User guide for Simplebox4nano

Rev 23th September 2019

[note: this user guide is written for Simplebox4nano, it remains relevant for Simplebox4plastic, with the exception that the fragmentation rate constant can now be defined as part of the degradation rate constant.]

Johannes Meesters, Joris Quik

Table of Contents

1. INTRODUCTION

SimpleBox4nano (SB4n) is a multimedia environmental fate model that is developed for the simulation of environmental fate and exposure of nanomaterials (Meesters, Koelmans et al. 2014). SB4n's mass balance equations and algorithms that are specifically derived for materials in the nano- or microform are embedded in the SimpleBox model, which is a nested multimedia environmental fate model for chemicals in which the environmental compartments air, water, sediment and soil are represented by boxes (Schoorl, Hollander et al. 2016). The user guide for the SimpleBox4.0 model written by Schoorl, Hollander et al. (2016) is available in the online library of the RIVM (see rivm.nl/simplebox), but does not yet include the extention for application to nanomateirals: SimpleBox4nano. The SimpleBox model is developed for chemical substances that are in atomic, ionic or molecular forms, dissolved in water or in the gas phase, whereas the specific SB4n module considers substances that occur in solid forms, like micro-or nanocolloids. Unlike SimpleBox, SB4n does not treat partitioning between dissolved and particulate forms of the chemical as equilibrium speciation but as nonequilibrium colloidal behavior. Therefore, within each compartment the micro- or nanomaterial can occur in different physical−chemical forms (species): (1) freely dispersed, (2) heteroaggregated with natural colloidal particles (<450 nm), or (3) attached to larger natural particles (>450nm) that are prone to gravitational forces in aqueous media. This guide provides instructions for the specific use of SimpleBox4nano, which is the nano extention to the SimpleBox 4.0 model. The model and manual can be downloaded from rivm.nl/simplebox4nano.

2. RUNNING THE MODEL

2.1. Model setup

After opening the MS Excel workbook called ‘SimpleBox4.01-nano’ the following sheet will appear containing version details, contact information references and disclaimer (Figure 1)

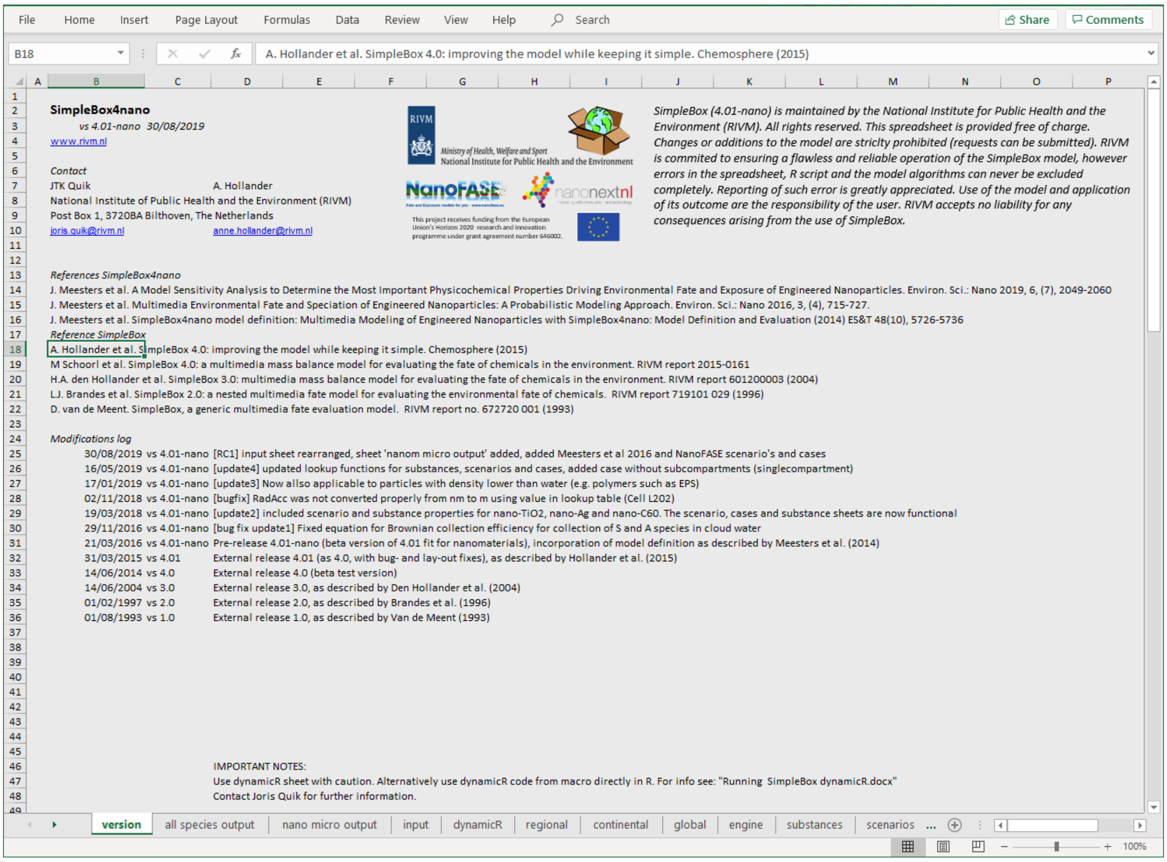
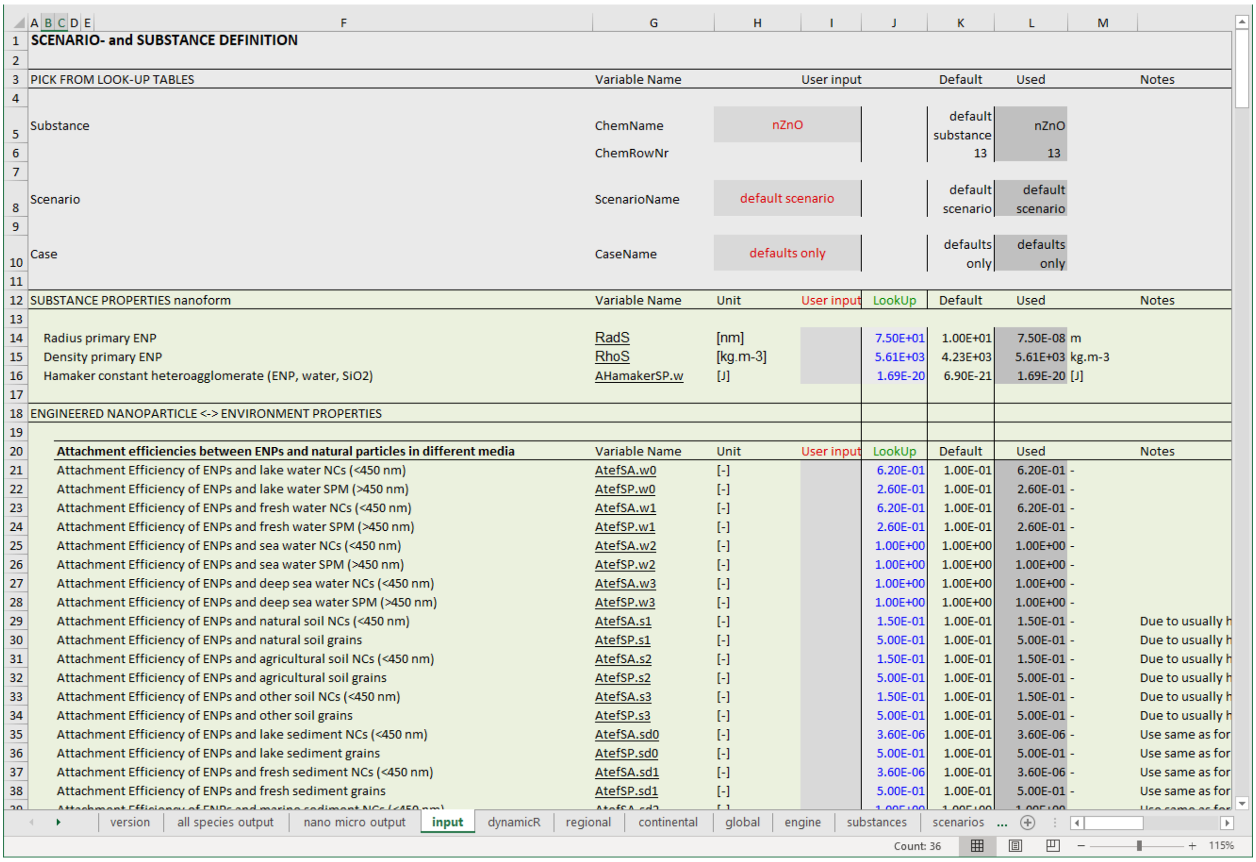


Figure 1. Opening sheet of SimpleBox4.0



1	**SCENARIO- and SUBSTANCE DEFINITION**								
2									
3	PICK FROM LOOK-UP TABLES	Variable Name		User input		Default	Used		Notes
4									
5	Substance	ChemName	nZnO			default substance	nZnO		
6		ChemRowNr				13	13		
7									
8	Scenario	ScenarioName	default scenario			default scenario	default scenario		
9									
10	Case	CaseName	defaults only			defaults only	defaults only		
11									
12	SUBSTANCE PROPERTIES nanoform	Variable Name	Unit	User input	LookUp	Default	Used		Notes
13									
14	Radius primary ENP	RadS	[nm]		7.50E+01	1.00E+01	7.50E-08	m	
15	Density primary ENP	RhoS	[kg.m-3]		5.61E+03	4.23E+03	5.61E+03	kg.m-3	
16	Hamaker constant heteroagglomerate (ENP, water, SiO2)	AHamakerSP.w	[J]		1.69E-20	6.90E-21	1.69E-20	[J]	
17									
18	ENGINEERED NANOPARTICLE <-> ENVIRONMENT PROPERTIES								
19									
20	**Attachment efficiencies between ENPs and natural particles in different media**	Variable Name	Unit	User input	LookUp	Default	Used		Notes
21	Attachment Efficiency of ENPs and lake water NCs (<450 nm)	AtefSA.w0	[-]		6.20E-01	1.00E-01	6.20E-01	-	
22	Attachment Efficiency of ENPs and lake water SPM (>450 nm)	AtefSP.w0	[-]		2.60E-01	1.00E-01	2.60E-01	-	
23	Attachment Efficiency of ENPs and fresh water NCs (<450 nm)	AtefSA.w1	[-]		6.20E-01	1.00E-01	6.20E-01	-	
24	Attachment Efficiency of ENPs and fresh water SPM (>450 nm)	AtefSP.w1	[-]		2.60E-01	1.00E-01	2.60E-01	-	
25	Attachment Efficiency of ENPs and sea water NCs (<450 nm)	AtefSA.w2	[-]		1.00E+00	1.00E+00	1.00E+00	-	
26	Attachment Efficiency of ENPs and sea water SPM (>450 nm)	AtefSP.w2	[-]		1.00E+00	1.00E+00	1.00E+00	-	
27	Attachment Efficiency of ENPs and deep sea water NCs (<450 nm)	AtefSA.w3	[-]		1.00E+00	1.00E+00	1.00E+00	-	
28	Attachment Efficiency of ENPs and deep sea water SPM (>450 nm)	AtefSP.w3	[-]		1.00E+00	1.00E+00	1.00E+00	-	
29	Attachment Efficiency of ENPs and natural soil NCs (<450 nm)	AtefSA.s1	[-]		1.50E-01	1.00E-01	1.50E-01	-	Due to usually h
30	Attachment Efficiency of ENPs and natural soil grains	AtefSP.s1	[-]		5.00E-01	1.00E-01	5.00E-01	-	Due to usually h
31	Attachment Efficiency of ENPs and agricultural soil NCs (<450 nm)	AtefSA.s2	[-]		1.50E-01	1.00E-01	1.50E-01	-	Due to usually h
32	Attachment Efficiency of ENPs and agricultural soil grains	AtefSP.s2	[-]		5.00E-01	1.00E-01	5.00E-01	-	Due to usually h
33	Attachment Efficiency of ENPs and other soil NCs (<450 nm)	AtefSA.s3	[-]		1.50E-01	1.00E-01	1.50E-01	-	Due to usually h
34	Attachment Efficiency of ENPs and other soil grains	AtefSP.s3	[-]		5.00E-01	1.00E-01	5.00E-01	-	Due to usually h
35	Attachment Efficiency of ENPs and lake sediment NCs (<450 nm)	AtefSA.sd0	[-]		3.60E-06	1.00E-01	3.60E-06	-	Use same as for
36	Attachment Efficiency of ENPs and lake sediment grains	AtefSP.sd0	[-]		5.00E-01	1.00E-01	5.00E-01	-	Use same as for
37	Attachment Efficiency of ENPs and fresh sediment NCs (<450 nm)	AtefSA.sd1	[-]		3.60E-06	1.00E-01	3.60E-06	-	Use same as for
38	Attachment Efficiency of ENPs and fresh sediment grains	AtefSP.sd1	[-]		5.00E-01	1.00E-01	5.00E-01	-	Use same as for

Figure 2. Go to the input sheet. Here you can select a predefined chemical, change the scenario or predefined case. Based on these selections, the Lookup column is populated.

2.2. Physicochemical properties

To insert the physicochemical properties of the material in micro- or nanoform, scroll down to the row called ‘engineered nanoparticle properties’. Here the radius, density and Hamaker constant of the material can be inserted in the ‘user input’ column.

Size and density

The size and density of the material in a nano- or microform can be inserted in the SB4n model in the ‘user input’ column in the rows called ‘Radius primary ENP’ and ‘Density primary ENP’. By default the substance is assumed to occur as a spherically shaped massive particle. In case the user sees it fit to follow this assumption, the size of the material can be inserted as the radius (nm) of such a sphere in the assigned user input cell. Following this assumption also means that the specific weight ($kg.m^{-3}$) assigned to the elemental composition of the material can be inserted as the density of the particles in the specific cell in the ‘user input’ column (Figure 4).

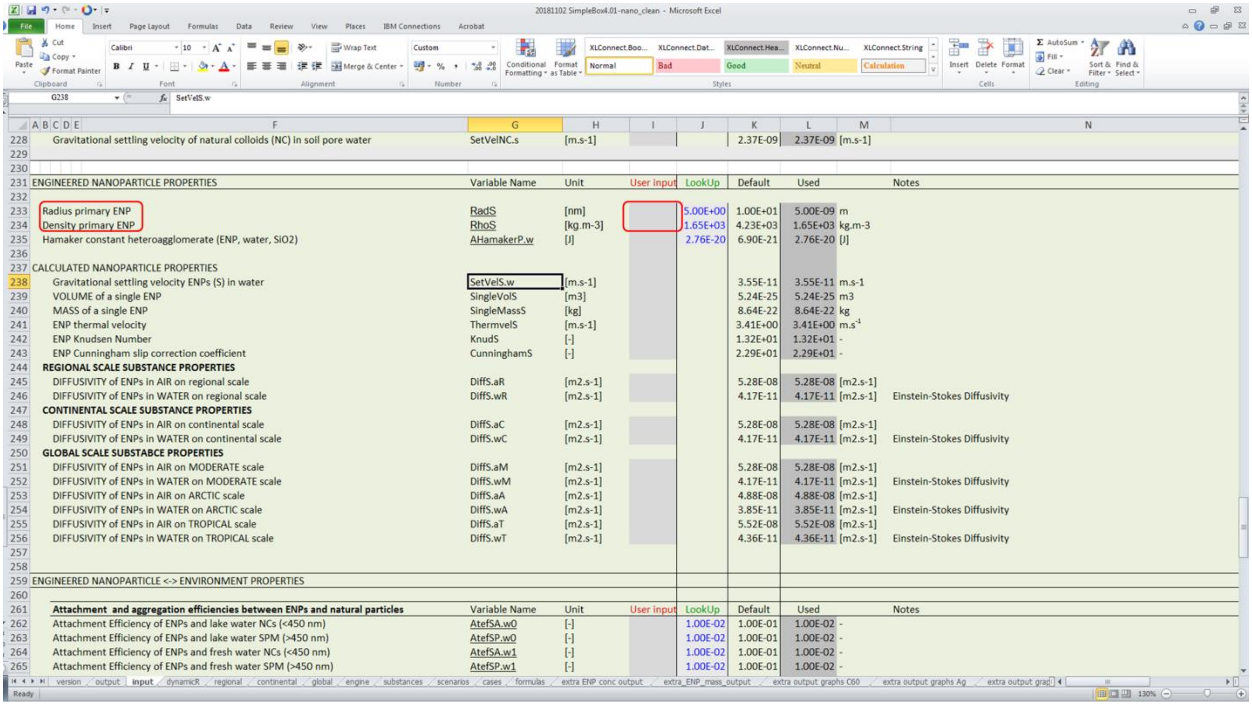


Figure 4. User input to insert the micro- or nanomaterial’s size and density

However, there are more options for the user in case the assumption of the material occurring as massive spherically shaped particles is not suitable for the model run. In these cases, the user should estimate the representative spherical size and density of the material (Figure 5).

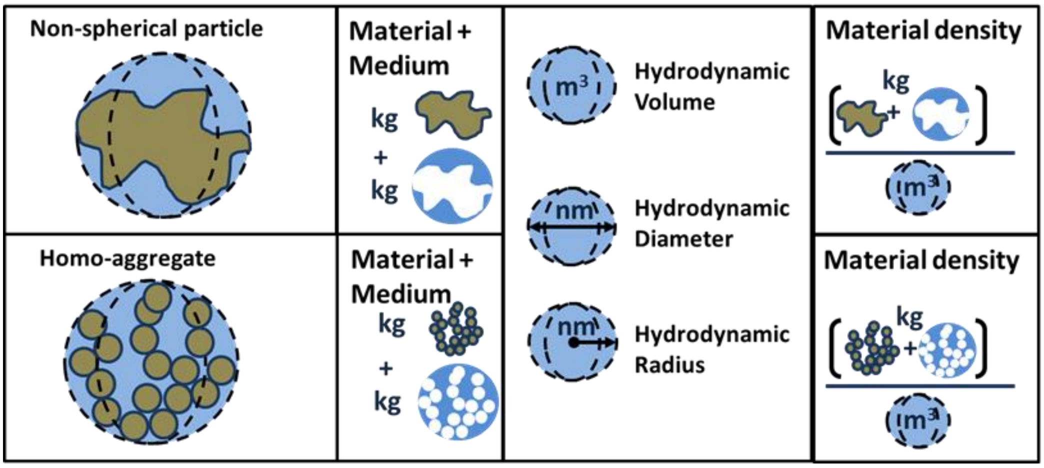


Figure 5. Consistency between particle size and density for non-spherical shaped materials and nanomaterial-homo-aggregates

For example, the environmental fate and exposure of non-spherical particles and homo-aggregates of nanomaterials in water can be simulated with SB4n by inserting the hydrodynamic radius as user input, but the material density ($kg.m^{-3}$) then refers to the weight of the particulate or homo-aggregate itself plus the weight of the surrounding medium within the hydrodynamic volume (kg) that is to be divided with the hydrodynamic volume (m^3) (Figure 5).

Hamaker constant

The Hamaker constant is a physicochemical property of the material in micro- or nanoform that expresses the coefficient that relates the interactive van der Waals energy to the distance of separation between two molecules where the interactive force is pair-wise additive and independent of the intervening media (Hamaker 1937). In SB4n, the Hamaker constant is required to determine the Van der Waals attraction between the nano- or micromaterial and natural particles in the environment. By default, the natural particles are characterized in SB4n as SiO_2-particles with water as the surrounding medium. Data on Hamaker constants can be collected from Bergstrom (1997), Israelachvili (1991) and Lefevre and Jolivet (2009). Hamakers constants derived for molecules with the same elemental composition in a vacuum can be recalculated for use within SB4n (Meesters, Quik et al. 2016):

$$A_{x,water,SiO_2} = \left(\sqrt{A_x} - \sqrt{A_{water}}\right)\left(\sqrt{A_{SiO_2}} - \sqrt{A_{water}}\right)$$

(Equation 1)

Here, $A_{x,water,SiO_2}$ refers to the Hamaker constant between nano- or micromaterial with elemental composition *x* and the natural particles that is to be inserted in SB4n, A_x is the Hamaker constant of material *x* in vacuum, A_{water} is the Hamaker constant of water and A_{SiO2} is the Hamaker constant of SiO_2. The Hamaker constant of water is 3.7 10^{-20} J according to Israelachvili (1991) and that of SiO_2. is 7.59 10^{-20} J according to Bergstrom (1997). As such, the equation for deriving the Hamaker constant for use in SB4n can be simplified to:

$$A_{x,water,SiO_2} = \left(\sqrt{A_x} - \sqrt{3.7\ 10^{-20}}\right)\left(\sqrt{7.59\ 10^{-20}} - \sqrt{3.7\ 10^{-20}}\right)$$

(Equation 2)

This Hamaker constant can be inserted in SB4n the designated cell in the 'user input' column (Figure 6).

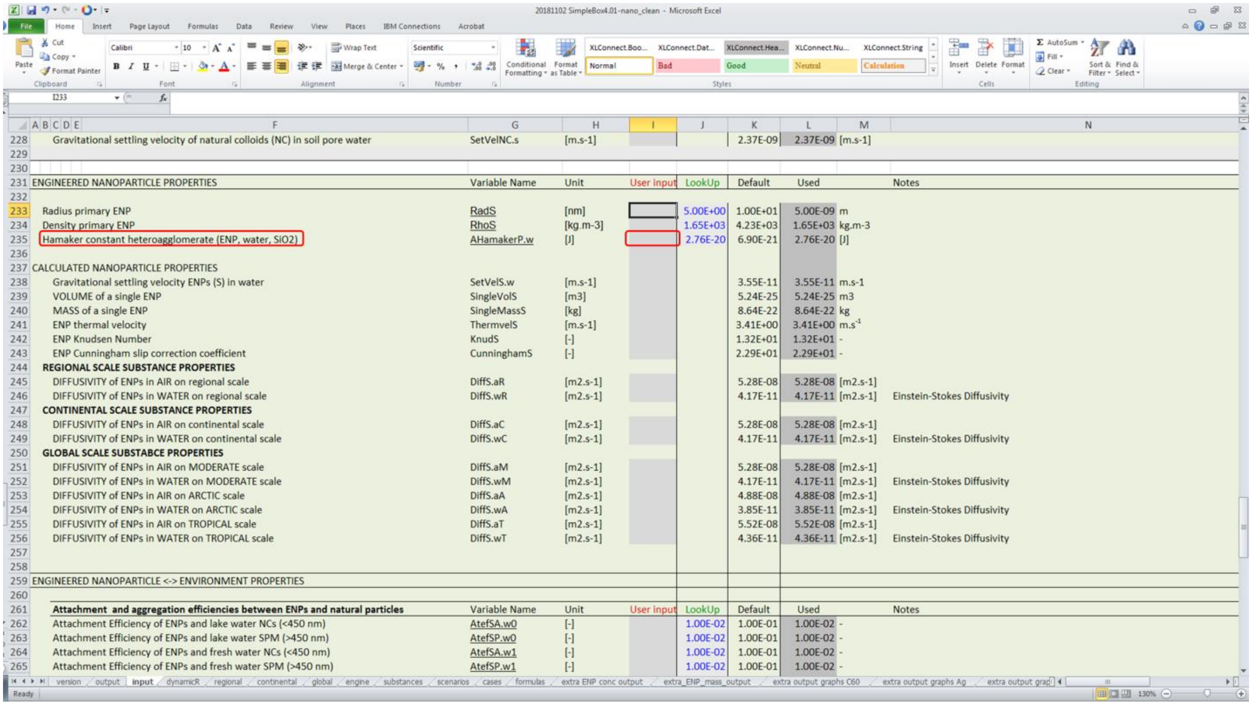


Figure 6. User input to insert the Hamaker constant between the nano- or micromaterial and natural particles.

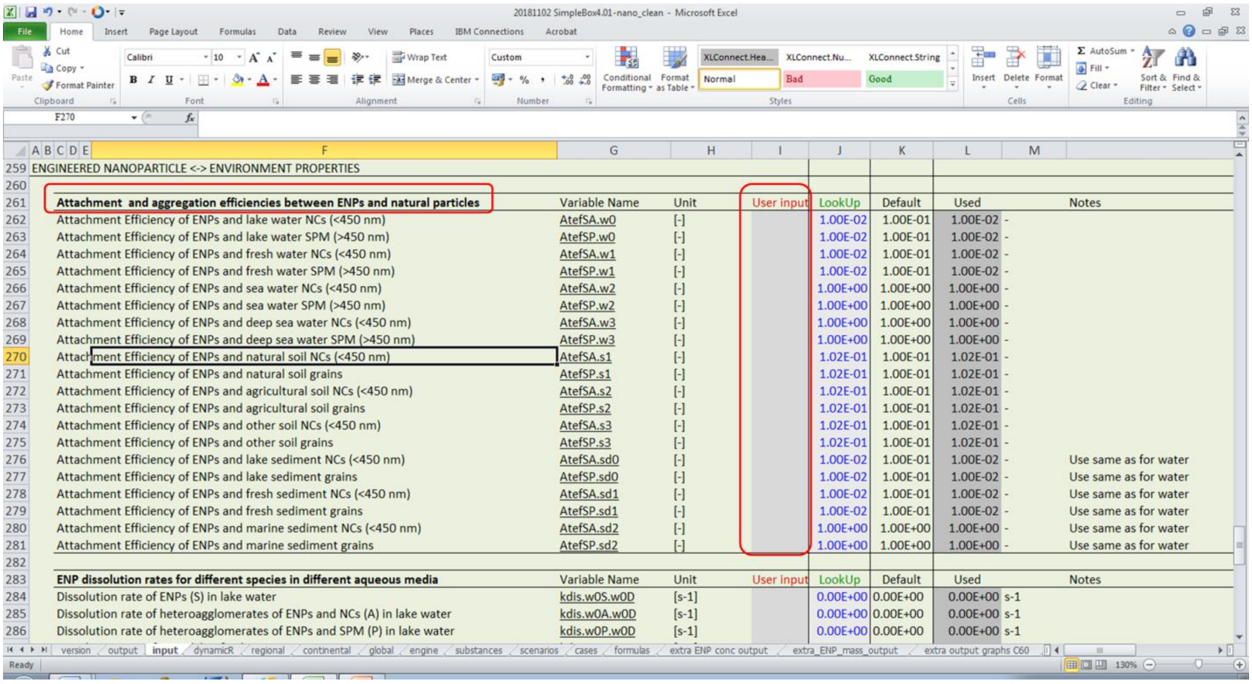
2.3. Functional assays

Functional assays here refer to interactions between the material and the environment that are characterized by physicochemical properties of the material. SB4n includes the attachment efficiencies between the nano- or micromaterial and the natural particles in the environment as functional assays and the dissolution rate constants in water bodies, sediments and soils (Meesters, Koelmans et al. 2014). The characterization and where to find the input cells for these functional assays are described below.

Attachment efficiencies with natural particles

Attachment efficiencies refer to the probability of two particles to stay attached to each other upon a collision event. SB4N requires attachment efficiencies between the micro- or nanomaterial and natural particles in the environment. The natural particles are divided into two size classes: natural colloidal particles (< 450 nm) and natural coarse particles (> 450 nm) that are more prone to gravitational forces in aqueous media (Meesters, Koelmans et al. 2014). It is preferred to obtain such attachment efficiencies from experimental work, but suitable data in the scientific literature are scarce and standardized technical guidance is yet to be developed. Moreover, experimental attachment efficiencies should be obtained under realistic environmental conditions of pH, dissolved organic carbon (DOC) concentrations and ionic strength.

In absence of experimental data on attachment efficiencies, the Derjaguin & Landau, Verwey, and Overbeek (DLVO) theory can be applied to theoretically derive them (Derjaguin and Landau 1941, Verwey and Overbeek 1948). However, many environmental conditions and nano- or micromaterial properties influence attachment efficiencies, which generally results in behavior not taken into account by the DLVO theory (non-DLVO). It is thus emphasized that experimentally derived attachment efficiencies are preferred over DLVO derived attachment efficiencies for simulations with SB4n (Meesters, Koelmans et al. 2014). Appendix tables 1-4 describe the outcomes of a DLVO calculator developed for deriving attachment efficiencies for the use of SB4n as a function of the material's size (nm), Hamaker constant (J), and zeta potential (mV) for attachment efficiencies with natural colloid and coarse particles in fresh water and soil.



259	ENGINEERED NANOPARTICLE <-> ENVIRONMENT PROPERTIES							
260								
261	**Attachment and aggregation efficiencies between ENPs and natural particles**	Variable Name	Unit	User input	LookUp	Default	Used	Notes
262	Attachment Efficiency of ENPs and lake water NCs (<450 nm)	AtefSA.w0	[-]		1.00E-02	1.00E-01	1.00E-02 -	
263	Attachment Efficiency of ENPs and lake water SPM (>450 nm)	AtefSP.w0	[-]		1.00E-02	1.00E-01	1.00E-02 -	
264	Attachment Efficiency of ENPs and fresh water NCs (<450 nm)	AtefSA.w1	[-]		1.00E-02	1.00E-01	1.00E-02 -	
265	Attachment Efficiency of ENPs and fresh water SPM (>450 nm)	AtefSP.w1	[-]		1.00E-02	1.00E-01	1.00E-02 -	
266	Attachment Efficiency of ENPs and sea water NCs (<450 nm)	AtefSA.w2	[-]		1.00E+00	1.00E+00	1.00E+00 -	
267	Attachment Efficiency of ENPs and sea water SPM (>450 nm)	AtefSP.w2	[-]		1.00E+00	1.00E+00	1.00E+00 -	
268	Attachment Efficiency of ENPs and deep sea water NCs (<450 nm)	AtefSA.w3	[-]		1.00E+00	1.00E+00	1.00E+00 -	
269	Attachment Efficiency of ENPs and deep sea water SPM (>450 nm)	AtefSP.w3	[-]		1.00E+00	1.00E+00	1.00E+00 -	
270	Attachment Efficiency of ENPs and natural soil NCs (<450 nm)	AtefSA.s1	[-]		1.02E-01	1.00E-01	1.02E-01 -	
271	Attachment Efficiency of ENPs and natural soil grains	AtefSP.s1	[-]		1.02E-01	1.00E-01	1.02E-01 -	
272	Attachment Efficiency of ENPs and agricultural soil NCs (<450 nm)	AtefSA.s2	[-]		1.02E-01	1.00E-01	1.02E-01 -	
273	Attachment Efficiency of ENPs and agricultural soil grains	AtefSP.s2	[-]		1.02E-01	1.00E-01	1.02E-01 -	
274	Attachment Efficiency of ENPs and other soil NCs (<450 nm)	AtefSA.s3	[-]		1.02E-01	1.00E-01	1.02E-01 -	
275	Attachment Efficiency of ENPs and other soil grains	AtefSP.s3	[-]		1.02E-01	1.00E-01	1.02E-01 -	
276	Attachment Efficiency of ENPs and lake sediment NCs (<450 nm)	AtefSA.sd0	[-]		1.00E-02	1.00E-01	1.00E-02 -	Use same as for water
277	Attachment Efficiency of ENPs and lake sediment grains	AtefSP.sd0	[-]		1.00E-02	1.00E-01	1.00E-02 -	Use same as for water
278	Attachment Efficiency of ENPs and fresh sediment NCs (<450 nm)	AtefSA.sd1	[-]		1.00E-02	1.00E-01	1.00E-02 -	Use same as for water
279	Attachment Efficiency of ENPs and fresh sediment grains	AtefSP.sd1	[-]		1.00E-02	1.00E-01	1.00E-02 -	Use same as for water
280	Attachment Efficiency of ENPs and marine sediment NCs (<450 nm)	AtefSA.sd2	[-]		1.00E+00	1.00E+00	1.00E+00 -	Use same as for water
281	Attachment Efficiency of ENPs and marine sediment grains	AtefSP.sd2	[-]		1.00E+00	1.00E+00	1.00E+00 -	Use same as for water
282								
283	**ENP dissolution rates for different species in different aqueous media**	Variable Name	Unit	User input	LookUp	Default	Used	Notes
284	Dissolution rate of ENPs (S) in lake water	kdis.w0S.w0D	[s-1]		0.00E+00	0.00E+00	0.00E+00 s-1	
285	Dissolution rate of heteroagglomerates of ENPs and NCs (A) in lake water	kdis.w0A.w0D	[s-1]		0.00E+00	0.00E+00	0.00E+00 s-1	
286	Dissolution rate of heteroagglomerates of ENPs and SPM (P) in lake water	kdis.w0P.w0D	[s-1]		0.00E+00	0.00E+00	0.00E+00 s-1	

Figure 7. User input for attachment efficiencies.

The user has the possibility to insert values for attachment efficiencies between the nano- or micromaterial and two size classes of natural particles within 10 different environmental compartments (e.g. fresh water, sea water, agricultural soil, etc.). In practice however, a dataset with these 20 different attachment efficiencies is rarely available for any nano- or micromaterial (calibrate D6.3 report). It is therefore proposed to simplify the input for attachment efficiency where possible. It is arguable to (i) use the same attachment efficiencies derived for water and sediment, (ii), use the same attachment efficiencies in fresh and lake water (ii) use the same attachment efficiencies for natural, agricultural and other soils, and (iii) assume an attachment efficiency of unity in the high saline conditions in marine water and sediment. As such, the number of required attachment efficiencies can be reduced to four, i.e. the attachment efficiency between the nano- or micromaterial with natural particles that are for attachment to (i) natural colloidal particles (<450 nm) in fresh water,(ii) coarse suspended particles (> 450 nm) in fresh water, (iii) natural colloidal particles in soil, and (iv) coarse soil grains. Estimates using DLVO theory for these four types of attachment efficiencies at varying zeta potential, radius and Hamaker constant are presented in Appendix 1.

Dissolution rate constants

The dissolution rate constant refers to how fast the material in nano- or microform dissolves into a molecular or ionic form. Dissolution is included in SB4N as an environmental fate process that transforms the nanomaterial into a molecular or ionic form (Meesters, Koelmans et al. 2014). As such, it is best represented by the sum of the rate constants of the chemical reactions known to drive such a transformation, e.g. oxidation, sulfidation, photolysis and spontaneous dissolution (Quik, Vonk et al. 2011). Hence, the dissolution rate constant is a functional assay that depends on the surface chemistry between the nanomaterial and the conditions of the surrounding medium such as pH, ionic strength or the concentration of natural organic matter. Technical guidelines to derive the specific dissolution rate constant for a specific nanomaterial within a specific environmental medium is under development, but not yet available (OECD 2019). In absence of experimental data on the specific dissolution rate constant, previously derived characteristic time frames of dissolution can be applied (Garner and Keller 2014). These dissolution time frames are characterized from dissolution experiments performed in aqueous media representing marine water, freshwater (storm water) and soil pore water, see Table 2. (Garner and Keller 2014).

Table 2. Timeframes for dissolution of nanomaterials

Material	**Cloud water**	**Freshwater**	**Groundwater**	**Marine**
Ag	"within weeks"	"within weeks"	"within weeks"	"within weeks"
Au	"no sign. diss."	"no sign. diss."	"no sign. diss."	"no sign. diss."
C	"no sign. diss."	"no sign. diss."	"no sign. diss."	"no sign. diss."
CeO2	"no sign. diss."	"no sign. diss."	"no sign. diss."	"no sign. diss."
CuO	"within weeks"	"within weeks"	"within months"	"within months"
NiO	"within months"	"within weeks"	"within months"	"within weeks"
TiO2	"no sign. diss."	"no sign. diss."	"no sign. diss."	"no sign. diss."
ZnO	"within weeks"	"within days"	"within weeks"	"within hours"

These timeframes can be converted to dissolution rate constants that SB4n requires as input, see Table 3.

Table 3. Dissolution rate constants calculated from characteristic dissolution timeframes (Table 2).

Dissolution timeframe	**Dissolution rate constant (s^{-1})**
“within hours”	1×10^{-5}
“within weeks”	4×10^{-7}
“within months”	3×10^{-8}
“no sign. diss. “	0

The user has the possibility to insert values for the dissolution rate constants of a substance in the nano- or microform in 10 different compartments for three different species, i.e. freely dispersed, hetero-aggregated, attached to coarse particles (Figure 8). In practice however, a dataset with these 30 different dissolution rate constants is rarely available for any nano- or micromaterial (calibrate D6.3 report). It is therefore proposed to simplify the input for dissolution rate constant where possible. It is arguable to (i) use the same dissolution rate constant for all three particle species within a compartment, (ii), use the same dissolution rate constant in fresh and lake water (ii) use the same dissolution rate constants for natural, agricultural and other soils, and (iii) use the same dissolution rate constants for water and sediment. As such the number of 30 different dissolution rate constants can be reduced to three, i.e dissolution in (i) fresh and lake water and sediment, (ii) marine water and sediment, (iii) soil.

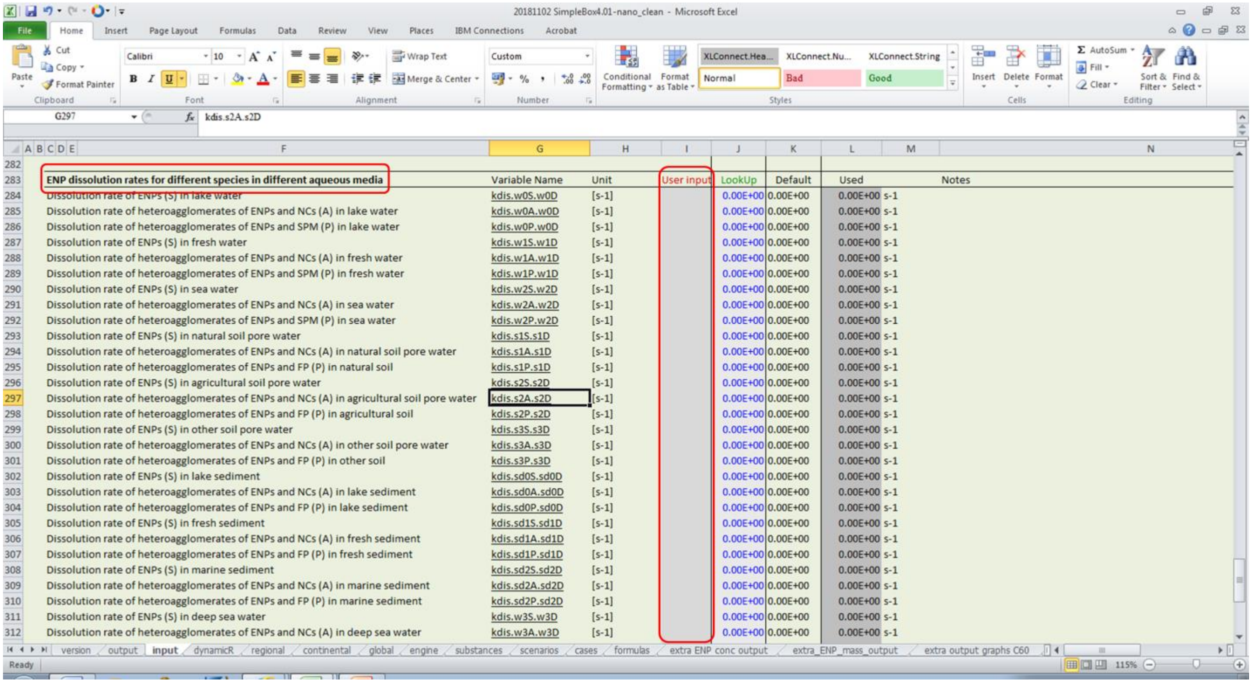


Figure 8. User input for dissolution rate constants

Degradation and transformation rate constants

Transformation or degradation can be included in the SB4N model as an environmental fate process removing the material as emitted in nano- or microform. The model however does not perform simulations of environmental fate and exposure of transformation products other than hetero-aggregated or dissolved species. Transformation processes may include processes such as biodegradation, photodegradation, physical break-up of nano or microparticles (i.e. microplastics). The input sheet contains 33 cells in which rate constants for such environmental removal mechanisms can be included in the environmental fate simulation (Figure 9).

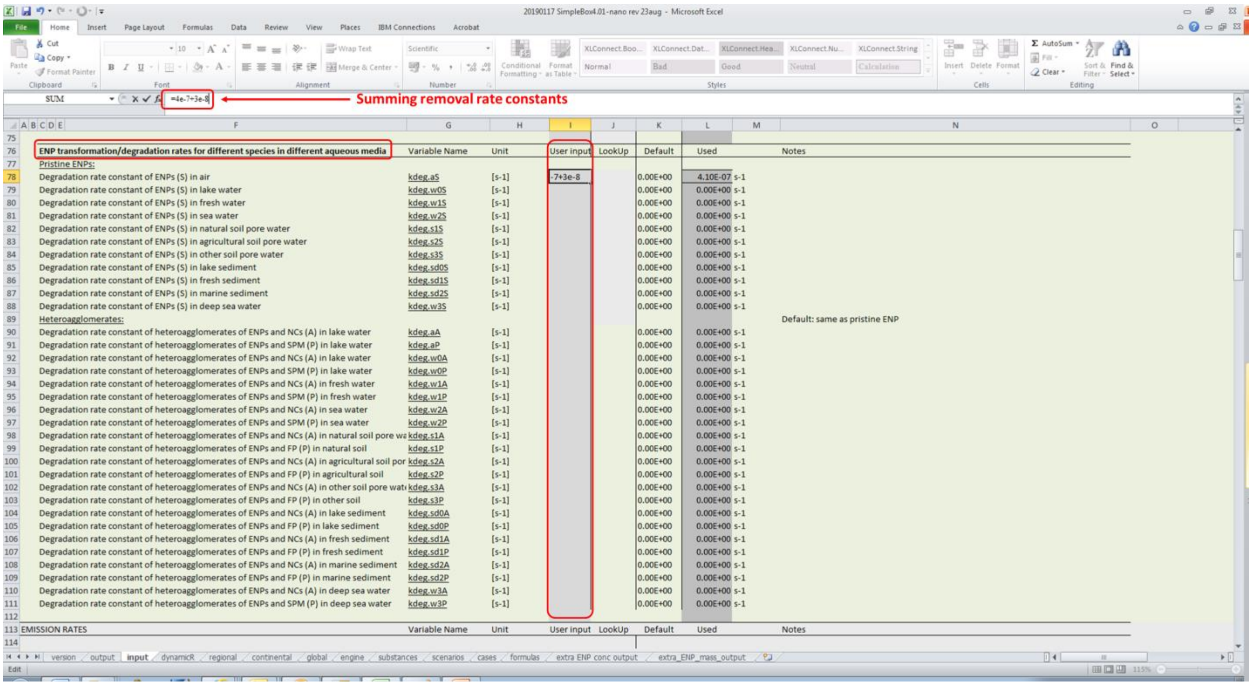


Figure 9. User input for transformation and /or degradation rate constants

The user is able to specify the removal rate constant per environmental species and compartment, because the 33 input cells refer to the species of the nano- or micromaterial as pristine solid (S), hetero-aggregated with natural colloids (A) or attached to a natural coarse particle (P) within a specific environmental compartment. The unit for such a rate constant is s^{-1}. Furthermore, the user is allowed to sum the rate constants of multiple environmental removal processes under the terms that the processes do not intervene with each other and apply to the same material species and environmental compartment. Such a sum of rate constants can be inserted in the formula bar. For example a rate constant one removal process of "within weeks" can be summed with a second removal process of "within months" as '4E-7 +3E-8', see Figure 9. The defaults for the transformation / degradation rates are set to zero, so that the cells can be left empty in case the user has no additional removal process to include in the environmental fate simulation with SB4n.

2.4. Emission rates

Scroll down until the row of 'EMISSION RATES' appears and then go to the table called 'Solid species ENPs (S)' appears. Here the emission rates of materials in a micro- or nanoform can be inserted per environmental compartment for every nested scale in the column called 'user input' in tons per year (Figure 3).

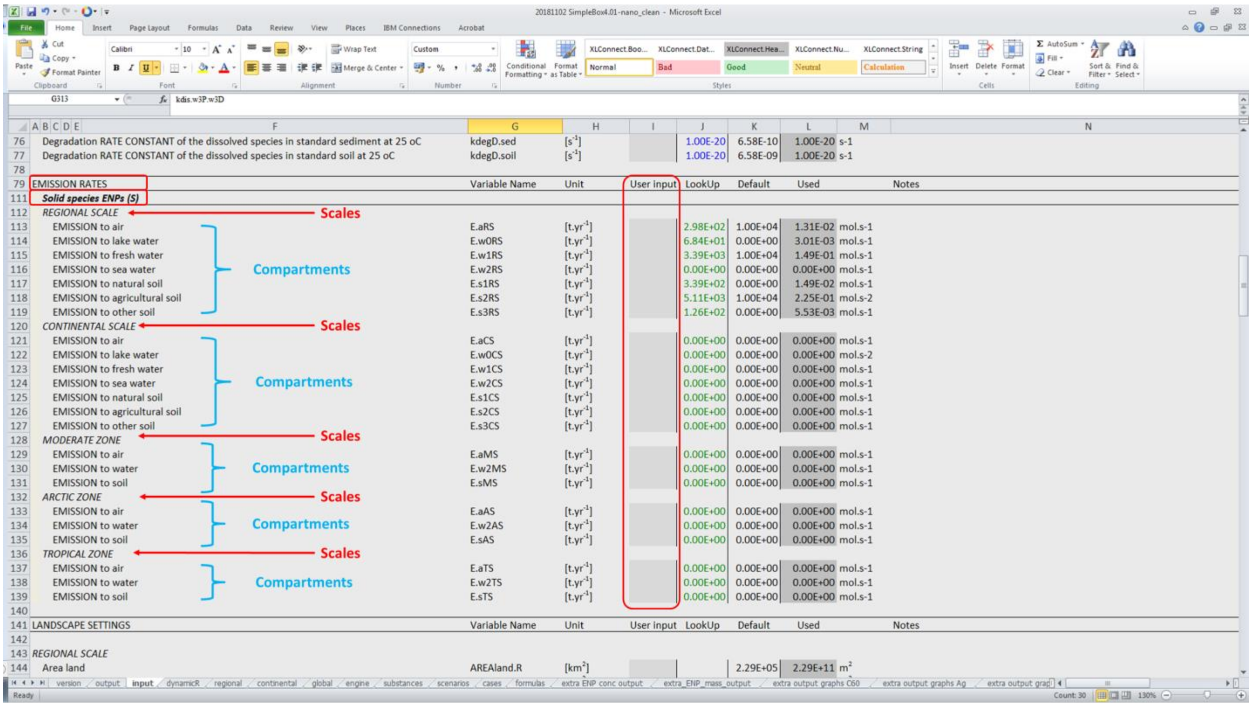


Figure 3. Inserting emission rates under user input

The emission rates inserted in the 'user input' column override any defaults or lookups referring to generic scenarios. In case there is no emission expected to a certain compartment within a certain scale, the user should enter the value of 0 in the assigned 'user input' cell instead of leaving the cells empty. This procedure ensures there are no emission rates simulated which are not intended by the user. Note that it is silently assumed that the materials are released as a 'freely dispersed' species.

2.5. Mass balance equations engine

SB4n is a classical multimedia mass balance modeling system ("box model") in which the masses, m (kg) of the nano- or micromaterial in the various environmental compartments (air, water, soil, etc.) are obtained as the steady-state solutions of the mass balance equations for all compartments:

$m = -A^{-1}e$

A represents the system matrix of rate constants (*s*−1), and *e* (kg·s−1) is the vector of rates of emission into the environment. The system matrix A holds (pseudo) first-order rate constants for (1) transport between compartments, (2) removal by transport to outside the system, (3) the rates at which the materials are taken up in aggregates or attach to the surfaces of larger particles, and (4) the rates at which the nano- or micromaterial dissolved, and (5) the rate the nano- or micromaterial may be subjected to removal processes such as degradation. SB4n's fate matrix and emission vector can be viewed under the sheet 'engine', the landscape settings and advective transport processes of the environmental system are described in Schoorl, Hollander et al. (2016).

3. PREDICTED ENVIRONMENTAL CONCENTRATIONS

The SB4n model delivers two sheets of output containing predicted environmental concentrations (PECs). The ‘nano micro output’ sheet displays the PECs for the solid nano- or micromaterials, whereas the ‘all species output’ also displays other species that are dissolved in water or sorbed to natural coarse particles or grains.

3.1. Nano- and micromaterial species

The PECs for nano- and micromaterials can be found under the tab ‘nano micro output’. The output sheet delivers PECs across the different scales and environmental compartments included in the SB4n model. Furthermore, the sheet delivers species concentrations of material in a nano- or microform occurring as free solid species (S), the alternate species (A) that are in a nano- or microform hetero-aggregated with natural colloid particles and the particulate species (P) that are in a nano- or microform attached to a natural coarse particle (Figure 10).

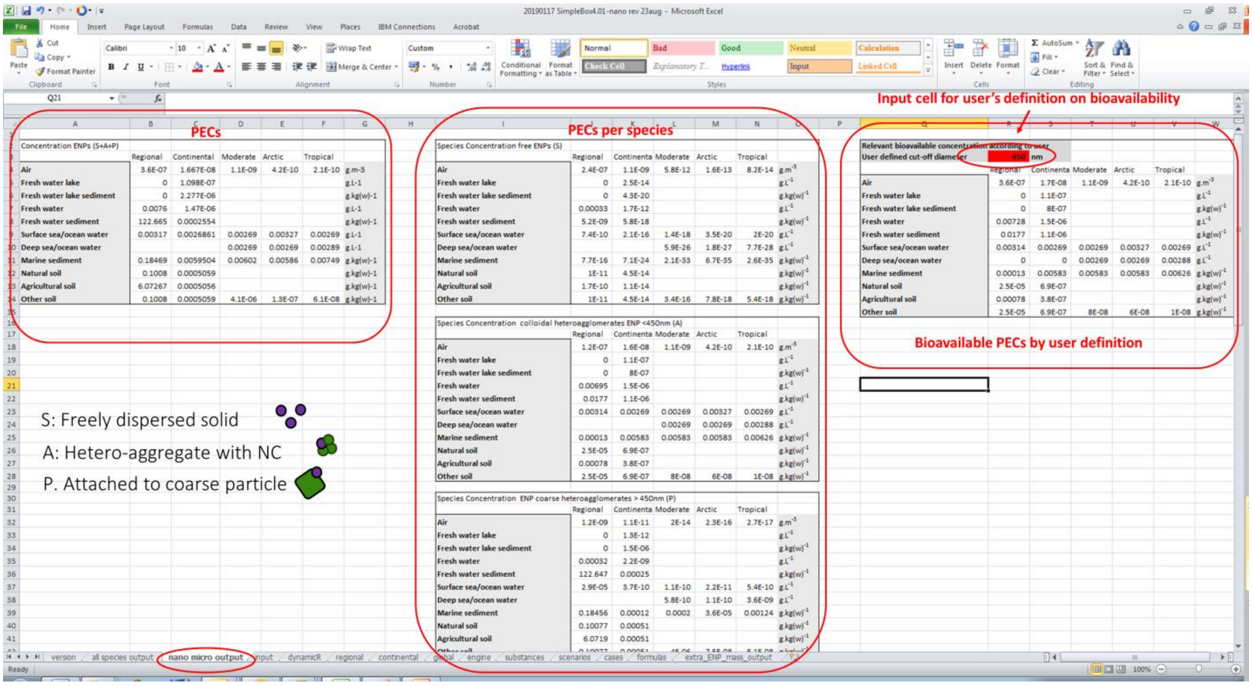


Figure 10. SB4n’s predicted environmental concentrations (PECs) material species in nano- or microform.

The ‘nano micro output’ sheet also provides an input cell for the user to define below what size the material is to be considered bioavailable. The predicted bioavailable concentrations relevant for the specific model run are calculated as the sum of the nano- or micromaterial species concentrations that are smaller than the user’s determined as cut-off diameter for bioavailability (Table 4).

Table 4. Summing of species concentrations relevant for bioavailability according to user

User defined cut-off diameter	Bioavailable concentration
User cut-off > Diameter P species	PEC (S+A+P)
Diameter A species < User cut-off < Diameter P species	PEC (S+A)
Diameter S species < User cut-off < Diameter A species	PEC (S)
User cut-off < Diameter S species	0

In earlier publications of the SB4n model (Meesters, Quik et al. 2016, Meesters, Peijnenburg et al. 2019), the cut-off diameter is set to 450 nm, because in environmental risk regulations the bioavailable fraction of a chemical or metal compound is arbitrary defined as the fraction that “is able to pass through a filter of <0.45 µm (ECHA, 2008). It is however uncertain whether the arbitrary split of <0.45 µm applies to environmental exposure estimation and risk assessment of nanomaterials (Koelmans, Diepens et al. 2015).

3.2. Other species

SB4n’s PECs for both dissolved and solid species can be viewed under the tab ‘all species output’ (Figure 11).

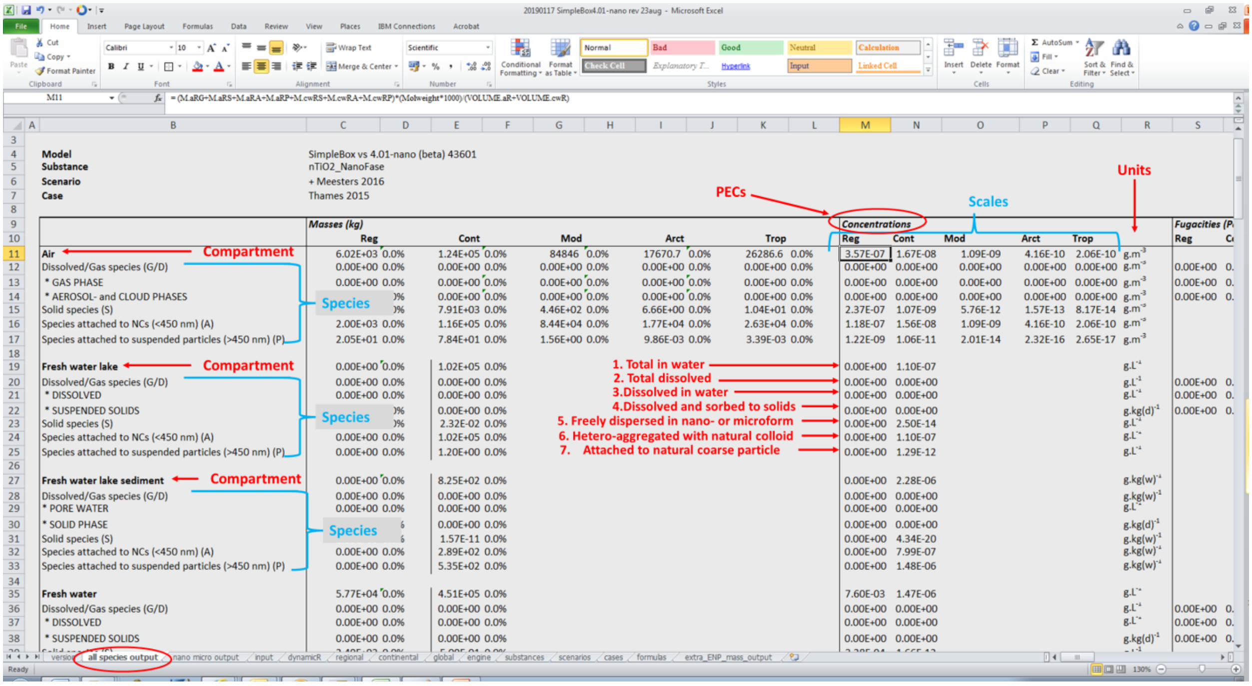


Figure 11. SB4n’s predicted environmental concentrations (PECs) under all species output.

The ‘output’ sheet is arranged per environmental compartment, species (Column B) and scale (Columns M-Q).

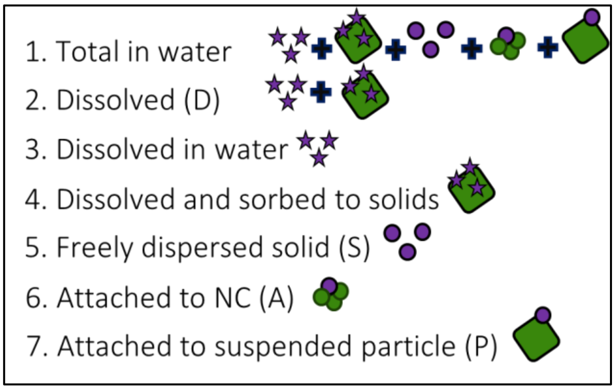


Figure 11. Substance forms considered within SimpleBox4nano.

The output sheet presents seven different predicted environmental concentrations per environmental compartment, one for each species considered in SB4n. The total concentration includes all species. The total dissolved (2) concentration refers to sum of the mass concentrations of the material that is dissolved into ions, atoms or molecules that is available for exposure or sorbed to solid particles. This concentration is also referred to as the dissolved species (D). The dissolved in water (3) refers to the dissolution products of the nano- or micromaterial that are available for exposure, whereas the 'dissolved and sorbed species' (4) are considered not bioavailable as they are sorbed to natural coarse particles. The freely dispersed solid species (S) refers to the parent nano- or micromaterial that is not dissolved, aggregated or attached (5). The alternate species (A) here refer to the species that are in a nano- or microform hetero-aggregated with natural colloid particles (6). The particulate species (P) refers to the species that are in a nano- or microform attached to a natural coarse particle (7). The relevant exposure concentration depends on the considerations of the user.

4. REFERENCES

Bergstrom, L. (1997). "Hamaker constants of inorganic materials." Adv. Colloid Interface Sci. **70**: 125-169.

Derjaguin, B. and L. Landau (1941). "Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes." Acta Physicochim **14**: 633-662.

Garner, K. L. and A. A. Keller (2014). "Emerging patterns for engineered nanomaterials in the environment: a review of fate and toxicity studies." Journal of Nanoparticle Research **16**(8): 1-28.

Hamaker, H. (1937). ""The London – van der Waals attraction between spherical particles"." Physica. **4**(10): 1058–1072.

Israelachvili, J. (1991). Intermolecular & Surface Forces.

Koelmans, A. A., et al. (2015). "Guidance for the prognostic risk assessment of nanomaterials in aquatic ecosystems." Sci Total Environ **535**: 141-149.

Lefevre, G. and A. Jolivet (2009). "Calculation of Hamaker constants applied to the deposition of metal oxide particles at high temperature." Proceed. of Intern.Conf. Heat Exchange Foul. and Clean **8**: 120-124.

Meesters, J. A. J., et al. (2014). "Multimedia Modeling of Engineered Nanoparticles with SimpleBox4nano: Model Definition and Evaluation." Environmental Science & Technology **48**(10): 5726-5736.

Meesters, J. A. J., et al. (2019). "A model sensitivity analysis to determine the most important physicochemical properties driving environmental fate and exposure of engineered nanoparticles." Environmental Science: Nano **6**(7): 2049-2060.

Meesters, J. A. J., et al. (2016). "Multimedia environmental fate and speciation of engineered nanoparticles: a probabilistic modeling approach." Environ. Sci.: Nano **3**(4): 715-727.

OECD (2019). Guidance Document for the testing and interpretation of data on dissolution rate and dispersion stability of nanomaterials for effects and exposure assessment. **1st DRAFT for WNT Comments (JULY2019)**.

Quik, J. T. K., et al. (2011). "How to assess exposure of aquatic organisms to manufactured nanoparticles?" Environment International **37**: 1068-1077.

Schoorl, M., et al. (2016). SimpleBox 4.0 : A multimedia mass balance model for evaluating the fate of chemical substances, Rijksinstituut voor Volksgezondheid en Milieu RIVM.

Verwey, E. J. W. and J. T. G. Overbeek (1948). Theory of the stability of lyophobic colloids. Amsterdam, Elsevier.

Appendix 1: Tables of DLVO derived attachment efficiencies

Annex I Table 1. DLVO derived attachment efficiencies between ENPs and natural colloids in fresh water

ENP		Diameter (nm)								
		1	10	20	30	40	50	100		
Zeta (mV)	20	1	1	1	1	1	1	1	1.00E-21	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.94	0.77	0.69	0.64	0.59	0.56	0.42		
	-20	0.88	0.55	0.39	0.27	0.19	0.13	2.80E-02		
	-30	0.83	0.38	0.18	0.08	0.036	0.017	9.50E-04		
	-40	0.78	0.25	0.075	0.021	0.0062	0.0021	3.40E-05		
	-50	0.74	0.17	0.031	0.0056	0.0012	0.00028	1.60E-06		
Zeta (mV)	20	1	1	1	1	1	1	1	5.00E-21	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.94	0.82	0.79	0.77	0.76	0.76	7.40E-01		
	-20	0.88	0.64	0.54	0.48	0.42	0.37	2.20E-01		
	-30	0.84	0.48	0.32	0.22	0.15	0.1	2.10E-02		
	-40	0.79	0.35	0.17	0.082	0.039	0.02	1.40E-03		
	-50	0.76	0.25	0.087	0.029	0.01	0.0038	1.07E-04		
Zeta (mV)	20	1	1	1	1	1	1	1	1.00E-20	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.95	0.85	0.85	0.85	0.85	0.86	0.87		
	-20	0.89	0.7	0.66	0.63	0.62	0.6	0.55		
	-30	0.84	0.56	0.46	0.39	0.33	0.29	0.14		
	-40	0.8	0.43	0.29	0.19	0.13	0.09	0.018		
	-50	0.77	0.33	0.17	0.088	0.045	0.024	0.0021		
Zeta (mV)	20	1	1	1	1	1	1	1	5.00E-20	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.96	0.95	0.97	0.98	0.98	0.99	0.99		
	-20	0.92	0.89	0.93	0.95	0.96	0.97	9.90E-01		
	-30	0.88	0.83	0.88	0.92	0.94	0.95	9.80E-01		
	-40	0.85	0.77	0.83	0.87	0.9	0.92	9.60E-01		
	-50	0.82	0.71	0.77	0.82	0.85	0.88	9.40E-01		
Zeta (mV)	20	1	1	1	1	1	1	1	1.00E-19	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.97	0.98	0.99	0.99	1	1	1		
	-20	0.93	0.96	0.98	0.99	0.99	1	1		
	-30	0.9	0.93	0.97	0.98	0.99	0.99	1		
	-40	0.88	0.91	0.96	0.98	0.99	0.99	1		
	-50	0.85	0.88	0.94	0.97	0.98	0.99	1		

Annex I Table 2. DLVO derived attachment efficiencies between ENPs and natural suspended coarse particles in fresh water

	Water	Diameter (nm)								
ENP		1	10	20	30	40	50	100		
Zeta (mV)	20	1	1	1	1	1	1	1	1.00E-21	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	1	0.96	0.89	0.81	0.69	0.54	4.50E-02		
	-20	0.99	0.89	0.62	0.26	0.067	0.14	5.20E-06		
	-30	0.99	0.77	0.23	0.024	0.0018	0.00014	4.90E-10		
	-40	0.99	0.61	0.054	0.0017	5.20E-05	1.60E-06	7.70E-14		
	-50	0.98	0.44	0.012	0.00015	1.90E-06	2.60E-08	2.60E-17		
Zeta (mV)	20	1	1	1	1	1	1	1	5.00E-21	
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	1	0.97	0.95	0.92	8.90E-01	8.50E-01	6.20E-01		
	-20	0.99	0.92	0.8	0.61	3.80E-01	1.90E-01	2.00E-03		
	-30	0.99	0.85	0.51	0.16	3.20E-02	5.60E-03	1.00E-06		
	-40	0.98	0.74	0.21	0.021	1.70E-03	1.30E-04	5.70E-10		
	-50	0.98	0.61	0.065	0.0026	9.70E-05	3.70E-06	5.60E-13		
Zeta (mV)	20	1	1	1	1	1	1	1	1.00E-20	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	1	0.98	0.97	0.96	0.95	0.94	0.93		
	-20	0.99	0.94	0.89	0.82	0.72	0.61	0.1		
	-30	0.99	0.89	0.72	0.44	0.2	0.071	0.0002		
	-40	0.99	0.82	0.44	0.11	0.019	0.00294	3.10E-07		
	-50	0.98	0.73	0.19	0.02	0.0016	0.00013	6.30E-10		
Zeta (mV)	20	1	1	1	1	1	1	1	5.00E-20	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	1	0.99	1	1	1	1	1.00E+00		
	-20	1	0.99	0.99	0.99	0.99	1	1.00E+00		
	-30	0.99	0.98	0.98	0.98	0.99	0.99	1.00E+00		
	-40	0.99	0.97	0.97	0.97	9.80E-01	9.80E-01	9.90E-01		
	-50	0.99	0.95	0.95	0.95	9.50E-01	9.50E-01	9.60E-01		
Zeta (mV)	20	1	1	1	1	1	1	1	1.00E-19	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	1	1	1	1	1	1	1		
	-20	1	1	1	1	1	1	1		
	-30	0.99	0.99	1	1	1	1	1		
	-40	0.99	0.99	1	1	1	1	1		
	-50	0.99	0.99	0.99	1	1	1	1		

Annex I Table 3. DLVO derived attachment efficiencies between ENPs and natural colloids in soil pore water

ENP	Soil	Diameter (nm)								
		1	10	20	30	40	50	100		
Zeta (mV)	20	1	1	1	1	1	1	1	1.00E-21	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.87	0.47	0.26	0.13	0.06	0.027	5.30E-04		
	-20	0.76	0.165	0.024	0.0029	0.00038	4.10E-05	3.90E-09		
	-30	0.67	0.052	0.0019	5.90E-05	2.00E-06	7.60E-08	5.30E-14		
	-40	0.597	0.017	0.000182	1.80E-06	2.00E-08	2.80E-10	2.70E-18		
	-50	0.54	0.0065	2.50E-05	9.30E-08	4.30E-10	2.50E-12	0		
Zeta (mV)	20	1	1	1	1	1	1	1	5.00E-21	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.87	0.56	4.10E-01	2.90E-01	2.10E-01	1.40E-01	0.018		
	-20	0.77	0.24	6.70E-03	1.60E-02	3.50E-03	7.90E-04	1.00E-06		
	-30	0.68	0.089	7.50E-03	5.40E-04	4.00E-05	3.30E-06	5.60E-11		
	-40	0.61	0.034	9.50E-04	2.40E-05	6.80E-07	2.20E-08	8.10E-15		
	-50	0.56	0.014	1.57E-04	1.70E-06	2.10E-08	3.10E-10	4.30E-18		
Zeta (mV)	20	1	1	1	1	1	1	1	1.00E-20	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.88	0.62	0.53	0.46	0.4	0.35	0.15		
	-20	0.78	0.31	0.13	0.051	0.018	0.0064	5.20E-05		
	-30	0.69	0.13	0.021	0.0027	0.00036	5.00E-05	8.40E-09		
	-40	0.62	0.057	0.0032	0.00016	8.80E-06	5.30E-07	2.60E-12		
	-50	0.57	0.026	0.00063	1.40E-05	3.60E-07	1.10E-08	2.50E-15		
Zeta (mV)	20	1	1	1	1	1	1	1	5.00E-20	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.9	0.85	0.89	0.91	0.94	0.99	9.80E-01		
	-20	0.82	0.67	0.7	0.75	0.79	8.20E-01	9.20E-01		
	-30	0.75	0.48	0.45	4.40E-01	4.20E-01	4.10E-01	3.00E-01		
	-40	0.69	0.33	0.23	1.50E-01	9.70E-02	5.90E-02	5.00E-03		
	-50	0.64	0.23	1.00E-01	4.00E-02	1.50E-02	5.80E-03	6.60E-05		
Zeta (mV)	20	1	1	1	1	1	1	1	1.00E-19	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.92	0.93	0.97	0.98	0.99	1	1		
	-20	0.85	0.85	0.92	0.96	0.98	0.98	1		
	-30	0.79	0.76	0.86	0.92	0.95	0.97	1		
	-40	0.74	0.66	0.77	0.86	0.91	0.94	1		
	-50	0.7	0.57	0.66	0.75	0.83	0.88	0.97		

Annex I Table 4. DLVO derived attachment efficiencies between ENPs and soil grains

ENP	Soil	Diameter (nm)								
		1	10	20	30	40	50	100		
Zeta (mV)	20	1	1	1	1	1	1	1	1.00E-21	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.99	0.83	0.39	0.07	0.008	0.00081	5.50E-09		
	-20	0.98	0.36	0.005	3.90E-05	2.50E-07	1.60E-09	1.00E-20		
	-30	0.97	0.057	3.80E-05	1.80E-08	8.50E-12	3.70E-15	0.00E+00		
	-40	0.96	0.0065	3.40E-07	1.40E-11	5.50E-16	2.00E-20	0		
	-50	0.95	0.00084	4.70E-09	2.20E-14	8.80E-20	0	0		
Zeta (mV)	20	1	1	1	1	1	1	1	5.00E-21	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.99	0.88	6.40E-01	2.90E-01	8.40E-02	1.90E-02	5.40E-06		
	-20	0.98	0.52	2.90E-02	6.10E-04	1.20E-05	2.10E-07	3.30E-16		
	-30	0.97	0.13	3.50E-04	6.40E-07	1.10E-09	1.80E-12	0		
	-40	0.96	2.00E-02	4.70E-06	8.80E-10	1.50E-13	2.60E-17	0		
	-50	0.95	3.10E-03	8.80E-08	2.10E-12	4.60E-17	0	0		
Zeta (mV)	20	1	1	1	1	1	1	1	1.00E-20	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.99	0.91	0.78	0.57	0.32	0.15	0.00064		
	-20	0.98	0.64	0.09	0.0047	0.00019	7.40E-06	5.40E-13		
	-30	0.97	0.23	0.0018	8.60E-06	3.80E-08	1.60E-10	0		
	-40	0.96	0.045	3.30E-05	1.90E-08	9.60E-12	4.80E-15	0		
	-50	0.95	0.0081	8.00E-07	6.30E-11	4.60E-15	3.30E-19	0		
Zeta (mV)	20	1	1	1	1	1	1	1	5.00E-20	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	0.99	0.97	0.98	0.98	0.98	0.99	1.00E+00		
	-20	0.99	0.93	0.89	8.40E-01	7.80E-01	7.10E-01	1.80E-01		
	-30	0.98	0.81	4.70E-01	1.40E-01	2.50E-02	3.90E-03	2.80E-07		
	-40	0.97	0.58	6.21E-02	2.50E-03	8.70E-05	3.00E-06	1.10E-13		
	-50	0.97	0.29	4.50E-03	4.00E-05	3.30E-07	2.60E-09	6.90E-20		
Zeta (mV)	20	1	1	1	1	1	1	1	1.00E-19	Hamaker (J)
	10	1	1	1	1	1	1	1		
	0	1	1	1	1	1	1	1		
	-10	1	0.99	1	1	1	1	1		
	-20	0.99	0.98	1	0.99	1	1	1		
	-30	0.98	0.95	0.96	0.97	0.97	0.98	1		
	-40	0.98	0.91	0.85	0.76	0.63	0.45	1.90E-02		
	-50	0.97	0.82	0.51	0.16	3.30E-02	5.70E-03	6.60E-07		