Principles for Evaluating the Human Health Risks from Petroleum Hydrocarbons in Soils:

A Consultation Paper

R&D Technical Report P5-080/TR1

Publishing Organisation
Environment Agency, Rio House, Waterside Drive, Aztec West, Almondsbury,
BRISTOL, BS32 4UD.

Tel: 01454 624400 Fax: 01454 624409
Website: www.environment-agency.gov.uk

© Environment Agency 2003 June 2003

ISBN 1 84432 0162

All rights reserved. No part of this document may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise without the prior permission of the Environment Agency.

The views expressed in this document are not necessarily those of the Environment Agency. Its officers, servants or agents accept no liability whatsoever for any loss or damage arising from the interpretation or use of the information, or reliance upon views contained herein.

Dissemination Status
Internal: Released to Regions
External: Released to Public Domain for Consultation

Statement of Use
This publication describes a proposed approach to the preparation of health criteria values, Soil Guideline Values and other supporting guidance for assessing the risks to health of petroleum hydrocarbons in soil. The report has been written for technical professionals familiar with the risks posed by land contamination to human health but who are not necessarily experts in risk assessment. It is expected to be of use to all parties involved with or interested in contamination, but in particular to those concerned with the assessment of land contamination.

Keywords
petroleum hydrocarbons, total petroleum hydrocarbons, TPH, land contamination, risk assessment, human health

Environment Agency Project Manager
Dr Raquel Duarte-Davidson, Risk Analyst, Environmental Policy - Risk and Forecasting, the Environment Agency, Kings Meadow House, Kings Meadow Road, Reading, RG1 8DQ

During the consultation period (before 3rd October 2003) copies of this report can be obtained from: Petroleum Hydrocarbons Consultation, MRC Institute for Environment and Health, University of Leicester, 94 Regent Road, Leicester, LE1 7DD.

After the consultation period

Further copies of this report are available from: Environment Agency R&D Dissemination Centre, c/o WRc, Frankland Road, Swindon, Wilts SN5 8YF

tel: 01793-865000 fax: 01793-514562 e-mail: publications@wrcplc.co.uk

ACKNOWLEDGEMENTS

This document is based on material collated and prepared by the Institute for Environment and Health (2001), TNO BIBRA (2002) and Cranfield University (2003). Entec UK Ltd provided assistance in the management and delivery of this document. The Environment Agency greatly acknowledges the valuable inputs from various independent experts and government agencies and departments, particularly the Department of Health and the Food Standards Agency.

EXECUTIVE SUMMARY

This document is an Environment Agency consultation paper on the principles for assessing the health risks from petroleum hydrocarbons in contaminated soil. A significant change to current UK practice is needed, in order to take account of the risk-based approach of Part IIA of the Environmental Protection Act 1990 and the requirements of Town and Country Planning Acts, in which land contamination is a material planning consideration. The Agency is inviting your views on the principles, before preparing a detailed risk-based approach to assessing health risks from petroleum hydrocarbons in soil.

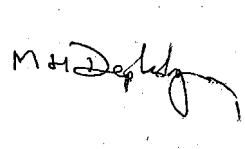
Petroleum hydrocarbon contamination is complex. The type of crude oil, its distillation, processing and blending, and the subsequent processes that act on the material once it is released into the environment all result in the development of petroleum residues of extreme chemical complexity. Yet sound, defensible and practical decisions are required on how to manage the risks to human health from exposure to petroleum hydrocarbons in soil.

Other industrialised countries have been faced with the same problem. The modern, risk-based approaches that have been developed, largely as a result of exhaustive reviews and consultations, offer some direction as to the approach that should be adopted in the UK. Decisions need to be made about the handling of compounds that exhibit threshold and non-threshold toxicological effects, about the degree of sophistication that should be adopted in a UK approach and about issues of implementation, including the practical aspects of analysis and the costs for site and risk assessments.

In this consultation we introduce the need for change, summarise the approaches used internationally and propose a way forward, outlining the key issues requiring input from consultees.

The outcome of this consultation will be a framework setting out the approach to be used and the representative substances or petroleum fractions to be considered in the health risk assessment of petroleum hydrocarbons in soils. Following this, detailed toxicological and fate and behaviour reviews will be prepared for those substances or fractions selected as representative of petroleum contamination. The framework and the review information will be combined to derive Soil Guideline Values (SGVs) for petroleum hydrocarbons in soils.

We look forward to receiving your input to this process and hearing of your practical experiences.



Professor Michael Depledge
HEAD OF SCIENCE

Toby Willison
HEAD OF LAND QUALITY

CONTENTS

1. INTRODUCTION

Petroleum hydrocarbons in soil

1.1 Past releases of petroleum hydrocarbons to the soil environment may pose potential risks to human health, water resources, ecosystems, property and other environmental receptors. Managing the potential risks requires an understanding of the impact of exposure to petroleum on each of these receptors, enabling the development of a structured risk assessment framework.

1.2 Unacceptable risks to human health and the environment from past land contamination are being addressed in the UK by Part IIA of the Environmental Protection Act 1990. Implementation of Part IIA provides the opportunity to develop a framework for the risk assessment of petroleum contamination in soils that addresses UK legislation and its supporting guidance and provides clarity in the process. This will also assist planning authorities to make decisions under the Town and Country Planning Acts, for which land contamination is a material consideration.

Purpose of consultation

1.3 This document deals only with risks to human health. It is an Environment Agency consultation paper on the principles for assessing the health risks from petroleum hydrocarbons in contaminated soil. A significant change to current practice is needed in order to take account of the risk-based approach in Part IIA. The Agency is inviting views on the principles, before preparing a detailed risk-based framework.

1.4 Understanding the toxicology of environmental contaminants in soil is essential if the risks to human health are to be managed responsibly. The toxicological evaluation of petroleum hydrocarbons is particularly difficult because these substances are present in the environment as complex mixtures, containing many hundreds of individual compounds, each with their own toxicological properties (IARC, 1989; ATSDR, 1999; CCME, 2000). Similarly, it is impractical to analyse for individual compounds when present in complex mixtures. Hence a scientifically sound and practical approach to managing risk is required that is protective of human health.

Who is being consulted?

1.5 Views are being sought from industry and its advisors, trade associations and trade bodies, Government departments and their agencies, non-government organisations, regulators, sector bodies, analytical laboratories, special interest groups, land remediation specialists, consultants and interested members of the public.

1.6 Views are welcomed on the specific issues and questions highlighted in section 4 of this document. Comments received will be considered and addressed in a separate publication. **Respondents should clearly state if they do not wish to be named, do not want their comments to be detailed in the publication and if they are commenting as individuals or on behalf of an organisation.**

What happens next?

1.7 The outcome of this consultation will be a framework setting out the approach to be used and the representative substances or petroleum fractions to be considered in the health risk assessment of petroleum hydrocarbons in soils. Following this, detailed toxicological and fate and behaviour reviews will be prepared for those substances or fractions selected as representative of petroleum contamination. The framework and the review information will be combined to derive Soil Guideline Values (SGVs) for petroleum hydrocarbons in soils.

Structure of this document

1.8 This consultation document is an extended summary of the issues and options rather than an exhaustive review. The remaining part of this document summarises the context and background to the need for a revised approach (section 2), briefly reviews other approaches adopted internationally (section 3), and presents a way forward, setting out the key technical issues on which the Environment Agency is inviting comment (section 4). Section 5 explains how comments can be submitted to the Agency. References are provided in section 6.

2. CONTEXT AND BACKGROUND

2.1 'Petroleum' is the term used for the naturally occurring liquid and gas produced when 'kerogen' is subject to high pressure and temperature, usually within the depths of the marine environment. Kerogen is the most abundant form of organic carbon in the earth's crust. It forms as organic matter from dead plants and animals decays and is deposited in marine sedimentary rocks. The organic matter is first broken down and then re-formed into complex chemical structures. As the temperature increases with increasing depth of burial below the sea, these complex chemical structures break down and some of the resulting hydrocarbons form oil (and gas), which then accumulate (Killops and Killops, 1993). The chemical structure of crude petroleum is complex and variable and alters according to both the nature of the parent material and conditions under which the crude petroleum has formed.

2.2 Petroleum refining is the process of distilling and processing various fractions of the crude oil for use as fuels (Table 2.1), petroleum products and feedstocks for many industrial products and synthetic chemicals.

Table 2.1 – Typical composition of some petroleum fuels

Composition / Product	Automotive gasoline [a]	Automotive diesel (DERV) [a]	No.6 Fuel oil
Alkane carbon number range	*n*-C_4–*n*-C_{12}	*n*-C_8–*n*-C_{21}	*n*-C_{12}–*n*-C_{34}
Boiling point range (°C)	40–200 (25–220) [b]	200–325 (160–390) [c]	350–700
Average composition (wt %)			
n-alkanes (straight chain)	>12.1	13.0	1.7
Total straight chain and iso-alkanes	47.0 (30–90 % vol) [b]	41.0	13.0
Total cycloalkanes	3.2 (1–35 % vol) [b]	37.0	15.2
Alkenes	10.0 (0–20 % vol) [b]	1.3	ND
Benzene	1.9	0.03	ND
Total xylenes	9.0	0.5	ND
Total monoaromatics	19.0 (BTXs) [d]	16	>4.0
Total polynuclear aromatics	ND	0.36	>0.37
Total aromatics	35.0 (5–55 % vol) [b]	22	34 (78.9) [e]

From TPHCWG, 1999a
ND, No data
[a]'Automotive gasoline' and 'Automotive diesel' are broadly synonymous with the UK terms 'Petrol' and 'Diesel', sold for use in motor vehicles, respectively
[b]Data from CONCAWE, 1992
[c]Data from CONCAWE, 1996, these values refer to fuels marketed in Europe
[d]BTXs, benzene, toluene and xylenes (commonly classified as BTEXs, which also includes ethylbenzene)
[e]Data from ATSDR, 1999, the large disparity between the percentage figures for total aromatics is probably due to the ATSDR data including heterocyclic (*O*, *N*, *S*-containing) aromatic compounds; the TPHCWG data on which the table is based detail No.6 fuel oil as containing 30% polar material

2.3 The refining, processing, transportation, blending, storage and use of petroleum products as fuels and feedstocks have resulted in the growth of numerous inland refinery, distribution, storage and auxiliary facilities. The petroleum

contamination of soils has often been an undesirable consequence of the operation of facilities, such as complex integrated refineries, manufacturing sites, power plants, distribution depots and retail service stations (Environment Agency, 1998). The nature and extent of contamination at these facilities can vary greatly from being insignificant to substantial, and the potential for human exposure to harmful components in the released oils can also vary widely. Site conditions, the local environmental setting, the extent and nature of contamination and the proximity to human populations all have a bearing on the nature of the risks to human health posed at these sites (Institute of Petroleum, 1993; CONCAWE, 1997).

2.4 The chemical complexity of petroleum releases to the soil arises, in part, from the chemical complexity of petroleum itself. Commercial fractions of petroleum (e.g. naphtha, gasoline, kerosene, gas oil, fuel oils, asphalt *etc*.), which are defined in terms of their boiling point range, each contain many hundreds of individual chemicals amassed together as a 'spectrum' of closely related compounds. The fractions produced from distillation, each of which is a characteristic subset of the crude oil from which it is distilled, overlap in their composition because there is never a perfect 'cut' or separation during distillation (API, 2001). Conventionally, the notation *n*-C_x–*n*-C_y for these fractions describes the carbon number range of straight chain *n*-alkanes in the fraction. The fraction C_6-C_9, for example, represents the fraction between *n*-hexane (6 carbon atoms) and *n*-nonane (9 carbon atoms).

2.5 The secondary processing of petroleum distillates adds further complexity. Thermal and catalytic 'cracking' is used to increase the yield and performance of petroleum products with high market demand, such as gasoline. Typically, the gaseous cracked products from kerosene or gas oil feedstocks are fed into a flash distillation chamber and further separated into gasoline and light gas oil, and the liquids are sent to a vacuum fractionator and separated into heavy gas oil and vacuum tar or residuum (Schobert, 1990).

2.6 Once released to the environment in a spill or leak, petroleum constituents partition, to differing extents, between the oil phase and the air, soil and water phases of the environment (Zemanek *et al*, 1997). Physical, chemical and biological processes 'weather' or age the spilled product, resulting in additional changes in composition and complexity (Westlake *et al*, 1974; Morgan and Watkinson, 1989; Pollard *et al,* 1999).

2.7 Decision-makers (e.g. site owners, developers, occupiers and regulators) charged with making informed and scientifically sound decisions about how to manage risks at petroleum-contaminated sites must take into account the complexity of the situation, within a practical decision framework. Among the factors they must take into account (section 4) are:

- the chemical and physical complexity of the source of contamination and the changes in composition of the contaminating material that have taken place since spillage;
- how to measure the extent and nature of contamination in a way that is meaningful and relevant to the risks it may pose;
- how to establish toxicological criteria for petroleum contamination in soil;

- how to account for the different toxicities of the thousands of individual compounds that may be present in the contaminating material and the range of potential adverse health effects that could result from short-, medium- or long-term exposure to these compounds; and

- how to make clear, consistent, pragmatic and sustainable decisions that protect human health but are not over-burdensome in terms of the societal costs of remediation.

2.8 These issues are not new. Many other countries have, in consultation with their stakeholders, developed decision frameworks that guide decision makers through a series of steps to determine how best to manage risks from petroleum contamination. Several reviews underpinning the development of these frameworks have been published (CCME, 2000; API, 2001; MaDEP, 2002a).

2.9 A formalised approach has yet to be established in the UK. Historically, *ad hoc* approaches have been applied to managing petroleum contamination, using simple analytical procedures to quantify the extent of contamination. Measurements such as 'total petroleum hydrocarbons (TPH)' have been used as surrogates for estimating the petroleum load of soils. This parameter, as with all analytical methods, is defined by the method used for analysis. Unless the spillage is well defined, reliance on a single parameter for petroleum hydrocarbons is unlikely to provide a sound basis for risk management. Surrogate measures, such as TPH analysis, indicate little about the risks posed by contamination (Gustafson, 2002). For example, TPH can be measured in material that is not derived from petroleum (API, 2001; Table 2.2).

Table 2.2 – Representative TPH measurements of naturally- and petroleum-derived materials

Sample	Grass	Dried oak leaves	No.6 Fuel oil	Household petroleum jelly
TPH (mg kg^{-1})	14,000	18,000	16,000	749,000

From API (2001)

2.10 Recognising this and other limitations, some of the international approaches to analysing and assessing the risks from petroleum-contaminated sites have been adopted in the UK over the last 10 years (*e.g.* ASTM, 1995, 2000; TPHCWG, 1997a,b; TNRCC, 2001). These approaches offer a more robust basis for assessing the risks from petroleum contamination as they focus on the components that pose most risk owing to their toxicological potency, presence in the environment and environmental fate and behaviour.

Legal framework

2.11 Two predominant pieces of legislation directly impact on contaminated land in the UK: The Town and Country Planning Acts, and Part IIA of the Environmental Protection Act 1990 (the contaminated land regime). Both Part IIA and the planning regime embrace the 'suitable for use' approach.

2.12 Under the Town and Country Planning Acts land contamination is a material planning consideration. This means that a planning authority has to consider the potential implications of contamination both when it is developing structure or local plans (or unitary development plans) and when it is considering individual applications for planning permission. Where contamination is suspected or known to exist at a site, a planning authority may require investigation before granting planning permission, or may include conditions on the permission requiring appropriate investigation and, if necessary, remediation.

2.13 Part IIA of the Environmental Protection Act 1990 (which was inserted by Section 57 of the Environment Act 1995) is a regime for the identification and remediation of contaminated land. This introduces a definition of contaminated land, for the purpose of the regime, and (as regards England) is described fully in DETR Circular 02/2000 (DETR, 2000). Part IIA has also been implemented in Wales and Scotland, with only minor differences from the regime implemented in England. The main functions under the regime are exercised by local authorities and, in certain circumstances, the Environment Agency or the Scottish Environment Protection Agency.

2.14 Part IIA is intended to complement the planning regime (which deals with risks to new development or land–uses arising from existing contamination). It also complements other regulatory regimes, including the Pollution Prevention and Control regime, Groundwater Regulations, Consents to Discharge and the system of waste management licensing, which control and limit future pollution.

2.15 Given the requirements of the contaminated land legislation (DETR, 2000) in England and Wales, the Environment Agency considers that a framework for the evaluation of human health risks from petroleum hydrocarbons in soils should:

- be scientifically authoritative and based on the principles of toxicology, exposure and risk;
- be based on a state-of-the-art understanding of petroleum in the environment;
- be able to be implemented by the full range of practitioners and disciplines involved in the contaminated site assessment and management processes;
- be proportionate to the risks posed; and
- enable decision-makers to arrive at practical, sound management decisions that are protective of human health.

2.16 The Environment Agency has concluded that a consistent approach is required and sets out its draft proposals in section 4 of this document. Prior to this, the international approaches that have been adopted elsewhere are briefly reviewed in the next section. More detailed descriptions of these approaches can be obtained from the references in section 6.

3. APPROACHES TO ASSESSING THE HEALTH RISKS FROM PETROLEUM HYDROCARBONS IN SOIL

3.1 A number of national organisations have proposed approaches for setting soil assessment criteria for petroleum hydrocarbon mixtures, using reviews of petroleum toxicology and existing regulatory approaches as a starting point. The approaches used fall broadly into two groups, as described below.

(1) *The use of generic assessment criteria for TPH or whole products* (diesel fuel, fuel oil etc.). These are usually developed following a review of international values for petroleum hydrocarbons in soil, and are levels above which action is required. Such criteria may or may not be risk based, and the toxicological basis for the criteria may be unclear. This approach was widely used for the development of soil assessment criteria in the late 1980s to mid 1990s. In practice, few sites have distinct, recent (i.e. unweathered), and well-characterised petroleum contamination, and the Environment Agency considers it necessary to progress to the adoption of authoritative risk-based approaches. Approaches based on TPH or whole products are, therefore, not reviewed in detail in this document.

(2) *The use of generic assessment criteria for indicator compounds and/or petroleum fractions together with the use of exposure models*. These criteria are *toxicologically driven* and developed from *risk-based approaches*. Here the emphasis is on identifying the key indicator compounds and/or petroleum fractions presenting risks at a site, by reference to their toxicology and/or environmental behaviour. These approaches usually start with simple initial assessments and build in complexity, as required, into a 'tiered' approach, similar to that adopted for environmental risk assessment in England and Wales (DETR *et al*, 2000). Screening criteria act as an initial check for site assessors; more detailed assessments are undertaken in later tiers if screening criteria are exceeded.

3.2 For evaluations of petroleum fractions rather than individual compounds, some working groups have adopted the 'Equivalent Carbon' (EC) number convention (Twerdok, 1999). The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) chose the concept of EC numbers because these values are logically related to compound mobility in the environment (TPHCWG, 1999b). The EC index is used to normalise petroleum constituents by reference to boiling point and to the carbon number of their *n*-alkane equivalents. For compounds with fewer than about 10 carbon atoms EC numbers are generally similar to the number of carbon atoms. However, above 10 carbon atoms EC values for aromatic compounds are smaller than those for aliphatic compounds with the same number of carbon atoms (MaDEP 2002a).

3.3 Most approaches in the second group, described in (2) above, distinguish between the risks posed by exposure to contaminants that exhibit threshold toxicological behaviour and those that exhibit non-threshold effects. For threshold effects many of the approaches adopt the US Environmental Protection Agency (USEPA) 'reference dose' (RfD) and 'reference concentration' (RfC) as the basis for the toxicological criteria that underpin soil assessment criteria (USEPA, 1986). The RfD is 'an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population that is

likely to be *without* an appreciable risk of deleterious effects during a lifetime'. The RfC is the inhalation equivalent and is expressed as an air concentration (USEPA, 1986).

3.4 Although reducing the number of petroleum hydrocarbon constituents to a smaller number of representative fractions simplifies the risk assessment process, it can still be complex. Some authorities have adopted s*treamlined approaches* in an attempt to develop risk assessment processes that are easier to use. These approaches are toxicologically based and recognise the costs of assessment. They attempt to reconcile thoroughness with efficient decision-making by reducing the number of petroleum fractions considered when assessing the risk from threshold substances.

3.5 The following paragraphs summarise the approaches adopted by various jurisdictions to evaluate the human health risks of petroleum hydrocarbons in soils. Most are risk-based approaches for indicator compounds or petroleum fractions (2, above).

The ASTM guides to risk-based corrective action

3.6 An example of a risk-based indicator compound approach is that developed by the American Society for Testing and Materials (ASTM). ASTM standards E1739-95 and E2081-00 represent three-tier approaches to risk-based corrective action (RBCA) at petroleum- and chemically-contaminated sites (ASTM, 1995, 2000) and are in wide use in North America and Europe. They rely on reviews of toxicology and environmental fate and exposure, which are used as the basis for the development of risk-based soil screening levels (RBSLs) and site-specific target levels (SSTLs) for assessing risks from contaminated soil. As site assessors move down the three tiers of the assessment, the tiers become less generic and less conservative, although each tier has the objective of compliance with an acceptable level of risk.

3.7 The RBCA approach assumes a significant proportion of the total impact on human health from all chemicals in soil is due to specific compounds, termed 'chemicals of concern', of significant toxicological potency. Other compounds or petroleum fractions are not considered. The most commonly selected chemicals of concern for sites contaminated by gasolines, kerosene and jet fuels are benzene, toluene, ethylbenzene and xylene (BTEX). Depending on the nature of the spill, it may also be necessary to test for lead and other fuel additives. For kerosene and fuel oils, polycyclic (or polynuclear) aromatic hydrocarbons (PAHs) are important, and twelve PAHs, including benzo[*a*]pyrene, are evaluated.

3.8 Under RBCA, a Tier 1 evaluation is a risk-based analysis that compares the environmental concentrations of chemicals of concern from an initial site assessment with conservative (health-protective) RBSLs. Where the RBSLs are exceeded, the site assessor proceeds to Tier 2. Tiers 2 (simple fate and transport analyses) and 3 (complex fate and transport analyses) require the derivation of SSTLs. Each tier involves increasingly sophisticated levels of data collection and analysis with the conservative assumptions of earlier tiers being replaced with site-specific data and information. A RBCA site remediation is governed by the most conservative RBSL or SSTL (depending on the tier of assessment). The use of whole mixture toxicity data and the assumption of additivity for chemicals in a

mixture are mentioned as options for Tiers 2 and 3, but neither approach is recommended by the ASTM (ATSDR, 1999).

The US State of Massachusetts Department of Environmental Protection approach

3.9 For assessing the threshold risk[1] at petroleum-contaminated sites, rather than evaluating individual compounds, another approach is the use of representative petroleum fractions. The Massachusetts Department of Environmental Protection (MaDEP, 1994, 1997, 2002a,b), which has been instrumental in implementing revised approaches to petroleum risk assessment since the early 1990s, proposes that focussing on a select few compounds is insufficient for characterising the risks posed by all hydrocarbons present (MaDEP, 2002a). MaDEP work from 1994 onwards (MaDEP, 1994; Hutcheson *et al,* 1996) on the petroleum fraction approach has influenced the work of the *ad hoc* TPHCWG and, in turn, that of the ATSDR (1999), described later in this section.

3.10 The MaDEP approach assesses key contaminants, 'target analytes', on an individual basis. Target analytes include non-threshold compounds (e.g. benzene, benzo[*a*]pyrene and some PAHs) and substances that have been conventionally used to characterise petroleum contamination (e.g. toluene, ethylbenzene, xylene and threshold PAHs). Toxicological criteria are derived for threshold risks by treating groups of petroleum compounds present in environmental samples as if all compounds in the group were all equally toxic. For each compound group or fraction, a 'reference compound' is identified. Oral and, more recently (MaDEP 2002 a,b), inhalation health criteria values for the reference compounds are then applied to the whole fraction. The underlying assumption is that the toxicity of each of the other compounds within the fraction is equal to that of the reference compound.

3.11 The original basis for the grouping of compounds was the segregation of petroleum constituents into four broad chemical classes, namely alkanes, cycloalkanes, alkenes and aromatics. The alkanes and cycloalkanes were treated together, owing to their toxicological similarities (MaDEP, 1994), as were the alkenes and aromatics, as they were separated together in the recommended analytical procedures (MaDEP, 1994). Toxicological justification for the consideration of aromatics and alkenes together was based on their similar metabolic pathways and the low proportion of alkenes in petroleum products (typically less than 5%) (MaDEP, 1994). Following a review of the toxicology of these groups of compounds, it was apparent that the toxicity of the alkanes/cycloalkanes decreased with an increase in the number of carbon atoms. For the aromatics/alkenes there was comparatively little variation in toxicity values. On this basis, rather than considering the four chemical classes originally proposed, four petroleum fractions were selected, three for alkanes/cycloalkanes and one for the aromatics/alkenes.

3.12 The 1994 MaDEP approach has since been updated (MaDEP, 2002a,b) to ensure that the most recent toxicological and analytical advances are incorporated into the guidance. Terminology was altered in accordance with that of the TPHCWG (see paragraphs 3.19 to 3.30) which divided petroleum hydrocarbons into

[1] MaDEP documents refer to carcinogenic and non-carcinogenic risks. MaDEP 1994 uses these terms synonymously with non-threshold and threshold risks (MaDEP, 1994).

aromatic and aliphatic fractions. Given the toxicological dominance of the alkanes and the aromatics MaDEP (2002 a,b) simply refers to aromatics/alkenes as aromatics and alkanes/cycloalkanes as aliphatics. Toxicological criteria for individual fractions have been revised in accordance with the recommended Volatile Petroleum Hydrocarbon (VPH) and Extractable Petroleum Hydrocarbon (EPH) methods of analysis. Although the four fractions identified in the 1994 guidance are retained, MaDEP (2002b) chose to designate six sub-fractions to minimise the use of both VPH and EPH methods on all samples. These fractions and sub-fractions are summarised in Table 3.1.

Table 3.1 – MaDEP hydrocarbon fractions

Toxicologically defined hydrocarbon fraction	Analytical/program defined hydrocarbon fraction	Analytical method	Reference dose (mg kg^{-1} bw d^{-1})	Reference concentration (mg m^{-3})
C_5-C_8 Aliphatics	C_5-C_8 Aliphatics	VPH	0.04	0.2
C_9-C_{18} Aliphatics	C_9-C_{12} Aliphatics	VPH	0.1	0.2
	C_9-C_{18} Aliphatics	EPH	0.1	0.2
C_{19}-C_{36} Aliphatics	C_{19}-C_{36} Aliphatics	EPH	2.0	N/A
C_9-C_{22} Aromatics	C_9-C_{10} Aromatics	VPH	0.03	0.05
	C_{11}-C_{22} Aromatics	EPH	0.03	0.05

From MaDEP 2002b
N/A, Not applicable

3.13 The MaDEP VPH Method (MaDEP 1998a) is a purge and trap, gas chromatography, with photoionisation detection or flame ionisation detection (GC/PID/FID), procedure. As well as measuring the petroleum fractions identified in Table 3.1, the VPH method may also be used to measure concentrations of the target VPH analytes, namely BTEX, methyl-tertiary-butylether and naphthalene.

3.14 The MaDEP EPH Method (MaDEP 1998b) is a solvent extraction/fractionation GC/FID procedure. As with the VPH method, the EPH method may also be used to measure concentrations of the PAH target EPH analytes.

3.15 The MaDEP approach for undertaking a risk assessment is implemented through the Massachusetts Contingency Plan (MCP). The MCP details the State regulations that govern the remediation of sites contaminated by oil or hazardous materials and now includes provisions for the VPH/EPH approach and standards (MaDEP, 2002b). The MCP offers three methods for assessing the risks associated with contamination, each of which requires an increasing level of site-specific knowledge and assessment:

- Method 1 - generic cleanup standards in soil and groundwater;
- Method 2 - site-specific modification of generic cleanup standards; and
- Method 3 - completely site-specific risk assessment.

Method 1 uses generic 'soil standards', which were designed to be protective at most sites. The standards were developed using a series of conservative site scenarios to evaluate risks to human health, public welfare, and the environment via a number of exposure routes and pathways, including direct contact, ingestion, leaching (soil), and volatilisation (groundwater). Method 2 involves the modification of the standards used in Method 1 to include consideration of site-specific fate and transport factors, such as depth to groundwater, soil permeability, soil organic carbon content, etc. Method 3 is entirely site-specific and involves the determination of quantitative risk levels for all contaminants present at a site, for comparison with specified risk management standards for threshold and non-threshold health effects.

3.16 Whichever method is chosen, analyses for appropriate target analytes and fractions are undertaken concurrently, helping assessors to identify the key risk drivers prior to any remedial activity. It is not a requirement to test for all target analytes and fractions - only those considered to be of interest, given knowledge of contamination at a site. To avoid the double counting of substances, the mass of target analytes present is subtracted from the corresponding mass fraction. For example, the mass of benzo[*a*]pyrene in a sample would not be included when determining the overall mass of the aromatic fraction.

3.17 In producing cleanup standards for each fraction based on toxicology alone, MaDEP recognised that the low toxicity of some of the components of petroleum hydrocarbons (e.g. heavy aliphatics) could result in significant levels of residual material being left behind in soils. At these levels other issues of 'public welfare' could be affected, such as staining, odour and other aesthetic concerns. To address the issue of public welfare, MaDEP introduced 'ceiling levels' of contaminants in soils, thereby limiting the potential for significant amounts of residual material to be left in the soil. Ceiling levels were derived for use in Method 1 and 2 assessments. For Method 3 assessments, the parties involved are required to demonstrate that 'public welfare' has been appropriately addressed.

3.18 A precautionary approach is used for the assessment of the additive effects of substances. For substances exhibiting non-threshold toxicological effects (e.g. benzene, benzo[*a*]pyrene), the overall risk is estimated using oral slope factors and unit risk estimates. If the resulting excess lifetime cancer risk exceeds 1 in 100,000, further investigation or remedial work is required. For the substances and fractions exhibiting threshold effects, a hazard index is calculated, based on the ratio of the expected dose or concentration to the toxicological criteria value. All of the ratios are added together to produce an overall hazard index. If this value exceeds 1, further assessment or site remediation is required.

The Total Petroleum Hydrocarbons Criteria Working Group approach

3.19 The TPHCWG (the Working Group) was established in 1993 as a US national *ad hoc* consortium with wide representation from the oil and gas industry, the environmental consulting community, the US military, academia and the US regulatory agencies to 'develop scientifically defensible information for establishing soil cleanup levels that are protective of human health at hydrocarbon contaminated sites' (TPHCWG, 1997a, Twerdok, 1999). Much of the work builds on the MaDEP (1994) proposals. Reports published to date (TPHCWG 1997a,b, 1998a,b, 1999a,b) are available on the internet at www.aehs.com.

3.20 The Working Group first considered whether human health toxicity associated with petroleum contamination should be evaluated using toxicity data on the whole product, on a fraction, or on indicator compounds (TPHCWG, 1999b). The whole product method is considered to be appropriate for fresh spills not subject to weathering. However, for the more common problem of weathered product, a hybrid method has been selected that employs fractions and carcinogenic (non-threshold) indicator compounds. The Working Group supports the use of appropriate indicator compounds, based on the type of petroleum used at the site (e.g., benzene and MtBE for gasoline sites, PAHs for heavy oil sites).

3.21 Understanding the potential exposures resulting from petroleum contamination is essential for reasonable estimates of human health risk (TPHCWG, 1999b). The Working Group has established petroleum hydrocarbon fractions based on transport properties of the compounds (TPHCWG, 1997a). The fractions selected are based on EC numbers (paragraph 3.2), as they are considered to be closely related to compound mobility in the environment (TPHCWG, 1999b).

3.22 In considering the transport properties of petroleum constituents, the Working Group calculated leaching factors and volatilisation factors for 250 individual petroleum compounds. Plotting these factors against EC numbers for each compound (TPHCWG, 1999b) indicated differing behaviours for aromatic and aliphatic compounds in the environment. Aromatic compounds tend to be more soluble in water and slightly less volatile than aliphatic compounds with similar EC numbers. On this basis, the Working Group has divided petroleum constituents into aromatic and aliphatic hydrocarbon fractions.

3.23 The data review undertaken by the Working Group shows that leaching and volatilisation factors for aromatic and aliphatic compounds cover several orders of magnitude. Thus in the TPHCWG approach the aromatic and aliphatic fractions are further divided into 13 transport fractions, with leaching and volatilisation factors that differ by approximately one order of magnitude. The Working Group considers a ‘one order of magnitude’ criterion for defining fractions is appropriate in view of the levels of uncertainty associated with toxicity assessments and exposure assessments (TPHCWG, 1999b).

3.24 The Working Group reviewed a number of methods for analysing petroleum contamination in soils (TPHCWG, 1998a). The recommended method for analysing petroleum hydrocarbon fractions is the ‘direct method’ (AEHS, 2000), which is a GC method developed by the Working Group to analyse for the 13 fractions. The first step of the direct method includes TPH quantification and identification of contamination type and EC number distribution. If more detailed data are needed, subsequent steps in the direct method can be followed to quantify the 13 transport fractions.

3.25 Having identified appropriate fractions and a suitable analytical technique, the Working Group has characterised the threshold toxicity of each fraction using RfDs and RfCs for ‘surrogate’ compounds or mixtures. A surrogate is an individual compound or mixture within each fraction that is representative of the toxicity of the fraction. The Working Group has preferred the use of mixtures as surrogates, as they include some of the interactions between compounds within the fraction. For fractions exhibiting similar toxicity, the same toxicity criterion is applied to each fraction. Thus, the toxicity of TPH can be estimated by

quantifying seven broader fractions. However, the Working Group has recommended (TPHCWG, 1999b) quantification of all 13 fractions, thus enabling the detailed modelling of the potential for human exposure owing to different transport properties.

3.26 In using fraction specific RfDs and RfCs, the Working Group (TPHCWG, 1999b) has assumed that the toxicity of all compounds present in a fraction does not vary significantly from the toxicity of the surrogate compound. To ensure that the risk is not underestimated, the toxicity criteria are designed to account for uncertainty in the underlying toxicity database; hence they are more likely to overestimate than underestimate the toxicity of any fraction.

3.27 Although surrogates are used as the basis for the toxicology of each fraction, the transport data used to evaluate exposure in risk assessments are based on correlations with EC numbers; hence transport data are representative of an entire fraction, rather than just a single material within it. A summary of the 13 fractions identified by the Working Group and the associated toxicity values is presented in Table 3.2.

Table 3.2 – TPHCWG petroleum fractions

Equivalent carbon number	Reference dose ($mg\ kg^{-1}\ bw\ d^{-1}$)	Reference concentration ($mg\ m^{-3}$)
Aliphatic fractions		
>5-6	5.0	18.4
>6-8	5.0	18.4
>8-10	0.1	1
>10-12	0.1	1
>12-16	0.1	1
>16-21	2.0	NA[a]
Aromatic fractions		
>5-7	0.004[b]	0.03[b]
>7-8	0.2	0.4
>8-10	0.04	0.2
>10-12	0.04	0.2
>12-16	0.04	0.2
>16-21	0.03	NA[a]
>21-35	0.03	NA[a]

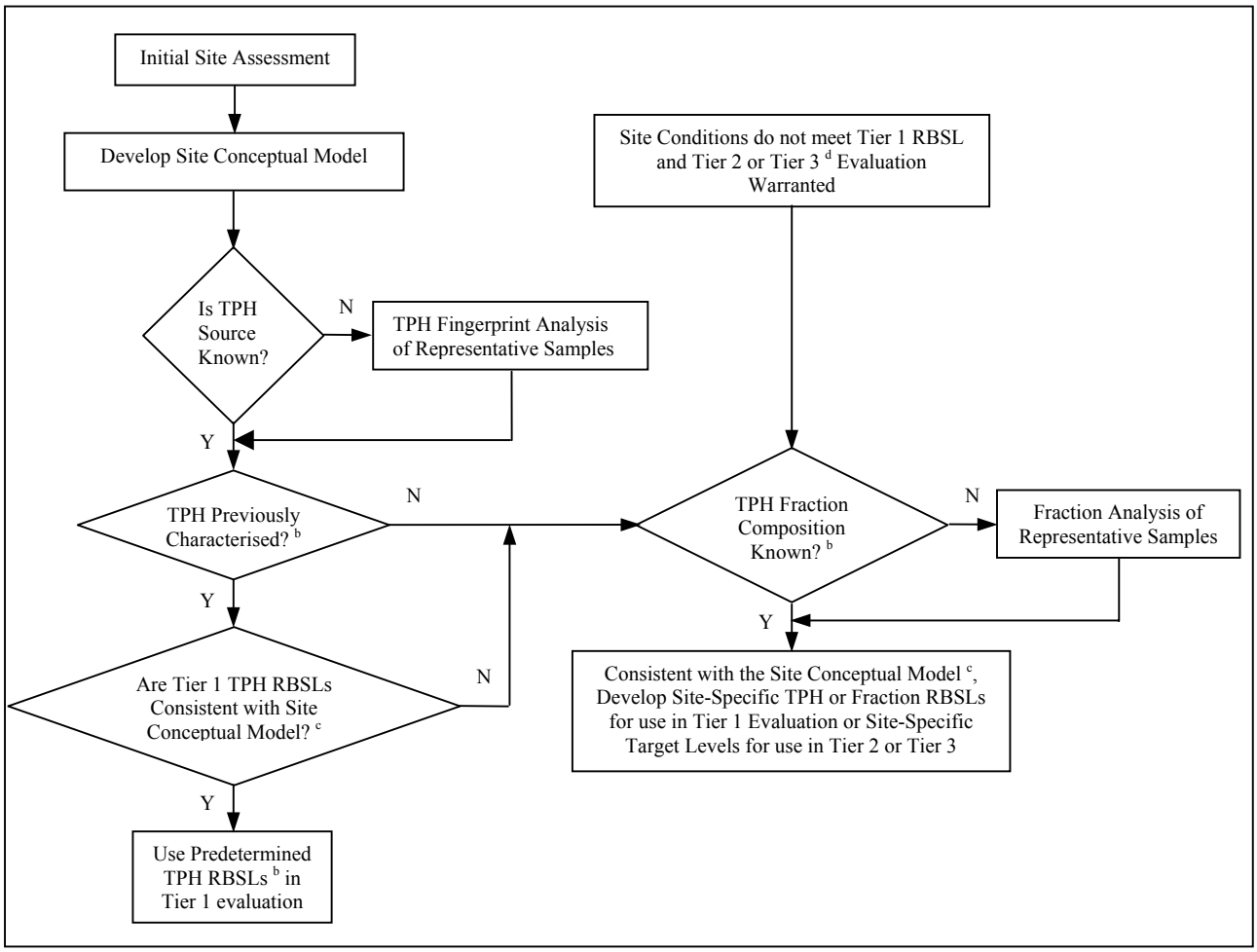
After TPHCWG (1999b)
[a]NA, Not available
[b]Based on USEPA benzene value (USEPA, 2003)

3.28 Application of the TPHCWG approach gives priority to the assessment of non-threshold compounds that are likely to be present at sites. These indicator compounds include benzene, lead, 1,3-butadiene, and carcinogenic PAHs. They are regulated individually in the USA, either federally or at state level. After

evaluation of indicator compounds, petroleum fractions are considered. The fractions are defined as mixtures of threshold toxicity compounds 'which represent the mass of petroleum remaining *after evaluation of the carcinogenic indicators*'. Thus, as with the MaDEP approach, when determining the mass of a fraction within a sample, indicator substances are subtracted to avoid double counting.

3.29 The approach developed by the Working Group can be incorporated into an ASTM RBCA programme (see paragraphs 3.6 to 3.8). The key difference between the two approaches is that the ASTM uses RBSLs and SSTLs for individual substances, whereas the Working Group uses petroleum fractions. In applying its approach, the Working Group has advocated the initial assessment and remediation of indicator substances, followed by a second phase of assessment and remediation for the petroleum hydrocarbon fractions (TPHCWG, 1997b). In practice however, it is recognised that, when applying the approach within a RBCA programme, it is more appropriate to consider indicator substances concurrently (TPHCWG, 1999b). The overall application of the Working Group approach in this context is presented in Figure 3.1.

Figure 3.1 – Implementation of risk-based TPH analysis within a 3-tiered RBCA framework [a]



From TPHCWHG, 1999b

[a] Assumes parallel assessment of potential indicator compounds (e.g. benzene, carcinogenic PAHs, lead, MtBE, etc., as appropriate)

[b] Assumes TPH RBSLs based on TPH fingerprints and associated fraction composition have been developed and approved by the appropriate regulatory agency

[c] RBSLs and SSTLs must be consistent with the site conceptual model

[d] Tier 3 evaluation similar to Tier 2 except based on more complex fate and transport models and site-specific exposure information

3.30 As with MaDEP, the Working Group approach assumes additivity of non-carcinogenic toxicity across the fractions. The assumption of additivity is claimed to ensure that TPH risk-based screening levels would be protective to human health, as not all fractions exert toxicity on the same target organ (TPHCWG, 1999b).

The US Agency for Toxic Substances and Disease Registry review

3.31 The toxicology of petroleum hydrocarbons has been reviewed by the US Agency for Toxic Substances and Disease Registry (ATSDR, 1999) as part of their national (US) 'toxicological profile' series. The philosophy of the MaDEP and the TPHCWG was identified as the preferred approach, with the initial step being an examination of the carcinogenic effects, using indicator compounds for which there are existing USEPA carcinogenic potency factors. At the time of the ATSDR report only benzene and benzo[*a*]pyrene had been evaluated in this way by USEPA. ATSDR (1999) concluded that the USEPA potency factors (relative to benzo[*a*]pyrene) 'can be applied' to the PAHs benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, chrysene, dibenz[*a,h*]anthracene and indeno[1,2,3-*c,d*]pyrene.

3.32 The petroleum fractions selected by the ATSDR for the threshold effects of petroleum hydrocarbons are similar to those favoured by the TPHCWG. One amendment made by ATSDR is the broadening of the aromatic EC_5–EC_8 fraction, used by TPHCWG, to EC_5–EC_9, to include all of the BTEX compounds. The ATSDR noted that 'these fraction-specific values are provisional values, reflecting the uncertainty inherent in this approach'. Also, the ATSDR adopted a precautionary approach and tended to use the most toxic representative compound or mixture to indicate the toxicity of the entire fraction.

3.33 The ATSDR (1999) report identifies the difficulties and uncertainties in analysing and modelling complex petroleum hydrocarbon mixtures in the environment. Although no specific analytical method or model for exposure assessment is recommended, physicochemical data determined for fractions (rather than individual compounds) are presented and the application of risk assessment methods within the ASTM RBCA framework are discussed.

3.34 The ATSDR addressed additivity across different petroleum indicators and fractions using an 'index of concern'. An assumption is made that the health effects are additive for all compounds or fractions that affect the same system or target organ. The index of concern is the sum of the ratios of the monitored level of exposure to the accepted level of exposure for each of the constituents of a mixture. Where this index is greater than 1, appropriate action must be taken. This approach to additivity is a refinement of the approaches of the MaDEP and TPHCWG, which assume additivity across fractions, irrespective of the nature of the toxic effect.

The Canada-Wide Standard for Petroleum Hydrocarbons in Soil

3.35 The Canada-Wide Standard for Petroleum Hydrocarbons in Soil (CCME, 2000, 2001a,b) was endorsed by the Canadian Council of Ministers of the Environment (CCME) in 2001. The Petroleum Hydrocarbons Canada-Wide Standard (PHC CWS) is a three-tiered, risk-based, remedial standard developed for four generic

land uses, namely agriculture, residential/parkland, commercial and industrial. It adopts many of the benefits of the US approaches, including, separate evaluation of indicator substances and petroleum hydrocarbon fractions, and provision of generic soil assessment levels for Tier 1 and 2 evaluations.

3.36 The approach is simplified through the use of only four fractions for the assessment of threshold effects and specifically removes the need for an aliphatic/aromatic split of the samples. The approach uses the 13 TPHCWG sub-fractions as the basis of four PHC CWS fractions:

- Fraction 1: nC$_6$-C$_{10}$;
- Fraction 2: >nC$_{10}$-C$_{16}$;
- Fraction 3: >nC$_{16}$-C$_{34}$;
- Fraction 4: >nC$_{34}$.

3.37 Based on an analysis of representative hydrocarbon products, the CCME (2001a) made the assumption that, within a TPHCWG sub-fraction, the balance between aromatic and aliphatic constituents was 20/80 (CCME, 2001a). The analyses were also used to determine appropriate proportions of different carbon ranges within a fraction. Toxicological information for each TPHCWG sub-fraction was combined with the information on the expected mass of each sub-fraction to produce a toxicological benchmark for each PHC CWS fraction. Using the toxicological criteria for each of the four fractions, Tier 1 soil assessment criteria were developed through the application of generic exposure assessment tools. Transport properties for the various fractions were also derived from the TPHCWG sub-fractions. The algorithms used for these calculations are described in the scientific rationale behind the PHC CWS approach (CCME, 2000).

3.38 A benchmark analytical method for determining petroleum hydrocarbons in soil has been developed to address major sources of variability and uncertainty in the extraction, purification and quantification of petroleum hydrocarbons and the data reported (CCME, 2001c). Fraction 1 is isolated through purge and trap procedures followed by GC/FID. Fractions 2–4, up to C$_{50}$, are extracted and 'cleaned up' on silica gel and determined by GC/FID. Petroleum hydrocarbons greater than C$_{50}$, if present, may be determined gravimetrically or through extended chromatography. The analytical method has been tested in laboratories across Canada and found to reduce variability in results significantly over previous tests where analytical procedures were not controlled (CCME, 2000).

3.39 Application of the PHC CWS involves separate assessments of the indicator compounds and the four fractions. Indicator compounds include the most toxic compounds (termed 'target compounds', including benzene and benzo[*a*]pyrene) and other hydrocarbons frequently tested for (toluene, ethylbenzene and xylenes). The mass of each fraction in a sample is determined by subtracting the mass of the indicator compounds from the overall value, thereby avoiding double counting (CCME, 2000).

3.40 The assessment process is based on the ASTM RBCA (1995, 2000) and CCME (1996) approaches. There are three successive tiers of evaluation, which can be described as follows:

- Tier 1 – the application of generic (national) assessment criteria that are protective of human health and the environment;
- Tier 2 – site-specific adjustments to the Tier 1 criteria to determine criteria that accommodate site-specific characteristics; and
- Tier 3 – levels that are developed from a site-specific ecological or human health risk assessment, when assumptions inherent in the Tier 1 values are not appropriate for a site.

3.41 The tiered approach essentially represents increasing levels of precision in a site assessment, through consideration of more specific site characteristics. Details on the phased acquisition of site information to support sound petroleum hydrocarbon management decisions are presented in separate guidance documents being developed by each Province (e.g. Saskatchewan Environment, 2002).

3.42 The approach to additivity of effects across the fractions, recommended by several US groups (MaDEP, TPHCWG, ATSDR), is not adopted by the PHC CWS[2].

3.43 In its evaluation of the overall impact of the PHC CWS, the Development Committee and Technical Advisory Groups identified a number of areas requiring additional research (CCME, 2000). There was concern about basing management decisions on aesthetic considerations, specifically odour, owing to the general adoption of qualitative, site-specific criteria. The need for a systematic and objective approach to the evaluation of aesthetic issues was identified, to ensure that site management decisions have a sound basis. The scope for including such guidance in a risk-based approach was also highlighted as an area for further consideration.

The Dutch National Institute for Public Health and the Environment approach

3.44 The Dutch National Institute for Public Health and the Environment (RIVM) recently undertook a critical review of the toxicology of petroleum hydrocarbons (RIVM, 2001). The review considered the advantages and limitations of a number of approaches and frameworks for evaluating the human health risks of exposure to petroleum hydrocarbons in soils. RIVM favoured the TPHCWG approach, with minor modifications. Taking account of the available toxicological data, RIVM assigned revised maximum permissible risk (MPR) levels to seven petroleum fractions and updated their 1991–1996 MPRs (Vermeire, 1993; Janssen *et al*, 1995) accordingly. These values are presented in Table 3.3.

[2] While the TPHCWG recognises that the additivity of health effects across fractions that might affect different organs is a precautionary approach, the CCME has confirmed that the PHC CWS Development Committee recommends a different approach. The Committee considers that, as different toxicological endpoints and/or routes of exposure are involved for each of the four PHC CWS fractions, it is not appropriate to add effects across the different fractions.

3.45 The revised (2001) MPRs can be used to develop 'so-called' serious risk concentrations (SRCs) by using the Dutch C-Soil generic exposure assessment model[3].

3.46 Influenced by both the ATSDR (1999) work on hazard indices and the TPHCWG approach, the RIVM decision framework (RIVM, 2001) can be described as follows:

(1) assess for indicator compounds (i.e. those with individual SRCs) – if the SRC for one or more of the compounds is exceeded, appropriate remedial measures should be considered or undertaken;

(2) assess fractions based on toxicity of surrogate compound or product – if the SRC for one or more of the compounds is exceeded, appropriate remedial measures should be considered or undertaken;

(3) if the petroleum fraction-specific SRCs are not exceeded, calculate an overall site specific contamination index by summing together the ratios of measured concentrations to the SRCs – where this exceeds 1, appropriate remedial measures should be considered or undertaken.

Table 3.3 – Human toxicological maximum permissible risk (MPR) levels for petroleum fractions

TPH fraction	TDI[a] (mg kg^{-1} bw d^{-1})	TCA[b] (mg m^{-3})
Aliphatic >EC_5-EC_8	2[c]	18.4
Aliphatic >EC_8-EC_{16}	0.1	1
Aliphatic >EC_{16}-EC_{35}	2	NA [d]
Aliphatic >EC_{35}	20	NA
Aromatic >EC_5-EC_9	0.2	0.4
Aromatic >EC_9-EC_{16}	0.04	0.2
Aromatic >EC_{16}-EC_{35}	0.03	NA

After RIVM (2001).
EC, equivalent carbon number – based on retention times on a non-polar gas chromatography column so as to normalise to *n*-alkane equivalents
[a]TDI, tolerable daily oral intake equivalent to TPHCWG RfDs except for aliphatics >EC5-EC8
[b]TCA, tolerable concentration in air, equivalent to TPHCWG RfC
[c]The value proposed by the TPHCWG was 5000 μg kg^{-1} bw d^{-1}; the basis of this was not considered to be robust, hence RIVM chose to adopt the more conservative value of 2000 μg kg^{-1} bw d^{-1}
[d]NA, not available (and not applicable due to extremely low volatilisation

3.47 The analytical procedure for petroleum hydrocarbons (NEN 5773) was developed for the initial 1991–1996 MPRs. The current recommended test method, modified to take account of the revised MPRs, is based on a GC/FID analysis and is designed to test for substances with carbon numbers from 6 to 40.

[3] In evaluating exposure potential, RIVM recommends the use of the fraction-based transport properties developed by the TPHCWG. However, where appropriate, site-specific information may be used to determine exposure.

Approaches in New Zealand / Australia

3.48 New Zealand has adopted the TPHCWG approach in its guidance for managing petroleum hydrocarbons from contaminated sites (Ministry for the Environment, 1999). However, the distinction between aromatic and aliphatic compounds in the TPH fractions has been dropped because the aromatic component is addressed separately by direct measurement of BTEX and PAH concentrations, and the analytical technique proposed for New Zealand does not distinguish between aromatic and aliphatic compounds. The criteria developed for New Zealand using this simplified approach apply principally to the aliphatic components of petroleum hydrocarbons. In combining the approach adopted by the TPHCWG with the standard analytical method technique being developed for use in New Zealand, Tier 1 soil and groundwater acceptance criteria have been developed on the basis of the following fractions:

- C_7 to C_9;
- C_{10} to C_{14}; and
- C_{15} to C_{36}.

3.49 Due to minor differences between the fractions selected for use in New Zealand and those proposed by the TPHCWG, some minor changes have been made to the toxicological (Table 3.4) and fate and transport properties adopted, based on a weighted averaging approach.

Table 3.4 – Toxicological reference doses for aliphatic petroleum fractions adopted in New Zealand

Fraction	C_7–C_9	C_{10}–C_{14}	C_{15}–C_{36}
Oral reference dose (mg kg^{-1} bw d^{-1})	5.0	0.1	1.5
Inhalation reference dose (mg kg^{-1} bw d^{-1})	5.0	0.3	1.5

After Ministry for the Environment (1999)

3.50 The assessment of petroleum contamination in Australia comes under the jurisdiction of individual states (Buddhadasa *et al,* 2002). Current approaches appear to be based on the use of generalised threshold concentration levels for hydrocarbons in soils. For example, in a recent draft guideline for the assessment of former gas-works sites (New South Wales Environment Protection Authority, 2002), 'threshold concentrations for sensitive land uses' were provided for two ranges of petroleum hydrocarbons (C_6–C_9 and C_{10}–C_{40}), BTEX, phenol, benzo[*a*]pyrene and total PAHs. Threshold concentrations are intended to protect both human and ecological health and are based on soil concentrations recommended by other expert groups (e.g. ANZECC/NHMRC, 1992). Although the expert groups initially proposing the values may have developed them using a risk-based approach, the guidance document issued by the New South Wales Environment Protection Authority does not demonstrate a risk basis in its adoption of these values as threshold concentrations.

Summary

3.51 A number of approaches to the evaluation of petroleum hydrocarbons in soil for the protection of human health have been described above. The key issues are addressed differently by the various approaches and an overall summary is presented in Table 3.5.

Table 3.5 – Summary of approaches to key issues

	ASTM	MaDEP	TPHCWG	ATSDR	PHC CWS	RIVM	New Zealand	New South Wales
Reference paragraphs	3.6 to 3.8	3.9 to 3.18	3.19 to 3.30	3.31 to 3.34	3.35 to 3.43	3.44 to 3.47	3.48 to 3.49	3.50
Indicator substances	Use of 'chemicals of concern' only.	Target analytes include most toxic compounds and others frequently tested for.	Indicator compounds include most toxic compounds only.	Indicator compounds include most toxic compounds only.	Indicator compounds include most toxic compounds (target compounds) and others frequently tested for.	Indicator compounds include most toxic compounds and others frequently tested for.	Use of 'contaminants of concern' to address most toxic substances and aromatics	Individual compounds identified
Fractions								
Number and basis	None	6 analytical fractions (3 aromatic and 3 aliphatic) using 4 toxicity values (3 aliphatic and 1 aromatic).	13 analytical fractions (6 aliphatic and 7 aromatic) using 7 toxicity values (3 aliphatic and 4 aromatic).	Similar to TPHCWG. Minor modification to aromatic groups to include all BTEX compounds in same fraction.	4 fractions based on 13 developed by TPHCWG. Separate evaluation of aromatic/aliphatic compounds not required.	7 fractions based on toxicity values (3 aliphatic and 4 aromatic).	3 aliphatic fractions only.	2 petroleum hydrocarbon fractions
		Fractions based on carbon number and driven by analytical methods and toxicology.	Fractions based on EC number, driven by fraction transport properties.	EC numbers, as per TPHCWG	EC numbers, as per TPHCWG	EC numbers, as per TPHCWG	EC numbers, as per TPHCWG	Various
Basis of toxicity and transport properties		Toxicity values based on surrogate compounds, transport properties based on TPHCWG approach (i.e. entire fraction).	Toxicity values based on surrogates, transport properties based on entire fraction.	Most toxic compound/mixture in fraction generally used as surrogate for toxicity values	Use of TPHCWG toxicity and transport data.	Toxicity values based on surrogates, transport properties based on entire fraction (as per TPHCWG).	Use of TPHCWG toxicity and transport data.	Basis unclear, as soil threshold concentrations taken directly from other expert groups

	ASTM	MaDEP	TPHCWG	ATSDR	PHC CWS	RIVM	New Zealand	New South Wales
Additivity of effects	Not recommended	Precautionary approach, based on addition of hazard quotients across fractions.	Precautionary approach, based on addition of hazard quotients across fractions.	Precautionary approach, developing 'index of concern', based on addition of hazard quotients across fractions for compounds affecting same target organs or systems.	Not advised due to different toxicological endpoints and exposure pathways of different fractions.	Precautionary approach, based on addition of hazard quotients across fractions.	Additivity of excess lifetime cancer risk for non-threshold substances Precautionary approach, as for ATSDR.	Not discussed in guidance document
Application of approach	Use of RBCA 3-tiered approach. Look up tables for Tier 1 and increasing use of site-specific information in Tiers 2 and 3.	Three Methods can be used, with generic standards for Method 1 and increasing use of site-specific information for Methods 2 and 3. Approach is not tiered, as appropriate Method is selected prior to assessment.	Use of RBCA 3-tiered approach. Look up tables for Tier 1 and increasing use of site-specific information in Tiers 2 and 3.	As for TPHCWG	Use of RBCA 3 -tiered approach. Look up tables for Tier 1 and increasing use of site-specific information in Tiers 2 and 3.	Use of a tiered approach, moving from generic guidelines to less conservative values using site-specific l	Use of a 3-tiered approach, moving from generic guidelines to less conservative values using site-specific l	Unclear
Recommended analysis	No specific method of analysis	Use Vapour Petroleum Hydrocarbon (VPH) and Extractable Petroleum Hydrocarbon (EPH) methods developed by MaDEP. Target analytes reported in these analyses.	Direct Method Indicator compounds not reported.	As for TPHCWG	2-step analytical method developed and benchmarked across laboratories in Canada. Indicator compounds not reported.	Single analytical method (NEN 5733) recommended. Indicator compounds not reported.	Based on American Petroleum Institute 'Method for Characterisation of Petroleum Hydrocarbons in Soil' Chemicals of concern not reported	Various, depending on source of threshold concentration
Other comments	Consideration given to aesthetic characteristics (e.g. odour) when identifying chemicals of concern	Address issues of 'public welfare', such as odour and staining, through the use of ceiling limits for soil concentrations			Aesthetic issues, such as odour, identified as a need for further research.		Aesthetic issues, such as odour, identified as consideration on a site-by-site basis	Basis of approach unclear and appears to be a mixture of ideas from various expert groups

4. PROPOSED APPROACH AND KEY ISSUES AND QUESTIONS FOR CONSULTATION

4.1 The review in section 3 raises a number of issues for consideration in developing an approach for assessing human health risks from petroleum hydrocarbons in the UK. Many of these issues are addressed by national conventions and accepted protocols already in place (Table 3.5). Thus it is not desirable to undertake an *a priori* review without considering them first, as they may influence the final way forward. Key issues to be addressed include:

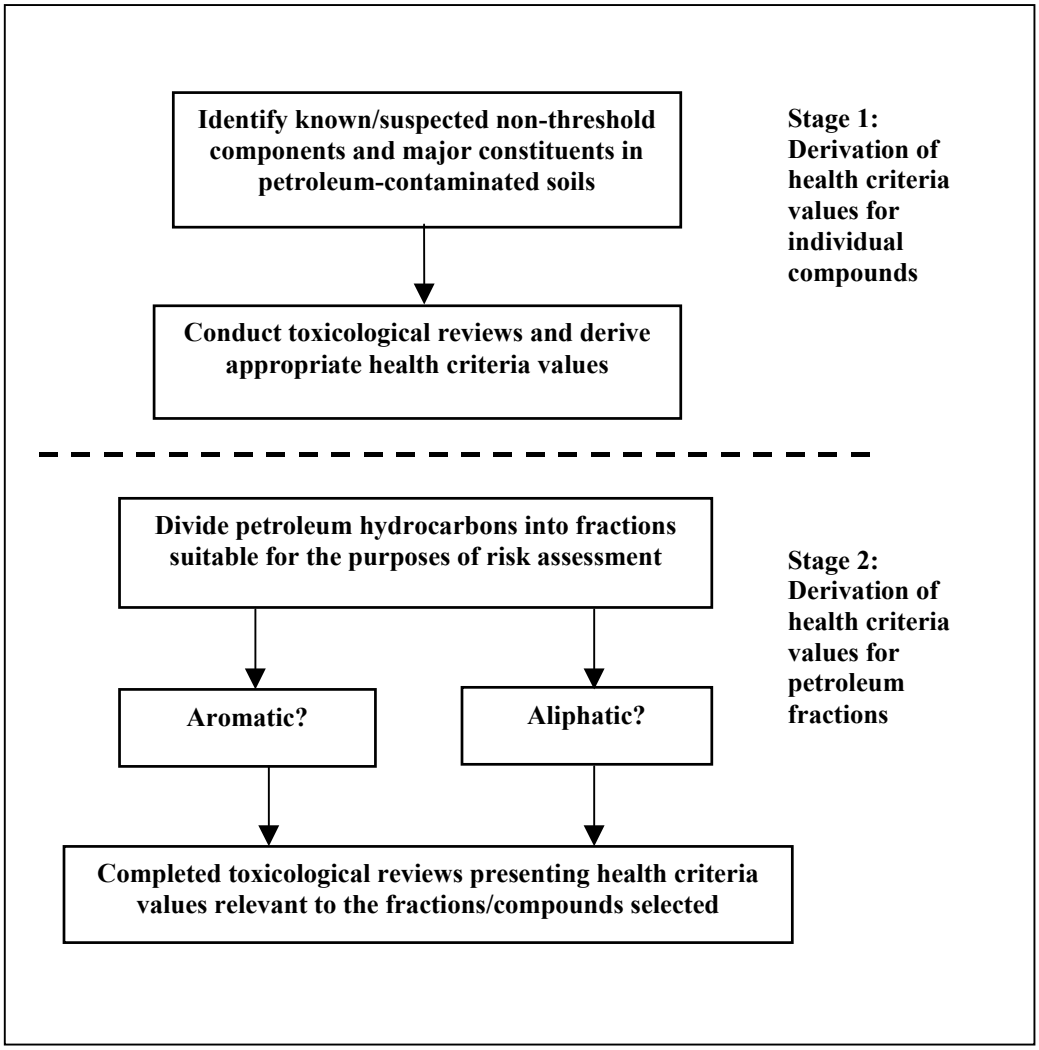
- the approach to assessing threshold and non-threshold risk;
- accepted approaches and philosophies of risk assessment and management;
- the availability and design of exposure assessment models for generating SGVs from toxicological criteria;
- the availability of standard analytical methods for the analysis of toxicologically relevant compounds and fractions in petroleum; and
- the cost of implementation and relative benefits in terms of improved decision-making.

4.2 The Environment Agency seeks to provide, for practitioners, clear guidance on the evaluation of human health risks from petroleum hydrocarbons in soils. The Agency recognises that some of the individual constituents of petroleum (e.g. benzene, PAH) may be assessed independently in establishing whether land is statutorily contaminated under Part IIA of the Environmental Protection Act 1990.

4.3 The Environment Agency proposes, for comment, a staged risk-based programme of research and development for the derivation of health criteria values for petroleum hydrocarbons in soil (Figure 4.1). Stage 1 will involve the development of Index Doses and Tolerable Daily Soil Intakes (health criteria values[4]) for individual compounds. Stage 2 will involve the development of health criteria values for petroleum fractions. The health criteria values from the two stages will then be used to derive SGVs for petroleum hydrocarbons. Key issues influencing the development of such an approach, on which the Agency seeks your views, are discussed below.

[4] see Defra and Environment Agency (2002c) for definitions of Index Dose and Tolerable Daily Soil Intake

Figure 4.1 – Environment Agency proposed programme of research and development to determine health criteria values for individual substances and fractions



Complexity of approach

4.4 The approaches summarised in section 3 vary in sophistication from those involving a full review of the available toxicology (ATSDR, TPHCWG, MaDEP), through the setting of generalised threshold concentrations (New South Wales Environment Protection Authority to approaches that are, to varying degrees, hybrids of both (CCME, RIVM, New Zealand Ministry for Environment). The Environment Agency seeks to ensure scientific integrity in its approach, alongside practicality in implementation.

Issue 1 ***The Environment Agency welcomes views on whether the UK should adopt a combined indicator and petroleum fraction approach to the evaluation of petroleum hydrocarbons in soil.***

Issue 2 ***What are consultees' experiences of applying these approaches in practice?***

Issue 3 ***The MaDEP has selected petroleum fractions on the basis of the available analytical techniques and the toxicology of petroleum compounds. The TPHCWG has selected fractions based on transport properties.***

If a petroleum fraction approach is favoured, what should be the basis for the selection of fractions?

Issue 4 ***Do consultees consider that a simplification of the TPHCWG approach is appropriate?***

4.5 One option, though not a necessary requirement, is the fractionation of the sample into aromatic and aliphatic sub-components (Figure 4.1).

Issue 5 ***The Environment Agency invites the views of consultees on the merits and practicalities of separating the aliphatic and aromatic class components (e.g. MaDEP, TPHCWG), compared with an approach based on carbon number alone (e.g. CCME).***

4.6 The major health risks associated with historic petroleum contamination in the environment are widely considered to be non-threshold effects posed by genotoxic carcinogens present in the complex mixture. Other threshold compounds are frequently present in petroleum contaminated soils. Some of these substances (Table 4.1) are listed in CLR8 (Department for Environment, Food and Rural Affairs (Defra) and Environment Agency, 2002a) and are currently being or have already been subject to review (Defra and Environment Agency, 2002b). The Agency proposes the separate toxicological review of each of these substances, to be termed 'indicator compounds', as part of Stage 1 (Figure 4.1) of the assessment.

Issue 6 ***The Environment Agency welcomes views on the proportions of sites where remediation is driven by the risks from non-threshold substances or threshold substances or both (and/or other assessment criteria).***

Table 4.1 – Some individual compounds to be considered during Stage 1 toxicological reviews

Non-threshold indicator compounds	Threshold indicator compounds
Benzene	Toluene
Benzo[*a*]pyrene	Ethylbenzene
Benz[*a*]anthracene	Xylene
Benzo[*b*]fluoranthene	Naphthalene
Benzo[*k*]fluoranthene	Fluoranthene
Chrysene	Phenanthrene
Dibenz[*a,h*]anthracene	Pyrene
Indeno[1,2,3-*c,d*]pyrene	

4.7 The Environment Agency proposes that Stage 2 of the assessment (Figure 4.1) will be the toxicological review and derivation of health criteria values for petroleum hydrocarbon fractions, based on vales for surrogate compounds or mixtures representative of each fraction. The basis for the selection of surrogates for each fraction can have considerable influence on the derivation of SGVs. For example, MaDEP (2002a) adopts *n*-hexane, with a RfD of 0.04 mg kg^{-1} bw d^{-1} and an RfC of 0.2 mg m^{-3}, as a surrogate compound for the aliphatic C_5–C_8 fraction because it is the most toxic constituent of this fraction. However, RIVM (2001) considers *n*-hexane to be a minor constituent and hence adopts less stringent criteria, based on *n*-heptane; that is, a tolerable daily oral intake of 2 mg kg^{-1} bw d^{-1} and a tolerable concentration in air of 18.4 mg m^{-3}, unless there is clear evidence for high amounts of *n*-hexane in contaminated soil.

Issue 7 ***If petroleum fractions are to be adopted, what should be the toxicological basis for the selection of surrogate compounds or mixtures?***

Issue 8 ***How many petroleum fractions do consultees consider to be toxicologically relevant?***

Issue 9 ***How, if at all, should additivity of health effects across the fractions be taken into account?***

Practicality – staged frameworks

4.8 Having established an approach for the derivation of health criteria values and SGVs for petroleum hydrocarbons, consideration needs to be given as to how these values will be applied in a site assessment. There are some differences in the practical application of the various approaches described in section 3. The approaches of the TPHCWG and ATSDR give precedence to non-threshold risks from individual compounds *within the framework* (i.e. initial evaluation of non-threshold risk, then subsequent evaluation of threshold risk). In contrast, the MaDEP approach explicitly assesses the risks from both individual compounds and fractions concurrently. The Environment Agency proposes use of the latter approach, in which all risks (and pollutant linkages) are determined prior to remedial activity.

Issue 10 ***The Environment Agency welcomes views on the concurrent assessment of all risks from both indicator compounds and petroleum fractions.***

Issue 11 ***However if an approach were adopted that gave precedence to the non-threshold risks (e.g. TPHCWG) over threshold risks, what are consultees' views on the practical application of such a staged approach in the context of identifying Part IIA pollutant linkages?***

4.9 A further consideration in the development of a decision-framework is the use of different *tiers* of approach – reflecting increased levels of sophistication as the assessment proceeds from the application of Tier 1 screening values through to site-specific risk-based endpoints. This feature is consistent with the Defra and Environment Agency guidelines on Environmental Risk Assessment and Management (DETR *et al,* 2000) and the forthcoming Model Procedures (Defra and Environment Agency, in preparation) and is a familiar concept of RBCA assessments (e.g. ASTM, 2000).

Issue 12 ***The Environment Agency seeks comments on the application of a tiered approach in the context of identifying the significance of Part IIA pollutant linkages.***

Analytical feasibility and approach

4.10 The limitations of TPH methods as a basis for the analysis of risks from petroleum hydrocarbons in soil are widely reported (Nyer and Skladany, 1989; Gustafson, 2002). No universal method exists for petroleum contamination owing to the complexity and specificity of the source, which can range from light distillates to heavy, residual fuels. In devising a risk-based framework for petroleum in soil, it is important to develop analytical strategies, methods and reporting conventions that are capable of reliably and reproducibly estimating the concentrations of risk-critical compounds and fractions. In the USA, the Texas Natural Resource Conservation Commission (TNRCC) direct method (AEHS, 2000) is gaining acceptance for the evaluation of the TPHCWG fractions. In Canada, the CCME reference method (CCME, 2001c) for the Canada wide standard (Tier 1 method) has been adopted. UK laboratories, using accredited methods for the analysis of petroleum hydrocarbons, apply a range of GC and mass spectrometric methods, including those for the analysis of:

- petrol- (C_5–C_{10}), diesel- (C_{10}–C_{30}) and 'total' petroleum (C_{10}–C_{40}) organics (using USEPA Modified method 8015M);
- TPH (using USEPA or modified USEPA Method 1664, the replacement for 418.1); and
- petroleum hydrocarbons in environmental samples (using TNRCC methods 1005 and 1006).

4.11 The analytical strategy and the methods developed for the UK will need to reflect the risk assessment approach chosen and the selection of toxicologically relevant compounds or fractions.

Issue 13 ***In devising its approach, the Environment Agency wishes to ensure that analytical methods can be suitably matched to the needs of the risk assessment.***

Consultees are invited to express their views on experiences in using the above (paragraph 4.10) and related analytical methods for characterising petroleum in environmental samples.

What are costs and requirements of these methods?

What are the implications for site investigation, soil sampling, analysis and analytical reporting?

What levels of uncertainty in analytical measurement are typically experienced in applying these methods?

Weathered petroleum contamination in the soil

4.12 Heavy and highly weathered oils present a particular challenge in terms of their chemical analysis, toxicological evaluation and risk assessment. The analysis of petroleum hydrocarbons using methods designed for lower boiling point compounds is inappropriate for highly weathered oils and residual fuel products (Pollard *et al*, 1994; Douglas *et al,* 2001; API, 2001). Their high boiling points, weathered composition and extreme chemical complexity mean that specialised analysis is often required. A common feature of the GC analysis of these oils is the presence of an unresolved complex mixture (UCM) of components in the mid-distillate range of the chromatogram (Hrudey and Pollard, 1993).

4.13 Acknowledging these constraints, recent revisions to the TPHCWG methodology have allowed the fractionation and detection of oils with a carbon number of up to C_{44}, that is with a carbon equivalent boiling point of > 548 °C (API, 2001). An oral RfD of 0.03 mg kg^{-1} bw day^{-1} and a dermal RfD of 0.8 mg kg^{-1} bw day^{-1} have been recently assigned to the C_{44+} fraction (API, 2001). Given that many petroleum-contaminated sites have oils present that are highly weathered, the Environment Agency wishes to incorporate within its risk-based framework clear guidance to practitioners on how these oils should be assessed.

Issue 14 ***The Environment Agency seeks views on appropriate methods for the chemical analysis of heavy, weathered and residual oils and on the approach to their toxicological evaluation.***

Aesthetics, costs and socioeconomic considerations

4.14 Petroleum, or more broadly hydrocarbon contamination, is found at most historically contaminated sites. Consequently the development and application of risk-based SGVs could have a considerable influence on the extent and cost of risk management measures.

Issue 15 ***The Environment Agency welcomes views on the implementation costs and implications of the various approaches described in section 3, specifically with respect to site and risk assessment.***

4.15 Petroleum oils present at historically contaminated sites often produce a residual odour, cause staining of materials and are unsightly at the surface. The MaDEP addressed this issue of 'public welfare' by introducing ceiling limits, based on aesthetic considerations, for Method 1 assessments, thereby limiting the amount of residual material remaining in the soil after remediation. Similar issues were raised during consultation with stakeholders in development of the CCME Canada Wide Standard (CCME, 2000), which recommended that risk management should include consideration of aesthetics and physico-chemical effects on soil.

Issue 16 ***Aesthetic impacts are not covered by Part IIA of the Environmental Protection Act 1990. However, the Environment Agency wishes to take this opportunity to consider separately views relating to aesthetic impacts of oil at contaminated sites.***

The Environment Agency invites practitioners to summarise their experiences of the influence that aesthetics currently play in risk management at petroleum-contaminated sites and their considered opinions on the influence they might play in the future.

What typical concentrations of petroleum hydrocarbons remain in the soil after remediation? Please relate concentration data to remedial techniques.

5. SUBMITTING YOUR COMMENTS

The Agency welcomes comments on this document and your responses to the issues and questions posed in section 4. In accordance with the Cabinet Office Code of Practice, the Agency has determined that a three-month review period for our proposals is appropriate. Please provide your response by 3rd October 2003 and send your response to:

- by e-mail to: ea_tph_consultation@leicester.ac.uk
- or by post to :

Petroleum Hydrocarbons Consultation,
MRC Institute for Environment and Health
University of Leicester
94 Regent Road
Leicester LE1 7DD
United Kingdom

In your response please:

- explain who you are and, where relevant, who you represent;
- state if you want your comments treated as confidential; and
- provide your comments against the issue numbering in the consultation document.

Please note that responses may be made public unless consultees specifically request confidentiality. All responses will be included in any statistical or other summary of results.

Code of Practice on written consultation

This consultation document has been produced in accordance with the Cabinet Office Code of Practice on written consultation.

The consultation criteria are:

1. Timing of consultation should be built into the planning process for a policy (including legislation) or service from the start, so that it has the best prospect of improving the proposals concerned, and so that sufficient time is left for it at each stage.

2. It should be clear who is being consulted, about what questions, in what timescale and for what purpose.

3. A consultation document should be as simple and concise as possible. It should include a summary, in two pages at most, of the main questions it seeks views on. It should make it as easy as possible for readers to respond, make contact or complain.

4. Documents should be made widely available, with the fullest use of electronic means (though not to the exclusion of others), and effectively drawn to the attention of all interested groups and individuals.

5. Sufficient time should be allowed for considered responses from all groups with an interest. Twelve weeks should be the standard minimum period for a consultation.

6. Responses should be carefully and open-mindedly analysed, and the results made widely available, with an account of the views expressed, and reasons for decisions finally taken.

7. Departments should monitor and evaluate consultations, designating a consultation co-ordinator who will ensure the lessons are disseminated.

6. REFERENCES

ANZECC/NHMRC 1992. *Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites*. Australian & New Zealand Environment & Conservation Council and National Health & Medical Research Council.

API (2001) *Risk-based Methodologies for Evaluating Petroleum Hydrocarbon Impacts at Oil and Natural Gas E&P Sites, API Publication 4709*, API Publishing Services, Washington DC. Available at http://api-ep.api.org/industry/index.cfm?bitmask=002007001005009000 (May 2003).

AEHS (2000) Characterization of C_6-C_{35} Petroleum Hydrocarbons in Environmental Samples – The Direct Method. Available at http://www.aehs.com/publications/catalog/contents/Direct%20Method.PDF (March 2003).

ASTM (1995) *Standard E1739-95e1 Guide for Risk-based Corrective Action Applied at Petroleum Release Sites,* American Society for Testing Materials, Philadelphia

ASTM (2000) *Standard E2081-00 Standard Guide for Risk-Based Corrective Action*, American Society for Testing Materials, Philadelphia

ATSDR (1999) *Toxicological Profile for Total Petroleum Hydrocarbons,* US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, Atlanta. Available at http://www.atsdr.cdc.gov/toxprofiles/tp123.html (March 2003).

Buddhadasa, S.C., Barone, S., Bigger, S.W. and Orbell, J.D. (2002) *Australian Approaches to Improving Methods for the Analysis of TPH Contamination in Soil,* Paper no. 1965, Symposium 41 in: Proc. 17th WCSS, 14-21st August, 2002, Thailand, 11pp.

CCME (1996) *A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines,* CCME-EPC-101E, Winnipeg, Manitoba, Canada

CCME (2000) *Canada-wide Standard for Petroleum Hydrocarbons in Soil: Scientific Rationale*, CCME, Winnipeg, Manitoba, Canada. Available at http://www.ccme.ca/initiatives/standards.html?category_id=9 (March 2003).

CCME (2001a) *Canada-wide Standard for Petroleum Hydrocarbons in Soil: Technical Supplement,* CCME, Winnipeg, Manitoba, Canada. Available at http://www.ccme.ca/initiatives/standards.html?category_id=9 (March 2003).

CCME (2001b) *Canada-wide Standard for Petroleum Hydrocarbons in Soil: Policy Statement, CCME, April 30-May 1, 2001,* Winnipeg, Manitoba, Canada

CCME (2001c) *Reference Method for the Canada-wide Standard for Petroleum Hydrocarbons in Soil – Tier 1 Method,* CCME, Winnipeg, Manitoba, Canada. Available at http://www.ccme.ca/initiatives/standards.html?category_id=9 (March 2003).

CONCAWE (1992) *Aromatic extracts. Product Dossier No. 92/101,* CONCAWE, Brussels.

CONCAWE (1996) *Gas Oils (Diesel Fuels/Heating Oils). Product Dossier No. 95/107,* CONCAWE Brussels. Available at http://www.concawe.be/Html/Reports.htm (March 2003).

CONCAWE (1997) *European Oil Industry Guidelines for Risk-bsaed Assessment of Contaminated Sites, Report 2/97,* CONCAWE, Brussels.

Defra and Environment Agency (2002a) *Priority Contaminants Report*, Report CLR8. Available from the R&D Dissemination Centre, WRc plc, Swindon, Wilts.

Defra and Environment Agency (2002b) *Contaminants in soil: Collation of Data and Intake Values for Humans. Benzo(a)pyrene.* Available from the R&D Dissemination Centre, WRc plc, Swindon, Wilts.

Defra and Environment Agency (2002c) *Contaminants in Soil: Collation of Toxicological Data and Intake Values for Humans. Consolidated Main Report*, CLR9. Available from the R&D Dissemination Centre, WRc plc, Swindon, Wilts.

Defra and Environment Agency (in preparation) *Model Procedures for the Management of Land Contamination.* Available from the R&D Dissemination Centre, WRc plc, Swindon, Wilts.

DETR (2000) Circular 2/2000, Environmental Protection Act 1990 – Part IIA – Contaminated Land, Department of Environment, Transport and the Regions, London. Available at http://www.defra.gov.uk/environment/landliability/circ2-2000/ (March 2002).

DETR, Environment Agency and Institute for Environment and Health (2000) Guidelines for Environmental Risk Assessment and Management, The Stationery Office, London, 88pp. Available at http://www.defra.gov.uk/environment/eramguide/ (March 2003).

Douglas, G., Naughton, G., Rhodes, I. and Kerr, J. (2001) In: *Risk-based Decision-Making for Assessing Petroleum Impacts at Exploration and Production Sites* (eds. McMillan S.J., Magaw, R.I. and Carovillano, R.L.), US Department of Energy, Tulsa, OK

Environment Agency (1998) *Oil and Gas in the Environment*, Environment Agency, Bristol

Gustafson, J. B. (2002) Using TPH in Risk-Based Corrective Action. Available at http://www.epa.gov/swerust1/rbdm/tphrbca.htm (March 2003).

Hutcheson MS, Pedersen D, Anastas ND, Fitzgerald J and Silverman D (1996) Beyond TPH: health-based evaluation of petroleum hydrocarbon exposures. *Regulatory Toxicology and Pharmacology* **24**, 85−101.

Hrudey, S.E. and Pollard, S.J. (1993) The Challenge of Contaminated Sites: Remediation Approaches in North America, *Environmental Reviews* **1**(1), 55-72

IARC (1989) *Occupational Exposures in Petroleum Refining: Crude Oil and Major Petroleum Fuels, IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 45,* International Agency for Research on Cancer, Lyon. Available at http://193.51.164.11/htdocs/indexes/vol45index.html (March 2003).

Institute of Petroleum (1993) *Code of Practice for the Investigation and Mitigation of Possible Petroleum-Based Land Contamination*, Institute of Petroleum, London

Janssen, P.J.C.M., Van Appledorn, M.E., Van Koten-Vermeulen, J.E.M. and Mennes, W.C. (1995) *Human Toxicological Criteria for Serious Soil Contamination – Compounds evaluated in 1993 and 1994,* National Institute of Public Health and the Environment, RIVM Report No. 715810009, August 1995, Bilthoven

Killops SD and Killops VJ (1993) *An Introduction to Organic Geochemistry,* Longman, Harlow, UK, 265pp.

MaDEP (1994) *Interim Final Petroleum Report: Development of Health-based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter,* Massachusetts Department of Environmental Protection, Bureau of Waste Site Cleanup, Boston. Available at http://www.state.ma.us/dep/bwsc/vph_eph.htm (March 2003).

MaDEP (1997) *Characterizing Risks Posed by Petroleum Contaminated Sites: Implementation of the MADEP VPH/EPH Approach. Draft for Public Comment,* Massachusetts Department of Environmental Protection, Bureau of Waste Site Cleanup, Boston. Available on-line at: http://www.state.ma.us/dep/bwsc/vph_eph.htm (March 2003).

MaDEP (1998a) *Method for the Determination of Volatile Petroleum Hydrocarbons (VPH)*, Massachusetts Department of Environmental Protection. Available at http://www.state.ma.us/dep/bwsc/vph_eph.htm (March 2003).

MaDEP (1998b) *Method for the Determination of Extractable Petroleum Hydrocarbons (EPH),* Massachusetts Department of Environmental Protection. Available at http://www.state.ma.us/dep/bwsc/vph_eph.htm (March 2003).

MaDEP (2002a) *Draft Updated Petroleum Hydrocarbon Fraction Toxicity Values for the VPH/EPH/APH Methodology*, Massachusetts Department of Environmental Protection, Bureau of Waste Site Cleanup, Massachusetts. Available at http://www.state.ma.us/dep/bwsc/vph_eph.htm (March 2003).

MaDEP (2002b) *Characterizing Risks Posed by Petroleum Contaminated Sites: Implementing the VPH/EPH/APH Approach, Policy #WSC-02-411,* Massachusetts Department of Environmental Protection, Executive Office of Environmental Affairs, Commonwealth of Massachusetts, dated 31/10/02. Available at http://www.state.ma.us/dep/bwsc/vph_eph.htm (March 2003).

Ministry for the Environment (1999) Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand, Ministry for the Environment, New Zealand, 1999. Available at http://www.mfe.govt.nz/publications/hazardous/oil-guide-jun99/ (March 2003).

Morgan P and Watkinson RJ (1989) Hydrocarbon degradation in soils and methods for biotreatment, *Critical Reviews in Biotechnology* **8**, 305-333.

New South Wales Environment Protection Authority (2002) *Draft Guidelines for the Assessment of Former Gasworks Sites,* NSW EPA, Sydney. Available at http://www.epa.nsw.gov.au/mao/servicestation.htm (March 2003).

Nyer EK and Skladany GJ (1989) Relating the physical and chemical properties of petroleum hydrocarbons to soil and aquifer remediation, *Groundwater Monitoring Review,* Winter 1989, 54-59.

Pollard SJT, Kenefick SL, Hrudey SE, Fuhr B, Holloway LR and Rawluk, M (1994) In: O'Shay, TA and Hodinott KB (eds.) *Analysis of Soils Contaminated with Petroleum Constituents*, ASTM STP 1221, American Society of Testing and Materials, Philadelphia, pp.38-52.

Pollard SJT, Whittaker, M and Risden GC (1999) The Fate of Heavy Oil Wastes in Soil Microcosms I: A Performance Assessment of Biotransformation Indices, *Science of the Total Environment* **226**, 1-22.

RIVM (2001) *Re-evaluation of Human Toxicological Maximum Permissible Risk Levels*. RIVM Report 711701 025. pp. 280 – 295. Available at http://www.rivm.nl/bibliotheek/rapporten/711701025.pdf (March 2003).

Saskatchewan Environment (2002) *Risk Based Corrective Actions for Petroleum Contaminated Sites, Environmental* Protection Branch, Saskatchewan Environment, EPB78, 30pp. + appendices

Schobert, H.H. (1990) *The Chemistry of Hydrocarbon Fuels*, Butterworth-Heinmann Limited, Oxford, 348pp.

TNRCC (2001) *Total Petroleum Hydrocarbons, TNRCC Method 1005, Revision 03*, June 1, 2001, Texas Natural Resource Conservation Commission, Austin, Texas, 26pp. Available http://www.tnrcc.state.tx.us/enforcement/csd/qa/method_1005.html (March 2003).

TPHCWG (1997a) Selection of Representative TPH Fractions Based on Fate and Transport Considerations, Volume 3. Total Petroleum Hydrocarbon Criteria Working Group Series. Amherst: Amherst Scientific Publishers. Available at http://www.aehs.com/publications/catalog/contents/tph.htm (March 2003).

TPHCWG (1997b) Development of Fraction Specific Reference Doses (RfDs) and Reference Concentrations (RfCs) for Total Petroleum Hydrocarbons, Volume 4. Total Petroleum Hydrocarbon Criteria Working Group Series. Amherst: Amherst Scientific Publishers. Available at http://www.aehs.com/publications/catalog/contents/tph.htm (March 2003).

TPHCWG (1998a) Analysis of Petroleum Hydrocarbons in Environmental Media, Volume 1. Total Petroleum Hydrocarbon Criteria Working Group Series. Amherst: Amherst Scientific Publishers. Available at http://www.aehs.com/publications/catalog/contents/tph.htm (March 2003).

TPHCWG (1998b) Composition of Petroleum Mixtures, Volume 2. Total Petroleum Hydrocarbon Criteria Working Group Series. Amherst: Amherst Scientific Publishers. Available at http://www.aehs.com/publications/catalog/contents/tph.htm (March 2003).

TPHCWG (1999a) Individual Sample Fuel Mixture Composition Data, Appendix 1. In Composition of Petroleum Mixtures, Volume 2. Total Petroleum Hydrocarbon Criteria Working Group Series. pp 102. Amherst: Amherst Scientific Publishers. Available at http://www.aehs.com/publications/catalog/contents/tph.htm (March 2003).

TPHCWG (1999b) Human Health Risk-based Evaluation of Petroleum Contaminated Sites: Implementation of the Working Group Approach, Volume 5. Total Petroleum Hydrocarbon Criteria Working Group Series. Amherst: Amherst Scientific Publishers. Available at http://www.aehs.com/publications/catalog/contents/tph.htm (March 2003).

Twerdok LE (1999) Development of toxicity criteria for petroleum hydrocarbon fractions in the Petroleum Hydrocarbon Criteria Working Group approach for risk-based management of total petroleum hydrocarbons in soil, *Drug and Chemical Toxicology* **22**, 275−291.

USEPA (2003) IRIS *Integrated Risk Information System, Benzene.* US Environmental Protection Agency, available at http://www.epa.gov/iris/subst/0276.htm (May 2003).

USEPA (1986) *US Environmental Protection Agency. Risk Assessment Guidelines*, EPA-600-8-87-045. Washington, DC. Available at http://www.epa.gov/clariton/clhtml/pubtitle.html (March 2003).

Vermeire, T.G. (1993) *Voorstel Voor de Human-Toxicologische Onderbouwing van C-(toetsings)warden.* Addendum op rapportnr. 75201005, National Institute of Public Health and the Environment, RIVM Report No. 715801001, May 1993, Bilthoven (in Dutch)

Westlake DWS, Jobson A, Phillippe R and Cook, FD (1974) Biodegradability and crude oil composition, *Canadian Journal of Microbiology* **20**, 915-928

Zemanek, M.G., Pollard, S.J.T., Kenefick, S.L. and Hrudey, S.E. (1997) Multiphase Partitioning and Co-solvent Effects for Polynuclear Aromatic Hydrocarbons (PAH) in Authentic Petroleum- and Creosote-Contaminated Soils, *Environmental Pollution* **98(2),** 239-252