concawe

**PETRORISK
version 7.0
Public: Manual**

CONCAWE

DRAFT

PETRORISK version 7.0 Public: Manual

Prepared by CONCAWE

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APPENDIX 1 COMPARISON OF PETRORISK v3.05 vs EUSESv123 HB FOR SELECTED INDIVIDUAL STRUCTURES: TOLUENE AND BENZO(a)PYRENE

ABBREVIATIONS

ACR – Acute to Chronic Ratio of toxicities
BP – Boiling Point
C# - Carbon Number
CSR – Chemical Safety Report
DNEL – Do Not Exceed Level vs Derived No Effect Levels
E – Product Emission(s)
EC – Equivalent Carbon Number
ECHA – European Chemicals Agency
EF – Exposure Factor
EUSES – European Union System for Evaluating Substances
FF – Fate Factor
GES – Generic Exposure Scenario
HB – Hydrocarbon Block
HC5 – Hazardous Concentration that affects 5% of species
HI – Human Intake fraction
IF – Intake Factor
PAH – Polycyclic Aromatic Hydrocarbon(s)
PEC – Predicted Environmental Concentration
PNEC – Predicted No-Effect Concentration
RCR – Risk Characterization Ratio
RMM – Risk Management Measures
RRE – Required Removal Efficiency
SPARC – SPARC Performs Automated Reasoning in Chemistry:
          (http://ibmlc2.chem.uga.edu/sparc/)
SpERC – Specific Environmental Release Category
TA – Total Aromatic Structure(s)
TLM – Target Lipid Model
TPH – Total Petroleum Hydrocarbons
UVCB – Unknown or Variable Composition, Complex reaction products of Biological materials
VP – Vapour Pressure
WS – Water Solubility
WWTP – Wastewater Treatment Plant

SECTION 1

CONCEPTUAL DESIGN OF PETRORISK

1.1   INTRODUCTION

PETRORISK is a spreadsheet tool that performs environmental risk assessments for petroleum substances using principles provided by the European Chemical Agency (ECHA) for fulfilling stakeholder obligations under the EU REACH regulation. It is designed to evaluate environmental exposure and ecological risks at both local and regional scales for a wide range of petroleum products from naphtha (gasoline), kerosene, gas oils, to heavy fuel and lubricant oils as well as hydrocarbon-based solvents. The spreadsheet tool can evaluate risks associated with different stages in the product life cycle. For example, the ecological risks can be evaluated at the production (manufacturing), formulation, and distribution stages as well as for generic uses in industrial, professional and consumer use sectors.

The tool was developed by Concawe to meet the Industry requirements under REACH. As such, there are a number of modules that are included in the model that are only applicable for Concawe. These are highlighted in the following sections.

The tool calculates the Predicted Environmental Concentrations (PECs) of representative hydrocarbons assigned within blocks (defined by compositional analysis) in various compartments of soil, air, water, waste water treatment plant (WWTP) effluent, drinking water, fish, meat and milk based on results obtained from the EUSES multimedia exposure model. For water, effluent, soil and sediment compartments, PECs are divided by Predicted No-Effect Concentrations (PNECs) derived with the Target Lipid Model (TLM) (McGrath et al., 2004) to compute environmental risk quotients for the representative hydrocarbons. Ecological risks for these compartments are then quantified by summation of the PEC/PNEC ratios for the representative hydrocarbon structures that are used to simulate the hydrocarbon blocks (HB) comprising the substance. A risk quotient of greater than or equal to one indicates a potential unsafe use. Human exposures are also calculated for total hydrocarbons using a default set of exposure pathways specified by EUSES. Appropriate Derived No Effect Levels, (DNELs), which can be based on marker compounds or expressed in terms of total hydrocarbon exposure or dose of the petroleum substance can be entered to perform human health risk assessment, obtaining a PEC/DNEL for the petroleum substance. This tool is based on the ECHA REACH Implementation Guidelines for performing risk assessments of complex petroleum substances using the hydrocarbon block method (ECHA, 2008a).

In 2015 the model was updated to version 7, following an extensive review of the TLM (McGrath et al., 2015) and changes to the blocking scheme in the high resolution mode.

1.2   SPREADSHEET TOOL

The spreadsheet model runs on a series of macros coded in Visual Basic with Excel. There are no special system requirements to run the model but the user will have to 'enable' macros to allow the model to run. The spreadsheet model with full model results is about 15 MB in size and requires <1 minute to run.

1.3   PRODUCT COMPOSITION

For complex UVCB petroleum products, compositional information allows quantification of the hydrocarbon components for which fate (e.g., PEC) and environmental hazards (e.g., PNEC), and resulting risk (PEC/PNEC ratio) should be based. PETRORISK makes use of an advanced Hydrocarbon Block (HB) method of risk assessment (see Section 4.2). A library of 1560 individual representative hydrocarbons has been mapped to the various HBs which are considered compositionally relevant for these complex substances; and which were used to derive physical-chemical properties relevant for environmental exposure and risk evaluations (see Section 2.11). The hydrocarbon library in PETRORISK is pre-loaded with these physical-chemical properties, fate factors (half-lives) and hazard endpoints (PNECs). Product compositional information (e.g., weight %, chemical class, boiling point intervals) is supplied by the user in either a high or low resolution format, based on the available analytical information. Product composition is used to define three distinct types of hydrocarbon complexity for predicting PECs, PNECs and RCRs of petroleum streams: 1) low (hydrocarbon) resolution based on equivalent carbon number from total petroleum hydrocarbon (TPH) analysis; 2) high (hydrocarbon) resolution; and 3) "Solvent Mode". The selection for compositional 'type' is presented in the 'Product Composition' worksheet, along with the explanation in the Notes comment:

Figure 1: Product Composition Tab, Composition Selection

The TPH –equivalent carbon number approach for composition is the basis for the low resolution format, which accepts compositional information using the same two structural classes for 9 boiling point intervals of n-alkanes. These intervals are often referred to as equivalent carbon numbers (EqC) (e.g., EqC 3-4, 5-6, 7-8, etc.) and is based on TPH fraction methods developed in support of risk-based corrective action at hydrocarbon contaminated sites;

(http://www.api.org/aboutoilgas/sectors/explore/resourcecenter.cfm).

The high resolution format (section 2.1.1), and the main focus of this guidance, allows information to be entered for up to 16 structural classes for 28 carbon numbers, with 1 carbon per block. This covers C4 to ≥C30. The sixteen structural classes are:

Normal alkanes or paraffins (n-P)

Branched alkanes or paraffins (i-P)

Normal olefins (n-O)

Branched olefins (i-O)

Mono-naphthenics (m-N)

Di-naphthenics (DiN)

Poly-naphthenics (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)

Aromatic sulphur compounds (ArS)

The analytical method (e.g., GCxGC) used to generate the required input data for high resolution calculations resolves complex products into structural classes by carbon number (Arey et al., 2007). Although Sulphur compounds are present, they are limited in

their quantity in most product related streams, and this, coupled with difficulty of gaining accurate quantification using GCxGC analysis, means that Sulphur classes have been ignored in recent applications of the tool. However, it is expected that the risk contribution from Sulphur classes are negligible compared with the other hydrocarbon classes that are predominant in a petroleum substance composition, and well within the uncertainty of this risk assessment methodology.

The third blocking scheme (also a low resolution strategy), "Solvent Mode", has been applied for hydrocarbon solvents, (assessed using the '); this scheme requires compositional input based on only two general structural classes (i.e., aliphatic, aromatic) as a function of individual carbon number.

Physical-chemical properties for the various hydrocarbon blocks (high or low resolution) are derived from a library of chemical properties for individual representative structures that are derived from basic structure types typically found in petroleum (see "Concawe Library" section). All the chemical properties except for sub-cooled liquid solubility, but including Henry's Law Constant (HLC), log Kow, molecular volume, boiling point, chemical class and molecular weight have been estimated using EPIWIN. The sub-cooled liquid solubility is estimated from SPARC v4.2 (May 2008), an on-line program that computes physical-chemical properties from chemical structure (Karickhoff et al., 1991). This set of parameters was used in all of the toxicity calculations consistent with the training datasets for the TLM and also to calculate the fate of these structures in the EUSES modelling framework. The individual structures are assigned to the HBs consistent with the user-defined blocking scheme and compositional input (see Section 4.1). In this manner, emissions, PECs, PNECs and risk characterization (PEC/PNEC) are calculated in terms of individual structures based on those physical-chemical properties associated with a given hydrocarbon block (HB) that are weighted by the products' hydrocarbon block composition. These calculations were performed outside of the PETRORISK model itself, using the EUSES model, and all values pre-loaded into the petroleum hydrocarbon library within PETRORISK.

Once the individual hydrocarbons are assigned to a block the mass fraction in that block is distributed among the assigned structures. In the high resolution scheme, the mass fraction for a particular HB is uniformly distributed among the individual library structures assigned to that block. In the low resolution scheme several detailed chemical classes are grouped into two general chemical classes; aliphatic and aromatic. Mass allocation under the low resolution scheme is performed in the same manner for most chemical classes, see Section 4.0 Technical Basis for details. The mass measured in the aliphatic blocks is evenly distributed among all the representative structures assigned to any given block in all cases. Briefly, the mass measured in the aromatic blocks is evenly distributed among all the

assigned hydrocarbons for compounds with boiling point (BP) < 350ºC. For compounds with BP > 350ºC aromatic mass 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 (HydroQual, 2009; Redman et al 2012).

1.3.1 Olefinic structures

The released version of PETRORISK has had the olefinic and Sulphur-hetero structures indexed in such a way that they are not picked up in the normal runs. If olefinic structures are required then the indexing in the Tab "Concawe Library", column titled "General Class" needs to be altered from 3 to 1.

1.4 EMISSION ESTIMATES

Annual emission estimates (tonne/yr.) are required from the user for various life stages and uses of a given petroleum product (see Section 3.2). Emission factors (fractional) are used to calculate the mass of hydrocarbons that are released to the three environmental compartments at regional (air, water, soil) and local (air, water, soil and effluent) scales. Product composition determines the speciation of the hydrocarbons emitted to a given compartment (see Section 4.3). Default emission factors and other exposure related default inputs (emission days, waste water flow, receiving water dilution factors) are provided for a broad range of relevant generic uses or generic exposure scenarios (GES) for the petroleum industry based on sector Specific Environmental Release Category (SpERC) factsheets (see Section 3.4). For each GES evaluated, default parameters are copied into the input deck but values can be over-written by the user if results indicate unsafe use and justification is available to refine initial assumptions.

1.5 PREDICTED ENVIRONMENTAL CONCENTRATIONS

As the concentrations of chemicals in the environment are approximately proportional to emission rates, it is common practice to report exposure modelling results in terms of concentrations per unit of emission, i.e. as emission normalized predicted exposure concentrations or environmental fate factors. Predicted environmental concentrations of the representative hydrocarbon structures, can then be calculated using a series of fate factors (FFs) that were derived with the EUSES multimedia fate model (van de Meent, 2008, van de Meent et al 2010). In this modelling framework, PECs (e.g., mg/L or mg/kg) are calculated as the product of the environmental Fate Factor (FF; d/L or d/kg) and the Product Emission (E; kg/d) using the general relationship

$$PEC(mg/L;kg/L) = FF(d/L;d/kg) \cdot E(kg/d) \qquad (1)$$

Fate factors for each hydrocarbon structure are included in the library database in the PETRORISK tool (see Section 3.12). The calculation is performed for each relevant structure following the mapping of library structures to the hydrocarbon blocks that are used to describe substance composition. The mass fraction of each structure is used to simulate the product composition is then determined by dividing the user-defined mass fraction for the block by the total number of structures in the block, i.e. each library structure mapped to a block is assumed to have equal weighting. For emissions to soil, the reported product composition is used. However, to estimate the speciation of air and water emissions in terms of library structures, the mass fractions of each library structure used to simulate the product composition is further scaled by Raoult's Law. This approach ensures that more volatile components are preferentially emitted to the air while the more water soluble components are released to water. Further details are provided in Section 4.0.

SECTION 2

INPUT DATA FOR SPREADSHEET MODEL PETRORISK

This section provides a description of how the essential data for running PETRORISK are input into the key worksheets;

1. product composition – Section 2.1

2. product lifecycle information – Section 2.3

3. DNEL – Section 2.4

The specific user-required inputs are addressed in this section. Details of the model calculations are provided in Section 4.0.

2.1 COMPOSITION INPUT

There are three different ways to input composition data, High Resolution mode, Low Resolution mode and Solvent Mode. Only the first two will be addressed in this manual.

TO CONTINUE IN THE MODEL – SELECT ONE OF THE THREE RADIO BUTTONS:
High Resolution
Low Resolution
Solvents

Depending upon the button selected a matrix will appear, which will fit the compositional data required. For further descriptions, see below.

2.1.1 High Resolution Mode

In this mode the compositional data (i.e., analytical results of GCxGC) needs to be entered into the matrix as percent mass;

The first block is for mass assigned to molecules with 4 carbon atoms, the second for molecules with 5 carbon atoms etc. Not all the cells need to have data and the mass does not have to add up to 100%.
- If the mass adds up to 100 +/- 0.5% the model will proceed.
- If the total entered mass is >100.5% then the model will stop and report the error and require the user to correct the entered mass fractions.
- If the mass is less than 99.5% a dialog box appears which allows the user to either
    - o 1) scale up all blocks evenly to reach 100%,
    - o 2) add the 'missing' mass to the highest aliphatic block or
    - o 3) To stop and fix the input errors.

Figure 2: Product Composition Worksheet: High Resolution Option

Block	C#i (>=)	C#f (<)	n-P (weight %)	I-P (weight %)	MonoN (weight %)	Di-N (weight %)	n-Olefins (weight %)	I-Olefins (weight %)	Poly-N (weight %)	AiS (weight %)	MoAr (weight %)	NMAr (weight %)	DIAr (weight %)	NDIAr (weight %)	TrIAr (weight %)	NTrIAr (weight %)	PolyAr (weight %)	ArS (weght %)
1	4	5																
2	5	6																
3	6	7																
4	7	8																
5	8	9																
6	9	10																
7	10	11																
8	11	12																
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19	22	23																
20	23	24																
21	24	25																
22	25	26																
23	26	27																
24	27	28																
25	28	29																
26	29	30																
27	30	>30																

2.1.2 Low Resolution mode

In this mode the user is required to input the percent mass allocated into 2 classes of hydrocarbons, aliphatics and aromatics that have been assigned to pre-defined 9 Boiling Point ranges (which have associated equivalent carbon numbers based on TPH analysis, section 1.3). It is possible to change these boiling point ranges, depending upon the information available on the substance being assessed.

Figure 3: Product Composition Worksheet: Low Resolution Option

Block	EqCi (>=)	EqCf (<)	BPi	BPf	Aliphatic (weight %)	Aromatic (weight %)
1	3	5	-51.6	34.5		
2	5	7	34.5	100.6		
3	7	9	100.6	155.4		
4	9	11	155.4	201.3		
5	11	13	201.3	240.9		
6	13	17	240.9	307.1		
7	17	22	307.1	373.9		
8	22	36	373.9	500.9		
9	36	>36	500.9	>500.9		

As with the High Resolution method, the assigned mass is assessed by the model, and depending on the actual value and the users' response, calculations will proceed (see Section 2.2.1).

2.2 ESTIMATION OF SOLUBILITY AND VAPOUR PRESSURE

The second step that users must follow is to estimate the product-specific vapour pressure (VP) and water solubility (WS). This is done by clicking on the 'Estimate VP and WS' button near cell E4, in the tab "product composition". This information is used to select default emission factors for generic exposure scenarios where default emission factor

inputs are specified as a function of the physical-chemical properties of the substance being evaluated.

Figure 4

2.3   USE INFORMATION AND TONNAGES

The next stage for the user is to input the data that specifies the use and tonnages of the petroleum substance. The tab required is "product lifecycle information".

To enter data in this section the user must have the following information:
1. The amount of material manufactured (in the region being assessed). This will be entered in the first line of the table, see below, Section 3.3.
2. The amount of the substance used as an Intermediate, which is usually entered in the next line.
3. The amount of the substance that will be distributed in the region, which will be the manufactured tonnage plus the imported tonnage. This is usually entered in the third line.
4. The tonnage associated with Formulation is entered next, and can be calculated from the manufactured tonnage plus the imported tonnage less the tonnage used for intermediates.
5. For each of the uses of the substance, the tonnage that is associated with that use.

NOTE: While the tonnages allocated in the list above are usual for the petroleum substances assessed by Concawe in the EU, there may be different circumstances, so the user should be clear about the way the substance they are assessing is distributed around the different uses.

2.4   DNEL

The final input for the user is to enter the appropriate DNELs that are used by the model to address the indirect effects to humans via the environment. These data are entered into the worksheet under tab "DNEL".

Two parameters are required;
- Human exposure via the environment
- Secondary exposure

Human exposure via the environment: Covers two possible endpoints, derived either from inhalation or food. The guidance available is in Guidance on information

requirements and chemical safety assessment, Chapter R.8: Characterisation of dose [concentration]-response for human health.

Secondary exposure: The guidance for choosing the right parameter is given in "Guidance on information requirements and chemical safety assessment, Chapter R.10: Characterisation of dose [concentration]-response for environment", section 10.8.

The data point used, usually a NOEC, should be derived from either bird or mammal studies via the food.

The data can be entered in cells F12 and F13 for Humans via the environment, and F23 for secondary poisoning.

2.5   SITE-SPECIFIC PRODUCTION

This section is principally designed for use by CONCAWE only, and the data is derived from the Industry supplied information from refineries.

2.6   RUNNING THE MODEL

Once all the data has been entered the user will need to navigate back to the "Use Information and Tonnages" tab.

To run the model the button "RUN PETRORISK" should be pressed once.

The model will take approximately 1 minute to run, when the model opens up the tab "LocalCSR". Two outcomes are available;

1. No message is seen, in which case the risk assessment has been successful, and all RCRs are <1. See section 3.7 for details of the content of this tab.
2. A message appears inside a button "RE-RUN", near to cell AY13. In this case there are RCRs which are >1.

If the reason for the RCRs being greater than 1, are due to water-borne emissions, then it is possible to "re-run" the model. When the "RE-RUN" button is pressed, the model will revise those RCRs for compartments that are driven by water-related emissions, deriving new on-site waste water removal efficiencies, to ensure safe use.

If the required waste water removal efficiency reported in row 15 is greater than the default off-site treatment that is determined using SimpleTreat, the implication is that advanced wastewater treatment (e.g. acclimated on-site biological treatment) is needed, and the exposure assessor must be sure to clearly communicate this additional level of RMM to the registrant.

It is important to understand that the re-run feature only addresses emissions via water and can only be re-run on one occasion.

Local risks can sometimes be driven by air emissions (e.g. RCR is driven by human inhalation, or terrestrial exposures as a result of atmospheric deposition). In such cases, the re-run feature **should not be used** and a manual revision to air emission factor inputs described in Section 3.3 will be required to determine conditions of safe use and associated risk management measures for air emissions. These revisions should be based on best achievable and reasonable available technology.

SECTION 3

DESCRIPTION OF SPREADSHEET MODEL PETRORISK

This section provides a description of the purpose for the various worksheets in the PETRORISK model. The specific user-required inputs, model outputs and spreadsheet formats are address in this section. Details of the model calculations are provided in Section 4.0.

3.1 OVERVIEW

PETRORISK provides detailed information on emissions, PECs, human intakes and Risk Characterisation Ratios (RCRs) for individual and summed hydrocarbon blocks at both local and regional scales. The spreadsheet model requires user inputs of hydrocarbon block composition, generic uses and tonnages, and substance-specific DNELs if applicable. There are also several worksheets that contain databases of fate factors, library structures and other supporting information as well as multiple output sheets that detail predicted local and regional exposures and risks and related risk management requirements. When finalizing the risk assessment from PETRORISK, the results are reported in a "clean" version, which has many of these databases and supporting information removed in order to limit the size of the spreadsheet and stream line reporting of model input and output (see Section 2.8). The purpose and function of the various worksheets in the spreadsheet model are described below. In several of the worksheets there are annotated comments provided to describe the use and function of a given set of cells. The descriptions are provided as documentation to 'PETRORISKv7.04', which is the latest publicly available version as of June 2016. The model can be accessed through the Concawe website (www.concawe.be) at no cost but requires registration so that downstream users may be notified of possible updates.

3.2 WORKSHEET 'product composition'

At this step, the user should SaveAs with a filename that is descriptive of the simulation being performed (e.g., "PETRORISKv7.04_substance name.xls"). The first step of an analysis with PETRORISK requires the user to enter compositional information for the substance under consideration (e.g., gasoline, kerosene, etc.). The buttons near cell B4 can be used to select the input format. The high resolution format allows users to enter compositional information using a blocking scheme that is defined by carbon number and up to 16 structural classes. This input format is consistent with information derived from GCxGC analytical methods. The user may enter information in single carbon number blocks as indicated in cells D9:F19. These functions are illustrated in Figure 5:

Figure 5: Product Composition Worksheet: High Resolution Data Input:

	1	2
	n-P	**i-P**
Block **C#i (>=)** **C#f (<)**	**(weight %)**	**(weight %)**

PETRORISK:
The user must enter compositional information (weight %) for a given petroleum product. High and Low Resolution input formats may be accessed through the radio buttons. The concentrations of individual priority substances may be specified below. Detailed model calculations and outputs will be generated using the RUN button. Mass must total to within <99.5 to <100.5% or model will report error and stop calculations.

(Pa)
ESTIMATED: 1.5E+02

- High Resolution
- Low Resolution
- Solvents

Estimate VP and WS

Block	C#i (>=)	C#f (<)	n-P (weight %)	i-P (weight %)
1	4	5	0.0E+00	0.0E+00
2	5	6	5.2E-03	1.5E-04
3	6	7	2.8E-02	4.5E-05
4	7	8	4.1E-02	2.9E-02
5	8	9	1.0E-01	6.9E-02
6	9	10	2.1E-01	1.7E-01
7	10	11	4.2E-01	3.5E-01
8	11	12	7.2E-01	6.0E-01
9	12	13	8.0E-01	6.7E-01
10	13	14	9.3E-01	8.5E-01
11	14	15	1.1E+00	1.1E+00
12	15	16	1.4E+00	1.3E+00
13	16	17	1.5E+00	1.6E+00
14	17	18	1.5E+00	1.3E+00
15	18	19	1.4E+00	1.6E+00
16	19	20	1.3E+00	2.1E+00
17	20	21	1.3E+00	1.9E+00
18	21	22	1.1E+00	1.3E+00
19	22	23	8.9E-01	9.6E-01
20	23	24	6.4E-01	8.5E-01
21	24	25	4.5E-01	7.6E-01
22	25	26	2.7E-01	5.5E-01
23	26	27	1.8E-01	3.8E-01
24	27	28	1.1E-01	2.4E-01
25	28	29	7.4E-02	1.9E-01
26	29	30	4.8E-02	1.3E-01
27	30	>30	7.2E-01	9.4E-02
		Sum:	100.00	

Low resolution format requires the user to enter composition information for up to two general chemical classes (e.g., aliphatic or aromatic) as a function of boiling point. The BP intervals are consistent with Total Petroleum Hydrocarbon (TPH) analytical protocols, see Figure 3, cells B9:F18. Previous work with PETROTOX (HydroQual, 2009; van de Meent et al 2010; van de Meent 2008) demonstrates that there are generally minor differences in the results between high and low resolution composition. The solvent blocking scheme option provides users with a third option allowing compositional input in terms of aliphatic and aromatic classes as a function of carbon number. This scheme is consistent with the latest nomenclature used to categorize various hydrocarbon-based

solvents under REACH (http://www.esig.org/uploads/documents/104-584-hspa_naming_convention.pdf).

The values entered into each composition input cell, or hydrocarbon block, are entered as weight percent of the total. The model allows for some variability in the overall reported composition of +/- 0.5% out of 100%. This means that the sum of total mass can be between 100.5 and 99.5% and the model will proceed with the calculations. However, if the total entered mass is >100.5% then the model will stop and report the error and require the user to correct the entered mass fractions. If the mass is less than 99.5% a dialog box appears which allows the user to either 1) scale up all blocks evenly to reach 100%, 2) add the 'missing' mass to the highest aliphatic block or 3) to stop and fix the input errors. For some lighter substances (e.g., naphtha, kerosene, gas oils) with reported mass fractions < 100% this is largely due to analytical variability. However, some heavier substances (e.g., bitumen, heavy fuel oil) there can be large fractions of mass present as resins or asphaltenes that cannot be quantified with GCxGC methods. In this case, the unreported mass are generally assigned to the highest aliphatic block, consistent with their generally inert behaviour, in order to preserve the mass balance.

The second step that users must follow is to estimate the product-specific vapour pressure (VP) and water solubility (WS). This is done by clicking on the 'Estimate VP and WS' button near cell E4. This executes a macro that calculates and reports the Raoult's Law-scaled VP and WS based on the simulated petroleum substance composition. This information is used to select default emission factors for specific environmental release categories (SpERCs) which are linked to generic exposure scenarios. These default emission factor inputs are specified as a function of the physical-chemical properties of the substance being evaluated (Sub-SpERCs), see Section 3.3.

3.3 WORKSHEET 'product lifecycle information'

The second step for running PETRORISK is to select Generic Exposure Scenarios using the dropdown menus in cells C7:C52 and to enter the total EU volume (tonnes/annum) in cells F7:F52 (Figure 6). Alternatively, the user may enter the PETRORISK ID (Section 3.13) that is associated with the GES into cells C7:C52. The dropdown menus are linked to the 'SpERCs' worksheet and provide default local emission volumes, emission factors and other information that are required for running the model.

Figure 6: Selecting SpERCs/ Conditions of Use For Each GES

The default values can be over-written, if justified. PETRORISK does not validate the entered EU volume or other parameters and it is assumed that the user is providing values that are consistent with the intended substance-specific generic use map. The first generic exposure scenario (GES) is always assumed to be Manufacturing (line 7) and cannot be changed. If this use is not required then the user may enter tonnage of zero into cell F7.

SpERC defined emission factors (EFs) to air, water, and soil are percent values of the EU volume that is emitted to these compartments from activities associated with the particular use. The EFs are applied at both the local and regional scale. Other factors affecting the emission calculations include the fraction of EU emissions emitted to the regional scale and assumed local site tonnage, emission duration, waste water flow and receiving water dilution. When the GES is selected from the drop-down menu, the EFs for the GES-linked SpERC are also selected. However, these defaults can be manually overwritten by the user. Exposure through land application of wastewater sludge can also be altered by modifying the Yes/No switch in column P.

Other input parameters include the organic carbon and moisture content in soils and sediments, see Cells D59:D61. The default values are 3% for sediments and 5% for soils with a dry weight fraction of 0.2. This information is used to calculate RCRs for emissions to soils and sediments. The model reports PECs in soils and sediments with units of 'mg/kg soil wet weight' while the PNECs are derived with units of 'µg/kg organic carbon'. Also, sediment and soil PNECs can be further reduced by a factor of 10 for compounds with log Kow >5. This feature is typically not used due to the technical basis of the TLM-derived PNEC and Equilibrium Partitioning (EqP) theory. While the technical basis of this additional assessment factor is debated the option is provided in cell F55. The user can enter a 'y', or 'Y' for Yes to invoke the application of this assessment factor. For petroleum products, the default and recommended setting is that no additional assessment factor is applied and is indicated by 'n' or 'N' for No. 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 and equilibrium partitioning theory do not understate observed toxicity (HydroQual 2009). Recent work suggests that the use of equilibrium partitioning theory maybe overly conservative in assessing ecological risks of petroleum hydrocarbons (Muijs and Jonker, 2010).

The tool is executed by clicking on the 'RUN Standard Mode' button near cell B29. This directs the model to read the compositional data (Section 3.2) and select the SpERC linked emission factors to calculate PECs, Human Intakes (HIs) and RCRs that are based on assigned library structures (Section 3).

3.4 WORKSHEET 'Site-Specific Production'

This mode allows the user to scale generic results obtained for the manufacturing GES (based on SpERC defaults) to specific manufacturing sites, and can only be accessed in the high or low resolution mode. The results of the generic calculation are referenced in cells C4:AS8. The generic results are scaled linearly based on the site-specific operating parameters provided by the user in cells C17:L153 for up to 137 individual sites (i.e. refineries).

Figure 8. Site-Specific Production Worksheet

The critical operating parameter inputs include total substance production (e.g., t/year of naphtha produced), the total crude oil throughput (t/year), the annually-averaged TPH in the effluent (mg/L) and the receiving water dilution factor. Other input data include the type of discharge environment (e.g., fresh water or sea water), waste water flow, which are only used if a site dilution factor is not provided by the user. Furthermore, to ensure conservatism, based on the type of discharge environment, the dilution factor applied in scaling is capped at 100 for fresh water and 1000 for marine discharges. The user also needs to specify whether waste water treatment is on-site or off-site. The reported TPH must be consistent with the treatment strategy (e.g., either after or before treatment, respectively). On-site WWTP are considered acclimated to industrial effluents and RCRs for WWTP microbes are not considered relevant for these scenarios and therefore not calculated nor provided in the output.

Results include PECs in the major environmental compartments (columns M:AD) and corresponding RCRs (columns AE:AM) where PNECs are applicable. Human intake via inhalation and indirect dose (e.g., dietary) is reported in columns AN:AP and corresponding RCRs (columns AQ:AS) if DNELs (Section 2.16) have been provided. RCRs that are greater than one are highlighted in bold red with grey shading (e.g., **10.0**). A 'required TPH removal efficiency' (column L) is calculated if any RCR greater than one is

calculated for a compartment where exposure concentrations are dictated by water emissions. Intermediate calculations are given in rows 169:189, which include the predicted solubility-scaled composition of TPH in the wastewater influent, resulting TPH speciation in effluent (after SimpleTreat removal), as well as the risk quotients for WWTP microbes by hydrocarbon block in the effluent. This information is provided to document assumptions regarding block emissions, fate during wastewater treatment and subsequent contributions to effluent toxicity.

3.5   WORKSHEET 'Multimedia Distribution'

This worksheet reports information on the fate of substance hydrocarbons emitted to air, water and soil through the use of the substance across all lifecycle stages at the regional scale as defined by 'product life cycle' worksheet discussed in Section 2.3. This calculation reflects the regional distribution results from EUSES, a level III type fugacity model. Mass and volume terms (cells M3:M10) in the mass balance calculations for the major compartments (e.g., soil, air, water, sediment) are the default dimensions specified in EUSES. Total mass (cells I3:I10) and the fractional contribution to the overall distribution (cells J3:J10) are the major outputs in this worksheet. This calculation is provided for characterizing the multi-media distribution of a complex substance as required in section 4.2 of International Uniform ChemicaL Information Database (IUCLID) and in section 5.4 in the REACH chemical safety report.

3.6   WORKSHEET 'ProductLibrary'

Once the '*RUN PETRORISK*' button is activated the tool assigns library structures to the appropriate hydrocarbon block based on user input of % mass, and then allocates the user-defined mass for that block evenly among the representative structures that are selected for simulating the block. All subsequent calculations are performed in terms of individual structures. The 'ProductLibrary' worksheet lists and assigned structures (column C:G) along with their physical-chemical properties and PNECs (identified as the estimated fifth percentile hazard concentration, or HC5 values in columns H:T). The reported physical-chemical properties include partition coefficients and compartment half-lives. The information is obtained from the "Concawe Library" Worksheet (Section 2.14) and is referenced by the unique compound ID (column D). The block assignment is given in column C by block (e.g., BP or C number) and structural class, see Figure 7.

Figure 7: Product Library

C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
A1:U1520		NOTES									Half-Lives						
HighResolution																	
Block ID	Compound ID	Chemical Name	SMILES	Chemical Class	Water Solubility (mg/L)	Law Constant (atm-m3/mol)	Log (K_{ow})	Log (K_{oc})	Air Hrs	Water Days	Soil Days	Sediment Days	Wastewater Hrs	Aqueous HC5 (ug/L)	Wastewater HC5 (ug/L)	Soil HC5 mg/kg WW	sediment HC5 mg/kg WW
Block, Class	ID	Name		Class	(mg/L)	(atm-m3/mol)			Hrs	Days	Days	Days	Hrs	(ug/L)	(ug/L)	mg/kg WW	mg/kg WW
					2.0.E+03	5.87	18.02	14.70	6.6.E+01	1.7.E+05	1.7.E+05	6.6.E+05	7.7.E+04	8.9.E+02	4.4.E+04	5.4.E+09	1.3.E+10
					2.7.E-12	-9.92	1.99	1.71	5.7.E-01	1.0.E+00	1.0.E+00	4.1.E+00	1.1.E-01	2.4.E-01	8.3.E-01	1.6.E-01	4.1.E-01
2,1	1455	n-pentane	CCCCC	n-Paraffins	5.0.E+01	-0.01	2.80	2.37	3.2E+01	4.0.E+00	4.0.E+00	1.6E+01	5.0.E-01	1.5E+02	7.1E+03	3.7E-01	7.7E-01
3,1	1456	n-hexane	CCCCCC	n-Paraffins	1.7.E+01	-0.01	3.29	2.77	2.4E+01	4.7E+00	4.7E+00	1.9E+01	5.9E-01	6.5E+01	2.9E+03	3.3E-01	7.7E-01
4,1	1005	n-heptane	CCCCCCC	n-Paraffins	3.6.E+00	0.23	3.78	3.16	1.9E+01	5.5E+00	5.5E+00	2.2E+01	7.1E-01	2.7E+01	1.2E+03	3.2E-01	7.8E-01
5,1	727	n-Octane	CCCCCCCC	n-Paraffins	1.2.E+00	0.29	4.27	3.56	1.5E+01	6.4E+00	6.4E+00	2.6E+01	8.4E-01	1.1E+01	4.6E+02	3.2E-01	7.9E-01
6,1	685	n-Nonane	CCCCCCCCC	n-Paraffins	4.1.E-01	0.31	4.76	3.96	1.3E+01	7.4E+00	7.4E+00	3.0E+01	1.0E+00	4.5E+00	1.8E+02	3.2E-01	7.9E-01

The Raoult's Law scaled (using water solubility and vapour pressure) and basic mass distribution assigned to each compound are also reported (columns U:W). Mass scaling for emissions to air or water via vapour pressure and water solubility, respectively, is intended to represent the actual composition of the emission to these compartments. The range of the physical-chemical properties of the assigned library structures is summarized in rows 5 (maximum of range) and 6 (minimum of range).

In some cases the PNECs provided for the library structures used in the substance simulation are highlighted in bold font and shaded, e.g. **1.1E+00.** This denotes that the PNEC for this structure exceeds its sub-cooled solubility limit. While this structure alone cannot result in ecotoxicity, it is conservatively assumed this structure can fractionally contribute to overall toxicity based on the additivity paradigm (see Section 4.6).

In summary, this worksheet provides a convenient description of the subset of library structures, associated fate and effect properties and assumed emission speciation that are used for a given substance evaluation. This relevant supporting information is provided for documentation purposes in the REACH chemical safety report.

3.7   WORKSHEET 'RegionalCSR'

This worksheet summarizes the emission, PECs, HIs and RCRs for all compartments considered at the regional scale. These results are intended to be submitted as part of the Chemical Safety Report. The results are obtained from the more detailed output worksheet for regional calculations (Section 3.10). Regional calculations are the sum of all emissions across all the uses listed in the 'product life cycle' worksheet discussed in Section 3.3.

3.8   WORKSHEET 'LocalCSR'

Similar to the 'RegionalCSR' worksheet, the LocalCSR summarizes the emissions, HIs, PECs, and RCRs for all compartments, for each GES considered, at the local scale. The worksheet is formatted so that the results for individual GESs (Section 2.3) are reported from left to right starting in column C. Information related to emissions and risk management measures is summarized in rows 3:22. Local scale PECs are summarized in rows 23:65 while resulting RCRs are reported in rows 68:88.

The worksheet can accommodate outputs for up to 46 GESs consistent with Section 2.3. If RCRs are greater than one, then the model automatically prompts the user to re-run the simulation with a revised wastewater emission factor (EF) (button near cell AY13). The revised EFs are calculated via the macro basic code by dividing the initial EF by the maximum RCR. This will result in RCRs less than one for all compartments that are driven by water-related emissions. This revision is done on a use-by-use basis, i.e. for each GES

Figure 9: Local CSR Worksheet output: PECs, RCRs example

Row	Table of Local Exposure and Risk Characterisation Results from PETRORISK	C (local output- Manufacture # 1)
2	Section 9 - Exposure Assessment	9.1
3	Regional Tonnage (T/yr)	7.7E+05
4	Fraction of regional tonnage used locally	7.8E-01
5	Local Site Tonnage (T/y)	6.0E+05
6	Site Tonnage (kg/d)	2.0E+06
7	Emission days (d/yr)	300
8	Release fraction (prior to RMM) - wastewater	3.0E-05
9	Release fraction (prior to RMM) - air	1.0E-02
10	Dilution Factor - Freshwater	10
11	Dilution Factor - Marine	100
12	On-site removal efficiency - Air (%)	90.0
13	Risk-driving Compartment	freshwater sediment
14	Wastewater Treatment Required (Yes/No)	Yes
15	Required Removal Efficiency - wastewater (%)	99.1
16	Onsite Removal Efficiency - wastewater (%)	85.8
17	Offsite Removal Efficiency - wastewater (%)	93.7
18	Total Removal Efficiency - wastewater (%)	99.1
19	Msafe (kg/d)	2.0E+06
20	Aquatic without Treatment (kg/d)	8.1E+00
21	Aquatic (with onsite and offsite treatment) (kg/d)	6.1E+00
22	Air (direct after on-site treatment) (kg/d)	2.1E+03
23	Environmental Exposure	
24	PEC effluent (mg/L)	5.3E-02
25	PEC sludge (mg/kg dw)	2.4E+02
26		
27	PEC air (mg/m³)	4.6E-01
28	C air (mg/m³)	4.6E-01
29		
30	PEC freshwater (mg/L)	5.3E-03
31	C freshwater (mg/L)	5.3E-03
32	PEC marine (mg/L)	5.3E-04
33	C marine (mg/L)	5.3E-04
34		
35	PEC freshwater sediment (mg/kg ww)	5.5E-01
36	C freshwater sediment (mg/kg ww)	5.4E-01
37	PEC marine sediment (mg/kg ww)	5.5E-02
38	C marine sediment (mg/kg ww)	5.5E-02
39		
40	PEC agricultural soil (mg/kg ww)	5.8E-03
41	C agricultural soil (mg/kg ww)	5.6E-03
42	PEC groundwater (mg/L)	2.5E-04
43	C groundwater (mg/L)	1.1E-05
44		
45	PEC oral freshwater fish (mg/kg ww)	8.6E-01
46	PEC oral marine top predator (mg/kg ww)	7.5E-01
47	PEC oral worm (mg/kg ww)	1.7E-02
48	PEC oral Top Predator (mg/kg ww)	7.5E-01
49	Indirect Human Exposure	

Row	Table of Local Exposure and Risk Characterisation Results from PETRORISK	C (local output- Manufacture # 1)
2	Section 9 - Exposure Assessment	9.1
49	Indirect Human Exposure	
50	PEC fish (mg/kg ww)	1.1E+00
51	C fish (mg/kg ww)	1.1E+00
52	PEC drinking water (mg/L)	2.8E-03
53	C drinking water (mg/L)	2.8E-03
54	PEC meat (mg/kg ww)	4.6E-01
55	C meat (mg/kg ww)	4.6E-01
56	PEC milk (mg/kg ww)	1.5E-01
57	C milk (mg/kg ww)	1.5E-01
58	PEC leaf (mg/kg ww)	5.8E-02
59	C leaf (mg/kg ww)	5.8E-02
60	PEC root (mg/kg ww)	2.0E-02
61	C root (mg/kg ww)	1.3E-02
62		
63	Dose inhalation (ug/kg/d)	1.3E+02
64	Dose oral exposure - excluding inhalation (ug/kg/d)	6.1E+00
65	Fraction from water pathways	1.4E-02
66		
67	Section 10 - Risk Characterisation	10.1
68	PNEC oral (mg/kg ww)	0.0E+00
69	DNEL inhalation (ug/kg/d)	1.3E+03
70	DNEL oral exposure (ug/kg/d)	1.3E+03
71		
72	Environmental Risk	
73	RCR effluent	2.1E-01
74	RCR freshwater	7.6E-01
75	RCR marine	7.6E-02
76	RCR freshwater sediment	9.1E-01
77	RCR marine sediment	9.1E-02
78	RCR oral freshwater fish	0.0E+00
79	RCR oral marine top predator	
80	RCR agricultural soil	1.5E-02
81	RCR worm oral	0.0E+00
82	RCR Top Predator	
83	Indirect Human Risk	
84	RCR inhalation	1.0E-01
85	RCR oral exposure - excluding inhalation	4.7E-03
86	RCR combined HI	1.1E-01
87	MaxRCR- Water-related compartments	9.1E-01
88	MaxRCR- Air-related compartments	1.0E-01
89	Max RCR - all compartments	9.1E-01

where the RCR is > 1, and does not require any additional user input. The revised waste water EF is used, in turn, to estimate the total (row 15) and additional on-site waste water removal efficiencies (row 16) beyond the default removal from SimpleTreat (row 17) that are required to ensure safe use. If the required waste water removal efficiency reported in row 15 is greater than the default off-site treatment that is determined using SimpleTreat, the implication is that advanced wastewater treatment (e.g. acclimated on-site biological treatment) is needed, and the exposure assessor must be sure to clearly communicate this additional level of RMM to the registrant. If cell 15 is less than 17, then no revision to the waste water EF is required since off-site treatment in a domestic sewage treatment plant (the default SpERC assumption) provides an adequate risk management measure (RMM) to provide safe use. If cell 15 is zero, secondary waste water treatment is not required. However, it is important to point out that the estimated RMMs (none, domestic off-site, advanced on-site) that is presented in this worksheet refers to a "hypothetical" site that is

defined by the default operating conditions assumed in the GES-specific SpERC. To translate the generic RMMs for downstream users into site-specific RMMs at actual sites, further scaling is required using key site operating parameters (i.e. site tonnage, wastewater flow dilution factor) as highlighted for manufacturing in section 3.4

One limitation to the re-run feature in the tool is the assumption that risks are driven by emissions to water. While this is often the case, local risks can sometimes be driven by air emissions (e.g. RCR is driven by human inhalation, or terrestrial exposures as a result of atmospheric deposition). In such cases, the re-run feature should not be used and a manual revision to air emission factor inputs described in Section 3.3 will be required to determine conditions of safe use and associated risk management measures for air emissions. These revisions should be based on best achievable and reasonable available technology. Reducing emission factors solely to achieve RCR values <1 based on stringent and impractical measures should be avoided if these are not possible to implement and maintain.

3.9   WORKSHEET 'speciated emission inventory'

This worksheet (Figure 10) displays the results of the emissions for the major environmental compartments (air, water, soil, and wastewater) at the regional and local scales for each hydrocarbon block in units of 'kg/day'. Emissions are only reported where there are non-zero emission factors entered in 'prod, cons & emis factors' worksheet. Separate outputs are reported for each use category where non-zero production/use volumes are entered.

Figure 10 Speciated Emissions Example

	REGIONAL	REGIONAL	REGIONAL	REGIONAL
		Emission to Air		
		SUM:	2.33E+03	
Summary of all uses		1	2	3
		n-P	i-P	MonoN
		(kg/day)	(kg/day)	(kg/day)
	1			
	2	1.2E+02	4.9E+00	1.4E+02
	3	1.9E+02	4.4E-01	1.4E+02
	4	8.8E+01	1.1E+02	2.3E+02
	5	7.1E+01	1.1E+02	2.2E+02
	6	4.9E+01	6.4E+01	9.6E+01
	7	3.4E+01	4.6E+01	6.7E+01
	8	2.1E+01	6.7E+01	4.3E+01
	9	8.8E+00	3.8E+01	2.0E+01

The overall emissions are on rows 7 to 26 and speciated emissions for each subsequent GES are reported in groups of ~20 rows each below the results of the overall emission calculation. Note that all calculations, including emissions, are performed in terms of individual structures as assigned during the mapping process. The emissions reported are

the sum of all the compounds in a given hydrocarbon block. The output format will change depending on the input resolution (Section 3.2).

3.10   WORKSHEET 'regional output-expo&risk'

The PECs, HIs and RCRs generated at a regional scale are reported in this worksheet. PECs are reported by hydrocarbon block for some select endpoints in rows 5 to 22. The corresponding RCRs are reported in rows 23 to 40 and the percent contributions to the RCR for each block are reported in rows 41 to 56. A summary of overall PECs and RCRs for each of the regional compartments is reported in cells B58:E71. This format changes slightly depending on the input resolution selected in the 'product composition' worksheet (Section 3.2).

The HIs ($\mu g/(kg*d)$) are reported in rows 75 to 97 for the major exposure routes (air, water, soil) by block. The sum across all compartments is reported in rows 98 to 123 and the fractional contribution from each exposure pathway that contributes to the HI for the overall product in rows 127 to 143. A summary of the human exposure and RCRs is given in a table at cells D139:G147.

Figure 11   WORKSHEET 'regional output-expo&risk example

		n-P	i-P	MonoN	Di-N	n-Olefins	i-Olefins	Poly-N	AIS	MoAr	NMAr	DiAr
		1	2	3	4	5	6	7	8	9	10	11
		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
	1											
	2	2.6E-09	2.6E-10	2.5E-08								
	3	4.4E-09	2.6E-11	2.7E-08						1.2E-07		
	4	1.2E-09	6.9E-09	2.8E-08						2.6E-07		
	5	8.7E-10	4.2E-09	2.1E-08	6.6E-09					3.0E-07		
	6	6.5E-10	3.6E-09	9.0E-09	1.5E-08					1.8E-07	1.2E-08	
	7	3.7E-09	2.2E-09	5.3E-09	2.1E-08					6.9E-08	1.5E-08	1.2E-07
	8	1.1E-09	1.1E-09	2.3E-09	1.2E-08					2.8E-08	8.1E-09	1.8E-07
	9	4.2E-10	3.8E-10	7.2E-10	5.4E-09					7.5E-09	7.6E-09	1.9E-07
	10	8.7E-11	1.0E-10	2.4E-10	2.5E-09					2.9E-09	2.9E-09	1.1E-07
	11	2.6E-11	3.5E-11	7.5E-11	9.1E-10					6.9E-10	5.6E-09	5.5E-08
	12	1.2E-11	1.3E-11	3.7E-11	2.6E-10					2.2E-10	2.4E-09	1.4E-08
	13	1.1E-11	1.4E-11	2.0E-11	1.0E-10					6.4E-11	9.6E-10	3.5E-09
	14	6.5E-12	2.7E-12	9.7E-12	8.0E-11					2.0E-11	7.9E-10	9.3E-10
	15	2.1E-12	1.8E-12	5.3E-12	5.3E-11					9.0E-12	1.0E-09	2.4E-10
	16	2.4E-12	1.5E-12	6.1E-12	5.0E-11					4.2E-12	2.6E-10	6.6E-11
	17	4.6E-12	8.3E-13	1.4E-12	2.3E-11					3.1E-12	3.2E-10	2.9E-11
	18	2.5E-13	3.3E-13	2.0E-12	1.4E-11					1.8E-12	2.8E-10	3.0E-11
	19	6.7E-13	1.4E-13	3.5E-13	5.5E-12					8.5E-13	7.4E-10	4.1E-12
	20	4.1E-14	6.8E-14	1.5E-13	2.3E-12					2.5E-13	2.2E-10	2.3E-12
	21	2.3E-14	4.0E-14	5.6E-14	7.9E-13					9.2E-14	1.1E-10	1.1E-12
	22	9.3E-15	2.3E-14	2.0E-14	3.0E-13					3.4E-14	3.6E-11	3.0E-13
	23	3.7E-15	5.8E-15	7.8E-15	1.6E-13					9.1E-15	1.3E-10	1.0E-13
	24	1.0E-15	2.0E-15	2.9E-15	6.8E-13					3.1E-15	5.3E-12	6.2E-14
	25	3.6E-16	8.1E-16	1.2E-15	1.1E-14					1.2E-15	1.2E-12	1.5E-14
	26	9.8E-17	3.8E-16	4.8E-16	3.1E-15					2.6E-16	3.0E-13	3.4E-15
	27	2.4E-16	8.9E-17	8.5E-17	4.7E-16			7.7E-11		4.9E-17	3.9E-12	1.1E-15

3.11   WORKSHEET 'local summary'

A summary of all local PECs, HIs and RCRs for each GES is reported in this worksheet. The local outputs (PECs and RCRs) are reported for each use given local emissions (see section 3.9). The PECs and RCRs are listed between rows 5 to 28 rows and 31-43, respectively. The results for each GES are reported starting in column F and up to column AY, consistent with the number of uses from Section 3.3. The compartments and units are labelled in columns D and E. For additional detail the user is referred to the 'local output-…" output worksheets that correspond to each GES that is summarized in this sheet (Section 3.12).

Figure 12   WORKSHEET 'local summary' example

PEC	units	Manufacture of substa	Use as Intermediate In	Distribution Industrial
Effluent	mg/L	4.1E-01	5.1E-02	5.2E-04
Fresh Water	mg/L	4.1E-02	5.1E-03	5.2E-05
Fresh Water Sediment	mg/kgw	4.2E+00	5.3E-01	5.4E-03
Marine Water	mg/L	4.1E-03	5.1E-04	5.2E-06
Marine Sediment	mg/kgw	4.2E-01	5.3E-02	5.4E-04
Agricultural Soil	mg/kgw	5.9E-03	3.2E-05	1.5E-06
Air	mg/m3	4.6E-01	2.4E-03	1.2E-04
Sludge	mg/kgw	1.9E+03	2.4E+02	2.4E+00
Groundwater	mg/kgw	2.5E-04	1.5E-06	6.4E-08
Fish	mg/kgw	8.4E+00	1.1E+00	3.6E-03
Leaf	mg/kgw	5.9E-02	4.5E-04	1.5E-05
Root	mg/kgw	2.0E-02	1.1E-04	5.2E-06
Meat	mg/kgw	4.6E-01	2.5E-03	1.2E-04
Milk	mg/kgw	1.5E-01	7.9E-04	3.7E-05
Drinking Water	mg/L	2.0E-02	2.5E-03	8.5E-06
fish.oral	mg/kgw	6.7E+00	8.3E-01	2.8E-03
predator.oral	mg/kgw	5.8E-01	7.3E-02	2.5E-04
worm.oral	mg/kgw	1.6E-02	1.1E-04	4.2E-06
Human Intake Fractions				
Air	ug/kg/d	1.3E+02	6.7E-01	3.4E-02
Water	ug/kg/d	1.5E+01	1.8E+00	6.2E-03
Soil	ug/kg/d	0.0E+00	0.0E+00	0.0E+00
Total	ug/kg/d	1.5E+02	2.5E+00	4.0E-02
RCR		cture of substances	Inciate Industion	Industrial (S
Effluent		1.7E+00	2.1E-01	2.1E-03
Fresh Water		5.9E+00	7.4E-01	7.5E-03
Fresh Water Sediment		7.0E+00	8.8E-01	8.9E-03
Marine Water		5.9E-01	7.4E-02	7.5E-04
Marine Sediment		7.0E-01	8.8E-02	8.9E-04
Agricultural Soil		1.5E-02	8.4E-05	3.8E-06
fish.oral				
predator.oral				
worm.oral				
Human Intake Fractions				
Inhalation		1.0E-01	5.3E-04	2.6E-05
Other Routes of Exposure		1.4E-02	1.4E-03	5.5E-06

3.12   WORKSHEET 'local output- …(use name and number) '

The 'local output-…' worksheets are reported for each GES where a local emission factor is specified. The name of the worksheet will reflect the name of the GES as indicated on the 'product lifecycle information' worksheets in cells B7:B27. A number corresponding (e.g., '#1') to the sequence of the entry is also provided to aid in record keeping. The format is similar to the 'regional output-expo&risk' worksheet (Section 3.10) with some additional endpoints specific to local exposure scenarios.   PECs and environmental compartment RCRs are reported in rows 1 to 77 and results related to Human Intake and RCRs are reported in rows 79 to 149.

3.13   WORKSHEET 'SPERCS'

This worksheet contains the database of emission related-parameters that were extracted from Specific Environmental Release Categories (SpERC) factsheets relevant to the petroleum industry.   SpERC factsheets can be accessed via the CEFIC website: http://www.esig.org/en/regulatory-information/reach/ges-library/ges-spercs-2.   As previously mentioned, SpERCs define key default inputs needed for local and regional environmental exposure assessment calculations such as local site tonnages, air, water and soil emission factors, emission duration plus additional information documenting the use sector (i.e. industrial point source or wide dispersive). The drop-down menus discussed in Section 3.3 are linked to the information in this worksheet. The default local site tonnage is typically less than or equal to the regional tonnage input by the user, the SpERC default is assumed in local exposure calculations. However, if the default local tonnage is greater than the regional tonnage for a given GES then the regional tonnage is applied for the local calculation (i.e. it is conservatively assumed that all of the regional tonnage is used locally). (See Section 4.0).

For some GESs, the emission factors for air and water are selected as a function of the substance-specific estimated VP and WS, these EF values are linked to Sub-SpERCs as was previously discussed in Section 3.2. GES titles and descriptors are given in columns B:G. Emission characteristics are given in columns H:O. PETRORISK references each GES title by a unique PETRORISK ID in column Q.

3.14   WORKSHEET 'Concawe Library'

The "Concawe Library" contains the physical-chemical properties for 1512 representative individual hydrocarbon structures. There are structures from 16 chemical classes that span a wide range in physical-chemical properties such as log Kow, boiling point half-lives in water and soil and carbon number.   These structures are assigned to the hydrocarbon blocks defined in the 'product summary' worksheet. The PNECs for each

structure for the water, wastewater and the soil/sediment compartments are also reported in columns Y to AD. The physical-chemical properties were estimated using the batch analysis feature in SPARC v4.2 (May 2008; http://ibmlc2.chem.uga.edu/sparc/). The physical-chemical properties from EPIWin 4.1 are used in the QSAR calculations for VP, WS, PNECs, etc. However, in order to be consistent with the partitioning calculation in EUSES, the Koc is modelled using the EUSES algorithms and EPIWIN-derived log Koc. PETRORISK references these structures by their unique ID in column A. This worksheet is password protected to prevent inadvertent manipulation or loss of these key data.

3.15 WORKSHEET 'ff & if library'

This library contains Fate Factors (FFs) and Intake Factors (IFs) for each of the structures in the Concawe Library. These are used to calculate the PECs for different compartments and HIs on a local and regional scale (See Section 4). There are FFs for each emission type (air, water, soil), for each scale (regional, local) for the relevant compartments. This is a large database with 181 (columns D:GE) containing FFs and related information for each of the 1512 structures in the 'Concawe Library' (Section 3.14). The FFs are based on EUSES model runs (EUTGDsheetvs123 HB 2008-715.xls) results and represent the environmental concentrations per unit emission for each compartment under consideration (van de Meent, 2008). Analogous IFs are used to estimate HIs. This worksheet is password-protected to prevent inadvertent manipulation or loss of these key data.

3.16 WORKSHEET 'DNEL'

Risk Characterization Ratios for humans exposed via the environment are derived using estimated HIs, with user-defined Derived No Effect Levels (DNEL) that are provided in this worksheet. The substance-specific DNELs are entered in cells F12:F13 for either inhalation exposures or overall exposure. If a DNEL of zero is entered then RCRs for human endpoints are reported as zero.

There is an option to enter a PNEC for secondary poisoning endpoints that can occur through multimedia exposure. A default PNEC is given that approximately equals the critical tissue residue concentration corresponding to the HC5 (McGrath and Di Toro 2009. This is the only environmental endpoint where RCRs are calculated using a unique PNEC that is applied to every structure in the tool that is included in the substance evaluation.

3.17 WORKSHEET 'Appendix1 Summary PNECS'

This worksheet has static outputs to summarize the median PNEC of the structures assigned to the HB. These do not vary with emission factors or product composition. This is provided for reference only. The individual PNECs reported in the 'Concawe library' are used in the risk calculations in PETRORISK based on insights gained from an

investigation of different blocking schemes and RCR calculation methods using the hydrocarbon block method (van de Meent et al., 2010; van de Meent 2008).

3.18   WORKSHEET 'Appendix2 Summary log Kow'

This worksheet reports the range (max, min and average) of the log Kow for the structures that are assigned to the various hydrocarbon blocks. This is a static output. Entries with "--" represent hydrocarbon blocks where there are no available representative structures. This information is consistent with data provided in the 'ProductLibrary' worksheet described in Section 3.6.

SECTION 3

TECHNICAL BASIS

This section provides the details of how the model calculations are performed. This section includes information on assignment of mass fraction to library structures, emission estimation and speciation, and calculation of PECs, HIs and RCRs.

4.1   OVERVIEW

PECs are calculated in PETRORISK based on a series of Fate Factors (FFs) that were derived from EUSES at the regional and local scales (van de Meent, 2008; van de Meent et al 2010). Using this framework, PECs scale linearly with emission estimates (Eq. 1). Human Intake Fractions (IFs) are calculated in a similar fashion. Environmental risk is estimated by the PEC to PNEC ratios (i.e., RCR) for all structures included in the simulation for the substance evaluated. PNECs for all library structures were estimated by applying a statistical extrapolation method (e.g., HC5) to the species sensitivity distribution derived from the published Target Lipid Model (TLM) database (McGrath and Di Toro, 2009; Di Toro et al., 2000; McGrath et al., 2004; Redman et al., 2007). The equations below are discussed in the order they are used in the PETRORISK calculations starting with structure assignments.

4.2   MASS ALLOCATION AND MAPPING OF LIBRARY STRUCTURES

Petroleum products are defined with individual structures from the "Concawe Library" (section 3.11). These structures are mapped to the user-defined hydrocarbon blocks as entered in the 'product composition' worksheet (section 2.4). Library structure assignments are performed by matching individual structures with bulk hydrocarbon blocks as a function of carbon number (for High Resolution) or Boiling Point (for Low Resolution) and chemical class (n=16, High Resolution; n=2, Low Resolution). Hydrocarbon blocks may have anywhere between 0 and >300 assigned structures. The user can refer to the 'ProductLibrary' worksheet for determining the actual assignments (Section 3.6).

Once the structures are assigned, the mass fraction for an individual structure (m_i) is determined by evenly dividing the mass of HB, j, (m_j) among the assigned structures (*structures$_j$*) according to the equation

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

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

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

In certain cases it is possible to have a HB with a specified mass where there are no available library structures for assignment. This can be due to subtle inconsistencies between the "Concawe Library" and the compositional analysis input, or simply a lack of representative structures for some high BP aliphatic, non-toxic structural classes. In these cases, the mass for that HB is re-assigned to a neighbouring block to preserve the overall mass balance and to assign structures with similar physical-chemical properties to these "orphan" blocks. This typically occurs for high C# aliphatic chemical classes that are mapped to neighbouring blocks with assigned structures exhibiting very limited solubility and reduced bioavailability, so this adjustment does not substantially affect risk assessment results.

The mole fraction, x_i for compound i in a substance is a key parameter which impacts vapour pressure and water solubility estimation. 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 $mole_i$ =mass x molecular weight.

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

If the high or solvent resolution blocking schemes are used to simulate substance composition, the mass allocations for each structure that is assigned to a block is determined by dividing the user-defined mass within the block by the number of structures in the block, i.e. assume each structure in a given block is equally weighted.

In the case of the low resolution scheme an additional weighting correction is applied to the aromatic mass distribution for relatively high BP (>350ºC) blocks in order to accurately predict ecotoxicity of heavy petroleum products (HydroQual, 2009; Redman et al 2012). 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. PAH structures receive approximately three times more mass than other compounds in these high BP blocks – but only at low resolution input scheme. The mass allocations to 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

$$\text{If } (1 - RATIO_{PAH}) < 0.7$$
$$\text{then } a_0 = 0.7$$
$$\text{else } a_0 = (1 - RATIO_{PAH}) \tag{5}$$

Where, the adjustment factor, a_0, is derived using an empirically derived constant of 0.7 (HydroQual, 2009; Redman et al 2012). The ratio of PAH structures to all aromatic structures ($RATIO_{PAH}$) is calculated as:

$$RATIO_{PAH} = NumberStructures_{PAH} \, / \, NumberStructures_{AllAromatic} = \text{PAH/TA} \tag{6}$$

Polycyclic aromatic compounds are weighted using a correction factor, a_1

$$a_1 = 1 + \left(\frac{a_0}{RATIO_{PAH}} \right) \tag{7}$$

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

$$a_2 = 1 - \left(\frac{a_0}{(1 - RATIO_{PAH})} \right) \tag{8}$$

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

$$m_{PAH,i} = m_i \cdot RATIO_{PAH} \cdot a_1 \tag{9}$$

where m_i is the initial mass assigned to this PAH structure (**eq 2**). Similarly, the re-adjusted mass assigned to the other high BP aromatic compounds ($m_{aro,i}$) is calculated as

$$m_{ARO,i} = m_i \cdot (1 - RATIO_{PAH}) \cdot a_2 \tag{10}$$

As stated above, this mass allocation correction for library structures assigned to the high boiling aromatic fraction as detailed in equations (5)-(10) is only applied when the low resolution blocking scheme is applied.

4.3   RE-SCALING MASS DISTRIBUTION USING RAOULT'S LAW

The mass allocation procedure in Section 3.2 describes the mapping of individual structures to simulate substance composition. This composition is used to model direct emissions to soil (as well as combustion related emissions for fuel uses since these emissions represent the composition of the unburned fuel), but does not reflect the differential partitioning behaviour of complex substances that modulate emissions 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

$$C_{W,i} = x_i \cdot S_i \qquad (11)$$

where x_i is the mole fraction for library structure i in the petroleum substance (calculated from **Eq 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 Kow 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

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

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)

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

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.

4.4   EMISSIONS

Emissions for each individual structure are calculated using the substance tonnages for each generic exposure scenarios and related emission factors to air, water, and soil at the regional and local scales as discussed in Section 3.3. The emissions of each individual structure assigned to a substance are further scaled as discussed in Section 4.3. Emissions to water are assumed to include contributions through emissions to waste water treatment plants. Land application of wastewater sludge can result in indirect emissions of petroleum hydrocarbons to soils and a special set of fate factors are used to account for increased soil emissions under this scenario.

Local emissions ($E_{local,compartment,i}$) via air, water and soil are calculated using the local site tonnage (EU_{local}), the Emission Factor ($EF_{compartment,i}$) to a given compartment (e.g., air, water, soil) as well as the corresponding scaled mass fractions ($m'_{compartment,i}$) for the appropriate compartment (air, water, soil). Scaled mass fractions are calculated using the molecular weight (MW) and the molar concentrations from Eq. 13.

$$E_{local,compartment,use,i} = EU_{local} \bullet EF_{compartment,i} \bullet m'_{compartment,i} \qquad (14)$$

Local site tonnage (EU_{local}) is calculated as either the regional tonnage (Eq. 15) or according to SpERC guidance (Column J, 'SPERCs', Section 2.13) – whichever is smaller. This method of establishing local site tonnages results in entries that are consistent with regional tonnages (e.g., less than or equal). For industrial uses an estimate of the local site tonnage is given in the SpERCs worksheet, but local tonnages for wide dispersive consumer and professional uses are estimated as a constant fraction (e.g., 0.002 or 0.0005) of the regional tonnage. The SpERC related parameters documented via factsheets have previously been discussed in Section 3.13.

The emissions for selected local compartments are further scaled by the days of operation ($Days_{use}$) within a year for a given GES (e.g., Eq. 14 * [365 / $Days_{use}$]). This conservative scaling approach results in higher PECs that occur during the shorter duration of emission compared to annual averages. Compartments that are scaled for the duration of the emissions include: effluent, sludge, fresh water, fresh water sediment, effluent, sludge, marine water and marine sediment. Other compartments that are not scaled include soil, ground water, air, leaf, fish, root, meat, milk, drinking water, as well as secondary poisoning endpoints predator.oral, fish.oral, and worm.oral since the corresponding PECs represent long-term exposures.

Consistent with REACH technical guidance (ECHA, 2008b), no direct emissions to soil ($EF_{soil} = 0$) are assumed at the local scale. All soil-related local PECs are attributable to

atmospheric deposition. Also, emissions from wide dispersive uses are considered regional in nature and are modelled by setting the EFair = 0 for local emissions. Wide dispersive uses include all non-industrial uses (e.g., professional or consumer) that are conducted in a variety of locations as opposed to industrial applications, which are considered as fixed emission point sources (e.g., refinery, blending plant).

Regional emissions ($E_{regional,compartment,i}$) are calculated in a similar manner using the total production tonnage (EU_{use}), regional emission fraction ($f_{regional,use}$), the Emission Factor ($EF_{compartment,i}$) and the corresponding scaled mass fractions ($m'_{compartment,i}$).

$$E_{\text{Regional,compartment,use,i}} = EU_{use} \cdot f_{regional,use} \cdot EF_{compartment,use} \cdot m'_{compartment,i} \quad (15)$$

Regional emissions are reported as the sum across all GES categories for annual emissions (e.g., no scaling for duration). For fuel related GESs, combustion related emissions to air of unburned fuel are considered as part of the waste stage that is included in the overall emission inventory for the substance. Waste stage emissions are included since this emission source is known to contribute significant to the overall emission inventory petroleum substances used principally as fuels, such as gasoline. Waste stage emissions use the reported mass distribution (e.g., no scaling for Air or Water) consistent with the emission speciation of combustion processes.

4.5   PECs AND HUMAN INTAKE FRACTIONS (HIs)

PECs and HIs are calculated using FFs and IFs (Section 3.15). At the regional scale there are 13 compartment PECs plus human exposure estimates (Table 1).

Table 1. Regional Scale Compartments	Units	PEC	RCR
Effluent	mg/L	x	x
Fresh Water	mg/L	x	x
Fresh Water Sediment	mg/kd ww	x	x
Marine Water	mg/L	x	x
Marine Sediment	mg/kd ww	x	x
Natural Soil	mg/kd ww	x	x
Air	mg/m^3	x	
Agricultural Soil	mg/kd ww	x	x
Fish	mg/kd ww	x	
Root	mg/kd ww	x	
Meat	mg/kd ww	x	
Milk	mg/kd ww	x	
Drinking Water	mg/L	x	

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Human Intake via Inhalation	µg/kg/d	x	x
Human Intake via Indirect Dose	µg/kg/d	x	x
Total Human Intake	µg/kg/d	x	x

Local PECs are calculated for 15 compartments (Table 2), plus 3 secondary poisoning endpoints (e.g., oral, or dietary, exposure) as well as human exposures.

Table 2. Local Scale Compartments	Units	PEC	RCR
Effluent	mg/L	x	x
Fresh Water	mg/L	x	x
Fresh Water Sediment	mg/L	x	x
Marine Water	mg/L	x	x
Marine Sediment	mg/kg ww	x	x
Natural Soil	mg/kg ww	x	x
Air	mg/m^3	x	
Sludge	mg/kg ww	x	
Ground water	mg/L	x	
Fish	mg/kg ww	x	
Leaf	mg/kg ww	x	
Root	mg/kg ww	x	
Meat	mg/kg ww	x	
Milk	mg/kg ww	x	
Drinking Water	mg/L	x	
fish.oral	mg/kg ww	x	x
predator.oral	mg/kg ww	x	x
worm.oral	mg/kg ww	x	x
Human Intake via Inhalation	µg/kg/d	x	x
Human Intake via Indirect Dose	µg/kg/d	x	x
Total Human Intake	µg/kg/d	x	x

The general form for calculating PECs is given in Equation 1 and is repeated here in more detail. This example is for PEC$_{air,local}$ though the same calculation is used for the other PECs and HIs reported in Tables 1 and 2 by using the appropriate set of FFs or IFs.

$$PEC_{local,use,Air,i} = FF^{Air}_{local,Air,i} \cdot E_{local,use,Air,i}$$
$$+ FF^{Water}_{local,Air,i} \cdot E_{local,use,Water,i} \cdot \left(\frac{10(fresh)\ or\ 100(marine)}{DF} \right) \cdot \left(\frac{2000}{EffFlow} \right) \quad (16)$$

The Local PEC ($PEC_{local,use,Air,i}$) is the sum of the product of the emissions to Air ($E_{local,use,Air,i}$) and water ($E_{local,use,Water,i}$) and their fate factors. In this example, the $FF^{Air}_{local,Air,i}$

is used for estimating the local air concentration (PEC) for structure i for a unit local air emission of structure i into air. Likewise, the $FF^{Water}_{local,Air,i}$ is used for estimating of air concentration of structure i for a unit emission to water. Emissions to soil are not considered at the local scale but may factor into regional scale emissions. The contribution to the PEC from emissions to water ($E_{local,use,Water,i}$) is further scaled by the user-defined dilution factor (DF) and the effluent flow from the wastewater treatment plant (*EffFlow*). The FFs were derived using a default DF of 10 for freshwater discharges and a default of 100 for marine water discharges. The default *EffFlow* of 2000 m^3/s was used in derivation of FFs so any emission scenario at a different DF or *EffFlow* requires this scaling step.

Air- and soil-related compartments (e.g., air, soil, root, meat, milk, leaf, ground water, worm.oral) are not affected by the DF since these PECs are driven by air deposition or through discharges to waste water prior to dilution such as volatilization through WWTP or land application of sludge, which only occurs at the regional scale. This calculation is repeated to calculate PECs for all local compartments using the applicable FFs.

These calculations are performed for each individual library structure used to simulate the substance being evaluated. The overall PEC is calculated as the sum of all individual library structures. At the local scale PECs are calculated for each GES considered (Section 2.3).

$$\text{PEC}_{local,GES,Air,Total} = \sum^{i} PEC_{local,GES,air,i} \qquad (17)$$

Most compartments are calculated using equations 16 and 17 at either the regional or local scale using appropriate fate factors. Predator.oral (e.g., secondary poisoning to top marine predator) is a special case since the derivation of these fate factors assumes that these organisms spend 10% of their time in local marine waters and 90% of their time in more remote (e.g., regional) marine waters. To account for this special case, a further correction is applied (predator.oral). The reported PEC* for predator.oral is calculated by scaling the initial PEC calculated from the fate factor approach (Eq. 16-17) by the regional and local seawater PECs using the equation:

$$PEC^*_{predator.oral,local} = PEC_{predator.oral,local} \left(\frac{0.9 PEC_{regional,seawater} + 0.1 PEC_{local,seawater}}{0.1 PEC_{local,seawater}} \right) \qquad (18)$$

Human Intakes ($HI_{local,Air,i}$) are calculated as the product of the emissions via the 3 major routes of exposure (air, water, soil) ($E_{local,use,compartment,i}$), the Intake Fraction ($IF_{local,Air,i}$) and the body weight ($W$). Body weight is assumed to by 70 kg, typical of adult humans. PECs are reported with appropriate unit conversions (Table 2).

$$HI_{local,use,Air,i} = (IF^{Air}_{local,Air,i} \cdot E_{local,use,Air,i})/W \qquad (19)$$

At the regional scale, the same approach is used except emissions and corresponding exposures are summed across GESs to reflect region-wide PECs and HIs (Table 1). The PEC calculation at the regional scale is similar to the local scale calculation in equation 16 with the important distinction that soil emissions can contribute to the overall PEC.

$$\begin{aligned}
PEC_{regional,use,Air,i} = {} & FF^{Air}_{regional,Air,i} \cdot E_{regional,use,Air,i} \\
& + FF^{Water}_{regional,Air,i} \cdot E_{regional,use,Water,i} \cdot \left(\frac{10(fresh)\ or\ 100(marine)}{DF}\right) \cdot \left(\frac{2000}{EffFlow}\right) \quad (20) \\
& + FF^{Soil}_{regional,Air,i} \cdot E_{regional,use,Soil,i}
\end{aligned}$$

The regional PEC ($PEC_{regional,use,Air,i}$) is the sum of the product of the emissions to Air ($E_{local,use,Air,i}$) water ($E_{local,use,Water,i}$) and soil ($E_{local,use,Soil,i}$) with their respective fate factors. In this example, the $FF^{Air}_{regional,Air,i}$ is used for estimating the regional air concentration (PEC) for structure i for a unit regional air emission of structure i into air. Likewise, the $FF^{Water}_{regional,Air,i}$ is used for estimating of air concentration of structure i for a unit emission to water and $FF^{Soil}_{regional,Air,i}$ is used for calculating the air concentration of structure i for a unit emission to soil. Soil emissions include atmospheric deposition as well as land application of WWTP sludge when specified by the SpERC. This calculation is repeated to calculate PECs for all regional compartments using the applicable FFs.

The 'FF and IF library' worksheet (Section 3.15) contains estimates of the fractional contribution from the various routes of exposure that are used in the human intake estimates including: inhalation, drinking water ingestion, and the consumption of fish, leaf, root, meat

and milk. This calculation is illustrated using the inhalation route of exposure at the regional scale but is similarly applied at the local scale.

$$HI - Inhalation_{regional,use,Air,i} = HI_{regional,use,Air,i} \cdot f_{regional,Air,i,inhalation} \qquad (21)$$

4.6 RISK CHARACTERIZATION RATIOS

Risk characterization ratios (RCRs) are used to quantify risks. Environmental effects for petroleum hydrocarbons are considered additive, so that the sum of all RCRs for individual structures is indicative of the overall risk of the complex petroleum substance. The RCR is calculated as the ratio of the PEC to the PNEC. The PNECs used in PETRORISK are the Target Lipid Model-derived HC5 extrapolation method for aquatic life (McGrath and Di Toro, 2009, McGrath et al., 2015) and waste water treatment plant microorganisms (Redman et al., 2007). The HC5 is the hazardous concentration that affects 5% of organisms. The HC5 is calculated for each library structure (column Y:Z in "Concawe library", section 2.14). The general form of the HC5 is based on the empirical statistics obtained from analysis of the distribution of critical body burdens (e.g., species sensitivity distribution, C_L^*) and acute to chronic ratios (ACRs), and is based on equation 22. See McGrath et al., 2004, McGrath and Di Toro, 2009, Redman et al., 2007 and McGrath et.al., 2015 for details.

$$\begin{aligned} logHC5 = E\{m\}logK_{OW} + E\{logC_\ell^*\} + \Delta c_\ell - E\{logACR\} \\ - k_Z \sqrt{V\{m\}logK_{OW}^2 + V\{logC_\ell^*\} + V\{logACR\}} \end{aligned} \qquad (22)$$

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 Kow^2), C_L^* and ACR. 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 protection (de Vries et al., 2010).

The HC5 makes use of the membrane-water partition coefficient (Kmw), which is an empirical bioavailability adjustment for high log Kow structures (>6) consistent with the

development and validation of the PETROTOX model (HydroQual, 2009; Redman et al 2012).

$$\log(K_{MW}) = \begin{bmatrix} 0.037 * \log(K_{OW}) + 5.78 & ; \ for \ \log(K_{OW}) \geq 6 \\ \log K_{OW} & ; \ for \ \log(K_{OW}) < 6 \end{bmatrix} \quad 0 \qquad (23)$$

PNECs for the soil and sediment compartments are calculated using Equilibrium Partitioning Theory and the estimated organic-carbon partition coefficient (Koc). The K_{OC} is calculated according to the algorithms used in EUSES based on log Kow. The EPIWIN-derived log Kow for each library structure is used as input to this equation to maintain consistency with the fate model in EUSES.

Soil and sediment compartments have units of mg/kg wet weight in PETRORISK to be consistent with the derivation of the FF so a conversion is required. The soil and sediment organic carbon content can be entered in to cells D59:61 in the 'product lifecycle information' worksheet (Section 3.3). The partition coefficient (Kd) for calculating soil and sediment PNEC is converted to a wet weight basis and is corrected for the pore water volume and densities (2500 L/kg for solids, 1000 L/kg for water) to be consistent with the fate model in EUSES.

$$K_{D,i} = \frac{(1 - f_{dry}) * 1000 + (f_{dry} f_{oc} HC) * 2500}{(1 - f_{dry}) * 1000 + f_{dry} * 2500} \qquad (24)$$

The direct risks of air PECs on terrestrial plants is not assessed since PNECs are not available. PECs calculated in milk, meat, root and leaf are used to estimate human intake, which is evaluated relative to the DNEL (section 3.16). Using the water compartment for illustration at the local scale for a specific GES, the RCR is calculated as:

$$RCR_{local,water,GES,i} = PEC_{local,water,GES,i} / PNEC_{water,i} \qquad (25)$$

Overall risks are estimated as the sum of each library structure RCR for a given compartment. Overall RCRs at the local scale are reported for each GES, whereas regional RCRs are reported as the sum across all GESs. Local RCRs are based on local PECs, which include contributions from regional (or background) PECs.

Risk to humans (RCR-H) via the environment can be estimated given a user-defined DNEL as discussed in Section 3.16. DNELs are normally established based on toxicity test data for the neat substance. However, in some circumstances, for example where there is a

single constituent that would drive this aspect of the risk characterization, that a constituent specific DNEL is used.

$$RCR - H_{\text{regional,water}} = HI_{regional,water} / DNEL \qquad (26)$$

Human RCRs are summed across library structures for each emission scenario (air, water, soil) for each GES at the local scale to calculate overall exposure. At the regional scale, human intakes are determined by further summing across GESs.

4.7 SCALING FOR SITE-SPECIFIC PRODUCTION

The site specific production worksheet may be used to scale default outputs to specific production sites with site-specific data, see Section 3.4. Since all PECs, HIs, and RCRs scale linearly with tonnage, generic results that are calculated with PETRORISK can be scaled linearly using site-specific operating parameters: production tonnage, crude throughput, DF and receiving water type (Marine or Freshwater), effluent TPH, and WWTP scenario (onsite or offsite).

The PECs (and resulting RCRs) are grouped into the following main categories: endpoints affected most by air emissions and endpoints affected most by water/waste water emissions. Effluent PECs are addressed separately. Each category uses different scaling factors (SF) based as explained below.

Compartments that are affected primarily by air emissions are: PEC_{air}, $PEC_{naturalsoil}$, $PEC_{groundwater}$, PEC_{leaf}, PEC_{root}, PEC_{meat}, PEC_{milk}, $PEC_{worm.oral}$, plus the HI_{air}, and HI_{soil} and their corresponding RCRs (when applicable).

Compartments that are affected primarily by water/wastewater emissions are: $PEC_{freshwater}$, $PEC_{freshwater\ sediment}$, PEC_{marine}, $PEC_{marine\ sediment}$, $PEC_{drinkingwater}$, PEC_{fish}, $PEC_{fish.oral}$, $PEC_{predator.oral}$, and their corresponding RCRs and the HI_{water}.

The scaling factor used to address air-related compartments (SF_{air}) is based on the ratio of the substance-specific site tonnage (t/a) relative to the manufacturing GES default tonnage.

$$SF_{\text{Air}} = Tonnage_{site} / Tonnage_{GES} \qquad (27)$$

Site-specific PECs and RCRs are calculated as the product of the scaling factor and the initial, default PEC. For example, the SF_{air} is used to calculate the $PEC_{site,air}$ (or related compartments) using the PETRORISK-modelled PEC

$$PEC_{site,air} = SF_{air} \bullet PEC_{GES,air} \qquad (28)$$

The human intake via inhalation ($HI_{inhalation}$, $\mu g/g/d$) for the site is calculated directly using the scaled air concentration ($PEC_{site,air}$, mg/m^3), the daily volume of air respired ($V_{respired}$) by typical human adults (e.g., 20 $m^3 d^{-1}$) and the body weight (W) of a typical human adult (70 kg).

$$HI_{site,air} = PEC_{site,air} * V_{respired}/W \tag{29}$$

The $RCR_{inhalation}$ for the site is calculated using the scaled $HI_{site,air}$ and the $DNEL_{inhalation}$.

$$RCR_{site,air} = HI_{site,air} / DNEL_{inhalation} \tag{30}$$

A scaling factor is derived to address water-related compartments that is based on site- and substance-specific parameters that will be applied to water emissions ($SF_{site,TPH}$). This scaling factor ($SF_{site,TPH}$) is the ratio of the annually average site TPH concentration in effluent (i.e., $PEC_{effluent,site}$) to the PETRORISK-predicted TPH (i.e., $PEC_{effluent,GES}$) using the default emission factors from the SpERC for the Manufacturing GES.

$$SF_{site,TPH} = TPH_{site} / TPH_{GES} \tag{31}$$

Next the TPH_{site} is scaled by the fraction of the substance production ($Tonnage_{Sub}$) relative to the total crude throughput ($Tonnage_{Crude}$) to give a effluent scaling factor.

$$SF_{effluent} = Tonnage_{Sub}/Tonnage_{Crude} \tag{32}$$

These parameters are combined to scale the default TPH in the effluent ($PEC_{effluent,GES}$) to calculate the site-specific TPH ($PEC_{effluent,site}$).

$$PEC_{effluent,site} = PEC_{effluent,GES} * SF_{effluent} \tag{33}$$

The $SF_{effluent}$ is adjusted using the ratio of the default DF to the site-specific DF in order to calculate a scaling factor that can be used to calculate water-related PECs. Site-specific DF can vary widely from default values. Based on the TGD the DF is capped at 1000 to provide conservative assessments. Default fresh water ('riverine') receiving waters have default DF = 10 and marine waters ('estuarine') have default DF = 100.

$$SF_{water} = SF_{effluent} * DF_{GES}/DF_{site} \tag{34}$$

The estimated concentration of concentration of TPH in the site's receiving water ($PEC_{water,site}$) is calculated as follows

$$PEC_{water,site} = PEC_{water,GES} * SF_{water} \qquad (35)$$

The RCRs are simply scaled as the ratio of the scaled to modelled PECs, which incorporate the scaling factors discussed in this section. The HI-RCRs are calculated by dividing the scaled HI by the DNEL.

4.8 ADDITIONAL CALCULATIONS AND SCALING APPLIED TO LOCALCSR AND REGIONALCSR

The PETRORISK results are formatted, and in some cases scaled for consistency between regional and local scales in the 'RegionalCSR' and 'LocalCSR' for reporting purposes. The CSR worksheets are intended to be attached to the Chemical Safety Report that is required for REACH registrations. This is intended to streamline the reporting and review of risk assessments by presenting the required data in two convenient spreadsheets. This section also discusses some special considerations and calculations that are presented only in the 'LocalCSR' worksheet.

RegionalCSR

The 'RegionalCSR' worksheet is simply a reformatted version of the 'Regional output-expr&risk' worksheet (section 3.10). This includes PECs, HIs and RCRs for all required compartments (Table 1) and the emission characteristics for the entire use map for the substance under consideration. Direct releases to the aquatic environment after WWTP are calculated as follows

$$\text{Aquatic releases (after WWTP, kg/d)} = \text{Volume}_{reg} \text{ (T/a)} * 1000/365 * \text{EF}_{water}$$
$$* \; [F_{connect\,WWTP\,.} + (1 - F_{connect\,WWTP}) * (1 - F_{direct\,regional\,marine})] * RE \qquad (36)$$

where the degree of connection for wastewater emissions to treatment facilities, $F_{connect\,WWTP}$, is 0.8; direct emissions of wastewater to marine environments, $F_{direct\,regional\,marine}$, is 0.01; the emission factor (EF_{water}) for releases to wastewater are from the SpERC and RE is the substance-specific SimpleTreat-estimated removal efficiency with fractional units. The terms in the brackets denote the fractional sum of bulk removal efficiencies for each assigned structure – reported in 'product composition' worksheet.

Releases to air either through direct volatilization or through releases via WWTP are calculated as follows

$$\text{Air releases (direct + WWTP, kg/d)} = [(\text{Volume}_{reg} \text{ (T/a)} * 1000/365 *$$
$$[EF_{air} + EF_{water} * F_{connect\,WWTP} * F_{WWTP\,air\,release.})] \qquad (37)$$

where $F_{WWTP.air.release}$ is the substance-specific SimpleTreat-estimated removal of a substance through WWTP via volatilization. The terms in the brackets denote the fractional sum of

removal efficiencies via air for each assigned structure – reported in 'product composition' worksheet.

Direct emissions to soil are calculated using the regional emission and EF_{soil} and are also reported in the 'speciated emissions' worksheets.

LocalCSR

The LocalCSR worksheet contains four classes of information:

1. Emission related parameters
2. Environmental PECs used to assess ecological risks
3. PECs that determine human exposure via direct and indirect pathways
4. RCRs for the environment and humans

<u>Emission Characterization</u>

The 'on-site removal efficiency - Air (%)' is taken directly from the SpERCs worksheet for a given GES. Based on the calculated RCRs obtained using the tool, The 'Risk driving compartment' is the selected. This corresponds to the compartment associated with the highest RCR.

The tool then determines if waste water treatment is required (RCR with no risk management measures (noRMM))

$$RCR_{noRMMs} = RCR_{Initial}/(1 – SimpleTreat\ Removal\ Efficiency) \tag{38}$$

If $RCR_{noRMMs} < 1$, then **NO SimpleTreat RE required**
If $RCR_{noRMMs} \geq 1$, then **YES SimpleTreat RE required**

The Required Removal Efficiency ($RRE_{overall}$) for Wastewater is then calculated:
$$RRE_{overall} = 1 – 1/RCR_{noRMMs} \tag{39}$$
Note: If $RCR_{noRMMs} < 1$; $RRE_{overall} = 0$

Assuming that effluent is discharged to an off-site unacclimated, domestic sewage treatment plant that exhibits a removal efficiency equal to SimpleTreat predictions, the additional Onsite Removal Efficiency that is required is determined by:

$$RE_{onsite} = 1 – [(1 – RRE_{overall}) / (1- SimpleTreat\ RE)] \tag{40}$$

If this term is zero, the implication is that the default assumption of off-site treatment via a domestic sewage treatment is adequate for safe use.

Water Emissions at the local scale without treatment is calculated by:

Aquatic releases (before WWTP, kg/d) = $Volume_{local}$ (T/a) * 1000/365 * EF_{water}

$$* \; [F_{\text{connect WWTP .}} + (1 - F_{\text{connect WWTP}}) * (1 - F_{\text{direct regional marine}}) \;] \qquad (41)$$

Water emissions at the local scale with on-site and off-site treatment based on the overall required removal efficiency (RRE) is

$$\text{Aquatic releases (after WWTP, kg/d)} = \text{Volume}_{\text{local}} \, (T/a) * 1000/365 * EF_{\text{water}}$$
$$* \; [F_{\text{connect WWTP .}} + (1 - F_{\text{connect WWTP}}) * (1 - F_{\text{direct regional marine}})] * RRE \qquad (42)$$

Similarly, local Air emissions are calculated by

$$\text{Air releases (direct + WWTP, kg/d)} = [(\text{Volume}_{\text{local}} \, (T/a) * 1000/365 *$$
$$[EF_{\text{air}} + EF_{\text{water}} * F_{\text{connect WWTP}} * F_{\text{WWTP air release.}})] \qquad (43)$$

Adjustment of PECs and RCRs

The derivation of the fate factors FFs used in scaling emissions to PECs assumes a factor of 10 difference between regional and local emissions. However, in practice the ratio of regional to local emissions in a substance evaluation can be quite different (Section 3.13, 4.4). This results in scenarios where the FF-calculated PEC_{local} is less than the PEC_{regional}. This is inconsistent with the derivation of the PEC_{local} in EUSES, which is intended to include background regional concentrations, meaning PEC_{local} should never be less than the PEC_{regional} since

$$PEC_{\text{local}} = C_{\text{local}} + PEC_{\text{regional}} \qquad (44)$$

For this reason local-scale calculations are considered intermediate results pending further comparison to the regional PECs. All PEC_{local} are compared to PEC_{regional} for compartments that are in common between the two scales (Table 1). If the PEC_{local} is less than the PEC_{regional} then the two are added together as the reported PEC_{local}^{*}, otherwise the initial PEC_{local} is reported.

$$\text{If } PEC_{\text{local}} < PEC_{\text{regional}} \text{ then, } PEC_{\text{local}}^{*} = PEC_{\text{local}} + PEC_{\text{regional}} \qquad (45)$$
$$\text{Else. } PEC_{\text{local}}^{*} = PEC_{\text{local}}$$

The local concentration (C_{local}) is calculated as either the difference between PEC_{local}^{*} and PEC_{regional} or as the PEC_{local} depending on whether or not the initial PEC_{local} is less than the PEC_{regional}.

$$\text{If } PEC_{\text{local}} < PEC_{\text{regional}} \text{ then, } C_{\text{local}} = PEC_{\text{local}}$$

Else, Clocal = PEC_{local}^* - $PEC_{regional}$ (46)

In a similar fashion the RCRs are adjusted for consistency. The $RCR_{regional}$ is added to the RCR_{local} only if the RCR_{local} is less than the $RCR_{regional}$.to calculate the reported RCR_{local}^*.

If RCR_{local} < $RCR_{regional}$ then, $RCR_{local}^* = RCR_{local} + RCR_{regional}$ (47)
Else. $RCR_{local}^* = RCR_{local}$

Similar adjustments are applied to HI and HI-RCR analogous to Eqn 40 and 41, respectively. This additional adjustment provides additional conservatism (i.e., higher PECs and RCRs) in substance evaluations.

Most PECs can be scaled according to Eq. 40, however, secondary poisoning compartments require special consideration. For example, there are no regional-scale PECs to support adjustments so related environmental compartments are used (e.g., $PEC_{freshwater}$ for $PEC_{fish.oral}$, and $PEC_{agric.soil}$ for $PEC_{worm.oral}$). The reported $PEC_{local.oral}^*$ is scaled by the ratio of the C_{local} to the PEC_{local}^* for fresh water (for fish.oral) or agricultural soil (for worm.oral), see also Eq. 40 and 41.

$$PEC_{local.oral}^* = PEC_{local.oral} * (PEC_{local}^* / C_{local}) \qquad (48)$$

Since the derivation of $PEC_{marine.oral}$ already includes regional contributions, Eq. 18. no additional scaling is applied to the reported $PEC_{marine.oral}$.

SECTION 4

EUSES VS PETRORISK COMPARISON

A direct comparison was made between PETRORISK and EUSES for two benchmark hydrocarbons, toluene and benzo(ghi)perylene These compounds were selected to represent two ends of the spectrum of physical-chemical properties (e.g., log Kow, VP) in the "Concawe library". This information is presented in Appendix 1. The major conclusion is that the results from PETRORISK and EUSES agree favourably (well within a factor of 2 typically). Most discrepancies are due to the differences in the emission assumptions in EUSES that were used to calculate the FF relative to the reported emission and use volumes in PETRORISK. For example, the FFs derived from EUSES assume a 100:10:1 allocation between continental, regional and local emissions, respectively. In practice, it is observed that the split between regional and local emissions can vary substantially more than the factor of 10 used in the FF derivation. This is accounted for in PETRORISK with the additional scaling calculations in the LocalCSR worksheet (Section 4.8).

SECTION 5

SUMMARY

PETRORISK provides a state of the science tool for performing environmental assessments for complex petroleum substance in order to meet REACH registration requirements. Selected worksheets are designed to be appended to registration dossiers to provide a consistent, concise documentation of the tool inputs and outputs used in the risk evaluation.

SECTION 6

ACKNOWLEDGEMENTS

SECTION 7

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

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SECTION 8

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Appendix 1. Comparison of PETRORISK v3.05 vs EUSESv123 HB for selected individual structures: Toluene and Benzo(a)pyrene

As noted, FFs and IFs in PETRORISK were compiled using EUTGDsheet v.123 hb. Consequently, predictions from the two models for single compounds (within the domain of substance applicability) should be similar if not equivalent under the same conditions of use. To evaluate differences that may exist over a range of physical-chemical properties, assessments were performed on toluene (relatively low Kow, high vapour pressure, high solubility compound) and benzo(ghi)perylene (relatively high Kow, low vapour pressure, low solubility compound); both of which are appropriate for modelling within PETRORISK.

The models were compared using the suite of local scale PECs reported in PETRORISK. The local scale calculations are the most transparent within EUTGDsheet and will typically be the greatest driver of risk. Five hypothetical scenarios (Table 1) were examined to highlight model differences resulting from variable system operating conditions, including; regional and local fractions, days emitting to the environment, and fractions released to the environment. Model comparison results, reported in Tables 2 and 3, are expressed as the ratio of predicted PECs generated using EUTGDsheet v.123 hb to those generated using PETRORISK v.3.05. Table 1 is a summary of the operational conditions used for each hypothetical scenario.

Table 1. Hypothetical scenarios defined on the basis of operational conditions used to compare PETRORISK v.3.05 and EUTGDsheet v.123 hb.

		Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
Fraction Regional		0.0909	0.0909	0.0909	**0.01**	0.01
Fraction Local		0.1	0.1	0.1	**0.0005**	0.0005
Days Emitting		365	365	365	365	**20**
Dilution Factors	FW	10	10	10	10	10
	MW	100	100	100	100	100
Emission Factors (%)	Air	0	**0.01**	**0.01**	0.01	0.01
	WW	**0.01**	0	**0.01**	0.01	0.01
	Soil	0	0	**0.01**	0.01	0.01

FW – fresh water; MW – marine water; WW - wastewater

Scenarios 1-3 reflect the fraction regional, fraction local, days emitting and dilution factors inputs that were used by van de Meent (2008) to derive the library of FFs and IFs. As shown in Tables 2 and 3, model differences are minimal for Scenarios 1 and 2, with the exception of the local marine environment for Scenario 2. The explanation for this difference is $PEC_{reg.seawater}$, which subsequently drives model differences for $PEC_{local.marine\ sediment}$ and $PEC_{oral.fishpredator,marine}$. There are a number of slight model differences for Scenario 3 for

toluene that are a consequence of an over-prediction of $PEC_{local.air}$ by PETRORISK. Within the EUTGDsheet, local air concentration is calculated using the maximum loading to air either from direct emissions or emissions coming from waste water treatment plant (SimpleTreat-Local). Within PETRORISK, when emission factors are greater than 0 for both air and waste water, these two loadings are summed to calculate the local air concentration. Because $PEC_{local.leaf}$, $PEC_{local.meat}$ and $PEC_{local.milk}$ are directly or partially driven by air concentration, these endpoints will also be over-estimated by PETRORISK. This in turn leads to a slight over-prediction of $DOSE_{local.human\,oral}$. This inconsistency is not observed for benzo(ghi)perylene (Table 3) because it is a sparingly volatile compound and thus indirect emissions from the waste water treatment plant will be insignificant relative to direct air emissions.

Table 2. Ratio of predicted PECs generated using EUTGDsheet v.123 hb to those generated using PETRORISK v.3.05, for toluene for each scenario defined in Table 1.

Endpoint	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
Effluent	1.000	N/A	1.000	1.000	1.000
Freshwater	1.000	1.000	1.000	1.167	1.008
Freshwater Sediment	1.000	1.000	1.000	1.167	1.008
Marine Water	1.001	*20.361*	1.001	1.126	1.007
Marine Sediment	1.001	*20.361*	1.001	1.126	1.007
Natural Soil	1.000	1.000	1.000	1.001	0.999
Air	1.000	1.000	0.695	1.230	1.230
Sludge	1.000	N/A	1.000	1.000	1.000
Groundwater	1.000	1.000	1.000	1.003	0.994
Fish	1.000	1.000	1.000	1.167	1.167
Leaf	1.000	1.000	0.695	1.230	1.240
Root	1.000	1.000	1.000	1.003	0.994
Meat	1.000	1.000	0.871	1.193	*0.114*
Milk	1.000	1.000	0.871	1.193	*0.114*
Drinking Water	1.000	1.000	0.999	1.166	*0.148*
Freshwater Fish	1.000	1.000	1.000	1.333	1.333
Marine Top Predator	1.005	2.036	1.005	2.150	2.257
Worm	1.000	1.000	1.000	1.024	0.995
Human Oral	1.000	1.000	0.864	1.191	*0.100*

In scenario 4 there is a deviation in fraction regional and fraction local from that used to derive the FFs and IFs. It is evident from Tables 2 and 3 that while this results in model differences for all environmental endpoints, these differences are minor; with the possible exception of $PEC_{oral.fishpredator,marine}$ for benzo(ghi)perylene. Differences are resultant of the fact that scaling of fraction regional does not translate linearly to the environmental concentrations in EUTGDsheet, which results in a slight, but consistent under-prediction by PETRORISK. Also, as for Scenario 3, PETRORISK will over-predict air concentrations for

more volatile compounds. Furthermore, $PEC_{oral.fishpredator.marine}$ reflects the largest difference (for benzo(ghi)perylene) because of the algorithm used for its calculation.

$$PEC_{oral.fishpredator,marine} = [0.1\ (PEC_{local.seawater}) + 0.9\ (PEC_{reg.seawater})]\ BCF \times BMF1 \times BMF2$$

The 90/10 split of regional to local emissions further complicates a simple scaling approach for this endpoint.

Table 3. Ratio of predicted PECs generated using EUTGDsheet v.123 hb to those generated using PETRORISK v.3.05, for benzo(ghi)perylene for each scenario defined in Table 1.

Endpoint	Scenario 1	Scenario 2	Scenario 3	Scenario 4	Scenario 5
Effluent	1.000	N/A	1.000	1.000	1.000
Fresh water	1.000	1.000	1.000	1.495	1.025
Fresh water Sediment	1.000	1.000	1.000	1.495	1.025
Marine Water	1.002	***10.086***	1.002	1.633	1.034
Marine Sediment	1.002	***10.086***	1.002	1.633	1.034
Natural Soil	1.000	1.000	1.000	1.015	0.996
Air	1.000	1.000	1.000	1.057	1.057
Sludge	1.000	N/A	1.000	1.000	1.000
Ground water	1.000	1.000	1.000	1.017	0.996
Fish	1.000	1.000	1.000	1.495	1.495
Leaf	1.000	1.000	1.000	1.057	1.146
Root	1.000	1.000	1.000	1.017	0.996
Meat	1.000	1.000	1.000	1.058	***0.156***
Milk	1.000	1.000	1.000	1.058	***0.156***
Drinking Water	1.000	1.000	0.996	1.489	0.776
Fresh water Fish	1.000	1.000	1.000	1.989	1.989
Marine Top Predator	1.019	1.009	1.020	***5.098***	***7.143***
Worm	1.000	1.000	1.000	1.055	0.998
Human Oral	1.000	1.000	1.000	1.155	0.706

Finally, scenario 5 highlights the model deviation resulting from differences in days emitted. While the same model anomalies exist in this scenario as in scenario 4, it is also the case that PETRORISK over-predicts PECs for meat, milk, and drinking water, which in-turn is reflected in $DOSE_{local.human\ oral}$. There are several reasons for this observation. Firstly, in EUTGDsheet, $PEC_{local.drinking\ water}$ (similar to $PEC_{local.air}$) is a function of the maximum between $PEC_{local.water\ annual}$ and $PEC_{local.groundwater}$. This will result in model differences (over-prediction by PETRORISK). This is further complicated by the fact that scaling for days emitted is only applicable for certain environment compartments and endpoints. In the above case, scaling is required for $PEC_{local.groundwater}$ but not for $PEC_{local.water\ annual}$; hence, a choice has to be made whether to scale $PEC_{local.drinking\ water}$ or not. It was decided to scale this endpoint in PETRORISK by days emitted in order to maintain conservatism. The same approach is required for $PEC_{local.meat}$ and $PEC_{local.milk}$ because each of these endpoints is

affected by a combination of sources – including air, drinking water, and grass, which is influenced by soil, air and groundwater – some of which should and should not be scaled by days emitted. Again, the choice was made to scale these PETRORISK endpoints by days emitted in order to maintain conservatism.

In summary, PETRORISK v.3.05 and EUTGDsheet v.123 hb compare well for individual compounds. While there are differences, especially as the operational conditions deviate from those used to derive FFs and IFs, good agreement is observed for the two benchmark hydrocarbons examined. Furthermore, for $DOSE_{local.human\ oral}$ and its associated endpoints, PETRORISK errs on the side of conservatism. The one exception may be for $PEC_{oral.fishpredator,marine}$, however, the under-prediction using PETRORISK is less than an order of the magnitude for higher log Kow compounds. Moreover, the bio-magnification factors (BMFs) used in EUTGDsheet for this endpoint are likely conservative; thus, this under-prediction by PETRORISK is considered acceptable.