# Identification and preliminary analysis of update needs for EUSES

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# Summary

The current report is dedicated to a preliminary analysis of the needs for update and improvement of EUSES, which have been identified over the recent years The aim of this project was to collect, describe and rank various corrections, improvements and extensions of EUSES developed in different contexts over the past years since EUSES 2.1 was released.
The report describes extensions of the applicability domain for different types of chemicals and model improvements that affect a wider range of chemicals. In order to compare the urgency of the various improvements, a qualitative ranking method was developed.

While documenting the various extensions or improvements, it became clear that without extensive comparisons, only qualitative judgements could be made on the overall utility of the improvements and extensions, and how these compare to each other. The ranking method and corresponding criteria should thus be seen as a first attempt to differentiate between rather obvious improvements and to facilitate the discussion on those improvements where the need depends on more strategic issues regarding the goals and ambitions of a revised EUSES program.

The Top 10 of improvements showed that the criteria for chemical domain, impact and maturity have the largest influence on priority setting. As a general rule, those changes that affect exposure for a whole or several chemical classes at (at least) the local scale and are well described and implemented are given the highest weight. Even if a change for a certain type of chemical (e.g. gaseous chemicals) affects a relatively small number of chemicals, it can have a high score if the impact and maturity of the changes are estimated to be high.

## Table of Contents

# 1. Introduction to the project and aim

The current report is dedicated to a preliminary analysis of the needs for update and improvement of EUSES, which have been identified over the recent years. The project was commissioned by the European Chemical Agency (ECHA) to the Netherlands Institute for Public Health and the Environment (RIVM) under contract number ECHA/2014/253.

The European Union System for the Evaluation of Substances (EUSES) is a decision-support instrument developed in the context of the legislation on New Notified Substances, Existing Substances and Biocides, before the REACH legislation entered into force. EUSES was developed to enable government authorities, research institutes and chemical companies to carry out rapid and efficient assessments of the general risks posed by chemical substances.  The system is fully described in the extensive EUSES documentation (EC, 2003)  and is based on the EU Technical Guidance Documents (TGD) on Risk Assessment for New Notified Substances, Existing Substances and Biocides (JRC, ).  The most recent version of EUSES (version 2.1.2, 2012) contains all Emission Scenario Documents for biocides (JRC,2012).

Within the context of REACH, the EUSES program is called from within ECHA's tool CHESAR (ECHA,2014). CHESAR is meant as a tool for the chemical safety assessment under REACH and assists registrants to prepare their chemical safety reports and exposure scenarios for communication in the supply chain. Environmental exposure estimates provided by CHESAR are based on the fate model of EUSES 2.1.

The aim of this project was to collect, describe and rank various corrections, improvements and extensions of EUSES developed in different contexts over the past years since EUSES 2.1 was released.

The project results should help ECHA to:
1.	Identify specific modifications needed for extending the applicability domain of the fate modules in EUSES (SimpleTreat, SimpleBox) for different types of chemicals, e.g. metals, ionisable chemicals, gases and nanomaterials.
2.	Identify improvements and extensions of the fate modelling within EUSES with regard to distribution in the environment including the waste water treatment, and accumulation in the food chain.
3.	Improve the understanding of the impact of the extensions or improvements by documenting
    a.	What are the types of substances affected
    b.	Which part of the exposure assessment is affected and how
    c.	References to the EUSES sections which may be affected.
4.	Rank the various extensions and improvements that are identified.   Ranking criteria were developed that take into account the relevance for 3a and 3b.

# 2. Methods: Description of the collection of issues and ranking criteria

### 2.1. Subject collection and use of documents

The environmental fate calculations in EUSES 2.1 are based on the fate models SimpleBox (Den Hollander et al., 2004) and SimpleTreat (Struijs, 1996). Recently, new versions of SimpleTreat and SimpleBox have been developed. The improvements and extensions implemented in these model updates are based on a critical review of recent developments that were documented in Struijs (2013), Meesters et al. (2014), Schoorl (2014) and Hollander et al. ( in prep., 2014).
In addition to these model updates, the EU FP6 project OSIRIS produced a detailed review of needs for improvement of EUSES (Franco et al., 2011). Based on these key documents, a list of topics was developed and discussed with ECHA in the tendering phase of the project. These topics are discussed in Chapter 3.

The current project does not allow for an extensive review of every publication on the EUSES fate modules, bioaccumulation or human exposure via the environment. Essential literature was cited when new publications have been made available.  Availability of new versions of SimpleBox, SimpleTreat  and other relevant models will be documented including relevant links. For each proposal for change or update of EUSES it was documented if the changes analysed are already implemented in updated versions of SimpleBox, SimpleTreat or other relevant models.

This report does not cover developments with respect to the release module in EUSES.

### 2.2. Relevance criteria and subject ranking

To determine the relevance of the extension, improvements or additions, a ranking method and corresponding criteria were developed. The ranking method is based on the assumption that it is possible to distinguish the relevance for each relevance criterion between the different proposed changes.  Ranking of the different proposed changes is then possible based on the sum of the scores for each relevance criterion.

An approach was chosen, where the criteria and boundaries for the classes were decided based on the expectation that it would lead to sufficient differentiation and insight in the need for implementation. The ranking method and corresponding criteria should thus be seen as a first attempt to differentiate between rather obvious improvements and to facilitate the discussion on those improvements where the need depends on more strategic issues regarding the goals and ambitions of a revised EUSES program.

*Criterion 1: Type of substance affected*
3.      All (e.g., due to errors that need correction, conceptual improvements, model extensions)
2.      Sizeable (One or several Chemical classes)
1.      Limited number of substances

*Criterion 2: Exposure calculation impact* *
3.      High impact (e.g., significant errors, extensions to chemical domain etc) and relevant, i.e. taking registration volume into account
2.      Unknown (e.g, because not implemented yet)
1.      Relatively low impact (small effect on exposure)

*Criterion 3: Maturity of improvement \*\**
3. Documented and implemented
2. Documented but not implemented
1. Neither documented nor implemented

*Criterion 4: Verification/validation status \*\**
3. A more extensive model verification/validation has been performed
2. Model sub-model or process is verified on a limited number of chemicals
1. Model is not verified or validated

*Criterion 5: Type of improvement \*\*\**
2. Refinement to existing calculations
1. Conceptual improvement or extension

\* The exposure impact may be variable, depending on substance properties and the environmental compartment(s) of interest. This may hamper scoring the impact on exposure calculation. Class boundaries between high/medium/low may not be easy to establish, so it is proposed to distinguish 'high', 'relatively low' and 'unknown' (i.e, undefined impact).

During the scoring, it was found that only the improvements on nanoparticles could not be scored for exposure impact, due to the difficulty establishing the relevant metric for exposure. Therefore, it was decided to assign an exposure score of '2' to nanoparticles, and all others with a score of 1 or 3.

\*\* In an initial discussion on ranking criteria, it was decided not to mix up maturity of improvements (related to documentation and implementation) and verification or validation status. Due to the nature and complexity of multi-media models, true validation is problematic, as reported in the scientific literature. However, verification of submodels, processes etc. on data is often possible. It was therefore proposed to distinguish three levels of verification.

\*\*\* The type of improvement may play a role in the assessment of the relevance of the various subjects.   Most of the extensions discussed in this report can be seen as refinements to existing calculations, although as discussed in Chapter 3, some are actually corrections of errors for specific types of chemicals or process descriptions.
Other conceptual improvements may be relevant if this will allow the fate modules of EUSES to be more robust or better equipped for future improvements, e.g. anticipating certain scientific or technical developments. While scoring the various extensions (Chapter 3), it was found that the suggested changes for nanomaterials, parent –metabolite and the nested local scale could be termed conceptual extensions. Because the impact on the relevance rating of such rather complex changes is hard to quantify, we propose to actually assign a lower score to conceptual changes than to proposed changes that are extensions of existing model implementations.

## 2.3.  Subject description
Based on the documentation provided in section 2.1, an inventory of extensions, improvements and additions mentioned above was made.

For each subject identified as a relevant improvement or extension, a brief description is given and an impact assessment is provided, based on

i) <u>Proposed change</u>. What is the actual proposed change, including a brief rationale and a short description of the topic.

ii) <u>Part of the exposure assessment influenced</u>. Describes which part of the exposure assessment is affected and where relevant, a clear reference to the relevant EUSES sections.

iii) <u>Model input and output,</u> describing if and how model input and output would change.

iv) <u>Substances affected,</u> describing what type of chemicals are covered by the proposed change

v) <u>Implementation</u>, describing if and how the proposed changed are implemented.

vi) <u>Importance ranking</u>, with scores according to the ranking criteria, including a brief justification (see section 2.2).

vii) <u>References</u> to the scientific literature.

Based on the ranking of the subjects, a top 10 list of improvements was identified that is described in more detail in chapter 4 and 5.

# 3. Improvements and extensions

## 3.1. Extension of the applicability domain for different types of chemicals

Similar to most of the multimedia mass balance models used in environmental fate and exposure modelling (Cowan et al., 1995), EUSES is designed primarily for use with 'well-behaved' non-polar, hydrophobic organic chemicals, which are sufficiently characterised by vapour pressure and octanol-water partition coefficient. Many of the newly marketed chemicals, particularly pharmaceutically active ones, are known to fall outside the chemical domain for which EUSES was designed originally. The following describes how EUSES can be made fit to serve such chemicals.

### 3.1.1. Sparingly soluble chemicals

Proposed change

Many (inorganic) chemicals (e.g. most metal oxides, many metal salts, some organic substances) are released to the environment in pure solid or liquid forms that are not readily transformed into the environmentally active (dissolved) form. Currently EUSES does not distinguish between physical or chemical forms in which chemical substances may occur, or in which form they are released, thereby silently assuming that chemicals appear entirely in the dissolved form, at least instantaneously upon release in the environment. This may lead to serious overestimation of exposure concentrations (particularly so for metals in water), which is described well in the literature (Gandhi et al., 2010; Diamond et al., 2010). Slow solubility and its consequences for exposure estimation have also been described for nanomaterials.

This can be improved by modelling the process of dissolution in EUSES, as proposed by Meesters et al. (2013). Instead of assuming instantaneous dissolution for all chemicals and silent disregard of the form in which the substance is released, EUSES could be modified to take account of (i) the form in which the substance is released, and (ii) estimate the rate of formation of the dissolved form as a first-order process, characterised by a first-order dissolution rate constant.

Part of the exposure assessment influenced

The proposed change affects exposure concentrations (local and regional PECs) in water, sediment and biota, particularly for substances emitted in solid form to water. Accounting for slow dissolution would lead to lower predicted concentrations in water and higher concentrations in (the solid phases of) sediments.

Model input and output

Accounting for slow dissolution requires that additional information is available: (i) registrants must specify the form in which the chemical is released, and (ii) in case the chemical is released as a solid, a first-order rate constant for dissolution must be provided. Such information can be obtained by laboratory testing according to OECD Guideline 29 (2001).

The proposed change would result in more realistic PEC assessments; no new model output will be produced.

Substances affected

The proposed change will affect sparingly soluble chemicals, notably trace metal oxides and salts, emitted as solids to water.

Implementation

Implementation of the changes proposed to turn EUSES 'fit for nano', as described by Meesters et al., 2013 (section 3.1.6) would include accounting for slow dissolution of solids. Meesters' model is a prototype, available for research purposes in spreadsheet format. Implementation of slow dissolution only would be a minor effort, compared to model adaptation necessary for nanomaterials.

Importance ranking

| Type of substance affected | 2. A sizeable number of chemicals is affected, notably trace metal oxides and salts. |
|---|---|
| Exposure calculation impact | 3.  The impact may be large because current calculations may seriously overestimate exposure concentrations. |
| Maturity of improvement | 2. Documented but not implemented. |
| Verification/validation status | 2. Sub-model or process is verified on a limited number of chemicals; see Gandhi et al., 2010; Diamond et al., 2010. |
| Type of improvement | 2. Refinement of existing calculations. |

References

Diamond ML, N Gandhi N, Adams WJ, Atherton J, Bhavsar SP,  Bulle C, Campbell PGC, Dubreuil A,  Fairbrother A, Farley K, Green A, Guinee J, Hauschild MZ, Huijbregts MAJ, Humbert S, Jensen KS,  Jolliet O, Margni M, McGeer JC, Peijnenburg WJGM, Rosenbaum R, van de Meent D, Vijver MG (2010). The clearwater consensus: the estimation of metal hazard in fresh water. Int J Life Cycle Asses 15(2010), 143–147

Gandhi N, Diamond M, van de Meent D, Huijbregts M, Peijnenburg W, Guinée  J(2010).  New method for calculating comparative toxicity potential of cationic metals in freshwater: Application to copper, nickel, and zinc. Environmental Science and Technology, 44(2010), 5195–5201

Meesters JA, Veltman K, Hendriks AJ, van de Meent D (2013) Environmental exposure assessment of engineered nanoparticles: why REACH needs adjustment. Integrated environmental assessment and management 9(3):e15-26 doi:10.1002/ieam.1446

OECD (2001). Series on testing and assessment Number 29: Guidance document on transformation/dissolution of metals and metal compounds in aqueaous media. Paris. OECD document ENV/JM/MONO(2001)9.

### 3.1.2. Extremely soluble chemicals

Proposed change

It has been demonstrated that the standard EUSES approach fails to correctly predict atmospheric fate of extremely soluble chemicals. The reason is that, like most multimedia fate models, EUSES assume atmospheric deposition to be continuous (i.e. at one constant rate all the time). This is unrealistic, as wet deposition (wash-out, rain-out) occurs only during relatively short episodes. A model formulation has been worked out and published (Jolliet and Hauschild, 2006) that can be easily implemented in existing multimedia mass balance models. It is proposed to replace the EUSES

'drizzle' model of wet deposition by Jolliet and Hauschild's episodic rain model, as done in SimpleBox4 already (Hollander et al., 2014; see also section 3.2.3).

Part of the exposure assessment influenced
The proposed change will affect predicted concentrations in air, water and soil at the larger spatial scales; local PEC would not be affected.

Model input and output
The proposed change affects the way atmospheric deposition is calculated. No additional input is required. No additional output is generated.

Substances affected
The proposed changes are known to predominantly affect substances with relatively high water solubility and/or low vapour pressure, i.e. substances with high air-water partition coefficients. This would certainly apply to chemicals released in air, but present in the environment as dissolved species in water: e.g. organic acids with pKa below ~6 and permanently charged anionic salt species. For such chemicals, the adapted EUSES would predict considerably lower concentrations in air, and higher concentrations in soil and water.

Model input and output
The proposed change affects the way atmospheric deposition is calculated. No additional input is required. No additional output is generated.

Implementation
The proposed changes have been implemented and tested in various multimedia mass balance models. Implementation in EUSES could follow the implementation in SimpleBox 4, described by Hollander et al. (2014). Implementation in EUSES would be a relatively minor operation.

Importance ranking

| *Type of substance affected* | 2. A sizeable number of chemicals is affected, e.g. organic acids with pKa below ~6 and permanently charged anionic salt species. |
|---|---|
| *Exposure calculation impact* | 1. The impact may be large at the regional scale, the updated model would predict considerably lower concentrations in air, and higher concentrations in soil and water. However, local PEC is not affected. |
| *Maturity of improvement* | 3. Documented and implemented. |
| *Verification/validation status* | 2. Sub-model or process is verified on a limited number of chemicals (Jolliet and Hauschild, 2006) |
| *Type of improvement* | 2. Refinement of existing calculations. |

References

Jolliet O and Hauschild M (2005). Modelling the Influence of Intermittent Rain Events on Long-Term Fate and Transport of Organic Air Pollutants. Environ. Sci. Technol. 39, 4513-4522

Hollander A, Schoorl M, Van de Meent D (2014, in prep). SimpleBox 4.0: improving the model while keeping it simple. Environmental Modeling & Software. In preparation. SimpleBox 4.0 is available via http://www.rivm.nl/en/Topics/S/Soil_and_water/SimpleBox_4_0_tool

### 3.1.3. Gaseous chemicals

Proposed change

In Chemical Safety Assessments for REACH registrations of some highly volatile chemical substances, registrants have encountered and communicated (Russell, 2010) a perceived flaw in the local exposure calculation in soil according to the TGD. Local PEC calculation assumes that net transport from air to soil depends on the concentration in air (which is correct), but independent of the concentration in soil (which is incorrect), yielding erroneously high local concentrations in soil for chemical substances with extremely high vapour pressures, which readily volatilize from soil upon deposition.

It has been shown in an unpublished study (Van de Meent, 2010) that this problem can be solved by including equilibrium exchange processes in EUSES' local PEC calculation, which is currently not the case. It is proposed that the local PEC calculation in EUSES is reformulated, which requires a rather fundamental reformulation of the current (TGD-conform) approach. This can be achieved best by modelling local PECs (in air, water, sediment and soil) in interdependence, as done for the larger spatial scales already.

Part of the exposure assessment influenced

The proposed change would correct the error in the calculation of local PECs in soil. Local PECs in water would be influenced to a lesser extent; local PEC in air is not expected to change noticeably.

Model input and output

The proposed change affects the way atmospheric deposition is calculated. No additional input is required. No additional output is generated.

Substances affected

The proposed changes would affect substances with high vapour pressures and/or low water solubilities, i.e. substances with high air-water partition coefficients, which is the case for chemicals that are in gaseous form at ambient pressure and temperature. It would affect other extremely volatile chemicals as well.

Implementation

The problem of erroneous calculation of local PECs in soil is best solved by applying multimedia mass balance calculation of local PECs, as done for the larger spatial scales. It is recommended that a local spatial scale is nested inside the existing regional scale, as described in a draft RIVM report by Roelofs et al. (2003) – see section 3.2.4. Implementation of this change in EUSES is to be considered a relatively large effort.

Importance ranking

| | |
|---|---|
| *Type of substance affected* | 1. A limited number of chemicals is affected, with extremely high vapour pressures. |
| *Exposure calculation impact* | 3. The impact may be large, the updated model would predict considerably lower concentrations in soil for these chemicals. |
| *Maturity of improvement* | 3. Documented but not implemented. |
| *Verification/validation status* | 2. Sub-model or process is verified on a limited number of chemicals. |
| *Type of improvement* | 2. Refinement of existing calculations. |

References

Roelofs W and Van de Meent D. 2003. Development of a local scale in multimedia fate model SimpleBox. Bilhoven, Draft RIVM report 601200002/2003.

Russell M. 2010. Question about EUSES, e-mail correspondence with attachment, Examples of TRAM runs for GASES.doc. Personal Communication with D van de Meent, Radboud University Nijmegen. Wilmington, DA, USA, 17 July 2010.

Van de Meent, 2010. Response Dik Examples of TRAM runs for GASES, e-mail correspondence with attachment. Personal Communication with M Russell, DuPont. Nijmegen, The Netherlands, 12 August, 2010.

### 3.1.4. Metals

Proposed change

Modelling local and regional PEC/PNEC ratios for direct exposure in EUSES requires that solids-water partition coefficients are available. For neutral organic substances, standard QSAR routines (based on $logK_{OW}$) are built in to estimate partition coefficients. No QSARs are available to estimate partition coefficients for metals. Current EUSES requires that, for metals, situation-specific effective water-sediment partition coefficients are known and can be used to describe the overall equilibrium distribution of metals over its various chemical forms, including adsorbed species, in the environment. Such knowledge is often unavailable, so that partitioning, e.g. from water to sediment, cannot be accounted for in chemical safety assessment, which may lead to serious overestimation of the (bio)availability of metals. It has been shown in the literature how calculation of trace metal speciation can be used to better describe metal partitioning and metal availability (Gandhi et al., 2011). It is proposed to expand calculation in EUSES of sediment-water, sediment-porewater and soil-porewater equilibrium constants and bioconcentration factors for metals with a basic metal speciation calculation according to Gandhi. Van de Meent and Huijbregts (2012) have proposed and explained how such an expansion can be realized for the USEtox model (Rosenbaum et al. 2011).

This implementation is to be added in USEtox 2.0, to be released soon in 2015 (Fantke et al. 2015). The current EUSES model cannot be used to calculate PEC/PNEC ratios metals and other ionized or ionizing substances from basic physical-chemical substance properties provided in IUCLID. In order to use EUSES to this end, risk assessors should feed the EUSES calculation with metal- and site-specific solids-water partition coefficients and bioconcentration factors. The current EUSES model does allow users to overrule the partition coefficients offered by default – note that these EUSES defaults apply to neutral organics only, and should never be used for metals! – by empirically

obtained partitioning information, but users will hardly ever have such information available, so that in practise, use of EUSES for calculating RCR of metals should be regarded misuse. The proposed model improvement would solve this for all metals for which biotic ligand modelling (BLM) according to Gandhi et al. (2010) is available.

It should be noted that no standardised modelling procedures exist for predicting secondary poisoning or human intake via the environment. The highly situation- and exposure-level -specific bioaccumulation and biomagnification cannot be solved by Gandhi's model improvement.

To use available empirical data to describe (and override EUSES default) ratios of internal and external metal concentrations in plants and higher organisms could be misleading, since metal accumulation is usually non-linear and exposure concentration-dependent. More details are provided in section 3.3.

Part of the exposure assessment influenced

The proposed change implements an estimation routine to calculate effective solids-water partition coefficients for metals. This will enable prediction of exposure concentrations in local and regional waters, in case measured partition coefficients are not available from IUCLID.

Model input and output

After the proposed change, input of empirical knowledge of situation-specific metal partition coefficients will no longer be necessary; such partition coefficients will be estimated by EUSES. No additional output is generated.

Substances affected

The proposed change will allow calculation of PECs for most trace metals, at least for the metals studied by Gandhi et al. (2011).

Implementation

The guidance provided by Van de Meent and Huijbregts (2012) for implementing the proposed change in USEtox could be followed directly to make the proposed changes to EUSES. Making the changes would require a moderately large (re)coding effort.

Importance ranking

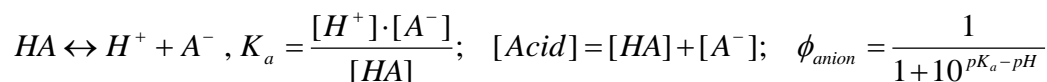| | |
|---|---|
| *Type of substance affected* | 1. A limited number of chemicals can be taken into account, because the underlying speciation model needs to be available for each specific metal. |
| *Exposure calculation impact* | 3. The impact may be large, the updated model could predict considerably lower bioavailability of metals, depending on environmental conditions. |
| *Maturity of improvement* | 2. Documented but not implemented. |
| *Verification/validation status* | 2. Sub-model or process is verified on a limited number of chemicals. |
| *Type of improvement* | 2. Refinement of existing calculations. |

References

Fantke P, Bengoa X, Chappert B, Guignard C, Hauschild M, Huijbregts M, Jolliet O, Kounina A, Magaud V, Margni M, McKone T, Rosenbaum R, Van de Meent D, Schoorl, M, Van Zelm R (2015). USEtox 2.0 Documentation. Lyngby, Denmark. The USEtox team. To be released soon.

Gandhi N, Diamond ML, Huijbregts MAJ, Guinée JB, Peijnenburg WJGM, Van de Meent D (2011). Implications of considering metal bioavailability in estimates of freshwater ecotoxicity: examination of two case studies. Int J Life Cycle Assess (2011) 16: 774–787.

Rosenbaum RK, Huijbregts MAJ, Henderson AD, Margni M, McKone TE, Van de Meent D, Hauschild MZ, Shaked S, Li D, Gold LS, Olivier Jolliet O   (2011). USEtox human exposure and toxicity factors for comparative assessment of toxic emissions in life cycle analysis: sensitivity to key chemical properties. Int J Life Cycle Assess (2011) 8: 710-727.

Van de Meent D and Huijbregts MAJ. 2012. USEtox for substances that occur in different physical and chemical forms. Unpublished report for the USEtox consortium. Nijmegen, 6 February, 2012.

### 3.1.5. Ionizing chemicals (organic acids and bases)

<u>Proposed change</u>

Current EUSES assumes all chemical substances to occur in one chemical form (viz. in its original, uncharged form) only. Any transformation of the original chemical into another chemical form is considered 'losses'; products of association or dissociation reactions are considered 'degradation products' (daughter products, metabolites). While this is generally sufficient to describe the partitioning behaviour of the relatively inert hydrophobic chemicals that were often used in the past, it is insufficient for many of the new chemicals which rapidly equilibrate between various forms of occurrence in the natural environment, all of which may be equally 'active'. This is the case for many organic acids and bases. When organic acids are brought into water, they partly dissociate to yield an equilibrium mixture of the original undissociated neutral acid and its dissociated anionic form:

$$HA \leftrightarrow H^+ + A^- \, , \, K_a = \frac{[H^+] \cdot [A^-]}{[HA]}; \quad [Acid] = [HA] + [A^-]; \quad \phi_{anion} = \frac{1}{1 + 10^{pK_a - pH}}$$

Similarly, organic bases associate with protons in water to yield their cationic (conjugated) acid form:

$$HB^+ \leftrightarrow H^+ + B \, , \, K_a = \frac{[H^+] \cdot [B]}{[HB^+]}; \quad [Base] = [HB^+] + [B]; \quad \phi_{cation} = \frac{1}{1 + 10^{pH - pK_a}}$$

As the different chemical forms usually have very different inter-media partition coefficients and chemical reactivities, behaviour of the mixtures depend on the the degree of association/dissociation. Current EUSES can account for one species (viz. the original, uncharged form) only, so that environmental fate of partly ionized chemicals cannot be described. In order to model (partly) ionized chemicals, two additional pieces of information must be accounted for (i) partition coefficients of neutral and ionic forms of the chemical, and (ii) degree of association/dissociation. By combining these two elements, 'overall' (i.e. of all chemical forms together) inter-media partition coefficients can be calculated.

Franco and Trapp (2008, 2010) have shown how partition coefficients of partly ionized substances can be estimated as the mass-weighted average of the partition coefficients of the neutral and ionized species, using the degree of ionization as weighting factors. They have derived and published useful QSAR equations to derive partition coefficients of the original (neutral) species and the (alternate) ionic species:

$\log K_{OC} \text{(acid, original (neutral) form)} = 0.54 \cdot \log K_{OW} + 1.11$

$$\log K_{OC}\,(\text{acid, alternate (anionic) form}) = 0.11 \cdot \log K_{OW} + 1.54$$

$$\log K_{OC}\,(\text{base, original (neutral) form}) = 0.37 \cdot \log K_{OW} + 1.7$$

$$\log K_{OC}\,(\text{base, alternate (cationic) form}) = pKa^{0.65} \cdot \left( \frac{K_{OW}\,(pH7)}{1 + K_{OW}\,(pH7)} \right)^{0.14}$$

By using Franco and Trapp's expressions to calculate intermedia equilibrium constants for neutral and ionic species of organic acids and bases, EUSES can account for pH-dependent intermedia partitioning of partly ionized organic acids and bases.

Part of the exposure assessment influenced

The proposed change implements an estimation routine to calculate effective air-water and solids-water partition coefficients for ionizable organic acids and bases. Without this modification, situation-specific empirical knowledge of effective partition coefficients must be entered into the model. Such empirical knowledge can be inserted by registrants into EUSES, but is usually not available from IUCLID, so that exposure concentrations for organic acids and bases cannot be modelled.

Model input and output

This modification requires that, in addition to the usual substance properties, acid dissociation constants (pKa) of the substances (for acids pKa, for bases pKa of the conjugated acid) are known. No additional output needs to be generated.

Substances affected

The proposed change affects predicted intermedia partitioning (and hence predicted concentrations) of organic acids and bases that have pKa's of such values that lead to a significant degree of ionization at environmental pH, which is the case for many strong and moderately weak acids and bases. Model predictions for ordinary, non-ionizing (neutral) organic chemicals remain unchanged.

Implementation

This model modification is extensively studied and described in detail by Franco and Trapp (2010) and summarised in Franco et al (2011). The Multimedia Activity Model for Ionizable compounds (MAMI) is available in spreadsheet format from the authors. Franco's algorithms have been applied and tested by Van Zelm et al. (2013) in their USES-LCA model. Van de Meent and Van Zelm (2011) have proposed to the USEtox consortium to implement these changes in the USEtox model, providing ratioale and a recipe for implementation. It is proposed that EUSES is adapted according to this recipe, following the example of SimpleBox 4.0 (Hollander et al., 2014).

Importance ranking

| | |
|---|---|
| *Type of substance affected* | 3. A large number of chemicals is affected. It was estimated that approximately one third of preregistered REACH substances is mostly ionised at pH 7 (Franco et al. 2010). |
| *Exposure calculation impact* | 3. The impact may be large, e.g. depending on the degree of ionisation at environmental pH |
| *Maturity of improvement* | 3. Documented and implemented. |
| *Verification/validation status* | 2. Sub-model or process is verified on a limited number of chemicals. |
| *Type of improvement* | 2. Refinement of existing calculations. |

References

Franco A et al., (2011) OSIRIS Deliverable D3.1.17 (6th Framework Program, EU, Project no. 037017) Recommendations for adaptations of ECHA Guidance Documents and EUSES.

Franco, A., Trapp, S. (2008). Estimation of the soil-water partition coefficient normalized to organic carbon for ionizable organic chemicals. Environmental Toxicology and Chemistry, Vol. 27, No. 10, pp. 1995–2004.

Franco, A., Trapp, S. (2010). Multimedia activity model for ionizable compounds - Validation study with 2,4-D, aniline and trimethoprim. Environ. Toxicol. Chem., 29(4), 789–799.

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### 3.1.6. Nanomaterials

Proposed change

The standard EUSES approach of the TGD cannot adequately model the environmental fate and exposure of engineered nanomaterials (ENMs) (Arvidsson et al. 2011; Meesters et al. 2013; Quik et al. 2011). The proposed change will make EUSES 'fit for nano'. This means that ENMs will be added to the current implementation of EUSES for conventional chemicals.

In relation to conventional chemicals, ENMs are of a particulate nature, meaning that they are not dissolved in solution but exist as two distinct phases (E.g. solid and liquid) which are thermodynamically unstable. For this reason, the fate of ENMs cannot be defined by thermodynamic equilibrium coefficients for partitioning. However the tendency of ENMs to reach (a more) thermodynamic stable state still makes it possible to define rates for transformation and transport. These transformation and transport rates can be quantified using already established theories, E.g. for sols or suspensions (Lyklema 2005; Petosa et al. 2010), aerosols (Friedlander 2000; Ketzel and Berkowicz 2004; Kulmala et al. 2001) and particle filtration (Tufenkji and Elimelech 2004). This gives the possibility to implement all relevant processes in a multi-media fate model as used in EUSES. No new conceptual transport processes are added; only the calculation methods for the transport rates are different. This means that new input parameters are needed which are specific for ENMs.

In addition to new ENM specific input parameters, new species need to be added. Just like conventional chemicals, ENMs interact with their environment, such as with organic matter and naturally occurring suspended particulate matter (SPM) in water. However, for ENMs these interactions have a much larger effect on their fate due to the inherently larger forces that drive this interaction (Afrooz et al. 2013; Batley et al. 2013; Huynh et al. 2012; Quik et al. 2012; Quik et al. 2014; Therezien et al. 2014; Velzeboer et al. 2014; Zhou et al. 2012). For this reason, the fate of heteroaggregates of ENMs with SPM need to be taken into account. Also dissolution of ENMs needs to be taken into account, meaning the transformation of ENMs to their dissolved counterpart, e.g. Ag (s) to Ag+(aq).

An additional note is that due to difficulty and therefore lack of available measurement techniques of ENMs in the environment, measurements currently do not contribute to the exposure assessment of ENMs. This leaves the use of modelling techniques for a first tier of exposure assessment. However this also means that any type of validation of modelling approaches is currently not possible, only sub-model or specific processes can be verified or validated, but at relatively low environmental complexity.

In summary EUSES can be changed to include nanomaterials for the reasons:

- Current model implementation not suitable due to fundamental differences between behaviour of dissolved and particulate chemicals.
- Different scientific fields have already developed models for describing fate of particulates, including nanomaterials.
- No adequate measurement methods of exposure concentrations of ENMs. Estimates based on modelling are the only option in the foreseeable future.

Part of the exposure assessment influenced

The currently implemented exposure assessment of conventional chemicals is not affected. This change adds the capacity to do an exposure assessment of nanomaterials and particulate chemicals in general. The model matrix would report additional species of a chemical in the nanomaterial form freely available or attached to other natural particulates. No adaption of the compartments or geographical scales as currently implemented in EUSES is required.

Model input and output

±112 new input parameters are needed as (default) internal variables of the model . Four additional internal PECs are calculated for different chemical species: (1) freely available ENMs, (2) heteroaggregates of ENMs with smaller natural colloids (Ø <450 nm), (3) heteroaggregates of ENMs with larger particulate matter (Ø >450 nm) and (4) the dissolved counterpart.

Output of exposure concentrations (PECnano,local;  PECnano,regional), is done as for conventional chemicals. For each spatial scale, 2 additional PECs are needed: the sum of all nano species that should be considered 'dispersed' or 'bound'. See the implementation section for more details.

Substances affected

Conventional chemicals are not affected, a new chemical class is added for ENMs. Because of the importance of natural particulate matter on ENM fate and likely effect on bioavailability to organisms, two species of ENM are taken into account: freely dispersed and attached to natural particulate matter.

Implementation

Meesters et al. (2014) have recently described a model definition: "SimpleBox4nano", which can be implemented in SimpleBox 4.0 in order to make it 'fit for nano'. This model can be seen as a standalone multimedia fate model for nanomaterials consisting of only one spatial scale for each environmental compartment. SimpleBox4nano uses nonequilibrium colloidal behaviour to describe transport of ENMs between environmental compartments. In order to capture the effect that natural particulate matter has on ENM fate two different fractions of natural particulate matter are considered. The interaction of ENMs with smaller natural colloids (Ø <450 nm) or larger particulate matter (Ø >450 nm). The heteroagglomerates that are formed when ENMs attach to particulate matter are more prone to gravitational forces compared to freely dispersed ENMs. Natural particulate matter plays a role in water, sediment, air and soil compartments, the agglomeration and attachment mechanisms have specific implementations in each of these compartments. In addition to the ENM species (in particulate form) the traditional implementation of simplebox can be used to model the conventional counterpart of the ENM (in dissolved form), which is the dissolved compound: e.g. Ag+ for Ag ENMs. This is currently not implemented in SimpleBox4nano, this addition would take dissolution of ENMs into account. This results in the technical capability of calculating PEC's for 4 different material species in all the environmental compartments at the different spatial scales. These 4 species are: (1) freely available ENMs, (2) heteroagglomerates of ENMs with smaller natural colloids (Ø <450 nm), (3) heteroagglomerates of ENMs with larger particulate matter (Ø >450 nm) and (4) the dissolved counterpart. However, in current effect assessment of ENMs at most two species of ENMs are considered which are the total and dissolved concentration of ENMs. The total ENM concentration can be calculated using the sum of species 1 to 3.

In general the implementation of SimpleBox4nano in EUSES would result in the following changes:

- 3 extra species in addition to conventional dissolved chemical for every compartment.
- New process formulations for speciation: aggregation and agglomeration between ENMs and natural particulate matter.
- Addition of particle dissolution.
- New model formulations for transport processes of particulate species.
- Addition of cloud water compartment for wet deposition of particulate species
- Output of exposure concentrations (PECnano,local, PECnano,regional), as done for conventional chemicals. The sums of all nano species that should be considered 'dispersed' or 'bound' would be reported to serve that purpose

These changes would result in an increase of the calculation matrix from 33x33 as used in SimpleBox 4.0 to 160x160 in the new 'fit for nano' variant. In order to fill the matrix, an additional 488 transport and removal rates need to be calculated or given. This requires about 112 new input parameters, to be specified in the model.

These input parameters are mainly related to ENM, natural colloid and SPM related characteristics such as size and density and related to descriptors of their behaviour in the respective environmental compartments, air, soil, water and sediment. Important descriptors are related to the efficiency and rate of attachment of ENMs to e.g. natural colloids and SPM. However, it might also be possible implement a more modular approach, where a 'plug-in' nano-simplebox model would be used in an only slightly adapted version of SB4.0.

Furthermore there are currently several projects working on developing standard test methods for several of the key input parameters related to aggregation and dissolution of ENMs, e.g. OECD (Kuhnel and Nickel 2014).

Currently RIVM is working on implementing the SimpleBox4nano model in SimpleBox 4.0. The model should eventually be made available through the RIVM website as SimpleBox 4.1 (for nano). Model definitions of the SimpleBox4nano model are available through the article and supporting information by Meesters et al. (2014).

Ranking

| *Type of substance affected* | 2. Chemical class: Nanomaterials and particulate chemicals |
|---|---|
| *Exposure calculation impact* | 2. Unknown |
| *Maturity of improvement* | 2. Documented not implemented |
| *Verification/validation status* | 1. Basic model formulations included for air, soil and water are verified independently of each other, this verification is not at scales used in EUSES. |
| *Type of improvement* | 1. Conceptual extension |

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### 3.1.7. Photolytically labile chemicals

<u>Proposed change</u>

Current EUSES offers users who prepare REACH registrations the possibility to account for photolytic stability of chemical substances by entering an environmental half-life for photolysis, which is often hard to find in (literature) reports of photolysis studies. Often, no more than half-lives of pure chemicals, measured with artificial light sources, under laboratory conditions are readily available to risk assessors (OECD, 2008). Castro Jiménez and Van de Meent (2011) have reviewed the available literature on photolytic degradation of chemical substances under environmental conditions and have proposed calculation tools to derive the environmentally relevant half-lives that EUSES accepts as input.

It is proposed that the formulations suggested by Castro Jiménez are implemented in EUSES. This will allow risk assessors to predict exposure concentrations, using only the information available from technical studies that report results of the standard photolysis test (OECD, 2008)).

The current EUSES model requires registrants enter field-specific half-lives of chemicals due to direct or indirect photolytic degradation into EUSES, without assistance offered from the model. This limits the applicability of EUSES for including the influence of photodegradation on environmental half-lives of persistent, but potentially photolabile, chemicals. Implementation of this change would offer risk assessors the option to evaluate the influence of photodegradation on persistent, only photolytically degradable, chemicals at larger spatial scales.  This is an element in the 'P' assessment of chemicals where environmental fate can be studied using fate modelling, supporting e.g. further P(BT) assessment for REACH.

Part of the exposure assessment influenced
The proposed change will affect exposure concentrations at the larger spatial scales (continental and global).

Model input and output
Evaluation of the influence of photodegradation on the persistence of chemicals in the environment requires that photolytic half-lives in environmental media are available, which is usually not the case. Application of the proposed change allows users to estimate half-lives under field conditions, which EUSES needs as input, from the half-lives or rate constants measured under laboratory conditions (OECD, 2008), which may be available from IUCLID. No additional output will be generated (unless the user is interested in the generated 'field relevant half-life for phototransformation').

Substances affected
The proposed change will affect exposure concentrations (PEC) in water and sediment for persistent chemicals that may undergo photolytic breakdown in the environment.

Implementation
Castro Jiménez and Van de Meent (2011) have described how first-order rate constants for photolytic degradation under environmentally relevant conditions can be (and should be) derived from information from studies under laboratory conditions, in cases where photolytic half-lives in the environment are not available from IUCLID. They have tested the proposed formulations by implementing them in SimpleBox vs. 3, available from the authors. This implementation can be copied into EUSES with relatively little coding effort.

Importance ranking

| Type of substance affected | 1. Substances that are persistent and where photolysis could be the dominant rate for removal from the dissolved fraction in the water column (both freshwater and seawater). |
|---|---|
| Exposure calculation impact | 1. Relatively low, currently EUSES does not take photolysis rates (determined in the lab) directly into account. If done properly, the outcome will usually be that photolysis will usually not be relevant under field conditions for persistent chemicals.  However, the transfer from lab to field-relevant rates will be supportive for the P assessment. |
| Maturity of improvement | 2. Documented not implemented |
| Verification/validation status | 2. Basic model extension for photolysis in water is verified |
| Type of improvement | 2. Refinement of existing calculations. |

References
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### 3.1.8. Simultaneous parent-metabolite(s) modelling

<u>Proposed change</u>

Many chemical substances undergo rapid transformation in the environment into daughter products that may be more persistent and/or more toxic than the substance used originally, DDT being the best documented example. The transformation may even be part of the application design, where the chemical daughter product is the actual active agent. In such situations, good risk assessment practise requires that exposure from relevant transformation products is evaluated simultaneously with evaluation of the chemical parent. Current EUSES does not provide possibility for such simultaneous parent-daughter evaluation, as EUSES merely regards formation of transformation products, even formation of potentially harmful metabolites, as 'degradation', resulting in loss of the parent only.

It is proposed that EUSES is upgraded to become capable of calculating (non-equilibrium) concentrations different chemical species of one chemical in parallel, as done regularly in pesticide risk assessment. Various studies have pointed out how parent-daughter relations in environmental fate can be modeled and how existing models can be adapted to include prediction of exposure concentrations for transformation products of the parent compound (Fenner et al., 2002; Cahill et al., 2003; Van Zelm et al., 2010; Franco et al., 2011; Ng et al. 2011). An example is the study by Van Zelm et al. (2008), who have created a multi-species version of the EU TGD spreadsheet to serve industry in analysing the environmental fate of perfluorinated octanoic acid (PFOA) based chemical substances.

<u>Part of the exposure assessment influenced</u>

The proposed change will affect the outcome of exposure calculations for the local and regional scales. Most of all, the proposed change will enhance possibilities for using EUSES in PBT assessment or risk assessment of degradation products. The guidance for environmental exposure assessment (Chapter R.16.5, ECHA (2012)) states that if stable and/or toxic degradation products are formed, these should be considered in the exposure assessment. The identification of the environmental compartment(s) is of primary importance for a PBT, vPvB or /and risk/exposure assessments. The compartments of highest exposure and risk should be tested first if testing is required for refinement of risk assessment. Multi-media modelling is employed in the exposure assessment to evaluate the environmental compartment(s) of primary concern (R.7.9.4.3, ECHA 2014b). We interpret this to be relevant for both parents and for degradation products.

<u>Model input and output</u>

*Input*: The information requirements for use of the MS-MM model are the same as for the EUSES regional model, except all physico-chemical properties and degradation rates required for the parent chemical are also required for the degradation products. In addition, the fractions of formation, or amount of each product generated from the parent, are needed. These need to be derived from the degradation pathway. The current guidance cites CATABOL, MultiCase and UM-BBD) (R.7.9.3.1). In addition the use of UMPPS has been recently described by Ng et al. (2011).

The multi-media compartments are not changed. In terms of the compartment characteristics (e.g. volume) and descriptions of mass transfer (e.g. rain rate, soil depth, sedimentation rate) the parameterization is identical to the EUSES model. The difference lies only in the inclusion of the degradation products and the ability to simultaneously calculate the persistence (P) and predicted environmental concentrations (PECs) of the parent compound and all its considered degradation products.

*Output*:  PECs are now available for the parent and the (main) metabolites simultaneously for all relevant compartments.

Substances affected

The proposed change will affect the assessment of chemicals that are transformed into persistent and/or toxic daughters.

Implementation

Van Zelm et al. (2008) have implemented multi-species mass balance modelling in the EU TGD spreadsheet, which closely follows EUSES 2.0. Van Zelm's spreadsheet model could serve as an example for recoding EUSES to simulate more than one chemical species. A similar implementation was done in the OSIRIS project, documented by Ng et al. (2011), however using a different format. Transformation of the current EUSES into a multi-species model should be considered a major task.

Importance ranking

| Type of substance affected | 2. Sizeable, not limited to chemical classes. Chemicals that are amenable to (bio)degradation. |
| --- | --- |
| Exposure calculation impact | 3. Expected to be high, many chemicals will form metabolites that could be more persistent and or toxic than the parent chemical; all depending on the rates of formation and degradation. |
| Maturity of improvement | 3. Documented and implemented |
| Verification/validation status | 2. Extensive model extension is verified |
| Type of improvement | 2. Refinement of existing calculations. |

References

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## 3.2. Model improvements

RIVM has recently released updated versions of SimpleTreat (Struijs, 2014) and SimpleBox (Hollander et al., 2014) and made them publicly available[1] ([http://www.rivm.nl/en/Topics/S/Soil_and_water/-SimpleBox_4_0_tool](http://www.rivm.nl/en/Topics/S/Soil_and_water/-SimpleBox_4_0_tool)). Many major and minor changes, made to the models since the releases of former versions (vs 3 for both models, both released in 2004, both used in EUSES 2.1), have been implemented in this new release. Some adjustments are corrections of issues that really should be considered erroneous in the models; most adjustments made reflect new insights in multimedia mass balance modelling and should be considered structural model improvements. A number of the changes introduced in SimpleBox 4 are deserve to be implemented in EUSES, too.

### 3.2.1. Structural improvements of the SimpleBox model

Proposed change

A number of changes introduced in SimpleBox 4 regard the parsimony principle, which, in Mackay's formulation of Occam's razor, reads: 'simple where possible, complex where needed' (Mackay, 2003). In the interest of parsimony, not often used or unneccessary compartments were removed from SimpleBox3, making room for others, while keeping the model simple (Hollander et al., 2014). The nested local spatial scale, which was first added in version 3[2] was omitted from SimpleBox 4, as it added complexity to the model without bringing added value to day-to-day fate model use, in which local scale calculation, although essential in REACH, is not frequently used. As it appears now, it could be re-introduced in version 4.1 (see section 3.2.4), to serve a new purpose. The same applies to the vegetation compartments, which were introduced in version SimpleBox version 2. Likewise, the complicated suspended solids bookkeeping, which has been part of SimpleBox ever since version 1, has been traded by assuming constant net sedimentation rate, which serves the same modelling purpose without its inevitable complexity. These and other minor examples of model complexity that have proven to be unnecessary for useful exposure assessment may be dropped from EUSES, too. Removing them may turn the model leaner (and thus more efficient and 'elegant'), but should be considered as luxury, as leaving them in does no harm.

In another line or reasoning, adding a few new compartments may be improvements that are worth following, mainly operating at higher than regional scales:
1. Addition of a large freshwater compartment at the continental scale
2. Addition of deep ocean compartments

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[1] SimpleTreat v4.0 will be released by early 2015 on the RIVM website.
[2] Not implemented as such in EUSES.

ad 1: current EUSES systematically models too little freshwater, which leads to underestimation of amounts of chemical in continental and global fresh water reservoirs, and to underestimation of the chemical residence times residence at continental scales; addition of large mountain water reservoirs solves this.

ad 2: persistent, relatively water soluble chemicals accumulate in oceans, but mainly hold up in the 100 m deep mixed upper layer; modelling upper and deep ocean water separately could account for this phenomenon.

These changes have been tested systematically and found useful by Schoorl (2014).

Part of the exposure assessment influenced
These structural adjustments influence PEC calculations at the larger spatial scales mainly.

Model input and output
No additional input parameters are foreseen. The adjusted model would generate new PECs for freshwater reservoirs and deep ocean compartments, which could/should be considered optional.

Substances affected
It has been shown that effects of these adjustments on calculated PECs are small for nearly all chemicals.

Implementation
SimpleBox 4 ([http://www.rivm.nl/en/Topics/S/Soil_and_water/SimpleBox_4_0_tool](http://www.rivm.nl/en/Topics/S/Soil_and_water/SimpleBox_4_0_tool)) and its technical descriptions (Brandes et al., 1996; Den Hollander et al., 2002; Schoorl, 2014; Hollander et al., 2014) are available as template for recoding EUSES.

Importance ranking

| *Type of substance affected* | 3. Structural changes that affect all chemicals |
| --- | --- |
| *Exposure calculation impact* | 1. Expected to be relatively small at local and regional scale |
| *Maturity of improvement* | 3. Documented and implemented |
| *Verification/validation status* | 2. Model changes were verified |
| Type of improvement | 1. (mostly) conceptual changes |

References

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### 3.2.2. Episodic rain

Proposed change

As described in section 3.1.2 for extremely soluble chemicals, most multimedia fate models, including the exposure modelling in EUSES, assume atmospheric deposition to be continuous (i.e. at one constant rate all the time), which is unrealistic. The recommendation of 3.1.2, that the alternative process formulations tested and published by Jolliet and Hauschild (2006) are implemented in EUSES instead of its traditional 'drizzle deposition model', is repeated and underpinned here.

Part of the exposure assessment influenced

The proposed change will affect predicted concentrations in air, water and soil, in particular those at the larger spatial scales (e.g. regional); local PECs would not be affected.

Substances affected

The proposed changes are known to predominantly affect substances with relatively high water solubility and/or low vapour pressure, i.e. substances with high air-water partition coefficients.

Implementation

The proposed changes have been implemented and tested in various multimedia mass balance models. Implementation in EUSES could follow the implementation in SimpleBox 4, described by Hollander et al. (2014). Implementation in EUSES would be a relatively minor operation.

Importance ranking

| *Type of substance affected* | 2. Structural changes that affect very soluble chemicals |
|---|---|
| *Exposure calculation impact* | 1. Expected to be relatively small at regional scale |
| *Maturity of improvement* | 3. Documented and implemented |
| *Verification/validation status* | 2. Sub-model or process is verified on a limited number of chemicals (Jolliet and Hauschild, 2006) |
| Type of improvement | 2. Refinement of existing calculations. |

References

Jolliet O and Hauschild M (2005). Modelling the Influence of Intermittent Rain Events on Long-Term Fate and Transport of Organic Air Pollutants. Environ. Sci. Technol. 2005, 39, 4513-4522

Hollander A, Schoorl M, Van de Meent D. SimpleBox 4.0: improving the model while keeping it simple. Environmental Modeling & Software. In preparation.

### 3.2.3. Correction for depth-dependent concentration in soil

Proposed change

Multimedia mass balance models typically assume compartments to be well-mixed, and that all processes obey first-order kinetics. This is the case also for soils, which are usually poorly mixed across depth. In real soils, concentrations of pollutants usually decrease exponentially with depth, in accord with theoretical understanding. At the soil-air interface, concentrations are found to be greater than the depth-averaged value. At the bottom of the (imaginary) top soil layer, concentrations are usually well below average. Assuming soils to be well-mixed leads to underestimation of volatilization and to overestimation of leaching. Mis-estimation of process rates from soils with depth-dependent soil concentration may be great, particularly for chemicals with low penetration depths (Hollander et al., 2007). This flaw has been recognized early in the development of multimedia mass balance calculation (Cowan et al., 1995; Brandes et al., 1996; Thibodeaux, 1996), but adequate correction for it has been proposed much later only. Hollander et al. (2004) have worked out a correction method, based on known or theoretically derived penetration depths of substances. Hollander's corrections have been implemented in SimpleBox 4, and are proposed here for implementation in EUSES.

Part of the exposure assessment influenced

The proposed change affects concentrations at all spatial scales in soil and air.

Model input and output

No additional input parameters. No changes in outputs.

Substances affected

The largest effects should be anticipated for substances that penetrate to small depths only, so that average concentrations in soil are much smaller than concentrations at the soil-air interface. Small penetration depths are expected (and observed) for substances that strongly adsorb to the solid phase of soil and/or rapidly degrade.

Implementation

Use of inhomogeneity correction factors is well described by Hollander et al. (2004) and can be implemented in EUSES with minor coding effort.

Importance ranking

| | |
|---|---|
| *Type of substance affected* | 2. Sizeable, mostly substances that strongly adsorb to the solid phase of soil and/or rapidly degrade |
| *Exposure calculation impact* | 3. Expected to be relatively high at local and regional scale for the relevant chemicals |
| *Maturity of improvement* | 3. Documented and implemented |
| *Verification/validation status* | 2. Sub model or process is verified |
| Type of improvement | 2. Refinement of existing calculations |

References
Brandes LJ, Den Hollander AH, Van de Meent D. 1996. SimpleBox 2.0: a nested multimedia fate model for evaluating the environmental fate of chemicals. Bilthoven, RIVM report 719101 029

Cowan C, Mackay D, Feijtel T, Van de Meent D, Di Guardo A, Davies J, Mackay N. 1995. The multimedia model: a vital tool for predicting the fate of chemicals. SETAC Press, Pensacola FL, USA.

Hollander A, Hessels L, De Voogt P, Van de Meent D. 2004. Implementation of depth-dependent soil concentrations in multimedia mass balance models. SAR and QSAR in Environmental Research 15, 457-468.

Hollander A, Baijens I, Ragas A, Huijbregts M, Van de Meent D. 2007. Validation of predicted exponential concentration profiles of chemicals in soils. Environmental Pollution 147, 757-763.

Thibodeaux LJ. 1996. Environmental chemodynamics: movement of chemicals in air, water and soil. New York, Wiley, 1996.

### 3.2.4. Nested local scale

Proposed change

At the time of conceptualization of the TGD and EUSES, local exposure calculation could not be done in full multimedia mode, as for the larger spatial scales. Although internal consistency called for a nested (i.e. global-continental-regional-local) approach to calculation of PECs at all spatial scales, a separate calculation of near-source (local) PECs had to be chosen instead. This unfortunate situation has never been corrected, although possibilities for improvement have been suggested. Not only has the lack of elegance yielded modelling results that were often hard to communicate, cases of plain error have been reported (see section 3.1.3). It is proposed that this internal model inconsistency that has existed ever since the conceptualization of the EU TGD, is corrected by implementing the nested model structure proposed by Roelofs et al. (2003) more than a decade ago. This would turn the calculation of PECs at local, regional and larger scales internally consistent. Parametrization of the nested local environment could be chosen to result in local concentrations that are approximately equal to the PECs calculated from the current, separate local EUSES model. Nesting the local PEC calculation inside the current regional spatial scale would also provide practical possibilities to accomodate the some adjustments proposed by ECHA in sections 3.3.4, 3.3.5 and 3.3.6.

Part of the exposure assessment influenced

This modification replaces the separate local scale of EUSES by a conceptually more correct nested local calculation. Implementation of this modification, which we believe should have been done long ago, also corrects the error in local PEC calculation in soil, mentioned in 3.1.2. The proposed change would affect the calculation of local PECs, leaving larger scales unaffected.

Model input and output

The adjusted model would run from the same inputs as used for the separate local scale calculation. The same outputs would be produced.

Substances affected

The aim of the proposed change is to not affect most substance at all; e.g. the dimensioning and parameterisation of the local scale should fit with the assumptions and scenarios for the current implementation of the local scale. However improvements that are possible for e.g. gaseous chemicals (see section 3.1.3) and the possibility to adapt the soil compartment to relevant (agricultural) soil emissions (see section 3.4.3.) will affect several classes of chemicals.

Implementation

Nested local scale modelling, according to Roelofs et al. (2003) has been implemented, used and tested in SimpleBox since the release of SimpleBox version 3 (Den Hollander et al., 2002). The local spatial scale was removed from SimpleBox in version 4 (Hollander et al., 2014) in the interest of parsimony, but has been re-introduced in the SimpleBox4 version that is now in use in the EU project 'SOLUTIONS', to allow analysis of local scale emission and exposure. The 'SimpleBox4solutions' spreadsheet will be documented as part of the SOLUTIONS project, and will be available as template for recoding EUSES. Implementation of nested local PEC modelling in EUSES should be considered a major coding effort.

Importance ranking

| *Type of substance affected* | 2. Sizeable; depending on changes made to the local scale scenarios |
|---|---|
| *Exposure calculation impact* | 3. Expected to be relatively high at local scale for the relevant chemicals |
| *Maturity of improvement* | 3. Documented and implemented |
| *Verification/validation status* | 2. Sub model or process is verified |
| Type of improvement | 1. Conceptual changes |

References

Roelofs W and Van de Meent D. 2003. Development of a local scale in multimedia fate model SimpleBox. Bilhoven, Draft 601200002/2003, August 2003.

Den Hollander HA, Van Eijkeren JCH and Van de Meent D. 2002. SimpleBox 3.0: multimedia mass balance model for evaluating the fate of chemicals in the environment. Unpublished RIVM report. Bilthoven, August 2002.

### 3.2.5. STP model update

Proposed change

Recently, SimpleTreat has been updated to take account of various new developments (Struijs, 2014). The model structure of SimpleTreat has not changed with respect to version 3.1. The adaptations can be grouped into three categories.

1. Flexible definition of wastewater properties, based on revised default or variable settings of existing parameters. In SimpleTreat 3.1, a fixed part (2/3) of the solids in domestic sewage is assumed to settle in the primary clarifier and a fixed part of the total BOD (biological oxygen demand) in raw sewage is dissolved. The remaining (also fixed) part resides in the solids. In version 4.0, these partitions can be chosen. This modification makes it possible to simulate the fate of chemicals in industrial wastewater (site specific situation), by setting some operational parameters of the STP by the user/ registrant:
   - Defining the activated sludge process, based on revised or more flexible settings of existing parameters: Sludge Rentention Time (SRT), Hydraulic Residence Time (HRT) and BOD (biologic oxygen demand) load. As shown in a recent study (Struijs et al., in prep.), these parameters, particularly the residence time (HRT) of sewage in the treatment facility, greatly

affects the elimination of moderately persistent chemicals during treatment of (industrial) waste water.

- Default values of the concentration of suspended solids in the Solids Liquid Separator (SLS) and in effluent have been lowered (Table 6 in Struijs et al.).

Table 1 Flow characteristics of raw sewage. Values in the last column are default settings typical for communal wastewater produced daily by one inhabitant (PE)

| symbol | meaning | Units | default |
|--------|---------|-------|---------|
| Q | Sewage flow | $m^3 \cdot d^{-1} \cdot PE^{-1}$ | 0.2 |
| SO | Mass of sewage solids | $kg \cdot d^{-1} \cdot PE^{-1}$ | 0.09 |
| BOD | Mass of $O_2$ binding material in sewage | $kg \ BOD \cdot d^{-1} \cdot PE^{-1}$ | 0.06 |

Table 2 Properties of raw sewage. Values in the last column are default settings representing communal wastewater

| symbol | Meaning | units | default |
|--------|---------|-------|---------|
| FB | Fraction BOD in sewage solids | - | 0.5417 |
| FS | Fraction sewage solids removed by primary settler | - | 0.667 |
| $foc_S$ | Fraction organic carbon in sewage solids | - | 0.3 |
| $d_S$ | Density of sewage solids | $kg \cdot L^{-1}$ | 1.5 |

2. A number of operational parameters have been updated to reflect a change in average operational conditions:
Default SLR and fixed suspended solids in effluent. The fixed parameter with respect to the concentration of suspended solids has been adjusted by a factor of 4. The concentration in SimpleTreat 3.1 was set at 30 mg dry weight/L and could be varied by the modeller. In version 4.0, it is set at 7.5 mg dry weight/L, which better reflects modern installations that treat domestic wastewater. The default value for the sludge loading rate (SLR) is now 0.1, instead of 0.15 kg/kg/d. The increase of the treatment rate in the EU and therefore also the average loading of STPs justifies this new default.
These parameter adjustments affect all uses and local and regional scales, but differently for different chemicals.

3. Partitioning of ionizing organic chemicals.
Ionic species have partition coefficients that may differ considerably from those of their neutral original species. The error is largely dependent on the degree of ionization, which, in turn, depends on the pKa of the substance and the pH of the environment. Recently, QSARs have become available to predict intermedia partitioning of partly ionized organic acids and bases, taking account of the above. SimpleTreat 4.0 is adapted to estimate partition coefficients of (partly) ionized substances to organic carbon according to algorithms described by Franco et al. (2009, 2013a), in pricesely the same way as implemented in SimpleBox 4, and described in section 3.1.5. Effects compared to SimpleBox 3.1 are shown in Struijs (2014, Ch.7).

Part of the exposure assessment influenced
The changes affect only the outcome of the SimpleTreat calculation at the local and regional scale (see EC 2004, section II.4.3.) : percentages released to air, surface water and soil (with sludge) will undergo noticeable change.

Model input and output

As described under 3.1.5, modelling ionizable substances requires that pKa are available as input to the new model calculation. No changes in output parameters.

Substances affected

All substances are affected by new default or variable settings for characteristics of the STP or sewage properties. This allows for claimed higher realism in current STP treatment and a wider range of STP operation than currently possible.

Acids and bases are affected, due to improved formulation of dissociation into neutral and charged species, and its accompanying QSARs for estimation of Koc for acids and bases.

Implementation

SimpleTreat 4.0 has implemented the changes 1-3 mentioned above. It is available in the following versions, documented in Struijs (2014):

- Version 4.0, standalone Windows version (to be released early 2015) via http://www.rivm.nl
- Version 4.0, spreadsheet version with an option to revert to Version 3.1 for comparison purposes (available via authors of this report on request).

Importance ranking

| | |
|---|---|
| *Type of substance affected* | 3. In principle, all substances are affected. In addition, predictions for ionisable organic substances (acids and bases) have been improved. |
| *Exposure calculation impact* | 3. A high impact can be expected for acids and bases, depending on the pKA of the substance. For some other parameters related to operational parameters of the STP, the may be relatively low. |
| *Maturity of improvement* | 3. Documented and implemented |
| *Verification/validation status* | 2. Most of the basic submodels are verified independently, however not as part of the SimpleTreat model and parameterization. Basic model formulations included for air, soil and water are verified independently of each other, this verification is not at scales used in SimpleTreat. |
| *Type of improvement* | 2. Refinement of existing calculations |

EC (2004) European Union System for the Evaluation of Substances 2.0 (EUSES 2.0). Prepared for the European Chemicals Bureau by the National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands (RIVM Report no. 601900005).

Franco A, Fu W, Trapp S (2009). The effect of pH on the sorption of ionizable chemicals: Modeling advances. Environ Toxicol Chem. 28:458–464.

Franco A, Struijs J, Gouin T, Price O (2013a). Evolution of the sewage treatment plant model SimpleTreat: applicability domain and data requirements. Integr Environ Assess Manag. 9: 560-568

Franco A, Struijs J, Gouin T, Price O (2013b). Evolution of the sewage treatment plant model SimpleTreat: use of realistic biodegradability tests in probabilistic model simulations. Integr Environ Assess Manag. 9: 569-579.

Struijs, J (2014). SimpleTreat 4.0: a model to predict fate and emission of chemicals in wastewater treatment plants. Background report describing the equations. Report 601353005, RIVM Bilthoven The Netherlands.

Struijs, J, Van de Meent D et al. (2015). Reparametrization of SimpleTreat 4.0 to simulate fate of persistent chemicals during treatment of industrial waste water flows. Water Research. In preparation.

### 3.3. Fate and accumulation in food chains for secondary poisoning and human exposure

Improvements were identified for the fate and accumulation of organic chemicals in biota and food chains (summarised by Franco et al., 2011) that are used to estimate bioconcentration potential in various trophic levels for prediction of secondary poisoning and human exposure via the environment.

In the OSIRIS project (a 6th FP program, EU ref.nr. Project no. 037017) the human daily dose predicted by EUSES and OSIRIS was compared for chemicals with a wide range of environmental partitioning properties. This comparison revealed significant differences between the two model predictions for transfer of chemicals to humans from the environment. The most important causes were differences in the predicted exposure via fish and vegetables, but smaller differences were also found for transfer via dairy products and meat. In general, the OSIRIS model predicted higher exposure to humans than EUSES for all but the superhydrophobic chemicals (i.e. those with a high octanol-water and octanol-air partition coefficients). This is consistent with another recent model comparison study where EUSES was compared to and found to yield lower predictions of human exposure than the mechanistic RAIDAR model (Arnot et al., 2010).

In another study (Rorije et al, 2011), bioaccumulation for fish is assessed as part of a PB(T) screening method. This can also be applied to EUSES as detailed below in section 3.3.1, as a competing simpler approach to that advocated by the OSIRIS project.

In order to be consistent with adapting EUSES for ionogenic organic chemicals (IOCs), uptake of IOCs in biota could also be improved (see REACH guidance on IR&CSA R7c, Appendix R7.10-1). Recent studies suggest that improvements for bioconcentration in fish can be made here as well (Fu et al. 2009, Armitage et al. 2013). However, accumulation in other consumption sources for human exposure are not as well advanced and consistency over all food sources seems not yet within reach (Franco et al., 2011, section 2.4.2).

Predicting metal concentrations in biota (fish and other food sources) with EUSES should general ly not be advocated. Metal bioaccumulation is not driven by log Kow  and concentration factors (e.g. BCF/BAF/BSAF/ BMF etc.) should not be regarded as constant for metals.

 Many processes will affect  bioaccumulation of metals. Essential elements such as zinc or copper can be accumulated or sequestered as part of homeostatic regulation for e.g. enzymatic and metabolic reactions which does not match with the bioconcentration concept for organic chemicals.
 A large volume of metal – and species-specific research shows that certain metal compounds are known to bioaccumulate in tissues . However,  the use of bioconcentration factor (BCF) and bioaccumulation factor (BAF) values is not supported when applied as generic  tools in  risk assessment  (Fairbrother et al, 2007, MERAG).  This is mostly due to the large dependency on exposure concentrations , environmental chemistry and species characteristics.
For regional assessments, BAF/BCFs should be expressed as a function of media chemistry and metal concentration for particular species (or closely related organisms). For local or site-specific assessments, single-value BAF/BCFs can be relevant because extrapolation across different exposure conditions is not intended. However, the relevancy of the BAF/BCFs for the local scenario would need to be established.

Trophic transfer can be an important route of exposure for metals (eg. (methyl)mercury and cadmium), although biomagnification of inorganic forms of metals in food webs is not a general phenomenon (Fairbrother et al, 2007, MERAG).

### 3.3.1. Bioccumulation in fish

Proposed change
It is proposed to replace the equations in the TGD for bioaccumulation of neutral organic chemicals in the aquatic food chain with updated equations to estimate the bioconcentration factors (BCF) and biomagnification factors (BMF), based on e.g. Franco et al., 2011 or Rorije et al. 2011.

Many improved methods are available and discussed elsewhere (e.g. Environment UK 1999, Arnot et al. , 2010) and additional consensus seeking may be needed to decide on the best overall approach. The choice for an updated model depends on the reliability of the model, the chemical domain that is covered by the model, and the appropriateness for risk assessment due to an explicit treatment of prediction uncertainty or degree of conservativeness.

This is especially significant for strongly bioconcentrating/bioaccumulating chemicals (log Kow >5) where potential biotransformation can have a great impact on the predicted fish BCF and associated risks for human consumption. The current approach in EUSES does not take biotransformation into account while the newer methods do.
In addition, biomagnification in the fish food chain (i.e., accounting for the fact that predatory fish are consumed as well; BMFs are needed to go up the food chain from a small fish to a predatory fish) is not taken into account in the calculations for fish consumed by humans in EUSES. It is not clear why the BMFs are not also employed in the calculations of human intake of chemicals via fish.

Part of the exposure assessment influenced
The exposure assessment as described in section II.5.1 (EC 2004) is affected, i.e. concentrations in fish (freshwater and saltwater). The comparison between the OSIRIS model and EUSES showed that the two models predict significantly different concentrations in fish, in particular for high KOW chemicals (Franco et al, 2011).

The revised BCFs are needed for calculating the RCR for birds and mammals (intermediate or top-predators) as identified in the following EUSES screenshot for the environmental risk characterisation, and detailed in section II.6.1.7 of the EUSES manual (EC 2004):
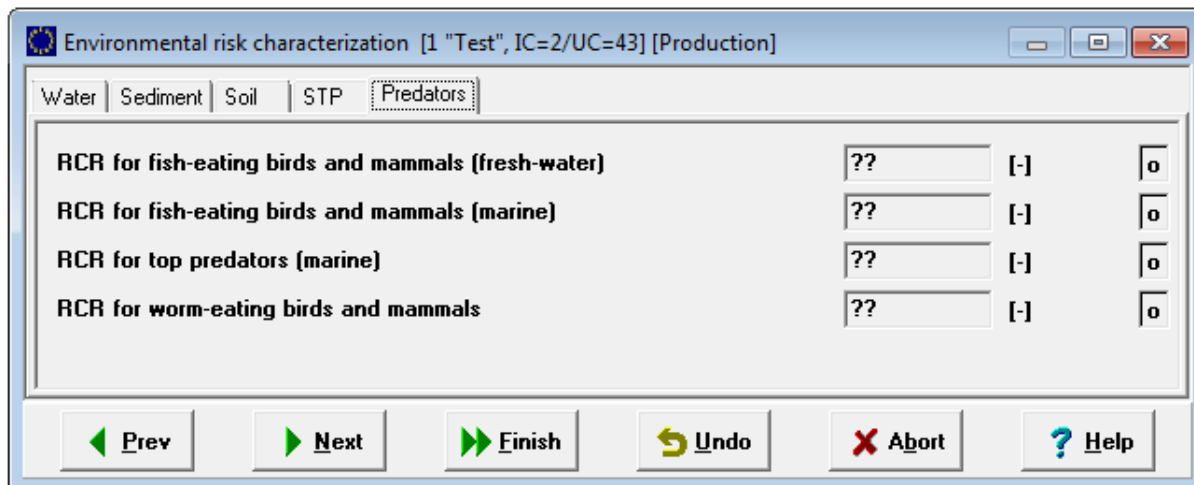
Model input and output
For input, both models (Franco et al., 2011; Rorije et al. 2011) require the same substance properties and environmental concentrations as the EUSES fish model (i.e. log $K_{OW}$ and the chemical's freely dissolved concentration in water). In addition, the biotransformation half-life in fish is required in both models.

The output of the refined bioaccumulation assessment remains the same.

Substances affected
In principle, all substances that undergo an assessment for secondary poisoning are affected due to the changes implemented, but on a general note, bioaccumulation is mostly of concern for substances with a log Kow value $\geq$ 5.  In addition, substances that undergo significant biotransformation will also be affected.

Implementation
Franco et al. (2011, OSIRIS model) suggested an improved model for a piscivorous fish feeding exclusively on a planktivorous fish (section 2.4.1.1.) The fish sub-model has a default parameterization that was based on the zooplankton – herring – cod food chain in the Baltic Sea. Therefore, two fish concentrations are reported: in a fish feeding on zooplankton and a predatory fish feeding on planktivorous fish. The current EUSES model only considers the first fish trophic level as food source where the potential biomagnification of (highly) lipophilic substances in the next trophic level for fish is ignored.

Rorije et al. (2011, section 2.2.2, (P)B score) used the REACH guidance R11 (ECHA, 2014, Appendix R11-1) as the basis for deriving an improved generic $BCF_{max}$ estimate for the first trophic fish level, without biotransformation

$$\log BCF_{max} = \frac{34.43}{2.93 \cdot (2 \cdot \pi)^{0.5}} \cdot e^{-0.5 \cdot \left( \frac{\log K_{ow} - 6.52}{2.93} \right)^2}$$

$BCF_{max}$ is then subsequently corrected for biotransformation, based on USE EPA EPIWeb v4.0.
An estimate for the half-life due to metabolism is calculated by the program BCFBAF v3.00.
This procedure can be seen as a more conservative RIVM modification of the overall BCFBAF model of EPA to correct for a too high biotransformation rate as predicted for specific known chemicals.

Importance ranking

| Type of substance affected | 2. Sizeable; Chemicals are affected with bioaccumulation potential with log Kow > 4. |
|---|---|
| Exposure calculation impact | 3.  The impact for bioaccumulating substances may be relatively high, due to additional bioaccumulation that is modelled in food chains. |
| Maturity of improvement | 2. Documented but not implemented for EUSES. |
| Verification/validation status | 2.  Submodel or process is verified.  The Franco model is verified on PCBs. Both models use empirical data to derive the BCF equations. |
| Type of improvement | 2. refinements to existing calculations. |

References

Armitage JM, Arnot JA, Wania F, Mackay D (2013). Development and evaluation of a mechanistic bioconcentration model for ionogenic organic chemicals in fish. Environ Toxicol. Chem 32: 115–128.

Arnot JA, Mackay D, Parkerton TF, Zaleski RT, Warren CS (2010). Multimedia modelling of human exposure to chemical substances: the roles of food web biomagnification and biotransformation. Environ Toxicol Chem 29: 45-55.

EC (2004). European Union System for the Evaluation of Substances 2.0 (EUSES 2.0). Prepared for the European Chemicals Bureau by the National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands (RIVM Report no. 601900005).

ECHA (2014). Guidance on Information Requirements and Chemical Safety Assessment Chapter R.11: PBT/vPvB Assessment. Report ECHA-14-G-07-EN, Helsinki Finland.

Environment UK (1999). Review of bioaccumulation models for use in environmental standards Science Report – SC030197/SR1.

Framework for Metals Risk Assessment

Fairbrother A, Wenstel R, Keith Sappington K, Wood W (2007). Framework for Metals Risk Assessment. Ecotoxicology and Environmental Safety 68 (2007) 145–227.

Franco A et al., (2011) OSIRIS Deliverable D3.1.17 (6th Framework Program, EU, Project no. 037017) Recommendations for adaptations of ECHA Guidance Documents and EUSES.

Fu W, Franco A, Trapp S. (2009). Methods for estimating the bioconcentration factor of ionizable organic chemicals. Environ Toxicol Chem 28:1372–1379.

Kelly BC, Ikonomou MG, Blair JD, Surridge B, Hoover D, Grace R, Gobas FA (2009) Perfluoroalkyl contaminants in an Arctic marine food web: trophic magnification and wildlife exposure. Environ Sci Technol. 43(11):4037-4043

MERAG. Metals Environmental Risk Assessment Guidance

Rorije E, Verbruggen EAJ, Hollander A, Traas TP, Janssen MPM (2011). Identifying potential POP and PBT substances. Development of a new Persistence/Bioaccumulation-score, RIVM Report 601356001/2011, Bilthoven the Netherlands.

## 3.3.2. Secondary poisoning

Proposed change
All changes related to BCF and BMF also relate to risk for secondary poisoning (birds and mammals) and will not be repeated here.
The additional proposed change is complementary to that suggested in section 3.3.1 and affects the derivation of RCRs based on accumulation and toxicity in birds and mammals.

A study by Verbruggen (2014) can be used to take account of the toxicology in secondary poisoning of birds and mammals in risks assessment of chemicals (EC 2004, section II.5.1) and extension of the food chains used.

Starting from the concentration in the environment, the resulting concentration in food of higher organisms is estimated. This exposure concentration is compared to the avian or mammalian toxicity of the chemical as an indication of possible effects on birds and mammals in the environment via the food chain. This relates to the following food chains already taken into account:
• Water (freshwater and marine environment) →fish → fish-eating predator
• Water (marine environment) → fish → fish-eating predator→top-predator
• Soil →earthworm → worm-eating predator

An addition of a new food chain in analogy with the aquatic food chain is advocated, as an extension to the current protection targets (for consistency reasons)[3]:
• Soil →earthworm → worm-eating predator -> top-predator

The new method differs from those in existing European guidance documents in some aspects. Although primarily aimed at the application in the Water Framework Directive (where PNECs are derived in water or soil to protect biota for secondary poisoning), the changes could equally apply to EUSES.

First, the energy content of food items is explicitly accounted for, resulting in different No-Effect levels for birds or mammals at the top of the food chains (See Verbruggen 2014, Ch2.7).
Second, the terrestrial food chain is extended with an extra step in the food chain to protect predators of small birds and mammals (similar to that for the aquatic food chain)[3].

Part of the exposure assessment influenced

The exposure assessment as described in section II.5.1 (EC 2004) is affected, i.e. concentrations in fish (freshwater and saltwater), worms and their predators. In addition, it is proposed to add another food chain for the terrestrial compartment covering terrestrial top predators in analogy with the freshwater compartment.

The revised calcuations are needed to update (improve) the calculation of the RCR for birds and mammals (intermediate or top-predators) as identified in the following EUSES screenshot for the environmental risk characterisation, and detailed in section II.6.1.7 of the EUSES manual (EC 2004):
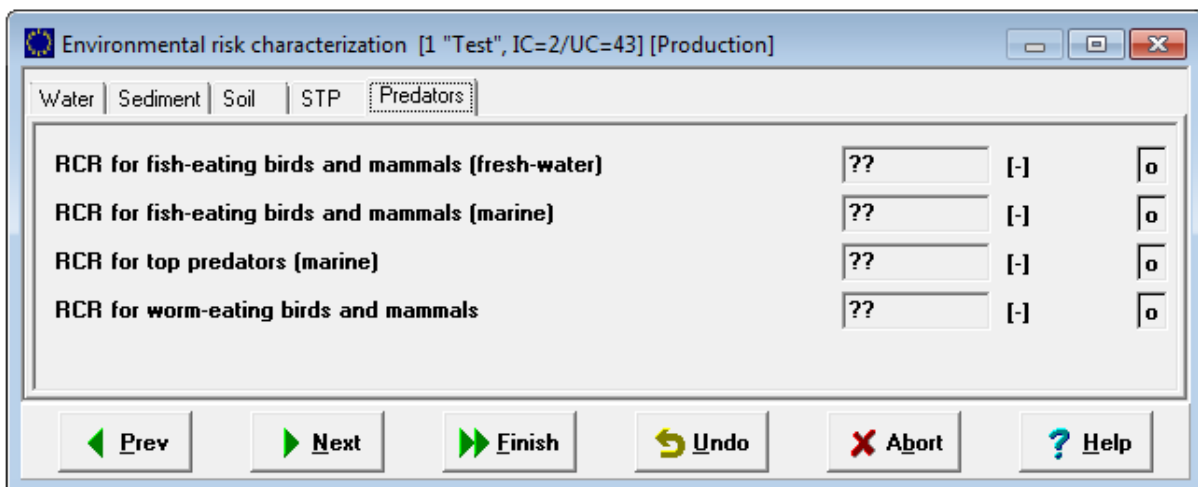


Model input and output
No substance specific parameters are added. Model formulation is adapted based on allometric equations, to estimate energy expenditure in the field.
Model output remains the same but is extended with the results for an RCR for terrestrial top predators.

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[3] A consistent set of protection targets for secondary poisoning may be considered when revising the relevant guidance.

Substances affected
In principle, all substances that undergo an assessment for secondary poisoning are affected due to the changes implemented, but on a general note, bioaccumulation is mostly of concern for substances with a log Kow value $\geq$ 4.

Implementation
The presented method relates to the interpretation of avian and mammalian toxicity studies. The method is different from the current methods for secondary poisoning that follow either a diet based approach or a dose based approach. This new method uses the body weight of a species to estimate its daily energy expenditure under field conditions, based on well-established relationships for birds and mammals (allometric relationships).

The daily dose that is administered to the bird or mammal in a toxicity study is related to this daily energy expenditure. This results in a concentration of a toxicant in food that is normalized to the energy content of food (Verbruggen 2014, section 2.7), which can be easily applied to different food items by taking the tabulated energy contents of these food items. This makes the method suitable to apply to various types of food items from different type of food webs, making a differentiation between these different food items, whih is considered an improvement in comparison with current European guidance documents.

In addition attention is paid to the extrapolation from sub-acute and sub-chronic exposure exposure times to real chronic exposure (Verbruggen 2014, Ch3).

Importance ranking

| | |
|---|---|
| *Type of substance affected* | 2. Sizeable; affects chemicals with bioaccumulation potential with log Kow > 4. |
| *Exposure calculation impact* | 1. The impact of these equations is expected to be relatively low for bioaccumulating substances |
| *Maturity of improvement* | 2. Documented but not implemented for EUSES. |
| *Verification/validation status* | 1. Knowledge on dependency of toxicity on feeding rate is documented, as is the importance of field derived BAFs over BCFs from lab or QSARs. |
| *Type of improvement* | 2. Refinements to existing calculations. |

References
Verbruggen EAJ (2014)  New method for the derivation of risk limits for secondary poisoning. RIVM Letter report 2014-0097, Bilthoven The Netherlands. Available via https:// www.rivm.nl.
EC (2004) European Union System for the Evaluation of Substances 2.0 (EUSES 2.0). Prepared for the European Chemicals Bureau by the National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands (RIVM Report no. 601900005).


### 3.3.3. Human exposure via the environment: crops, meat and milk


Indirect human exposure to chemicals via food intake is described in Chapter R.16.6.8 (Humans exposed indirectly via the environment) of the ECHA Technical Guidance (ECHA 2008). Previous sections (3.3.1 and partly 3.3.2) have already dealt with fish.

This section will not take metals into account since uptake and bioaccumulation are highly non-linear and metal-specific processes, hence beyond the scope of the present study.

Proposed change

*Plant leaves:* In EUSES, uptake to leaves from soil water is calculated using the transpiration stream concentration factor (TSCF) based on Briggs et al., 1982, which is the quotient between the chemical concentrations in the transpiration stream and the soil pore water. Based on the work of Dettenmaier et al. (2009), this equation should be modified.

*Root crops:* A validation study showed that EUSES (section III.5.2) severely overestimates root concentrations, due to the effect of growth dilution (Legind and Trapp, 2009). Because this is recognized in the Guidance (Chapter R7.10.10), EUSES should be updated.

*Meat and milk:* The current regression equations in EUSES for estimating the biotransfer factors (BTFs) (see ECHA Guidance (2008 R.16.6.8.5) should be replaced by a mechanistic steady state model for bioaccumulation in cattle. The OSIRIS model is based on McLachlan, 1994.

Part of the exposure assessment influenced

Indirect human exposure to chemicals via food intake is described in Chapter R.16.5.8 (Humans exposed indirectly via the environment) (ECHA, 2012). It influences the calculation of human exposure and associated risk characterisation ratios via the environment (EC 2004, section II.5.2.) .for a combination of intake via both the local and the regional scale  in EUSES:



Model input and output

Additional input is needed for biomagnification in food chains: the (measured or estimated) octanol-air partitioning coefficient ($K_{oa}$), which can be obtained as $K_{oa}=K_{ow}/K_{aw}$, from standard input.
The output in EUSES does not change.

Substances affected

Due to the different biotic compartments affected, both soluble and liphophilic compounds are affected.
For plant leaves, a higher uptake is predicted for hydrophilic compounds compared to EUSES. For root crops, a validation on the improved equation showed that EUSES severely overestimates root concentrations.  For cattle fairly constant (and higher than EUSES) BAFs for persistent chemicals are

predicted in the log KOW range of 3-6. The BAF values then drop at higher KOW (i.e. where EUSES BAFs are at maximum value).

Implementation

*Plant leaves:*  Based on the work of Dettenmaier et al. (2009), the equation should be modified to: TSCF = 11 / (11+ 2.6 log Kow).

*Root crops:* An updated model is recommended for the calculation of the concentration in roots from the concentration in soil water (Legind and Trapp 2009),as discussed by Franco et al (p. 40-41).

*Meat and milk:* Concentrations in beef and milk are calculated according to mechanistic model, in analogy to the more sophisticated models for fish as discussed earlier. The rather elaborate equations are given in Franco et al, section 2.4.1.4. The model may be parameterized to represent a generic steer or cow by default.

Importance ranking

| | |
|---|---|
| *Type of substance affected* | 3. A large number of chemicals is affected, both hydrophilic and lipophilic |
| *Exposure calculation impact* | 1.  Relatively low. Although the impact may be relatively large especially for strongly bioaccumulating substances in fish and meat/milk, indirect human exposure is not often criticl for the risk assessment (Bodar et al, 2003) |
| *Maturity of improvement* | 3. Documented and implemented. |
| *Verification/validation status* | 2. Validation of all submodels discussed in this paragraph is documented. |
| *Type of improvement* | 2. Refinements to existing calculations. |

References
Bodar CWM, Berthault F, De Bruijn JHM, Van Leeuwen CJ, Pronk MEJ, T G Vermeire TG (2003). Evaluation of EU risk assessments existing chemicals (EC Regulation 793/93).Chemosphere 53(8):1039-47
Briggs G, Bromilow RH, Evans AA (1982). Relationships between lipophilicity and root uptake and translocation of nonionized chemicals by barley. Pesticide Science 13: 495-504.
Dettenmaier EM, Doucette WJ, Bugbee B (2009). Chemical Hydrophobicity and Uptake by Plant Roots. Environ. Sci. Technol. 43: 324-329.
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## 3.4. Topics identified by ECHA

Specific topics were identified *a priori* by ECHA and discussed in this section.

### 3.4.1. PECregional for sediment

Proposed change

The current EUSES guidance is not clear if, and how to use the regional predicted concentration for sediment in EUSES (PECregional_sed) as a background concentration to calculate local predicted concentration in sediments (PEClocal_sed). For concentrations in air and water at the local scale, local and regional concentrations are added (EC (2004), section II.4.5.2). This source provides no instruction to derive PEClocal_sed.

Alternate calculation options for local exposure calculation for Chemical Safety Assessment under REACH (EU TGD spreadsheet, Ecetoc TRA), calculate the concentration in freshly deposited sediment (i.e., derived from suspended matter) is taken as the PEC for sediment and the properties of suspended matter are therefore used (EC (2004), section II.4.5.2). The concentration in suspended matter is based on the ambient water concentration (i.e. sum of local and regional water concentrations) and the sorption of the chemical to organic carbon in the suspended matter. The EU TGD spreadsheet derives PEClocal_sed from PEClocal_water , assuming thermodynamic equilibrium partitioning (see also Di Toro et al., 1991). It is assumed that calculation of PEClocal_sed in EUSES (which still needs to be confirmed by looking into the source code) is implemented in the same way.

This way of calculating local concentrations in sediment is in agreement with the spirit of exposure estimation in the TGD. It correctly reflects and implements the influence of regional releases and exposures on local concentrations in sediment and correctly accounts regional influence on local PEC/PNEC ratios in sediment.

Part of the exposure assessment influenced

Anticipating the outcome of further confirmatory action, it is foreseen that no adjustments of the current EUSES calculation are needed. If it needs to be implemented however, changes would affect PEC values at the local scale for sediment, and all corresponding related measures where sediment concentrations are used at the local scale.

Model input and output

No additional input and output is needed, the proposed change only affects calculation of water and sediment concentrations at the local scale (local PECs).

Substances affected

In principle, all substances are affected due to this change.

Implementation

Implementation follows a simple addition of local and regional scale concentrations, either via addition of local and regional PECs for sediment, or via equilibrium partitioning of the sum of local water and regional water concentrations.

Importance ranking

| Type of substance affected | 3. A large number of chemicals is affected. |
|---|---|
| Exposure calculation impact | 1. Relatively low due to the expected dominance of local concentrations over regional sediment concentrations. |
| Maturity of improvement * | 2. Documented |
| Verification/validation status | 2. The proposed change was verified (simple change) |
| Type of improvement | 2. Refinements to existing calculations. |

*  Because this issue is a check on an existing calculation, this category is not really applicable.

References

EC (2004) European Union System for the Evaluation of Substances 2.0 (EUSES 2.0). Prepared for the European Chemicals Bureau by the National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands (RIVM Report no. 601900005).

EU TGD spreadsheet (2008). Available from Radboud University, Nijmegen NL via http://www.ru.nl/environmentalscience/research/themes-0/risk-assessment/eutgdsheet/

## 3.4.2. Different Kp(susp) and Kp(sed) for seawater and freshwater

Proposed change

Currently, EUSES does not differentiate the following partitioning coefficients between freshwater and seawater(nor do alternative models):

*Solids-water partition coefficient sediment (Kp.sed, L/kg)*

*Solids-water partition coefficient suspended matter solids (Kp.sus, L/kg)*

The possibility to have 2 different partitioning coefficients Kp (sediment, suspended solid) for marine and freshwater would allow to differentiate for substances where different partitioning behaviour is expected between sea water and freshwater (mostly for ionising substances or (metal)salts) due to different ionic strength or pH. It is proposed to adjust EUSES to allow entry of separate Kp values for marine and freshwater environments, and to add QSAR estimations of marine Kp, based on Kow, pH, pKa and salinity.

Part of the exposure assessment influenced

This change would affect water and sediment concentrations (PECs) in the marine part of the local and regional scale, and risk characterisation dependent on it.

Model input and output

In principle, no additional model input would be needed if a QSAR estimate can be made to estimate different marine and freshwater partitioning coefficients based on known substance properties and water composition parameters (e.g influence of ionic strength in sea water or differences in pH between freshwater and oceans (for ionising chemicals). However, measured Kp's would need to be specified if the user would want to override the default Kp's.

Substances affected

The proposed change is supposed to mostly affect metal partitioning and other ionising chemicals.

Implementation
As discussed in section 3.1.5., pH  affects the calculation of partitioning to organic carbon  and thus will result in different Kp values for freshwater and seawater, depending on average pH and pKa of a specific chemical.
Ionic strength impacts the activity coefficients and thus the relation between activity and concentration in MAMI (Franco and Trapp 2010). Only the ionic content of seawater and sediments was found to have a moderate effect on model outputs.

Importance ranking

| | |
|---|---|
| *Type of substance affected* | 1. A relatively small number of chemicals is affected. |
| *Exposure calculation impact* | 3. Relatively high due to the expected moderate influence of (average) pH differences and ionic strength (at regional scale). |
| *Maturity of improvement* | 3. Documented, and implemented |
| *Verification/validation status* | 2. Validation this paragraph is documented (simple change) |
| *Type of improvement* | 2. Refinements to existing calculations. |

References
Franco, A., Trapp, S. (2010). Multimedia activity model for ionizable compounds - Validation study with 2,4-D, aniline and trimethoprim. Environ. Toxicol. Chem., 29(4), 789–799.

### 3.4.3. Local and regional releases to soil

Proposed change
The local soil model in EUSES distinguishes between agricultural soil and grass land.  At the regional scale, natural soil, agricultural soil and industrial soil are distinguished.
Currently, release to soil at the local scale only occur via application of sludge from an STP to agricultural soil and via atmospheric deposition of substances released to air. Direct releases to soil from industrial settings are not assessed at the local scale, but only at the regional scale.

The possibility for releases to soil compartments other than industrial soil (i.e., via ERC 1-7), was suggested to account for other types of direct emissions,  e.g. release to agricultural soil due to application of co-formulants in pesticides. In principle, direct emissions to soil compartments can be accounted for at both the local and regional scale, to any soil type that is present at the difference scales in EUSES.
However, the current EUSES does not offer the possibility for registrants to enter data for direct emissions to local soil. It is proposed to correct this and offer this option in a modified version of the exposure model.  When the local scale is nested inside the regional scale, it is even easier to make a consistent matrix of emissions to the local scale (and associated intermedia transport processes such as runoff) that considers the same compartments as for the regional scale.

Part of the exposure assessment influenced
The proposed changes affect soil concentrations at the local or regional scale (see previous paragraph).

Model input and output
Model inputs would need to be extended with additional (direct) soil emissions at the local or regional scale (as specified for other emissions (EC (2004), e.g. section III.3.4) , e.g. for co-formulants of pesticides or other direct soil applications.
Model output will not need to be extended, unless ' industrial/urban soil' is added to the local scale (this is possible when nesting the local scale within the regional scale as done in SimpleBox 3.0). In that case, a PEC for local industrial/urban soil would be added. So far this has not been considered a protection target in the context of EUSES and there seems to be no need to change this.

Substances affected
The change would affect substances where direct releases to soil, other than industrial activity under ERC[4] 1-7, would be relevant, e.g. direct-loss chemicals in (agricultural) machinery such as lubricants, co-formulants of pesticides etc.

Implementation
At the local scale, the concentration in soil would need to be averaged over a certain time period (when following a similar model as for sludge application (EC (2004), section II 4.5.3) or other more sophisticated models could be relevant (for agricultural use, FOCUS models can be considered, cf FOCUS 2014).
At the regional scale, intentional direct emissions to agricultural soil can be coded with little effort as for direct emissions to industrial/urban soil.

Importance ranking

| | |
|---|---|
| *Type of substance affected* | 2. Sizeable, based on several types of use categories as specified |
| *Exposure calculation impact* | 1. Depending on the type of chemical and application, impact could be high but not a priori high for the whole category |
| *Maturity of improvement* | 2. Documented, not implemented |
| *Verification/validation status* | 2. Validation this paragraph is documented (simple change) |
| *Type of improvement* | 2. Refinements to existing calculations. |

References
EC (2004) European Union System for the Evaluation of Substances 2.0 (EUSES 2.0). Prepared for the European Chemicals Bureau by the National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands (RIVM Report no. 601900005).
FOCUS (2014). FOrum for Co-ordination of pesticide fate models and their USe, in the framework of the EU Directive 91/414/EEC. Website http://focus.jrc.ec.europa.eu/

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[4] ERC is an abbreviation for Industrial Release Category, see Guidance document R.12: Use descriptor system Reference: ECHA-2010-G-05-EN, section R12.3.4.

**3.4.4. Metals**

See sections 3.1.4. and section 3.3.

**3.4.5. Additional predictions and fate calculations for degradation products**

See section 3.1.8

# 4. Discussion of the improvements/extensions

## 4.1. Model updates and implementation

Many of the various improvements that were described in Chapter 3 are implemented in some for or other. An overview table was made of the model implementation as discussed for each topic in Chapter 3 listing the available models or model updates. All of the listed topics were described as documented in Chapter 3 but not all issues are implemented as can be seen in the overview table. The regional background calculation for sediment (topic 3.4.1) is, based on the EU-TGD spreadsheet, in all likelihood implemented (hence the * indication). This needs to be confirmed based on the EUSES source code.

*Table 1: Overview of model implementation of the various topics of Chapter 3.*

| Section | Topic | Implemented | Model |
|---------|-------|-------------|-------|
| 3.1.1. | Sparingly soluble chemicals | no | |
| 3.1.2. | Extremely soluble chemicals | yes | SimpleBox 4.0 |
| 3.1.3. | Gaseous chemicals | no | SimpleBox 3.0 |
| 3.1.4. | Metals | no | |
| 3.1.5. | Ionising organic chemicals | yes | SimpleBox 4.0, SimpleTreat 4.0 |
| 3.1.6. | Nano materials | no | |
| 3.1.7. | Photolytically labile chemicals | yes | via RIVM (prototype) |
| 3.1.8. | parent-metabolite(s) | yes | MSC EUTGD spreadsheet |
| 3.2.1. | Model structure changes | yes | SimpleBox 4.0 |
| 3.2.2. | Episodic rain | yes | SimpleBox 4.0 |
| 3.2.3. | depth-dependent concentration in soil | yes | SimpleBox 4.0 |
| 3.2.4. | Nesting the local scale | yes | SimpleBox 3.0 |
| 3.2.5. | SimpleTreat update | yes | SimpleTreat 4.0 |
| 3.3.1. | Bioaccumulation in fish | yes | OSIRIS, PB score |
| 3.3.2. | Secondary poisoning | no | |
| 3.3.3. | Human exposure via the environment | yes | OSIRIS |
| 3.4.1. | Regional background sediment | yes* | |
| 3.4.2. | Kp values for seawater and freshwater | yes | SimpleBox 4.0, MAMI 2010 |
| 3.4.3. | Additional release to soil | no | |

The various models and their availability is summarized in Table 2.

*Table 2: Availability of model updates or improvements. Public means that the source model (not necessarily model code) is available via the internet.*

| Model | availability | Resource |
|-------|--------------|----------|
| SimpleBox 3.0 | on request | via authors RIVM, EUSES (without nested local scale) |
| SimpleBox 4.0 | public | http://www.rivm.nl/en/Topics/S/Soil_and_water/SimpleBox_4_0_tool |
| SimpleTreat 4.0 | on request | spreadsheet via authors, standalone via www.rivm.nl by early 2015 |
| multi-species model EU-TGD | on request | via authors RIVM |
| OSIRIS | public | via webtool: http://osiris.simpple.com/OSIRIS-ITS/itstool.do |
| MAMI | public | http://homepage.env.dtu.dk/stt/Homepage%20anf/Website.htm |
| PB Score | on request | via authors RIVM |

## 4.2.  Importance ranking

For each model change that was discussed in Chapter three, a summary was made of the arguments that could help to decide on the importance and relevance of each model change or update. Five different criteria were scored according to the procedure described in Chapter Two:
1) Type of substance affected;  2) Exposure calculation impact;  3) Maturity of improvement
4) Verification/validation status;   5) Type of improvement.

While documenting the various extensions or improvements, it became clear that without extensive comparisons, only qualitative judgements could be made on the overall utility of the improvements and extensions, and how these compare to each other (see Section 5).  The ranking method and corresponding criteria should thus be seen as a first attempt to differentiate between rather obvious improvements and to facilitate the discussion on those improvements where the need depends on more strategic issues regarding the goals and ambitions of a revised EUSES program.

*Table 3: Importance ranking overview of the topics in Chapter 3,  based on the criteria described in Chapter 2.  The topic with the highest score is listed at the top.*

| Rank | Section | Topic | Chemical domain | Impact | Maturity | Validation | Type of change | Sum |
|------|---------|-------|-----------------|--------|----------|------------|----------------|-----|
| 1 | 3.1.5. | Ionising organic chemicals | 3 | 3 | 3 | 2 | 2 | 13 |
| 2 | 3.2.5. | SimpleTreat update | 3 | 3 | 3 | 2 | 2 | 13 |
| 4 | 3.2.3. | depth-dependent concentration in soil | 2 | 3 | 3 | 2 | 2 | 12 |
| 3 | 3.1.8. | parent-metabolite(s) | 2 | 3 | 3 | 2 | 1 | 11 |
| 5 | 3.1.1. | Sparingly soluble chemicals | 2 | 3 | 2 | 2 | 2 | 11 |
| 6 | 3.1.3. | Gaseous chemicals | 1 | 3 | 3 | 2 | 2 | 11 |
| 7 | 3.2.4. | Nesting the local scale | 2 | 3 | 3 | 2 | 1 | 11 |
| 8 | 3.3.1. | Bioaccumulation in fish | 2 | 3 | 2 | 2 | 2 | 11 |
| 9 | 3.3.3. | Human exposure via the environment | 3 | 1 | 3 | 2 | 2 | 11 |
| 10 | 3.4.2. | Kp values for seawater and freshwater | 1 | 3 | 3 | 2 | 2 | 11 |
| 11 | 3.1.2. | Extremely soluble chemicals | 2 | 1 | 3 | 2 | 2 | 10 |
| 12 | 3.1.4. | Metals | 1 | 3 | 2 | 2 | 2 | 10 |
| 13 | 3.2.1. | Model structure changes | 3 | 1 | 3 | 2 | 1 | 10 |
| 14 | 3.2.2. | Episodic rain | 2 | 1 | 3 | 2 | 2 | 10 |
| 15 | 3.4.1. | Regional background sediment | 3 | 1 | 2 | 2 | 2 | 10 |
| 16 | 3.4.3. | Additional release to soil | 2 | 1 | 2 | 2 | 2 | 9 |
| 17 | 3.1.6. | Nano materials | 2 | 2 | 2 | 1 | 1 | 8 |
| 18 | 3.1.7. | Photolytically labile chemicals | 1 | 1 | 2 | 2 | 2 | 8 |
| 19 | 3.3.2. | Secondary poisoning | 2 | 1 | 2 | 1 | 2 | 8 |

The overview table of the importance ranking reveals that the criteria for chemical domain, impact and maturity have the largest influence on priority setting. As a general rule, those changes that affect exposure for a whole or several chemical classes at (at least) the local scale and are well described and implemented are given the highest weight. Even if a change for a certain type of chemical (e.g. gaseous chemicals, section 3.1.3) affects a relatively small number of chemicals, it can have a high score if the impact and maturity of the changes are estimated to be high.

The first conceptual change that ends up high in the top 10 is adding parent-metabolite modelling (section 3.1.8) due to the many potentially relevant chemicals, the relative degree of maturity and verification. This change, although relevant and important, would require a significant implementation effort due to the  simultaneously calculation of predicted environmental concentrations (PECs) of the parent compound and all its considered degradation products.

The second conceptual change that gets a somewhat lower score is the nesting of the local scale (section 3.2.4), due to the advantages this has in terms of calculation for highly volatile chemicals and the consistency of local scale emissions to the general concept of nested spatial scales.

Modernising human exposure also receives a high score, partly due to the large number of chemicals affected. It should be noted that human exposure via the environment also includes the aquatic foodchain, which received a slightly higher score. It seems logical to address all environmental and human exposure routes (uptake in biota) if it is decided to update this part of EUSES.

The proposed changes that are outside the top 10 usually receive a lower score on expected impact (for further discussion) based on an expert judgement on the expected numerical change in predicted exposure concentrations and the expected effect on the overall risk characterisation.
It can also be expected that the developments for nano materials receive a relatively low score due to the fact that the model is still under development and validation for this chemical class is still a hot topic.  This shows that although some topics are hotly debated in the scientific literature, not all are already mature enough to implement in EUSES.

Some improvements need to be made to correct conceptual or accidental error in the model. Examples are error in calculation of sparingly soluble chemicals (3.1.1.), extremely soluble chemicals (3.1.2.),  local soil concentrations in case of local release of gaseous chemicals to air (3.1.3.) the unrealistic assumption of continuous wet deposition (3.2.2.) and correction for depth-dependent concentration in soil (3.2.3.). Of these five topics, only two closely related topics on extremely soluble chemicals (3.1.2.) and correction of continuous wet deposition (3.2.2.) fall outside the top 10.

Although the current ranking is prelimary and largely based on expert judgement, it seems to fulfil its purpose of distinguishing between improvements that address a relatively large number of chemicals, are described and implemented and at least verified at the submodel or process level. These 'top 10' improvements therefore seem to be a good working list for EUSES improvements on the relatively short term.  These observations do not imply that topics that received a lower score are not relevant, but they can be implemented at a later stage when the more urgent issues have been addressed.

The criterion that was most difficult to score is the exposure calculation impact, because the impact may vary based on the substance properties of specific (classes of) chemicals. To actually quantify such an impact, a comparison of model predictions with and without the addition/ extension must be available which isn't always the case. Even if such an exercise is done as for SimpleBox 4.0, it is complicated due to the many relevant compartments that are the basis for RCR calculations at the various spatial scales and for various protection targets. The inter-comparability of various improvements is even more difficult, due to the different scope of the improvements.

A valid ambition, although much more difficult to prioritise, is that all relevant processes in EUSES should be updated or corrected to the current state of the science, regardless whether the impact on actual risk assessment is large or small. Some of the conceptual extensions in the top 10 that have been discussed would require a substantial effort to implement. It could be argued that for efficiency reasons' sake, a major overhaul would be more efficient in one go. However, the current review

shows that some improvements seem more urgent than others in the context or REACH registration requirements.

# 5. General references

Den Hollander HA, Van Eijkeren JCH, Van de Meent D (2004). SimpleBox 3.0. RIVM report 601200003/2004, RIVM Bilthoven The Netherlands.

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JRC (2003). Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances; Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances; Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. JRC report  part II: EUR 20418 EN/2 ()http://ihcp.jrc.ec.europa.eu/our_activities/public-health/risk_assessment_of_Biocides/doc/tgd).

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Struijs J (1996). SimpleTreat 3.0: a model to predict the distribution and elimination of chemicals by sewage treatment plants. RIVM report no. 719101025/1996, RIVM Bilthoven, The Netherlands.

Struijs J (2014). SimpleTreat 4.0: a model to predict fate and emission of chemicals in wastewater treatment plants. Background report describing the equations. Report 601353005, RIVM Bilthoven The Netherlands.

## Annex 1

The importance ranking and tables on the various model extensions/ improvements are available via the embedded object included here.

Overview
tables_ECHA 2014_2!