environmental risk assessment of petroleum substances: the hydrocarbon block method

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ABSTRACT

This report describes an approach to environmental risk assessment for petroleum substances compatible with the principles described in EU Technical Guidance Documents.

KEYWORDS

Risk assessment, environment, petroleum substance, hydrocarbon mixture, fate, distribution, modelling, QSAR, effects.

CONTENTS

SUMMARY

The principles of environmental risk assessment for Existing Substances are outlined in a Commission Regulation No. 1488/94 and the procedures are elaborated in extensive technical guidance notes. The procedures were developed for assessment of the risks posed by single chemicals. This report describes an approach to environmental risk assessment of petroleum substances, which although described by single EINECS numbers, are complex mixtures of hydrocarbons.

Individual components of petroleum substances will have specific and differing physico-chemical properties and potentials to be degraded in the environment. Accordingly, each will be subject to different distribution and fate processes on release. In reality, groups of closely-related hydrocarbons may be considered together without introducing significant inaccuracies in respect of their predicted environmental concentrations (PECs). The aquatic toxicity of each "block" of constituent hydrocarbons should also be considered separately to enable the calculation of a corresponding predicted no effect concentration (PNEC) and hence PEC/PNEC ratio. This report describes the scientific basis for this approach to the evaluation of the environmental risk posed by petroleum substances, including combining the PEC/PNEC ratios calculated for each block of constituent hydrocarbons to derive an overall ratio for the complex substance.

By appropriate definition of hydrocarbon "blocks", this approach to risk assessment provides an opportunity to estimate the environmental impact of particular groups of hydrocarbons, or by defining a block to contain a single component, to derive the concentration of the particular hydrocarbon in each environmental compartment. Furthermore, the variable composition of UVCB substances can be addressed by adjusting the contribution of individual blocks to examine any effect on the overall PEC/PNEC ratio for a suitably defined range of compositions.

Data to be used in the risk assessment process are discussed, along with the main technical details of the proposed approach.

1. INTRODUCTION

EU Council Regulation No. 793/93 [1] provides for the assessment of the risks to man and the environment of existing substances. Such risk assessments are to be conducted according to the principles outlined in EC Regulation No. 1488/94, [2] which is supported by Technical Guidance Documents. [3] The fundamental steps in this process are exposure assessment, hazard identification, determination of dose-response relationship and risk characterisation. For each environmental compartment, it is necessary to identify a PEC (Predicted Environmental Concentration) and a PNEC (Predicted No Effect Concentration) for a substance, in order to calculate the PEC/PNEC ratios. If the ratio is ≤ 1, there is no perceived risk, but if the ratio is >1, then either further data may be needed to refine the assessment, or risk reduction measures may need to be considered.

The Technical Guidance Document for existing substances was developed mainly from the experience gained with individual organic chemicals. The procedure described cannot be applied directly to a complex mixture like a petroleum substance because of the different fate and effects of individual components of the mixture in the environment.

The purpose of this report is to describe an approach to the environmental risk assessment of petroleum substances which is consistent with the principles outlined in the Technical Guidance Document. The approach, the Hydrocarbon Block Method (HBM), was developed by CONCAWE Petroleum Products Ecology Group and presented at a Workshop organised by EC DGXI held at the Joint Research Centre, Ispra in December 1994. The intention of this workshop was to consider approaches to risk assessment of petroleum substances and to develop recommendations for consideration by the expert working groups developing a single consolidated Technical Guidance Document for risk assessment of both new and existing substances. An appendix to this consolidated draft Technical Guidance Document describing the HBM has been prepared and this is due to be published in 1996.

2. BACKGROUND

The petroleum refinery streams identified in the EINECS (European Inventory of Existing Commercial Chemical Substances) are all complex combinations of hydrocarbons. Many may contain sulphur and nitrogen compounds which may influence their toxicological characteristics. In Chemical Abstracts terms, they are UVCB substances (UVCB - Unknown or Variable Composition, Complex Reaction Products and Biological Materials) meaning that they cannot be denoted by conventional molecular formulae.

It is recognised that some of the EINECS numbers used for petroleum substances are also used for hydrocarbon solvents. The latter fit the same definitions, but are essentially "narrow cuts" containing a predominance of carbon numbers around the centre of a given carbon number range. This illustrates that complex hydrocarbon substances having the same CAS numbers may have significantly different carbon number distributions.

The individual hydrocarbon components of petroleum substances will have specific and different physico-chemical properties and potentials to be degraded in the environment. As such, hydrocarbon components will be subject to different distribution and fate processes on release and each will reach its own concentration in each environmental compartment. It follows that a PEC for a whole petroleum substance, i.e. a complex hydrocarbon mixture, does not exist. However, it would be theoretically possible to determine a PEC value for each individual hydrocarbon constituent of a complex mixture. This approach demands a degree of analytical resolution that is not achievable for most petroleum substances. However, since hydrocarbons of similar structure and size will behave very similarly in terms of environmental distribution and fate, it is possible to block or group such hydrocarbons, so that components having similar properties may be considered together. PEC values can then be calculated for hydrocarbon blocks for each environmental compartment.

PNEC values for each hydrocarbon block can also be assigned based on ecotoxicity data. Based on the assumption of the additivity of effects for substances with the same mode of action, the PEC/PNEC ratios which are derived for each block can then be added proportionately to derive an overall PEC/PNEC ratio of the mixture. This approach to risk assessment is referred to as the Hydrocarbon Block Method (HBM).

3. OUTLINE OF METHOD

The distribution and fate of a chemical is dependent on its physico-chemical properties and its susceptibility to degradation. In the case of a mixture, each component will be distributed and subjected to fate processes independent of the other components of the mixture. Estimations of PECs can therefore only be made for the individual components, although in reality, groups of closely related chemicals, such as isomers and adjacent members of homologous series of hydrocarbons, may be so similar in their properties that they can be grouped and treated as single compounds without introducing serious errors.

Given that PECs can only be derived for components or blocks of similar components, it follows that PNECs must also be estimated for such components, or blocks. [It is to be noted that ecotoxicity data obtained with **whole** petroleum products, whether obtained using water accommodated fractions (WAFs) or dispersions, cannot be used for the estimation of PNECs for individual blocks.]

From these considerations, it is clear that the PEC/PNEC ratio of a mixture cannot be derived directly; it must be calculated using the PEC/PNEC ratios of the (blocks of) components. The scientific rationale underpinning the additivity of aquatic toxicity effects and of PEC/PNEC ratios is detailed in **Section 5** and assuming such additivity, the PEC/PNEC ratio of a mixture can be calculated using the equation:

$$\frac{\text{PEC}}{\text{PNEC}}\ \text{mix} = \frac{\text{PEC}_{\text{A}}}{\text{PNEC}_{\text{A}}} + \frac{\text{PEC}_{\text{B}}}{\text{PNEC}_{\text{B}}} + \frac{\text{PEC}_{\text{C}}}{\text{PNEC}_{\text{C}}} \quad \text{etc.}$$

where the mixture contains known amounts of components, or groups of components, A, B, C, etc. It is to be noted that the proportion of each component that is present must be taken into account.

Most experience during the development and subsequent application of the Hydrocarbon Block Method has been with the aquatic environment. However, similar principles are applicable to all environmental compartments.

The principal steps in the application of HBM may then be summarised as follows:

- Obtain compositional data for the substance that are sufficient to assign components to "blocks".

- Define "blocks" by grouping components on the basis of similar structural/physico-chemical and ecotoxicological properties. If desired, "blocks" can be defined as single components.

- Obtain production data.

- Establish release estimates for each "block". A single release estimate for a petroleum substance may not always be adequate ("blocks" with markedly different physico-chemical properties may require different release estimates).

- Assign representative values for physico-chemical properties, degradation rate constants and toxicity values for each "block". Note that NOEC (No Observed Effect Concentrations) values may be obtained directly or by applying safety factors to the conventional $LC_{50}/EC_{50}/IC_{50}$ expressions of lethality.

- Determine a PEC value for each compartment for each "block".

- Determine a PNEC value for each compartment for each "block".

- For each compartment, calculate the PEC/PNEC ratio for each "block" and sum proportionately.

Definition of "blocks"

"Blocks" will primarily be defined on the basis of those physico-chemical and degradation properties that are key in determining the distribution and fate of their components. Care should be taken to ensure that "blocks" are not so wide as to encompass components that will not have broadly similar fates and distributions on release. Similarly "blocks" should, whenever possible, contain substances with a similar mode of action and not too wide a range of toxicity. Both the fate and toxicity criteria for "block" definition need to be satisfied simultaneously.

4. PREDICTED ENVIRONMENTAL CONCENTRATION

For substances containing only a single component, sound monitoring data provide the best estimate of exposure. For petroleum substances there are a number of difficulties related to the use of monitoring data that need consideration.

Some monitoring data for petroleum hydrocarbons have been collected using methods which only provide information on the total quantity of hydrocarbon present and these data cannot therefore, be directly related to the predicted environmental concentrations (PECs) for the individual components of the mixture.

Where monitoring data on specific hydrocarbons are available, it will rarely be possible to attribute them to a particular petroleum substance (except in some local situations), as many petroleum substances will contain the same components and might therefore be contributing to the monitored values. In most situations, monitoring data will therefore, only provide an estimate of environmental concentration reflecting all sources of release of a particular “block".

The general lack of reliable monitoring data in the form required, forces a reliance on the use of modelling to arrive at the PECs for individual hydrocarbons or blocks. However, the application of computer-based modelling* does allow for the possibility of multiple iterations of the risk characterisation process to refine risk estimates. Furthermore, it also allows for example, investigation of the influence of composition variation within a particular petroleum substance on the PECs of particular blocks or components, or of the effects of alternative blocking schemes on the overall outcome of the process.

Modelling of the PEC requires information on composition, amounts released to the environment, their distribution in the environment (dependent on physico-chemical properties) and on rates of degradative processes.

Product composition

Compositional data are required in sufficient detail to allow petroleum substances to be described in "blocks". For some petroleum substances, it may be necessary to generate the required data to pursue this approach; development of the required information may be more difficult for the heavy, complex petroleum substances. Complete analytical resolution of petroleum substances into individual hydrocarbons is possible for gases and gasoline components, up to C_{12}, but it is not practicable for higher carbon numbers due to the rapid increase in the number of isomers. However, techniques are available for finding carbon number distributions and for identifying and quantifying the hydrocarbon types that are present, sufficient for the purposes of risk assessment.

However, as explained below (see **Section 5**), such data are only required for components or "blocks" that have a potential to cause chronic toxic effects. Those components which do not demonstrate chronic effects will not be of concern and as such, can all be "blocked" together. Furthermore, for products that have no, or negligible, chronic toxicity in the environment (e.g. paraffinic lubricant base oils),

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* Such as the Dutch Uniform System for the Evaluation of Substances (USES) programme

there should be no requirement to carry out extensive environmental risk characterisation.

Release Estimates

Data on the tonnages of the different petroleum substances produced in the EU are available from open literature sources e.g. an OECD publication. [4]

The USES computer model [*] contains default values for the proportion of any substance released to air, water and soil through the product life cycle. Where possible, the use of actual data for petroleum substances is preferable. Release factors are estimated for each "block", based on physico-chemical properties. Data on environmental concentrations of petroleum substances and individual constituent hydrocarbons are being collated by CONCAWE and it is hoped to gather a more extensive base of "real-world" data to improve on the current default values included in the USES program. These data should allow some validation and refinement of some of the calculated PEC values.

Octanol - water partition coefficient (K_{ow})

The calculation method for Log K_{ow} values, CLOGP, is considered to be accurate for hydrocarbons and calculated values agree well with experimentally verified values, up to Log K_{ow} values around 6.

The major difficulty is with homologues having calculated log K_{ow} values above 6. The experimental methods to determine log K_{ow} are only valid up to values of 6 to 8 and, therefore, calculation methods cannot be validated beyond that point. Accordingly, it follows that any prediction based on a Log K_{ow} value (BCF, toxicity, etc.), may not be valid for chemicals with calculated log K_{ow} values greater than around 6. Calculation methods yield log K_{ow} values that increase incrementally with carbon number. It is inherently unlikely that the "real" log K_{ow} values above 6, if they could be measured, behave in this way. It is equally unlikely that other parameters estimated from log K_{ow} above 6, such as acute toxicity, BCF, soil sorption coefficient, etc., change in a linear way with changing carbon number. Indeed it is likely that values of some of these parameters may at least plateau. Experimental data on water solubility shows some indications of this (see above), as do data relating to BCF at values of log K_{ow} greater than approximately 6.7. [8]

Vapour pressure

Data are available on most of the lower homologues; extrapolation to higher homologues is uncertain and is complicated by the transition from liquid to solid phases. Methods for estimating vapour pressure have also been published. [6]

Water solubility

The best reference sources on measured solubilities of hydrocarbons in water are the IUPAC Solubility Data Series, [5,6] which review the published data critically. However data for many of the higher molecular weight hydrocarbons are variable and authors frequently state that measured values are in excess of values predicted by extrapolation from lower homologues.

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[*] A European version of the USES programme is currently being developed.

Methods for estimating water solubility have been published; [7] there are sufficient data and adequate quantitative structure activity relationships (QSARs) to provide water solubility estimates for "simple" hydrocarbons with log Pow values up to about 6. Above this point, data are unreliable and therefore, there is no firm basis for extrapolation. It may be necessary to carry out some accurate determinations of solubility in order to establish validated QSARs for such components.

Biodegradation

The issue of rate constants for biodegradation, whether in sewage treatment plants or in the environment, is extremely complex. For the purpose of running the risk assessment model (at least in the first instance) it should, however, be adequate to categorise "blocks" as either readily, inherently or not biodegradable. The model will assign set rate constants depending on the category chosen.

Limited data on biodegradation are available for single hydrocarbons, and it should be possible to assign each block to an appropriate category using chemical structure as a basis. Those "blocks" comprised solely of normal alkanes, normal alkenes and simple aromatics will qualify as being readily biodegradable.

Photooxidation

Photodegradation by reaction with OH radicals is the major loss process for hydrocarbons released to air. Data for the rates of reaction of many hydrocarbons with tropospheric ozone and OH radicals are available in the literature, [9] and there are also published calculation methods that can be used to predict rate constants. [9]

5. PREDICTED NO EFFECT CONCENTRATION

Ecotoxicity

Experimental data are available for comparatively few single hydrocarbons, but the use of $LC_{50}/EC_{50}/IC_{50}$ values derived from QSARs is well established for simple hydrocarbons. [3, 10, 11]

It is generally accepted that for chemicals with the same mode of action, acute toxicities can be considered as additive. [12, 13] There is increasing evidence that this is also true for chronic toxicity (see next section). [14] Petroleum hydrocarbons are for the great part composed of hydrocarbons which all act via a similar mode of toxic action, non-polar narcosis. [15, 16, 17] Thus it can be assumed that at least for the hydrocarbon components of petroleum substances, there will be simple additivity of toxicity.

The situation is less clear with regard to the additivity of toxicity for those components with different modes of action. However, even for these chemicals, it is possible to argue that at concentrations below their chronic toxicity effect level, those which have a specific mode of action will not contribute to the overall toxicity of a complex mixture, other than through their contribution to the non-polar narcosis effect of the mixture.

Certain petroleum substances contain non-hydrocarbon components, and special care must be taken when assessing these substances to ensure that "blocking" is appropriate and in particular, that the range of toxicities of components within the "block" is not unacceptably large. Where necessary, due account must be taken of differences in mode of action.

In running the USES model, PNEC may be estimated from values for acute toxicity subject to an "assessment factor" of 1000. For long-term ecosystem effects, the application of this assessment factor of 1000 is accepted as being conservative.

For particular petroleum substances, there may be a number of "blocks" for which no acute toxicity is indicated at the limit of water solubility for those "blocks". This does not necessarily mean that these "blocks" will not contribute to chronic toxic effects. Therefore, it is proposed that if no experimental data on chronic toxicity are available, default values for acute toxicity, equal to the water solubility value for the "block", be used in the initial assessment. If this leads to an indication of risk, then it may be necessary to generate specific chronic toxicity data.

There are experimental data to support a "cut-off" of acute aquatic toxicity for hydrocarbons with a carbon number greater than 14 and evidence to indicate that chemicals with a molecular weight greater than 700 are not taken up. [16, 18, 19] There is a need to determine experimentally if there is a non-linear dose-response relationship for chronic toxicity. The existence of such a relationship for chronic toxicity is considered to be likely as there is experimental evidence to support a non-linear dose response for bioaccumulation which indicates that for molecules with a Log K_{ow} greater than 6.7 prolonged exposure will not lead to an increase in body burden. [8, 10, 20]

Joint toxic action of mixtures of chemicals

On the basis of current knowledge Calamari and Vighi [21] and Broderius [12, 22] have concluded that the hypothesis of simple addition effects for molecules with similar modes of action constitutes the most reliable approach to establishing water quality objectives with respect to the combined toxic effects of chemical mixtures.

The concentration-addition model of Anderson and Weber [23] is based upon the precept that toxic components of a mixture, with a similar mode of action, act additively in expressing their effects on an organism - providing that neither component modifies the action of the other. To allow for differences in the potency of components, exposure concentrations are expressed in terms of "Toxic Units (TU)" i.e. as a proportion of their individual effect threshold concentration. Summing TUs for components of a mixture in solution provides an indication of whether a toxic threshold is likely to be exceeded as in the following example:

If xA and yB are the concentrations of two components in aqueous solution expressed as a proportion of its effect threshold concentration

- a toxic threshold is unlikely to be exceeded if: $xA + yB$ is <1
- but a toxic threshold is likely to be exceeded if: $xA + yB$ is >1

The principle of additivity of TU for chemicals with the same mode of acute toxic action has been widely demonstrated. [12, 24-34] Furthermore, the principle has been shown to apply even to very complex mixtures. For example, Konemann [30] and Deneer et al [25] have demonstrated additivity for mixtures containing 50 non-reactive organic chemicals, where each is represented by 0.02 TU.

Specific evidence that the principle of concentration addition can be applied to predicting the acute toxicity of hydrocarbon mixtures has been provided by Lee and Nicol [35] in tests with mixtures of naphthalene, 1,2,4-trimethylbenzene, o-cresol and o-toluidine. Cooper et al [36] has achieved similar results in tests with mixtures of hydrocarbons present in JP4 Jet Fuel.

Extension of the principle of concentration addition to predicting the chronic toxicity of chemical mixtures has been less extensively studied. However, Hermens et al [30] have shown that, for mixtures of alcohols and chlorobenzenes, the no observed effect concentration (NOEC) for effects on growth of Daphnia magna could be predicted on the basis of concentration addition. Similarly, Hermanutz et al [37] have shown that for mixtures of two pesticides (endrin and malathion) chronic effects on growth followed a simple additive effects model. Although Hermens et al [29] have demonstrated a slight deviation from concentration addition with mixtures of between 5 and 50 chemicals with the same anticipated mode of action, they are unable to conclude that the deviation is systematic on the basis of the limited information.

Although concerns have been expressed that chemical mixtures may exert greater than additive toxic effects (synergism), there is no clear experimental evidence to support this hypothesis. Indeed, following a series of experiments carried out with pesticide tank mixes, Matthiessen et al [32] concluded that synergism will prove to be "a rare occurrence" - a statement supported by Calamari and Vighi [17] and by Broderius [12] with respect to chemical contaminants likely to be found in rivers.

Undissolved product

An additional factor that needs to be considered with petroleum products is that they can enter the aquatic environment either in solution or as non-dissolved material in slicks or dispersions. The blanketing effects of non-dissolved material can be significant in some situations, but any effect will be relatively local. Within a few days of release, the lighter (more volatile) components, which are the most toxic to aquatic organisms, can be expected to have dissolved or evaporated. Non-dissolved material is, therefore, not considered when running a regional risk characterisation model for the aquatic compartment; it may however need to be taken into account when carrying out a local risk characterisation.

6. USE OF DATA DERIVED FROM QUANTITATIVE STRUCTURE-ACTIVITY RELATIONSHIPS (QSARS)

As outlined, the application of HBM will frequently be dependent on the use of QSARs for the estimation of physico-chemical properties (e.g log K_{ow}, water solubility, melting point and vapour pressure) and degradation rates (e.g. photodegradation and biodegradation rates) when measured values are not available. There are reasonably well accepted methods for the generation of these data using readily available databases or QSARs.

As noted, it is considered adequate, at least for initial assessments, if experimentally determined rate constants for the "blocks" of interest are not available, to classify "blocks" as readily, inherently or not biodegradable and to use appropriate estimates of rate constants.

The use of QSARs is well established for predicting the acute toxicity of simple hydrocarbons, and can be used to supplement the available ecotoxicity data. [3, 9] Whilst the accuracy of QSARs for more complex hydrocarbons and for chronic toxicity may need further consideration they provide an adequate default where experimental data are not available (in particular where the values are found not to be key to the outcome of the risk assessment).

7. RISK CHARACTERISATION

For a given petroleum substance, the PEC/PNEC ratios for each of the defined blocks are calculated and refined by reference to available monitoring data, etc. Finally, the proportionate sum of PEC/PNEC ratios can be calculated to derive an overall assessment of the risk to the environment posed by the "whole" petroleum substance.

Consideration of the PEC/PNEC ratios estimated for individual blocks may provide valuable information to help with the identification of those blocks which are the principal contributors to the overall PEC/PNEC ratio for the whole substance and, therefore, where refinement of the data, through for example the generation of experimental values as opposed to QSAR estimates, would be most valuable.

Risk characterisation for other environmental compartments

The present report has focused in particular on risk characterisation for the aquatic environment; this is due to the following reasons:

- this is generally considered to be the environmental compartment most at risk;
- as yet, there is little experience with the methodology for formally undertaking risk assessment of other environmental compartments;
- at the present time, relatively little ecotoxicity data for other environmental compartments exists.

However, the principles of the HBM are applicable to all environmental compartments and it is anticipated that as familiarity with the approach extends, knowledge will increase and it will prove possible to apply the method to the soil, sediment and air compartments.

Risk characterisation of other petroleum substances

The PEC/PNEC ratios developed for particular blocks of related hydrocarbons will be applicable to any of the petroleum substances in which these components are identified. Thus the risk characterisation process will be facilitated by the establishment of a database of information on blocks which are common to more than one petroleum substance.

Practical application of the HBM

The steps followed in applying the HBM approach to gasoline for the aquatic environment using data derived from measurement, computer calculation and QSAR predictions, are outlined in an Appendix to this report.

8. FUTURE DEVELOPMENT

It is apparent that this method may be applicable to other UVCB substances but this will need to be explored on a case-by-case basis. Its broader applicability will be determined by the ability to define acceptable "blocks" and to provide the necessary data to support the derivation of PECs and PNECs for the "blocks". Further, it will be necessary to justify the additivity of these blocks in order to derive an overall PEC/PNEC ratio.

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GLOSSARY

Terms used in environmental risk assessment.

BCF	Bioconcentration Factor (a measure of the potential of a substance to accumulate in organisms)
CAS	Chemical Abstracts Service
CLOGP	A widely-used computer program for estimating K_{ow} values
EC DGXI	Directorate General XI of the European Commission
EINECS	European Inventory of Existing Commercial Chemical Substances
EC_{50}	The concentration of a substance estimated to have a specified effect on 50% of an exposed group of organisms
HBM	Hydrocarbon Block Method
IC_{50}	The concentration of a substance estimated to have an inhibitory effect (on growth) in 50% of an exposed group of organisms
IUPAC	International Union of Pure and Applied Chemistry
K_{ow}	Octanol-water partition coefficient (physico-chemical parameter providing a first indication of the potential of a substance to bioaccumulate)
LC_{50}	The concentration of a substance estimated to kill 50% of an exposed group of organisms
OECD	Organisation for Economic Co-operation and Development
OH radicals	Hydroxyl radicals (reactive species formed in the atmosphere by photochemical reactions)
PEC	Predicted Environmental Concentration
PEC/PNEC ratio	Environmental risk quotient (ratio of PEC to PNEC)
PNEC	Predicted No Effect Concentration (estimated environmental concentration of a substance that should not cause adverse effects on environmental organisms)
QSAR	Quantitative Structure Activity Relationship (enabling reliable prediction of a physico-chemical property or biological effect)
TU	Toxic Unit (an expression of the toxicity of a component within a mixture)
USES	Dutch Uniform System for the Evaluation of Substances (computer program for estimating risk)
UVCB	Unknown or Variable Composition, complex reaction products and Biological materials
WAF	Water Accommodated Fraction (aqueous medium produced by mixing oil with water, followed by phase separation)

APPENDIX

APPLICATION OF THE HYDROCARBON BLOCK METHOD TO A BLENDED GASOLINE

The HBM is intended to be used in conjunction with a computerised fate model such as USES. An example of its application might be to undertake a local and regional risk characterisation for the aquatic compartment of the environment for a typical blended gasoline. The steps to be taken are summarised as follows:

1. The detailed composition of the gasoline would be obtained, by for example GC-MS analysis.

2. The hydrocarbons would be assigned to blocks based upon carbon number and generic hydrocarbon type. The number of blocks would be dependent on the actual species present. The number of blocks for a blended gasoline might be as follows:

Hydrocarbon type	Carbon number range	Number of blocks
n-Alkanes	C_3-C_{10}	7
iso-Alkanes	C_4-C_{10}	7
Cycloalkanes	C_5-C_{10}	5
Olefins	C_4-C_9	5
Benzene	C_6	1
Toluene	C_7	1
Alkylbenzenes	C_8-C_{11}	4
Naphthalene	C_{10}	1
Alkylnaphthalenes	C_{11}-C_{13}	3

3. The following technical data would be used in PEC and PNEC estimation for each of these 34 blocks:

   Water solubility
   log K_{ow} (K_{ow} = octanol/water partition coefficient)
   Vapour pressure
   Molecular weight
   Melting point
   Half life in air from reaction with hydroxyl radicals
   Half life in water from biodegradation
   Ecotoxicity data (fish, Daphnia, algae)

4. The annual production quantity of gasoline for a region would be estimated, together with the likely local production.

5. Annual release estimates for each block to waste-water would be estimated based on the physical properties of each block and the total gasoline release. The latter would depend on the production level of the gasoline.

6. For each block, fate models such as waste-water treatment, environmental partitioning, degradation, etc. are applied. Such models are contained within USES. The model then develops PEC values for each block.

7. PNEC values for each block are assigned based upon measured toxicity or QSAR values, using the appropriate application factors.

8. PEC/PNEC values for each block are then calculated and are summed proportionately, in order to calculate ratios for the blended gasoline, at both the local and regional levels.