Reference Doses for Petroleum Mixtures

Petroleum products are complex mixtures that include hundreds of compounds. How to estimate the toxicity of such mixtures was subject to considerable discussion throughout the rule-making process, involving the Department of Ecology, the Department of Health, the TPH Project Oversight Group (POG), the U.S. EPA, and numerous stakeholders. Based on this work, consensus was reached on three principles:

1. Where reference doses and cancer potency factors are available for individual substances that are part of the petroleum mixture, these values should be used for these substances.
2. The remainder of the mixture should be divided into several groups of substances, or fractions, and a reference dose assigned to each fraction based on known toxicological information about substances found in those fractions or with a similar chemical structure.
3. Because of the wide range of chemicals and potential health effects, the noncarcinogenic toxicity posed by the various fractions should be assumed to be additive for the purposes of estimating the toxicity of a petroleum mixture.

Based on information developed by the National TPH Criteria Working Group, it was determined that the mixture of substances should be split into two main groups – aliphatic hydrocarbons and aromatic hydrocarbons. Each of these main groups was then further subdivided into fractions with similar physical properties.

Initial reference doses were derived from work done by the National TPH Criteria Working Group and the Massachusetts Department of Environmental Protection. At the request of EPA Region 10, the EPA's National Center for Environmental Assessment (NCEA) reviewed these values and recommended some adjustments. These recommendations were endorsed by the POG and the MTCA Science Advisory Board and published in the November 2001, Version 3.1 of CLARC. After publication of Version 3.1 of CLARC, EPA's National Center for Environmental Assessment, Superfund Technical Support Center published the provisional risk assessment issue paper "Derivation Support Document for Total Petroleum Hydrocarbons" (SRC SF 01-031/10-16-2002). The following memoranda documents the deliberations between the Department of Ecology and EPA and the changes made to the table "Recommended Reference Doses for Petroleum Fractions and Individual Hazardous Substance", Part IV, published in Version 3.1 of CLARC, November 2001. The information in the table "Reference Doses For Total Petroleum Hydrocarbon (TPH) Fractions and Individual Hazardous Substances Related to TPH" is to be used to establish cleanup levels for petroleum mixtures consistent with the guidance "Calculation of Method B and C Cleanup Levels For Petroleum Mixtures."

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10
1200 Sixth Avenue
Seattle, Washington 98101

February 14, 2005

Reply to
Attn of: OEA-095

Craig M. McCormack, Pharm.D.
Toxics Cleanup Program
Department of Ecology
P. O. Box 47600
Olympia, WA 98504-7600

Dear Dr. McCormack:

Thank you for your letter of February 9, 2006, describing the changes to the table "Updated Reference Doses for Total Petroleum Hydrocarbon (TPH) Fractions and Individual Hazardous Substances Related to TPH." The updated table is to be incorporated into Ecology's Cleanup Levels and Risk Calculations under the Model Toxic Control Act regulations

The changes appear to be consistent with our discussions over the past few months. I concur with the changes made to the table and its footnotes and believe they represent appropriate interpretations of information available from the IRIS and HEAST databases and from EPA's National Center for Environmental Assessment, including the Superfund Technical Support Center.

Sincerely,

Marcia L. Bailey

Marcia L. Bailey, D Env.

cc: Patricia Cirone, Ph.D.

STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY
PO Box 47600 • Olympia, WA 98504-7600 • 360-407-6000
TTY 711 or 800-833-6388 (for the speech or hearing impaired)

February 9, 2006

Marcia Bailey, D.Env.
US EPA Region 10, MS: OEA-095
1200 6th Avenue
Seattle, Washington 98101

Dear Dr. Bailey:

The enclosed table, *Updated Reference Doses For Total Petroleum Hydrocarbon (TPH) Fractions And Individual Hazardous Substances Related to TPH – Revised January 2006*, consolidates our discussions, e-mails, and overall review of the reference doses appropriate for inclusion in the Department of Ecology's updated TPH table to be incorporated into the Cleanup Levels and Risk Calculations under the Model Toxics Control Act Cleanup Regulation (CLARC). This constitutes an update to the TPH CLARC table that was prepared with your support, in 2004. The information in the updated table will be used by the Department of Ecology's Toxics Cleanup Program to evaluate and develop cleanup levels for dangerous waste sites contaminated with petroleum and selected chemicals that may be associated with petroleum products.

The 2006 table recognizes updates that have been made to the EPA Integrated Risk Information System (IRIS) database as of January 2006 and information from EPA's National Center for Environmental Assessment, Superfund Technical Support Center (STSC). For individual hazardous substances, the following changes have been made to the revised January 2006 table:

- 1-Methylnaphthalene has been deleted from the table, because the oral reference dose (RfDo) is no longer supported by STSC. The toxicity of 1-methylnaphthalene in a mixture will now be accounted for by including its measured concentration in the aromatic fraction >EC 10 to EC 12 for both oral and inhalation pathways.
- 2-Methylnaphthalene remains in the table with an oral RfD of 0.004 mg/kg-day, supported on IRIS. 2- Methylnaphthalene is to be evaluated individually for oral exposure only. There is no inhalation RfD for 2-methylnaphthalene, because STSC does not recommend a route-to-route extrapolation for this chemical. The measured concentration of 2-methylnaphthalene should be included in the aromatic >EC 10-12 fraction for purposes of evaluating inhalation exposures.
- Toluene has an oral RfD of 0.08 mg/kg-day and an inhalation RfD of 1.4 mg/kg-day, supported by IRIS.

- N-hexane has an oral RfD of 0.06 mg/kg-day and an inhalation RfD of 0.2 mg/kg-day, supported by EPA's Health Effects Assessment Summary Table and IRIS, respectively.

For purposes of documentation, I would appreciate receiving from you, in writing, verification that the information in the enclosed table accurately reflects our mutual understanding and interpretation of the current technical information regarding measures of toxicity for TPH and related hazardous substances.

Thank you for your helpful and continued technical support.

Sincerely,

Craig R. McCormack, Pharm.D.
Toxics Cleanup Program

Enclosure

Updated Reference Doses For Total Petroleum Hydrocarbon (TPH) Fractions and Individual Hazardous Substances Related to TPH - Revised January 2006				
Equivalent Carbon (EC) Chain Length For TPH Fraction	**Toxicity Surrogate Descriptive Of The TPH Fraction**	**Oral RfD (mg/kg-day)**	**Inhalation RfD (mg/kg-day) (4)**	**Documentation**
Aliphatic TPH Fractions				
Aliphatic EC 5 to EC 6	Cyclohexane (1)	1.7	1.7	EPA / IRIS
Aliphatic >EC 6 to EC 8	Cyclohexane (1)	1.7	1.7	EPA / IRIS
Aliphatic > EC 8 to EC 10	See footnote (2)	0.03	0.085	(1)
Aliphatic > EC 10 to EC 12	See footnote (2)	0.03	0.085	(1)
Aliphatic > EC 12 to EC 16	See footnote (2)	0.03	0.085	(1)
Aliphatic > EC 16 to EC 21	White Mineral Oil	2	Not Applicable (3)	(4)
Aliphatic > EC 21 to EC 36	White Mineral Oil	2	Not Applicable (3)	(4)
Aromatic TPH Fractions				
Aromatic EC 5 to EC 8	BTEX Compounds, Toxicity Assessed Individually (5)	See individual chemical below	See individual chemical below	EPA / IRIS
Aromatic > EC 8 to EC 10	Isopropyl benzene (Cumene)	0.1	0.114	EPA / IRIS
Aromatic > EC 10 to EC 12	Naphthalene	0.02	0.00086	EPA / IRIS
Aromatic > EC 12 to EC 16	1,1 - Biphenyl	0.05	0.05 (6)	EPA / IRIS
Aromatic > EC 16 to EC 21	Pyrene	0.03	Not Applicable (2)	EPA / IRIS
Aromatic > EC 21 to EC36	Fluoranthene	0.04	Not Applicable (2)	EPA / IRIS
Reference Doses For Individual Chemicals With Noncancer Toxicities That May Be Associated with TPH*				
Chemical	**Toxicity Surrogate Descriptive Of The TPH Fraction**	**Oral RfD (mg/kg-day)**	**Inhalation RfD (mg/kg-day) (7)**	**Documentation**
2- methylnaphthalene	No Surrogate Necessary	0.004	Include in Aromatic > EC 10- EC 12	EPA/IRIS, (8,9)
Benzene	No Surrogate Necessary	0.004	0.00855	EPA/IRIS
Ethylbenzene	No Surrogate Necessary	0.1	0.286	EPA/IRIS
Toluene	No Surrogate Necessary	0.08	1.4	EPA/IRIS
Xylene(s)	No Surrogate Necessary	0.2	0.029	EPA/IRIS
Styrene	No Surrogate Necessary	0.2	0.285	EPA/IRIS
1,2-dibromoethane	No Surrogate Necessary	0.009	0.00257	EPA/IRIS
n-hexane	No Surrogate Necessary	0.06	0.2	EPA/HEAST, IRIS
Methyl-tert-butyl-ether	No Surrogate Necessary	None	0.857	EPA/IRIS

(1) Where n-hexane is quantitatively analyzed for as an individual chemical, use cyclohexane as the toxicity surrogate for the aliphatic EC 5 to EC 8 fraction, and assess n-hexane based on its own toxicity; if n-hexane is not quantitatively analyzed for as an individual chemical, use n-hexane toxicity as the toxicity surrogate for the entire fraction.

(2) The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) and EPA/NCEA PPRTV Derivation Support Document for Total Petroleum Hydrocarbons (SRC SF 01-031/10-16-2002). The oral reference dose (RfD) for the aliphatic fractions > EC 8 to EC 16 is based on TPHCWG's analysis of a mixture of alkanes and JP-8 fuel, plus a safety factor of 3 as recommended by NCEA/EPA. The inhalation RfD is based on the ATSDR chronic inhalation minimum risk level (MRL), as recommended by NCEA/EPA.

(3) Not Applicable due to non-volatility

(4) TPHCWG recommendation based on feeding studies of white mineral oils and EPA/NCEA PPRTV Derivation Support Document for Total Petroleum Hydrocarbons (SRC SF 01-031/10-16-2002).

(5) BTEX: **B**enzene; **T**oluene; **E**thylbenzene; **X**ylene(s); IRIS: **I**ntegrated **R**isk **I**nformation **S**ystem developed by U.S Environmental Protection Agency

(6) The inhalation RfD for 1, 1 - biphenyl is a direct extrapolation from the oral RfD.

(7) Derivation of inhalation RfDs from inhalation reference concentrations (RfCs) are based on the following: RfDi mg/(kg-day) = RfC (mg/m^3) X 20 m^3/ day X 1/ 70 kg, where 20 m3/day is the assumed adult inhalation rate, and 70 kg is the assumed adult body weight

(8) 2-Methylnaphthalene is included in the aromatic >EC 10 to EC 12 fraction when evaluating its hazards from inhalation exposure. 2-Methylnaphthalene does not have an inhalation RfD because STSC does not recommend route to route extrapolation from the oral RfD for this chemical. Use the oral RfD (0.004 mg/kg-day) for 2-methylnaphthalene when evaluating its hazards from the oral route of exposure, and subtract it from the aromatic >EC 10 to EC 12 fraction.

* The information provided in this table is for TPH-related chemicals with reference doses. As has been the case in the past, TPH-related chemicals with cancer potency factors only, or cancer potency factors in addition to reference doses, must be evaluated independently for purposes of estimating risks and calculating cleanup levels. In addition to benzene, these may include the following chemicals, if required to be analyzed, pursuant to Table 830-1 in MTCA: 1,2-dibromoethane, 1,2-dichloroethane, carcinogenic PAHs and PCBs. In addition, lead, which has neither a reference dose nor a cancer potency factor, must be evaluated based on prevention of unacceptable blood lead levels, when it is a potential contaminant at TPH sites.