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ENVIRONMENTAL SCIENCE FOR THE EUROPEAN REFINING INDUSTRY

Evaluating environmental risks associated to petroleum products

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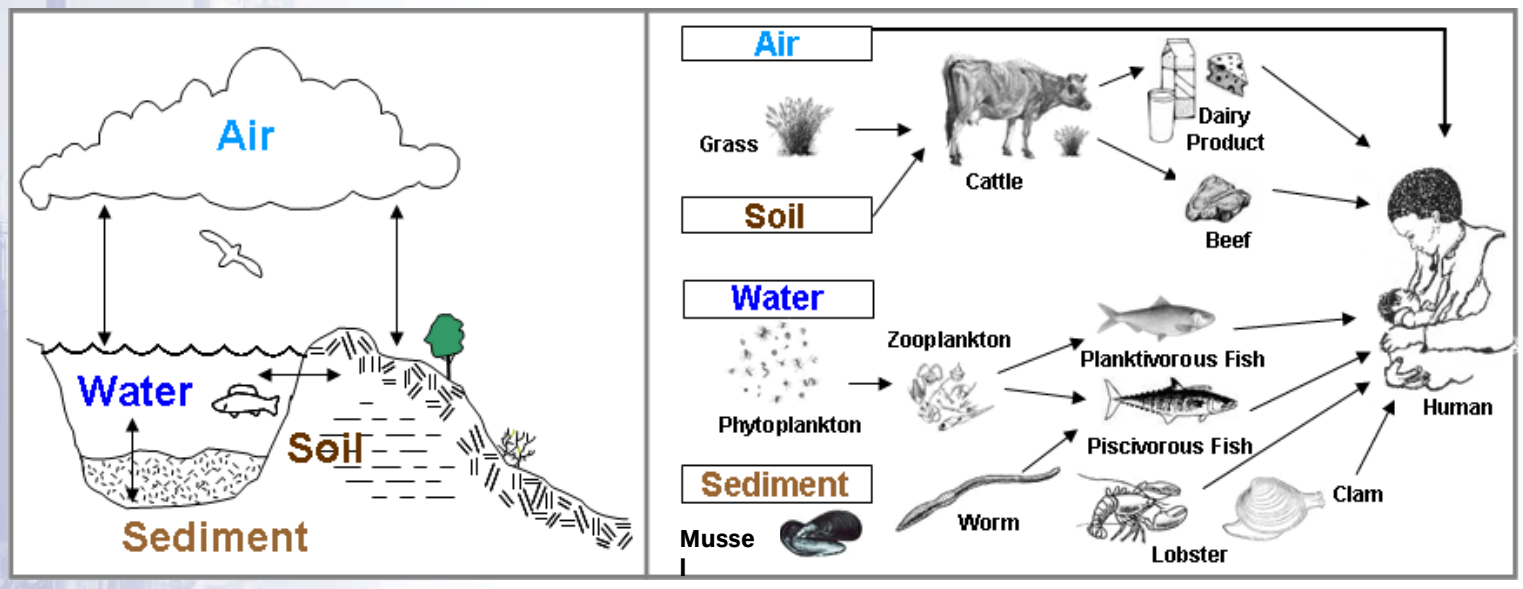
Outline

- REACH exposure scenarios - GES
- Petroleum substances - UVCBs
- Modeling risk of petroleum products
  - Estimating emissions and exposure
    - spERCs
  - Estimating hazard
    - PETROTOX
  - Estimating risk
    - PETRORISK
- Latest developments

REACH exposure scenarios

SUBSTANCE

Exposure pathways



Environmental distribution

EXPOSURE

HAZARD

RISK

REACH environmental exposure scenarios

- Exposure Scenarios developed for generic uses of petroleum products
  - Only for substances hazardous to the environment
  - Embedded in the Generic Exposure Scenarios (GESs)
- GESs were developed to cover worker activities associated with the use of petroleum substances
- GESs for the environment contain specific Environmental Release categories (spERCs)
- Exposure and risk of uses of petroleum substances in the environment is quantified using models

REACH environmental ESs

- Hydrocarbon block methodology (HBM)
  - Originally proposed by CONCAWE
    - Complex substance is divided into “pseudo-components”, constituents with known physico-chemical, fate and hazard properties, stored in CONCAWE library
    - PECs and PNECs for individual constituents are determined
    - Overall substance risk is assessed by summing PEC/PNEC ratios across constituents
    - Accepted by regulators, incorporated in REACH guidance
- HBM implementation: **PETRORISK tool**
  - Based on EUSES
  - Specific features to make hydrocarbon UVCB risk assessment possible, e.g. composition matrix

PETRORISK development by Concawe

Different steps in PETRORISK development:

- **Exposure**: development of new / updated QSPRs
  - Prediction of K_{OA}
  - Prediction of Biodegradation ½ Lives
  - Prediction of Bioconcentration Factor in Fish
- Development of library containing phys/chem, partitioning and degradation properties for over 1500 “representative” hydrocarbons
  - Based on Quann et al. 1998
- **Hazard**: development of PETROTOX model

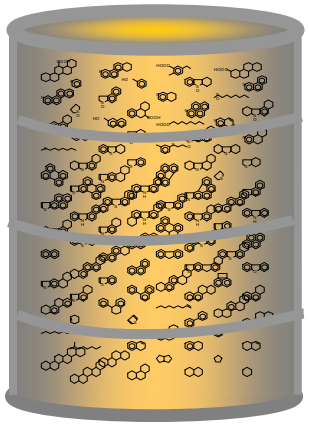
Outreach:

- Several presentation and workshops with scientists and regulators
  - Poster series at SETAC EU in 2006
  - Workshop at ECHA in 2010
  - Poster series at SETAC EU in 2014

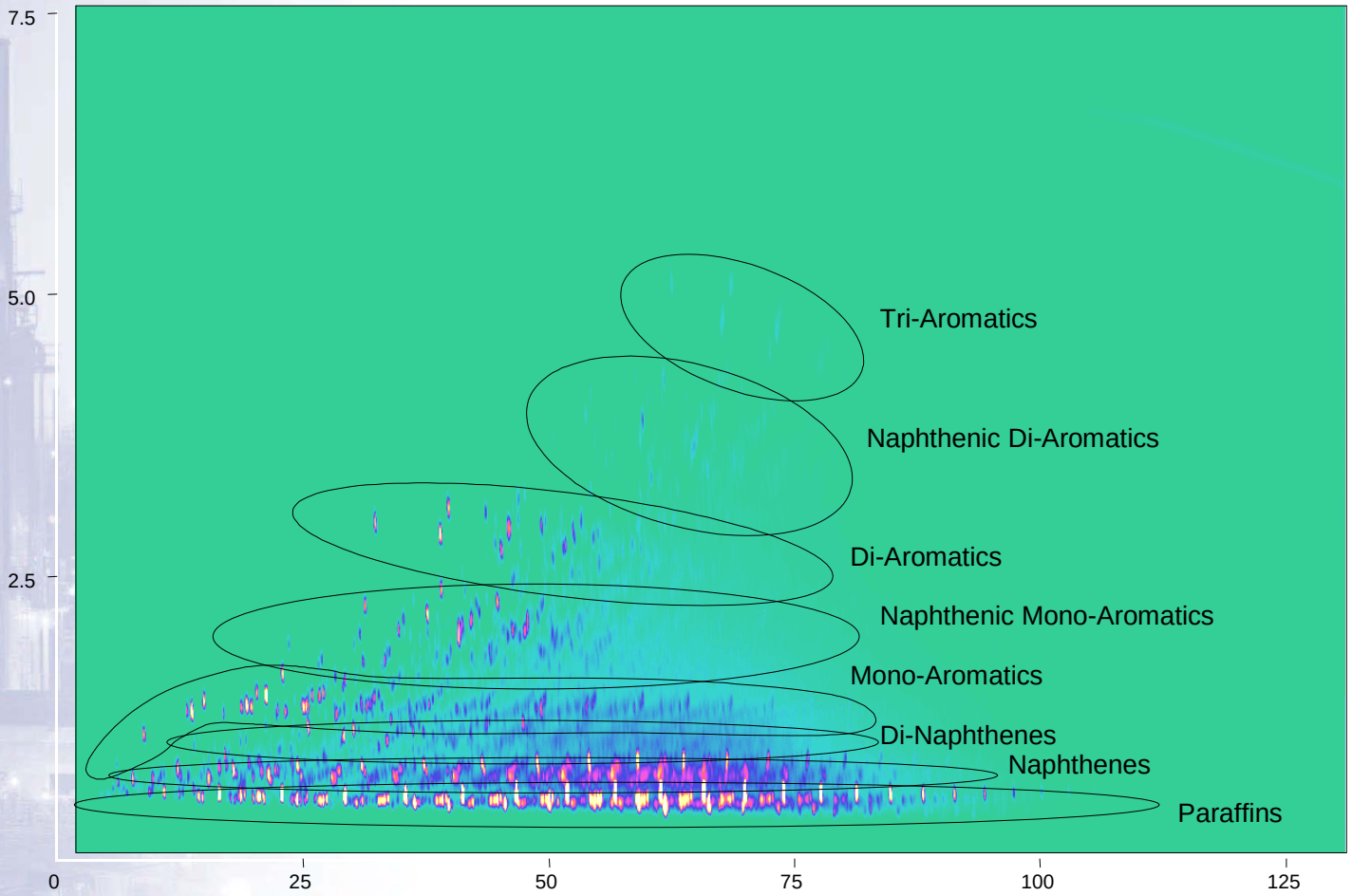
Petroleum substances are UVCBs

***U**nknown or **V**ariable composition, **C**omplex reaction products and **B**iological materials*

- Produced according to technical performance specifications
- Not intentional mixtures of specific chemicals
- Typically defined by refining process, distillation range, carbon number range, viscosity and hydrocarbon classes, etc.
- Petroleum substances are grouped together into major product categories
  - e.g. kerosines, gas oils, base oils, aromatic extracts, etc.
- Petroleum substances contain numerous hydrocarbon structures



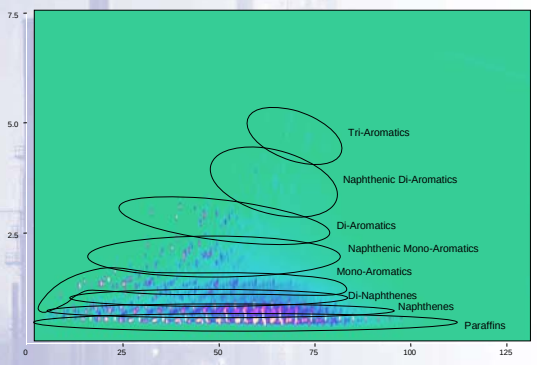
GCxGC plot of a middle distillate



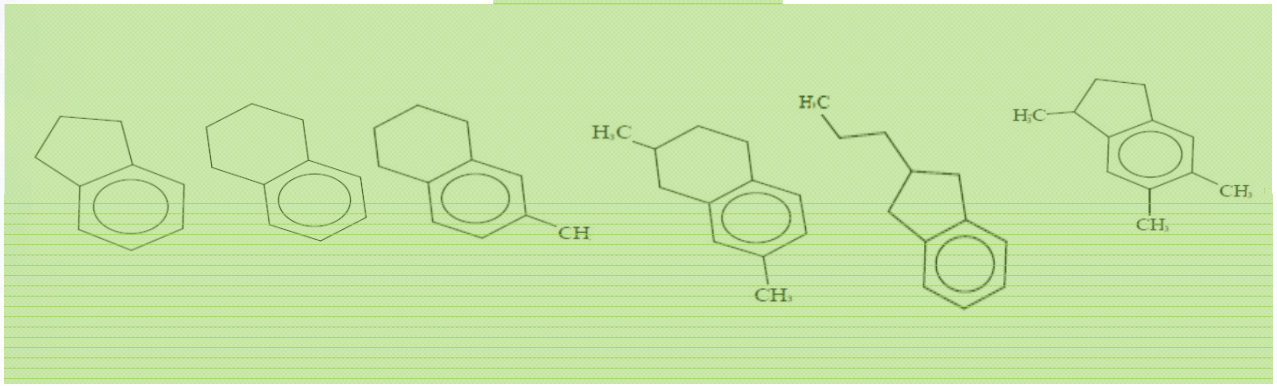
Second dimension separation (polarity - functionality)

First dimension separation (volatility - carbon number)

Concawe library – assigning structures and mass



HB	C#	n-P	i-P	n-CC6	i-N	Di-N	Poly-N	MoAr	NMAr	DiAr	NDiAr	PolyAr
		wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
1	3-5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2	6-8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3	9-11	0.1	0.2	0.0	0.3	0.2	0.0	0.1	0.4	0.4	0.1	0.0
4	12-14	2.1	2.9	0.3	3.3	1.6	0.0	1.4	1.6	0.9	0.6	0.3
5	15-17	4.6	9.1	1.1	7.6	4.2	0.0	3.0	2.2	1.0	0.4	0.4
7	etc	"	"	"	"	"	"	"	"	"	"	"



Input for exposure assessment petroleum substances

- Environmental Release Categories (ERCs) and Sp(ecific)ERCs

	ERC	Specific ERC (SpERC)
Emission Estimation	Standardized	Standardized
Defaults	Worst case	Good practice
Risk Management Measures (RMMs)	Not included	Considered
Responsibility	ECHA	Sector Groups/Trade Associations

- Industry evaluation of ERCs
  - Conservative emission estimate (initial screening)
  - Refinement often required
  - Applicable to manufacturers and downstream users

Example: 'Solvent-borne' SpERCs

- Set of SpERCs for 'Uses in Coatings' & 'Uses in Cleaning Agents'

GES Title	Area of Application / UD	max site tonnage t/day	Number of emission days	release to air before RMM (%)	efficiency of air emission controls (%)	release to air (%)	release to wastewater (%)	release to soil (%)
Identified Solvent								
Uses in Coatings	Industrial (SU3)	50	300	95.0	98.0	1.9	f(WS) WS < 1mg/L = 0.002 WS 1-10 mg/l = 0.007 WS 10-100 mg/L = 0.07 WS 100-1000 mg/L = 0.7 WS > 1000 mg/l = 2	0.0
	Professional (SU22)	EU Tonnage for use x 0.1 x 0.0005	365	99.0	N/A	99.0	0.0	1.0
	Consumer (SU21)	EU Tonnage for use x 0.1 x 0.0005	365	99.0	N/A	99.0	0.0	1.0
Use in Cleaning Agents	Industrial (SU3)	5.0	100	95.0	95.0	4.8	f(WS) WS < 1mg/L = 0.00001 WS 1-10 mg/l = 0.00003 WS 10-100 mg/L= 0.0003 WS 100-1000 mg/L= 0.003 WS > 1000 mg/l = 0.01	0.00
	Professional (SU22)	EU Tonnage for use x 0.1 x 0.0005	365	99.0	N/A	99.0	0.0	1.0
	Consumer (SU21)	EU Tonnage for use x 0.1 x 0.0005	365	99.0	N/A	99.0	0.0	1.0

Estimating emissions for petroleum substances

CONCAWE production / use questionnaires

tonnages per use per category

GES allocation

spERCs

emissions to air, water and soil for library structures

Local

Regional

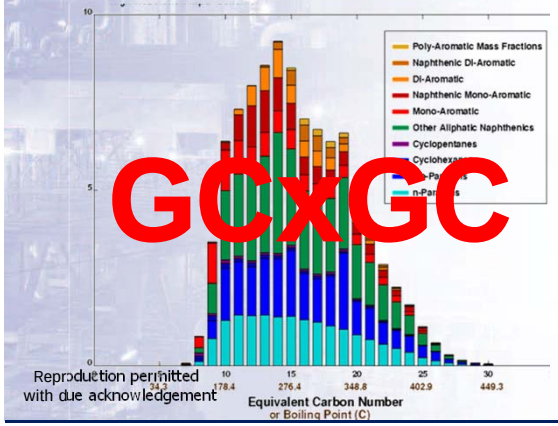
MULTIMEDIA MODEL (PECs)

HC COMPONENTS

map to CONCAWE library

allocate components to environmental compartments using simulated composition / Raoult's Law

GCxGC



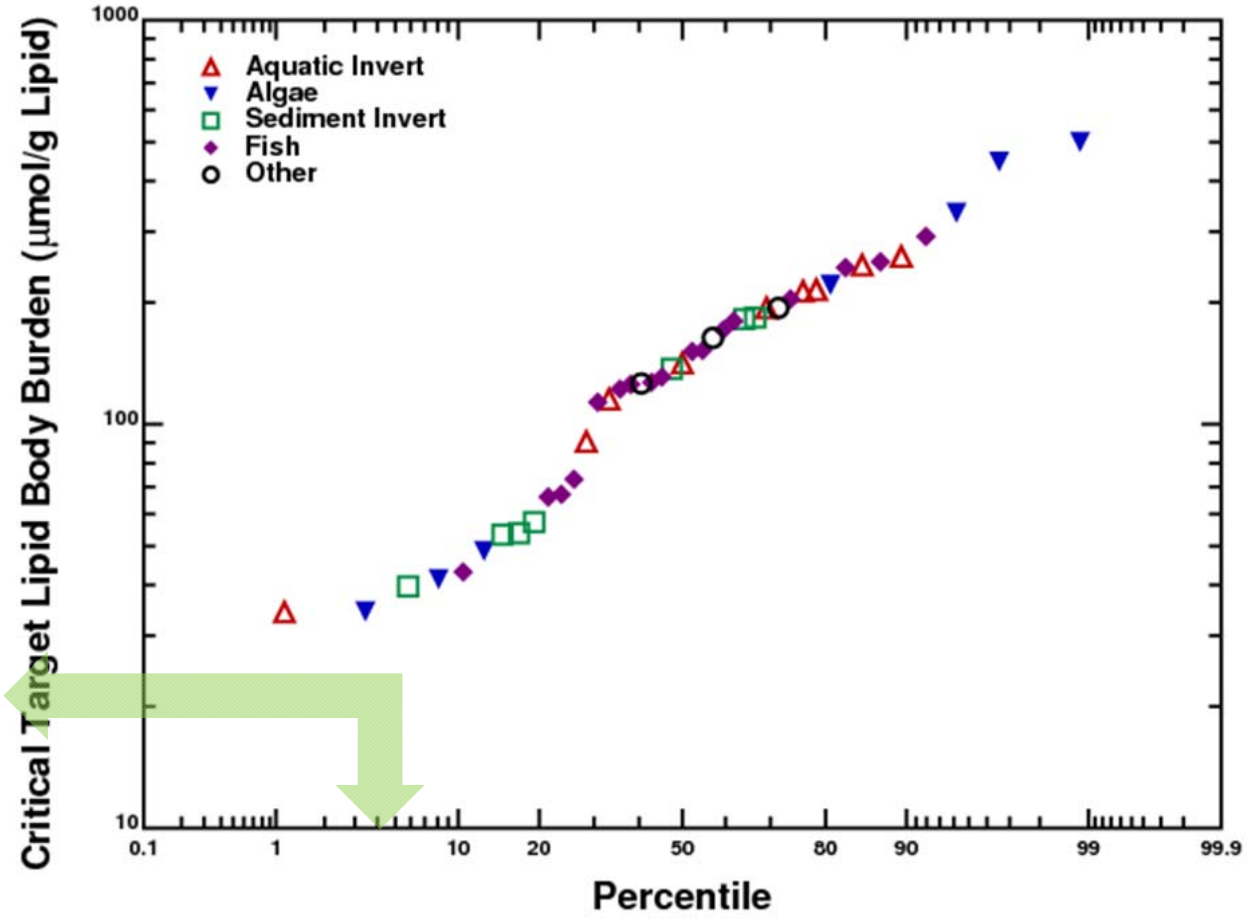
approach conservative since category emissions applied to substance registrations

Estimating hazard for petroleum substances

- Toxicity testing performed using Water Accommodated Fractions (WAF)
  - Results used for classification and labeling
  - Results not relevant for risk assessment as results from the laboratory do not reproduce behavior of hydrocarbons on the environment
- Modeling tool developed to reproduce WAFs
  - **PETROTOX**
  - Includes all components in Concawe library
  - Implements the Target Lipid Model with a Water Accommodated Fraction (WAF) model to predict toxicity of petroleum substances in water
  - Model assumes narcotic mode of action and additive hydrocarbon toxicity
  - PETROTOX is used to fill toxicity data gaps in REACH dossiers

Estimating hazards for petroleum substances

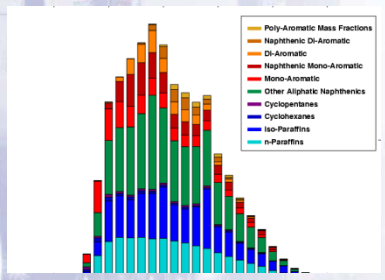
- PETROTOX is used to predict HC5 based on Species Sensitivity Distribution (SSD)



Used to calculate 5% Hazard Concentration for the environmental compartment (HC5)

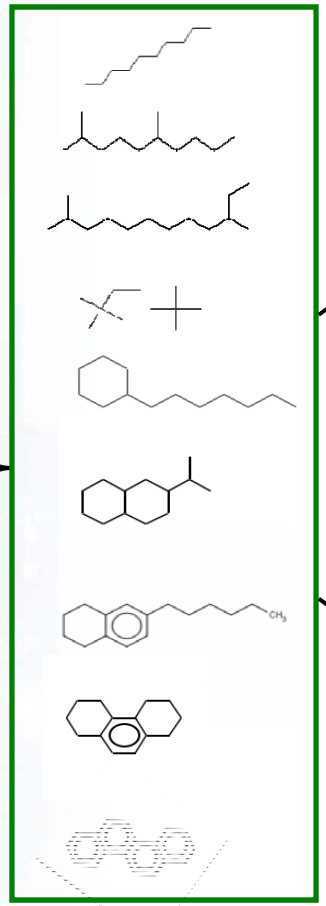
Estimating risks of petroleum substances - PETRORISK

Petroleum Category Composition



Petroleum Category Emissions

Structure



Library

FF / IFs from EUSES Model

- Air
- Water
- Soil
- Sediment

Predicted Exposure Concentrations

$PEC_{1, media}$
$PEC_{2, media}$
.....
.....
$PEC_{n, media}$

Safe Use

Yes

$$\text{Risk Ratio} = \sum_{i=1}^{n} (PEC_i / PNEC_i) < 1?$$

No

Toxicity Model

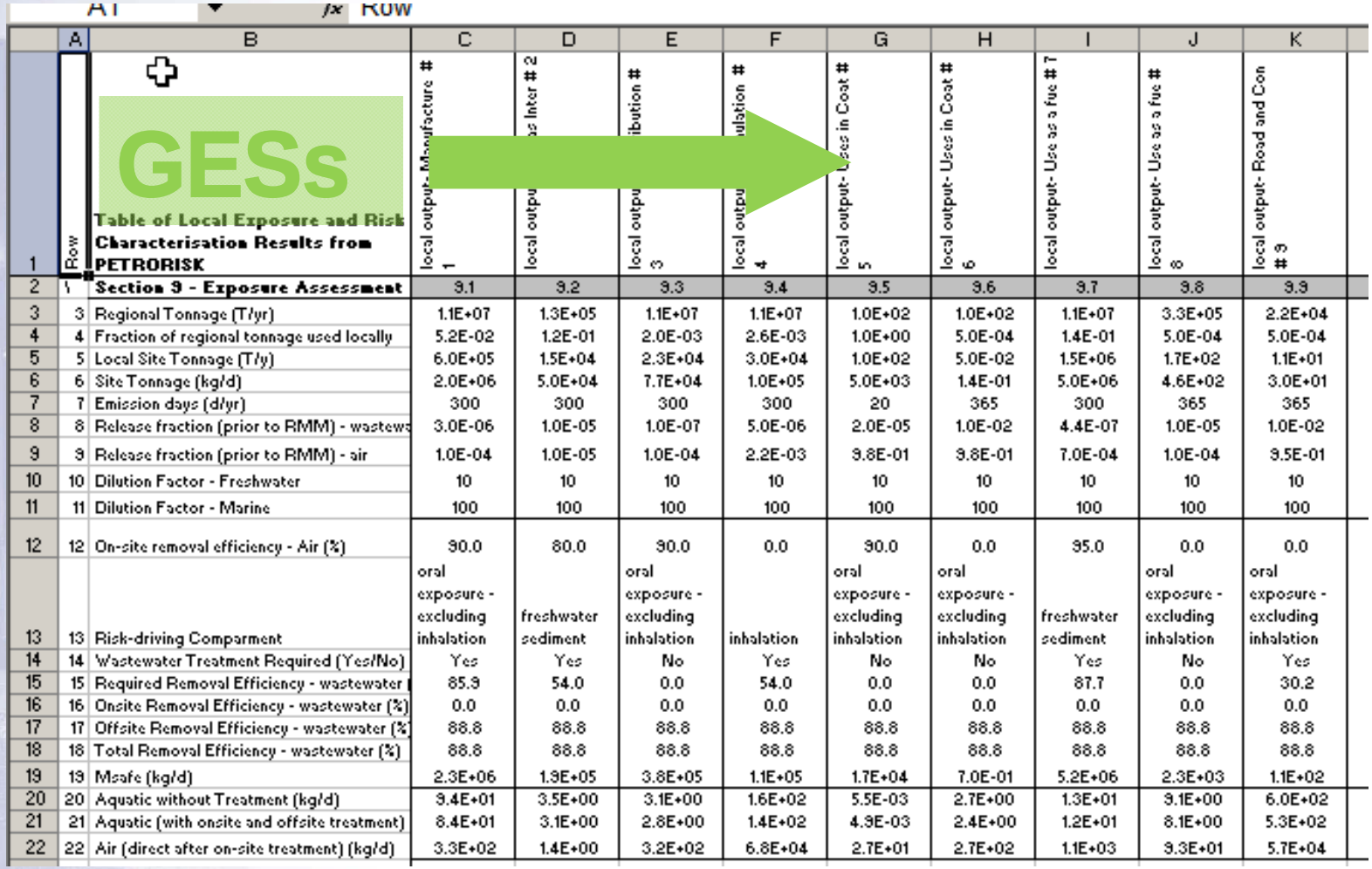
Target Lipid Model

Predicted No Effect Concentrations

$PNEC_{1, media}$
$PNEC_{2, media}$
.....
.....
$PNEC_{n, media}$

Refine emissions or risk management measures

PETRORISK output for petroleum substances



Row		local output- Manufacture # 1	local output- Uses Inter # 2	local output- Distribution # 3	local output- Formulation # 4	local output- Uses in Coat # 5	local output- Uses in Coat # 6	local output- Use as a fue #7	local output- Use as a fue # 8	local output- Road and Con # 9
2	Section 9 - Exposure Assessment	9.1	9.2	9.3	9.4	9.5	9.6	9.7	9.8	9.9
3	Regional Tonnage (T/yr)	1.1E+07	1.3E+05	1.1E+07	1.1E+07	1.0E+02	1.0E+02	1.1E+07	3.3E+05	2.2E+04
4	Fraction of regional tonnage used locally	5.2E-02	1.2E-01	2.0E-03	2.6E-03	1.0E+00	5.0E-04	1.4E-01	5.0E-04	5.0E-04
5	Local Site Tonnage (T/y)	6.0E+05	1.5E+04	2.3E+04	3.0E+04	1.0E+02	5.0E-02	1.5E+06	1.7E+02	1.1E+01
6	Site Tonnage (kg/d)	2.0E+06	5.0E+04	7.7E+04	1.0E+05	5.0E+03	1.4E-01	5.0E+06	4.6E+02	3.0E+01
7	Emission days (d/yr)	300	300	300	300	20	365	300	365	365
8	Release fraction (prior to RMM) - wastewa	3.0E-06	1.0E-05	1.0E-07	5.0E-06	2.0E-05	1.0E-02	4.4E-07	1.0E-05	1.0E-02
9	Release fraction (prior to RMM) - air	1.0E-04	1.0E-05	1.0E-04	2.2E-03	9.8E-01	9.8E-01	7.0E-04	1.0E-04	9.5E-01
10	Dilution Factor - Freshwater	10	10	10	10	10	10	10	10	10
11	Dilution Factor - Marine	100	100	100	100	100	100	100	100	100
12	On-site removal efficiency - Air (%)	90.0	80.0	90.0	0.0	90.0	0.0	95.0	0.0	0.0
13	Risk-driving Comparment	oral exposure - excluding inhalation	freshwater sediment	oral exposure - excluding inhalation	inhalation	oral exposure - excluding inhalation	oral exposure - excluding inhalation	freshwater sediment	oral exposure - excluding inhalation	oral exposure - excluding inhalation
14	Wastewater Treatment Required (Yes/No)	Yes	Yes	No	Yes	No	No	Yes	No	Yes
15	Required Removal Efficiency - wastewater	85.9	54.0	0.0	54.0	0.0	0.0	87.7	0.0	30.2
16	Onsite Removal Efficiency - wastewater (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
17	Offsite Removal Efficiency - wastewater (%	88.8	88.8	88.8	88.8	88.8	88.8	88.8	88.8	88.8
18	Total Removal Efficiency - wastewater (%)	88.8	88.8	88.8	88.8	88.8	88.8	88.8	88.8	88.8
19	Msafe (kg/d)	2.3E+06	1.9E+05	3.8E+05	1.1E+05	1.7E+04	7.0E-01	5.2E+06	2.3E+03	1.1E+02
20	Aquatic without Treatment (kg/d)	9.4E+01	3.5E+00	3.1E+00	1.6E+02	5.5E-03	2.7E+00	1.3E+01	9.1E+00	6.0E+02
21	Aquatic (with onsite and offsite treatment)	8.4E+01	3.1E+00	2.8E+00	1.4E+02	4.9E-03	2.4E+00	1.2E+01	8.1E+00	5.3E+02
22	Air (direct after on-site treatment) (kg/d)	3.3E+02	1.4E+00	3.2E+02	6.8E+04	2.7E+01	2.7E+02	1.1E+03	9.3E+01	5.7E+04

Latest developments environmental ESs

- Discussion with ECHA on environmental assessments for UVCBs
  - PBT assessment
  - Risk assessment
    - Assessment entity concept, currently not possible to implement for complex UVCBs
- ECHA Decision letters October 2013
  - Concerning uncertainties in PETROTOX and PETRORISK tools
    - SSD
    - ACR
    - Toxicity of heterocyclic hydrocarbons
    - PAH phototoxicity
    - HC5 derivation
  - Uncertainties were discussed with involved regulators (RIVM in NL)
  - Action plan underway to address decision letters involves several steps, deadline January 2016