Calculation of Aquatic Biota Toxicity Reference Values (TRVs) for Petroleum Alkanes, Alkenes, Cycloalkanes, BTEX and PAH Compounds

Total Petroleum Hydrocarbon (TPH) Mixture TRV Derivation

We are unaware of any promulgated ecological screening level toxicity reference values (TRVs) for total petroleum hydrocarbon mixtures. The only efforts to date to derive TPH TRVs (Michelsen 1997, URS 1996c, Golder Associates 1995) have all utilized a tissue residue approach. These three efforts, performed originally for sites in Washington, Alaska and British Columbia, respectively, have more similarities than differences in their methodologies. All are limited to some extent by the amount of residue-effects literature for individual components of TPH mixtures, and by publicly available petroleum mixture toxicity data in the scientific literature.

The tissue residue approach starts with a critical body residue of a toxicant, then in essence runs a bioaccumulation model backwards to calculate the maximum chemical concentration in water or sediment which does not result in exceedance of the critical body residue (CBR). These maximum media concentrations which do not result in exceedance of a CBR are the TRVs used to evaluate ecological risks from media concentrations of TPH mixtures.

The original derivation of ecological TRVs for TPH mixtures was based on State of Alaska definitions of three TPH fractions: gasoline range organics (alkanes, alkenes, cycloalkanes and BTEX with a carbon chain length between C_6 and C_{10}), diesel range organics (C_{10} to C_{25}) and residual range organics ($>C_{25}$). Most of this discussion is based on the Alaska defined TPH fractions.

A strength of the TRV derivation methodology discussed in this paper is that the procedure is adaptable to any number of defined TPH fractions. TRVs will also be derived herein for State of Oregon's 12 defined TPH fractions, seven of which are aliphatic fractions (C_5 to C_6, C_6 to C_8, C_8 to C_{10}, C_{10} to C_{12}, C_{12} to C_{16}, C_{16} to C_{21}, and C_{21} to C_{34}), five of which are aromatic fractions (C_8 to C_{10}, C_{10} to C_{12}, C_{12} to C_{16}, C_{16} to C_{21}, and C_{21} to C_{34}).

Petroleum alkanes, alkenes and cycloalkanes are considered to elicit their toxicity to aquatic life by a mode of toxic action termed narcosis (CONCAWE 2001, Schultz 1997, Snyder 1987). Many aromatic compounds in petroleum, such as the BTEX chemicals, also elicit toxicity to aquatic life via narcosis. Short-term PAH toxicity to many aquatic species, particularly invertebrates with poor metabolic transformation capabilities for organic chemicals, is also due to narcotic toxicity (DiToro et al. 2000). Narcotic chemicals do not have a specific site or organ in the body where they elicit their toxicity. Instead, they are believed to elicit their toxic effects after dissolution of the chemical in the lipid layer of membranes, resulting in an increased volume fraction of the chemical in tissue and disruption of cellular function (Franks and Lieb 1978). Symptoms of narcotic toxicity include decreased nervous system activity, lethargy, loss of equilibrium and ultimately death. Narcotic toxicity is reversible if the environmental concentration of the chemical is reduced below that required to elicit toxicity. Narcosis is perhaps better known as the mode of toxic action of anaesthetics used in medicine.

As is the case with nearly all chemicals, narcotic chemicals must first be accumulated in the tissues of an aquatic species to a concentration which elicits the toxic response. Toxicity does not occur until the chemical concentration in tissues exceeds a critical body residue. Critical body residues in a number of aquatic species for a number of narcotic chemicals have been measured. These studies (summarized in McCarty and Mackay 1993, Van Wezel and Opperhuizen 1995, Escher and Hermens 2002) have observed that when expressed on a molar concentration basis, the critical body residue of narcotic chemicals associated with mortality is constant within a narrow range centered on 2 - 8 millimoles per kilogram (mmol/kg) whole body, wet weight. Limited information is available regarding narcotic chemical residues associated with chronic toxicity, defined here as any adverse effect other than mortality. What information is available indicates that chronic narcotic toxicity begins to occur at tissue residues approximately an order of magnitude lower (0.2 - 0.8 mmol/kg) than the lethal body burden of 2 - 8 mmol/kg. A database of tissue residues associated with adverse toxic effects in aquatic biota (Bridges and Lutz 1999, Shephard 1998) contains some information on petroleum alkane residues associated with toxicity. The data indicates that alkane toxicity begins to occur at around 0.24 mmol/kg, within the range of critical body residues predicted to be associated with chronic toxicity. Table 6 provides a summary of the residue-effects literature for alkanes and BTEX chemicals in aquatic biota.

Narcotic toxicity is often referred to as "baseline toxicity", as narcosis corresponds to the minimal level of toxicity exerted by any chemical. Chemicals with specific modes of toxic action are more toxic (i.e. require lower body burdens to elicit toxicity) than would be expected on the basis of narcotic toxicity.

The toxicity of mixtures of narcotic chemicals has been found to be strictly concentration additive (Deneer et al. 1988, Hermens et al. 1984), implying that the composition of a mixture of narcotic chemicals causing toxicity is not important. Toxicity from a mixture of narcotic chemicals, such as petroleum alkanes, alkenes and cycloalkanes occurs when the sum of individual chemical molar concentrations of the mixture in tissue exceeds the critical body residue. This additivity of individual narcotic chemical toxicity is what permits derivation of TRVs for petroleum alkane mixtures, all of whose individual components elicit their toxicity via narcosis.

Starting with a critical body residue of petroleum alkanes (0.24 mmol/kg) believed to be a threshold for chronic toxicity, a one compartment first order kinetic (1CFOK) toxicological model (Shephard 1998) has been used to predict the concentration of alkanes in water required for an aquatic animal to bioconcentrate the critical body residue of 0.24 mmol/kg. The approach is based on the concentration of freely dissolved chemical in water. The differential equation form of the 1CFOK model used to calculate waterborne chemical concentrations of alkanes that will result in bioconcentration of 0.24 mmol/kg petroleum alkanes is given in Equation 1.

Equation 1:

$$\frac{dC_a}{dt} = (k_u \times C_W) - (k_e \times C_a)$$

where: C_a = chemical concentration in an animal (mg/kg)
t = time (hours)
C_W = chemical concentration in water (mg/L)
k_u = chemical uptake rate constant (L/kg/hour)
k_e = chemical elimination rate constant (hour^{-1})

If the chemical concentration in water is assumed to be constant, Equation 1 may be exactly integrated to yield Equation 2.

Equation 2:

$$C_a = C_w \times \frac{k_u}{k_e} \times (1 - e^{-k_e t}) + (C_{a(t=0)} e^{-k_e t})$$

where all terms are defined as per Equation 1. For an animal being modeled, which has not been exposed to a chemical at the start of an experiment, $C_{a(t=0)}$ equals zero, and the last term of Equation 2 drops out of the integrated form of the 1CFOK model. If it is assumed that the animal has been exposed to the chemical in water for a sufficiently long period to establish steady state between the chemical concentration in the animal and the water, Equation 2 reduces to Equation 3.

Equation 3:

$$C_a = C_w \times \frac{k_u}{k_e}$$

The term k_u / k_e in Equation 3 is the bioconcentration factor (BCF) of the chemical into the animal from the water, and has units of L/kg. If the animal accumulated its body burden of alkanes from multiple sources (e.g. water and diet), the term k_u / k_e becomes a bioaccumulation factor. Alkane bioaccumulation factors (Chapman and Connell 1986) for a benthic deposit feeding gastropod (*Strombus luhuanus*) were used to derive ecological TRV's for petroleum alkanes in sediment. For water, reexpressing k_u / k_e as a BCF and rearranging Equation 3 to solve for C_w yields Equation 4, which is the equation used to calculate the ecological TRV for alkanes/cycloalkanes in water.

Equation 4:

$$C_w = \frac{C_a}{BCF}$$

Bioconcentration factors for petroleum alkanes were derived from the logarithm of the octanol-water partition coefficient (log K_{OW}) of individual petroleum compounds. For TRVs which encompass a range of alkane carbon chain lengths, a log K_{OW} for the compound at the center of the range was chosen. Bioconcentration factors and log K_{OW} were related to each other using Equation 5, the regression equation used by U.S. EPA in the derivation of national ambient water quality criteria (U.S. EPA 1980).

Equation 5:

$$\log BCF = (0.85 \times \log K_{ow}) - 0.70$$

Compilations of log K_{OW} values for alkanes, particularly the longer carbon chain length alkanes are not readily available. Alkane log K_{OW} values were derived by combining available information from U.S. EPA and the Alaska Department of Environmental Conservation (ADEC). The derivation of the K_{ow} values for the various alkane/cycloalkane size classes starts with Equation 6, which is the regression used by the U.S. Environmental Protection Agency (1993) to convert K_{ow} values to the organic carbon-water partition coefficient (K_{OC}) needed to derive sediment quality criteria for hydrophobic organic chemicals.

Equation 6:

$$\log K_{OC} = 0.00028 + (0.983 \times \log K_{ow})$$

Where: K_{OC} = organic carbon - water partition coefficient

The State of Alaska (ADEC 1996) has derived Equation 7, which relates K_{OC} and carbon chain length for petroleum alkanes.

Equation 7:

$$\log K_{OC} = (0.45 \times N_C) + 0.43$$

Where: N_C = number of carbons in the alkane (i.e. N_C = 8 for octane)

Substituting Equation 7 into Equation 6 and solving for log K_{OW} yields Equation 8, which was used to derive log K_{OW} values for determination of bioconcentration factors (Equation 5).

Equation 8:

$$\log K_{OW} = \frac{(0.45 \times N_C) + 0.43}{0.983} - 0.00028$$

Results of the TRV calculations (Equation 5) are presented in Table 7.

Some of the petroleum alkane TRVs (Table 7) at first glance appear to represent low concentrations in water. As stated earlier, the toxicological model used to derive the TRVs is based on freely dissolved chemical concentrations in water. Chemicals associated with suspended particulates are not available for uptake by biota in the model used. To compare the predicted TRVs to the maximum water solubility of the alkane fraction, Equation 9 (ADEC 1996) was used to estimate water solubility of petroleum alkanes.

Equation 9:

$$\log S = 4.5 - (0.55 \times N_C)$$

Where: S = water solubility, mg/L

Finally, if it is desired to obtain a single TRV for two or more fractions measured in an environmental mixture, knowledge of the weight percent of the total composition of the environmental mixture each individual fraction constitutes can be used with Equation 10 to generate a TRV for multiple fractions.

Equation 10:

Using a no adverse effect tissue residue of 0.24 mmol/kg, the narcosis model predicts that alkanes with a carbon chain length greater than $C_{16\text{-}17}$ (the actual chain length at which this occurs varies with the value of the octanol-water partition coefficient and the log K_{OW} – log BCF regression selected as starting points for the calculations) would have to exceed their maximum water solubility before any chronic toxicity could be elicited. As the narcotic toxicological model is based on the concentration of freely dissolved alkanes, the approach used to derive ecological TRV's does not apply for alkanes with carbon chain lengths greater than $C_{16\text{-}17}$. Toxicity of the heavier alkanes to aquatic life in the water column requires a supersaturated solution (in essence, an oil sheen, slick or spill) before toxicity would be observed.

In supersaturated solutions, toxicity is more likely to occur from physical toxicity or changes in the environment, such as suffocation or habitat degradation. These processes do not result from narcosis, thus, narcosis is not predicted to be the toxic mode of action to aquatic biota for alkanes in surface water with a carbon chain length greater than $C_{16\text{-}17}$. Surface water TRV's therefore have not been calculated for alkane fractions heavier than C_{16}, and for aromatic fractions in Oregon with more than 12 carbons, as the narcotic mode of toxic action is not responsible for any observed adverse effects of alkanes heavier than C_{16} or aromatics heavier than C_{12}. Any detected concentrations of diesel range or residual range alkanes in surface waters which are greater than their maximum water solubility are assumed to represent either material surface adsorbed on particulate matter, which should have limited bioavailability and toxicity to aquatic life, or represent free product, which may pose unacceptable risks to aquatic biota. As the available analytical data do not permit a distinction between particulate sorbed and free product alkanes, any detected diesel range or residual range organics at concentrations in excess of their maximum solubility are assumed to pose potential risks to ecological receptors. Unfortunately, the potential for these toxicological risks cannot be quantified given the current state of the art. The potential for risks from supersaturated solutions of diesel range and residual range organics will be discussed in the uncertainty section of the risk assessment.

Additional details of the procedures used to derive TRVs for petroleum alkane mixtures are provided in Shephard and Webb (1998) and Shephard and McCarty (1997). Although the literature on water and sediment concentrations of petroleum alkanes associated with toxicity to aquatic life is limited, the existing data support the TRV derivation methodology used in this risk assessment. Additional support for the utility of the basic approach of this TRV development approach is found in Dyer et al. (2000), who found that TRVs, although not specifically petroleum alkane TRVs, derived by the methodology described herein overpredict adverse effects to field populations of fish. In the initial stages of risk assessment, overprediction of toxicity (i.e. a conservative risk assessment) is generally desired.

Some experimental data are available that illustrates the acute toxicity of gasoline mixtures to aquatic species. Methodological difficulties occur when testing the aquatic toxicity of sparingly soluble and volatile chemical mixtures such as petroleum hydrocarbons. These include the preparation of testing solutions, and maintaining constant concentrations of the test material during the performance of bioassays. The common adage “oil and water don’t mix” is a crude but accurate description of the difficulties in preparing test solutions of petroleum mixtures for use in toxicity testing. A chemically more accurate description of the problem is “oil is sparingly soluble in water”. Attempting to mix oil and water often results in a two phase system. A number of approaches have been historically used to prepare media for toxicity testing of petroleum mixtures, including testing of the two phase system, suspensions of petroleum maintained in solution by addition of carrier solvents, studies of water extracts of petroleum added at high mass loading rates (water soluble fraction), and removal of the water insoluble phase followed by testing of the water phase (water accommodated fraction). Open static and flow through exposure systems both permit volatilization of some petroleum fractions, making it difficult to maintain constant exposure concentrations and composition of the petroleum mixture.

Current recommendations for testing the toxicity of petroleum mixtures (CONCAWE 2001, OECD 2000) call for the use of water accommodated fraction extracts in closed systems with no head space, and under flow through or renewal conditions. Acute toxicity studies of water accommodated fractions in sealed containers with no head space evaluating mortality of aquatic species have been summarized by CONCAWE (2001).

Results from 7 species found mortality occurring at 2 – 27 mg/L (median 5.9 mg/L). Using the tissue residue approach described in this measures of effects section, the acute toxicity of gasoline, using octane (C_8H_{18}) as the surrogate alkane for the gasoline mixture results in an estimated acute toxicity range between 0.95 – 3.8 mg/L, within the lower end of the measured gasoline toxicity range. This estimate uses an estimate critical body residue of 2 – 8 mmol/kg for octane, with a molecular weight of 114.

An earlier CONCAWE (1992) literature review, evaluating gasoline toxicity of the water soluble fraction in closed containers with no head space, found the acute toxicity range for ten aquatic species to be 0.3 – 8.3 mg/L gasoline (median 3.0 mg/L). The median gasoline LC_{50} from the CONCAWE (1992) review falls within the estimated range of gasoline toxicity using the tissue residue approach in this measures of effects section. Neither CONCAWE (2001, 1992) study reports information on the chronic toxicity of gasoline. However, a literature review of non-closed system toxicity tests with TPH mixtures by Tsvetnenko (1998) identified one study (Carr and Reish 1977) that reported chronic NOEC values for reproduction of a No. 2 fuel oil on the polychaetes *Ctenodrilus serratus* and *Ophryotrocha sp*. of 0.397 and 0.301 mg/L, respectively. These chronic NOECs are 3-4 times higher than the calculated gasoline TRVs of 0.114 and 0.101 mg/L for use in Alaska and Oregon, respectively. The accuracy of the acute toxicity estimates of gasoline using the procedures in this section provide support for the use of the derived chronic LOEC TRV for gasoline.

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Table 2. Calculation of ecological toxicity reference values (TRV's) for petroleum components in water and sediment using a no effect tissue residue approach TRV development methodology.

Chemical	Surrogate Compound	Molecular Weight	Surrogate Carbon Content	BCF(a)	log BCF	log Koc(b)	log Kow(c)	---------- Toxic tissue residues ----------				Estimated maximum water solubility (µg/L)	Water TRV(f, i) µg/L	Sediment TRV mg/kg(g, j)	Sediment TRV mg/kg OC(h)
								Acute mmol/kg(d)	LOER(e) mmol/kg	Acute mg/kg	LOER mg/kg				
Alaska ecological TPH TRV's															
C_6 - C_{10} (Alaska gasoline range organics)	n-Octane	114	8	240	2.38	4.03	4.10	2	0.24	228	27.4	1259	114	12.2	1219
C_{10} - C_{25} (Alaska diesel range organics)	n-Heptadecane	240	17	764072	5.88	8.08	8.22	2	0.24	480	57.6	0.014	0.014	90.6	9063
C_{25} - C_{36} (Alaska residual range organics)	n-Hentriacontane	437	31	2.1E+11	11.33	14.38	14.63	2	0.24	874	104.9	2.8E-10	NA	1175	117476
Aliphatics (Oregon definitions)															
C_5 - C_6	n-Hexane	86.17	6	161	2.21	3.23	3.29	2	0.24	172	20.7	15849	128	2.20	220
C_6 - C_8	n-Heptane	100.203	7	447	2.65	3.72	3.78	2	0.24	200	24.0	4467	54	2.80	280
C_8 - C_{10}	n-Nonane	128.257	9	3256	3.51	4.68	4.76	2	0.24	257	30.8	355	9.5	4.52	452
C_{10} - C_{12}	n-Undecane	156.31	11	14624	4.17	5.64	5.74	2	0.24	313	37.5	28	2.6	11.3	1127
C_{12} - C_{16}	n-Tetradecane	198.4	14	4292	3.63	7.10	7.22	2	0.24	397	47.6	0.63	NA	1389	138874
C_{16} - C_{21}	n-Octadecane	254.5	18	41	1.62	9.02	9.18	2	0.24	509	61.1	0.0040	NA	NC	NC
C_{21} - C_{34}	n-Heptacosane	380.75	27	0.00081	-3.09	13.37	13.60	2	0.24	762	91.4	0.000000045	NA	NC	NC
Aromatics (Oregon definitions)															
C_8 - C_{10}	Ethylbenzene	106.2	8	120	2.08	3.10	3.15	2	0.24	212	25.5	1259	212	2.65	265
C_{10} - C_{12}	2-Methylnaphthalene	142.19	11	395	2.60	3.66	3.72	2	0.24	284	34.1	28	NA	3.93	393
C_{12} - C_{16}	Phenanthrene	178.24	14	1803	3.26	4.38	4.46	2	0.24	356	42.8	0.63	NA	5.75	575
C_{16} - C_{21}	Chrysene	228.3	18	12864	4.11	5.51	5.61	2	0.24	457	54.8	0.0040	NA	13.9	1394
C_{21} - C_{34}	Coronene	300.36	24	3783	3.58	7.16	7.28	2	0.24	601	72.1	0.0000020	NA	2732	273241

a - BCF is the bioconcentration factor, the ratio between a chemical concentration in tissue and water, L/kg
b - Koc = organic carbon-water partition coefficient
c - Kow = octanol-water partition coefficient
d - mmol/kg = millimoles/kilogram
e - LOER = Lowest Observed Effect Residue
f - TRV = Toxicity Reference Value
g - Bulk sediment TRV's in this column based on an assumed 1% organic carbon content of sediment
h - mg/kg OC = mg chemical/kg organic carbon in sediment
i - NA = Not Applicable, TRV would have to exceed maximum water solubility of these fractions
j - NC = Not Calculable, calculated TRV exceeds 100% pure surrogate compound