Appendix 4B
Basis for total petroleum hydrocarbon (TPH) criteria protective of human health

Hydrocarbon fuels of interest in the context of petroleum contaminated sites are generally complex mixtures of compounds, including alkanes, alkenes and a range of aromatic compounds. Analysis of soil and groundwater samples for total petroleum hydrocarbons (TPH) parameter measures the total concentration of all petroleum related hydrocarbons, expressing the results in terms of the concentration of hydrocarbon compounds within various carbon ranges, e.g. C6 to C9. The TPH parameter is a useful indicator of hydrocarbon contamination, but it is of limited use in the assessment of health risk, but as it refers to the concentration of a complex mixture of compounds which do not exhibit toxicological or fate and transport properties.

The health risk associated with exposure to petroleum hydrocarbons may be considered to consist of the risk associated with a number of well defined compounds of known and significant toxicity (e.g. benzene and other monocyclic aromatic hydrocarbons, and PAHs, such as benzo(a)pyrene) and a much larger number of less well defined, generally less toxic compounds.

Acknowledging the variability in the criteria nominated for TPH in the United States, the TPH Criteria Working Group (TPHCWG) was established to develop a technically defensible approach to the development of soil clean-up levels for TPH that are protective of human health. The TPHCWG includes representatives from academia, industry (e.g. Shell, Exxon, Chevron, API, Association of American Railroads) and government (e.g. USEPA and some state regulators, Department of Defense).

The TPHCWG have developed an approach for the derivation of health based soil clean-up levels based on normal procedures for the derivation of such values. In order to facilitate this TPHCWG have assigned representative toxicological and fate and transport properties to each of the fractions. The representative properties give consideration to the range of properties exhibited by the chemicals comprising the fraction considered.

The work of the TPHCWG is reaching a final draft stage. Volume 3 *Selection of Representative TPH Fractions Based on Fate and Transport Considerations* was released as a final draft in February 1997. Volume 4, which will address the representative toxicological issues is due to be released as a final draft shortly.

In 1994, the Massachusetts Department of Environmental Protection (MDEP) adopted a similar approach in *Interim Final Petroleum Report: Development of Health-based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter*. The MDEP considered the information available regarding the toxicity and fate and transport of whole products (e.g. unleaded gasoline) and individual key components (e.g. benzene). The MDEP adopted an approach based on developing specific acceptance criteria for the contaminants of primary concern (e.g. benzene, benzo(a)pyrene) and the development of acceptance criteria based on indicator chemicals for each of the TPH fractions considered. A key difference between the MDEP and TPHCWG approaches is that the MDEP assigned a surrogate chemical to each of the fractions considered and then assessed each fraction as it if were comprised entirely of the surrogate compound, e.g. the C6 to C9 fraction was assessed as if it was all n-hexane. In practice, this approach is conservative as the C7 to C9

compounds are less toxic than n-hexane. The TPHCWG approach therefore has the advantage of considering the properties of each of the range of chemicals included in each fraction.

The TPHCWG split the range of petroleum hydrocarbons into six fractions, considering separately the aromatic and aliphatic components of each as follows:

- C6 to C8 (or C7 to C8 for aromatics)
- C9 to C11
- C11 to C12
- C13 to C16
- C17 to C21
- C22 to C34

The distinction between aromatic and aliphatic compounds in the TPH fractions has been dropped for the purposes of these guidelines as the aromatic component will be addressed separately by direct measurement of BTEX and PAH concentrations, and because the analytical technique proposed for New Zealand will not distinguish between aromatics and aliphatics. Therefore the criteria developed for New Zealand using this approach apply principally to the aliphatic component.

In considering toxicological properties the TPHCWG considered only three fractions, as follows (due to the inability of the toxicological data to achieve a greater level of resolution):

- C6 to C8
- C9 to C16
- C17 to C34

In integrating this approach proposed by the TPHCWG and the standard analytical method technique being developed on behalf of the OIEWG for use in New Zealand, Tier 1 soil and groundwater acceptance criteria have been developed on the basis of the following fractions:

- C7 to C9
- C10 to C14
- C15 to C36

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

The toxicological and fate and transport properties assumed for each of the fractions are summarised in Tables 4B1 and 4B2.

Table 4B1 Adopted toxicological properties for TPH

Fraction	C7 - C9	C10 - C14	C15 - C36
Oral reference dose (mg/kg/d)	5.0	0.1	1.5
Inhalation reference Dose (mg/kg/d)	5.0	0.3	1.5

Table 4B2 Adopted fate and transport properties for TPH

Fraction	C7 - C9	C10 - C14	C15 - C36
Molecular weight (g/mol)	120	185	245
Solubility (mg/L)	3.3	4.3×10^{-3}	2.3×10^{-5}
Vapour pressure (atm)	2.2×10^{-2}	1.7×10^{-4}	6.5×10^{-6}
Henry Coefficient (c/c)	120	160	135
log Koc	4.0	6.1	8.7
log Kow	5.2	7.6	9.3
Dair (cm^2/s)	6.0×10^{-2}	4.2×10^{-2}	3.3×10^{-2}
Dwat (cm^2/s)	7.1×10^{-6}	4.8×10^{-6}	3.8×10^{-6}