# PETRORISK - an Excel based tool for conducting environmental risk assessment of petroleum substances

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***This poster is number 4 of a series of 5 posters on the risk assessment of petroleum substances. See also posters TU 282, 283, 284 and 286.***

## Abstract

PETRORISK is a modeling framework used to evaluate the environmental risk of petroleum substances under typical use conditions. Petroleum substances are complex substances comprised of hundreds to thousands of individual constituents. The physicochemical, fate and effect properties of the individual constituents within a petroleum substance can vary over several orders of magnitude, which complicate the risk assessment.

PETRORISK combines the risk assessment strategies used on single chemicals with the hydrocarbon block approach for modeling complex substances:

- Blocks are usually defined by available analytical chemistry, which characterizes substances in terms of mass fractions for discrete blocks based on chemical class and physicochemical properties (e.g., carbon number or boiling point).
- Emissions and predicted exposure concentrations (PEC) are modeled using mass-weighted representative constituents.
- Overall risk for environmental compartments at the regional and local level is evaluated by comparing the PECs for individual representative constituents to their predicted-no effect concentrations (PNEC) derived with the Target Lipid Model.

## Hydrocarbon blocks

PETRORISK uses three different compositional resolution schemes depending on the analytical data available:

- Low resolution - Aliphatic/Aromatic hydrocarbons vs. Equivalent Boiling point
- Solvents resolution - Aliphatic/Aromatic hydrocarbons vs. Carbon Number
- High resolution – 16 hydrocarbon classes vs. 3-carbon blocks
    - n- and isoalkanes
    - n-cyclopentanes and n-cyclohexanes
    - mono- , di- and polynaphthenics
    - n- and isoolefins
    - mono-, di- and polyaromatics
    - naphthenic mono- and diaromatics
    - sulfur containing aliphatics and aromatics

For petroleum substances the high resolution composition option is used, filled in with data obtained from GCxGC characterization (see poster TU 283)

## Specific Environmental Release Categories (spERCs)

Operating conditions and release factors used to calculate emissions to the environment are essential inputs into the PETRORISK tool. For all relevant petroleum substance uses, specific Environmental Release Categories (spERCs) have been standardized in order to include process and use knowledge available in the solvents and petroleum industry.

Main features of the spERCs are:

- spERCs improve the emission estimates included in the standard Environmental Release Categories (ERCs) by applying industry knowledge to describe emissions associated to main industrial processes
- The main component of a spERC are emission factors to air, water and soil
    - Emission factors for air vary with vapor pressure
    - Emission factors to water vary with water solubility
- spERCs include site operating conditions: tonnage used per day, emission days per year
- spERCs include efficiency of the risk management measures for the air compartment
- Justification factsheets for the spERCs were developed by the European Solvents Industry group, see http://www.esig.org/en/regulatory-information/reach/ges-library/ges-spercs-2

spERC example: **Use of coatings**

| Area of Application (Sector of Use) | max (typical) site tonnage /day | Number of emission days | max (typical) site tonnage /yr | release to air before RMM % | efficiency of air emission controls (%) | release to air % | release to wastewater (%) | release to soil (%) | Notes |
|---|---|---|---|---|---|---|---|---|---|
| Industrial (SU3) | 50 | 300 | 15000 | 98.0 | 90 | 9.8 | f(WS)<br>WS < 1mg/L = 0.002<br>WS 1-10 mg/l = 0.007<br>WS 10-100 mg/L = 0.07<br>WS 100-1000 mg/L = 0.7<br>WS > 1000 mg/l = 2 | 0 | Releases to air before RMM based OECD Coatings ESD July 2009; Assumed air RMM efficiency selected based on typical values in CEFIC RMM library for technologies used at medium sites; Emissions factors to WW conservatively calculated based on WW volume gene |
| Professional (SU22) | EU Tonnage (bld) for use x0.1 x 0.0005 | 365 | | 98.0 | N/A | 98.0 | 1.0 | 1.0 | Based on the OECD Coatings ESD (July 2009) solvent losses to air are 98-100%; To conserve mass, emissions to WW and soil are conservatively assumed to each equal 1%. Note many professional users must comply with the EU solvents directive which require R |
| Consumer (SU21) | EU Tonnage (bld) for use x0.1 x 0.0005 | 365 | | 98.5 | N/A | 98.5 | 1.0 | 0.5 | Based on the OECD Coatings ESD (July 2009) solvent losses to air and WW are 93% and 1%, respectively; To conserve mass, emissions to soil are conservatively assumed to equal 6%. |

## Estimating emissions to the environment

Emissions to the environment in PETRORISK are estimated using four different elements:

- The composition in the hydrocarbon blocks mapped to the CONCAWE library (see poster TU 283)
- Emission factors and operating conditions contained in the ESIG spERCs (hard-coded)
- Fate Factors and Intake Fractions calculated using EUSES (hard-coded)
- Use/tonnage information for all relevant uses of petroleum substances

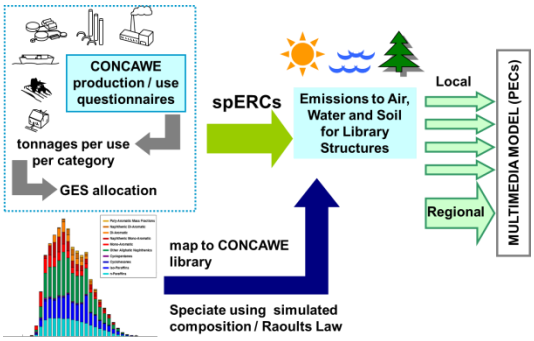
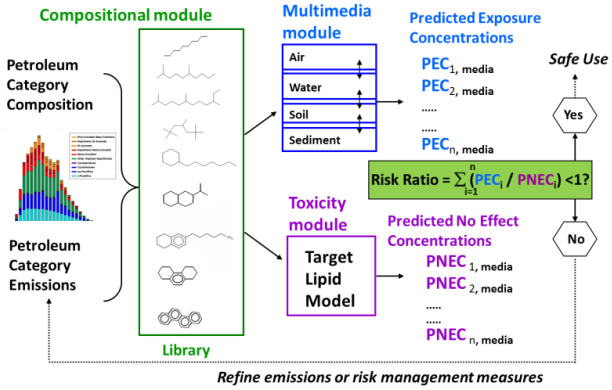



Figure 2. Emission calculation scheme used for all representative hydrocarbons

## Predicting environmental risks

The PETRORISK tool consists of three different modules shown in the scheme below:

1. The compositional module (see "Hydrocarbon blocks")
2. The multimedia module (see "Estimating emissions") to estimate PECs
3. The toxicity module (Target Lipid Model) to estimate PNECs




The toxicity predictions for each representative hydrocarbon are derived using the target lipid model (see poster TU 284). As hydrocarbons cause toxicity via the narcotic mode of action additivity can be assumed, and the sum of all Risk Characterization Ratios (RCRs) for the relevant representative hydrocarbons will be the RCR for the product for that specific use and environmental compartment.

The PETRORISK tool calculates both the regional and local risk assessment for all known uses of a substance. The results per Generic Exposure Scenario (GES, generic use) are included in he output worksheet. The tool also calculates indirect exposure to humans via the environment using Derived No Effect Levels (DNELs).

## Risk assessment for manufacturing sites

The PETRORISK tool performs site specific assessments using data for the 119 CONCAWE refineries in Europe. The site specific assessment is performed in two steps:

- A generic assessment for a standardized refinery is performed using the operating conditions included in the Manufacturing spERC
- The "generic" risk assessment output (PECs and RCRs) is scaled to the operating conditions of the specific EU refineries, which are:
    - Total Refinery Production & Feedstock throughput
    - TPH in effluent
    - WWTP flow, Receiving water type (marine or riverine)
    - Reported Dilution factor
    - Presence of a final Wastewater Treatment On-Site

## PETRORISK validation

In order to validate PETRORISK predictions, a case study using kerosene was developed (published in Redman et. al., 2014).

Model input:

- GCxGC compositional information,
- EU tonnage,
- spERC values for relevant uses

**Results:**

- Emissions and PECs for manufacturing life cycle stage much larger than emissions of wide dispersive uses (100 fold), as expected
- Predicted Environmental Concentrations (PECs) for air are conservative compared to monitoring data for kerosene components (PEC=460 µg/m$^3$ compared to 5 µg/m$^3$)
- Regional emissions for industrial uses 10 to 1000 fold lower than local emissions
- For wide dispersive uses regional and local emissions more similar
- For distribution and fuel uses RCR values < 1
- For manufacturing, risk assessment indicated effluent RCR > 1. Emission estimates were refined and additional risk management measures (e.g. WWTP efficiency) were identified

## Conclusion

The PETRORISK tool is the successful practical implementation of the hydrocarbon block risk assessment methodology for petroleum substances.

- It allows to calculate all risk assessment parameters required by the REACH regulation
- It uses standardized information – included in the spERCs – to calculate emissions for the main uses of petroleum substances
- It uses representative components to derive PECs and PNECs, which are added to calculate RCRs for each use of the substance
- The PETRORISK tool generates output spreadsheets showing:
    - The product library used in the risk assessment
    - The risk assessment output (regional and local)
    - Tailored risk assessments for the 119 CONCAWE manufacturing sites in Europe
- Risk assessment values calculates using the PETRORISK tool has been validated using kerosene as an example

REFERENCES

Redman, A., Parkerton, TF, Comber, MHI, Leon Paumen, M, Eadsforth, CV, Dmytrasz, B, King, D, Warren, CS, den Haan, K, Djemel, N. PETRORISK, a risk assessment framework for petroleum substances. IEAM, DOI 10.1002/ieam.1536.