PETROTOX—CONCAWE's ecotoxicity predictor for petroleum products

A user-friendly tool to assess aquatic toxicity hazard of complex petroleum and related substances

Background

CONCAWE has been conducting a voluntary programme assessing the risks to man and the environment of petroleum substances in anticipation of proposed legislation (REACH). The process by which the risk assessments are being conducted is based on the guidance issued by the European Union in a technical guidance document (TGD) (EU, 2003). The TGD contains an extensive description of how to conduct a risk assessment for man and the environment, but was written primarily to address single pure substances. At the time the first TGD was written, CONCAWE proposed a technical framework to address complex petroleum substances referred to as the Hydrocarbon Block Method (Peterson, 1994; King *et al.,* 1996). This approach was subsequently adopted as an Appendix to the TGD and applied to a risk assessment on gasoline. In the case of gasoline, the individual constituents can be readily identified and logically grouped into hydrocarbon blocks with similar fate and effect properties. It was recognised at the time that the Hydrocarbon Block Method required further adaptation in order to be applied to higher boiling substances where detailed information on the identity of individual constituents cannot be obtained.

PETROTOX

As one part of this further work, CONCAWE has sponsored an external contractor (Hydroqual) to develop a general purpose spreadsheet-based model (PETROTOX) to predict the ecotoxicity of the petroleum substances under different test conditions for various aquatic organisms. PETROTOX is a user-friendly tool to assess aquatic toxicity hazard of complex petroleum and related substances; it:

- predicts toxicity of substances to different aquatic organisms (based on the Narcosis Target Lipid Model);
- assesses impact of composition/test design on toxicity results; and
- estimates Predicted No-Effect Concentrations (PNECs) needed as input to environmental risk assessments of petroleum substances using the Hydrocarbon Block Method.

The model can accommodate two types of inputs, low resolution or high resolution, which depend on the information known about the mass distribution of hydrocarbon classes in the petroleum substance. In the low-resolution approach, the mass distribution of two generic classes (aliphatic and aromatic) is entered over user-defined boiling point intervals. This format is patterned after the information derived from a Total Petroleum Hydrocarbon (TPH) method of analysis. In the high-resolution approach, the mass distribution for up to 16 classes of hydrocarbons can be entered: n-paraffins, iso-paraffins, n-substituted cylcohexanes, n-substituted cylcopentanes, other mono-naphthenics, di-naphthenics, poly-naphthenics, n-olefins, iso-olefins, sulphur-bearing aliphatics, mono-aromatics, naphthenic mono-aromatics, di-aromatics, naphthenic di-aromatics, poly-aromatics and sulphur-bearing aromatics. This format is patterned after the information derived from highly detailed 2D-GC that provides mass distribution information for the 16 chemical classes over 26 boiling point intervals. In both cases, the physical/chemical properties of the chemical classes that are used in the model to characterise the product are derived from a library of representative hydrocarbon structures that are included as a separate worksheet in the spreadsheet. A generic version of the model (User-Defined version) has also been developed that allows input of user-defined hydrocarbon blocks and associated properties.

Both the Default and User-Defined versions of the PETROTOX spreadsheet model are available on the CONCAWE website (www.concawe.org/Content/Default.asp?PageID=241) or by contacting Bo Dmytrasz at CONCAWE (bo.dmytrasz@concawe.org). For both versions of the model, there are user's guides that include tutorials which give detailed examples with step-by-step instructions to guide the user through various features of

the model. PETROTOX is being made available without charge. However, certain restrictions apply. For complete details, please refer to the User Agreement and Disclaimer that is included in the user guide.

For those readers interested in more technical details, further discussion follows on the topics that underpin PETROTOX, namely target lipid models and aquatic toxicity of petroleum substances.

Target lipid models

In carrying out the gasoline risk assessment, a method for predicting the no-effect concentrations (PNECs) to aquatic organisms was needed. The method chosen was based on the Narcosis Target Lipid Model (NTLM), developed by Di Toro *et al.* (Di Toro *et al.*, 2000a,b).

The first observation of interest when trying to understand the relationships between chemicals and mortality of aquatic organisms, is that if a chemical causes death, without a specific mode of action, when quantified, the range of concentrations (expressed in molar terms per kg) in the body of the aquatic organisms is approximately similar regardless of the chemical. This body burden is a result of the bioconcentration of the chemical up to a critical concentration, and is thus the product, for a range of narcosis chemicals, of the BCF and the LC50 of the chemicals. As BCF increases and LC50 decreases with increasing octanol-water partition coefficient, K_{OW}, the result is approximately constant.

This also gives rise to the frequently observed inverse relationship between the LC50 and K_{OW}:

$$\log(LC50) = a \log(K_{OW}) + b \qquad \textit{(Equation 1)}$$

The NTLM extends this observation by assuming a single universal slope for the log (LC50) versus log (K_{OW}) relationship, independent of the species. The universal slope is the slope of a linear free energy relationship between octanol and the target lipid in the organism. The y-intercepts are the species-specific critical target lipid body burdens (CTLBB), C_L^*, for narcosis mortality. These body burdens are adjusted for chemical classes that are slightly more potent than baseline narcotics. Further details on model theory and calibration with available aquatic toxicity data sets are provided by Di Toro *et al.*, 2000a and McGrath *et al.*, 2004.

Aquatic toxicity of petroleum products

Experimental evidence shows that the aquatic toxicity of individual narcotic chemicals, including hydrocarbons, can be categorised into two broad classes of hydrocarbons that:

- exhibit aquatic toxicity spanning several orders of magnitude and inversely correlated to K_{OW} (see Equation 1); and
- do not exhibit toxicity due to their low aqueous solubility.

Thus, to be able to predict the aquatic toxicity of petroleum substances both the nature and concentration of individual hydrocarbons in solution need to be understood. To account for compositional differences, the toxicity of individual compounds in a mixture can be conveniently expressed in terms of toxic units (TUs). A toxic unit is the ratio of the measured concentration of a chemical and the corresponding effect concentration in the same medium. Assuming additivity, toxic units for individual constituents can be summed to estimate toxicity of the mixture.

In the recent gasoline risk assessment, this approach was adopted and based on the hydrocarbon blocks chosen, sharing similar physiochemical properties, the toxicity of water accommodated fractions (WAFs) of six gasoline blending streams to an algae (*Selenastrum capricornutum*), a fish (*Oncorhynchus mykiss*) and a daphnid (*Daphnia magna*) were successfully predicted using the NTLM (McGrath *et al.* 2005). During this project, the NTLM was modified by expressing aquatic toxicity of petroleum products based on membrane-water partitioning (K_{MW}) rather than K_{OW}. This was required because at a log(K_{OW}) greater than approximately 5.5, the log(K_{MW})–log(K_{OW}) relationship that is assumed deviates from linearity resulting in higher predicted toxicity of higher boiling point products when compared to observed toxicity. This revision allowed NTLM predictions to be reconciled with

measured toxicity data and provided a mechanistic model that could be used to derive PNEC values for hydrocarbon blocks comprising higher boiling point petroleum substances such as kerosines and gas oils.

Solubility limitations on chronic aquatic toxicity

A key finding from the gas oils and kerosine risk assessments is that the approximate chain lengths at which aliphatic hydrocarbons cease to exert aquatic toxicity need to be confirmed to ensure proper calibration of the revised target lipid model that is based on membrane-water rather than octanol-water partition coefficients. This work has commenced and the research now being conducted will better define chronic cut-offs for various aliphatic hydrocarbon classes in the C12–C16 range. The work will first concentrate on establishing high quality toxicity data on algae, before confirming that invertebrates follow a similar pattern, as predicted from the toxicity model.

References

EU (2003) EU Technical Guidance Document: 2nd edition of the Technical Guidance Document in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. Office for Official Publications of the European Communities, Luxembourg.

Di Toro, D.M., McGrath, J.A. and Hansen, D.J. 2000a. Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. I. Water and Tissue. *Environmental Toxicology and Chemistry*. 19:1951–1970.

Di Toro, D.M. and McGrath, J.A. 2000b. Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. II. Mixtures and sediments. *Environmental Toxicology and Chemistry*. 19:1971–1982.

Peterson, D.R. 1994. Calculating the aquatic toxicity of hydrocarbon mixtures. *Chemosphere*. 29:2493–2506.

King, D.J., Lyne, R.L., Ginberg, A., Peterson, D.R., Stephenson, R. and Short, D. 1996. *Environmental Risk Assessment of Petroleum Substances: The Hydrocarbon Block Method*, CONCAWE Report No. 96/52, Brussels, Belgium.

McGrath, J.A., Parkerton, T.F. and Di Toro, D.M. 2004. Application of the narcosis target lipid model to algal toxicity and deriving predicted no-effect concentrations. *Environmental Toxicology and Chemistry*. 23(10):2503–2517.

Mcgrath, J.A., Parkerton, T.F., Hellweger, F.L. and Di Toro, D.M. 2005. Validation of the narcosis target lipid model for petroleum products: gasoline as a case study, *Environmental Toxicology and Chemistry*. 24(9):2382–2394.

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