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RIVM report 711701015

A proposal for revised Intervention Values for petroleum hydrocarbons ('minerale olie') on base of fractions of petroleum hydrocarbons

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Abstract

The Dutch intervention value ‘Total Petroleum Hydrocarbons - TPH’ (in Dutch ‘minerale olie’), has been revised using ecotoxicological and human toxicological data with respect to TPH fractions. Mainly in connection with the work of the Total Petroleum Hydrocarbon Criteria Working Group, human toxicological data were used to calculate the potential human risk for several TPH fractions in soil. The report presented here distinguishes serious soil contamination concentrations for 5 fractions of aliphatics and 5 fractions of aromatics. Since sound terrestrial ecotoxicological data related to TPH fractions are scarce, no HC50 levels could be calculated. The present Dutch method of analyzing TPH was concluded as possibly underestimating the (non-carcinogenic) human-toxicological risk of TPH from light fuels, like petrol. Replacing this method by a method to distinguish the TPH fractions (C5-C40) reviewed and to adopt the ten indicative levels for TPH fractions presented is recommended.

Preface

In the framework of the RIVM project ‘Main Evaluation of Intervention Values’ the Dutch Intervention Value for petroleum hydrocarbons (‘minerale olie’) has been reviewed in a literature study supervised by a TPH Working Group (‘Werkgroep minerale olie’), including the authors and the following members: Ir.J. Kuyper, province of Noord Holland; Dr.R. Theelen, TAUW Milieu, Ir.J. Tuinstra, IWACO, Soils Dept. and Dr.W. Veerkamp Shell, All Products.

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Samenvatting

De interventiewaarde voor minerale olie is geëvalueerd. De huidige interventiewaarden voor minerale olie zijn 5000 mg/kg droge stof voor bodem en 600 µg/l voor grondwater en hebben betrekking op de som van C10 tot en met C40 al dan niet vertakte alkanen. Deze interventiewaarden hebben geen (humaan- noch eco-) toxicologische basis.
Literatuuronderzoek is verricht naar ecotoxicologische en humaan-toxicologische data gericht op oliefracties, Total Petroleum Hydrocarbons (TPH). Betrouwbare terrestrisch data voor TPH-fracties zijn schaars, om deze reden zijn geen HC50 waarden (ecotoxicologische ernstige bodemverontreinigingsconcentraties) afgeleid. Aanbevolen wordt om TPH-fracties te onderscheiden welke relevant zijn voor het beschrijven van terrestrische ecotoxicologische effecten van petroleum hydrocarbons, om vervolgens de benodigde ecotoxicologische data te genereren om HC50 waarden voor minerale-oliefracties vast te kunnen stellen.
Humaantoxicologische data zijn gebruikt om het potentiële humane risico te berekenen voor diverse TPH fracties; het gaat hierbij om het niet-carcinogene risico. Hierbij is gebruik gemaakt van het werk van de Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). In het voorliggende rapport worden voor 5 fracties aliphaten en 5 fracties aromaten humaantoxicologische ernstige-bodemverontreinigings-concentraties voorgesteld. Vooral alifatische fracties (≤EC12) en aromatische fracties (≤EC16) zijn relevant voor het (niet-carcinogene) humane risico (zie hoodstuk 5 General conclusions and recommendations, Table 5.1).

Het beschouwen van TPH-fracties is zowel van belang voor humane als ecologische risico's; risico's bij blootstelling aan TPH kunnen op deze wijze genuanceerder geschat worden. Geconcludeerd wordt dat de huidig analysemethode onvoldoende informatie geeft om de humane risico van lichte oliefracties, als bijvoorbeeld benzine, te beschouwen. Aanbevolen wordt om de huidige analysemethoden voor het bepalen van de concentratie minerale olie (welke de som van C10-C40 verbindingen beschouwt) te vervangen door een analysemethode welke TPH-fracties onderscheidt in de range van C5-C40 en om de toetsing van in de praktijk gemeten gehalten te laten plaatsvinden aan de hand van de voorgestelde indicatieve niveaus (humane EBVC's) voor 10 TPH-fracties.
Analyse van BTEX en / of PAK in geval van TPH-mengsels blijft noodzakelijk om de carcinogene risico's van bodemverontreiniging met TPH te beschouwen.

Summary

The present Dutch Intervention Value for “mineral oil” (i.e. ‘Total Petroleum Hydrocarbons’), has been reviewed with respect to fractions of TPH and using ecotoxicological and human toxicological data. These present Intervention values are 5000 mg/kg dw for soil and 600 µg/l for groundwatertaking the sum of C10-C40 petroleum hydrocarbons into account. These Intervention Values are not (human- toxicologically or ecotoxicologically) risk based. Since sound terrestrial ecotoxicological data related to TPH fractions are scarce, no HC50 levels (ecotoxicologic serious soil contamination concentration) could be calculated. It is recommended to identify relevant TPH fractions to describe terrestrial ecotoxicological effects of petroleum hydrocarbons and then generating the necessary ecotoxicological data to derive HC50 values (ecotoxicologic serious soil contamination concentration).
Human toxicological data have been used to calculate the potential human (non carcinogenic) risk for several TPH fractions. These data are related mainly to the work of the Total Petroleum Hydrocarbon Criteria Working Group. The report presented distinguishes serious soil contamination concentrations for 5 fractions of aliphatics and 5 fractions of aromatics. Especially aliphatic fractions (to EC12) and fractions aromatics (to EC16) are relevant with respect to the (non-carcinogenic) human risk (see chapter 5 General conclusions and recommendations, Table 5.1).

Review of the TPH fractions is significant with respect to both human and ecological risks, since risks by exposure to TPH could be more pronounced.
It is concluded that the present method of analysing TPH (which considers the sum of C10-C40 petroleum hydrocarbons) gives insufficient information to consider the (non-carninogenic) human-toxicological risk of TPH in light fuels like petrol. It is recommended to replace this method by a method to distinguish aliphatic and aromatic fractions in the range C5-C40 and to adopt the 10 indicative levels presented for TPH fractions is recommended. Besides analysis of TPH fractions, BTEX and /or PAH analysis should be maintained to consider the carcinogenic risk of TPH.

1. Introduction

1.1 Scope of the report

The Dutch intervention value for petroleum hydrocarbons ('mineral oil') has been reviewed in the framework of the RIVM project 'Main Evaluation Intervention Values'. The present Dutch intervention values for 'mineral oil' are 5000 mg/kg dw for soil and 600 µg/l for groundwater. These intervention values, not founded on a risk-based approach, consider the sum of the fraction C10-C40. In this report, the present intervention value for 'mineral oil' (TPH) are reviewed, given the present state of scientific knowledgde; if reasons are found, revised intervention values for (fractions of) petroleum hydrocarbons will be proposed. The review is based on literature studies on ecotoxicological and human toxicological data.

This report will use the international conventional term 'Total Petroleum Hydrocarbons' (TPH) instead of 'mineral oil' to avoid confusion since the term 'mineral oil' (in English) is used to characterise particular petroleum hydrocarbon products known as 'medicinal white oils'.

In the case of soil contamination with mixtures (petroleum hydrocarbon products) Dutch regulations stipulate that the content of individual aromatic hydrocarbons (BTEX) and /or the sum of polyaromatic hydrocarbons (PAHs) also have to be considered. However, evaluation of the intervention values for BTEX and PAH are not considered in this report, but will be within the framework of the RIVM project 'Main Evaluation Intervention Values'.
Neither are additives (like TEL, TML and MTBE) considered.

The reviews of ecotoxicological and human toxicological available scientific knowledge are presented in Chapters 2 and 3, respectively. In Chapter 4 the human toxicogical information (MTRs and TCA) are used as input to calculate the potential human risk for several fractions of petroleum hydrocarbons. Chapter 5 gives general conclusions and recommendations.

1.2 Petroleum hydrocarbon products

Total petroleum hydrocarbons (TPHs) originate from crude oils. According to the WHO (1982) these petroleum crude oils can be broadly divided into paraffinic, asphaltic and mixed crude oils. Paraffinic crude oils are composed of aliphatic hydrocarbons (paraffins), paraffin wax (longer chain aliphatics) and high grade oils. Naphtha is the lightest of the paraffinic fraction, followed by kerosene fractions. Asphaltic crude oils contain larger concentrations of cycloaliphatics and high viscosity lubricating oils. Petroleum solvents, the product of crude oil distillation, are generally classified by boiling point range. Lubricants, greases and waxes are high boiling point fractions of crude oils. The heaviest, solid, fraction of crude oils are the residuals or bitumen.

TPHs are principally composed of carbon and hydrogen but may also contain oxygen, sulfur and nitrogen; hydrocarbons containing the latter two elements are referred to as heterocyclic compounds. General classes of TPH include (in order of increasing carbon number) petroleum-derived gases, liquefied gases, solvents, white spirits (C9-C11), kerosenes (C10-C16), jet fuels, diesel, automotive and railroad fuels, fuel and lubricating oils, bitumen compounds

and waxes. Chemically, the TPH can be broadly classified as straight and branched chain alkanes, straight and branched chain alkenes, cycloalkanes, cycloalkenes, straight-chain alkynes, alkyl benzenes, alkyl naphthalenes, naphtheno-benzenes and polynuclear aromatics. Mineral oil products appearing on the market are the result of treatment and blending processes of (primary and secondary) refinery products, the goal of which is to maintain a relatively constant composition and quality independent of the kind of crude oil that forms the starting point of the production. Appendix 2 summarises several important process streams in oil refinery, Appendix 3 summarises the main characteristics of refinery products (data taken from the product dossiers of CONCAWE).

An important feature of the TPH analytical methods is the use of the *equivalent carbon number* index (EC). The EC, representing equivalent boiling points for hydrocarbons (HCs), is based on equivalent retention times on a boiling point gaschromatographic column (a non-polar capillary column) normalised to n-alkanes. In other words, the EC number of a compound X represents the number of carbon atoms that an imaginary n-alkane should have in order to present exactly the same boiling point as compound X. Thus the EC numbers of n-alkanes equals their number of carbon atoms, while the EC numbers start to differ from the number of carbon atoms for the branched alkanes and the unsaturated and aromatic HCs. Some examples: n-hexane (C_6H_{14}), being a n-alkane, naturally has an EC of 6.0; 2,2-dimethyl butane (C_6H_{14}) has an EC of 5.37; methyl cyclopentane (C_6H_{14}) has an EC of 6.27, cis-2-hexene (C_6H_{12}) of 6.14 and benzene (C_6H_6) of 6.5.

Characterisation according to EC numbers is thus the physical characteristic that forms the basis for separating petroleum (and other) components in chemical analysis, and is also typically the way by which analytical laboratories routinely report carbon numbers for HCs evaluated by (boiling-point) gas chromatographic analysis.

1.3 Dutch Intervention Values for soil and groundwater

The Dutch Intervention Values for soil and groundwater are based on a potential human toxicological and potential ecotoxicological risk assesment. Above these Intervention Values a soil is considered to be seriously contaminated (VROM, 1994).

Restrictions have been put with respect to the minimum size of a contaminated area. In case that an average soil volume concentration of at least 25 m^3 or an average concentration in the porewater of a water-saturated soil volume of at least 100 m^3 exceeds the Intervention Value means that in principle remediation will be necessary. If so, the urgency of remediation has to be determined by actual risk assesment (VROM, 1994).

In 1994 the Intervention Values for soil and groundwater of the first series (Van den Berg and Roels, 1991) were formalized (VROM, 1994); 70 compounds were considered a.o. petroleum hydrocarbons (“minerale olie”). In 1997 the Soil Protection Guideline was extended by incorporating Intervention Values for the second (Van den Berg et al., 1994) and the third series (Kreule et al., 1995) of contaminants. In 1999 the Soil Protection Guideline was extended by incorporating standards for the fourth series of contaminants (Kreule and Swartjes, 1998) via Ministerial Circulars (VROM, 1997, 1999).

Derivation of the Intervention Values will be discussed in chapter 1.4.

1.4 Procedure leading to proposal for Intervention Values of soil and groundwater.

To derive a new Intervention Value the *human-toxicological* serious soil contamination concentrations (HUM-TOX SCCs) are derived and combined with the *ecological* serious soil contamination concentration (ECOTOX SCCs). The HUM-TOX SCCs are derived using the CSOIL human exposure model with the compound-specific physicochemical data and the Maximum Persmissible Risk values for intake (MPR_{human} values) as input data. Figure 1.1 shows the relation between the different steps leading to proposals for Intervention Values for soil and groundwater. In this report these different steps are discribed in chapter 2 (ECOTOX), chapter 3 (HUMTOX) and chapter 4 (Integration / proposal for intervention values for fractions of TPH).
All relevant information for the derivation of the HUM-TOX SCC and the integration of the ECOTOX SCC and HUM-TOX SCC has been summarised in the present report.

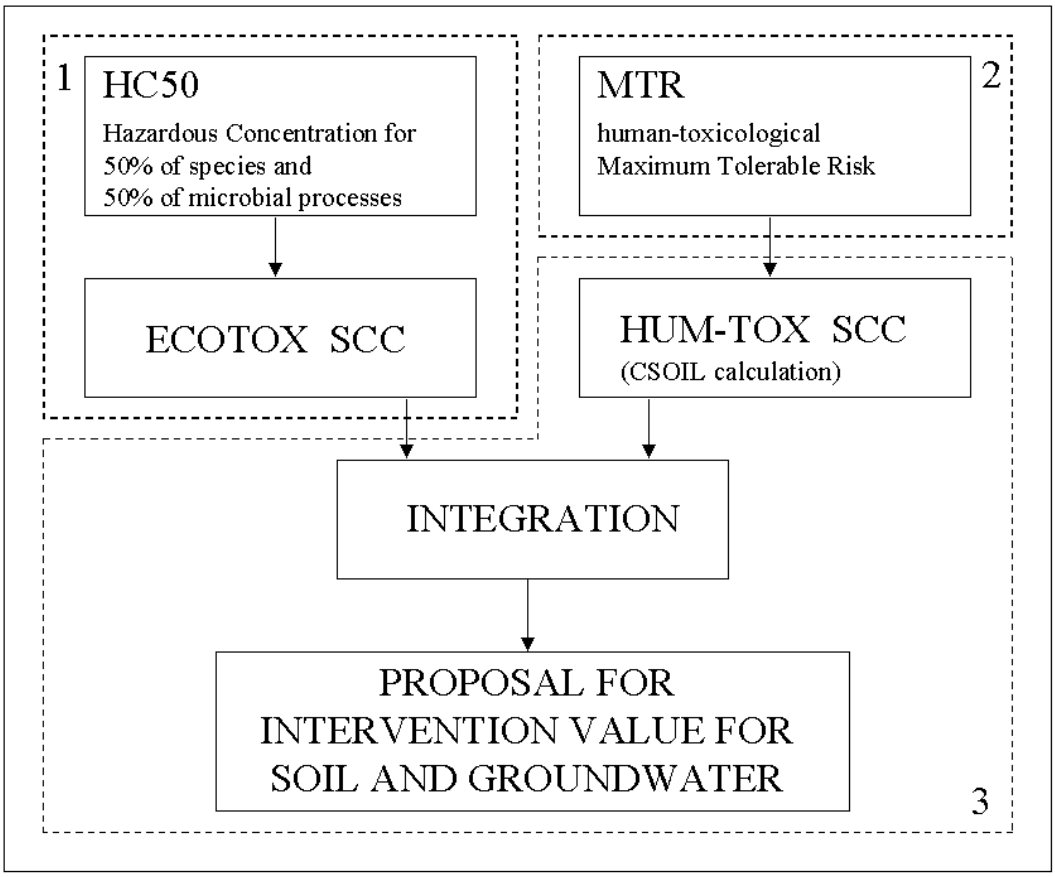

Figure 1.1 Steps leading to proposals for Intervention Values of soil and groundwater

The ecotoxicological criterion for serious soil contamination concentration is represented by the threat to 50% of the species and 50% of the microbial processes. It is assumed that species and processes are threatened if the NOEC (No-Observed-Effect-Concentration) for effects on vital life functions of species (like survival, growth and reproduction) and/or microbial and enzymatic processes are exceeded. If a substance has a potential for secondary poisoning, the possible adverse effects due to secundary poisoning are incorporated in the

criterion. The methodology used to derive the ecotoxicological criterion for serious soil contamination is described in as stepwise protocol (Crommentuijn et al., in prep).

The humantoxicological criterion for serious soil contamination is determined by the soil quality corresponding with the Maximum Permissible Risk for intake (MPR_{human}). For this reason, the HUM-TOX SCC is defined as the concentration of a contaminant in the soil which would result in an exposure equal to the MPR_{human} under standardized conditions (*potential* exposure), see figure 1.2. More information on derivation of "Maximum Permissible Risk levels for human intake of soil contaminants" is included in a guidance document (Janssen et al., 1997).

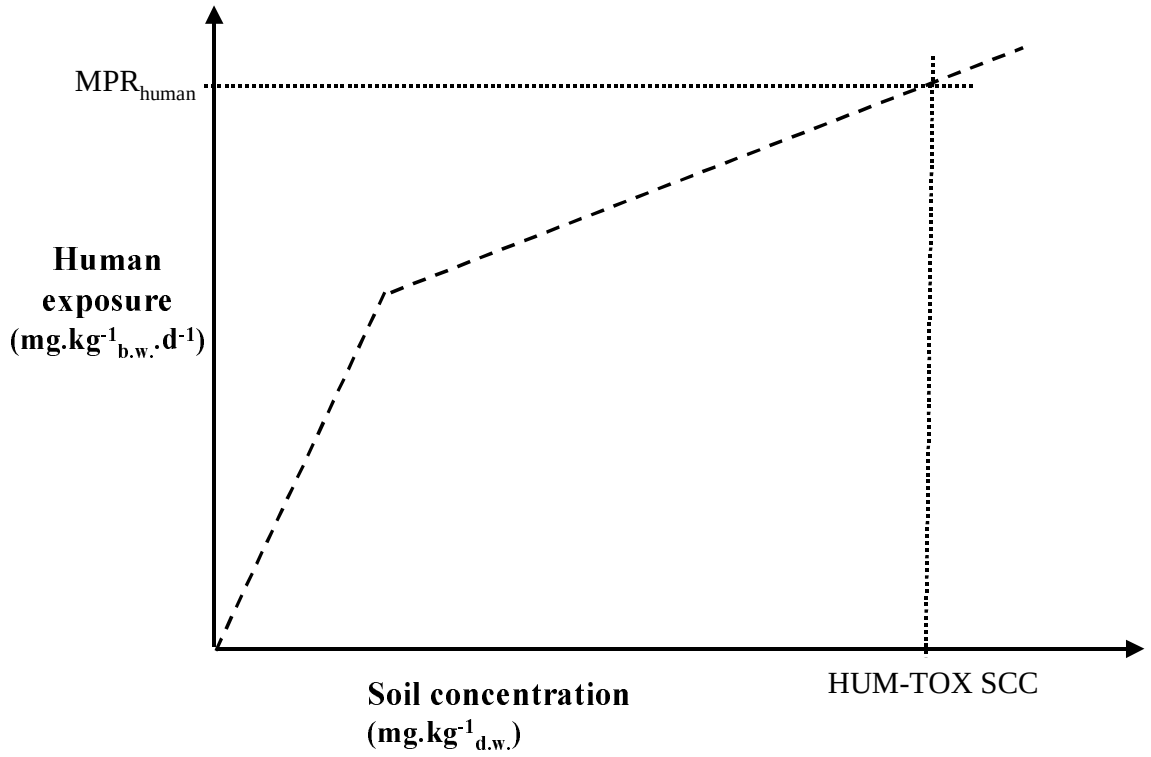

Figure 1.2 Derivation of the HUM-TOX SCC

The potential exposure is calculated using the CSOIL model. A standard exposure scenario has been defined to describe the standardized conditions (Van den Berg, 1995). In this scenario, all exposure pathways in CSOIL are assumed to be operational on the basis of exposure to contaminants in a residential situation. In case that the calculated indoor air concentration (an intermediate result) exceeds the TCA, the human toxicological intervention value for soil is corrected in such a way that the calculated indoor air concentration equals the TCA. In the next step the exposure from all pathways is calculated for children and adults separately. Finally, the mean lifelong exposure is calculated by summing up exposure of children and adults with a relative weight of $^{6}/_{70}$ (child during six years) and $^{64}/_{70}$ (adult during 64 years), respectively.

Groundwater

Direct human exposure to contaminants in groundwater in the Netherlands is unlikely. For this reason, the Intervention Values for groundwater have been derived from the Intervention Values for soil. The Intervention Value for groundwater is defined as the concentration in groundwater that is related to a soil concentration that equals the Intervention Value. This Intervention Value for groundwater is calculated on the basis of both the partitioning between the solid phase and pore water, and leaching into the groundwater. In a first step the equilibrium concentration in the pore water is calculated by dividing the Intervention Values for soil by an average partition coefficient. The equilibrium concentration in the groundwater is calculated by simply dividing the pore water concentration by a factor of 10, taking into account the uncertainty in the partition coefficient, lack of partitioning equilibrium, dilution processes and the heterogeneity of the leaching process. Degradation has not been taken into account.

However, the possible consumption of contaminated groundwater as drinking water has also been considered in a final step. When using groundwater that is contaminated to the level of the Intervention Value directly as drinking water results in unacceptable human exposure (i.e. exposure exceeds the MPR_{human}), the Intervention Value for groundwater is corrected in such a way that drinking this contaminated groundwater would result in an exposure exactly equal to the MPR_{human}. Finally, the Intervention Values for groundwater were compared to existing quality objectives for soil and groundwater, and with data generally representative of the groundwater in the Netherlands (data for relatively "clean" groundwater from the Dutch National Groundwater Quality Monitoring Network).

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2. Review of ecotoxicological data

2.1 Introduction

A literature search was performed to evaluate whether it is possible to derive ECOTOX SCCs for fractions of petroleum hydrocarbons.

The results of the literature search will be described in this section, starting with the standard procedure to derive ECOTOX SCCs in 2.2.1, proceeding to remarks on this procedure when considering petroleum hydrocarbons in 2.2.2, followed by publications dealing with possible approaches to derive ECOTOX SCCs for fractions of petroleum hydrocarbons, as described in 2.3.1. The publications dealing with terrestrial ecotoxicological effects from oil are described in section 2.3.2. In the summary and conclusions (section 2.4) proposals are made for possible steps to be taken to derive ECOTOX SCCs for fractions of petroleum hydrocarbons.

2.2 Procedure to derive ECOTOX SCCs

2.2.1 Standard Procedure to derive ECOTOX SCCs for single compounds

The procedure followed to derive ECOTOX SCCs is described in detail in Crommentuijn et al. (1994), which will be revised by Crommentuijn et al. (in prep). Figure 2.1 gives a schematic presentation of the procedure. A detailed description of quality criteria applied when evaluating the literature is described in the Quality System of the Centre for Substances and Risk Assessment CSR (1996).

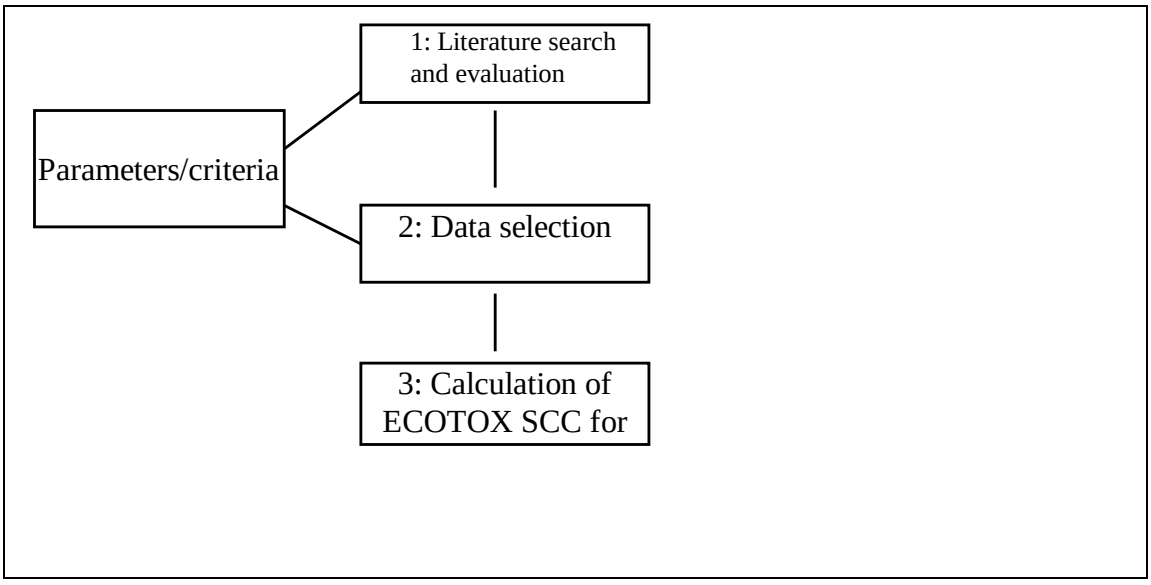

Figure 2.1 Schematic presentation of the procedure to derive the ECOTOX SCC.

2.2.2 Remarks on standard procedure when considering TPH

1) ECOTOX SCCs are derived for single compounds. Group or sum values are derived only when it is known or can be assumed that the individual compounds considered in the group value have the same mode of action. Group values for ecotoxicological effects have been proposed, for instance, for the chloroanilines (Reuther et al., 1998; Posthumus et al., 1998). TPH is a complex mixture of different compounds (see, for instance, Van Dijk-Looyard et al., 1988 and Evers et al., 1997). Hydrocarbons are the most dominant fraction in TPH. Besides this, most oils also contain other elements (e.g. N, S, P) and metals (V, Ni, Fe). These different compounds have different physico-chemical characteristics and different modes of action. Each type of TPH is a different mixture of compounds; since these compounds having different modes of action, it is not possible to derive one single value for TPH.

2) If no, or only a limited amount, of terrestrial data are available, the equilibrium partitioning method (EP-method) can be used to derive a preliminary ECOTOX SCCs. Applying the EP-method leads to derivation of an ECOTOX SCC on the basis of aquatic toxicity data and using a partition coefficient. But even aquatic toxicity data for TPH are not available (see 1). Besides this, it is also impossible to derive one single partition coefficient for TPH-fractions. Based on these two considerations a value based on the EP-method, cannot be derived when the standard procedure is followed.

3) Besides toxic effects, physical effects may also occur if soil organisms are exposed to fractions of petroleum hydrocarbons. It is not clear yet at what concentrations these effects occur and, when considered relevant, how to incorporate them in an ECOTOX SCC.

2.3 Results

Two types of publications were searched: 1) Publications describing approaches that can be used to derive ECOTOX SCCs for fractions of petroleum hydrocarbons, 2) Publications dealing with ecotoxicological effects of fractions of petroleum hydrocarbons on terrestrial species and processes. Besides this, so-called grey literature was searched by contacting scientists doing research on fractions of petroleum hydrocarbons and quality standards in general.

2.3.1 Possible approaches to deriving ECOTOX SCCs

The literature describes several approaches that may be used to derive ECOTOX SCCs for fractions of petroleum hydrocarbons. The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) has proposed three different approaches for evaluating actual human risks of soil oil pollution (TPHCWG, 1997b): (1) Indicator approach, (2) Whole product approach and (3) Fraction approach (the TPHCWG representing an USA consortium of state regulatory agencies, academia, the US Department of Defence and Department of Energy, USEPA, ATSDR, petroleum, power and transportation industries and consulting firms). Although intended to deal with actual human risks, these approaches can be used for evaluating potential ecotoxicological risks as well. Depending on the approach chosen, it is, however, necessary that effect data for terrestrial species and processes be expressed in a specified 'format'. The Hydrocarbon Block Method is proposed by CONCAWE (King et al., 1996) to derive PNECs (Potential No Effect Concentration) for oil. This approach is in principle the

same as the fraction approach, proposed by the (TPHCWG, 1997b). The different approaches are summarised below:

1. *Indicator approach*. (TPHCWG, 1997b). This approach is based on the most toxic compounds of mineral oil. Data for these extremely toxic compounds should be available. Values have been derived in the past for several compounds, also included in TPH, e.g. PAHs (Denneman and Van Gestel, 1990; Kalf et al., 1995) and metals (Denneman and Van Gestel, 1990; Crommentuijn et al., 1998). Although this approach has already been dealt with, it is not clear which compounds should be considered as the most toxic for the terrestrial environment, making it therefore difficult to evaluate whether the most toxic compounds have been covered already.

2. *Whole product approach*. (TPHCWG, 1997). This approach is based on petroleum hydrocarbons products. Terrestrial data on ecotoxicological effects for total TPH should be available. However, the mixtures referred to as petroleum hydrocarbons products are different in composition. The varying composition of petroleum hydrocarbons makes it difficult to compare results from different experiments. (see remarks made considering the standard procedure, section 2.2.2). Besides this, the process of ageing will change the composition of oil in time. This makes the comparison of results from short-term fieldexperiments, in which oil is added to soil at the start of the experiment, difficult.

3. *Fraction approach* or *Hydrocarbon Block Method* (King et al., 1996; TPHCWG, 1997). This approach is based on specified hydrocarbon fractions of petroleum hydrocarbons and the assumption that the individual compounds of the fraction have the same mode of action. In principle, the toxicity of such groups can be evaluated as a group. Data should be expressed as the concentration of a certain specified fraction in soil. It is not clear yet, whether the seven fractions proposed by the TPHCWG (1997) can also be used for ecotoxicological effects. From experiments with the sediment organism *Corophium volutator* it was concluded that the C5-C20 attributed the most to the toxicity of the oils tested (Scholten et al., 1997). An advantage of this method is that concentrations are expressed in such a way that results from freshly added oil in laboratory experiments are directly comparable with aged concentrations in the field.

Several steps are necessary to derive a Predicted No Effect Concentration (PNEC) (see King et al., 1996). The PNEC has to be specified on the basis of a predefined tolerable effect. In the case of the ECOTOX SCCs it is proposed to specify the PNEC as the concentration representing in a serious threat for the ecosystem. This is the concentration that is potentially hazardous for 50% of the species in an ecosystem or the HC50. The following steps are then necessary to derive ECOTOX SCCs for different 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 effect data such as NOECs and/or L(E)C50s, expressed as a concentration of the defined block.
- Calculate the HC50 for each block.

This method has been proposed for use in risk characterisation for the aquatic environment by CONCAWE (King et al., 1996) and has been validated by Verbruggen and Hermens (1997).

However, recalculating an aquatic value based on a block into a terrestrial value has the disadvantage that one single partition coefficient is not available. Besides this, the HBM method takes care of hydrocarbons only, without considering effects of other elements and compounds in petroleum hydrocarbons.

The fraction approach is also proposed to derive HUM-TOX SCCs (see Chapter 3) and a Maximum Permissible Concentration (MPC) for the sediment compartment (Evers et al., 1997; Scholten et al., 1997). Considering the sediment MPC ecotoxicological effect data are generated, at the moment, using four different sediment species. Results for the sediment compartment will be available at the end of 1999.

2.3.2 Data availability

At the start of the literature survey data on aquatic species, both on terrestrial species and processes, have been searched for. A large number of publications were found in which effects of petroleum hydrocarbons on, especially, marine aquatic species, are considered. Scholten et al. (1993), Evers et al. (1997) and CONCAWE (1996) have reviewed aquatic effects of petroleum hydrocarbons. All aquatic publications describe effects of different types of oil and drilling fluids typical for the marine environment; these are often expressed as the Water Accommodated Fraction (WAF). For effects on marine species EC50 concentrations ranging from 20 ug/l – 300,000 ug/l for different types of oil were found (Scholten et al., 1993). Because of the limitations of the aquatic data to be used to derive ECOTOX SCCs for soil (see 2.2 remarks 1 and 2), the resulting references have not been evaluated.

All publications dealing with terrestrial effects are based on experiments with different types of petroleum hydrocarbons. From a first selection of 41 papers, nine references were selected for further evaluation. (Dorn et al., 1998; Salanitro et al., 1997). EC50s for the earthworm species *Eisenia foetida* could be derived from two publications. All the EC50s are, however, based on experiments with different types of oil and show a large variation. EC50s for this species ranged from 30-71,000 mg/kg oil. As already indicated in section 2.2, no accurate proposal for ECOTOX SCCs for fractions of petroleum hydrocarbons could be derived.

Publications dealing with bioassays were not selected for further evaluation. Bioassays are performed to evaluate the actual risks at a certain site or to evaluate the effectiveness of bioremediation (Brouwer et al., 1998; Van den Munckhof et al., 1998). Although very useful for the intended aim, the results of these bioassays are not useful for deriving generic risk limits like the ECOTOX SCC. In bioassays different field soils with different characteristics are used in one experiment and treatments are therefore not comparable. A control treatment is not always included and the field soils used may contain other toxic substances as well. (in Appendix 4 summaries of two bioasssay studies are given as an example).

After evaluating the selected nine publications in detail according to the evaluation procedure as described in the Quality System (CSR, 1996) no effect data could be derived. In Appendix 5 a short summary of these nine studies is presented. When deriving ECOTOX-SCCs or MPCs publications as summarised in Appendix 5 are normally included in a report as ‘evaluated but rejected’. These data are not used to derive risk limits. The studies are rejected for the following reasons:

1) Different types of oil are used which are not comparable.

2) No control treatment is included. In this case it is not possible to relate the performance found in the treatments with the performance if no oil is added.

3) Not enough treatments are included. In this case no dose-effect relationship can be evaluated.

4) There is no specification of soil characteristics. It is not possible to recalculate risk limits into results for a standard soil.

5) No soil is used in experiment. For instance, filter paper test results cannot be converted to soil concentrations. Besides this, test conditions are created that may be stressful for the species. Effects may be related to test conditions themselves instead of to the toxic substance.

The American Petroleum Institute (API) and Environment Canada have been consulted to find (as yet) unpublished tests, but no results are available yet. Both Environment Canada and the API are developing tests for ecotoxicological risk assessment for petroleum hydrocarbons in soils.

Results of tests for the sediment compartment using *Corophium volutator* have been published by Scholten et al. (1997). This study was performed in order to explore the possibilities for deriving a MPC for the sediment compartment based on toxicity tests with sediment dwelling organisms. Based on this study, tests with three other sediment organisms have been performed. Results will be available at the end of 1999. It should, however, be discussed whether data for the sediment compartment can be used for terrestrial effect assessment as well.

2.4 Summary and Conclusions

Three possible approaches for deriving an ECOTOX SCCs follow:

1. Indicator approach. This approach has already been dealt with because for some single compounds included in petroleum, e.g. PAHs, hydrocarbon values have been derived. It is however not clear which compounds should be considered as the most toxic for the terrestrial environment and it is therefore difficult to evaluate whether the most toxic compounds are already covered.

2. Whole product approach. Reliable data on terrestrial species and processes are not available. Besides this, it is not possible to derive one single value for petroleum hydrocarbons as the composition of different oils is not comparable. Deriving a value on the basis of aquatic data is not proposed, because most effect data for the aquatic environment are based on TPH and drilling fluids typical for the marine environment. Besides this, it is not possible to derive one single partition coefficient for TPH, necessary to recalculate an aquatic HC50 into a terrestrial value.

3. The fraction approach or Hydrocarbon block method. This approach seems to be the most promising for derivation of ECOTOX SCCs for three reasons: a) effect concentrations from laboratory experiments are directly comparable with concentrations in the field; b) the approach has been proposed by several other organisations and countries; c) the approach is also chosen for deriving the HUM-TOX SCCs.

The relevant terrestrial ecotoxicological data for deriving ECOTOX SCCs following the fraction approach or Hydrocarbon block method are not yet available. The available data are all based on bioassays and do not pass the quality criteria proposed to evaluate data from literature (CSR, 1996). As argued by the Technical Soil Protection Committee (TCB, 1996), in the absence of any available terrestrial data, ECOTOX SCCs should not be proposed. In this case terrestrial data would have to be generated. ECOTOX SCCs should preferably be based on terrestrial data and EP can be used if at least some terrestrial data are available, since applying the EP method will introduce extra uncertainties.

Another argument for not proposing an ECOTOX SCC at the moment is the fact that data will become available in the near future (Environment Canada, American Petroleum Institute, tests with sediment species). It is, however, not clear at the moment whether these data will be suitable for deriving ECOTOX SCCs applying the Hydrocarbon block method for soil.

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3. Review of human toxicological data

3.1 Introduction

A human-toxicological MPR (Maximum Permissible Risk *1) for ‘mineral oil’ was established in 1993 [Vermeire, 1993], while in 1995 a MPR was derived for high boiling aromatic solvents or ‘C9 aromatic Naphtha’ *2 [Janssen et al., 1995].

The relevant exposure to ‘mineral oil’ was considered to be oral [Vermeire, 1993]. There were only very limited toxicity data and the available studies did not allow for the estimation of a NOAEL or LOAEL. However, a dietary dose of 5 % for rats (equivalent to 2500 mg/kg body weight [bw] per day) during full life-span was not harmful. Applying a safety factor of 100 resulted in a MPR of 25 mg/kg bw per day.
Remark: According to the present state-of-the-art, however, this approach (i.e. the assumption that a dietary dose of 5 % is not harmful) is no longer considered very reliable.

Oral, inhalatory and dermal exposure were all considered relevant for 'C9 aromatic Naphtha' [Janssen et al., 1995]. Toxicity data were scarce, so the basis for the TDI estimation was a 12 months inhalatory study in the rat, which resulted in a NOAEL of 450 mg/m^3 (corrected for exposure time: 80 mg/m^3). Applying a safety factor of 100 resulted in a TCA of 0.8 mg/m^3, and via route-to-route extrapolation in a provisional MPR of 0.17 mg/kg bw per day.

The present report deals with an approach to evaluate TPH contaminated soil by splitting up the oil mixture in a limited number of fractions of hydrocarbon compounds, which are then evaluated on the basis of their physical-chemical and toxicological characteristics. Only carcinogenic oil compounds (like benzene and some polycyclic aromatic hydrocarbons) need to be evaluated separately; this carcinogenic risk evaluation is not discussed here.

3.2 Toxicology

3.2.1 Introduction

The toxicology of some mixtures such as diesel fuel, fuel oils and petrol, and of chemicals such as benzene, 1,3-butadiene, toluene and xylenes, has been extensively evaluated by regulatory and governmental agencies and institutes such as the US Agency for Toxic Substances and Disease Registry (ATSDR), the International Agency for Research on Cancer (IARC), the International Programme on Chemical Safety (IPCS), the US Environmental

*1 For practical use the MPR is equivalent to the TDI (Tolerable Daily Intake)

*2 High boiling aromatic solvents is a standard mixture of substances indicated as ‘C9-aromatic Naphtha’ and defined by the International Research and Development Corporation to include oxylene (3.2%), i-isopropyl benzene (2.74%), n-propyl benzene (3.97 %), 1-methyl-4-ethyl benzene (7.05%), 1-methyl-3-ethyl benzene (15.1%), 1-methyl-2-ethyl benzene (5.44%), 1,3,5-trimethyl benzene (8.37%), 1,2,4-trimethyl-benzene (40.5%), 1,2,3-trimethyl benzene (6,18%) and ≥C10 alkyl benzenes (6,.19%).

Protection Agency (USEPA), the UK Health and Safety Executive (UKHSE) and the Dutch National Institute of Public Health and the Environment (RIVM).
The toxicological information of many constituents is limited. In 1997 the TPHCWG, examining information on 254 chemicals in the C3-C26 range, identified approximately 65 compounds as possible surrogates for other petroleum hydrocarbons; useful toxicological information was also available on these compounds [TPHCWG, 1997a,b], which was essentially confirmed and adopted by the ATSDR [1998]. In addition, CONCAWE has started publication of some 11 reports summarising the available information on toxicity etc. of a number of principal oil products; nine of these reports have already appeared since 1992 [CONCAWE 1992a-c; 1993; 1994; 1995; 1997; 1998].

3.2.2 Acute exposure

In general, low molecular weight petroleum distillates are poorly absorbed from the gastrointestinal tract and do not cause appreciable systemic toxicity by ingestion unless inhalation occurs, in which case primary effects include pulmonary damage and transient CNS depression or excitation. Inhalation exposure to volatile petroleum hydrocarbons such as low molecular weight aromatics and aliphatics, including petrol, may result in cardiac arrhythmias and CNS depression. Case reports of renal and haematological effects have also been recorded from acute high exposure. Gases such as methane, ethane and propane may cause asphyxiation in confined spaces.

Dermal effects from short-term exposure to relatively high concentrations of solvents may include irritant and defatting effects; exposure to lubricating oils, greases and waxes may result in skin disorders such as primary irritation, oil acne, hyperkeratosis and photosensitivity.

Testing the acute oral toxicity of 19 selected petroleum hydrocarbons in rats resulted in LD_{50} values from 4700 mg/kg bw (heavy fuel oil “#6”, containing 1.2% S) to 17,500 mg/kg bw (home heating oil 50% “#2”). Of the 19 petroleum hydrocarbons evaluated, six did not induce mortality at 23,000 mg/kg bw and lubricating oils did not induce mortality at 5000 mg/kg bw. The selection included unleaded petrol, five middle distillates (three “#2” fuel oils, four “#6” fuel oils) and seven lubricating oils (5 paraffinic and 2 naphthenic base stocks).

The middle distillates (HCs with carbon numbers of approximately 6-20) proved to be the most irritating and toxic of the streams examined. Heavy fuel oils produced the most severe eye irritation while the middle distillates produced the most severe dermal irritation. Contact with diesel fuel resulted in dermal blisters while paraffinic and naphthenic oils were the least reactive. Only “#6” heavy fuel oil (0.8% S) demonstrated dermal sensitising potential, with mild reactions being produced.

The category of heavy fuel oils was shown to have a dermal LD_{50} in the rabbit of >2000 to >5000 mg/kg bw.

3.2.3 Subacute and (sub)chronic exposure

The scarce data available are restricted to inhalation studies and indicate mainly nephrotoxic and pulmonary effects. Rats exposed to jet fuel (JP-5) vapour for 60 days developed slight nephropathy at an exposure level of 2900 mg/m^3 (male rats only); in a 90-days study with rats and dogs exposed to vapour concentrations of 150 and 750 mg/m^3 jet fuel (JP-5), male rats

showed dose-related slight nephropathy; the same effects were seen in a 12-month study with rats exposed to jet fuel (JP-5) vapour at concentration levels of 1000 and 5000 mg/m^3 (6 h per day, 5 days per week). A further a 90-day study with rats and mice continuously exposed to marine diesel fuel vapour in the concentration range of 150-750 mg/m^3 resulted also in dose-dependant nephropathy in male rats only. Exposure of rats to vaporised unleaded petrol for 3 months (6 h per day, 5 days per week) at concentrations levels of 90, 1250 or 9950 mg/m^3 resulted likewise in male rat nephropathy. The toxic effects in male rat kidney observed with various HCs are the result of a complex accumulation process that starts with the interaction of HC metabolites and alpha-2μ-globulin. The accumulation causes tubular cell damage and increased cellular proliferation, which enhances the probability of tumour development. Neither nephrotoxicity nor the subsequent carcinogenesis occurs when alpha-2μ-globulin is not produced in substantial amounts (such as in female rats, mice or other animal species, including humans).

Rats exposed to aerosolised diesel fuel concentrations of 1300-6000 mg/m^3 (for 2 hours, 3 times per week for 3 weeks, or once per week for a total of 6 hours over 9 weeks) did not show signs of neurotoxicity, but did show an increase in focal accumulation of free cells in the lungs, thickening and hypocellularity of alveolar walls, and a decreased total lung capacity. Reductions in respiratory rate, pulmonary hyperaemia, leucocytosis, monocytosis and decreased erythrocyte sedimentation rate were observed in a study in which rats, mice, rabbits and cats were exposed to kerosene aerosol concentrations of 50-120000 mg/m^3 for up to four weeks (the kerosenes used were characterised as standard lighting grade, and export grades A and B). Histological examination revealed inflammatory changes in the respiratory tracts. Rats exposed to an aerosol of solvent-extracted paraffin oil for 9 days at concentrations of 50, 500 or 1500 mg/m^3 developed dermal irritation and clinical signs of CNS depression at the two highest dose levels, accompanied by microscopic evidence of inflammation and irritation in pulmonary tissue at the highest dose level. A 4-week study with rats exposed to aerosol concentrations of 50, 210 or 1000 mg/m^3 (6 h per day, 5 days per week) of solvent-extracted 100 SUS oil or washed white oils showed a dose-related increase of lung weights associated with accumulations of foamy alveolar macrophages, but no clinical signs of toxicity.

3.2.4 Developmental and reproductive toxicity

Heavy fuel oils showed maternal and foetal toxic effects in rats (19 days dermal exposure starting at day 0 of gestation) at the respective doses of 8 mg and 30 mg (LOAELs), catalytically cracked clarified oil per kg bw per day. In similar experiments, clarified slurry oil had a LOAEL of 30 mg/kg bw per day, for heavy coker oil this value was 125, and for heavy vacuum gas oil it was 500 mg/kg bw per day (both maternal and foetal toxicity).

In a study to evaluate adverse reproductive effects, dermal application of clarified slurry oil to rats showed non-reproductive toxic effects in males and females with NOAELs of 1 and 10 mg/kg bw per day, respectively, while the reproductive NOAEL rats showed >250 mg/kg bw per day (both sexes).

No abnormal development was seen in the offspring of rats dermally exposed to three lubricating oil basestocks (up to 2000 mg/kg bw per day) on gestation days 0-19. Gavage administration to rats of 5 ml/kg bw per day of a highly refined white oil on days 6-19 of gestation did not produce any sign of teratogenicity. The same dose regimen applied for 13

weeks after which treated male and female rats were allowed to breed, did not show any abnormality in the offspring.

Diesel fuel (inhalatory exposure) or gas oils (dermal application) did not show foetotoxic or teratogenic effects in rats at dose levels below the level(s) at which maternal toxicity was observed (maternal LOAELs varying between 30 and 1000 mg/kg bw per day). Rats exposed to kerosene (760 or 2,600 mg/m^3, 6 h/day, gestation days 6-15) did not show adverse effects in either the dams or the progeny. Similar results were obtained in a study with jet fuel A (0, 700 and 2800 mg/m^3).

3.2.5 Carcinogenicity

The carcinogenic risk classification of a number of TPHs as evaluated by the IARC [1987; 1989] is shown in Table 3.1.

Table 3.1 Carcinogenic risk evaluations for some TPH [IARC, 1987; 1989]

Chemical	IARC classification group *)
Crude oil	3
Mineral oil - untreated and mildly-treated	1
Mineral oil - highly refined	3
Petrol/gasoline(unleaded)	2B
Jet fuel	3
Light fuel oils and light diesel oils	3
Residual (heavy) fuel oils and marine diesel fuel	2B
Mineral based crankcase oil	3
Benzene	1
Ethyl benzene	NR
Toluene	3
Xylene	3
n-Hexane	NR
Benzo(a)pyrene	2A
Benzo(b)fluoranthrene	2B
Dibenzo(a,h)anthracene	2A
Methyl *tert.* butyl ether (MBTE)	NR
1,2-Butadiene	2A

*) Group 1: human carcinogen
Group 2A: probably carcinogenic to humans
Group 2B: possibly carcinogenic to humans
Group 3: not classifiable
NR: not reviewed

Human epidemiological studies have demonstrated the association of petroleum hydrocarbon exposures with various adverse health outcomes. Exposure to TPHs that have been used in a variety of occupations, including mulespinning, metal machining and jute processing, has been intensely and consistently associated with the occurrence of squamous-cell cancers of the skin, and especially of the scrotum. Occupational exposure to twelve petroleum-derived liquids suggested increased risk of cancers from exposure to automotive and aviation petrol, mineral spirits, diesel fuel, and lubricating and cutting oils. Oil and gas fieldwork seemed to be associated with acute myelogenous leukaemia, but this was not found in more updated studies. An increased risk of renal adenocarcinomas was seen for refinery and petrochemical workers and from occupational exposures to petrol.

Environmental exposures within residential localities have been reported to increase bone, brain and bladder cancer deaths of children and adolescents living in a residential area near three large petroleum and petrochemical complexes. Neurophysiological and neurological

impairment in residents (with up to 17 years residence) living adjacent to an oil processing and Superfund site was also reported.

Dermal carcinogenic potential of petroleum hydrocarbons was demonstrated by an increased incidence of squamous cell carcinomas and fibrocarcinomas in male mice treated with dewaxed heavy paraffin distillate in lifetime skin painting studies. Petroleum distillates with boiling points below those of polycyclic aromatic hydrocarbons (generally responsible for dermal carcinogenic responses) were reported to have weak tumourigenic activity, a finding that was supported in three other studies.
Chronic (life-time) studies are not available.

3.3 Approaches to asses the maximum permisible risk for intake of TPH

3.3.1 Introduction

In order to develop human health-based TDI(s) as the starting point for estimating cleanup levels for petroleum hydrocarbons in contaminated areas, three principally different approaches are conceivable: (1) the use of toxicity data for the whole mixture or parent product (e.g. diesel fuel, petrol, jet fuel, etc.), (2) the identification and quantification of all individual components, followed by a full risk assessment of these components and (3) the use of an indicator and/or surrogate approach to assess the toxicity and risk posed by the mixture.

Ideally any hazard assessment should be based on the compounds (that is: all individual compounds) to which the receptor of concern is exposed. On the other hand, utilising data on the actual mixture present would account accurately for the interactive effects of all compounds in the mixture. However, data on all individual components are currently not available, making these approaches impractical and in fact inapplicable. The data available are: (1) data on some whole mixtures or parent products, (2) data on some individual compounds, namely important indicators such as benzene and benzo(a)pyrene, and (3) data on some fraction-specific mixtures.

Toxicity data on whole mixtures or parent products are only available for some petrols, some jet fuels, and medicinal white oil. Thus for other parent products (such as bunker fuel, diesel, lube oils, etc.) a whole mixture approach is not possible. Moreover, once released in the environment the parent product separates into fractions based on differences in fate and transport. Thus the mixture to which a receptor is exposed will vary with space, time and by media. Finally, there are no toxicity data on weathered fraction-specific mixtures or mixtures of parent compounds (such as mixtures of diesel and petrol). Hence, a whole mixture approach is not appropriate for a weathered release, but is only feasible for the hazard assessment of a fresh release of a single, known product for which toxicity data are available.

Recently (1994-1998) a number of approaches were reported, all of which recognised the need to be based upon reliable scientific data and at the same time the necessity to be feasible in generally encountered polluted situations. All apply the indicator/surrogate principle outlined above; these include the methods developed by the Massachusetts Department of

Environmental Protection (MDEP-USA) [Hutcheson et al., 1996], the method described by Staats et al. [1997], the results of efforts of the TPHCWG [TPHCWG, 1997a,b, and finally the recent ATSDR draft report [1998].

Comparing these approaches, the one developed by Hutcheson et al. [1996] offers the virtual advantage of a fairly simple level of operation, only discriminating between 4 subgroups, 3 of which are concerned with saturated HCs (alkanes, cycloalkanes and isoalkanes) and the 4th covering all aromatic compounds. However, this approach is considered to be an oversimplification of the complex composition of TPH at contaminated sites seen in practice. Moreover, the scientific basis of 2 out of the 4 RfDs [1]) is rather weak.

The method as developed by Staats et al. [1997] is not only more detailed but has a better scientific basis as well, and offers the possibility to discriminate between soils contaminated with neat petroleum products of known composition and (weathered) soils contaminated with unknown TPH. However, as with Hutcheson et al., this method too requires a detailed chemical analysis; if this analysis does not allow a risk assessment based on one or more neat petroleum products, then also here rather few surrogates/indicator data are available to serve as the basis for risk assessment, again resulting in an oversimplification of the complex composition of the TPH at contaminated sites seen in practice.

In contrast with Hutcheson et al. [1996] and Staats et al. [1997] the TPHCWG approach [1997a,b] discriminates between a reasonable number of groups (defined as 'fractions') and thus allows a more detailed risk assessment while still being feasible in practice. The approach has its scientific basis in an in-depth evaluation of the available toxicity data. In short, the TPHCWG-methodology (see Figure 3.1) evaluates as the first step individual carcinogenic indicators to which the receptor is exposed, which is consistent with USEPA methodology for carcinogens. If these indicators are not present, or are present below levels of concern, the remaining mass of petroleum is evaluated using fraction-specific surrogates. The fraction-specific composition of the mixture to which the receptor is exposed is determined, and surrogate RfDs/RfCs are utilised to determine the risk or to develop cleanup goals. The use of fraction-specific surrogates accounts for the effect of fate and transport on the whole mixture or parent products in that changes in the relative mass of each fraction at the receptor are accounted for in the risk assessment. This TPHCWG approach is described in further detail below.

3.3.2 The TPHCWG approach

Recently, the TPHCWG [1997a,b] extensively evaluated the toxicity data on individual TPH compounds. Petroleum is known to consist of thousands of individual HCs and related compounds. Of these, some 250 are actually identified. Of these 250 identified compounds only 95 had toxicity data. Of these 95, only 25 have sufficient data to develop toxicity criteria. Most of these 25 have USEPA-derived RfDs/RfCs or slope factors.

Considering the scarce data available and the need to assess the risks of petroleum mixtures, there is no other choice than to use the indicator/surrogate approach (see Chapter 3.3.1). Based on the uncertainties discussed above, the TPHCWG decided on a combination of data

[1]) Reference Dose (RfD) and Reference Concentration (RfC) are terms introduced by the US-EPA as 'neutral' replacements of the ADI/TDI and TCA, respectively.

on individual compounds *(indicators)* and fraction-specific mixtures *(surrogates)* as the hazard assessment methodology.

Firstly, the ***indicator approach*** is used to assess the hazard of (human) carcinogenic compounds (such as BTEX and certain PAHs). Secondly, if possible and applicable, the ***whole product approach*** is applied (only rarely possible). Finally, the TPHCWG ***surrogate approach,*** outlined in Figure 3.1, is applied.
Remark: This surrogate approach is outlined in more detail below. The current report does not deal with the first steps in evaluating TPH-contaminated areas (i.e. the indicator approach for carcinogenic risks, and the whole product approach).
Evaluation of the intervention values for BTEX and PAH are not considered in this report, but will be within the framework of the RIVM project 'Main Evaluation Intervention Values' (see Chapter 1.1 Scope of the report).

Over 200 HCs were considered in the development of fraction-specific characteristics. Because the fate and transport of a chemical in the environment largely defines its exposure potential to the receptors at risk, partition modelling according to ASTM standards was applied to each chemical in order to quantify, individually, the chemical's relative ability to leach from soil to groundwater and to volatilise from soil to air. Based on these results, the chemicals were grouped into fractions using one order of magnitude in relevant physical-chemical parameters as the cut-off point. Within each fraction, the HCs are grouped according to their EC (equivalent carbon) numbers (EC numbers are based on equivalent retention times on a boiling point gaschromatographic column; see section 2.2). Physical characteristics of the resulting 13 fractions are shown in Table 3.2. Although the ATSDR [1998] has adopted these fractions, section 4.3 of the ATSDR-report should be referred to for a remark on the exact classification of aromatic compounds with ECs of approximately 8.

To evaluate the human health effects, the number of fractions, as shown in Table 3.2, was reduced to seven, mainly due to the limited toxicity data available and the similarity in toxic effects. The toxicity data available on fraction-specific mixtures cover the aliphatic fractions of TPH and the aromatic fraction >EC5 - EC8. Data on the >EC8 - EC16 and >EC16 - EC35 aromatic fractions consist of mixture data in the EC8 - EC11 range only. In addition, there are no data on petroleum components with >EC35. However, since compounds >EC20 are not volatile or soluble in groundwater, they are likely to remain at the release site; moreover, compounds >EC35 are likely to possess low bioavailability by the oral, inhalatory and dermal route. The RfDs/RfCs for aliphatic fractions are at least one order of magnitude greater than those for the aromatic fractions. This is a result of both a difference in uncertainty and potency. The TPH fraction-specific RfDs and RfCs are summarised in Table 3.3.

Table 3.2 Representative physical parameters for TPH fractions [TPHCWG, 1997a; ATSDR, 1998]

Fraction	Solubility (mg/l)	Vapour pressure (atm)	Henry's Law constant (cm^3/cm^3)	Log K_{oc}
Aliphatics				
EC5 - EC6	36	0.35	47	2.9
>EC6 - EC8	5.4	0.063	50	3.6
>EC8 - EC10	0.43	0.0063	55	4.5
>EC10 - EC12	0.034	0.00063	60	5.4
>EC12 - EC16	0.00076	0.000076	69	6.7
>EC16 - EC35	0.0000025	0.0000011	85	8.8
Aromatics				
EC5 - EC7 [1])	220	0.11	1.5	3
>EC7 - EC8 [2])	130	0.035	0.86	3.1
>EC8 - EC10	65	0.0063	0.39	3.2
>EC10 - EC12	25	0.00063	0.13	3.4
>EC12 - EC16	5.8	0.000048	0.028	3.7
>EC16 - EC21	0.65	0.0000011	0.0025	4.2
>EC21 - EC35	0.0066	0.00000000044	0.000017	5.1

EC: Equivalent carbon number index.

Table 3.3 TPH fraction-specific RfDs and RfCs according to the TPHCWG method [TPHCWG,1997b]

TPH fraction [1])	**Oral RfD mg/kg bw/day**	**Inhalation RfC mg/m^3**	**Critical effect (studies) [2])**
Aliphatic >EC5 - EC8	5.0	18.4	neurotoxicity (6 studies n-heptane; 10 studies commercial hexane)
Aliphatic >EC8 - EC16	0.1	1.0	hepatic & haematological changes (5 studies on JP-8 and de-aromatised petroleum streams)
Aliphatic >EC16 - EC35	2.0	NA [3])	hepatic granulomas (1 extensive study on 5 white mineral oils)
Aliphatic >EC35	20	NA	hepatic granulomas (1 extensive study on 3 white mineral oils)
Aromatic >EC5 - EC8	0.20	0.4	hepato- & nephrotoxicity (based on the available /RfCs in this range) [4])
Aromatic >EC8 - EC16	0.04	0.2	decreased body weight, increased liver and kidney weight (based on 8 RfDs and 2 RfCs, respectively)
Aromatic >EC16 - EC3	0.03	NA	nephrotoxicity (1 study on pyrene)

[1]) EC : Equivalent carbon number index, based on equivalent retention times on a boiling-point gaschromatographic column (non-polar capillary column) to normalise to n-alkanes (compare section 2.2).
[2]) The toxicity studies, in parentheses, from which RfDs/RfCs were developed according to the USA-EPA methodology.
[3]) NA: not available (and not applicable due to extremely low volatilisation).
[4]) RfD : 6 out of the 7 compounds in this range (ethyl benzene, styrene, toluene, o-, m-, p-xylene).
RfC : toluene, ethyl benzene, styrene.

Remark: see critical note in section 4.3 (ATSDR, 1998) on an error in the aromatic fraction >EC5 - EC8 in this table.

Table 3.4 Human toxicological TDIs for TPH fractions; based on TPHCWG [1997b] and ATSDR [1998]

TPH fraction	Oral RfD [1]) mg/kg bw/day	Inhalation RfC [1]) mg/m^3	TDI (oral) [2])	Uncertainty factor applied [3])
Aliphatic >EC5 - EC8	2.0 [4])	18.4	2.0	100
Aliphatic >EC8 - EC16	0.1	1.0	0.1	1000/5000
Aliphatic >EC16 - EC35	2.0	NA [5])	2.0	100
Aliphatic >EC35	20	NA	20	100
Aromatic >EC5 - EC9	0.20	0.4	0.20	100/1000
Aromatic >EC9 - EC16	0.04	0.2	0.04	100/3000
Aromatic >EC16 - EC35	0.03	NA	0.03	1000

EC: Equivalent carbon number index, based on equivalent retention times on a boiling-point gas-chromatographic column (non-polar capillary column) to normalise to n-alkanes (compare section 3.1).

[1]) 'Oral RfDs' and 'Inhalation RfCs' directly adopted from the TPHCWG method (see Table 3.3).

[2]) 'TDI (oral)': equal to the estimated (USEPA) RfDs, except for aromatics >EC5 - EC9: the uncertainty resulting from route-to-route extrapolation of the RfC to the RfD (which would result in an RfD of 0.11 mg/kg bw per day) is considered to outweigh the apparent accuracy.

[3]) For an explanation see section 3.3.2

[4]) The oral RfD of 2 mg/kg bw per day of n-heptane is preferred to the rather feebly-argued RfD of 5 mg/kg bw per day (calculated from the RfC by route-to-route extrapolation), as recommended by the TPHCWG for this fraction (Table 3.3; see also section 3.4).

[5]) NA: not available (and not applicable due to extremely low volatilisation).

Remarks:

A. These TDIs replace the earlier MPR for 'mineral oil' [Vermeire, 1993].

B. These TDIs explicitly exclude carcinogenic risks, meaning that carcinogenic risks are expected to have been evaluated using the appropriate indicator compounds before these other toxic risks are considered (see Figure 3.1).

The EC is based on equivalent retention times on a boiling-point gaschromatographic column (non-polar capillary column) to normalise to n-alkanes (compare section 2.2).

[1]) The only compound in this fraction is benzene.

[2]) The only compound in this fraction is toluene.

Of the aliphatic >EC5-EC8 fraction, n-hexane is the only compound for which the USEPA has developed a RfD. Because of its unique toxicity, however, the use of the n-hexane RfD of 0.06 mg/kg bw per day as basis for the fraction-specific RfD would considerably overestimate the risks of HCs in this fraction. The composition of petroleum products containing n-hexane is well known and ranges from 0.05% to 7.0% in some petrols up to 15.7% in sweetened naphtha. Thus the levels of n-hexane are generally low (approx. 2 % in petrols). The available data sets on n-heptane and on solvent mixtures containing hexane isomers allowed us to conclude that n-heptane can be considered an appropriate surrogate for the EC6-EC8 HCs (with the exception of hexane); consequently, the TPHCWG recommended an RfD for the EC6-EC8 aliphatics of 5 mg/kg bw per day [2]). In all studies an uncertainty factor (UF) of 100 (10 for animal to human, 10 for most sensitive) was applied to arrive at the RfDs/RfCs.

Toxicity data on individual components in the aliphatic >EC8-EC16 fraction are minimal. The data used were from studies on jet fuel JP-8 (EC9-EC16) and on de-aromatised

[2]) Only in the rare cases of a release of high purity n-hexane the RfD of n-hexane (i.e., 0.06 mg/kg bw per day) should be used.

petroleum streams (10 studies in total), which, together, cover the entire range of the fraction. Although data on n-nonane are available, the data on petroleum streams were preferred since these data refer more to on mixtures rather than on an individual compound at the low end of the fraction. The UFs used in these studies varied from 1000 (which includes an additional factor of 10 to compensate for the use of subchronic studies) to 5000 in one study (the additional factor of 5 was applied to compensate for the use of a LOAEL instead of a NOAEL).

The RfDs for the aliphatic >EC16-EC35 and >EC35 fractions were based on a recent and extensive BIBRA study in which Fischer rats were exposed to various white mineral oils (these are complex mixtures of highly refined mineral HCs, predominantly branched chain alkanes and alkenes with one or more saturated cyclic structures, and no aromatics or other contaminants, extensively used as food additives and in cosmetics and pharmaceutical products). The RfD for the EC17-EC35 fraction (2 mg/kg bw per day) is based on the NOAEL for low molecular weight oils for liver granulomas (200 mg/kg bw per day) and a UF of 100. The RfD for the >EC35 fraction (20 mg/kg bw per day) is based on the NOAEL for high molecular weight oils for liver granulomas (2000 mg/kg bw per day) and a UF of 100. An recent similar study in Japan showed comparable results.

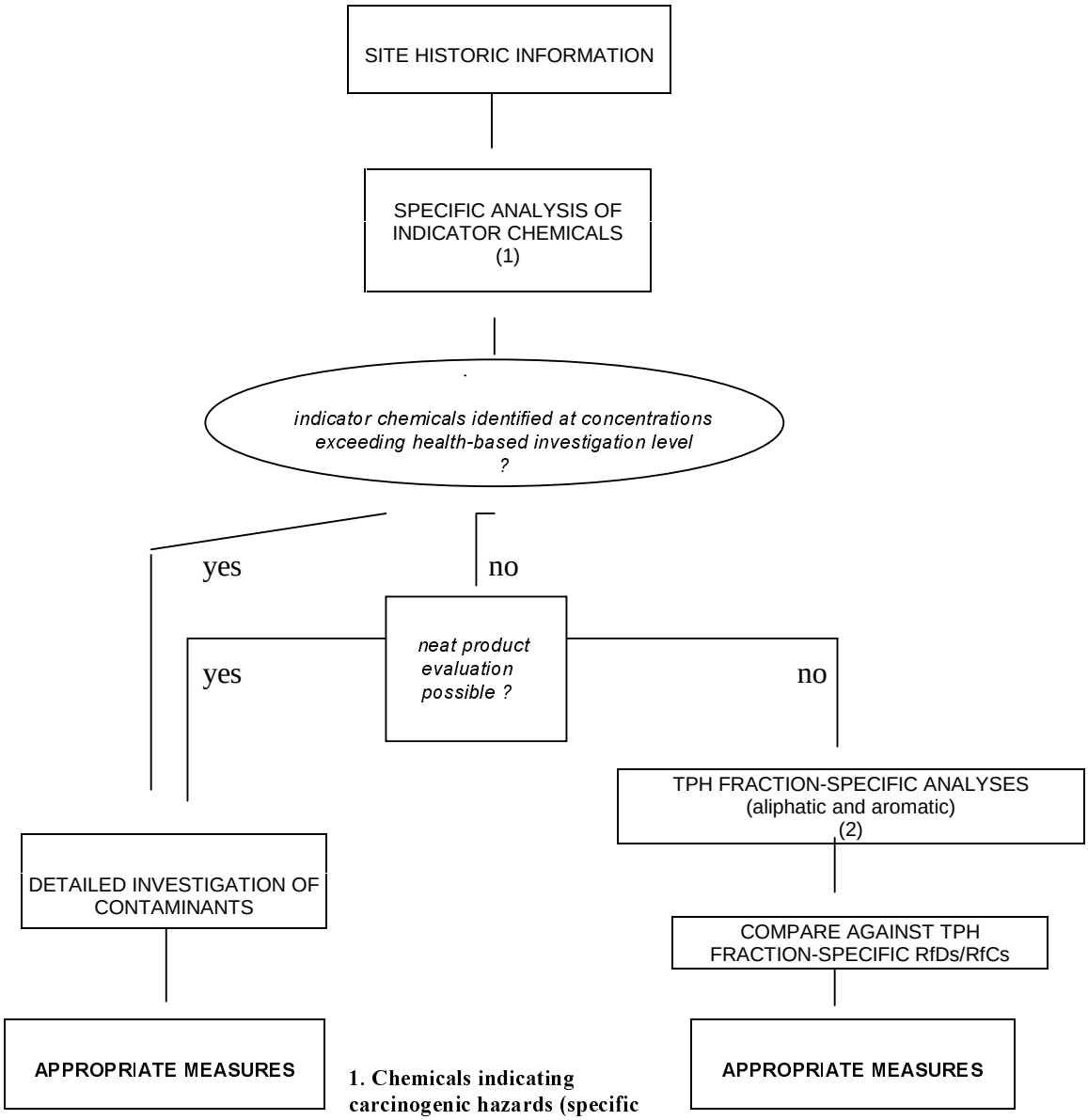
In petroleum products of the aromatic >EC5-EC8 range, seven compounds were identified. RfDs are available for six of these: ethyl benzene, styrene, toluene, m-, o- and p-xylene. The values range from 0.1 to 2.0 mg/kg bw/ day. On reviewing the toxicity and compositional information of this fraction, the TPHCWG considered a RfD of 0.2 mg/kg bw per day appropriate. RfCs are available for three compounds: toluene, ethyl benzene and styrene, ranging from 0.4 to 1.0 mg/m^3; the TPHCWG recommended a RfC of 0.4 mg/m^3 for this fraction. The UFs range from 100 (xylenes) to 1000 (toluene, ethyl benzene and styrene), the additional factor of 10 for these latter ones compensates for the use of subchronic studies.

In the aromatic >EC8-EC16 fraction 77 compounds have been identified; RfDs have been developed for 8 of these (all with ECs > 9), ranging from 0.03 to 0.3 mg/kg bw per day. There are also data available on a mixture within this range: naphthalene/methyl naphthalenes; for this mixture a RfD of 0.03 mg/kg bw per day was developed. After reviewing the information, a fraction-specific RfD of 0.04 mg/kg bw per day was considered to be appropriate (of the 8 available individual RfDs, 4 were 0.04 mg/kg bw per day, the only exceptions are fluorene and the naphthalene/methyl naphthalenes mixture with values of 0.03 mg/kg bw per day). Inhalation data for the EC9-EC16 fraction are extremely limited, there are RfCs for isopropyl benzene (0.09 mg/m^3) and naphthalene (0.0013 mg/m^3), but these compounds are not at all representative for this fraction. In addition there are several inhalation studies on EC9 aromatic mixtures that allowed the development of an RfC, resulting in values ranging from 0.2 to 1.3 mg/m^3. The TPHCWG determined the more conservative value (0.2 mg/m^3) to be representative of this entire fraction. The UFs range from 100 (biphenyl), via 1000 (naphthalene, fluorene), to 3000 (isopropyl benzene, methyl naphthalene, anthracene); the additional factor of 10 (naphthalene, fluorene) originates from the use of subchronic studies, the additional factor of 3 (isopropyl benzene, methyl naphthalene, anthracene) compensates for the inadequate databases.

There are no previous developed RfDs for aromatic HCs in the >EC16-EC35 range, and a literature review did not result in data which allowed for the development of a RfD. Thus the TPHCWG considered the RfD for pyrene ($C_{16}H_{10}$), i.e. 0.03 mg/kg bw per day, to be the best

option as a surrogate for the fraction-specific RfD. Pyrene is considered a conservative surrogate because its carbon number is lower than any of the compounds in this fraction. The UF was 3000 (which includes a factor of 10 to compensate for the use of a subchronic study, and a modifying factor of 3 for lack of adequate toxicity data in a second species and reproductive/developmental data).

The TPHCWG approach is based on some implicit assumptions. It assumes:
(1) that the toxicity of the fraction as tested does not significantly change with weathering in the environment,
(2) that the composition of the fraction will not vary significantly from the surrogate tested (i.e. the surrogate tested represents the TPH fraction), and
(3) that the interaction of the various fractions can be assumed to be additive.
The resulting uncertainties warrant a careful use of the methodology. Comments are presented in section 3.3.4



1. Chemicals indicating carcinogenic hazards (specific analysis), e.g.: lead, benzene, 1,3-butadiene, and the PAHs benzo(a)pyrene, benzo(a)anthracene, dibenzo(a,h)anthracene, benzo(k)fluoroanthrene, benzo(b)fluoroanthrene, benzo(j)fluoroanthrene, dibenzo(a,h)acridine, dibenzo(a,j)acridine, dibenzo(a,e)pyrene, dibenzo(a,h)pyrene, dibenzo(a,i)pyrene, dibenzo(a,l)pyrene, indeno(1,2,3-cd)pyrene, 5-methylchrysene; **if necessary also:** ethyl benzene, toluene, xylene, n-hexane.

2. TPH fraction-specific analyses (aromatic and aliphatic):

aliphatic >EC5 - EC8	aromatic >EC5 - EC9
aliphatic >EC8 - EC16	aromatic >EC9 - EC16
aliphatic >EC16 - EC35	aromatic >EC16 - EC35
aliphatic >EC35	

EC: Equivalent carbon number index. The EC is based on equivalent retention times on a boiling-point gas-chromatographic column (non-polar capillary column) to normalise to n-alkanes (compare section 2.2).

Remark: In this figure the classification of the fractions has been corrected and redefined according to the remark in section 4.3: 'aromatic >EC5 - EC8' is now 'aromatic >EC5 - EC9'.

Figure 3.1 Schematic outline of the TPHCWG methodology [1997].

3.3.3 The ATSDR toxicological profile for TPH

In late 1998 the ATSDR published the draft of its toxicological profile for TPH [ATSDR, 1998]. In its approach to the health assessment of TPH, ATSDR has drawn on the experience of others who have been developing approaches to a health-based assessment of TPH, particularly on Hutcheson et al. [1996] and the TPHCWG [1997a,b].

The ATSDR adopted the TPH fraction approach as developed by the TPHCWG, who considered this approach the most useful. However, the ATSDR adjusted the classification of compounds into appropriate fractions because xylene and styrene were misclassified on the basis of actual rather than equivalent carbon index numbers (these compounds have ECs of 8.5-8.81 and should thus belong to the TPHCWG >EC8 - EC16 category). Hence, the aromatic >EC5 -EC8 fraction has been redefined as an >EC5 - EC9 fraction, so that it includes all the BTEXs. Consequently, the aromatic >EC8 - EC16 fraction has been redefined as an >EC9 - EC16 fraction.

3.3.4 Comments

As outlined above, the TPHCWG approach [1997a,b] discriminates between a reasonable number of fractions, thus allowing a more detailed risk assessment, while still being feasible in practice. With respect to the underlying assumptions (uncertainties) of the approach as such, the careful consideration of these assumptions has shown them to a certain extent irrelevant.

For example, there are no toxicity data on weathered products. Whittaker and Pollard [1997] recently suggested the use of certain marker compounds in oil and oil products to determine the origin of a crude oil contamination and the state of weathering. They propose oil weathering indices based on petroleum microbiology, in particular on the differential rates at which oil components are metabolised and transformed. Microbial catabolism of n-alkanes proceeds via successive oxidation and cleavage of the terminal methyl groups of a hydrocarbon molecule. Branched or cyclic compounds experience slower biotransformation rates due to the presence of secondary, tertiary and quaternary carbon atoms that render these compounds more difficult to metabolise. Thus in terms of oil class fractions, the open chain alkanes are generally the most labile oil components, followed by aromatic compounds, then polar resins, and finally the highly condensed bitumen compounds.

However, although this methodology allows - to a certain extent - the determination of the origin of a crude oil or a particular petroleum product (such determinations are performed in the Netherlands by the RIZA), only a determination of the ‘weathering status’ is allowed in relation to this origin. If, for example, a spillage of a particular jet fuel occurred in the past, the use of marker compounds makes it possible to estimate the weathering of this jet fuel spillage. In contrast, if the origin of a contamination (that is, the product or its composition at the time it was spilled) is not known, the methodology is unable to identify the weathering status. Assuming that the risk assessment of any petroleum-contaminated site inevitably always starts with a full chemical analysis of the contamination (which aims at a classification according to the fractions as defined by the TPHCWG), this presents the actual composition in terms of these fractions. In this way the question ‘if?’ and ‘to what extent’? weathering has occurred becomes irrelevant.

The same argument holds for the second assumption, i.e. that the composition of the fraction will not vary significantly from the surrogate tested. Again, assuming that a chemical analysis will always precede the actual risk assessment makes this assumption irrelevant.

The third assumption (the interaction of the various fractions are assumed to be additive) is more serious. Current knowledge, however, does not present clear and scientifically based indications that interactions other than addition of effects should be applied. Unfortunately the TPHCWG does not explain how and when interaction, and thus additivity, becomes an important issue in the evaluation of contaminated areas. The ATSDR, however, does pay some attention to the question how to account for exposure to more than one fraction. ATSDR's approach is based on the assumption of additivity (in accordance with the TPHCWG), an approach which is claimed to be reasonable for compounds or fractions that affect the same system or target organ. The ATSDR then defines a 'hazard index', being the sum of the ratios of monitored level of exposure to the accepted level of exposure for each of the constituents of a mixture:

$$HI = \Sigma E_i/AL_i$$

HI : hazard index
E_i : actual exposure level to the i^{th} component
AL_i : accepted exposure level for the i^{th} component

A proposal to manage this 'hazard index' approach in the Dutch situation is presented in section 3.5.

3.4 Background exposure

No data are available on the daily oral or inhalatory background exposure to TPH. Oral exposure can be assumed to be negligible in agreement with Vermeire [1993]. Inhalatory background exposure can be expected only from rather volatile TPH-based compounds. However, only for a few neat petroleum products are some limited data available, for example, petrol fumes and exhausts, and TPH-based solvents used in industry and households, like Stoddard solvent ('white spirit' or 'turpentine').

Petrols are mixtures of volatile HCs (C3-C11, composed of 30-90% alkanes and 5-55% aromatics with a boiling range of 30-260 °C). For petrol fumes and exhausts, air concentrations measured in Germany in the mid-seventies indicate arithmetic mean values for non-methane HCs ranging from 42 (rural areas) to 756 (city streets with heavy traffic) $\mu g/m^3$ [BUA, 1998], with an average value of approximately 300 $\mu g/m^3$. Since the indoor concentration will hardly differ from the outdoor concentration, this figure results in a background exposure of the average population of 86 µg/kg bw per day for an adult of 70 kg with a breathing volume of 20 m^3 per day. The MAC for petrol in air (Dutch occupational limit value, 8 h per day, 40 h per week) is 240 mg/m^3 [MAC, 1997].

Stoddard solvent (a mixture of saturated aliphatic and alicyclic C7-C12 HCs with a maximum content of 25% aromatics and a boiling range of 130-230 °C) was reviewed by the IPCS [1996]: no estimations were reported on the background exposure of the general population. Painters and industrial workers were reported to be exposed to widely varying concentrations of white spirit. A reasonable time–weight average exposure level (8 h per day) to indoor

painting appeared to be approximately 150 mg/m^3 [IPCS, 1996]. Assuming a 14-day, 8-h per day exposure per year for the general population (amateur painting and cleaning), this results in a mean daily exposure of 550 µg/kg bw per day for an adult of 70 kg bw (breathing volume 20 m^3 per day) [3]). Alternatively, a time-weight average air concentration can be estimated at approximately (2 mg/m^3)[4]). The MAC-value for Stoddard solvent in air (Dutch occupational limit value, 8 h per day, 40 h per week) is 575 mg/m^3 [MAC, 1997].

The estimations presented above are probably rather conservative, taken into account that the measurements were done in the mid-eighties (Stoddard solvent) and the mid-seventies (petrol), and that since then the use of alkyd paints has decreased in favour of water-soluble paints, and vehicle engines have improved considerably the efficiency with which petrol is burned. Moreover, the estimations apply to two neat petroleum products only. Nevertheless, the background exposition is apparently already in the order of magnitude of the TDIs for the light TPH fractions (compare section 3.5 and Table 3.4). On the other hand, the data indicate air concentrations well below the occupational limit values.

3.5 Conclusion

Based on current knowledge and in view of the complexity of the vast majority of petroleum-contaminated areas the TPHCWG methodology (after correction of the mistake noted by ATSDR [1998]) offers the best possible methodology at the moment to perform a human health-based risk assessment giving an optimal reliability while at the same time being feasible in practice. Basically, a tiered approach is applied, as outlined in Figure 3.1. Detailed site historic information is followed by specific chemical analysis with particular emphasis on the carcinogenic indicator compounds, like benzene and selected PAHs. If these are present, indicating a hazard for human carcinogenic health effects, further investigation is needed, followed by the appropriate measures (this first step is not further discussed in the present report). If these indicator compounds are not present in concentrations causing concern, the possibility of applying a whole product approach is considered (only possible in cases of very recent spillages with known product). Finally, a TPH fraction-specific analysis is made, and the resulting concentrations are compared with fraction-specific TDIs as summarised in Table 3.4.

This approach ultimately leads to seven (human) TDI (MPR) values for TPH fractions, and explicitly excludes carcinogenic risks (meaning that carcinogenic risks are expected to be evaluated before the other toxic risks considered). These TDIs are summarised in Table 3.4, and replace the earlier MPR for 'mineral oil' [Vermeire, 1991], which was based on a whole product approach.

There is one differentiation with regard to the recommendations of the TPHCWG. The TPHCWG suggests an RfD of 5 mg/kg bw per day for the aliphatic >EC5 - EC8 fraction. The reasoning for this, however, is quite unclear. TPHCWG review a large number of studies with n-heptane (C_7H_{16}), bringing them to the conclusion of a RfD of 2 mg/kw bw per day, and then calculate a RfD of 5 mg/kg bw per day by route-to-route extrapolation using a RfC of 18.4 mg/m^3 resulting from an inhalatory study with commercial hexane. Furthermore they

[3]) (14 x 8/24 x 20 x 150) ÷ (365 x 70) = 548 µg/kg bw per day.
[4]) (14 x 8/24 x 150) ÷ 365 = 1.92 mg/m^3.

review seven studies with various petroleum products, in all of which the RfDs varied between 1.5-2.0 and (one with cyclohexane, one with methyl cyclohexane), but do not develop a RfD from these data. The proposed RfD of 2 mg/kg bw per day, based on six studies with n-heptane and seven studies with different petroleum products, has evidently a better scientific basis.

From these human-toxicological TDIs summarised in Table 3.4 the corresponding SCCs (serious soil contamination concentrations) for the various TPH fractions can be calculated using the CSOIL model. Given a contaminated area in which exposure to more than one fraction is under discussion, the approach should be as follows, depending on the specific situation:

1. If the SCC for one or more fractions is exceeded, appropriate measures should be considered or taken.
2. If (and only if) none of the fraction-specific SCCs is exceeded, an overall site-specific contamination index should be calculated assuming additivity, according to the following equation:

$$\text{site-specific contamination index} = \Sigma \frac{\text{measured concentration}_i}{\text{SCC}_i}$$

If this index is ≥ 1, the appropriate measures should be considered or taken [ATSDR, 1998].

A serious objection to this approach is the issue of whether or not it is correct to assume additivity. However, as already outlined in section 3.3.4, current knowledge does not present clear and scientifically based indications that interactions other than addition of effects can be applied. Thus at present there is simply is no better way of meaningfully dealing with this problem. This approach is also followed by the ATSDR [1998] as the default assumption if no other (more detailed) information is available.

Remark: It should be noted that the chemical analysis of contaminated sites, which the proposed method requires, should include the HCs with the equivalent carbon numbers of 6 - 10. This implies an extension of the current methodology according to NEN 5733, which defines 'mineral oil' as the sum of all alkanes (including branched alkanes) with carbon numbers 10 - 40, requiring additional analysis of the amount of aromatic and/or polycyclic aromatic HCs if their presence is indicated. The NEN 5733 definition is based on a GC-FID analysis and refers to the detector signal between n-decane ($C_{10}H_{22}$) and n-tetracontane ($C_{40}H_{82}$).

3.6 Comparison with earlier derived MPRs

Next to the earlier referred MPRs for 'mineral oil' and 'C9-aromatic Naphtha' (see section 3.1), a number of MPRs for individual TPH components were derived in the years 1991-1996 (Vermeire et al., 1991; Vermeire, 1993; Janssen et al., 1995; Janssen et al., 1998]. The accompanying TDIs, TCAs and QCRAs are summarised in Table 3.5, together with the TDIs/TCAs as estimated in the present report (compare Table 3.5), and arranged according to the present TPH fractions.

The earlier derived MPRs are mostly limited to the aliphatic >EC5-EC8 and the aromatic >EC5-EC9 fractions; in the aromatic >EC16-EC35 fraction almost all MPRs are related to the carcinogenic risk.
A comparison of the available values shows good agreement. The only significantly differing value is the TCA for petrol of 71 $\mu g/m^3$, which is very low compared to the proposed TCA range of the aliphatic/aromatic EC5-EC16 fractions. However, this particular TCA, developed in 1991, was based on two studies published in 1978 and 1979 (cited in IARC [1989]), reporting interstitial fibrosis in lung parenchyma of female rats in semichronic studies. In more recent studies, however, these effects were not reported (compare section 3.3, CONCAWE [1992b] and TPHCWG [1997b]). Moreover, also the Dutch occupational limit value of 240 mg/m^3 is considerably higher than the above cited TCA [MAC, 1997]. Hence it seems justified to adjust the 1991 TCA for petrol of 71 $\mu g/m^3$, unless there are important reasons for doing so e.g. specific petrol-contaminated areas.

Table 3.5 Comparison of the present TDIs/TCAs with earlier derived values

		Values 1991-1996		Values 1999 (this report)	
TPH fraction/compounds	EC	TDI	TCA	TDI	TCA
Aliphatic >EC5-EC8				2000	18400
Hexane	6	23 (P)	200 (P)		
Heptane	7	3100	-		
Octane	8	3100	-		
Aliphatic >EC8-EC16				100	1000
--					
Aliphatic >EC16-EC35				2000	NA
--					
Aliphatic >EC35				20000	NA
--					
Aromatic >EC5-EC9				200	400
Benzene	6.5	4.3	30		
Benzene	6.5	170 (R)	1200 (R)		
Toluene	7.58	430	3000		
Ethyl benzene	8.5	136	77		
Xylenes	8.7	10	54		
Styrene	8.83	77	800		
Aromatic >EC9-EC16				40	200
Naphthalene	11.69	50	-		
'C9-aromatic Naphtha'	±10.1	170 (P)	800		
Aromatic >EC16-EC35				30	NA
Dodecylbenzene	±18.5	5	NA		
Phenanthrene	19.36	20 (R)	-		
Anthracene	19.43	50	-		
Pyrene	20.80	20 (R)	-		
Fluoranthene	21.58	20 (R)	-		
Benzo(a)anthracene	26.37	20 (R)	-		
Chrysene	27.41	2 (R)	-		
Benzo(k)fluoranthrene	30.14	20 (R)	-		
Benzo(a)pyrene	31.34	2 (R)	-		
Benzo(ghi)perylene	34.01	20 (R)	-		
Indeno(1,2,3cd)pyrene	35.01	20 (R)	-		
PAHs total	-	6.3 (R)	-		
Others				-	-
Petrol	-	3100	71		
TPH	-	25000	-		

TDI tolerable daily intake (µg/kg bw per day).

TCA tolerable concentration in air (µg/m^3).

R quantitative carcinogenic risk assessment (QCRA; µg/kg bw per day c.q. µg/m^3).

EC equivalent carbon number index, based on equivalent retention times on a boiling-point gas-chromatographic column (non-polar capillary column), in order to normalise to n-alkanes.

NA not applicable.

P provisional.

'C9-aromatic Naphtha' high boiling aromatic solvents, also known as 'aromatic naphtha' or 'high-flash aromatic naphtha', is a mixture that remains after evaporation of the more volatile constituents from petrol or other petroleum products. Generally this mixture is rich in C3- and C4-alkylated benzenes, i.e. trimethyl benzenes, methylethyl benzenes, tetramethyl benzenes and methylpropyl benzenes. Its boiling range is approximately 155-210 °C; the ECs range from 9.6 - 10.7 (average approximately 10.1).

Petrol petrols are mixtures of volatile HCs (C3-C11, composed of 30-90% alkanes and 5-55% aromatics) with a boiling range of 30-260 °C.

TPH 'mineral oil' in the 1993 report.

3.7 References

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4. Derivation of serious soil contamination concentrations (SCCs) for TPH

4.1 Derivation of ECOTOX SCCs

Since there are no ECOTOX serious soil contamination available for TPH fractions, only indicative levels for TPH fractions could be proposed based on HUMTOX SCCs.

4.2 Derivation of HUMTOX SCCs

Chapter 3 presented MTRs and TCAs for seven fractions of petroleum hydrocarbons. On the basis of physico-chemical characteristics these fractions could be further differentiated. We used the same data as presented by the TPHCWG (1997a); see Table 3.2.

As noted by the ATSDR [1998], the TPHCWG [1997b] included ethylbenzene, styrene and the xylenes in the >EC7-EC8 aromatic fraction, although they belong to the >EC8-EC10 fraction. Only toluene belong to the >EC7-EC8 fraction (benzene belongs to the >EC5-EC7 fraction). However, since the RfD and RfC for the aromatic >EC7-EC8 fraction were developed from toxicity data for toluene, toxicity data developed for this fraction have been deemed appropriate.

Ethyl benzene, styrene and the xylenes should have been included in the >EC8-EC10 aromatic fraction. Based on comparable toxicity this fraction was combined with the aromatic fraction >EC10-EC16 into the aromatic fraction >EC8-EC16. The compounds mentioned have RfDs and RfCs that are higher than other compounds in this combined fraction, and since the toxicity criteria for each fraction are expected to represent conservative estimates, there is no need to change the current values for this >EC8-EC16 fraction [TPHCWG, 1997b errata].
Finally, because of the physico-chemical properties of the earlier defined, more detailed, aromatic fractions, it is desirable to maintain these, despite the (slight) errors mentioned above (which have no consequences for the toxicity criteria).
In conclusion, the TDIs/TCAs, as presented in Table 4.1, have been used for the calculation of the HUMTOX SCCs.

Table 4.1 TDIs and TCAs for serveral aromatic fractions

	TDI (µg/kg bw/day)	TCA (µg/m3)	
Aromatic fraction EC5-EC7	4.3	30	(benzene) [1])
Aromatic fraction >EC7-EC8	200	400	(toluene) [2])
Aromatic fraction >EC8-EC10	40	200	(ethylbenzene, styrene, xylenes) [2])
Aromatic fraction >EC10-EC12	40	200	(alkylbenzenes, -naphthalenes) [2])
Aromatic fraction >EC12-EC16	40	200	(alkylbenzenes,-naphthalenes, naphtheno-benzenes) [2])

[1]) According to Vermeire [1993]. Note that in Vermeire et al. [1991] the QCRA (for carcinogenic risk) was estimated at 170 µg/kg bw per day and 1200 µg/m^3, respectively (see also Table 3.5).

[2]) According to the present report.

On the basis of these data theHUMTOX SCCs for several fractions of petroleum hydrocarbons has been calculated with the model CSOIL (version 8.0), as described by Van den Berg (1995). Model parameters for the fractions: solubility, Vp, H, Koc etc. were taken from the TPHCWG (see Appendix 6a and 6b). A revision of the CSOIL exposure model, planned in 2000, could change the calculated HUM-TOX SCC.
Since there are no ECOTOX SCCs available for TPH fractions, a proposal for Intervention Values for TPH fractions could only be based on HUMTOX SCCs. The results are presented in Table 4.2.

Table 4.2 MTRs, TCAs and proposals for the Intervention Value soil (HUMTOX SCC) and groundwater for standard soil.

	MTR Mg/kg bw/d	**TCA µg/l**	**HUMTOX SCCs Proposal for Intervention Value soil mg/kg**	**Proposal for Intervention Value groundwater** *1 **(µg/l)**
Aliphatics				
EC 5-6	2	18.4	28	61
EC>6-8	2	18.4	99	43
EC>8-10	0.1	1	27	1.47
EC>10-12	0.1	1	155	1.06
EC>12-16	0.1	1	52170 *2	0.59
EC>16-21	2	0	- *3	- *3
Aromatics				
EC 5-7	0.2	NA	*4	*4
EC>7-8	0.2	0.4	*3	*3
EC>8-10	0.04	0.2	95	104
EC>10-12	0.04	0.2	363	249
EC>12-16	0.04	0.2	860 *2	296 *2
EC>16-21	0.03	0	10118 *2	509 *2
EC>21-35	0.03	0	17563 *2	6.6 *2

NA - Not Available

*1 The Intervention Value groundwater is calculated with the formula IVgroundwater = (IVsoil / Kd) / 10 whereas Kd = Koc * Foc.
The Foc (fraction organic carbon) for a "standard soil" = 5,8 %.
The Kocs are presented in appendices 6A en 6B. If the calculated IVgroundwater is crossing the solubility, the solubility is taken as IVgroundwater.

*2 Since colloids are not considered, exposure could be underestimated and thus the calculated HUMTOX SCCs could be too high.

*3. For the aliphatic fraction EC>16-21, a daily intake of 150 mg soil does not result in human risk.
A daily intake of 150 mg soil is a default assumption (in the model CSOIL) to calculate the human toxicological serious soil contamination concentrations (SCCs).

*4 Since benzene (EC = 6.5) and toluene (EC = 7.5) are the only representatives of these groups, both will be measured individually, therefore these fractions could be skipped.

*5 The calculated Intervention Values are calulated for a "standard soil" with the model CSOIL (version 8.0). Parameters for "standard soil" are pH=6, OM=10 (= 5.8% OC), L=25%, SD=1,5, Va=0,2, Vw=0,2, Vs=0.6.

Striking are the large differences of HUMTOX SCCs of lower aliphatics (EC≤12) compared to higher aliphatics (EC>12) and of lower aromatics (EC ≤16) compared to higher aromatics

(EC>16). These differences are caused by the decline of vapour pressure, solubility and partition coefficients (Kow); see Appendix 6a and 6b.
Also striking is the relatively low HUMTOX SSC of the EC>8-10 compared to EC>6-8 aliphatic fraction; this could be explained by the lower MTR for the EC>8-10 aliphatic fraction. The calculated HUMTOX SCC suggests that the present assessment of the human toxicological risk of petroleum hydrocarbons should be replaced by a procedure which distinguishes aliphatic and aromatic fractions of petroleum hydrocarbons.

The accuracy of the predicted fate and effects are affected by the quality of the physicochemical data. Reliable available data on solubility (and other physico-chemical data) for higher alkanes (C>10) are, however, limited (De Maagd et al., 1997; Verbruggen, 1999). Verbruggen [1999] found that on the basis of a literature survey on hydrophobicity, the solubility of higher alkanes (>C13) only slightly decreases. This result is in conflict with the data presented by TPHCWG (1997a), which suggest a linear relation between the increase of EC and decrease of solubility (from EC = 5 to EC = 26). Verbruggen concluded that this split reflects a change from true aqueous solubility for the lower alkanes to a colloidal accommodation for higher alkanes (C>13). This means that for the exposure to higher aliphatics (C>13) colloids also have to be considered (besides the true aqueous solubility) to overcome underestimation of exposure for TPH C>13. It is expected that for higher aromatics (C>13) there will also be colloid accommodation.
If the solubility for aliphatics EC>13 is similar to the solubility for the fraction EC>10-12 (suggested by Verbruggen, 1999) the calculated HUMTOX SCC will be a few factors lower. For example, for the aliphatic fraction EC>12-16, a HUMTOX of 15431 mg/kg is calculated instead of 52170 mg/kg.

Indicative levels for serious soil contamination were derived earlier for ‘C9 aromatic naptha’ (see Chapter 3.1); a human MTR of 170 µg/kg_{bw}/d has been deduced. Indicative levels of 200 mg/kg dw for soil and 150 µg/l for groundwater are presented (Janssen et al., 1995; Kreule et al., 1995) on the basis of scarce ecotoxicological data. Since then, new human toxicological data were included, which resulted in a substantial lower MTR (40 ug/kg_{bw}/d) and thus a lower Intervention Value (95 mg/kg dw for soil and 103 µg/l for groundwater). It is proposed to lapse the present “indicative level” for ‘C9 aromatic Naphtha’, if this proposal for revised Intervention Values for petroleum hydrocarbons is accepted.

Table 4.3 presents an overview of exposure routes which determine the human toxicological risk related to the considered TPH fractions; the information is generated with the model CSOIL.

Table 4.3 TPH fractions and dominant exposure routes which dominate the human exposure to TPH fractions

Fraction	**Dominant risk factor**
Aliphatics	
EC 5-6	Inhalation of indoor air
EC>6-8	Inhalation of indoor air
EC>8-10	Inhalation of indoor air
EC>10-12	Inhalation of indoor air
EC>12-16	Ingestion of soil
EC>16-21	Ingestion of soil
Aromatics	
EC>8-10	Inhalation of indoor air
EC>10-12	Inhalation of indoor air & ingestion of crops
EC>12-16	Ingestion of crops
EC>16-21	Ingestion of soil
EC>21-35	Ingestion of soil

4.3 Discussion

The TPHCWG presented data related to the petroleum hydrocarbon composition of fuels, sorted by fuel type (TPHCWG, 1997a). Although there is a large variety in the composition per fuel type, these data give an impression of frequently used fuels. For example, the TPH fraction of petrols is mainly related to the range C4-C10, whereas diesel and fuel oil are mainly related to the range C8-C20. This means that the present Dutch analytical procedure, which determines the sum of C10-40 alkanes, could lead to an underestimation of the human-toxicological risk, especially in the case of light fuels like petrol, but even for diesel and fuel oil.

It will remain uncertain if analysing BTEX will overcome this underestimation of the lower TPH fraction, since the variety in composition per fuel type is large. Adoption of the present analytical procedure will be necessary to overcome underestimation of human-toxicological risks. Replacing the present analytical procedure by a procedure which distinguishes aliphatic and aromatic fractions of TPH within a range of EC5-EC40 is recommended; for example, by a GC-MS screening as proposed by the TPHCWG (in preparation).

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5. General conclusions and recommendations

I. General

- Distinguishing TPH fractions in contaminated soil is significant with respect to ecotoxicology and human risk assessment.
- Reliable physicochemical data for higher aliphatics (C>10) are scarce. Experimental research is recommended, since the accuracy of the predicted fate and effects is, for example, determined by the quality of the physicochemical data. For the exposure to higher aliphatics (C>13) colloid formation has to be considered (besides the true aqueous solubility); with the purpose to overcome underestimation of exposure of TPH C>13.

II. Ecotoxicology

- Relevant ecotoxicological data to derive HC50-values (ECOTOX SCC) for fractions of 'petroleum hydrocarbons' is lacking.

There are severe indications (based on ecotoxicological experiments with light, medium and heavy oils) that it is significant to distinguish TPH fractions.

The most promising approach is the fraction approach or Hydrocarbon Block Method; however, before an ecological serious soil contamination concentration can be derived it is recommended:

- first, to identify the blocks relevant to quantifying ecotoxicological effects of petroleum hydrocarbons and
- second, to generate the relevant terrestrial ecotoxicological data and discussing the use of sediment data, which will become available at the end of 1999.

III. Human toxicology

- In general, there are enough human toxicological data to determine MTRs for several fractions of petroleum hydrocarbons. The described methodology to distinguish human risks for fractions of TPH fits well with the present methodology for deriving human risks.
- Especially aliphatic fractions (to EC12) and fractions of aromatics (to EC16) are relevant with respect to the (non-carcinogenic) human risks.

Table 5.1 Proposals for the Intervention Value soil (HUMTOX SCC) and groudwater for standard soil.

	ECOTOX SCC mg/kg	HUMTOX SCCs Proposal for Intervention Value soil mg/kg	Proposal for Intervention Value groundwater conc. (µg/l)
Aliphatics			
EC 5-6	-	28	61
EC>6-8	-	99	43
EC>8-10	-	27	1.47
EC>10-12	-	155	1.06
EC>12-16	-	52170 *1	0.59 *1
EC>16	-	- *2	- *2
Aromatics			
EC≤ 8		*3	*3
EC>8-10	-	95	104
EC>10-12	-	363	249
EC>12-16	-	860 *1	296 *1
EC>16-21	-	10118 *1	509 *1
EC>21-35	-	17563 *1	6.6 *1

*1 Since colloids are not considered, exposure could be overestimated and thus the calculated HUMTOX SCCs could be too high.

*2.For the aliphatic fraction EC>16-21 a daily intake of 150 mg soil a day does not result in human risk. A daily intake of 150 mg soil is a default assumption (in the CSOIL model) to calculate the human toxicological serious soil contamination.

*3 Since benzene (EC = 6.5) and toluene (EC = 7.5) are the only representatives of these groups, both will be measured individually; therefore these fractions could be skipped.

The proposed Intervention Values for soil (HUMTOX SCCs) and groundwater concentrations (see Table 5.1) are calculated with the human exposure model CSOIL version 8.0; revision of CSOIL, planned in 2000, could change these values.

IV. Proposal for intervention values for TPH fractions

- Since no HC50 (ECOTOX serious soil contamination) could be derived, the proposed. Intervention Values for several TPH fractions are only based on HUMTOX SCCs and groundwater contamination concentrations (see Table 5.1).
- The present method of analysing TPH (which considers the sum of C10-C40 petroleum hydrocarbons) provides insufficient information to consider the (non-carninogenic) human-toxicological risks of TPH in light fuels like petrol (which contain a substantial TPH fraction <C10).
- If the proposal for Intervention Values for TPH fractions are adopted, the Dutch Intervention Value for ‘mineral oil’ could lapse. However, besides analysing TPH fractions, analysing BTEX and/or PAH should be maintained.
- It is proposed to lapse the present “indicative level” for ‘C9 aromatic Naphtha’, if the

proposal for revised Intervention Values for petroleum hydrocarbons is accepted.

- It is recommended to consider concentration addition for TPH fractions if (and only if) none of the fraction-specific SCCs is exceeded. Additivity is only applicable for TPH-fractions that affect the same system or target organ. An overall site-specific contamination index should be calculated according to the following equation:

$$\text{site-specific contamination index} = \Sigma \frac{\text{measured concentration i}}{\text{SCC}_i}$$

If this index is ≥ 1, appropriate measures should be considered or taken.

V. Analytical procedure

- To overcome underestimation of the human-toxicological risk, the analytical procedure has to be changed. A wider range of TPH has to be considered (C5-C40) related to aliphatic and aromatic fractions. The analytical procedure could be changed: for example, as proposed by the TPHCWG. It is recommended to investigate the consequences of a new analytical proposal (including costs) before adapting the indicative levels for TPH fractions proposed in this report.

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Appendix 2 Principal refinery process streams

			→		Fuel gas
			→		Liquefied petroleum gas
	→	→			
		polymerisation	Polymerisation naphtha		
	gas	→	n-Butane	*treatment*	Aviation petrol
	separation	*alkylation*	Full-range alkylate naphtha		
		→	Isomerisation naphtha	& →	Automotive petrol
	→	*catalytic*	Light straight-run naphtha		
		isomerisation	Full-range reformed naphtha	*blending*	Solvents
	atmospheric	→	Light hydrocracked naphtha		
	distillation	*naphtha hydro-*			
→		*desulfurisation*	Light catal. cracked naphtha		
		→	HDS heavy naphtha	*treatment*	Jet fuel
Crude oil	→	*catalytic*	Straight-run kerosene		Kerosene
		hydrocracking	Straight-run middle distillate	& →	Solvents
→		→	HDS middle distillate		Distillate fuel oils
	vacuum	*middle distillate*	Light catal. cracked distillate	*blending*	Diesel fuel oils
	distillation	*hydrodesulfurisation*			
		→	Heavy vacuum distillate	*treatment*	
	→	*catalytic*	Heavy catal. cracked distillate		
		cracking	Catal. cracked clarified oil	& →	Residual fuel oils
	solvent	→	Thermally cracked residue		
	De-	*coking*	Vacuum residue	*blending*	
	asphalting				
		→	Atmospheric tower residue		
	→	*visbreaking*			
		→	→		Bitumen
			→		Petroleum coke

HDS: hydrodesulfurised

Catal.: catalytical

Source: TPHCWG (Total Petroleum Hydrocarbon Criteria Working Group, Toxicology Technical Action Group)(1998), Analysis of petroleum hydrocarbons in environmental media, TPHCWG Series Volume 1. Amhers Scientific Publishers, Amhers MA, USA.

Appendix 3 Characteristics of principal refinery streams

Substance	CAS nr.	Carbon distribution	Boiling range	Remarks
Crude oil (petroleum)	8002-05-9	2 - >50	-80 - >600	Naturally occurring substance
Petroleum gases (fuel gas)	68131-75-9	3 - 4	-51 - -1	Mainly propane and propylene
Liquefied petroleum gas	68476-85-7	3 - 7	-40 - 80	Mainly propane and butanes
Polymerisation naphtha	64741-72-6	6 - 12	65 - 270	Mainly monoolefinic HCs
Full-range alkylate naphtha	64741-64-6	7 - 12	90 - 220	Mainly branched-chain saturated HCs
Isomerisation naphtha	64741-70-4	4 - 6	-10 - 60	Mainly branched-chain saturated HCs
Light straight-run naphtha	64741-46-4	4 - 10	-20 - 180	Mainly aliphatic HCs
Full-range reformed naphtha	68919-37-9	5 - 12	35 - 230	Complex combination of HCs
Light hydrocracked naphtha	64741-69-1	4 - 10	-20 - 180	Mainly saturated HCs
Light catal. cracked naphtha	64741-55-5	4 - 11	-20 - 190	Large proportion unsaturated HCs
HDS heavy naphtha	64742-82-1	7 - 12	90 - 230	Complex combination of HCs
Straight-run kerosene	8008-20-6	9 - 16	150 - 290	Complex combination of HCs
Straight-run middle distillate	64741-44-2	11 - 20	205 - 345	Complex combination of HCs
HDS middle distillate	64742-80-9	11 - 25	205 - 400	Complex combination of HCs
Light catal. cracked distillate	64741-59-9	9 - 25	150 - 400	Large proportion bicyclic arom. HCs
Hvy vacuum distillate	64741-57-7	20 - 50	350 - 600	Contains ≥ 5% 4-6 rings arom. HCs
Hvy catal. cracked distillate	64741-61-3	15 - 35	260 - 500	Contains ≥ 5% 4-6 rings arom. HCs
Catal. cracked clarified oil	64741-62-4	> 20	> 350	Contains ≥ 5% 4-6 rings arom. HCs
Thermally cracked residue	64741-80-6	> 20	> 350	Contains ≥ 5% 4-6 rings arom. HCs
Vacuum residue	64741-56-6	> 34	> 495	Complex combination of HCs
Atmospheric tower residue	64741-45-3	> 20	> 350	Contains ≥ 5% 4-6 rings arom. HCs
Bitumen (asphalt) *)	8052-42-4	> 25	400 - >550	Large proportion of HCs with high C/H ratio
Petroleum coke	64741-79-3	--	--	Carbonaceous material

Arom.: aromatic
Catal.: catalytical
Hvy: heavy
HC: hydrocarbon
HDS: hydrodesulfurised
*) In the USA ‘asphalt’ refers to ‘bitumen’ as defined in most parts of the world outside North America.

Sources:

CONCAWE (1992a): Liquefied petroleum gas. Product Dossier No. 92/102.
CONCAWE (1992b): Gasolines. Product Dossier No. 92/103.
CONCAWE (1992c): Bitumen and bitumen derivatives. Product Dossier No. 92/104.
CONCAWE (1993): Petroleum coke. Product Dossier No. 93/105.
CONCAWE (1994): Kerosenes/jet fuels. Product Dossier No. 94/106.
CONCAWE (1995): Gas oils (diesel fuels/heating oils). Product Dossier No. 95/107
CONCAWE (1997): Lubricating oil basestocks. Product Dossier No. 97/108.
CONCAWE (1998): Heavy fuel oils. Product Dossier No. 98/109.

Appendix 4 Examples of literature on terrestrial bioassays

1. Van den Munckhof, G.P.M., Veul, M.F.X., van Gestel, C.A.M. en Bloem, J. (1998) Bodemkwaliteitsparameters stimulering gebruik ecotesten. Rapporten Programma geïntegreerd bodemonderzoek, deel 14.

   Bioassays with four different soils are performed. The soils are from different locations, but soil characteristics are comparable. Concentrations of oil in the different soils are: <50 mg/kg, <50 mg/kg, 53 mg/kg and 370 mg/kg. Sample 1 is considered as a control sample. Effects in samples 2 to 4 are therefore compared with effects in sample 1. For *Eisenia fetida* no effect on activity is found. Growth is significantly affected in sample 4. No effects on survival and growth of *Folsomia candida* are found. Reproduction is significantly affected in sample 2 to 4.

2. Brouwer, L., van den Broek Humphrey, G.C., Breuking, C.M., Keidel, H., Bongers, A.M.T., Ma, W. en Meuldijk, P. (1998) Preofsanering meetstation 1 NAM Schoonbeek. Fase 2: Interpretatie en rapportage. NOBIS 95-1-44.

   Results are described of bioassays with three worm species, *Lumbricus rubellus, Eisenia veneta* and *Aporrectodea caliginosa,* in soils with varying total oil concentrations. Five different soils with concentrations of 240, 1900, 2700, 3700 and 8800 mg/kg oil and a laboratory reference are used. Soil characteristics are not reported. The effects studied are cocoon production and growth. In all the experiments reported effects occurred in the soil with the lowest oil concentration (240 mg/kg) compared with the reference value.

Appendix 5 Literature on effects of TPH on terrestrial species and processes: evaluated but rejected

1. Amadi, A., Abbey, S.D. and NMA, A. (1996) Chronic effects of oil spill on soil properties and microflora of a rainforest ecosystem in Nigeria. *Water, Air and Soil Pollution,* **86,** 1-11.

   Soil and microbiological properties of samples from tropical rain forest soil were evaluated 17 years after oil spillage to access chronic effects on hydrocarbon utilising and nitrifying micro-organisms. The spatial distribution of petroleum hydrocarbons, the nutrient status and the abundance of microbes along transect lines in the contaminated zone are assessed. Nutrient status and abundance of microbes between samples from a Heavy Impact zone (HI) and Moderate Impact zone (MI) are compared. The HI zone contained about 39 mg/kg Total Petroleum Hydrocarbons, the MI zone about 0.17 mg/kg Total Petroleum Hydrocarbons.

   This reference rejected because: 1) no control value was present, 2) soils with different characteristics used in one experiment, 3) no specification of mixture was given; results expressed as Total Petroleum Hydrocarbons.

2. Bombick, D.W., Arlian, L.G. and Livingston, J.M. (1987) Toxicity of jet fuels to several terrestrial insects. *Archives of Environmental Contamination and Toxicology,* **16,** 111-117.

   The acute toxicity of a variety of air force jet fuels was evaluated for several terrestrial insects. Results are expressed as LC50s in per cent fuel in acetone as pipetted on the surface of filter paper.

   Reference rejected because: 1) no control value was present (only a treatment - acetone - control used, 2) no soil was used, 3) no specification of mixture given; results expressed as added total oil concentrations.

3. Dorn, P.B., Vipond, T.E., Salanitro, J.P. and Wisniewski, H.L. (1998) Assessment of the acute toxicity of crude oils in soils using earthworms, microtox and plants. *Chemosphere,* **37,** 845-860.

   Heavy, medium and light crude oils were spiked into field soils in the laboratory. Tests were performed with earthworms (*Eisenia foetida*), bacteria and plants. Results expressed as percentage of total oil added to the soils. LC50 values expressed as mg/kg oil can be calculated. For earthworms in Norwood soil (0.3% organic carbon = 1.8 % organic matter) LC50s of 5300 and 6200 mg/kg oil were found for heavy oil, for medium oil thiese were 1300 and 1900 mg/kg oil, and for light oil, 1300, 1800 and 17000 mg/kg. LC50 values found for earthworms in Norwood/Baccto soil (4.7% organic carbon = 28% organic matter) were 71,000 and 63,500 mg/kg oil for the heavy oil, 23,400 and 25,600 mg/kg oil for the medium oil and 8500, 18,300 and 7300 mg/kg oil for the light oil.

   In summary, earthworm LC50s in a low organic carbon soil ranged from 1300-17,000 mg/kg oil for different types of oil. In a high organic carbon soil, LC50s for earthworms range from 8500-71,000 mg/kg oil for different types of oils.

   Reference rejected because: 1) no specification of mixtures was given; results expressed as per cent added oil to the soil.

4. Frankenberger, W.T. and Johansen, J.B. (1982) Influence of crude oil and refined petroleum products on soil dehydrogenase activity. *Journal of Environmental Quality,* **11,** 602-607.

   The effects of crude oil, leaded gasoline, kerosene, diesel fuel and motor oil on soil dehydrogenase activity were investigated by contaminating three different soils. The dehydrogenase activity is expressed as formazan (ug per g soil per 24 hours). Intercomparisons between soils loaded with 20%, 40% and 60% of different oil types were made.

Reference rejected because: 1) no control value given, 2) no specification of mixtures given; results expressed as per cent added oil to the soil.

5. Kireyeva, N.A. and Galimzyanova, N.F. (1996) Influence of soil pollution by oil and petroleum products on the population and species composition of micromycetes. *Eurasian Soil Science,* **28,** 96-105.

Laboratory and field experiments conducted with two types of soils. Oil and petroleum products added and fungal population analysed after different time-intervals. In the field experiment the influence of three different treatments (8, 16 and 25 l oil/m^3 on population and species composition of fungi were studied. No control value included. In the laboratory experiment 1,2,4,6,8,10 and 25 per cent oil of the weight of soil were added. Fungal biomass is determined three days after pollution .

Reference rejected because: 1) only three treatments are used in field experiments, 2) laboratory experiment has only one observation per treatment (reported), 3) no specification of soils given, 4) no specification of mixture and concentrations in soil; results expressed as total oil added per m^{-2}.

6. Pirhonen, R. and Huhta, V. (1984) Petroleum fractions in soil: effects on populations of nematoda, enchytraeidae and microarthropoda. *Soil biology and biochemistry,* **16,** 347-350.

Effects of light fuel oil and hydraulic oil on invertebrate populations of deciduous forest soil were investigated, with 6.25 l oil/m^2 spread on test plots. Total oil content was analysed at three time intervals. Soil animals were collected at six time intervals. Both types of oil almost totally destroyed the populations of microarthropods and practically no recovery was observed by the end of the study. Most Enchytraeidae were destroyed by the fuel oil but half of the population survived the hydraulic oil. Numbers of nematods decreased after application of the fuel oil and their numbers were twice those found in control plots at the end of the experiment. Hydraulic oil had no direct negative effects on nematods and numbers increased to many times that of the control.

Reference rejected because: 1) only one treatment for each oil was used in field experiments, 2) no specification of soil was used, 4) no specification of mixture given; results expressed as total oil added.

7. Riis, V., Stimming, M., Miethe, D. and Babel, W. (1996) Investigations into the toxicity of persistent fractions of mineral oils. *Chemosphere*, **32,** 1435-1443.

Effects on bioluminescence, dehydrogenase activity and respiration of oils or extracts from long-term contaminated soils were investigated. Exposure of cell-suspensions in solution, effects measured at start and after three time-intervals.

Reference rejected because: 1) results of oil (extracts) taken at beginning and after three time-intervals, 2) no soil was used, 3) no specification of oil(extracts) given; results expressed as total oil added in solution.

8. Salanitro, J.P., Dorn, P.B., Huesemann, M.H., Moore, K.O., Rhodes, I.L., Rice, L.M., Vipond, T.E., Western, M. and Wisniewski, H.L. (1997) Crude oil hydrocarbon bioremediation and soil ecotoxicity assessment. *Environmental Science and Technology,* **31,** 1769-1776.

Effects of two contaminated and bioremediated soils containing low (0.3%) or high (4.7%) organic carbon on earthworms (*Eisenia foetida*), bacteria and plants were investigated. Concentrations added varied from 12,000 to 14,000 mg/kg, from 26,000 to 27,000 mg/kg and from 4000 to 9600 mg/kg Total Petroleum Hydrocarbons (TPH) for a heavy, medium and light oil, respectively. For different time intervals after bioremediation, experiments with earthworms and plants were performed. Earthworms and plants were added to five different treatments and a control (bioremediated soil diluted with control soil). Survival at each time interval expressed as per cent of bioremediated soil in the treatment, resulting in 50% survival (earthworms) or effect on growth (plants). LC50 values expressed as mg/kg TPH can be calculated by combining TPH-analysis results and LC50s expressed asper cent bioremediated soil. For earthworms in Norwood soil (0.3% organic carbon = 1.8 % organic matter) LC50s ranged from 2860-8000 mg/kg TPH for the heavy oil, 880-9000 mg/kg TPH for the medium oil and 30-465 mg/kg TPH for the light oil. LC50 values for earthworms in Norwood/Baccto soil (4.7% organic carbon = 28% organic matter) ranged from

4420-13,000 mg/kg TPH for the heavy oil, 2600-11,000 mg/kg TPH for the medium oil and 96-2000 mg/kg TPH for the light oil.

In summary, earthworm LC50s in a low organic carbon soil ranged from 30-9000 mg/kg TPH for different types of oil. In a high organic carbon soil LC50s for earthworms range from 96-13,000 mg/kg TPH for different types of oils.

Reference rejected because: 1) no specification of oils given; results expressed as concentration Total Petroleum Hydrocarbons.

9. Song, H.-G. and Bartha, R. (1990) Effects of jet fuel spills on the microbial community of soil. *Applied and Environmental Microbiology*, **56,** 646-651.

Effects of jet fuel spills on a loamy soil were investigated for bacteria and fungi numbers and microbial activity. Changes in number of bacteria and fungi in contaminated soil and bioremediated soil at different time intervals are covered. In one experiment a control treatment is included, but only two treatments are used.

Reference rejected because: 1) effects were at different time intervals of two, 2) no specification of oils given; results expressed as concentration Total Petroleum Hydrocarbons

Appendix 6a Aliphatic TPH fractions: Hum-Tox SCCs, related groundwater concentrations and parameter involved

		EC 5-6	EC >6-8	EC >8-10	EC >10-12	EC >12-16	EC >16-21
M	$g.mol^{-1}$	81	100	130	160	200	270
S	Mol. m^{-3}	3.46E-01	4.2E-02	2.54E-03	1.63E-04	2.95E-06	3.70E-09
Vp	Pa	5.07E+04	8.61+03	8.21E+02	7.90E+01	3.55E+00	1.72E-01
Klw	-	47	50	55	60	69	87
log Kow	-	3286	3986	4886	5786	7086	9385
log Koc	$Dm^3.kg^{-1}$	2.9	3.6	4.5	5.4	6.7	9
Koc	$Dm^3.kg^{-1}$	7.94E+02	3.98E+03	3.16E+04	2.51E+05	5.01E+06	1.00E+09
MTR	Mg/kg $bw.d^{-1}$	2	2	0.1	0.1	0.1	2
TCL	Mg/m^3	18.4	18.4	1	1	1	0
HUMTOX SCC	Mg/kg	28	99	27	155	52000	>100000 *1
IV-ground Water	µg/l	51	41	1.47	1.06	0.59 *2	0.001 *2

*1 With a daily intake of 150 mg/kg (assumption in CSOIL) there are no Hum-Tox restrictions.
*2 The solubility is less than the calculated IVgroundwater value; the IVgroundwater is based on solubility.

Appendix 6b Aromatic TPH fractions; Hum-Tox SCC, related groundwater concentration and parameters involved

		EC 5-7	EC >7-8	EC >8-10	EC >10-12	EC >12-16	EC >16-21	EC >21-35
M	$g.mol^{-1}$	78	92	120	130	150	190	240
S	Mol. m^{-3}	2.82E+00	1.41E+00	5.42E-01	1.92E-01	3.87-02	2.68E-03	2.75E-05
Vp	Pa	1.11E+04	3.24E+03	8.21E+02	7.90E+01	3.55E+00	1.72E-01	8.00E-04
Klw	-	1.5	0.82	0.39	0.13	0.028	0.0019	0.000017
log Kow	-	3386	3.486	3586	3786	4086	4586	5486
log Koc	$Dm^3.kg^{-1}$	3	3.1	3.2	3.4	3.7	4.2	5.1
Koc	$Dm^3.kg^{-1}$	1.00E+03	1.26E+03	1.58E+03	2.51E+03	5.01E+03	1.58E+04	1.26E+05
MTR	Mg/kg $bw.d^{-1}$	0.11	0.11	0.04	0.04	0.04	0.03	0.03
TCL	Mg/m^3	nb	0.4	0.2	0.2	0.2	0	0
HUMTOX SCC	Mg/kg	58	130	95	363	860	10118	17563
IV-ground Water	µg/l	99	177	103	249	296	509 *1	6.6 *1

*1 The solubility is less than the calculated IVgroundwater value; the IVgroundwater is based on solubility.