. This can easily be simulated by setting In_Susp_WWTP to 0.

The positive difference between the gross and the net sedimentation rate is the resuspension rate:

$$\begin{aligned}
 U_RS \text{ [m.d}^{-1}] &= \text{IF (GrossSedimentationRate} > \text{NetSedimentationRate)} \quad (33) \\
 &\quad \text{THEN GrossSedimentationRate} - \text{NetSedimentationRate} \\
 &\quad \text{ELSE 0}
 \end{aligned}$$

$$\text{Resuspension [g.d}^{-1}] = A_SW \cdot U_RS \cdot \text{PollutantConc} \quad (34)$$

Next, diffusion is calculated based on mass transfer coefficients at the water and sediment side of the sediment-water interface:

$$\text{DiffusionToWater [g.d}^{-1}] = \frac{A_SW \cdot \text{PollutantConc}}{\frac{K_SW}{\text{masstransfer_k_WS}} + \frac{1}{\text{masstransfer_k_SW}}} \quad (35)$$

Note that this equation, similar to equation (25), differs from the equation used in SimpleBox (see Table 1). The factor K_SW is needed to convert the denominator's first term's units from $(\text{m}^3 \text{ water} \cdot \text{m}^{-2} \cdot \text{d}^{-1})^{-1}$ to $(\text{m}^3 \text{ sediment} \cdot \text{m}^{-2} \cdot \text{d}^{-1})^{-1}$, but was used incorrect in SimpleBox.

Removal from the sediment compartment by biological breakdown is calculated as a first order process:

$$\text{RemovalByReaction [g.d}^{-1}] = k_S \cdot A_SW \cdot H_S \cdot \text{PollutantConc} \quad (36)$$

The sediment burial rate is derived from the net sedimentation rate:

$$\text{Burial [g.d}^{-1}] = A_SW \cdot \text{NetSedimentationRate} \cdot \text{PollutantConc} \quad (37)$$

Finally, the mass balance and concentration are derived:

$$\begin{aligned}
 \frac{d \text{ PollutantMass}}{d t} \text{ [g.d}^{-1}] &= \text{Import} - \text{DiffusionToWater} - \text{Resuspension} \\
 &\quad - \text{RemovalByReaction} - \text{Burial} \quad (38)
 \end{aligned}$$

The Import term is calculated as in equation (3), as a part of the GenericCompartmentModel. Next to the eight generic input variables, compartment specific interface variables are $In_DiffusionFromWater$ and $In_DepositionFromWater$.

$$\text{PollutantConc [g.m}^{-3}] = \frac{\text{PollutantMass}}{A_SW \cdot H_S} \quad (39)$$

3.8 Groundwater compartment model

In SimpleBox, the water flow rate transporting the pollutant from soil to groundwater was calculated as a fixed fraction of the rainfall (see equation (15)), but this was considered to be transport across the boundaries of the modeled system, as no groundwater compartment is included in SimpleBox.

3.8.1 Model inputs

Table 7 lists the needed model inputs and default values in case they cannot be obtained from the dataserver node.

Table 7. Model inputs for the groundwater compartment model.

Name	Meaning	Default value	Units
A_{EA}	Surface area of the soil-air interface	(from dataserver)	m ²
F_{RE}	Fraction of rainwater that infiltrates the soil	(from dataserver)	-
U_R	Rain intensity	(from dataserver)	m.d ⁻¹
V	Volume of groundwater present in the system		m ³

3.8.2 Dynamic equations

As the groundwater compartment is considered to be a completely mixed tank with a fixed volume, the water flow rate leaving the groundwater compartment is equal to the incoming flow rate, i.e. a fixed fraction of the rainfall.

Leaching from the groundwater to the water compartment is therefore modeled as:

$$\text{LeachingToWater} = U_R \cdot F_{RE} \cdot A_{EA} \cdot \text{PollutantConc} \quad (40)$$

Reaction is not supposed to be relevant in the groundwater compartment.

$$\frac{d \text{PollutantMass}}{d t} [\text{g.d}^{-1}] = \text{Import} - \text{LeachingToWater} \quad (41)$$

$$\text{PollutantConc} [\text{g.m}^{-3}] = \frac{\text{PollutantMass}}{V} \quad (42)$$

3.9 Dataserver

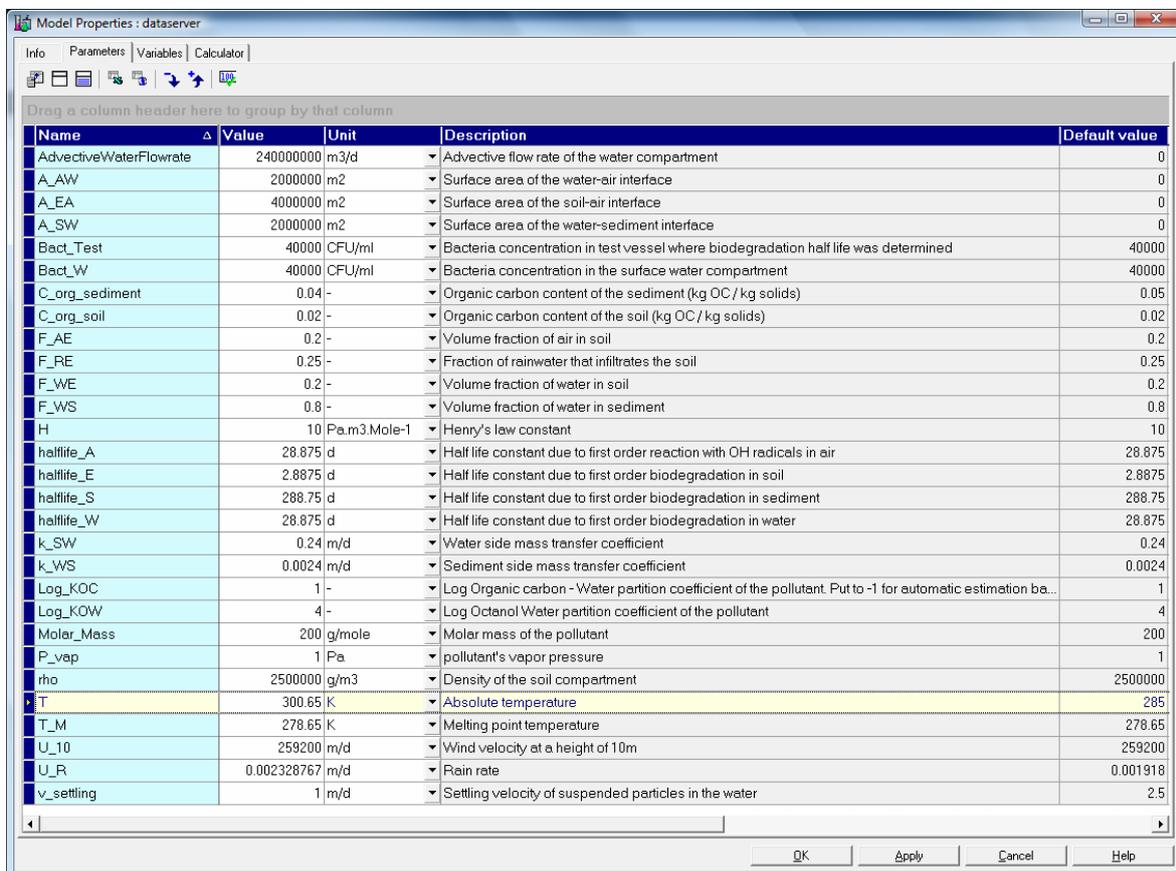
In the above sections, many default parameter values can be obtained from the dataserver model discussed in this section. In the following, the input to the dataserver block will be called “input parameters” and their names will be in italics. The output of the dataserver model, i.e. the values which are passed on to the compartment models, are called “outputs” and their names will be in normal typeface.

The outputs can have either calculated or estimated values, as shown in Table 8. The reference for the estimation equations is SimpleBox 2.0 (Brandes *et al.*, 1996) and SimpleBox 3.0 (den Hollander *et al.*, 2003), unless mentioned differently. The input parameters needed to calculate the outputs’ values, are listed in Table 9 together with their default values. Figure 4 shows a screenshot of the user interface which allows changing the dataserver’s input parameters. Some intermediate state variables needed in the calculation of the outputs are given in Table 10. Figure 5 shows some

of the intermediate state variables and the outputs available for coupling with the compartment models.

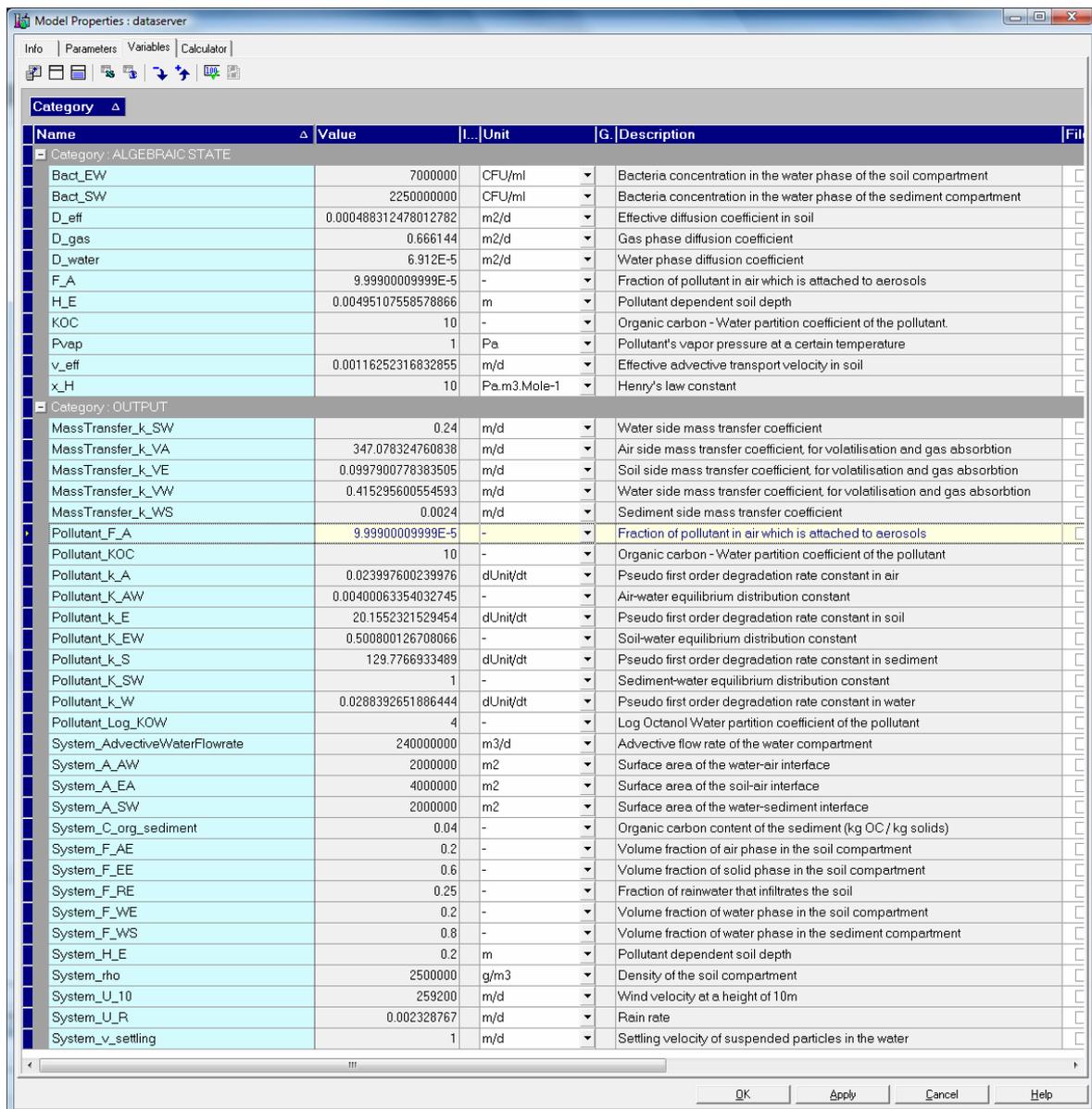
Some outputs are simply equal to an input parameter. The advantage of having them in the dataserver node is that they can be passed on to all compartment models needing their value. To avoid mistakes, these parameters occurring in the multiple compartments should be coupled. This can either be done through parameter coupling in the WEST Configuration Builder, or by obtaining the parameter value from the dataserver block. The last option could be more transparent because the visual representation of the links reduces the risk of linking too many or not enough parameters.

It must be emphasized that the only purpose of the dataserver node is to make the estimation of parameter values easier and centralized in one model instead of distributed in the environmental compartment models. This implies that the modeler is not forced to use the estimates provided by the dataserver: parameter values needed in the environmental compartment models can simply be entered in the compartment node, which will overrule the dataserver's estimated values.



Name	Value	Unit	Description	Default value
AdvectiveWaterFlowrate	240000000	m3/d	Advective flow rate of the water compartment	0
A_AW	2000000	m2	Surface area of the water-air interface	0
A_EA	4000000	m2	Surface area of the soil-air interface	0
A_SW	2000000	m2	Surface area of the water-sediment interface	0
Bact_Test	40000	CFU/ml	Bacteria concentration in test vessel where biodegradation half life was determined	40000
Bact_W	40000	CFU/ml	Bacteria concentration in the surface water compartment	40000
C_org_sediment	0.04	-	Organic carbon content of the sediment (kg OC / kg solids)	0.05
C_org_soil	0.02	-	Organic carbon content of the soil (kg OC / kg solids)	0.02
F_AE	0.2	-	Volume fraction of air in soil	0.2
F_RE	0.25	-	Fraction of rainwater that infiltrates the soil	0.25
F_WE	0.2	-	Volume fraction of water in soil	0.2
F_WS	0.8	-	Volume fraction of water in sediment	0.8
H	10	Pa.m3.Mole-1	Henry's law constant	10
halflife_A	28.875	d	Half life constant due to first order reaction with OH radicals in air	28.875
halflife_E	2.8875	d	Half life constant due to first order biodegradation in soil	2.8875
halflife_S	288.75	d	Half life constant due to first order biodegradation in sediment	288.75
halflife_W	28.875	d	Half life constant due to first order biodegradation in water	28.875
k_SW	0.24	m/d	Water side mass transfer coefficient	0.24
k_WS	0.0024	m/d	Sediment side mass transfer coefficient	0.0024
Log_KOC	1	-	Log Organic carbon - Water partition coefficient of the pollutant. Put to -1 for automatic estimation ba...	1
Log_KOW	4	-	Log Octanol Water partition coefficient of the pollutant	4
Molar_Mass	200	g/mole	Molar mass of the pollutant	200
P_vap	1	Pa	pollutant's vapor pressure	1
rho	2500000	g/m3	Density of the soil compartment	2500000
T	300.65	K	Absolute temperature	285
T_M	278.65	K	Melting point temperature	278.65
U_10	259200	m/d	Wind velocity at a height of 10m	259200
U_R	0.002328767	m/d	Rain rate	0.001918
v_settling	1	m/d	Settling velocity of suspended particles in the water	2.5

Figure 4. The WEST user interface to change the dataserver's input parameter values.



Name	Value	Unit	Description
Category: ALGEBRAIC STATE			
Bact_EW	7000000	CFU/ml	Bacteria concentration in the water phase of the soil compartment
Bact_SW	2250000000	CFU/ml	Bacteria concentration in the water phase of the sediment compartment
D_eff	0.000488312478012782	m ² /d	Effective diffusion coefficient in soil
D_gas	0.666144	m ² /d	Gas phase diffusion coefficient
D_water	6.912E-5	m ² /d	Water phase diffusion coefficient
F_A	9.999000099999E-5	-	Fraction of pollutant in air which is attached to aerosols
H_E	0.00495107558578866	m	Pollutant dependent soil depth
KOC	10	-	Organic carbon - Water partition coefficient of the pollutant
Pvap	1	Pa	Pollutant's vapor pressure at a certain temperature
v_eff	0.00116252316832855	m/d	Effective advective transport velocity in soil
x_H	10	Pa.m3.Mole-1	Henry's law constant
Category: OUTPUT			
MassTransfer_k_SW	0.24	m/d	Water side mass transfer coefficient
MassTransfer_k_VA	347.078324760838	m/d	Air side mass transfer coefficient, for volatilisation and gas absorption
MassTransfer_k_VE	0.0997900778383505	m/d	Soil side mass transfer coefficient, for volatilisation and gas absorption
MassTransfer_k_VW	0.415295600554593	m/d	Water side mass transfer coefficient, for volatilisation and gas absorption
MassTransfer_k_WS	0.0024	m/d	Sediment side mass transfer coefficient
Pollutant_F_A	9.999000099999E-5	-	Fraction of pollutant in air which is attached to aerosols
Pollutant_KOC	10	-	Organic carbon - Water partition coefficient of the pollutant
Pollutant_k_A	0.023997600239976	dUnit/dt	Pseudo first order degradation rate constant in air
Pollutant_K_AW	0.00400063354032745	-	Air-water equilibrium distribution constant
Pollutant_k_E	20.1552321529454	dUnit/dt	Pseudo first order degradation rate constant in soil
Pollutant_K_EW	0.500800126708066	-	Soil-water equilibrium distribution constant
Pollutant_k_S	129.7766933489	dUnit/dt	Pseudo first order degradation rate constant in sediment
Pollutant_K_SW	1	-	Sediment-water equilibrium distribution constant
Pollutant_k_W	0.0288392651886444	dUnit/dt	Pseudo first order degradation rate constant in water
Pollutant_Log_KOW	4	-	Log Octanol Water partition coefficient of the pollutant
System_AdvectiveWaterFlowrate	240000000	m ³ /d	Advective flow rate of the water compartment
System_A_AW	2000000	m ²	Surface area of the water-air interface
System_A_EA	4000000	m ²	Surface area of the soil-air interface
System_A_SW	2000000	m ²	Surface area of the water-sediment interface
System_C_org_sediment	0.04	-	Organic carbon content of the sediment (kg OC / kg solids)
System_F_AE	0.2	-	Volume fraction of air phase in the soil compartment
System_F_EE	0.6	-	Volume fraction of solid phase in the soil compartment
System_F_RE	0.25	-	Fraction of rainwater that infiltrates the soil
System_F_WE	0.2	-	Volume fraction of water phase in the soil compartment
System_F_WS	0.8	-	Volume fraction of water phase in the sediment compartment
System_H_E	0.2	m	Pollutant dependent soil depth
System_rho	2500000	g/m ³	Density of the soil compartment
System_U_10	259200	m/d	Wind velocity at a height of 10m
System_U_R	0.002328767	m/d	Rain rate
System_v_settling	1	m/d	Settling velocity of suspended particles in the water

Figure 5. The dataserver's calculated state variables and outputs available for use in the compartment models.

Table 8. Outputs calculated or estimated in the Dataserver node.

Name	Meaning	Equation yielding the default value	Units
A_AW	Total surface area of the water-air interface	$= A_{AW}$	m ²
A_EA	Total surface area of the soil-air interface	$= A_{EA}$	m ²
A_SW	Surface area of the water-sediment interface	$= A_{SW}$	m ²
AdvectiveWaterFlowrate	Advective flow rate of this compartment.	$= AdvectiveWaterFlowrate$	m ³ .d ⁻¹
C_org_sediment	Organic carbon content of the sediment top layer (kg OC / kg solids)	$= C_{org_sediment}$	-
F_A	Fraction of pollutant in air which is attached to aerosols	$= \begin{cases} \text{IF } (T > T_M) \\ \text{THEN } \frac{10^{-4}}{P_{vap} + 10^{-4}} \\ \\ \text{ELSE } \frac{10^{-4}}{P_{vap} \cdot e^{6.79 \cdot \left(1 - \frac{T_M}{T}\right)} + 10^{-4}} \end{cases}$	-
F_EE	Volume fraction of the solid phase in the soil compartment	$= 1 - F_{WE} - F_{AE}$	-
F_RE	Fraction of rainwater that infiltrates in the soil	$= F_{RE}$	-
F_WS	Volume fraction of the water phase in the sediment compartment	$= F_{WS}$	-
H_E	Height (depth) of the soil compartment.	$= \begin{cases} \text{IF } \left(\frac{v_{eff} + \sqrt{v_{eff}^2 + 4 \cdot D_{eff} \cdot k_E}}{2 \cdot k_E} \geq 0.20 \right) \\ \text{THEN } \frac{v_{eff} + \sqrt{v_{eff}^2 + 4 \cdot D_{eff} \cdot k_E}}{2 \cdot k_E} \\ \\ \text{ELSE } 0.20 \end{cases}$	m
k_A	Pseudo first order degradation rate constant in air	$= \frac{0.693}{halflife_A} \cdot 2^{\frac{T-298}{10}} \cdot F_A$	d ⁻¹

K_AW	Air-water equilibrium distribution constant	$= \frac{H}{8.314 \cdot T}$	-
k_E	Pseudo first order degradation rate constant in soil	$= \frac{0.693}{halflife_E} \cdot 2^{\frac{T-298}{10}} \cdot \frac{F_WE}{K_EW} \cdot \frac{Bact_EW}{Bact_Test}$	d ⁻¹
K_EW	Soil-water equilibrium distribution constant	$= F_AE \cdot K_AW + F_WE + (1 - F_WE - F_AE) \cdot K_P_soil \cdot \frac{rho}{1000000}$	-
k_S	Pseudo first order degradation constant in sediment	$= \frac{0.693}{halflife_S} \cdot 2^{\frac{T-298}{10}} \cdot \frac{F_WS}{K_SW} \cdot \frac{Bact_SW}{Bact_Test}$	d ⁻¹
K_SW	Sediment-water equilibrium distribution constant	$= F_WS + (1 - F_WS) \cdot K_P_sediment \cdot \frac{rho}{1000000}$	-
k_W	Pseudo first order degradation constant in water	$= \frac{0.693}{halflife_W} \cdot 2^{\frac{T-298}{10}} \cdot \frac{Bact_W}{Bact_Test}$	d ⁻¹
KOC	Organic carbon – water partition coefficient of the pollutant	$= \begin{cases} \text{IF } (Log_KOC == -1) \\ \text{THEN } 1.26 \cdot (10^{Log_KOW})^{0.81} \\ \text{ELSE } 10^{Log_KOC} \end{cases}$	-
Log_KOW	Log Octanol-Water partition coefficient of the pollutant	$= Log_KOW$	-
masstransfer_k_SW	Water side mass transfer coefficient	$= k_SW$	m.d ⁻¹
masstransfer_k_VA	Air side mass transfer coefficient, for volatilisation and gas absorbtion	$= 3600 \cdot 24 \cdot 0.01 \cdot \left(0.3 + 0.2 \cdot \frac{U_10}{24 \cdot 3600} \right) \cdot \left(\frac{18}{Molar_Mass} \right)^{0.335}$	m.d ⁻¹
masstransfer_k_VE	Soil side mass transfer coefficient, for volatilisation and gas absorbtion	$= v_eff + \frac{D_eff}{H_E}$	m.d ⁻¹
masstransfer_k_VW	Water side mass transfer coefficient, for volatilisation and gas absorbtion	$= 3600 \cdot 24 \cdot 0.01 \cdot \left(0.0004 + 0.00004 \cdot \left(\frac{U_10}{24 \cdot 3600} \right)^2 \right) \cdot \left(\frac{32}{Molar_Mass} \right)^{0.25}$	m.d ⁻¹
masstransfer_k_WS	Sediment side mass transfer coefficient	$= k_WS$	m.d ⁻¹
rho	Density of the solid phase of the sediment	$= rho$	g.m ⁻³

	compartment		
U_10	Wind velocity at a height of 10m	$= U_{10}$	m.d ⁻¹
U_R	Rain intensity	$= U_R$	m.d ⁻¹
v_settling	Settling velocity of suspended particles	$= v_{settling}$	m.d ⁻¹

Table 9. Intermediate state variables needed in the calculation of the outputs.

Name	Meaning	Equation	Units
Bact_EW	Bacteria concentration in the water phase of the soil compartment	$= \frac{1.4E6}{F_{WE}}$	CFU.ml ⁻¹
Bact_SW	Bacteria concentration in the water phase of the sediment compartment	$= \frac{1.8E9}{F_{WS}}$	CFU.ml ⁻¹
K_P_sediment	Solid-water partition constant in sediment	$= C_{org_sediment} \cdot KOC$	-
K_P_soil	Solid-water partition constant in soil	$= C_{org_soil} \cdot KOC$	-
D_gas	Gas phase diffusion coefficient	$= 2.57E-5 \cdot \sqrt{\frac{18}{Molar_Mass}} \cdot 3600 \cdot 24$	m ² .d ⁻¹
D_water	Water phase diffusion coefficient	$= 2E-9 \cdot \sqrt{\frac{32}{Molar_Mass}} \cdot 3600 \cdot 24$	m ² .d ⁻¹
D_eff	Effective diffusion coefficient in soil	$= \frac{D_{water} \cdot F_{WE}^{1.5} + D_{gas} \cdot F_{AE}^{1.5} \cdot K_{AW}}{K_{EW}}$	-
v_eff	Effective advective transport velocity in soil	$= \frac{U_R \cdot F_{RE}}{F_{WE} + F_{AE} \cdot K_{AW} + (1 - F_{WE} - F_{AE}) \cdot K_{P_soil} \cdot \frac{rho}{1000000}}$	m.d ⁻¹

Table 10. Input parameters which require user specified values and their default values.

Name	Meaning	Default value	Units
<i>A_{AW}</i>	Total surface area of the water-air interface	(*)	m ²
<i>A_{EA}</i>	Total surface area of the soil-air interface	(*)	m ²
<i>A_{SW}</i>	Surface area of the water-sediment interface	(*)	m ²
<i>Advective WaterFlowrate</i>	Advective flow rate of the water compartment.	(*)	m ³ .d ⁻¹
<i>Bact_Test</i>	Bacteria concentration in test vessel where biodegradation half life was determined	4E4	CFU.ml ⁻¹
<i>Bact_W</i>	Bacteria concentration in the surface water compartment	4E4	CFU.ml ⁻¹
<i>C_{org_sediment}</i>	Organic carbon content of the sediment top layer (kg OC / kg solids)	0.05	-
<i>C_{org_soil}</i>	Organic carbon content of the soil (kg OC / kg solids)	0.02	-
<i>F_{AE}</i>	Volume fraction of air in soil	0.20	-
<i>F_{RE}</i>	Fraction of rainwater that infiltrates the soil	0.25	-
<i>F_{WE}</i>	Volume fraction of water in soil	0.20	-
<i>F_{WS}</i>	Volume fraction of the water phase in the sediment compartment	0.80	-
<i>H</i>	Henry's law constant	(**)	Pa.m ³ .mole ⁻¹
<i>halflife_A</i>	Half life constant due to first order reaction with OH radicals in air	(**)	d
<i>halflife_E</i>	Half life constant due to first order biodegradation in soil	(**)	d
<i>halflife_S</i>	Half life constant due to first order biodegradation in sediment	(**)	d
<i>halflife_W</i>	Half life constant due to first order biodegradation in water	(**)	d
<i>k_{SW}</i>	Water side mass transfer coefficient for sediment-water diffusion	(**)	m.d ⁻¹
<i>k_{WS}</i>	Sediment side mass transfer coefficient for sediment-water diffusion	(**)	m.d ⁻¹
<i>Log_KOC</i>	Organic carbon – water partition coefficient (put to -1 for automatic estimation based on <i>Log_KOW</i>)	-1	-
<i>Log_KOW</i>	Log octanol-water partition coefficient	(**)	-
<i>Molar_Mass</i>	Molar mass of the pollutant	(**)	g.mole ⁻¹
<i>Pvap</i>	Vapor pressure	(**)	Pa
<i>rho</i>	Density of solid phase of the soil compartment	2500000	g.m ⁻³
<i>T</i>	Ambient temperature	285	K
<i>T_M</i>	Melting point temperature	(**)	K
<i>U₁₀</i>	Wind velocity at a height of 10m	259200	m.d ⁻¹
<i>U_R</i>	Rain intensity	0.001918	m.d ⁻¹
<i>v_{settling}</i>	Settling velocity of suspended particles in the water	2.5	m.d ⁻¹

*: Case dependent parameters have no default values.

** : The default values for pollutant dependent parameters are included for different pollutants in the models specializing the generic dataserver model.

From the above, it is clear that all values calculated in the dataserver are static (time-independent), although it is easy to include dynamics. For instance, the output *U_R* (rainfall intensity) now equals the static parameter *U_R*, but this can easily be replaced by a dynamic value obtained from an input file containing a rainfall series. The same holds for ambient temperature *T*, which is now equal to the static parameter *T*, but could easily be replaced by a sine function or a measured value from an input file. However, as the aim of the multimedia model within ScorePP is to provide long-term boundary conditions to the integrated urban water system model, such dynamics on a relatively short term time scale are unnecessary and therefore not implemented yet.

4 Model verification by comparison with SimpleBox

4.1 Setup

To verify the implementation of the multimedia model in WEST, the simple model configuration shown in Figure 1 was built and a SimpleBox 3.0 equivalent was set up. For this test, no direct emissions into the environmental compartments were considered. This means that only the pollutant input by advection of water and air, together with the initial amounts of pollutant present in the system, determine which environmental concentrations are reached after a certain simulation time. The final steady state only depends on the advective input via water and air import into the system. This “Level III” test (steady state solution of the dynamic mass balances) forms a basic verification to assure the implementation quality.

The difficulty in the SimpleBox spreadsheet is that the differential equations for all scales (local, regional, continental, moderate global, arctic global, tropical global) are solved together by matrix inversion. This means that even if only the regional scale is needed for this verification, sufficient data must be provided to the model to calculate concentrations and mass flow rates in all compartments (i.e. no divisions by zero (#DIV/0!)) are allowed throughout the whole spreadsheet). To realize these conditions, all unneeded parameter values were put to very small numbers, e.g. 1E-200. As this is not what SimpleBox was meant for, this workaround might have a slight influence on the calculated (steady state) concentrations.

The verification was performed for the PP benzene, with the case-specific or pollutant-dependent parameter values listed in Table 11. All other parameter values were put to their default values mentioned in the tables in the above sections.

4.2 Results

The described setup provides two measurable outputs. First, the steady state concentrations in the different compartments can be compared, as shown in Table 12. Secondly, the process rates of the different intermedia mass transfer processes and degradation processes can be compared in Table 13.

Table 11. Pollutant-specific or case-dependent input parameters used for model verification.

Name	Meaning	Value	Units
<i>A_{AW}</i>	Total surface area of the water-air interface	7.500 E7	m ²
<i>A_{EA}</i>	Total surface area of the soil-air interface	4.925 E9	m ²
<i>A_{SW}</i>	Surface area of the water-sediment interface	7.500 E7	m ²
<i>Advective AirFlow</i>	Advective flow rate of the air compartment.	2.068 E13	m ³ .d ⁻¹
<i>Advective WaterFlowrate</i>	Advective flow rate of the water compartment.	8.64 E6	m ³ .d ⁻¹
<i>C_{susp_in}</i>	Suspended matter 'background concentration' in the inflowing water.	15	g.m ⁻³
<i>H</i>	Henry's law constant	551.04	Pa.m ³ .mole ⁻¹
<i>H_W</i>	Height (depth) of the water compartment	3	m
<i>halflife_A</i>	Half life constant due to first order reaction with OH radicals in air	17	d
<i>halflife_E</i>	Half life constant due to first order biodegradation in soil	16	d
<i>halflife_S</i>	Half life constant due to first order biodegradation in sediment	16	d
<i>halflife_W</i>	Half life constant due to first order biodegradation in water	16	d
<i>In_{Susp}WWTP</i>	Suspended matter (TSS) input massflux into the water compartment above the sediment.	0	g.d ⁻¹
<i>InflowConcentration (air comp.)</i>	Pollutant concentration in inflowing air	5 E-6	g.m ⁻³
<i>InflowConcentration (water comp.)</i>	Pollutant concentration in inflowing water	5 E-4	g.m ⁻³
<i>k_{SW}</i>	Water side mass transfer coefficient for sediment-water diffusion	2.4 E-1	m.d ⁻¹
<i>k_{WS}</i>	Sediment side mass transfer coefficient for sediment-water diffusion	2.4 E-3	m.d ⁻¹
<i>Log KOW</i>	Log octanol-water partition coefficient	2.13	-
<i>Molar Mass</i>	Molar mass of the pollutant	78.1121	g.mole ⁻¹
<i>Pvap</i>	Vapor pressure	6692	Pa
<i>T_M</i>	Melting point temperature	278.65	K
<i>V</i>	Volume of groundwater present in the system (only in the ScorePP model as groundwater is not included in SimpleBox)	2.5 E8	m ³

Table 12. Steady state concentrations in the different compartments as obtained with the ScorePP model in WEST and with the SimpleBox model in Excel, as well as the relative difference between both ($C_{WEST} - C_{SimpleBox}$)/ C_{WEST} .

Compartment	Steady state concentration (g.m ⁻³)		Relative difference (%)
	WEST implementation	SimpleBox 3.0	
Air	4.95 E-06	4.95 E-06	2.09 E-04
Water	9.97 E-05	9.97 E-05	-3.00 E-04
Soil	2.37 E-05	2.37 E-05	6.27 E-03
Sediment	2.74 E-08	2.73 E-08	5.54 E-01
Groundwater	1.05 E-05	-	-

Table 13. Steady state process rates as obtained with the ScorePP model in WEST and with the SimpleBox model in Excel, as well as the relative difference between both $(k_{WEST} - k_{SimpleBox})/k_{WEST}$.

Process	Steady state process rate (g.d ⁻¹)		Relative difference (%)
	WEST implementation	SimpleBox 3.0	
Deposition of PM in water bodies	1.88 E+00	1.88 E+00	-1.00 E-03
Resuspension of sediment particles	1.21 E-04	1.20 E-04	5.51 E-01
Diffusion from water to sediment	1.79 E+01	1.78 E+01	5.90 E-01
Diffusion from sediment to water	1.99 E-03	1.96 E-03	1.14 E+00
Soil and water runoff to water	2.48 E+01	2.48 E+01	1.69 E-02
Diffusion from air to soil (absorption)	1.23 E+04	1.25 E+04	-1.66 E+00
Diffusion from soil to air (volatilization)	6.05 E+03	6.05 E+03	-1.24 E-02
Wet and dry deposition on soil (incl rain dissolution)	2.01 E+02	2.01 E+02	1.02 E-02
Diffusion from air to water (absorption)	8.35 E+02	8.38 E+02	-3.67 E-01
Diffusion from water to air (volatilization)	3.91 E+03	3.91 E+03	-2.99 E-04
Wet and dry deposition on water (incl rain dissolution)	3.07 E+00	3.06 E+00	1.02 E-02
Advective input into air	1.03 E+08	1.03 E+08	0.00 E+00
Advective input into water	4.32 E+03	4.32 E+03	0.00 E+00
Advective output from air	1.02 E+08	1.02 E+08	2.09 E-04
Advective output from water	8.61 E+02	8.61 E+02	-3.00 E-04
Direct emission into air	0.00 E+00	0.00 E+00	0.00 E+00
Direct emission into water	0.00 E+00	0.00 E+00	0.00 E+00
Direct emission into soil	0.00 E+00	0.00 E+00	0.00 E+00
Direct emission into sediment	0.00 E+00	0.00 E+00	0.00 E+00
Removal from air by reaction	1.01 E+06	1.01 E+06	-2.10 E-02
Removal from water by reaction	3.94 E+02	3.94 E+02	-2.15 E-02
Removal from soil by reaction	6.37 E+03	6.37 E+03	-1.43 E-02
Removal from sediment by reaction	1.97 E+01	1.96 E+01	5.33 E-01
Removal from sediment by burial	3.34 E-05	3.32 E-05	5.64 E-01
Leaching from soil to groundwater	2.48 E+01	2.48 E+01	1.69 E-02

From the relative differences in these tables, it can be concluded that both model implementations yield the same results within acceptable margins, despite the differences in equations (25) and (35). The reason for this is that the process rates DiffusionToSediment in the water compartment and DiffusionToWater in the sediment compartment are not very sensitive to the value of the parameter K_{SW} , because the difference in magnitude between k_{SW} and k_{WS} is a factor 100.

4.3 Mass balance

Another check can be performed independently from SimpleBox, i.e. it should be checked whether the total pollutant mass balance is closed. Due to the conservation of mass, the total input to the system should equal the total removal from the system in steady state conditions.

The only inputs to the system are the advective water and air flows. Together these flows import $1.034 \text{ E}+08 \text{ g.d}^{-1}$ into the system (see Table 14).

The total output from the system consists of removal by reaction, burial of sediment, leaching from groundwater and advective output flows of water and air. The sum of these mass fluxes also equals $1.034 \text{ E}+08 \text{ g.d}^{-1}$.

Table 14. Steady state process rates calculated in WEST and the resulting overall mass balance.

Input		Output	
Process	Rate (g.d^{-1})	Process	Rate (g.d^{-1})
Advective input into air	1.034 E+08	Advective output from air	1.024 E+08
Advective input into water	4.320 E+03	Advective output from water	8.610 E+02
		Removal from air by reaction	1.009 E+06
		Removal from water by reaction	3.944 E+02
		Removal from soil by reaction	6.368 E+03
		Removal from sediment by reaction	1.974 E+01
		Removal from sediment by burial	3.342 E-05
		Leaching from groundwater	2.480 E+01
Total:	1.034 E+08	Total:	1.034 E+08

5 Verification by comparison with another multimedia fate model

In the previous chapter the main focus was on showing that the multimedia model implemented in WEST yields the same results as the SimpleBox models, on which the WEST equations were based.

In this chapter, however, the ScorePP multimedia model results are compared with the results obtained with a fugacity-based multimedia model.

5.1 Benzene partitioning in a simple evaluative environment

The approach suggested by Mackay (2001) and discussed briefly in section 2.1 was implemented in a stand-alone software tool by the Canadian Environmental Modelling Centre (CEMC), Trent University, and can be obtained from their website (<http://www.trentu.ca/academic/aminss/envmodel/models/VBL3.html>). The level III fugacity model was run with the same parameter values as the ScorePP model (listed in Table 11 or as default values in chapter 3) and yields environmental steady state concentrations in the same order of magnitude for all environmental compartments except for the sediment (see Table 15).

Table 15. Steady state Benzene concentrations in the different compartments as obtained with the ScorePP model in WEST and with the Mackay model implemented by CEMC, as well as the relative difference between both $(C_{WEST} - C_{Mackay})/C_{WEST}$.

Compartment	Steady state concentration (g.m ⁻³)		Relative difference (%)
	ScorePP	Mackay	
Air	4.95 E-06	4.95 E-06	0.00 E+00
Water	9.97 E-05	9.08 E-05	8.93 E+00
Soil	2.37 E-05	3.64 E-05	-5.36 E+01
Sediment	2.74 E-08	7.60 E-05	-2.77 E+05
Groundwater	1.05 E-05	-	-

The reason for the discrepancy in sediment concentration was found to be caused by two conceptual differences, the second being more important than the first:

- The affection of the pollutant for sediment particles is estimated by a different function of the octanol-water partitioning coefficient: $K_{OC} = 1.26 \cdot K_{OW}^{0.81}$ in the ScorePP model, compared to $K_{OC} = 0.41 \cdot K_{OW}$ in the Mackay model.
- The reaction rate parameter for pollutant removal by microbial breakdown in the sediment k_S is estimated as $\ln(2)/t_{1/2}$ in the Mackay model, while a correction factor for the actual temperature and sediment bacteria concentration is applied in the ScorePP model, as was suggested in SimpleBox (see equation in Table 8).

Concerning the $K_{OC} - K_{OW}$ relation, it must be emphasized that both correlation equations provide rough estimates. In SimpleBox 3.0 the regression coefficients a and b of the relation $\log K_{OC} = a \cdot \log K_{OW} + b$ are fixed to resp. 0.81 and 0.1 ($= \log(1.26)$), but in fact these coefficients should be different according to the type of chemical, as can be seen in Table 16, taken from Schwarzenbach *et al.* (2003). In WEST, the multimedia model user is therefore allowed to specify a more precise $\log K_{OC}$ value that will overrule the $\log K_{OW}$ based estimation (see equation for KOC in Table 8).

Figure 6 is a graphical representation of the simulation results obtained with the Mackay level III software tool by CEMC, not only showing the steady state environmental concentrations but also the inter-media mass fluxes in kg.h⁻¹.

Table 16. Slopes and intercepts of the linear correlation $\log K_{OC} = a \cdot \log K_{OW} + b$. After Schwarzenbach *et al.* (2003), Table 9.2.

Compound class	a	b
Alkylated and chlorinated benzenes, PCBs (\pm apolar)	0.74	0.15
PAHs (monopolar)	0.98	-0.32
Chlorinated phenols (neutral species, bipolar)	0.89	-0.15
C1- and C2-halocarbons (apolar, monopolar and bipolar)	0.57	0.66
Only chloroalkanes (mix)	0.42	0.93
Only chloroalkenes (\pm apolar)	0.96	-0.23
Only compounds including bromine (mix)	0.50	0.81
All phenylureas (bipolar)	0.49	1.05
Only alkylated and halogenated phenylureas, phenyl-methylureas and phenyl-dimethylurea (bipolar)	0.59	0.78
Only alkylated and halogenated phenylureas (bipolar)	0.62	0.84

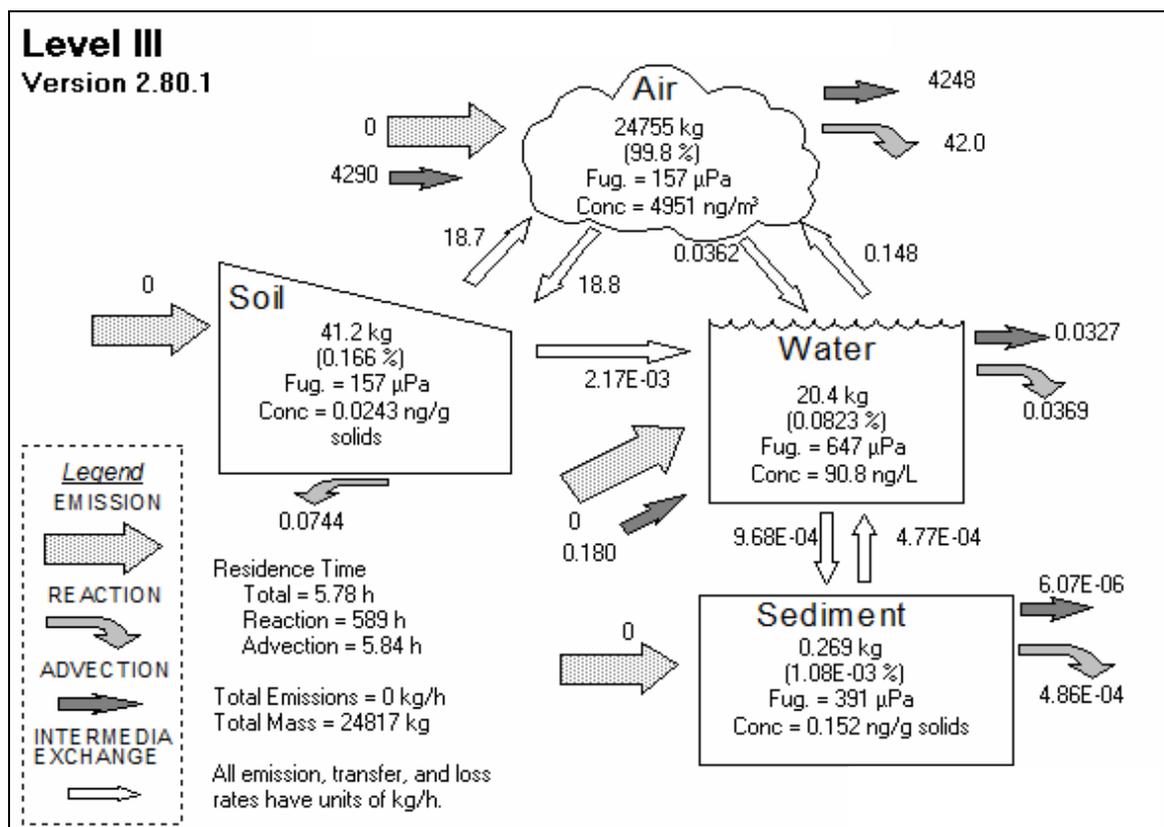


Figure 6. Steady state partitioning of Benzene, as obtained with the Mackay Level III software tool by CEMC, with the same parameter values as were used in chapter 4.

5.2 Hexachlorobiphenyl partitioning in a “real” environment

Mackay and Paterson (1991) described the use of their fugacity-based multimedia model to evaluate the fate of six chemicals in the region of Southern Ontario, Canada. The same system was modeled with the ScorePP multimedia model in WEST, using the system’s properties as described in the paper, for the PCB group of hexachlorobiphenyls. The system’s key properties are listed in Table 17. The steady state simulation results are compared with the values reported by Mackay and Paterson (1991) in Figure 7.

The chemical’s partitioning between the four compartments is similar in orders of magnitude, although some mass fluxes differ, e.g. diffusion between air and soil. The main reason for this was found to be the concept of availability to diffusion. In SimpleBox (and thus also in the ScorePP model) the diffusion mass flux from a compartment is calculated as a function of the compartment’s concentration and the fraction of the pollutant available for diffusion (e.g. the fraction which is not attached to aerosols in the air, see equations (5) and (6)), while the Mackay model doesn’t take this available fraction into account.

However, this verification exercise shows that similar partitioning results are obtained with both approaches, given the uncertainty inherent to all multimedia models – usually only orders of magnitude are considered, as the conceptual errors (e.g. by assuming intra-medium equilibrium distribution of the chemical between the different phases of the medium) are hardly quantifiable.

Table 17. Key properties of the modeled system, representing the region of Southern Ontario, Canada, and the chemical hexachlorobiphenyl (if different from the default values mentioned earlier in this Deliverable).

Name	Meaning	Value	Units
<i>A AW</i>	Total surface area of the water-air interface	8.00 E10	m ²
<i>A EA</i>	Total surface area of the soil-air interface	1.20 E11	m ²
<i>A SW</i>	Surface area of the water-sediment interface	8.00 E10	m ²
<i>Advective AirFlow</i>	Advective flow rate of the air compartment	7.92 E13	m ³ .d ⁻¹
<i>Advective WaterFlowrate</i>	Advective flow rate of the water compartment	7.92 E9	m ³ .d ⁻¹
<i>C_org_sediment</i>	Organic carbon content of the sediment top layer (kg OC / kg solids)	0.04	-
<i>C_org_susp</i>	Organic carbon content of the suspended particles (kg OC / kg solids)	0.2	-
<i>C_susp</i>	Suspended matter concentration in the water	12	g.m ⁻³
<i>C_susp_in</i>	Suspended matter 'background concentration' in the inflowing water.	0	g.m ⁻³
<i>F RE</i>	Volume fraction of rain that infiltrates the soil	0.40	-
<i>F WE</i>	Volume fraction of water in the soil	0.30	-
<i>F WS</i>	Volume fraction of water in the sediment	0.70	-
<i>Gross Sedimentation Rate</i>	Gross sedimentation rate	3.653 E-6	m.d ⁻¹
<i>H</i>	Henry's law constant	50	Pa.m ³ .mole ⁻¹
<i>H A</i>	Height of the air compartment	2000	m
<i>H E</i>	Height (depth) of the soil compartment	0.10	m
<i>H S</i>	Height (depth) of the sediment compartment	0.01	m
<i>H W</i>	Height (depth) of the water compartment	50	m
<i>halflife_A</i>	Half life constant due to first order reaction with OH radicals in air	1E18 (*)	d
<i>halflife_E</i>	Half life constant due to first order biodegradation in soil	6.94 (*)	d
<i>halflife_S</i>	Half life constant due to first order biodegradation in sediment	7411 (*)	d
<i>halflife_W</i>	Half life constant due to first order biodegradation in water	1925 (*)	d
<i>In_Susp_WWTP</i>	Suspended matter (TSS) input mass flux into the water compartment above the sediment.	0	g.d ⁻¹
<i>InflowConcentration (air comp.)</i>	Pollutant concentration in inflowing air	1.05 E-9	g.m ⁻³
<i>InflowConcentration (water comp.)</i>	Pollutant concentration in inflowing water	1.05 E-6	g.m ⁻³
<i>k_SW</i>	Water side mass transfer coefficient for sediment-water diffusion	2.4 E-1	m.d ⁻¹
<i>k_WS</i>	Sediment side mass transfer coefficient for sediment-water diffusion	8 E-4	m.d ⁻¹
<i>Log KOW</i>	Log octanol-water partition coefficient	6.80	-
<i>masstransfer_k_VA</i>	Air side mass transfer coefficient, for volatilisation and gas absorption	72	m.d ⁻¹
<i>masstransfer_k_VW</i>	Water side mass transfer coefficient, for volatilisation and gas absorption	0.72	m.d ⁻¹
<i>Molar Mass</i>	Molar mass of the pollutant	350	g.mole ⁻¹
<i>Net_Sedimentation_Rate</i>	Net sedimentation rate. (gross sedimentation minus resuspension)	2.74 E-6	m.d ⁻¹
<i>Prod_Susp</i>	Production rate of suspended matter in the water compartment above the sediment	0	g.m ⁻² .d ⁻¹
<i>Pvap</i>	Vapor pressure	5.00 E-4	Pa

ρ	Density of the solids	2400000	g.m^{-3}
U_{EW}	Solids runoff rate from soil	1.096 E-6	m.d^{-1}
U_Q	Dry deposition velocity	259.2	m.d^{-1}
U_R	Rain intensity	0.0023288	m.d^{-1}
v_{settling}	Settling velocity of suspended particles in the water	0.219178	m.d^{-1}

*: the half-lives were calculated to fit the degradation rate constants k_A , k_E , k_S and k_W to the ones mentioned in Mackay and Paterson (1991).

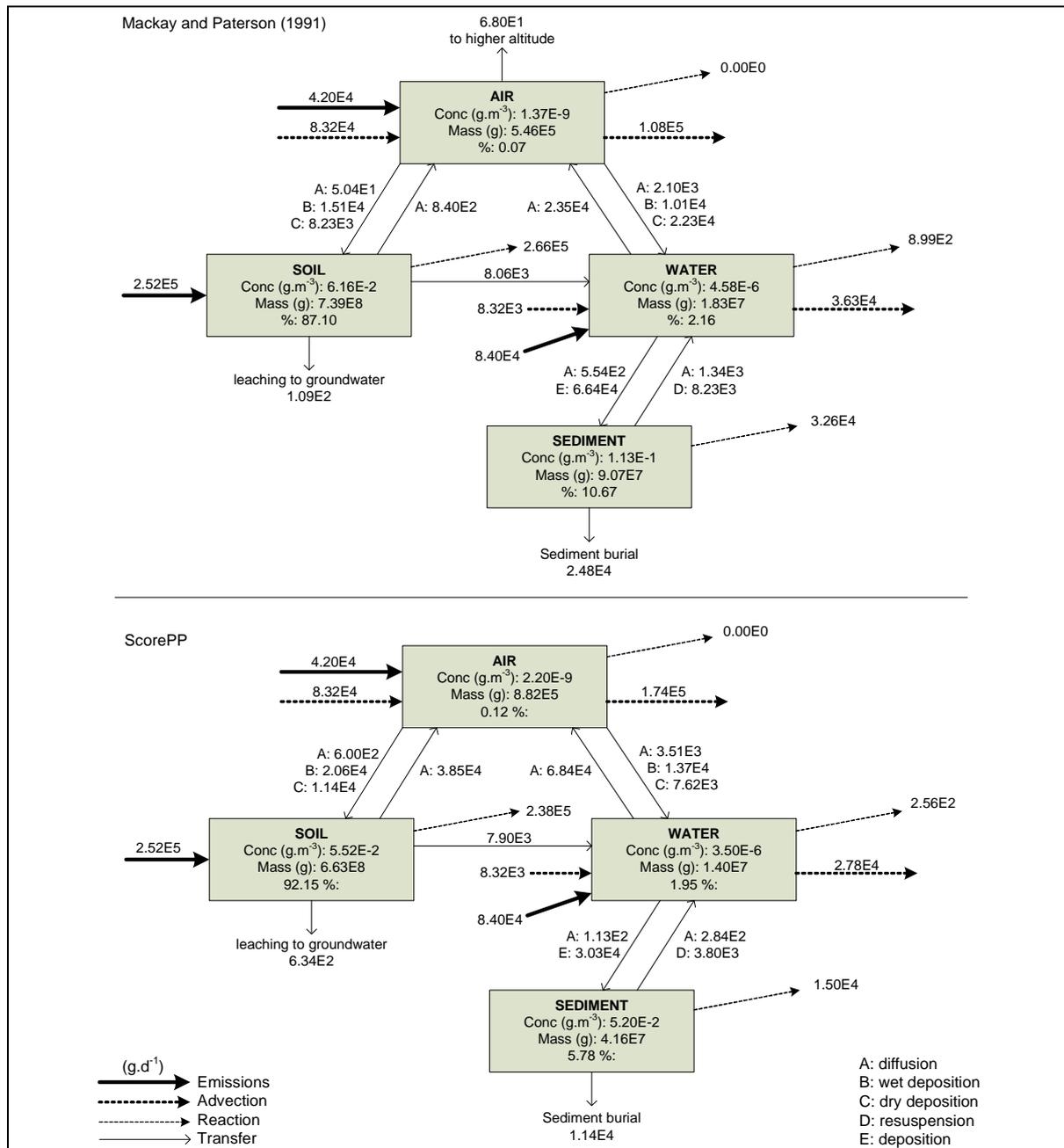


Figure 7. Steady state simulation results obtained with the fugacity-based model (upper figure, adapted from Mackay and Paterson (1991)) and with the ScorePP multimedia model (lower figure).

6 Conclusions

To provide boundary conditions for the integrated urban scale PP exposure model, under development in Task 7.4, a multimedia model at river basin scale had to be developed. At the same time this multimedia environmental fate model allows predicting and evaluating the PP concentrations in other environmental compartments and on other spatial scales beyond the focus of the dynamic urban scale integrated model, allowing a more global risk assessment.

The multimedia modeling framework based on a chemical's fugacity and often referred to as the Mackay models, was analyzed and compared with the SimpleBox models, which are a less abstract adaptation of the Mackay-type models implemented in MS Excel. The SimpleBox models contain equations for the estimation of parameter values on the basis of well-known properties, which makes the use of the model more appropriate compared to the more theoretical framework used in the Mackay-type models. It was decided to implement a multimedia model analogous to the SimpleBox models in WEST in order to provide full compatibility with the integrated urban scale model of Task 7.4.

The multimedia box model implementation in WEST features full flexibility:

- processes can easily be added or removed from each compartment's mass balance in the MSL editor;
- compartments can be inserted and connected as desired in the configuration editor;
- default values for many parameters are calculated in a datasever, but the estimated values can be overruled by user input values.

Steady state partitioning (comparable to Mackay level III) as well as dynamic simulations (level IV) can be run with the multimedia model, either as a stand alone model or in connection with a dynamic integrated model.

The model implementation was verified by comparing steady state simulation results obtained with a basic multimedia setup built in WEST and comparable to the regional scale of the SimpleBox model. The same steady state environmental concentrations and process rates were obtained.

In an additional verification the multimedia model's environmental fate predictions were compared with results obtained with a "Mackay-type" fugacity based multimedia model for two test cases: benzene, with the air as a main sink, and hexachlorobiphenyl, with the soil as main sink compartment. The chemical's partitioning between the included environmental compartments has the same order of magnitude. However, several mass fluxes differed significantly due to differences in some of the implemented equations.

As a major conclusion, it can be stated that a fully flexible, comprehensible and easy to use dynamic multimedia model was successfully implemented in WEST.

References

- Brandes, L.J., den Hollander, H. and Van de Meent, D. (1996). SimpleBox 2.0: a nested multimedia fate model for evaluating the environmental fate of chemicals. Report 719101 029. National Institute for Human Health and the Environment (RIVM), Bilthoven, the Netherlands. 156p. Available from www.rivm.nl.
- Cahill, T. M. and Mackay, D. (2003). A high-resolution model for estimating the environmental fate of multi-species chemicals: application to malathion and pentachlorophenol. *Chemosphere* 53(5), 571-581.
- Cousins, I.T. and Mackay, D. (2001). Strategies for including vegetation compartments in multimedia models. *Chemosphere* 44(4), 643-654.
- den Hollander, H.A., van de Meent, D. and van Eijkeren, J.C.H. (2003). SimpleBox 3.0. Spreadsheet. National Institute for Human Health and the Environment (RIVM), Bilthoven, the Netherlands.
- Devillers, J. and Bintein, S. (1995). CHEMFRANCE: a regional level III fugacity model applied to France. *Chemosphere*, 30(3), 457-476.
- Diamond, M.L., Priemer, D.A. and Law, N.L. (2001). Developing a multimedia model of chemical dynamics in an urban area. *Chemosphere* 44(7), 1655-1667.
- Fenner, K., Scheringer, M. and Hungerbühler, K. (2000). Persistence of parent compounds and transformation products in a level IV multimedia model. *Environmental Science and Technology* 34(17), 3809-3817.
- Jury, W.A., Spencer, W.F. and Farmer, W.J. (1983). Behavior assessment model for trace organics in soil: I. Model description. *Journal of Environmental Quality*, 12(4), 558-564.
- Kirkby, M.J., Jones, R.J.A., Irvine, B., Gobin, A, Govers, G., Cerdan, O., Van Rompaey, A.J.J., Le Bissonnais, Y., Daroussin, J., King, D., Montanarella, L., Grimm, M., Vieillefont, V., Puigdefabregas, J., Boer, M., Kosmas, C., Yassoglou, N., Tsara, M., Mantel, S., Van Lynden, G.J. and Huting, J. (2004). Pan-European Soil Erosion Risk Assessment: The PESERA Map, Version 1 October 2003. Explanation of Special Publication Ispra 2004 No.73 (S.P.I.04.73).
- Mackay, D. (2001). Multimedia environmental models: the fugacity approach, second edition. Lewis Publishers, Florida, US. 261p.
- Mackay, D. and Paterson, S. (1981). Calculating fugacity. *Environmental Science and Technology* 15(9), 1006-1014.
- Mackay, D. and Paterson, S. (1991). Evaluating the multimedia fate of organic chemicals: a level III fugacity model. *Environmental Science and Technology* 25(3), 427-436.
- Mackay, D., Paterson, S. and Joy, M. (1983). Application of fugacity models to the estimation of chemical-distribution and persistence in the environment. ACS Symposium Series 225, 175-196.
- Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M. (2003). Environmental organic chemistry. Second Edition. Wiley-Interscience, New York, US. 1313p.
- Severinsen, M. and Jager, T. (1998). Modelling the influence of terrestrial vegetation on the environmental fate of xenobiotics. *Chemosphere* 37(1), 41-62.
- Suzuki, N., Murasawa, K., Sakurai, T., Nansai, K., Matsuhashi, K., Moriguchi, Y., Tanabe, K., Nakasugi O. and Morita, M. (2004). Geo-referenced multimedia environmental fate model

(G-CIEMS): model formulation and comparison to the generic model and monitoring approaches. *Environmental Science and Technology* 38(21), 5682-5693.

Toose, L., Woodfine, D.G., MacLeod, M., Mackay, D. and Gouin, J. (2004). BETR-World: a geographically explicit model of chemical fate: application to transport of alpha-HCH to the Arctic. *Environmental Pollution* 128(1-2), 223-240.

Vanhooren, H., Meirlaen, J., Amerlinck, Y., Claeys, F., Vangheluwe, H. and Vanrolleghem, P.A. (2003). WEST: Modelling biological wastewater treatment. *Journal of Hydroinformatics*, 5(1), 27-50.

Woodfine, D.G., MacLeod, M., Mackay, D. and Brimacombe, J.R. (2001). Development of continental scale multimedia contaminant fate models: integrating GIS. *Environmental Science and Pollution Research* 8(3), 164-172.