2. OVERVIEW OF TOTAL PETROLEUM HYDROCARBONS

This document presents information in a way that is more summary in nature than the usual comprehensive toxicological profile. Total petroleum hydrocarbons (TPH) is such a broad family of compounds that it would be a large undertaking to present comprehensive environmental, chemical/physical, and health information on all the individual chemical components or on all petroleum products. This and subsequent chapters are designed to aid the reader in understanding what TPH is, what we know about it, the chance of significant exposure, and possible health consequences. Appendices are provided that present more detailed information.

2.1 DEFINITION OF TOTAL PETROLEUM HYDROCARBONS

TPH is defined as the measurable amount of petroleum-based hydrocarbon in an environmental media. It is, thus, dependent on analysis of the medium in which it is found (Gustafson 1997). Since it is a measured, gross quantity without identification of its constituents, the TPH "value" still represents a mixture. Thus, TPH itself is not a direct indicator of risk to humans or to the environment. The TPH value can be a result from one of several analytical methods, some of which have been used for decades and others developed in the past several years. Analytical methods are evolving in response to needs of the risk assessors. In keeping with these developments, definition of TPH by ATSDR is closely tied to analytical methods and their results. The ATSDR approach to assessing the public health implications of exposure to TPH is presented in Section 2.3.

There are several hundred individual hydrocarbon chemicals defined as petroleum-based, with more than 2.50 petroleum components identified in Appendix D of this profile. Further, each petroleum product has its own mix of constituents. One reason for this is that crude oil, itself, varies in its composition. Some of this variation is reflected in the finished petroleum product. The acronym PHC (petroleum hydrocarbons) is widely used to refer to the hydrogen- and carbon-containing compounds originating from crude oil, but PHC should be distinguished from TPH, because TPH is specifically associated with environmental sampling and analytical results.

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

Some products are highly predictable (e.g., jet fuels) with specific fractions of defined components; others, for example, automotive gasolines, contain broader ranges of hydrocarbon types and amounts. Table D- 1 in Appendix D provides a comprehensive list of petroleum hydrocarbons.

Petroleum products, themselves, are the source of the many components, but do not define what is TPH. They help define the potential hydrocarbons that become environmental contaminants, but any ultimate exposure is determined also by how the product changes with use, by the nature of the release, and by the hydrocarbon's environmental fate. When petroleum products are released into the environment, changes occur that significantly affect their potential effects. Physical, chemical, and biological processes change the location and concentration of hydrocarbons at any particular site.

Petroleum hydrocarbons are commonly found environmental contaminants, though they are not usually classified as hazardous wastes. Many petroleum products are used in modern society, including those that are fundamental to our lives (i:e., transportation fuels, heating and power-generating fuels). The volume of crude oil or petroleum products that is used today dwarfs all other chemicals of environmental and health concern. Due to the numbers of facilities, individuals, and processes and the various ways the products are stored and handled, environmental contamination is potentially widespread.

Soil and groundwater petroleum hydrocarbon contamination has long been of concern and has spurred various analytical and site remediation developments, e.g., risk-based corrective actions (ASTM's Risk-Based Corrective Action [RBCA]), EPA and state government underground storage tank (UST) programs, British Columbia's Ministry of Environment's development of remediation criteria for petroleum contamination (primarily environmental risks) (BC 1995), and the annual Amherst Massachusetts conference from which the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) was formed. The TPHCWG is made up of industry, government, and academic scientists, working to develop a broad set of guidelines to be used by engineering and public health professionals in decisions on petroleum contaminated media. In 1997 the criteria working group published a technical overview of their risk management approach to TPH (TPHCWG 1997a), which represents the most comprehensive effort in this area to date. In 1997 the TPHCWG published two volumes, *Selection of Representative TPH Fractions Based on Fate and Transport Considerations* (Vol. 3) and *Development of Fraction Specific Reference Doses (RfDs) and Reference Concentrations (RfCs) for Total Petroleum Hydrocarbons (TPH)* (Vo1.4) (TPHCWG 1997b, 1997c). In 1998 the TPHCWG published Volume 1*, Analysis of Petroleum Hydrocarbons in Environmental Media* (TPHCWG 1998a) and Volume 2*, Composition of Petroleum Mixtures* (TPHCWG 1998b).

2.2 TOTAL PETROLEUM HYDROCARBONS ANALYSIS OVERVIEW

The TPH method of analysis often used, and required by many regulatory agencies, is EPA Method 4 18.1. This method provides a "one number" value of TPH in an environmental media; it does not provide information on the composition (i.e., individual constituents of the hydrocarbon mixture). The amount of TPH measured by this method depends on the ability of the solvent used to extract the hydrocarbon from the environmental media and the absorption of infrared (IR) light by the hydrocarbons in the solvent extract. EPA Method 418.1 is not specific to hydrocarbons and does not always indicate petroleum contamination (e.g., humic acid, a non-petroleum hydrocarbon, may be detected by this method).

An important feature of the TPH analytical methods is the use of an Equivalent Carbon Number Index (EC). The EC represents equivalent boiling points for hydrocarbons and is the physical characteristic that is the basis for separating petroleum (and other) components in chemical analysis. Petroleum fractions as discussed in this profile are defined by EC.

Another analytical method commonly used for TPH is EPA Method 8015 Modified. This method reports the concentration of purgeable and extractable hydrocarbons; these are sometimes referred to as gasoline and diesel range organics, GRO and DRO, respectively, because the boiling point ranges of the hydrocarbon in each roughly correspond to those of gasoline (C_6 to C_{10-12}) and diesel fuel (C_{8-12} to C_{24-26}), respectively. Purgeable hydrocarbons are measured by purge-and-trap gas chromatography (GC) analysis using a flame ionization detector (FID), while the extractable hydrocarbons are extracted and concentrated prior to analysis by GUFID. The results are most frequently reported as single numbers for purgeable and extractable hydrocarbons. Before the TPHCWG began publishing its TPH guides, the Massachusetts Department of Environmental Protection (MADEP) developed risk assessment and analytical methodologies for TPH (Hutcheson et al. 1996). MADEP developed a method based on EPA Method 801.5 Modified which gives a measure of the aromatic and aliphatic content of the hydrocarbon in each of several carbon number ranges (fractions). The MADEP method is based on standard EPA methods, which allows it to be easily implemented by laboratories, though there are limitations with the method (see Section 3.3). EPA has proposed a modification in its test procedure for analysis of “oil and grease and total petroleum hydrocarbons” that not only overcomes the problem of using freon as a solvent, but also provides more refined separation of aliphatic and aromatic fractions (EPA 1998a).

The Risk-Based Corrective Action (RBCA) guidance of American Society for Testing and Materials (ASTM), published in 1995, is an important document for public and private institutions that remediate petroleum contaminated sites (ASTM 1995). EPA is telling agencies implementing risk- based decision-making that the ASTM standard may be a good starting point for risk management (EPA 1995c).

2.3 TPH FRACTIONS AND THE ATSDR APPROACH TO EVALUATING THE PUBLIC HEALTH IMPLICATIONS OF EXPOSURE TO TPH

The public health implications associated with TPH are common to the broader questions of chemical mixtures. What does one know about the makeup and adverse health effects associated with the whole mixture? Does one select the most toxic or carcinogenic elements or representative chemical(s), or does one rely on whole product toxicity results? In the case of TPH, one sample is likely to vary significantly in content from other samples, even with similar “single value” results.

This profile builds on the efforts by the TPHCWG and MADEP to group chemicals into fractions with similar environmental transport characteristics (i.e., transport fractions). An important difference is ATSDR’s concern with all possible exposure periods, from acute through chronic, whereas other agencies or groups have focused on longer-term exposures. The common characteristic of all of these approaches is the attempt to gather the available information about the toxicity and the risks associated with transport fractions.

Although chemicals grouped by transport fraction generally have similar toxicological properties, this is not always the case. For example, benzene is a carcinogen, but toluene, ethylbenzene, and xylenes are not. However, it is more appropriate to group benzene with compounds that have similar environmental transport properties than to group it with other carcinogens such as benzo(a)pyrene that have very different environmental transport properties. Section 6.1.1 provides a more detailed discussion of the various transport fractions.

ATSDR's mission of providing public health support to communities with potential exposure to hazardous wastes is different from that of the ASTM, for example, which developed the RBCA guide for the purpose of remediation of petroleum-contaminated sites. Also, ecological risk assessment is a fundamental feature of the ASTM and British Columbia methodologies, though not for ATSDR.

Because a critical aspect of assessing the toxic effects of TPH is the measurement of the compounds, one must first appreciate the origin of the various fractions (compounds) of TPH. Transport fractions are determined by several chemical and physical properties (i.e. solubility, vapor pressure, and propensity to bind with soil and organic particles). These properties are the basis of measures of leachability and volatility of individual hydrocarbons and transport fractions. The TPHCWG approach defines petroleum hydrocarbon transport fractions by equivalent carbon number grouped into 13 fractions (see Section 6.1.2). The "analytical fractions" are then set to match these transport fractions, using specific *n*-alkanes to mark the analytical results for aliphatics and selected aromatics to delineate hydrocarbons containing benzene rings. ATSDR has used the basic TPHCWG approach and modified the fractional groups (see Chapter 6). Fate and transport considerations are discussed in more detail in Chapter 5. The TPHCWG transport fractions' physical properties are presented in Table 2-l.

The approach to evaluating the potential health effects for these transport fractions taken by ATSDR and the TPHCWG, however, uses a reduced number of fractions, namely three aliphatic fractions and three aromatic fractions. Health effects screening values based on representative chemicals or-mixtures for each of the fractions were developed using ATSDR minimal risk levels (MRLs). Table 2-2 presents the ATSDR TPH fractions and their representative compounds or mixtures. In general, the most toxic representative compound or mixture for each fraction is used to indicate the potential toxicity of the entire fraction. Selection of the representative compounds and mixtures is discussed in detail in Sections 6.2,

Table 2-1. Representative Physical Parameters for TPH Analytical Fractions Based on Correlation to Relative Boiling Point Index

Fraction	Solubility, mg/L	Vapor pressure, atm	Henry's law constant, cm^3/cm^3	Log K_{oc}
Aromatics				
EC_5–EC_7[a]	220	0.11	1.5	3
$EC_{>7}$–EC_8[b]	130	0.035	0.86	3.1
$EC_{>8}$–EC_{10}	65	0.0063	0.39	3.2
$EC_{>10}$–EC_{12}	25	0.00063	0.13	3.4
$EC_{>12}$–EC_{16}	5.8	0.000048	0.028	3.7
$EC_{>16}$–EC_{21}	0.65	0.0000011	0.0025	4.2
$EC_{>21}$–EC_{35}	0.0066	0.00000000044	0.000017	5.1
Aliphatics				
EC_5–EC_6	36	0.35	47	2.9
$EC_{>6}$–EC_8	5.4	0.063	50	3.6
$EC_{>8}$–EC_{10}	0.43	0.0063	55	4.5
$EC_{>10}$–EC_{12}	0.034	0.00063	60	5.4
$EC_{>12}$–EC_{16}	0.00076	0.000076	69	6.7
$EC_{>16}$–EC_{35}	0.0000025	0.0000011	85	8.8

[a] The only compound contained in this fraction is benzene.
[b] The only compound contained in this fraction is toluene.

EC = equivalent carbon number

Source: TPHCWG 1997b

Table 2-2. ATSDR TPH Fractions and Representative Compounds

Chemical fraction, in EC[a]	Representative compounds
Aromatics	
EC_6 - EC_9	Benzene, toluene, ethylbenzene, xylenes
$EC_{>9}$ - EC_{16}	Isopropyl benzene, naphthalene
$EC_{>16}$ - EC_{35}	Fluorene, fluoranthene, benzo(a)pyrene
Aliphatics	
EC_5 - EC_8	*n*-Hexane
$EC_{>8}$ - EC_{16}	JP-5, JP-7, JP-8, kerosene, dearomatized petroleum stream
$EC_{>16}$ - EC_{35}	Mineral oils

[a] EC = equivalent carbon number index. EC is based on equivalent retention times on a boiling point GC column, normalized to n-alkanes

6.3, and 6.6. In addition, existing cancer assessments for each fraction are presented and discussed in Chapter 6 and Appendix A.

Despite the large number of hydrocarbons found in petroleum products and the widespread nature of petroleum use and contamination, only a relatively small number of the compounds are well characterized for toxicity. The health effects of some fractions can be well characterized, based on their components or representative compounds (e.g., light aromatic fraction-BTEX-benzene, toluene, ethylbenzene, and xylenes). However, heavier TPH fractions have far fewer well characterized compounds. Systemic and carcinogenic effects are known to be associated with petroleum hydrocarbons, but ATSDR does not develop health guidance values for carcinogenic end points (ATSDR 1996b). See Chapter 6 for further discussion of the ATSDR approaches and the approaches of other groups (MADEP, TPHCWG, and ASTM).