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Environmental hazard and risk characterisation of petroleum substances: A guided "walking tour" of petroleum hydrocarbons

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ABSTRACT

Petroleum substances are used in large quantities, primarily as fuels. They are complex mixtures whose major constituents are hydrocarbons derived from crude oil by distillation and fractionation. Determining the complete molecular composition of petroleum and its refined products is not feasible with current analytical techniques because of the huge number of molecular components. This complex nature of petroleum products, with their varied number of constituents, all of them exhibiting different fate and effect characteristics, merits a dedicated hazard and risk assessment approach. From a regulatory perspective they pose a great challenge in a number of REACH processes, in particular in the context of dossier and substance evaluation but also for priority setting activities. In order to facilitate the performance of hazard and risk assessment for petroleum substances the European oil company association, CONCAWE, has developed the PETROTOX and PETRORISK spreadsheet models.

Since the exact composition of many petroleum products is not known, an underlying assumption of the PETROTOX and PETRORISK tools is that the behaviour and fate of a total petroleum substance can be simulated based on the physical–chemical properties of representative structures mapped to hydrocarbon blocks (HBs) and on the relative share of each HB in the total mass of the product. To assess how differing chemical compositions affect the simulated chemical fate and toxicity of hydrocarbon mixtures, a series of model simulations were run using an artificial petroleum substance, containing 386 (PETROTOX) or 160 (PETRORISK) HBs belonging to different chemical classes and molecular weight ranges, but with equal mass assigned to each of them. To this artificial petroleum substance a guided series of subsequent modifications in mass allocation to a delineated number of HBs belonging to different chemical classes and carbon ranges was performed, in what we perceived as a guided "walking tour" through the chemical space of petroleum substances. We show that the PETROTOX and PETRORISK predictions reflect changes in mass distribution introduced to selected HBs by affecting hazard and risk estimates in correspondence with what is expected based on physical-chemical properties of individual constituents in the corresponding HBs.

1. Introduction

Petroleum substances and refinery streams are derived from crude oil, using one or more refinery processes, but due to their method of production, different origin and complex composition, it is not possible to characterise many petroleum substances in terms of exact chemical composition, molecular formula or structure. From a regulatory perspective they are collectively called UVCBs or Substances of Unknown or Variable composition, Complex reaction products or Biological materials (Carrillo et al., 2010). UVCBs pose a great challenge in a number of REACH processes, in particular in the context of dossier and substance evaluation but also for priority setting activities of the European Chemical Agency (ECHA).

Under the CLP[1] (Classification, Labelling and Packaging of substances and mixtures) and REACH regulation it is possible to group substances together into categories where their physical hazards, human and environmental toxicological properties and environmental fate properties are likely to be similar or follow a regular pattern as a result of structural similarities. As such, in this category approach petroleum substances can be grouped together according to the processes by which they are manufactured and basic physical properties (Carrillo et al., 2010). Examples of categories are kerosines, untreated distillate aromatic

Abbreviations: 2D-GC, 2-dimensional gas chromatography, or GC × GC; CLP, classification, labelling and packaging of substances and mixtures (Regulation (EC) No. 1272/2008); C-range, carbon range; CSR, Chemical Safety Report; CONCAWE, Conservation of Clean Air and Water in Europe; CTLBB, Critical Target Lipid Body Burden; DAE, untreated distillate aromatic extracts; DNEL, derived no effects level; ECHA, European Chemicals Agency; IF, intake fractions; FF, fate factors; GES, Generic Exposure Scenario; HB, hydrocarbon block; HBM, hydrocarbon block method; HFO, heavy fuel oil components; LL_{50}, lethal loading to 50% of the organisms; NOEL, No Observed Effect Level; PEC, Predicted Environmental Concentration; PNEC, Predicted No Effect Concentration; QSAR, Quantitative Structure Association Relationships; REACH, Registration, Evaluation, Authorisation and Restriction of Chemicals (Regulation (EC) No 1907/2006); RCR, risk characterisation ratio; SpERC, Specific Environmental Release Category; TLM, target lipid model; UVCBs, Substances of Unknown or Variable composition, Complex reaction products or Biological materials; VP, vapour pressure; WS, water solubility.

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[1] Regulation (EC) No 1272/2008.

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extracts (DAE) and heavy fuel oil components (HFO). In total 27 different categories are defined (Carrillo et al., 2010).

In order to facilitate the performance of hazard and risk assessments of petroleum substances CONCAWE has developed the PETRORISK (HydroQual, 2011) and PETROTOX (HydroQual, 2009; Redman et al., 2012) spreadsheet models, both based on the Hydrocarbon Block Method (HBM). In the HBM approach groups of closely related constituents of petroleum substances, such as isomers and adjacent members of a homologous series of hydrocarbons are thought to possess such similar properties, that it is assumed that they can be grouped in hydrocarbon blocks and treated as single compounds without introducing serious errors in their hazard and risk assessments (King et al., 1996). A library of 1512 individual structures has been constructed (Howard et al., 2006) to represent all types of structures that are present in petroleum substances. This range of individual hydrocarbons is subsequently mapped to the various HBs. Mass is allocated to each structure based on the relative share of each HB in the total mass of the product, in order to simulate the complex petroleum substance and derive physical–chemical properties relevant for environmental exposure and risk evaluations. In PETRORISK and PETROTOX petroleum substances are modelled as being composed of 160 and 386 HBs, respectively. Product compositional information (e.g. weight % of each HB, chemical class, boiling point intervals reflecting carbon number ranges) can be obtained by two-dimensional gas chromatography (2D-GC) or more conventional total petroleum hydrocarbon (TPH) analysis (mass distribution for aliphatic and aromatic classes vs boiling point) (Gustafson et al., 1997; Weisman, 1998, 1999).

The Total Petroleum Hydrocarbon Criteria Working group (TPHWG) fractionation approach is one of the most commonly used methods for characterisation and risk assessment of petroleum products (Gustafson et al., 1997; Verbruggen et al., 2008; Weisman, 1998, 1999). Similar approaches grouping petroleum hydrocarbons in pseudo-components (Lee et al., 1993; Mackay and Paterson, 1980; Reijnhart and Rose, 1982), hydrocarbon blocks (King et al., 1996; EC, 2003), chemical groups (Van de Weghe et al., 2006; Mao et al., 2008), fractions (Gustafson et al., 1997; Park and Park, 2010, 2011) or a combination of fractions and individual components (Pinedo et al., 2013) have also been shown successful for the assessment of petroleum hydrocarbons. Methods may differ in the analytical techniques, number of fractions and chemical classes considered and have evolved over time. The HBM approach at different stages of its development, the most recent version of which is implemented in the PETRORISK and PETROTOX models, has demonstrated its utility for exposure and risk assessment of gasoline (Macload et al., 2004; McGrath et al., 2005; Foster et al., 2005). The PETROTOX model performance was recently further validated by Redman et al., 2012 by comparing the predicted toxicity distributions for different petroleum substances from different petroleum categories with independent, empirical distributions of toxicity data for these same categories. Whale et al. (2013) successfully applied the PETROTOX model to predict the toxicity of refinery spot samples based on their hydrocarbon composition. Comparing hydrocarbon block (HBM) and TPHWG methods Bamard et al. (2011) conclude that the characterisation factors (CF) used in life cycle assessment obtained using these different blocking methods yield similar results and are both relevant for characterising the potential impact for aquatic ecotoxicity of petroleum substances.

Given the variable composition of petroleum substances lumped together in a single category – variability due to geographical differences of origin and different production processes – it is crucial to understand how well the PETRORISK and PETROTOX modelling tools are able to reflect compositional mass distribution over different carbon ranges and chemical classes as obtained from 2D-GC, i.e. to explore to what extent the different HBs covering the chemical space of petroleum UVCBs contribute to the overall hazard and risk outcome. Several approaches can be followed to better understand the effect of variable compositional input on the hazard and risk estimates of both models. In this paper we report on the results of model simulations for which an artificial petroleum substance was constructed, containing 160 (PETRORISK) or 386 (PETROTOX) HBs belonging to different chemical classes and molecular weight ranges, but with equal mass assigned to each block. Subsequently, a controlled or "guided" series of modifications in mass allocation to a delineated number of HBs belonging to different chemical classes and carbon ranges was made to this artificial petroleum substance, in what we perceived as a guided "walking tour" through the chemical space of an artificial petroleum UVCB. The main purpose of these model simulations was to investigate the influence of the inherent variability in product composition on predicted environmental distribution, hazard and risk of petroleum substances as calculated by the PETRORISK and PETROTOX models.

2. Methods and materials

2.1. Guided "walking tour" of petroleum hydrocarbons

In order to test the overall performance of both modelling tools the models were run multiple times and for each run changes were made to the composition of the hydrocarbon product. Two distinct modifications were performed: (i) adding 30% mass to HBs in incremental molecular weight ranges (carbon (C)-ranges) from C3–5 up to C21–23 (larger structures are highly insoluble), each range encompassing 3 carbon numbers, in PETRORISK and from C3–5 up to C18–20 (larger structures are highly non-toxic) in PETROTOX and (ii) adding 30% mass to different chemical classes representing the product, i.e. Paraffins and iso-Paraffins (n- & i-P), Cyclo-Pentanes and –Hexanes (n-CC5 & -6), Naphthenics (i- & Di-N), Mono-Aromatics (Mo- & NM-Ar), Di-Aromatics (Di- & Ndi-Ar) and Poly-Aromatics (Poly-Ar). When adding mass to HBs in incremental molecular weight ranges distinction has been made between a first set of runs including both aliphatics and aromatics and a second set of runs targeting aromatic classes only. As no aromatic structures <C6 exist the range C3–5 has not been addressed in the second set of model runs.

During the mass re-allocation process mass added to targeted HBs was subtracted from mass in all other HBs in order to preserve 100% mass in the total product. In the original (unmodified) artificial petroleum each HB was assigned equal mass, i.e. 1.0490% in case of PETRORISK and 0.3497% in case of PETROTOX. Differences in the initial mass allocated to each of the HBs in PETRORISK and PETROTOX result from the use of 3 carbon versus 1 carbon intervals in the input matrix in PETRORISK and PETROTOX, respectively. Also, as a result of the unequal number of HBs in both models—the weight % after the mass redistribution process in both models is not identical because the mass added to the targeted blocks is subtracted evenly from a different number of remaining HBs in both model inputs. In our approach the weight % in the PETRORISK input matrix was obtained by summing the weight % of 3 successive C-ranges in the PETROTOX 1C matrix (for example: the sum of the weight % of C6, C7 and C8 of PETROTOX, equals the weight % of block 2 (C-range 6–8) in PETRORISK). Matrices illustrative of the targeting process for each model are given in Tables 1 and 2, respectively. For PETROTOX an example is given of targeting the chemical classes n- & i-P. In case of PETRORISK an example is given of mass addition to Block 2, i.e. C-range 6 to 8. In subsequent model runs 3C-ranges up to C23 and different chemical classes specified above were targeted in a similar way. Notice that as Blocks 1 and 10 only contain structures with 5 and 30 carbons, respectively, they were assigned only 1/3 of the weight % of the other blocks. Blocks 8 to 10 which contain highly insoluble and non-toxic structures (>C23) were excluded from the mass re-allocation process targeting incremental C-ranges.

Normal olefins (n-O), branched olefins (i-O) and aliphatic sulphur compounds (Al–S) were excluded from the targeting experiments (mass set to zero) as no information on these classes is provided in the category composition by CONCAWE (Leonards et al., 2010). Because of their limited quantity in most petroleum products, coupled also with the difficulty of separating them from the other hydrocarbon groups