

Report

Report no. 14/22

PetroRisk version 8.01 User Manual



PetroRisk version 8.01

User Manual

Prepared with support of **Penman Consulting Ltd.**

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M. Comber (Mike Comber Consulting Ltd.)
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ABSTRACT

This report provides a detailed description of version 8.01 of Concawe's PetroRisk model: (1) conceptual design, (2) main improvements compared to previous versions, (3) KNIME, the open-source software wherein PetroRisk is developed, (4) use instructions, and a (5) technical basis.

PetroRisk calculates the environmental exposures and risks resulting from the different lifecycle stages of multi-constituent hydrocarbon substances, using the principles provided by the European Chemical Agency (ECHA) under the EU REACH regulation. Environmental exposures and risks can be predicted at the manufacture/formulation/distribution stages and at industrial/professional/consumer use stages for multi-constituent hydrocarbon substances, such as naphthas (gasolines), kerosenes, gas oils, heavy fuel and lubricant oils, and solvents. PetroRisk version 8.01, including its Generic Exposure Scenario (GES) scaling tool, can be downloaded free-of-charge from our website.

KEYWORDS

ECHA, Exposure, Hydrocarbon Block, KNIME, Guidance, Man via environment, Secondary poisoning, exposure scenario, scaling tool, Risk, SimpleTreat, SimpleBox, spERC, UVCB, multi-constituent

INTERNET

This report is available as an Adobe pdf file on the Concawe website (www.concawe.eu).

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1. PETRORISK - CONCEPTUAL DESIGN

1.1. A BRIEF SUMMARY

PetroRisk calculates the environmental exposures and risks resulting from the different lifecycle stages of multi-constituent hydrocarbon substances, using the principles provided by the European Chemical Agency (ECHA) under the EU REACH regulation. Environmental exposures and risks can be predicted at the manufacture/formulation/distribution stages and at industrial/professional/consumer use stages for multi-constituent hydrocarbon substances, such as naphthas (gasolines), kerosenes, gas oils, heavy fuel and lubricant oils, and solvents.

PetroRisk implements the ECHA Guidance on [environmental exposure estimation](#) and [risk characterization](#) with refinements to improve its applicability to complex hydrocarbon substances. The tool extrapolates the user-provided substance analytical information to individual hydrocarbon concentrations via the [Hydrocarbon Block Method](#) (HBM)¹, and subsequently calculates the Predicted Environmental Concentrations (PECs) of the representative hydrocarbons in soil, air, water, sediment, sewage treatment plant (STP) effluent, and drinking water and foodstuff. Compared to the REACH Guidance approach (as implemented in for example [EUSES](#)²), PetroRisk uses tailored methods to estimate [organic carbon-water partitioning coefficients](#) (K_{oc})³ and [Biomagnification Factors](#) (BMF)⁴, and implements version 4 of [SimpleBox](#)⁵ and [SimpleTreat](#)⁶, including an adapted version of the latter for a better representation of [industrial wastewater treatment](#)⁷.

For the water, soil, sediment and STP compartments, a risk characterization ratio (RCR) is calculated for each representative hydrocarbon:

$$RCR = PEC/PNEC$$

wherein the hydrocarbon-specific Predicted No-Effect Concentration (PNEC) is derived with the [Target Lipid Model](#) (TLM)⁸. The RCRs are subsequently summed to reflect the ecological risk of the entire substance in each compartment.

Human exposures are calculated for each representative hydrocarbon by multiplying the PECs in air, drinking water and foodstuff with the related daily human intake rates. Compared to the Guidance approach, PetroRisk uses a [refined 'Man via Environment' model](#)⁹, resulting in more realistic human exposure predictions. The hydrocarbon-specific human exposure via inhalation and ingestion are summed to reflect the respiratory and dietary exposure to the entire substance. Both human exposures are subsequently divided by the related Derived No Effect Levels (DNEL) to obtain substance-specific respiratory and dietary RCRs. The applied substance DNELs are usually derived from available mammalian toxicity data on the substance or a marker compound (e.g., benzene).

RCR values above 1 indicate that the assessment does not support safe use, and may require further refinement or consideration of additional RMMs or process controls. In such case, the user should consider refining the applied operational conditions (OC) that describe the Generic Exposure Scenario (GES) of the use. PetroRisk can automatically calculate and mathematically implement a set of Risk Management Measures (RMMs) that achieves 'safe' air and wastewater emission levels (i.e., resulting in RCRs ≤ 1).

The tool can successfully handle large batches of input files, if these are set up appropriately and provided in a single folder. The results are captured both as a single data table at the end of the PetroRisk workflow and as individual, substance-specific Excel-based output files.

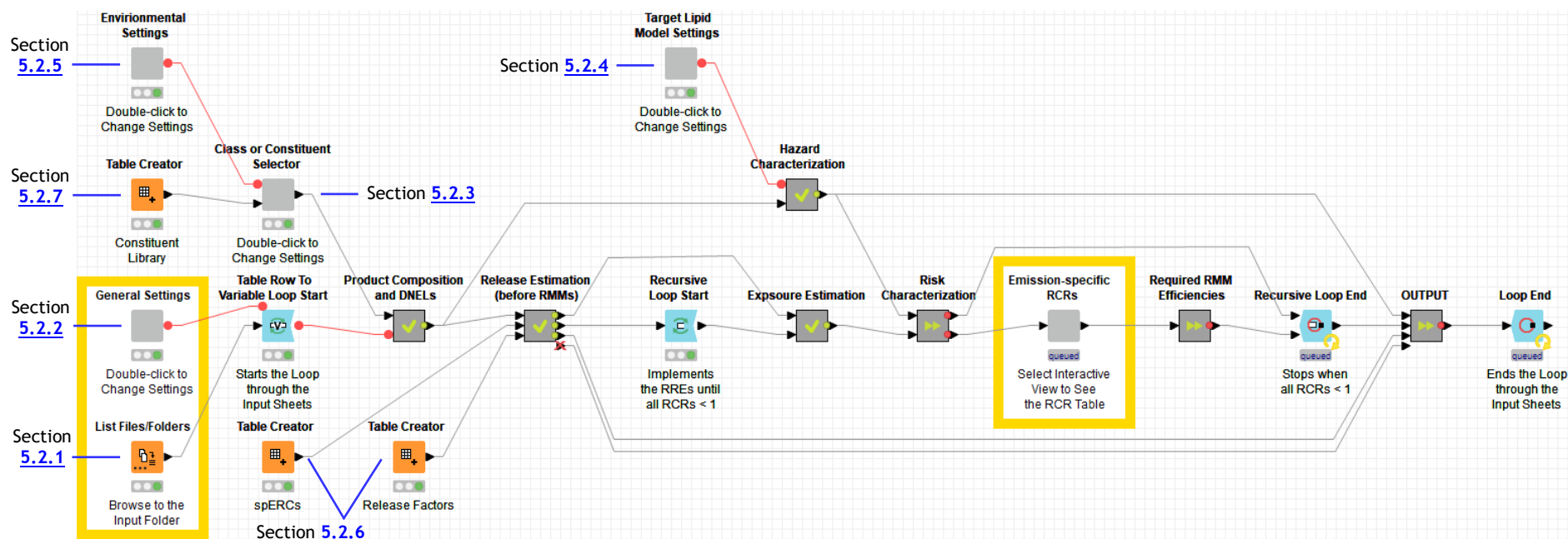


Figure 1 The PetroRisk 8.01 KNIME workflow.

PetroRisk has been programmed as a workflow in the [Konstanz Information Miner](#)¹⁰ (KNIME), which is an open source data analytics, reporting and integration platform based on Eclipse and written in Java. An intuitive drag and drop style graphical user interface allows visual assembly, execution and analysis of complex workflows without the extensive need for coding (see [Section 3](#)).

In addition, a user-friendly Excel-VBA based tool is provided to ‘scale’ the PetroRisk generated GESs of industrial lifecycle stages and uses to site specific OCs. More information on the Scaling Tool can be found in [Section 7](#).

1.2. PRODUCT COMPOSITION

PetroRisk makes use of the Hydrocarbon Block (HB) method¹ to extrapolate available compositional information to individual concentrations of representative hydrocarbons (see [Section 6.2](#)).

Available product compositional information can be supplied by the user as weight percentages via 4 different HB schemes: for each chemical class (aliphatics vs. aromatics) or subclass (see below), and per carbon number or boiling point intervals.

The sixteen chemical subclasses are: normal alkanes or paraffins (nP), branched alkanes or paraffins (iP), normal olefins (nO), branched olefins (iO), mono-naphthenics (MoN), di-naphthenics (DiN), polynaphthenics (PolyN), mono-aromatics (MoAr), di-aromatics (DiAr), tri-aromatics (TriAr), poly-aromatics (PolyAr), naphthenic mono-aromatics (NMoAr), naphthenic di-aromatics (NDiAr), naphthenic tri-aromatics (NTriAr), aliphatic sulphur compounds (ALS) and aromatic sulphur compounds (ArS).

Block	Starting Carbon number (>=)	Ending Carbon number (<)	n-Paraffins	iso-Paraffins	Mono-Naphthenics	Di-Naphthenics	Mono-Aromatics	Naphthenic Mono-Aromatics	Di-Aromatics	Naphthenic Di-Aromatics	Tri-Aromatics	Naphthenic Tri-Aromatics	Poly-Aromatics
2	5	6			0.000472								
3	6	7	0.00055		0.00484		0.004826						
4	7	8	0.01339	0.01117	0.052269		0.029061						
5	8	9	0.09141	0.06459	0.354499	0.009069	0.250074						
6	9	10	0.40716	0.36996	0.746283	0.130382	0.741676	0.036261					
7	10	11	0.71322	0.88572	1.215395	0.549769	0.79498	0.427629	0.046606				
8	11	12	1.00838	1.15822	1.431089	1.0186	0.800314	0.951538	0.192321				
9	12	13	1.10493	1.27563	1.716085	1.134372	0.775708	1.296903	0.422927	0.001525			
10	13	14	1.19152	1.52264	1.778257	1.226912	0.795384	1.28121	0.582175	0.04143			
11	14	15	1.34196	1.69463	1.896399	1.576976	0.811701	1.11946	0.655287	0.156132	0.020489		
12	15	16	1.456	1.75839	1.935965	1.142167	0.726854	0.922732	0.512696	0.265697	0.075006		
13	16	17	1.35334	1.86107	1.884772	0.87133	0.629418	0.705623	0.4453	0.266012	0.142022	0.002862	0.002124
14	17	18	1.3237	1.44888	1.826345	0.780654	0.571668	0.61984	0.403518	0.236931	0.149855	0.009075	0.005203
15	18	19	1.16117	1.76995	1.646253	0.736836	0.521115	0.527375	0.313047	0.167229	0.12105	0.012838	0.007761
16	19	20	0.99301	1.91656	1.530744	0.694241	0.469581	0.45913	0.220679	0.094107	0.079709	0.012375	0.007674
17	20	21	0.85358	1.50637	1.316542	0.488926	0.425395	0.447323	0.165898	0.071038	0.058294	0.010842	0.004678
18	21	22	0.70365	1.0383	1.094237	0.400298	0.31606	0.310313	0.115071	0.034823	0.038017	0.007447	
19	22	23	0.584	0.75484	0.953014	0.220455	0.261693	0.178263	0.078181	0.017506	0.021405	0.003588	
20	23	24	0.45743	0.67457	0.740255	0.154207	0.210819	0.117067	0.041444	0.011835	0.003191		
21	24	25	0.34819	0.55201	0.516659	0.067573	0.146836	0.080357	0.019676	0.004995	0.001971		
22	25	26	0.22856	0.42169	0.338308	0.049973	0.09958	0.04537	0.013203	0.003788			
23	26	27	0.15176	0.3109	0.216815	0.025093	0.054594	0.030184	0.008985	0.000208			
24	27	28	0.08559	0.17937	0.114382	0.012458	0.034613	0.017578	0.004474	0.000208			
25	28	29	0.04661	0.10671	0.067002	0.005597	0.018178	0.006402	0.000809				
26	29	30	0.02617	0.06876	0.036999	0.001937	0.01155	0.003055	0.000362				
27	30	> 30	0.01881	0.05179	0.032486	0.015753	0.009907	0.00272	0.00093	0.02093	0.000999		

Figure 2 An example of the subclass versus Carbon Number interval HB scheme as used in the PetroRisk input file.

For the extrapolation of the user provided analytical information to a representative substance composition (in the metanode “Product Composition and DNELs”, please see Figure 1), the mass fraction assigned to a particular HB is evenly distributed among the individual library structures representing that block. The PetroRisk

representative constituent library (in the component “Class or Constituent Selector”, please see Figure 1) currently contains 1,560 hydrocarbons representing different carbon number and boiling point intervals, and different hydrocarbon classes and subclasses (please see Figure 3 and Figure 4).

When using the structure class (aliphatics and aromatics) versus boiling point range HB-format, which in previous PetroRisk versions was described as the “Solvent mode”, the mass measured in the aromatic blocks with BP > 350°C is weighted towards PAHs by approximately a factor of 3, and the mass assigned to other aromatic classes is decreased accordingly. This adjustment was required to better describe the available toxicity and is consistent with compositional data for heavier classes of petroleum products^{11,12}.

Block	Starting Carbon number (≥)	Ending Carbon number (<)	n-Paraffins	iso-Paraffins	Mono-Naphthenics	Di-Naphthenics	n-Olefins	iso-Olefins	Poly-Naphthenics	Sulfur-containing Aliphatics	Mono-Aromatics	Naphthenic Mono-Aromatics	Di-Aromatics	Naphthenic Di-Aromatics	Tri-Aromatics	Naphthenic Tri-Aromatics	Poly-Aromatics	Sulfur-containing Aromatics
1	4	5	1	1			1	1										
2	5	6	1	1	2		1	1										
3	6	7	1	1	3		2	1			1							
4	7	8	1	3	4	1	1	3			1							
5	8	9	1	2	11	2	3	4		1	4							2
6	9	10	1	7	11	3	2	4		1	7	2						2
7	10	11	1	7	17	2	2	6		1	9	2	1					2
8	11	12	1	9	10	1	2	7		2	8	3	2					
9	12	13	1	11	14	8	2	7		2	13	11	10	1	1			6
10	13	14	1	12	13	12	2	7		2	7	8	13	2	1			6
11	14	15	1	19	16	11	2	7	1	2	12	11	11	3	3			10
12	15	16	1	15	12	7	2	7	1	1	9	9	10	4	5	1		4
13	16	17	1	14	13	7	2	5	1	2	11	9	12	6	15	1		9
14	17	18	1	3	5	4	2	5	2	1	8	10	10	8	10	1	2	7
15	18	19	1	3	4	3	2	5	3	1	2	12	10	13	17	1	7	8
16	19	20	1	3	4	1	2	5	4		2	12	8	10	9	4	6	
17	20	21	1	5	4	2	2	5	3	1	2	7	6	7	10	4	14	5
18	21	22	1	2	4	1			4	1	2	9	2	8	7	6	17	4
19	22	23	1	2	4	2			4	1	2	8	4	7	5	7	22	5
20	23	24	1	2	4	1			3		2	9	2	5	3	5	17	
21	24	25	1	2	4	3			3	1	2	7	2	5	1	4	11	
22	25	26	1	1	4	1			3		2	7	2	5	1	4	8	
23	26	27	1	2	4	2			6		2	7	2	4	1	3	6	
24	27	28	1	2	4	1			5		2	5	2	4	1	3	5	
25	28	29	1	3	4	2			5		2	6	2	4	1	3	6	
26	29	30	1	2	4	2			5		2	6	2	4	1	3	5	
27	30	31	1	2	4	2			5		2	7	2	4	1	3	5	
28	31	32	1	1	3	2			2		2	4			1		1	
29	32	33	1		2	1			3		1	2						
30	33	34	1		1				1				1					
31	34	35	1		1	1												
32	35	36			1													
33	36	37	1		1				1									
34	37	38				1												
35	38	39																
36	39	40				1												
37	40	41																
38	41	42							1									

Figure 3 Chemical subclass versus Carbon number interval-based HB summary of the PetroRisk hydrocarbon library.

Block	Starting Boiling point (°C)	Ending Boiling point (°C)	n-Paraffins	iso-Paraffins	Mono-Naphthenics	Di-Naphthenics	n-Olefins	iso-Olefins	Poly-Naphthenics	Sulfur-containing Aliphatics	Mono-Aromatics	Naphthenic Mono-Aromatics	Di-Aromatics	Naphthenic Di-Aromatics	Tri-Aromatics	Naphthenic Tri-Aromatics	Poly-Aromatics	Sulfur-containing Aromatics
1	0	15.4		1														
2	15.4	30.8	1	1			1	1										
3	30.8	46.2	1															
4	46.2	61.6		2			1	1										
5	61.6	77	1	1	2		1	3										
6	77	92.4		1	2		1	1										
7	92.4	107.8	1	2	5	1	1	2			1							
8	107.8	123.2	1	4	6		2	2										
9	123.2	138.6		7	8	2	1	5			1							
10	138.6	154	1	4	8	2	2	2			4							
11	154	169.4	1	7	14	1	1	5			1							
12	169.4	184.8		9	9	2	2	6			6	2						
13	184.8	200.2	1	6	5	1	1	7		1	9	1						
14	200.2	215.6	1	19	14	8	2	3		1	8	3						1
15	215.6	231	1	17	11	11	2	8		1	13	5						
16	231	246.4	1	9	15	11	1	5		1		11	1					2
17	246.4	261.8	1	9	12	11	2	4	1		7	9	2					2
18	261.8	277.2	1	4	14	4	2	7	1	1	12	11	11	1	1			1
19	277.2	292.6		4	5	4	2	4	2	1	9	10	13	2	1			1
20	292.6	308	2	4	4	3	2	5	2	3	12	10	12	3	1			3
21	308	323.4	1	3	4	2	2	5	4	1	9	10	12	5	2			5
22	323.4	338.8	1	4	6	2	3	4	6	3	3	13	17	8	5			5
23	338.8	354.2	1	4	7	3			3	3	3	13	10	12	14	1		8
24	354.2	369.6	2	3	4	2			6		2	14	11	15	15	1		7
25	369.6	385	1	2	6	4			5	2	3	13	6	12	19	2	2	4
26	385	400.4	1	3	7	2			5	1	3	9	6	10	12	3	6	6
27	400.4	415.8	2	3	4	2			8		3	10	2	6	10	7	7	5
28	415.8	431.2	1	1	5	3			7	1	3	10	4	8	6	10	12	3
29	431.2	446.6	1	2	7	2			7		2	8	3	8	2	6	21	2
30	446.6	462	1	1	2	2			4		3	7	3	6	1	5	18	3
31	462	477.4	2		2	1			3		2	2	2	5	2	6	16	5
32	477.4	492.8			2	1						2		3	1	5	15	4
33	492.8	508.2	1			1			1				1		2	5	10	1
34	508.2	523.6	1													2	8	1
35	523.6	539				1											10	
36	539	554.4															3	1
37	554.4	569.8							1								2	
38	569.8	585.2															2	

Figure 4 Chemical subclass versus Boiling point (in °C) interval-based HB summary of the PetroRisk hydrocarbon library.

1.3. EMISSION ESTIMATION

PetroRisk can execute environmental exposure and risk assessments on a predefined set of 44 lifecycle stages and uses: from the manufacture of the substance to its inclusion in articles. For each relevant lifecycle stage of the substance for which the user has provided an annual EU tonnage in the tab ‘product lifecycle information’ of the input file, a regional and local fraction is used to estimate a continental, regional and local annual tonnage from the user provided EU tonnage (in tonnes/yr). For each stage, a default number of annual release days is used to extrapolate the annual local tonnage to a daily local tonnage. Subsequently, the release factors (RF) provided in the spERCs are used to extrapolate these tonnages to annual continental, regional and daily local emissions to air, wastewater and soil¹. The applied regional and local fractions, number of release days, and RFs have been predefined in the [sector-specific Environmental Release Categories \(spERCs\)](#) by the European Solvents Industry Group (ESIG), and are based on use information obtained from Downstream Users (DUs) and on default generic approaches proposed in Guidance [Part D - Chapter R.16](#).

¹ Please note that, as per REACH Guidance Chapter R.16, direct releases to (‘non-agricultural’, ‘other’, or ‘industrial’) soil are considered at the regional and continental scale, but not at the local scale.

The chemical composition of the substance fractions emitted to air and wastewater will differ from the composition of the unreleased substance: the emission to air will mainly comprise the most volatile constituents of the substance, while the emission to wastewater will mainly comprise the most water-soluble constituents². To estimate the composition of the air and wastewater emissions, PetroRisk applies Raoult's Law on the representative product composition (see [Section 6.3](#))

The exposure estimation finally results in use-specific local (in T/d), regional and continental (in T/y) emissions to air, wastewater and soil for each representative hydrocarbon.

1.4. SITE-SPECIFIC INFORMATION

In the 'Site-specific Production' sheet of the input file, PetroRisk 8.01 allows the user to provide site-specific use conditions (e.g. annual site tonnage, wastewater flow, dilution factors) for the life cycle stage 'Manufacture'³. In the meta-node 'Release Estimation (before RMMs)', PetroRisk will use the provided site information, generating a more representative 'worst-case' set of use conditions to override the generic 'worst-case' use conditions defined by the spERCs.

1.5. PREDICTED ENVIRONMENTAL CONCENTRATIONS

In PetroRisk, an environmental exposure estimation is performed on each representative hydrocarbon according to REACH Guidance [Part D - Chapter R.16](#). All Guidance calculations to derive the relevant Predicted Environmental Exposure Concentrations (PECS) and human exposure doses have been implemented in the PetroRisk metanode "Exposure Estimation". The Guidance approach relies on 2 rather complex multimedia partitioning models: SimpleTreat, for estimating the fate in a wastewater treatment plant, and SimpleBox, for estimating the fate in the regional (and continental) environment, where, in contrast to the local environment, degradation and intermedia partitioning is assumed to play an important role. The complex calculations from within these models were not transcribed into PetroRisk, as it would require a substantial programming effort and would slow down the PetroRisk tool. Instead, a 'Fate Factor' (FF) approach¹³ was implemented (see [Section 6.7](#)).

1.6. HAZARD CHARACTERIZATION

In the metanode 'Hazard Characterization' (see Figure 1), PNECs for aquatic species and Sewage Treatment Plant (STP) micro-organisms are generated based on the Target Lipid Model (TLM) for each representative hydrocarbon. PNECs for sediment and soil are derived from the aquatic PNEC by an Equilibrium Partitioning (EqP) based extrapolation. For addressing the secondary poisoning endpoints (fish-eating predators, marine top predators, and terrestrial (worm-eating) predators), a default 'oral' PNEC of 8.77 mg/kg wet weight (ww) is assigned to each hydrocarbon in the representative constituent library. Please see [Section 6.4](#) for further details.

In the 'substance DNELs' worksheet of the PetroRisk input file, the user can provide the 'whole product' oral and inhalation Derived No Effect Levels (DNEL, in µg/kg BW/day). If no DNELs are provided, PetroRisk will assume that the substance is not considered hazardous to the general human population, and hence the 'Man via Environment' (or 'Indirect Human Exposure') assessment will not be performed.

² The fraction directly released to soil is assumed to have the same composition as the 'parent' substance.

³ For the next PetroRisk update, Concawe plans to facilitate the derivation of a representative worst-case scenario for all industrial uses.

1.7. RISK CHARACTERIZATION

In the metanode 'Risk Characterization', PetroRisk will compare, for each identified use, the calculated PECs with the calculated PNECs via the Risk Characterization Ratio (RCR) concept:

$$RCR = PEC/PNEC$$

A RCR is generated for each representative hydrocarbon for each of the 10 environmental protection goals (STP micro-organisms, freshwater organisms, sediment organisms, seawater organisms, marine sediment organisms, agricultural soil organisms, freshwater (fish-eating) predators, marine (fish-eating) predators, marine top predators, and terrestrial (worm-eating) predators).

With the additive nature of the narcotic mode of toxic action which characterizes hydrocarbons, the individual RCRs can be summed to represent the environmental risks related to the entire UVCB substance.

For the 'Man via Environment Assessment', the human intake doses via ingestion (diet) and via inhalation of each representative hydrocarbon are first summed to the UVCB substance level, and then compared to the oral DNEL and inhalation DNEL, respectively, that were provided by the user in the input file.

1.8. IDENTIFYING APPROPRIATE RISK MANAGEMENT MEASURES (RMMS)

A use of a substance is demonstrated to be 'safe' if the resulting exposures do not exceed toxic threshold concentrations or, in other words, if all use related RCRs are at or below a value of 1. If the risk assessment fails to demonstrate safe use, then the described use operational conditions (OC) need to be refined. More guidance on RMMs and OCs can be found in [REACH Guidance Part G - Chapter R.13](#).

In PetroRisk, the user can opt for the model, if 1 or more RCRs are above a value of 1, to automatically calculate and mathematically implement the air and/or wastewater RMM removal efficiencies that would be required to achieve 'safe' emission levels. The approach considers the contributions from all emissions from all uses of the substance, and will prioritize the emissions who contribute most to the predicted risks during an incremental calculation process (see [Section 6.9](#)). It is up to the user to judge whether the calculated treatment efficiencies are representative and practically implementable.

1.9. DOWNSTREAM USER (DU) SCALING

PetroRisk is developed to create Generic 'worst-case' Exposure Scenarios (GES) for the uses of hydrocarbon based UVCB substances. The OCs as defined in the (specific) Environmental Release Categories (spERC) are applied⁴ to generate the GESs. A simple Excel-VBA based tool is provided with PetroRisk to 'scale' the GESs of industrial lifecycle stages and uses to site specific OCs. More information on the Scaling Tool can be found in [Section 7](#).

⁴ For the lifecycle stage 'Manufacture', the user can provide site-specific conditions to refine the GES. For the next PetroRisk update, Concawe plans to facilitate the derivation of a representative worst-case scenario for all industrial uses.

2. PETRORISK VERSION 8 - MAIN IMPROVEMENTS

Compared to previous Microsoft Excel-VBA based versions, the PetroRisk tool has been largely reprogrammed in the KNIME analytics platform. The main improvement within the updated model is the **refined Fate Factor (FF) approach**: an environmental exposure and risk assessment according to REACH Guidance is based on linear algorithms. Estimated exposures and risks resulting from a use of a chemical will thus linearly depend on the emission levels, with intercepts at 0 and slopes which are specific to the chemical, emission (air, wastewater or soil), and end-compartment (e.g. marine sediment). Thus, the entire exposure estimation and risk characterisation can be abbreviated if these slopes, or Fate Factors (FF), have previously been quantified.

In earlier PetroRisk versions, FFs were generated using EUTGDsheet v1.24 (Excel based implementation of the Guidance concept) with fixed continental, regional and local annual emissions of 100, 10 and 1 Tonnes/year, respectively^{13,14}. This approach had 2 major draw backs:

- 1) The generated FF libraries represented the entire EUTGDsheet tool. Thus, the generated FFs relied on the models and parameters that were applied within, and the chemical specific data that was provided into EUTGDsheet. This 'exhaustive' FF approach did not facilitate the implementation of improvements to the PetroRisk tool, as with every refinement the EUTGDsheet would have to be adapted and all FF libraries regenerated.

EUTGDsheet is a more transparent and more flexible implementation of EUSES in Microsoft Excel, developed and maintained until 2008 by the Netherlands Centre for Environmental Modelling (NCEM). EUTGDsheet is no longer updated or publicly available. Some of the approaches adopted in the REACH Guidance (and thus in the EUTGDsheet and EUSES models) are meanwhile also outdated and/or more applicable approaches exist for hydrophobic chemicals.

- 2) FFs from continental, regional and local emissions were generated simultaneously using a 100:10:1 continental:regional:local emission ratio. However, this approach is flawed due to 2 aspects:
 - a. that ratio in practice largely differs between uses. For example, for a default industrial use, it is worst-case assumed that the total EU tonnage (continental + regional tonnage) is manufactured or used at both the regional and the local scale (a 0:100:100 ratio is applied), while for a default wide dispersive use (professional or consumer use) it is assumed that 10% of the EU tonnage is used at the regional scale, and 0.05% of the regional tonnage is used at the local scale (a 90:10:0.005 ratio is applied).
 - b. continental emissions can significantly contribute to the regional scale, and continental and regional emissions to the local scale. The derived regional and local FFs however assumed a fixed continental and regional background.

Thus, briefly, the generated FFs were only correctly applicable to a 100:10:1 continental:regional:local emission ratio. Generally, the FF approach led to an overestimation of exposures and risks for wide dispersive use scenarios and an underestimation for industrial use scenarios.

The new 'minimalistic' FF approach only encompasses 2 FF libraries, representing SimpleTreat and SimpleBox, which are 2 rather complex multimedia fate partitioning models that are embedded in the Guidance (and thus in EUTGDsheet

and EUSES). All other parameters and calculations from the Guidance are now transparently encoded in the PetroRisk tool.

One remaining drawback of the new approach is that the SimpleTreat and SimpleBox FFs were generated with fixed settings (e.g. a default environmental temperature of 12 °C), and that current SimpleTreat or future SimpleBox versions are/will no longer be available in Excel format. Future-wise however, it may be feasible to integrate Java-based models (such as SimpleTreat version 4) directly into the PetroRisk KNIME workflow.

The major advantages of the new FF approach are:

- 1) The FF concept correctly applies to all continental:regional:local emission ratios. After having implemented the new FF concept, but before having implemented additional improvements (see below), the new PetroRisk Tool estimated exposure concentrations and risk characterization ratios between 98.5 and 101% identical to those estimated with EUTGDSheet v1.24 for 3 different hydrocarbons (toluene, benzo[a]pyrene and n-pentadecane) and various use conditions.
- 2) Parameters and calculations outside of SimpleTreat and SimpleBox are accessible within the PetroRisk workflow and can thus be easily adjusted or improved by the PetroRisk developers and users. For example, PetroRisk 8.01 by default implements improved estimations of K_{oc} , BMF and of indirect human exposure ('Man via Environment').
- 3) SimpleTreat or SimpleBox updates, or alternative models, can be incorporated more easily into PetroRisk. PetroRisk 8.01 by default encompasses SimpleBox and SimpleTreat versions 4, including a SimpleTreat model specific for industrial scenarios.

The second large improvement to PetroRisk is the optional **automated calculation and mathematical implementation of the onsite air and wastewater treatment efficiencies** required to achieve 'safe' emission levels. The approach considers the contributions from all emissions from all uses of the substance, and will prioritize the emissions who contribute most to the predicted risks.

As a result of the automated calculation of required treatment efficiencies, PetroRisk has now the ability to **handle input files in batches**: once the user has defined the PetroRisk settings, including the input and output folder locations, the model will 'loop' through the input files and generate related output files without further user interaction. Once the batch is completed, the results of all inputs can also be retrieved at the end of the PetroRisk KNIME workflow as a single dataset.

3. KNIME - A BRIEF INTRODUCTION

The [Konstanz Information Miner](#) (KNIME) is an open source data analytics, reporting and integration platform based on Eclipse and written in Java. An intuitive drag and drop style graphical user interface allows visual assembly, execution and analysis of complex data flows (termed workflows) without the extensive need for coding.

3.1. NODES AND WORKFLOWS, META-NODES AND SUB-WORKFLOWS

A node is the smallest processing unit in KNIME. Each node has been dedicated to perform a specific task with minimal programming. For example, training a decision tree, filtering data rows, calculating a pivoting matrix, applying a model. Nodes in the editor appear with their icon, their name, their background (indicating the node type), their ports and a traffic-light status display. A KNIME user can choose from over 2 000 nodes from the node repository, including nodes which integrate external tools (see 2.4) into a workflow. After being created, a node needs to be configured to execute the task. After configuration, a node needs to be executed to actually carry out the assigned task.

The available node types are: source (any kind of data source, green), sink (any kind of persisting nodes, blue), manipulator (data transforming nodes, brown), miner (orange), predictor (red), view (nodes that display data, dark-yellow), meta (nodes that can contain other nodes, violet) and other (grey-blue).

Ports on the left of the node icon are input ports, the ones on the right are output ports. Ports with a black triangle are data ports. Data model ports are represented by small blue squares.

Each node has a state, and a traffic light depicted under each node represents the node's state. The red light means the node has been created, but it is not ready to do anything, it needs to be configured (it is either not fully connected, some settings may be missing or incorrect, or the state of the predecessor node is also red). The amber light means that the node has been configured and it is ready to run its task. The green light indicates that the node has executed its task successfully. The crossed red light indicates that the node has executed its task unsuccessfully.

A sequence of nodes makes a workflow. A workflow is the graphic equivalent to a script as a sequence of instructions. Nodes can be connected to each other through their input and output ports to form a workflow.

Meta nodes are nodes that contain sub-workflows, i.e. in the workflow they look like a single node, although they can contain many nodes and even more meta nodes. They are created with the help of the meta node wizard, which contains customisable pre-defined meta-nodes. Meta nodes look different to normal nodes: the icon is not rounded and has a dark grey background. There is no status light and no progress. The state of a meta node is displayed by an icon in the meta node (seen from outside). The states of a meta node are the same as the states of a workflow. A meta node can be: (1) idle/configured if there is at least one node inside the meta node that is neither executed nor executing (an orange clock icon); (2) executing if at least one node is executing (a green 'fast forward' icon); (3) executed if all contained nodes are executed (a green 'check' icon) (see Figure 9).

3.2. USER INTERFACE

The KNIME Workbench is made up of the following components:

KNIME Explorer: Overview of the available workflows and workflow groups in the active KNIME workspaces, i.e. your local workspace. Once imported, you will have PetroRisk there.

Workflow Coach: Lists node recommendations based on the workflows built by the wide community of KNIME users. It is inactive if you don't allow KNIME to collect your usage statistics and it won't be useful to run PetroRisk.

Node Repository: All nodes available in core KNIME Analytics Platform and in the extensions you have installed are listed here. The nodes are organized by categories but you can also use the search box on the top of the node repository to find nodes. If you don't create new workflows or change the current one you don't need to use this component either.

Workflow Editor: Canvas for editing and running the currently active workflow.

Description: Description of the currently active workflow, or a selected node (in the Workflow Editor or Node Repository).

Outline: Overview of the currently active workflow.

Console: Shows execution messages indicating what is going on under the hood. In PetroRisk you will get useful information such as RCRs above one, and the steps you need to perform in order to re-run PetroRisk if you desire to recalculate emission factors, for instance.

You can select what components you want to see from the "View" menu. To use PetroRisk you just need the KNIME Explorer, the workflow editor and the Console. A more detailed explanation can be found online at: https://docs.knime.com/2020-12/analytics_platform_workbench_guide/index.html#workspaces.

3.3. VISIBILITY & TRACEABILITY

All data processed by KNIME is visible at every step of the calculations. This allows for: (1) analysis of intermediary data, (2) validation of the model, (3) explanation of model details to regulators and auditors, and (4) debugging.

3.4. EXTENSIBILITY

KNIME has many different integrations such as database connectors, molecular viewers, export formats, and more. This makes the PetroRisk workflow a tool that can easily be modified to fit into a wide range of more complex business processes. It also allows the workflow to be easily adjusted to add more visualisations, charts, or reports depending on the user's needs.

4. INSTALLATION OF KNIME AND PETRORISK

In order to run PetroRisk, KNIME (version 4.5.2 or newer) should be installed on your computer. You can get the latest version from the webpage (<https://www.knime.com/downloads/download-knime>). We suggest using the Analytics Platform version of KNIME, and not the Server version, as the former will run faster. Additionally, we would advise you to download the installer which allows you to easily define the amount of memory that KNIME can use, and thus to maximize the processing speed of the PetroRisk KNIME workflow: we advise to allocate at least 4Gb less and maximally 1 Gb less than your computer's total Random Access Memory (RAM) size to be available to KNIME. In Microsoft Windows, you can identify your computer's total RAM size via Start > Settings > About.

The first time you launch KNIME, you will be asked to create a workspace. Please create it on the local drive and not on a network folder, otherwise you could have problems loading workflows (<https://www.knime.com/forum/knime-users/problem-with-workflow-opening>).

The most recent PetroRisk workflow, release notes, input template file and input example files can be extracted from the PetroRisk ZIP archive file available at [Concawe's website](#). Open the PetroRisk workflow via "File-> Import KNIME Workflow...". Click on the "Browse..." option at the right of the "Select file..." input box and select the PetroRisk workflow (.knwf format). You will probably receive an error message asking for the installation of some packages (e.g. "KNIME Virtual Nodes"). Please proceed with the installation of the packages and accept the terms and conditions.

Please also ensure that "KNIME Analytics Platform 4.0 Update site" and "KNIME Community Contributions (4.0)" are enabled via "File → Preferences → Install/Update → Available Software Sites" (see Figure 5).

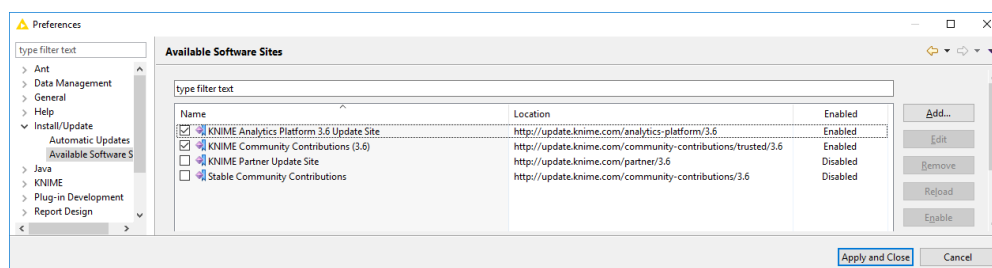


Figure 5 The 'Available Software Sites' tab in the KNIME 'Preferences' window.

5. RUNNING PETRORISK

5.1. PREPARING THE INPUT FILE

5.1.1. Product Composition

1. Open the Excel template file “PetroRisk_INPUT_TEMPLATE.xlsx”, which you have downloaded within the PetroRisk ZIP archive file.
2. In Row 2 of the first worksheet (‘product composition’), select whether you wish to import ‘high resolution’ (up to 16 predefined hydrocarbon subclasses) or ‘low resolution’ (‘aliphatics’ vs. ‘aromatics’), and boiling point or carbon number range data.
3. In columns C and D, you can define the boiling point or carbon number ranges manually. In the last row populated in column D, you can use a ‘higher than’ character (e.g. ‘> 30’) if you wish the last blocks to also encompass all available constituents with higher carbon numbers or boiling points.
4. As from cell E5, input the masses of each hydrocarbon block (HB) in the corresponding cell. HBs which are not relevant can be left blank.

5.1.2. Product Lifecycle Information

5. On the second sheet (product lifecycle information), input the corresponding tonnages (as T/yr) for each area of application, leaving blank tonnages for the ones that are not relevant.
6. If no tonnages have been provided, PetroRisk will not perform an exposure (and hence risk) assessment but will only generate the representative substance composition. Typically, the user will leave the worksheet empty if the substance is not classified according to CLP as ‘hazardous’ and if it does not fulfil the PBT criteria (REACH Article 14(4)).

5.1.3. Site-specific Production

7. Optionally, on the third sheet (Site-specific Production), add manufacture site (i.e. refinery) specific conditions: Annual Site Tonnage (T/y), Wastewater Flow (m³/d), Receiving water type (‘Riverine’ or ‘Marine’) and the Dilution factor (DF). The provided information will be used to define the worst-case use conditions, instead of the generic use conditions defined by the ‘Manufacture’ spERC. The Refinery Code is facultative and is not captured or used by PetroRisk. Default wastewater flow and DFs will be used if no site-specific values are provided.

5.1.4. Substance DNELs

8. For the ‘Man via Environment’ assessment (MvE), an oral and inhalation systemic, long-term DNEL should be provided by the user in the fourth sheet (Substance DNELs). If cells C3 or C4 is left blank, then a MvE will not be performed.

5.2. PETRORISK SETTINGS

1. Please ensure that KNIME is properly installed and the PetroRisk workflow properly imported (see [Section 4](#)).
2. Open KNIME, and open the PetroRisk workflow by double-clicking it in the ‘KNIME Explorer’ window. The workflow should load into the KNIME workflow editor.

5.2.1. Select the Input Folder

- Once the workflow is loaded, double click on the orange 'List Files/Folders' node (Fig. 1). A dialog box will pop-up (see Figure 6).

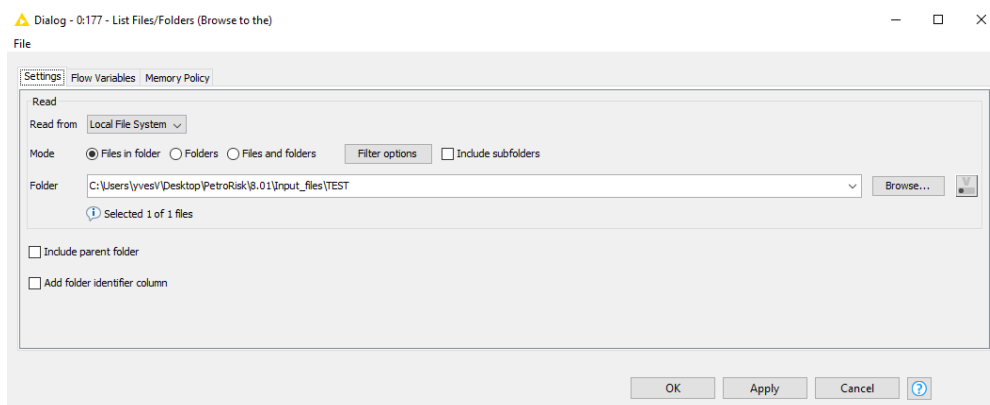


Figure 6 The 'Browse to the Input Folder' List Files/Folders Dialog box.

- Browse to select the folder containing the input files. PetroRisk will execute all the files within the folder. You can also opt to execute all files within the folder and its subfolders. Press the 'OK' button when done.

5.2.2. General Settings

- Next, back in the PetroRisk main workflow, double-click the 'General Settings' component to open the related Dialog box (see Figure 7). This dialog box allows the user to easily alter the main parameters and settings of the PetroRisk model.

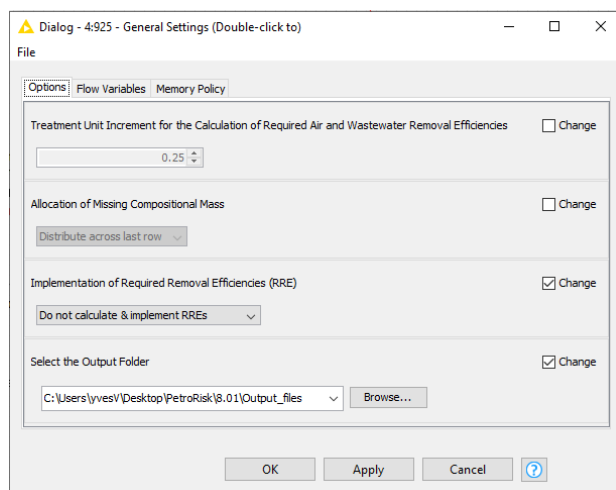


Figure 7 The 'General Settings' Dialog box.

a. Select the Output Folder

The user can indicate the folder in which the output files should be stored. If no output folder has been selected, the output files will be stored in the input file folder. The output file names will be deduced from the input file name, removing 'input' where applicable and extend the file name with '_OUTPUT'.

a. Allocation of Missing Compositional Mass

If the user has provided, via the input Excel workbook, a total HB mass less than 100% w/w, PetroRisk can scale the provided composition via 2 approaches: evenly scaling each HB for which a mass was provided, or assign the missing mass to the last boiling point or carbon number range. The latter approach is typically applicable to incompletely resolved compositions of ‘heavier’ substances (i.e. containing a substantial w/w fraction of constituents with a molecular weight above 400 g/mol): the ‘missing’ mass is reallocated to the highest BP/C interval of each (sub)class according to the total detected mass for each (sub)class.

b. Implementation of Required Removal Efficiencies

The user can opt to have PetroRisk calculate and mathematically implement an optimal set of applied onsite air and wastewater treatment efficiencies, or Required Removal Efficiencies (RRE)s, to achieve “safe” use conditions (i.e. all RCR values ≤ 1) for all uses of the substance. The calculations mimic the stepwise manual approach risk assessors would typically apply to derive an adequate set of RREs (see [Section 6.9](#)). However, while the calculation and implementation of the RREs takes additional computing time, the user also may be rather interested in the exposures and risks resulting from the provided use conditions regardless whether the RCRs are above a value of 1.

c. Treatment Unit Increment for the Calculation of Required Air and Wastewater Removal Efficiencies

If the user has opted to calculate and apply RREs, these will be calculated via an iterative process: at each step of the process, PetroRisk will calculate, for each air and wastewater emission of each use of the substance, the overall ‘risk reduction’ resulting from an increase in applied ‘Treatment Units’ (see [Section 6.9](#)), and only retain the increase in treatment units which would result in the highest overall ‘risk reduction’. This process is repeated until all RCR values are ≤ 1 , and it results in a mathematical implementation of RREs across all emissions and uses of the substance with a minimal overall number of ‘treatment units’. In the ‘General Settings’ Dialog, the user can define the unit increment to any value above 0. The lower the value, the higher the precision but the slower the processing speed. A default increment of 0.25 has shown to give a good balance between precision and processing speed.

5.2.3. Limiting the Analysis to Specific (Sub)classes or Constituents

After double-clicking the ‘Class or Constituent Selector’ component, the user can deliberately exclude specific hydrocarbons, or entire hydrocarbon subclasses or classes, for example when the user has the knowledge that certain hydrocarbons are not present in the substance.

Following settings and parameters can also be adjusted relatively easily, but doing so should be done with caution.

5.2.4. Hazard Characterisation Settings

The user can alter the main parameters used to derive the PNECs after double-clicking the ‘Target Lipid Model Settings’ component. For more details on the Target Lipid Model and how it is applied to compute the concentrations above which 95% of species should be protected (HC5), please read [Section 6.4](#).

5.2.5. Environmental Settings

Environmental parameters and settings which are used throughout the PetroRisk model can also be reviewed and altered easily by the user after double-clicking the 'Environmental Settings' component.

a. Use Dissolved or Total Effluent Concentration

While SimpleTreat does calculate the dissolved and associated effluent fraction separately, EUSES and EUTGDsheet use the total (dissolved + associated to suspended matter) effluent concentration predicted by SimpleTreat for assessing STP microorganism toxicity and as input to the aquatic compartments. The Guidance (appendix A.16-3.3.1) states that 'the effluent concentration approximates the really dissolved concentration in activated sludge', which is incorrect when association to suspended matter is considered for (very) hydrophobic substances. This approach mathematically overestimates STP microorganism toxicity, as only the dissolved effluent fraction should be regarded as bioavailable (according to REACH Guidance appendix A.16-3.3.1). This approach will also (largely) overestimate dissolved fresh- and seawater concentrations of hydrocarbons, despite dissolved effluent concentrations released into the aquatic environment are further reduced by dilution and adsorption to suspended sediment in the freshwater and marine environment (according to Guidance equation R.16-29). Thus, it may be more correct to use the SimpleTreat dissolved instead of the total effluent concentration for these purposes. As a default, PetroRisk uses the predicted dissolved effluent concentration, but the user can still opt to use the total effluent concentration.

b. Cap Onsite WWTP Effluent Concentration to Water Solubility

According to REACH Guidance paragraph R.16.3.2.1, the effluent concentration predicted by SimpleTreat may be re-set to a value closer to the water solubility if the predicted effluent concentration significantly exceeds the water solubility. The guidance however states that this approach might not be valid for substances with a density lighter than water, and/or that are suspended or emulsified (thus generally including hydrocarbons). In a typical Sewage Treatment Plant (STP), hydrocarbons would partition mainly into the floating 'scum' layer in the primary settler or clarification unit, and would be skimmed off for treatment in (a) digester unit(s) together with the sludge. SimpleTreat however currently does not consider the 'scum' layer as a separate 'box'. As a result, the SimpleTreat estimated (dissolved) effluent concentration can (largely) exceed the substance water solubility. Also the SimpleTreat model adapted by Thunnissen et al.⁷ to better reflect the fate in an industrial wastewater treatment plant, may still predict effluent concentrations (far) above the water solubility.

Therefore, the user can select to have PetroRisk capping the onsite WWTP effluent concentration to the water solubility (at environmental temperature, by default 12 °C). The fraction that is thereby 'removed' from the effluent is added to the waste fraction (which could be recovered, recycled or disposed, e.g. by incineration)⁵, which in PetroRisk is the default fate of onsite generated sludge and scum.

c. Cap Regional Dissolved Water Concentrations to Water Solubility

SimpleBox versions 3 and 4 use different approaches to deduce dissolved from total (fresh and sea) water concentrations. While both versions correct for partitioning onto suspended organic matter, v3 additionally corrects for partitioning into biota ('biodilution'), while v4 additionally corrects for partitioning onto suspended and

⁵ Estimation of exposure from waste life is currently not covered by PetroRisk. For more information, please read [Guidance Part G - Chapter R.18](#).

colloid organic matter. Both model versions however regularly predict dissolved concentrations (far) above water solubility for (very) hydrophobic hydrocarbons. Therefore, an optional refinement is included in PetroRisk to limit the dissolved regional freshwater, seawater and groundwater concentrations to the water solubility limit at environmental temperature (which is 12 degrees Celsius by default).

d. Indirect Human Exposure Model

By default, PetroRisk applies the approach from Legind and Trapp (2009)⁹, which is basically a refined Guidance ‘Man via Environment’ assessment (see [Section 6.6](#)): it uses realistic dietary consumption data and crop-specific plant uptake models (i.e. roots, potatoes, leafy vegetables, lettuce, fruits and cereals). Nonetheless, the user can opt to implement the Guidance default approach, which is explained in detail in the [EUSES background report](#)².

e. Soil and Sediment Assessment Factor

While the technical basis of it is debated, sediment and soil PNECs can be further reduced by an assessment factor of 10 for compounds with $\log K_{ow} > 5$ (see also Guidance R.7b, R.7c, R.10 and E). For petroleum products, Concawe recommends to apply a default factor of 1 (thus no correction applied). This is based on a detailed compilation and analysis of soil and sediment toxicity data for hydrocarbons indicating predictions derived using the target lipid model (TLM) and equilibrium partitioning theory (EqP) do not underestimate observed toxicity¹². Recent work suggests that the use of EqP may be overly conservative in assessing ecological risks of petroleum hydrocarbons¹⁵.

All other parameters within the ‘Environmental Settings’ Dialog Box have been by default assigned the Guidance values. Changing these parameters should be done with caution however, as the default values have been used for deriving the SimpleTreat and SimpleBox FFs, and the FFs won’t be automatically updated.

5.2.6. spERC Parameters

The generic use conditions and release factors that have been assigned to each use can be reviewed and altered within Table Creator nodes ‘spERCs’ and ‘Release Factors’, respectively. The ‘Release Factors’ table contains the use specific, and often also vapour pressure and water solubility class specific release factors to air, wastewater, soil and waste. Double-clicking on both ‘Table Creator’ nodes will allow you to review or alter the spERC details.

5.2.7. PetroRisk Constituent Library

Double-click the orange ‘Constituent library’ Table Creator node in the main workflow to review or update it. More information regarding the constituent library can be found in [Section 6.1](#). Please note that, if you have added or altered constituents, you need to also generate and provide (updated) SimpleTreat and SimpleBox FFs for these (see [Section 6.7](#)).

If you have made changes to the default PetroRisk settings, we would advise you to capture these in your communication to any relevant stakeholder (e.g. when compiling the Chemical Safety Report to support your REACH registration). If you have made multiple and/or ‘deeper’ changes to the workflow (e.g. altered spERCs or constituent library) we would additionally advise you to save and export the altered workflow and share it together with your communication.

5.3. RUNNING THE PETRORISK WORKFLOW

With the PetroRisk main workflow back in the Workflow Editor Window, push the green ‘fast-forward’ button (“Execute All”) in the KNIME Toolbar (see Figure 8), or press “Shift+F7”.

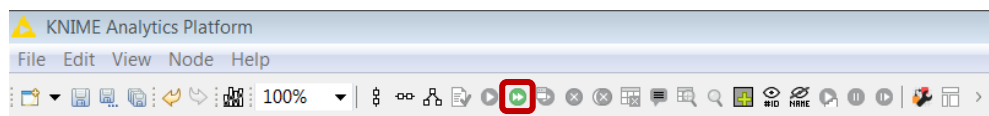


Figure 8 Detail of the KNIME toolbar, with the “Execute all executable nodes” button highlighted.

You will see the workflow icons changing status.

The status of nodes and components is represented by a ‘traffic light’ underneath the node or component. A red ‘light’ means the node or component is not properly configured, a yellow ‘light’ means the node or component is properly configured but not yet executed, a green ‘light’ means the node or component is successfully executed. An ‘alert signal’ (a triangle with an exclamation mark) on top of the traffic light indicates that (one of) the calculation(s) has failed (typically an input parameter is missing).

Typically, such errors would occur in the early stages of the workflow (e.g. the ‘List Files/Folders’ node, or the ‘Release Estimation’ metanode), and are caused by 1 or more errors in the input file. In case you continue to encounter a ‘red’ traffic light or an alert signal, please contact Concawe at admin@super-sief.eu.

The status of metanodes is represented by a clock (paused), a fast forward icon (in execution) and finally to a ‘check icon’ (finished task).



Figure 9 The different meta-node states.

Ports on the left of the node icon are input ports, the amber, red and green dots graphically represent the output ports.

If one of the calculations within a metanode failed, the metanode state will remain ‘Paused’. You can search where the workflow halted by opening the metanode by double-clicking it.

You can reset individual nodes, components, metanodes (and automatically all the subsequent parts of the workflow) or the entire workflow (press CTRL+A on your keyboard), by either selecting it and pressing F8, or by right-clicking it and selecting ‘Reset’ in the appearing menu. You can run individual nodes, components or metanodes by selecting it and pressing F7, or by pressing the ‘play’ button in the Toolbar.

5.4. MODEL OUTPUT

The output is available in 2 formats: individual Excel workbooks for each substance, or a single data-table at the end of the PetroRisk workflow.

5.4.1. Excel Output File

The generated Excel output files are stored in the output folder. If no output folder was specified in the 'General Settings' node, then the output files are stored in the input file folder. The output file will have the same name as the input files with the suffix "_OUTPUT.xlsx" (if the input file contains "input", that will be deleted). The PetroRisk Excel output file is made up of the following sheets:

Composition: Contains the compositional information provided by the user (see [Section 6.2](#)).

Constituents: Contains the hydrocarbon structures from the PetroRisk constituent library (see [Section 6.1](#)) which are representative of the product composition, and includes the predicted mass fractions of each structure emitted to soil, water and air (see [Section 6.3](#) for a detailed description of the calculations).

Lifecycle information: Shows the uses and related EU tonnages provided by the user.

Local assessment: Contains, for every lifecycle stage and use of the substance, the generic use conditions used for the assessment, the estimated local concentrations (i.e. without a regional background concentration) and Predicted Environmental Concentrations (PECs, i.e. with regional background concentrations), and the resulting RCRs. For scaling the generic assessment for a use to a site-specific assessment, the relevant column within this sheet should be copy-pasted into the Scaling Tool (see [Section 7](#)).

Regional assessment: Contains the calculated regional PECs and RCRs (both environmental and indirect human exposure) for all uses combined. These PECs and RCRs serve as background concentrations for the use specific local assessments.

Properties: Contains parameters which are specific to the substance, and not to individual hydrocarbons: the user provided oral and inhalation DNEL and the estimated vapour pressure and water solubility of the substance (which are based on the vapour pressure and water solubility of the individual representative hydrocarbons and their mass contribution to the substance).

5.4.2. Data Table Output

Once the complete workflow has been successfully executed, you can also gather the results as a single database, containing all the output for all substances within the assessed batch. This approach is of particular interest to database handlers. It is useful to generate an overview of the performed exposure and risk assessments, or it can be used in subsequent KNIME programming (e.g. other output formats). You can view the full data-table by right-clicking the 'Loop-End' node at the end of the PetroRisk workflow, and subsequently clicking on the 'Collected results' icon at the bottom of the pop-up menu (see Figure 10). From the 'Collected results' table, you can select the aggregated output by pressing CTRL+A on your keyboard and subsequently copy it either via the Menu Bar (via 'Edit' > 'Copy with Column Header') or by pressing CTRL+SHIFT+C on your keyboard. The aggregated output contains the results of the release estimation, exposure estimation and hazard characterization for each use of each substance.



Figure 11 Example of the collected results at the end of the PetroRisk workflow, highlighting the menu option to copy the entire table with column headers.

In a similar fashion, you can also gather intermediate output from any node, component or metanode within the workflow.

6. TECHNICAL BASIS

PetroRisk is designed to enable and facilitate the environmental exposure and risk assessment of hydrocarbon UVCB substances according to REACH Guidance. The exposure and risk assessment concept is applied on individual hydrocarbons which are selected to be representative for the product composition provided by the user.

The technical approaches are described in full detail in ECHA Guidance and in the EUSES background document, and will not be discussed in further detail in this report:

- Appendix R.7.13-1 (Technical Guidance for Environmental Risk Assessment of Petroleum Substances) of [Part G - Chapter R.7c](#) (Endpoint specific Guidance)
- [Part D - Chapter R.16](#) (Environmental Exposure Estimation)
- [Part E](#) (Risk Characterization)
- [EUSES 2.0 Background Report](#).

The approaches which are different or additional to the Guidance approaches will be discussed in more detail below. This section includes information on assignment of mass fractions to representative hydrocarbons, improved prediction methods for several hydrocarbon properties, and an improved 'Man via Environment' assessment approach.

6.1. CONSTITUENT LIBRARY AND HYDROCARBON PROPERTIES

The library currently consists of 1,512 hydrocarbons which are considered compositionally relevant for petroleum UVCBs. The hydrocarbons are described by their name, SMILES code, carbon number, and hydrocarbon class and subclass. Molecular weight, Boiling point, vapour pressure, log K_{ow} , Molecular Connectivity Index (MCI), melting point, water solubility, specific degradation rate constant with OH-radicals (kOH) have been estimated using EPI Suite 4.1. Other properties are discussed more in detail below. All physicochemical parameters correspond to conditions at standard temperature (25°C) and pressure (1 atm).

6.1.1. Organic Carbon-water Partitioning Coefficient (K_{oc})

As applied in EUSES and EUTGDsheet, the Guidance approach prescribes the K_{ow} -based prediction of K_{oc} developed by Sabljic et al. (1995)³ for 'predominantly hydrophobic' chemicals. Accordingly, the wastewater treatment, regional exposure and Man via Environment models also rely on these K_{oc} predictions. The K_{ow} based prediction has a x-variable domain for Log K_{ow} 1-7.5, with an accuracy of 0.83 log units. Sabljic et al (1995) state that the method has large uncertainties for the predominantly hydrophobic chemicals, particularly in the log K_{ow} range from 4 to 7.5. Therefore, Sabljic et al have developed a MCI based method, which has a x-variable domain for log K_{ow} 3-22 with an accuracy of 0.54 log units. By default, PetroRisk implements the K_{ow} based method for hydrocarbons with a MCI value lower than 3 (i.e., for 19 hydrocarbons), and the MCI based approach for hydrocarbons with a MCI value at or above 3. For reference, the smallest MCI value in the constituent library is 1.73, the largest value is 19.9. MCI based K_{oc} predictions were also used to generate the SimpleTreat and SimpleBox FFs.

6.1.2. Degradation Half-lives

The aquatic biodegradation half-life has been estimated using BioHCWin v1.01a¹⁶. The aquatic half-life is extrapolated to soil and sediment half-lives using extrapolation factors of 1 and 4, respectively¹⁷.

To estimate the biodegradation half-life in a STP, open literature was examined in 2005 for activated sludge treatment studies that monitored removal of hydrocarbons. Hydrocarbons with more than one reported removal value from full scale studies and with an experimental environmental half-life (extracted from the BioHCWin training set) were retained for further analysis. As removal was generally measured as total removal and not specifically for biodegradation, SimpleTreat 3.1 was used to back-calculate a representative STP biodegradation half-life from the median total removal values obtained from the literature (see [Annex 1](#) for further details).

Regression of the estimated STP biodegradation half-lives with the experimental environmental aquatic half-lives results in an equation which is suitable for a relatively crude correction of BioHCWin predicted half-lives to half-lives in activated sludge reactors (see Figure 12 Experimentally derived environmental (aquatic) biodegradation half-lives vs. STP biodegradation half-lives derived via SimpleTreat from experimental activated sludge treatment studies.).

$$HL_{bio_{WWTP}}(\text{in hrs}) = 0.1045 \times HL_{bio_{water}}(\text{in d})^{1.1239} \quad (1)$$

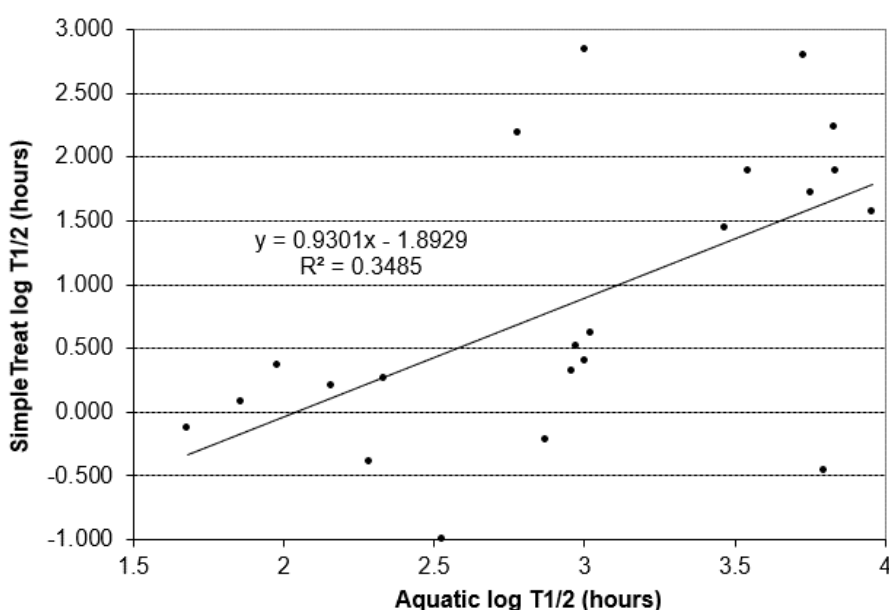


Figure 12 Experimentally derived environmental (aquatic) biodegradation half-lives vs. STP biodegradation half-lives derived via SimpleTreat from experimental activated sludge treatment studies.

For the generation of the SimpleTreat FFs, first order biodegradation rate constants were deduced ($k_{biodeg1} = (\ln 2) / HL_{bio_{WWTP}}$) to represent the biodegradation in the aqueous phase of the activated sludge.

6.1.3. Bioconcentration Factor (BCF)

BCFs were predicted according to approaches proposed in Guidance Chapter R7.c. The Veith et al. 1979¹⁸ model was chosen to be more representative for the 'lower-end' K_{ow} structures (applicability domain $\log K_{ow}$ 1 - 7.05), while the Bintein et al. 1993¹⁹ model was chosen for the 'higher-end' K_{ow} structures (applicability domain $\log K_{ow}$ 1.12 - 8.60). Both model predictions overlap at a $\log K_{ow}$ of 5.71. For hydrocarbons with a $\log K_{ow} \leq 5.71$, the BCF was predicted using the Veith et al.

model. For methane ($\log K_{ow} = 0.78$), the $\log K_{ow}$ cut-off 1 was applied in the Veith et al. model, resulting in a BCF of 1.40 L/kg. For constituents with a $\log K_{ow} > 5.71 - \leq 8.60$, the BCF was predicted using the Bintein et al. model. For constituents with a $\log K_{ow} > 8.60$, the $\log K_{ow}$ cut-off of 8.6 was applied in the Bintein et al. model, resulting in a BCF of 171 L/kg.

6.1.4. Biomagnification Factor (BMF)

The BMFs are predicted by the 'BMFpred consensus' model⁴ using AlvaScience's Alvarunner tool (<https://www.alvascience.com/alvarunner/>). A comparison between predicted BMFs and available experimentally derived BMFs indicate the model performs well for petroleum hydrocarbons (see Figure 13): 119 out of 158 predictions (or 75%) were less than 0.5 log unit different than the experimental results. 8 (or 5%) of the predictions underestimated the experimental results by more than a 0.5 log unit of error (see Annex 2).

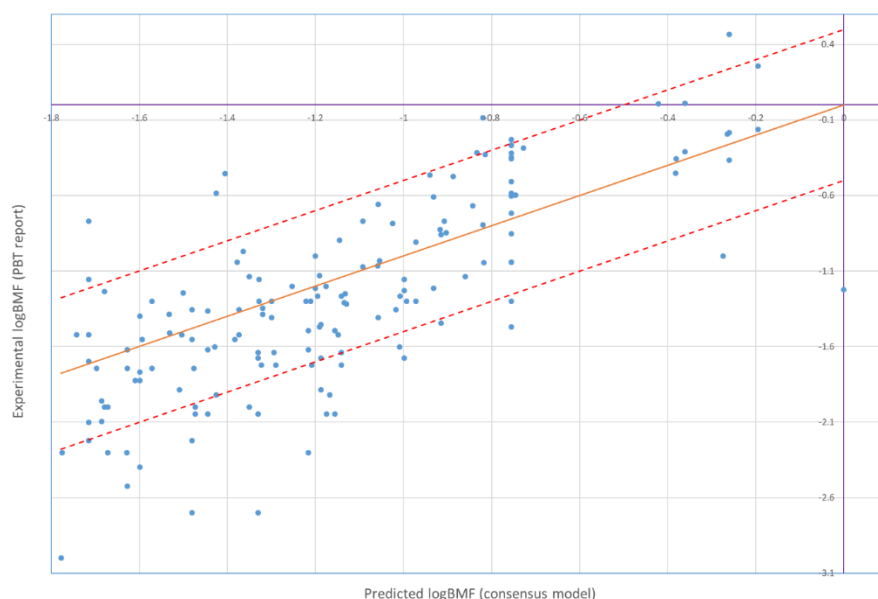


Figure 13 Observed vs predicted Biomagnification Factors (BMF).
The orange line is the 1 to 1 line (experimental = predicted). The red lines indicate ± 0.5 log units of error from the prediction.

The BMFpred consensus model overpredicts BMFs by factors between 0.1 and 33.5, and on average by a factor of 2.3 ± 0.6 (95% CI). In contrast, the Guidance default approach (as described in Guidance Table R.16-9) overpredicts BMFs by factors between 1 and 10,000, and on average by a factor of 352.1 ± 140.5 (95% CI).

6.2. FROM HYDROCARBON BLOCK TO CONSTITUENT CONCENTRATIONS

For most petroleum substances and other complex nonpolar organic mixtures, it is currently not technically feasible to separate or resolve the majority of constituents within the analyte. To date, comprehensive two-dimensional gas chromatography (GCxGC) generally provides the most detailed chemical characterisation for such substances. Due to the underlying physical principles of the GCxGC separation process, hydrocarbon constituents of the same structure class and size tend to elute in clusters. The resulting 2D chromatogram can be delineated into Hydrocarbon Blocks (HB) to approximate the total mass concentration of structures of a particular chemical class and carbon number range.

From its ‘constituent library’ (see [Section 6.1](#)), PetroRisk 8 can assign up to 1,560 representative hydrocarbon structures to up to 512 predefined HBs, based on carbon number or Boiling Point and chemical class or subclass. HBs can have anywhere between 0 and >300 assigned structures. Once the hydrocarbons are assigned to the HBs, the mass fraction for an individual structure (m_i) is determined by evenly dividing the HB mass, j , (m_j) among the assigned hydrocarbon structures ($structures_j$) according to the equation

$$m_{i,j} = \frac{m_j}{structures_j} \quad (2)$$

where $m_{i,j}$ is the mass of structure i in block j

$$m_j = \sum_n^i m_{i,j} \quad (3)$$

In certain cases, it is possible to have a HB with an allocated mass where there are no available library structures for assignment. This can be due to subtle inconsistencies between the constituent library and the compositional analysis input, or simply by a lack of representative structures for the HB (see Figure 3 and Figure 4). In these cases, the mass for that HB is re-assigned to the closest neighbouring block within the (sub)class to preserve the overall mass balance and to assign structures with similar physico-chemical properties to these “orphan” blocks.

The mole fraction, x_i for compound i in the substance is a key parameter which impacts the substance’s estimated vapour pressure and water solubility. This parameter is determined as the ratio of the moles of constituent, i , to the sum of all constituents in the petroleum substance. The molecular weight is used to convert between mass and molar units, where $mole_i = \text{mass} \times \text{molecular weight}$.

$$x_i = \frac{mole_i}{\sum_n^i mole_i} \quad (4)$$

The mass allocations for each hydrocarbon is determined by dividing the user-defined HB mass by the number of structures in the block, i.e. assuming each hydrocarbon in a HB is equally weighted.

When the user has provided weight percentages in the boiling point range vs. hydrocarbon class (i.e. aliphatics and aromatics) HB format, an additional weighting correction is applied to the aromatic mass distribution for relatively high BP (>350°C) blocks in order to accurately predict ecotoxicity of heavy petroleum products^{11,12}. This correction is based on observed mass distributions of polycyclic

aromatic hydrocarbon (PAH) structures and comparisons between observed and predicted toxicity for these heavy product types. Basically, high BP PAHs are currently underrepresented in the PetroRisk constituent library. Therefore, the mass allocations to high BP PAH structures are scaled up by approximately three times, while other aromatic structures (mono-, dicyclic aromatics, etc.) are scaled down proportionately to preserve the overall mass balance. This re-adjustment is performed in a step-wise process where the ratio of PAH to total aromatic structures (TA) is considered in order to consistently scale the mass assignments to individual structures in PAH and other aromatic classes. The adjusted mass allocation is performed as follows

$$\begin{aligned} &\text{If } (1 - \text{RATIO}_{PAH}) < 0.7 \\ &\text{then } a_0 = 0.7 \\ &\text{else } a_0 = (1 - \text{RATIO}_{PAH}) \end{aligned} \quad (5)$$

Where, the adjustment factor, a_0 , is derived using an empirically derived constant of 0.7^{11,12}. The ratio of PAH structures to all aromatic structures (RATIO_{PAH}) is calculated as:

$$\text{RATIO}_{PAH} = \text{NumberStructures}_{PAH} / \text{NumberStructures}_{AllAromatic} = \text{PAH/TA} \quad (6)$$

Polycyclic aromatic compounds are weighted using a correction factor, a_1

$$a_1 = 1 + \left(\frac{a_0}{\text{RATIO}_{PAH}} \right) \quad (7)$$

and all other aromatic compounds are scaled downward proportionately using a second correction factor, a_2

$$a_2 = 1 - \left(\frac{a_0}{(1 - \text{RATIO}_{PAH})} \right) \quad (8)$$

The mass assigned to the PAH structures ($m_{PAH,i}$) in these high BP blocks is calculated as

$$m_{PAH,i} = m_i \cdot \text{RATIO}_{PAH} \cdot a_1 \quad (9)$$

where m_i is the initial mass assigned to this PAH structure. Similarly, the re-adjusted mass assigned to the other high BP aromatic compounds ($m_{ARO,i}$) is calculated as

$$m_{ARO,i} = m_i \cdot (1 - \text{RATIO}_{PAH}) \cdot a_2 \quad (10)$$

6.3. RE-SCALING MASS DISTRIBUTION USING RAOULT'S LAW

The mass allocation procedure describes the mapping of individual structures to simulate substance composition. This composition is used to model direct emissions to soil but does not reflect the differential partitioning behaviour of complex substances to air and water. To account for the influence of library structure partitioning properties on the composition of air and water emissions, the substance composition is further scaled by the vapour pressure or water solubility of the structure, respectively. This ensures that the more volatile structures are enriched in the simulated emissions to air, while the water-soluble structures are given greater weight in estimated water releases, respectively.

Emissions to water are scaled by first calculating the individual aqueous solubilities ($C_{w,i}$) of each structure using Raoult's Law.

$$C_{w,i} = x_i \cdot S_i \quad (11)$$

where x_i is the mole fraction for library structure i in the petroleum substance (calculated from equation 4) and S_i is the corresponding sub-cooled aqueous solubility. The sub-cooled aqueous solubility is the theoretical solubility of a compound as if it were in the liquid state. For example, many PAHs and other high log K_{ow} compounds are crystalline as pure substances. However, the presence of other hydrocarbons in a petroleum substance acts as a solvent to dissolve crystalline phases in the petroleum substance. This has the effect of increasing the relative aqueous solubility of these sparingly soluble compounds. The overall aqueous solubility is calculated as the sum of all individual aqueous solubilities.

$$C_{w,Total} = \sum_{i=1}^n C_{w,i} \quad (12)$$

The revised mole fractions (x'_i) for emissions to water are calculated as the ratio of the individual water solubility to the overall solubility in molar units (e.g., moles/L)

$$x'_i = \frac{C_{w,i}}{C_{w,Total}} \quad (13)$$

Emissions to air are scaled in the same manner but instead using vapour pressure. The assumption is that volatilization is the primary driver for most air emissions.

6.4. HAZARD CHARACTERIZATION USING THE TARGET LIPID MODEL

6.4.1. Toxic Threshold Concentrations for Aquatic Organisms

Environmental effects for petroleum hydrocarbons are considered additive, so that the sum of all RCRs for the individual hydrocarbon structures is indicative of the overall risk of the UVCB substance. The PNECs used in PetroRisk are derived from the Target Lipid Model-derived chronic HC5 values for aquatic species^{8,20} and waste water treatment plant microorganisms²¹. The HC5 is the hazardous concentration that affects 5% of organisms. The general form of the HC5 is based on equation 14.

$$\log(HC_5) = E\{m \log(K_{MW})\} + E\{\log(C_L^*)\} - E\{\log(ACR)\} - k_Z \sqrt{V\{m \log(K_{MW})^2\} + V\{\log(C_L^*)\} + V\{\log(ACR)\} + 2 \log(K_{OW}) Cov} \quad (14)$$

The HC5 is based on the median (E) critical target lipid body burden (C_L^*) and the acute to chronic ratio (ACR), which is further modified by the variance (V) in the slope ($\log K_{ow}^2$), C_L^* , ACR and the covariance. The sample size extrapolation factor (k_Z) is based on the number of organisms in the database and related to the lower 5% of the distribution. The HC5 is based on an extensive database of critical body burdens (n=79 species) and ACRs (n=20 species) for fish, algae and invertebrates and explicitly accounts for variability in the acute species sensitivity distribution and acute to chronic effects extrapolation across diverse taxa (covering the 8 taxonomic groups included in the REACH guidance). This effects database includes aquatic and marine as well as pelagic and benthic species. The application of additional assessment factors (AF) is, therefore, not warranted and the HC5 is used as the PNEC (e.g., AF = 1). Recent work indicates that the HC5 statistic is very likely

(>99.6%) to be an effective concentration threshold for ensuring biodiversity protection²².

The HC5 makes use of the membrane-water partition coefficient (K_{mw}), which is an empirical bioavailability adjustment for high $\log K_{ow}$ structures (>6) consistent with the development and validation of the PetroTox model^{11,12}.

$$\log(K_{mw}) = \begin{cases} 6 & \cdots \text{ for } \log(K_{ow}) \geq 6 \\ \vdots & \\ \log K_{ow} & \cdots \text{ for } \log(K_{ow}) < 6 \end{cases} \quad (15)$$

For more details on the Target Lipid Model, please read McGrath et al. 2018⁸

6.4.2. Toxic Threshold Concentrations for Soil and Sediment Organisms

PNECs (in mg/kg ww) for the soil and sediment compartments are extrapolated from the TLM derived aquatic PNECs (in mg/L) using Equilibrium Partitioning Theory:

$$PNEC_{\text{sediment or soil}} = K_D \times \frac{PNEC_{\text{water}}}{\text{Assessment Factor}} \quad (16)$$

Wherein K_D is the sediment-water or soil-water distribution coefficient, which is deduced from the K_{OC} , converted to a wet weight basis and corrected for the pore water volume and density (2500 L/kg for solids, 1000 L/kg for water), in consistency with the Guidance:

$$K_D = \frac{1 - f_{dry} \times 1000 + (f_{dry} \times f_{oc} \times K_{oc} \text{ (in L/kg)}) \times 2500}{(1 - f_{dry}) \times 1000 + 2500 \times f_{dry}} \quad (17)$$

Wherein f_{dry} is the fraction of dry matter in the soil or sediment (0.2 default) and f_{oc} is the fraction organic carbon present in the soil (0.02 default) or sediment (0.05 default).

6.4.3. Toxic Threshold Concentrations for Aquatic and Terrestrial Predators

For addressing the secondary poisoning endpoints (fish-eating predators, marine top predators, and terrestrial (worm-eating) predators), a default 'oral' PNEC of 8.77 mg/kg wet weight (ww) is assigned to each hydrocarbon in the constituent library. The default $PNEC_{\text{oral}}$ is derived from the critical tissue lipid body burden (CTLBB) corresponding to the HC5²⁰ (in $\mu\text{mol/g}$ lipid), adjusted to 5% w/w lipid content and to an average molecular weight of 247 g/mol.

6.4.4. Toxic Threshold Concentrations for Indirect Human Exposure

For the 'Man via Environment' assessment (MvE), an oral and inhalation systemic, long-term DNEL should be provided by the user. The Derived No-Effect Level (DNEL) is the exposure limit of a substance below which no adverse health effects in humans are expected. In practice, DNELs are based on applying safety factors on observational (non-experimental, epidemiological) human data and/or non-human experimental mammalian toxicity studies. In REACH terms, the human health risk assessment is carried out for the different exposure routes (oral, dermal and/or inhalation), the different population groups (workers and general population), for different durations of exposure (short-term and long-term) and according to the type of effects (systemic and local).

6.5. REFINING THE GENERIC USE CONDITIONS FOR THE MANUFACTURE STAGE

In the 'Site-specific Production' sheet in the input workbook, the user can add manufacture site (i.e. refinery) specific use conditions: Annual Site Tonnage (T/y), Wastewater Flow (m^3/d), Receiving water type ('Riverine' or 'Marine') and the Dilution factor (DF). The provided information will be used to define the worst-case use conditions, instead of the generic use conditions defined by the 'Manufacture' spERC. If no wastewater flow is provided for a site, a default value of $10,000 \text{ m}^3/\text{d}$ will be assigned. If no DF is provided, the default values of 10 and 100 will apply for sites releasing to riverine and marine environments, respectively. Additionally, the provide site-specific riverine and marine DFs are capped to 100 and 1000, respectively.

The resulting generic wastewater flow, and generic riverine and marine DF will be different than the provided individual worst-case values (and the DFs might be higher than the accepted 'caps', although these have actually been implemented): the lowest wastewater flow/site tonnage ratio is selected and then multiplied with the maximum site tonnage to derive the generic wastewater flow. Subsequently, the lowest $(\text{DF} \times \text{wastewater flow})/\text{site tonnage}$ ratio is selected and then divided by the generic wastewater flow and multiplied with the maximum site tonnage to derive the generic riverine and marine DF. As a result, the derived generic values cover all site-specific conditions without being overly conservative. This section is principally designed for use by Concawe only, and the data is derived from the industry supplied information from refineries.

6.6. MAN VIA ENVIRONMENT ASSESSMENT

The Guidance approach for assessing 'Indirect human exposure' or 'Man via Environment' (MvE) uses regressions and models from various sources. Although most of these approaches have quite a broad regression range, the common range is only between $\log K_{ow}$ 3.0 and 4.7. This means that for polar and lipophilic chemicals, the use of these regressions gives uncertain and probably wrong results²³. Petroleum substances mostly contain very lipophilic hydrocarbons: in the PetroRisk representative constituent library, 1,401 out of 1,560 hydrocarbons have a predicted $\log K_{ow}$ above a value of 4.6. 1,081 of these have a predicted $\log K_{ow}$ above a value of 6, 124 have a predicted value above 12. The Guidance approach further leads to overprediction due to the use of unrealistic consumption data (the 'EU Food Basket') and a false root uptake model⁹. Although the PetroRisk user can still opt to implement the Guidance approach (see [Section 5.2.2](#)), PetroRisk will by default implement the New Model Framework (NMF) developed by Legind and Trapp (2009)⁹. The NMF implements additional crop-specific models (potato, lettuce, cereals, fruit), corrects the root crop model, and implements realistic human intakes based on food consumption data for Danish 4-5-year-old children and 14-75-year-old women. The NMF calculated daily intakes of benzo(a)pyrene and 2,3,7,8-TCDD are in good agreement with measured data from diet studies, while the Guidance approach largely overestimated these. PetroRisk currently implements the 95th percentile consumption data for Danish women of the age 14-75 years. In PetroRisk, 1 correction is made to the NMF framework: soil concentrations in the lettuce and corn models are converted from dry weight to wet weight ($\times \text{RHO}_{\text{soil-dry}}/\text{RHO}_{\text{soil-wet}}$).

6.7. SIMPLETREAT AND SIMPLEBOX FATE FACTORS

SimpleTreat⁶ and SimpleBox⁵ are rather complex multimedia partitioning models that form the basis of the Guidance exposure estimation. Transcribing these models into PetroRisk would require a large programming effort, and would result in a slower PetroRisk tool. In both models, predicted fractions or concentrations linearly relate to the input emission rates (e.g. wastewater emission). While using the same model parameters, the slope of that linear relationship will only vary with the physicochemical properties of the chemical (while the intercept is zero).

These slopes were generated using default settings and parameters in batch versions of both models⁶, for each of the 1,560 representative hydrocarbons in the PetroRisk constituent library. The generated slope values are referred to as Fate Factors (FFs), and allow for the implementation of the SimpleTreat and SimpleBox models into PetroRisk, without the need incorporate these models in the tool. For SimpleTreat, 2 sets of FFs have been generated: one set representative of a municipal Sewage Treatment Plant (STP), and one set representative of an industrial wastewater treatment plant (WWTP). SimpleTreat is designed to represent a STP with or without a primary settler ('9-Box' and '6-Box' model, respectively). The 9-Box model was used to generate the 'municipal' FFs. However, as defined in the ESIG spERCs, a primary oil-water separation step is typically implemented in industrial wastewater treatment plants dealing with a high load of (petroleum) hydrocarbons. At petroleum refineries, a Dissolved Air Flotation Unit (DAF) is typically used as primary treatment to efficiently capture hydrocarbons from the aqueous phase. Thunnissen et al.⁷ have adapted the primary settler unit in the SimpleTreat model to better represent a DAF unit. In PetroRisk, this updated model is used by default for industrial uses. The SimpleTreat FF library and SimpleBox FF library contain, for each of the representative hydrocarbons, 8 and 70 FFs, respectively.

For the SimpleTreat FF library: 4 resulting fractions (to air, sludge (and scum), dissolved effluent, and associated to suspended solids) times 2 models (with a primary settler, or with a primary Dissolved Air Flotation (DAF) unit⁷).

For the SimpleBox FF library: 7 resulting PECs (in air, freshwater, sediment, seawater, marine sediment, natural soil, and groundwater) times 5 emission routes (via air, freshwater, seawater, agricultural soil, and other soil) times 2 emission scales (regional and continental).

As the FFs have been generated using default parameters in SimpleTreat and SimpleBox, both FF libraries should be updated when changing environmental settings (e.g. temperature, suspended solid fractions) or hydrocarbon physicochemical properties (e.g. organic carbon-water partitioning coefficient (K_{oc}), vapour pressure) in PetroRisk. You can access the SimpleTreat and SimpleBox FF libraries within the 'Exposure Assessment' metanode, within the underlying 'SimpleTreat' and 'SimpleBox' metanodes, respectively.

PetroRisk by default uses SimpleTreat and SimpleBox versions 4, and K_{oc} s predicted by the more appropriate Molecular Connectivity Index (MCI) approach for hydrocarbons with a MCI above a value of 3. Nonetheless, the user can opt to use previous SimpleTreat and SimpleBox versions 3, using K_{ow} based K_{oc} predictions for all hydrocarbons. This approach would be identical to the EUSES 2.2 and EUTGDsheet approaches. Therefore, the user would need to connect the 'Joiner' nodes to the version 3 'Table Creator' nodes, and update 2 other nodes:

Exposure Estimation > Wastewater Treatment > Local Wastewater Treatment: double-click the 'Offsite Concentration in sludge' Math Formula node to manually update the SURPLUSsludge parameter. SimpleTreat v4 uses a value of 0.0255, while v3 uses 0.0190 kg;d-1.eq-1.

Class or Constituent Selector > Constituent Properties > PhysChem: double click the 'Koc' Math Formula node to manually change the K_{oc} calculation:

K_{ow} based formula: $10^{(0.81 * \text{LogKow} (-) + 0.1)}$

⁶ Unlike for SimpleBox, SimpleTreat v4 is not publicly available in Excel format. To generate SimpleTreat v4 FFs, the v3 workbook was upgraded according to the SimpleTreat v4 RIVM report ⁶, and compared with version 4 results for consistency.

MCI based formula: $\text{if}(\$MCI\$ < 3, 10^{(0.81 * \$LogKow (-) \$ + 0.1)}, 10^{(0.52 * \$MCI\$ + 0.7)})$

6.8. DERIVATION OF THE LOCAL PEC SEDIMENT

In EUSES and EUTGDsheet, the PEC sediment is extrapolated from the PEC (sea)water directly, and is not a sum of the local concentration (LC) in sediment and the regional PEC in sediment. Regional sediment PECs (via SimpleBox) and local sediment concentrations are derived via different mathematical approaches. In some cases, this leads to local sediment PECs to be lower than the regional sediment PEC. In PetroRisk, LCsediment is extrapolated from the LC(sea)water and added to the regional PECsediment to obtain the local PECsediment, which is in line with the general approach to derive local PECs.

6.9. REQUIRED ONSITE AIR AND WASTEWATER REMOVAL EFFICIENCIES

For each representative hydrocarbon and for each use, the exposure and risk assessment within PetroRisk is performed separately for air, wastewater and soil emissions. This slows down the PetroRisk tool, but it enables for:

- 1) the user to easily judge which emissions of which uses are driving the risks: right-click on the “Emission-specific RCRs” component, and press “Interactive View: Emission-specific RCRs” in the pop-up menu.
- 2) PetroRisk to calculate (and mathematically implement) an adequate and minimal set of onsite air and wastewater REs in the meta-node “Required RMM Efficiencies”, if required.

In the ‘spERCs’ Table creator node, industrial life cycle stages are assumed to be connected to an onsite biological WWTP equipped with a primary oil-water separation unit, while wide dispersive uses are assumed to be connected to an offsite biological STP equipped with a primary settler. For both industrial and wide dispersive stages, no onsite air treatment is initially assumed. In the ‘spERCs’ Table creator node, the user can change these settings for each life cycle stage.

The removal efficiency (RE) of the total substance by the default STP or WWTP (RE_{default}) is determined by the predicted influent concentration and SimpleTreat FF_{effluent} of each representative constituent. The RE_{default} typically ranges between 90.0-99.9%, with the default onsite WWTP generally being more performant than the municipal STP. Although no air treatment is initially assumed, a RE_{default} for air emissions is required to allow subsequent calculations. As no air treatment model is currently available, it is assumed the air treatment is equally efficient in removing all constituents, and a RE_{default} of 0.9 is applied to the total substance.

During the first iteration, PetroRisk implements the onsite WWTP RE_{default} for industrial wastewater emissions ($RE_{\text{required}} = RE_{\text{default}}$), and no onsite treatment for air emissions and for wide dispersive wastewater emissions ($RE_{\text{required}} = 0$). Offsite STP treatment is only assumed for wide dispersive uses (unless indicated otherwise by the user in the ‘spERCs’ table). If a wastewater emission should be (further) reduced in the next iteration, PetroRisk will apply additional onsite WWTP treatment, instead of increasing the default offsite STP RE, for both industrial and wide dispersive uses. Similarly, it will increase onsite air treatment for a use if its air emission needs to be reduced.

For predicting the additionally required air and/or wastewater treatment, the applied ‘treatment unit’ concept assumes that a treatment facility will require more serially connected hypothetical treatment units to achieve increasing RE, wherein each unit has the same predefined RE (RE_{unit}). The concept is graphically represented in Figure 14. The RE_{unit} can have any value between > 0 and < 1 , but by default has the same pre-set value (of 0.5) for each emission of each identified use. The user can (de)prioritize emissions for reduction by altering the RE_{unit} values in the ‘spERC’ Table creator node.

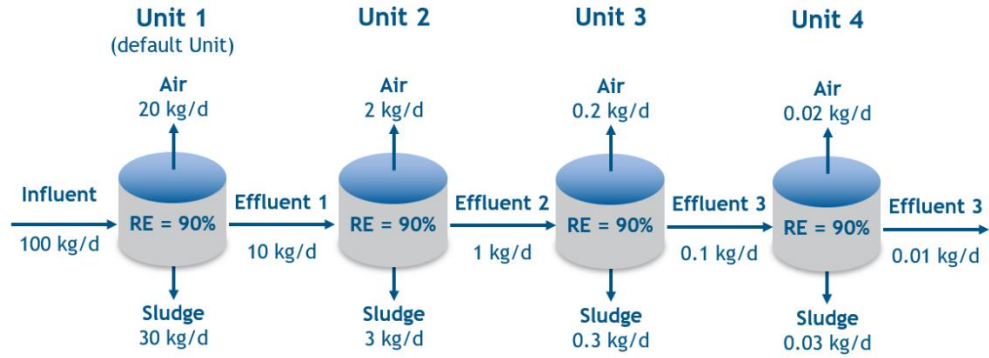


Figure 14 Graphical representation of the treatment unit concept for a hypothetical wastewater treatment facility.

In this example, each hypothetical unit will emit 20% of its influent concentration to air, 30% to sludge and 10% to effluent, while 40% will be degraded. The overall RE for this set-up would be equal to $1 - (1 - 0.9)^4$ or 99.99%.

The default and required number of hypothetical treatment units are calculated as:

$$U_{default} = \log_{1-RE_{Unit}}(1 - RE_{default}) \quad (18)$$

$$U_{required} = \log_{1-RE_{Unit}}(1 - RE_{required}) \quad (19)$$

After each iteration, PetroRisk identifies the air or wastewater emission for which (further) increasing the number of treatment units (by a user predefined 'increment' value, e.g. + 0.25) leads to the largest overall reduction in RCRs (for those RCRs which have a value above 1), and subsequently adopts this increase for the identified 'priority' emission. This process is repeated, i.e. stepwise adopting the most effective increases in treatment units, until all RCRs are at or below a value of 1. At the end, the process has identified a combination of adequate RMMs at an overall minimal 'investment'.

Contributions of local wastewater emissions to the RCRs which are mainly driven by air emissions (agricultural soil, terrestrial predators, and 'man via environment'), are excluded during this process, to avoid situations where increased air emissions from increased wastewater treatment will erroneously result in further increases in wastewater treatment.

The identified increases in treatment units are then mathematically implemented in the exposure and risk assessment. For increases in onsite wastewater treatment, the default SimpleTreat FFs of each representative hydrocarbon are rescaled:

$$FF_{effluent,required} = FF_{effluent,default} \frac{U_{required}}{U_{default}} \quad (20)$$

$$FF_{air,required} = FF_{air,default} \times \frac{1 - FF_{effluent,required}}{1 - FF_{effluent,default}} \quad (21)$$

$$FF_{sludge+scum,required} = FF_{sludge+scum,default} \times \frac{1 - FF_{effluent,required}}{1 - FF_{effluent,default}} \quad (22)$$

By default, the fraction to sludge (and scum) from offsite STP treatment is applied on agricultural soil, while the fraction of sludge (and scum) from onsite WWTP treatment is added to the use's waste fraction.

For increases in onsite air treatment, the mathematical approach is straightforward due to the lack of an air treatment model. The fraction being withheld by air treatment is added to the waste fraction of the use:

$$FF_{air,required} = 0.1 \frac{U_{required}}{U_{default}} \quad (23)$$

$$FF_{waste,required} = 1 - FF_{air,required} \quad (24)$$

The UVCB nature of the substance however complicates the exact estimation of required wastewater REs: with increasing required wastewater units, the hydrocarbons with lower default $FF_{effluent}$ will be removed even more efficiently compared to the hydrocarbons with higher default $FF_{effluent}$. Thus, while, with increasing treatment, the total concentration of hydrocarbons decreases in the effluent, it is relatively enriched with hydrocarbons which are less easily removed. This results in RCRs which are not ‘scaling’ linearly but rather exponentially with increasing wastewater treatment (see Figure 15). The exact relationship can only be determined empirically, as it mainly depends on both the influent concentration and the SimpleTreat $FF_{effluent}$ of each representative hydrocarbon. As a result, the required wastewater treatment units ($U_{required}$) calculated in the ‘Required RMM Efficiencies’ metanode are linear approximations: the exposure estimation, risk characterization and estimation of required RMM efficiencies may need to be iterated a few times before all RCRs are effectively below a value of 1. The PetroRisk tool is currently limited to 10 iterations, but it can be easily adjusted in the ‘Stops when all RCRs <1’ Recursive Loop End node. Usually less than 5 iterations are required.

7. PETRORISK SCALING TOOL FOR SITE-SPECIFIC ASSESSMENTS

A simple Excel-VBA based tool is provided with PetroRisk to ‘scale’ the GESs of industrial lifecycle stages and uses to match site specific Operating conditions (OC). The OCs that can be provided by the user include: daily site tonnage (kg/d), release days (d/yr), Release Factor (RF) to air (%), RF to wastewater (%), RF to soil (%), wastewater flow (L/d), (freshwater and/or marine) dilution factor, and the presence (and RE) of ‘end-of-pipe’ air and/or wastewater treatment facilities. The user also has the option to provide measured site effluent concentrations (e.g. based on Total Petroleum Hydrocarbon (TPH) measurements).

The scaling tool will adjust the PECs, human intake doses and resulting RCRs according to the user provided information. The user also has the option to have the scaling tool recalculate the applied onsite air and wastewater REs to the lowest acceptable values (i.e. resulting in the maximal RCR at a value of exactly 1).

Due to the UVCB nature of the PetroRisk assessed substances, rescaling the onsite wastewater treatment RE should be performed with caution. In PetroRisk, changing wastewater treatment RE will correctly change the relative composition of the effluent: when the RE is increased, the effluent will be relatively further enriched with hydrocarbons which are less easily removed from the wastewater, i.e. less volatile, less biodegradable but more water soluble and generally more toxic hydrocarbons. As a consequence, risks related to wastewater emissions do not scale linearly, but rather exponentially with wastewater RE, with the equation parameters depending on the predicted influent concentrations and REs of each hydrocarbon. The PetroRisk Scaling Tool however assumes the effluent constituents will be equally ‘diluted’ with increasing RE (or equally ‘concentrated’ with decreasing RE). The Scaling Tool will thus underestimate risks when the applied onsite wastewater RE is increased, but will conservatively overestimate risks when the RE is decreased (see Figure 15).

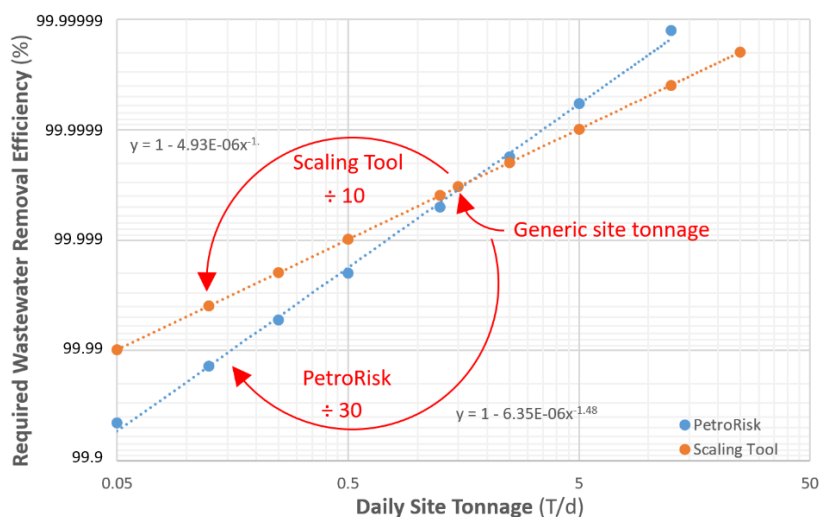


Figure 15 For an undisclosed use of an undisclosed substance, the required wastewater RE (Y-axis) as a result of the daily site tonnage (X-axis). Calculated via PetroRisk (blue markers and trendline), and estimated via the Scaling Tool from the generic risk assessment (orange markers and trendline).

More detailed guidance on GES scaling is provided in the “README” sheet of the Scaling Tool Excel workbook.

8. GLOSSARY

ACR	Acute to Chronic Ratio
AF	Assessment Factor
ALS	Aliphatic Sulphur compounds
ArS	Aromatic Sulphur compounds
BCF	Bio Concentration Factor
BMF	Bio Magnification Factor
BP	Boiling point
BW	Body Weight
C	Carbon number
C _L *	Critical toxic Lipid body burden
CLP	Classification, Labelling and Packaging (Regulation ((EC) No 1272/2008)
Concawe	Conservation of Clean Air and Water Europe
CTLBB	Critical Toxic Lipid Body Burden
CTRL	Control key
C _w	aqueous solubility
CSR	Chemical Safety Report
DAF	Dissolved Air Flotation
DF	Dilution Factor
DiAr	Di-Aromatics
DiN	Di-Naphthenics
DNEL	Derived No Effect Level
DU	Downstream User
E	median
ECHA	European Chemicals Agency
EPI	Estimation Programs Interface
EqP	Equilibrium Partitioning method
ESIG	European Solvents Industry Group
EU	European Union
EUSES	European Union System for the Evaluation of Substances
EUTGD	European Union Technical Guidance Document
FF	Fate Factor
GES	Generic Exposure Scenario
HB	Hydrocarbon Block
HC5	Hazardous Concentration that affects 5% of species
HLbio	biodegradation Half-Life
iO	branched (or iso) Olefins
iP	branched (or iso- alkanes or Paraffins

K _d	partition (or distribution) coefficient
K _{mw}	Membrane-Water partition coefficient
KNIME	Konstanz Information Miner
K _{oc}	organic carbon-water (or soil, or sediment) partitioning coefficient
k _{OH}	specific degradation rate constant with OH-radicals
K _{ow}	octanol-water partitioning coefficient
k _z	sample size extrapolation factor
LC	Local Concentration
m _{ARO}	mass assigned to other (than PAH) high BP aromatic compounds
MCI	Molecular Connectivity Index
MoAr	Mono-Aromatics
MoN	Mono- Naphthenics
m _{PAH}	mass assigned to the PAH structures
MvE	Man via Environment assessment
NDiAr	Naphthenic Di-Aromatics
NMF	New Model Framework
NMoAr	Naphthenic Mono-Aromatics
nO	normal Olefins
nP	normal alkanes or Paraffins
NTriAr	Naphthenic Tri-Aromatics
OC	Operating Conditions
PAH	Poly(cyclic) Aromatic Hydrocarbon(s)
PBT	Persistent, Bioaccumulative and Toxic
PEC	Predicted Environmental Concentration
PNEC	Predicted No Effect Concentration
PolyAr	Poly-Aromatics
PolyN	Poly-Naphthenics
RAM	Random Access Memory
RATIO _{PAH}	Ratio of PAH structures to all aromatic structures
RCR	Risk Characterization Ratio
RE	Removal Efficiency
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals (Regulation (EC) No 1272/2008)
RF	Release Factor
RHO	bulk density (ρ)
RMM	Risk Management (or Mitigation) Measure
RRE	Required Removal Efficiency
S	sub-cooled aqueous solubility
SAS	Statistical Analysis System

SMILES	Simplified Molecular Input Line Entry System
spERC	(industry) specific Environmental Release Category
STP	Sewage Treatment Plant
TA	Total aromatic structures
TCDD	Tetrachlorodibenzo-p-dioxin
TLM	Target Lipid Model
TriAr	Tri-Aromatics
UVCB	Unknown or Variable Composition, Complex reaction products of Biological materials
V	Variance
VBA	Visual Basic A
WW	Wet Weight
WWTP	Waste Water Treatment Plant
x'	revised mole fraction for emissions to water

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10. ANNEX 1: EXTRAPOLATION OF AQUATIC TO STP BIODEGRADATION HALF-LIVES

Table 1. Data used for the regression of predicted STP vs. experimental environmental biodegradation half-lives.

Name	Total activated sludge removal			SimpleTreat biodegradation half-life (hours)	Environmental biodegradation half-life (days)
	No. samples	Range	Median		
Benzo(a)pyrene	3	86-95.2%	88%	630.09	224
Benzo(b)fluoranthene	3	88-95.4%	89.5%	173.28	282
Benzo(a)anthracene	5	64-99.65%	94.7%	77.88	285
Chrysene	5	83.6-99.69%	96.8%	37.46	378
Pyrene	7	50-99.88%	78% ¹	52.31	237
Fluoranthene	7	41-99.25%	86%	77.44	147
2-Methyl anthracene	2	>99-99.99	99.5%	0.35	260 ³
2-Methylnaphthalene	2	>99-99.99	99.5%	0.10	14
Acenaphthylene	4	84-99.11%	98.45%	2.08	38
Biphenyl	4	92.2-99.94%	96.95%	0.61	31
1,2,4-Trimethylbenzene	5	89-99.98%	94%	2.31	4
Anthracene	9	0-100%	90%	27.40	123
Phenanthrene	10	17-100%	97%	2.52	42
Fluorene	10	33-99.17%	92.5%	4.12	44
Acenaphthene	11	69-99%	99%	3.29	39
Xylene	21	21->99%	94.4% ²	1.82	9 ⁴
Benzene	52	44->99%	92.15%	1.61	6
Naphthalene	54	2-99.99%	94%	1.20	3
Ethylbenzene	82	22-100%	97%	0.41	8
Toluene	103	0-100%	95%	0.75	2
Pristane	5	80-99.73%	94%	693.43	42
n-Eicosane	2	92.4-99.5%	95.98%	154.03	25

¹ Values ranged widely

² Includes all available data on the various isomers (m-, o-, and p-xylene, as well as any data on m- and p-xylene combined and on xylene (isomer unspecified)

³ Half-life is from 9-methylanthracene

⁴ Half-life values for o-, m-, and p-xylene are 6, 10, 9 days, respectively

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11. ANNEX 2: BMFPRED CONSENSUS MODEL

Table 3: Substances with BMF underpredicted > 0.5 log units (consensus model)

Structure	Log BMF (model)	LogBMF (experimental)	Delta (obs-pred)	BMF Exp
benzo(a)pyrene	-1.715	-1.1549	0.560098	0.07
benzo(a)pyrene	-1.715	-0.76955	0.945449	0.17
1-phenylnaphthalene	-1.426	-0.58503	0.840973	0.26
1-methyl-7-(isopropyl)-hydrophenanthrene	-1.405	-0.45593	0.949068	0.35
1,4-diisopropylcyclohexane	-0.833	-0.31605	0.516947	0.483
o-terphenyl	-0.755	-0.22915	0.525852	0.59
trans-decalin	-0.82	-0.08672	0.733284	0.819
n-hexadecane	-0.26	0.465829	0.725829	2.923

Table 4: Substances with BMF overpredicted > 0.5 log units (consensus model)

Structure	Log BMF (model)	LogBMF (experimental)	Delta (obs-pred)	BMF Exp
9-methyl anthracene	-1.475	-3	-1.525	0.001
Perylene	-1.778	-3	-1.222	0.001
Anthracene	-1.33	-2.69897	-1.36897	0.002
Fluoranthene	-1.48	-2.69897	-1.21897	0.002
Triphenylene	-1.627	-2.52288	-0.89588	0.003
Chrysene	-1.599	-2.39794	-0.79894	0.004
Naphthalene	-1.775	-2.30103	-0.52603	0.005
4-ethyl-1,1'-biphenyl	-1.216	-2.30103	-1.08503	0.005
acenaphthylene	-1.628	-2.30103	-0.67303	0.005
7-methylbenz(a)anthracene	-1.672	-2.30103	-0.62903	0.005
benzo(a)pyrene	-1.715	-2.22185	-0.50685	0.006
Fluoranthene	-1.48	-2.22185	-0.74185	0.006
n-octylbenzene	-1.156	-2.04576	-0.88976	0.009
3,3',4,4'-tetramethyl 1,1'-biphenyl	-1.175	-2.04576	-0.87076	0.009
Anthracene	-1.33	-2.04576	-0.71576	0.009
2-methylanthracene	-1.473	-2.04576	-0.57276	0.009
benzo(b)fluorene	-1.445	-2.04576	-0.60076	0.009
phenanthrene	-1.35	-2	-0.65	0.01
2-methylanthracene	-1.473	-2	-0.527	0.01
6-n-butyl-2,3-dimethylnaphthalene	-1.168	-1.92082	-0.75282	0.012
2,6-dimethyloctane	-1.188	-1.88606	-0.69806	0.013
3-methyldecane	-1.209	-1.72125	-0.51225	0.019
2-isopropyldecalin	-1.141	-1.72125	-0.58025	0.019
2,6-dimethyldecane	-0.998	-1.67778	-0.67978	0.021
4,5,9,10-tetrahydropyrene	-1.009	-1.60206	-0.59306	0.025
o-terphenyl	-0.755	-1.46852	-0.71352	0.034
2,2,3-trimethyldecane	-0.915	-1.4437	-0.5287	0.036
o-terphenyl	-0.755	-1.30103	-0.54603	0.05
cyclohexylbiphenyl (hexahydroterphenyl)	NP	-1.22185	NP	0.06
2,7-diisopropyldecalin	-0.274	-1	-0.726	0.1

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ISBN 978-2-87567-162-2



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