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Review of Chemical, Physical, and Toxicologic Properties of Components of Total Petroleum Hydrocarbons

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ABSTRACT: Risk is a function of exposure and hazard, and both aspects must be incorporated into sound risk assessment efforts. However, risk assessment for sites contaminated with petroleum products is complicated by a general lack of information relevant to exposure to and toxicity of petroleum mixtures (especially total petroleum hydrocarbons, or TPH). Specifically, there is often inadequate information about the components of the TPH present at the site and the physical and chemical properties and toxicities of these components. Such information is crucial to developing a strong conceptual model of exposure to and risk from petroleum hydrocarbons at contaminated sites. This article presents information that can be incorporated into risk assessments for sites contaminated with petroleum hydrocarbons.

KEY WORDS: petroleum contamination, total petroleum hydrocarbons, risk assessment, toxicity, physical/chemical properties.

I. BACKGROUND

Environmental contamination by petroleum products is a significant concern throughout the U.S. It is estimated that there are over 2 million underground storage tanks subject to the federal underground storage tank regulations designed to minimize potential releases (Valentinetti, 1989). Not included in this figure are other sources of petroleum product contamination, such as heating oil tanks (which are not subject to the regulations), refineries, aboveground tanks, terminals, pipelines, or accidental spills from other sources. An understanding of the risks associated with releases from these sources is crucial to effective decision making about both prevention and remediation of releases. However, as lamented by Bauman of the American Petroleum Institute (1989), risk assessment efforts for petroleum hydrocarbons in environmental media are frustrated significantly by the complex nature of petroleum products, the lack of adequate knowledge about the movement of petroleum components in soil, and the lack of knowledge about the

toxicity of these components. This article provides information that can be used to develop a better understanding of the petroleum components present at sites, their movement in the environment, and their toxicity.

Once a release has occurred, environmental media at petroleum-contaminated sites are typically sampled and analyzed for a handful of specific compounds (such as benzene, toluene, ethylbenzene, xylenes (BTEX), and lead), and for total petroleum hydrocarbons (TPH). The BTEX components of petroleum products can be identified and quantified, and their toxicity and mobility in the environment are relatively well understood. However, although chemical analysis for TPH is relatively simple and inexpensive, this measure of petroleum components presents challenges to risk assessors. For instance, the label "total" implies that analysis for TPH includes all petroleum hydrocarbons, which is far from true. Although several methods are available, each actually measures only a specific range of the hydrocarbon components (Bauman, 1991). Because petroleum product composition varies among sources and over time (as a result of weathering and environmental fate and transport processes), the same concentration of TPH at two different sites may represent very different mixtures and, therefore, very different risks to human health and the environment (Bauman, 1991; Millner *et al.,* 1992).

Although the analytical approaches for TPH in the environment may satisfy the informational needs of regulatory agencies and engineers designing remediation activities, the level of detail (or lack thereof) presents significant challenges to risk assessors who must evaluate the movement of petroleum components in the environment, consider the inherent hazards associated with these chemicals (toxicity), and estimate the risks these releases pose to human and ecological receptors. For instance, the polycyclic aromatic hydrocarbon content of diesel varies significantly across diesel products and could significantly affect the toxicity of the TPH mixtures present in the environment (Block *et al.,* 1991). Risk assessors typically select surrogate compounds (or combinations of compounds) to represent TPH so that movement in the environment and toxicity can be evaluated manageably.

Three types of information contribute to selection of surrogate compounds for TPH: (1) the composition of TPH at the site, (2) information about the chemical and physical properties of the TPH components, and (3) information quantifying the inherent toxicity of the components. This paper presents a compilation of information about the composition of TPH from various sources, available chemical and physical information about these components, and available toxicity information about them. This information can be applied to select surrogate compounds for TPH.

II. COMPONENTS OF TPH

Information about the composition of TPH from a variety of sources is summarized in Tables 1 and 2. The considered petroleum product sources include gasoline,

TABLE 1
Composition of Gasoline-Based TPH

Constituents	Gasoline weight (%)	Regular unleaded gasoline volume (%)	Premium unleaded gasoline volume (%)	Leaded gasoline volume (%)	Water-soluble-phase regular leaded gasoline (ppb)	Water-soluble-phase regular unleaded gasoline (ppb)	Water-soluble-phase super unleaded gasoline (ppb)
Alcohols							
2-Butoxyethanol							16,800
Ethyl alcohol		<5	<5				
Methyl alcohol		0.2	0.2				
t-Butyl alcohol					22,300	15,900	933,000
Cycloalkanes							
Cyclopentane	0.19–0.58						
1-*trans*-3-Dimethylcyclohexane	0.05–0.12						
1-*cis*-2-Dimethylcyclopentane	0.07–0.13						
1-*trans*-2-Dimethylcyclopentane	0.06–0.20						
Ethylcyclohexane	0.17–0.42						
Ethylcyclopentane	0.14–0.21						
1-Methyl-*cis*-2-ethylcyclopentane	0.06–0.11						
1-Methyl-*trans*-3-Ethylcyclopentane	0.06–0.12						
Isopropylcyclopentane	0.01–0.02						
n-Propylcyclopentane	0.01–0.06						
1,1,2-Trimethylcyclopentane	0.06–0.11						
1-*trans*-2-*cis*-3-Trimethylcyclopentane	0.01–0.25						
1-*trans*-2-*cis*-4-Trimethylcyclopentane	0.03–0.15						
Cycloalkenes							
Cyclohexene	0.03						
Cyclopentene	0.12–0.18				5190		
3-Methylcyclopentene	0.03–0.08						
Chlorinated aliphatics							
Dibromoethane				190 mg/l	576		
1,2-Dichloroethane	150–300				1330		
1,1-Dichloroethane				210 mg/l			
Ethylene dibromide	0.7–177.2 mg/kg						

TABLE 1 (continued)
Composition of Gasoline-Based TPH

Constituents	Gasoline weight (%)	Regular unleaded gasoline volume (%)	Premium unleaded gasoline volume (%)	Leaded gasoline volume (%)	Water-soluble-phase regular leaded gasoline (ppb)	Water-soluble-phase regular unleaded gasoline (ppb)	Water-soluble-phase super unleaded gasoline (ppb)
Ethyl alkanes/alkenes							
5-Ethylheptane	0.02–0.16						
3-Ethylhexane	0.01						
3-Ethyl-2-pentene	0.03–0.04						
Ether							
Methyl-*t*-butyl ether		<12	<12		43,700	35,100	966,000
Methyl alkanes							
2,2-Dimethylbutane	0.17–0.84						
2,3-Dimethylbutane	0.59–1.55						
2,4-Dimethyl-3-ethylpentane	0.03–0.07						
2,2-Dimethylheptane	0.01–0.08						
2,3-Dimethylheptane	0.13–0.51						
2,6-Dimethylheptane	0.07–0.23						
3,3-Dimethylheptane	0.01–0.08						
3,4-Dimethylheptane	0.07–0.33						
2,4-Dimethylhexane	0.34–0.82						
2,5-Dimethylhexane	0.24–0.52						
3,4-Dimethylhexane	0.16–0.37						
2,6-Dimethyloctane	0.06–0.12						
2,3-Dimethylpentane	0.32–4.17						
2,4-Dimethylpentane	0.23–1.71						
3,3-Dimethylpentane	0.02–0.03						
2-Methyl-3-ethylhexane	0.04–0.13				9,930		
2-Methylbutane							
2-Methylheptane	0.48–1.05						
3-Methylheptane	0.63–1.54						
4-Methylheptane	0.22–0.52						
2-Methylhexane	0.36–1.48						
3-Methylhexane	0.3–1.77						

TABLE 1 (continued)
Composition of Gasoline-Based TPH

Constituents	Gasoline weight (%)	Regular unleaded gasoline volume (%)	Premium unleaded gasoline volume (%)	Leaded gasoline volume (%)	Water-soluble-phase regular leaded gasoline (ppb)	Water-soluble-phase regular unleaded gasoline (ppb)	Water-soluble-phase super unleaded gasoline (ppb)
2-Methylnonane	0.06–0.41						
3-Methylnonane	0.06–0.32						
4-Methylnonane	0.04–0.26						
2-Methyloctane	0.14–0.62						
3-Methyloctane	0.34–0.85						
4-Methyloctane	0.11–0.55						
2-Methylpentane	2.91–3.85						
3-Methylpentane	2.4						
2,2,3-Trimethylbutane	0.01–0.04						
2,2,4-Trimethylheptane	0.12–1.7						
3,3,5-Trimethylheptane	0.02–0.06						
2,2,4-Trimethylhexane	0.11–0.18						
2,2,5-Trimethylhexane	0.17–5.89						
2,3,3-Trimethylhexane	0.05–0.12						
2,3,5-Trimethylhexane	0.05–1.09						
2,4,4-Trimethylhexane	0.02–0.16						
2,2,3-Trimethylpentane	0.09–0.23						
2,2,4-Trimethylpentane	0.32–4.58						
2,3,3-Trimethylpentane	0.05–2.28						
2,3,4-Trimethylpentane	0.11–2.8						
Methyl alkenes							
2,3-Dimethyl-1-butene	0.08–0.1						
2,3-Dimethyl-1-pentene	0.01–0.02						
2,4-Dimethyl-1-pentene	0.02–0.03						
4,4-Dimethyl-1-pentene	0.6 (vol.)						
4,4-Dimethyl-*cis*-2-pentene	0.02						
2-Methyl-1-butene	0.22–0.66						
2-Methyl-2-butene	0.96–1.28						
2-Methyl-1-pentene	0.2–0.22						
2-Methyl-2-pentene	0.27–0.32						
3-Methyl-1-butene	0.08–0.12	0.06–0.08	0.06–0.08	0.06–0.08			
3-Methyl-*cis*-2-pentene	0.35–0.45						
3-Methyl-*trans*-2-pentene	0.32–0.44						
4-Methyl-*cis*-2-pentene	0.04–0.05						
4-Methyl-*trans*-2-pentene	0.08–0.3						

TABLE 1 (continued)
Composition of Gasoline-Based TPH

Constituents	Gasoline weight (%)	Regular unleaded gasoline volume (%)	Premium unleaded gasoline volume (%)	Leaded gasoline volume (%)	Water-soluble-phase regular leaded gasoline (ppb)	Water-soluble-phase regular unleaded gasoline (ppb)	Water-soluble-phase super unleaded gasoline (ppb)
Monocyclic aromatic hydrocarbons							
Benzene	0.12-3.5	2-5	2-5	2-5	30,500	28,100	67,000
n-Butylbenzene	0.04-0.44	0.08	0.08	0.2-0.5			
sec-Butylbenzene	0.01-0.13						
t-Butylbenzene	0.12						
1,2-Diethylbenzene	0.57						
1,3-Diethylbenzene	0.05-0.38						
1,2-Dimethyl-3-ethylbenzene	0.02-0.19						
1,2-Dimethyl-4-ethylbenzene	0.5-0.73						
1,3-Dimethyl-2-ethylbenzene	0.21-0.59						
1,3-Dimethyl-4-ethylbenzene	0.03-0.44						
1,3-Dimethyl-5-ethylbenzene	0.11-0.42						
1,3-Dimethyl-5-t-butylbenzene	0.02-0.16						
1,4-Dimethyl-2-ethylbenzene	0.05-0.36						
Ethylbenzene	0.36–2.86	5	5	5	4,040	2,420	7,400
Isobutylbenzene	0.01–0.08						
Isopentylbenzene	0.07–0.17						
eip-Isopropylbenzene	<0.01–0.23						
1-Methyl-4-ethylbenzene	0.18–1						
1-Methyl-2-ethylbenzene	0.19–0.56						
1-Methyl-3-ethylbenzene	0.31–2.86						
1-Methyl-2-*n*-propylbenzene	0.01–0.17						
1-Methyl-3-*n*-propylbenzene	0.08–0.56						
1-Methyl-3-isopropylbenzene	0.01–0.12						
1-Methyl-3-*t*-butylbenzene	0.03–0.11						
1-Methyl-4-*t*-butylbenzene	0.04–0.13						
n-Pentylbenzene	0.01–0.14						
n-Propylbenzene	0.08–0.72	0.6	0.6				
1,2,3,4-Tetramethylbenzene	0.02–0.19						
1,2,3,5-Tetramethylbenzene	0.14–1.06						
1,2,4,5-Tetramethylbenzene	0.05–0.67						
Toluene	2.73–21.8	6–7	6–7	6–7	31,400	31,100	107,400
1,2,3-Trimethylbenzene	0.21–0.48	0.73	0.73	0.73			
1,2,4-Trimethylbenzene	0.66–3.3						
1,3,5-Trimethylbenzene	0.13–1.15	1.3	1.3	1.3			

TABLE 1 (continued)
Composition of Gasoline-Based TPH

Constituents	Gasoline weight (%)	Regular unleaded gasoline volume (%)	Premium unleaded gasoline volume (%)	Leaded gasoline volume (%)	Water-soluble-phase regular leaded gasoline (ppb)	Water-soluble-phase regular unleaded gasoline (ppb)	Water-soluble-phase super unleaded gasoline (ppb)
o-Xylene	0.68–2.86						
m-Xylene	1.77–3.87				13,900	10,900	11,500
o,p-Xylenes						4,840	5,660
p-Xylene	0.77–1.58						
Xylenes		6–7	6–7	6–7			
Polycyclic aromatic hydrocarbons							
Anthracene		1.55–1.84 mg/l	1.55–1.87 mg/l	1.55 mg/l			
Benzo*[a]*pyrene	0.19–2.8 mg/kg						
Benzo*[b]*fluoranthene		3.9 mg/l	3.9 mg/l	3.9 mg/l			
Benzo*[e]*pyrene		0.3 mg	0.3 mg	0.3 mg/l			
Fluoranthene		1.84 mg/l	1.84 mg/l	1.84 mg/l			
Naphthalene	0.09–0.49	0.2–0.5	0.2–0.5	0.08			
Simple alkanes							
n-Butane	3.93–4.7	4–5	4–5	4–5			
n-Decane	0.04–0.5						
n-Dodecane	0.04–0.09						
n-Heptane	0.31–1.96						
n-Hexane	0.24–3.5						
Isobutane	0.12–0.37	0.7–1	0.7–1	0.1			
Isopentane	6.07–10.17	9–11	9–11	9–11			
Neopentane	0.02–0.05						
n-Nonane	0.07–0.83						
n-Octane	0.36–1.43						
n-Pentane	5.73–10.92	2.6–2.7	2.6–2.7	2.6–2.7			
Propane	0.01–0.14	0.07–0.08	0.07–0.08	0.07–0.08			
n-Undecane	0.05–0.22						

TABLE 1 (continued)
Composition of Gasoline-Based TPH

Constituents	Gasoline weight (%)	Regular unleaded gasoline volume (%)	Premium unleaded gasoline volume (%)	Leaded gasoline volume (%)	Water-soluble-phase regular leaded gasoline (ppb)	Water-soluble-phase regular unleaded gasoline (ppb)	Water-soluble-phase super unleaded gasoline (ppb)
Simple alkenes							
2-Butene		0.16–0.17	0.16–0.17	0.16–0.17	5,870	4,740	8,790
cis-2-Butene	0.13–0.17						
trans-2-Butene	0.16–0.2						
cis-3-Heptene	0.14–0.17						
trans-3-Heptene	0.06–0.1						
cis-2-Hexene	0.15–0.24						
trans-2-Hexene	0.18–0.36						
cis-3-Hexene	0.11–0.13						
trans-3-Hexene	0.12–0.15						
1-Pentene	0.33–0.45						
2-Pentene						22,500	
cis-2-Pentene	0.43–0.67						
trans-2-Pentene	0.52–0.9						
Unknown							
Indan	0.25–0.34						
1-Methylindan	0.04–0.17						
2-Methylindan	0.02–0.1						
4-Methylindan	0.01–0.16						
5-Methylindan	0.09–0.3						
Tetralin	0.01–0.14						
Tricresyl phosphate		<0.2	<0.2				

From State of California, Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure, Appendix I, 1989; Watts, *Groundwater Monitoring Parameters and Pollution Sources,* 3rd ed., Tables 7.3.1 and 7.3.2, 1989; Kramer and Hayes, *N.J. Geol. Surv. Tech. Memo.,* 87, 87, 1987a.

TABLE 2
Composition of Diesel-, Jet Fuel A-, Diesel Fuel No. 2-, and Fuel Oil No. 2-Based TPH

Constituents	Diesel (wt. %)	Jet fuel A (vol. %)	Diesel fuel no. 2 (vol. %)	Water-soluble-phase fuel oil no. 2 (ppb)
Cycloalkanes				
Cyclopentane		0.59		
Cyclopropane, 1-methyl-2-(3-methylpentyl)				450
cis-1,2-Dimethylcyclohexane				460
Ethylcyclohexane		0.04		2400
1-Ethyl-4-methylcyclohexane				1900
Methyl cyclohexane				950
cis-Octahydropentalene				250
Propylcyclohexane		0.07		
Tetramethylcyclopentane		0.01		
Trimethylcyclohexane				4800
1,1,3-Trimethylcyclohexane		0.03		
Chlorinated aliphatics				
Dibromoethane		0.05		
Ether				
Methyl-*t*-butyl ether				117
Ketone				
Methyl isobutyl ketone				97

TABLE 2 (continued)
Composition of Diesel-, Jet Fuel A-, Diesel Fuel No. 2-, and Fuel Oil No. 2-Based TPH

Constituents	Diesel (wt. %)	Jet fuel A (vol. %)	Diesel fuel no. 2 (vol. %)	Water-soluble-phase fuel oil no. 2 (ppb)
Methyl alkanes				
3,6-Dimethyl undecane				590
6-Ethyl-2-methyl decane				680
2-Methylbutane		0.2–0.26		
3-Methyldecane		0.14		
2-Methylnonane		0.2		
4-Methylnonane		0.22		
3-Methyloctane		2.5		
2-Methyl-6-propyl dodecane				510
2,6,10-Trimethyldodecane	0.45			
2,7,10-Trimethyldodecane				510
2,3,7-Trimethyl octane				800
Methyl alkenes				
3,3-Dimethyl-1-octene				3,100
Monocyclic aromatic hydrocarbons				
Benzene		0.02	Trace	646
Benzene, methyl (1-methylethyl)				490–4,400
Butylbenzene		2		
1,2-Diethylbenzene		0.24		
1,2-Dimethyl-3-propylbenzene		5.4		
1,4-Dimethyl-2-ethylbenzene		0.2		

TABLE 2 (continued)
Composition of Diesel-, Jet Fuel A-, Diesel Fuel No. 2-, and Fuel Oil No. 2-Based TPH

Constituents	Diesel (wt. %)	Jet fuel A (vol. %)	Diesel fuel no. 2 (vol. %)	Water-soluble-phase fuel oil no. 2 (ppb)
Ethylbenzene		0.02	Trace	1,360
1-Ethyl-3-methyl benzene				6,200
1-Methylethyl benzene				12,000–20,000
1-Methylpropyl benzene				2,200
1-Methyl-4-propylbenzene		3.3		
Propylbenzene		3–5		2,500
n-Propylbenzene			Trace	
1,2,4,5-Tetramethylbenzene		9		
Toluene		Trace	Trace	1,680
1,2,3-Trimethylbenzene		6.6		
1,3,5-Trimethylbenzene			Trace	
m-Xylene				3,760
o,p-Xylenes				3,770
Xylenes		0.07	Trace	
Polycyclic aromatic hydrocarbons				
Anthracene			0.013–0.02	
Benzo*[a]*pyrene	0.07 μg/kg			
1,2-Dimethylnaphthalene				540
1,3-Dimethylnaphthalene		0.15		
1-Ethylidene-1*H*-indene				720
Fluorene			0.07–0.1	175
Methylnaphthalene	0.57–0.91			
1-Methylnaphthalene				1,230
2-Methylnaphthalene		0.34		

TABLE 2 (continued)
Composition of Diesel-, Jet Fuel A-, Diesel Fuel No. 2-, and Fuel Oil No. 2-Based TPH

Constituents	Diesel (wt. %)	Jet fuel A (vol. %)	Diesel fuel no. 2 (vol. %)	Water-soluble-phase fuel oil no. 2 (ppb)
Naphthalene	0.13	0.14	0.14–0.11	
Phenanthrene			0.26–0.3	296
Pyrene				65
Simple alkanes				
Decane		16.5		375
n-Decane	0.5–2			
n-Docosane	<0.2			
Dodecane		0.7		
n-Dodecane	0.96–11			
n-Eicosane	0.23–3			
n-Heneicosane	1			
n-Heptadecane	1.2–6			
Hexadecane				350
n-Hexadecane	1.2–6			
n-Nonadecane	0.53–4			
n-Nonane	0.1			
n-Octadecane	0.82–5			
Pentadecane				1,170
n-Pentadecane	1–7			
7-Propyl tridecane				925
n-Tetradecane	1.1–9			
Tridecane		0.5		1,030
n-Tridecane	1.1–10			
Undecane		36		590
n-Undecane	0.98–9			

TABLE 2 (continued)
Composition of Diesel-, Jet Fuel A-, Diesel Fuel No. 2-, and Fuel Oil No. 2-Based TPH

Constituents	Diesel (wt. %)	Jet fuel A (vol. %)	Diesel fuel no. 2 (vol. %)	Water-soluble-phase fuel oil no. 2 (ppb)
Unknown				
Alkyl nitrate			0.2	
Methylindane		0.3		
Pentacozane				1,380

From State of California, Guidelines for Site Assessment, Cleanup, and Underground Storage Tank Closure, Appendix I, 1989; Watts, *Groundwater Monitoring Parameters and Pollution Sources,* 3rd ed., Tables 7.3.1 and 7.3.2, 1989; Kramer and Hayes, *N.J. Geol. Surv. Tech. Memo.,* 87, 87, 1987b.

diesel, jet fuel, and water-soluble components of gasolines and fuel oil. Units of quantification used in the table are the same as those provided in the original source.

Most of the these analyses were performed on fresh petroleum products. Environmental media are not expected to contain these same distributions of components due to volatilization following releases, biodegradation, selective migration through soils and into ground water, and other processes. These processes must be considered when identifying surrogates for TPH at a particular site.

It is clear from Tables 1 and 2 that the composition of TPH varies significantly. For instance, gasoline products contain more straight-chain hydrocarbons than do diesel products. This will affect both the movement of the products in the environment and their toxicity. A greater number and variety of components have been identified in gasoline than in other petroleum products, suggesting complex characteristics affecting movement in the environment and toxicity, as well as a wide range of options for evaluating these characteristics.

The following sections provide available information on the components identified in Tables 1 and 2. This information can be used to evaluate the effects of weathering and movement in the environment on the composition of TPH at release sites and the toxicity of TPH.

III. CHEMICAL AND PHYSICAL PROPERTIES

Information about chemical and physical properties is presented in Table 3 for the TPH components identified in Tables 1 and 2. The following properties are included in the table: molecular weight, water solubility, specific gravity, vapor pressure, Henry's law constant, diffusivity, organic carbon/water partition coefficient (K_{oc}), octanol/water partition coefficient (log K_{ow}), fish bioconcentration factor (BCF), and surface-water half-life. The information was obtained from readily available sources and does not represent an exhaustive search of the literature. Rather, it is adequate for appropriate identification of surrogates to represent the weathering and movement of petroleum hydrocarbons in the environment. The information also illustrates what is readily available in the open scientific literature.

Solubility is an important property affecting constituent migration in soils, ground water, and surface water. Solubility is expressed in terms of the number of milligrams of a constituent that can be dissolved in 1 l of water (mg/l) under standard conditions of 25°C and one atmosphere of pressure (atm). The higher the value of solubility, the greater the tendency of a constituent to dissolve in water. For inorganic constituents, solubility depends on the form of the constituents.

Volatility is another important property affecting the mobility and persistence of organic constituents and several forms of inorganics. Henry's law constant (H) is an indication of the tendency of a constituent to volatilize, or "partition," from the

TABLE 3

Chemical and Physical Properties of TPH Components

Constituents	Molecular wt.	Water solubility (mg/L 25°C)	Specific gravity	Vapor pressure (mmHg 25°C)	Henry's law constant (atm-m³/mol 25°C)	Diffusivity (cm²/s)	K_{oc} (ml/g)	Log K_{ow}	Fish BCF (L/kg)	Surface-water $T_{1/2}$ (days) Low high
Alcohols										
Ethyl alcohol	46.07	280,000	0.789	59	1.2E – 05	0.12368	0.3	3.1	0.34	
Methyl alcohol	32	300 ,000		130	2.0E – 05	0.16211	0.1	1.5	2.3	
t-Butyl alcohol	74.1		0.788	42		0.09752		0.37		
Cycloalkanes										
Cyclopentane	70.14	160	0.751	42.4	1.9E + 0.1					
Methyl cyclohexane	98.19	14	0.77	6.18	4.3E + 01					
Cycloalkenes										
Cyclohexene	84.16	55 (20°C)	0.779	77 (20°C)						
Cyclopentene	68.12		0.77							
Chlorinated aliphatics										
1,2-Dichloroethane	99	7,986–8,650	1.23	87	1.3E – 03	0.09451	65	1.48–2.13	5.6	28–180
Dibromoethane	187.88	4.31 (30°C)	2,701	17 (30°C)						
1,1-Dichloroethane	99	5060	1.1757	182.1	5.9E – 03	0.0959	30.2	1.79		
Ether										
Methyl-*t*-butyl ether	88	4800	0.74	250	5.9E – 03	0.10172	41	1.2	1.5	28–180
Ketone										
Methyl isobutyl ketone	100.2	20,400	0.8017	14.5	9.4E – 05	0.07588	19–106	1.19		
Methyl alkanes										
2,3-Dimethylbutane	86.7	19.1		31.3	1.3E + 02					
2,3-Dimethylpentane	100.21	5.25		9.18	1.8E + 02					
2,4-Dimethylpentane	100.21	5.5		13.1	3.0E + 02					
3,3-Dimethylpentane	100.21	5.94		11	1.9E + 02					
2-Methylheptane	114.23									
3–Methylheptane	114.23	0.792		2.6	3.8E + 02					
4-Methylheptane	114.23									

TABLE 3 (continued)

Chemical and Physical Properties of TPH Components

Constituents	Molecular wt.	Water solubility (mg/L 25°C)	Specific gravity	Vapor pressure (mmHg 25°C)	Henry's law constant (atm-m³/mol 25°C)	Diffusivity (cm²/s)	K_{oc} (ml/g)	Log K_{ow}	Fish BCF (L/kg)	Surface-water $T_{1/2}$ (days) Low high
2-Methylhexane	100.21	2.54		8.78	3.5E + 02					
3-Methylhexane	100.21	4.95		8.21	2.4E + 02					
4-Methyloctane	128.26	0.115		0.903	1.0E + 03					
2-Methylpentane	86.17	13	0.654	28.2	1.7E + 02					
3-Methylpentane	86.17	13.1	0.6645	25.3	1.7E + 02					
2,2,4-Trimethylhexane	128.26									
2,2,5-Trimethylhexane	128.26	1.15		2.21	3.5E + 02					
2,3,3-Trimethylhexane	128.26									
2,3,5-Trimethylhexane	128.26									
2,4,4-tTrimethylhexane	128.26									
2,2,3-Trimethylpentane	114.23									
2,2,4-Trimethylpentane	114.23	2.44		6.56	3.3E + 02					
2,3,3-Trimethylpentane	114.23									
2,3,4-Trimethylpentane	114.23	2.3		3.6	1.9E + 02					
Methyl alkenes										
2-Methyl-1-butene	70.14		0.65							
2-Methyl-2-butene	70.14		0.668							
3-Methyl-1-butene	70.14	130	0.648	120	5.5E + 01					
2-Methyl-1-pentene	86.16	78	0.6817							
2-Methyl-2-pentene	86.16									
3-Methyl-*cis*-2-pentene	86.16									
3-Methyl-*trans*-2-pentene	86.16		0.67							
4-Methyl-*cis*-2-pentene	86.16		0.67							
4-Methyl-*trans*-2-pentene	86.16									
Monocyclic aromatic hydrocarbons										
Benzene	78	1780	0.88	95	5.5E – 03	9.30E – 02	49–100	1.56–2.15	5.2	5
Butylbenzene	134		0.86	1 (23°C)			1500			
n-Butylbenzene	134	50	0.86	1 (23°C)	1.3E + 00					
sec-Butylbenzene	134	30.9	0.87	1.5 (20°C)	1.4E + 00					
t-Butylbenzene	134	34	0.862	1.1 (20°C)	1.2E + 00					
1,2-Diethylbenzene	136						1500			
1,3-Diethylbenzene	136						1500			
Ethylbenzene	106	152–208	0.87	9.5	8.7E – 03	6.70E – 02	95–260	3.05–3.15	37.5	3
Isobutylbenzene	134.2	10.1		0.248	3.3E + 00					
eip-Isopropylbenzene	120	50 (20°C)	0.862	3.2 (20°C)	1.0E – 02			3.66		2
n-Pentylbenzene	149						2520			

TABLE 3 (continued)

Chemical and Physical Properties of TPH Components

Constituents	Molecular wt.	Water solubility (mg/L 25°C)	Specific gravity	Vapor pressure (mmHg 25°C)	Henry's law constant (atm-m³/mol 25°C)	Diffusivity (cm²/s)	K_{oc} (ml/g)	Log K_{ow}	Fish BCF (L/kg)	Surface-water $T_{1/2}$ (days) Low	high
Propylbenzene	120.2	60		0.449	7.0E – 01						
n-Propylbenzene	120	60 (15°C)	0.862	2.5 (20°C)	5.6E – 03 (15°C)			3.57–3.68			
1,2,3,4-Tetramethylbenzene	215.9	4.31		0.00876	2.6E – 01		1500				
1,2,3,5-Tetramethylbenzene	215.9	3.5		0.0186	5.9E – 01		1500				
1,2,4,5-Tetramethylbenzene	134.2	3.48		0.0659	2.5E + 00		1500				
Toluene	92	490–627	0.87	28	6.7E – 03	7.80E – 02	115–150	2.11– 2.8	10.7	4	
1,2,3-Trimethylbenzene	120						884				
1,2,4-Trimethylbenzene	120	57 (20°C)	0.88	1.4	3.9E – 01 (20°C)		1600	3.4	230	7	
1,3,5-Trimethylbenzene	120	64	0.865	1.4	3.7E – 01	1.60E + 03	3.4	230			
m-Xylene	106	173	0.8684	10	6.3E – 03		1585	3.2			
o-Xylene	106	204	0.87596	10	5.4E – 03		129	2.77–3.16			
p-Xylene	106	200	0.85665	10	6.3E – 03		204	3.15			
Xylenes	106	162—200	0.87	6.6—8.8	6.3E – 03	7.20E – 02	128—1,580	2.77—3.2	132	7	
Polycyclic aromatic hydrocarbons											
Anthracene	178	0.030—0.1125	1.24	1.7E – 5—1.95E – 4	6.5E – 05	5.90E – 02	16,000—26,000	4.34—4.54	30	0.071	0.024
Benzo*[a]*pyrene	252	0.0038—0.004	1.35	5.5E – 09	<2.4E – 6	4.70E – 02	398,000—1,900,000	5.81—6.50	30	0.015	0.046
Benzo*[b]*fluoranthene	252	0.0012	. ND	5.0E – 07	1.2E – 05	4.40E – 02	550,000	6.57	ND	0.36	
Benzo*[e]*pyrene	252					4.70E – 02					
1,2-Dimethylnaphthalene	158						4230				
1,3-Dimethylnaphthalene	158						4230				
Fluoranthene	202	0.206—0.373	1.25	0.000005	1.7E – 02	42,000	5.22	1.150	0.875	2.6	
Fluorene	166	1.66—1.98	1.2	1E – 3—1E – 2	2.1E – 04	5.70E – 02	5000	4.12—4.38	30	32	
Methylnaphthalene	142	27									
1-Methylnaphthalene	142	28	1.025	ND	ND	ND	ND	ND	129	ND	
2-Methylnaphthalene	142	25	1.001	0.045	3.4E – 04	6.20E – 02	7,400—8,500	3.86—4.11	190	ND	
Naphthalene	128	30—34	1.16	2.3E – 1—8.7E – 1	4.6E – 04	8.20E – 02	550—3,160	3.2—4.7	10.5	0.5	
Phenanthrene	178	0.71—1.29	1.18	0.00068	2.6E – 05	5.40E – 02	5250—38,900	4.2—4.6	30	0.125	1.04
Pyrene	202	0.013—0.171	1.27	6.85E – 07—2.5E – 05	1.1E – 05	5.00E – 02	46,000—135,000	4.88—5.32	30	0.028	0.085

TABLE 3 (continued)

Chemical and Physical Properties of TPH Components

Constituents	Molecular wt.	Water solubility (mg/L 25°C)	Specific gravity	Vapor pressure (mmHg 25°C)	Henry's law constant (atm-m³/mol 25°C)	Diffusivity (cm²/s)	K_{oc} (ml/g)	Log K_{ow}	Fish BCF (L/kg)	Surface-water $T_{1/2}$ (days) Low high
Simple alkanes										
n-Butane	58.13	61	0.6	1.82E + 03	9.6E – 01					
Decane	148.28	0.008								
n-Decane	148.28	0.052		0.175	7.0E + 02					
Dodecane	170.33	0.0037		0.0157	7.5E + 02					
n-Dodecane	170.33									
n-Eicosane	282.6	0.0019		2.67E – 06	2.9E – 01					
n-Heptane	100.21	3		0.06872	2.3E + 02					
n-Hexadecane	226.44	0.00628		0.000917	2.3E + 01					
n-Hexane	86	18 (20°C)	0.66	1.2E – 2 (20°C)	7.7E – 01	7.50E – 02	890	2.77	ND	ND
Isobutane	58.13	48.19		357	1.2E + 02					
Isopentane	72.15	48		92.6	1.4E + 02					
n-Nonane	128.26	0.07		0.571	5.0E + 02					
n-Octadecane	254.4	0.0021		2.50E – 05	2.9E + 00					
n-Octane	114.23	0.66		1.88	3.0E + 02					
n-Pentane	72.15	35		68.4	1.3E + 02					
Propane	44.09	63	0.58	8.5						
n-Tetradecane	190.38	0.00696		0.00127	1.1E + 02					
Undecane	156.32	0.044		0.0522	1.9E + 03					
n-Undecane	156.32									
Simple alkenes										
2-Butene		210								
cis-2-Butene	56.1		0.64							
trans-2-Butene	56.1		0.64							
cis-3-Heptene	98	9								
trans-3-Heptene	98									
cis-2-Hexene	84	50	0.86							
trans-2-Hexene	84	50	0.86							
cis-3-Hexene	84									
trans-3-Hexene	84									
1-Pentene	70.14	150		85	4.0E + 01					
2-Pentene	70.14	203		66	2.3E + 01					
cis-2-Pentene	70.14									
trans-2-Pentene	70.14									

From Bidleman, T. F. *et al.* (1986); Budavari, S. (1989); Dixon, D. and E. Rissmann (1985); Howard, P. H. (1989); Howard, P. H. (1990); Howard, P. H. *et al.* (1991); Lyman, W. J. *et al.* (1982); Mackay, D. *et al.* (1983); Mackay, D. and W. Y. Shiu (1981); Montgomery, J. H. and L. M. Welkom (1990); Shen, T. J. (1982); Strenge and Peterson (1989); U.S.EPA (1991); Verschueren, K. (1983).

aqueous or water phase to the vapor phase and is dependent on the vapor pressure and solubility of the constituent. Organic constituents having H values of 10^{-3} atm-m^3/mol or greater tend to volatilize from water; those with H values $<10^{-3}$ atm-m^3/mol may volatilize from water, but other processes such as adsorption to soil or sediment may be more important (Howard, 1989). In evaluating volatilization from water used within the home, U.S. Environmental Protection Agency (EPA) guidance (1991) recommends including constituents with an H of $>10^{-5}$ atm-m^3/mol and a molecular weight of <200 g/mol.

The potential for a constituent to adsorb to soil and sediment particles affects migration through soil and aquifer materials as well as migration from surface water to sediments. The potential for adsorption usually is expressed in terms of a partition coefficient, K_d. A K_d is the ratio of the concentration of adsorbed constituent to the concentration of aqueous-phase constituent and, although a unitless quantity, typically it is reported in units of milliliters per gram (ml/g). Higher values of K_d indicate greater potential for the constituent to sorb to soil, sediment, and aquifer materials. This partition coefficient may be determined empirically or estimated using constituent-specific and sediment- or soil-specific parameters. The parameters used to calculate K_d for organic constituents are the organic carbon/water partition coefficient (K_{oc}), which measures the selective affinity for soil organic carbon vs. water, and the fraction of organic carbon (f_{oc}) in soil, because K_d is commonly expressed as the product of the K_{oc} and f_{oc} (EPA, 1989a).

The octanol/water partition coefficient (K_{ow}) is a measure of the selective affinity for *n*-octanol vs. water. The fish BCF is used as an indication of the ability of a constituent to bioaccumulate in fish.

Persistence is the "lasting power" of constituents and is commonly expressed in terms of half-lives ($t_{1/2}$) for specific environmental media. A half-life is the time required for one half of the mass of a compound to be transformed into other constituents.

IV. **TOXICITY VALUES**

For purposes of quantitative risk assessment, the inherent toxicity of each chemical must be reduced to numerical values. A distinction is made between carcinogenic and noncarcinogenic effects. For potential carcinogens, the current regulatory guidelines (EPA, 1989b) use an extremely conservative approach in which it is assumed that any level of exposure to a carcinogen could hypothetically cause cancer. This is contrary to the traditional toxicological approach, in which finite thresholds are identified below which toxic effects are not expected to occur. This traditional approach still is applied to noncarcinogenic health effects.

Identification of constituents as known, probable, or possible human carcinogens is based on an EPA weight-of-evidence classification scheme in which chemicals are systematically evaluated for their ability to cause cancer in mammalian species and conclusions are reached about the potential to cause cancer in humans. The EPA classification scheme (EPA, 1989b) contains six classes based on the weight of available evidence, as follows:

- A: known human carcinogen
- B1: probable human carcinogen, limited evidence in humans
- B2: probable human carcinogen, sufficient evidence in animals and inadequate data in humans
- C: possible human carcinogen, limited evidence in animals
- D: inadequate evidence to classify
- E: evidence of noncarcinogenicity.

Some constituents in class D may have the potential to cause cancer, but adequate data are not currently available to change the classification.

The toxicity value used to describe the potency of a class A, B1, B2, or C carcinogen is the cancer slope factor (CSF). The slope factor is generated by the EPA through the use of a mathematical model that extrapolates from the high doses in animal studies to the low doses characterizing human exposures. The CSF represents the 95% upper confidence limit on the slope of the dose-response curve generated by the model.

For many noncarcinogenic effects, protective mechanisms must be overcome before the effect is manifested. Therefore, a finite dose (threshold), below which adverse effects will not occur, is believed to exist for noncarcinogens. For a given constituent, the dose that elicits no effect when evaluating the most sensitive response (the adverse effect that occurs at the lowest dose) in the most sensitive species is combined with uncertainty factors ("safety" factors, "modifying" factors) to establish an acceptable dose (toxicity value) for noncarcinogenic effects. Acceptable doses that are sanctioned by the EPA are called verified reference doses (RfDs) for oral or inhalation exposure or reference concentrations (RfCs) for inhalation exposure.

Most federal and state regulatory agencies expect that slope factors, cancer classifications, RfDs, and RfCs will be taken from the Integrated Risk Information System (IRIS, 1992) or, in the absence of IRIS data, the EPA Health Effects Assessment Summary Tables (HEAST) (EPA, 1992). Potential alternatives include in-depth review of the literature pertaining to toxicity of a particular constituent, resulting in independent development of a toxicity value, or estima-

tion of toxicity based on structure-activity relationships. However, most agencies lack the time or resources to evaluate such efforts. Thus IRIS and HEAST are the preferred sources of information. IRIS is an online data base containing up-to-date health risk and regulatory information provided by the EPA and contains only toxicity values that have been verified by the RfD or Carcinogen Risk Assessment Verification Endeavor Workgroups. HEAST is a tabular presentation, also prepared by the EPA, of interim RfDs and slope factors. HEAST is updated periodically. Available toxicity information from IRIS and HEAST is provided in Table 4.

Toxicity values were available for only a small number of the components identified in Tables 1 and 2. Although significant additional information is available in the literature for a number of the other components, many regulatory agencies are reluctant to accept toxicity values derived on the basis of the literature if confirmatory information is not available on either IRIS or HEAST. Therefore, from the perspective of real-world applications for most petroleum release sites, the information provided here is most pertinent to selection of surrogate compounds for TPH.

V. DISCUSSION

The composition of released petroleum products varies significantly, depending on the source, weathering of the product over time, and differential movement of the components in the environment. For most release sites, detailed information about the composition of TPH will not be available. Information presented in Tables 1 and 2 can be used to determine roughly what the initial composition of TPH in the released product might have been, thereby providing a starting point for evaluation of petroleum product releases. The next important step is to consider the effects of weathering on the ultimate composition of TPH remaining in the environment as a result of the release. Information presented in Table 3 describing chemical and physical properties of TPH components can contribute to evaluation of the effects of weathering and to consideration of the impact of fate and transport processes on the composition of TPH both close to and away from the original release point. Surrogate compounds can be selected to depict movement of TPH (or fractions of TPH) in the environment. Information provided in Table 4 can be used to identify one or more surrogate compounds to represent the toxicity of TPH associated with a particular release.

When properly integrated, the information presented in this article can contribute to selection of surrogate compounds that represent the movement of site-specific TPH in the environment and the toxicity of TPH that reaches human and ecological receptors. This approach can contribute to meaningful decision making about regulation and remediation of petroleum releases to the environment.

TABLE 4
Reference Doses, U.S. EPA Cancer Classifications, and Cancer Slope Factors for TPH Components

Constituents	RfDi[a] (mg/kg/d) subchronic	RfDi[a] (mg/kg/d) chronic	RfDo[b] (mg/kg/d) subchronic	RfDo[b] (mg/kg/d) chronic	Cancer class	CSFo[c] (mg/kg/d)$^{A-1}$	CSFi[d] (mg/kg/d)$^{A-1}$
Alcohols							
t-Butyl alcohol	NA	NA	1.0E + 00	1.0E – 01	D	NC	NC
Methyl alcohol	NA	NA	5.0E + 00	5.0E – 01	D	NC	NC
Cycloalkanes							
Dibromoethane	NA	NA	NA	NA	B2	8.5E + 01	7.7E – 01
1,1-Dichloroethane	5.0E + 00	5.0E – 01	1.0E + 00	1.0E – 01	B2	1.4E – 01	NA
Ethylene dibromide	NA	NA	2.0E – 01	2.0E – 02	C	8.4E – 02	NA
Ether							
Methyl-*t*-butyl ether	1.4E + 00	1.4E – 01	NA	NA	D	NC	NC
Monocyclic aromatic hydrocarbons							
Benzene	NA	NA	NA	NA	A	2.9E – 02	2.9E – 02
Ethylbenzene	2.9E – 01	2.9E – 01	1.0E + 00	1.0E – 01	D	NC	NC
eip-Isopropylbenzene	2.6E – 02	2.6E – 03	3.0E – 02	4.0E – 02	D	NC	NC
Toluene	5.7E – 01	1.1E – 01	2.0E + 00	2.0E – 01	D	NC	NC
Xylenes	NA	NA	4.0E + 00	2.0E + 00	D	NC	NC

TABLE 4 (continued)
Reference Doses, U.S. EPA Cancer Classifications, and Cancer Slope Factors for TPH Components

Constituents	RfDi[a] (mg/kg/d) subchronic	RfDi[a] (mg/kg/d) chronic	RfDo[b] (mg/kg/d) subchronic	RfDo[b] (mg/kg/d) chronic	Cancer class	CSFo[c] (mg/kg/d)^{A}–1	CSFi[d] (mg/kg/d)^{A}–1
Polycyclic aromatic hydrocarbons							
Anthracene	NA	NA	3.0E + 00	3.0E – 01	D	NC	NC
Benzo*[a]*pyrene	NA	NA	NA	NA	B2	7.3E + 00	6.1E + 00
Fluoranthene	NA	NA	4.0E – 01	4.0E – 02	D	NC	NC
Fluorene	NA	NA	4.0E – 02	4.0E – 02	D	NC	NC
Naphthalene	NA	NA	4.0E – 02	4.0E – 02	D	NC	NC
Pyrene	NA	NA	3.0E – 01	3.0E – 02	D	NC	NC
Simple alkanes							
n-Hexane	5.7E – 02	5.7E – 02	6.0E – 01	6.0E – 02	D	NC	NC

[a] RfDi = inhalation reference dose.
[b] RfDo = oral reference dose.
[c] CSFo = oral cancer slope factor.
[d] CSFi = inhalation cancer slope factor.

From U.S. EPA HEAST, 1992, and IRIS, 1992.

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