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Preventing Recalcitrant Organic Mobile Industrial chemicalS for Circular Economy in the soil-sediment-water System

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D2.6 - An improved SimpleBox model for improved environmental risk assessment and life cycle impact assessments

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Authorisation

Authorisation	Name	Status	Date
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Validation	Martine Bakker	WP leader	April 9, 2024 (version 1) September 13, 2024 (version 2)
Approval	Julie Lions	Project Coordinator	April 21, 2024 (version 1) September 13, 2024 (version 2)

Executive Summary

Persistent, Mobile and Toxic (PMT) substances are of concern for organisms living in surface water bodies because of their indication of high (eco)toxicity in combination with high environmental persistence, due to poor removal from the water phase. Assessment of environmental persistence requires the use of multimedia chemical fate models such as SimpleBox, because these models are able to integrate the impact of substance properties, emission patterns and the dynamics of the environmental system over time. In the current deliverable report the environmental persistence is specified further into aquatic persistence, being the extent to which substances persist in surface water bodies.

Just as for environmental persistence, the assessment of aquatic persistence needs the use of multimedia fate models to integrate the impact of the three factors mentioned above. To this end, the Aquatic Persistence Dashboard has been developed as an improvement of the SimpleBox model. At the end of the PROMISCES project the Simple Box version with the Dashboard will become publicly available at https://github.com/rivm-syso/SimpleBox. The Aquatic Persistence Dashboard enables the user to evaluate the time that a substance remains in the water phase and hence its tendency to flow downstream and eventually reach the ocean. SimpleBox simulates the degradation and transport as dynamic environmental fate processes occurring at regional, continental and global scale systems. By deriving aquatic persistence in this manner, these dynamic processes are integrated. The Aquatic Persistence Dashboard enables the user (exposure/risk assessor or policy maker) to screen the combined PMT properties of a substance as it directly indicates the timescale over which a chemical is anticipated to maintain in surface water bodies.

The sensitivity analyses performed with the Aquatic Persistence Dashboard show that vapor pressure and air-water partitioning behavior of a substance can be of great impact on the aquatic persistence. However, these substance properties are currently not included as PM criterium. As such, it is possible that a volatile substance is defined as a PM substance as it fits the criteria, whereas in reality the substance resides in the atmosphere. The results of the sensitivity analyses thus shows the need to discuss whether vapor pressure or air-water partitioning coefficient should be considered a PM criterium as well.

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List of Abbreviations

$\Sigma e_{environment}$	The sum of all emissions into the environment
$\Sigma m_{environment}$	The sum of all chemical mass present in the environment
Σm_{water}	The sum of all chemical mass present in water bodies
A	Fate matrix
ChemRowNr	Chemical Row Number
CS	Case study
e	Emission vector
ECHA	European Chemical Agency
EUSES	European Union System for the Evaluation of Substances
f_{oc}	Organic carbon content
FR_{orig}	Fraction of original species
K_{aw}	Air-water partitioning coefficient
$K_{aw\ arctic}$	Air-water partitioning coefficient in the arctic system
$K_{aw\ regional}$	Air-water partitioning coefficient in the regional scale system
$K_{aw\ tropic}$	Air-water partitioning coefficient in the tropic scale system
$k_{deg\ air}$	Degradation rate constant in air
$k_{deg\ sed}$	Degradation rate constant in sediments
$k_{deg\ soil}$	Degradation rate constant in soil
$k_{deg\ water}$	Degradation rate constant in water
K_{oc}	Organic carbon-water partitioning coefficient
K_{ow}	Octanol-water partitioning coefficient
m	Environmental load
M	Mobility
OECD	Organisation for Economic Co-operation and Developmen
P	Persistence
P_{aq}	Aquatic Persistence
pHw	Acidity of the water medium
pKa	Dissociation constant
P_{ov}	Overall environmental persistence
PM	Persistent and Mobile
PMT	Persistent Mobile and Toxic
PROMISCES	Preventing Recalcitrant Organic Mobile Industrial chemicalS for Circular Economy in the soil-sediment-water System
PSA	Probabilistic Sensitivity Analysis
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SB	SimpleBox
SB-AP Dashboard	SimpleBox Aquatic Persistence Dashboard
vPvM	Very Persistent and very Mobile
WP	Work Package

1 Introduction

1.1 Introduction to this deliverable

Substances that are well soluble, but hardly volatile, barely degradable and have a small tendency to sorb to organic carbon may stay in the aquatic environment as persistent and mobile (PM) substances. Consequently, aquatic organisms can be exposed to PM substances for a long time, which can lead to undesirable effects once ecotoxicological threshold concentrations are exceeded.

In the context of the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) the persistence (P) and mobility (M) of a substance are currently evaluated using separate indexes based on the (bio)degradation half-life and the organic carbon-water partitioning coefficient (EC, 2022). Although the separate indexes are of great significance, the *combined* effect of P and M, determining the time that a substance remains bioavailable in water bodies, is a factor of importance as well. In the PROMISCES project, we have introduced the term aquatic persistence for this substance property. In the current evaluation system procedure of PMT substances under REACH, aquatic persistence is not explicitly assessed. This is an omission, since aquatic persistence is crucial for the exposure and risk of substances to aquatic organisms.

In this deliverable we studied aquatic persistence of substances and implemented an equation for this property in the existing multimedia fate model SimpleBox (SB) (rivm.nl/simplebox, 2024).

The SimpleBox model is prescribed for chemical safety assessment within REACH (ECHA, 2012) and EUSES. In the current task, the model has been improved by extending it with the SimpleBox Aquatic Persistence Dashboard (SB-AP Dashboard). This dashboard simulates the time a substance resides in a water body based on its substance properties (solubility, vapor pressure, octanol-water partitioning coefficient), (bio)degradation rate, emission patterns and characteristics of the water bodies such as depth, volume, suspended matter concentration and water flow rates. The SB-AP Dashboard enables its users, e.g. exposure/risk assessors or policy makers, to evaluate the combined impact of a substance's P and M as well as the environmental fate processes that influence the time a substance remains bioavailable in water bodies (e.g. volatilization and advective transport via flowing water).

The development of the SB-AP Dashboard proceeded parallel to a series of case studies in the PROMISCES project, in which the fate and transport of PMT substances is evaluated in different local environments. Examples are the interaction between groundwater and soil, river bank filtration, urban settings, and upstream catchments by using models such as Hydrus (Simunek et al., 2012) and Modflow (USGS, 2024). These fate and transport models include routines to simulate the evaporation of substances. However, the extent to which a substance is prone to volatilization is currently not included as a PMT criterion. Therefore, we developed the SB-AP Dashboard which evaluates the potential for volatilization. This is performed by expressing the aquatic persistence by including vapor pressure and solubility as input parameter and plotting air-water partitioning behavior against aquatic persistence. The aim of this exercise is to study the potential impact of volatilization as a fate process removing PMTs from water bodies.

1.2 Behaviour of PMT substances

PM substances with low ecotoxicological thresholds are considered Persistent Mobile and Toxic (PMT). The higher ecotoxicological threshold concentrations of less toxic substances may be

exceeded nonetheless for very Persistent and very Mobile (vPvM) substances, because higher exposure concentrations can be reached over time. In that case, the fate processes that remove these substance from water, e.g. biodegradation, carbon sorption and evaporation, are slow.

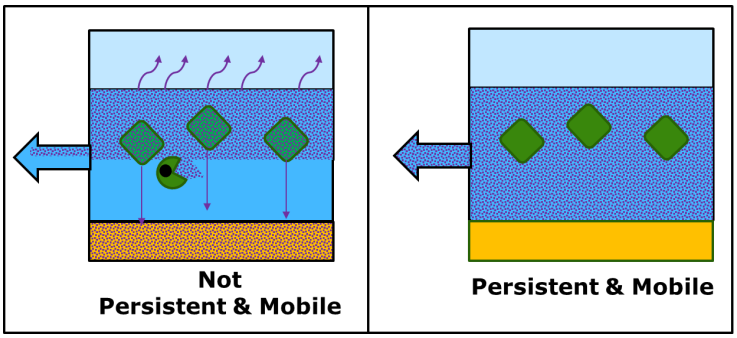


Figure 1. Difference between PM and not-PM substance in aquatic fate and concentrations

The potential of a chemical for leading to an exposure burden that will continue into the future time or be displaced to remote regions can be screened and assessed with the so called overall environmental persistence (Webster et al., 1998; OECD, 2004). Overall environmental persistence (P_{ov} in *s*) of chemical emissions is estimated as the sum of all chemical mass present in the environment ($\Sigma m_{environment}$ in *g*) divided by the sum of all emissions into the environment ($\Sigma e_{environment}$ in $g.s^{-1}$).

$$P_{ov} = \frac{\sum m_{environment}}{\sum e_{environment}} \quad (1)$$

The considered (v)P(v)M substances mainly reside in aqueous media, whereas overall persistence also covers other environmental compartments such as the atmosphere and soil. Aquatic persistence (P_{aq}) is therefore introduced in WP 2.4 as a component of the overall persistence in order to be able to focus on the potential exposure burden of aquatic organisms to (v)P(v)M substances that persist and displace in water bodies. Aquatic persistence (P_{aq} in *s*) is expressed as the sum of all chemical mass present in water bodies (Σm_{water} in *g*) divided by the sum of the emissions to water (Σe_{water} in $g.s^{-1}$).

$$P_{aq} = \frac{\sum m_{water}}{\sum e_{water}} \quad (2)$$

Overall environmental persistence is not acknowledged as an intrinsic substance property, but as a combination of joint properties of chemical pollutants, their emission patterns, and the characteristics of the environment (OECD, 2004). Consequentially, overall persistence cannot be assessed directly from information about the chemical and/or from emission data only. Therefore, multimedia chemical fate models are used for such assessment (OECD, 2004). This also applies for the aquatic persistence of (v)P(v)M substance emissions, because their tendency to persist and displace in aquatic environments is difficult to characterize. It depends on a variety of substance properties such as vapour pressure, solubility, octanol-water partition coefficient, and degradation half-life as well as at what type of water body the emission takes place, e.g. slowly streaming lake waters or rapidly running river water. Therefore, a new tool to express and evaluate aquatic

persistence of substances emitted to water has been developed within Task 2.4.1 as an additional module to the existing multimedia chemical fate model SimpleBox.

1.3 SimpleBox

SimpleBox (SB) is a model for the prediction of environmental concentrations of chemical substances. It is a multimedia mass balance model that simulates environmental fate of chemicals as fluxes (mass flows) between a series of well-mixed boxes of air, water, sediment and soil on regional, continental and global spatial scales. SimpleBox does so by simultaneously solving mass balance equations for each environmental compartment box in the model (Schoorl et al., 2015).

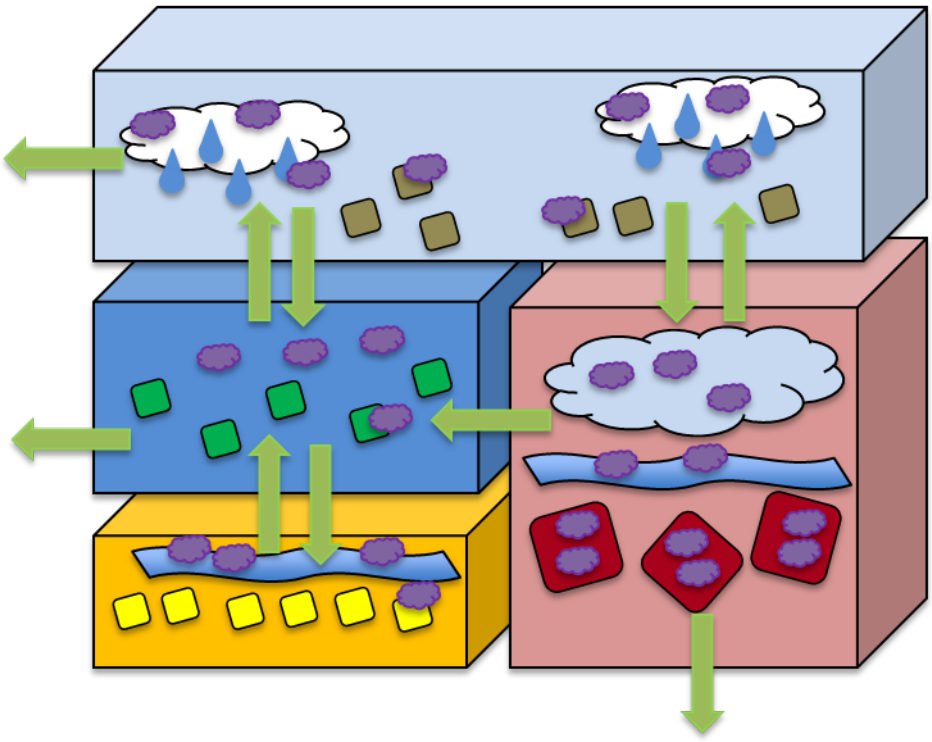


Figure 2. Visualization of the SimpleBox model

The mass balance equations delivers the environmental load per compartment (*m* in *mo*l) and are performed by multiplying a vector of emission (*e* in *mol.s*$^{-1}$) with the inverse of matrix *A* that holds rate constants (in s^{-1}) for the environmental fate processes within and between the compartments, such as (bio)degradation, advective and diffusive transport.

$$m = e \times -A^{-1} \quad (3)$$

The SB model has served as 'regional distribution module' in the European Union System for the Evaluation of Substances (EUSES). Currently, SB is used for environmental exposure estimation as part of the chemical safety assessment for registration of chemical substances under REACH (ECHA, 2015). SB was designed originally as a research tool and has proven most useful in dedicated environmental fate studies, focused at understanding and predicting environmental fate from fundamental physical and chemical substance properties (www.rivm.nl/simplebox , 2024). The latest version of the SB model includes model routines for predicting environmental concentrations of neutral organic substances, acids, bases, ionizable substances and nano- and micromaterials (Schoorl et al., 2015).

The assessment of the aquatic persistence of (v)P(v)M substances in Task 2.4.1 is also a dedicated environmental fate study for which is SB is used. The SimpleBox – Aquatic Persistence Dashboard (SB-AP Dashboard) has been developed as a new tool to study the extent to which PMT substances persist in water bodies as a function of their chemical substance properties and emission distribution over different water bodies. The current document is a demonstration manual that describes how to use the SB-AP Dashboard for:

- Expressing the aquatic persistence of emitted substances as a single value from deterministic input values for chemical properties and emissions
- Expressing a probabilistic range for the aquatic persistence of emitted substances from ranges of input values for chemical properties and emissions
- Performing probabilistic sensitivity analyses (PSAs) to investigate the influence of one or more input parameters on the aquatic persistence of emitted substances.

SB is operated as a Microsoft Excel spreadsheet, supported by numerical computations in R, which are linked to the spreadsheet via RExcel (www.rivm.nl/simplebox, 2024). The SB-AP Dashboard is added to the SimpleBox version 4.01 as new worksheets that link with SB's emission and landscape scenarios, substance data, the simulation of environmental fate processes and the derived chemical mass in the water compartments.

The demonstration manual (Chapter 2) describes some general settings of the SB model, because the SB-AP Dashboard is used within SimpleBox version 4.01. At the end of the project the model will be made publicly available in the GitHub platform of SimpleBox (https://github.com/rivm-syso/SimpleBox/).

2 SB-AP Dashboard demonstration manual

2.1 Opening version sheet

At first use the SB-AP Dashboard opens with the 'version' tab that describes the documentation of the Microsoft Excel spreadsheet that contains the engine and model routines of SimpleBox version 4.01. The development of the SB-AP Dashboard does not include modifications to the engine or model routines. Rather SB-AP Dashboard is an additional module with a newly developed dashboard screen, simulation data and graph tab (Figure 3).

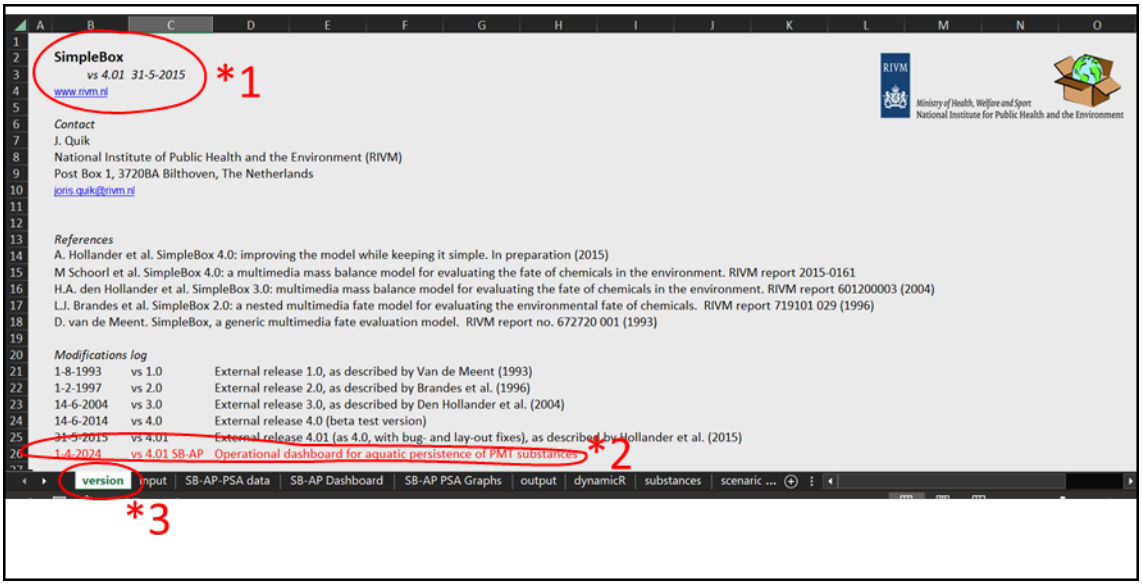


Figure 3. Screenshot of the opening sheet of SimpleBox version that included SB-AP Dashboard with 1: Description of the SimpleBox version, 2: added SB-AP added to the modifications log, 3: opening 'version' tab of the SB-AP Dashboard spreadsheet.

2.2 Setting up the SB-AP Dashboard scenario and substance data in SimpleBox

The SB landscape and emission settings for the SB-AP Dashboard are implemented in SB as a new and separate scenario. The *'SB-AP Dashboard'* scenario can be selected in the general 'input tab' of the SB model in input cell *I8*.

The SB-AP dashboard is made fit for substances dissolving in water as an acid, base or as a neutral substance, but the substance data that SB uses to calculate the chemical load in the aquatic compartments needs to be consistent with the input data inserted in the SB-AP Dashboard (Figure 4).

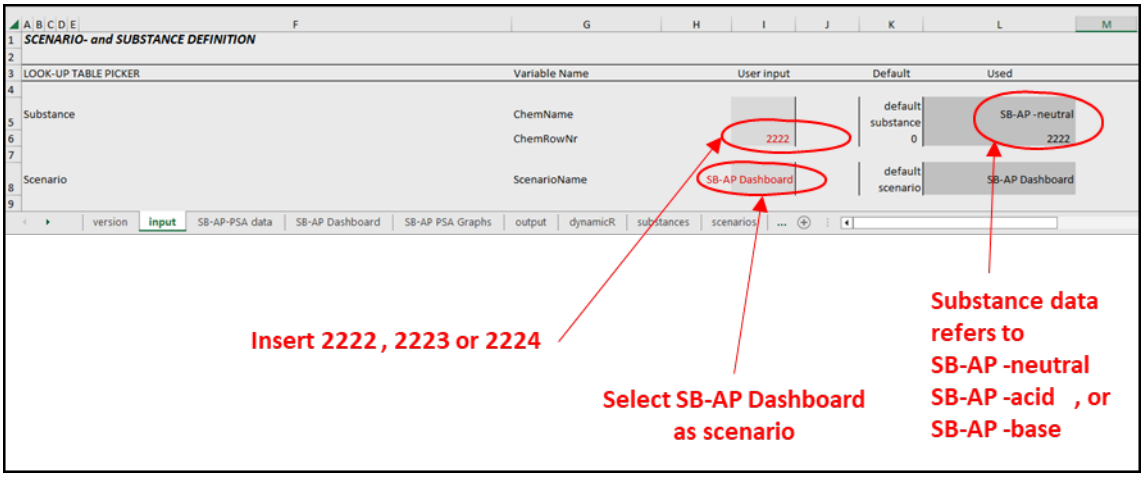


Figure 4. Rows 1 to 9 of SB's Input tab.

The chemical class of a substance as neutral, base or acid can be selected within the SB-AP Dashboard by choosing the accurate *'ChemRowNr'* in cell *I7* under the '*input tab'*. This number needs to be *'2222', '2223'*, or *'2224'* as these row numbers correspond to the chemical substance database records that link with SB-AP Dashboard for PMT substances that are neutral, acid or base respectively (Figure 4).

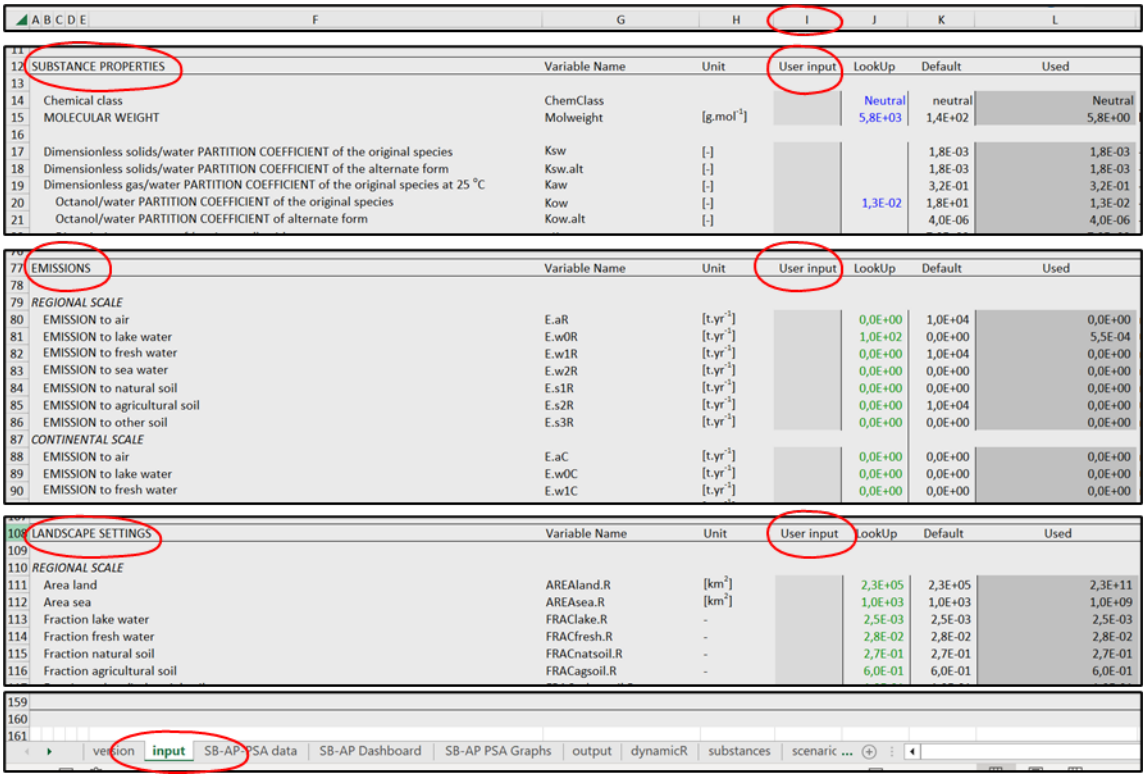
SB employs the dissociation constant for acids and bases (*pKa*)to estimate the fraction of the substance that is dissolved as original species, i.e. without dissociation of H+ or OH- ions. This *pKa* is used to determine the fraction of original species in waters, sediments and soils and to calculate the apparent octanol-water partitioning coefficient. For substances that may occur to a significant extent in their alternate (i.e. non-neutral) forms, it is essential that a *pKa* value is available. By default, a 50-50 split between original and alternate forms at neutral pH is assumed using a pKa value of 7 (Schoorl et al., 2015). The fraction original species (FR_{orig}) in aerosol water, in fresh water, in sea water, in sediments, in soils and in soil pore water are calculated in SB as a function of the *pKa* and pH of the medium (*pHw*) for acids as:

$$FR_{orig.acid} = 1/(1 + 10^{pHw-pKa}) \quad (4)$$

And for bases as

$$FR_{orig.base} = 1/(1 + 10^{pKa-pHw}) \quad (5)$$

The *'user input cells'* in the *'input'* tab to characterise emissions (*cells I79:I106*), landscape settings (*cells I111:I158*)) and substance properties (*I14:I39 and I66:I75*) should be left blank (Figure 5). Inserting a SB user input value in these cells will overwrite the SB-AP dashboard compromising its outcomes.



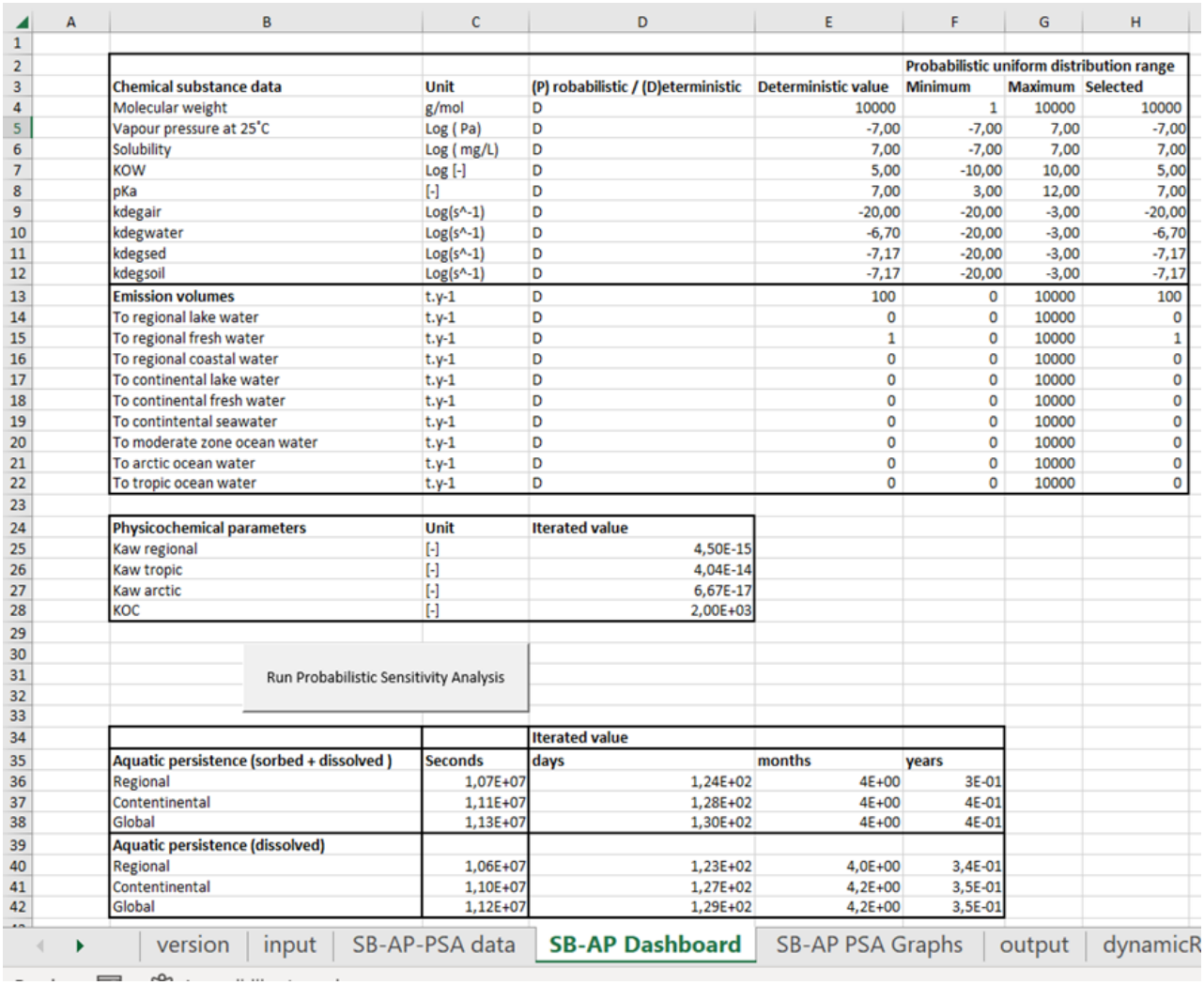
	F	G	H	I	J	K	L
12	SUBSTANCE PROPERTIES	Variable Name	Unit	User input	LookUp	Default	Used
13							
14	Chemical class	ChemClass			Neutral	neutral	Neutral
15	MOLECULAR WEIGHT	Molweight	[g.mol^{-1}]		5,8E+03	1,4E+02	5,8E+00
16							
17	Dimensionless solids/water PARTITION COEFFICIENT of the original species	Ksw	[-]			1,8E-03	1,8E-03
18	Dimensionless solids/water PARTITION COEFFICIENT of the alternate form	Ksw.alt	[-]			1,8E-03	1,8E-03
19	Dimensionless gas/water PARTITION COEFFICIENT of the original species at 25 °C	Kaw	[-]			3,2E-01	3,2E-01
20	Octanol/water PARTITION COEFFICIENT of the original species	Kow	[-]		1,3E-02	1,8E+01	1,3E-02
21	Octanol/water PARTITION COEFFICIENT of alternate form	Kow.alt	[-]			4,0E-06	4,0E-06
77	EMISSIONS	Variable Name	Unit	User input	LookUp	Default	Used
78							
79	*REGIONAL SCALE*						
80	EMISSION to air	E.aR	[t.yr^{-1}]		0,0E+00	1,0E+04	0,0E+00
81	EMISSION to lake water	E.w0R	[t.yr^{-1}]		1,0E+02	0,0E+00	5,5E-04
82	EMISSION to fresh water	E.w1R	[t.yr^{-1}]		0,0E+00	1,0E+04	0,0E+00
83	EMISSION to sea water	E.w2R	[t.yr^{-1}]		0,0E+00	0,0E+00	0,0E+00
84	EMISSION to natural soil	E.s1R	[t.yr^{-1}]		0,0E+00	0,0E+00	0,0E+00
85	EMISSION to agricultural soil	E.s2R	[t.yr^{-1}]		0,0E+00	1,0E+04	0,0E+00
86	EMISSION to other soil	E.s3R	[t.yr^{-1}]		0,0E+00	0,0E+00	0,0E+00
87	*CONTINENTAL SCALE*						
88	EMISSION to air	E.aC	[t.yr^{-1}]		0,0E+00	0,0E+00	0,0E+00
89	EMISSION to lake water	E.w0C	[t.yr^{-1}]		0,0E+00	0,0E+00	0,0E+00
90	EMISSION to fresh water	E.w1C	[t.yr^{-1}]		0,0E+00	0,0E+00	0,0E+00
108	LANDSCAPE SETTINGS	Variable Name	Unit	User input	LookUp	Default	Used
109							
110	*REGIONAL SCALE*						
111	Area land	AREAland.R	[km^2]		2,3E+05	2,3E+05	2,3E+11
112	Area sea	AREAsea.R	[km^2]		1,0E+03	1,0E+03	1,0E+09
113	Fraction lake water	FRAClake.R	-		2,5E-03	2,5E-03	2,5E-03
114	Fraction fresh water	FRACfresh.R	-		2,8E-02	2,8E-02	2,8E-02
115	Fraction natural soil	FRACnatsoil.R	-		2,7E-01	2,7E-01	2,7E-01
116	Fraction agricultural soil	FRACagsoil.R	-		6,0E-01	6,0E-01	6,0E-01
159							
160							
161							

version | input | SB-AP PSA data | SB-AP Dashboard | SB-AP PSA Graphs | output | dynamicR | substances | scenaric ...

Figure 5. SB user input cells in the input tab that need to remain blank.

2.3 Inserting values in the SB-AP Dashboard

The tab 'SB-AP Dashboard' includes the input cells for inserting the chemical substance data and emission volumes for the evaluation of an aquatic persistence scenario (Figure 6). It consists of a chemical substance data table (*cells B3:H12*) and an emission volumes table (*cells B13:H22*) in which the user can configure the aquatic persistence scenario.



Chemical substance data	Unit	(P) robabilistic / (D)eterministic	Deterministic value	Probabilistic uniform distribution range Minimum	Maximum	Selected
Molecular weight	g/mol	D	10000	1	10000	10000
Vapour pressure at 25°C	Log (Pa)	D	-7,00	-7,00	7,00	-7,00
Solubility	Log (mg/L)	D	7,00	-7,00	7,00	7,00
KOW	Log [-]	D	5,00	-10,00	10,00	5,00
pKa	[-]	D	7,00	3,00	12,00	7,00
kdegair	Log(s^-1)	D	-20,00	-20,00	-3,00	-20,00
kdegwater	Log(s^-1)	D	-6,70	-20,00	-3,00	-6,70
kdegsed	Log(s^-1)	D	-7,17	-20,00	-3,00	-7,17
kdegsoil	Log(s^-1)	D	-7,17	-20,00	-3,00	-7,17
Emission volumes	t.y-1	D	100	0	10000	100
To regional lake water	t.y-1	D	0	0	10000	0
To regional fresh water	t.y-1	D	1	0	10000	1
To regional coastal water	t.y-1	D	0	0	10000	0
To continental lake water	t.y-1	D	0	0	10000	0
To continental fresh water	t.y-1	D	0	0	10000	0
To contintental seawater	t.y-1	D	0	0	10000	0
To moderate zone ocean water	t.y-1	D	0	0	10000	0
To arctic ocean water	t.y-1	D	0	0	10000	0
To tropic ocean water	t.y-1	D	0	0	10000	0

Physicochemical parameters	Unit	Iterated value
Kaw regional	[-]	4,50E-15
Kaw tropic	[-]	4,04E-14
Kaw arctic	[-]	6,67E-17
KOC	[-]	2,00E+03

Run Probabilistic Sensitivity Analysis

		Iterated value		
Aquatic persistence (sorbed + dissolved)	**Seconds**	**days**	**months**	**years**
Regional	1,07E+07	1,24E+02	4E+00	3E-01
Contentinental	1,11E+07	1,28E+02	4E+00	4E-01
Global	1,13E+07	1,30E+02	4E+00	4E-01
Aquatic persistence (dissolved)				
Regional	1,06E+07	1,23E+02	4,0E+00	3,4E-01
Contentinental	1,10E+07	1,27E+02	4,2E+00	3,5E-01
Global	1,12E+07	1,29E+02	4,2E+00	3,5E-01

Figure 6. The SB-AP Dashboard

The user can choose to insert deterministic values for these data tables by typing the letter *D* in the 'Probabilistic / Deterministic' column (cells *D3:D22*). The spreadsheet then selects the deterministic values that are inserted by the user for the simulation of the aquatic persistence and expresses this value in the 'Selected' column (H3:H22). The user may also choose to insert a (uniformly distributed) range of input values to include uncertainty/variability for the purpose of performing probabilistic sensitivity analyses. In that case the user must type the letter *P* in the respective cell in the 'Probabilistic / Deterministic' column (cells *D3:D22*) and insert a minimum (cells *F3:F22*) and a maximum (cells G3:G22) value to define the probabilistic uniformly distributed range. The spreadsheet then randomly selects a value that is within the given range and expresses this value in the 'Selected' column (H3:H22).

2.4 Iterated values for physicochemical parameters

The 'physicochemical parameters' table (cells B24:D28) displays parameter values for the temperature dependent air-water partitioning coefficients at regional ($K_{aw\ regional}$), tropic ($K_{aw\ tropic}$) and arctic scale ($K_{aw\ arctic}$) and the organic carbon-water coefficient (K_{oc}) derived from the inserted octanol-water partitioning coefficient (K_{ow}) as calculated by the SB model based on the selected chemical substance properties (cells *H3: 12*).

2.5 Iterated values for aquatic persistence

The SB-AP Dashboard directly delivers the aquatic persistence calculated from the substance data and emission volumes as given in the '*Selected*' values (cells H3:22). There are six different aquatic persistence values calculated, because both the total and dissolved chemical load is estimated for the water compartments at the regional, continental and global scale (*cells B35:F42*). The '*aquatic persistence (sorbed + dissolved)*' table refers to the presence of chemical that is sorbed to organic carbon in suspended matter and the chemical dissolved in the water phase, whereas the '*aquatic persistence (dissolved only)*' table refers to presence of chemical dissolved in the water phase only. Aquatic persistence is expressed in unit of time to express the extent to which (v)P(v)Ms reside in water compartment. The units of time given here are in *seconds*, *days*, *months* and *years*, because the predicted aquatic persistence for different substances may differ in orders of magnitude.

2.6 Run probabilistic sensitivity analysis

Pressing the button '*run probabilistic sensitivity analysis*' starts a Microsoft Excel Macro that draws 10,000 iterations. Per iteration the spreadsheet model (i) randomly selects a value between the minimum and maximum of the probabilistic uniform distribution range for each chemical substance property and emission volume indicated with the letter *P* and (ii) calculates values for the physicochemical properties and aquatic persistence of *dissolved only* and *sorbed plus dissolved* chemicals at the regional, continental and global scale. The selected input values, iterated parameter values and calculated aquatic persistence values are written down in the 'SB-AP-PSA data' tab (a part of which is shown Figure 7), which stands for *SimpleBox –Aquatic Persistence – Probabilistic Sensitivity Analysis (SB-AP-PSA*).

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
1														
2		Molecular we	Vap 25	Solubility	KOW	pKa	kdegair	kdegwater	kdegsed	kdegsoil	Kaw region	Kaw tropic	Kaw arctic	KOC
3	Iteration	5340,7794	-2,42248	-5,88591	4,61622	5,63953	-4,97958	-14,9151	-13,613	-12,4582	1466,44	6266,23	90,0634	826,514
4	1	9562,7277	2,68583	-1,05883	1,48725	11,3334	-17,1438	-12,2238	-5,71825	-14,591	11474,6	21439,5	3442,83	0,61415
5	2	4938,4529	-1,33236	-5,41162	6,0029	8,83916	-3,56124	-4,20386	-5,83126	-13,1036	6679,65	23923,7	575,505	20133,9
6	3	9590,5524	0,52341	-3,18161	7,16203	3,01664	-7,52228	-11,7758	-4,10196	-7,47426	7400,69	19626	1134,57	290440
7	4	5521,6273	0,43015	-2,0124	2,65931	6,97159	-7,02986	-9,75407	-6,38332	-12,939	229,336	617,435	34,1552	9,12734
8	5	5323,3313	2,56284	-4,09069	-0,4301	9,56324	-4,93261	-19,7391	-7,91677	-16,4985	5076395	9675724	1466048	0,00743
9	6	3604,7702	0,32493	-2,55055	-1,82516	10,4455	-4,67224	-4,32907	-15,091	-15,4851	398,85	1092,26	57,4913	0,0003
10	7	4795,1703	-4,08482	-4,16495	-4,39443	9,61621	-14,6387	-7,69791	-7,83096	-10,4681	0,41615	2,32757	0,01525	8,1E-07
11	8	2627,3277	-5,66443	6,28431	8,6893	7,72146	-15,0344	-6,522	-6,59993	-8,6009	1,7E-13	1,2E-12	3,7E-15	9779888
12	9	4863,576	-4,60871	4,9498	9,91614	3,05264	-3,2562	-6,50621	-15,6116	-11,8418	8,9E-11	5,4E-10	2,8E-12	1,6E+08

version | input | SB-AP-PSA data | SB-AP Dashboard | SB-AP PSA Graphs | output | dynamicR | substances

Figure 7. A part of the SB-AP-Probabilistic Sensitivity Analysis data tab.

The *'SB-AP-PSA data'* tab includes 10,000 rows of iterations for which the selected values for molecular weight, vapour pressure (*Vap 25*), solubility, octanol-water partitioning coefficient (K_{ow}) the *pKa* and the degradation rate constant in air (k_{degair}), water($k_{degwater}$), sediment (k_{degsed}) and soil ($k_{degsoil}$) are given as well as the calculated air-water and organic carbon -water partitioning coefficient (K_{OC}) and the aquatic persistence of total and dissolved chemical in water compartments at the regional, continental and global scale. The simulation data in the '*SB-AP-PSA data'* tab is the data source for the graphs in the '*SB-AP Graphs'* tab (Figure 6).

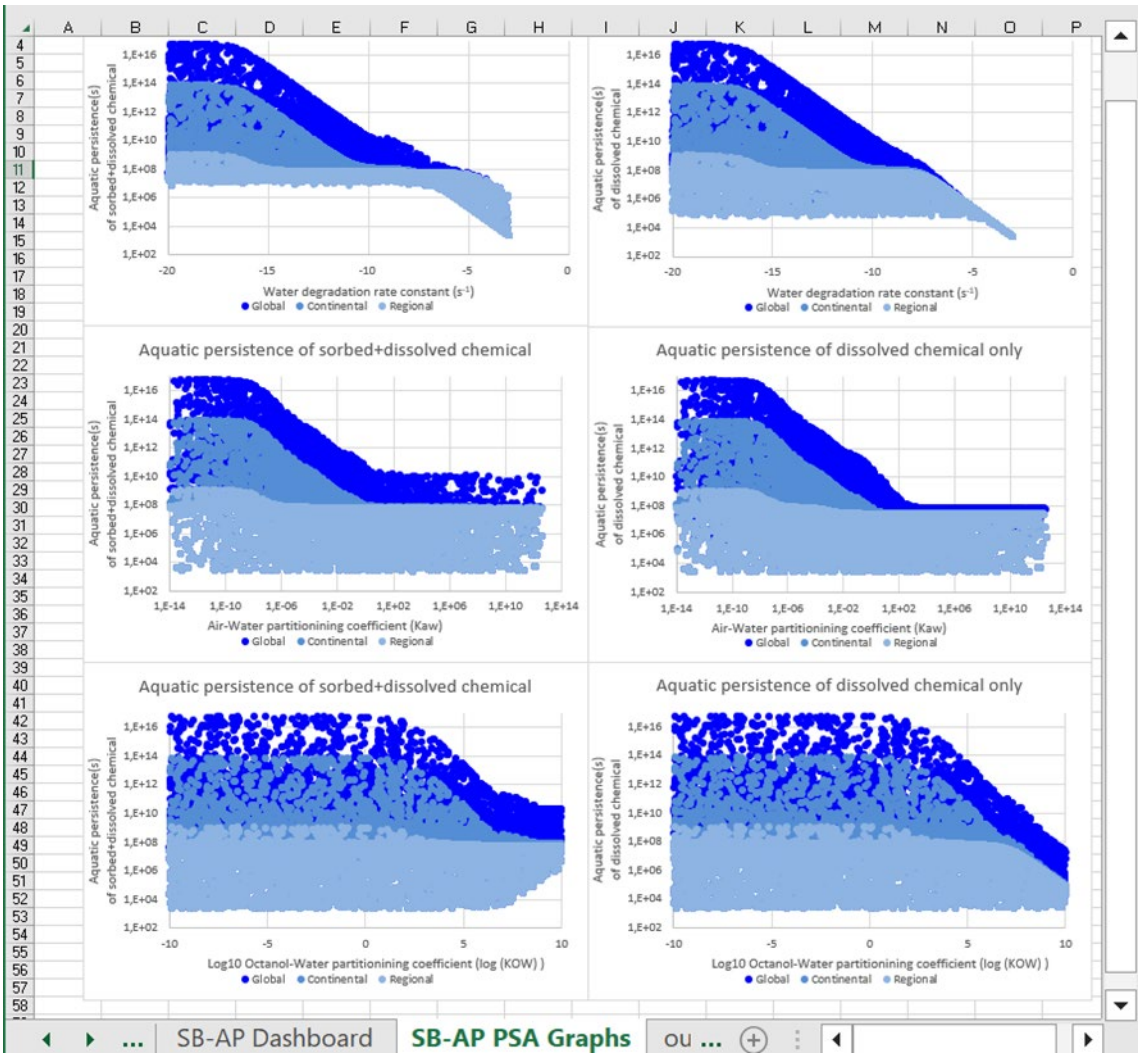


Figure 8. The SB-AP PSA Graphs tab

The *'SB-AP Graphs'* tab (Figure 8) displays six scatter plot graphs in which the aquatic persistence of '*dissolved'* or '*sorbed + dissolved'* chemicals are on the y-axes. The x-axes refer to inserted ranges for rate constants for degradation in water, calculated air-water partitioning coefficient (K_{aw}) or inserted octanol-water partitioning coefficients (K_{ow}).

3 Using the SB-AP Dashboard in novel exposure assessments for better risk assessment

The SB-AP Dashboard is a novel tool in the exposure assessment of PM(T) substances. This chapter explains how exposure assessors can use it for policy implications (Section 3.2). A number of advancements to the SB-AP Dashboard were made to make the tool fully operational for this purpose. These are described below.

3.1 Advancements in the SB-AP Dashboard

Several advancements have been made to the SB-AP Dashboard since the first model runs of a prototype version have been presented, such as the development of a MS Excel macro and the possibility to evaluate acids and bases as well as the bioavailability of sorbed and dissolved chemical species.

3.1.1 Development of MS Excel macro

The SB-AP Dashboard (available after the end of the project at https://github.com/rivm-syso/SimpleBox) has been optimized for MS Excel users as it no longer requires the licensed software add-in of @RISK (Lumivero, 2024). The @RISK software add-in has been replaced with a MS Excel Macro that runs probabilistic sensitivity analyses (Figure 6). Replacing the @RISK software add-in with the MS Excel macro has made the SB-AP Dashboard more user friendly as it is no longer required to install and get acquainted with @RISK. Instead, the user directly enters input values as described in section 2.3. Furthermore, the MS Excel macro directly delivers a datasheet (Figure 7) that comprises all simulated data.

3.1.2 Evaluation of acids and bases

The earlier versions of the SB-AP Dahsboard only included the possibility of evaluating substances that occur in the environment in a neutral form, excluding the evaluation of acids and bases. For this reason, the SB-AP Dashboard has been extended with routines to simulate acidic and basic substances (Figure 4) and an input field to insert values the dissociation constant (*pKa*) as substance property (Figure 6).

3.1.3 Bioavailability of sorbed and dissolved chemical species

Chemical substances in water bodies are considered bioavailable when they are actually dissolved in water and not sorbed to the organic carbon in suspended matter. Exposure estimation should thus account for the extent to which a chemical substance occurs as sorbed or dissolved species (ECHA REACH R.16). The earlier versions of the SB-AP Dashboard only delivered results for the sum of the dissolved and sorbed species. As such, the relatively large impact of K_{ow} on bioavailability was neglected. The latest version of the SB-AP Dashboard delivers results for both dissolved and summed species, so that the user can include the impact of bioavailability in its exposure assessment exercise. The paragraph below describes how the dissolved and sorbed species are calculated in the model.

The K_{oc} of a substance refers to the ratio between the concentration sorbed to organic carbon and the concentration dissolved in water. SB calculates K_{oc} s as the product of the substance's K_{ow} and the organic carbon content (f_{oc}) in the suspended matter ($K_{oc} = f_{oc} \times K_{ow}$). As such, dissolved substances with high K_{ow} are effectively sorbed by the organic carbon in suspended matter. The

impact of the K_{ow} on the sum of dissolved and sorbed chemical species is relatively small compared to the impact on dissolved species only (Figure 6). The process of sorption to suspended particles directly reduces the presence of dissolved chemical species in the water columns. The sorbed species are only indirectly removed from the water column, because the suspended particles to which the chemical is sorbed settle to the sediments at the bottom. Hence, the impact of high K_{ow} is relatively large for the aquatic persistence of the bioavailable dissolved chemical species only, but small for the summed species. Application of the SB-AP Dashboard in environmental risk assessment

3.2 Aquatic persistence as screening index for PM properties

Aquatic persistence (P_{aq}) is introduced in the current deliverable as a component of the overall persistence in order to focus on the potential exposure burden of aquatic organisms to (v)P(v)M substances that persist and displace in water bodies. The SB-AP Dashboard is a tool developed to express the aquatic persistence of chemical substances in water bodies. As such, it can be used in a similar manner as existing model tools developed for overall persistence and long range transport potential, but with a focus on the water compartments. Overall persistence tools have proven to be useful in chemical risk assessment in the identification and evaluation of persistent organic pollutants and the understanding of their environmental fate (Wegmann et al., 2009).

Just as for overall environmental persistence, the assessment of aquatic persistence needs the use of multimedia fate models to integrate the impact of the substance properties, emission patterns and landscape characteristics. The SB-AP Dashboard enables environmental exposure assessors to evaluate the time that a substance remains in the water phase and hence its tendency to flow downstream and eventually reach the ocean. SB simulates the degradation and transport as dynamic environmental fate processes occurring at regional, continental and global scale systems. Such dynamics are integrated in the way aquatic persistence is derived. The SB-AP Dashboard is a tool to screen the PMT properties of a substance as it directly indicates the timescale over which a chemical is anticipated to maintain in surface water bodies. Such screening supports decision making as substances can be identified to be PM in case the calculated aquatic persistence for the substance of interest is higher than the aquatic persistence calculated for substances representing the current PM or vPvM criteria (Table 1). In Annex I it is documented how the PM and vPvM criteria are translated into input values for the SB-AP Dashboard.

Table 1. Calculated aquatic persistences representing PM and vPvM criteria*

	Aquatic persistence of PM substance		Aquatic persistence of vPvM substances	
Scale	Dissolved species only	Sorbed + dissolved species	Dissolved species only	Sorbed + dissolved species
Regional	> 131 days	> 131 days	>187 days	> 187 days
Continental	> 137 days	> 137 days	>203 days	> 203 days
Global	> 140 days	> 140 days	> 215 days	> 215 days

* See annex I for derivation of aquatic persistence of substances representing PM and vPvM criteria

Moreover, the SB-AP Dashboard provides the user the opportunity to insert input values as ranges which can quantify uncertainty. The calculated Probabilistic Sensitivity Analysis graphs (Figure 8) and

data (Figure 7) resulting from such input ranges can then be used to evaluate the level of uncertainty in the aquatic persistence of a substance.

4 Conclusions

This deliverable report presents the SimpleBox Aquatic Persistence Dashboard (SB-AP Dashboard) developed within the PROMISCES project as a tool to evaluate the aquatic persistence of chemical substance emissions to surface waters. The SB-AP Dashboard, at the end of the project available at https://github.com/rivm-syso/SimpleBox, provides model users (e.g. risk assessors and policy makers) with the opportunity to directly gain insight into the *combined* effect of P and M, being the time a substance resides in the water phase (i.e. aquatic persistence). An application of the Dashboard is the comparison of the aquatic persistence of a specific substance to that of substances with properties corresponding with PM and vPvM criteria, for different scales (regional, continental, global).

The fate and transport models used in the PROMISCES case studies contain routines to simulate the volatilization of substances. Nevertheless this transport process removing substances from soil or water is not reflected in the current PM criteria. Thus, the impact of volatilization on the presence of PM in aqueous media demanded further investigation. The SB-AP Dashboard was applied in a dedicated fate modeling study to investigate the impact of air-water partitioning behavior (driven by volatilization and solution behavior of a substance) on aquatic persistence. The sensitivity analyses demonstrate an linearly increasing trend of aquatic persistence with decreasing air-water partitioning coefficients smaller than 100. Consequentially, volatile substances suitable to be considered PM because of their low K_{OC} and slow (bio)degradation can nonetheless still effectively be removed from water via volatilization leading to low aquatic persistence.

SimpleBox, as well as the fate and transport models used in the PROMISCES case studies, do contain model routines to account for volatilization. Hence, it is concluded that including volatilization in the evaluation of PM substances is a feasible effort. With the SB-AP Dashboard risk assessors and/or policy makers are able to include the volatilization of a suspected PM substance in prioritizing exercises for PM substances.

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Annex I Simulation of aquatic persistence representing PM and vPvM criteria

Here it is explained how the SB-AP Dashboard can be used to screen and index the aquatic persistence of a substance emission, by comparing it to aquatic persistence values the SB-AP Dashboard yields when the PM or vPvM criteria (EC, 2022) are inserted as input values (Table 1). Currently, a substance is proposed to be persistent if it meets one of the following criteria (EC, 2022):

i) the degradation half-life in marine water (at 9˚C) is higher than 60 days
ii) the degradation half-life in fresh or estuarine water at (12 ˚C) is 40 days
iii) the degradation half-life in marine sediment (at 9˚C) is higher than 180 days
iv) the degradation half-life in fresh or estuarine water sediment (at 12˚C) is higher than 120 days
v) the degradation half-life in soil (at 12 ˚C) is higher than 120 days

A substance is proposed to be very persistent (vP) if it meets one of the following criteria (EC, 2022)

i) the degradation half-life in marine, fresh or estuarine water is higher than 60 days
ii) the degradation half-life in marine, fresh or estuarine water sediment is higher than 180 days
iii) the degradation half-life in soil is higher than 180 days.

A substance shall be considered to fulfil the mobility criterion (M) when the log K_{oc} is less

than 3 (EC, 2022) and a substance shall be considered to fulfil the 'very mobile' criterion (vM) when the log K_{oc} is less than 2.

The half-life values ($t_{1/2}$) in persistence criteria are translated values for the input fields of the SB4.0 that refer to degradation rate constants in water, sediment and soil as:

$$k_{deg} = \frac{-\ln(\frac{1}{2})}{t_{1/2}}$$

The K_{oc} of a substance is included in SB as the product of the K_{OW} and the organic carbon content of the natural solid matter (f_{OC}) that is included in SB4.0 as parameter values characterising the environmental system with mass percentages of 2% for soil, 5% for sediments and 10% for the suspended particles in water compartments.

$$K_{OC} = f_{OC} \times K_{OW}$$

Here, the KOC is calculated for the suspended particles in the water compartments, because aquatic persistency refers to the time a substances resides in surface water bodies.

Table A1.1 Inserted values in SB-AP Dashboard to derive aquatic persistence matching PM and vPM criteria

SB-AP Dashboard input field	**Inserted value to derive PM index**	**Inserted value to derive vPvM index**	**Unit**
Molecular weight[A]	10,000	10,000	g/mol
Vapor pressure[A]	10^{7}	10^{7}	Pa
Solubility[A]	10^{8}	10^{8}	mg/l
pKa	7	7	[-]
K_{OW}[B]	10^{4}	10^{3}	[-]
$k_{degwater}$	$2\ 10^{-7}$	$1.34\ 10^{-7}$	s^{-1}
k_{degsed}	$6.7\ 10^{-8}$	$4.46\ 10^{-8}$	s^{-1}
$k_{degsoil}$	$6.7\ 10^{-8}$	$4.46\ 10^{-8}$	s^{-1}

A: a maximum value is inserted as the substance property is not include as PM or vPvM criterium

B: *pKa* is set to 7 to represent a default neutral substance

C: calculated as $K_{OW} = K_{OC} / f_{OC}$ with f_{OC} = 10%

D: calculated as $k_{deg} = -\ln(1/2) / t_{1/2}$