Canadian Council of Ministers of the Environment

Canada-Wide Standards for Petroleum Hydrocarbons (PHCs) in Soil: Scientific Rationale

Supporting Technical Document

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Executive Summary

1.1 Synopsis

The Canada-Wide Standard for Petroleum Hydrocarbons in Soil (PHC CWS) was developed by the Canadian Council of Ministers of the Environment (CCME) under the Harmonization Sub-Agreement on Standards. The PHC CWS is a 3-tiered remedial standard for soil and subsoil protective of human and environmental health under four generic land uses – agriculture, residential/parkland, commercial and industrial. The purpose of this document is to provide an overview of the land use-based framework for the PHC CWS and the detailed scientific rationale in support of the derivation of the Tier 1 values. These values form the numerical basis of the PHC CWS and reflect the risk management and environmental quality goals of the standard as determined by CCME in consideration of scientific, technical and socio-economic factors and the substantive input of stakeholders.

1.2 Background

Petroleum hydrocarbons (PHC) describe a mixture of organic compounds found in or derived from geological substances such as oil, bitumen and coal. Petroleum products released to the environment, such as gasoline, crude oil and jet fuel, typically contain hundreds to thousands of compounds in varying proportions.

PHCs in the environment are a concern for a number of reasons. First, their reduced nature and volatility pose a fire/explosion hazard. Second, most PHC constituents are toxic to some degree. Third, lighter hydrocarbons are mobile and can be a problem at considerable distances from their point of release due to transport in ground, water or air. Fourth, larger and branched chain hydrocarbons are persistent in the environment. Fifth, PHCs may create aesthetic problems such as offensive odour, taste or appearance in environmental media. Finally, under some conditions PHCs can degrade soil quality by interfering with water retention and transmission, and with nutrient supplies.

Because PHC composition at a release site is a function of the source (e.g., gasoline vs. crude oil), site factors (e.g., soil texture, climate), time since release, and management, the effects noted above occur to varying degrees. Knowledge of the distribution and abundance of PHC types is necessary for accurate assessment and management response. However, most Canadian regulatory approaches and guidelines in the late 1990s did not consistently address this assessment requirement and also differed widely in other important ways, including the analytical methods required or accepted, scientific basis for assessment, and risk management objectives. This meant that PHC contaminated sites were not consistently evaluated and managed and that results were reported in a widely differing array of parameters and formats.

This condition is unsatisfactory and made more serious by the scope of the PHC problem. Throughout Canada, many tens of thousands of PHC release sites exist, and environmental liabilities have been estimated in the 10 billion $Can. range. Consistent, science-based assessment tools are needed to protect the environment and control costs. The PHC CWS was developed to address this need.

1.3 Framework for PHC CWS

The PHC CWS framework is based on a synthesis of the ASTM (1995) and CCME (1996) frameworks for the assessment and management of contaminated sites, and incorporates at successive tiers: (1) the application of generic (national) Tier 1 levels that are protective of human health and the environment, (2) site-specific adjustments to the Tier 1 levels to calculate Tier 2 levels that accommodate unique site characteristics, and (3) Tier 3 levels that are developed from a site-specific ecological or human health risk assessment, when assumptions inherent in the Tier 1 values are not appropriate for a site. The level of protection afforded, and the associated underlying guiding principles, are preserved throughout this tiered process. The tiered approach essentially represents increasing levels of precision in a site assessment through consideration of more specific site characteristics. Details on the phased acquisition of site information to support a sound PHC management decision are presented in a separate User Guidance document.

1.4 Approach to Development of Tier 1 Levels

The PHC CWS Tier 1 levels were developed using risk assessment and risk management techniques. In this approach, the primary environmental and human health values to be protected are identified, an analysis of how these values could be affected by PHC contamination is undertaken, and benchmark concentrations or levels of PHC in soil are calculated to provide an environmentally acceptable endpoint. The primary task is to develop an exposure scenario for each land use that adequately captures the receptors of concern and the pathways by which these can be exposed by PHC contamination in soil or subsoil. A summary of the receptor/pathway combinations addressed under each land use in the PHC CWS is presented in Table E1. Each combination is discussed further in the appropriate section of this Technical Supplement.

Tabular Tier 1 levels (see Chapter 5) are calculated for pathway/receptor combinations wherever the pathway is deemed applicable and sufficient data are available to support the derivation.

Table E1: Land-uses, key receptors and exposure pathways.

Exposure Pathway	Agriculture	Residential/ Parkland	Commercial	Industrial
Soil Contact	Nutrient cycling Soil invertebrates Crops (plants) Human (child)	Nutrient cycling Invertebrates Plants Human (child)	Nutrient cycling Invertebrates Plants Human (child)	Nutrient cycling Invertebrates Plants Human (adult)
Soil Ingestion	Herbivores Human (child)	(wildlife)* Human (child)	(wildlife)* Human (child)	(wildlife)* Human (adult)
Groundwater/ Surface Water	Aquatic Life/ Livestock Watering Human (child)	Aquatic Life Human (child)	Aquatic Life Human (child)	Aquatic Life Human (adult)
Vapour Inhalation (humans only)	Child, indoor**	Child, indoor	Child, indoor	Adult, indoor
Produce, meat and milk produced on site (humans only)	Child	Child (produce only)		
Off-site migration of Soil/Dust				Human/Eco

* wildlife dermal contact and ingestion data may be particularly important for PHCs (e.g., oiling of feathers, etc., although this should be addressed with an initial assessment of the presence of non-aqueous phase liquids - NAPL), but there are unlikely to be sufficient data to develop guidelines that address this exposure pathway

** a 30m horizontal offset is assumed between the farm residence and the PHC contamination, consistent with oil and gas development practices. Contamination nearer a farm residence triggers a residential assessment.

To address the diversity of PHC contamination types, including various crudes and product admixtures, PHCs are considered in four broad physico-chemical fractions synthesized from the sub-fractions defined by the US Total Petroleum Hydrocarbons Criteria Working Group. The fractions are defined in equivalent carbon numbers as follows:

F1: C6 to C10
F2: >C10 to C16
F3: >C16 to C34
F4: C34+

Aliphatic and aromatic sub-fractions are handled separately in the human health assessment.

Whereas the primary focus in PHC CWS standard development is prevention of toxic effects from F1-F4 on the receptors listed in Table E1, in certain situations these pathways may be of little immediate concern and PHC management is governed by other factors including:

- ignition hazard
- odour and appearance
- effects on buried infrastructure

- formation of non-aqueous phase liquids (NAPL)
- socio-economics and technological capabilities

Such factors are considered at the Tier 1 level in the integration phase, described below.

1.5 Human Health Protection

Inadvertent ingestion of soil can be a significant pathway of human exposure to contaminated soil. Studies indicate that children ingest much greater amounts of soil and dust each day than adults, primarily due to greater hand-to-mouth activity and a greater time spent playing outdoors and on the floor. In the PHC CWS children were assumed to ingest four times the amount of soil as an adult. Tier 1 levels were calculated using an algorithm common to both CCME (1996) and Atlantic PIRI (1999).

Dermal absorption of soil-borne PHC is addressed through the algorithm presented in Atlantic PIRI (1999). In no case was this pathway found to govern remedial response at the Tier 1 level.

Ingestion of cross-contaminated groundwater is addressed through use of a simple leaching/dilution model common to CCME (1996) and Atlantic PIRI (1999). It is conservatively assumed that the PHC contamination is underlain by an unconfined aquifer and that a potable well is located at the downgradient boundary of the site. At the Tier 1 level, this pathway, where applicable, would govern remedial response for F1 and F2 on sites with fine-textured soils, and F2 only on coarse-textured soils.

Migration of soil PHC vapours through cracks and imperfections in building foundations can lead to human inhalation exposure. This pathway is assessed through application of the vapour intrusion model of Johnson and Ettinger (1991), restricting transport to diffusion only in fine-textured soils and including advection in coarse soils. The vapour inhalation pathway governs remedial response at the Tier 1 level for F1 on coarse-textured sites.

1.6 Ecological Health Protection

Tier 1 levels are derived to protect key ecological receptors that sustain normal activities on the four previously defined land use categories: agricultural, residential/parkland, commercial and industrial. The derivation of Tier I levels for ecological receptors focuses on the effects of PHCs on the biotic component of a terrestrial ecosystem. Specifically, it evaluates the potential for adverse effects to occur from exposures to soil-based PHCs at point-of-contact or by indirect means (e.g., soil to groundwater pathways, food chain transfer).

Chronic, sub-chronic, acute and lethal responses of plants and invertebrates relevant to the sustainable functioning of soil under the four land uses are used to derive Tier 1 levels. A “weight of evidence” approach is used to arbitrate among the

various data sources. The direct soil contact pathway governs remedial response at the Tier 1 level for F3 and F4 under all land uses.

Concentrations of PHC in soil that would not be expected to pose a threat to aquatic life in nearby streams, rivers and lakes is estimated by modeling transport from soil through groundwater to a default discharge point 10 m downgradient from the PHC contaminated site. A dynamic, advective-dispersive model incorporating first-order biodegradation in the saturated zone (Domenico and Robbins 1984 as adapted by BC Environment) is used for this purpose. Remedial response for F2 at the Tier 1 level is governed by the Aquatic Life Protection pathway on coarse-textured sites when the surface water body is immediately adjacent to the PHC contamination. The lateral distance may be varied in Tier 2 up to a maximum of 500 m.

1.7 Integration of Human Health and Ecological Levels

A summary of the risk-based values developed for each pathway/receptor combination in the individual land use categories is presented in Chapter 5. In addition, rationale is provided for certain risk management decisions made in the final integration of human health and ecotoxicological inputs.

The principal features added to the PHC CWS at the integration stage were:

- Adjustment of eco-contact levels with respect to soil texture; and
- Addition of generic levels for subsoils – defined as earthy materials below 1.5 m depth.

In the process of developing these features the Development Committee considered several factors that are not easily accommodated in explicit, quantitative exposure and risk estimates. These factors included:

- Capabilities of current and emerging remediation technologies;
- Likelihood of subsoil disturbance and excavation under different scenarios;
- Potential effects of PHC on buried infrastructure;
- Aesthetics;
- Role of subsoil in terrestrial ecology;
- Costs of risk reduction measures; and
- Property values and environmental stewardship.

The objective of the integration is development of environmentally protective Tier 1 levels that are practical and attainable with proven remedial technologies. Remediation and conservation of PHC-affected soils is preferred over disposal.

1.8 Analytical Method

A benchmark method for determination of PHC in soil is presented that addresses major sources of variability and uncertainty related to the extraction, purification,

quantification and reporting. F1 PHC are isolated though purge and trap procedures followed by gas chromatography with a flame ionization detector (GC-FID). F2 – F4 PHC up to C50 are extracted by a Soxhlet procedure, “cleaned up” on silica gel and determined by GC-FID. C50+ PHC, if present, may be determined gravimetrically or through extended chromatography. Specific chromatographic calibration standards are required.

The analytical method has been tested in round-robin trials and found to drastically reduce variability in results over previous round robins where analytical procedures were not controlled. Performance-based alternatives to the benchmark procedures are permitted.

1.9 Recommendations for Future Research and Development

A number of important gaps in understanding were identified through the development of the PHC CWS and these are summarized in Chapter 7. Scientific review of the PHC CWS is planned for 2003, such that the standard may be revised in 2005. Key opportunities for research in the immediate future include:

- Toxicity testing of PHC fractions on aquatic receptors;
- Biodegradation rates of volatile PHC in the vadose zone;
- Toxicity assessment of gamma-diketone forming F1 aliphatics;
- Effects of soil PHC on buried infrastructure; and
- Aqueous and vapour-phase partitioning of F1, F2 PHC in the presence of residual F3, F4 PHC.

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The Canada-Wide Standard for Petroleum Hydrocarbons in Soil came to be as a result of the cooperative efforts of a great many people. While it is not possible to acknowledge all participants, the contributions of some key individuals and groups must be noted.

George Murphy was the Alberta champion for the PHC CWS and kept the Development Committee on track and communicating effectively with the CCME parent committee. The Development Committee was co-chaired by Ted Nason and David Thornton, both of whom provided frequent after hours service to the project. The Development Committee was advised and supported by the Technical Advisory Groups. The Development Committee is deeply appreciative of the dedication and skill of the TAG chairs in facilitating discussions with stakeholders, providing sound technical advice, and vetting the ideas of the Development Committee. Doug Bright (Royal Roads University) chaired the Ecological Technical Advisory Group, Warren Kindzierski (University of Alberta) chaired the Human Health Fate and Transport Technical Advisory Group (HHFT TAG), Richard Turle (Environment Canada) chaired the Analytical Methods Technical Advisory Group, and Doug Younie (Alberta Environment) chaired the Socio-Economic Analysis Technical Advisory Group. The complete memberships of the Development Committee and Technical Advisory Groups are provided in Appendix A.

In addition to chairing the HHFT TAG through two separate phases, Warren Kindzierski also chaired the Protocol Improvement Working Group, which carried out an intensive nine-month review and development of the human health basis of the PHC CWS. Lin Callow (Gulf Canada Resources), Claude Chamberland (Shell Canada), Sharon Vervaet (NS Environment) and Ted Nason/Mike Zemanek (Alberta Environment) provided insights, data and substantial sweat equity.

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Glossary

absorption: The uptake of a chemical by a cell or an organism across biological membranes and including any transport to other tissues.

adsorption: The physical process of attracting and holding molecules of other substances or particles to the surfaces of solid bodies with which the former are in contact with.

advective flow: A process that transports a chemical from one location to another by virtue of the fact that the chemical is a component of a moving physical system (e.g. wind, flowing water, sediment transport).

aliphatic compounds: Organic compounds in which the carbon atoms exist as either straight or branched chains. Examples include pentane, n-hexane (not cyclohexane), and octane. The alkane group of aliphatics have maximum hydrogen content (saturated hydrocarbons), whereas alkenes have one or more double bond between adjacent carbon atoms. Alkynes have at least one triple bond between adjacent carbon atoms. Alkenes and alkynes are termed “unsaturated” hydrocarbons..

aromatic compounds: Contain ring structures formed from closed loops of carbon chains (most often containing six C atoms) where carbons in the ring have resonant double bonds. Aromatic compounds include compounds such as benzene, toluene, ethylbenzene, and xylene (*BTEX*), as well as polyaromatic compounds such as naphthalene. Because of the double bonding between carbon atoms, the molecules are not saturated with hydrogen atoms (un-saturated hydrocarbons).

asphaltene: Generally defined by the solution properties of petroleum residuum in various solvents. Asphaltenes are, broadly speaking, n-heptane insoluble and aromatic soluble. Structurally, asphaltenes are condensed polynuclear aromatic ring systems bearing mainly alkyl sidechains. The number of rings in oil asphaltenes can vary from 6 to 15. Tars or asphaltenes occur in many crude oils as colloidally suspended solid particles. Precipitation takes place when the crude loses it ability to keep those particles dispersed.

assessment endpoint: The characteristic of the ecological system that is the focus of the risk assessment. Formal expressions of the actual environmental value to be protected (e.g., fishable, swimmable water)

benefits: Positive changes resulting from an activity or project (e.g., increased income or productivity, reduced health risks, increased recreational opportunities).

bioaccumulation: The process by which chemical compounds are taken up by terrestrial and aquatic organisms directly from the surrounding environmental medium and/or through consuming contaminated food.

bioavailability: The amount of chemical available for uptake from environmental media to the target tissues of a receptor following exposure.

biodegradation: A microbiologically mediated process (e.g., due to the action of bacteria, yeasts, and fungi) that chemically alters the structure of a chemical,

the common result being the breakup of the chemical into smaller components (ultimately CO_2 and H_2O for aerobic biodegradation of hydrocarbons).

BTEX: Abbreviation for benzene, toluene, ethylbenzene and xylenes. These compounds are somewhat soluble, volatile and mobile in the subsurface environment and are useful indicators of contaminant migration.

Canada-wide standard (CWS): National standards that can include qualitative or quantitative standards, guidelines, objectives and criteria for the protection of the environment and human health. Included in the CWSs are numeric limits (e.g. ambient, discharge, or product standards), a commitment and timetable for attainment, a list of preliminary actions required to attain the standard and a framework for reporting to the public.

carbon-fractions: Petroleum hydrocarbons are categorized by fractions (F1 to F4) according to the equivalent normal straight-chain hydrocarbon (nC) boiling point ranges (Fraction #1: nC6 to nC10; Fraction #2: >nC10 to nC16; Fraction #3: >nC16 to nC34; and, Fraction #4: nC35+). In general, each carbon fraction contains all extractable hydrocarbon constituents which, on a DB1 *gas chromatographic column*, elute between and thus have a boiling point between the lower and higher indicated normal straight chain hydrocarbon.

clay: Soil components of equivalent diameter <0.002 mm usually consisting of clay minerals but commonly including amorphous free iron oxides, humic materials and trace quantities of primary minerals.

coarse-grained soils: Soil which contains greater than 50% by mass particles greater than 75 µm mean diameter (D_{50} > 75 µm).

conservative exposure scenario: A site conceptual model that includes receptors and pathways characteristic of a sensitive but plausible use of the land and water resources.

consumers: Organisms which require energy in the form of organic material from external food sources (heterotrophs).

costs: Negative changes resulting from an activity or project (e.g., capital and annual costs of a project, land removed from agricultural production, increased health risk, reduction of wildlife habitat).

critical receptor: The taxon, cohort, and developmental stage believed to be the most biologically sensitive among a larger target group that is potentially exposed to a contaminant (e.g. for humans, toddlers 6 months to 4 years old are often critical receptors for non-cancer causing substances).

critical threshold: The dose/concentration below which no adverse effect is expected to occur.

crude oil: Complex mixture of thousands of *petroleum hydrocarbon* and non-hydrocarbon compounds, extracted from natural deposits and prior to any distillation or other substantive refinement. Hydrocarbons comprise more than 75% of crude and refined oils, however heavy crude oils can contain more than 50% nonhydrocarbons (molecules containing oxygen, sulfur, nitrogen, or metals in addition to carbon and hydrogen). Crude oil

classification depends on specific gravity (light, medium or heavy) which can be further separated into fractions based on their boiling point.

decomposers: Organisms which derive their energy from breaking down organic matter from other deceased organisms (detritus).

downstream industry: *Petroleum hydrocarbon* industry sectors which are responsible for the marketing, sales, and re-distribution of a wide variety of end products and intermediates derived from refining crude oil. (e.g. petroleum retailers, refuelling stations such as airports, shipping ports, etc.). The downstream industry and its customers (including individuals, government and private sector entities) constitute a potential source for soil contamination of *PHCs* (e.g. leaky underground storage tanks, overflow spills, etc.).

ecological receptors: A non-human organism potentially experiencing adverse effects from exposure to contaminated media either directly (contact) or indirectly (food chain transfer). In the context of the PHC CWS, ecological receptors are the range of non-human organisms that might be found at a *PHC* release site and thus exposed to PHCs in the environment.

effects concentration low (ECL): A level of protection determined for commercial and industrial lands above a threshold effect concentration. It is derived from the distribution of effects data (*LOEC*, EC_{50} , LC_{50}) only and is preferably calculated using the weight of evidence approach, or alternatively by obtaining the geometric mean of available *LOEC* data. (see also Appendix D)

environmental quality benchmarks: Risk-based numerical values for the protection of sensitive ecological receptors from potentially toxic substances. Any value below which environmental risks to humans or ecological receptors are deemed to be unlikely, based on an evaluation of the existing scientific knowledge, in concert with policy decisions concerning biological effects levels above which environmental quality might be compromised.

equivalent carbon number (ECN): ECN is empirically related to the boiling point of a chemical normalized to the boiling point of the n-alkanes (straight-chain alkanes), or its retention time in a boiling point gas chromatographic column. It allows for the determination of an equivalent number of carbon atoms for chemicals where only the boiling point is known. The ratio of the number of C atoms to ECN for compounds with an ECN < ~12 is very similar to 1:1. See *carbon-fractions* for ECN ranges for individual PHC fractions.

estimated daily intake: Total “background” exposure to a chemical experienced by most Canadians. Estimated daily intake arises from the low levels of contamination commonly found in air, water, food, soil, and consumer products (e.g. tobacco, paints, and medicines). Estimated daily intake of a chemical is determined through a multimedia exposure assessment.

exposure pathway: The means by which organisms are exposed to contaminants. The possible categories of exposure pathways for humans or terrestrial ecological receptors include (i) direct transfer from the surrounding medium of contaminants (from air, water soil or sediment – by dermal uptake or absorption across external epithelial solution, (ii) ingestion of contaminated

soil or sediment, (iii) ingestion of contaminated water, (iv) inhalation of contaminated vapours or particulates, and (v) ingestion in food substances (including trophic transfer). The exposure pathway may also refer to the media from which an organism is exposed (air, water, soil, sediment, or combination thereof) and route of contaminant transport from source to receptor.

fine-grained soils: Soil which contains greater than 50% by mass particles less than 75 µm mean diameter (D_{50} < 75 µm).

gas chromatography: An analytical technique used in the quantification of PHC compounds. A sample is vaporized and injected into a carrier gas (e.g. helium or nitrogen) which passes through a solid-state elution column (a 100% polydimethylsiloxane column is used for PHCs). The sample is thereby separated into its component compounds according to the unique affinity of each compound for the stationary phase. The components appear separately at the effluent end of the column where they can be quantified using a flame ionization detector (for *PHC*s). The signal peak for each separated component compound is proportional to the quantity of the compound injected, making it possible to provide a quantitative analysis by calibration with known standards.

geo-environment: The *vadose* and saturated zones of the earth –excluding surface water bodies – participating in or communicating with the biosphere.

groundwater recharge: Process which occurs when the water content of the unsaturated zone becomes high enough to cause excess water to percolate downward to the water table, usually as a result of the infiltration of snow melt or rainwater into surface soils. Using a water balance approach, recharge is equal to the total amount of precipitation less the amount of surface runoff and evapotranspiration.

groundwater: Subsurface water beneath the water table in fully saturated geologic formations.

Hazard Quotient: An indication of potential risk from non-carcinogenic contaminants. It is estimated by dividing the expected exposure level by the associated *reference dose* for that contaminant. A value of <1 is presumed to be protective of the human population.

Heinz bodies: Molecules that accumulate at the red-blood-cell membrane, where they can damage or destroy red blood cells.

Henry's Law constant: A partition coefficient defined as the ratio of a chemical's concentration in air to its concentration in water at steady state. The dimensionless Henry's Law constant is obtained by dividing the Henry's Law constant by the gas constant, R.

hydraulic conductivity (*K*): The proportionality factor between hydraulic gradient and flux in Darcy's Law. It is a measure of the ease with which water is conducted through porous material and is primarily dependent on the characteristics of the porous material and to a minor extent, changes in viscosity of water.

lipophilicity: From lipophilic: literally – lipid-loving. The degree to which a substance will dissolve in organic, non-polar solvents. Lipophilic substances have very low water solubility.

LOEC (*Lowest Observed Effect Concentration*): The lowest concentration of a chemical used in a toxicity test that has a statistically significant adverse effect on test organisms relative to a control.

measurement endpoint: An effect on an ecological component that can be measured and described in some quantitative fashion (e.g., EC_{50}).

mogas: A commonly used refinery blend of motor gasoline. A special additive-free formulation of mogas was used to determine the toxicity of the F1 fraction (nC6 to nC10). Mogas contains approximately 30% aromatic and 70% total aliphatic compounds by weight.

monetizable benefits: Benefits to which a dollar value can be attached.

Monte Carlo simulation: An iterative process involving the random sampling of stochastic model parameter values from specified frequency distributions, simulation of the system, and output of predicted values. The distribution of the output values can be used to determine the probability of occurrence of any particular value.

multimedia exposure assessment: The simultaneous assessment of potential contaminant exposure from several environmental media (e.g. air, water, soil, etc.) by applicable exposure pathways (i.e., inhalation, dermal contact, ingestion).

NOEC (*No Observed Effect Concentration*): The highest concentration of a contaminant used in a toxicity test that has no statistically significant adverse effect on the exposed population of test organisms.

non-specific narcosis-type effects: General, reversible mode of toxic action to most biota from organic chemicals which disrupt normal cellular functions, presumably through either indiscriminate protein binding or disruption of the fluid mosaic architecture of cell membranes, resulting in impaired ion transport and polarization across cell membranes.

petroleum hydrocarbon (PHC): A hydrocarbon is a molecule consisting solely of carbon and hydrogen. Hydrocarbon groups present in *petroleum* products include: alkanes, alkenes, alkynes, aromatics, polynuclear aromatics, and complex hydrocarbon compounds containing oxygen, nitrogen, and sulfur. PHC compounds are found in or derived from geological sources such as oil, coal and bitumen.

petroleum: Products which consist of crude oils and a wide variety of refined-oil products.

porewater: The water occupying the space between particles of sediment or soil.

producers: Organisms which undergo photosynthesis to convert CO_2 and H_2O into sugars (autotrophs).

Qsoil: The advective flow of gas through soil.

reference concentration (RfC): An estimate (with *uncertainty* spanning perhaps an order of magnitude) of continuous inhalation exposure to the human population, including sensitive subgroups, that is likely to be without

appreciable risk of deleterious effects during a lifetime. RfC is used to evaluate potentially noncarcinogenic effects only.

reference dose (RfD): An estimate (with *uncertainty* spanning perhaps an order of magnitude) of daily exposure to the human population, including sensitive subgroups, that is likely to be without appreciable risk of deleterious effects during a lifetime. RfD is used to evaluate potentially noncarcinogenic effects only.

sand: A soil particle between 0.075 and 2 mm in diameter

silt: A soil particle between 0.002 and 0.075 mm in equivalent diameter.

slab-on-grade: Building foundation built as a concrete slab directly on the ground surface with no basement.

socio-economic factors: Includes benefits, costs, and technological considerations.

soil allocation factor (SAF): The relative proportion which soil constitutes in the total exposure from various environmental pathways (air, soil, food, water, consumer products).

soil organic matter: The organic fraction of the *soil*; includes plant and animal residues at various stages of decomposition, cells and tissues of soil organisms, and substances synthesized by the soil population. It is usually determined on soils that have been sieved through a 2.0 mm sieve.

soil: Normally defined as the unconsolidated material on the immediate surface of the earth that serves as a natural medium for terrestrial plant growth. Here limited to unconsolidated, surficial, mineral materials.

solubility: The maximum concentration of a chemical that can be dissolved in water when that water is both in contact and at equilibrium with the pure chemical.

standard deviation: A measure of the dispersion of samples in a data set from the mean value. The standard deviation is equal to the square root of the sum of squares (sum of differences between individual values and the mean) divided by the degrees of freedom (sample size minus one). A small standard deviation indicates that the values are clustered close to the mean, while a large standard deviation indicates a wide range in values in the data set.

statistical significance: In hypothesis testing a sample is said to be significantly different from a hypothetical population if the observed test statistic differs from the associated critical value at a specified probability level ($P \leq \alpha$; where α is a probability error of rejecting a true null hypothesis). Generally, α-levels > 0.05 are not considered to be statistically significant.

stomatal functioning: Stomata (sing. stoma) are minute pores or openings in the epidermis of leaves and herbaceous stems. They are flanked by two guard cells which open and close to regulate the rate of gas exchange and transpiration in the plant.

subsoil: Unconsolidated regolith material above the water table not subject to *soil* forming processes. Nominally includes *vadose zone* materials below 1.5 m depth.

surrogate: A representative compound used to assess the toxicity of the individual *CWS PHC* fractions.

texture: A categorical description of the proportions of sand, silt, and clay present in a soil.

threshold effects concentration (TEC): The concentration of a chemical below which no adverse effect is expected to occur. Ideally, it is derived from the distribution of the no-effects and effects data (i.e. *NOEC*, *LOEC*, LC_{50}, EC_{50}).

Tier 1 levels: Numerical values (soil concentrations) which form the basis of the *CWS* for *PHC*s and reflect the risk management and environmental quality goals of the standard as determined by CCME. This level represents the first of a three-tiered approach recommended for the assessment and remediation of petroleum contaminated sites.

Tier 2 levels: Numerical values calculated from Tier 1 levels in consideration of site-specific factors.

tolerable daily intake (TDI): The level/rate of chemical exposure to which a person may be exposed with no expected adverse effects. A tolerable daily intake can only be determined for chemicals with threshold effects (i.e., non-carcinogens).

transmissivity (*T*): The rate of water movement (m^2/sec) within a specified thickness of an aquifer. *T* is equal to the product of the *hydraulic conductivity* and the height of the modeled aquifer boundary.

trophic levels: Position in the food chain determined by the number of energy transfer steps to that level. Primary producers such as plants occupy the first trophic level, herbivores occupy the second trophic level, animals that prey on herbivores occupy a third trophic level, and so on.

uncertainty factor: A unitless numerical value applied to a reference toxicological value (e.g., EC_{50}) to account for the uncertainty in the estimate of a final soil quality guideline. Uncertainty factors may be applied, for example, when there is a need for extrapolation to long-term values from short-term data, extrapolation from laboratory to field conditions, or to account for inter- or intra-specific variation between individual test organisms and species.

uncertainty: The relative confidence in a scientific result owing to (1) variability in identified, contributing parameters and (2) ignorance regarding certain processes and phenomena. Uncertainty related to (1) can be reduced through data acquisition whereas uncertainty related to (2) cannot.

unconfined aquifer: A region of saturated ground material unbound by an impermeable or low-permeability layer such as clay. These systems allow for the draining of soil *porewater* and the subsequent movement of air (or water) to fill the spaces vacated by the moving water.

upstream industry: Petroleum hydrocarbon industry sectors which are responsible for the exploration and extraction of crude oil from subterranean reservoirs and oil sands, transfer to refineries, and the refining. As such, upstream industries pose a potential source for soil contamination of *PHCs* (e.g. leaks or spills occurring during the extraction procedure or by pipeline delivery, etc.).

vadose zone: Refers to the upper portion of the unsaturated zone in the subsurface environment, where both air and water are present between mineral grains.

volatilization: The chemical process by which chemicals spontaneously convert from a liquid or solid state into a gas and then disperse into the air above contaminated soil.

weathering: As applied to PHC, the change in composition and bioavailability with time as related to natural processes including volatilization, differential mobility, biodegradation and stabilization.

weight-of-evidence approach: Procedures that combine multiple, often disparate, toxicological data sources to develop an *environmental quality benchmark*. As applied in the *PHC CWS*, uses a percentile of the effects data set to estimate a concentration in the soil expected to cause no adverse biological effects.

whole Federated crude oil: Un-fractionated *crude oil* obtained from the Federated pipeline in west central Alberta.

Acronyms

ACH: air changes per hour
AEHS: Associates for the Environmental Health of Soils
AENV: Alberta Environment
AEP: Alberta Environmental Protection
AM TAG: Analytical Methods Technical Advisory Group
ASHRAE: American Society of Heating, Refrigerating and Air-Conditioning Engineers
ASTM: American Society for Testing and Materials
ATSDR: Agency for Toxic Substances and Disease Registry
BCMELP: British Columbia Ministry of Environment, Lands and Parks
BTEX: benzene, toluene, ethylbenzene, xylene
CAPP: Canadian Association of Petroleum Producers
CCME: Canadian Council of Ministers of the Environment
CFLRI: Canada Fitness and Lifestyle Research Institute
CMHC: Canada Mortgage and Housing Corporation
CPPI: Canadian Petroleum Products Institute
CSST: Contaminated Sites Soil Taskgroup of British Columbia
CWS: Canada-Wide Standards
DRO: diesel range organics
EC-L: effects concentration - low
ECN: equivalent carbon number
EcoTag: Ecological Task Advisory Group
ECx: effective concentration for x percentage of the test population
EDI: estimated daily intake
GC-FID: gas chromatography - flame ionization detector
GC-MS: gas chromatography - mass spectrometry
GRO: gasoline range organics
HC: Health Canada
HEPH: heavy extractable petroleum hydrocarbons
HHFT TAG: Human Health, Fate and Transport Technical Advisory Group
K_d: distribution coefficient
K_{OC}: organic carbon - water partition coefficient
K_{OW}: octanol - water partition coefficient
LCx: lethal concentration for x percentage of the test population
LEPH: light extractable petroleum hydrocarbons
LF: leaching factor
LO(A)EL: lowest observed (adverse) effects level
LOEC: lowest observed effect concentration
MADEP: Massachusetts Department of Environmental Protection
MEFQ: Ministère de L'Environnement et de la Faune Québec
MOEE or OMEE: Ontario Ministry of Environment and Energy

MOG: mineral oil and grease
NAPL: non-aqueous phase liquids
NHW: National Health and Welfare
NO(A)EL: no observed (adverse) effects level
NOEC: no observed effect concentration
OAEI: O'Connor Associates Environmental Inc.
OMEE: Ontario Ministry of Environment and Energy
PAHs: polycyclic aromatic hydrocarbons
PHC CWS: Canada-Wide Standard for Petroleum Hydrocarbons in Soil
PHC: petroleum hydrocarbon
PIRI: Partners in *RBCA* Implementation
PIWG: Protocol Improvement Working Group
PST: petroleum storage tank
PTAC: Petroleum Technology Alliance Canada
QA/QC: quality assurance/quality control
RAFs: relative absorption factors
RBC: red blood cells
RBCA: Risk - Based Corrective Action
RBSLs: Risk - Based Screening Levels
RfC: reference concentration
RfD: reference dose
RRfC: residual reference concentration
RTDI: residual tolerable daily intake
SAF: soil allocation factor
SQG: soil quality guideline
TDI: tolerable daily intake
TEC: threshold effect concentration
TED_{LDW}: daily threshold effect dose for livestock drinking water
TPHCWG: Total Petroleum Hydrocarbon Criteria Working Group
TRPH: total recoverable petroleum hydrocarbon
UF: uncertainty factor
US EPA: United States Environmental Protection Agency
VF: volatilization factor
VPH: volatile petroleum hydrocarbons
WIR: water ingestion rate

1. Introduction

The Canada-Wide Standard for Petroleum Hydrocarbons in Soil (PHC CWS) was developed by the Canadian Council of Ministers of the Environment (CCME) under the Harmonization Sub-Agreement on Standards. Alberta championed the PHC CWS and co-chaired the national Development Committee with Canada. The Development Committee was assisted immeasurably by the participation of key stakeholders from the oil and gas and environmental consulting industries, environmental non-governmental organizations and universities. An overview of the consultative processes used to develop the PHC CWS is provided in Appendix A.

The purpose of this document is to provide an overview of the land use-based framework for the PHC CWS and the detailed technical scientific rationale in support of the derivation of the Tier 1 values. The Tier 1 values are also presented in brief in the 'approved in principle' PHC CWS and Technical Supplement (www.ccme.ca). These values form the numerical basis of the PHC CWS and reflect the risk management and environmental quality goals of the standard as determined by CCME in consideration of scientific, technical and socio-economic factors and the substantive input of stakeholders.

This document outlines the goals and principles used in developing the standard (Chapter 1), the risk management and environmental quality objectives within the land use-based framework (Chapter 2), and details the approach adopted for the derivation of the human health (Chapter 3) and ecological Tier 1 values (Chapter 4). Chapter 5 includes the tabulated Tier 1 values for surface soils and generic values for sub-surface soils. This chapter discusses the integration of the ecological and human health values, and the role of risk management in the derivation process. Chapter 6 discusses the critical role of the recommended analytical method in defining the standard and supporting its consistent use. Chapter 7 (Summary and Recommendations) summarizes the features and benefits of the PHC CWS, indicates gaps in the current understanding of PHC as related to standard development and provides recommendations for future priority research.

This document is not intended as guidance to users on implementation of the PHC CWS. Technical options available to jurisdictions in implementing the PHC CWS are being developed in a separate volume (CCME 200X).

1.1 Background

Petroleum hydrocarbons (PHC) describe a mixture of organic compounds found in or derived from geological substances such as oil, bitumen and coal. Petroleum products released to the environment, such as gasoline, crude oil and jet fuel,

typically contain hundreds to thousands of compounds in varying proportions, composed predominantly of carbon and hydrogen, with minor amounts of nitrogen, sulphur and oxygen. PHC contamination in soils varies with the petroleum source, soil type, the composition, degree of processing (crude, blended or refined) and the extent of weathering caused by exposure to the environment. Such factors have complicated the assessment of the human and environmental health risks associated with PHC contamination in soils.

PHCs in the environment are a concern for a number of reasons. First, their reduced nature and volatility pose a fire/explosion hazard. Second, most PHC constituents are toxic to some degree. Third, lighter hydrocarbons are mobile and can be a problem at considerable distances from their point of release due to transport in ground, water or air. Fourth, larger and branched chain hydrocarbons are persistent in the environment. Fifth, PHCs may create aesthetic problems such as offensive odour, taste or appearance in environmental media. Finally, under some conditions PHCs can degrade soil quality by interfering with water retention and transmission, and with nutrient supplies.

Canadian regulatory agencies have responded to these problems with assessment and remediation requirements applicable where PHCs are released to soils and groundwater. A blend of generic guidelines and site-specific, risk-based approaches has emerged across Canada, but there is very little consistency across jurisdictions in the rationale for guidelines, numerical values provided, or application to land uses. Moreover, a vast array of analytical options exist for quantifying hydrocarbons in soil. Various methods have been developed to quantify all or part of the hydrocarbons present in a sample based on different extraction, purification, detection and data treatment approaches. Lack of standardization in sampling, storage and analytical procedures has led to high variability in results and confusion for users of the data.

This condition is unsatisfactory and made more serious by the scope of the PHC problem. When both production (“upstream”) and marketing (“downstream”) sectors are considered, over a quarter million actual or potential PHC release sites exist in Canada. Liabilities are estimated in the billion dollar plus range (Komex 2000). It is important that guidelines and other assessment tools be as accurate and reproducible as possible to protect the environment and control costs. The costs of failing to control risks are very high; for example, losses of community water supplies have occurred as a result of PHC releases.

The PHC CWS was developed in recognition of the above factors.

1.2 Goals and Principles

The overall goal of the PHC CWS is to provide a sound Canadian framework and scientific toolkit for the assessment and management of PHCs in soil and subsoil consistent with the principles of the Harmonization Accord and Sub-Agreement on Environmental Standards.

While all principles of these two enabling agreements apply, the following are especially significant to the PHC CWS:

- Performance-based, results oriented and science-based;
- Openness, transparency, accountability and effective participation of stakeholders in decision making;
- Allow for flexible implementation required to reflect variations in ecosystems and local, regional, provincial and territorial conditions;
- Consensus-based and driven by the commitment to attain the highest level of environmental quality within the context of sustainable development;
- Pollution prevention is the preferred approach to environmental protection.

More specific goals and principles were identified by stakeholders at the two national workshops and captured in the workshop reports posted on the CCME website (www.ccme.ca). Key stakeholders recommendations included:

- Protection of ecological and human health;
- A risk-based, 3-tiered framework for assessment of PHC contamination consistent with CCME and ASTM approaches;
- Tier 1 standards based on four boiling point range fractions to meaningfully group fate, behaviour and toxicological properties;
- Incorporation of socio-economic factors to ensure that Tier 1 standards are practical and appropriate for many sites – while not compromising human and ecological health;
- Provision for a flexible Tier 2 process that responds to influential site factors while maintaining symmetry and consistency with Tier 1 standards;
- Risk management should include consideration of aesthetics and physical-chemical effects on soil;

- Development of a standard analytical method based on gas chromatography;
- Inclusion of a means to review and update standards in response to new data and insights.

1.3 Overview of PHC CWS Features

The PHC CWS is based in the science of environmental risk assessment and management. This approach defines acceptable environmental quality in terms of receptors (living things and other valued ecosystem components), their susceptibility to contaminants, and the pathways along which exposure to contamination may occur. The objective is to ensure that exposures are kept below levels at which adverse effects are expected.

Meeting these risk management objectives for complex and variable mixtures such as PHCs requires a systematic approach and a number of simplifying assumptions. The PHC CWS considers PHCs in four fractions that provide broad groupings with respect to environmental fate, behaviour and effects. These fractions are defined with respect to analytical procedures (boiling point range – Chapter 2) but correlate roughly with gasoline, diesel, lubricant and heavy lubricant ranges. The PHC CWS in soils presents for these four fractions a three-tiered, risk-based remedial standard developed for four generic land uses - agriculture, residential/parkland, commercial and industrial (Figure 1.1). Tier 1 levels for each land use are derived through a systematic evaluation of all pathways of exposure that apply to the receptors of concern identified under the land use. Tier 2 levels may be generated and used when site conditions exist that significantly modify the exposure and risk scenarios. At Tier 3, a site-specific ecological and/or human health risk assessment is conducted. The objective of the standard is to improve the protection of human health and the environment and to provide consistency and accuracy in the management of PHC contaminated soils.

An appropriate remediation decision can be identified through consideration of site characterization data, site and surrounding land use factors, technical factors, and benefits and costs attached to options at Tiers 1, 2 and 3. General risk management objectives do not change among the Tiers, however, the means of minimizing or eliminating exposure can vary. This provides good flexibility in responding to PHC contamination of soils and subsoils. Details can be found in CCME (200X).

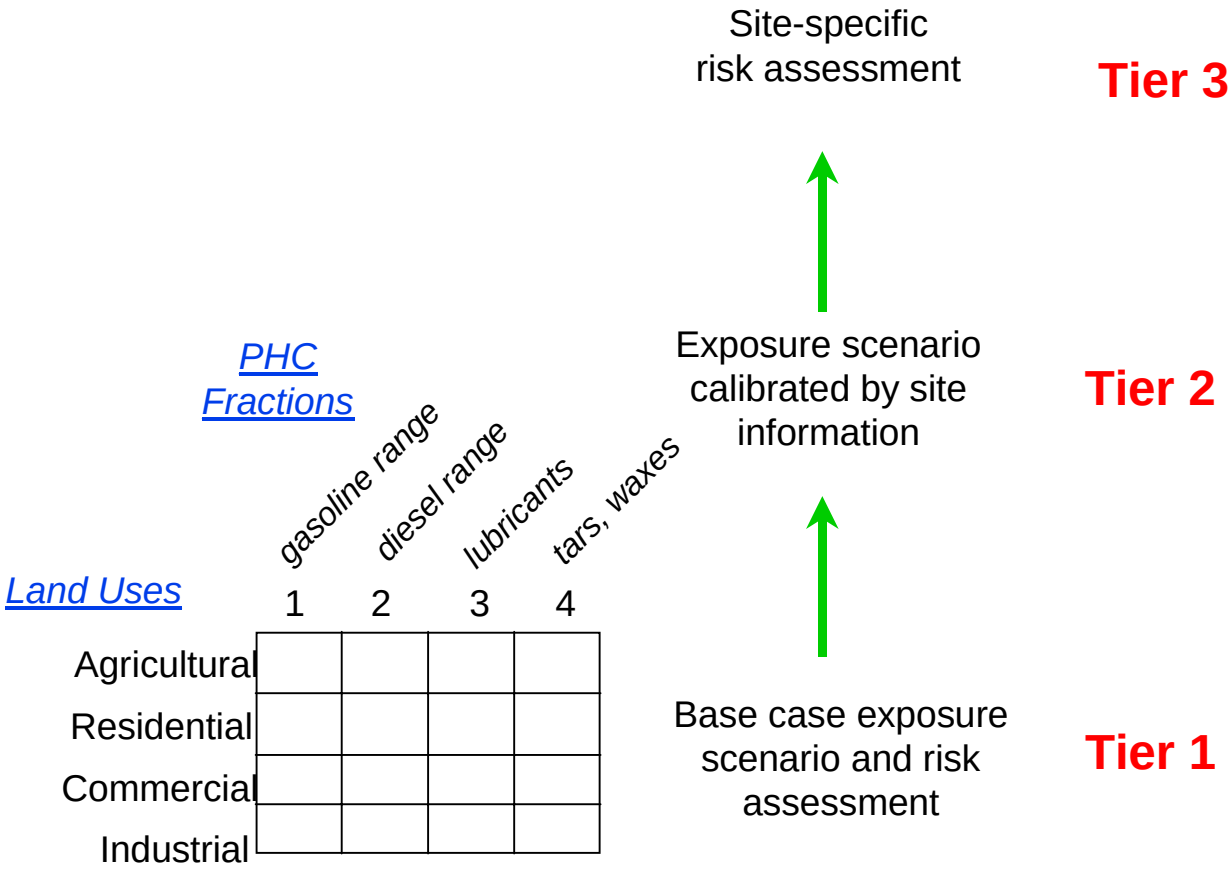


Figure 1.1: Tiered risk-based approach to managing PHC-contaminated soils.

2. Development of Tier 1 Generic Soil Quality Levels

2.1 Sources of Information

The PHC CWS is founded on documented and scientifically defensible risk-based methodology. The chief sources were:

1. 1996 *CCME Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines*;
2. American Society for Testing & Materials (ASTM) *Risk-based Corrective Action (RBCA) Standard Guide 1739-95* - and additions/improvements thereon, including the Atlantic *Partners in RBCA Implementation (Atlantic PIRI 1999);*
3. US TPH Criteria Working Group Series Vols. 1-5 (1997-1999);
4. British Columbia Environment Matrix Standards for VPH, LEPH and HEPH (1998).

Consequently, the derivation of the Tier 1 levels of the CWS involves explicitly listed receptors - both human and ecological, and the levels of protection accorded. It also involves defined exposure scenarios, and documented underlying assumptions and equations as outlined in more detail in Sections 3 and 4 of this document.

Very important additional concepts and features were adopted or adapted from numerous other sources including Alberta Environment's Petroleum Storage Tank Guidelines (AEP 1994) and Ontario Ministry of Environment's Guideline for Use at Contaminated Sites in Ontario (OMEE 1996).

A discussion of risk-based approaches adopted in North America for the assessment and management of PHC contaminated soils is presented in Appendix B. In summary, several primary initiatives have been established for the assessment of PHC contaminated soils. These include the Massachusetts Department of Environmental Protection (MADEP 1994, 1996, 1997); the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG; Weisman 1998; Potter and Simmons 1998; Gustafson et al. 1997; Edwards et al. 1997); the B.C. Ministry of Environment (Golder Assoc. 1995); CanTox Inc. (1997); and the Atlantic provinces (Atlantic PIRI 1999).

The development of human health-protective Tier 1 values is based predominantly on the work of the TPHCWG. This resulted from a review of the available information concerning the various approaches to risk-based assessment/management of PHCs, and following discussions with members of the PHC Development Committee, the Eco TAG, the AM TAG, and the HHFT TAG (Appendix A). Based on a consideration of both physical-chemical properties and

toxicological RfDs for the TPHCWG fractions, 4 carbon-fractions (F1, F2, F3, F4) have been identified and described in more detail below.

The PHC CWS is unique in the development of risk-based values that are protective of ecological health. A paucity of scientifically-defensible toxicological data on the ecological responses to PHCs rendered it necessary to generate ecotoxicological data on a carbon fraction-specific basis for the development of the standard. Data for F2 and F3, and mogas (motor gasoline) toxicity (as an approximation of F1 toxicity) and fresh Federated whole crude oil were conducted with support from CAPP/PTAC/AENV and CPPI/Crestech. Additional testing was facilitated through support from Environment Canada, Alberta Environment, Quebec Ministry of Environment, Ontario Ministry of Environment, and B.C. Ministry of Environment, Lands and Parks.

Collectively, the well-founded risk-based methodology for human and ecological receptors, generation of ecotoxicology data and the standard analytical methodology (Chapter 6) form the scientific basis of the PHC CWS. In addition, the science-based component of the PHC CWS is complemented by a consideration of socio-economic and policy based factors as illustrated in Figure 2.1. The contributions of these latter factors are further discussed in Chapter 5.

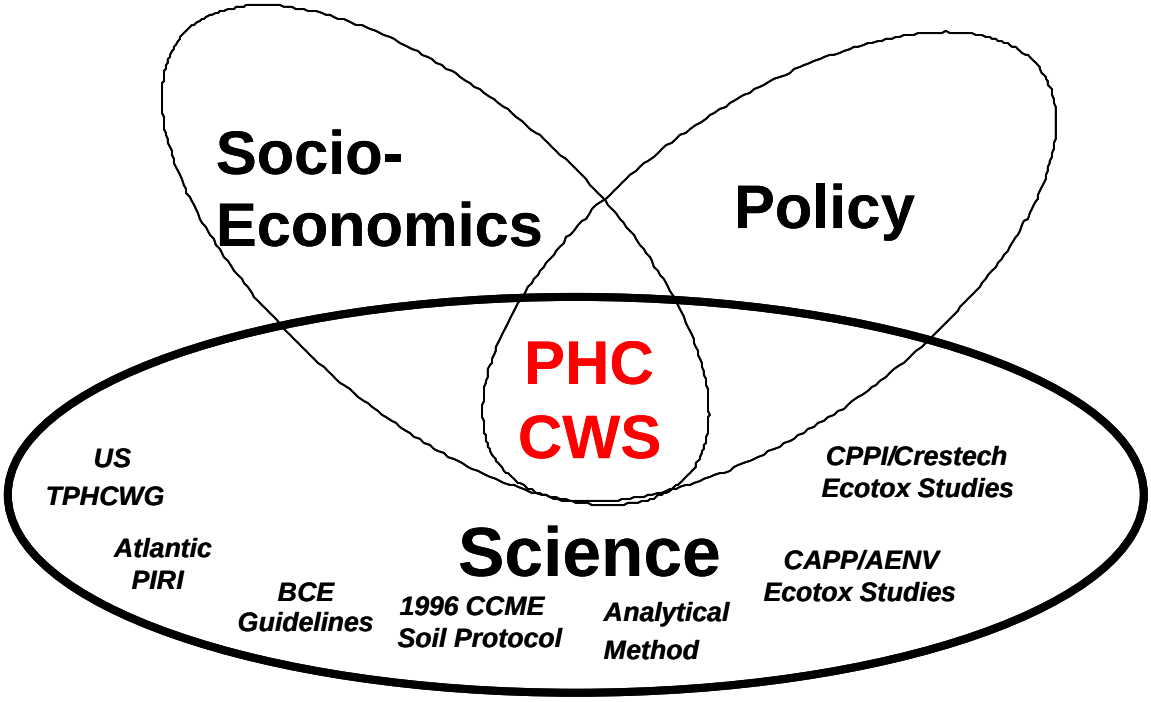


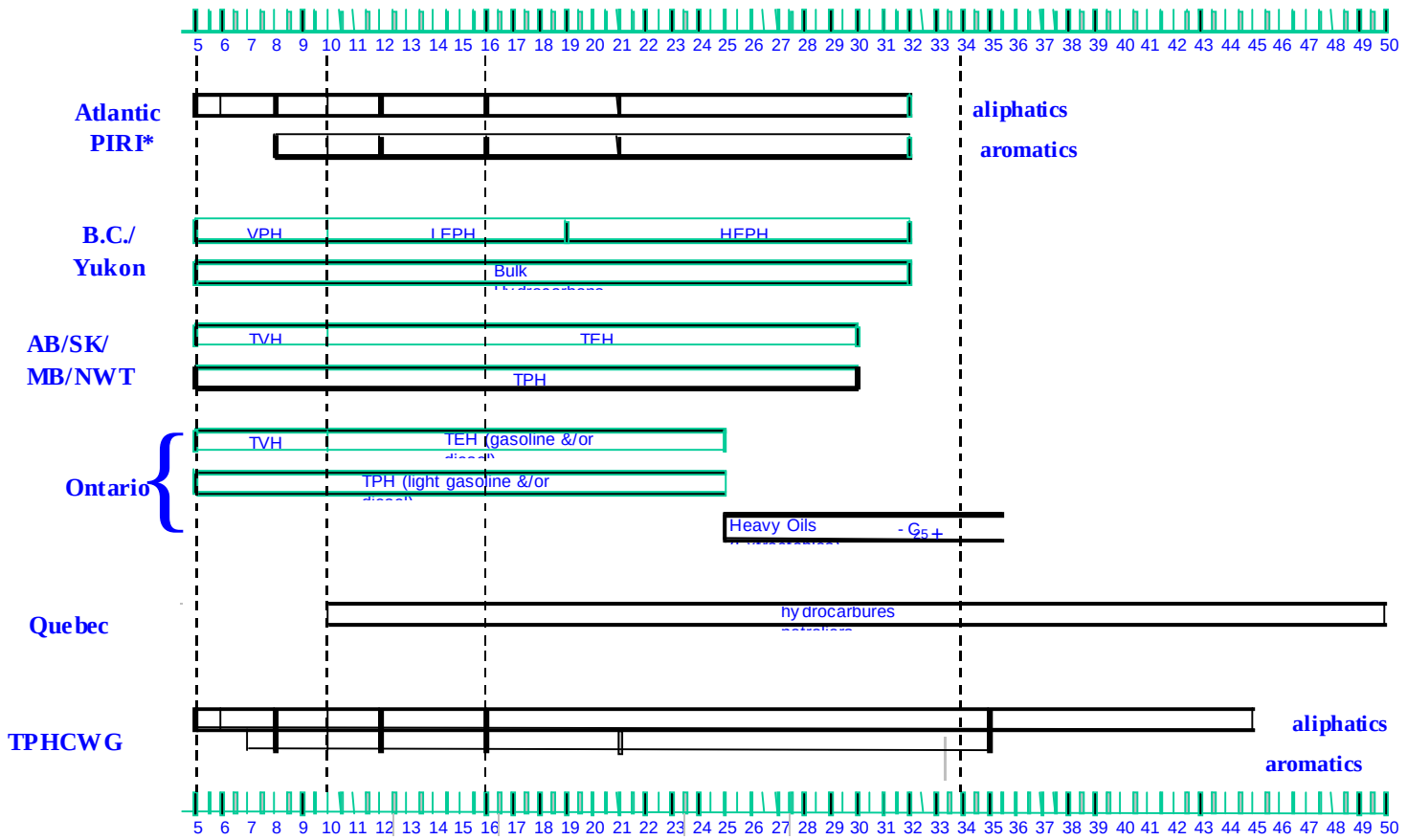
Figure 2.1. Scientific, socio-economic and policy based components of the PHC CWS.

2.2 Functional Definition of PHC Fractions

For purposes of the PHC CWS, petroleum hydrocarbons are sub-divided into fractions according to specified ranges of equivalent carbon number (ECN). Each fraction is, in turn, made of subfractions as previously defined by the TPHCWG. These subfractions that form the four CWS fractions have been described according to their relevant physical-chemical properties (e.g., solubility, Henry's Law constant, etc.) and toxicological characteristics (i.e., RfD and/or RfC) which permitted the prediction of chemical fate, exposure and potential risk. Within the CWS fractions, the balance between aromatic and aliphatic constituents is assumed to be 20/80 based on an analysis presented by TPHCWG and the petroleum industry (CAPP, CPPI) of some representative hydrocarbon products. The breakpoints defined for the 4 fractions that form the basis of Tier 1 levels were selected in consideration of analytical factors, the fit with TPHCWG subfractions and expected relevance to biological response in soils. These are described below (Figure 2.2).

I. Fraction 1 encompasses the range of ECN from C_6 to C_{10}
   - A. This fraction is composed of the following TPHCWG sub-fractions:
     1. aromatics $C_{>7}$-C_8, $C_{>8}$-C_{10}
     2. aliphatics C_6-C_8, $C_{>8}$-C_{10}
   - B. Physical-chemical properties are well defined for TPHCWG sub-fractions within this range;
   - C. Unique RfDs and RfCs are defined for each aromatic or aliphatic subfraction in the range;
   - D. BTEX should be analyzed separately and their concentrations subtracted from aromatics in this fraction;
   - E. Aliphatics in this range are represented by two RfD and RfCs; for C6-C8, and for C>8-C10;
   - F. Non-BTEX aromatics are represented by two RfD and RfCs; for C>7-C8 and C>8-C10.

II. Fraction 2 encompasses $C_{>10}$ to C_{16}
   - A. This fraction is composed of the following TPHCWG sub-fractions:
     1. aromatics $C_{>10}$-C_{12}, $C_{>12}$-C_{16}
     2. aliphatics $C_{>10}$-C_{12}, $C_{>12}$-C_{16}
   - B. Physical-chemical properties are well defined for TPHCWG sub-fractions within this range;
   - C. Aliphatics in this range are represented by a single RfD and RfC;
   - D. Aromatics are represented by a single RfD and RfC.



* PIRI guidelines presented for gasoline, diesel and heating oil.

Figure 2.2: CWSPHC carbon-fractions in relation to the TPHCWG subfractions.

III. Fraction 3 encompasses the range of ECN from $C_{>16}$ to C_{34}
   A. This fraction is composed of the following TPHCWG sub-fractions:
      1. aromatics $C_{>16}$-C_{21}, $C_{>21}$-C_{34}
      2. aliphatics $C_{>16}$-C_{21}, $C_{>21}$-C_{34}
   B. Physical-chemical properties are well defined for TPHCWG sub-fractions within this range;
   C. Aliphatics in this range are represented by a single RfD;
   D. Aromatics are represented by a single RfD.

IV. Fraction 4 encompasses the range of ECN from $C_{>34}$ to C_{50}
   A. This fraction is composed of the following TPHCWG sub-fractions:
      1. aromatics $C_{>34}$
      2. aliphatics $C_{>34}$
   B. This fraction can represent a substantial and significant proportion of environmental PHC contamination, and of petroleum products and crude oils;
   C. Although the physical-chemical properties are less well defined in this fraction, the material is not volatile and is expected to have minimal environmental migration;
   D. A study of mixtures provides the basis for an RfD for aliphatics in this range;
   E. There are no data available to derive an RfD for aromatic PHCs in this range, specifically. However, the toxicity of aromatics can be conservatively assumed to be equivalent to that of pyrene, as is currently done for all aromatics with an ECN $C_{>16}$ under the TPHCWG scheme.

2.2.1 Relative Proportion of Aromatics to Aliphatics in Each PHC Fraction

The carbon number ranges encompassed by each PHC fraction may be further classified or subdivided in terms of aliphatics and aromatics. The composition of each PHC "fraction" to be used for deriving Canada Wide Standards for PHCs in soil is summarized in Table 3.11. Also included in Table 3.11 is the recommended composition of petroleum products to be employed to derive Tier 2 soil quality guidelines for such products, in a manner that would be consistent with the Tier 1 Canada Wide Standards for PHC fractions. The recommended ratio of aliphatic to aromatic hydrocarbons in each PHC fraction is 80:20, based on a review of data presented by the TPHCWG, and on data provided by CAPP and CPPI. This requires that the content/concentrations of benzene, toluene, ethylbenzene and xylenes (BTEX) are subtracted from the content of total PHCs at the contaminated site, thus requiring that BTEX be analyzed, assessed and managed separately from PHCs.

2.3 Representing PHC Fractions: Whole Fraction Properties vs. Surrogates

TPHCWG Vol. 4 describes whole product- and surrogate-based approaches to evaluating the toxicity of mixtures such as PHC. The pros and cons of each approach are discussed and a case made that the surrogate method is best suited to deal with PHC source variability and environmental modifications related to differential mobility and dissipation. All agencies proposing risk-based approaches to PHCs have defined or selected surrogates to represent the environmental mobility (physico-chemical properties) and toxicity (RfDs, RfCs) of individual PHC fractions. Most efforts prior to the TPHCWG have focused on individual compounds within the carbon number range of specified PHC fractions. Generally, the most toxic known constituent of a given fraction was selected to represent the toxicity of the entire fraction. The physico-chemical properties of this toxic constituent were also generally employed for purposes of predicting environmental fate of each fraction.

For the purposes of developing human health Tier 1 values under the CWS for PHCs, the physicochemical properties and RfDs/RfCs described by the TPHCWG were adopted rather than selected *de novo* surrogates for defining the environmental mobility or toxicity of the four designated PHC fractions. The relevant variables are applied to each of the TPHCWG sub-fractions and these sub-fractions are added or 'rolled-up' into the four 'super' fractions defined herein. The addition of TPHCWG sub-fractions is undertaken on the basis of the weight percent of each sub-fraction within the CCME PHC fractions.

Rather than relying on a strict, surrogate approach for the derivation of ecological Tier 1 values, a *weight of evidence* approach was used that combined whole product, whole fraction and compound surrogate information. Responses to whole Federated crude oil (drawn from the Federated pipeline in west central Alberta), distillate cuts prepared from that crude, and chemical surrogates were used. Surrogate compounds were identified to represent the aromatic and aliphatic portions of each fraction as follows: F2- napthalene and decane, F3- pyrene and eicosane. In addition, a critical body residue approach was taken in the assessment of F1 and F2 effects on aquatic receptors through potential movement of PHC through groundwater. Details of how these toxicity information sources were combined are presented in Chapter 4.

2.4 Land Use Definitions

The PHC CWS in soils has been developed for four generic land uses - agriculture, residential/parkland, commercial and industrial. A generic land use scenario has been envisioned for each category based on the 'normal' activities on these lands (Figure 2.3). The risk-based nature of the PHC CWS means that, for each land use, all values to be protected (life-forms or receptors, ecosystem properties) are

explicitly documented as well as the contaminants considered within PHCs and the pathways by which PHCs can affect these values. This approach provides great flexibility; it allows assessment and management of different variations within a land use and even extension of the standard to other land use categories (e.g., wildlands). The vision, or exposure scenario, attached to each land use is the heart of the PHC CWS. The four land uses are defined as follows:

Agricultural lands: where the primary land use is growing crops or tending livestock. This also includes agricultural lands that provide habitat for resident and transitory wildlife and native flora. The portion of a farm that houses people is considered a residential land use.

Residential/Parkland: where the primary activity is residential or recreational activity. The ecologically-based approach assumes parkland is used as a buffer between areas of residency, but this does not include wild lands such as national or provincial parks, other than campground areas.

Commercial: where the primary activity is commercial (e.g., shopping mall) and there is free access to all members of the public, including children. The use may include, for example, commercial day-care centres. It does not include operations where food is grown.

Industrial: where the primary activity involves the production, manufacture or construction of goods. Public access is restricted and children are not permitted continuous access or occupancy.

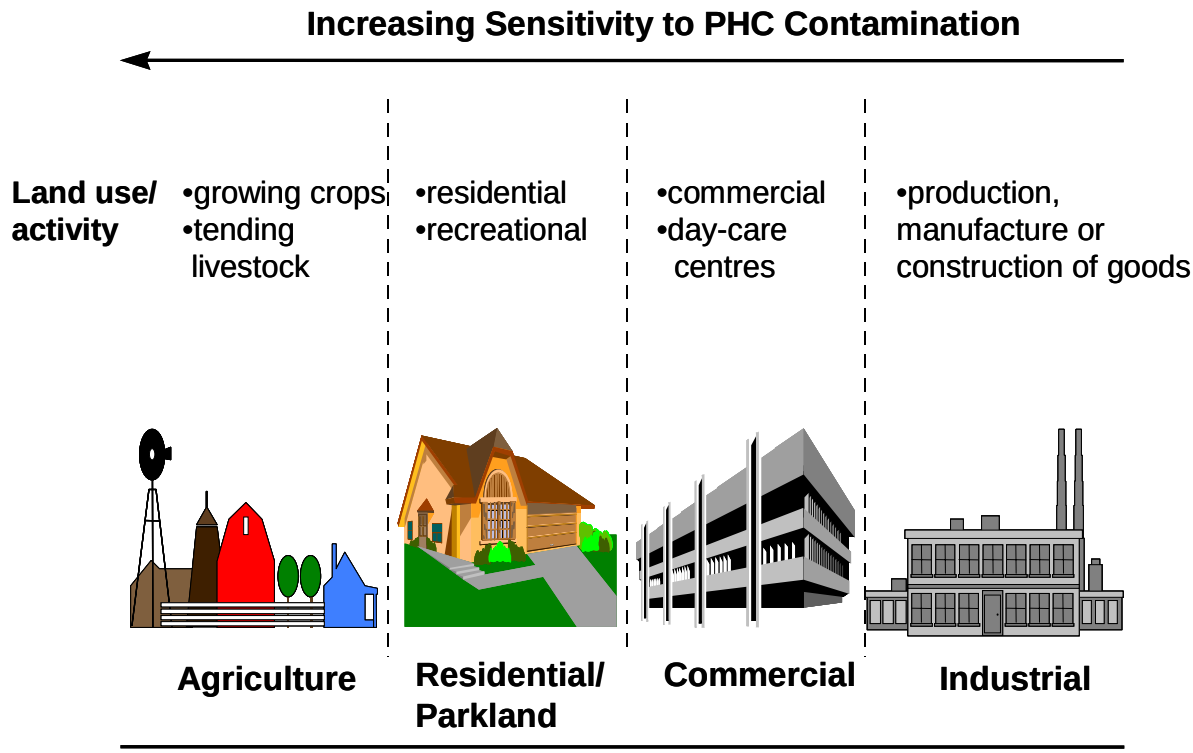


Figure 2.3: Generic land-use scenarios and their associated activities.

2.5 Receptors and Pathways

Tier 1 levels for each land use are derived through a systematic evaluation of all pathways of exposure that apply to the receptors of concern, including human health and ecological, identified under that land use. A summary of the receptor/pathway combinations addressed under each land use in the PHC CWS is presented in Table 2.1. Each combination is discussed further in the appropriate section of this document.

Tier 1 levels in the PHC CWS are presented as a summary of the above pathway/receptor combinations where data were sufficient to support the derivation procedure. In application, users will gather information on relevant pathways and will frequently require information on secondary pathways. Decisions are made in relation to the governing pathway(s) applicable at individual sites. Procedures supporting this decision-making process are presented in the user guidance (CCME 200X).

Table 2.1: Land-uses, key receptors and exposure pathways.

Exposure Pathway	Agriculture	Residential/ Parkland	Commercial	Industrial
Soil Contact	Nutrient cycling Soil invertebrates Crops (plants) Human (child)	Nutrient cycling Invertebrates Plants Human (child)	Nutrient cycling Invertebrates Plants Human (child)	Nutrient cycling Invertebrates Plants Human (adult)
Soil Ingestion	Herbivores Human (child)	(wildlife)* Human (child)	(wildlife)* Human (child)	(wildlife)* Human (adult)
Groundwater/ Surface Water	Aquatic Life/ Livestock Watering Human (child)	Aquatic Life Human (child)	Aquatic Life Human (child)	Aquatic Life Human (adult)
Vapour Inhalation (humans only)	Child, indoor**	Child, indoor	Child, indoor	Adult, indoor
Produce, meat and milk produced on site (humans only)	Child	Child (produce only)		
Off-site migration of Soil/Dust				Human/Eco

* wildlife dermal contact and ingestion data may be particularly important for PHCs (e.g., oiling of feathers, etc., although this should be addressed with an initial assessment of the presence of non-aqueous phase liquids - NAPL), but there are unlikely to be sufficient data to develop guidelines that address this exposure pathway

** a 30m horizontal offset is assumed between the farm residence and the PHC contamination, consistent with oil and gas development practices. Contamination nearer a farm residence triggers a residential assessment.

Jurisdictional approaches to implementation of the CCME land use categories differ somewhat but frequently make use of land zoning systems to capture “compliant” and “non-compliant” uses. A scientific basis for decisions on how specific site uses connect with the CCME categories lies in an examination of the specific receptors and exposure pathways.

In addition to the toxic risks addressed by the receptor/pathway analyses, certain other management considerations apply. Chief among these are:

- ignition hazard
- odour and appearance
- formation of non-aqueous phase liquids (NAPL)

Whereas the primary focus in PHC CWS standard development is prevention of toxic effects to the receptors in Table 2.1, in certain situations these pathways may be of little immediate concern and PHC management is driven by consideration of policy factors. Aesthetics and avoidance of free product considerations have been incorporated as policy factors in the development of the Tier 1 levels as indicated in Fig. 2.1.

2.5.1 Treatment of Soil-to-Groundwater Exposure Pathways

Soils are hydrologically linked to groundwater systems. A major concern with soil contamination is that it can and does lead to groundwater contamination, which may be technically, economically, or otherwise difficult or currently impossible to remediate. Tier 1 levels for the PHC CWS are designed to prevent unacceptable transfers of contaminants to groundwater systems.

Procedures are undertaken to assess and manage the soil-to-groundwater pathway with respect to three uses of groundwater (Table 2.1):

- Human consumption (potable water);
- Aquatic life;
- Livestock watering.

In order to address these pathways at Tier 1, soil contamination is considered to exist in a reasonably sensitive hydrogeological setting. It is assumed that the site is underlain by an unconfined aquifer and that soil contamination extends to the water table (this assumption can be adjusted in relation to site data at Tier 2). Petroleum hydrocarbons in F1 and F2 partition between soil organic matter, soil water and soil air. Petroleum hydrocarbons dissolved in soil water move with recharge water to the water table and are diluted with the groundwater flow. At some distance downgradient groundwater is either withdrawn for the specified use - typically through a well - or discharged to a natural or engineered surface water body.

The precise treatment of these soil-to-groundwater pathways at Tier 1 differs somewhat depending on the groundwater protection goal. In the case of potable groundwater, it is assumed that use or potential use occurs on the PHC-contaminated site. For the other two groundwater uses, it is assumed that a minimum lateral distance of 10 m exists between the contamination source in soil and the point of discharge or withdrawal. These different assumptions necessitate different technical approaches.

Details on the technical description of movement and attenuation of PHCs in groundwater for potable use and aquatic life/livestock watering are provided in Chapters 3 and 4 respectively. In overview, potable groundwater protection at Tier 1 involves use of a simple, steady state mixing-dilution model that assumes a well exists at the downgradient boundary of a site uniformly contaminated to the Tier 1 soil standard. This model has been used previously in CCME (1996), US EPA (1997) and Atlantic PIRI (1999). Under this model description, on-site groundwater quality is assured because PHC concentrations increase with site length; concentrations are maximal at the downgradient boundary. A vertical mixing depth must be specified and a nominal 2 m value is used here in consideration of practical factors cited in CCME (1996).

A simple mixing-dilution model is inappropriate for supporting aquatic life and livestock watering uses of groundwater because it is assumed that a minimum

separation of 10 lateral meters exists between the PHC contaminated soil and the point of groundwater use/discharge. A dynamic advective-dispersive model is needed to describe such an arrangement. Tier 1 values in PHC CWS were calculated using solutions to the advective-dispersive flow equation published by Domenico and Robbins (1984). Under this mathematical description attenuation of PHC includes:

- retardation by organic matter in the aquifer;
- a conservative, anaerobic biodegradation process;
- a vertical mixing zone calculated from a dispersive relationship that depends on lateral distance travelled.

The method of determining the vertical mixing zone differs from that used for on-site potable groundwater and generally gives values less than 2 meters over practical lateral separation distances. While different vertical mixing results are obtained by the two methods each is considered appropriate in the circumstances. In the potable water case, vertical mixing is assured through depth averaging related to well construction and operation details (see CCME 1996). In contrast, it is difficult to assume any particular mixing pattern related to withdrawal or discharge for the other groundwater uses. In such applications groundwater may be discharging to a dugout or natural standing water body where mixing prior to or during exposure is very uncertain. Thus, for aquatic life and livestock watering uses of groundwater, the vertical mixing zone is determined using a dispersive algorithm described in Chapter 4.

Throughout the PHC CWS, a distinction is made between fine-textured and coarse textured soils. While “texture” is used in the normal connotation for soil (e.g., see Soil Classification Working Group 1998) the terms fine-textured and coarse textured are based solely on the geo-technically accepted size cutoff between sand and silt (75 µm; ASTM 2000). Specifically, fine textured soils are defined as having greater than 50% by mass particles less than 75 µm mean diameter (D_{50} < 75 µm). Coarse textured soils are defined as having greater than 50% by mass particles greater than 75 µm mean diameter (D_{50} > 75 µm). Simply put, coarse soils are defined as having more than 50% sand by mass and fine soils are defined as having less than 50% sand by mass.

2.6 Approach for PHCs

This section summarizes the approaches adopted for deriving Tier 1 human health and ecological levels. A more detailed description of each approach and the toxicological basis and methods to calculate the Tier 1 values are presented in the appropriate sections (Chapters 3, 4).

Human Health Summary

Petroleum hydrocarbons are grouped by physico-chemical properties into 4 carbon chain length fractions. Group toxicological and physico-chemical properties are used to estimate concentrations of PHC in soil that would not lead to an exposure exceeding a hazard quotient of 1 along 4 pathways – inhalation of vapours, dermal contact, incidental ingestion of soil and ingestion of cross-contaminated groundwater. The same pathways and same exposure equations are used for all land uses, however, exposure duration and frequency vary between land uses and only an adult's exposure is considered for the industrial land use. Average values for most parameters and characteristics are used which, when combined, gives a conservative but practical result. There are insufficient data to evaluate PHC exposure through the food chain. The few data available suggest that plant uptake of PHC and subsequent exposure at higher trophic levels is not a concern (see discussion in Section 4.1).

Ecological Health Summary

Tier 1 levels are derived to protect key ecological receptors that sustain normal activities on the four previously defined land use categories: agricultural, residential/parkland, commercial and industrial. The derivation of Tier I levels for ecological receptors focuses on the effects of PHCs on the biotic component of a terrestrial ecosystem. Specifically, it evaluates the potential for adverse effects to occur from exposures to soil-based PHCs at point-of-contact or by indirect means (e.g., soil to groundwater pathways, food chain transfer).

The approach adopted for the derivation of Tier 1 levels of PHCs in soils for the protection of ecological receptors is based on a 'weight of evidence' method as outlined in the CCME 1996 Protocol with some modifications. This approach facilitates the incorporation of disparate types of high quality information on the risks of PHCs to ecological receptors by calculating a percentile of the effects data set to estimate a concentration in soil expected to cause no adverse biological effects.

2.7 Incorporating Scientific Uncertainty and Socio-Economic Considerations

Estimates of exposure and risk to receptors related to environmental contamination are subject to many uncertainties and these considerations apply in standards development as well. Indeed, in developing generic standards it is generally necessary to make a number of conservative assumptions concerning uncertain exposure and toxicity factors such that the conservative exposure scenario does not lead to adverse environmental and health effects. Examples of sources of uncertainty include toxic response in humans in relation to test animals, contact rates of biota with contamination (reasonably certain for soil organisms, less certain for humans), construction details affecting entry rates of vapours into enclosed spaces, hydrological factors affecting the rate of contaminant movement between soil and groundwater, soil and groundwater conditions affecting the rate of biodegradation, and variability in primary scientific measurements during toxicity testing. Generally, conservative assumptions are made regarding these uncertainties such that a standard is protective. Many conservative assumptions were made in the development of the PHC CWS.

However, conservatism must be balanced with practical considerations in order to achieve an attainable, yet environmentally protective standard. Provided decisions concerning receptors, pathways, and exposure remain within the scientific uncertainty associated with a conservatively chosen exposure scenario, we can be confident that a protective standard will result. Chapters 3 and 4 include information on the uncertainties considered and the assumptions made in developing the PHC CWS.

2.7.1 Socio-Economic Analyses

Socio-economic analyses were undertaken at two stages in the development of the PHC CWS. A largely qualitative scoping analysis was undertaken at the outset to identify major release scenarios, affected parties, remedial technologies and benefits of their application (ChemInfo Services 1998). This was useful in showing the extreme diversity of PHC releases and the corresponding need for a *general* approach to PHC assessment and management. Such information was influential in pointing the way to a fraction-based approach and a flexible, tiered framework.

In a second stage, a quantitative screening analysis was carried out under the guidance of a multistakeholder advisory committee (Komex 2000). Eleven scenarios were developed to represent the more common and important PHC releases to the geo-environment. Typical volumes of contaminated soil for each scenario were estimated based on exceedance of “seed values” – screening estimates of risk-based Tier 1 guidelines available from the Development Committee in 1999 – and 5-fold adjustments of the seed values up (less stringent case: LS) and down (more stringent case: MS). Site remediation to Tier 1 levels was considered to occur via excavation/landfill for more contaminated material and biotreatment for less contaminated material. For screening purposes, other

technologies were not investigated and no Tier 2 or Tier 3 remediations were considered. Estimated costs of remediation were compared to monetizable benefits including recovery of property value, avoidance of property "blight", and avoidance of agricultural crop damage. Human health and ecological benefits were not monetized.

Under the assumptions and constraints described above, projected costs were roughly 2.5 to 3 times the monetizable benefits. While this outcome appears disjunct from societal experience with PHCs in the geo-environment, it is largely explained by the incomplete monetization of benefits and conservative description of remedial response. Nevertheless, the study describes well the distribution of releases by sector and region and provides useful screening estimates of liabilities under varying standard stringency. Very broadly, the study shows that costs of Tier 1 remediation are in the 10 billion dollar range. Even the LS standard, which includes values exceeding the most liberal guidelines presently in use in Canada, leads to estimated Tier 1 remediation costs of about $5 billion Cdn. Thus, *any* generic remediation standard (for example, merely removing free product) will generate liability estimates in excess of a billion dollars.

Because of the large upstream oil and gas industry in Western Canada (many sites) and the fact that benefits, as monetized in the screening study, are greater in populous areas, about 70% of costs are centred in Western Canada while about 70% of the benefits are in Eastern Canada.

The PHC CWS Development Committee duly considered these screening socio-economic studies in rendering its final risk management recommendations. These recommendations included:

- A tiered framework that encourages acquisition and application of site information useful in refining estimates of exposure and risk;
- Provision for flexible risk management within the framework;
- Inclusion of soil texture and depth within the generic standards;
- Careful selection of receptor and exposure pathways as appropriate to each land use;
- Careful consideration of the model and parameter uncertainty in the major exposure pathways.

Details on how these responses to socio-economic considerations were implemented appear in subsequent chapters.

2.8 Generic Subsoil Levels

One important way in which socio-economic considerations were applied in the PHC CWS is in the development of exposure scenarios and generic levels for subsoils. The rationale for, and details of the development of these generic subsoil levels are presented in Chapter 5. The approach is based on the reduced exposure and hence, risk, posed by contamination at depth. However, it is recognized that a stratified approach to PHC remediation does pose certain potential limitations on use within a land use category. For this reason, the subsoil levels are not considered Tier 1 levels, where remediation to specified levels is consistent with full site use flexibility within a land use category and thus no need for administrative notifications or controls.

3. Human Health Soil Quality Levels

Tier 1 levels for PHCs have been developed for four general land uses (agricultural, residential/parkland, commercial, industrial) and two soil textures (coarse-grained and fine-grained). Surface and sub-surface levels are also developed to account for the location of the contaminant in the soil stratum, recognizing the influence of contaminated soil accessibility and availability on human exposure and health risk.

3.1 Land Uses

The frequency, duration and intensity with which people contact pollutants at a contaminated site are proportional to the nature of the land use. Also, the critical receptor in any land category is dependent on the ease of public access and the activities inherent to that land use. CCME has defined four general land uses for developing PHC soil quality levels: agricultural, residential/parkland, commercial, industrial.

3.1.1 Agricultural

Agricultural land encompasses a wide range of activities including dairy, livestock and/or crop production. Most farms include a homestead so that the land immediately surrounding and beneath the home is assumed to be a residential property to which the assumptions and guidelines for residential land use apply (see below). Agricultural lands are generally accessible by the farmer and his/her family members, including children, which represent the more sensitive human receptor category. Therefore, the critical human receptor in the agricultural land use category is assumed to be a toddler who receives 100% of his/her daily intake of soil and drinking water (groundwater) from the property. For exposure to PHC vapours, it is assumed that agricultural land is at least 30 m from the residential building and that volatile PHCs must migrate a minimum of 30 m through clean soil before reaching and penetrating the building foundation.

3.1.2 Residential/Parkland

The generic residential property assumed for PHC Tier 1 derivation is a typical detached, single family home with a backyard where children, particularly toddlers, play. The critical receptor assumed on a residential property is a toddler who receives 100% of his/her daily intake of soil, drinking water (groundwater), and air (indoors) from the property. Separate Tier 1 levels have been developed for two house foundation construction styles - 1) below-grade concrete foundation wall and floor slab (basement); and 2) concrete slab-on-grade foundation. The two foundation construction styles only affect the indoor infiltration pathway by which volatile PHCs penetrate the building envelope via foundation cracks and gaps.

Parks may serve as areas for children's play and other family activities and are therefore also included in the residential land use category.

3.1.3 Commercial

Commercial properties span a wide variety of uses with varying degrees of public access. For purposes of deriving PHC Tier 1 levels, the generic commercial property is assumed to contain a daycare facility, a sensitive commercial property use that is permitted in many municipal jurisdictions in Canada. It is assumed that the critical receptor (toddler) spends a substantial portion of the weekdays at a daycare. In particular, it is assumed that the toddler spends 10 hours per day, 5 days per week for 48 weeks per year at the daycare. The toddler thereby receives an amount of his/her daily intake of soil, drinking water (groundwater), and air (indoors) from the commercial property proportional to the number of hours per day, days per week and weeks per year spent at the facility. Most commercial buildings are constructed with concrete slab-on-grade foundations. Therefore, PHC Tier 1 levels for commercial properties only consider slab-on-grade foundation construction, which influences the indoor infiltration pathway by which volatile PHCs penetrate the building envelope via foundation cracks and gaps.

3.1.4 Industrial

Industrial properties span a wide variety of uses but generally do not permit direct public access and therefore, children are not likely or frequently present. For purposes of deriving PHC Tier 1 levels, the generic industrial property is assumed to be a site with a building frequented by an adult worker who spends 10 hours per day, 5 days per week for 48 weeks per year on the property. The adult receptor thereby receives an amount of his/her daily intake of soil, drinking water (groundwater), and air (indoors) from the industrial property proportional to the number of hours per day, days per week and weeks per year spent at the facility. Most industrial buildings are constructed with concrete slab-on-grade foundations. Therefore, PHC Tier 1 levels for industrial properties only consider slab-on-grade foundation construction, which influences the indoor infiltration pathway by which volatile PHCs penetrate the building envelope via foundation cracks and gaps.

3.2 Soil Texture

Tier 1 levels for PHCs in soil have been derived herein for both coarse-grained and fine-grained soils. Soil texture is defined herein according to ASTM (2000). Fine textured soils are defined as having greater than 50% by mass particles less than 75 µm mean diameter (D_{50} < 75 µm). Coarse textured soils are defined as having greater than 50% by mass particles greater than 75 µm mean diameter (D_{50} > 75 µm). Simply put, coarse soils are defined as having more than 50% sand by mass and fine soils are defined as having less than 50% sand by mass.

3.3 Exposure Pathways

As discussed in Chapter 2, exposure to PHCs from contaminated soil may occur by a variety of pathways. However, not all of these pathways are relevant for each and every land use. Also, not all pathways are well understood or their parameters adequately quantified for PHC Tier 1 levels derivation. For purposes of deriving Tier 1 levels for PHCs, the following pathways were considered (see Figure 3.1):

(a) inadvertent ingestion of PHC contaminated soil;
(b) dermal absorption of PHCs from contaminated soil deposited on the skin;
(c) inhalation of volatile PHCs emanating from the soil following their infiltration to the indoor environment; and/or
(d) ingestion of soluble PHCs which have infiltrated to, and contaminated, local groundwater used as a source of drinking water.

Following the policies and procedures set out in the CCME Protocol (CCME 1996), the recommended human health-based soil quality level is based on the single pathway that results in the greatest exposure, thereby providing the lowest overall protective numerical Tier 1 value.

3.4 Models and Assumptions

For the purpose of PHC Tier 1 level, human exposure to PHC contamination in soil is assumed to occur primarily via the four pathways described in Section 3.3. Numerous models exist with which to assess these exposures. In selecting models to support Tier ½ objectives, CCME has sought a balance among scientific rigour, complexity, ease of use, transparency and history of use in regulatory decision-making. Appendix C presents the equations developed to derive risk-based Tier 1 levels that ensure that the residual soil contamination will not result in human exposure in excess of prescribed tolerable daily intakes (TDIs) or reference air concentrations (RfCs; applicable to volatile PHCs only).

Calculations performed for vapour intrusion and water ingestion pathways involve partitioning of PHC constituents among dissolved, sorbed and vapour phases. Tier

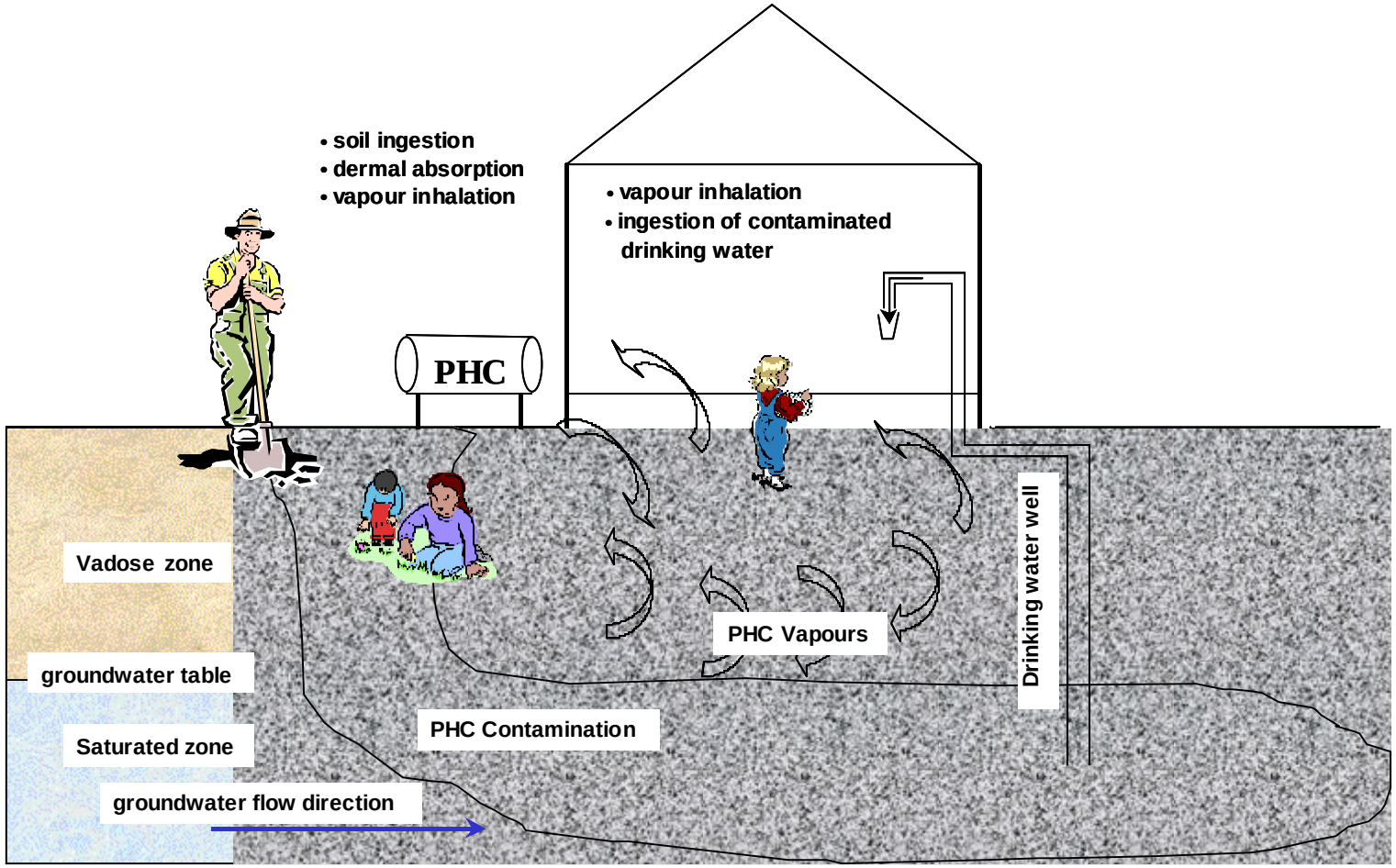


Figure 3.1. Human health exposure pathways to PHC contaminated soil.

1 levels calculated for these pathways are based on the *total* (three phase) soil concentration as would be observed through the analytical method.

3.4.1 Ingestion of PHC-contaminated soil

Inadvertent ingestion of soil can be a significant pathway of human exposure to contaminated soil. Studies indicate that children ingest much greater amounts of soil and dust each day than adults, primarily due to greater hand-to-mouth activity and a greater time spent playing outdoors and on the floor. The equation to estimate risk-based Tier 1 levels that prevent unacceptable exposure via inadvertant direct ingestion of PHC-contaminated soil is presented in Appendix C. This equation is identical to that employed within the Atlantic PIRI tool kit and by CCME (1996).

Assumptions concerning rates of daily soil ingestion by the various critical receptors (toddlers in agricultural, residential and commercial land uses and adults in industrial land uses) are included in Table 3.1.

Table 3.1: Receptor characteristics.

	Toddler [1]	Adult [2]
Body Weight (BW) (kg)	16.5	70.7
Exposure Time (ET) (agricultural)	1	1
Exposure Time (ET) (residential) [3]	1	1
Exposure Time (ET) (commercial) [3]	(10/24)*(5/7)*(48/52)	(10/24)*(5/7)*(48/52)
Exposure Time (ET) (industrial) [3]	(10/24)*(5/7)*(48/52)	(10/24)*(5/7)*(48/52)
Soil Ingestion Rate (SIR) (g/d) [3]	0.08	0.02
Surface Area - hands (SA_{HANDS})(m2)	0.043	0.089
Surface Area - other (SA_{OTHER}) (m2)	0.258	0.250
Dermal Loading to Skin (mg/m2-event) [4]		
Hands (DL_{HANDS})	1000	1000
Surfaces other than hands (DL_{OTHER})	100	100
Exposure Frequency (EF) (events/d)	1	1
Inhalation Rate (IR) (m3/d)	9.3	16.2
Water Ingestion Rate (IR_W) (L/d)	0.6	1.5

(after Richardson, 1997, unless otherwise noted)

1 Toddlers are the critical receptors for residential and commercial (day care) land uses.
2 Adults are the critical receptors for industrial land uses.
3 Source: CCME (1996)
4 Source: Kissel et al. (1996, 1998)

3.4.2 Dermal Absorption of Soil-borne PHCs

In most cases, human skin provides a relatively good barrier to passage of substances into the human body. However, depending on their chemical properties, absorption of some contaminants through the skin is potentially an important route of human exposure. To be absorbed through the skin, the invading substance must pass through the epidermis or through appendages on the skin such as sweat glands or hair follicles. Dermal absorption of organic compounds is primarily limited to substances that are very lipid (fat)-soluble. The equation to estimate risk-based Tier 1 levels that prevent unacceptable exposure via dermal absorption of PHC from contaminated soil deposited to the skin is presented in Appendix C. This equation is identical to that employed within the Atlantic PIRI tool kit. Assumptions concerning exposed skin surface area and soil loading to skin are included in Table 3.1.

3.4.3 Migration To, and Contamination of Groundwater

Protection of potable groundwater was considered in the derivation of the Tier 1 objective for the PHC Tier 1 level for hydrocarbon fractions F1 and F2. The Tier 1 levels for F1 and F2 are intended to provide acceptable drinking water quality on the down-gradient boundary of a site underlain by an unconfined aquifer, as described in Section 2.5.1. Whereas the primary focus in PHC CWS standard development is the prevention of toxic effects to potential receptors, in some cases it is possible that PHC groundwater contamination by fractions F1 and F2 may create taste or odor concerns at concentrations lower than the Tier 1 level concentrations derived to prevent health effects. Unfortunately guidelines for aesthetic factors, such as taste and odor, do not currently exist for broad PHC fractions as defined herein; guidelines for such aesthetic qualities may require future development.

Guidelines for potable groundwater protection for fractions F3 and F4 were not necessary due to their inherent low solubilities and high affinity for adsorption on soil organic carbon which significantly reduces their potential for movement into groundwater.

As shown in Figure 3.1, soil contamination is assumed to extend to the water table, though this assumption can be adjusted in a Tier 2 case if supported by relevant site-specific data. Concentration of PHCs distributed between the adsorbed, dissolved and vapour phases in soil were estimated using the linear partitioning methods described in TPHCWG Vol. 2 (1997). This method assumes there is no free hydrocarbon phase present. PHC partitioned to soil water is assumed to leach to groundwater at a rate determined by groundwater recharge. The PHC-contaminated groundwater recharge is diluted by the lateral groundwater flow as described by the relationship provided in Appendix D of CCME (1996). A Tier I soil objective that protects groundwater quality for human health consumption for PHC fractions F1 and F2 is determined by:

- Back-calculating from the applicable drinking water quality guideline derived from the residual tolerable daily intake for each TPHCWG sub-fraction within the F1

and F2 categories. In this back-calculation, the water quality guideline is multiplied by a dilution factor representing groundwater recharge and lateral flow to estimate the soil porewater concentration at the soil source. Linear partitioning constants are then applied to the porewater concentration to determine the equilibrium soil concentration as shown in Appendix C, and

- Using the algorithm provided for summing TPHCWG sub-fractions provided at the beginning of Appendix C to determine the value for the entire PHC CWS fraction.

Partitioning Relationship

Physico-chemical parameters (including log Koc) for TPHCWG sub-fractions are provided in Table B.1. Based on a review of organic C content of Canadian subsoils conducted for the PHC CWS, Foc was set at 0.5% for both coarse and fine-textured soil.

Dilution Expression

The vertical mixing zone was set at 2 m as described in Section 2.5.1. Other parameters needed for the dilution expression are listed in Table 3.2.

Table 3.2: Additional assumptions required for the migration to groundwater pathway and the indoor infiltration pathway.

Migration to Groundwater

Assumption	Value
Effective Mixing Depth (B) (m)	2
Hydraulic Gradient (*i*) (unitless)	0.05
Site Length (L) (m)	10

Indoor Infiltration

Assumption	Value
Vapour viscosity (μ) (g/cm-s)	1.73 E-04
Gas Constant (R) (atm-m^3/mol-K)	8.20 E-05
Soil temperature (T) (degrees K)	294
Vapour migration path length (L_t) (m)	
Agricultural	30
Residential, commercial, industrial	0.3

The following rationales apply:

- Recharge values were derived from Atlantic PIRI (1999) to reflect high precipitation conditions in the western and eastern coastal regions of Canada. Most other areas in Canada will have lower recharge rates and lower sensitivity to soil-to-groundwater cross contamination;

- A 10 m site length was selected to be representative of upper lateral dimensions at typical small release sites such as oil and gas wellsites and fuel stations. *Note that this value cannot be assumed to be protective at large release sites such as pipeline breaks and refineries. A Tier 2 or 3 approach should be applied in such cases.*

- Hydraulic conductivities were selected to represent a good-yielding aquifer in the coarse textured case and, for the fine textured case, a lower end yield consistent with a threshold transmissivity of 10^{-4} cm/s to support consumptive use for a small family.

Toxicological Benchmark

Toxicological endpoints and reference doses for TPHCWG sub-fractions are given in Table 3.8. A soil allocation factor of 1.0, was used for derivation of Tier 1 soil quality levels protective of potable groundwater, as described in Section 3.8.

3.4.4 Indoor infiltration of Volatile PHCs

The receptor characteristics developed to derive PHC Tier 1 levels to protect against risks posed by the indoor infiltration of PHC vapours from fine-grained soils and coarse-grained soils are presented in Table 3.1. Soil parameters and other site-specific variables assumed for these models are presented in Table 3.3 while assumptions concerning buildings into which the vapours might infiltrate are presented in Table 3.4. Table 3.5 presents assumptions for chemical-specific variables. These models are taken from the work of Johnson and Ettinger (1991).

Table 3.3: Assumed soil characteristics required for the Tier 1 indoor infiltration of vapours pathway.

	Coarse-Grained	Fine-Grained
Retention of grains on a 75 µm screen (D50) (%)	> 50	≤ 50
Saturated Hydraulic Conductivity (K) (m/y)	320	32
Recharge (R) (m/y)	0.28	0.20
Organic Carbon Fraction (f_{OC}) (g/g)	0.005	0.005
Water Content (= Mw/Ms) (θ_m)	0.07	0.12
Soil Bulk Density (ρ_B) (g/cm3)	1.7	1.4
Total Soil Porosity (θ_T)	0.4	0.3
Vapour-Filled Porosity (θ_a)	0.281	0.132
Moisture-Filled Porosity (θ_w)	0.119	0.168
Soil Vapour Permeability to Vapour Flow (K_v) (cm2)	10^{-8}	10^{-9} *
Median particle diameter, D_{50}	> 75 um	< 75 um
Distance from contamination to foundation slab, Lt (cm)**	30 (soil, and subsoil basement scenario) 139 (subsoil, slab-on-grade)	30 139

* not required for Tier 1 calculations.

**a general 30 cm separation between contamination and building slab is assumed, except for subsoil values in slab-on-grade scenarios, where a separation of roughly 139 cm is created by the distance from the bottom of the slab to the defined 150 cm+ depth of subsoil.

Table 3.4: Building characteristics assumed for indoor infiltration pathway.

	Residential Scenario (with basement)	Residential Scenario (slab-on-grade)	Commercial Scenario (slab-on-grade)
Building Length (L_B) (cm)	1225	1225	2000
Building Width (W_B) (cm)	1225	1225	1500
Building Area (A_B) (cm2)	1.50E+06	1.50E+06	3.00E+06
Building Height, including Basement (H_B) (cm)	488	488	300
Thickness of Building Foundation (cm) - L_{crack}	11.25	11.25	11.25
Area of Cracks (cm2) - A_{crack}	994.5	994.5	1846
Radius of Idealized Cylinder (cm) - r_{crack}	A_{crack} / X_{crack}	A_{crack} / X_{crack}	A_{crack} / X_{crack}
Length of Idealized Cylinder (cm) - X_{crack}	4900	4900	7000
Distance below grade to Idealized Cylinder (cm) - Z_{crack}	244	11.25	11.25
Air Exchanges per Hour (ACH) (h^{-1})	1	1	2
Pressure Differential (ΔP) (g/cm-s2)	40	40	20
Diffusivity in cracks, D^{crack}, (cm2/sec)	4.5E-04	4.5E-04	4.5E-04

Table 3.5: Chemical-specific assumptions required for the indoor infiltration of vapours pathway and/or the migration to groundwater pathway.

AROMATICS	**$C_{>7}$ - C_8**	**$C_{>8}$ - C_{10}**	**$C_{>10}$ - C_{12}**	**$C_{>12}$ - C_{16}**	**$C_{>16}$ - C_{21}**	**$C_{>21}$ - C_{34}**	**$C_{>34}$ - C_{50}**
Tolerable Daily Intake (TDI) (mg/kg/d) [a]	0.2	0.04	0.04	0.04	0.03	0.03	0.03
Estimated Daily Intake (EDI) (mg/kg/d) [b]	0.00477	0.00938	0	0	0	0	0
Reference Concentration (RfC) (mg/m3) [a]	0.4	0.2	0.2	0.2	NA	NA	NA
Background Indoor/Outdoor Air Conc'n (C_a) (mg/m3) [b]	0.01776	0.03745	0	0	0	0	0
Henry's Law Constant (H) (atm-m3/mol) [a]	6.49E-03	1.20E-02	3.40E-03	1.30E-03	3.10E-04	1.61E-05	4.40E-07
Organic Carbon Partition Coefficient (K_{OC}) (mL/g) [a]	$10^{2.4}$	$10^{3.2}$	$10^{3.4}$	$10^{3.7}$	$10^{4.2}$	$10^{5.1}$	$10^{6.25}$
Diffusion Coefficient in Air (D_a) (cm2/s) [c]	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Diffusion Coefficient in Water (D_w) (cm2/s) [d]	n/c	n/c	n/c	n/c	n/c	n/c	n/c
Absorption Factor for Gastrointestinal Tract (AF_G) (unitless) [e]	1	1	1	1	1	1	1
Absorption Factor for Skin (AF_D) (unitless) [e]	0.2	0.2	0.2	0.2	0.2	0.2	0.2

ALIPHATICS	**$C_{>6}$ - C_8**	**$C_{>8}$ - C_{10}**	**$C_{>10}$ - C_{12}**	**$C_{>12}$ - C_{16}**	**$C_{>16}$ - C_{21}**	**$C_{>21}$ - C_{34}**	**$C_{>34}$ - C_{50}**
Tolerable Daily Intake (TDI) (mg/kg/d) [a]	5	0.1	0.1	0.1	2	2	20
Estimated Daily Intake (EDI) (mg/kg/d) [b]	0.02334	0.0103	0	0	0	0	0
Reference Concentration (RfC) (mg/m3) [a]	18.4	1	1	1	NA	NA	NA
Background Indoor/Outdoor Air Conc'n (C_a) (mg/m3) [b]	0.09111	0.03881	0	0	0	0	0
Henry's Law Constant (H) (atm-m3/mol) [a]	1.2	1.9	2.9	12.5	118	13500	2.90E+06
Organic Carbon Partition Coefficient (K_{OC}) (mL/g) [a]	$10^{3.6}$	$10^{4.5}$	$10^{5.4}$	$10^{6.7}$	$10^{8.8}$	10^{13}	$10^{18.2}$
Diffusion Coefficient in Air (D_a) (cm2/s) [c]	0.05	0.05	0.05	0.05	0.05	0.05	0.05

Diffusion Coefficient in Water (D_w) (cm2/s) [d]	n/c	n/c	n/c	n/c	n/c	n/c	n/c
Absorption Factor for Gastrointestinal Tract (AF_G) (unitless) [e]	1	1	1	1	1	1	1
Absorption Factor for Skin (AF_D) (unitless) [e]	0.2	0.2	0.2	0.2	0.2	0.2	0.2

Footnotes to Table 3.5

a - based on TPHCWG

b - incorporated where data permit; estimated by OAEI

c - recommended by PIWG

d - not considered (n/c) as the contribution due to diffusion through the soil moisture will be insignificant in comparison with vapour-phase diffusion

e - assumed

NA - not available

Johnson and Ettinger (1991) provided one of the first screening level models to assess potential risks posed by the indoor infiltration of volatile contaminants emanating from soil and/or groundwater, and it has become a widely accepted work in this area. A risk assessment modelling tool based on Johnson and Ettinger (1991) has been published by the U.S.EPA (1997), and a modified version of the Johnson and Ettinger model has been adopted within ASTM Standard 1739-95 (RBCA) (ASTM 1995) and subsequently by the Atlantic Provinces PIRI initiative. Such models are routinely used in Canada and elsewhere for assessment of soil-borne volatile contaminants, particularly petroleum hydrocarbons.

Johnson and Ettinger (1991) demonstrated the mathematical rigour of their model by solving for a number of hypothetical, limiting situations. This work demonstrated that the solutions to these limiting cases agreed with what was anticipated theoretically. As yet there are insufficient data from field trials or controlled experimentation on full scale buildings to 'field validate' the model. However, laboratory research has demonstrated the validity of various components, at least at bench scale.

3.4.4.1 Mass Transfer Phenomena Controlling Vapour Migration Through Soil. A modified version of the Johnson and Ettinger model has been adopted within ASTM Standard 1739-95 (RBCA) (ASTM 1995). The primary modification within RBCA is the omission of advective (also termed convective) vapour transport through cracks and spaces in the building envelope at Tier 1. Although all the Johnson and Ettinger equations (and quantification of the necessary variables) are provided within RBCA, the RBCA Tool Kit assigns the critical variable for advective flow (Q_{soil}) a value of zero for the default case. This effectively restricts the model to diffusion-driven infiltration only. No explanation is provided within the RBCA documentation to rationalize or justify this modification. However, Nazaroff et al. (1985, 1987) report Q_{soil} values ranging from 280 cm^3/s to 2800 cm^3/s for indoor to outdoor barometric pressure differentials of 5 to 30 Pa (lower pressure indoors). Given that such pressure differentials are routinely observed in the range up to 12 Pa, depending on construction details (CMHC 1997), then the default assumption of $Q_{soil} = 0$ is inappropriate in all default cases.

Numerous authors indicate that advective (pressure-driven) flow, which moves volatile contaminants from the soil-foundation interface into the living space of the building under a net negative barometric pressure differential (possibly due to wind effects, temperature differentials, appliance fans, stack effect, etc.) must be considered when quantifying the indoor infiltration and potential health risks of soil-borne volatile hydrocarbons (Johnson and Ettinger 1991; CMHC 1997; Williams et al. 1996; U.S.EPA 1997; Hers and Zapf-Gilje 1999; Little et al. 1992; and references therein). Coarse-grained soils such as sand lack significant resistance to air flow in the soil matrix. Therefore, advective flow must be considered for coarse-textured soils and building characteristics and site features that influence advective flow must be defined.

For fine-grained soils, however, the 'tightness' of these soils and their consequently lower air space, diffusivity and permeability characteristics are anticipated to inhibit air flow through the soil matrix. As a result, only diffusion of volatile components of PHCs are considered for fine-textured soils.

Careful consideration of soil properties influencing diffusive and advective flow was undertaken in the preparation of the Tier 1 levels. Under conditions differing from those specified for Tier 1 levels (i.e., at Tier 2) it will be necessary to consider the potential contributions of both mechanisms of vapour movement.

3.4.4.2 Site Characteristics Required for Indoor Infiltration Modelling. Indoor to outdoor pressure differential (ΔP):

Recommended values are:

- Residential buildings: 4.0 Pa
- Commercial buildings: 2.0 Pa
- Industrial buildings: 2.0 Pa

One of the over-riding factors contributing to advective flow of volatile contaminants to the indoor environment is a net negative pressure differential in indoor environments, relative to outdoor environments. Indoor to outdoor barometric pressure differences have been investigated by a variety of researchers (reviewed by U.S.EPA 1997; CMHC 1997; Johnson and Ettinger 1991). In general, a net negative pressure difference on the order of 1 to 12 Pa has been observed, with this pressure difference being observed primarily during the heating season, and being influenced by factors such as house height, presence/absence of chimney, presence/absence of appliance fans, below grade versus slab on grade construction (CMHC 1997). CMHC (1997) indicates that pressure differentials between the indoor and outdoor environment during the winter heating season for 1 or 2 storey dwellings span from 2 Pa (no chimney, mild winter) to 12 Pa (severe winter, chimney, no fresh air intake for combustion air supply, frequently used exhaust fan and/or fireplace). The expected modal or average condition during winter would be a 7 Pa negative pressure differential. Assuming that the heating season lasts 6 months, and that a zero pressure difference exists for the remainder of the year, then the annual average or typical pressure differential would be 4 Pa (rounded to one significant digit from a value of 3.5 Pa). Application of an annual average pressure differential is appropriate in the derivation of Tier 1 levels for PHCs because chronic exposures ($\geq$ 365 days) are being considered and chronic reference doses and reference air concentrations are being applied to prevent potential health effects.

For commercial and industrial buildings, a lower default negative pressure differential of 2 Pa was selected. Commercial and industrial buildings are expected to maintain a lower overall pressure differential, compared to residential buildings, because of forced, calibrated air exchange designed into heating systems, and due

to the more regular and routine movement of building occupants into and out of the structure.

3.5 Air exchange rates

- Residential buildings: 1.0 ach
- Commercial buildings: 2.0 ach
- Industrial buildings: 2.0 ach

Information on air exchange rate (or air changes per hour; ACH) is required to estimate the degree of dilution of infiltrating PHC vapours in fresh (uncontaminated) indoor air. A large variety of studies have been published documenting measurements of ACH in homes. Most of those studies suggest an average ACH of between 0.3 and 0.5 for homes in Canada or homes from northern regions of the United States. However, these ACH measurements are routinely collected with conditions that simulate Canadian winter conditions: all windows and doors tightly closed. Also, these measurements are often taken in unoccupied homes. As a result, average ACH values from reported data generally do not reflect typical 'lived-in' house conditions, nor do they reflect annual average conditions. Pandian et al. (1993) reported data collected on air change rates for more than 4000 U.S. homes. Their data include measurements collected during all four seasons. Average summer measurements were between 2.8 times greater, 13.5 times greater, and 10.8 times greater than measurements collected in spring, fall and winter, respectively. The fact that ACH increases significantly with open doors and/or windows is corroborated by Otson et al. (1998) and Lamb et al. (1985).

CMHC (1997) indicates that more recently built residences have lower ACH than older homes. CMHC suggests that ACH values for homes built pre-1960 may range from 2 to 10 times greater than recently constructed 'airtight' homes. This is generally supported by data from Pandian et al. (1993), Grimsrud et al. (1983), Gerry et al. (1986) and King et al. (1986) and likely reflects building practices which increase energy efficiency in more recent construction. Based on data presented by Grimsrud et al. (1983) the geometric mean ACH for homes built prior to 1970 was 0.69, whereas homes built during or after 1970 had a geometric mean ACH of 0.46. This difference was statistically significant.

ACH values for multi-level homes tend to be greater than ACH values for single storey residences. Pandian et al. (1993) report ACH values of 0.6 and 2.8 for one-level and two-level homes, respectively. Data from Grimsrud et al. (1983) indicate geometric mean ACH values of 0.47 and 0.52 for one-level and two-level homes, respectively. Again, these latter values are statistically significantly different.

Data comparing natural air exchange rates in commercial properties are limited compared to residential homes. Greater door traffic is anticipated to result in greater natural air exchange in commercial versus residential buildings. Data

reported by Kailing (1984) on natural air exchange rates indicate ACH values ranging from 0.09 to 1.54 for commercial structures compared to 0.01 to 0.85 for residences. Many commercial properties (especially malls and other large facilities) will have mechanical ventilation systems to maintain adequate ventilation to ensure indoor air quality (see ASHRAE Standard 62-1989, for example). Sherman and Dickerhoff (1994) and Weschler et al. (1996) report ACH values of 1.5 to 1.8 ACH for small commercial buildings under mechanical ventilation.

Diffusional path length for volatile PHCs

For residential, commercial and industrial properties, it has been assumed that the soil-borne PHC contamination is a minimum of 30 cm (L_t = 0.3 m) from the building foundation. The PHC vapours must migrate through this 0.3 m of clean fill before reaching and penetrating the building foundation. When L_t is less than 0.3 m, a Tier 2/3 analysis is required because the performance of the vapour intrusion model is uncertain in this parameter range. Soil gas to indoor air dilution factors for a range of values of $L_T \geq 0.3$ m, for both fine-grained and coarse-grained soils are presented in Table 3.6.

Table 3.6: Soil gas to indoor air dilution factor (DF) as a function of depth/distance from building to contamination (L_t).

	Dilution Factors for Indoor Infiltration (DF)					
L_T (cm)	Residential, with basment		Residential, slab-on-grade		Commercial/Industrial, slab-on-grade	
	f/g	c/g	f/g	c/g	f/g	c/g
30	512931	23142	512931	14350	678631	44825
100	527516	25231	527516	16439	696563	47394
200	548351	28216	548351	19424	722181	51063
300	569187	31201	569187	22409	747799	54733
500	610859	37170	610859	28378	799034	62073
1000	715038	52094	715038	43302	927123	80422
2000	923396	81942	923396	73150	1183301	117120
3000	1131754	111790	1131754	102998	1439479	153818

For agricultural land uses, the homestead site is considered residential land use and PHC contamination located on the homestead site is subject to the 0.3 m path length applicable to the derivation of residential Tier 1 levels for volatile PHCs. However, where PHC contamination is located in agricultural fields, it is assumed that PHC vapours must migrate 30 m through clean soil before reaching and penetrating the residential structure (farm homestead). This separation distance was selected to be consistent with minimum setbacks required for oil and gas development in Canada.

3.6 Receptor Characteristics

The critical human receptor, that may experience the hypothetical (modeled) exposure to PHCs, is dependent on the prescribed land use. For residential land use, the critical receptor is assumed to be a toddler, that has the greatest exposure (on a dose per unit body weight basis) of any age group. Likewise for commercial properties, the toddler was selected as the critical receptor due to the possible operation of day care facilities, which are permitted by all provincial and municipal zoning bylaws in Canada. For industrial properties, an adult was identified as the critical receptor due to the (generally) restricted public access to such sites.

The receptor characteristics relevant to developing Tier 1 human health-based soil quality values for PHCs include body weight, inhalation rate, water ingestion rate, soil ingestion rate, skin surface area, exposure duration, soil loading to skin. Receptor characteristics assumed for purposes of deriving soil quality quidelines for PHCs under the Canada Wide Standard are summarized in Table 3.1.

Available Canadian studies on exposure factors were identified and analysed by Richardson (1997). The purpose was to thoroughly and critically evaluate Canadian data, in a fashion similar to that undertaken by the U.S.EPA in their *Exposure Factors Handbook*. Additionally, through extensive biostatistical analyses, Richardson (1997) proposed statistically-derived probability density functions to facilitate defensible probabilistic risk assessments. Therefore, where Canadian data exist, receptor characteristics required to derive soil quality levels have been defined from the data presented by Richardson (1997). In cases where empirical Canadian data do not exist for receptor characteristics (soil ingestion rate, for example), alternate sources for assumptions have been used. These included, in order of preference:

- *A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* (CCME 1996);
- *Human Health Risk Assessment for Priority Substances* (HC 1994); and
- Relevant published scientific literature.

3.6.1 Body weight

Recommended values:

- Adult: 70.7 kg
- Toddler: 16.5 kg

Recommended body weights represent arithmetic average values from empirical Canadian data as presented by Richardson (1997). These data were derived from three Canadian surveys conducted in 1970-72, 1981 and 1988 (Demirjian 1980, CFLRI 1981, CFLRI 1988). Toddler body weight was based on data from Demirjian (1980), but adjusted for evident weight increases in the Canadian population observed between 1970 and 1988. Adult body weight was based on CFLRI (1988).

These values are based on the most recent, publicly available data in Canada; the same data upon which Health Canada (1994) recommended deterministic assumptions for risk assessments. These body weight values have also been adopted for use by the Atlantic provinces within the PIRI Tool Kit and are now widely employed throughout Canada for contaminated site risk assessments.

3.6.2 Inhalation rate

Recommended values:

- Adult: 16.2 m^3/24 hours
- Toddler: 9.3 m^3/24 hours

Recommended inhalation rates were taken from Richardson (1997) and Allan and Richardson (1998). These inhalation rates were based on a Monte Carlo simulation incorporating quantitative time-activity data with minute volume data for various levels of physical activity for each age group considered. The methods for derivation of these inhalation rates have been published in the peer-reviewed scientific literature (Allan and Richardson 1998). The recommended values are slightly conservative (higher) compared to those based on metabolic studies (see Layton 1993). These inhalation rate values have been adopted by Atlantic provinces for the PIRI Tool Kit and are now widely used in contaminated site risk assessments in Canada.

3.6.3 Water ingestion rate

Recommended values:

- Adult: 1.5 L/day
- Toddler: 0.6 L/day

Recommended water ingestion rates were taken from Richardson (1997). Adult water intake rate was based on NHW (1981). The toddler rate was based on data presented by Ershow & Cantor (1989), as the data in NHW (1981) did not adequately represent younger age groups. For adult intake, the original raw data from NHW (1981) have been lost. Therefore, Monte Carlo analysis of water ingestion rate frequencies derived from the original survey data were undertaken to simulate the original data and to generate standard deviations for these age groups.

For toddlers, Canadian data do not exist. Therefore, a mean rate was derived by calculating a weighted mean for sub-groups reported by Ershow & Cantor (1989) within the desired age range. Mean rates reported by Ershow & Cantor (1989) for adults and teens were within 0.1 L/day of mean rates reported by NHW (1981). Therefore, data for younger age groups from Ershow & Cantor were assumed to be representative of Canadians in the same age groups. The recommended assumptions concerning drinking water intake have been adopted by the Atlantic

provinces within the PIRI Tool Kit and are now widely employed throughout Canada for contaminated site risk assessments.

3.6.4 Soil ingestion rate

Recommended values:

- Adult: 20 mg/day
- Toddler: 80 mg/day

Unintentional ingestion of soil occurs in all age groups of the population (Sedman and Mahmood 1994). This results from the mouthing of unwashed hands and other surfaces, from transfer from unwashed hands to food, and from the ingestion of inhaled dirt particles deposited in the mouth and upper respiratory tract which are transferred to the esophagus by ciliary action, etc. Quantitative data concerning the inadvertent ingestion of soil by Canadians are not available. Available data on soil ingestion are limited and extremely uncertain (U.S.EPA 1997). Recent studies by Stanek and Calabrese (and co-workers) (Stanek et al. 1998, 1999, Stanek and Calabrese 1994a,b, 1995, among others) have employed tracer techniques whereby 6 to 8 inorganic tracer elements are quantified in soil, diet and human faeces in order to determine the net content in faeces that might originate from soil. However, the different tracers provide inconsistent estimates, with some occasionally suggesting negative ingestion rates.

As a result of the lack of Canadian data, and the uncertainty in existing soil ingestion data, assumptions regarding this variable are still considered “best professional judgement”. Therefore, for consistency with previous methods and assumptions regarding soil ingestion by different age groups of the Canadian population, the assumptions presented within the CCME *Protocol* (CCME, 1996) have been adopted for derivation of Canada Wide Standards for PHCs.

3.6.5 Skin surface area

Recommended values:

- Adult:
  - hands: 890 cm^2
  - Other (upper and lower arms): 2500 cm^2
- Toddler:
  - hands: 430 cm^2
  - other (upper and lower arms + upper and lower legs): 2580 cm^2

Recommended skin surface areas were taken from Richardson (1997). These values are based on equations developed by U.S.EPA for estimating skin surface area from measurements of weight and height; Canadian weight and height data were then employed for calculations of skin surface areas of various body parts.

Assumptions proposed by Richardson (1997) on skin surface area have been adopted within PIRI Tool Kit by the Atlantic provinces, and are now routinely employed for site-specific risk assessments across Canada.

3.6.6 Soil to Skin Adherence

Recommended values:

- adult and toddler:
  - hands: 0.1 mg/cm^2
  - other: 0.01 mg/cm^2

Recent research on soil loading to skin, from both field and controlled trials, has been published by Kissel et al. (1996, 1998). Loadings are consistently greatest on the hands, with lower loadings to face, forearms and lower legs. Loadings are generally greater for activities involving direct contact with soil (gardening, pipe laying, for example). Duration of activity has little or no significant influence on total loading to the hands. Loadings of moist soil are about an order of magnitude greater than loadings of dry soil. Loadings on children and adults engaged in similar activities are not markedly different.

From these studies, loadings to hands for typical activities anticipated on residential and commercial properties ranged from 0.019 to 0.19 mg/cm^2 with an arithmetic average value of 0.075 mg/cm^2. Loadings to leg and arm surfaces for these same activities ranged from 0.0008 mg/cm^2 to 0.023 with an arithmetic average of 0.0077 mg/cm^2. Based on these data, an assumption of 0.1 mg/cm^2 for hands, and 0.01 mg/cm^2 for exposed surfaces of other body parts (arms, legs, face), are appropriate.

3.6.7 Exposure frequency

Recommended values are:

- Agricultural land use: 365 days/year
- Residential land use: 365 days/year
- Commercial land use: 100 days/year
  - 10 hr/d x 5 d/wk x 48 wk/yr
- Industrial land use: 100 days/year
  - 10 hr/d x 5 d/wk x 48 wk/yr

Recommendations concerning exposure frequency, for derivation of Canada Wide Standards for PHCs, were adopted from CCME (1996) to maintain consistency with previous methods and assumptions regarding exposure frequency for soil quality guidelines derivation and site-specific risk assessment in Canada.

3.6.8 Exposure duration

For purposes of deriving Canada Wide Standards for PHCs, shorter-than-lifetime exposures were not amortized (averaged) over a lifetime (70 years). Therefore,

explicit definition of a default exposure duration is not required for derivation of Tier 1 soil quality levels.

3.6.9 Route-specific absorption rates

3.6.9.1 Ingestion. Tolerable daily intakes (reference doses) for environmental contaminants are normally derived based on delivered dose, rather than the absorbed dose. Therefore, it has been assumed that the relative gastrointestinal absorption rate for all PHCs is 100%.

3.6.9.2 Inhalation. Tolerable air concentrations (TCs) (RfCs) for volatile environmental contaminants are normally derived based on the exposure concentration in test subjects or animals, rather than the absorbed dose. For those PHCs lacking TCs (RfCs), little or no data exist to accurately quantify respiratory absorption. However, such absorption does approach 100% for various individual hydrocarbon compounds. Therefore, it has been assumed that the relative respiratory absorption rate for all PHCs is 100%.

3.6.9.3 Dermal. There are two basic approaches used to quantify absorption following dermal exposure: 1) a total absorption factor; and 2) to define absorption rate as a function of the duration of dermal contact (Ryan et al. 1987). A total absorption factor, typically as a percent relative to ingestion exposure, is routinely employed for the derivation of generic soil quality guidelines (MADEP 1991, OMEE 1997). However, for site-specific risk assessment, the flux of contaminant penetrating the skin (mg/cm^2-hour) may be combined with information on duration of exposure to provide a more (theoretically) accurate estimate of dermal absorption (Ryan et al. 1987, U.S.EPA 1992a).

For the purpose of prescribing soil quality levels for the CWS PHC initiative, it is recommended that a total absorption factor approach be employed. This recommendation is based on the following:

- the nature of the generic Tier 1 derivation process prevents an accurate quantification of the duration of dermal loading;

- the uncertainties introduced by the total absorption factor approach are not anticipated to significantly increase the overall uncertainty in Tier 1 derivation, given the numerous uncertainties inherent in other assumptions made in the process.

The dermal absorption of aromatic and aliphatic petroleum fractions has been reviewed by the Agency for Toxic Substances and Disease Registry (ATSDR 1999a), but studies on the total applied dose absorbed or on skin penetration rates have not been published for the vast majority of hydrocarbon compounds. The

dermal absorption of benzene, toluene, ethylbenzene and xylenes has been summarized by the ATSDR (1995a, 1997, 1998,1999b). Generally less than 1% of a dermally-applied dose of benzene was absorbed following single dermal applications in both humans and animals (ATSDR 1997). Dermal absorption of a single dermal application of ethybenzene resulted in 3.4% absorption (ATSDR 1995b). Research indicates that absorption of a single dermal application of PAHs in an organic solvent may amount to between 50 and 80% of applied dose, but declines to less than 20% when the PAHs were applied in a soil matrix (ATSDR 1995b).

Tsuruta (1982) determined that the skin penetration rate (nMoles/cm^2-min) of volatile hydrocarbons decreased in the following order:

> benzene > toluene > styrene > ethylbenzene > o-xylene > n-pentane > 2-methylpentane > n-hexane > n-heptane > n-octane

This research indicated that, for volatile aliphatic and aromatic hydrocarbons at least, the skin penetration rate is generally proportional to water solubility (with more soluble compounds penetrating the skin at a greater rate) and that aromatic compounds are absorbed at a greater rate than aliphatic compounds of similar carbon number.

It has also been noted that dermal absorption from a soil matrix is less than dermal absorption from an aqueous solution and of the pure compound (U.S.EPA 1992a; see also ATSDR 1995b). This seems particularly true for chlorinated organics such as dioxins and may be a function of compound interactions with organic carbon (U.S.EPA 1992a).

Relative absorption factors (RAFs) have been proposed by the Ontario Ministry of Environment and Energy to quantify dermal absorption for the purpose of deriving generic soil quality guidelines (OMEE 1997). The RAF values defined by OMEE for hydrocarbon compounds are presented in Table 3.7. These values were adopted from the Massachusetts Department of Environmental Protection (MADEP 1989, 1991). OMEE RAF values for hydrocarbon compounds range from 8% (benzene) to 26% (phenol, 2,4-dimethylphenol) with the majority of hydrocarbon RAF values being 20%.

Based on the foregoing discussion, it is recommended that an absorption factor of 20% be applied to the derivation of soil quality levels for all aromatic and aliphatic PHC fractions. Although it is anticipated that dermal absorption will decrease with increasing carbon number (decreasing solubility), data are insufficient to prescribe a rigorous and defensible regression analysis with which to derive separate dermal RAF values for each TPHCWG PHC sub-fraction.

Table 3.7: Ontario Ministry of Environment and Energy relative absorption factors for dermal exposure.

CHEMICALS	OMEE RAF
Acenaphthene	0.2
Acenaphthylene	0.18
Anthracene	0.29
Benzene	0.08
Benzo(a)anthracene	0.2
Benzo(a)pyrene	0.2
Benzo(b)fluoranthene	0.2
Benzo(g,h,i)perylene	0.18
Benzo(k)fluoranthene	0.2
Chrysene	0.2
Dibenzo(a,h)anthracene	0.09
Dimethylphenol, 2,4-	0.26
Ethylbenzene	0.2
Fluoranthene	0.2
Fluorene	0.2
Indeno(1,2,3-cd)pyrene	0.2
Methylnapthalene	0.1
Naphthalene	0.1
Phenanthrene	0.18
Phenol	0.26
Pyrene	0.2
Styrene	0.2
Toluene	0.12
Xylenes (Mixed Isomers)	0.12

(from OMEE 1997)

3.7 Tolerable Daily Intakes and Reference Concentrations for TPHCWG Sub-fractions

3.7.1 Application of RfCs Versus TDIs

Soil quality levels for PHCs were derived for non-carcinogenic PHCs only. Soil quality levels for carcinogenic PHCs (benzene, PAHs) have been published elsewhere (CCME 1997). These carcinogenic components, as well as toluene, ethylbenzene and xylenes should be directly quantified and subtracted from total PHC contamination prior to application of these PHC Tier 1 levels (see Chapter 6 for analytical methods and methods for quantification of PHC concentrations).

The Development Committee for Canada Wide Standards for PHCs has opted to employ route-specific reference exposure levels for the derivation of soil quality levels for those PHCs. Route-specific reference levels are considered most appropriate for Tier 1 derivation. This eliminates necessary adjustment for relative absorption efficiencies when TDIs are applied to inhalation exposures, for example, and also eliminates the necessary assumption that the toxic effect(s) are independent of exposure route. Therefore, RfCs were applied for derivation of Tier 1 levels for PHC fractions that are volatile (F1 and F2) and for those pathways involving indoor or outdoor inhalation of vapours (penetration of the building envelope with indoor inhalation (agricultural - 30 m offset, residential, commercial, industrial). For PHC fractions considered non-volatile (F3 and F4) or for those pathways involving exposure routes other than inhalation (direct soil ingestion, ingestion of contaminated groundwater, dermal absorption), tolerable daily intakes (TDIs, also known as reference doses (RfDs)) were applied.

RfCs are defined by the U.S. Environmental Protection Agency (U.S.EPA 2000) as an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. RfCs are analogous to TDIs. As with TDIs, RfCs are derived with the application of uncertainty factors to address, among other considerations, potential human receptors with greater sensitivity to effects, compared to the norm. One such potential sensitive receptor group is toddlers, young children being potentially more sensitive to effects than adults. Given the application of an uncertainty factor for potentially-sensitive receptors, the Development Committee considers RfCs to provide adequate human health protection for all age groups.

RfCs were derived by the TPHCWG, following methods delineated by the U.S. EPA (1994a), for aromatic and aliphatic sub-fractions spanning C_6 to C_{16} (Edwards et al. 1997).

3.7.2 Toxicology of PHCs

An extensive review of the toxicity of components and fractions of PHCs has been presented by Edwards et al. (1997), along with the derivation of tolerable daily

intakes (TDIs) and reference air concentrations (RfCs) for the petroleum hydrocarbon sub-fractions defined by the TPHCWG. Edwards et al. (1997) reviewed available toxicological studies for individual compounds falling within the prescribed TPHCWG sub-fractions and also reviewed available toxicological investigations of a variety of petroleum hydrocarbon mixtures. As a result of that review, the TDIs and RfCs outlined in Table 3.8 were established. Those reference exposure values were based on studies investigating the indicated toxicological endpoints (hazards) and it is anticipated, based on current knowledge and on current reference level derivation methods, that they should prevent such hazards from arising in the vast majority of the population throughout lifelong exposure. It should be noted that reference values were generally derived from exposure levels that were free of observable effects (i.e., no-observed-adverse-effect-levels; NOAELs) in exposed animals.

3.7.2.1 Aromatics. For aromatics in the $C_{>7}$ to C_8 range, styrene is the only compound for which toxicological data are available once benzene, toluene, ethylbenzene and xylenes (BTEX) are deducted. The U.S.EPA (2000) has published a TDI for styrene of 0.2 mg/kg-d. This is based on a sub-chronic oral study in beagle dogs in which increased numbers of Heinz bodies in the red blood cells (RBC), decreased packed cell volume, and sporadic decreases in hemoglobin and RBC counts were observed at the higher dose levels. In addition, increased iron deposits and elevated numbers of Heinz bodies were found in the livers. The TDI was derived from the NOAEL of 200 mg/kg-day and an uncertainty factor of 1000 (10 for intraspecies variability, 10 for interspecies variability, and 10 for extrapolation of subchronic effects to chronic effects).

The U.S.EPA (2000) has also established an RfC of 1.0 mg/m3 based on a NOAEL from human occupational studies investigating effects on the central nervous system. However, the published RfC for toluene is lower, at 0.4 mg/m3. Despite toluene being excluded from PHCs in this range (as they are analyzed separately and deducted from total PHCs), the TPHCWG opted to apply the lower RfC for toluene to the remaining PHCs in the $C_{>7}$ to C_8 range.

In the $C_{>8}$ to C_{16} range, eight aromatic hydrocarbon compounds (isopropylbenzene, naphthalene, acenaphthene, biphenyl, fluorene, anthracene, fluoranthene, pyrene) exist for which TDIs and/or RfCs were published by the U.S.EPA. In addition, unpublished data on the effects of oral exposure of rats to a mixture of naphthalene/methylnaphtalenes were available to the TPHCWG, along with a variety of published studies on the effects of inhalation exposure to C_9 aromatics in rats and mice, from which TDIs or RfCs could be derived (following EPA methodology). Published or derived TDIs ranged from 0.03 mg/kg-d to 0.3 mg/kg-d for the various compounds and mixtures. Only two published RfCs existed (isopropylbenzene = 0.09 mg/m^3; naphthalene = 0.0013 mg/m^3), while the RfC

Table 3.8: Toxicological endpoints for tolerable daily intakes (reference doses) and reference concentrations developed by the Total Petroleum Hydrocarbon Criteria Working Group.

TPH Sub-fraction	TDI	RfC	Critical Effect
Aliphatics			
C_6-C_8	5.0	18.4	Neurotoxicity
$C_{>8}$-C_{10}	0.1	1.0	Hepatic and hematolotical changes
$C_{>10}$-C_{12}	0.1	1.0	Hepatic and hematolotical changes
$C_{>12}$-C_{16}	0.1	1.0	Hepatic and hematolotical changes
$C_{>16}$-C_{21}	2.0	N/A [1]	Hepatic granuloma
$C_{>21}$-C_{34}	2.0	N/A	Hepatic granuloma
$C_{>34}$	20.0	N/A	Hepatic granuloma
Aromatics			
$C_{>7}$-C_8	0.2	0.4	Hepatotoxicity, neurotoxicity
$C_{>8}$-C_{10}	0.04	0.2	Decreased body weight
$C_{>10}$-C_{12}	0.04	0.2	Decreased body weight
$C_{>12}$-C_{16}	0.04	0.2	Decreased body weight
$C_{>16}$-C_{21}	0.03	N/A	Nephrotoxicity
$C_{>21}$-C_{34}	0.03	N/A	Nephrotoxicity
$C_{>34}$	0.03	N/A	Nephrotoxicity

(from Edwards et al. 1997)

[1] N/A = not applicable; sub-fraction of PHCs is not sufficiently volatile to present air-borne exposure.

derived for C_9 aromatics was 0.2 mg/m^3. In consideration of the range of TDI values, and emphasizing studies of mixtures (for RfC determination), the TPHCWG selected a TDI of 0.04 mg/kg-d and an RfC of 0.2 mg/m^3 for aromatic petroleum hydrocarbon sub-fractions in the $C_{>8}$ to C_{16} range.

For aromatic PHCs in the $C_{>16}$ range, there are no published TDIs or RfCs, nor available data, for surrogates or mixtures in this range. Therefore, the TDI for pyrene (C_{16}) was selected to be applied to aromatic sub-fractions in the $C_{>16}$ range. No RfC was defined, as PHCs with $C_{>16}$ are insufficiently volatile to pose an inhalation risk.

3.7.2.2 Aliphatics. Within the aliphatic sub-fraction C_6 to C_8, n-hexane is the only compound for which the U.S.EPA has established a TDI, that value being 0.06 mg/kg-d. However, toxicity data for a variety of other hydrocarbons exists, which has been reviewed by Edwards et al. (1997). These hydrocarbons include cyclohexane, methylpentanes and methylcyclohexane. Also, data exist on commercial hexanes, and mixture containing 53% or less n-hexane. An analysis of petroleum products (Edwards et al. 1997) indicated that the n-hexane content of the $C_{>5}$ to C_8 sub-fraction of petroleum products and crude oils was generally less than 20%, while the n-hexane content of commercial hexane was 53%. Therefore, it is inappropriate to apply the TDI for n-hexane to the entire C_6 to C_{10} aliphatic sub-fraction. Toxicological investigations indicate that commercial hexane is some 80 times less toxic than n-hexane (TDIs are 5 mg/kg-d and 0.06 mg/kg-d for commercial hexane and n-hexane, respectively), suggesting a strong inhibitory/antagonistic effect on n-hexane toxicity in the commercial hexane mixture. As a result, a TDI of 5.0 mg/kg-d, based on the toxicity of commercial hexane, has been selected as the most appropriate toxicological benchmark for the C_6 to C_8 aliphatic sub-fraction, reflecting the preferred emphasis on data for mixtures to establish TDIs for mixtures of PHC. The RfC for commercial hexane was determined to be 18.4 mg/m^3 (Edwards et al. 1997).

Ten investigations of the toxicity of PHC mixtures including or spanning $C_{>8}$ to C_{16} have been conducted; these were reviewed by Edwards et al. (1997). Based on these studies of PHC mixtures, the TPHCWG determined a suitable TDI of 0.1 mg/kg-d and an RfC of 1.0 mg/m^3. These values have been adopted for the derivation of human health-based soil quality levels under the CCME Canada Wide Standard for PHCs in soil.

Studies of the toxicity of white mineral oils have been selected as the basis for a TDI for aliphatics in the range of $C_{>16}$ to C_{34}. Seven mineral oils, containing PHCs spanning C_{15} to C_{45} aliphatic hydrocarbons, had been toxicologically investigated in rats (Smith et al., 1995, 1996). Based on no-observed-effects-levels in these studies, the TPHCWG derived a TDI for C_{16} to C_{34} aliphatic hydrocarbons of 2 mg/kg-d, and derived a TDI for $C_{>34}$ aliphatics of 20 mg/kg-d. Due to the low potential volatility of C_{16} to C_{50} aliphatics, no RfC has been determined for aliphatic PHCs in this range.

3.7.3 Background Exposures, Residual TDIs and Residual RfCs

Excluding PAHs, no reports of generalized background contamination of air, water, food or soil (unrelated to contaminated sites) were located for component PHCs in fractions 2, 3 and 4 (i.e., $C_{>10}$). This likely stems from their generally low or negligible solubility and volatility. PAHs are evaluated separately from PHCs for purposes of risk assessment of contaminated sites and, therefore, they are not considered within the various PHC fractions being evaluated here.

Due to the lack of evidence for, and low probability of, ubiquitous environmental contamination with PHCs in fractions 2, 3 and 4, the estimated daily intakes (EDI) of PHCs in fractions 2, 3 and 4 from background sources are considered to be zero.

PHCs in fraction 1 (C_6 to C_{10}) are relatively volatile and soluble. As a result, aliphatic and aromatic compounds in this carbon range have been reported in drinking water, outdoor air, ambient air and some foods. These reports and available data have been summarized previously. With regard to drinking water monitoring in Canada, no provincial authority was identified that routinely monitors drinking water for non-BTEX PHCs. Therefore, it was concluded that the occurrence of these PHCs in drinking water is rare and likely related only to site-specific contamination problems.

Based on an examination of available data, contamination of foods with hydrocarbons in the C_6 to C_{10} range is sporadic and limited, and appears either to be site-specific or to be a function of food preparation (as has also been observed for PAHs in grilled and barbecued foods, for example).

Based on the available data and above-noted considerations, only inhalation exposure to PHCs in the C_6 to C_{10} range is anticipated to contribute significantly to typical background exposures (excluding BTEX and PAHs).

The estimated daily intakes (EDI) and estimated background air concentrations for TPHCWG sub-fractions within fraction 1 were calculated and these values were subtracted from their respective TDIs and RfCs in order to derive the residual TDI (RTDI) and residual reference air concentration (RRfC) for each TPHCWG sub-fraction within Fraction 1. These RTDIs and RRfCs are presented in Table 3.9.

3.8 Soil Allocation Factors to be Employed for Tier 1 Levels

People can receive exposure to contamination from five different media – vis. air, water, soil, food and consumer products. In addition, within soil there are a number of pathways by which a person can be exposed (ingestion, inhalation, dermal contact). A major objective in standards development is to ensure that total exposure does not exceed the applicable reference dose. Confidence that human health is protected by environmental quality guidelines for threshold substances can be increased by taking a *multimedia* approach. This approach, which takes account of known background exposures and “allows room” for other uncharacterized exposures from other media, was first developed and applied in the *Protocol for the Derivation of Human Health and Environmental Soil Quality Guidelines* (CCME 1996).

Table 3.9: EDIs and residual TDIs and RfCs for TPHCWG sub-fractions in PHC fraction 1.

TPHCWG Sub-fraction	Outdoor Air Concen-tration [1]	Estimated Indoor Air Concen-tration [1]	Estimated Daily Intake (EDI)			TPHCWG RFC	RESIDUAL RFC [5]	TPHCWG TDI	RESIDUAL TDI [6]
			Outdoor [2]	Indoor [3]	Total [4]				
	mg/m^3	mg/m^3	mg/kg-d	mg/kg-d	mg/kg-d	mg/m^3	mg/m^3	mg/kg-d	mg/kg-d
Aromatics, C7-C8	0.43	17.33	0.02	4.75	4.77	400	382.24	200	195.23
Aromatics, C9-C10	3.98	33.47	0.22	9.16	9.38	200	162.55	40	30.62
Aliphatics, C5-C6	23.41	161.37	1.28	44.18	45.46	18400	18215.22	5000	4954.53
Aliphatics, C7-C8	7.33	83.78	0.4	22.94	23.34	18400	18308.89	5000	4976.66
Aliphatics, C9-C10	1.49	37.32	0.08	10.22	10.3	1000	961.19	100	89.7

[1] Data provided by the Ontario Ministry of Environment.
[2] Based on outdoor air concentration and assuming 4 hour/day outdoors, 23 m^3/day inhalation rate, and 70 kg body weight.
[3] Based on indoor air concentration and assuming 20 hour/day outdoors, 23 m^3/day inhalation rate, and 70 kg body weight.
[4] Total = outdoor exposure + indoor exposure.
[5] Calculated as RFC - (Outdoor air concentration + indoor air concentration)
[6] Calculated as TDI - Total exposure.

The *Protocol* describes management of exposure within a tolerable daily intake (TDI) or reference dose (RfD) by first subtracting estimated daily (background) intake (EDI) from the TDI to generate a residual tolerable daily intake (RTDI). Subsequently, a portion of the RTDI is allocated to each of five possible media (air, water, soil, food and consumer products). Allocation to all five media is undertaken for two reasons. First, background exposure may be occurring from non-soil media that is not reported or observed – i.e., the EDI may be underestimated. Second, by reserving an allocation for each medium, room is provided for the development of guidelines for other media.

In the most general case discussed in the *Protocol*, a substance is considered to have the potential to be present in all media and therefore, on a default basis, an allocation of 20% of the RTDI is assigned to each of the 5 media. However, for specific substances, in this case PHCs, there may be properties that preclude the presence or limit the concentration in various media. When this is the case, both

the issues of uncharacterized exposure and the potential creation of a new guideline are negated or mitigated. In such cases a greater proportion of the RTDI can be allocated to critical media, such as soil.

Recommended soil allocation factors (SAF) for PHC are presented in Table 3.10 with corresponding rationale based on properties, occurrence in various media, and likelihood that guidelines for other media could be developed. These SAFs have been applied to soil ingestion, dermal contact and inhalation pathways only. The water ingestion pathway uses a SAF of 1, as consistent with the development of many Canadian Drinking Water Guidelines.

It should be noted that in using the SAF to account from each of the contaminated soil pathways, the Development Committee has assumed that there is an imbalance in exposure form the different pathways. If exposure from each of two pathways was expected to be equal and the toxic endpoint for each was the same, then it would be appropriate to assign a SAF of 0.5 to each pathway. However, based on physico-chemical properties and partitioning among media, balanced exposure is rarely expected.

3.9 Derivation of Human Health Tier 1 Soil Quality Levels

Presented in Appendix C is a sample calculation of Tier 1 values for PHC Fraction 1, for residential properties with a below-grade basement and a toddler as the critical receptor. All equations are presented in Table 3.1. Necessary assumptions for input variables are presented in Tables 3.3 through 3.9. Default characteristics for critical receptors are presented in Table 3.1. Calculations for individual TPHCWG sub-fractions are combined into CCME “super-fractions” on a weight-percent basis, employing the formula for combining fractions presented in Appendix C and the weight percents presented in Table 3.11.

Table 3.10 : Soil allocation factors (SAF) for deriving soil quality levels for PHCs*.

Fraction	SAF	Rationale
F1	0.5	Physico-chemical properties and environmental measurements indicate co-residency in air and water. Not likely to occur in significant quantities in food due to poor contact with primary sources and volatility. Consumer products are known to off-gas PHC and data are available for some F1 sub-fractions that indicate fairly low concentrations in indoor air compared to the reference concentration. However, there is little to no information on background exposures to other F1 sub-fractions and there are other known exposures that have not yet been quantified (e.g., patrons at filling stations, adjacent residents). F1 levels may be formally developed for water.
F2	0.5	Physico-chemical properties and environmental measurements indicate co-residency in air and water but at lower concentrations than for F1. No reliable data on background exposure from indoor or outdoor air were identified. F2 to F4 fractions are known to occur in consumer products such as leather and furniture polishes, pharmaceuticals, lubricants, dust control products and motor oils. Probability of occurrence in food greater than for F1. There is potential for exposure along all four of the contaminated soil pathways. Some likelihood that levels for F2 could be developed for water.
F3	0.6	Sparingly soluble in water and very low volatility. F2 to F4 fractions are known to occur in consumer products such as leather and furniture polishes, pharmaceuticals, lubricants, dust control products and motor oils. Some exposure in food likely from barbecued and grilled foods. Exposure from soil likely to occur mainly from soil ingestion and dermal contact. Unlikely that levels will be developed for media other than soil.
F4	0.8	Physico-chemical properties indicate PHC of $C_{>34}$ cannot dissolve in water or volatilize significantly. Whatever non-soil exposure may occur is likely related principally to consumer products such as heavy lubricants, greases and waxes. Exposure from soil likely to occur mainly from soil ingestion and dermal contact. Unlikely that levels will be developed for media other than soil.

* SAF set to 1 for protection of potable groundwater (see Section 3.8)

Table 3.11: Recommended composition of designated petroleum "fractions".

TPH Sub-fraction	Fraction 1	Fraction 2	Fraction 3	Fraction 4
Aliphatics				
C_6-C_8	0.55			
$C_{>8}$-C_{10}	0.36			
$C_{>10}$-C_{12}		0.36		
$C_{>12}$-C_{16}		0.44		
$C_{>16}$-C_{21}			0.56	
$C_{>21}$-C_{34}			0.24	
$C_{>34}$				0.8
Aromatics				
$C_{>7}$-C_8				
$C_{>8}$-C_{10}	0.09			
$C_{>10}$-C_{12}		0.09		
$C_{>12}$-C_{16}		0.11		
$C_{>16}$-C_{21}			0.14	
$C_{>21}$-C_{34}			0.06	
$C_{>34}$				0.2
Sum all sub-fractions	1	1	1	1

4. Ecological Soil Quality Levels

4.1 Protocol Summary and General Issues

A necessary first step in the development of Tier 1 levels for site investigation and soil remediation is to establish the suite of ecological receptors deemed to be potentially at risk from PHC contamination. The choice of ecosystem components that should be protected must necessarily be generically applicable at Tier I; that is, sufficiently protective when applied at the vast majority of terrestrial sites within Canada where PHC releases might be encountered. Figure 4.1 illustrates a simplified set of exposure scenarios for potential ecological receptors at PHC contaminated sites.

Potentially exposed organisms across the entire landmass of Canada span a range of phylogenetic diversity, trophic levels, and physioecological attributes. The overall range includes, for example, soil-dependent organisms (plants, soil invertebrates, soil microbes) and higher order consumers (wildlife, livestock) that may be categorized as primary consumers (herbivores), secondary, tertiary and quaternary consumers. The larger conceptual model for ecological receptors also includes aquatic life in surface water bodies (wetlands, ponds, lakes, streams, rivers) which may occur at or adjacent to PHC-contaminated sites.

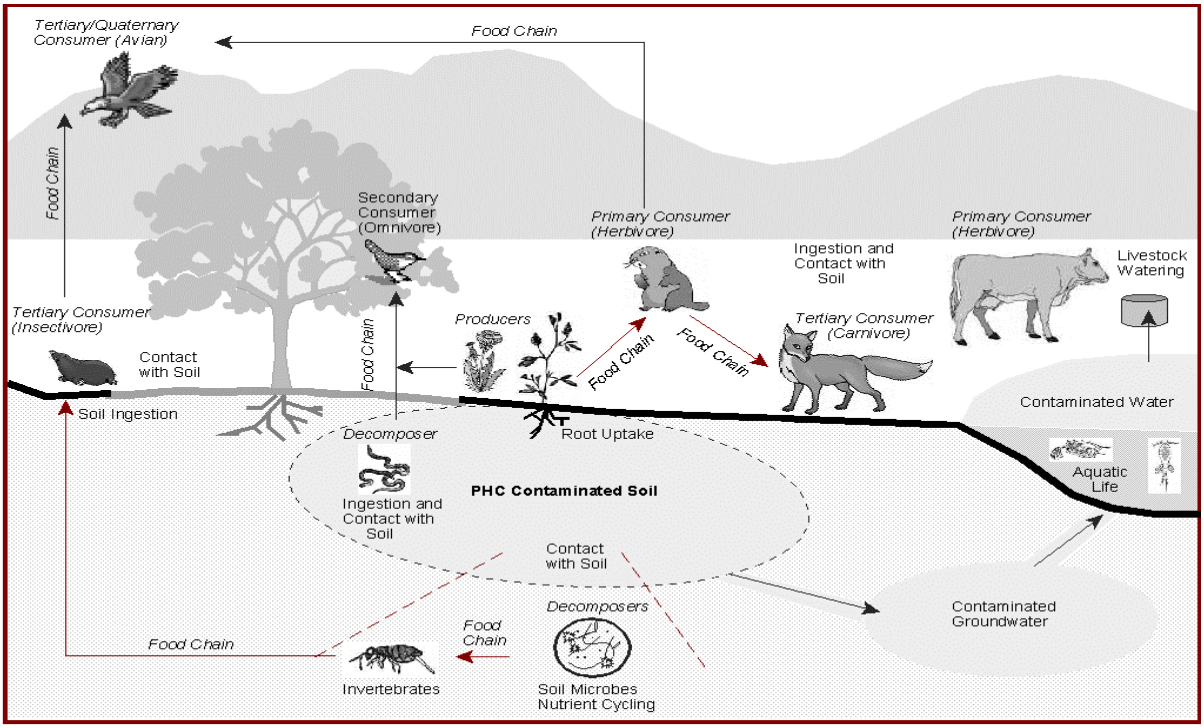


Figure 4.1. Key ecological receptors and exposure pathways of PHC contaminated soils.

The PHC CWS Tier I guidance was developed in consideration of a range of ecological receptors that might otherwise be exposed to petroleum hydrocarbons at unacceptably high levels. Because of the scarcity of ecological effects information for terrestrial organisms, however, selected key ecological receptors that maintain land activities were chosen for the development of Tier 1 levels. In particular, Table 4.1 lists the major categories of ecological receptors for each of the land uses considered as described in more detail in Chapter 2.

Specifics of the scientific rationale for the protection of soil invertebrates and plants, or protection of other ecological receptors (aquatic life, livestock drinking surface water) are provided in Sections 4.2 and 4.3, respectively.

Table 4.1: Ecological receptors and exposure scenarios used in developing the PHC CWS.

Land Use		
Agricultural	***Residential/Parkland***	***Commercial and Industrial***
· Direct contact by soil invertebrates and plants · Aquatic life in adjacent water bodies · Livestock drinking surface water (dugouts) · Livestock ingesting soil	· Direct contact by soil invertebrates and plants · Aquatic life in adjacent water bodies	· Direct contact by soil invertebrates and plants[1] · Aquatic life in adjacent water bodies

Notes: (1) Subsequent to deliberations by EcoTAG and the PHC CWS Development Committee, it was decided that soil quality levels for commercial and industrial sites would be derived primarily in consideration of plant health.

In some non-Canadian jurisdictions, as well as in detailed ecological risk assessments, the development of soil screening or remediation guidance for PHCs has focused more on vertebrate receptors – especially avian or mammalian domesticated and wild species. In Canada, the greater emphasis has been placed on exposure pathways based on direct contact between plant roots or soil invertebrates and the contaminated soils. This emphasis is based on the need to preserve the principal ecological functions performed by the soil resource. Less emphasis has been placed than in some jurisdictions on the estimation of contaminant concentrations in soils beyond which wildlife or domesticated animals might be at risk.

The focus on off-site migration and associated effects on aquatic organisms was deemed to be necessary based on the potential for the introduction of more water-soluble fractions of PHCs to surface water runoff and groundwater at PHC contaminated sites, and was supported by collective practical experience at various PHC contaminated sites. The maintenance of soil integrity based on its ability to support plant and soil invertebrate communities is deemed to be important for both

short and long term ecological sustainability, as demonstrated – for example – through no substantial decrease in primary productivity or impairment of nutrient and energy cycling within the area of interest.

The relative lack of emphasis on terrestrial vertebrate animals such as mammalian or avian wildlife is probably acceptable for PHC release sites as most PHCs are readily metabolized by vertebrates, modified into a more readily excretable form, and thus do not tend to accumulate in tissues. In addition, PHCs are not readily absorbed into and accumulated into plant tissues. The net result is that the consumption of either plants or other animals (as opposed to soil ingestion) does not tend to constitute the major component of exposure for PHCs in wildlife and livestock populations.

It was recognized when deriving the PHC CWS that both livestock and wildlife could be at risk from direct ingestion of released petroleum products. In waterfowl, for example, direct oiling of feathers from PHC spills leads to loss of insulation value and may directly lead to hypothermia. In addition, there is a huge volume of veterinary and toxicological literature that demonstrates that direct ingestion of petroleum products from the preening of feathers or fur can lead to acute toxic effects, including death. This exposure scenario, however, is based largely on the presence of free-phase petroleum hydrocarbons in the environment. For the purpose of the PHC CWS it is assumed as a starting point that the presence of free-phase PHCs from anthropogenic releases to the environment is unacceptable and that remedial activities are necessary wherever free-phase PHCs are observed.

The derivation of Canada Wide Standards for petroleum hydrocarbons (PHCs) represents one of the first attempts in Canada to develop environmental quality benchmarks for complex mixtures. The challenges in defining environmentally protective benchmarks for the complex suite of constituents in PHCs are greater than for other mixtures such as polychlorinated biphenyls (PCBs) or polychlorinated dioxins and furans (PCDDs, PCDFs), where there is thought to be a common toxicological mode of action that prevails across different constituents of the mixture. The constituents found in any petroleum hydrocarbon mixture encountered in the upstream industry, in downstream products, or in releases to the environment generally exhibit a very large range of chemical structures and properties relative to other complex mixtures, which are of direct relevance to environmental redistribution, persistence, bioavailability and toxicity.

When defining environmentally protective soil or water quality guidelines for complex mixtures, the issues go well beyond the uncertainties associated with the interactive effects of two or more individual potential contaminants. There are challenges associated with how to reconcile the disparate data types that have arisen given the diversity of analytical and experimental techniques that have been used to operationally define the mixture.

The Ecological Task Advisory Group (EcoTAG), under the direction of the PHC CWS Development Committee, recommended a strategy for deriving soil quality guidelines from complex mixtures (EcoTAG 2000). This is illustrated in Figure 4.2.

PHC toxicity data and studies for ecological receptors were used to the extent possible in order to bring the maximum amount of information to bear on the development of PHC Tier 1 soil values. For convenience, the approach adopted was described as a "weight-of-evidence" approach, which is defined as the critical evaluation and adoption of new numerical protocols, where required, to facilitate the incorporation of otherwise high quality but disparate types of information on the risks of PHCs to ecological receptors. This approach builds on the weight-of-evidence procedure introduced in the CCME (1996) soil quality guideline derivation protocol.

For the purpose of the derivation exercise, the recommended order of preference for toxicity data utilization (Figure 4.2) was –

- new toxicity data for the PHC CWS fractions;
- surrogate data "standardized" to whole fraction values, to the extent that broadly disparate estimates of PHC toxicity are not produced;
- whole product data from controlled laboratory studies and with toxicity subsequently assigned to the PHC CWS fractions; and
- field data from PHC contaminated sites.

This order of preference was established based on both data availability and perceived relevance to risks when PHC concentrations in soil are quantified as the four CWS fractions, and based on generic applicability across Canadian sites.

There were a number of critically important issues which were examined as part of the overall derivation exercise. These included –

- Conversion of effects endpoints from laboratory studies as calculated from nominal, or spiked, soil concentrations to estimates based on expected soil exposure concentrations;
- Biases in estimates of soil quality benchmarks associated with data manipulation to reconcile redundant toxicity endpoints (e.g., multiple data points for a specific taxon - toxicity endpoint combination). See Appendix D for a more detailed discussion; and
- Differences in toxicological thresholds for soil invertebrates and plants based on fresh PHC exposures versus historical releases, as well as strategies for incorporating at Tier 1 an appreciation of the importance of weathering for bioavailability and toxicity.

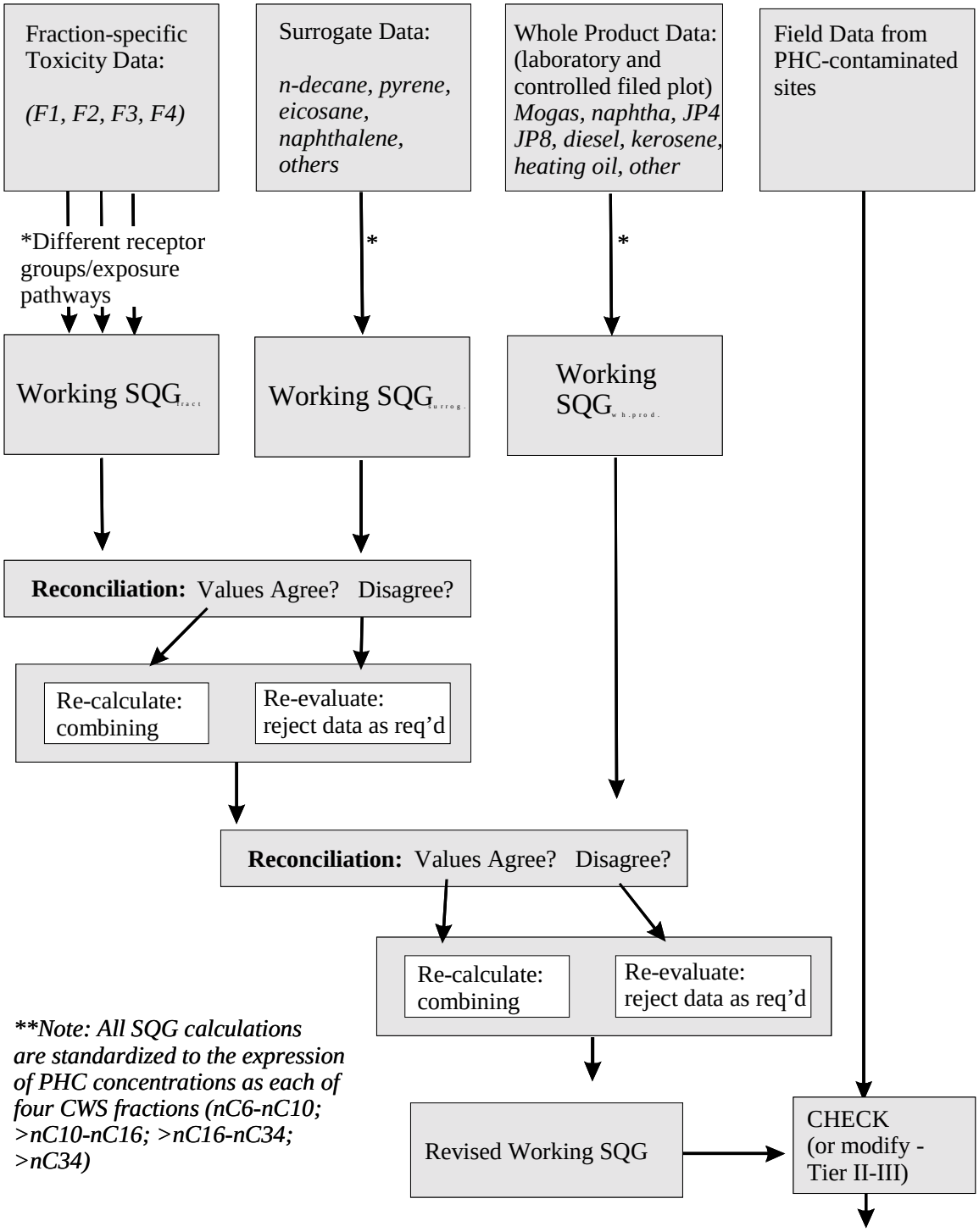


Figure 4.2: Summary of framework used for reconciling disparate data types when developing PHC Soil Quality Tier levels.

4.2 Direct Soil Contact – Protection of Soil Invertebrates and Plants

The approach taken herein was to critically evaluate the resulting soil quality benchmarks for the four PHC fractions based on a number of different data screening scenarios. The intent of description provided herein is to create as much transparency as possible in documenting how the PHC CWS Tier 1 levels were derived based on direct contact to soil invertebrates and plants.

Methods used to derive soil quality benchmarks from the PHC toxicity data, as adapted from CCME (1996), are documented in more detail in Appendix D.

4.2.1 Methods

Prior to the initiation of efforts to develop a PHC CWS, the scientific literature contained little if any information that would allow a confident prediction of the organismic and ecological responses to petroleum hydrocarbons when measured as the designated fractions (CWS F1, F2, F3, F4). A series of toxicity tests, therefore, was conducted in order to address the large data gaps for the effects of PHC mixtures on ecological receptors. The major portion of the data presently available for the derivation of PHC CWS based on effects in plants and/or soil invertebrates due to direct soil contact were produced by Stephenson *et al.* of ESG International through funding provided by the Petroleum Technology Alliance of Canada (PTAC), Alberta Environment and Canadian Association of Petroleum Producers (CAPP). Additional studies were facilitated through financial support from the Canadian Petroleum Producers Industry (CPPI), Environment Canada, Alberta Environment, Quebec Ministry of Environment, and B.C. Ministry of Environment, Lands and Parks.

Details of studies on fraction-specific toxicity for fractions F2 and F3 were provided in Stephenson *et al.* (2000a, b), while studies on motor gas toxicity (prior to the introduction of additives) as an approximation of F1 toxicity were provided in Stephenson (2000). These reports include details of:

- the larger study objectives;
- preparation of the individual fractions as vacuum distillates from fresh “Federated Crude Oil”;
- detailed chemical characterization, using various pre-established analytical techniques;
- comparison of different soil spiking techniques and soil test unit configurations, based on minimizing loss of volatile PHC constituents through the test period;
- composition of and relative acute toxicities to soil invertebrates and plants of PHCs in an artificial soil and sandy loam reference soil
- acute versus chronic responses; and

- appropriate methods for the estimation or realized exposure concentrations from nominal and measured concentrations.

The entire toxicity database for mogas (without additives), F2, F3 and fresh Federated Whole Crude Oil is tabulated in Appendix E. The studies were based on the use of either whole products or vacuum distillates of fresh as opposed to weathered whole Federated Crude Oil, using coarse textured soils (either a standardized field soil or an artificial sandy loam). The results, therefore, are expected to be most closely applicable to coarse-grained surface soils to which a fresh petroleum hydrocarbon product has been introduced. Additional considerations pertaining to finer grained site soils, or contamination at depth, are discussed in Chapter 5.

4.2.2 Departures for the PHC CWS from the CCME (1996) Protocol

In consideration of the challenges associated with the application of the CCME (1996) protocol to the available petroleum hydrocarbon toxicity data for terrestrial receptors, the following methodological departures were applied:

- Only effects-endpoints (EC_x or LC_x) were used, as derived from interpolation within linear or non-linear regression-type approaches of appropriately constructed dose response curves;
- NOEC and LOEC data were not used if corresponding EC_x data were available;
- Toxicity endpoint response levels were standardized at or near the 50% response level for sublethal studies. Where studies provided endpoints that were not based on a 50% response, the EC_x value for the data point where 'x' was the closest to 50% was used;
- For the same species, individual toxicity data points were considered to be redundant if they (i) represented different response levels for the same type of response and under the same or highly similar exposure conditions; (ii) were for different soil types, but the objective was not to evaluate effects of soil properties; or (iii) were based on different response measures which are known to be directly, causally connected. For data points that were deemed to be redundant, a single composite response concentration was calculated as the geometric mean[1];
- For toxicity data for the same species, response type, response level and exposure conditions, but based on different exposure periods, the data for the longer exposure period were given precedence;

[1] In virtually all cases, combining ecotoxicity data for the same test species, exposure period and toxicity endpoint did not substantially reduce the number of useable toxicity endpoints available to estimate the species sensitivity distribution. Use of the geometric mean in these cases provided a conservative estimate of soil concentrations leading to toxicological responses. In theory, however, the toxicity endpoints from different soil types might have also been considered as distinct endpoints, since it is part of the overall expected variation in species and between-site sensitivity.

- Separate anaylses of the plant and soil invertebrate data sets were carried out initially to establish the relative sensitivity of these two major functional groups;
- Subsequently, the 25th, percentile of the combined effects data set for soil invertebrates and plants was used in order to derive a soil quality benchmark for agricultural and residential/parkland sites. This is very similar to the protocol for application of an Effects Concentration - Low (EC-L) under the existing CCME (1996) protocol (Appendix D)[1];
- The 50th percentile of the plant effects (not mortality) data was used to derive a soil quality benchmark for commercial and industrial land uses.

The above-mentioned procedures were adopted in direct response to some of the data manipulation issues that arose for the PHC fraction-specific toxicity results, and may or may not have value for use in the development of soil quality guidelines for other substances. The rationale for the recommendations is provided through a detailed exploration of the effects of the data manipulation protocols on the resulting soil quality benchmarks for F3, as described below.

Overall, the approach taken for the PHC CWS was based on two explicit assumptions:

(i) Effects endpoints for reduced plant growth, yield, seed germination, or productivity, or for increased mortality or reduced growth or fecundity in soil invertebrates are ecologically relevant.

(ii) Different toxicological response endpoints in the same species provide useful individual measures of intra-taxon variability in sensitivity provided that the endpoints are not directly, causally linked.

Different measurement endpoints represent an inherent part of the within-species sensitivity distribution if they arise from perturbations of different biochemical/ physiological processes. Such variability is deemed to be a relevant part of the overall species sensitivity distribution. Plant root and shoot growth responses to PHCs in soils are likely to be at least partially correlated; however, the orthogonality of the individual toxicity endpoint is not required for a ranks-based approach.

Scientific substantiation for the first of the two assumptions is as follows. The overall approach would lead to a soil quality concentration equivalent to the 25th percentile

[1] EcoTAG originally felt that the separate evaluation of soil invertebrate and plant sensitivity to the PHC CWS fractions was likely to provide a more precise indication of soil PHC levels at which risks to the different groups were likely to be elevated. This decision was based, in part, on expectations regarding the importance of different toxicological mechanisms for the vastly different phyletic groups. Indeed, soil invertebrates were observed to be generally more sensitive to mogas, F2 and F3 than plants. In comparing the relative sensitivity of the two groups, however, EcoTAG concluded that the establishment of soil protective levels based on the combined soil invertebrate and plant data would still provide adequate protection for a large proportion of the soil invertebrate community at any given site.

of the species sensitivity distribution, standardized around a 50% reduction in growth, yield, fecundity or survivorship. This, in turn, assumes that the available, screened toxicity database allows an accurate reconstruction of a species sensitivity distribution for all possible taxa that might occur at a site within Canada. The potential for biases in the re-construction of species sensitivity distributions is likely to be inversely proportional to the number and diversity of information for different taxa, toxicological endpoints, and soil types in the underlying database.

The approach is not amenable to easy translation into - for example - percent of species in the environment protected, or percentage of community diversity at risk; measures with a more intuitive appeal from a policy perspective. The only known and credible method for translating a 25^{th} percentile of an EC_x or LC_x distribution into a true community- or ecosystem-based measure of the level of protection is through the design of specific field studies, using complex ecological communities.

4.2.3 Development of Soil Quality Benchmarks for: Fraction 4 (>nC34)

No specific studies have been undertaken of the toxicity to soil invertebrates or plants of the PHC CWS Fraction 4 [petroleum hydrocarbon constituents with a greater boiling point than an nC34 aliphatic hydrocarbon (>nC34)]. Work is presently underway to characterize the toxicity of a representative F4 mixture, obtained through the distillation of fresh Federated Crude Oil. The results, however, were not available in time to guide the first round derivation of the Tier 1 levels for F4. It is anticipated that the new toxicity data will be useful in re-assessing the Tier 1 levels for F4 as part of the larger PHC CWS implementation process.

The Ecological Technical Advisory Group (EcoTAG) was of the opinion that laboratory toxicity testing is unlikely to adequately capture the range of issues associated with heavy hydrocarbons, such as asphaltenes or residual heavy hydrocarbons that may dominate soils following bioremediation or long-term weathering. The bioavailability of individual hydrocarbon constituents with molecular weights larger than nC34 is likely to be very limited (TPHCWG 1997); therefore, ecological risks are likely to be only poorly linked to internalization of the heavier PHCs and subsequent perturbation of biochemical/physiological functioning.

On the other hand, heavier hydrocarbon constituents, as potentially captured in the F4 fraction have been demonstrated to exert negative impacts on soil properties at release sites, including the production of “hydrophobic” soils. Hydrophobic soils have a severely impaired water-holding capacity, which, in turn would affect the rhizosphere and plant uptake of water and nutrients. There appears to be little relationship between either the types of PHCs introduced into soils or the total PHC concentration and the tendency for formation of hydrophobic soils. As yet to be defined soil properties appear to have a large influence on the tendency for formation of hydrophobic soils.

Given the current limitations in the scientific understanding of the possible range of mechanisms of soil ecosystem impairment, and the risks associated with the >nC34 PHC fraction, alternate approaches for the derivation of an F4 Tier 1 level were considered, including either the derivation of a value based on alternative toxicological information or a policy-based decision. A strictly policy-based Tier 1 value was rejected in favour of using toxicity data for whole Federated Crude Oil. The unfractionated fresh product probably provides a conservative estimate of toxicological thresholds for this fraction. Since the whole product contained appreciable portions of CWS fractions F1, F2 and F3 in addition to the heavier hydrocarbon fraction (including asphaltenes) found in F4, there is a strong likelihood that the actual observed toxicity thresholds would occur at higher soil concentrations had the test organisms been exposed to F4 alone. There is a limited possibility, however, that the lighter PHC fractions could exert antagonistic influence on the F4 toxicity – which cannot be ruled out without additional evidence.

The toxicity of fresh whole Federated Crude Oil is analyzed in detail in Section 4.2.9, and illustrated in Figures 4.17 and 4.18. Based on this analysis, the following endpoints were derived:

- The 25th %ile of the combined plant and soil invertebrate EC_x/LC_x toxicity data for whole Federated Crude Oil was estimated to be 4,800 mg/kg in soil, based on the nominal, or spiked concentration.
- The 50th %ile of the plant toxicity data alone was estimated to be 9,100 mg/kg in soil, based on the nominal, or spiked concentration.

As will be noted in Sections 4.2.4 through 4.2.6, the nominal concentration did not adequately represent the true exposure concentration in the soil invertebrate or plant toxicity tests. Depending on the volatility of the fractions being considered, the actual initial exposure concentration at time ‘zero’ was estimated to vary from <10% of the nominal concentration for mogas, to between 31 and 65% for the F3 distillate of Federated Whole Crude. The percent loss was also observed to be dependent on the magnitude of the nominal concentration.

To account for possible PHC losses from toxicity trials on whole Federated Crude Oil, the soil quality benchmarks for PHC CWS Fraction 4 were established at 2,800 mg/kg for agricultural, residential and parkland sites (i.e. – 58% of the nominal 25th %ile EC_{50}/LC_{50} soil concentration for the combined soil invertebrate and plant toxicity data). Similarly, the soil quality benchmarks were established as 3,300 mg/kg for commercial and industrial sites (i.e. – 36% of the 50th %ile of the EC_{50} soil concentration for plant toxicity test data).

4.2.4 Development of Soil Quality Benchmarks for Fraction 3 (>nC16 to nC34)

Stephenson *et al.* (2000b) derived toxicity endpoints for exposure to PHC CWS fraction F3 in soil for three species of plants; *Medicago sativa* (alfalfa), *Hordeum*

vulgare (barley), *Agrophyron dasystachyum* (northern wheatgrass) and three species of soil invertebrates; Collembola: *Onychiuris folsomi* (springtail), and *Eisenia fetida* and *Lumbricus terrestris* (earthworms). Table 4.2 provides a summary of the available data on the toxicity of Fraction 3 of Federated crude, with a boiling point range from >nC16 and nC34, inclusive.

For the barley and for acute exposure periods, the toxicity tests were carried out in two soil types: a field-collected sandy loam reference soil, and an artificial soil [details provided in Stephenson et al. (1999)]. In addition, various regression-based statistical techniques were used to calculate an EC_{20} and EC_{50} response level. Finally, tests in field soils included measurement of responses after an acute exposure period, usually 7 days, as well as a longer, chronic or "definitive" exposure period.

A pair-wise comparison was undertaken to assess the effects on calculated toxicological endpoints of soil type, exposure period, and effect size. This was done through the independent use of paired-sample t-tests for each of the three plant species, and for each factor of interest. The results are summarized below:

- **Alfalfa exposure to F3 in soil:**
  - ⇒ Tests were conducted only in field soil.
  - ⇒ EC_{20} and EC_{50} endpoints were not significantly lower after 26 day exposure than 7 day exposure [n = 4, t(1) = 1.48, p = 0.14]; however, the lack of statistical significance was due to the small number of paired data available. The 26 day and 7 day exposure endpoints were significantly correlated (Pearson r = 0.86)**. *The ECx soil concentrations were on average 80% lower for the longer exposure period***.
  - ⇒ The EC_{20} soil concentrations were significantly lower than EC_{50} concentrations, with an average difference of 69% [n = 10, t(1) = -2.48, p = 0.017]. Toxicity endpoints for specific endpoint types were highly correlated (Pearson r = 0.86).

- **Barley exposure to F3 in soil:**
  - ⇒ Acute (7 day) tests were conducted in both field and artificial soil. The toxicity in field soil was consistently and significantly lower, by 46% on average, than in the artificial soil [n = 6, t(2) = -9.17, p = 0.0003; Pearson r = 0.90].
  - ⇒ EC_{20} and EC_{50} endpoints were significantly lower after 14 day exposure than 7 day exposure [n=6, t(1) = 2.24, p = 0.038]. *The 14 day exposure endpoints were on average 52% lower than 7 day endpoints.* (Pearson r = 0.22)**.**

⇒ The EC_{20} soil concentrations were significantly lower than EC_{50} concentrations, with an average difference of only 28% [n=15, t(1) = -6.05, p < 0.0001]. Toxicity endpoints for specific endpoint types were highly correlated (Pearson r = 0.956).

- **Northern wheatgrass exposure to F3 in soil:**

  ⇒ Acute (7 day) tests were conducted in both field and artificial soil. The toxicity in field soil was consistently and significantly lower, by 52% on average, than in the artificial soil (n = 7, t(2) = -2.67, p = 0.037; Pearson r = 0.53).

  ⇒ EC_{20} and EC_{50} endpoints were significantly lower after 25 day exposure than 7 day exposure [n = 3, t(1) = -3.26, p = 0.0031]. *The 25 day exposure endpoints were on average 89% lower than 7 day endpoints.* (Pearson r = 0.21)**.**

  ⇒ The EC_{20} soil concentrations were significantly lower than EC_{50} concentrations, with an average difference of 59% [n=13, t(1) = -3.26, p=0.003]. Toxicity endpoints for specific endpoint types were highly correlated (Pearson r = 0.941).

Table 4.2: Summary of Fraction 3 (>nC16 to nC34) toxicity data.

Organism	Endpoint	Parameter[1]	Value (mg/kg nominal)	# conc. in test series	# Reps. for ea. conc.	Soil	pH	Comment
Plants								
alfalfa	EC50	shoot length	51900	7(0, 15, 30, 50, 60, 70, 80 mg/g)	4	field soil: Delacour Orthic Black Chernozem		8 day test. n=10
alfalfa	EC20	shoot length	2800	as above	4	as above		as above
alfalfa	EC50	root length	10000	as above	4	as above		as above
alfalfa	EC20	root length	7200	as above	4	as above		as above
alfalfa	EC50	whole ww	72300	as above	4	as above		as above
alfalfa	EC20	whole ww	15800	as above	4	as above		as above
alfalfa	EC50	whole dw	98200	as above	4	as above		as above
alfalfa	EC20	whole dw	50200	as above	4	as above		as above
alfalfa	EC50	shoot length	8300	12 (0, 1, 3, 6, 12, 15, 20, 40, 60, 80, 100, 120 mg/g)	3-6	as above		26 day test n= 10 clear lids kept on till plants 3cm in height
alfalfa	EC20	shoot length	620	as above	3-6	as above		as above
alfalfa	EC50	root length	6300	as above	3-6	as above		as above
alfalfa	EC20	root length	920	as above	3-6	as above		as above
alfalfa	EC50	shoot ww	2100	as above	3-6	as above		as above
alfalfa	EC20	shoot ww	510	as above	3-6	as above		as above
alfalfa	EC50	shoot dw	2300	as above	3-6	as above		as above
alfalfa	EC20	shoot dw	620	as above	3-6	as above		as above
alfalfa	EC50	root ww	4400	as above	3-6	as above		as above
alfalfa	EC20	root ww	860	as above	3-6	as above		as above
alfalfa	EC50	root dw	5500	as above	3-6	as above		as above
alfalfa	EC20	root dw	1100	as above	3-6	as above		as above
barley	EC50	shoot length	53400	6 (0, 4, 10, 30, 50, 80 mg/kg)	4	field soil: Delacour Orthic Black Chernozem		6 day test. n =5

[1] ww = wet weight; dw = dry weight

Organism	Endpoint	Parameter[1]	Value (mg/kg nominal)	# conc. in test series	# Reps. for ea. conc.	Soil	pH	Comment
barley	EC20	shoot length	39400	as above	4	as above		as above
barley	EC50	root length	58200	as above	4	as above		as above
barley	EC20	root length	47600	as above	4	as above		as above
barley	EC50	shoot ww	50300	as above	4	as above		as above
barley	EC20	shoot ww	36700	as above	4	as above		as above
barley	EC50	shoot length	98200	7 (0, 15, 30, 50, 60, 70, 80 mg/g)	4	artificial: 70% silica sand; 20% kaolinite clay;10% sphagnum peat	6-7	7day test. n = 5
barley	EC20	shoot length	74800	as above	4	as above	6-7	as above
barley	EC50	root length	119600	as above	4	as above	6-7	as above
barley	EC20	root length	79000	as above	4	as above	6-7	as above
barley	EC50	shoot ww	85900	as above	4	as above	6-7	as above
barley	EC20	shoot ww	73800	as above	4	as above	6-7	as above
barley	EC50	shoot dw	87200	as above	4	as above	6-7	as above
barley	EC20	shoot dw	73600	as above	4	as above	6-7	as above
barley	EC50	root ww	90800	as above	4	as above	6-7	as above
barley	EC20	root ww	61200	as above	4	as above	6-7	as above
barley	EC50	root dw	95300	as above	4	as above	6-7	as above
barley	EC20	root dw	67400	as above	4	as above	6-7	as above
barley	EC50	shoot length	27600	10 (0, 10, 20, 30, 40, 50, 60, 70, 80, 100 mg/g)	3-6	field soil: Delacour Orthic Black Chernozem		14day test. n = 5 clear lids kept on till plants 3cm in height
barley	EC20	shoot length	3700	as above	3-6	as above		as above
barley	EC50	root length	3200	as above	3-6	as above		as above
barley	EC20	root length	120	as above	3-6	as above		as above
barley	EC50	shoot ww	54100	as above	3-6	as above		as above
barley	EC20	shoot ww	48200	as above	3-6	as above		as above
barley	EC50	shoot dw	53300	as above	3-6	as above		as above
barley	EC20	shoot dw	48700	as above	3-6	as above		as above
barley	EC50	root ww	8700	as above	3-6	as above		as above
barley	EC20	root ww	1700	as above	3-6	as above		as above

Organism	Endpoint	Parameter[1]	Value (mg/kg nominal)	# conc. in test series	# Reps. for ea. conc.	Soil	pH	Comment
barley	EC50	root dw	35100	as above	3-6	as above		as above
barley	EC20	root dw	10000	as above	3-6	as above		as above
northern wheat grass	EC50	shoot length	42100	7 (0, 15, 30, 50, 60, 70, 80 mg/g)	4	as above	0	8 day test. n = 5
northern wheat grass	EC50	root length	51100	as above	4	as above	0	as above
northern wheat grass	EC20	root length	20400	as above	4	as above	0	as above
northern wheat grass	EC50	whole ww	26700	as above	4	as above	0	as above
northern wheat grass	EC20	whole ww	13700	as above	4	as above	0	as above
northern wheat grass	EC50	whole dw	24800	as above	4	as above	0	as above
northern wheat grass	EC20	whole dw	12100	as above	4	as above	0	as above
northern wheat grass	EC50	shoot length	81900	as above	4	artificial: 70% silica sand; 20% kaolinite clay; 10% sphagnum peat	6-7	12 day test. n = 5
northern wheat grass	EC20	shoot length	17100	as above	4	as above	6-7	as above
northern wheat grass	EC50	root length	121000	as above	4	as above	6-7	as above
northern wheat grass	EC20	root length	54900	as above	4	as above	6-7	as above
northern wheat grass	EC50	whole ww	73400	as above	4	as above	6-7	as above
northern wheat grass	EC20	whole ww	34000	as above	4	as above	6-7	as above
northern wheat grass	EC50	whole dw	63900	as above	4	as above	6-7	as above
northern wheat grass	EC20	whole dw	33500	as above	4	as above	6-7	as above
northern wheat grass	EC50	shoot length	12700	11 (0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80 mg/g)	3-6	field soil: Delacour Orthic Black Chernozem	0	25 day test. n = 5 clear lids kept on till plants 3cm in height
northern wheat grass	EC20	shoot length	330	as above	3-6	as above	0	as above
northern wheat grass	EC50	root length	7300	as above	3-6	as above	0	as above
northern wheat grass	EC20	root length	4300	as above	3-6	as above	0	as above
northern wheat grass	EC50	shoot ww	610	as above	3-6	as above	0	as above
northern wheat grass	EC20	shoot ww	13	as above	3-6	as above	0	as above
northern wheat grass	EC50	shoot dw	1400	as above	3-6	as above	0	as above
northern wheat grass	EC20	shoot dw	50	as above	3-6	as above	0	as above

Organism	Endpoint	Parameter[1]	Value (mg/kg nominal)	# conc. in test series	# Reps. for ea. conc.	Soil	pH	Comment
northern wheat grass	EC50	root ww	890	as above	3-6	as above	0	as above
northern wheat grass	EC20	root ww	180	as above	3-6	as above	0	as above
northern wheat grass	EC50	root dw	1100	as above	3-6	as above	0	as above
northern wheat grass	EC20	root dw	210	as above	3-6	as above	0	as above
Soil Invertebrates								
springtail (*O.folsomi*)	LC50	mortality	6670	6 (0, 2, 4, 8, 12, 15 mg/g)	3-4	artificial 70% silica sand 20% kaolinite clay 10% sphagnum peat	6-7	7 day test n = 10 covered loosely
springtail (*O.folsomi*)	LC50	mortality	5970	as above	3-4	field soil: Delacour Orthic Black Chernozem	0	as above
springtail (*O.folsomi*)	LC50	adult mortality	3695-4280	10 (0, 0.5, 1, 2, 3, 4, 5, 5.5, 6, 7 mg/g)	10	as above	0	35-36 day test n = 10 loosely closed lids removed biweekly for air exchange. value for IC & LC
springtail (*O.folsomi*)	LC20	adult mortality	3120	as above	10	as above	0	as above
springtail (*O.folsomi*)	EC50	# juvenile	1490	as above	10	as above	0	as above
springtail (*O.folsomi*)	EC20	# juvenile	910	as above	10	as above	0	as above
springtail (*O.folsomi*)	EC50	adult fecundity	1410	as above	10	as above	0	as above
springtail (*O.folsomi*)	EC20	adult fecundity	620	as above	10	as above	0	as above
springtail (*O.folsomi*)	NOEC	adult mortality	3000	as above	10	as above	0	as above
springtail (*O.folsomi*)	LOEC	adult mortality	4000	as above	10	as above	0	as above
springtail (*O.folsomi*)	NOEC	# juvenile	1000	as above	10	as above	0	as above
springtail (*O.folsomi*)	LOEC	# juvenile	2000	as above	10	as above	0	as above
springtail (*O.folsomi*)	NOEC	adult fecundity	1000	as above	10	as above	0	as above
springtail (*O.folsomi*)	LOEC	adult fecundity	2000	as above	10	as above	0	as above
worm (*E. foetida*)	LC50	mortality	22360	10 (0, 0.5, 1, 2, 4, 8, 12, 15, 20, 50 mg/g)	3-4	as above	0	14 day test n = 5 perforated lids
worm (*E. foetida*)	IC50	# juveniles	776	11 (0, 0.5, 1, 3, 5, 7, 10, 12.5, 15, 20, 25 mg/g)	10	as above	0	57 day test n = 2 perforated lids. adults removed at day 37 & cocoons allowed to hatch. value for IC & LC
worm (*E. foetida*)	EC20	# juveniles	240	as above	10	as above	0	as above

Organism	Endpoint	Parameter[1]	Value (mg/kg nominal)	# conc. in test series	# Reps. for ea. conc.	Soil	pH	Comment
worm (*E. foetida*)	EC50	juvenile ww	854	as above	10	as above	0	as above
worm (*E. foetida*)	EC20	juvenile ww	272	as above	10	as above	0	as above
worm (*E. foetida*)	EC50	juvenile dw	809	as above	10	as above	0	as above
worm (*E. foetida*)	EC20	juvenile dw	213	as above	10	as above	0	as above
worm (*E. foetida*)	NOEC	# juveniles	0	as above	10	as above	0	as above
worm (*E. foetida*)	LOEC	# juveniles	500	as above	10	as above	0	as above
worm (*E. foetida*)	NOEC	juvenile ww	0	as above	10	as above	0	as above
worm (*E. foetida*)	LOEC	juvenile ww	500	as above	10	as above	0	as above
worm (*E. foetida*)	NOEC	juvenile dw	0	as above	10	as above	0	as above
worm (*E. foetida*)	LOEC	juvenile dw	500	as above	10	as above	0	as above
worm (*L. terrestris*)	LC50	mortality	19150	6 (0, 8, 12, 15, 20, 50 mg/g)	3-4	artificial: 70% silica sand; 20% kaolinite clay; 10% sphagnum peat	6-7	14 day test n = 3 perforated lids
worm (*L. terrestris*)	LC50	mortality	17220	7 (0, 4, 8, 12, 15, 20, 50 mg/g)	3-4	field soil: Delacour Orthic Black Chernozem	0	as above

(from Stephenson et al. 2000b)

Figure 4.3 illustrates the distribution of all plant F3 toxicity data tabulated above, irrespective of differences in exposure period or effect size of the end point. The plant data were ranked (from 1 to 77) and the rank percentile (on the y-axis) plotted against the estimated nominal F3 soil concentrations for the tabulated toxicity endpoints. The graphing of the ranked data in this plot is functionally equivalent to the CCME (1996) protocol for deriving the Threshold Effects Concentration, based on the 25^{th} percentile of the ranked data (around 3,000 mg/kg PHCs as F3 in Figure 4.3). The plant toxicity endpoints, however, do not include any NOEC values, since these were not provided. Rather, the entire F3 plant database is made of interpolated 20% and 50% effects (EC) or inhibitory (IC) soil concentrations.

The advantage of plotting the data as shown in Figure 4.3 is that it allows better scrutiny of the underlying data distribution. Data points plotted as their rank percent in the database tend to follow a straight line when plotted along a y-axis with a probability-type scale. The fact that the data approximate a straight line distribution when the soil concentrations are plotted along a logarithmic scale suggests that the sensitivity of the plant species tested adheres to a log-normal distribution, as might be predicted. A close inspection of Figure 4.3 further suggests that the composite data actually includes two major distinct log-normal sensitivity distributions, since the plot approximates two separate straight lines that meet at a nominal F3 soil concentration of around 50,000 mg/kg. The fact that there are two major distributions within the larger database merits critical evaluation.

Figure 4.4 shows the data distribution, and corresponding 25^{th} percentile value when the EC_{50} endpoints are used, and the EC_{20} data are omitted. The EC_{20} data where excluded in this scenario based on several reasons:

- The reduction in growth endpoints for the plants are not mortality-based endpoints; hence, it is not obvious that a twenty percent reduction in root or shoot length or mass would lead to population level effects in the environment;
- Some provincial jurisdictions (e.g., British Columbia) specify a level of protection for soil invertebrates and plants which is equivalent to an EC_{50} or an LC_{20}, not the EC_{20}; and
- The database provided for plants from the toxicity tests on the F2 fraction did not include EC_{20} data. It was deemed advantageous to screen the toxicity data for F2 and F3 in similar ways, to better allow a direct comparison of the 25^{th} percentile values (TECs or EC-Ls) for fractions F2 and F3.

The EC_{50} endpoints for barley and northern wheatgrass, furthermore, were provided based on studies using both an artificial and standardized field soil (see Table 4.2). In most cases, EC_{50} values were similar for each plant response measured between the two soil types.

The endpoint-specific toxicological response was estimated as the geometric mean of the EC_{50}s for F3 PHC exposure in the artificial and field soil.

As shown in Figure 4.4, a 25th percentile value based on only the EC_{50} data for plants (approx. 7,000 mg/kg nominal) was higher than when the EC_{20} and EC_{50} data were combined, as in Figure 4.3 (approx. 3,000 mg/kg). The data also approximate a bimodal log-normal sensitivity distribution.

Figure 4.5 illustrates the ranked data distribution based on a further reduction of the database to exclude acute and intermediate exposure periods, in favour of "definitive" (Stephenson *et al.,* 2000b) exposure periods (i.e., the longest exposure period used in the experiment). It is clear that, for the F3 fraction, growth or yield inhibition increased substantially with longer, chronic exposure periods (26, 14, and 25 day for alfalfa, barley and northern wheat grass, respectively) relative to more acute exposures (8, 6, and 8 days, respectively). A strong unimodal log-normal sensitivity distribution is apparent in Figure 4.5. This suggests that the reduction in plant growth or yield when exposed to F3 PHCs follows a distinct log-normal sensitivity distribution. An approximate estimate of the 25th percentile of the ranked data in Figure 4.5 is 2,000 mg/kg F3, expressed as a nominal exposure concentration. The use of the term "definitive" may be a bit misleading, since there is no evidence that longer, chronic exposure periods would not have resulted correspondingly larger reductions in growth or yield relative to uncontaminated controls.

As a final check against the biases associated with possible inclusion of redundant toxicity endpoints, all available EC_{50} values for definitive exposure periods and for a single test species were combined (aggregate EC_{50}s were derived from endpoints based on shoot or root length or mass based on wet and dry weight measurements). A single EC_{50} for each plant species was calculated both as the geometric and arithmetic mean of the constituent data. Figure 4.6 shows the consolidated data based on the geometric means. The arithmetic mean EC_{50}s were similar.

The severe reduction through either culling or combination of the toxicity endpoints data as shown in Figure 4.6 shows that, while the three data points produced are too few to adequately define a reasonable 25th percentile effects concentration, the value of 1,700 mg/kg nominal F3 that was derived is close to the 25th percentile provided in Figure 4.5. Overall, an estimate of a nominal F3 exposure concentration of 2,000 mg/kg appears to be a reasonable estimate of a threshold concentration above which there may be elevated risks for plants.

Figure 4.7 and 4.8 provide a parallel analysis for the F3 soil invertebrate data set. The entire invertebrate toxicity endpoint data set is shown in Figure 4.7. The use of the entire data set in a ranks-based procedure would result in a 25th percentile nominal concentration of approximately 400 mg/kg.

The data plotted in Figure 4.8 are based on the exclusion of NOEC, LOEC and $LC(EC)_{20}$ estimates. The mortality data have been circled to distinguish them from sublethal endpoints. The lowest LC_{50} value was observed at an F3 nominal concentration of around 5,000 mg/kg, which is more than five-fold higher than the 25^{th} percentile nominal concentration of around 800 mg/kg, based on the combined mortality-type and non-lethal endpoints.

Figure 4.9 compares the underlying data distributions and 25^{th} percentile estimates of toxicity endpoints for plants and soil invertebrates, based on the most appropriate data manipulations as discussed above. The ranked data distribution for the combined data sets is also shown.

The preceding analysis is based entirely on the evaluation of toxicological responses of soil invertebrates or plants based on the “nominal”, or spiked soil concentration of F3. The loss of compound during toxicity testing is expected to be less severe for F3 than for fractions F1 and F2; however, the actual changes in exposure concentration of F3 PHCs from the nominal to the initial or final soil concentration were examined as by Stephenson et al. (2000b) as a means of adjusting the broader suite of nominal data. Table 4.3 provides an excerpt of the data on F3 losses during toxicity testing.

Table 4.3: Change in the soil concentration during sampling unit preparation and over the exposure period.

Nominal F3 Concentration (spiked)	Initial Measured Concentration (t=0)[A]	Init.: Percent of Nominal	Final (14 day) Measured Concentration[B]	Final: Percent of Nominal
6,000 mg/kg	1,910 mg/kg	31%	550 mg/kg	9%
20,000 "	6,170 "	31%	3,440 "	17%
60,000 "	32,030 "	53%	22,160 "	37%
100,000 "	56,330 "	56%	52,580 "	53%
120,000 "	79,660 "	66 %	78,380 "	65%

Notes:
A. Based on GC analysis of TPH for a subset of test soils.
B. TPH analysis of alfalfa definitive (14 day) test units.

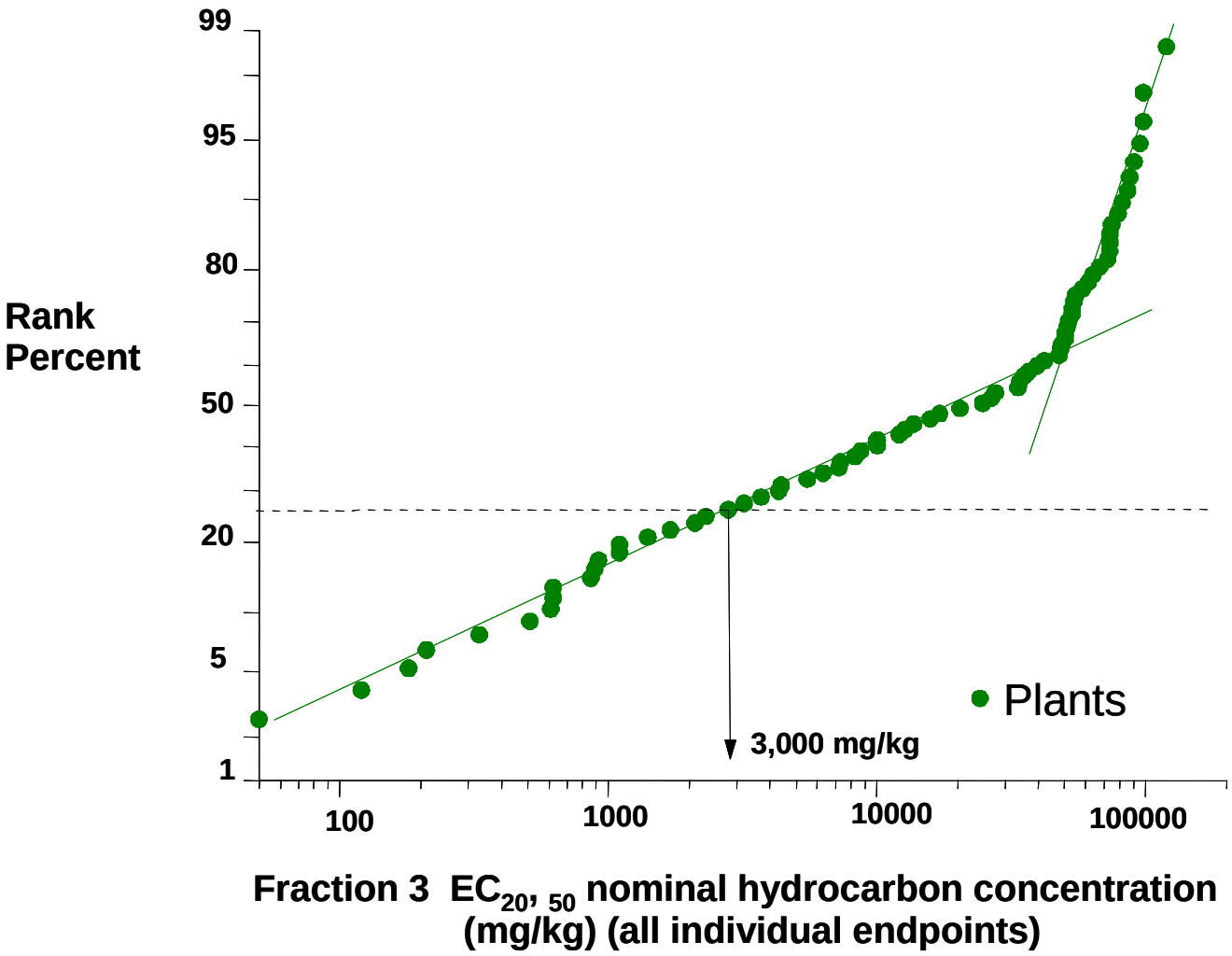


Figure 4.3: Distribution of plant toxicological endpoints for studies on F3 PHCs based on all data provided in Table 4.2.

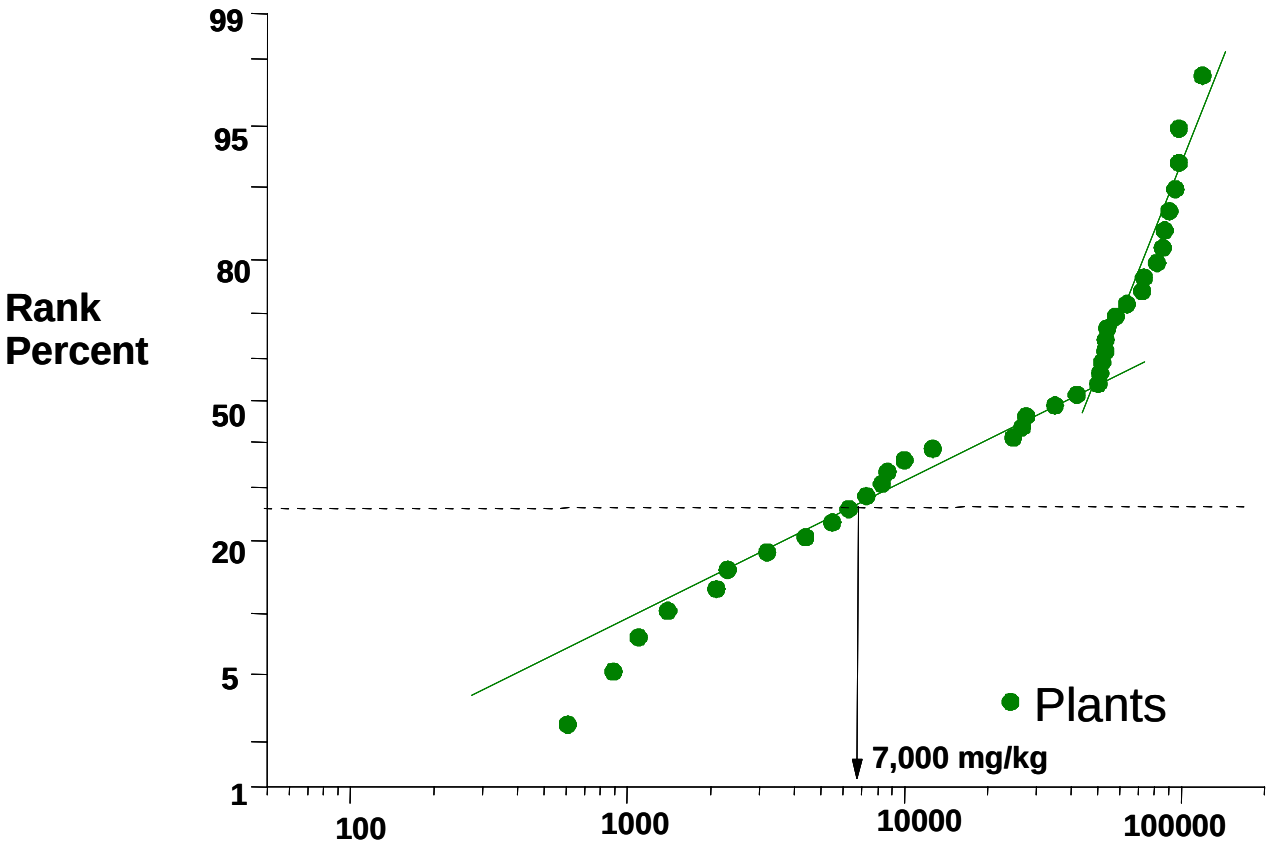


Figure 4.4: Distribution of plant toxicological endpoints for studies on F3 PHCs based on EC_{50} data.

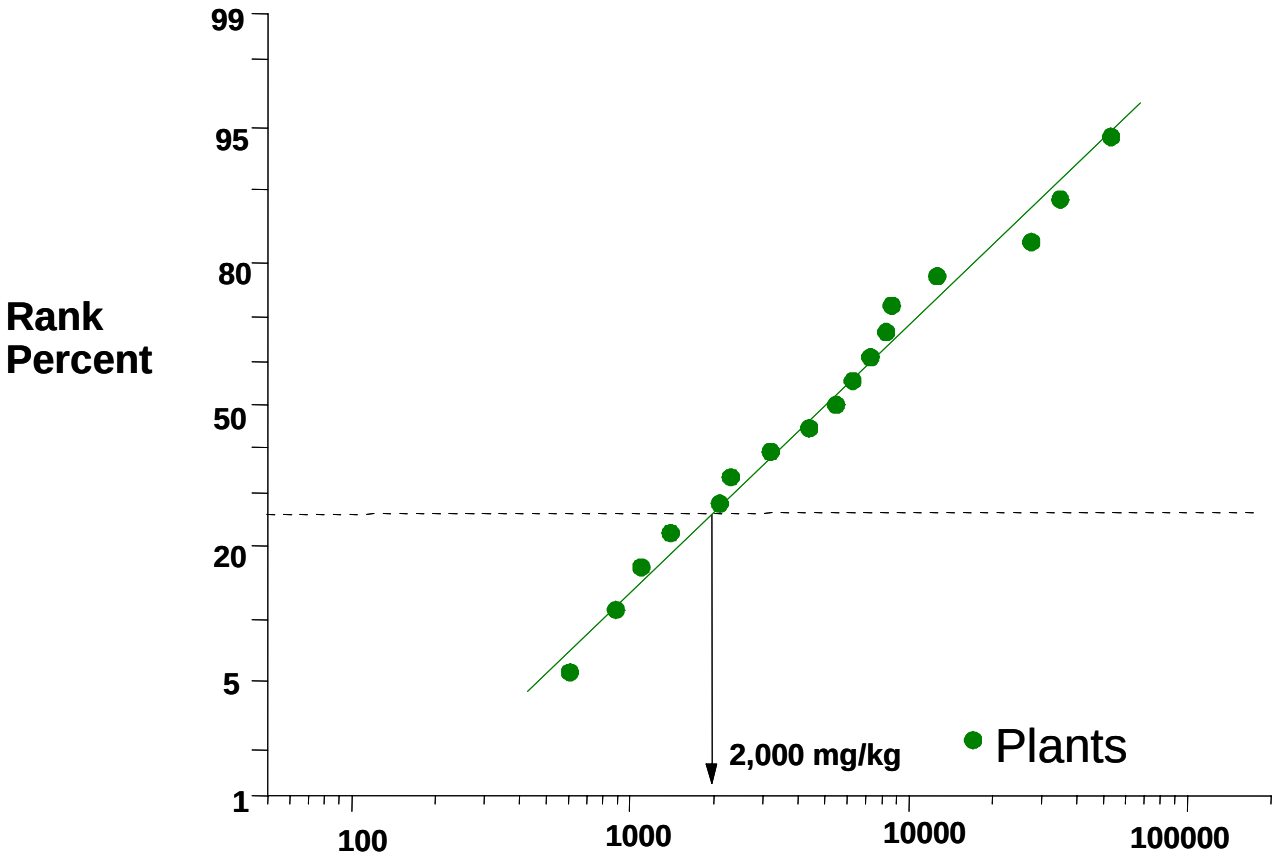


Figure 4.5: Distribution of plant toxicological endpoints for studies on F3 PHCs based on EC_{50} data and chronic ("definitive") exposure periods only.

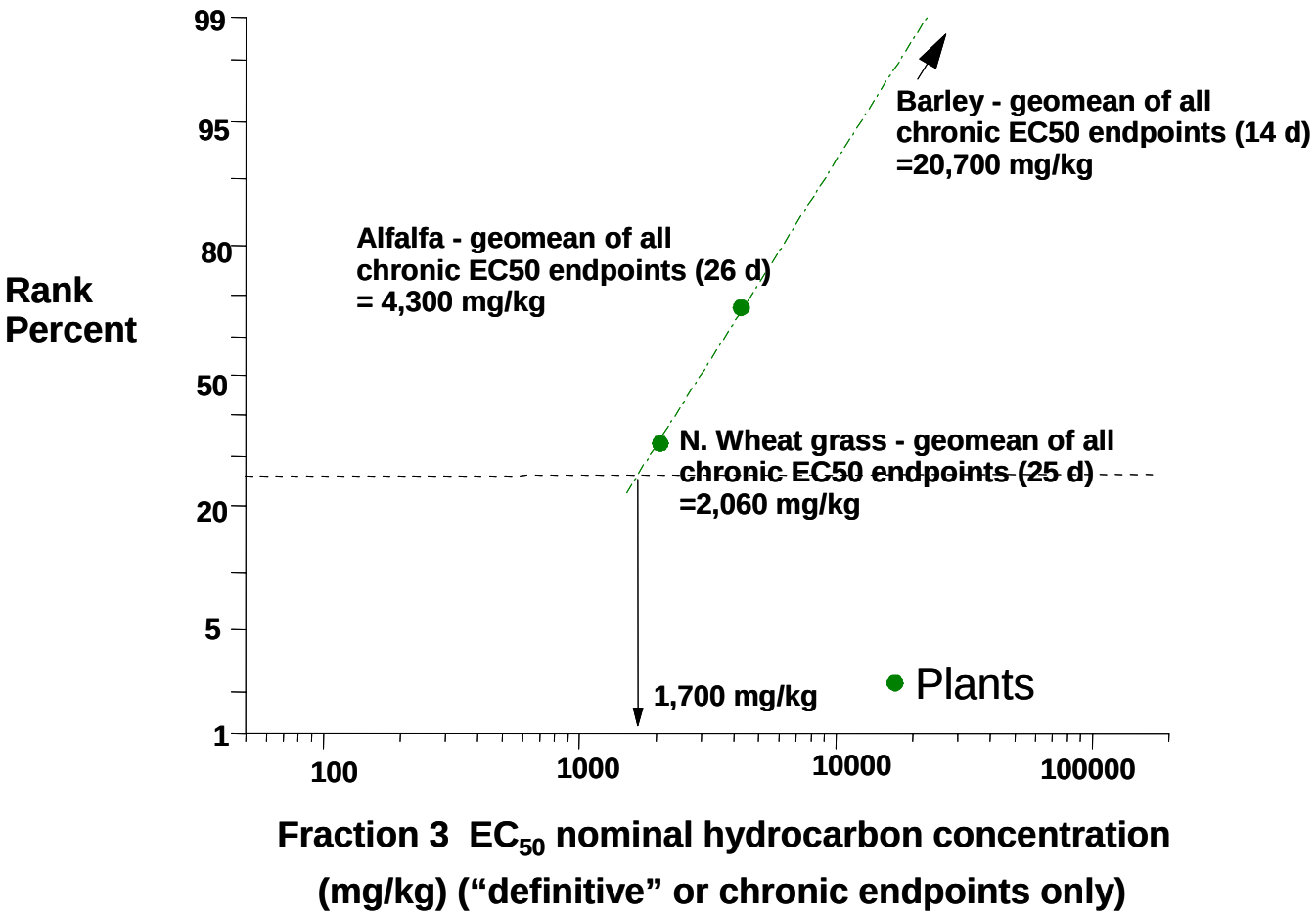


Figure 4.6: Distribution of plant toxicological endpoints for studies on F3 PHCs - consolidated EC_{50} estimates for three plant species for chronic ("definitive") exposure periods only.

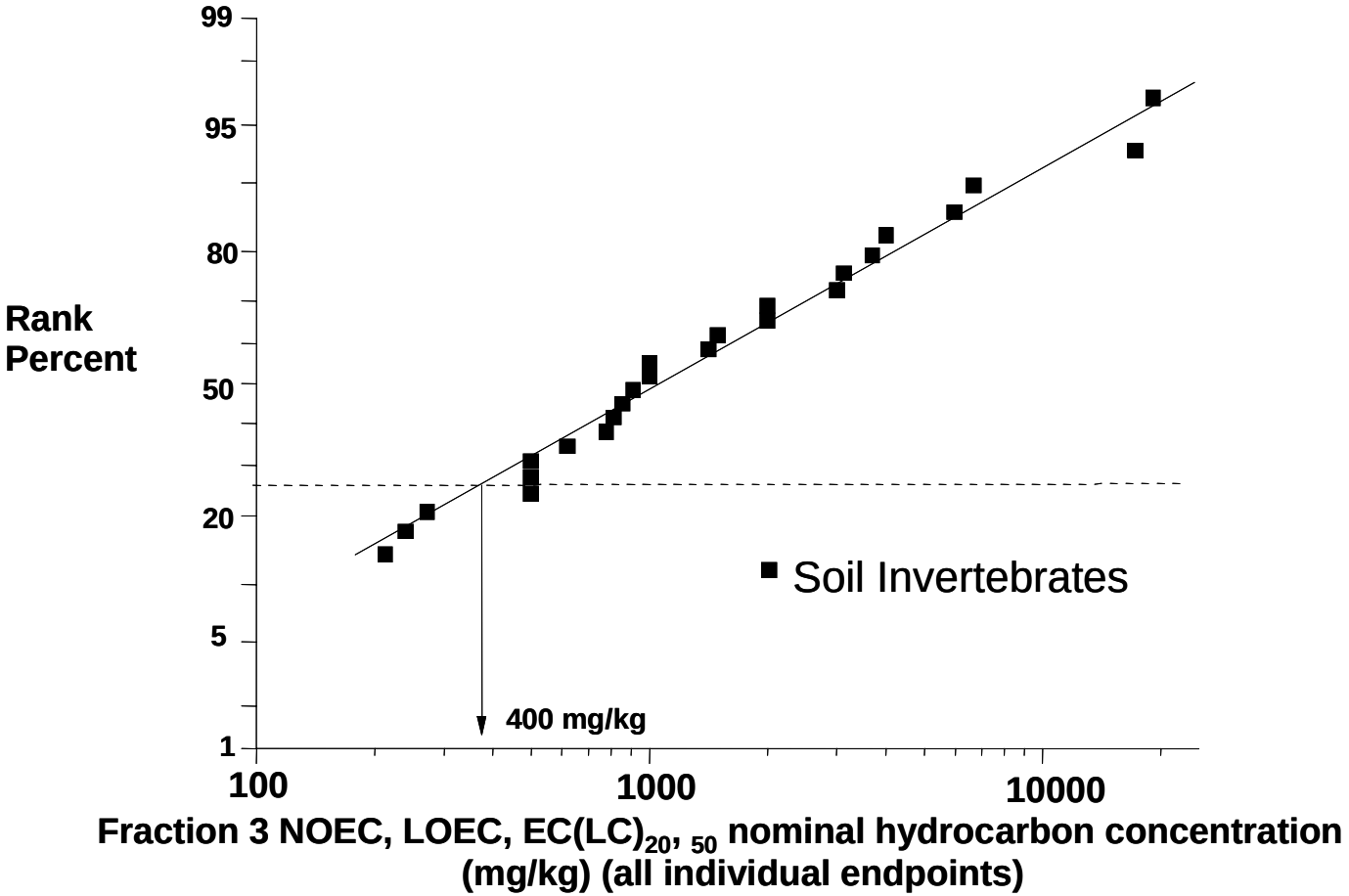


Figure 4.7: Distribution of soil invertebrate toxicological endpoints for studies on F3 PHCs based on LOEC, NOEC, $EC(LC)_{20}$ and $EC(LC)_{50}$ data across two different soil types and acute and chronic ("definitive") exposure periods.

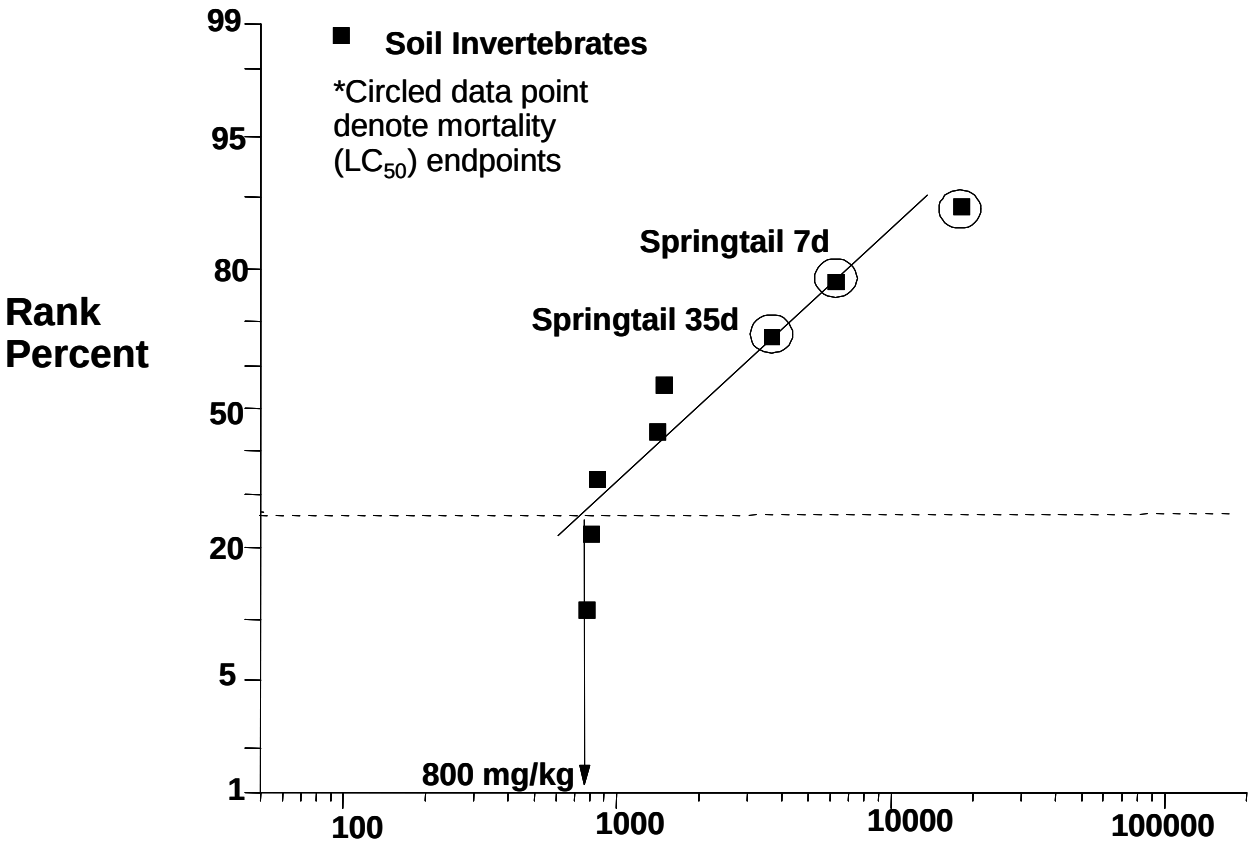


Figure 4.8: Distribution of soil invertebrate toxicological endpoints for studies on F3 PHCs based on $EC(LC)_{50}$ and primarily chronic ("definitive") exposure periods.

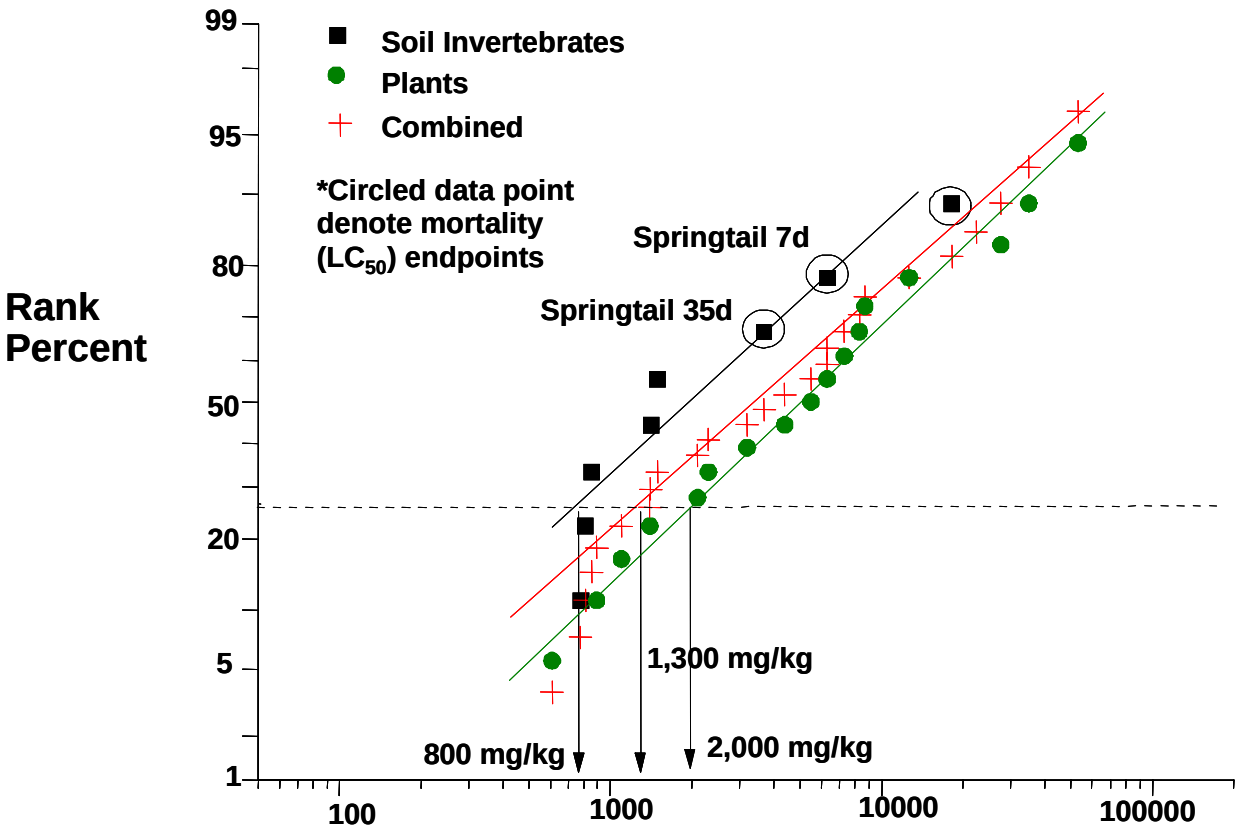


Figure 4.9: Comparison of data distributions for soil invertebrate and plant toxicological endpoints for studies on F3 PHCs.

Based on the above-documented analysis, the 25th percentile of the $EC(LC)_{50}$ nominal concentrations of F3, distilled from Federated Crude Oil, was estimated as shown in Table 4.4. The 50^{th} percentile of the $EC(LC)_{50}$ data distribution, as illustrated in Figure 4.9 is also shown. This shows the effect of the defined ranks level on the resulting soil concentration.

Table 4.4: Threshold effects concentrations for PHC CWS fraction F3.

	Soil Invertebrates Only	Plants Only	Soil Invertebrates and Plants Combined
Est. 25^{th} percentile of effects data based on "nominal" exposure levels: F3	**800 mg/kg**	**2,000 mg/kg**	**1,300 mg/kg**
Estimated "initial" exposure concentration as percent of "nominal" F3 concentration (see Table 4.3, above)	31%	31%	31%
Est. 25^{th} percentile of effects data based on "initial" realized exposure levels: F3	**250 mg/kg**	**620 mg/kg**	**400 mg/kg**
Est. 50^{th} percentile of effects data based on "nominal" exposure levels: F3	2,000 mg/kg	5,500 mg/kg	4,000 mg/kg
Est. 50^{th} percentile of effects data based on "initial" realized exposure levels: F3	**620 mg/kg**	**1,700 mg/kg**	**1,200 mg/kg**

The resulting Threshold Effects Concentrations for the F3 fraction, based on the 25^{th} percentile of the effects database (EC_{50}s and LC_{50}s) are lower than might have been initially anticipated. Referring back to Table 4.2, it can be seen that the following were among the lowest EC_{50}s for F3:

- northern wheatgrass shoot wet wt., 25 day EC_{50} 610 mg/kg nominal **= 190 mg/kg initial**
- worm (*E. foetida*) number of juveniles, 57 day EC_{50} 776 mg/kg nominal **= 240 mg/kg initial**
- worm (*E. foetida*) juvenile dry wt., 57 day EC_{50} 810 mg/kg nominal **= 250 mg/kg initial**
- northern wheatgrass root wet wt., 25 day EC_{50} 890 mg/kg nominal **= 280 mg/kg initial**

- springtail (*O. folsomi*) adult fecundity, 35-36 day EC_{50} 1410 mg/kg nominal
  = 440 mg/kg initial

- alfalfa shoot wet wt, 26 day EC_{50} 2100 mg/kg nominal
  = 650 mg/kg initial

4.2.5 Development of Soil Quality Benchmarks for Fraction 2 (> nC10 to C16)

Using an approach similar to that applied for the Fraction 3, the available draft data from Stephenson *et al.* (2000a) were plotted. Figure 4.10 shows the relative data distribution and corresponding 25th percentile nominal F2 concentrations for plants and soil invertebrates. The data for artificial and standardized field soil were first combined using a geometric mean. In addition, the acute exposure endpoints for plants were omitted.

For the barley and for acute exposure periods, the toxicity tests were carried out in two soil types: a field-collected sandy loam reference soil, and an artificial soil (details provided in Stephenson *et al.* (1999). In addition, various regression-based statistical techniques were used to calculate an EC_{50} response level only. Unlike F3 toxicity tests, no acute endpoints were provided for alfalfa or northern wheatgrass. In addition, the definitive tests conducted in these two plant species were carried out only in one soil type – a field collected "Delacour Orthic Black Chernozem" sandy loam.

A pair-wise comparison was undertaken to assess the effects on calculated toxicological endpoints of soil type, and exposure period for barley. This was carried out through the independent use of paired-sample t-tests for each of the three plant species, and for each factor of interest. The results are summarized below:

- **Barley exposure to F2 in soil:**
  - $\Rightarrow$ Acute (8 day) tests were conducted in both field and artificial soil. The toxicity in the two soil types was similar: There was a difference of only 0.3% in average EC_{50} values between the two soil types. [n = 6, t(2) = 0.068, p = 0.945; Pearson r = 0.95].
  - $\Rightarrow$ EC_{50} endpoints were significantly lower after 13 day exposure than 8 day exposure [n = 6, t(1) = 2.42, p = 0.030]. *The 13 day exposure endpoints were on average 46 % lower than 8 day endpoints.* (Pearson r = -0.30)**.**

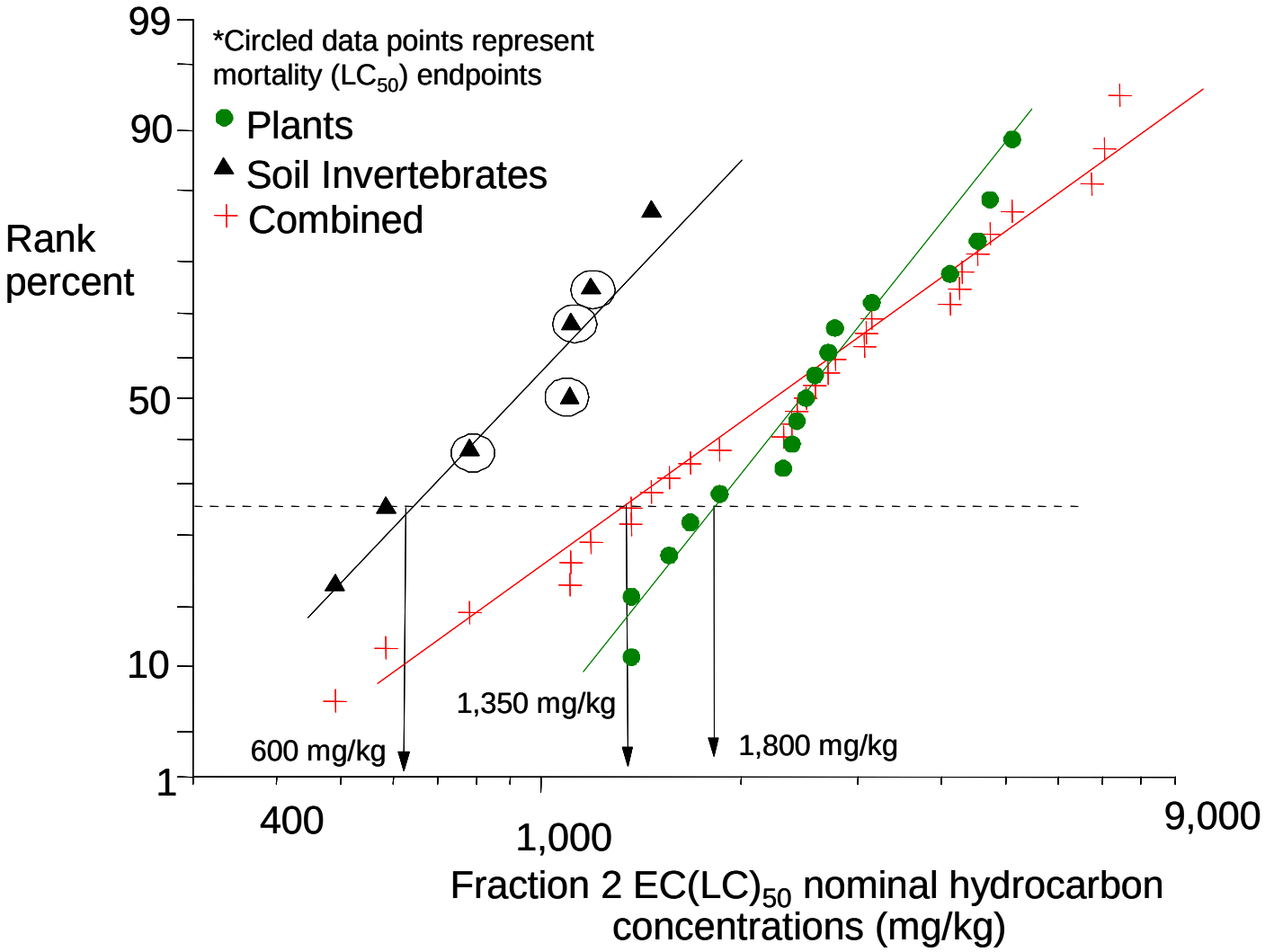


Figure 4.10: Comparison of data distributions for soil invertebrate and plant toxicological endpoints for studies on F2 PHCs.

The preceding analysis is based entirely on the evaluation of toxicological responses of soil invertebrates or plants based on the “nominal”, or spiked soil concentration of F2. The actual changes in exposure concentration of F2 PHCs from the nominal to the initial or final soil concentration were examined as by Stephenson et al. (2000a) as a means of adjusting the broader suite of nominal data. Table 4.5 provides an excerpt of the F2 losses during toxicity testing:

Table 4.5: Change in the soil concentration during sampling unit preparation and over the exposure period.

Nominal F2 Concentration (spiked)	Initial Measured Concentration (t=0)[A]	Init.: Percent of Nominal	Final (14 day) Measured Concentration[B]	Final: Percent of Nominal
500 mg/kg	150 mg/kg	29%	not avail.	
1,000 "	340 "	33%	not avail.	
6,000 "	2,160 "	36%	not avail.	
8,000 "	3,380 "	42%	not avail.	
30,000 "	14,280 "	47%	not avail.	

Notes:
A. Based on GC analysis of TPH for a subset of test soils.
B. TPH analysis of northern wheatgrass definitive (14 day) test units.

Based on the above-documented analysis, the 25th percentile of the $EC(LC)_{50}$ nominal concentrations of F2, distilled from Federated Crude Oil, was estimated as shown in Table 4.6.

Table 4.6: Draft threshold effects concentrations for PHC CWS fraction F2.

	Soil Invertebrates Only	Plants Only	Soil Invertebrates and Plants Combined
Est. 25th percentile of effects data based on "nominal" exposure levels: F2	600 mg/kg	1,800 mg/kg	1,350 mg/kg
Estimated "initial" exposure concentration as percent of "nominal" F2 concentration (see Table 4.5, above)	33%	33%	33%
Est. 25th percentile of effects data based on "initial" realized exposure levels: F2	**200 mg/kg**	**600 mg/kg**	**450 mg/kg**
Est. 50th percentile of effects data based on "nominal" exposure levels: F2	900 mg/kg	2,300 mg/kg	2,100 mg/kg
Est. 50th percentile of effects data based on "initial" realized exposure levels: F2	**300 mg/kg**	**760 mg/kg**	**690 mg/kg**

The following were among the lowest LC(EC)$_{50}$s for F2:

- worm (*E. foetida*) number of juveniles, 62-63 day EC$_{50}$ — 490 mg/kg nominal **= 160 mg/kg initial**
- worm (*E. foetida*) mortality 14 day LC$_{50}$ — 530 mg/kg nominal **= 170 mg/kg initial**
- worm (*L. terrestris*) mortality 7 day LC$_{50}$ — 1,100 mg/kg nominal **= 330 mg/kg initial**
- worm (*L. terrestris*) mortality 14 day LC$_{50}$ — 1,100 mg/kg nominal. **= 330 mg/kg initial**
- alfalfa shoot dry wt. 21 day EC$_{50}$ — 1,370 mg/kg nominal **= 450 mg/kg initial**
- northern wheatgrass 14 day EC$_{50}$ — 1,370 mg/kg nominal **= 450 mg/kg initial**

- springtail (*O. folsomi*) number of juveniles 35 day EC_{50} 1,470 mg/kg nominal
  = **490 mg/kg initial**

4.2.6 Development of Soil Quality Benchmarks for Fraction 1 (C6-nC10)

Limitations in time and funding prevented the generation of new data for the toxicity of F1, distilled from Federated crude, to soil invertebrates and plants. Toxicity data were provided by Stephenson (2000), however, for motor gas, or Mogas.

Mogas is a very common, light-end distillate which is predominantly F1 hydrocarbons when fresh. Following release to the environment, however, the relatively high volatility of mogas constituents tends to result in rapid loss from soils, often within hours to days, depending on which constituent is considered.

The characteristics of the mogas used in the soil invertebrate and plant toxicity tests is provided in Stephenson (2000). The aliphatics in the mixture were predominantly in the >C6 to C8 range. The aromatics were predominantly in the >C8 to C10 range. The mixture was approximately 70% aliphatics and 30% aromatics, including BTEX. In addition, the mogas, provided by the Environmental Technology Group of the Imperial Oil Research Department, was an additive-free refinery blend. Toxic responses, therefore, were not due to additives.

Using an approach similar to that applied for the Fraction 3, the available draft data from Stephenson (2000) were plotted. Figure 4.11 illustrates the plant and soil invertebrate $EC(LC)_{50}$ data distributions.

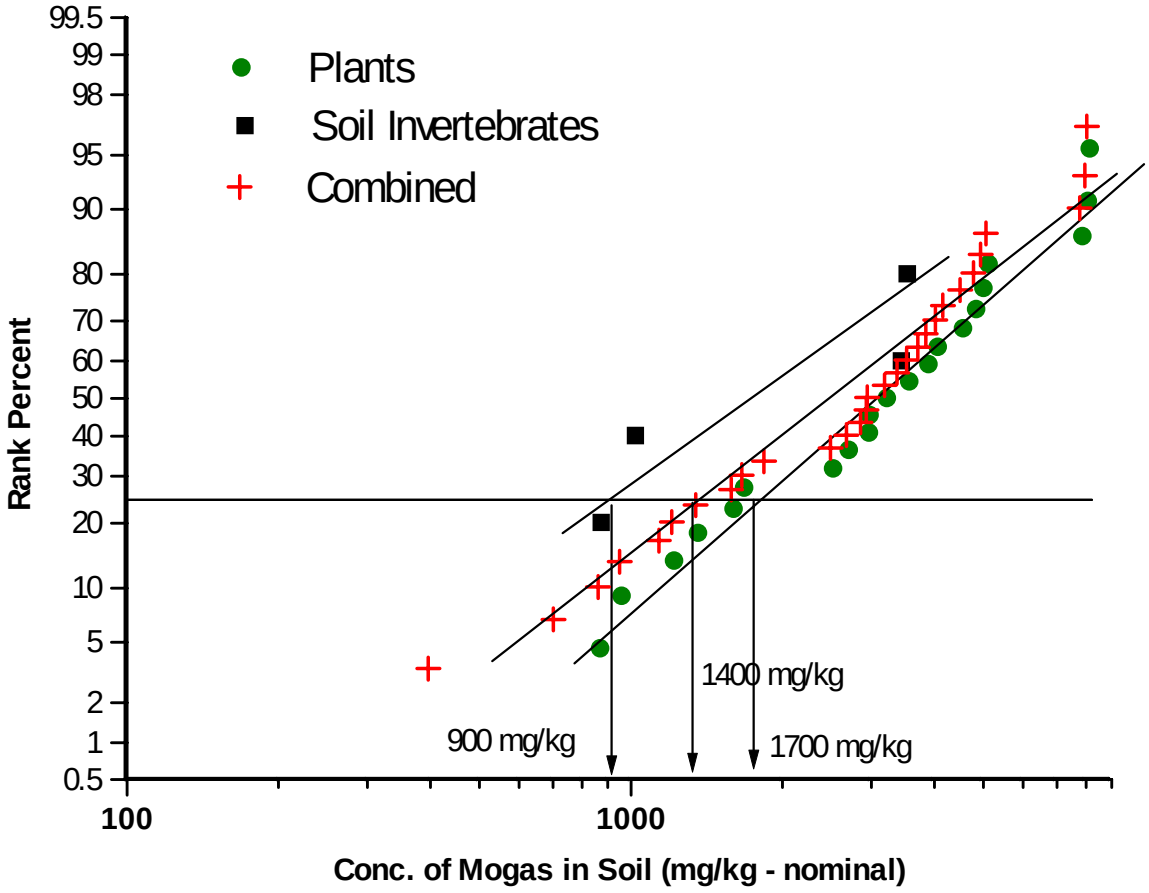


Figure 4.11: Comparison of data distributions for soil invertebrate and plant toxicological endpoints for studies on mogas.

Table 4.7 provides a brief summary of the comparative toxicity of additive-free mogas to alfalfa in two soil types, based on different exposure periods, and at a 20% versus 50% response level.

Table 4.7: Comparison of alfalfa response thresholds [mg/kg (nominal) mogas as TPH] by soil type, exposure duration, and effect size.

Soil Type	Sandy Loam Ref				Artificial Soil			
Exposure time	11 day		21 d		11 d		21 d	
Response Level	EC20	EC50	EC20	EC50	EC20	EC50	EC20	EC50
Endpoint								
shoot length	**2410**	**6600**	**2570**	**5130**	**3210**	**5450**	ND	ND
root length	**3080**	**4580**	**1890**	**2710**	**3310**	**5010**	ND	ND
whole plant ww	**5900**	**8220**	ND	ND	**3390**	**5320**	ND	ND
whole plant dw	**5100**	**6750**	ND	ND	**3400**	**4910**	ND	ND
shoot ww	ND	ND	**1850**	**2520**	ND	ND	ND	ND
shoot dw	ND	ND	**2240**	**3900**	ND	ND	ND	ND
root ww	ND	ND	**2310**	**2980**	ND	ND	ND	ND
root dw	ND	ND	**2120**	**2970**	ND	ND	ND	ND

There were differences in the variability between different response endpoints between the two soils. Overall, however, there was no significant difference in the soil concentration at which comparable response levels (EC_{20} or EC_{50}) were elicited between the artificial soil and sandy loam field soil (two-tailed paired-sample t-test; n = 8. t = 2.17, p = 0.066).

As expected, there was a highly significant difference between EC_{20} and EC_{50} values (one-tailed paired-sample t-test; n = 14. t = -6.94, $p < 0.0001$): EC_{20} soil concentrations were on average 36% lower than EC_{50} values. Finally, 11 day EC_x soil concentrations were significantly higher than 21 day EC_x soil concentrations (one-tailed paired-sample t-test; n = 4, t = 2.48, p = 0.04): the resulting effects endpoint was on average 26% lower for 21 days than 11 days exposure.

Based on the above-documented analysis, the 25th percentile of the $EC(LC)_{50}$ nominal concentrations of additive-free mogas, as an estimate of F1, was as follows (Table 4.8):

Table 4.8: Draft threshold effects concentrations for PHC CWS fraction F1, based on the toxicity of mogas:

	Soil Invertebrates Only	Plants Only	Soil Invertebrates and Plants Combined
Est. 25th percentile of effects data based on "nominal" exposure levels: F1 (mogas)	**900 mg/kg**	**1,700 mg/kg**	**1,400 mg/kg**
Estimated "initial" exposure concentration as percent of "nominal" F1 (mogas) concentration	Note A	Note A	Note A
Est. 25th percentile of effects data based on estimate of "initial" realized exposure levels: F1 (mogas)	**75 mg/kg**	**165 mg/kg**	**130 mg/kg**
Est. 50th percentile of effects data based on "nominal" exposure levels: F1 (mogas)	**1,700 mg/kg**	**3,000 mg/kg**	**2,300 mg/kg**
Est. 50th percentile of effects data based on estimate of "initial" realized exposure levels: F1 (mogas)	**170 mg/kg**	**330 mg/kg**	**240 mg/kg**

Notes:

A: Stephenson evaluated the relationship between the nominal concentration of mogas, and the initial measured concentration. For the preparation method used in Stephenson's laboratory, there was a strong correlation ($r^2 = 0.98$) over 5 orders of magnitude concentration range between the nominal concentration and initial (t = 0) concentration. The simple least-squares regression was as follows:

log (initial) = 1.232 log (nominal) -1.762 (all values in mg mogas/ kg soil dw)

This formula was used to convert at 25th percentile $EC(LC)_{50}$ concentration based on nominal concentration to one based on the expected initial realized exposure concentration in soil test units.

The following were among the lowest $LC(EC)_{50}$s for additive-free mogas:

- worm (*E. foetida*) mortality; 14 day LC_{50} (sandy loam field soil) — 710 mg/kg nominal **= 56 mg/kg initial**
- barley root wet mass; 13 day EC_{50} (sandy loam field soil) — 870 mg/kg nominal **= 72 mg/kg initial**
- alfalfa shoot dry mass, 21 day EC_{50} (artificial soil) — 2,520 mg/kg nominal **= 270 mg/kg initial**
- springtail (*O. folsomi*) number of juveniles 35 day EC_{50} nominal (artificial soil) — 2,890 mg/kg **= 320 mg/kg initial**
- springtail (*O. folsomi*) number of juveniles 35 day EC_{50} nominal (sandy loam field soil) — 4,210 mg/kg **= 500 mg/kg initial**

4.2.7 Surrogate PHC Data

4.2.7.1 - F4 Surrogate Ecotoxicity. No surrogates have been identified to the present time for the F4 fraction.

4.2.7.2 - F3 Surrogate Ecotoxicity. Of the large number of possible PHC compounds found within the >C16 to C34 equivalent boiling point range, pyrene and eicosane were selected as a minimum data set representing an aromatic and aliphatic, respectively. Sufficient data were not available for the round 1 derivation of the PHC CWS, however.

Benzo(a)pyrene (B(a)P) is a C20, five ring unsubstituted aromatic hydrocarbon that has been studied much more extensively than any other individual constituent falling in the F3 fraction. While much of the interest in benzo(a)pyrene is related to its known carcinogenicity to vertebrates, it also has the potential to produce non-specific narcosis-type effects in soil invertebrates in a manner that is similar to other non-carcinogenic aromatics and aliphatics which might be found in the F3 fraction.

Environment Canada (1996a) provides the following summary of plant and soil invertebrate toxicity studies for benzo(a)pyrene (Table 4.9).

Table 4.9: Collated data on soil invertebrate and plant responses to Benzo(a)Pyrene in soil.

Organism	Effect Endpoint	B(a)P conc. (mg/kg soil)
Worm (*E. foetida)*	Mortality 14 day – NOEC	26,000[A]
Lettuce (*Lactuca sativa*)	Seedling emergence 5 day – NOEC	4,400
	LOEC (40% red'n)	8,800
Radish *(Raphanus sativa*)	Seedling emergence 3 day – NOEC	17,500

(from Environment Canada 1996a)

Notes:
A) Initial conc.

The comparison of toxicity endpoints derived using different methodologies, and in different soil types, is undermined by the possible influence of inconsistent exposure regimes. Such comparisons, therefore, should be evaluated with some degree of skepticism, pending a more detailed analysis of the methodological details.

The toxicological response concentrations for benzo(a)pyrene in Table 4.9 are much higher in general than for the F3 fraction for soil invertebrates or plants (estimated 25^{th} percentile for F3 was 250 to 620 mg/kg initial concentration). The F3 data, however, clearly demonstrate that exposure period is of critical importance for the effects endpoint. The F3 fraction was progressively more toxic with an increase in exposure time for both soil invertebrate and plant toxicity tests.

As will be discussed further in Section 4.2.9, the range of equivalent toxicity values across different test organisms was greater for the F3 fraction than for F2, mogas, or even the whole Federated crude oil. This might be attributable to the fact that F3 (>C16 to C34) contains compounds with a broad range of water solubility and lipophilicity. Benzo(a)pyrene is a C20 hydrocarbon; however, its strong lipophilicity (K_{ow} = 6.06; Env. Can., 1996a) and low water solubility (2.3×10^{-3} mg/L) probably make it among the least water soluble, most tightly soil sorbed, and least bioavailable of PHC constituents within the F3 fraction.

4.2.7.3 – F2 Surrogate Ecotoxicity. Of the large number of possible PHC compounds found within the >nC10 to C16 equivalent boiling point range, naphthalene and n-decane were selected as a minimum data set representing an aromatic and aliphatic, respectively. Toxicity studies on naphthalene were carried out in support of the PHC CWS initiative using barley, by Ministère de l'Environnment et de la Faune - Quebec, (MEF-QC), Ontario Ministry of the Environment (OMOE), Environment Canada and ESG International Inc.

The most recent data on effects of naphthalene on barley augment earlier documented data (Environment Canada, 1996b), as follows:

Table 4.10 Collated and new data on soil invertebrate and plant responses to naphthalene in soil.

Organism	Effect Endpoint	Naphthalene conc. (mg/kg)	Notes
Worm (*E. foetida)*	Mortality 14 day – NOEC	204	A
	LOEC (56%)	408	
	EC_{25}	287	
	EC_{50}	**362**	
	Mortality 7 day – NOEC	63 (33)	B
	LOEC (47%)	125 (70)	
	EC_{25}	97 (54)	
	EC_{50}	137 (**77**)	
	Mortality 7 day – **LC_{50}**	(**56.3**)	
	Mortality 14 day – LC_{50}	108	A
Lettuce (*Lactuca sativa*)	Seedling emergence 5 day – NOEC	350	A
	LOEC (62%)	700	
	EC_{25}	470	
	EC_{50}	**630**	
	NOEC	8 (2)	B
	LOEC (62%)	16 (5)	
	EC_{25}	10 (3)	
	EC_{50}	144 (**64**)	
Radish *(Raphanus sativa*)	Seed germination 3 day – NOEC		A
	LOEC (62%)	63 (58)	
	EC_{25}	125 (121)	
	EC_{50}	66 (61)	
		90 (**86**)	

(from Environment Canada 1996b)

Notes:
(A) Nominal;
(B) Nominal conc. with conc. measured at end of exposure period in brackets.

Limited studies are also underway to examine the toxicological effects of n-decane, by MEF-QC and OMOE. The results are forthcoming. The n-decane studies will allow a direct comparison of the relative toxicity of an aromatic compound (naphthalene) and aliphatic (n-decane) with a similar effective carbon size to a representative plant (barley).

Figure 4.12 shows the most recent data for the toxicity of naphthalene to barley. All researchers calculated an EC_{20} and EC_{50} effect level, which are plotted separately in Figure 4.12. This underscores the importance of decisions around data screening prior to applying a ranks-based procedure for defining toxicological thresholds.

The spread in the data (i.e., EC_{50} values that vary from around 500 to 3,000 mg/kg nominal naphthalene concentration) for a single test species is attributable to the different measurement endpoints incorporated (root and shoot length, wet weight, dry weight). The lower concentration effects endpoints tended to be for the inhibition of root growth or mass, whereas the higher endpoints tended to be for shoot growth or mass.

As shown in Table 4.6, the estimated 25^{th} percentile of the EC_{50} data (adjusted for actual initial exposure concentration) for the F2 fraction was **200 mg/kg** for invertebrates and **600 mg/kg** for plants. The 25^{th} percentile EC_{50} for naphthalene effects on barley (Figure 4.12) was 820 mg/kg. Assuming losses from soil during the preparation of test units similar to those documented by Stephenson for naphthalene (initial concentration of ~30% nominal), this would yield a barley growth naphthalene EC_{50} of around **250 mg/kg**. The $EC(LC)_{50}$ values shown in Table 4.9 were in the range of **56 to 86 mg/kg** initial exposure concentration.

Overall, comparison of the available naphthalene toxicity data with the F2 data indicates that naphthalene alone may be slightly more toxic to soil invertebrates and plants on a soil concentration basis than F2 distilled from Federated whole crude (by a factor of approximately two to four).

4.2.7.4 – F1 Surrogate Ecotoxicity. Surrogate compounds previously deemed to represent the F1 fraction include the aromatic toluene and the aliphatic n-hexane. No attempt was made as part of the PHC CWS development initiative to acquire additional toxicity data for surrogates that are potentially representative of the F1 fraction.

Limited data for benzene (Environment Canada, 1996c) toluene (Environment Canada, 1996d), ethylbenzene (Environment Canada, 1996d) and xylenes (Environment Canada, 1996d) on soil invertebrates and plants were collated as part of previous efforts to derive soil quality guidelines. Figure 4.13 provides a graphical summary of the Environment Canada collated ecotoxicity data for benzene.

The soil invertebrate and plant toxicity data for toluene, ethylbenzene, and xylenes is even more limited than for benzene and is not shown graphically herein.

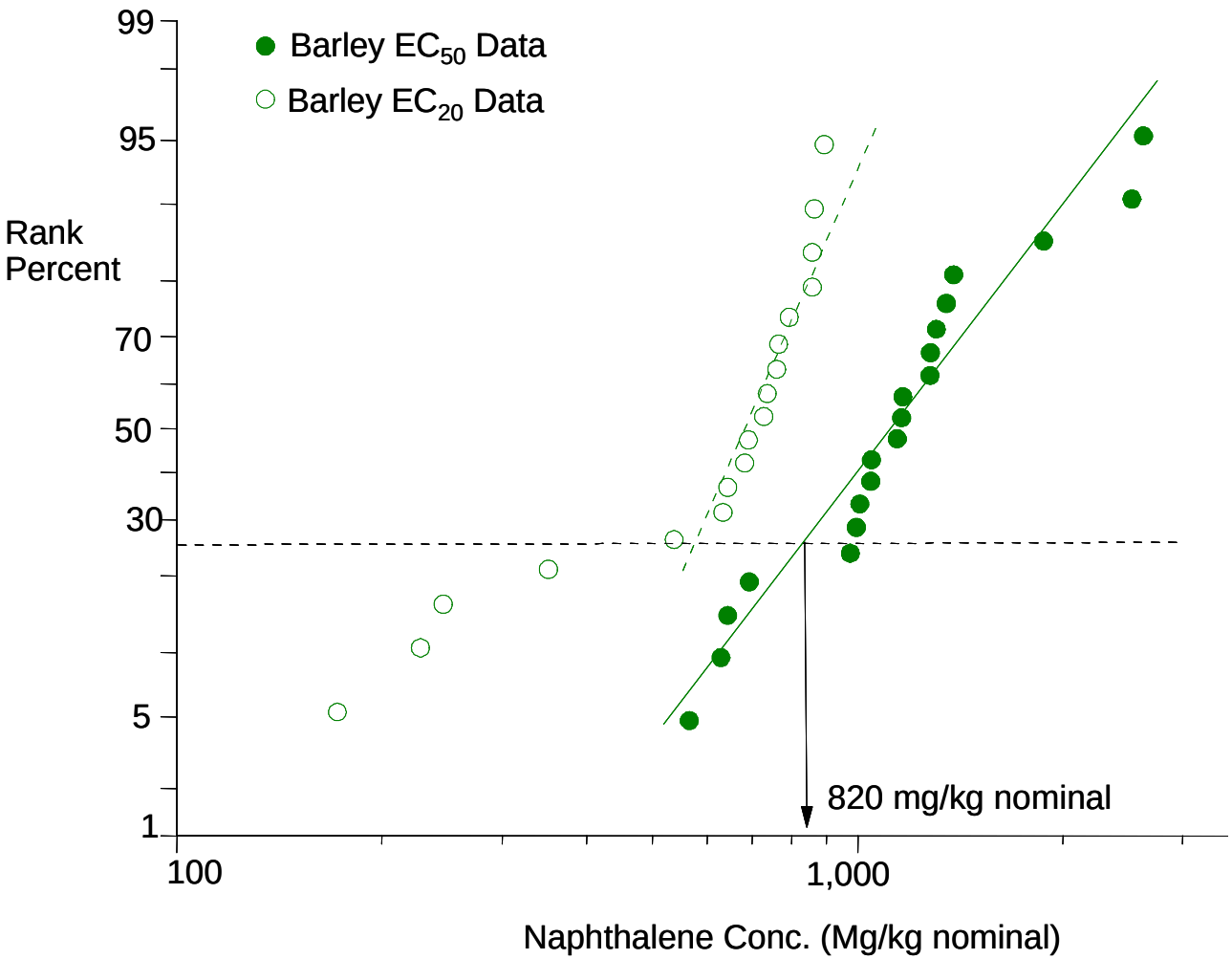


Figure 4.12: Distribution of barley ecotoxicological endpoints for studies on naphthalene based on EC_{50} and EC_{20} endpoints from four different laboratories.

There are considerable methodological challenges in conducting bulk soil toxicity tests for highly volatile compounds. Major portions of the toxicant tend to be lost during preparation of the soil test units, and substantial chemical losses are also experienced during the exposure period. Such losses might not be as great in a typical field situation with a much larger contaminated soil mass, including substantial subsurface mass of volatile organics which tend to re-supply and saturate the soil vapour phase and result in residual contaminant concentrations over much longer periods of time.

Overall, it is difficult to draw any firm conclusions based on comparison of the toxicity of mogas or F1 hydrocarbons with individual surrogates in the C6 to nC10 range.

4.2.8 Whole Product Data

Several of the peer-reviewed studies may provide useful toxicological data based on laboratory or field studies of whole upstream or downstream petroleum products, such as crude oil, mogas, diesel, or JP4 (jet fuel). The carbon range and proportion of CWS carbon-fractions for some of the whole product data are provided in Table 4.11.

Table 4.11: Comparison of whole products and the PHC CWS fractions.

Product	Carbon Range	CWS Fraction
Mogas (fresh)		15% BTEX portion; 65% Non-BTEX portion, include in F1; 20% F2
Mogas (slightly weathered)		25% BTEX; 25% non-BTEX F1; 50% F2
Naphtha (light catalytic cracked)		
	C4 to nC12	F1
Diesel (fresh)	nC9 to nC20.	50% F2; 50% F3
Kerosene	nC9 to nC17	F2
JP4	C4 to nC16	50% F1; 50% F2 (?)
Heavy fuel oils and lube oils (fresh)		
	> nC12-14	F3, F4 (?)

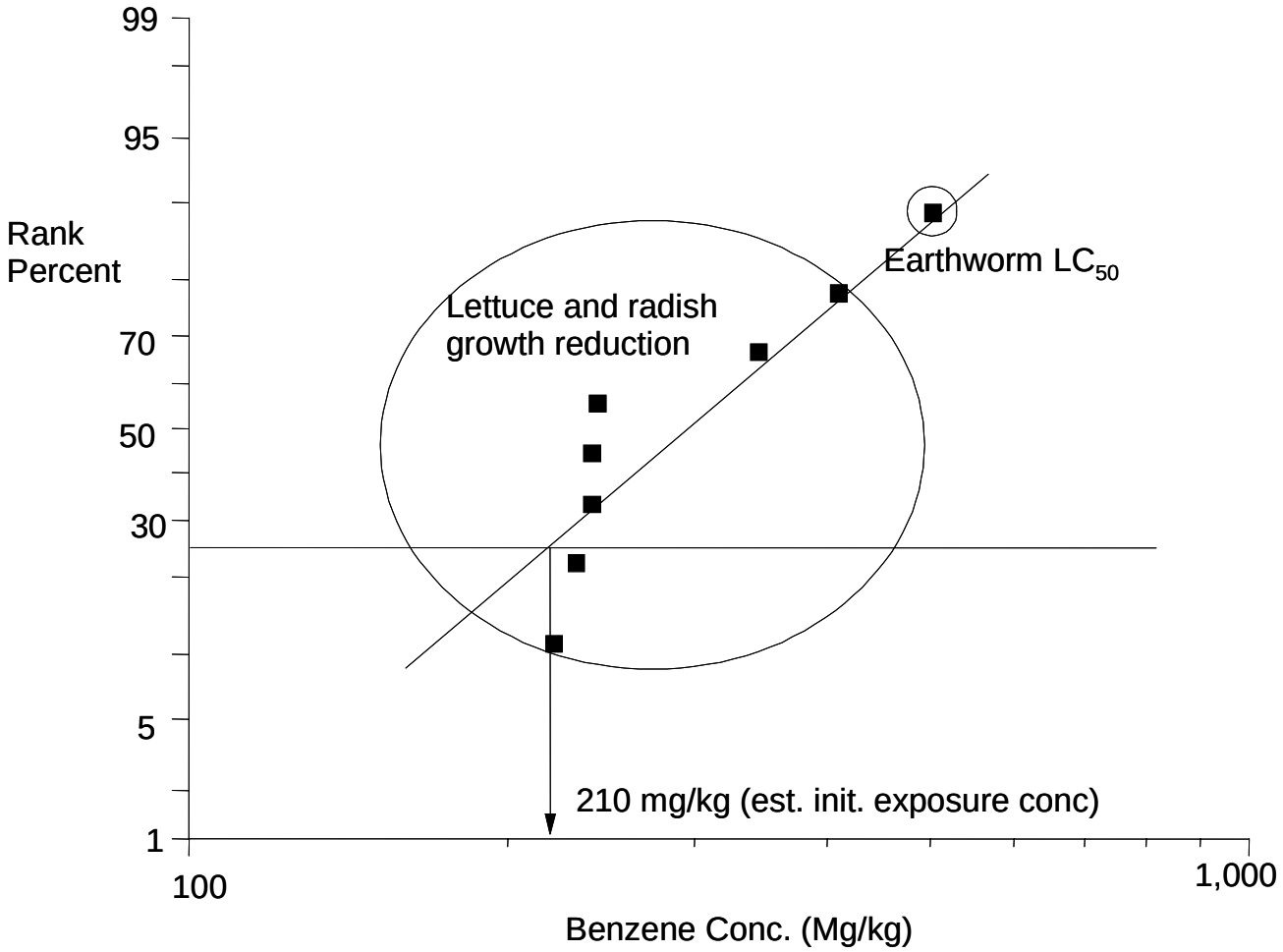


Figure 4.13: Distribution of plant and soil invertebrate ecotoxicological endpoints for benzene based on EC_{50} and LC_{50} endpoints.

In the case of products that fall entirely, or nearly so, within a single PHC CWS fraction, the studies may have value for deriving from scratch a fraction-specific sediment quality guideline (SQG). Naphtha and kerosene toxicity data, for example, may be useful for deriving an SQG for F1 and F2 respectively. Cases where a whole product spans several fractions are clearly more complicated; for example, diesel may be apportioned roughly equally between F2 and F3 (Table 4.11). It is not clear how the relative toxicity of individual fractions can be accounted for, and therefore, how whole product data can be used in the derivation of SQGs for individual carbon fractions.

The diesel or other whole product toxicity data are clearly useful as a validation check against soil values that have been derived from other data types, including fraction-specific and surrogate data. As discussed in section 4.1, this is primarily the context in which the use of whole product studies has been advocated.

4.2.9 Toxicity of Whole Federated Crude Versus CWS Fractions

Stephenson *et al.* (1999) conducted soil toxicity testing on a similar battery of test organisms, using directly comparable endpoints, for whole Federated crude oil and the F3 and F2 fractions obtained from Federated crude through careful distillation. The data are summarized in Appendix F. It is also possible to compare the toxicity of Federated crude with mogas as a reflection of F1 toxicity, based on the data generated by Stephenson (2000).

The ratios of the EC (or $LC)_{50}$ for fractions F1, F2, and F3 to whole Federated crude are summarized as frequency distributions in Figures 4.14 to 4.16.

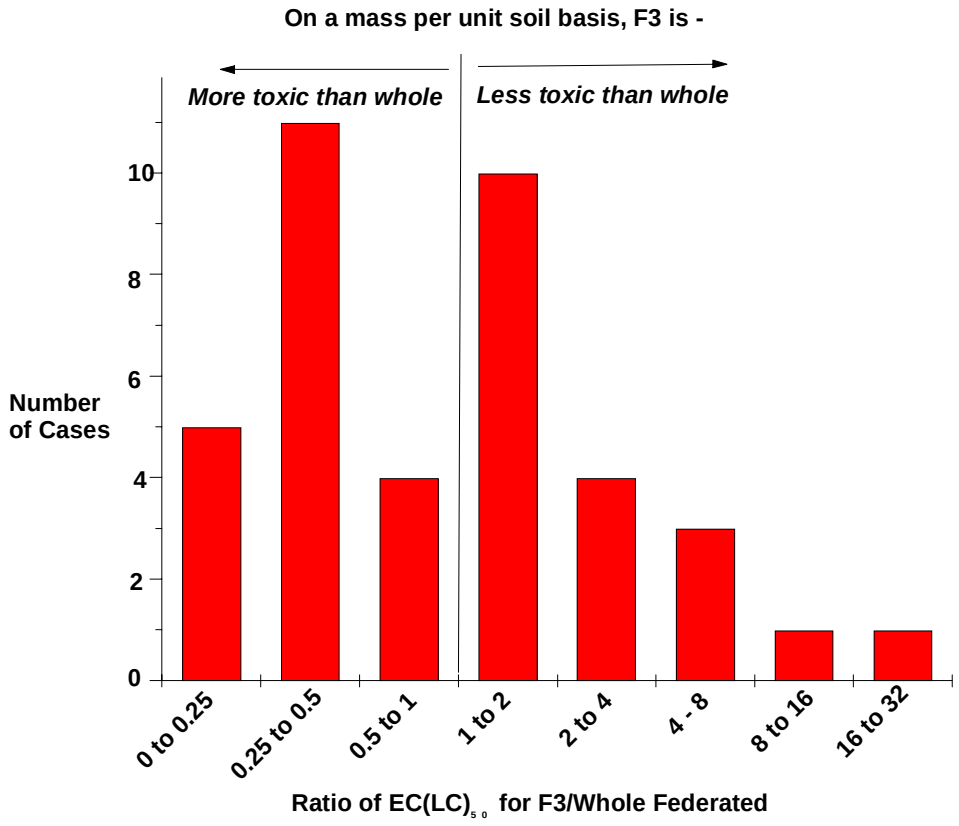


Figure 4.14: Frequency histogram of the relative toxicity of F3 to Federated Whole Crude, based on $EC(LC)_{50}$ endpoints.

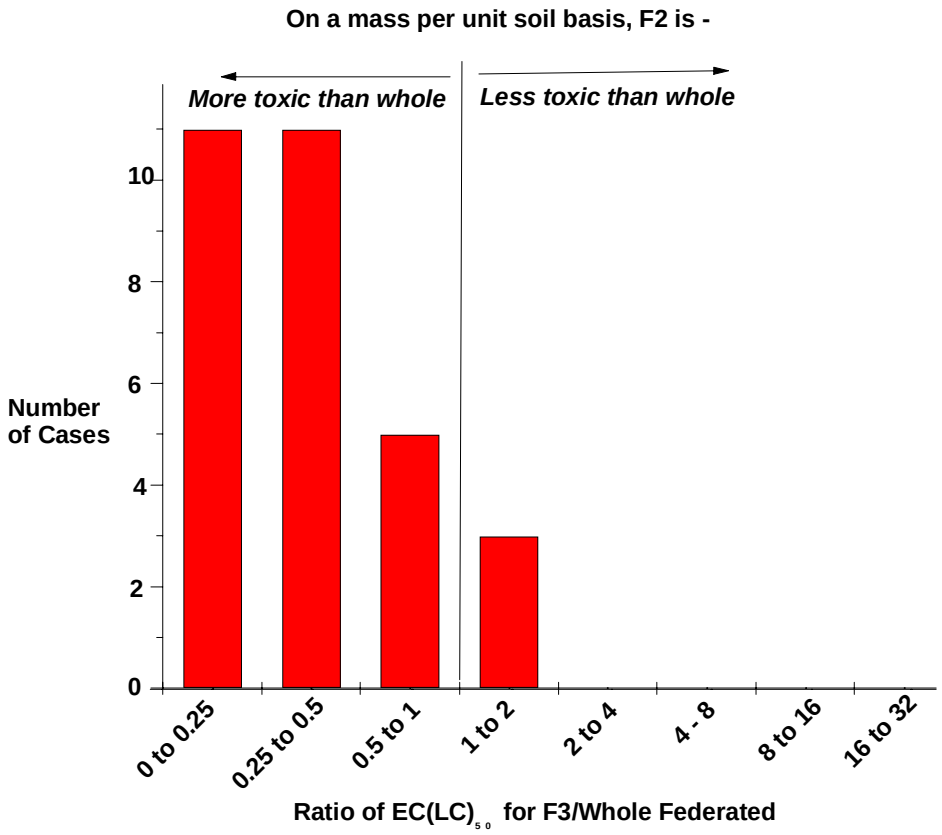


Figure 4.15: Frequency histogram of the relative toxicity of F2 to Federated Whole Crude, based on EC(LC)$_{50}$ endpoints.

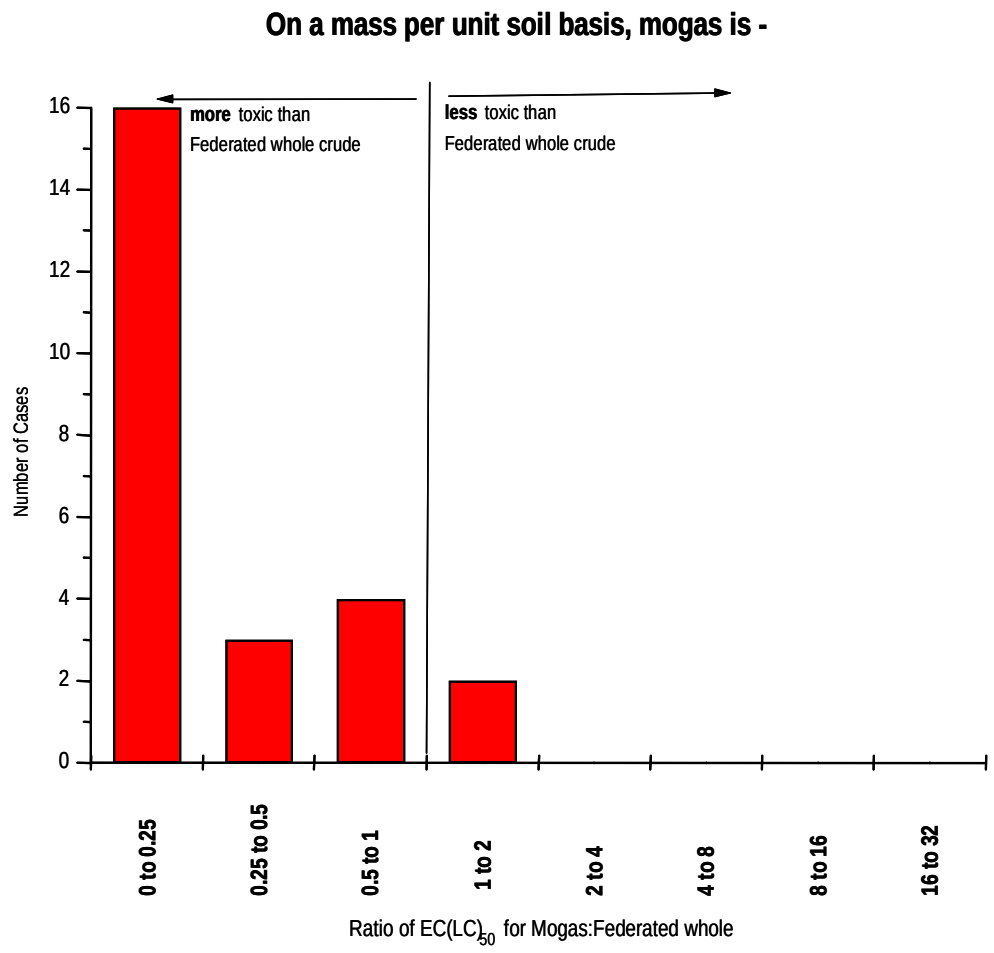


Figure 4.16: Frequency histogram of the relative toxicity of Mogas to Federated Whole Crude, based on $EC(LC)_{50}$ endpoints.

A major portion of the TPH concentration of Federated whole crude might be associated with F4 constituents (>C34) as well as F3 constituents (>C16 to C34) with a limited bioavailability, since the strong hydrophobicity would limit partitioning from soil particles. It would be expected, therefore, that a substantial portion of the whole product toxicity would be associated with the F1 and F2 portions. If these relatively more toxic fractions are isolated, then they alone should exhibit higher toxicity and lower $EC(LC)_{50}$ values than Federated whole crude. Figures 4.15 and 4.16 bear this out. Fraction 2 alone tended to be between two and ten times more toxic, per unit concentration, than whole Federated crude (Appendix F).

The range of toxicity encountered for different taxa and different endpoints for the F3 distillate was much greater than for either F2 alone or for whole crude. The $EC(LC)_{50}$ ratio for F3 to whole crude varied from 0.09 to 19. In other words, F3 alone varied from being around ten times more toxic to twenty times less toxic than whole Federated crude, depending on the test species and endpoint employed.

Figures 4.17 and 4.18 also demonstrate the spread in data for F3 toxicity endpoints relative to either the whole product or various other fractions. This further suggests that the toxicity of F3 across different taxa and exposure conditions will be less easy to predict than for F1 and F2. One possible reason for the spread in data is the large range of physicochemical properties encompassed in F3, based on constituents with a boiling point range bracketed by >C16 and C34. The mixture, therefore, is likely to include a great diversity of branched and straight-chain aliphatics, heterocyclics, N- and S-substituted compounds, and alkylated PAHs. Overall, F3 merits additional future scrutiny in terms of the associated environmental risks.

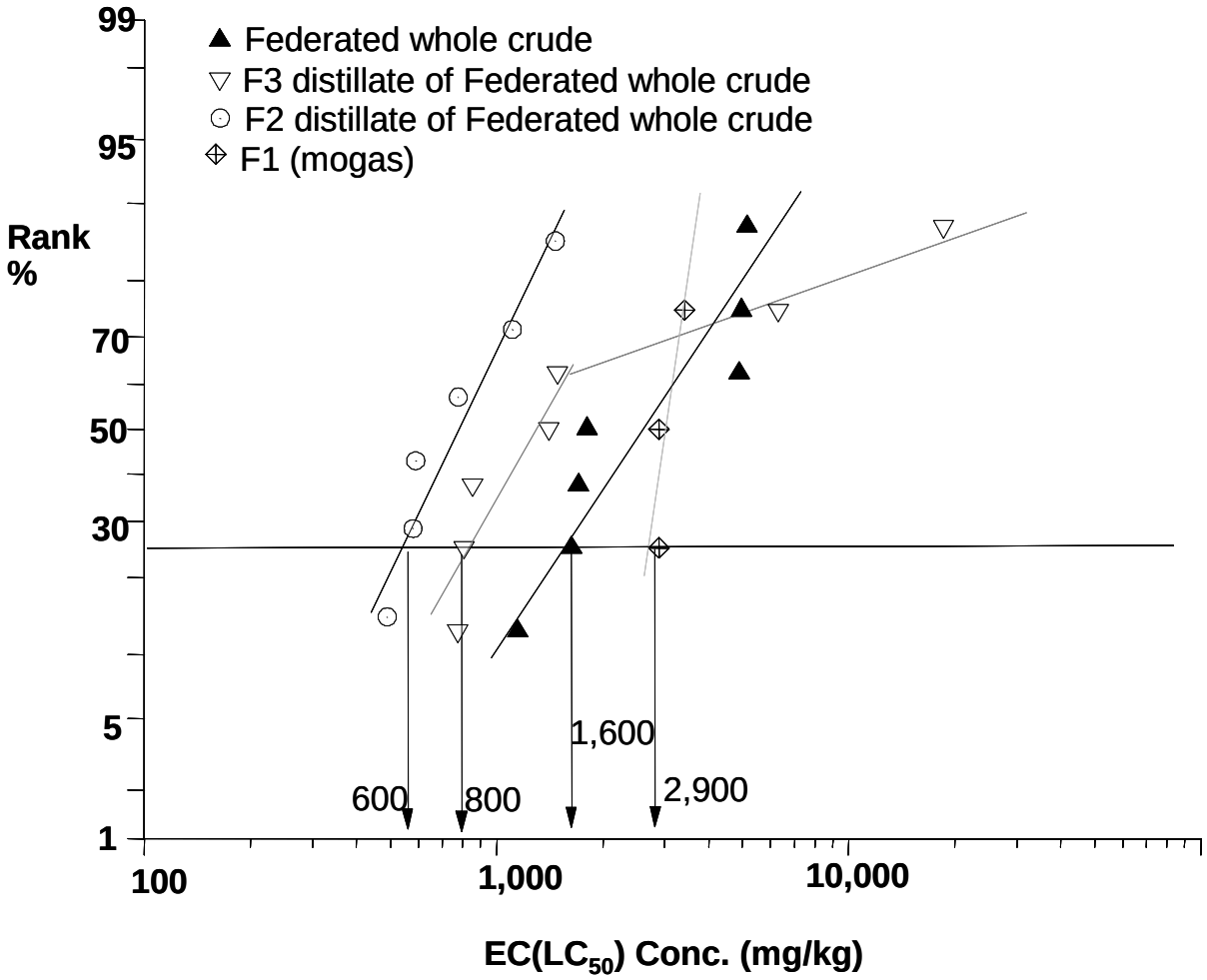


Figure 4.17: Comparison of ranked data for soil invertebrate toxicity effects.

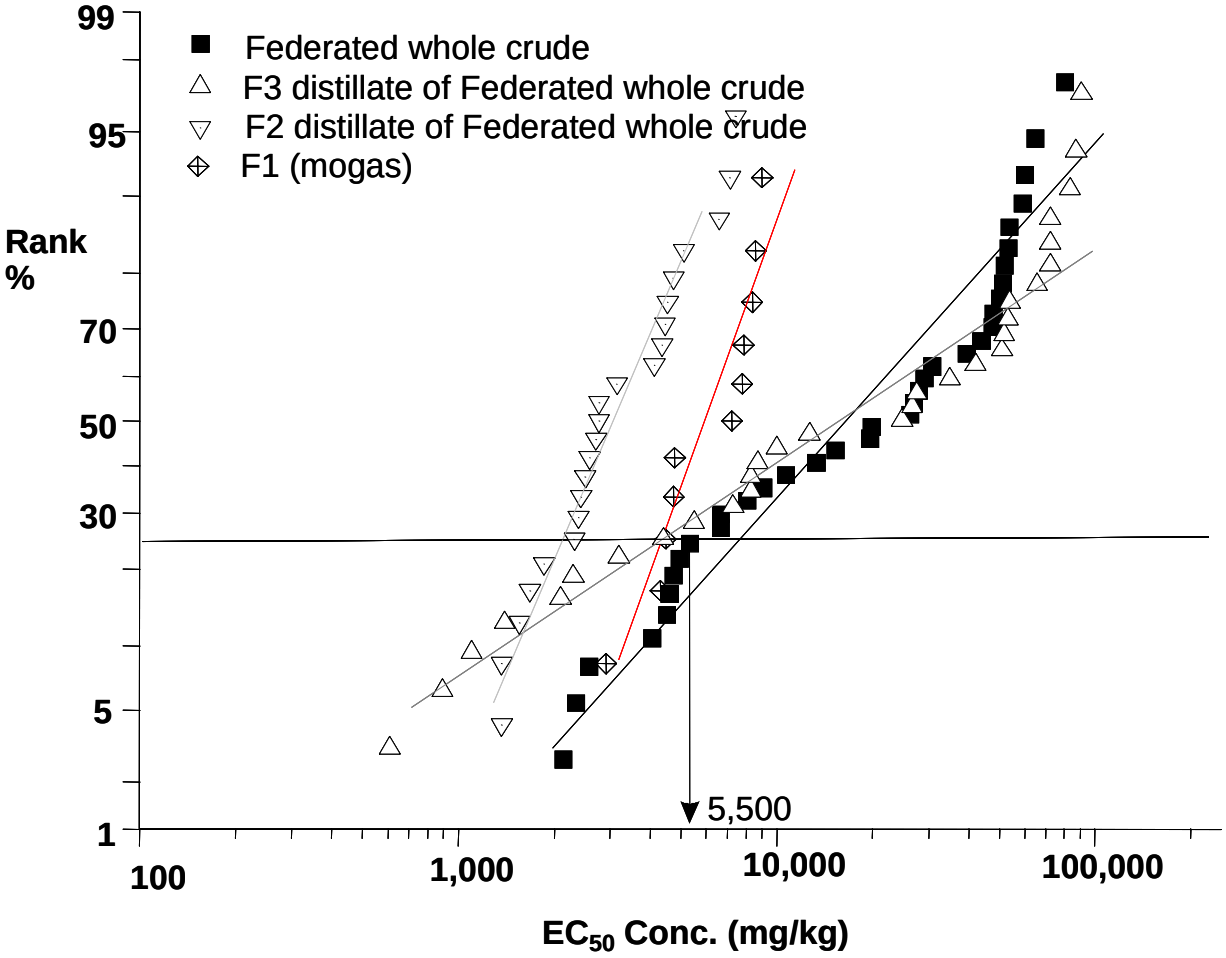


Figure 4.18: Comparison of ranked data for plant toxicity effects endpoints [EC_{50} estimates].

4.2.10 Toxicity of Weathered versus Fresh PHCs

It is commonly held that the natural or enhanced attenuation and biodegradation of PHC mixtures decreases the toxicity and risks over time, as well as the concentrations of various PHC input types. The decrease in toxicological risk is generally attributed to one or more of the following:

- Changes in composition (change in the relative proportions of the original fractions) with biases in loss of more versus less toxic substances.

- Decreased solubility and bioavailability relative to total soil concentrations, due to changes in the PHC-soil particle interaction (enhanced sorption; transfer to intercrystalline layer and/or other deeper internal portions of soil particles).

A conceptual model based on biochemical perturbations in target receptors, which includes issues around bioavailability, is as follows:

PHC input source

↓

↓

Total concentration in soil

↓

↓

Compositional change associated with partitioning and differential loss

↓

Bioavailable fraction (0 to 100% bioavailable)

↓

Internalized or surface contact dose

It is important to differentiate between changes in the toxicity following weathering or bioremediation that are associated with shifts in chemical composition as opposed to bioavailability. In particular, it has been hypothesized that the solubility, leachability, and – hence – bioavailability of petroleum hydrocarbon mixtures rapidly declines after even short periods following introduction into a soil environment (Parkerton and Stone, *in press*).

One of the major advantages of managing PHCs as four discrete fractions, as opposed to using TPH or Oil and Grease measurements, is that compositional shifts associated with weathering may be recognized through the shift in soil concentrations of CWS fractions F1 through F4. The loss of highly volatile hydrocarbons, therefore, would necessarily result in a lower residual concentration of PHCs in the F1 and F2 range. The lower toxicity of residual petroleum hydrocarbons based on loss of volatiles is expected to be reflected in

the lower F1 and F2 concentrations in the soil.

There may be compositional shifts due to weathering, however, within a fraction such that ecotoxicity data on fresh product may not be a good predictor of the risks associated with soils from historical release sites or bioremediated soils. This issue is probably the most important in the context of the CWS F3 fraction (>nC16 to C34), which may comprise a broad spectrum of PHC mixtures, and probably a broader range of relative toxicity than F1 or F2. It has been hypothesized that PHC compounds in the boiling point range >nC16 to C21 (lower molecular weight portion of F3) are relatively more toxic, but less environmentally persistent than constituents in the range >C21 to C34. If this were the case, a change in relative composition within F3 due to weathering and differential attenuation could render overly conservative any F3 soil quality value based on toxicity testing of F3 from fresh product.

The major portion of good quality data to calculate an ecological soil contact Tier 1 value is from either fresh mogas (for F1) or F2 and F3 range distillate of fresh Federated whole crude. This may bias the Tier 1 standards toward lower values typical of fresh releases, as opposed to weathered PHCs. This section specifically evaluates whether the use of laboratory-based plant and soil invertebrate toxicity tests on vacuum distillates from fresh whole product is likely to over-estimate risks at the major portion of field sites.

In particular, one or more of three specific conditions were deemed to constitute direct evidence that the Tier 1 values derived from ecotoxicity data for distillates from fresh Federated Crude Oil are overly protective when applied to a field site with a more weathered mixture:

a. There is a shift toward heavier constituents within each of the CWS fractions (especially F3) as a result of weathering and/or biodegradation;
b. Residual soil concentrations, when expressed according to boiling point ranges equivalent to those encompassed by the PHC CWS fractions, generally result in a higher concentration at which soil invertebrates or plants are affected (higher LC_x or EC_x) than has been documented for fractions derived from fresh Federated Whole Crude (Section 3); and/or
c. No-observed effect levels for F1, F2 or F3 equivalent concentrations are generally substantially higher than would be predicted by the 25^{th} % ile of the EC/LC_{50} distributions documented in Sections 4.2.4 through 4.2.6.

Considerable new information has been brought to bear on the relative risks of fresh versus weathered petroleum products within the last few years. Several studies are presently under way, and the results that will not be available until

after adoption of the first round of Tier I PHC CWS. Four major studies conducted by 1) Visser *et al.* 2) Saterbak *et al.* 3) Alberta Research Council 4) Montreal Refinery site, however, were consulted for evidence of limitations in the applicability of laboratory-based ecotoxicity data on fresh PHC fractions to field sites in Canada. A summary of the major findings is presented below. A detailed discussion of these preliminary results is provided in Appendix G.

Based on the analysis documented in Appendix G, it is concluded that it is not presently possible to adjust generic soil quality benchmarks to reflect the degree of PHC weathering at a specific release site. While some of the studies provisionally support the assertion that PHCs of an equivalent composition are less toxic following weathering, there are also clear-cut cases where the opposite has been observed.

A further rationale for rejection of any measures to adjust generic (Tier I) PHC soil quality benchmarks is as follows:

- Loehr and Webster (1997) stated that –

  "Insufficient data was available to evaluate the relationship between chemical mobility and terrestrial (bulk soil) toxicity". (p. 224)

  In other words, there is insufficient knowledge at the present time to derive defensible numerical models which account for weathering effects of PHC mixtures in bulk soils.

- Loehr and Webster (ibid.) further stated –

  "The results of these evaluations indicated the following:

  There was no apparent relationship between the measured chemical concentrations in a soil or sludge and the associated toxicity of that soil or sludge, before or after bioremediation;"

- Existing studies of mixtures have generally failed to differentiate changes in toxicological thresholds for TPH associated with mixture compositional changes (which would be better reflected in the PHC CWS analysis of 3+1 fractions) as opposed to changes in bioavailability. The existing literature, therefore, offers little guidance.

- Existing studies of weathered versus fresh toxicity thresholds for individual PHC surrogates have underlined the importance of variations in soil type (and possibly other site-specific variations) that cannot presently be accounted for in a Tier I generic site application.

- Use of a fresh/weathered conditional application at Tier I would require some robust means of defining the age of the PHC release and/or degree of weathering.

4.2.11 Reconciliation of Data Types

The toxicity of various PHC constituents in soils to plants and/or invertebrates, based on various measures of PHC concentration as discussed above, is summarized in Table 4.12.

Overall, the data generated for fractions F1, F2, F3 are within the lower effects range (25^{th} percentile of the effects endpoints) as calculated for whole products. The F1, F2 and F3 lower effects concentration were substantially higher than previously documented for individual BTEX constituents; however – as noted above – the degree of confidence in the BTEX plant and soil invertebrate toxicity test results is low.

Based on a weight-of-evidence type analysis, as previously defined (Section 4.1), the new information generated on the ecotoxicity of mogas (for F1), F2, F3, and whole Federated crude (for F4) were deemed to provide the best estimates of toxicological thresholds for the purpose of deriving Tier 1 levels.

Table 4.12: Plant and invertebrate toxicity endpoints for various PHC constituents, based on the 25th percentile of the effects [EC(LC)$_{50}$] database, or range of effects concentrations (in brackets).

PHC Measure	Soil Protective Benchmark for PHCs in Soils (in mg/kg estimated soil exposure concentration or as indicated)		
	Soil Invertebrate 25th percentile	**Plant 25th percentile**	**Combined 25th percentile**
Fraction-specific			
F4 (>nC34)	note A	note A	note A
F3 (>nC16 to C34)	**250**	**620**	**400**
F2 (>nC10 to C16)	**200**	**600**	**450**
F1 (C6 to nC10)[B]	**75**	**165**	**130**
Surrogate data			
F4	not avail.	not avail.	not avail.
F3			
Benzo(a)pyrene	NOEC = 26,000	LOEC = 8,800	
Pyrene	not avail.	note C	not avail.
Eicosene	not avail.	note C	not avail.
F2			
Naphthalene	(56 to 108)	(64 to 86) 250 (barley)	
N-decane	not avail.	note C	not avail.
F1			
Benzene	(55, 342)[D]	(26-102)[D]	210
Toluene	(5-126)[D]	(7-84)[D]	
Ethylbenzene	(155)[D]	(9-71)[D]	
Xylene	(79)[D]	(9-97)[D]	
Whole Product Data			
Fresh Federated Whole Crude	1,600 nominal	5,500 nominal	4,800 nominal
Weathered Crude Oil	800 nominal	600 nominal	
Fresh Crude Oil	1,200 nominal	8,400 nominal	
Fresh Diesel or Heating Oil	800 nominal	800 nominal	
Weathered Diesel or Heating Oil	not avail.	20,000	

Notes:
A: To be determined based on toxicity tests on asphaltene.
B: As estimated from toxicity tests on mogas.
C: In progress.
D: Excerpted from CCME (1996), Supporting Documents. Canadian Soil Quality Guidelines for Benzene, Ethylbenzene, Toluene, and Xylenes. The bracketed concentrations are final measured concentrations, which are underestimates of initial exposure concentration.

4.3 Exposure Scenarios for Ecological Receptors Based on PHCs in Groundwater

This section describes the derivation of draft petroleum hydrocarbon (PHC) concentration limits in surface and subsurface soils beyond which there might be elevated risks to ecological receptors via groundwater exposure pathways. Two different groups of ecological receptors were examined:

i) **Aquatic life** in nearby streams, rivers, and lakes, where PHC contaminated groundwater infiltration might be an issue; and

ii) **Livestock watering**, where livestock (especially cattle) might obtain drinking water from a dugout or other water body within a short distance, and with the potential to receive contaminated groundwater from petroleum hydrocarbon contaminated soils.

The exposure pathway for aquatic life is applicable to all sites and all land-use types where there is potential for risks to aquatic life in surface water bodies at or near a contaminated site. The pathway assumes the presence of a shallow aquifer that interacts directly or indirectly with contaminated soil upgradient from the water body. The exposure pathway for livestock drinking water supplies is intended to apply in agricultural settings only.

The approach used herein to model fate of PHCs in the subsurface environment is adapted from that developed by the British Columbia Contaminated Sites Soil Task Group (CSST) for “soil matrix standards” based on groundwater flow to surface water used by aquatic life. The CSST approach is outlined in “Overview of CSST Procedures for the Derivation of Soil Quality Matrix Standards for Contaminated Sites” [British Columbia Environment (BCE), 1996a]. The US EPA draft document “Soil Screening Guidance” (1994) was used as the framework for the BCE model and the mathematical simulation for the saturated groundwater transport was based on work by Domenico and Robbins (1984). The mathematical equations incorporated in the model are provided in Appendix H.

4.3.1 PHC Chemical Property Assumptions for Tier I Groundwater Fate Modeling

The input parameters to the BCE model were modified using estimates of chemical-specific characteristics for the CWS PHC fractions (Table 4.13), as well as standardized assumptions (based on input from the CWS technical advisory groups) regarding generic site properties (Appendix H).

Soil quality benchmarks for two of the four PHC CWS fractions were developed following preliminary analysis, based on the likelihood of solubilization into groundwater and subsurface transport toward a surface water body containing

aquatic organisms. As discussed previously, the PHC CWS Fraction 1 (F1) includes both aromatic and aliphatic hydrocarbon constituents in the effective boiling point range spanned by n-hexane (nC6) and n-decane (nC10), but excluding BTEX (benzene, toluene, ethylbenzene, and xylenes). The PHC CWS fraction 2 (F2) is designated as the sum of concentrations of aliphatic and aromatic PHCs in the boiling point range between nC10 and nC16. No attempt was made to derive soil quality guidelines based on groundwater transport to ecological receptors for PHC CWS fractions F3 (>nC16 to C34) or F4 (>C34): The strong hydrophobicity of heavier hydrocarbons in these fractions generally precludes significant mobilization in the groundwater in the dissolved phase.

Table 4.13: Representative physical parameters for TPHCWG sub-fractions, based on correlation to relative boiling point index (source: TPHCWG, Vol. 3; 1997).

Fraction (based on boiling point range)	Solubility (mg/L)	Henry's Law Constant (cm^3/ cm^3)	Log K_{oc}
Aliphatic			
C5-C6	3.6E+01	3.3E+01	2.9E+00
>C6-C8	5.4E+00	5.0E+01	3.6 E+00
>C8-C10	4.3E-01	8.0E+01	4.5 E+00
>C10-C12	3.4E-02	1.2E+02	5.4 E+00
>C12-C16	7.6E-04	5.2E+02	6.7 E+00
>C16-C21	2.5E-06	4.9E+03	8.8 E+00
Aromatic			
C5-C7 (benzene only)	1.8E+03	2.3E-01	1.9 E+00
>C8-C10	6.5E+01	4.8E-01	3.2 E+00
>C10-C12	2.5 E+01	1.4E-01	3.4 E+00
>C12-C16	5.8 E+00	5.3E-02	3.7 E+00
>C16-C21	6.5E-01	1.2E-02	4.2 E+00
>C21-C35	6.6E-03	6.7E-04	5.1 E+00

In order to predict PHC fate and transport in the subsurface environment, it was necessary to establish applicable physical transport properties for constituent mixtures of the CWS F1 and F2 fractions**.** A singular estimate for the relevant physical properties was estimated for the sub-fractions designated by the Total Petroleum Hydrocarbon Criterion Working Group (TPHCWG - Vol. 3, 1997), which serves as a good starting point for the PHC CWS groundwater-based soil quality guideline efforts. In general, the TPHCWG fractions were established to limit the range of physical properties of individual constituents within the fraction to around one order of magnitude. The PHC CWS fractions, however, represent a further amalgamation of 17 TPHCWG sub-fractions into only four fractions (F1: nC6 to nC10; F2: >nC10 to nC16; F3: >nC16 to nC34; F4: >nC34). Under the

PHC CWS scheme, aliphatics and aromatics are combined. As noted previously, the BTEX fraction is subtracted from F1.

In assigning values for solubility, organic carbon partition coefficients, Henry's Law Constants or other physical properties to F1 and F2, it is important to appreciate that a given fraction is likely to be a complex mixture of individual compounds. Each of these compounds may have unique physical properties, and a set of assigned values for either the TPH CWG sub-fractions that make up CWS F1 or F2, or for F1 and F2 themselves, as a whole assume that the entire mixture behaves according to some average property which is captured in a singular estimate. This assumption neglects the change in composition of a PHC complex mixture as it moves through the subsurface environment, based on differential partitioning between various matrices, such as soil particle surfaces, interstitial air, interstitial water, or organic matrices.

For the purpose of this exercise, it is assumed herein that the chemical properties of the TPHCWG seventeen sub-fractions (Table 4.13) as previously estimated accurately reflect the environmental partitioning behaviour of these mixtures as a whole. Should relevant new scientific information arise on the fate and transport of complex PHC mixtures, this assumption may need to be re-visited.

The assumed composition of the modeled CWS fractions, as previously applied for human health protective pathways, is as follows:

(i) **CWS Fraction 1 (F1):** 55% >C6 to nC8 (100% aliphatics); 45% >nC8 to nC10 (80% aliphatics and 20% aromatics).

(ii) **CWS Fraction 2 (F2):** 45% >nC10 to nC12 (80% aliphatics and 20% aromatics); 55% >nC12 to nC16 (80% aliphatics and 20% aromatics).

For the CWS, groundwater modeling of the soil concentration below which risks to aquatic life is likely to be elevated was based on the additive contribution of the relevant TPHCWG sub-fractions contained in each PHC CWS fraction. Potential additive or other interactive effects between F1 and F2 fractions were ignored in the derivation exercise. The use of the TPHCWG sub-fractions as the basic chemical unit for modeling represents a compromise along a continuum. The choice of chemical descriptors potentially occupies the entire range from use of single PHC compounds (for example, isopropylbenzene) to the use of a whole product (for example, motor gas) as a singular chemical entity. This is shown conceptually below (Figure 4.19):

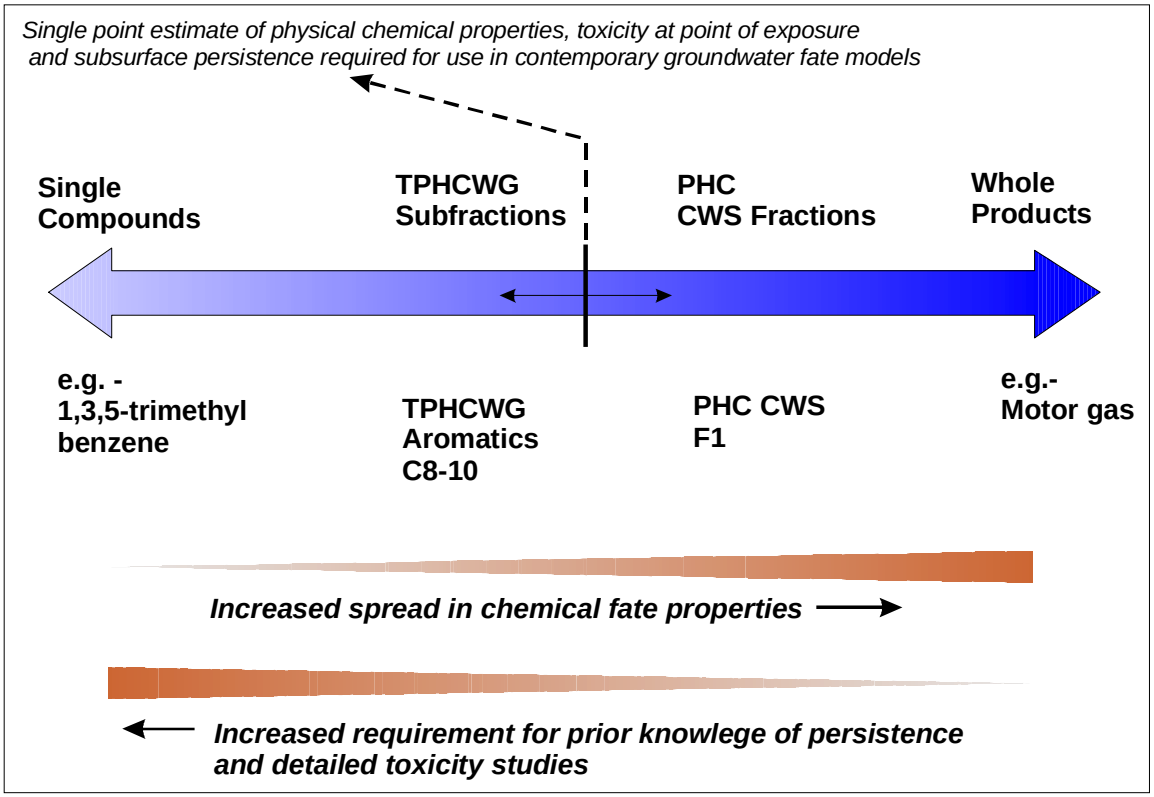


Figure 4.19: Compromise between precision of estimates and level of detailed knowledge of chemical-specific toxicity.

In order to back-calculate an environmentally acceptable soil concentration for PHCs based on groundwater transport to an ecological receptor, the following information is required for each designated chemical unit:

(i) a single point estimates of aqueous solubility, Henry's constant, and K_{oc};

(ii) an estimate of environmental persistence unless it is very conservatively assumed that no subsurface degradation occurs; and

(iii) an aquatic toxicity reference value (TRV) above which risks to relevant ecological receptors may be elevated.

This parallels the informational requirements for estimation of an environmentally acceptable soil concentration based on human health considerations (Chapter 3) although there are key differences between the modeling exercises since the aquatic life or livestock exposure scenario is largely dependent on lateral migration of PHCs in groundwater, as opposed to on-site exposure via drinking water. Where the available scientific knowledge does not adequately support

confident assignation of unique values of the above to each designated chemical unit, then it is necessary to make some more generic assumptions about point estimates that span several of the chemical units. This is discussed in more detail below.

Soil protective benchmarks calculated for the chosen chemical units - in this case the TPHCWG sub-fractions - can be combined to produce an environmentally acceptable concentration in soil for CWS F1 or F2 based on the following formula:

$$SQG_{slice\_i} = \frac{1}{\sum\left(\frac{MF_{subfraction\ j}}{SQG_{subfraction\ j}}\right)}$$

Where -

SQG_{slice_i} = soil quality guideline for the CWS fraction *i* (mg/kg)
$SQG_{subfraction\ j}$ = soil quality guideline (mg/kg) for each sub-fraction within fraction *i* for the target water quality guideline for fraction *i*
$MF_{subfraction\ j}$ = mass fraction of each sub-fraction within the fraction *i*

4.3.2 Estimation of PHC Toxicity to Aquatic Receptors

One of the challenges for developing soil quality guidelines for PHC CWS fractions that are protective of aquatic life in nearby surface water bodies was the absence of formally adopted guidance on appropriate water quality benchmarks for each of the four CWS fractions. The derivation of such soil guidelines necessarily relies on assertions about concentrations of PHCs in water that are acceptably low, and at what level in water there is a potential for elevated risks to aquatic biota.

This derivation exercise focused on CWS fractions F1 and F2, since analysis of the literature indicated that PHCs found in fractions F3 and F4 are sufficiently insoluble that movement via dissolution in groundwater is not likely to be an operable exposure pathway. In the absence of pre-existing guidance, two different approaches were investigated for defining environmentally acceptable concentrations of F1 and F2 PHCs in water bodies containing aquatic life. These were –

- **use of individual surrogates** to define the expected toxicity reference value (toxicological threshold) of the entire CWS fraction in the surrounding water, based on pre-existing aquatic toxicity studies of these surrogates; and

- **use of a "Critical Body Residue" approach**, assuming that the major portion of toxicity is associated with a narcosis-type endpoint, and that the concentration of PHC constituents in the surrounding water is less important for narcosis than the cumulative fraction on a molar basis of all PHCs present in either CWS F1 or F2.

The two approaches are described in more detail below.

4.3.2.1 Use of a Surrogates-Based Approach to Define Acceptable Ambient Water Concentrations. B.C. Environment[1] initially provided to EcoTAG and the PHC CWS Development Committee draft recommendations on aquatic life toxicity reference values for volatile (nC5-nC9) and light (nC10-C19) extractable petroleum hydrocarbons [Volatile Petroleum Hydrocarbons (VPH), and Light Extractable Petroleum Hydrocarbons (LEPH), respectively] based on aquatic life protection.

The BCE draft water quality guidelines employed a surrogates-based approach. For VPH, which is directly equivalent to CWS F1, the surrogates initially used were n-hexane to represent aliphatics toxicity, and toluene to represent the toxicity to aquatic life of the aromatics portion. For the Light Extractable Petroleum Hydrocarbons (LEPH: nC10-C19) fraction, n-decane and naphthalene were used as surrogate compounds for the aliphatics and aromatics respectively. The CWS F2 fraction (nC10-C16) employs a different cut-off than LEPHs at the upper end; however, the previously screened surrogate toxicity data (for naphthalene and n-decane) were deemed to be applicable to F2 since both are at the lighter end of this boiling point range.

For each of the VPH and LEPH fractions, toxicity data for an aliphatic and aromatic surrogate were obtained from US EPA's AQUIRE database. Following an initial review, the BCE toxicity reference values were further modified as described herein.

For the PHC CWS fractions F1 and F2, the toxicity data for each of the chosen surrogates and associated uncertainty factors initially applied were as follows:

[1] Memorandum from Mike Macfarlane and Glyn Fox to John Ward, January 7, 2000. Re: Recommendations for Aquatic Life Criteria for VPH/LEPH/HEPH.

CWS F1:

- **n-hexane**: geometric mean of 48-h LC_{50} for *Daphnia magma* and 24-h LC_{50} for *Artemia salina* = 3,700 µg/L, then divided by a twenty-fold uncertainty factor = 185 µg/L.
- **toluene**: Based on CCME (1996) re-assessment of toluene WQG. Lowest effect level for 27-d rainbow trout LC_{50} of 20 µg/L, then divided by a ten-fold uncertainty factor = 2 µg/L.

CWS F2:

- **decane**: A 48-h acute NOAEL for *Daphnia magna* of 1,300 µg/L was then divided by a ten-fold uncertainty factor to yield a WQG of 130 µg/L.
- **naphthalene**: The geometric mean of rainbow trout hatchability in embryo-stage larvae was 11 µg/L. This was adopted with no uncertainty/application factor.

Through application of the assumed relative percent composition of either F1 or F2 as aliphatics and aromatics, a single toxicity reference value for the entire fraction was obtained. The appropriate mathematical procedure includes the use of the "inverse weighted means" formula as was used elsewhere to combine modeling results for multiple constituent TPH CWG fractions; i.e. –

$$\textit{Toxicity Reference Value (CWS Fraction)} = \frac{1}{\Sigma \{MF_{sub\text{-}f\,j}/TRV_{sub\text{-}f\,j}\}}$$

where –

$MF_{sub\text{-}f\,j}$ = mass fraction of subfraction j 0.2 for aromatic surrogate; 0.8 for aliphatic surrogate

$TRV_{sub\text{-}f\,j}$ = toxicity reference value of subfraction j

For the F1 fraction, the result overall TRV was calculated as follows:

$$\textit{Toxicity Reference Value (CWS F1-draft)} = \frac{1}{[(0.8/185\ \mu g/L.)+(0.2/2\ \mu g/L)]}$$

$$= 9.6\ \mu g/L$$

Similarly, for the F2 fraction, the result overall TRV was calculated as follows:

$$\textit{Toxicity Reference Value (CWS F2-draft)} = \frac{1}{\quad}$$

$$[(0.8/\ 130\ \mu g/L.)+(0.2\ /\ 11\ \mu g/L)]$$

$$= \quad 42\ \mu g/L$$

The use of n-hexane as a surrogate for the toxicity of aliphatics in a typical F1 mixture appears to be reasonable. The use of toluene, or indeed any of the BTEX suite, to characterize the toxicity of the aromatics fraction merited a more detailed examination, however – especially given the potential to strongly influence assumptions regarding the overall toxicity of the CWS F1 fraction. This fraction, by definition, excludes BTEX.

The aromatics found in F1 for a range of whole products are shown in Table 4.14, based on data provided in TPH CWG – Vol. 3.

Approximately 6% to 36% of the composition of gasoline by weight is made up of BTEX. Non-BTEX aromatics in the F1 boiling point range are estimated to comprise an additional 2% to 12% by weight of gasoline. The non-BTEX aromatic composition for the other products was estimated to account for between 0.2% and 3.9% by weight. The preceding estimates, however, are not directly equivalent to an expected aromatic composition in F1 (as opposed to in the whole product), since an appreciable portion of the overall weight percent even for gasoline would be expected to have an Effective Carbon (EC) range greater than nC10 or less than C6. The actual percent composition would be estimated as –

$$\%\ \text{composition (F1)} = \frac{\text{contribution to composition of the whole product}}{\text{fraction of whole product comprised of F1}}$$

If it is reasonably assumed that gasoline is 60% F1 (and 40% <C6 or >nc10) then the maximum percent composition of F1 would be calculated as follows:

$$\%\ \text{composition (F1)} = \frac{12\%}{0.6} = 20\%$$

An upper (worst-case) estimate that CWS F1 is comprised of 20% non-BTEX aromatics, as was previously assumed, appears to be a reasonable assumption

Table 4.14: Whole product composition of F1 aromatics (adapted from TPH CWG, Vol. 3).

Compound	Number of Carbons	EC	Crude Oil Wt%		Gasoline Wt.%		JP-4 Wt.%	JP-5 Wt.%	Diesel Wt.%	
			l.r.	*u.r.*	*l.r.*	*u.r.*	*value*	*value*	*l.r.*	*u.r.*
Benzene	6	6.5	0.04	0.4	0.12	3.5	0.5		0.003	0.1
Toluene	7	7.58	0.09	2.5	2.73	21.8	1.33		0.007	0.7
ethylbenzene	8	8.5	0.09	0.31	0.36	2.86	0.37		0.007	0.2
o-xylene	8	8.81	0.03	0.68	0.68	2.86	1.01	0.09	0.001	0.085
m-xylene	8	8.6	0.08	0.2	1.77	3.87	0.95	0.13	0.018	0.512
p-xylene	8	8.61	0.09	0.68	0.8	1.58	0.35		0.018	0.512
sub-total (% by wt)			***0.42***	***4.8***	***6.4***	***36***	***4.5***	***0.22***	***0.054***	***2.1***
Styrene	9	8.83							<0.002	<0.002
1-methyl-4-ethylbenzene	9	9.57	0.03	0.13	0.18	1	0.43			
1-methyl-2-ethylbenzene	9	9.71	0.01	0.09	0.19	0.56	0.23			
1-methyl-3-ethylbenzene	9	9.55	0.04	0.4	0.31	2.86	0.49			
1,2,3-trimethylbenzene	9	10.1	0.1	0.1	0.21	0.48				
1,2,4-trimethylbenzene	9	9.84	0.13	0.9	0.66	3.3	1.01	0.37		
1,3,5-trimethylbenzene	9	9.62	0.05	0.18	0.13	1.15	0.42		0.09	0.24
n-propylbenzene	9	9.47			0.08	0.72	0.71		0.03	0.048
isopropylbenzene (cumene)	9	9.13			<0.01	0.23	0.3		<0.01	<0.01
n-butylbenzene	10	10.5			0.04	0.44			0.031	0.046
isobutylbezene	10	9.96			0.01	0.08				
sec-butylbenzene	10	9.98			0.01	0.13				
t-butylbenzene	10	9.84			0.12	0.12				
1-methyl-2-n-propylbenzene	10				0.01	0.17				
1-methyl-3-n-propylbenzene	10				0.08	0.56				
1-methyl-4-isopropylbenzene	10	10.1							0.003	0.026
1-methyl-2-isopropylbenzene	10				0.01	0.12	0.29			
sub-total (% by wt)			***0.36***	***1.8***	***2.0***	***12***	***3.9***	***0.4***	***0.2***	***0.4***

Note: l.r. – lower value of reported range; u.r. – upper value of reported range.

The expected relative contribution of individual non-BTEX aromatics to F1 is also shown in Figure 4.20: Based on expected composition, some of the alkylbenzene compounds were deemed be potentially more representative aromatic surrogates of CWS F1 than toluene. The dominant non-BTEX aromatics in the F1 fraction of gasoline and crude oil tend to be trialkylbenzenes such as (in order of relative contribution) 1,2,4-trimethylbenzene; 1-methyl-3-ethylbenzene; 1,3,5-trimethylbenzene; and 1–methyl-4-ethylbenzene. Ideally, assertions about the toxicity of non-BTEX aromatics in CWS F1 using a surrogates approach should be based on studies of these dominant trialkylbenzenes.

The results of a subsequent search for aquatic toxicity data for C9 and C10 alkylbenzenes are provided as Table 4.15, and summarized in Figures 4.21 through 4.23. The lowest tabulated value was for *Daphnia magna* exposed to isopropylbenzene (cumene): Bobra *et al* (1983) observed a 48 h EC_{50} for immobilization of 5 mmol/m^3, or 601 µg/L. As noted in the figures and table, this value falls below the 5th %ile of the species sensitivity distribution for effects on aquatic organisms (including mortality) observed for several C9 and C10 alklybenzenes. In fact, this low value for a 48 h LC_{50} is in disagreement with observed toxicity endpoints derived by others (Table 4.15), and is deemed to be a perhaps overly protective surrogate value for the aquatic risks of CWS F1 aromatics. Immobility in aquatic animals, especially as associated with narcosis-type effects (see below) will generally be followed by mortality unless exposure to the stressor is curtailed. One of the challenges in assessing immobility endpoints in daphnids and other small aquatic animals is that a high degree of variability between different observers sometimes occurs.

In order to account for chronic versus sub-chronic response, a five-fold uncertainty factor was applied to the Bobra *et al.* endpoint, to arrive at an aromatics surrogate toxicity threshold of 120 µg/L. The application of a lower uncertainty factor than is often applied for extrapolating from acute or sub-chronic to chronic endpoints is justified by the fact that the data point falls well below the 5th %ile of the reconstructed species sensitivity distribution, and the endpoint was an immobility EC_{50}, not – strictly speaking – an acute endpoint. No further uncertainty factor was applied to account for additional inter-taxon variability, given that alkylbenzene toxicity data were available for a wide variety of organisms, spanning invertebrates, fish, and algae.

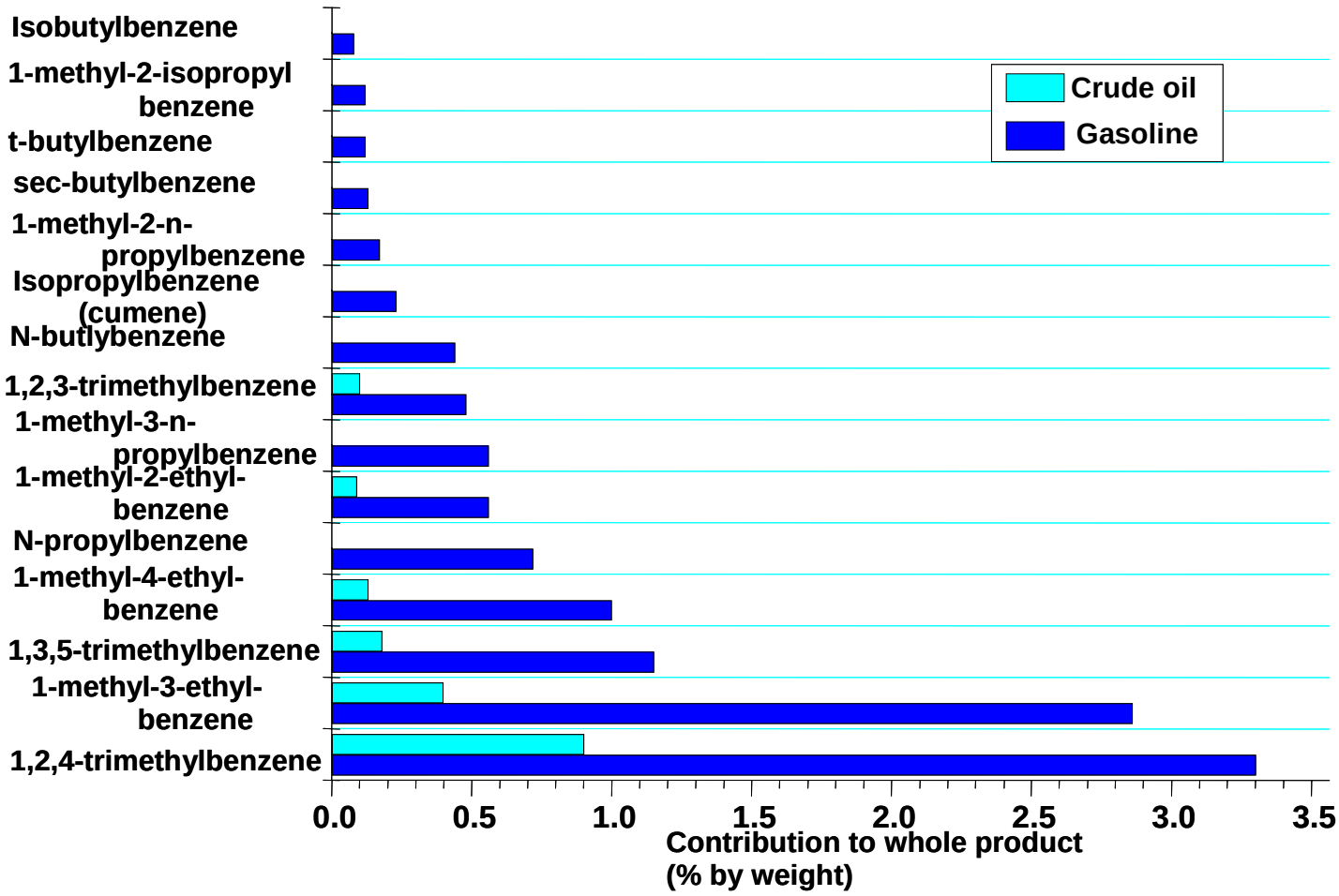


Figure 4.20: Relative abundance of different non-BTEX aromatics in F1.

Table 4.15: Compiled aquatic toxicity data for F1 alkylbenzenes.

Chemical Name	mol. Wt.	sol (mg/L)	H[c/c]	log Kow	Scientific Name	Common Name	Endpoint	Effect	Media Type	Test Duration	Duration Units	Concentration Mean (ug/L)	Author	Title
1,2,4-Trimethylbenzene	120.2	57	2.30E-01	3.60E+00	*Artemia salina*	Brine shrimp	LC50	MOR	SW	24	H	**12020**	ABERNETHY, S., A.M. BOBRA, W.Y. SHIU, P.G. WELLS, AND D. MACKAY	1986. Acute Lethal Toxicity of Hydrocarbons and Chlorinated Hydrocarbons to Two Planktonic Crustaceans: The Key Role of Organism-Water Partitioning.Aquat Toxicol 8(3):163-174 (Publ in Part As 11936)
1,2,4-Trimethylbenzene	120.2	57	2.30E-01	3.60E+00	*Daphnia magna*	Water flea	EC50	Immobil.	FW	48	H	**3606**	BOBRA, A.M., W.Y. SHIU, AND D. MACKAY	1983. A Predictive Correlation for the Acute Toxicity of Hydrocarbons and Chlorinated Hydrocarbons to the Water Flea (Daphnia magna). Chemosphere 12(9-10):1121-1129
1,2,4-Trimethylbenzene	120.2	57	2.30E-01	3.60E+00	*Pimephales promelas*	Fathead minnow	LC50	MOR	FW	96	H	**7720**	GEIGER, D.L., S.H. POIRIER, L.T. BROOKE, AND D.J. CALL	1986. Acute Toxicities of Organic Chemicals to Fathead Minnows (Pimephales promelas), Vol. 3. Center for Lake Superior Environmental Studies, University of Wisconsin, Superior, W I:328
Mesitylene (1,3,5-Trimethylbenzene)	120.2	50	3.15E-01	3.58	*Artemia salina*	Brine shrimp	LC50	MOR	SW	24	H	**14184**	ABERNETHY, S., A.M. BOBRA, W.Y. SHIU, P.G. WELLS, AND D. MACKAY	As above
Mesitylene	120.2	50	3.15E-01	3.58	*Carassius auratus*	Goldfish	LC50	MOR	FW	24	H	**20570**	BRENNIMAN, G., R. HARTUNG, W.J. WEBER, AND J	1976. A Continuous Flow Bioassay Method to Evaluate the Effect of Outboard Motor Exhausts and Selected Aromatic Toxicants on Fish. Water Res 10(2):165-169
Mesitylene	120.2	50	3.15E-01	3.58	*Carassius auratus*	Goldfish	LC50	MOR	FW	48	H	**16170**	BRENNIMAN, G., R. HARTUNG, W.J. WEBER, AND J	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Carassius auratus*	Goldfish	LC50	MOR	FW	72	H	**13650**	BRENNIMAN, G., R. HARTUNG, W.J. WEBER, AND J	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Carassius auratus*	Goldfish	LC50	MOR	FW	96	H	**12520**	BRENNIMAN, G., R. HARTUNG, W.J. WEBER, AND J	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Daphnia magna*	Water flea	LC0 (NOEC)	MOR	FW	24	H	**40000**	KUHN, R., M. PATTARD, K. PERNAK, AND A. WINTER	1989. Results of the Harmful Effects of Water Pollutants to Daphnia magna in the 21 Day Reproduction Test. Water Res 23(4):501-510.
Mesitylene	120.2	50	3.15E-01	3.58	*Daphnia magna*	Water flea	EC50	Immobil.	FW	24	H	**50000**	KUHN, R., M. PATTARD, K. PERNAK, AND A. WINTER	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Daphnia magna*	Water flea	EC50	Immobil.	FW	48	H	**6010**	BOBRA, A.M., W.Y. SHIU, AND D. MACKAY	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Daphnia magna*	Water flea	NOEC	REP	FW	21	D	**890**	KUHN, R., M. PATTARD, K. PERNAK, AND A. WINTER	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Scenedesmus subspicatus*	Green algae	EC10	absorb. @578 nm	FW	48	H	**8100**	KUHN, R. AND M. PATTARD	1990. Results of the Harmful Effects of Water Pollutants to Green Algae (Scenedesmus subspicatus) in the Cell Multiplication Inhibition Test. Water Res 24(1):31-38.

Chemical Name	mol. Wt.	sol (mg/L)	H[c/c]	log Kow	Scientific Name	Common Name	Endpoint	Effect	Media Type	Test Duration	Duration Units	Concentration Mean (ug/L)	Author	Title
Mesitylene	120.2	50	3.15E-01	3.58	*Scenedesmus subspicatus*	Green algae	EC50	absorb. @578 nm	FW	48	H	**25000**	KUHN, R. AND M. PATTARD	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Scenedesmus subspicatus*	Green algae	EC10	turbidity as est. of pop'n density	FW	48	H	**53000**	KUHN, R. AND M. PATTARD	As above.
Mesitylene	120.2	50	3.15E-01	3.58	*Scenedesmus subspicatus*	Green algae	EC50	turbidity as est. of pop'n density	FW	48	H	**53000**	KUHN, R. AND M. PATTARD	As above.
o-Ethyltoluene (1-methyl-2-ethylbenzene)	120.2	75	2.14E-01	3.63	*Chlamydomonas angulosa*	Green algae	EC50	PHY	NR	3	H	**18631**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	1980. The Correlation of the Toxicity to Algae of Hydrocarbons and Halogenated Hydrocarbons with Their Physical-Chemical Properties. Environ Sci Res 16:577-586.
o-Ethyltoluene	120.2	75	2.14E-01	3.63	*Chlorella vulgaris*	Green algae	EC50	PHY	NR	3	H	**40868**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
p-Ethyltoluene (1-methyl-4-ethylbenzene)	120.2	94	2.02E-01	3.63	*Chlamydomonas angulosa*	Green algae	EC50	PHY	NR	3	H	**54090**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
p-Ethyltoluene	120.2	94	2.02E-01	3.63	*Chlorella vulgaris*	Green algae	EC50	PHY	NR	3	H	**48080**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
Propyl benzene (n-propylbenzene)	120.2	52	4.20E-01	3.69	*Chlamydomonas angulosa*	Green algae	EC50	PHY	NR	3	H	**18030**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
Propyl benzene	120.2	52	4.20E-01	3.69	*Chlorella vulgaris*	Green algae	EC50	PHY	NR	3	H	**16227**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.

Chemical Name	mol. Wt.	sol (mg/L)	H[c/c]	log Kow	Scientific Name	Common Name	Endpoint	Effect	Media Type	Test Duration	Duration Units	Concentration Mean (ug/L)	Author	Title
Propyl benzene	120.2	52	4.20E-01	3.69	*Daphnia magna*	Water flea	LC50	MOR	FW	24	H	**2000**	TOSATO, M.L., L. VIGANO, B. SKAGERBERG, AND S. CLEMENT	1991. A New Strategy for Ranking Chemical Hazards. Framework and Application. Environ Sci Technol 25:695-702.
Propyl benzene	120.2	52	4.20E-01	3.69	*Oncorhynchus mykiss*	Rainbow trout,donaldson trout	LC50	MOR	FW	96	H	**1550**	GALASSI, S., M. MINGAZZINI, L. VIGANO, D. CESAREO, AND M.L. TOSATO	As above.
Propyl benzene	120.2	52	4.20E-01	3.69	*Selenastrum capricornutum*	Green algae	EC50	GRO	FW	72	H	**1800**	GALASSI, S., M. MINGAZZINI, L. VIGANO, D. CESAREO, AND M.L. TOSATO	As above.
Cumene (isopropylbenzene)	120.2	50	5.92E-01	3.63	*Artemia*	Brine shrimp	EC50	ITX	FW	48	H	**7400**	MACLEAN, M.M. AND K.G. DOE	1989. The Comparative Toxicity of Crude and Refined Oils to Daphnia magna and Artemia. Environment Canada, EE-111, Dartmouth, Nova Scoti a:64
Cumene	120.2	50	5.92E-01	3.63	*Artemia*	Brine shrimp	EC50	ITX	FW	48	H	**7500**	MACLEAN, M.M. AND K.G. DOE	As above.
Cumene	120.2	50	5.92E-01	3.63	*Artemia*	Brine shrimp	LC50	MOR	FW	48	H	**7400**	MACLEAN, M.M. AND K.G. DOE	As above.
Cumene	120.2	50	5.92E-01	3.63	*Artemia*	Brine shrimp	LC50	MOR	FW	48	H	**8000**	MACLEAN, M.M. AND K.G. DOE	As above.
Cumene	120.2	50	5.92E-01	3.63	*Artemia salina*	Brine shrimp	LC50	MOR	SW	24	H	**13703**	ABERNETHY, S., A.M. BOBRA, W.Y. SHIU, P.G. WELLS, AND D. MACKAY	As above.
Cumene	120.2	50	5.92E-01	3.63	*Artemia salina*	Brine shrimp	LC50*	MOR	SW	24	H	**1E+05**	PRICE, K.S., G.T. WAGGY, AND R.A. CONWAY	1974. Brine Shrimp Bioassay and Seawater BOD of Petrochemicals. J Water Pollut Control Fed 46(1):63-77.
Cumene	120.2	50	5.92E-01	3.63	*Chlamydomonas angulosa*	Green algae	EC50	PHY	NR	3	H	**8775**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
Cumene	120.2	50	5.92E-01	3.63	*Chlorella vulgaris*	Green algae	EC50	PHY	NR	3	H	**21275**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
Cumene	120.2	50	5.92E-01	3.63	*Daphnia magna*	Water flea	EC50	ITX	FW	24	H	**1400**	TOSATO, M.L., L. VIGANO, B. SKAGERBERG, AND S. CLEMENT	As above.
Cumene	120.2	50	5.92E-01	3.63	*Daphnia magna*	Water flea	EC50	ITX	FW	48	H	**601**	BOBRA, A.M., W.Y. SHIU, AND D. MACKAY	As above.

Chemical Name	mol. Wt.	sol (mg/L)	H[c/c]	log Kow	Scientific Name	Common Name	Endpoint	Effect	Media Type	Test Duration	Duration Units	Concentration Mean (ug/L)	Author	Title
Cumene (listed as "cumol" in German)	120.2	50	5.92E-01	3.63	*Daphnia magna*	Water flea	LC0	MOR	FW	24	H	**83000**	BRINGMANN, G. AND R. KUHN	1977. The Effects of Water Pollutants on Daphnia magna. Z Wasser-Abwasser-Forsch 10(5):161-166 (GER) (ENG ABS).
Cumene (listed as "cumol" in German)	120.2	50	5.92E-01	3.63	*Daphnia magna*	Water flea	LC50	MOR	FW	24	H	**95000**	BRINGMANN, G. AND R. KUHN	As above.
Cumene (listed as "cumol" in German)	120.2	50	5.92E-01	3.63	*Daphnia magna*	Water flea	LC100	MOR	FW	24	H	**1E+05**	BRINGMANN, G. AND R. KUHN	As above.
Cumene	120.2	50	5.92E-01	3.63	*Oncorhynchus mykiss*	Rainbow trout,donaldson trout	LC50	MOR	FW	96	H	**2700**	GALASSI, S., M. MINGAZZINI, L. VIGANO, D. CESAREO, AND M.L. TOSATO	As above.
Cumene	120.2	50	5.92E-01	3.63	*Pimephales promelas*	Fathead minnow	LC50	MOR	FW	96	H	**6320**	GEIGER, D.L., S.H. POIRIER, L.T. BROOKE, AND D.J. CALL	As above.
Cumene	120.2	50	5.92E-01	3.63	*Poecilia reticulata*	Guppy	LC50	MOR	FW	96	H	**5100**	GALASSI, S., M. MINGAZZINI, L. VIGANO, D. CESAREO, AND M.L. TOSATO	As above.
Cumene	120.2	50	5.92E-01	3.63	*Selenastrum capricornutum*	Green algae	EC50	GRO	FW	72	H	**2600**	GALASSI, S., M. MINGAZZINI, L. VIGANO, D. CESAREO, AND M.L. TOSATO	As above.
tert-Butylbenzene	134.2	30	5.17E-01	4.11	*Daphnia magna*	Water flea	LC50	MOR	FW	24	H	**41000**	BRINGMANN, G. AND R. KUHN	As above.
Isobutyl benzene	134.2	10.1	1.34	4.01	*Chlamydomonas angulosa*	Green algae	EC50	PHY	NR	3	H	**3087**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.
Isobutyl benzene	134.2	10.1	1.34	4.01	*Chlorella vulgaris*	Green algae	EC50	PHY	NR	3	H	**3490**	HUTCHINSON, T.C., J.A. HELLEBUST, D. TAM, D. MACKAY, R.A. MASCARENHAS, AND W.Y. SHIU	As above.

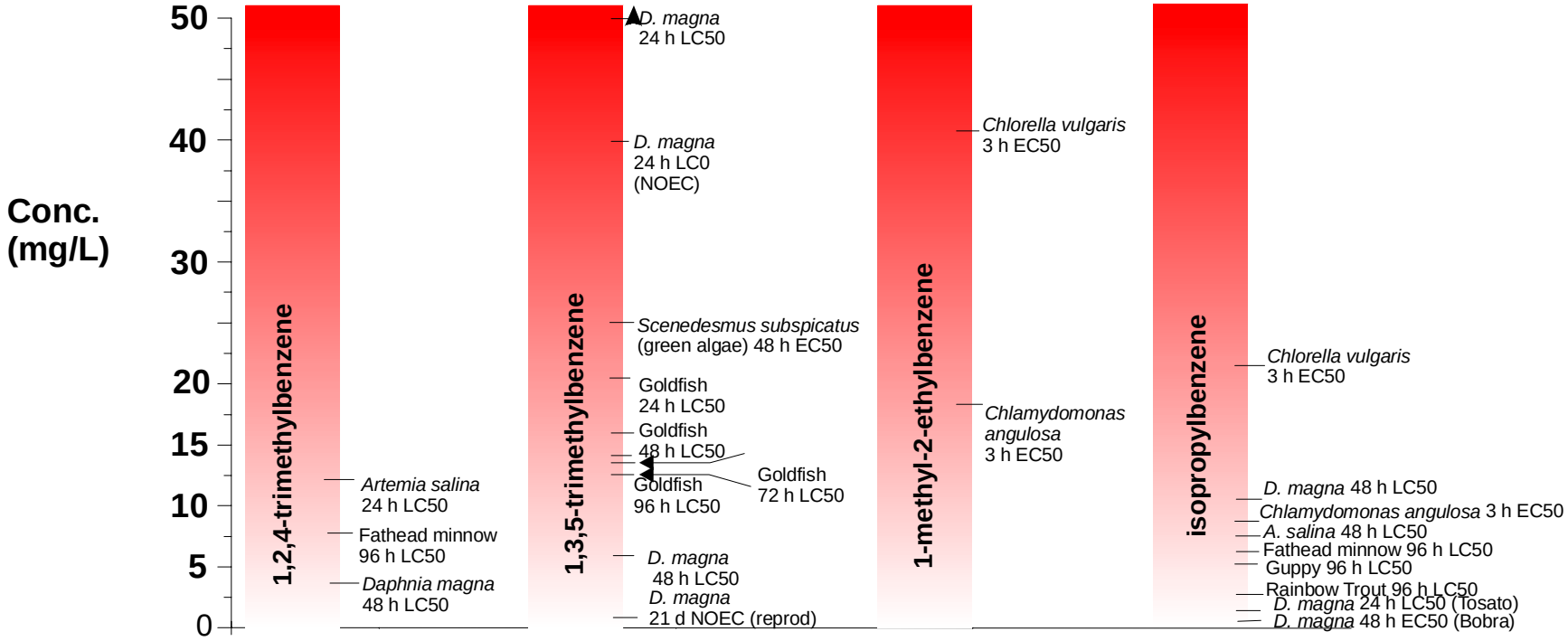


Figure 4.21: Illustration of the aquatic toxicity of alkylbenzenes.

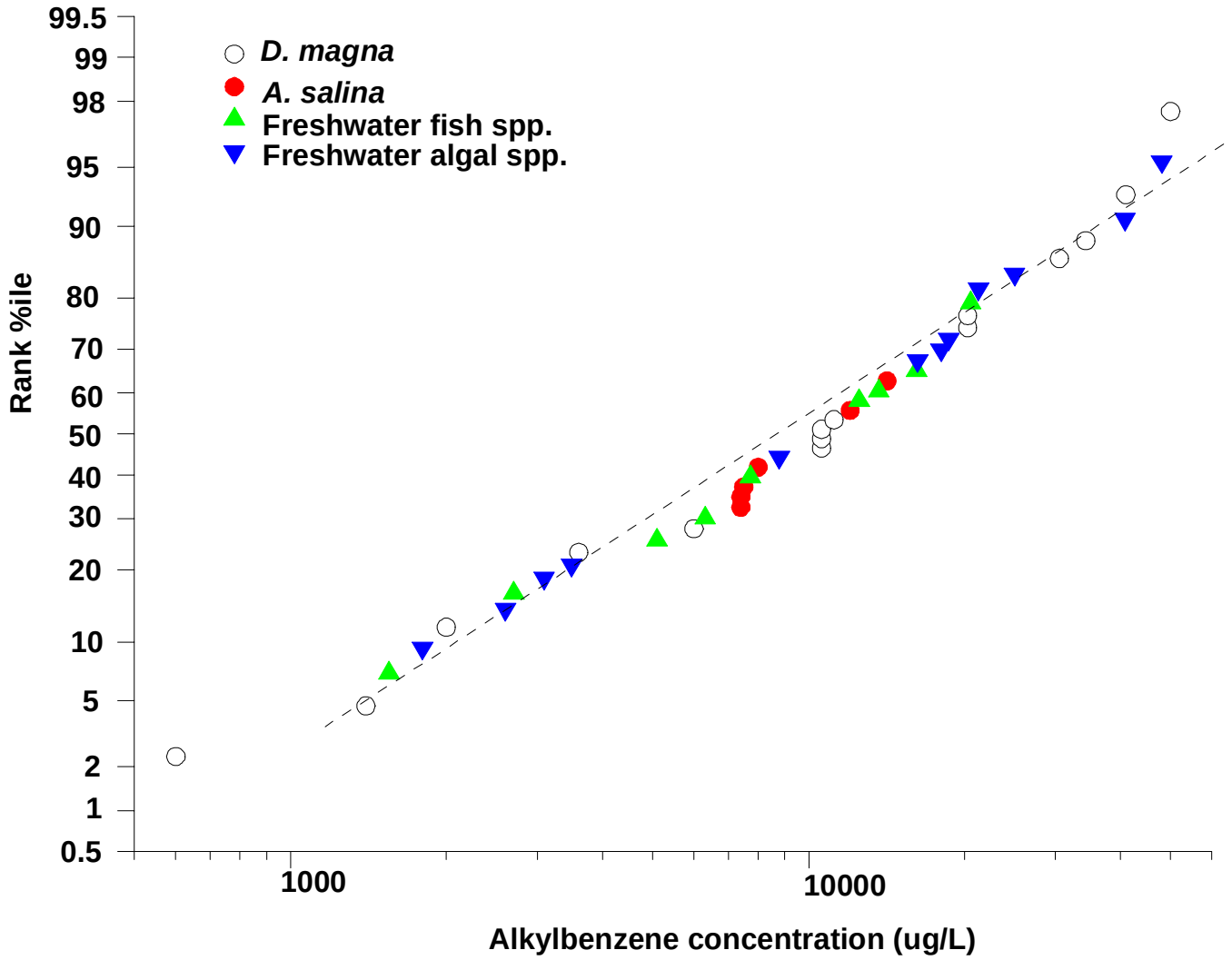


Figure 4.22: Re-constructed aquatic species sensitivity distribution based on the available toxicity data for alkylbenzenes.

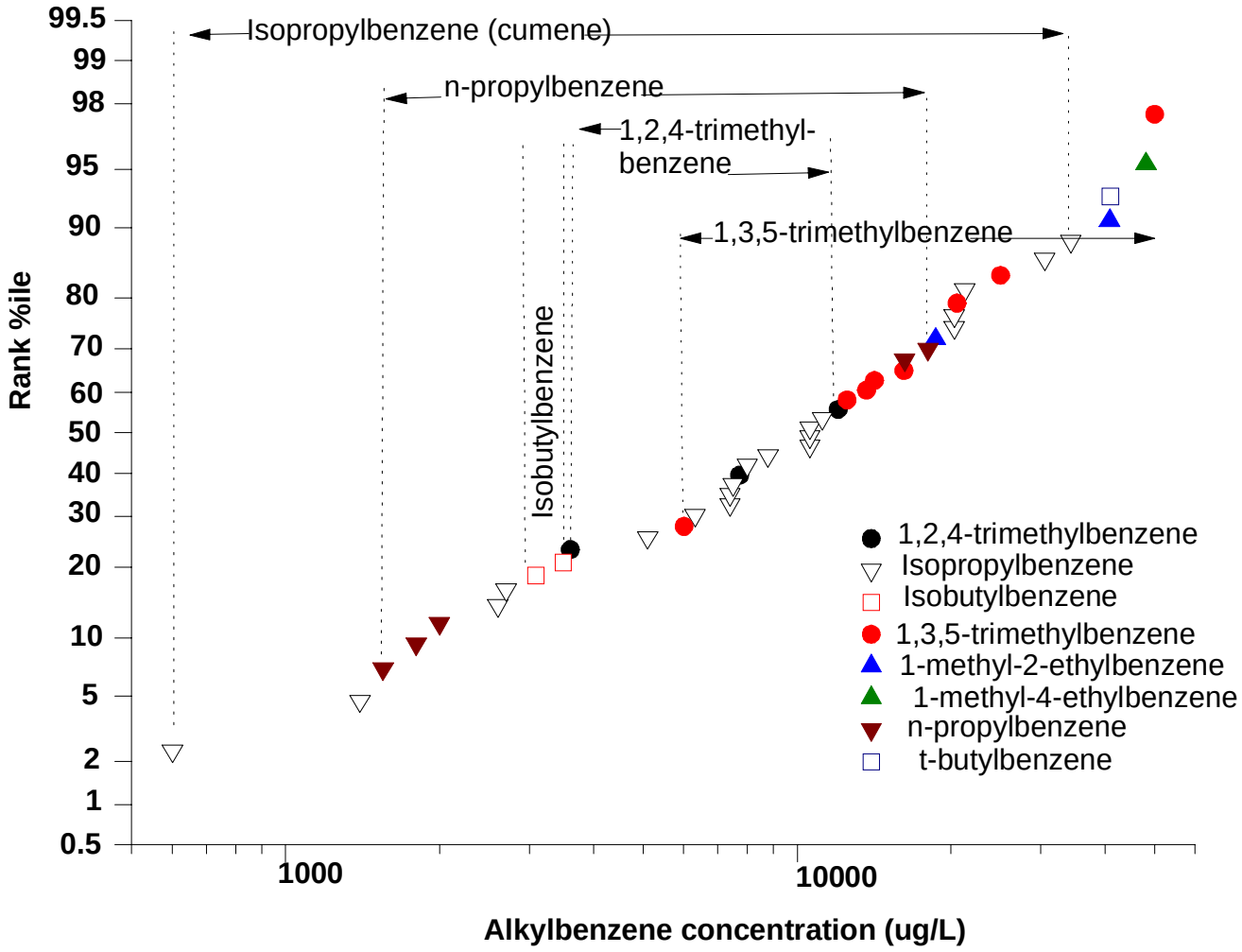


Figure 4.23: Re-constructed aquatic species sensitivity distribution based on the available toxicity data for alkylbenzenes – Relative toxicity of different alkylbenzenes.

The combined aliphatics and aromatics draft toxicity reference value for CWS F1, therefore, was modified as follows:

$$\textit{Toxicity Reference Value (CWS F1- Draft)} = \frac{1}{[(0.8/185\ \mu g/L.)+(0.2/120\ \mu g/L)]}$$

$$= 167\ \mu g/L$$

Within British Columbia, Contaminated Sites Soils Taskgroup policy decisions further allow for a ten-fold dilution within an initial mixing zone once the contaminant has reached the surface water body. A ten-fold dilution was not used herein, since policy decisions regarding allowances for dilution within the receiving environment vary across jurisdictions within Canada.

4.3.2.2 The Critical Body Residues Approach. Michelson (1997) recently refined a regulatory approach for establishing narcosis-type toxicity thresholds based on the internalized 'dose' of lipophilic substances. Such an approach is well suited for evaluating and managing the risks of complex, predominantly hydrophobic mixtures such as petroleum hydrocarbons. Michelson's (1997) work builds on studies and suggested approaches by Golder Associates and McCarty (1995), which are in turn based on studies by Abernathy et al. (1988), McCarty and Mackay, (1993), (McCarty, 1991) and EPA (1988). These authors have variously demonstrated and established conceptual models asserting that narcotic effects of hydrophobic organic contaminants occur at similar levels for different taxa as well as different compounds when the 'dose' is expressed based on the cumulative molar fraction of the contaminant(s) taken up into lipid membranes. A dose expressed in this form has been termed the "critical body residue" (CBR).

Narcosis is a long-recognized, non-specific type of toxicity, in which the internalization of lipophilic contaminants in lipid-rich structures in an organism broadly interferes with a myriad of biochemical functions. For example, critically high residues of hydrophobic organic contaminants in the lipid bilayer cell membrane of nerve fibres within animals could adversely affect membrane potential, depolarization and re-polarization, nerve transition, and ultimately behavioural and locomotory function. Manifestations of narcosis in animals might include lethargy and anaesthetic-type effects. Strictly speaking, narcosis occurs only in animals (protozoa and metazoa); however, there are undoubtedly functional equivalents in algae, plants, and fungi. Any internalization of lipophilic contaminants into the lipid bilayer membranes of cells and organelles in living organisms at critically high concentrations is expected to be accompanied by an increased potential for disruption of the fluid mosaic, including embedded proteins.

The "critical body residues" (CBR) approach is predicated on the following assumptions:

- A major component of the toxicity of PHCs to aquatic life is via narcosis-type effects. This ignores more specific toxicological mechanisms based on toxicant-molecular receptor interactions, such as endocrine disruption, MFO induction, mutagenesis, or carcinogenesis.

- The risks of narcosis are directly related to the cumulative molar fraction of all lipophilic toxicants taken up into lipid pools within an organism, and the tendency of different toxicants to induce narcosis once internalized in lipid is similar.

- The concentration of hydrophobic contaminants in internal lipid pools of aquatic organisms at any given time is related to equilibrium partitioning from the exposure medium.

- The risks are much less directly related to the actual concentration in water of individual toxicants or mixtures thereof; the internalized dose (on a molar/lipid weight basis) is a much better predictor of narcotic effects.

- Toxicants are neither substantially metabolized nor eliminated from internal lipid pools. While we know that this is not true for the major portion of organic contaminants, and is highly dependent of phyletic differences, the assumption is conservative and thus protective by driving a routine over-estimate of CBR toxicity.

As stated by Michelson (1997) –

> "In addition, the narcotic effect is not dependent on the specific lipophilic chemical or chemicals present (Call *et al*., 1985). Various studies (Ferguson, 1939; McGowan, 1952; Hermens *et al*., 1984; Hermens *et al*., 1985a,b; Deneer *et al*., 1988) have demonstrated that the narcotic effect is instead related to the total number of foreign molecules present, and therefore effects in tissue can be predicted from the total molar concentration of contaminants in the tissue. Thus it is not necessary to know the identity or toxicity of each individual chemical, just the molar concentration of all the chemicals in tissue combined".

In the context of soil quality guidelines, the CBR approach would be viable if –

- firstly, there is a definable CBR below which risks from narcosis to aquatic life are likely to be negligible;

- secondly, the CBR can be related to concentrations of the toxicant(s) in the surrounding medium;

- thirdly, the major uptake pathway for CBRs is from the surrounding water (as opposed to through diet or from sediments); and,

- fourthly, threshold soil contaminant concentrations can reasonably be predicted from water ambient concentrations using an appropriate fate and transport model.

The third and fourth requirements hold for both a CBR-based and other approaches for the derivation of soil quality guidelines that are protective of aquatic life.

Critical body residues have been related to concentrations of various contaminants in the surrounding water through the development of and subsequent predictive use of fugacity-type approaches and physical-chemical properties. This is an approach that has a long history of use in environmental fate and toxicity studies, spanning more than three decades. The critical body residue is related to the concentration in the surrounding water for any given contaminant based primarily on its octanol-water partition co-efficient (K_{ow}), which is expected to be directly equivalent to the chemical specific bioconcentration factor. This, in turn, assumes that octanol is a reasonable surrogate for functional lipids in the myriad of aquatic life, an assertion that has been challenged by some researchers.

Non-polar contaminant body residues are based on contaminant molar concentrations in lipid, as follows:

$$BR_L = C_W \times BCF_l$$
$$= C_W \times K_{ow}$$

where:

BR_L	=	body residue, expressed as molar concentration in the lipid (mmol/kg lipid)
C_W	=	concentration in the water (mmol/L)
BCF_l	=	lipid-normalized bioconcentration factor (unitless)
K_{ow}	=	octanol-water partitioning coefficient (unitless)

The second of the two equations assumes that the lipid-normalized BCF is essentially equal to the K_{ow}, which in turn is based on an assumption that octanol is a very similar substance to lipid tissues, and can be used as a surrogate for lipid partitioning. Michelson (1997) reviews the scientific support for this assumption.

A body residue value based on whole tissue wet weight rather than lipid-normalized weight could also be used, provided that percent lipid (by weight) is measured and subsequently applied; however, this further complicates the task of deriving generically protective contaminant benchmarks, since different organisms vary in their lipid content.

Michelson (1997) discusses the range of BR_Ls for at which narcosis-type effects are likely to be manifested. The following is excerpted without amendment:

> "Much of the literature is reported as whole-body critical body residues (CBRs) at which acute mortality is observed. However, lipid content is generally also reported, allowing calculation of lipid-normalized CBRs. The whole body acute CBR is reported to range from approximately 2-8 mmol/kg wet tissue (McCarty and Mackay, 1993; McCarty, 1991; van Hoogan and Opperhuizen, 1998; Carlson and Kosian, 1987; McKim and Schmieder, 1991). Lipid-normalization of these values (using actual lipid data provided in the references), along with additional lipid-normalized values in the literature (Abernathy et al., 1998; van Wezel et al., 1995), produces a range of lipid-normalized acute CBRs of 30-200 mmol/kg-lipid.
>
> State and federal water quality laws require that water quality standards be protective of both acute and chronic toxicity. Chronic exposure by benthic organisms to a groundwater plume continuously discharging into surface water would be expected, so it is reasonable to set a tissue criterion that represents a chronic narcosis endpoint. Fewer data are available on chronic CBRs, and none are lipid-normalized. Whole-body chronic CBRs are reported in McCarty and Mackay (1993), Donkin et al. (1989), Carlson and Kosian (1987), Borgmann et al. (1990), Mayer et al. (1977), Mauck et al. (1978) and Opperhuizen and Schrap (1988), producing a range of 0.2 - 0.8 mmol/kg (wet tissue) and an acute-chronic ratio of 10. An acute-chronic ratio of about 10 has been reported by a number of researchers for a wide variety of organisms (Abernathy et al. 1988; McCarty, 1986; Call et al., 1985)."

Based on this analysis, a lipid-based CBR of 30-200 mmol/kg-lipid might be used as a basis for establishing aquatic life acute toxicity reference values for petroleum hydrocarbons. As discussed, chronic toxicity based on narcosis would be expected to occur over a lower range of body residues.

It was of interest to evaluate whether this approach would lead to more or less conservative water-based levels of F1 and F2 PHCs relative to the previously described approach (Section 4.3.2.1). Hence, the available aquatic toxicity data for alkylbenzenes (Table 4.15) were converted first to molar concentrations in water, and subsequently to lipid-based body residue concentrations, by assuming that the bioconcentration factor is directly equivalent to the K_{ow} for each of the alkylbenzenes.

The reconstructed species sensitivity distribution based on the available toxicity data as plotted in Figure 4.22 was re-plotted (Figure 4.24), with dose expressed as BR_L instead of as the concentration in water. Also indicated on the figure is the expected CBR range as defined by Michelson (1997)

The conversion of the water-based, chemical-specific toxicity data to critical body residue values did not substantively affect the spread in the data. The variability in

experimentally derived acute toxicity was around two orders of magnitude regardless of whether it was expressed based on water concentration (µg/L) or as a CBR (mmol/kg-lipid). The relative ranking of the various data points was not substantively altered either.

It is concluded, therefore, that for C9-C10 alkylbenzenes, and expression of dose that accounts for differences in potential for bioaccumulation and evaluation of toxicity on a molar rather than gravimetric basis did not substantively alter perceptions about toxicity (nor the value of F1 aromatic PHCs in water on which to model acceptable soil concentrations). A different result may have been achieved had the CBR approach been applied to mixtures of narcotic compounds with a much larger variation in K_{ow} or molecular weight (e.g. – if one were interested in the combined narcotic effects of F1 and F2 PHCs, or if the preceding analyses were conducted on the larger range of aliphatics and aromatics likely to be found in CWS F1.

The CBR acute threshold as defined by Michelsen (20-300 mmol/kg-lipid) falls at the lower end of the range of CBR estimates from experimentally derived data. This would be expected, since – as previously stated – it is derived based on some conservative assumptions. This approach merits additional development.

Only one toxicity data point was observed at a concentration lower than the lowest range of the CBR. As discussed in Section 4.3.2.1, *Daphnia magna* exposed to isopropylbenzene (cumene) exhibited a 48 h EC_{50} for immobilization of 5 mmol/m^3, or 601 µg/L [the lower and upper 95% confidence interval estimates for the EC50 value as provided Bobra *et al* (1983) was 1 mmol/m^3 and 30 mmol/m^3, respectively – underscoring the limited confidence in the accuracy of this endpoint]. There is no technical basis, however, in light of the methods description in the Bobra *et al.* paper for the exclusion of this data point when considering alkylbenzene toxicity. It is, nonetheless, recognized to be an outlier relative to the larger probability distribution. In section 4.3.2.1, the uncertainty factor applied in extrapolating from a sub-chronic to chronic endpoint was adjusted in light of this.

Di Toro *et al.* (2000) recently applied the critical body residue approach to develop water quality criteria for narcotic contaminants in general, and PAHs in particular. The reader is referred to the original paper for a state-of-the-science validation and application of the CBR approach. The authors note that, while the underlying mechanisms of toxicity are similar across widely different aquatic animal taxa, there are variations in toxicity and the CBR associated with acute toxicity. Such variation is

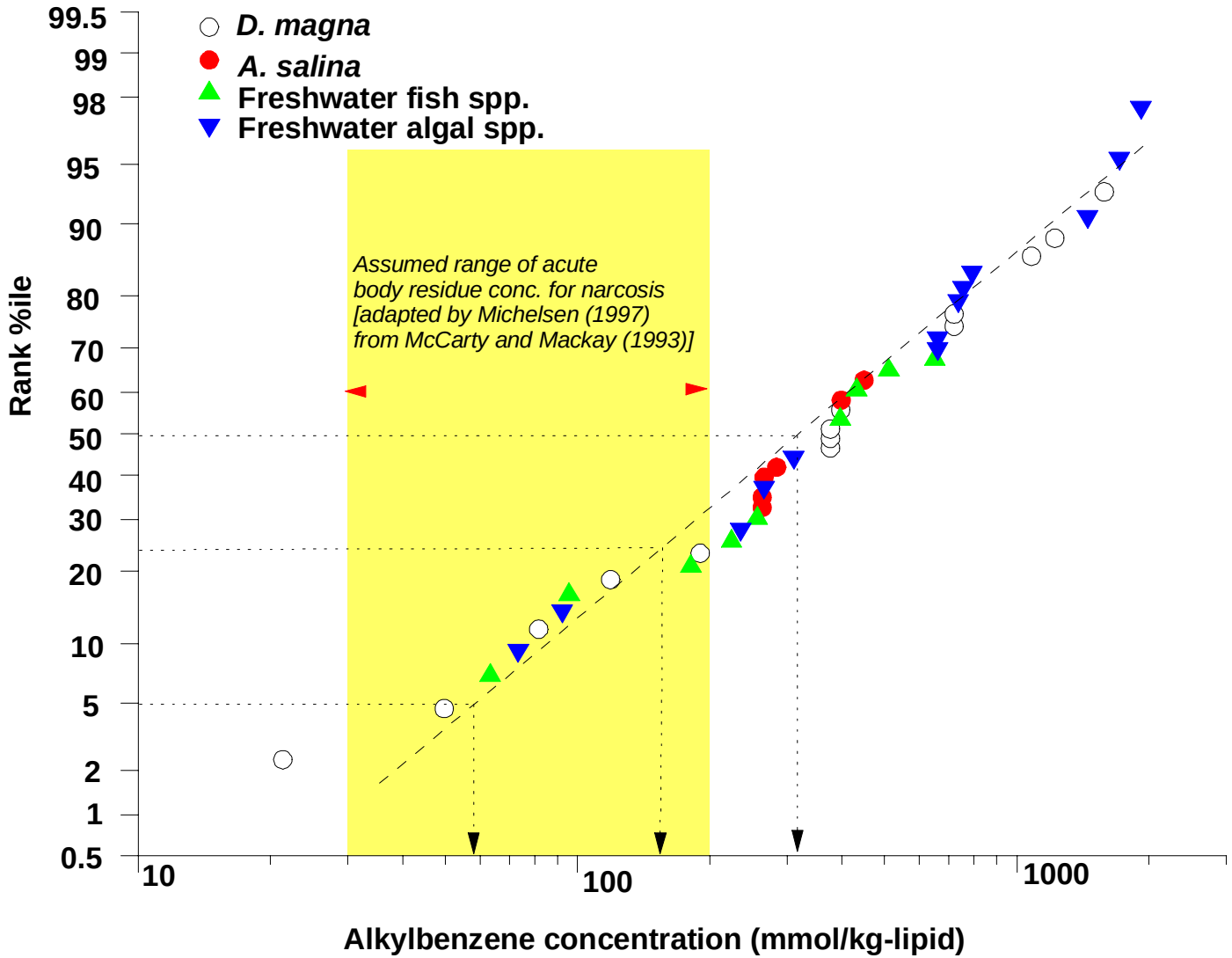


Figure 4.24: Range of critical body residues calculated from experimentally derived acute toxicity (primarily LC_{50}) endpoints for alkylbenzenes. [NB: plant endpoints were acute impairment of photosynthetic pigments (absorbance) and cell division (culture turbidity)].

predictable, however, and Di Toro *et al*. provide validated models that account for the inter-taxon variability. The authors provide a species sensitivity distribution for toxicity based on body burden, develop multi-species thresholds based on the 5th %ile of the ranked data (as specified in the USEPA guidelines for establishing water quality criteria), and provide a universal acute-chronic ratio adjustment.

Table 4.16 is adapted from Di Toro *et al*. (2000), and shows the "Final Chronic Values for Narcotic Chemicals" as calculated using the CBR approach, and based on application of an acute-chronic ratio (ACR) of 5.09. This ACR was derived as the geometric mean value of 35 data pairs of acute and chronic toxicity, encompassing 20 individual chemicals and six distinct aquatic species of animals.

Table 4.16: Final chronic values for narcotic contaminants and aquatic life - Lipid-based tissue residue concentration thresholds for chronic toxicity across multiple taxa (mmol/kg-lipid).

Chemical Class					
Baseline	**Halogenated Baseline**	**Ketones**	**Halogenated Ketones**	**PAHs**	**Halogenated PAHs**
6.94	3.96	3.95	2.25	3.79	2.16

Among the above-listed CBR-based chronic toxicity thresholds for aquatic life, the value for PAHs is most directly applicable to CWS F1 or F2 petroleum hydrocarbon constituents in general. In the absence of more detailed evaluation, however, a chronic CBR-based value of 3.0 mmol/kg-lipid appears to be a reasonable threshold for protection against adverse aquatic effects due to narcosis.

Using a chronic CBR-based toxicity threshold of 3.0 mmol/kg-lipid, it is then possible to calculate a toxicity reference value (C_w) for each of the TPHCWG sub-fractions that make up CWS F1 or F2. As shown above -

$$C_W = \frac{BR_L}{K_{ow}}$$

Table 4.17: Derivation of sub-fraction chronic toxicity reference values using a CBR-based chronic tissue residue benchmark of 3.0 mmol/kg-lipid.

TPHCWG sub-fraction	$logK_{oc}$ [A]	$logK_{ow}$ [B]	Mol. Wt. [A] (g/mole)	Solubility (mg/L)	C_w - Estimated CBR-based tox. ref. value (µg/L)
Aliphatics					
AlC6-8	3.6	3.81	100	5.4	46.5
AlC8-10	4.5	4.71	130	0.43	7.6
AlC10-12	5.4	5.61	160	0.034	1.18
AlC12-16	6.7	6.91	200	0.00076	0.074
Aromatics					
ArC8-10	3.2	3.41	120	65	140
ArC10-12	3.4	3.61	130	25	96
ArC12-16	3.7	3.91	150	5.8	55.4

A: from TPHGWG Vol. 3
B: Based on empirical relationship between Koc and Kow developed by Karickhoff *et al*. (1979).

4.3.2.3 Final Reconciliation of Approaches. The F1 (167 µg/L) and F2 (42 µg/L) toxicity reference values developed in Section 4.3.2.1 were compared to LC_{50} values for a variety of whole products, including fuel oil #2 and gasoline. The whole product LC_{50}s for a variety of fish or invertebrate species were in the range of 1,500 to > 560,000 µg/L (Table 4.18).

These lethality endpoints for whole products are generally an order of magnitude or more higher than the previously documented F1 and F2 toxicity reference values; however, sub-lethal effects endpoints are generally considered to be more appropriate for the calculation of environmentally protective thresholds than mortality endpoints. In addition, it is not unreasonable to assume that chronic sensitivity to PHCs and more sensitive toxicity endpoints (e.g. reproduction) would be up to an order of magnitude or more lower than acute mortality thresholds.

Using gasoline as comparable with F1, the lowest LC_{50} was 1,500 µg/L (for grass shrimp; based on five fish or invertebrate spp. total). If this is divided by an uncertainty factor (UF) of 20 to account for the fact that LC_{50} endpoints were the only ones available and to account for the likelihood that at least some species may be lower on the overall species sensitivity distribution, then a whole product toxicity reference value would be around 75 µg/L. If a 10-fold UF is applied (assuming that inter-taxon variability has been adequately addressed based on the species examined and choice of the lowest relevant LC50) the value derived is 150 µg/L - not far different from 167 ug/L.

Table 4.18: PHC Whole Product literature values for toxicity to aquatic life (adapted from MacFarlane and Fox, Jan. 7, 2000).

Product	Organism	LC_{50} value (µg/L)	Ref.
Fuel Oil #2	Juvenile American Shad	2E+05	A
	Bluegill	9.8e+3 to >1.8e+5	"
	Banded Killifish	1.1e+3 to 2.9e+4	"
	Striped Bass	9.1e+2 to 3.1e+4	"
	Pumpkin Seed	1.1e+3 to 4.3e+4	"
	White Perch	1.4e+3 to 4.2e+4	"
	American Eel	4.6e+3 to 2.8e+4	"
	Carp	6.2e+3 to 5.3e+4	"
	Rainbow trout (eggs)	1.2e+4 to 2.0e+4	"
	Gulf Menhaden	7.0e+5	"
	Sand Lance	5.8e+3 to 1.4e+4	"
	Striped Mullet	3.2e+5 to > 5.6e+5	"
	Mullet	1.3e+4	"
	Menhaden	5e+3	"
	Grass Shrimp	2e+3	"
	Paleomonetes vulgaris	1.8e+5	"
Gasoline	Rainbow trout	4.0e+4 to 1.0e+5	"
	Salmon fingerling	1.0e+5	"
	Juvenile American shad	6.8e+4 to >1.1e+5	"
	Mullet	2e+3 to 4e+4	"
	Menhaden	2e+3	"
	Grass Shrimp	1.5e+3	"
Diesel	*Daphnia magna*	7.2e+3	B
"	*Salmo gairdneri* (= *O. mykiss)*	2.5e+3	C
#2 Fuel Oil	*Daphnia magna*	2.2e+3	B
Leaded gasoline	" "	5.4e+3	"
Unleaded gasoline	" "	5.0e+4	B
" "	*Salmo gairdneri* (= *O. mykiss)*	5.4e+3	C
New crankcase oil	*Daphnia magna*	3.8+2	B
Used crankcase oil	" "	4.9e+4	"

References" A) 1997 Micromedex Inc., Vol. 32 OHM/TADS – Oils and Hazardous Materials/Technical Assistance Data System; B) MacLean (1988), as summarized in MADEP (1996); C) Lockhart (1987), as summarized in MADEP (1996)

For F2, diesel and fuel oil #2 have some relevance. The lowest tabulated LC50 was 1,100 μg/L. Using an UF of 10, a whole product toxicity threshold of 110 μg/L is calculated. Using 20-fold UF, a toxicity threshold of 55 μg/L is calculated (close to but still higher than the originally 'calculated' 42 μg/L).

We might expect that the whole product toxicity data, surrogate-based toxicity data and CBR-based water concentrations would be similar provided that a petroleum product has been introduced directly to surface water at a sufficiently low concentration that the proportion of constituents in the bioavailable water-accommodated fraction is similar to that of the original mixture, at least within the EC range encompassed by each of CWS F1 and F2. For example, a lower value for F2 than for F1 would be expected based on a Critical Body Residue approach - since the potential for bioconcentration increases from F1 to F2.

Using a CBR approach, the aromatics toxicity reference value derived for C8-C10 aromatics based on an assumed chronic threshold body residue of 3.0 mmol/kg-lipid was 140 μ/L (Table 4.17). This compares favourably with a threshold toxicity reference value of alkylbenzenes as discussed in Section 4.3.2.1 based on dividing the Bobra *et al*. (1983) 48 h EC_{50} value of 601 μg/L by an uncertainty factor of five, to arrive at a chronic value of 120 μg/L.

The preceding discussion illustrates that different approaches for defining aquatic toxicity provide similar conclusions regarding toxicological thresholds, at least where aquatic organisms have been directly exposed to the narcotic contaminant suite of interest. In light of the need to also account for compositional change between source and aquatic receptor, due to differential partitioning in along subsurface pathways, the use of a CBR approach was chosen for subsequent modeling. This allowed the derivation of a chronic toxicity reference value for each of the TPHCWG sub-fractions, and therefore better accounted for compositional change during leaching into groundwater and subsurface transport than if a single toxicity reference values had been used for each of CWS PHC fractions F1 and F2.

In conclusion, the water quality benchmarks for the TPHCWG sub-fractions, as shown in Table 4.17 were used in the modeling exercise: i.e. -

CWS F1

TPHCWG Aliphatics C6-8	46.5 μg/L
TPHCWG Aliphatics C8-10	7.6 μg/L
TPHCWG Aromatics C8-10	140 μg/L

CWS F2

TPHCWG Aliphatics C10-12	1.18 μg/L
TPHCWG Aliphatics C12-16	0.074 μg/L
TPHCWG Aromatics C10-12	96 μg/L
TPHCWG Aromatics C12-16	55.4 μg/L

4.3.3 Estimation of PHC Toxicity to Livestock Based on Drinking Water Uptake From a Surface Water Body

A literature review was undertaken of the documented effects of petroleum hydrocarbons on livestock, based on ingestion-type studies. Cattle, in particular, might be exposed to PHCs through:

- ingestion of contaminated surface soils, especially during grazing;
- ingestion of contaminated plants, where there has been uptake from the soil;
- internalization through drinking water from surface dugouts and other water bodies affected by PHC-contaminated soils;
- dermal absorption; and
- inhalation in the vapour phase.

For a multi-media exposure, CCME (1996) established an allocation factor for the allowable or threshold dose of 0.75 based on the evaluation of contaminated soil and plants in isolation from the other three pathways. This allocation factor is set based on the recognition that these are likely to be the quantitatively the major contributors to internalized dose. For PHCs, many scientific studies have shown that the phyto-accumulation is very limited, suggesting that soil ingestion alone will account for the vast majority of the contribution to internal dose at the majority of PHC-contaminated agricultural sites.

Dermal absorption is thought to have very limited contribution to contaminant exposure in terrestrial mammals with thick coats, including cows, except where the contaminant is directly ingested from the skin through grooming activities. In addition, vapour-phase accumulation is assumed herein to be a minor contributor to expected dose, relative to direct soil and water ingestion.

This section provides estimates of toxicological thresholds based on chronic drinking water ingestion by livestock, especially cattle. An allocation factor of 0.2 is assumed, recognizing that cattle inhabiting an area where PHCs have been released may also be exposed through the other four pathways, and may also experience limited background exposure, especially through proximity to farm machinery being operated and maintained.

A limited number of studies are available with which to estimate a “Daily Threshold Effects Dose” for livestock drinking water ($DTED_{LDW}$). In particular, Coppock and Campbell, in Chalmers (1999), provided a thorough and up-to-date review of PHC risks to livestock. This document should be consulted for more information on the state of the science. There is a large body of published information, especially in veterinary journals, on the accidental poisoning of livestock, often through the ingestion of mineral spirit carriers for topical remedies applied to the coat, or through the direct ingestion of

petroleum products such as mogas or diesel. Many of these studies provide details of symptoms and acute pathology, which may be diagnostic of PHC poisoning.

Less than a half-dozen studies have value in assigning a threshold PHC dose for cattle. Page 56 of Chalmers (1999) includes tabulated threshold dose estimates for crude oil in cattle, which range from > 1.25 to 8 mL/kg bw. This table is reproduced herein (Table 4.19). Unweathered oil (with a specific gravity of 0.843) exhibited a threshold dose of 2.5 mL/kg (adapted from Stober, 1962).

Table 4.19: Threshold doses for crude oil in cattle (adapted from Chalmers, 1999).

Oil Type	Composition	Threshold Dose
Unweathered Oil	100 mL = 84.3 g Carbon = 84.6% (19% arom.) Hydrogen = 11.92% Nitrogen = 0.71% Sulfur = 2.46%	2.5 to 5 mL/kg bw = 2.1 to 4.2 g/kg bw
Weathered oil	Water 10% by wt. 100 mL = 91.0 g Carbon = 83.6% (21% arom.) Hydrogen = 11.56% Nitrogen = 0.49% Sulfur = 2.8%	8 mL/kg bw = 7.3 g/kg bw
Venezeule crude oil (naphtha-based)	100 mL = 87.5 g Carbon = 85.6% (19% arom.) Hydrogen = 12.95% Nitrogen = 0.46% Sulfur = 1.58%	= 4.0 mg/kg
Bunker “C” oil	Carbon = 86% (19% arom.) Hydrogen = 11% Nitrogen and Oxygen = 0.46% Sulfur = 2.5%	> 1.25 mL/kg = > 1.1 g/kg bw

Coppock and Campbell (in Chalmers, 1999) more formally evaluate risks, including safe PHC exposure levels for cattle. They used a “Tolerable Daily Intake” (TDI) approach, based on CCME (1993) for crude oil, as follows:

- Cited Literature value LOAEL (after Stober, 1962) = 2.5 mL/kg bw
- Oil Specific gravity = 0.85 g/ml
- LOAEL = 2.5 mL/kg bw x 0.85 g/mL = 2.1 g fresh crude/kg bw

- Estimated NOAEL = LOAEL/5.6 = 2.13 g/kg bw/5.6 = 0.38 g/kg bw

(i) Livestock TDI = $(LOAEL \times NOAEL)^{0.5}/UF = (2.13 \text{ g/kg bw} \times 0.38 \text{ g/kg bw})_{0.5}/UF$

Where -

UF = Uncertainty Factor: set at 10

and –

(ii) TDI = 0.9 g fresh crude/kg bw/10 = 0.09 g fresh crude/kg bw

It is assumed that Coppock and Campbell implicitly assume this to be a daily exposure threshold, in other words – 0.09 g/kg bw/day.

The CCME (1993) TDI approach was intended to apply to human health risk assessments. CCME (1996) provides a protocol for estimating toxicological thresholds for livestock and wildlife based on the "Daily Threshold Effects Level" (DTED) for livestock drinking water (LDW). The DTED is estimated as follows:

(iii) **$DTED_{LDW}$** = Lowest Documented Effects Dose (ED)/ Uncertainty Factor

(iv) = 2.1 g fresh crude/kg bw/day / UF of 10 = 0.21 g/kg bw/d

= 210 mg/kg bw/d

(Assuming that the Lowest Effects Dose is the previously discussed LOAEL of 2.1 g/kg bw/d)

From this, a reference concentration (RfC_{LDW}) for whole fresh crude ingested in livestock drinking water is established as follows:

(v) **RfC_{LDW}** = $(DTED_{LDW} \times AF \times BW)/WIR$,

where -

$DTED_{LDW}$ = Daily Threshold Effects Dose for Livestock Drinking Water (as above)

AF	=	Allocation Factor for allowable dose (set at 0.2)
BW	=	Cow Body Wt., set at 550 kg for an adult cow
WIR	=	Water Ingestion Rate (set at 100 L/day)

Coppock and Campbell (in Chalmers, 1999) consulted a study by Pal (1988), which demonstrated that cattle drink between 25 and 66 L/cow/day. Additional consumption occurs in lactating cows (an additional 5.4 L of water/L milk produced, as well as for cows fed on dry feed (3 to 10 L of water/kg dry feed consumed). An appropriate water ingestion rate (WIR) for adult cows is taken to be around 100 L/d.

The final RfC_W is estimated as follows:

(vi) **RfC_W** = (210 mg/kg bw/d x 0.2 x 550 kg bw)/100 L/d

= 23 mg/L fresh crude

Coppock and Campbell, based on the study by Stober (1962), suggested that the value for a weathered crude oil (after adjusting for calculations areas) would be 3.7 x higher, or 85 mg/L weathered crude.

The preceding calculations assume a proportional transfer of the different constituents of a crude oil to a drinking water reservoir, such that the dose derived from drinking water would be equivalent to experimental doses in the consulted studies. Such an assumption ignores known differential solubilities and partitioning of different hydrocarbon classes. In addition, the RfC_W must be converted to an RfC_W for each of the CWS fractions, in order to back-calculate a soil protective benchmark based on a livestock drinking water exposure scenario.

If it is assumed that the fresh crude used in cattle toxicology experiments had a composition similar to Federated Whole crude, then the relative composition of the original dose as PHC CWS F1-F4 can be estimated. The underlying studies do not allow us to know which of the fractions (or single compounds within the fractions) might have resulted in the toxicological response. In subdividing the original RfC_W among the CWS fractions, therefore, one runs the risk of attributing a LOAEL response to one of the non-toxic CWS fraction. It can be confidently stated, however, that the redefined composition as CWS fractions represents the lowest possible dose for each fraction, below which toxicity would be unlikely (for each Fraction, the concentration would represent either the LOAEC, or – if not the responsible toxicant, a documented NOAEC.

Recent studies sponsored by PTAC/CAPP (Stephenson et al, 1999) provided the following carbon distribution for fresh Federated Crude Oil. Fresh Federated Crude (from Swan Hills area of Alberta) had the following composition:

C1-C5:	2.8%
C6-C10 (CWS F1):	23.2%
C11-C16 (CWS F2):	21.3%
C17-C22:	16.0%
C23-C35:	8.5%
SUM OF LAST 2 (CWS F3):	34.5%
>C35 (CWS F4):	18.2%

Assuming that the unweathered crude oil has a similar composition, the $DTED_{LDW}$ can be apportioned among the CWS fractions, to produce the following provisional RfC_{LDW} estimates:

PHC CWS F1:	= 0.232 x 23 mg/L	=	**5.3 mg/L;**
PHC CWS F2:	= 0.213 x 23 mg/L	=	**4.9 mg/L;**
PHC CWS F3:	= 0.345 x 23 mg/L	=	**7.9 mg/L;**
PHC CWS F4:	= 0.182 x 23 mg/L	=	4.2 mg/L.

Fraction F4 was removed from further consideration since (i) the bioavailability and gastrointestinal absorption of petroleum hydrocarbons >C34 is expected to be exceedingly limited, and (ii) the particulars of groundwater transport would preclude any substantial migration of this fraction into adjacent surface water bodies, including livestock watering dugouts.

4.3.3.1 Additional Toxicological Literature Review. Mitchell et al (1978) exposed cross-bred barrow pigs to 0, 1, 2, or 3 ppm (µL/L) gasoline in drinking water (8 pigs per treatment level: approximate initial weight was 85 kg). No effect was detected over a five week exposure period on weight gain, feed efficiency, or water consumption rates. In a second experiment, young, recently weaned swine were fed ad libitum drinking water with gasoline at the solubility limit. There was no difference between control and exposed swine.

The study by Rowe et al (1973) involved the treatment of 11 cattle (varying in age from 6 mo. to 3.5 y) total with either a sweet crude, sour crude, or kerosine. Crude oil dosages ranged from 37 mL/kg body weight, given as a single dose, to 123 mL/kg bw given as five doses over a five day period. Kerosine dosages ranged from a single dose of 19.8 mL/kg bw to 61.6 mL/kg bw given as five doses over five days. In addition, 3 separate groups of five calves were administered crude oils and kerosine at a rate of 8 mL/kg bw/d for up to 14 consecutive days. A dose of 8 mL/kg bw/day to one calf

produced only mild signs of pneumonia, from which recovery occurred. Higher single doses to calves or adults resulted in a variety of more severe effects, including mortality for some doses and individuals. A threshold dose of 8 ml/kg bw/day for 14 day is consistent with the LOAEL derived by Coppock and Campbell (1997).

4.3.4 Model Predictions – Aquatic Life

For the CWS Tier I default site assumptions, preliminary model calculations were run for each of the F1 and F2 fractions, and sensitivity analyses were run on a number of model inputs, as follows:

- *Fraction Physical Properties:*
  - ⇒ solubility
  - ⇒ Henry's Law Constant
  - ⇒ Log K_{oc}
  - ⇒ Subsurface degradation half-life

- *Site Generic Parameters:*
  - ⇒ soil organic carbon content (F_{oc})
  - ⇒ Darcy's velocity
  - ⇒ distance to surface water body

Preliminary analyses revealed that model estimates of soil concentrations for various TPHCWG subfractions were very sensitive to estimates of solubility and the organic carbon – water partition coefficient (K_{oc}), but insensitive to variations in the Henry's Law Constant. This is likely due to the relative unimportance of PHC fate in the unsaturated zone, since generic site assumptions provide for the direct interaction between the bottom of the contaminated soil zone and the saturated zone. Varying the depth of the unconfined aquifer had no influence on model predictions.

Preliminary analyses further revealed that the resulting soil quality benchmarks for each TPHCWG sub-fraction, as well as for the CWS fractions derived from these, were heavily influenced by assumptions regarding the possibility of and rate of subsurface hydrocarbon degradation. The allowance of even highly conservative degradation rates produced much higher soil quality benchmarks for PHCs in the CWS F1 range, in particular, than if attenuation through *in situ* biodegradation is discounted entirely. In response to this issue, the default assumption of infinite subsurface half-lives for PHCs was re-visited. This assumption was initially adopted in parallel with guidance by PIWG in the context of human health-protective pathways, and parallels Tier I assumptions within the Risk Based Corrective Action (RBCA) model. The assumption merited re-consideration in the context of exposure pathways for ecological receptors, since the primary compartment of interest for fate calculations is the subsurface saturated zone. An environmental persistence half life in the saturated zone should be less variable across sites than in the unsaturated zone, and there are probably fewer factors that influence biodegradation rates.

Appendix G provides a brief summary of the environmental persistence of PHCs in the subsurface environment. In addition, generic environmental persistence half-lives are defined for the CWS F1 and F2 fractions using conservative estimates which in their application would tend to over-estimate rather than underestimate the of an ecological receptor at the vast majority of Canadian sites. The consequences of the environmental degradation rate estimates are further explored in this section, as part of the detailed derivation exercise.

The existing environmental persistence data are insufficient to allow a confident derivation of degradation half-lives (t1/2) at a chemical unit lower than the CWS fractions (F1, F2). Even at this level, the derived values are highly conservative, given the uncertainty in their applicability and any given PHC release site in Canada. Degradation half-lives in both the saturated and unsaturated zone, therefore, where established as follows:

CWS F1: t1/2 (saturated and unsaturated zone) = 712 d (~ 2 yr)

(and t1/2 for TPHCWG Aliphatics C6-8; Aliphatics C8-10; and Aromatics C8-10 = 712 d)

CWS F2: t1/2 (saturated and unsaturated zone) = 1750 d

(and t1/2 for TPHCWG Aliphatics C10-12; Aliphatics C12-16; Aromatics C10-12 and C12-16 = 1750 d)

As discussed in Section 4.3.1, a necessary first step in calculating a soil quality benchmark for the protection of aquatic life for PHC CWS fractions F1 and F2 is the modeling of an appropriate SQG for each of the constituent TPHCWG subfractions. For CWS F1, the TPHCWG subfractions included –

TPHCWG Aliphatics C6-C8 (55% of CWS F1 by mass);

TPHCWG Aliphatics C8-C10 (36% of CWS F1 by mass);

TPHCWG Aromatics C8-C10 (9% of CWS F1 by mass).

Similarly, the assumed composition of PHC CWS F2 is –

TPHCWG Aliphatics C10-C12 (36% by mass);

TPHCWG Aromatics C10-C12 (9% by mass);

TPHCWG Aliphatics C12-C16 (44% by mass);

TPHCWG Aromatics C12-C16 (11% by mass).

4.3.4.1 TPHCWG Aliphatics C6-C8. Table 4.20 provides the output of runs on the

BCE groundwater model for TPHCWG subfraction C6-C8 (aliphatics), using the PIWG/CWS default site assumptions for a coarse-textured site (Appendix H) and chemical property assumptions as documented in Table 4.13.

Table 4.20: Calculated SQGs (mg/kg) for the TPHCWG aliphatics C6-C8 subfraction.

	Assumed Environmental Degradation Half Live (t1/2) in Days							
Distance from source area (m)	**1.0E+09**	**1.0E+06**	**1.0E+05**	**1.0E+04**	**6.0E+03**	**3.0E+03**	**1.5E+03**	**712**
10	4.8	4.8	5.0	7.4	9.5	18	51	357[A]
20				11	18	51		
30	4.8	4.9	5.5	16	31	130		
40					53			
50	5.0	5.1	6.2	32	86			
60					141			
70								
80				93				
90				131				
100	6.8	7.1	10					
150			15					
200	12	13	27					

No solution provided since fraction at solubility limit at source would still be too low to result in toxic concentration at aquatic receptor

Notes: A) Solubility limit increased 10X to obtain model solution

4.3.4.2 TPHCWG Aliphatics C8-C10. Even at a distance of 10 m from source to receptor, and without allowing for any subsurface degradation of this fraction, model runs failed to provide an appropriate sub-fraction SQG. This is due to the fact that the overall transport toward the aquatic receptor is constrained by the limited solubility of the fraction at the interface between the PHC contaminated soil mass. Introduction of leachate into the subsurface environment at the solubility limits provides an upgradient concentration that is lower than that required to result in a threshold toxic concentration at the aquatic receptor, after accounting for attenuation through dilution and degradation. Furthermore, relaxing solubility constraints by increasing the assumed solubility of the TPHCWG sub-fraction by and order of magnitude did not alleviate this constraint.

4.3.4.3 TPHCWG Aromatics C8-C10. Table 4.21 provides the output of runs on the BCE groundwater model for TPHCWG subfraction C8-C10 (aromatics), using the PIWG/CWS default site assumptions for a coarse-textured site and chemical property assumptions as documented in Table 4.13.

Table 4.21: Calculated SQGs (mg/kg) for the TPHCWG aromatics C8-C10 subfraction.

Distance from source area (m)	Assumed Environmental Degradation Half Live (t1/2) in Days							
	1.00E+09	1.00E+06	1.00E+05	1.00E+04	6.00E+03	3.00E+03	1.50E+03	712
10	4.1	4.1	4.2	4.9	5.5	7.2	12	33
20							30	161
30				6.9	9.4	19	66	
40							138	
50	4.3	4.3	4.7	9.7	16	46	277	
60								
70								
80					28	110		
90						253		
100	5.8	5.9	6.9	27	63	376		
150				70	221			
200	10	11	14	164				

4.3.4.4 TPHCWG Aliphatics C10-C12 and C12-C16. Even at a distance of 10 m from source to receptor, and without allowing for any subsurface degradation of this fraction, model runs failed to provide an appropriate SQG for these two subfractions. In the case of C12-C16 (aliphatics) the model algorithms failed to converge on a solution, even after manipulation of assumed solubility limits. Thus, the concentration of PHCs in the soil would not theoretically impose limits on the concentration in groundwater down gradient from the source area at a distance of 10 m or more, assuming transport in dissolved form. Rather, the solubility limits at the point where contaminated soil and groundwater interacts is deemed to be the major limiting factor.

Table 4.22: Calculated SQGs (mg/kg) for the TPHCWG Aliphatics C10-C12 subfraction.

Distance from source (m)	Assumed Environmental Degradation Half Live (t1/2) in Days							
	1.00E+09	1.00E+06	1.00E+05	1.00E+04	6.00E+03	3.00E+03	1.75E+03	875
10	35	44	[A]285					
20								
30								
40								
50								
60								
70								
80								
90								
100								
150								
200								

Notes: A) Solubility limit increased 10X to obtain model solution

4.3.4.5 TPHCWG Aromatics C10-C12. Table 4.23 provides the output of runs on the BCE groundwater model for TPHCWG subfraction C10-12 (aromatics), using the PIWG/CWS default site assumptions for a coarse-textured site (Appendix H) and chemical property assumptions as documented in Table 4.13.

Table 4.23: Calculated SQGs (mg/kg) for the TPHCWG aromatics C10-C12 subfraction.

Distance from source (m)	Assumed Environmental Degradation Half Live (t1/2) in Days							
	1.00E+09	1.00E+06	1.00E+05	1.00E+04	6.00E+03	3.00E+03	1.75E+03	875
10	4.5	4.5	4.6	5.8	6.9	10	18	56
20						22	57	
30				9.7	15	43	152	
40						80		
50	4.6	4.7	5.3	16	32	145		
60						259		
70					68			
80					98			
90					140			
100	6.3	6.4	8.2	61	198			
150				204				
200	11	12	19					

4.3.4.6 TPHCWG Aromatics C12-C16. Table 4.24 provides the output of runs on the BCE groundwater model for TPHCWG subfraction C12-C16 (aromatics), using the PIWG/CWS default site assumptions for a coarse-textured site (Appendix H) and chemical property assumptions as documented in Table 4.13.

Table 4.24: Calculated SQGs (mg/kg) for the TPHCWG aromatics C12-C16 subfraction.

Distance from Source (m)	Assumed Environmental Degradation Half Live (t1/2) in Days							
	1.00E+09	1.00E+06	1.00E+05	1.00E+04	6.00E+03	3.00E+03	1.75E+03	875
10	5.1	5.1	5.4	8.6	12	25	63	
20				14	25	89		
30			6.0	22	48			
40				33	90			
50	5.3	5.4	6.9	50				
60				76				
70				115				
80			9.6					
90								
100	7.2	7.6	12					
150			21					
200	13	14	34					

4.3.4.7 Associated Issues: The Influence of Soil Organic Carbon Content (Foc). The calculated sub-fraction soil quality guidelines presented in Tables 4.20-4.24 show that the derivation methods, and resulting Tier I guidance for soil concentration thresholds that are protective of aquatic life, are strongly influenced by both the expected rate of hydrocarbon biodegradation in the saturated zone and the distance separating the contaminated soil mass and the aquatic receptor.

The assumed hydrophobicity of several of the sub-fractions prevented the calculation of a sub-fraction SQG. Even for those fractions addressed in Tables 4.20-4.23 however, the calculated SQG is highly sensitive to minor changes in the assumed (or measured) organic carbon content of subsurface soils at a site. This is shown graphically in Figure 4.25:

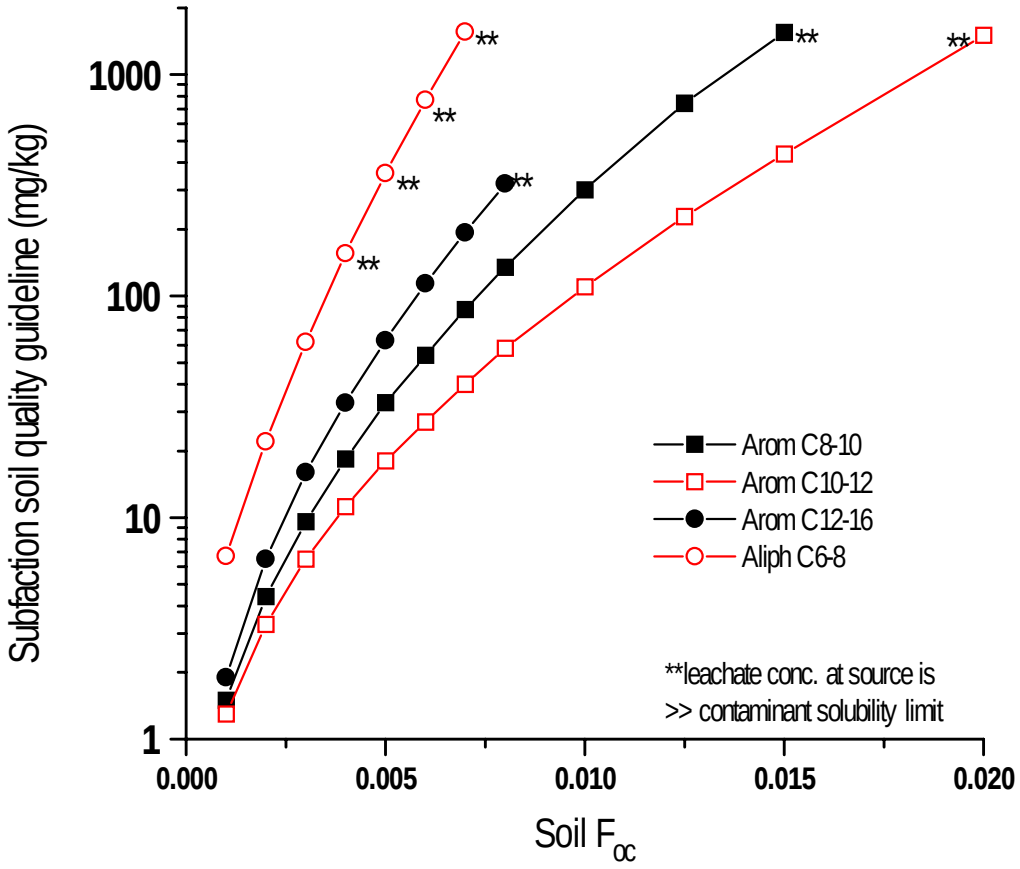


Figure 4.25: Change in modeled PHC soil quality benchmarks based on changes in soil organic carbon content.

4.3.4.8 Calculation of SQGs for PHC CWS Fractions F1 and F2. For Tier I calculations, based on a generic site wherein a surface water body is separated from petroleum hydrocarbon contaminated, coarse-grained soil by a distance of 10 m, the following estimates of appropriate sub-fraction soil quality thresholds were calculated:

i) **PHC CWS F1:**

TPHCWG Aliphatics C6-C8 (55% of CWS F1 by mass): **357 mg/kg**
TPHCWG Aliphatics C8-C10 (36% of CWS F1 by mass): no value
(assume **20,000 mg/kg**; i.e. limits below which free product would be expected)
TPHCWG Aromatics C8-C10 (9% of CWS F1 by mass): **33 mg/kg**

ii) **PHC CWS F2:**

TPHCWG Aliphatics C10-C12 (36% by mass): no value
(assume **20,000 mg/kg**; i.e. limits below which free product would be expected)
TPHCWG Aromatics C10-C12 (9% by mass): **18 mg/kg**
TPHCWG Aliphatics C12-C16 (44% by mass): no value
(assume **20,000 mg/kg**; i.e. limits below which free product would be expected)
TPHCWG Aromatics C12-C16 (11% by mass): **63 mg/kg**

The sub-fractions for which no SQG could be calculated are not deemed to be limiting for aquatic life based on transport in the dissolved phase, up to a concentration of 100% in soil: The solubility limits at the point of interception between contaminated soil and groundwater are the major limiting factor to increased concentrations in groundwater and surface water down –gradient from the site. Based on inclusion of the "no value" subfractions at a 20% soil concentration (an approximate threshold for the presence of free product), the following CWS SQGs are calculated:

$$SQG_{slice\_i} = \frac{1}{\sum\left(\frac{MF_{subfraction\ j}}{SQG_{subfraction\ j}}\right)}$$

Where -

SQG_{slice_i} = soil quality guideline for the CWS fraction *i* (mg/kg)
$SQG_{subfraction\ j}$ = soil quality guideline (mg/kg) for each sub-fraction within fraction *i* for the target water quality guideline for fraction *i*
$MF_{subfraction\ j}$ = mass fraction of each sub-fraction within the fraction *i*

CWS F1:

SQG = 1/[(0.55/357 mg/kg) + (0.36/20000 mg/kg) + (0.09/33 mg/kg)]

= 233 mg/kg

CWS F2:

SQG = 1/[(0.36/20000 mg/kg) + (0.44/20000 mg/kg) + (0.09/18 mg/kg) + (0.11/6.3 mg/kg)]

= 147 mg/kg

Rounding these numbers to two significant figures, the following provisional guidelines are derived:

i) PHC CWS F1:	**SQG_{AL}** (provisional) = 230 mg/kg
ii) PHC CWS F2:	**SQG_{AL}** (provisional) = 150 mg/kg

Based on the analysis provided herein, the recommended Tier I SQG_{AL} for coarse-grained soils for CWS fractions F1 and F2 is 230 mg/kg and 150 mg/kg respectively.

PIWG also provided default assumptions for Tier I sites with fine-grained (silt-clay) soils. Use of an assumed Darcy velocity of 0.016 m/y, coupled with other assumed model input parameters for fine textured soils did not lead to reasonable estimates of subfraction SQGs for any of the TPHCWG subfractions. It is recommended, therefore, that a soil quality guideline based on groundwater transfer to surface water bodies should not apply to fine-grained sites at Tier I. Not withstanding the absence of an adopted soil protective standard based on the aforementioned exposure scenario, the regulator or other stakeholder may require additional investigation and/or risk management activities in cases where there is evidence of PHC inputs to adjacent water bodies containing aquatic life, either through aeolian transport and particle erosion, groundwater transport, or other pathways.

4.3.5 Model Predictions – Livestock Watering

Estimates of toxicological thresholds for livestock drinking water, as fraction-specific reference concentrations (RfC_{LDW}s), are provided in Section 4.3.5. These RfC_{LDW}s were used to back-calculate soil concentrations for PHCs above which risks to livestock ingesting drinking water might be expected – based on an approach similar to that used calculating soil benchmarks for the protection of aquatic life.

The BCE groundwater model was used to estimate appropriate threshold source soil concentrations, using the assumptions for a generic site with coarse-textured soil, as documented in Table 4.13. In addition, the model was run firstly under the assumption

that no PHC degradation would occur in the saturated or unsaturated environment. Model calculations were subsequently run assuming an environmental persistence in both the saturated and unsaturated zone of 2 years (712 days) and slightly less than 5 years (1750 days) for CWS fractions F1 and F2, respectively (as applied to the TPHCWG sub-fractions). Table 4.25 summarizes the model runs.

Table 4.25: Back-calculated predictions of soil quality benchmarks (in mg/kg) for TPHCWG subfractions based on protection of livestock ingesting drinking water.

	$t_{1/2}$ = 1.0e+09			$t_{1/2}$ (F1: 712 days; F2: 1,750 days)		
CWS F1						
TPHCWG-AlC6-8	>sol [A]	390	at 4x sol [C]	>sol	29,000	at 350x sol
TPHCWG-AlC8-10	>sol	3100	at 10x sol	>sol	no solution at sol = 100% conc	
TPHCWG-ArC8-10	**155 mg/kg** [B]			>sol	920	at 3x sol
CWS F2						
TPHCWG-AlC10-12	>sol	28000	At 100x sol	>sol	no solution at sol = 100% conc	
TPHCWG-AlC12-16	>sol			>sol	no solution at sol = 100% conc	
TPHCWG-ArC10-12	**230 mg/kg**			**360 mg/kg**		
TPHCWG-ArC12-16	>sol	450	at 4x sol	>sol	5600	at 20x sol

Notes: A) No solution returned based on TPHCWG estimates for subfraction physico-chemical properties. The groundwater leachate concentration at the source soils would exceed the assumed sub-fraction solubility limits in order to result in a surface water concentration deemed to constitute a risk.
B) Bolded values are model calculations that were reached within the TPHCWG estimated solubility limits for the subfraction.
C) Where the solubility limits were exceeded by the leachate concentration, an arbitraily elevated solubility limit was used to back-calculate a soil concentration that would result in the target RfCs if solubility was not a limiting factor.

Note that no results are provided for the TPHCWG subfractions that fall within the CWS F3 fraction. Model runs reinforced the view that the strong hydrophobicity of >nC16 to C34 PHCs would render groundwater exposure pathways inoperative.

The tabulated TPHCWG subfraction values were used to calculate a soil quality benchmark for CWS fractions F1 and F2 using the following algorithm (see also Section 4.3.2):

$$SQG_{slice\_i} = \frac{1}{\sum\left(\frac{MF_{subfraction\ j}}{SQG_{subfraction\ j}}\right)}$$

Where -

SQG_{slice_i} = soil quality guideline for the CWS fraction *i* (mg/kg)

$SQG_{subfraction\ j}$ = soil quality guideline (mg/kg) for each subfraction within fraction *i* for the target water quality guideline for fraction *i*

$MF_{subfraction\ j}$ = mass fraction of each subfraction within the fraction *I*

The SQGs for subfractions for which the groundwater leachate concentration at the source soils would exceed the assumed sub-fraction solubility limits were estimated as either (i) the soil concentration required to produce the target surface water concentration had solubility not been a limiting factor, or (ii) a 100% soil concentration. This resulted in the following soil quality guideline estimates for CWS fractions F1 and F2:

CWS Fraction	$T_{1/2}$ = 1.0e+09 day	$T_{1/2}$ = 712 and 1750 days for F1,2
F1	**550 mg/kg**	**9,000 mg/kg**
F2	**1,500 mg/kg**	**4,000 mg/kg**

4.4 Tier I Guidance for Ecological Receptors

An analysis was undertaken to derive a soil quality guideline for PHCs which will be protective of aquatic life where there is an adjacent surface water body. Based on the sensitivity analysis contained herein, this exposure pathway would be important when the aquatic-life containing water body is less than 100 m from the contaminant source area. In addition risks to aquatic life in an adjacent water body would be important to consider where massive PHC releases have occurred, and/or there are aspects of PHC transport which fall outside of the assumptions of the modeling exercise (channelized flow, presence of non-aqueous phase lipids or large co-solvent concentrations).

Detailed new toxicology studies, coupled with a detailed analysis of existing and new data (herein) provided guidance on environmentally protective thresholds for PHCs in relatively coarse surface soils of relevance to soil invertebrates and plants.

Table 4.26 provides a summary of Tier I guidance for ecological receptors in surface, coarse soils, based on the preceding analysis. Toward the final derivation of the Tier I PHC CWS, additional values were provided based on the prevention of ecological risks, for fine-grained soils as well as subsurface soils. The extension of the numbers provided in Table 4.26 to fine-textured and/or subsurface soils is discussed in Chapter 5.

Table 4.26: Summary of generic PHC soil quality guidelines (mg/kg soil) recommended for coarse-textured surface soils in Canada.

Receptor	PHC CWS Fraction				Rationale
	F1	F2	F3	F4	
Soil Invertebrates and Plants					
· *Agricultural and Residential/ Parkland*	130	450	400	2,800[1]	-25th percentile of combined soil invertebrates and plants species sensitivity dist'n - 50th percentile of plant effects dist'n
· *Commercial and Industrial*	330	760	1,700	3,300	
Aquatic Life · *All land use categories*	230	150	NA[2]	NA	-Based on a narcosis/ critical body residue approach. A chronic lipid-based threshold of 3.0 mmol PHCs/kg-lipid was used to establish acceptable water concentrations in a surface body 10 m away from the mass of PHC-contaminated soils for each of seven TPHCWG sub-fractions.
Livestock Drinking surface Water · *Agricultural*	9,000	4,000	NA	NA	

Notes: (1) provisional guidance only, based on ecotoxicity of fresh whole Federated Crude Oil (Section 4.2.3); (2) NA – not applicable

Some direct scientific guidance is also provided herein on groundwater mediated exposure pathways and risks to aquatic life or livestock in fine soils. The groundwater model exercise predicts that the transport of PHCs (especially the F1 and F2 fractions) within the dissolved phase in groundwater in a homogeneous, fine-textured soil in unlikely to lead to exposure concentrations in surface water bodies of concern. One possible exception to this is when a mass of PHC contaminated soil is in intimate contact with a surface water body. Such a situation is deemed to be outside of the assumptions used in the derivation of Tier I PHC CWS.

5. Integration of Ecological and Human Health Levels

5.1 General

Tabular Tier 1 levels in the PHC CWS present the lower of the values generated for human health and ecological protection such that both are protected when Tier 1 levels are applied. This roll-up is essential to establish the risk management goals applicable to the most sensitive sites under each land use – i.e., sites where all potential receptors and exposure pathways are operative. In practice, the number of such sites in a particular jurisdiction may be small and detailed results applicable to individual pathway/receptor combinations are needed in order to identify practical management strategies. This chapter provides a summary of the risk-based values developed for each pathway/receptor combination in the individual land use categories. In addition, rationale is provided for certain risk management decisions made in the final integration of human health and ecotoxicological inputs.

The principal features added to the PHC CWS at the integration stage were:

- Adjustment of eco-contact levels with respect to soil texture, and
- Addition of generic levels for subsoils – defined as earthy materials below 1.5 m depth.

In the process of developing these features the Development Committee considered several factors that are not easily accommodated in explicit, quantitative exposure and risk estimates. These factors included:

- Capabilities of current and emerging remediation technologies,
- Likelihood of subsoil disturbance and excavation under different scenarios,
- Potential effects of PHC on buried infrastructure,
- Aesthetics,
- Role of subsoil in terrestrial ecology,
- Costs of risk reduction measures,
- Property values and environmental stewardship.

A description of the roles played by the above scientific, technical and socio-economic factors in finalizing the Tier 1 PHC CWS levels is provided in this chapter.

5.2 Eco Soil Contact Pathway – Role of Soil Texture

Soil texture, and clay content in particular, has long been recognized as an important influence on the behaviour of chemicals in soils. The clay fraction is responsible for most of the surface area of soils and also provides unique colloidal properties that support well-documented phenomena such as cation exchange. It is now accepted that clay plays an important role in stabilizing naturally occurring organic residues against microbial attack (Stevenson 1983). As a result, fine

textured soils tend to accumulate greater amounts of organic matter and exhibit lower rates of decomposition than coarse textured soils under similar climatic and vegetative conditions.

Colloidal properties are now being shown to be influential on contaminant behaviour in soils also. Recent scientific literature indicates that toxicity of PHCs in soils declines with time (see, for example Loehr and Webster 1996, Salanitro et al. 1997). In part, as discussed in Chapter 4, this is due to dissipative mechanisms such as volatilization, leaching and biodegradation. However, some evidence suggests that "aging" of PHCs results in reduced bioavailability as well. Several mechanisms of aging have been hypothesized and investigated including, attrition of lower molecular components due to biodegradation, physical occlusion of PHCs in pores inaccessible to organisms, and stabilization of PHCs by association with soil colloidal material. Irrespective of which of these mechanisms predominates, there is agreement that "aging" is a factor in ecotoxicological response in the field. The degree of amelioration has been observed to be greater in fine textured soils; consistent with predictions from consideration of colloidal properties.

Chung and Alexander (1998) and Kelsey and Alexander (1997) described differences in bioavailability of individual hydrocarbons added to soils of varying texture and how bioavailability decreases with aging. Salanitro et al. (1997) reported similar trends in soils contaminated by crude oil and concluded that soil conditions are among the chief determinants of hydrocarbon phytotoxicity in soil. While mechanisms by which soil colloids reduce bioavailability of PHCs are not clearly established, it is highly likely that they include those applicable to biological residues, such as H-bonding, van der Waals forces, ion exchange, geometric complementarity, physical occlusion, etc. Many researchers ascribe reductions in bioavailability of hydrocarbons in soil to a generalized "sequestration".

5.2.1 Socio-Economic and Technological Factors

Considerable work has been carried out over the past two years to provide information on response of soil dwelling organisms to the PHC CWS fractions and certain whole products. Chapter 4 describes how standardized acute and chronic bioassays of plant and invertebrate toxicity response in artificial and coarse textured field soils have been conducted on Federated Crude, Mogas and four fractions cut from the Federated Crude. Analyses of these data using modified concepts and procedures from the CCME (1996) soil protocol indicate an appreciable toxicity for all investigated fractions. However, direct application of the Tier 1 values calculated for coarse textured surface soils to fine textures and deep subsoils would pose significant challenges to the biotreatment technologies typically applied to PHC contaminated soils.

CCME carried out a screening socio-economic analysis in support of the PHC CWS (Komex 2000) that analyzed theoretical Tier 1 values ("seed values" and upper and lower limit values around the seed values) in order to estimate options and costs for

remediation of affected Canadian soils. This analysis indicated to the Development Committee that well-established biotreatment technologies can be used to attain Tier 1 values for coarse soils as derived above but would often fail to meet these same targets were they applied to fine textured soils. Attainment of Tier 1 levels for F3 would be particularly problematic. The analysis further indicated that the probable outcome of application of Tier 1 eco contact values for coarse soils to fine soils would be that extensive volumes of soil and subsoil would be directed to landfills rather than receiving remedial treatment. This, in turn, would fail to conserve otherwise useful soil and put additional pressure on scarce landfilling capacity. The CCME Development Committee considered this information carefully and concluded that some amendment to eco-contact values applicable to fine textured soils should provide a net geo-environmental benefit.

5.2.2 Risk Management Decision

While systematic, quantitative relationships between soil toxicity of PHC and texture are not yet published, it was judged to be a conservative assumption that, over practical exposure durations in field soils, toxic response in fine textured soils would be not greater than half that seen in coarse textured soils. As described in Chapter 4, the bulk of the contributing data for development of the PHC CWS were derived from coarse textured soils (e.g., OECD mix). Thus, a risk management decision was made to increase Tier 1 levels for eco-contact in surface soils by 2-fold over those derived for coarse textured soils. Eco Soil Contact entries in Table 5.1 (applicable to fine-textured soils) are, with one exception, double those in Table 5.2 (applicable to coarse textured soils). An upset limit of 2,500 mg/kg was used for commercial and industrial lands in consideration of the relatively non-conservative ecotoxicity endpoint used for the coarse textured case (see Chapter 4).

Note that this risk management decision regarding soil texture applies only to the eco-contact pathway, where experimental evidence for the adjustment exists. It should be further noted that this is strictly a practical decision that responds to the differences in biotreatment efficiency in soils of differing efficiency. Loehr and Webster (1996) showed that fine textured soils reached a non-toxic biotreatment endpoint at higher residual hydrocarbon concentrations than did coarse textured soils.

As research results accumulate, it will be possible to re-visit the professional judgment basis of eco-contact values for fine textured soils.

5.3 Approach to Subsoil Values

Information is presented in Tables 5.3 and 5.4 on generic levels applicable to subsoils, defined as earthy materials below 1.5 m depth. This section describes the general rationale for subsoil values, principles used in their derivation, pathway analysis and specific risk management decisions supporting the generic values.

Experience has shown that technical and socio-economic factors constrain risk management decision-making at contaminated sites. At larger and/or more severely contaminated sites this frequently means that numerical guidelines are applied only to surface soils and deeper contamination is addressed using site-specific risk assessment and management. Commonly, risk management plans based on site-specific risk assessment allow higher contamination concentrations at depth than would be acceptable under a guideline-based approach. Details vary but reduced accessibility of contamination at depth is a very common rationale for these higher concentrations. Monitoring of these higher concentrations and some form of notification or administrative control is usually required for regulatory acceptance. Recently, some jurisdictions have incorporated this form of risk management - stratified remediation - into their generic guidelines (e.g., MADEP 1994, OMEE 1996, Atlantic PIRI 1999). This approach has the advantage of presenting an economical risk management option without triggering the need for a site-specific risk assessment. CCME decided to develop generic values for subsoils as a risk management option under the PHC Canada-Wide Standard.

5.3.1 Principles for Development of Generic Subsoil Levels

While practical advantages have been identified, these could be realized only if a number of principles and conditions were followed:

- Generic subsoil levels must be risk-based and take account of all relevant and applicable pathways for both human and ecological receptors;
- All pathways applicable to surface soil must be assessed in the determination of appropriate subsoil pathways;
- Generic subsoil levels must not compromise aesthetic values or pose an unacceptable risk to infrastructure;
- An acceptable subsoil definition must exclude zones of high biological activity;
- Subsoil contamination must not serve as significant source for upward contamination of overlying soil through diffusion or “wicking” under evapotranspiration gradients;
- Subsoil contamination should not pose an unacceptable risk to workers who may occasionally come into contact with contamination through excavation or infrastructure service activities.

5.3.2 Review of Pathways

Human Health

(a) Soil ingestion – Not applicable under non-disturbance conditions. Could apply to construction and infrastructure workers under occasional conditions. For surface soil, only residential land use shows values below residual levels -“RES” - (>3%) for surface – 1.6% and 2.9% for F2 and F3 respectively. Given these values and the sharply reduced exposure for

workers as compared to continuously exposed children, a worker exposure scenario would be expected to return a value of “RES”.

(b) Soil dermal contact -- Not applicable under non-disturbance conditions. Could apply to construction and infrastructure workers under occasional conditions. All surface exposure pathways assessed as “RES”. Occasional, short duration exposure to subsoil would be expected to return “RES” also.

(c) Vapour inhalation – Risk-based values for soil are based on a minimum vertical distance from base of slab to contamination (“L_t”) of 30 cm. For the basement and subsoil scenario, the same 30 cm vertical distances applies. However, for slab-on-grade construction, the default value of L_t is 139 cm – 150 cm to subsoil less the nominal slab thickness of 11 cm. L_t may be further increased for contamination positioned below 150 cm depth.

(d) Potable groundwater protection – Applies in same manner as for surface soil.

Ecological Health

(a) Direct soil contact – Very deep-rooted species may explore soil to this depth. Also, certain invertebrates may migrate deeply to avoid moisture stress periodically (Coleman and Crossley 1995). In the former case, the proportion of root biomass involved is minor and would be expected to pose minimal risk so long as values do not exceed those applicable to surface soil by a wide margin. In the latter case, the proportion of species making deep vertical migrations is small, and of those that do, time spent at depth is small and may be partially avoided. Given the present reliance on fresh product ecotoxicity data, which provide a conservative estimate of biological response, a five-fold increment in the Tier 1 value applicable to surface soil should be protective of ecological functions at depth.

(b) Soil and food ingestion/bioaccumulation – Does not apply.

(c) Protection of groundwater for aquatic life, livestock watering – Applies in same manner as for surface soil.

Miscellaneous

(a) Off-site migration of Soil/Dust – Does not apply for subsoils.

5.3.3 Risk Management Decisions

Depth to Subsoil

Based on consideration of the depth of soil development in Canada and zones of high biological activity, including rooting depths of common and valued plants, and common depths of routine excavation, a depth of 1.5 m was used to define the transition from soil to subsoil. This is also consistent with OMEE (1996).

Applicable Pathways

Based on the pathways analysis in Section 5.3.2 generic subsoil values are presented only for the vapour inhalation pathway, groundwater protection pathways, and Eco-soil contact pathways. The values for vapour inhalation and groundwater protection were calculated as indicated in Section 5.3.2 and differ very little, if at all, from values applicable to surface soils. The Eco Soil Contact pathway includes the factors discussed in Section 5.3.2 as well as any considerations related to aesthetics and protection of infrastructure. This decision was taken in consideration of the following points:

- At some sites, neither the vapour inhalation pathway nor groundwater protection pathways will apply whereas the Eco Soil Contact pathway is considered applicable at all times;
- There is a need, generically, to indicate an upset limit for subsurface PHC contamination;
- Definitive studies clearly delineating tolerable limits for PHC contamination from a standpoint of aesthetics and infrastructure protection are lacking. Nevertheless, there is evidence that high levels of PHC in subsoil can adversely affect aesthetics and infrastructure.

Thus, data were judged insufficient to allow “standalone” risk-based derivations for aesthetics and infrastructure, and they were addressed qualitatively as risk management considerations constraining the degree of expansion of surface ecotoxicity values applicable to subsoil.

Upset Limits

Free Product Formation – Theoretically, free-phase hydrocarbon can form in soil once a constituent exceeds its solubility limit in soil water, which is reached at a total soil concentration determined by the partitioning isotherm applicable to the particular soil and substance under consideration. For lower molecular weight constituents of particular environmental concern, these saturation limits can be reached at concentrations less than 50 mg/kg for C12-C16 aliphatics to about 1600 mg/kg for C5-C7 aromatics (TPHCWG 1999). In practice, lower molecular weight constituents tend to partition strongly into any residual (immobile) hydrocarbon phase that may be present. Appearance of residual hydrocarbon as a perceptible free phase in soil depends on a number of factors including soil texture, porosity, aeration porosity and hydrocarbon type (US EPA 1992b). Nevertheless, across a range of soil and petroleum hydrocarbon types, 3% PHC is generally sufficient for many to identify a hydrocarbon phase. Allowing for a margin of safety, a decision was taken that generic subsoil concentrations should not exceed 2%, of which not more than 1% should be in the sum of F1-F3. In consideration of the mobility and flammability risk posed by F1, it was further decided that F1 concentrations should not exceed 1,000 mg/kg.

Effect of Texture -- It was felt that clay content would contribute to general stabilization of F1-F3 at depth. Within a land use and fraction, fine textured soils were assigned higher generic subsoil PHC values than were coarse textured soils. Given the viscosity, insolubility, low bioavailability and resistance to attack of F4 it was felt that texture was relatively unimportant in the environmental risk posed by PHC in subsoil. Consequently, an upset limit of 10,000 mg/kg was established for F4 for both coarse- and fine-textured subsoil.

Technological Factors -- Bioremediation is presently the preferred technology for dealing with percent range PHC contamination of soils and subsoils, based on its effectiveness and cost (Komex 2000). Several studies have shown that bioremediation is most effective on low- to mid-range PHC (i.e., less than about C25). Larger PHC are biodegraded, but at much slower rates and, possibly, at lower rates still with soil "aging". This means that the major challenge for bioremedial systems is in dealing with F3, which is present in varying amount across a broad range of PHC release types and, unlike F4, is substantially toxic to plants and soil invertebrates (see Chapter 4). The following upset limits were established for F3 in subsoils in consideration of toxic risk, aesthetics, effects on infrastructure and bioremedial capabilities:

- Coarse textured subsoil, agricultural and residential uses: 2,500 mg/kg
- Coarse textured subsoil, commerical and industrial uses: 3,500 mg/kg
- Fine textured subsoil, agricultural and residential uses: 3,500 mg/kg
- Fine textured subsoil, commerical and industrial uses: 5,000 mg/kg

Subsoil Procedures for F1

Generic levels for F1 in fine textured subsoil under commercial/industrial uses were established at the upset limit of 1,000 mg/kg described above under "free product formation". Subsoil values for coarse textures under commercial/industrial use were established at twice the value applied to agricultural and residential uses. For agricultural and residential uses, an approximate 3-fold increment over the surface soil values was used for subsoil values.

Subsoil Procedures for F2

Generic levels for coarse textured were established at approximately 3-fold above the values applicable to coarse textured surface soil. Finally, generic levels for fine-textured subsoil were established at the approximate means of values established for F1 and F3 within the same texture and land use class.

5.4 Summary of Risk Management Decisions

Generic subsoil levels for PHC are judged to be protective of human health and environment so long as subsoil remains at depth. In addition, allowance has been made for certain exposures that could occur as a consequence of excavation.

A number of assumptions and interpretations have been made with respect to effects of subsoil PHC contamination on ecological functions, infrastructure and aesthetics. The risk management decision made in regard to these factors rely principally on input from stakeholders and experts. More quantitative information from future studies will allow validation or adjustment of these risk management decisions.

It is recognized that jurisdictions have discretion in the application of generic subsoil PHC levels with regard to any relevant conditions for on-going management.

5.5 Tabular Presentation of Generic PHC CWS Levels

Tables 5.1 through 5.4 on the following pages summarize the outcomes of the risk assessment and risk management procedures discussed in detail in Chapters 1 through 5. Four tables are presented:

- Table 5.1: Tier 1 levels for fine-grained surface soil.
- Table 5.2: Tier 1 levels for coarse-grained surface soil.
- Table 5.3: Generic levels for fine-grained subsoil.
- Table 5.4: Generic levels for coarse-grained subsoil.

Generic subsoil values are not listed as Tier 1 because their use may pose on-going risk management considerations in some situations.

Table 5.1. Tier 1 levels (mg/kg soil) for PHCs for fine-grained surface soils.

Land Use	Exposure Pathways	F1 (C6-C10)	F2 (>C10-C16)	F3 (>C16-C34)	F4 (>C34)
Agricultural	Soil Ingestion	15,000	8000	18,000	25,000
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor, 30 m offset)	2100	11,400	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Protection of GW for Livestock Watering[3]	TBD	TBD	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[4]	260	900	800	5600
	Eco Soil Ingestion	TBD	TBD	TBD	TBD
	Produce, Meat and Milk	NC	NC	NC	NC
Residential	Soil Ingestion	15,000	8000	18,000	25,000
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor)	940	5200	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[4]	260	900	800	5600
	Produce	NC	NC	NC	NC
Commercial	Soil Ingestion	RES	29,000	RES	RES
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor)	4600	25,000	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[4]	660	1500	2500	6600
Industrial	Soil Ingestion	RES	RES	NA	NA
	Dermal Contact	RES	RES	RES	NA
	Vapour Inhalation (indoor)	4600	25,000	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[4]	660	1500	2500	6600
	Offsite Migration	NA	NA	12,000	RES

NA = Not applicable. Calculated value exceeds 1,000,000 mg/kg or pathway excluded.
RES = Residual PHC formation. Calculated value exceeds 30,000 mg/kg and solubility limit for PHC fraction.
NC = Not calculated. Insufficient data to allow derivation.
TBD = To be determined

1 = Assumes site is underlain by groundwater of potable quality in sufficient yield (K of 10^{-4} cm/sec or greater).
2 = Assumes surface water body at 10 m from site.
3 = Generally applicable for this land use as related to use of dugouts and wells for supply of livestock water.
4 = Tier 1 values based primarily on laboratory bioassay response to fractions derived from fresh Federated Crude Oil and adjusted for textural factors.

Table 5.2 Tier 1 levels (mg/kg soil) for PHCs for coarse-grained surface soils.

Land Use	Exposure Pathways	F1 (C6-C10)	F2 (>C10-C16)	F3 (>C16-C34)	F4 (>C34)
Agricultural	Soil Ingestion	15,000	8000	18,000	25,000
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor, 30 m offset)	200	1100	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Protection of GW for Livestock Watering[2]	*9000*	*4000*	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[3]	130	450	400	2800
	Eco Soil Ingestion	TBD	TBD	TBD	TBD
	Produce, Meat and Milk	NC	NC	NC	NC
Residential	Soil Ingestion	15,000	8000	18,000	25,000
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor, basement)	50	240	NA	NA
	Vapour Inhalation (indoor, slab-on-grade)	30	150	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[3]	130	450	400	2800
	Produce	NC	NC	NC	NC
Commercial	Soil Ingestion	RES	29,000	RES	RES
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor)	310	1700	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[3]	330	760	1700	3300
Industrial	Soil Ingestion	RES	RES	NA	NA
	Dermal Contact	RES	RES	RES	NA
	Vapour Inhalation (indoor)	310	1700	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Nutrient Cycling	TBD	TBD	TBD	TBD
	Eco Soil Contact[3]	330	760	1700	3300
	Offsite Migration	NA	NA	RES	RES

NA = Not applicable. Calculated value exceeds 1,000,000 mg/kg or pathway excluded.
RES = Residual PHC formation. Calculated value exceeds 30,000 mg/kg and solubility limit for PHC fraction.
NC = Not calculated. Insufficient data to allow derivation.
TBD = To be determined
1 = Assumes surface water body at 10 m from site.
2 = Includes use of dugouts and wells for supply of livestock water.
3 = Tier 1 values based mainly on laboratory bioassay response to fractions derived from fresh Federated Crude Oil.

Table 5.3. Generic levels for PHCs in fine-grained subsoil (> 1.5 m depth).

Land Use	Exposure Pathways	F1 (C6-C10)	F2 (>C10-C16)	F3 (>C16-C34)	F4 (>C34)
Agricultural	Soil Ingestion	RES	RES	RES	RES
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor, 30 m offset)	2100	11,400	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Protection of GW for Livestock Watering[3]	TBD	TBD	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[4]	750	2200	3500	10,000
	Eco Soil Ingestion	TBD	TBD	TBD	TBD
	Produce, Meat and Milk	NA	NA	NA	NA
Residential	Soil Ingestion	RES	RES	RES	RES
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor: basement, slab)	(940, 990)	(5200, 5500)	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[4]	750	2200	3500	10,000
	Produce	NA	NA	NA	NA
Commercial	Soil Ingestion	RES	RES	RES	RES
	Dermal Contact	NA	RES	NA	NA
	Vapour Inhalation (indoor)	4800	26,000	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[4]	1000	3000	5000	10,000
Industrial	Soil Ingestion	NA	NA	NA	NA
	Dermal Contact	NA	NA	NA	NA
	Vapour Inhalation (Indoor)	4800	26,000	NA	NA
	Protection of Potable GW[1]	180	250	NA	NA
	Protection of GW for Aquatic Life[2]	TBD	TBD	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[4]	1000	3000	5000	10,000
	Offsite Migration	NA	NA	NA	NA

NA = Not applicable. Calculated value exceeds 1,000,000 mg/kg or pathway excluded.
RES = Residual PHC formation. Calculated value exceeds 30,000 mg/kg and solubility limit for PHC fraction.
NC = Not calculated. Insufficient data to allow derivation.
TBD = To be determined
1 = Assumes site is underlain by groundwater of potable quality in sufficient yield (K of 10^{-4} cm/sec or greater).
2 = Assumes surface water body at 10 m from site.
3 = Generally applicable for this land use as related to use of dugouts and wells for supply of livestock water.
4 = Values based primarily on laboratory bioassay response to fractions derived from fresh Federated Crude Oil and adjusted for texture, depth factors and other physical hazard considerations.

Table 5.4. Generic levels for PHC in coarse-grained subsoil (> 1.5 m depth).

Land Use	Exposure Pathways	F1 (C6-C10)	F2 (>C10-C16)	F3 (>C16-C34)	F4 (>C34)
Agricultural	Soil Ingestion	RES	RES	RES	RES
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor, 30 m offset)	200	1100	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Protection of GW for Livestock Watering[2]	*9000*	*4000*	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[3]	350	1500	2500	10,000
	Produce, Meat and Milk	NA	NA	NA	NA
Residential	Soil Ingestion	RES	RES	RES	RES
	Dermal Contact	RES	RES	RES	RES
	Vapour Inhalation (indoor, basement)	50	240	NA	NA
	Vapour Inhalation (indoor, slab-on-grade)	40	190	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[3]	350	1500	2500	10,000
	Produce	NA	NA	NA	NA
Commercial	Soil Ingestion	RES	RES	RES	RES
	Dermal Contact	NA	RES	NA	NA
	Vapour Inhalation (indoor)	340	1800	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[3]	700	2000	3500	10,000
Industrial	Soil Ingestion	NA	NA	NA	NA
	Dermal Contact	NA	NA	NA	NA
	Vapour Inhalation (indoor)	340	1800	NA	NA
	Protection of Potable GW	860	1200	NA	NA
	Protection of GW for Aquatic Life[1]	230	150	NA	NA
	Nutrient Cycling	NA	NA	NA	NA
	Eco Soil Contact[3]	700	2000	3500	10,000
	Offsite Migration	NA	NA	NA	NA

NA = Not applicable. Calculated value exceeds 1,000,000 mg/kg or pathway excluded.
RES = Residual PHC formation. Calculated value exceeds 30,000 mg/kg and solubility limit for PHC fraction.
NC = Not calculated. Insufficient data to allow derivation.
TBD = To be determined
1 = Assumes surface water body at 10 m from site.
2 = Includes use of dugouts and wells for supply of livestock water.
3 = Values based primarily on laboratory bioassay response to fractions derived from fresh Federated Crude Oil and adjusted for depth factors and other physical hazard considerations.

6. Background to the Development of Analytical Methodology

6.1 Introduction

Methods for quantifying and reporting environmental contaminants generally influence the scope and interpretation of the results, and this is particularly important in the case of PHCs. Petroleum hydrocarbons in soil have been reported as extractable, purgeable or total depending on how they have been recovered from soil and measured. In addition, variations in the degree of analytical "clean up" and the manner of detection/quantification affect the results obtained and the reporting terminology. Analytical cleanup is normally undertaken to reduce interference from co-extracted biochemicals that are not PHCs. Quantification can occur by gravimetric, spectrophotometric or chromatographic methods.

Various combinations of extraction, cleanup and detection methods contribute to a proliferation of terms, which include oil and grease, mineral oil and grease, extractable hydrocarbons, purgeable hydrocarbons, and total petroleum hydrocarbons. This array of terms is confusing to users and contributes to uncertainty around what is being observed and what environmental significance a given set of data might have.

Inter laboratory studies of PHC analytical methods conducted by Environment Canada's Wastewater Technology Centre in the mid-1990s showed highly variable results from laboratory to laboratory when extraction, purification and detection steps were not specified. However, much of the variability depended on systematic factors – i.e., fundamental differences in extraction, detection, quantification and reporting. Stakeholders confirmed the need for consistent nomenclature, analytical methodology and linkage between the two at the first national PHC workshop in October 1997. The CCME PHC CWS thus includes a reference analytical method that must be followed to ensure the validity of the assessment and remediation program. The reference method combines prescriptive and performance-based elements.

6.2 Sampling and Analysis of PHC in Soil

The reference method for measurement of PHC in soil and subsoil described in this section was developed under the guidance of a national, multistakeholder Analytical Methods Technical Advisory Group (AM TAG). The method was developed to ensure that measurements made in support of the PHC CWS:

- Link to the fractions used in the risk analysis;
- Are technically and scientifically defensible;
- Provide users with accurate and consistent results;

- Can be delivered by competent laboratories using routine equipment;
- Can incorporate knowledge and experience of analysts to improve results and costs within a performance-based framework.

While the procedures described below are required to characterize contamination and confirm remedial results, it is recognized that certain simplifications will occur on a site-by-site basis or within the overall management process at a given site. As examples:

a) Site characterization may confirm that only a subset of CWS PHC fractions is present at a particular release site and this information may be used to reduce the cost and complexity of PHC analysis. For example, investigation of a site confirmed to be contaminated by fresh gasoline need not include observations on F3 and F4. Similarly, if weathered lubricants are the sole PHC contaminants, observations on F1 and possibly F2 will not be needed.

b) It may be possible at many sites to correlate inexpensive screening analyses with standardized reference analyses (CCME 2000). While such analyses would not be adequate for confirmation or regulatory purposes, they may be useful in the delineation of contamination and preparation of remedial action plans.

It is further recognized that analytical results are strongly influenced by sampling procedures including the approach to delineation, sample collection technique, handling and storage. These considerations are touched on only briefly below but are considered in greater detail in both the analytical method documentation (CCME 2000) and the PHC CWS User Guidance (CCME 200X).

6.3 Sample Collection and Handling

Sampling is generally undertaken to assess the nature and extent of contamination and, depending on assessment outcome, guide any necessary remedial actions and confirm their effectiveness. Ultimately, sampling and analysis information will be used to create a record of environmental condition that will allow stakeholders to make appropriate land and water use decisions. Concentrations of the PHC fractions in contaminated soil and subsoil are needed to assess management options including the urgency of any indicated remedial action and the technologies that may be able to deal with the contamination.

Given the above applications, sampling for site characterization must be conducted so as to:

- delineate the lateral and vertical extent of “non-compliant” soil and subsoil,

- maximize retention of all fractions (F1, F2, F3, F4) in the sample,
- determine the concentration of contamination in the non-compliant areas.

Sampling for confirmation of site condition must be able to show that non-compliant soil and subsoil has been remediated and that margins of the affected area “test clean”. The definitions of compliant and non-compliant material depend on land use, texture, depth and various site properties and use patterns as described in CCME (200X).

Retention of PHC in soil and subsoil samples is critical in achieving valid analytical results, especially for the volatile fraction F1. Dissipation of low molecular weight PHC via volatilization and biodegradation is the principal concern. Biodegradation is also a concern for other PHC fractions. Use of air-tight vessels and low temperature storage for minimizing this dissipation is described in CCME (2000).

Technical guidance to assist in achieving the goals of accurate and precise characterization of site conditions is provided in **CCME (1993, 1994**, 200X). The CWS PHC method does not address in detail sampling of PHC contaminated sites. It does provide general guidance using CCME and U.S.EPA published procedures and the necessity of following a strict protocol and the need for samplers to develop QA/QC procedures for sampling and transfer to the laboratory.

The quality and quantity of site characterization data necessary for assessment and closure of a PHC-contaminated site are determined by jurisdictions.

It is essential to note that many different sampling strategies can yield acceptable and comparable site characterization data. The choice of strategy is up to the user.

6.4 Analysis of PHC in Soil Samples

Determination of PHC in solid matrices such as soils generally includes extraction and detection steps and may include a purification or clean-up step in between. Historically, a great diversity of extraction and detection systems have been used. The CCME reference method (CCME 2000) is based on proven approaches that mate well with the four PHC fractions and make use of technologies that are routinely available in laboratories accredited by the Canadian Association of Environmental Analytical Laboratories or the Ministère de l’environment du Quebèc. The method blends prescriptive (procedures that must be followed) and performance-based elements (a range of procedures meeting performance criteria which may be used). The balance between prescriptive and performance-based procedures was reached by consensus among members of the AM TAG in consideration of professional experience and results of round robin trials aimed at identifying sources of error in PHC methods.

6.4.1 Outline of Method

PHCs are divided into two practical categories that differ in analytical procedures: (1) volatile PHCs (F1), and (2) extractable PHCs (F2-F4). Depending on the amount of F4 material in the sample and user/analyst preferences, extractable PHCs may be further sub-divided on the basis of detection method (chromatographic/gravimetric).

Volatile PHCs are recovered by extracting the sample with methanol in a sealed container. Volatile PHCs dissolved in the methanol are then purged directly to a gas chromatograph (GC) equipped with a 100% poly(dimethylsiloxane) (DB-1 or equivalent) column and flame ionization detector (FID). Area counts between C6 and C10 are then integrated and adjusted for BTEX (which are measured and reported separately) and reported in concentration units as F1.

Extractable PHCs are recovered by Soxhlet extraction in 50:50 hexane-acetone. The extract is dried over sodium sulfate and treated with silica gel to remove polar material (fats, plant waxes etc.). A sample of the extract is then injected into a GC-FID equipped with a poly(dimethylsiloxane) column. Area counts are integrated and then quantified in the following ranges: (1) nC10 to nC16 – “F2”, (2) nC16 to nC34 – “F3”, and (3) nC34 to nC50 - “F4”. This determination of F4 is adequate provided the GC-FID chromatogram has returned to the baseline at nC50. If this is not the case, or other evidence suggests that PHCs greater than nC50 are present in appreciable quantities, residual PHCs may be determined gravimetrically or through extended, high temperature chromatography. If determinations of target PAH (e.g., napthalene, phenanthrene, chrysene, benzo(a)pyrene) have been made, these should be subtracted from the appropriate PHC CWS fractions (generally F3, except F2 for naphthalene).

Comparison to other methods for PHCs:

There is an incredible diversity of methods for analyzing PHCs. This meant that compromises had to be struck. For example, considerable debate was held by the AMTAG regarding use of solvents e.g. dichloromethane (DCM) versus hexane or hexane/acetone. The success of silica gel clean up to remove compounds other than hydrocarbons before gas chromatography is very much dependent on experience, degree of activation, and the solvent used for elution. This confirms the need for on-going improvement and further standardization in analytical methods for PHCs.

6.5 Linkage to Effects Database

The toxic response of plants and invertebrates to the above analytically-defined fractions was determined in soil microcosms. Concentrations of the fractions were measured at various times during the exposure period using the reference method.

No uncertainty factors were added to the toxic response endpoints (see Section 4.2). Thus, to maximize applicability of results, analytical determinations from field sites should use the reference method.

Similarly, human health toxicological endpoints were drawn from work of the TPHCWG and are specific to sub-fractions defined within the four PHC CWS fractions. Again, appropriate comparison to the risk-based endpoints derived from the TPHCWG toxicological reference values requires that PHC be measured and reported consistent with the reference method.

6.6 Notes on the PHC CWS Analytical Method

6.6.1 Development, Validation, and Calibration Issues

Although it is the intention of the CCME that jurisdictions adopt the analytical method as a standard, jurisdictions may choose to use it as a benchmark against which laboratories can establish their performance using equivalent methods (in areas where flexibility is indicated). The need to follow the four fractions in the CWS and a need for a consistent approach to calibration have been captured within the method. Reference Materials are not available at this time. However, the Canadian Association for Environmental Analytical Laboratories have been approached to consider one more preliminary inter-laboratory study, followed by a regular Proficiency Testing program. This program would allow Canadian laboratories accredited by the Standards Council of Canada to include PHCs by this method in their scope of accreditation.

6.6.2 Data Quality Objectives

Method detection limits are not available at this time. Consideration is being given to the development of a single laboratory validation to determine method detection limits. This could be verified by the preliminary inter-laboratory study discussed earlier. Recoveries, as normally defined, are not addressed in the method due to a lack of appropriate surrogates. One of the conclusions from a recent inter-laboratory study was that good laboratories, with experience in the PHC CWS method, routinely generated results within 25% of design values -- a vast improvement on past inter laboratory performance.

6.6.3 BTEX and PAH Analysis

The method does require analysis of BTEX so that values for BTEX can be subtracted from fraction F1. However, it is left to jurisdictions to choose among a variety of good, available methods. Most use GC-MS to aid identification of BTEX

components. It is not possible to measure BTEX components by the PHC CWS method as compounds are not uniquely resolved in the C6-C10 region by GC-FID. The PHC CWS method also requires subtraction of selected PAHs if they are present in sufficient quantity to affect the PHC result. Sites showing considerable quantities of PAHs would have to be treated as such.

6.6.4 Constraining PHC Quantitation Range

Inclusive procedures in the analytical method are provided on the assumption that PHC contamination may be "broad-band" and poorly characterized – as might occur in the case of a crude oil release, or when different product/waste streams coalesce in a downstream scenario. However, in some cases, reliable information exists to indicate that a PHC release is of a single type that is well-characterized and confined to (1) three or less of the PHC CWS fractions, or (2) F1-F3 plus only a portion of F4. The latter case is discussed in some detail in the analytical method – the go/no-go decision regarding extending chromatography beyond C50 or performing a gravimetric determination based on chromatogram characteristics and knowledge of release type.

In principle, similar approaches may be applied with respect to the first case. For example, if PHC contamination is understood to be related to a recent release of a single grade of gasoline, and comprehensive gas chromatography of representative samples confirms this knowledge, F4 and possibly F3 can be eliminated from the analysis. Similarly, other simple fuel types may be confirmed by return of the chromatographic trace to the baseline region within the F3 envelope. In such cases it may be unnecessary to extend chromatography to the C50 range.

Specific approved procedures must be confirmed with the jurisdictional authority.

6.6.5 Additional Comments

Screening approaches were not considered. They exist but generally are not applicable to what is essentially a reference method, the results of which will decide which action is to be taken. Screening or rapid on-site techniques can be useful during remediation and in defining site boundaries.

It was noted that unusual soils may require different treatments of the results (e.g. soils with very organic levels or soils partially remediated with straw and manure). Such results are useful, despite their limitations, in deciding which Tier-level provides the best approach to remediation.

7. Summary and Recommendations

7.1 Scientific Overview

PHCs released to soil pose a variety of risks in the geo-environment. These risks include combustion hazards, direct toxic risks to humans, plants and animals, effects on soil processes such as water retention and nutrient cycling, movement to water and air, and aesthetic problems such as objectionable odour and sheen. Left unmanaged, PHCs in the geo-environment can cause important adverse effects.

PHC release sites are present in all Canadian jurisdictions and the total number of actual and potential sites number in the hundreds of thousands. Jurisdictions presently assess and manage PHC-contaminated sites under different processes with different yardsticks and different terminologies, producing a patchwork of environmental results and costs. This is both confusing to stakeholders and an inefficient use of resources. Nationally consistent understandings and outcomes are needed.

This document presents the consensus recommendations of the CCME Development Committee for the Tier 1 standards of the Canada-Wide Standard for Petroleum Hydrocarbons in Soil. These Tier 1 standards for soil and subsoil reside within a 3-tiered, risk-based framework that can be applied to assess and manage sites contaminated by petroleum hydrocarbons in the range of C6 to C50+. Tier 2 and Tier 3 procedures are described in CCME (200X).

The Tier 1 standards are science-based and designed to be protective of human and ecological health for four land use categories – agricultural, residential, commercial and industrial. For each of these land-use categories an exposure scenario was developed to illustrate a sensitive use. The exposure scenario defined the receptors present and pathways by which these could be exposed to contamination in soil, subsoil and cross-contaminated groundwater. Knowledge of receptor response to PHC contamination was used to calculate or estimate environmentally acceptable concentrations in the soil and subsoil.

Because environmental behaviour and effects of PHCs in the geo-environment are related to chemical properties (e.g., size, geometry and extent of oxidation) it was advantageous to consider these substancesin broad categories or fractions. Four fractions were defined by combining sub-fractions provided in the work of the US TPH Criteria Working Group. For the purposes of human health protection, it was assumed that within the four fractions aliphatics and aromatics were present in a ratio of 4:1. The combined sub-fractions in the appropriate ratios then served as surrogates for the entire fraction.

A review of scientific literature indicated that there was insufficient information to support a similar approach for protection of ecological receptors. Research was commissioned by several stakeholder groups to provide information to support a weight-of-evidence approach that combined biological response data from chemical surrogates, whole fractions, and whole products. Both on-site and off-site receptors were considered.

Offsite receptors were considered primarily as users of PHC-contaminated groundwater. Groundwater protection goals were defined either at the downgradient boundary of a PHC-contaminated area (potable uses) or at a nominal 10 m offset (livestock watering or aquatic life receptor). This distance can be replaced by site data in a Tier 2 assessment.

The above procedures taken together provide a strong and much-improved scientific basis for Tier 1 standards applicable to PHC contamination of soil and subsoil in Canada. Coupled to the tiered assessment framework (CCME 200X), it is expected that greater precision and efficiency in remedial efforts will be realized.

7.1.1 Uncertainty

Many uncertainties are present in the science underlying the PHC CWS. Some of the uncertainty represents lack of knowledge. For example, the intrusion rates of F1 vapours into enclosed spaces are generally not known. Rather, these rates are estimated through use of mechanistic vapour transport models. It is expected that models will improve through testing and refinement, also less reliance on models will be required as methods for on-site vapour intrusion measurement evolve. Some uncertainty is caused also by random and or complex future events such as the likelihood that groundwater not presently used will be used.

Efforts were made throughout the PHC CWS development process to identify key areas of uncertainty that could be reduced through research. These areas are discussed under the Recommendations section below.

Uncertainties in exposure and effects were generally addressed by ensuring that conservative assumptions were made regarding contaminant types, mobilities, toxicities and exposure patterns. This approach was balanced with the need for practical Tier 1 standards that take account of technological capabilities and socio-economic factors.

7.2 Socio-economic Considerations

The PHC CWS Tier 1 standards were designed to be attainable. Socio-economic screening analyses were undertaken that confirmed that liabilities for remediation of PHC-contaminated sites in Canada are in the multi-billion dollar range. It was noted

that bioremedial technologies are the most accessible, affordable and reliable approaches presently available.

Performance capabilities of bioremedial technologies were considered in the interpretation of scientific uncertainties in development of the Tier 1 standards. For example, bio-treatability was influential in the interpretation of ecotoxicological response to F3. Dispersion in data between laboratory and field conditions, fresh versus weathered PHC and coarse versus fine textures indicated that the 400 mg/kg ecotoxicity standard applicable to coarse textured surface soils under sensitive land uses could safely be relaxed to 800 mg/kg for fine textures and better accommodate bioremedial performance factors.

Similarly, socio-economic factors were the principal risk management consideration in basing ecological protection for commercial and industrial soils solely on the response of plants. The PHC CWS is a practical standard. Practical endpoints and management decisions are delivered, however, within the scientific uncertainty around the definition of acceptable environmental quality. In other words, soils remediated to the Tier 1 standards are expected to pose no adverse effects to human health or the environment within the conservative exposure scenarios used.

The principal benefits expected from implementation of the PHC CWS include:

- Documented scientific basis for risk management decisions for PHC-contaminated sites;
- Standards are protective of human and environmental health;
- Consistent approach to measurement, assessment and remediation levels the playing field for responsible parties and stakeholders;
- Attainable standards encourages responsible action and brings affected areas back into use at a faster rate;
- Tiered assessment framework allows efficient use of remedial resources while ensuring protection – avoids over- and under-management of sites;
- Clear land and water use decisions at PHC-contaminated sites.

7.3 Recommendations for Further Development and Research

Significant progress was made in applying current science to the development of the PHC CWS. Nevertheless, there are still important gaps in information and understanding that, if filled, would lead to further improvements in the management of PHC in Canada's geo-environment. The following sections list the principal areas

where the Development Committee and Technical Advisory Groups felt that research investment was needed.

7.3.1 Research Related to Human Health Protection

Toxicity of PHC fractions

- deficiencies were noted in understanding of toxic actions of aromatic components of F3 and F4. Pyrene was used as a surrogate but this will not be satisfactory in the long term because it does not chromatograph with F4 compounds. An appropriate, non-carcinogenic F4 aromatic compound needs to be identified.

- Commercial hexane was used as a surrogate for F1 aliphatics. However, some components of the F1 aliphatics – those, such as n-hexane, metabolized to gamma-diketones - have unique modes of toxic action and, apparently, high potencies. These may need to be managed separately or F1 aliphatic potency may need revision. There are presently inconsistencies in the available regulatory toxicity evaluations for commercial hexane and pure hexane.

- Heterocyclic components of PHCs were not considered in the present development work. Certain thiophenes and quinolines exhibit ecotoxicity and may be present at low levels in a variety of PHC sources. Further information is needed on their occurrence in common PHC release types and effects in mammalian systems. Once this information is available, the appropriateness of the toxicological benchmarks for F3 and F4 must be assessed to identify any necessary changes.

Vapour Intrusion to Buildings

- Vapour movement under and around building foundations – relative contributions of advective and diffusive transport. In the PHC CWS, advection is included only for coarse-textured soils. However, the relative contributions of the two transport mechanisms in soils of intermediate texture are not known and may be important in the vapour intrusion process.

- Adaptation of Darcy's Law to gaps and imperfections in building foundations. The PHC CWS applies a description of vapour intrusion based on movement of gases to a buried perimeter pipe adapted by Johnson and Ettinger (1991) from research on radon infiltration. Research is needed to explore infiltration through differing spacings and geometries in response to pressure and concentration gradients across building substructures.

- Development of field methods for determination of peri-foundational PHC concentrations and rates of intrusion – such that reliance on models may be reduced. While improvements to models are needed to support pro-active

management – including better generic standards – in cases where vapours are at or near the foundation some form of exposure management is often required on an urgent basis. Improved methods are needed for obtaining relevant and representative soil gas measurements near foundations and interpreting these data such that appropriate interventions are taken.

Aesthetics

Management decisions regarding PHC contamination of soils are sometimes driven by odour considerations. These decisions are generally made on the basis of qualitative, site-specific information – i.e., the material is deemed unsuitable for the present or proposed use on the basis of odours disagreeable to one or more stakeholders. Such situations are difficult to forecast and are therefore a potential concern in re-development of PHC-affected sites. A systematic and objective approach to evaluation of PHC odours could reduce the frequency of such events. Information is needed on:

- Odour thresholds of commonly occurring PHC constituents;
- Occurrence and abundance of malodorous components in common PHC release types;
- Vapour pressures and mobilities of these compounds;
- Options for incorporation of this information into a risk-based approach.

7.3.2 Research Related to Ecological Protection

Effects of PHCs in Field Trials

- Information is needed on the fate of individual fractions over time. Current data present information on dissipation and toxicity of mainly whole products. Effects from balance of fractions cannot be segregated from bioavailability within fractions.

Effects of Different PHC Mixtures

- Ecotox information is needed on cuts prepared from different PHC sources. It is not known how well the Federated Crude oil represents the diversity of PHC sources in Canada.

Bioassay

- A broader range of plants and soil organisms need study. Effects of vapour perfusion from below on roots, soil organisms have not received much study.

- Thorough, toxicity-based guidelines for aquatic receptors are needed based on direct testing of F1 and F2 fractions.

7.3.3 Research Related to Fate, Behaviour and Effects of PHC in and on the Geo-Environment

- Genesis of hydrophobicity. What soil properties, PHC properties and management histories lead to this phenomenon?

- Aqueous and vapour phase partitioning of low molecular weight PHCs in the presence of variable amounts of F2, F3 and F4 material. The practical application of Raoult's Law to better estimate vapour and dissolved phase concentrations contributing to leaching and vapour intrusion fluxes.

- Biodegradation rates in the vadose zone in relation to season, soil moisture content, depth and nutrient availability. Methods to measure biodegradation rates throughout the year at individual sites are needed.

- Harmonization of groundwater modeling for on- and off-site receptors. Research to identify a single modeling approach that can be applied to receptors at various distances from a source is needed. Also needed is a review of vertical mixing and dispersion phenomena and appropriate mathematical descriptions.

- Guidance on sampling, storage and handling of PHC-contaminated soil, subsoil and groundwater is also required.

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Appendix A: Overview of CCME developmental and consultative processes for the PHC CWS

A.1 Canada-Wide Standards

In January of 1998 twelve Canadian Ministers of the Environment (members of the Canadian Council of Ministers of the Environment (CCME)) signed a Harmonization Accord and three associated sub-agreements, including the Sub-Agreement on Environmental Standards[1]. The Canada-wide Environmental Standards Sub-Agreement is a framework for federal, provincial and territorial Environmental Ministers to work together to address key environmental protection and health risk reduction issues that require a common standard across the country. The standards sub-agreement sets out principles for governments to jointly agree on priorities, to develop standards, and to prepare complementary workplans to achieve those standards, based on the unique responsibilities and legislation of each government.

Six priority substances were announced at the time of signing of the Canada-wide Environmental Standards Sub-Agreement. PHCs in soil were one such priority; a problem shared by all jurisdictions throughout Canada.

In June 2000, the PHC CWS was accepted in principle by the Canadian Council of Ministers of the Environment[2] (CCME).

A.1.1 Developmental Process for the PHC CWS

Release of the PHC CWS represents the culmination of a three-year multi-stakeholder development process, reflecting the efforts of representatives from government, petroleum and environmental industries, academia and non-governmental organizations.

The PHC CWS was developed under the direction of a national Development Committee co-chaired by Alberta and Canada. Alberta was the champion of the PHC CWS, having responsibility for providing leadership and overall management of the development of the standard including preparation of workplans; initiating, tracking and integrating the necessary pieces; liaising with stakeholders and the Environmental Planning and Protection Committee; coordinating activities with other Development Committees; and presenting the standard to the Council of Ministers.

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[1] Nunavut Signed on to the Harmonization Accord and Subagreements when they joined the Council in November 1999.

[2] The CCME is the major inter-governmental forum in Canada for discussion and joint action on environmental issues of national and international concern. The council is made up of environment ministers from the federal, provincial and territorial governments. The CCME undertakes activities associated with environmental protection and sustainable development through coordinated action, which includes the development of Canada-wide Standards.

Four multi-stakeholder technical advisory groups and one working group supported the work of the Development Committee. Consensus process was used to generate recommendations to the Development Committee from the advisory and working groups, and consensus among jurisdictions was used to generate recommendations in the Development Committee. National, multi-stakeholder workshops were used to set the initial direction of development (October 1997) and confirm results and direction as development proceeded.

In the early stages of the development of the standard, technical advisory groups (TAGs) were tasked to provide expert scientific advice to the PHC CWS Development Committee including the: Analytical Methods TAG (AMTAG), Human Health Fate and Transport TAG (HHFTTAG), Ecological TAG (ECOTAG), and Socioeconomic Analysis TAG (SEATAG). In addition, the Protocol Improvement Working Group (PIWG) was established to evaluate and compare established protocols for the derivation of human health-based soil quality assessment values for petroleum hydrocarbons. In particular, the PIWG reviewed the CCME Protocol for the derivation of environmental and human health soil quality guidelines (CCME 1996) and the Atlantic Partnership in RBCA (Risk-Based Corrective Action) for Petroleum Impacted (PIRI) Sites (Atlantic PIRI 1999). The establishment of the TAGs and PIWG, which reported on a regular basis to the Development Committee, resulted in a process that ensured a high level of multi-stakeholder consultation and transparency throughout the development of the standard.

A.2.0 Membership of PHC CWS Committees

A.2.1 PHC CWS Development Committee

Member	Jurisdiction
Ted Nason (co-chair)	Alberta
Glyn Fox	British Columbia
David Thornton (co-chair) Connie Gaudet, Kathie Adare	Canada
Edwin Yee	Manitoba
Ray Morin	New Brunswick
Toby Matthews	Newfoundland
Harvey Gaukel	Northwest Territories

John Henderson, Sharon Vervaet	Nova Scotia
Earle Baddaloo	Nunavut
Marius Marsh	Ontario
Danny McInnis	Prince Edward Island
Renée Gauthier	Quebec
Sam Ferris	Saskatchewan
Kevin McDonnell, Ruth Hall	Yukon
Fred O'Brien (Yukon)	CEOH
Scott Tessier, Margaret Gibbs, Nancy Gehlen	CCME

A.2.2 Human Health Fate and Transport Technical Advisory Group (HHFT TAG)

The CCME Human Health/Fate and Transport Technical Advisory Group (HHFT TAG) was mandated to assist with delivery of of the PHC CWS by:

- providing advice on technical issues or questions posed by the PHC DC;
- assisting in the selection of optimum solutions from technical options;
- evaluating models for best predictive power under diverse Canadian conditions.

The primary purpose of the HHFT TAG is to enable the PHC DC to deliver on a timely basis Tier 1 levels for petroleum hydrocarbons (PHCs) in soil that are scientifically sound and consistent with stakeholder advice on consideration of direct and indirect exposure pathways for humans under the four land uses defined in the CCME framework.

Membership of the HHFT TAG was designed to ensure the required complement of expertise in toxicology, soil science, hydrogeology and risk analysis. As well, a balance was sought across sectors and between basic and applied fields.

Name	Affiliation
HHFT TAG I:	
Warren Kindzierski (Chair)	University of Alberta
Adolfo Silva	Canadian Petroleum Products Institute
Chris Severson-Baker	Pembina Institute
Donna Vorhees	Menzie-Cura
Glyn Fox	BC Environment
Jean-Pierre Trepanier	Sanexen
John Cracknell	Jacques-Whitford
Mark Allen	New Brunswick Health Committee for Environmental and Occupational Health (CEOH)
Michel Charbonneau	University of Quebec
Reidar Zapf-Gilje	Golder Associates
Rob Hoffman	Chevron Canada
Corresponding Members:	
Christine Moore	CanTox
David Williams	O'Connor Associates
John Wiens	AGRA
Mike Zemanek	Alberta Environment
Paul Kostecki	University of Massachusetts
Reginal North	Keystone Environmental
HHFT TAG II:	
Warren Kindzierski (Chair)	University of Alberta
Adolfo Silva	Canadian Petroleum Products Institute
Andrea Walters	Petro Canada
Claude Chamberland	Shell Canada
Donna Vorhees	Menzie-Cura
Eliot Sigal	CanTox
Glyn Fox	BC Environment
Ian Hers	Golder Associates
Mark Cameron	Keystone Environmental
Mike Zemanek	Alberta Environment

A.2.3 Ecological Technical Advisory Group (Eco TAG)

Name	Affiliation
EcoTAG core members:	
Doug Bright, Chair	Royal Roads University
Lin Callow	Gulf Canada Resources Inc.
Anne-Marie Lafortune	Ministère de l'Environnement et de la Faune
Wayne Landis	Western Washington University
Bill McGill	University of Alberta
Peter Miasek	Imperial Oil
Christine Moore	CanTox
Norman Sawatsky	Alberta Environment
Rick Scroggins	Environment Canada
Gladys Stephenson	ESG International Inc.
Graham van Aggelen	Environment Canada
Susanne Visser	University of Calgary
Ex officio:	
Kathie Adare	Environment Canada
Connie Gaudet	Environment Canada
Trisha Murray	Environment Canada
Sylvain Ouellet	Environment Canada
Tracy Schneider	Environment Canada
Sherri Smith	Environment Canada
Corresponding Members:	
Nigel Blakley	Washington State Department of Ecology
James Clark	
Anne Fairbrother	ParaMetrix
Stephen Goudey	HydroQual Labs
Sue Halla	Alberta Energy and Utilities Board
Michael Kangas	
Francis Law	Simon Fraser University
Mike MacFarlane	BC Environment
Lynn McCarty	Golder Associates
Rodger Melton	
Charles Menzie	Menzie-Cura and Associates
Dwayne Moore	Cadmus Group
Stan Pauwels	Mclaren-Hart.com
Mike Rankin	Golder Associates Ltd.
Andrew Teal	Imperial Oil

A.2.4 Analytical Methods Technical Advisory Group (AM TAG)

The CCME Analytical Methods Technical Advisory Group (AM TAG) was mandated to assist with delivery of the PHC CWS by:

- Providing advice on technical issues or questions posed by the PHC DC;
- Reviewing existing methods for the determination of PHC in solid matrices;
- Developing recommendations for a benchmark analytical method to support the PHC CWS;
- Testing the recommended benchmark method and providing advice on operating parameters, data analysis and performance-based measures for validation of equivalent or better methods.

The primary purpose of the AM TAG was to enable the PHC DC to deliver on a timely basis a Canada-Wide Standard for petroleum hydrocarbons (PHC) in soil that is scientifically sound and accompanied by a reliable, accurate, precise and practical analytical method.

Membership of the AM TAG was designed to ensure the required complement of expertise in environmental and analytical chemistry and experience with analysis of organic mixtures in solid matrices. As well, a balance was sought among private, government and industrial laboratories.

The following members of the Analytical Methods Technical Advisory Group (AMTAG) of the CCME contributed to the establishment and validation of this method.

Name	Affiliation
Richard Turle	Environment Canada (AMTAG Chair)
Renée Gauthier	Ministère de l'Environnement du Québec
Scott Hannam	ASL Analytical Service Laboratories Ltd.
George Kanert	Ontario Ministry of the Environment
Abdel Kharrat	Alberta Research Council
Don Laberge	Envirotest Laboratories (CAEAL Representative)
Todd Arsenault	Environment New Brunswick
Tim Munshaw	Philip Analytical (IAETL Representative)
Carol Drury	Shell Canada (Petroleum industry Representative)
Ileana Rhodes	Equilon Enterprises LLC (Petroleum industry representative)
François Messier	CEAEQ, Ministère de l'Environnement du Québec
Dave Morse	Ontario Ministry of the Environment
Peter Fowlie	Cornerstone Science

A.2.5 Socio-Economic Technical Advisory Group (SEA TAG)

The CCME Socio-Economic Assessment Technical Advisory Group (SEA TAG) was mandated to assist with delivery of the PHC CWS by:

- providing advice on technical issues or questions posed by the PHC DC;
- assisting in the selection of scenarios and models for assessment of socio-economic factors;
- evaluating recommendations for incorporation of socio-economic factors into the PHC CWS.

The primary purpose of the SEA TAG was to enable the PHC DC to deliver on a timely basis a Canada-Wide Standard for petroleum hydrocarbons (PHC) in soil that is scientifically sound and takes account of the limitations and potentials posed by social, economic and technological factors.

Membership of the SEA TAG was designed to ensure the required complement of expertise in environmental science and engineering, risk analysis, social science, and economics. As well, a balance as sought across sectors and between basic and applied fields.

Name	Affiliation
Dana Atwell	Shell Canada
Robert Lee	Cantox Environmental Inc., Calgary, AB
Charles Hammond	Independent Retail Gasoline Marketers Association, St. Marys, ON
Chris Severson-Baker	Pembina Institute, Drayton Valley, AB
Alan Wood	Insurance Bureau of Canada, Edmonton, AB
Paul Young	Petro-Canada
Doug Younie	Alberta Environment, Edmonton, AB

A.2.6 Protocol Improvement Working Group (PIWG):

The Protocol Improvement Working Group (PIWG) was a fixed-duration working group created to compare human health protection aspects of the Canadian Council of Ministers of the Environment (CCME) and the Atlantic Partnership in Risk-based Corrective Action Implementation (Atlantic PIRI) protocols for development of a Canada Wide Standard for petroleum hydrocarbons in soil. An objective of the comparison was to identify and make recommendations for a new protocol that integrates these best aspects of each. A main priority of the PIWG was the direct comparison and consideration of the two protocols in making their recommendations. The PIWG also considered additional fate and transport information from other protocols. Ecological protection aspects of the protocols was

not considered by this group. The PIWG provided its recommendations to CCME Petroleum Hydrocarbon Committee Technical Advisory Groups. The PHC Development Committee considered recommendations of the Technical Advisory Groups in preparing a complete Canada Wide Standard for consideration by senior CCME committees and, ultimately, the Council of Ministers.

Name	Affiliation
Warren Kindzierski (Chair)	University of Alberta
Claude Chamberland	Shell Canada
Lin Callow	Gulf Canada Resources
Sharon Vervaet	Nova Scotia Department of Environment and Labour
Ted Nason / Mike Zemanek (Alternate)	Alberta Environment

Appendix B: Brief historical review of soil quality guidelines for PHCs

B.1.0 History of PHC Management Tools for Contaminated Sites

The CCME *Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* (CCME 1996) was published in 1996 following 4 years of developmental work by the CCME Subcommittee on Environmental Quality Criteria for Contaminated Sites to devise science-based procedures for deriving soil quality guidelines for human and ecological receptors which have a basis in risk assessment. That *Protocol* underwent extensive peer review and has now been applied to the derivation of risk-based soil quality guidelines for a variety of inorganic and organic contaminants. However, the CCME *Protocol* had not been applied to petroleum hydrocarbon mixtures due to scientific difficulties in applying that framework to complex mixtures.

Currently in Canada, various provinces have existing regulations and/or regulatory policies that prescribe soil quality criteria for sites contaminated with PHCs. A graphical depiction of the carbon fractions represented by these current guidelines is presented in Figure 2.2.

Existing Canadian PHC guidelines differ in their definition of the substance. PHCs have been varyingly defined in terms of:

- petroleum products (gas, diesel, heavy oils) (Ontario);
- physical-chemical characteristics, particularly boiling point (volatile, light extractable, heavy extractable) (B.C.);
- carbon range (C_{10}-C_{50}; that encompasses the potential full range of gas, diesel and heavy oils in the “extractable” range, but excludes BTEX and other more volatile components) (Quebec);
- analytical methods without necessarily defining other characteristics of the mixture (Alberta);
- limited sub-fractions of the carbon number range, (C_5-C_{10}, $C_{>10}$-C_{12}, $C_{>12}$-C_{16}, etc.) adopting definitions, physical-chemical properties, reference doses, and other assumptions, as proposed by the Total Petroleum Hydrocarbon Criteria Working Group (Atlantic provinces).

B.2.0 Review of Some Risk-based Approaches to PHC Assessment / Management

Over the past few years, there have been four primary initiatives in North America to establish a viable, scientifically defensible, risk-based approach to the assessment and management of PHC-contaminated sites. These four approaches have been undertaken by the Massachusetts Department of Environmental Protection (MADEP 1994, 1996, 1997); the Total Petroleum Hydrocarbon Criteria Working Group (Edwards et al. 1997, Gustafson et al. 1997, Potter and Simmons 1998, Weisman

1998); the B.C. Ministry of Environment (Golder Assoc. 1995); by CanTox Inc. (1997); and by the Atlantic provinces (which modified the work of the TPHCWG). These approaches are similar in that they propose to subdivide the complex mixture that is PHC according to specified ranges of equivalent carbon number (ECN), and assign to each 'fraction' the necessary physical-chemical properties (solubility, Henry's Law constant, etc.) and toxicological characteristics (i.e., TDI and/or RfC) which permit the prediction of chemical fate, exposure and potential risk. Refer to Figure 2.2 for a graphical depiction of the carbon number ranges encompassed by the fractions defined by each of these approaches.

These methods differ in the number of, and classification of, carbon number fractions. They also differ in the values that have been assigned for physical-chemical properties and toxicological tolerable daily intakes (TDIs).

In North America, three approaches have been proposed for establishing reference doses for PHC fractions and to subsequently derive risk-based soil quality guidelines. Methods have been proposed by: 1) the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) established by the U.S. Air Force; 2) the Massachusetts Department of Environmental Protection (MADEP); and 3) by CanTOX Inc. Atlantic PIRI has adapted the TPHCWG methodology to the maritime provinces' needs, modifying the approach to reflect risk-based methods, procedures and assumptions prescribed by Health Canada and the Canadian Council of Ministers of Environment.

Other provincial and state agencies have PHC criteria but they are not generally derived via a risk-based approach. A review of the available PHC guidelines/methodologies of these various agencies and organizations follows.

B.3.0 The Total Petroleum Hydrocarbon Criteria Working Group

In 1994, the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) was established in the United States as a result of an initiative of the U.S. Department of Defence. The goal was to devise a scientific basis for assessment of petroleum-contaminated sites within a risk assessment/risk management framework (in particular, the framework provided by the ASTM Standard for Risk Based Corrective Action - RBCA). The work of the TPHCWG culminated in the publication of a four volume series of documents (Edwards et al. 1997, Gustafson et al. 1997, Potter and Simmons 1998, Weisman 1998) evaluating and defining the characteristics of TPH related to environmental fate, toxicity, and other factors pertinent to applying the ASTM RBCA framework to petroleum-contaminated soil and groundwater.

The TPHCWG recommended that PHCs be considered as 14 separate and independent (toxicologically, and with respect to environmental fate) sub-fractions defined by effective carbon number ranges, and further divided between aliphatics and aromatics. This large number of sub-fractions was devised based on a thorough and extensive compilation and evaluation of environmental fate and

transport considerations. The TPHCWG defined the effective carbon number ranges for PHC sub-fractions such that solubility, leachability and the volatility did not span more than approximately one order of magnitude. This degree of uncertainty was considered acceptable within the overall uncertainties of PHC risk assessment/risk management.

The TPHCWG specifically set out to apply the ASTM RBCA (1995) risk-based approach to the issue of PHC contamination. TPHCWG evaluated 275 individual hydrocarbon compounds from the following 11 homologous series:

- straight chain alkanes
- straight chain alkenes
- straight chain alkynes
- branched chain alkanes
- branched chain alkenes
- cylcloalkanes
- cycloalkenes
- alkyl benzenes (including benzene)
- naphtheno benzenes
- alkyl naphthalenes (including naphthalene)
- polynuclear aromatics

Of the 275 individual compounds evaluated, information on all required physico-chemical parameters (carbon number, equivalent carbon number, molecular weight, solubility, specific gravity, vapour pressure, Henry's Law constant, octanol-water partition coefficient, organic carbon partition coefficient, boiling point, diffusivity in air, diffusivity in water) were available for about 180, while partial information existed for the remainder.

As previously mentioned, the TPHCWG methodology was defined as an extension of the ASTM's standard E-1739 for Risk Based Corrective Action (1995). Within the ASTM RBCA approach to deriving risk-based screening levels, two factors have significant influence: LF - leaching factor; and VF - volatilization factor. Due to the influence of these two variables, the TPHCWG grouped carbon sub-fractions of PHC where individual components had values of LF and VF ranging about one order of magnitude. This was considered a reasonable degree of accuracy or consistency given the numerous uncertainties in the risk assessment process. Also, specified carbon sub-fractions were further divided between aromatics and aliphatics. Selected carbon sub-fractions are presented in Table B.1.

Physico-chemical properties of individual components and homologous series were extensively evaluated by direct comparison and correlation. Representative properties for carbon sub-fractions were estimated by arithmetic averaging, weighted averaging and correlation techniques. Sub-fraction-specific physico-

chemical properties ultimately selected by the TPHCWG are also presented in Table B.1.

Sub-fraction specific TDIs and RfCs selected by TPHCWG are presented in Table B.1. Toxicity data were evaluated for both individual compounds and for specific hydrocarbon mixtures where data were available. Emphasis was placed on data pertaining to mixtures as these studies were considered most applicable to, and representative of, PHCs.

On behalf of the TPHCWG, Exxon Biomedical Sciences Inc. conducted a comprehensive search for literature pertaining to the toxicity of all individual hydrocarbon compounds identified in Volume 3 of the TPHCWG's methodology. Literature pertaining to the toxicity of hydrocarbon mixtures was also searched. All relevant studies and reports identified by this search were compiled and are summarized in volume 4 of the TPHCWG Methodology (Edwards et al. 1997). All data were evaluated relevant to the PHC sub-fractions identified in Table B.1.

Where possible and appropriate, suggested TDIs and RfCs were based on the evaluation of studies pertaining to mixtures of hydrocarbons spanning or including the carbon sub-fractions under consideration. Where data and information on mixtures were unavailable or of insufficient quality or relevance, RfCs for individual compounds were selected/defined and used as a surrogate for an entire specified PHC sub-fraction. In some cases, TDI/RfC values for a mixture were based on the weighted averaging of the TDI/RfC of two or more individual components of the mixture.

For the most part, TDIs and RfCs for individual compounds were drawn from U.S.EPA's Integrated Risk Information System and Health Effects Assessment Summary Tables. In some cases, TDIs and RfCs for individual compounds were derived from appropriate studies identified via the literature search, employing methods prescribed by U.S.EPA for the derivation of these reference exposure values. In all cases, TDI/RfC values based on toxicity data pertaining to mixtures were derived by the TPHCWG following procedures prescribed by U.S.EPA.

Demonstration of the TPHCWG approach to PHC mixtures has been completed by the Association of American Railroads (Nakles et al. 1996). Following the TPHCWG proposed approach, Nakles et al. (1996) derived PHC fraction-specific risk-based screening levels (RBSLs). Nakles et al. (1996) also derived RBSLs for gasoline and diesel fuel (BTEX excluded), expressed as the sum of the relative concentrations of these PHC fractions in the weathered whole products.

B.3.1 General Acceptance of the TPHCWG Approach

The work and proposals of the TPHCWG are now widely accepted in the U.S.A., and are becoming accepted in Canada, for the assessment and management of petroleum-contaminated sites. Its root in the ASTM RBCA framework, and the

broad inter-disciplinary and inter-jurisdictional participation in this Working Group has resulted in its general acceptance. In Canada, the Atlantic provinces have adopted this approach within their PIRI (Partnership In RBCA Implementation) initiative. Other provinces have been generally accepting of site-specific risk assessments of PHC-contaminated soils using the TPHCWG approach, particularly the recommended TDIs/RfCs and the assigned physical-chemical properties, with or without the use of the RBCA models and framework.

Based on the foregoing work of the TPHCWG, and on its general regulatory acceptance in North America, the CCME Development Committee on Canada Wide Standards for Petroleum Hydrocarbons has adopted the work of the TPHCWG into the Canada Wide Standard on Petroleum Hydrocarbon. However, some modifications have been introduced in order to accommodate the need for soil quality guidelines for specified “fractions” of PHC.

B. 4.0 Massachusetts Department of Environmental Protection (MADEP)

In 1994, MADEP was the first regulatory agency to formally propose a fraction-specific approach to PHCs (MADEP 1994). Draft regulations respecting numerical criteria were published for public comment on November 1, 1996 and subsequently revised and re-released for further comment on January 17, 1997.

MADEP proposed that PHC be evaluated as the sum of exposures to specific PHC fractions, each with a specified human reference dose thus providing human health risk-based PHC criteria. MADEP established fraction-specific TDIs for individual (surrogate) hydrocarbon compounds published by the U.S.EPA. Where a specified PHC fraction had only one compound with a published TDI (n-hexane within the alkanes, for example), that TDI was adopted as the TDI for the entire fraction. Where a specified fraction had two or more components with published TDIs, the TDI of lowest value (i.e., the TDI for the most potent component) was selected as the representative TDI. Again, the selected TDI was applied to the entire hydrocarbon fraction.

Following comments provided during the public consultation period following the release of proposed revisions to the PHC criteria dated November 1, 1996, and considering recent developments in PHC criteria, particularly the work of TPHCWG, MADEP revised the November 1996 proposals, releasing these revisions for further public consultation on January 17, 1997. Revisions addressed concerns expressed regarding over-conservatism of the proposed guidelines. Research conducted by MADEP on the partitioning of volatile petroleum hydrocarbons between adsorbed, dissolved and vapour phases in soil (which suggested earlier assumptions over-estimated partitioning to the gaseous phase by an order of magnitude) and the toxicological review by the TPHCWG (which indicated uncertainty in the toxicity of certain fractions spanning an order of magnitude) resulted in revised PHC criteria that reflected considerable professional judgement in addition to the calculation of

risk-based criteria derived following standard procedures outlined in the Massachusetts Contingency Plan.

B.5.0 CanTOX Inc.

CanTOX Inc. (1997) has proposed a risk-based approach for petroleum hydrocarbons which it has applied at a variety of sites for the military and other clients. Their approach is similar to that of MADEP in that the toxicological and physico-chemical characteristics of specific, individual compounds within particular PHC fractions are assumed to be representative to the entire fraction. CanTOX increased the representativeness of a surrogate compound for the toxicological characteristics of the specified fraction by defining oral or inhalation reference doses/slope factors for numerous individual petroleum hydrocarbons, thereby eliminating these compounds of known toxicity from PHC fraction analysis to which surrogates would be applied. These compounds of known toxicity would be quantified through chemical analysis of site samples and subtracted from the remaining PHC components. Surrogate toxicities are then applied only to the remaining, chemically-undefined PHC fractions. The prescribed reference doses lend themselves to application to ASTM Standard E-1739 or other risk-based methods of risk assessment and guidelines development.

B.6.0 B.C. MOE - Working Document: Recommendations to B.C. Environment for Development of Remediation Criteria for Petroleum Hydrocarbons in Soil and Groundwater

On behalf of B.C.MOE, Golder Associates prepared a review of national and international approaches to developing risk-based criteria for PHCs (Golder Assoc. 1995). The proposals and recommendations do not represent B.C.MOE policy, and current B.C.MOE guidelines for PHCs in soil and groundwater were based largely on professional judgement rather than quantitative risk assessment (G. Fox, B.C.MOE, personal communication).

This working document was used as a resource document by the TPHCWG and, therefore, many of its components are similar to the TPHCWG methodology. A unique aspect of the proposed approach was to define the proportion of each surrogate in its respective PHC fraction and derive exposures and risks only for the proportion of the fraction that was the surrogate chemical. This approach effectively assumed that the remaining components of the mixture have no toxicity or at least that their toxicity is negligible compared to the remaining components.

B.7.0 Atlantic Partnership in RBCA Implementation

The Atlantic provinces, through the efforts of the Partnership In Risk-Based Corrective Action Implementation (PIRI) initiative, have established a quantitative risk assessment/risk management approach for PHC-contaminated sites. This approach is based on the work of the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) and the American Society for Testing and Materials (ASTM)

Risk-Based Corrective Action (RBCA) framework (ASTM, 1995c).

In 1997, New Brunswick initiated a project to evaluate the applicability of the ASTM RBCA Standard and the work of the TPHCWG to assessing risks posed by petroleum-contaminated soils in that province. A modified RBCA standard was devised which substituted Canadian data and assumptions within the ASTM RBCA framework. Subsequently, the Partnership in RBCA Implementation (PIRI) was established whereby regulatory representatives of the Atlantic Provinces (New Brunswick, Nova Scotia, Prince Edward Island and Newfoundland), affected industries (Canadian Petroleum Products Institute), as well as environmental engineering and remediation consulting firms, combined their efforts to devise and implement a risk-based approach to assessing and managing petroleum-contaminated sites. The approach that evolved was based largely on the modified RBCA standard developed by New Brunswick.

Modifications introduced to reflect Canadian approaches and assumptions for risk assessment included:

- Canadian reference doses or tolerable daily intakes, where available;
- Alteration of numerous assumptions (averaging times, exposure rates and frequencies, water and air intake rates, etc.) to reflect the Canadian population;
- Alteration of assumed site characteristics (required to derive screening level criteria) to reflect conditions of Atlantic Canada.

B.8.0 Other Canadian Provincial PHC Criteria

PHC criteria for soil and groundwater currently in use by the Ontario Ministry of Environment and Energy (MOEE), the Ministère de L'Environnement du Québec (MENV), Alberta Environment and the British Columbia Ministry of Environment, Lands and Parks (BCMELP) are presented in Table B.2.

MOEE criteria are based primarily on the recommendations of a multi-stakeholder workgroup (OMEE 1993) with some modifications to reflect additional considerations and information presented by OMEE (1996). The current OMEE PHC criteria have a qualitative but not a quantitative basis in risk. OMEE derived a Generic Site Sensitivity Analysis flowchart to differentiate sites into three relative levels of risk/concern (high, moderate and low). Subsequently, guidelines were proposed for PHCs as gasoline/diesel, and PHC as heavy oils. Alternate analytical procedures were also prescribed for extraction and quantification of total PHC in these different products.

MENV has recently released a revised strategy for the rehabilitation of contaminated lands (MENV 1996). Criteria for petroleum hydrocarbons (carbon range C_{10} to C_{50}) replaced earlier criteria for oil and grease as of January 1996. MEFQ prescribes soil and groundwater criteria for three qualitatively different levels of risk:

Level A Typical background concentrations for inorganic parameters; limit of analytical detection for organics (analytical methods available on Quebec Ministry's website).

Level B Maximum acceptable concentrations for residential, recreational and institutional lands and commercial properties near residential areas.

Level C Maximum acceptable concentration for commercial (not situated near residential properties) and industrial lands.

No scientific rationale for the prescribed A, B and C PHC criteria is presented.

PHC soil criteria have been promulgated by BCMELP in Part 3.1 (Contaminated Site Remediation) of the Waste Management Amendment Act, 1993 (BCMELP 1993). Under that Act, criteria have been published (Schedule 4: Generic Numerical Soil Standards) for volatile petroleum hydrocarbons (VPHs), light extractable petroleum hydrocarbons (LEHPs) and heavy extractable petroleum hydrocarbons (HEPHs). Generic standards for these parameters range from 200 to 5000 ppm and vary according to land use (agricultural, urban park, residential, commercial, industrial). The standards are based on professional judgement; no rationale for their derivation has been published (G. Fox, BCMELP, personal communication).

On behalf of Alberta Environmental Protection, OAEI undertook the Development of Remediation Guidelines for Petroleum Storage Tank Sites (OAEI 1996), which included total petroleum hydrocarbons among numerous other contaminants. A variety of methods were examined as a basis for the derivation of quantitative and qualitative risk-based PHC criteria. Final criteria were based on qualitative considerations including human organoleptic, aesthetic and phytotoxicological/ecotoxicological considerations. Criteria were defined for three levels of site sensitivity, loosely interpretable as residential (Level I), commercial (Level II) and industrial (Level III) sites. Potential off-site receptors located on a more sensitive site were also considered.

B.9.0 State-by-State Summary of PHC Criteria from the US

A state-by-state summary of soil PHC action and cleanup standards used across the United States has been recently presented in the *Journal of Soil Contamination* (Anonymous 1997). State criteria respecting PHCs are summarized in Table B.3. These PHC and related criteria are largely based on professional judgements. MADEP, the only state to actively evaluate a risk basis for PHC criteria, has not yet promulgated risk based PHC criteria.

Table B.1: Carbon sub-fractions (as Equivalent Carbon number - EC), physico-chemical parameters, reference doses and reference air concentrations proposed by the Total Petroleum Hydrocarbon Criteria Working Group.

TPH Sub-fraction	BP (^{o}C)	EC (n)	MW (g/mole)	S (mg/L)	VP (atm)	H (cm^3/cm^3)	log Koc	TDI (mg/kg-day)	RfC (mg/m^3)
Aliphatics									
EC 5-6	5.1 E+01	5.5 E+00	8.1 E+01	3.6 E+01	3.5 E-01	3.3 E+01	2.9 E+00	5.0	18.4
EC >6-8	9.6 E+01	7.0 E+00	1.0 E+02	5.4 E+00	6.3 E-02	5.0 E+01	3.6 E+00	5.0	18.4
EC >8-10	1.5 E +02	9.0 E+00	1.3 E+02	4.3 E-01	6.3 E-03	8.0 E+01	4.5 E+00	0.1	1.0
EC >10-12	2.0 E+2	1.1 E+01	1.6 E+02	3.4 E-02	6.3 E-04	1.2 E+02	5.4 E+00	0.1	1.0
EC >12-16	2.6 E+02	1.4 E+01	2.0 E+02	7.6 E-04	4.8 E-05	5.2 E+02	8.8 E+00	0.1	1.0
EC >16-21	3.2 E +02	1.9 E+01	2.7 E+02	2.5 E-06	1.1 E-06	4.9 E+03	9.0 E+00	2.0	NA [1]
Aromatics									
EC >8-10	1.5 E+02	9.0 E+00	1.2 E+02	6.5 E+01	6.3 E-03	4.8 E-01	3.2 E+00	0.04	0.2
EC >10-12	2.0 E+02	1.1 E+01	1.3 E+02	2.5 E+01	6.3 E-04	1.4 E-01	3.4 E+00	0.04	0.2
EC >12-16	2.6 E+02	1.4 E+01	1.5 E+02	5.8 E+00	4.8 E-05	5.3 E -02	3.7 E+00	0.04	0.2
EC >16-21	3.2 E+02	1.9 E+01	1.9 E+02	6.5 E-01	1.1 E-06	1.3 E-02	4.2 E+00	0.03	NA [1]
EC >21-34	3.4 E+02	2.8 E+01	2.4 E+02	6.6 E-03	4.4 E-10	6.7 E-04	5.1 E+00	0.03	NA [1]

(from Gustafson et al. 1996; Edwards et al., 1996)

1 NA = not available; specified sub-fraction considered non-volatile.

Table B.2: Criteria for "Petroleum Hydrocarbons" (mg/kg soil) currently in use in Ontario, Quebec, Alberta and British Columbia.

Ontario Ministry of Environment and Energy (OMEE)					
	Agricultural [1]	Residential/Parkland [1]		Industrial/Commercial [1]	
	Potable or Nonpotable GW	Potable GW	Nonpotable GW	Potable GW	Nonpotable GW
gas/diesel	100	100	1000	100	1000
heavy oils	1000	1000	1000	1000	5000
Ministère de L'Environnement et de la Faune Québec (MEFQ)					
	Level A - Background/Detection Limit	Level B- Maximum for Residential, Parkland and Institutional Properties		Level C - Maximum for Commercial and Industrial	
C_{10} - C_{50}	<100	700		3500	
British Columbia Ministry of Environment, Lands and Parks (BCMELP)					
	Agricultural	Urban Park	Residential	Commercial	Industrial
VPHs [2]	200	200	200	200	200
LEPHs [2]	1000	1000	1000	2000	2000
HEPHs [2]	1000	1000	1000	5000	5000
Alberta Environment – PST Guidelines [3]					
		Level I [4]		Level II [4]	Level III [4]
Product or fraction not specified		Coarse-grained soil: 1000 Fine-grained soil: 2000		2000 4000	5000 5000
Alberta Environment – Tier I Criteria for Contaminated Soil Assessment and Remediation [5]					
	Agricultural	Residential			
Mineral oil and grease	1,000	1,000			

(from BCMELP 1993; MEFQ 1996; OAEI 1996; OMEE 1996)

[1] Criteria apply to both surface and subsurface soils;

[2] VPH=volatile petroleum hydrocarbon, LEPH=light extractable petroleum hydrocarbon, HEPH=heavy extractable petroleum hydrocarbon (extraction and analytical methods not specified in B.C. Contaminated Sites regulations)

[3] Petroleum Storage Tank (PST) guidelines applied to downstream facilities (gas stations, etc.) and refinery sites.

[4] Level I, II and III sites approximate but do not match precisely the categories residential, commercial and industrial

[5] Tier I guidelines applied to upstream oil and gas sites and to sensitive sites, such as agricultural and residential lands, with surface soil contamination.

Table B.3: Total petroleum hydrocarbon cleanup levels for contaminated soils in the United States of America*.

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Alabama	Gasoline	TPH**	EPA 4030, 9071, 418.1 SM 5520	100	Alabama Department of Environmental Management	
	Diesel	TPH	EPA 4030, 9071, 418.1, SM 5520	100		
	Waste Oil	TPH	EPA 4030, 9071, 418.1, SM 5520	100		
Alaska	See AEHS, 1999.				Alaska Department of Environmental Conservation	
Arkansas	NA	NA	NA	NA	Arkansas Department of Environmental Quality	Note: Hydrocarbon remediation based on ASTM Method, E 1739.
Arizona	Gasoline	TPH (1)	AZ 418.1	7,000 (3) 24,000 (4)	Arizona Department of Environmental Quality	(1) Applies only to sites characterized prior to 12/4/97, and remediating pursuant to interim soil remediation standards (final rule doesn't have TPH standard). (2) Refer to AAC R18-7-201. (3) Cleanup Level Residential. (4) Cleanup Level Non-Residential.

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
	Kerosene	C10-C32	AZ 8015	(2)		
	Diesel	C10-C32	AZ 8015	(2)		
	Jet Fuel	C10-C32	AZ 8015	(2)		
	Heavy Fuel Oil	TPH(2)	AZ 418.1	(2)		
		C10-C32	AZ 8015	(2)		
	Waste Oil	TPH(2)	AZ 418.1	(2)		
		C10-C32	AZ 8015	(2)		
California	Gasoline	TPH	(1)	Site Specific	California Regional Water Quality Control Board	(1) There is no statewide requirement for a specific laboratory test. Contact the lead agency for guidance.
	Diesel	TPH	(1)	Site Specific		
		TAPH	(1)	Site Specific		
Colorado	Subsurface Soil	TPH(1)	NA	500	Colorado Department of Labor and Employment, Oil Inspection Section	(1) TPH threshold values (2) For Residential and Industrial Land Uses.
	Surficial Soil	TPH(1)	NA	500(2)		
Connecticut	NA***	NA	NA	NA	Department of Environmental Protection Underground Storage Tank Program	Contact Department
DC	Gasoline	GRO*	EPA 8015 M	100	NA	Note: Soil Quality Standards are from UST Regulation (20 DCMR Chapter 55).
	Diesel	DRO**	EPA 8015 M	100		
	Waste Oil	DRO	EPA 8015 M	100		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Deleware	Gasoline	TPH GRO	(1)	100	Deleware Department of Natural Resources & Environmental Control	Note: Contact Deleware's UST Branch for required methodologies. (1) Different Tiers, TPH criterion may be replaced by a list of COCs (Chemicals of Concern) (2) Tier O Action/Cleanup Level; Applies to all new sites entering the program, such as removal or abandonment. Note: Above Tier O, TPH-GRO and TPH-DRO are replaced by a list of chemicals of concern.
	Kerosene	TPH GRO	(1)	100**		
		TPH DRO	(1)	1000(2)		
	Jet Fuel	TPH GRO	(1)	100(2)		
		TPH DRO	(1)	1000(2)		
	Diesel	TPH DRO	(1)	1000(2)		
	Heating Fuel	TPH DRO	(1)	1000(2)		
	Used Oil	TPH GRO	(1)	100(2)		
		TPH DRO	(1)	1000(2)		
	Aviation Gas	TPH GRO	(1)	100(2)		
Florida	TRPHs***	TRPH	FL-PRO	340(1)	Florida Department of Environmental Protection	(1) For Direct Exposure Residential and Leachability Based on Groundwater Criteria.

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Georgia	Gasoline, Aviation Gas	TPH	EPA 8015 (GRO)	10	Georgia Department of Natural Resources	**Note: Soil cleanup levels shown are the most stringent threshold values for average or higher groundwater pollution susceptibility area and public or non-public water supplies or surface water are located less than or equal to 500 feet away.** Note: For information on lower susceptibility areas and/or different distances from water sources or withdrawal points, call the department.
	Diesel, Kerosene, Jet Fuel A, #2 and #4 Fuel Oil	TPH	EPA 8015 (GRO & DRO)	10		
	Hydraulic Oil, #5 and #6 Fuel Oil, Motor Oil, Used Oil	TPH	EPA 418.1	10		
	Mineral spirits, Jet Fuel B, or unknown petroleum contents	TPH	EPA 8015 (GRO & DRO)	10		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Hawaii	Gasoline	TPH as Gasoline	EPA 5030/8015, LUFT	Site-Specific	Hawaii Dept. of Health, Solid and Hazardous Waste Branch	Note: Hawaii Risk Based Corrective Action (RBCA) program can be used to develop more site-specific action levels for soil.
		TPH as Residual Fuels	EPA 5030/8015, LUFT	Site-Specific		
		TPH as Residual Distillates	EPA 5030/8015 LUFT	Site-Specific		
Idaho	Gasoline	NA	NA	NA	Iowa Department of Natural Resources	Note: Idaho has developed a RBCA program for assessment and cleanup of petroleum contamination.
Illinois	NA	NA	NA	NA	Illinois Environmental Protection Agency	Note: The Illinois EPA has adopted RBCA Regulations to determine cleanup objectives.
Indiana	Kerosene, Gasoline	TPH	EPA 8015 M or 8240/8260	<100[(1)] 20[(2)]	Indiana Department of Environmental Management (IDEM)	(1) On-site cleanup level. (2) Off-site cleanup level. Note: IDEM is currently developing RBCA guidance.
	Naplha, Diesel	TPH	EPA 8015 M or 8270	<100[(1)] 20[(2)]		
	Aviation Gas	TPH	EPA 4181	<100[(1)] 20[(2)]		
Iowa	See AEHS, 1999.				Idaho Division of Environmental Quality	Note: Iowa has adopted the ASTM RBCA method for addressing Petroleum Contaminated Sites.

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Kansas	Gasoline	TPH	(1)	100	Kansas Department of Health & Environment	(1) Purge and trap with summation of peaks chromatography; EPA 418.1 can be used for TPH analysis of waste oil only. Note: Kansas expects to implement a Risk-Based Corrective Action approach but these standards will remain in place as baseline standards.
	Diesel	TPH	(1)	100		
	Waste Oil	TPH	(1)	100		
Kentucky	See AEHS, 1999.				Kentucky Division of Waste Management	
Louisiana	See AEHS, 1999.				Louisiana Department of Environmental Quality	Note: Has a Risk Evaluation/Corrective Action Program similar to RBCA.
Maryland	Gasoline	TPH	EPA 8015M GRO	Site specific or 10	Maryland Department of the Environment	Note: There are no promulgated cleanup standards. All decisions are made via site-specific risk characterization.
	Diesel Fuel, #2 Heating Oil	TPH	EPA 8015M DRO	Site specific or 10		
	Heavy Oil #4, 5, and 6, Bunker Oil	TPH	EPA 1664	Site specific or 10		
	Used Oil	TPH	EPA 1664	Site specific or 10		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Massachusetts	Gasoline	C5-C8 Aliphatic Hydrocarbons	MADEP VPH	0.1-0.5[(1)] or site specific	Massachusetts Department of Environmental Protection	(1) Nine generic cleanup standards have been established depending upon exposure potential/accessibility of soil, and use/classification of underlying groundwater.
		C9-C12 Aliphatic Hydrocarbons	MADEP VPH	1.0-5.0[(1)] or site specific		
		C9-C10 Aliphatic Hydrocarbons	MADEP VPH	0.1-0.5[(1)] or site specific		
	Diesel, #2 Fuel Oil	C9-C18 Aliphatic Hydrocarbons	MADEP EPH	0.1-0.5[(1)] or site specific	Massachusetts Department of Environmental Protection	
		C19-C36 Aliphatic Hydrocarbons	MADEP EPH	2.5-5.0[(1)] or site specific		
		C11-C22 Aliphatic Hydrocarbons	MADEP EPH	0.2-0.5[(1)] or site specific		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Maine	Gasoline	Total Gasoline	GRO	5(1)	Maine Department of Environmental Protection (DEP)	Note: Maine DEP uses a Decision Tree approach to establish remediation standards. Four Categories of sites exist: Baseline 1 (BL-1), Baseline 2 (BL-2), Intermediates (IN), and Stringent (ST). (1) Applies to ST and IN sites only. BL-1 sites require only removal of tree product and product-saturated soils. BL-2 sites may be cleaned to 500-1000 mg/kg measured by field/headspace for gasoline or 200-400 mg/kg for diesel.
	Diesel	Total Fuel Oil	DRO	10(1)		
Michigan	NA	NA	NA	NA	Michigan Department of Environmental Quality; Environmental Response Division	
Minnesota	Gasoline	TPH	Wisconsin DNR GRO	Site Specific	Minnesota Pollution Control Agency	
	Diesel	TPH	Wisconsin DNR GRO	Site Specific		
	Waste Oil	TPH	Wisconsin DNR GRO	Site Specific		
Missouri	See AEHS, 1999.			50-100	Missouri Department of Natural Resources	Note: Site gets assigned a score based on site features – TPH criteria depends on score.
Mississippi	Gasoline	NA	NA	NA	Mississippi Underground Storage Tank Division	(1) If no sensitive environmental receptors are present.

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
	Diesel	TPH	EPA 418.1	<100[1]		
	Waste Oil	TPH	EPA 418.1	<100[1]		
North Carolina	See AEHS. 1999.				North Carolina Division of Waste Management	Note: Contact UST section of NC Department of Natural Resources, Division of Waste Management.
North Dakota	Gasoline	TPH	EPA 8015M	Site Specific	North Dakota State Department of Health	
	Diesel	TPH	EPA 8015M	Site Specific		
	Waste Oil	NA	NA	NA		
Nebraska	Gasoline	TRPH	OA1	Site Specific[1]	Nebraska Department of Environmental Quality	(1) Soil cleanup levels are based on site specific contaminants and exposure parameters.
	Diesel	TRPH	OA1, OA2	Site Specific[1]		
	Waste Oil	TRPH	OA1, OA2	Site Specific[1]		
New Hampshire	Gasoline	TPH (as gasoline)	(1)	10 000	New Hampshire Department of Environmental Services	(1) Initially EPA 8250 plus MTBE and P&T – GC/FID for TPH. All other samples EPA 8020 plus MTBE and P&T GC/FID for TPH. (2) Initially EPA 8260, 8270/8310 and extraction GC/FID for TPH. All other samples 8020, 8240, 8260, 8270/8310 and extraction GC/FID for PAH.
	No's 2,4,5,6 Fuel Oil and Diesel	TPH (as oil)	(2)	10 000		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
New Jersey	NA	NA	NA	NA	New Jersey Department of Environmental Protection; Site Remediation	
New Mexico	Gasoline	TPH	EPA 8021	100	New Mexico Environment Department	
	Diesel	TPH	EPA 8015M	100		
	Waste Oil	TPH	EPA 8015M	100		
Nevada	Gasoline	TPH	EPA 8015M	100	Nevada Department of Conservation and Natural Resources	
	Diesel	TPH	EPA 8015M	100		
	Waste Oil	TPH	EPA 8015M	100		
New York	NA	NA	NA	NA	New York Department of Environmental Conservation	
Ohio	Gasoline	TPH	EPA 8015M	Site Specific	Ohio Department of Commerce	
	Diesel	TPH	EPA 418.1	Site Specific		
	Waste Oil	TPH	EPA 418.1	Site Specific		
Oklahoma	Gasoline, Diesel, and Kerosene	TPH	EPA 8015	Site Specific	Oklahoma Corporation Commission, UST Program	Note: Oklahoma uses a Remediation Index in determining cleanup standards on a site-by-site basis. EPA 418.1 is not accepted testing method for TPH.
Oregon	See AEHS, 1999.				Oregon Department of Environmental Quality	Note: Oregon's UST Cleanup Rules (OAR 340-122-0205 through 340-122-0360) provide responsible parties with four options for remediating sites.
Pennsylvania	NA	NA	NA	NA	Commonwealth of Pennsylvania Department of Environmental Protection	

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Rhode Island	See AEHS, 1999.				Rhode Island Department of Environmental Management	Note: Rhode Island has Direct Exposure TPH criteria and Leachability criteria for contaminated soils. See AEHS for more information.
South Carolina	Gasoline, Diesel, and Kerosene	NA	NA	NA	South Carolina Department of Health & Environmental Control	(1) No action or cleanup levels. TPH is used solely to determine necessity of performing expanded analyses.
	Waste Oil	TPH	EPA 9071	(1)		
South Dakota	Gasoline	TPH	(1)	(2)	South Dakota Department of Environmental and Natural Resources	(1) California/USGS method or similar methods that can quantify TPH by integrating all detectable peaks within the time period in which 95% of the recoverable hydrocarbons are eluted. (2) Cleanup is not required if no risks to human health present. Source removal required. If risks present – site specific.
	Diesel	TPH	(1)	(2)		
	Waste Oil	TPH	(1)	(2)		
Tennessee	Gasoline	TPH-GRO	TN TPH-GRO	100-1000[(1)]	Tennessee Department of Environment and Conservation; Division of UST	(1) Cleanup levels are based on groundwater classification and soil permeability.
	Diesel	TPH-EPH	EPH	100-1000[(1)]		
	Waste Oil	TPH-EPH	EPH	100-1000[(1)]		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
Texas	Gasoline	TPH	TNRCC 1005	Site Specific/ Risk Based	Texas Natural Resource Conservation Commission	
	Diesel	TPH	TNRCC 1005	Site Specific/ Risk Based		
	Used Oil	TPH	TNRCC 1005	Site Specific/ Risk Based		
Utah	NA	NA	NA	Site Specific	Utah Division of Environmental Response and Remediation	Note: Utah has RBCA Tier 2 process for determining site-specific cleanup values.
Virginia	Gasoline	TPH	CA UFT Method	Site Specific/ Risk Based	Virginia Department of Environmental Quality	
	Diesel	TPH	CA UFT Method	Site Specific/ Risk Based		
	Waste Oil	TPH	EPA – approved GC Methods	Site Specific/ Risk Based		
Vermont	Gasoline	NA	NA	NA	Vermont Agency of Environmental Conservation	
	Diesel	TPH	EPA 418.1 or Extended GC	Site Specific/ Risk Based		
	Waste Oil	NA	NA	NA		
Washington	Gasoline	TPH	NWTPH-GX	100	Washington Department of Natural Resources	Note: Cleanup level shown is for Method A for routine cleanups. Method B and C also exist for residential and industrial cleanups which are risk-based.
	Diesel	TPH	NWTPH-DX	500		
	Waste Oil	NA	NA	NA		
Wisconsin	Gasoline	GRO	WI DNR Modified GRO	Site Specific	Wisconsin Department of Natural Resources	
	Diesel	GRO	WI DNR Modified DRO	100 or Site Specific		
	Waste Oil	DRO	WI DNR Modified DRO	Site Specific		
West Virginia	Gasoline	TPH	EPA 5015 M(1)	Site Specific	West Virginia Department of Environmental Protection	(1) Report GRO and DRO separately.

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
	Diesel	TPH	EPA 5015 M[(1)]	Site Specific		
Wyoming	Gasoline	NA	NA	NA	Wyoming Department of Environmental Quality	(1) If groundwater is <50 feet. (2) If groundwater is >50 feet.
	Leaded Gas	TPH	EPA 8015 M GRO C5-C10	30[(1)] 100[(2)]		
	Fuel Oils	TPH	EPA 8015 M GRO C10-C32	100		
	Lubricating Oils	TPH	EPA 8015 M GRO C10-C32	100		
	Waste Oil	TPH	EPA 8015 M GRO (GC)	100		

(from: Komex Inc., 2000)

NOTES:

* Information obtained from Associates for the Environmental Health of Soils (AEHS) State by State Soil Survey

** TPH = Total Petroleum Hydrocarbon

*** NA = Not Available

\+ GRO = Gasoline Range Organics

++ DRO = Diesel Range Organics

+++ TRPH = Total Recoverable Petroleum Hydrocarbon

Appendix C: Equations used for the derivation of human health-based Tier 1 Levels and example derivation.

Part A: Tier 1 Level Equations

Algorithm used to sum TPHCWG sub-fractions within each fraction:
To derive soil quality guidelines for a PHC fraction, guidelines must first be estimated for each individual TPHCWG sub-fraction, for the target Hazard Quotient desired. Then, the guidelines for sub-fractions must be combined according to their mass fraction within the fraction, according to the algorithm below.

$$SQG_{Fraction\_i} = \frac{1}{\sum\left(\frac{MF_{subfraction\ j}}{SQG_{subfraction\ j}}\right)}$$

$SQG_{fraction\_i}$ = soil quality guideline for the fraction *i* (mg/kg)
$SQG_{sub\text{-}fraction\ j}$ = soil quality guideline (mg/kg) for each sub-fraction within fraction *i* for the target Hazard Quotient for fraction *i*
$MF_{sub\text{-}fraction\ j}$ = mass fraction of each sub-fraction within the fraction *i*

Soil Ingestion Pathway:

$$SQG_{SI} = [(TDI - EDI)(SAF)(BW)(10^3\ g/kg)]/[(SIR)(AF_G)(ET)] + BSC$$

Where:
SQG_{SI} = soil quality guideline by soil ingestion (mg/kg)
TDI = tolerable daily intake (reference dose) (mg/kg-d)
EDI = estimated daily intake (mg/kg-d)
SAF = Soil Allocation Factor (unitless)
BW = body weight (kg)
SIR = soil ingestion rate (g/d)
AF_G = gastrointestinal absorption factor (unitless)
ET = exposure term (unitless)
BSC = background soil concentration (mg/kg)

Dermal Contact Pathway:

$$SQG_{DC} = [(TDI - EDI)(SAF)(BW)(10^6 mg/kg)]/[(AF_D)\{SA_{HANDS})(DL_{HANDS}) + (SA_{OTHER})(DL_{OTHER})\}(EF)(ET)] + BSC$$

Where:
- SQG_{DC} = soil quality guideline by soil ingestion (mg/kg)
- TDI = tolerable daily intake (reference dose) (mg/kg-d)
- EDI = estimated daily intake (mg/kg-d)
- SAF = Soil Allocation Factor (unitless)
- BW = body weight (kg)
- AF_D = dermal absorption factor (unitless)
- SA_{HANDS} = surface area of hands (m^2)
- SA_{OTHER} = surface area of exposed body surfaces other than hands (m^2)
- DL_{HANDS} = dermal loading of soil to hands (mg/m^2-event)
- DL_{OTHER} = dermal loading of soil to other skin surfaces (mg/m2-event)
- EF = exposure frequency (events/d)
- ET = exposure term (unitless)
- BSC = background soil concentration (mg/kg)

Protection of Potable Groundwater:

$$SQG_{GW} = [(TDI - EDI)(K_d + (\theta_m / \rho_w))(SAF)(BW)(DF_W)] / (IR_W)$$

Where:
- SQG_{GW} = soil quality guideline to protect potable groundwater (mg/kg)
- TDI = tolerable daily intake (reference dose) (mg/kg-d)
- EDI = estimated daily intake (mg/kg-d)
- K_d = distribution coefficient (mL/g)
- θ_m = ratio: mass of water in soil / dry mass of soil (unitless)
- ρ_w = density of water (g/cm^3)
- SAF = Soil Allocation Factor (unitless)
- BW = body weight (kg)
- IR_W = water ingestion rate (L/d)
- DF_W = aquifer dilution factor (unitless)
  = {[(B x K x *i)* / (R x L)] + 1}/(L_1/L_2)
  where: B = effective mixing depth in aquifer (m)
  K = saturated hydraulic conductivity of aquifer (m/y)
  i = hydraulic gradient (unitless)
  R = recharge rate (m/y)
  L = site length (m)
  L_1 = thickness of affected subsurface soils (cm)
  L_2 = distance from top of affected soils to groundwater (cm)

Indoor Infiltration and Inhalation Pathway:

$$SQG_{ii,a} = [(TDI - EDI)(BW)\{\theta_w + (K_{oc})(f_{oc})(\rho_b) + (H/RT)(\theta_a)\}(SAF)(DFi)(10^3 g/kg)]/$$
$$[(IR)(H/RT)(\rho_b)(ET)(10^6 cm^3/m^3)] + BSC$$

$$SQG_{ii,b} = [(RfC - C_a)\{\theta_w + (K_{OC})(f_{OC})(\rho_b) + (H/RT)(\theta_a)\}(SAF)(DFi)(10^3 g/kg)]/$$
$$[(H/RT)(\rho_b)(ET)(10^6 cm^3/m^3)] + BSC$$

Where:

$SQG_{ii,a}$	= soil quality guideline by indoor infiltration for volatile PHCs using TDI (i.e., sub-fraction has no prescribed RfC) (mg/kg)
$SQG_{ii,b}$	= soil quality guideline by indoor infiltration for volatile PHCs using RfC (mg/kg)
TDI	= tolerable daily intake (reference dose) (mg/kg-d)
EDI	= estimated daily intake (mg/kg-d)
RfC	= reference air concentration (mg/m^3)
C_a	= background indoor/outdoor air concentration (mg/m^3)
SAF	= Soil Allocation Factor (unitless)
BW	= body weight (kg)
IR	= inhalation rate (m^3/d)
θ_w	= moisture-filled porosity (unitless)
θ_a	= vapour-filled porosity (unitless)
K_{OC}	= organic carbon partition coefficient (mL/g)
f_{OC}	= fraction organic carbon (g/g)
ρ_b	= dry bulk density (g/cm^3)
H	= Henry's Law Constant (atm-m^2/mol)
R	= gas constant (8.2 x 10^{-5} atm-m^2/mol-^{O}K)
T	= absolute temperature (^{O}K)
DF_i	= dilution factor from soil gas to indoor air (unitless): ***see derivation below***
ET	= exposure term (unitless)
BSC	= background soil concentration (mg/kg)

Calculation of DF for indoor infiltration pathway:

$$DF_i = \frac{1}{\alpha}$$

DF_i = dilution factor from soil gas concentration to indoor air concentration (unitless)
α = attenuation coefficient
= (contaminant vapour concentration in the building)/(vapour concentration at the contaminant source)

Coarse textured soils (considers advection only)

$$\alpha = \frac{\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right)}{\left(\frac{D_T^{eff} A_B}{Q_{soil} L_T}\right) + 1}$$

D_T^{eff} = effective porous media diffusion coefficient (cm^2/s)
A_B = building area (cm^2)
Q_B = building ventilation rate (cm^3/s)
L_T = distance from contaminant source to foundation (cm)
Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s)

$$D_T^{eff} \approx D_a \left(\frac{\theta_a^{10/3}}{n^2}\right)$$

D_T^{eff} = overall effective porous media diffusion coefficient based on vapour-phase concentrations for the region between the source and foundation (cm^2/s)
D_a = diffusion coefficient in air (cm^2/s)
θ_a = air-filled porosity (unitless)
n = total soil porosity (unitless)

$$Q_B = L_B W_B H_B (ACH) / (3600\ s/h)$$

Q_B = building ventilation rate (cm^3/s)
L_B = building length (cm)
W_B = building width (cm)
H_B = building height, including basement (cm)
ACH = air exchanges per hour (h^{-1})

$$Q_{soil} = \frac{2\pi\ \Delta P\ k_v\ X_{crack}}{\mu \ln\left[\frac{2\left(Z_{crack}\right)}{r_{crack}}\right]}$$

Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s)
ΔP = pressure differential ($g/cm{\cdot}s^2$)
k_v = soil vapour permeability to vapour flow (cm^2)
X_{crack} = length of idealized cylinder (cm)
μ = vapour viscosity ($g/cm{\cdot}s$)
Z_{crack} = distance below grade to idealized cylinder (cm)
r_{crack} = radius of idealized cylinder (cm)

Fine textured soils (considers diffusion only)

$$\alpha = \frac{\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right)}{1+\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right)+\left(\frac{D_T^{eff} A_B L_{crack}}{D^{crack} A_{crack} L_T}\right)}$$

D_T^{eff} = effective porous media diffusion coefficient (cm^2/s)
A_B = building area (cm^2)
Q_B = building ventilation rate (cm^3/s)
L_T = distance from contaminant source to foundation (cm)
L_{crack} = thickness of the foundation (cm)
D^{crack} = effective vapour-pressure diffusion coefficient through the crack (cm^2/s)
A_{crack} = area of cracks through which contaminant vapours enter building (cm^2)

Tier 2: (requires consideration of both advection and diffusion)
For derivation of site-specific soil quality objectives, calculations must consider both advective and diffusive vapour transport mechanisms, according to the following equations.

$$DF_i = \frac{1}{\alpha}$$

DF_i = dilution factor from soil gas concentration to indoor air concentration (unitless)
α = attenuation coefficient
= (contaminant vapour concentration in the building)/(vapour concentration at the source)

$$D_T^{eff} \approx D_a \left(\frac{\theta_a^{10/3}}{n^2} \right)$$

D_T^{eff} = overall effective porous media diffusion coefficient based on vapour-phase concentrations for the region between the source and foundation (cm^2/s)
D_a = pure component molecular diffusivities in air (cm^2/s)
θ_a = air-filled porosity (unitless)
n = total soil porosity (unitless)

$$Q_B = L_B W_B H_B (ACH) \big/ (3600\ s/h)$$

Q_B = building ventilation rate (cm^3/s)
L_B = building length (cm)
W_B = building width (cm)
H_B = building height, including basement (cm)
ACH = air exchanges per hour (h^{-1})

$$Q_{soil} = \frac{2\pi\ \Delta P\ k_v\ X_{crack}}{\mu \ln\left[\frac{2\left(Z_{crack}\right)}{r_{crack}}\right]}$$

Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s)
ΔP = pressure differential ($g/cm \cdot s^2$)
k_v = soil vapour permeability to vapour flow (cm^2)
X_{crack} = length of idealized cylinder (cm)
μ = vapour viscosity ($g/cm \cdot s$)
Z_{crack} = distance below grade to idealized cylinder (cm)
r_{crack} = radius of idealized cylinder (cm)

$$\alpha = \frac{\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right)\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right)}{\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right)+\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right)+\left(\frac{D_T^{eff} A_B}{Q_{soil} L_T}\right)\left[\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right)-1\right]}$$

D_T^{eff} = effective porous media diffusion coefficient (cm^2/s)
A_B = building area (cm^2)
Q_B = building ventilation rate (cm^3/s)
L_T = distance from contaminant source to foundation (cm)
Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s)
L_{crack} = thickness of the foundation (cm)
D^{crack} = effective vapour-pressure diffusion coefficient through the crack (cm^2/s)
A_{crack} = area of cracks through which contaminant vapours enter the building (cm^2)

Part B: Example Derivaton

The equations presented in Part A are applied as appropriate for the PHC fraction and soil texture under consideration. Derivations for F1 in a coarse textured soil case are the most complex and inclusive case. Complete calculations for this fraction/texture combination are presented below.

Fraction 1, Aliphatics $C_{>6}$-C_8, Coarse-grained soil, Residential with Basement, Toddler

Soil Ingestion Pathway:

$$SQG_{SI} = [(TDI - EDI)(SAF)(BW)(10^3 g/kg)]/[(SIR)(AF_G)(ET)] + BSC$$

Where:

TDI = tolerable daily intake (reference dose) (mg/kg-d) = 5
EDI = estimated daily intake (mg/kg-d) = 0.02334
SAF = Soil Allocation Factor (unitless) = 0.5
BW = body weight (kg) = 16.5
SIR = soil ingestion rate (g/d) = 0.08
AF_G = gastrointestinal absorption factor (unitless) = 1
ET = exposure term (unitless) = 1
BSC = background soil concentration (mg/kg) = 0

Therefore,

SQG_{SI} = soil quality guideline by soil ingestion (mg/kg)
= 513 218 mg/kg

Dermal Contact Pathway:

$$SQG_{DC} = [(TDI - EDI)(SAF)(BW)(10^6 mg/kg)]/[(AF_D)\{SA_{HANDS})(DL_{HANDS}) + (SA_{OTHER})(DL_{OTHER})\}(EF)(ET)] + BSC$$

Where:

TDI = tolerable daily intake (reference dose) (mg/kg-d) = 5
EDI = estimated daily intake (mg/kg-d) = 0.02334
SAF = Soil Allocation Factor (unitless) = 0.5
BW = body weight (kg) = 16.5
AF_D = dermal absorption factor (unitless) = 0.2
SA_{HANDS} = surface area of hands (m^2) = 0.0430
SA_{OTHER} = surface area of exposed body surfaces other than hands (m^2) = 0.2580

DL_{HANDS} = dermal loading of soil to hands (mg/m^2-event) = 1000
DL_{OTHER} = dermal loading of soil to other skin surfaces (mg/m2-event) = 100
EF = exposure frequency (events/d) = 1
ET = exposure term (unitless) = 1
BSC = background soil concentration (mg/kg) = 0

Therefore,
SQG_{DC} = soil quality guideline by soil ingestion (mg/kg)
= 2 983 826 mg/kg

Protection of Potable Groundwater:

$$SQG_{GW} = [(TDI - EDI)(Kd + (\theta_m / \rho_w))(SAF)(BW)(DF_W)] /(IR_W)$$

Where:

TDI = tolerable daily intake (reference dose) (mg/kg-d) = 5
EDI = estimated daily intake (mg/kg-d) = 0.02334
K_d = distribution coefficient (mL/g) = 19.905
= Koc x foc
where: Koc = organic carbon partition coefficient (mL/g) = $10^{3.6}$
foc = fraction organic carbon (g/g) = 0.005
θ_m = ratio: mass of water in soil / dry mass of soil (unitless) = 0.07
ρ_w = density of water (g/cm^3) = 1.0
SAF = Soil Allocation Factor (unitless) = 1.0
BW = body weight (kg) = 16.5
IR_W = water ingestion rate (L/d) = 0.6
DF_W = aquifer dilution factor (unitless) = 12.4
= {[(B x K x *i)* / (R x L)] + 1}/(L_1/L_2)
where: B = effective mixing depth in aquifer (m) = 2
K = saturated hydraulic conductivity of aquifer (m/y) = 320
i = hydraulic gradient (unitless) = 0.05
R = recharge rate (m/y) = 0.28
L = site length (m) = 10
L_1 = thickness of affected subsurface soils (cm)
L_2 = distance from top of affected soils to groundwater (cm)
L_1/L_2 = 1 (i.e., the affected soils are in contact with groundwater)

Therefore,

SQG_{GW} = soil quality guideline to protect potable groundwater (mg/kg)
= 33 898 mg/kg

Indoor Infiltration and Inhalation Pathway:

$$\mathbf{SQG_{ii,a}} = [(TDI - EDI)(BW)\{\theta_w + (K_{oc})(f_{oc})(\rho_b) + (H/RT)(\theta_a)\}(SAF)(DFi)(10^3 g/kg)]/$$
$$[(IR)(H/RT)(\rho_b)(ET)(10^6 cm^3/m^3)] + BSC$$

$$\mathbf{SQG_{ii,b}} = [(RfC - C_a)\{\theta_w + (K_{OC})(f_{OC})(\rho_b) + (H/RT)(\theta_a)\}(SAF)(DFi)(10^3 g/kg)]/$$
$$[(H/RT)(\rho_b)(ET)(10^6 cm^3/m^3)] + BSC$$

Where:

$SQG_{ii,a}$	= soil quality guideline by indoor infiltration for volatile PHCs using TDI (i.e., sub-fraction has no prescribed RfC) (mg/kg)
$SQG_{ii,b}$	= soil quality guideline by indoor infiltration for volatile PHCs using RfC (mg/kg)
TDI	= tolerable daily intake (reference dose) (mg/kg-d)
EDI	= estimated daily intake (mg/kg-d)
RfC	= reference air concentration (mg/m^3) = 18.4
C_a	= background indoor/outdoor air concentration (mg/m^3) = 0.09111
SAF	= Soil Allocation Factor (unitless) = 0.5
BW	= body weight (kg) = 16.5
IR	= inhalation rate (m^3/d) = 9.3
θ_a	= vapour-filled porosity (unitless) = 0.281
θ_w	= moisture-filled porosity (unitless) = 0.119
K_{OC}	= organic carbon partition coefficient (mL/g) = $10^{3.6}$
f_{OC}	= fraction organic carbon (g/g) = 0.005
ρ_b	= dry bulk density (g/cm^3) = 1.7
H	= Henry's Law Constant (atm-m^2/mol) = 1.2
R	= gas constant (atm-m^2/mol-^{O}K) = 8.2 x 10^{-5}
T	= absolute temperature (^{O}K) = 294
DF_i	= dilution factor from soil gas to indoor air (unitless): ***see derivation below***
ET	= exposure term (unitless) = 1
BSC	= background soil concentration (mg/kg) = 0

Calculation of DF for indoor infiltration pathway:

$$DF_i = \frac{1}{\alpha}$$

DF_i = dilution factor from soil gas concentration to indoor air concentration

(unitless)

α = attenuation coefficient
= (contaminant vapour concentration in the building)/(vapour concentration at the source)

$$D_T^{eff} \approx D_a \left(\frac{\theta_a^{10/3}}{n^2} \right)$$

D_T^{eff} = overall effective porous media diffusion coefficient based on vapour-phase concentrations for the region between the source and foundation (cm^2/s)
D_a = diffusion coefficient in air (cm^2/s) = 0.05
θ_a = vapour-filled porosity (unitless) = 0.281
n = total soil porosity (unitless) = 0.4

$$Q_B = L_B W_B H_B (ACH) / (3600\ s/h)$$

Q_B = building ventilation rate (cm^3/s)
L_B = building length (cm) = 1225
W_B = building width (cm) = 1225
H_B = building height, including basement (cm) = 488
ACH = air exchanges per hour (h^{-1}) = 1

$$Q_{soil} = \frac{2\pi\ \Delta P\ k_v\ X_{crack}}{\mu \ln\left[\frac{2(Z_{crack})}{r_{crack}} \right]}$$

Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s)
ΔP = pressure differential ($g/cm \cdot s^2$) = 40
k_v = soil vapour permeability to vapour flow (cm^2) = 10^{-8}
X_{crack} = length of idealized cylinder (cm) = 4900
μ = vapour viscosity ($g/cm \cdot s$) = 1.73 x 10^{-4}
Z_{crack} = distance below grade to idealized cylinder (cm) = 244
r_{crack} = radius of idealized cylinder (cm) = A_{crack} / X_{crack} = 0.20296

$$\alpha = \frac{\left(\frac{D_T^{eff} A_B}{Q_B L_T} \right) \exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}} \right)}{\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}} \right) + \left(\frac{D_T^{eff} A_B}{Q_B L_T} \right) + \left(\frac{D_T^{eff} A_B}{Q_{soil} L_T} \right) \left[\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}} \right) - 1 \right]}$$

D_T^{eff} = effective porous media diffusion coefficient (cm^2/s) = 0.00454
A_B = building area (cm^2) = 1 500 625

Q_B = building ventilation rate (cm^3/s) = 203 418
L_T = distance from contaminant source to foundation (cm) = 30
Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s) = 9.14382
L_{crack} = thickness of the foundation (cm) = 11.25
D^{crack} = effective vapour-pressure diffusion coefficient through the crack (cm^2/s)
= 0.00454 (i.e., coarse-grained soil in the crack with θ_a = 0.281 and n = 0.4)
A_{crack} = area of cracks through which contaminant vapours enter the building (cm^2)
= 994.5

Therefore,

α = 4.3211×10^{-5}

DF_i = $1/\alpha$ = 23 142

$SQG_{ii,b}$ = soil quality guideline by indoor infiltration for volatile PHCs using RfC (mg/kg)
= 120 mg/kg

Algorithm used to sum TPHCWG sub-fractions within Fraction 1 (soil ingestion pathway):

To derive soil quality guidelines for Fraction 1, guidelines must first be estimated for each individual TPHCWG sub-fraction within Fraction 1, for the desired target Hazard Quotient (equivalent to the soil allocation factor discussed herein). Then, the guidelines for sub-fractions must be combined according to their mass fraction within Fraction 1, according to the algorithm below.

$$SQG_{Fraction\_i} = \frac{1}{\sum\left(\frac{MF_{subfraction\ j}}{SQG_{subfraction\ j}}\right)}$$

$SQG_{Fraction\_i}$ = soil quality guideline for the fraction *i* (mg/kg)
$SQG_{sub\text{-}fraction\ j}$ = soil quality guideline (mg/kg) for each sub-fraction within fraction *i* for the target Hazard Quotient for fraction *i*
$MF_{sub\text{-}fraction\ j}$ = mass fraction of each sub-fraction within fraction *i*

For the soil ingestion pathway:

$SQG_{sub\text{-}fraction\ C>6\ to\ C8\ aliphatics}$ = 513 218 mg/kg

(as shown in calculations above)

$SQG_{sub\text{-}fraction\ C>8\ to\ C10\ aliphatics}$ = 9 250 mg/kg

$SQG_{sub\text{-}fraction\ C>8\ to\ C10\ aromatics}$ = 3 158 mg/kg

And,

$MF_{sub\text{-}fraction\ C>6\ to\ C8\ aliphatics}$ = 0.55
$MF_{sub\text{-}fraction\ C>8\ to\ C10\ aliphatics}$ = 0.36
$MF_{sub\text{-}fraction\ C>8\ to\ C10\ aromatics}$ = 0.09

Therefore,

$SQG_{Fraction\ 1}$ = 1 / { [0.55/513218] + [0.36/9250] + [0.09/3158]}

= 14 600 mg/kg

Appendix D: Application of the CCME 1996 Soil Protocol to the derivation of Tier 1 ecological values.

The CCME protocol for the derivation of soil quality guidelines based on direct soil contact to soil invertebrates and plants is provided in CCME (1996). Briefly, where sufficient data exist (at least ten data points from at least three studies; minimum of each of two soil invertebrate and two crop/plant data points), the following protocol is applied:

> "**Threshold Effects Concentration" (TEC).** Applicable to Agricultural and Residential/ Parkland land use, where -
>
> TEC = 25^{th} percentile of the effects and no effects data distribution;
>
> **"Effects Concentration - Low" (EC-L).** Applicable to Commercial and Industrial land use, where -
>
> EC-L = 25^{th} percentile of effects data distribution (LOEC, ECx, LCx values from toxicity database).

Where the above-mentioned minimum data requirements have not been met, the "*Provisional Method: Toxicity to Soil Invertebrates and Plants"* is applied as follows:

> For Agricultural and Residential/Parkland, use lowest of toxicity values (usually EC_{25} values) in published literature and divide by uncertainty factor (UF) based on the following: Uncertainty Factors: 5 if EC_{50} is the lowest toxicity value, 10 if LC_{50}.
>
> For Commercial and Industrial land use, use geometric mean of available endpoints (usually LOECs or EC_{25}s). Commerical/Industrial - $1 \leq UF \geq 5$.

The minimum data requirements for the Provisional Method include a minimum of three studies, and at least one terrestrial plant and one soil invertebrate toxicity endpoint.

EcoTAG (2000a) specifically advocated against the use of the provisional method where possible to avoid the use of uncertainty factors. Part of the discomfort in the provisional method is associated with the long history of use of petroleum hydrocarbon products, their relative ubiquity, and recognition that PHCs are neither highly persistent, nor highly bioaccumulative.

In addition, most EcoTAG members felt that the separate evaluation of soil invertebrate and plant endpoints was scientifically more defensible than combining the two highly disparate groups, and that the separation of the two major taxa would result in more accurate and precise estimates of the range of toxicological thresholds. There was concern, however, that the further subdivision of the available

plant and soil invertebrate toxicity data might result in a reduction in the size of data set which might be used for defining species sensitivity distribution based on direct soil contact.

The CCME (1996) protocol for calculating either the Threshold Effects Concentration or the Effects Concentration - Low is often difficult to apply when there is a relatively large database to work with as is the case of various PHC categorizations. This is due to the amount of latitude available in screening and either rejecting or including no effects or effects data prior to ranking and subsequently establishing a 25th percentile soil concentration.

Following an initial screening to ensure minimum quality requirements for toxicity data, scientific/professional judgment is routinely used to ascertain whether there is further redundancy, or inappropriate co-variations between individual data points that would lead to biases in establishing environmental quality benchmarks which are suitably protective when extrapolated to the larger soil invertebrate and plant communities present at a given locale. For example, Stephenson *et al.* (2000b) derived the following toxicity endpoints based on studies of the toxicity of the F3 fraction, distilled from federated crude oil, on springtail collembolans (*Onychiuris folsomi*) (Table D.1, below)

Table D.1: Example of soil invertebrate toxicity endpoints available.

Endpoint		Response		Exposure Period
• NOEC • LOEC • $EC(LC)_{20}$ • $EC(LC)_{50}$	X	• fecundity • no. of juveniles • adult mortality	X	• 7 day (acute) • 35-36 day (definitive)

For plants tested with the F3 fraction, the individual endpoints examined included -

- shoot length
- root length
- shoot wet weight
- shoot dry weight
- root wet weight
- root dry weight

A toxicologist might derive from a single dose-response curve a large number of EC_x or LC_x endpoints (e.g., an EC_5, EC_{10}, EC_{25}, EC_{50}, EC_{75}, EC_{90}, and EC_{95} as well as NOEC and LOEC). The soil invertebrate and plant LOECs defined from the Stephenson *et al.* (2000b) study on the toxicity of the F3 fraction where generally

associated with an effect size greater than 50% (i.e., the nominal F3 soil concentration for the LOEC endpoint was greater than the calculated nominal concentration for the EC_{50} or LC_{50}).

One of the questions which invariably arises when screening data before applying a ranks-based approach is whether two data points are effectively redundant and should be combined. For example, it might be argued that plant shoot wet weight and dry weight measurements capture essentially the same suite of physiological and biochemical responses to a toxicant. Alternatively, it might be argued that dry weight measurements capture perturbations in the deposition of structural proteins and carbohydrates, and starches for energy storage, whereas perturbations in wet weight might independently reflect hydration state, plant water balance, and/or stomatal functioning.

The use of NOEC and LOEC values to examine risks has been challenged by a number of researchers, since the values derived are in large part an artifact of (i) the experimental protocol (specific concentrations to which the test organism is exposed), and (ii) shortcomings of the Analyis of Variance (ANOVA) model in allowing the identification of statistically significant differences between different exposure concentrations and the control (issues associated with statistical power).

The CCME (1996) TEC and EC-L protocols allow the combination of mortality endpoints (LC_x) with ecologically-relevant sublethal endpoints such as decreased plant growth or crop yield, which may or may not be accompanied by corresponding mortality. This aspect of the protocol has been rejected by the Contaminated Sites Soils Taskgroup (B.C.MELP 1996) of the British Columbia Ministry of Environment in favour of methods that separately utilize the ECx and LCx portions of an available database. If due care and attention is not paid to the relative proportion of either short-term/acute versus longer-term/chronic, or sublethal effects versus mortality data, then the resulting TEC or EC-L might result in a highly variable realized level of environmental protection achieved.

There is invariably considerable latitude in how toxicological data are screened and occasionally transformed prior to being subjected to a weight-of-evidence ranks-based protocol for the derivation of environmentally protective benchmarks. While some aspects of data manipulation are amenable to standardization of methods through detailed guidance, others invariably will not be – especially when ecotoxicity data have been salvaged from a variety of sources. The challenges are actually greater in cases where the underlying database is larger, since the amount of latitude available in screening data is correspondingly larger.

Appendix E: New ecotoxicity data for soil invertebrates and plants exposed to PHC CWS fractions of fresh Federated Whole Crude, and unfractionated whole product.

Table E.1: PHC CWS fraction F3 (>nC16 to nC34) toxicity data for direct contact to soil invertebrates and plants.

Organism	Parameter	Endpoint	Value *(mg/kg)*	Exposure conc. *# (conc.)*	# reps.	Conc. type *nom./init./final*	Soil type	Comments
Alfalfa	shoot length	EC20	2800	7 (0,15,30,50,60, 70,80 mg/g)	4	nominal	field soil - Delacour Orthic Black Chernozem	8d test. n=10
	root length	EC20	7200					
	whole ww	EC20	15800					
	whole dw	EC20	50200					
	shoot length	EC50	51900	7 (0,15,30,50,60, 70,80 mg/g)	4	nominal		8d test. n=10
	root length	EC50	10000					
	whole ww	EC50	72300					
	whole dw	EC50	98200					
	shoot length	EC20	620	12 (0,1,3,6,12, 15,20,40,60,80, 100,120 mg/g)	3-6	nominal		26d test. n=10 clear lids kept on till plants 3cm in height
	root length	EC20	920					
	shoot ww	EC20	510					
	shoot dw	EC20	620					
	root ww	EC20	860					
	root dw	EC20	1100					
	shoot length	EC50	8300	12 (0,1,3,6,12,15, 20,40,60,80, 100,120 mg/g)	3-6	nominal		26d test. n=10 clear lids kept on till plants 3cm in height
	root length	EC50	6300					
	shoot ww	EC50	2100					
	shoot dw	EC50	2300					
	root ww	EC50	4400					
	root dw	EC50	5500					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments	
Barley	shoot length	EC20	74800	7 (0,15,30,50, 60,70, 80 mg/g)	4	nominal	Artificial - 70%	7d test. n=5	
	root length	EC20	79000				silica sand, 20%		
	shoot ww	EC20	73800				keolinite clay		
	shoot dw	EC20	73600				10% sphagnum		
	root ww	EC20	61200				peat		
	root dw	EC20	67400						
	shoot length	EC50	98200	7 (0,15,30,50,60, 70, 80 mg/g)	4	nominal		7d test. n=5	
	root length	EC50	119600						
	shoot ww	EC50	85900						
	shoot dw	EC50	87200						
	root ww	EC50	90800						
	root dw	EC50	95300						
	shoot length	EC20	39400	6 (0,4,10,30,50,80 mg/kg)	4	nominal	field soil	6d test. n=5	
	root length	EC20	47600				- Delacour Orthic		
	shoot ww	EC20	36700				Black Chernozem		
	shoot length	EC50	53400	6 (0,4,10,30,50,80 mg/kg)	4	nominal		6d test. n=5	
	root length	EC50	58200						
	shoot ww	EC50	50300						
	shoot length	EC20	3700	10 (0,10,20,30,40, 50,60,70,80,100 mg/g)	3-6	nominal		14d test. n=5 3cm in height	clear lids kept on till plants
	root length	EC20	120						
	shoot ww	EC20	48200						
	shoot dw	EC20	48700						
	root ww	EC20	1700						
	root dw	EC20	10000						
Barley (cont'd)	shoot length	EC50	27600	10 (0,10,20,30,40, 50,60,70,80,100 mg/g)	3-6	nominal	field soil	14d test. n=5 3cm in height	clear lids kept on till plants
	root length	EC50	3200				- Delacour Orthic		

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	shoot ww	EC50	54100				Black Chernozem	
	shoot dw	EC50	53300					
	root ww	EC50	8700					
	root dw	EC50	35100					
Northern wheat-grass	root length	EC20	20400	7 (0,15,30,50,60, 70,80 mg/g)	4	nominal		8d test. n=5
	whole ww	EC20	13700					
	whole dw	EC20	12100					
	shoot length	EC50	42100	7 (0,15,30,50,60, 70,80 mg/g)	4	nominal		8d test. n=5
	root length	EC50	51100	7 (0,15,30,50,60, 70,80 mg/g)	4	nominal		8d test. n=5
	whole ww	EC50	26700					
	whole dw	EC50	24800					
	shoot length	EC20	330	11 (0,5,10,15,20, 30,40,50,60,70, 80 mg/g)	3-6	nominal		25d test. n=5 clear lids kept on till plants 3cm in height
	root length	EC20	4300					
	shoot ww	EC20	13					
	shoot dw	EC20	50					
	root ww	EC20	180					
	root dw	EC20	210					
	shoot length	EC50	12700	11 (0,5,10,15,20, 30,40,50,60,70, 80 mg/g)	3-6	nominal		25d test. n=5 clear lids kept on till plants 3cm in height
	root length	EC50	7300					
	shoot ww	EC50	610					
	shoot dw	EC50	1400					
Northern wheat-grass (cont'd)	root dw	EC50	1100				field soil	
	root ww	EC50	890					
	shoot length	EC20	17100	7 (0,15,30,50,60,	4	nominal	Artificial - 70%	12d test. n=5

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
				70,80 mg/g)				
	root length	EC20	54900				silica sand, 20% keolinite clay 10% sphagnum peat	
	whole ww	EC20	34000					
	whole dw	EC20	33500					
	shoot length	EC50	81900	7 (0,15,30,50,60, 70,80 mg/g)	4	nominal		12d test. n=5
	root length	EC50	121000					
	whole ww	EC50	73400					
	whole dw	EC50	63900					
Worms (*E.foetida*)	# juveniles	EC20	240	11 (0,0.5,1,3,5,7, 10,12.5,15,20,25 mg/g)	10	nominal	field soil - Delacour Orthic Black Chernozem	57d test. n=2 perforated lids. adults removed at D37 & cocoons allowed to hatch. value for IC & LC
	# juveniles	EC50	776					
	juvenile ww	EC20	272					
	juvenile ww	EC50	854					
	juvenile dw	EC20	213					
	juvenile dw	EC50	809					
	# juveniles	NOEC	0					
	# juveniles	LOEC	500					
	juvenile ww	NOEC	0					
	juvenile ww	LOEC	500					
	juvenile dw	NOEC	0					
	juvenile dw	LOEC	500					
	mortality	LC50	22360	10 (0,0.5,1,2,4,8, 12,15,20,50 mg/g)	3-4	nominal	field soil Delacour Orthic Black Chernozem	14d test. n=5 perforated lids
Worms (*L. terrestris*)	mortality	LC50	19150	6 (0,8,12,15,20,50 mg/g)	3-4	nominal	Artificial - 70%silica sand, 20% keolinite clay, 10% sphagnum peat	14d test. n=3 perforated lids

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	mortality	LC50	17220	7 (0,4,8,12,15,20, 50 mg/g)	3-4	nominal	field soil Delacour Orthic Black Chernozem	14d test. n=3 perforated lids
Springtail (*O. folsomi*)	mortality	LC50	6670	6 (0,2,4,8,12,15 mg/g)	3-4	nominal	artificial 70% silica sand 20% keolinite clay 10 % sphagnum peat	7d test. n=10 covered loosly
	mortality	LC50	5970					
	# juvenile	NOEC	1000	10 (0,0.5,1,2,3,4,5, 5.5,6,7 mg/g)	10	nominal	field soil Delacour Orthic Black Chernozem	35-36d test. n=10. loosely closed lids removed biweekly for air exchange. value for IC & LC
	# juvenile	LOEC	2000					
	# juvenile	EC20	910					
	# juvenile	EC50	1490					
	adult fecundity	NOEC	1000	10 (0,0.5,1,2,3,4,5, 5.5,6,7 mg/g)	10	nominal	field soil Delacour Orthic Black Chernozem	35-36d test. n=10. loosely closed lids removed biweekly for air exchange. value for IC & LC
	adult fecundity	LOEC	2000					
	adult fecundity	EC20	620					
	adult fecundity	EC50	1410					
Springtail (*O. folsomi*) (cont'd)	adult mortality	NOEC	3000	10 (0,0.5,1,2,3,4,5, 5.5,6,7 mg/g)	10	nominal	field soil Delacour Orthic Black Chernozem	35-36d test. n=10. loosely closed lids removed biweekly for air exchange. value for IC & LC
	adult mortality	LOEC	4000					
	adult mortality	EC20	3120					

Organism	Parameter	Endpoint	Value *(mg/kg)*	Exposure conc. *# (conc.)*	# reps.	Conc. type *nom./init./final*	Soil type	Comments
	adult mortality	EC50	3695-4280					

(after Stephenson et al., 2000b)

Table E.2: PHC CWS fraction F2 (>nC10 to nC16) toxicity data for direct contact to soil invertebrates and plants.

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Alfalfa	shoot length	EC50	2710	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	nominal	field soil – Delacour, Orthic Black Chernozem	21d test. n=10
	root length	EC50	1860					
	shoot ww	EC50	1680					
	shoot dw	EC50	1370					
	root ww	EC50	4740					
	root dw	EC50	5120					
Barley (*H.vulgare*)	shoot length	EC50	6370	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	nominal	Artificial: 70% sand; 20% clay; 10% peat	8d test. n=5
	root length	EC50	3440					
	shoot ww	EC50	7510					
	shoot dw	EC50	7830					
	root ww	EC50	4160					
	root dw	EC50	4180					
	shoot length	EC50	7150	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	nominal	field soil – Delacour, Orthic Black Chernozem	8d test. n=5
	root length	EC50	2770					
	shoot ww	EC50	6610					
	shoot dw	EC50	8240					
	root ww	EC50	4460					
	root dw	EC50	4370					
	shoot length	EC50	4130	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	nominal	field soil – Delacour, Orthic Black Chernozem	13d test. n=5
	root length	EC50	4550					
	shoot ww	EC50	2430					
	shoot dw	EC50	2590					
	root ww	EC50	2390					
	root dw	EC50	2510					
Northern	shoot length	EC50	7440	11 (0, 0.5, 1, 3, 5, 6,	3-6	nominal	field soil – Delacour,	14d test. n=5

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
wheatgrass				8, 12, 15, 20, 30 mg/g)			Orthic Black Chernozem	
	root length	EC50	2320					
	shoot ww	EC50	2770					
	shoot dw	EC50	3150					
	root ww	EC50	1560					
	root dw	EC50	1370					
Worms (*E.foetida*)	mortality	LC50	1190	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	nominal	Artificial: 70% sand; 20% clay; 10% peat	7d test. loose lids. n=5
	mortality	LC50	1030	8 (0, 0.1, 0.3, 0.5, 1, 2, 3, 6 mg/g)	3	nominal	field soil – Delacour, Orthic Black Chernozem	7d test. loose lids. n=5
	mortality	LC50	1150	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	nominal	Artificial: 70% sand; 20% clay; 10% peat	14d test. loose lids. n=5
Worms (*E.foetida*)	mortality	LC50	530	8 (0, 0.1, 0.3, 0.5, 1, 2, 3, 6 mg/g)	3	nominal	field soil – Delacour, Orthic Black Chernozem	14d test. loose lids. n=5
	# of juveniles	EC50	490	10 (0, 0.029, 0.041, 0.059, 0.084, 0.12, 0.17, 0.245, 0.35, 0.5 mg/g)	10	nominal	field soil – Delacour, Orthic Black Chernozem	62-63d test. n=2. perforated lids. adults removed at D27 & cocoons allowed to hatch
	juvenile ww	EC50	590					
	juvenile dw	EC50	580					
Worms (*L.terrestris*)	mortality	LC50	1100	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	nominal	Artificial: 70% sand; 20% clay; 10% peat	7d test. loose lids. n=3
	mortality	LC50	1290	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	nominal	field soil – Delacour, Orthic Black Chernozem	7d test. loose lids. n=3
	mortality	LC50	1100	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	nominal	field soil – Delacour, Orthic Black Chernozem	14d test. loose lids. n=3

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Worms (*L.terrestris*) (cont'd)	mortality	LC50	1120	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	nominal		14d test. loose lids. n=3
Springtail (*O.folsomi*)	mortality	LC50	2920	9 (0, 0.5, 1, 2, 3, 5, 8, 10, 25 mg/g)	3	nominal	Artificial: 70% sand; 20% clay; 10% peat	7d test. loose lids. n=10
	mortality	LC50	3230	9 (0, 0.5, 1, 2, 3, 5, 8, 10, 25 mg/g)	3	nominal	field soil – Delacour, Orthic Black Chernozem	7d test. loose lids. n=10
	# juveniles	EC50	1470	(0, 0.025, 0.05, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	10	nominal	field soil – Delacour, Orthic Black Chernozem	35-36d test. n=10. loose lids

(after Stephenson et al., 2000a)

Table E.3: Additive-free mogas toxicity data as an estimate of CWS F1 (C6 to nC10) toxicity, based on direct contact to soil invertebrates and plants.

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
Alfalfa	shoot length	EC20	**3210**	10 (0,1,2,3,5, 6,8,12,15, 25)	3	nominal	artificial	11 d test (n=3 closed test units mech. mixing
	root length	EC20	**3310**					
	ww	EC20	**3390**					
	dw	EC20	**3400**					
	shoot length	EC20	**2410**	10 (0,1,2,3,5, 6,8,12,15, 25)	3	nominal	SLR	11 d test (n=3 closed test units mech. mixing
	root length	EC20	**3080**					
	ww	EC20	**5900**					
	dw	EC20	**5100**					
	shoot length	EC50	**5450**	10 (0,1,2,3,5, 6,8,12,15, 25)	3	nominal	artificial	11 d test (n=3 closed test units mech. mixing
	root length	EC50	**5010**					
	ww	EC50	**5320**					
	dw	EC50	**4910**					
	shoot length	EC50	**6600**	10 (0,1,2,3,5, 6,8,12,15, 25)	3	nominal	SLR	11 d test (n=3 closed test units mech. mixing
	root length	EC50	**4580**					
	ww	EC50	**8220**					
	dw	EC50	**6750**					
	shoot length	EC20	**2570**	10 (0,1,2,3,5, 6,8,12,15 25)	3	nominal	SLR	21 d test (n=3-6; closed test units for first 7 d only; mech. mixing)
	root length	EC20	**2240**					
	shoot ww	EC20	**1890**					
	shoot dw	EC20	**1850**					
	root ww	EC20	**2310**					
	root dw	EC20	**2120**					
Alfalfa	shoot	EC50	**5130**	10 (0,1,2,3,5,	3	nominal	SLR	21 d test (n=3-6; closed test units for

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
(cont'd)	length			6,8,12,15, 25)				first 7 d only; mech. mixing)
	root length	EC50	**3900**					
	shoot ww	EC50	**2710**					
	shoot dw	EC50	**2520**					
	root ww	EC50	**2980**					
	root dw	EC50	**2970**					
Barley (*H.vulgare*)	shoot length	EC20	**4430**	7 (0,2.5,5, 10,25,50, 100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	7d test. n=5 open plastic test units. mech mix
	shoot ww	EC20	**5530**					
	shoot dw	EC20	**5740**					
	root length	EC20	**2310**					
	root ww	EC20	**2180**					
	root dw	EC20	**2320**					
	shoot length	EC20	**2850**	7 (0,2.5,5, 10,25,50, 100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	7d test. n=5 closed plastic test units. mech mix
	shoot ww	EC20	**4390**					
	shoot dw	EC20	**3560**					
	root length	EC20	**1590**					
	root ww	EC20	**1930**					
	root dw	EC20	**1620**					
	shoot length	EC20	**1900**	7 (0,2.5,5, 10,25,50, 100 mg/g)	3	nominal	SLR	7d test. n=5 closed plastic test units. mech mix
	shoot ww	EC20	**1210**					
	shoot dw	EC20	**1210**					
	root length	EC20	**1380**					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
	root ww	EC20	**1130**					
Barley	root dw	EC20	**910**					
(cont'd)	shoot length	EC50	**3100**	7 (0,2.5,5, 10,25,50, 100 mg/g)	3	nominal	SLR	7d test. n=5 closed plastic test units. mech mix
	shoot ww	EC50	**2320**					
	shoot dw	EC50	**2520**					
	root length	EC50	**2220**					
	root ww	EC50	**1770**					
	root dw	EC50	**1950**					
	shoot length	EC50	**5000**	7 (0,2.5,5, 10,25,50, 100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	7d test. n=5 closed plastic test units. mech mix
	shoot ww	EC50	**5500**					
	shoot dw	EC50	**5440**					
	root length	EC50	**2760**					
	root ww	EC50	**3660**					
	root dw	EC50	**3590**					
	shoot length	EC50	**7240**	7 (0,2.5,5, 10,25,50, 100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	7d test. n=5 open plastic test units. mech mix
	shoot ww	EC50	**7860**					
	shoot dw	EC50	**7790**					
	root length	EC50	**4480**					
	root ww	EC50	**4310**					
	root dw	EC50	**4780**					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
Barley (cont'd)	shoot length	EC20	**890**	10 (0, 0.25, 0.5,0.75,1, 1.5,2,4,6, 10)	3	nominal	SLR	13d test. n=5 closed plastic test units, for firt seven days only, mech mix
	shoot ww	EC20	**770**					
	shoot dw	EC20	**680**					
	root length	EC20	**640**					
	root ww	EC20	**580**					
	root dw	EC20	**590**					
	shoot length	EC50	**1680**	10 (0, 0.25, 0.5,0.75,1,1 .5,2,4,6,10)	3	nominal	SLR	13d test. n=5 closed plastic test units, for firt seven days only, mech mix
	root length	EC50	**1600**					
	shoot ww	EC50	**1360**					
	shoot dw	EC50	**1220**					
	root ww	EC50	**870**					
	root dw	EC50	**960**					
Corn (*Zea mays*)	shoot length	EC20	**3230**	11 (0,1,2,3,5, 6,8,15,25, 50,100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	acute test. n=5 closed glass jars. tumble mixing
	shoot ww	EC20	**5260**					
	shoot dw	EC20	**4230**					
	root length	EC20	**1920**					
	root ww	EC20	**6830**					
	root dw	EC20	**6730**					
	shoot length	EC20	**3080**	11 (0,1,2,3,5, 6,8,15,25, 50,100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	acute test. n=5 closed glass jars. mech. mixing
	shoot ww	EC20	**6670**					
	shoot dw	EC20	**6250**					
	root length	EC20	**1000**					
	root ww	EC20	**6750**					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
	root dw	EC20	**5470**					
Corn (cont'd)	shoot length	EC50	**4880**	11 (0,1,2,3,5,6, 8,15,25,50, 100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	acute test. n=5 closed glass jars. tumble mixing
	shoot ww	EC50	**7590**					
	shoot dw	EC50	**7710**					
	root length	EC50	**3140**					
	root ww	EC50	**9090**					
	root dw	EC50	**9610**					
	shoot length	EC50	**4650**	11 (0,1,2,3,5, 6,8,15,25, 50,100 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	acute test. n=5 closed glass jars. mech. mixing
	shoot ww	EC50	**9250**					
	shoot dw	EC50	**9620**					
	root length	EC50	**2700**					
	root ww	EC50	**8930**					
	root dw	EC50	**8440**					
	shoot length	EC20	**3840**	11 (0,1,2,3,5, 6,8,15,25, 50,100 mg/g)	3	nominal	SLR	acute test. n=5 closed glass jars. mech. mixing
	shoot ww	EC20	**6270**					
	shoot dw	EC20	**6240**					
	root length	EC20	**2290**					
	root ww	EC20	**6260**					
	root dw	EC20	**6020**					
	shoot length	EC50	**5020**	11 (0,1,2,3,5, 6,8,15,25, 50,100 mg/g)	3	nominal	SLR	acute test. n=5 closed glass jars. mech. mixing
	shoot ww	EC50	**6960**					
	shoot dw	EC50	**7100**					
	root length	EC50	**3960**					
	root ww	EC50	**6910**					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
	root dw	EC50	**6650**					
Red fescue	shoot length	EC20	**2790**	10 (0,1,2,3,5, 6,8,12,15, 25 mg/g)	3	nominal	artificial	9 d. acute test. n=5 closed glass jars. mech. mixing
	root length	EC20	**2440**					
	ww	EC20	**4240**					
	dw	EC20	**3370**					
	shoot length	EC20	**2680**	10 (0,1,2,3,5, 6,8,12,15, 25 mg/g)	3	nominal	SLR	9 d. acute test. n=5 closed glass jars. mech. mixing
	root length	EC20	**1430**					
	ww	EC20	**3400**					
	dw	EC20	**2970**					
	shoot length	EC50	**5070**	10 (0,1,2,3,5, 6,8,12,15, 25 mg/g)	3	nominal	artificial	9 d. acute test. n=5 closed glass jars. mech. mixing
	root length	EC50	**4350**					
	ww	EC50	**5790**					
	dw	EC50	**4250**					
	shoot length	EC50	**4110**	10 (0,1,2,3,5, 6,8,12,15, 25 mg/g)	3	nominal	SLR	9 d. acute test. n=5 closed glass jars. mech. mixing
	root length	EC50	**2930**					
	ww	EC50	**4330**					
	dw	EC50	**3890**					
Springtails (*O.folsomi*)	adult mortality	LC50	**3420**	10 (0,0.025, 0.05,0.1, 0.5,1,2,3,5, 8 mg/g)	10	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	35-36d test. n=10. ? results due to low repro of control. closed units till D7 then loosely closed
	# juveniles	EC50	**2890**					
Springtails (cont'd)	adult mortality	LC50	**3760**					
	# juveniles	EC50	**4210**					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
	mortality	LC50	**4720**	8 (0,0.5,1,2, 3,5,8,10 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	7d test. n=? closed units
	mortality	LC50	**5960**	8 (0,0.5,1,2, 3,5,8,10 mg/g)	3			
	mortality	LC50	**4190**	8 (0,0.5,1,2, 3,5,8,10 mg/g)	3	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	7d test. n=? closed units
	adult mortality	LC20	**1940**	10 (0,0.025, 0.05,0.1, 0.5,1,2,3,5, 8 mg/g)	10	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	35-36d test. n=10. ? results due to low repro of control. closed units till D7 then loosely closed
	# juveniles	EC20	**2170**					
	adult mortality	LC20	**2630**	10 (0,0.025, 0.05,0.1, 0.5,1,2,3,5, 8 mg/g)	10	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	35-36d test. n=10. ? results due to low repro of control. closed units till D7 then loosely closed
	# juveniles	EC20	**2350**					
	adult mortality	LOEC	**3000**	10 (0,0.025, 0.05,0.1, 0.5,1,2,3,5, 8 mg/g)	10	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	35-36d test. n=10 ? results due to low repro of control. closed units till D7 then loosely closed
	# juveniles	LOEC	**25**		10	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	35-36d test. n=10 ? results due to low repro of control. closed units till D7 then loosely closed. ? inclusion because higher concent were not stat signif from control - son not dose-dep responce!
	adult mortality	NOEC	**2000**		10	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	35-36d test. n=10 ? results due to low repro of control. closed units till D7 then loosely closed
	# juveniles	NOEC	**0**		10	nominal	artificial	35-36d test. n=10 ? results due to low repro of control. closed units till D7 then

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
								loosely closed
Worms (*E.fetida*)	mortality	LC50	**630**	7 (0,0.1,0.5, 1,2,3,5 mg/g)	2	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	mech. mixing. container 7d test. closed test
	mortality	LC50	**1230**		2	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	mech. mixing. contaner 7d test. closed test
	mortality	LC50	**710**		2	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	mech. mixing. container 7d test. open test
	mortality	LC50	**2080**		2	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	mech. mixing. container 7d test. open test
	mortality	LC50	**1150**	7 (0,0.1,0.5, 1,2,3,5 mg/g)	2	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	mech. mixing. container 14d test. closed test
	mortality	LC50	**400**		2	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	mech. mixing. container 14d test. closed test
	mortality	LC50	**1860**		2	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	mech. mixing. container 14d test. open test
	mortality	LC50	**710**		2	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	mech. mixing. container 14d test. open test

(after Stephenson 2000)

Table E.4: Toxicity of fresh, Whole Federated Crude Oil to soil invertebrates and plants.

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Alfalfa	shoot length	EC20	6550	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	11d test. n=10
	root length	EC20	339					
	whole dw	EC20	587					
	shoot length	EC20	3382	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	11d test. n=10
	root length	EC20	277					
	whole dw	EC20	113882					
	whole ww	EC20	66114					
	shoot length	EC50	149054	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	11d test. n=10
	root length	EC50	1054					
	whole dw	EC50	302221					
	whole ww	EC50	152357					
	shoot length	EC50	10506	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	11d test. n=10
	root length	EC50	5175					
	whole dw	EC50	242415					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Alfalfa (cont'd)	shoot length	EC20	3109	13 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 135, 150 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	20d test. n=10
	root length	EC20	9905					
	shoot ww	EC20	1526					
	shoot dw	EC20	5286					
	root ww	EC20	131344					
	root dw	EC20	36276					
	shoot length	EC50	19877	13 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 135, 150 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	20d test. n=10
	root length	EC50	30768					
	shoot ww	EC50	5358					
	shoot dw	EC50	13330					
	root ww	EC50	50187					
	root dw	EC50	60194					
Barley (CDC Buck)	shoot length	EC20	61622	9 (0, 0.5, 1, 5, 10, 15, 30, 60, 120 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	9d test. n=5
	root length	EC20	16683					
	shoot dw	EC20	54832					
	shoot ww	EC20	39386					
	root dw	EC20	45332					
	shoot length	EC50	80598	9 (0, 0.5, 1, 5, 10, 15, 30, 60, 120 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	9d test. n=5
	root length	EC50	44004					
	shoot ww	EC50	53712					
	shoot dw	EC50	64965					
	root dw	EC50	59161					
Barley (Chapais)	shoot length	EC20	3431	13 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100, 120,	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	13d test. n=5

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
				135, 150 mg/g)				
	root length	EC20	2982					
	shoot ww	EC20	2570					
	shoot dw	EC20	723					
	root ww	EC20	1370					
	root dw	EC20	1171					
	shoot length	EC50	15268	13 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 135, 150 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	13d test. n=5
	root length	EC50	10682					
	shoot ww	EC50	9060					
	shoot dw	EC50	4519					
	root ww	EC50	4052					
	root dw	EC50	4740					
Corn (Kandy Korn)	shoot length	EC20	103361	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	7d test. n=3
	root length	EC20	2434					
	root ww	EC20	100632					
	root dw	EC20	104951					
	shoot length	EC50	116500	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	7d test. n=3
	root length	EC50	62041					
	root ww	EC50	111257					
	root dw	EC50	108321					
	shoot length	EC20	94723	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	6d test. n=3
Corn (Kandy Korn) (cont'd)	root length	EC20	2604					
	shoot ww	EC20	97670					
	shoot dw	EC20	92670					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments	
	root ww	EC20	82248						
	root dw	EC20	67736						
	shoot length	EC50	130639	10 (0, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	6d test. n=3	
	root length	EC50	26485						
	shoot ww	EC50	140732						
	shoot dw	EC50	132712						
	root ww	EC50	125753						
	root dw	EC50	114903						
	shoot length	EC20	10928	13 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 135, 150 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	14d test. n=5	initial measures are provided
	root length	EC20	1168						
	shoot ww	EC20	34031						
	shoot dw	EC20	34458						
	root ww	EC20	8452						
	root dw	EC20	35224						
	shoot length	EC50	47680	13 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 135, 150 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	14d test. n=5	initial measures are provided
	root length	EC50	8103						
	shoot ww	EC50	53532						
	shoot dw	EC50	51973						
	root ww	EC50	26253						
	root dw	EC50	47964						
Northern wheatgrass	shoot length	EC20	7373	11 (0, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	9d test. n=5	
	root length	EC20	3505						
	whole ww	EC20	22917						
	whole dw	EC20	6538						

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	shoot length	EC50	29862	11(0, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	9d test. n=5
	root length	EC50	16636					
	whole ww	EC50	51836					
	whole dw	EC50	22371					
	shoot length	EC20	10557	11 (0, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	9d test. n=5
	root length	EC20	7794					
	whole ww	EC20	25588					
	whole dw	EC20	21342					
	shoot length	EC50	26120	11 (0, 1, 2.5, 5, 10, 30, 60, 80, 100, 120, 150 mg/g)	4 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	9d test. n=5
	root length	EC50	23187					
	whole ww	EC50	50899					
	whole dw	EC50	37791					
	shoot length	EC20	837	10 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	20d test. n=5
	root length	EC20	782					
	shoot ww	EC20	2140					
	shoot dw	EC20	525					
	root dw	EC20	1598					
	root ww	EC20	1480					
Northern Wheatgrass	shoot length	EC50	6671	10 (0, 0.5, 1, 2.5, 5, 10, 30, 60, 80, 100 mg/g)	6 control 3-4 trt	nominal	Field soil Delacour Orthic Black Chernozem	20d test. n=5
(cont'd)	root length	EC50	5876					
	shoot ww	EC50	2140					
	shoot dw	EC50	2576					
	root ww	EC50	4598					
	root dw	EC50	4963					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Springtails (***O. folsomi***)	mortality	LC50	7588	9 (0, 0.5, 1, 2, 4, 8, 15, 25, 50 mg/g)	6 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	7d test. n=10 loosely sealed lids
	mortality	LC50	4858	10 (0, 1, 2, 4, 6, 8, 10, 15, 25, 50 mg/g)	6 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	7d test. n=10 loosely sealed lids
	mortality	LC50	4678					
	# juveniles	EC50	4882	9 (0, 0.5, 1, 2, 4, 5, 6, 7, 7.5 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	35-36d test. n=10 loosely fitting lids. air exchanged biweekly
	fecundity	EC50	4977					
Worms (***E.fetida***)	mortality	LC50	3984	8 (0, 0.5, 1, 3, 5, 7, 10, 15 mg/g)	6 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	14d test. n=10 perforated lids
	mortality	LC50	5251	7 (0, 1, 3, 6, 8, 10, 24 mg/g)	6 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	14d test. n=10 perforated lids
	mortality	LC50	5729	7(0, 1, 3, 6, 8, 10, 24 mg/g)	6 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	14d test. n=10 perforated lids
	mortality	LC50	4200	8 (0, 1, 2, 3, 4, 6, 8, 10 mg/g)	6 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	14d test. n=3 perforated lids
Worms (***E.fetida***) **(cont'd)**	# juveniles	EC20	842	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1, 2, 3, 4 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids. values for IC/EC
	juvenile ww	EC20	1183	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1, 2, 3, 4 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids. values for IC/EC
	juvenile dw	EC20	968	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1, 2, 3, 4 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids. values for IC/EC
	# juveniles	EC50	1633	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1, 2, 3, 4 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids. values for IC/EC

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	juvenile ww	EC50	1807	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1, 2, 3, 4 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids. values for IC/EC
	juvenile dw	EC50	1714	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1, 2, 3, 4 mg/g)	10	nominal	Field soil Delacour Orthic Black Chernozem	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids. values for IC/EC
Worms (***L. terrestris***)	mortality	LC50	4112	8 (0, 1, 2, 3, 4, 6, 8, 10 mg/g)	6 control 3 trt	nominal	Artificial: 70% silica sand; 20% keolinite clay;10% sphagnum peat	14d test. n=3 perforated lids
	mortality	LC50	64158	8 (0, 1, 2, 3, 4, 6, 8, 10 mg/g)	6 control 3 trt	nominal	Field soil Delacour Orthic Black Chernozem	14d test. n=3 perforated lids

(after Stephenson et al., 1999)

Appendix F: Toxicity comparison of Federated Whole Crude Oil and its derived fractions.

Table F.1: Direct comparison of the toxicity of Federated Whole Crude with CWS fractions derived from it (and with Mogas) (expressed as $EC(LC)_{50}$ nominal soil concentrations, in mg/kg).

Taxon	Endpoint	Exposure Period	$LC(EC)_{50}$ PHC conc.						
			whole crude	F3	F3/ whole	F2	F2/ whole	mogas (F1)	mogas/ crude
springtail (*O.folsomi*)	mortality	7 day (all)	6070	6300	**1.04**	3070	**0.51**	5000	**0.82**
	# juveniles	35-36 day (all)	4880	1490	**0.31**	1470	**0.30**	2890	**0.59**
	fecundity		4980	1410	**0.28**			3420	**0.69**
worms (*E. foetida)*	mortality (open container)	14 day (all)	1150	22360	**19.4**	780	**0.68**	1860	**1.62**
	# juveniles	61, 57, 62 day	1,630	776	**0.48**	490	**0.30**		
	juvenile ww		1,810	854	**0.47**	590	**0.33**		
	juvenile dw		1,710	809	**0.47**	580	**0.34**		
worm (*L.terrestris*)	mortality	14 day (all)	5,140	18,600	**3.62**	1110	**0.22**		
alfalfa	shoot length	11, 8, n/a, 11 day	39,600	51900	**1.31**			6600	**0.17**
	root length		2,340	10000	**4.27**			4580	**1.96**
	whole dw		27,100	72300	**2.67**			8220	**0.30**
	whole ww		270,000	72300	**0.27**			6750	**0.03**
	shoot length	20, 26, 21, 21 day	19877	8300	**0.42**	2710	**0.14**	5130	**0.26**
	root length		30768	8300	**0.27**	1860	**0.06**	3900	**0.13**
	shoot wet wt		5358	2100	**0.39**	1680	**0.31**	2710	**0.51**
	shoot dry wt		13330	2300	**0.17**	1370	**0.10**	2520	**0.19**
	root wet wt		50187	4400	**0.09**	4740	**0.09**	2980	**0.06**
	root dry wt		60194	5500	**0.09**	5120	**0.09**	2970	**0.05**
barley (*H. vulgare*)	shoot length	7, 7, 8, 7 day	80598	72400	**0.90**	7150	**0.09**	7240	**0.09**
	root length		44004	83400	**1.90**	2770	**0.06**	4480	**0.10**
	shoot ww		53712	65700	**1.22**	6610	**0.12**	7860	**0.15**
	shoot dw		64965	87200	**1.34**	8240	**0.13**	7790	**0.12**
	root ww			90800		4460		4310	
	root dw		59161	95300	**1.61**	4370	**0.07**	4780	**0.08**
barley (Chapais)	shoot length	13, 14, 13, 13 day	15268	27600	**1.81**	4130	**0.27**	1680	**0.11**
	root length		10682	3200	**0.30**	4550	**0.43**	1600	**0.15**
	shoot ww		9060	54100	**5.97**	2430	**0.27**	1360	**0.15**

Taxon	Endpoint	Exposure Period	$LC(EC)_{50}$ PHC conc.						
			whole crude	F3	F3/ whole	F2	F2/ whole	mogas (F1)	mogas/ crude
	shoot dw		4519	53300	**11.79**	2590	**0.57**	1220	**0.27**
	root ww		4052	8700	**2.15**	2390	**0.59**	870	**0.21**
	root dw		4740	35100	**7.41**	2510	**0.53**	960	**0.20**
corn (*Z. mays*)	shoot length	6 day						8379	
	root length							9006	
	shoot ww							2912	
	shoot dw							9010	
	root ww							8612	
	root dw							4764	
corn (Kandy Korn)	shoot length	14 day	47680						
	root length		8103						
	shoot ww		53532						
	shoot dw		51973						
	root ww		26253						
	root dw		47964						
northern wheat grass	shoot length	9, 7 day	27900	42100	**1.51**				
	root length		19600	51100	**2.61**				
	whole ww		51400	26700	**0.52**				
	whole dw		29100	24800	**0.85**				
	shoot length	20, 25, 14 day	6671	12700	**1.90**	7440	**1.12**		
	root length		6671	7300	**1.09**	2320	**0.35**		
	shoot ww		2140	610	**0.29**	2770	**1.29**		
	shoot dw		2576	1400	**0.54**	3150	**1.22**		
	root ww		4598	890	**0.19**	1560	**0.34**		
	root dw		4963	1100	**0.22**	1370	**0.28**		

Appendix G: Toxicity of PHCs in weathered soils.

For soil invertebrates and plants, toxicity tends to occur when the molar concentration of the organic toxicant in an organism's lipid pool exceeds a critical threshold (McCarthy and Mackay 1993). Non-specific mechanisms associated with membrane disruption, increased membrane fluidity, loss of membrane polarization, and a host of related biochemical perturbations (often termed 'narcosis' in animals) are often assumed to be the major mode of toxicological action (Van Wenzel *et al*. 1996). The contribution of individual non-polar toxicants to such a common, non-specific toxicological response is often assumed to be additive, with the contribution of individual toxicants being influenced primarily by bioavailability, lipophilicity, and resistance to rapid metabolic modification and elimination from the body. The bioavailability, in particular, is expected to be controlled by specifics of the interaction between an organism and the immediate soil microenvironment. Narcosis-type modes of action are often taken as the base case for toxicity in soil invertebrates and plants (Parkerton and Stone, *in press*); however, more specific toxicological modes of action should not be discounted – e.g., for PAHs effects on earthworms through photo-induced toxicity (Erickson et al. 1999).

Weathering of petroleum hydrocarbons in a soil environment through biodegradation and other loss mechanisms results in the differential loss of more easily degraded constituents among the original mix of unsubstituted and alky-PAHs, alkane, hopanes, isoprenoids (aliphatic and non-aromatic cyclic hydrocarbons) and other compounds. The loss of PHC mass can occur through either partial or complete mineralization, to produce CO_2 and H_20. Partial breakdown can lead to metabolic intermediates with similar or greater toxic potency than the parent substance.

The relative composition of PAHs, n-alkanes and isoprenoids has been used to evaluate the degree of weathering, and specific processes involved during biodegradation and environmental partitioning (Didyk and Simoneit 1989, Rogues *et al.* 1994, Wang *et al.* 1995). A slightly degraded oil is usually indicated by the partial depletion of n-alkanes; a moderately degraded one is often indicated by the substantial loss of n-alkanes and partial loss of lighter PAHs. Highly degraded mixtures may be accompanied by almost complete loss of n-alkanes along with unsubstituted, but less so more highly alkylated PAHs. Several indices have been proposed to provide a measure of weathering (Rogues et al. 1994). One index is the nC17/pristine and nC18/phytane ratios. As the more easily degraded normal hydrocarbons (nC17 and nC18) are lost, the more recalcitrant isoprenoids (pristane and phytane) are conserved. The corresponding n-alkane/isoprenoid ratio in a moderately weathered sample is less than one. In very highly weathered samples, a substantial proportion of the isoprenoids is also lost. Hopanes, however, tend to be preserved until the latter stages of overall PHC degradation, and are especially prevalent if weathering occurs by biodegradation.

One of the challenges in assessing the relative toxicity of fresh versus weathered PHCs is that the relative toxicity of the above-mentioned classes of PHCs is not

known. Where residual hydrocarbons fall in the >nC34 range, the relative toxicity is likely not an issue, since the bioavailability, and – hence – toxicity of all individual constituents is expected to be very limited (TPHCWG 1999). For the F3 fraction, however, it is not known whether n-alkanes, isoprenoids, and hopanes have equivalent bioavailability and ecotoxicity.

The above-mentioned indices are applicable primarily to crude oils, and the degree of weathering is most easily assessed when complex compositional data are available for the fresh product that was released at a site. If a management approach is to be used that accounts for effects of weathering at a field site, then there is an added requirement to be able to objectively and transparently define the degree of weathering which has occurred, either generically or on a site-specific basis.

According to Irwin et al. (1997) –

> “The word "fresh" cannot be universally defined because oil breaks down faster in some environments than in others. In a hot, windy, sunny, oil-microbe-rich, environment in the tropics, some of the lighter and more volatile compounds (such as the Benzene, Toluene, Ethyl Benzene, and Xylene compounds) would be expected to disappear faster by evaporation into the environment and by biodegradation than in a cold, no-wind, cloudy, oil-microbe-poor environment in the arctic. In certain habitats, BTEX and other relatively water-soluble compounds will tend to move to groundwater and/or subsurface soils (where degradation rates are typically slower than in a sunny well aerated surface environment). Thus, the judgement about whether or not oil contamination would be considered "fresh" is a professional judgement based on a continuum of possible scenarios.
>
> The closer in time to the original spill of non-degraded petroleum product, the greater degree the source is continuous rather than the result of a one-time event, and the more factors are present which would retard oil evaporation or breakdown (cold, no-wind, cloudy, oil-microbe-poor conditions, etc.) the more likely it would be that in the professional judgement experts the oil would be considered "fresh." In other words, the degree of freshness is a continuum which depends on the specific product spilled and the specific habitat impacted. Except for groundwater resources (where the breakdown can be much slower), the fresher the middle distillate oil contamination is, the more one has to be concerned about potential impacts of BTEX compounds, and other lighter and more volatile petroleum compounds.”

G.1.0 Studies by Visser et al. (in progress)

Visser (in progress) is conducting a study of the effects of aging on the toxicity of Federated Whole Crude to soil invertebrates and plants. The experiment was conducted in three different soil types:

i) Sandy soil (82.5% sand, 9% silt, 9% clay);
ii) Loam (18% sand, 48% silt, 34% clay); and
iii) Clay (16% sand, 33% silt, 51% clay).

Toxicity endpoints included a 14 day survival assay for earthworms *(E. fetida*) and 4-5 day germination and root elongation test for lettuce and barley. Residual soil concentrations for PHCs were generated by adding fresh crude oil to each soil treatment and incubating the soil at room temperature for three months; at this point all of the treatments had achieved a stable or near stable endpoint (Visser, pers. comm.). Preliminary results are shown in Tables G.1 through G.6.

Visser et al., as well as Stephenson et al. (1999) also characterized the fresh Federated Whole Crude oil. The initial composition, prior to weathering is as follows:

C1-C5:	2.8%
C6-C10 (CWS F1):	**23.2%**
C11-C16 (CWS F2):	**21.3%**
C17-C22:	16.0%
C23-C35:	8.5%
SUM OF LAST 2 (CWS F3):	**34.5%**
>C35 (CWS F4):	**18.2%**

Table G.1: Ecotoxicity of artificially weathered Federated Whole Crude residuals in sand: Earthworm (*Eisenia fetida)* survival.

- 14 days exposure in soil (Data are means ± standard deviation) (n = 3; 15 worms/replicate)

Original Oil Dosage (mg/kg)	Crude Oil Residual (mg/kg)					% Earthworm Survival
	Total	CWS F1 (C6-C10)	CWS F2 (>C10-C16)	CWS F3 (>C16-C34)	Fraction 4 (>C34-C60+)	
0	137	0 (0%)	0 (0%)	19 (13.95)	118 (86.1%)	**100**
6000	1785	0 (0%)	21 (1.2%)	645 (36.1%)	1119 (62.7%)	**100**
12000	3473	0 (0%)	49 (1.4%)	1145 (3.0%)	2279 (65.6%)	**96.7 ± 5.8**
***24000**	7433	**1** (0%)	**240** (3.2%)	**2711** (36.5%)	**4481** (60.3%)	**100**
48000	17251	6 (0%)	794 (4.6%)	6797 (39.4%)	9654 (56.0%)	**13.3 ± 15.3**
96000	44465	15 (0%)	3097 (7.0%)	20842 (46.9%)	20511 (46.1%)	**0**

*shaded row represents NOEC.

Table G.2: Ecotoxicity of artificially weathered Federated Whole Crude residuals in sand: Seed germination, root elongation by lettuce and barley in soil.

- Butter lettuce – 5 day assay (30 seeds/rep); Barley – 4 day assay (20 seeds/rep)
- Data are means ± standard deviation (n = 3)

Orig. Oil Dosage (mg/ kg)	Crude Oil Residual (mg/kg)					Lettuce % germin.	Lettuce (cm root/ plant)	Barley (% germ.)	Barley (cm root/ plant)
	Total	CWS F1	CWS F2	CWS F3	CWS F4				
0	137	0	0	19	118	78.9± 11.7	4.7±0.1	85±8.7	8.0±0.6
6000	1785	0	21	645	1119	71.1± 7.7	8.6±0.6	85±13	8.4±0.4
12000	3473	0	49	1145	2279	81.1± 5.1	8.2±1.3	90±0	9.9±0.6
*24000	7433	**1**	**240**	**2711**	**4481**	70.0± 23.3	6.6±1.4	80±10.0	10.0±0.9
48000	17251	6	794	6797	9654	28.9± 28.8	3.2±2.8	73.3±34	4.6±3.1
96000	44465	15	3097	20842	20511	0	0	50± 32.8	1.3±0.2

*shaded row represents NOEC.

Table G.3: Ecotoxicity of artificially weathered Federated Whole Crude residuals in loam: Earthworm (*Eisenia fetida)* survival.

– 14 days exposure in soil (Data are means ± standard deviation) (n = 3; 15 worms/replicate)

Original Oil Dosage (mg/kg)	Crude Oil Residual (mg/kg)					% Earthworm Survival
	Total	CWS F1	CWS F2	CWS F3	CWS F4	
0	1416	0 (0%)	7 (0.5%)	106 (7.5%)	1303 (92.0%)	100
6000	6906?	0 (0%)	68 (1.0%)	1637 (23.7%)	5201 ((75.3%)	100
12000	7990	1 (0.0%)	143 (1.8%)	2435 (30.5%)	5411 (67.7%)	100
24000	11240	1 (0.0%)	209 (1.9%)	3915 (34.8%)	7115 (63.3%)	100
48000	23912	2 (0.0%)	662 (2.8%)	8535 (36.7%)	14713 (61.5%)	100
*96000	29603	**3 (0.0%)**	**780 (2.6%)**	**10253 (34.6%)**	**18567 (62.7%)**	100

*shaded row represents NOEC.

Table G.4: Ecotoxicity of artificially weathered Federated Whole Crude residuals in loam: Seed germination, root elongation by lettuce and barley in soil.

- Butter lettuce – 5 day assay (30 seeds/rep); Barley – 4 day assay (20 seeds/rep)
  - Data are means ± standard deviation (n = 3)

Original Oil Dosage (mg/kg)	Crude Oil Residual (mg/kg)					Lettuce % germ.	Lettuce (cm root/ plant)	Barley (% germin.)	Barley (cm root/ plant)
	Total	CWS F1	CWS F2	CWS F3	CWS F4				
0	1416	0	7	106	1303	78.9± 10.7	4.7±0.5	86.7±7.6	7.1±0.3
6000	6906	0	68	1637	5201	38.7± 18.9	4.6±0.3	86.7±2.9	7.2±0.7
12000	7990	1	143	2435	5411	56.7± 12.1	5.2±0.3	95±5	7.0±0.4
24000	11240	1	209	3915	7115	55.6± 11.7	6.1±0.2	91.7±10.4	7.8±0.6
48000	23912	2	662	8535	14713	51.1±7.7	8.9±0.3	91.7±2.9	10.3±0.7
*96000	29603	**3**	**780**	**10253**	**18567**	57.8± 11.7	9.2±0.6	88.3± 7.6	10.2±0.6

*shaded row represents NOEC.

Table G.5: Ecotoxicity of artificially weathered Federated Whole Crude residuals in clay: Earthworm (*Eisenia fetida)* survival.

- 14 days exposure in soil (Data are means ± standard deviation) (n = 3; 15 worms/replicate)

Original Oil Dosage (mg/kg)	Crude Oil Residual (mg/kg)					% Earthworm Survival
	Total	CWS F1	CWS F2	CWS F3	CWS F4	
0	904	0 (0.0%)	2 (0.2%)	70 (7.7%)	832 (92.0%)	100
6000	3765	1 (0.0%)	128 (3.4%)	1359 (36.1%)	2277 (60.5%)	100
12000	6201	3 (0.0%)	243 (3.9%)	2290 (36.9%)	3665 (59.1%)	100
24000	16514	8 (0.0%)	993 (6.0%)	7462 (45.2%)	8051 (48.8%)	100
*48000	28554	**13 (0.0%)**	**1942 (6.8%)**	**13717 (48.0%)**	**12882 (45.1%)**	100
96000	62427	22 (0.0%)	6049 (9.7%)	32430 (51.9%)	23926 (38.3%)	23.3±40.4

*shaded row represents NOEC.

Table G.6: Ecotoxicity of artificially weathered Federated Whole Crude residuals in clay: Seed germination, root elongation by lettuce and barley in soil.

- Butter lettuce – 5 day assay (30 seeds/rep); Barley – 4 day assay (20 seeds/rep)
- Data are means ± standard deviation (n = 3)

Original Oil Dosage (mg/kg)	Crude Oil Residual (mg/kg)					Lettuce % germin.	Lettuce (cm root/ plant)	Barley (% germin.)	Barley (cm root/ plant)
	Total	CWS F1	CWS F2	CWS F3	CWS F4				
0	904	0	2	70	832	67.8± 10.7	5.6±0.1	93.3±2.9	10.0±1.0
6000	3765	1	128	1359	2277	67.8±5.1	6.9±0.3	88.3±2.9	10.2±0.7
12000	6201	3	243	2290	3665	70.0± 10.0	9.2±0.8	95.0±5.0	11.8±0.6
24000	16514	8	993	7462	8051	57.8± 15.7	9.2±0.9	91.7±7.6	11.4±0.1
48000	28554	13	1942	13717	12882	57.8±8.4	8.7±0.5	93.7±7.1	10.4±0.2
*96000	62427	**22**	**6049**	**32430**	**23926**	50.0±8.8	7.5±0.5	96.7± 5.8	9.5±0.6

*shaded row represents NOEC.

These results clearly show that a measured F3 soil concentration between 2,700 and 32,000 mg/kg soil did not correspond to increased mortality to earthworms (14 day exposure), or reduced germination or reduced root elongation in lettuce and barley (4-5 day exposure). This is substantially higher than the estimated 25th percentile of the LC/EC_{50} data (250 to 620 mg/kg F3) for toxicity of F3 from fresh federated crude oil to soil invertebrates and plants (Section 4.2.4). It should be noted, however, that the lowest ECx from the Stephenson et al (2000b) study were for much longer exposure periods, and for potentially more sensitive endpoints, such as worm reproduction, as opposed to mortality.

The most sensitive EC_{50} endpoints from Stephenson et al (2000b) for F3 are reproduced immediately below for direct comparison:

- northern wheatgrass shoot wet wt., 25 day EC_{50} — 610 mg/kg nom. = 190 mg/kg init.
- worm (*E. foetida*) number of juveniles, 57 day EC_{50} — 776 mg/kg nom. = 240 mg/kg init.
- worm (*E. foetida*) juvenile dry wt., 57 day EC_{50} — 810 mg/kg nom. = 250 mg/kg init.
- northern wheatgrass root wet wt., 25 day EC_{50} — 890 mg/kg nom. = 280 mg/kg init.
- springtail (*O. folsomi*) adult fecundity, 35-36 day EC_{50} — 1410 mg/kg nom. = 440 mg/kg init.
- alfalfa shoot wet wt, 26 day EC_{50} — 2100 mg/kg nom.

The NOEC levels from Visser (in progress) for the CWS F2 fraction also occurred at much higher residual PHC concentrations that the 25th percentile of EC/LC_{50} concentration based on the study by Stephenson et al. (2000a) with one exception. The plant germination/growth or worm mortality NOEC test unit had a measured F2 concentration of 240 mg/kg. The sand test unit with a residual F2 and F3 concentration of around 790 mg/kg and 6800 mg/kg, respectively, corresponded to an average earthworm survivorship of 13%, and a reduction in germination or root length from around 10 to 70%.

Visser's study also shows that weathering has the potential to reduce PHC concentrations for the F1 and F2 fractions to levels that are lower than the previously discussed 25th percentile of soil invertebrate EC(LC)$_{50}$ values, but less so for the F3 fraction.

The degree to which weathering changes the relative proportions of the light to heavy CWS fractions varies as a function of both soil type and initial soil concentration.

G.2.0 Studies by Saterbak et al.

Saterbak et al. have carried out extensive studies on the effects of PHC weathering and bioremediation on toxicity to soil invertebrates and plants, using methods similar to those of Stephenson et al. and Visser (summarized briefly above). Details of the larger set of studies are provided in Saterbak et al. (1999; in press) and in Wong et al. (1999).

Seven field-collected soils contaminated with crude oil and one contaminated with a spilled lubricating oil, were used for toxicity testing before and after a period of 11-13 months of bioremediation, simulated in the laboratory. Toxicity test organisms and endpoints included earthworm (*E. fetida*) avoidance, survival and reproduction, as well as seed germination and root elongation in four plant species. Saterbak (*in press*) clearly demonstrated that the survival, reproduction, or growth of test organisms remained high or was improved following bioremediation.

Saterbak et al (1999) focused their objectives on the evaluation of ecotoxicity test methods applicable to use in Tier II or III evaluations of PHC contaminated sites. This guidance, along with subsequent work by Stephenson et al., is directly applicable to the possible adoption of site-specific toxicity test methods for PHC CWS Tier II evaluations.

The study by Wong et al. (1999) applied multivariate statistical techniques to detailed physical and chemical soil characterization data (e.g. soil particle size, asphaltenes, TPH, aromatics, ring saturates) for the same eight PHC-contaminated soils as predictors of toxicity to earthworms and plants.

Saterbak kindly made the larger ecotoxicity and soil chemistry database available to EcoTAG, in support of PHC CWS derivation efforts. The eight soils studied were analyzed prior to and following a year of laboratory-based remediation for TPH (C6 to C25) by GC-FID, following pentane extraction. Results are provided in Figures G.1 and G.2.

The results of this analysis allowed the re-allocation of TPH results into the PHC CWS fractions F1 and F2, as well as the lighter end of F3 (>nC16 to C25). A more complex speciation of samples prior to bioremediation provided a more complete breakdown from C5 up to C60+, and included the quantification of *n*- and *iso*-alkanes, aromatics, polar compounds, and asphaltenes. This allowed for the further reconstruction of soil (and exposure) concentrations of all four CWS fractions including all of F3 and F4; however, similar data were lacking for the post-remediation soils.

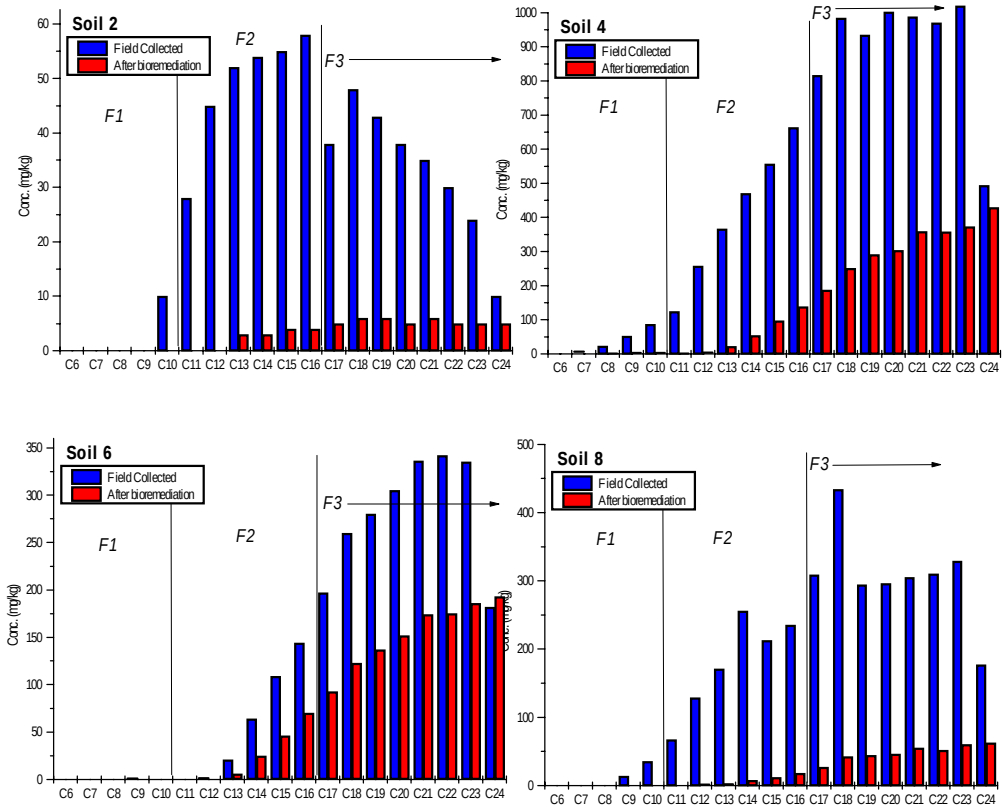


Figure G.1: C6 to C24 PHC carbon profiles for field collected and subsequently bioremediated soils.

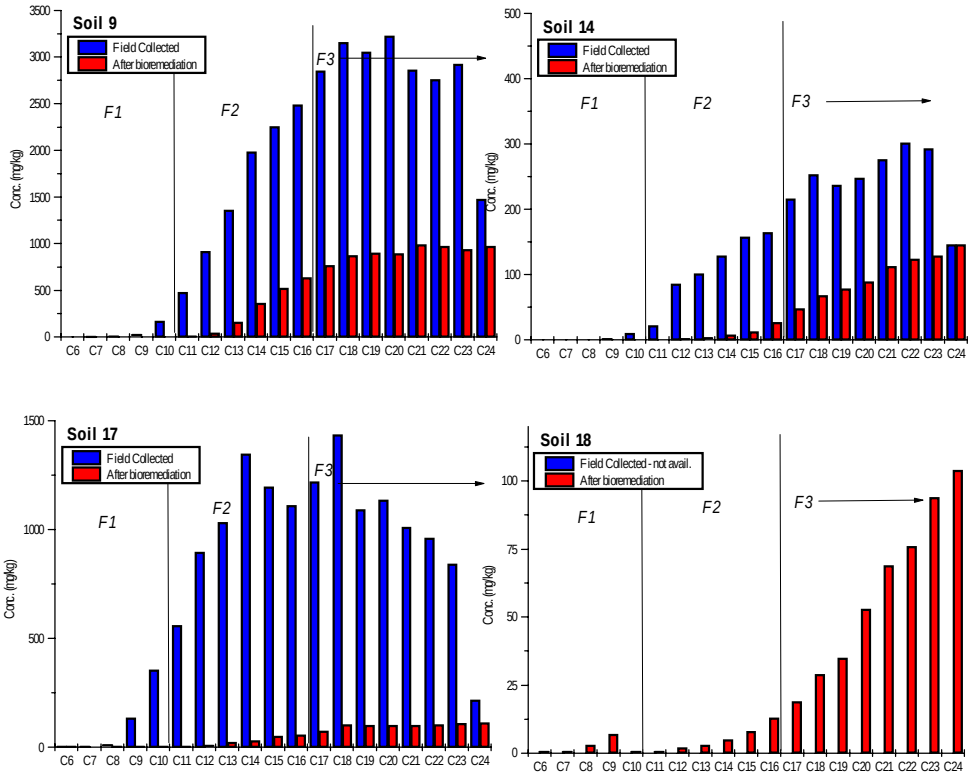


Figure G.2: C6 to C24 PHC carbon profiles for field collected and subsequently bioremediated soils.

Table G.7: Summary of ecotoxicity data from Saterbak et al.

		Soil Conc. (mg/kg)															
		Soil 2		Soil 4		Soil 6		Soil 8		Soil 9		Soil 14		Soil 17		Soil 18	
Date		**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**
Carbon Number																	
c6-nC10		0	0	88	5.3	1.6	0	14	0	54	0	2	0	155	3		12
>nC10-C16		244	10	1864	185	196	77	871	25	7176	1103	505	28	5388	123		20
>C16-C34		1053		25539		9474		4518		38735		4144		14870		10379	
>C16-C21	TPH	224	26	4402	1172	1187	575	1568	178	14784	4076	1117	311	5998	437	0	150
>C16-C21	BDC data	392		7633		2238		1336		10511		975		5704		735	
>C21-C34	BDC data	662		17906		7236		3181.6		28224		3168		9166		9644.1	
>C34	BDC data	1415		21596		16935		2799.2		28827		6103		4484		8928	
TPH by GC		567	56	9830	2880	2580	1380	3580	433	32000	9050	2640	851	14600	992	1490	523
Soil - percent of original, mixed with clean site ref.																	
Earthworm - E. fetida - Average																	
7-Day Acute	LC25		>100		>100		>100		>100		15.2		>100		>100		>100
14-Day Acute	LC25	>100	>100	7.8	>100	78	>100	>100	>100		15.0	>100	>100	10	>100	>100	>100
Chronic	LC25		>100		>100		>100		>100	-	15.0		>100		>100		>100
Juveniles/Adult/Week	EC25	28	no data	10	6.3	23	0.91	0.9	8.9	-	0.36	-	17.4	1.2	6.6	4.0	50
Cocoons/Adult/Week	EC25	no data	no data	7.9	12.1	24	32	4.3	7.8	-	0.39	-	16.5	2.8	22	1.7	>100
Plant germination - Average																	
Corn	EC25	100	100	100	100	90	100	100	100	50	23	100	100	100	100	100	100
Lettuce	EC25			4.9	14	26	94	7.5	99	1.4	0.26	2.0	94	31	21	77	79
Mustard	EC25	8.0	55	8.7	15	18	88	23	98	0.70	0.17	1.3	41	18.8	100	87	88
Wheat	EC25	100	100	87	90	64	88	100	100	32	25	100	100	100	100	100	100
Plant root elongation - Average																	
Corn	EC25	100	100	25	45	35	100	14	19	20	18	100	100	28.75	100	100	46
Lettuce	EC25			7.8	1.8	14	70	14	65	0.90	0.14	1.5	32	20	7.3	100	74
Mustard	EC25	24		14	38	7.4	53	81	100	0.55	0.23	18	70	14	100	100	100
Wheat	EC25	100	100	55	41	30	72	100	89	17	3.8	50	88	50	100	100	100

Table G.8: Estimation of F2 and F3 EC25-equivalent concentrations for eight field-collected and subsequently bioremediated PHC contaminated soils (after Saterbak et al).

	Soil 2		Soil 4		Soil 6		Soil 8		Soil 9		Soil 14		Soil 17		Soil 18	
Date	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**	**Dec-95**	**Jul-97**
Lowest observed EC25 (% of PHC contaminated soil)																
min (%)	**8.0**	**55**	**4.9**	**1.8**	**7.4**	**0.91**	**0.90**	**7.8**	**0.55**	**0.14**	**1.3**	**17**	**1.2**	**6.6**	**1.7**	**46**
Estimated concentration of PHCs in test unit, expressed as PHC CWS F2 and F3 (in mg.kg soil)																
F2	*20*	*5.4*	*91*	*3.3*	*15*	*0.7*	*7.8*	*2.0*	*39*	*1.5*	*6.6*	*4.7*	*65*	*8.1*		*8.9*
F3a	*18*	*14*	*214*	*21*	*88*	*5.2*	*14*	*14*	*81*	*5.7*	*15*	*51*	*72*	*29*		*68*
F3	*85*		*1243*		*701*		*41*		*213*		*54*		*178*		*176*	
Lowest observed EC25, excluding worm reproductive endpoints (% of PHC contaminated soil)																
min(2)(%)	**8.0**	**55**	**4.9**	**1.8**	**7.4**	**53**	**7.5**	**19**	**0.55**	**0.14**	**1.3**	**32**	**10**	**7.3**	**77**	**46**
Estimated concentration of PHCs in test unit, expressed as PHC CWS F2 and F3 (in mg.kg soil)																
F2	*20*	*5.4*	*91*	*3.3*	*15*	*41*	*65*	*4.8*	*39*	*1.5*	*6.6*	*9.1*	*539*	*8.9*		*8.9*
F3a	*18*	*14*	*214*	*21*	*88*	*306*	*117*	*34*	*81*	*5.7*	*15*	*101*	*600*	*32*		*68*
F3	*85*		*1243*		*701*		*337*		*213*		*54*		*1487*		*7940*	

Notes: 1) F3a comprises all PHCs in the boiling point range spanned by >nC16 to nC21.

The re-interpreted results shown in Table G.7 and G.8 show that both field collected and bioremediated soils can result in inhibition of growth and plant germination, as well as mortality in earthworms, when they contain concentrations between 2 and 540 mg/kg when expressed as CWS F2, or between 54 and 8000 mg/kg when expressed as CWS F3.

Because the soils used in these series of experiments were field-collected soils, there is a possibility that an appreciable portion of the observed toxicity was due to the presence of co-contaminants such as metals, as opposed to the PHCs present.

The lack of detailed chemical characterization of the soils following bioremediation for the >C24 range limits the conclusions that can be drawn regarding environmentally protective thresholds for this PHC fraction. It also limits any examination of the relative compositional change within the F3 fraction as a result of bioremediation; e.g., the relative composition of F3 as >nC16 to C21 versus >C21 to C34.

PERF (1999) concluded–

> "…that acute toxicity to earthworms was unlikely to occur at concentrations less than 4,000 mg/kg TPH (by GC) and should be expected to occur at TPH concentrations in excess of 10,000 mg/kg. Within the range of 4,000 mg/kg to 10,000 mg/kg, it is uncertain whether acute effects on individual earthworms will occur."

It is difficult to understand the basis for this conclusion based on the underlying studies. In addition, PERF (1999) ignored the data on worm reproduction and plant responses in their conclusions regarding "Hydrocarbon Uptake by Ecological Receptors".

Of the original eight soils, all induced detrimental effects in at least one test organism and endpoint prior to remediation. In most cases, bioremediation reduced the presence or severity of adverse effects, as indicated by an improvement in the EC_{25} (as % of soil used in test unit). It is interesting to note, from Table G.8, however, that there was evidence for an increase in the toxicity of some bioremediated soils relative to pre-remediation soils (e.g.: Soil 18: corn and lettuce root elongation; Soil 9: virtually all plant growth and germination endpoints). The studies suggest that earthworm mortality endpoints are relatively insensitive to PHCs relative to other measures. In addition, the studies highlight very large variability in ecotoxicological concentration-response curves across different soil types. Finally, this study highlights the large variations in toxicity associated with soil type.

G.3.0 Alberta Research Council, 1999 Studies

Slaski et al (1999) and Sawatski and Li (1999) summarized studies on the bioremediation of three different land-treated soils (crude oil and brine contaminated top soil; diesel invert mud residue; flare pit sludge). All three wastes were bioremediated using a bioreactor system for 1, 2 or 3 years, and subsequently land-farmed in 1996. Subsequent land-based remediation has been followed for three years after the initial

placement. As of 1998, decreased ecotoxicity of the three wastes has been observed; however, all three materials exhibited significantly greater toxicity than controls in 1998.

The results of this study do not lend themselves to an evaluation of toxicological thresholds (a dilution series was not used to estimate a soil dilution with clean soil corresponding to a pre-defined ECx).

Sawatski and Li (1999) documented changes over time in the n-alkane composition. This is shown in Table G.9, based on the relative composition of C15-C20, C20-C30, and >C30.

Table G.9: PHC Compositional change in three bioremediated wastes.

		Time 1	Time 2	Time 3	Time 4
Waste 1					
	c10-c15	0	0	15.9	15.3
	c15-c20	2690	821	400	138
	c20-c25	8740	3000	1065	1300
	c25-c30	6160	2200	827	1240
	>c30	9860	3890	3260	2650
	sum	27450	9911	5567.9	5343.3
	c15-20 (% of ~F3)	**15.3%**	**13.6%**	**17.5%**	**5.2%**
Waste 2					
	c10-c15	50700	84	56	0
	c15-c20	41000	2410	1550	745
	c20-c25	3900	1340	792	1600
	c25-c30	0	54	140	494
	>c30	0	0	13	0
	sum	95600	3888	2551	2839
	c15-20 (% of ~F3)	**91.3%**	**63.4%**	**62.4%**	**26.2%**
Waste 3					
	c10-c15	675	270	0	0
	c15-c20	12730	3700	1995	1630
	c20-c25	16100	6960	1570	4230
	c25-c30	15800	9460	1425	1530
	>c30	19900	14900	9785	4740
	sum	65205	35290	14775	12130
	c15-20 (% of ~F3)	**28.5%**	**18.4%**	**40.0%**	**22.1%**

(Adapted from Sawatski and Li, 1999)

G.4.0 Study of Soils from a Former Refinery Site in Montreal

Miasek (pers. com.) provided a summary of a study commenced in 1996 and undertaken jointly by Imperial Oil, Exxon Biomedical Sciences Inc., Environment Canada, and Quebec MEF on the remediation and ecotoxicity of PHC-contaminated soils found at a former refinery site in Montreal, Quebec. Five soils were tested, as follows:

Table G.10: Summary of Montreal former refinery test soils.

Soil	Mineral Oil and Grease Conc. (mg/kg)	GC Boiling Pt. Range, C	Weight percent of – saturated/ aromatics/ polars	Weight percent of aromatic carbon	No. of soil toxicity tests (4 different test organisms ea.)
Reference	< 40	n/a	n/a	n/a	0
Thermally treated	< 40	n/a	n/a	n/a	3
Contam.at < criterion	2,000	170/430/640	26/48/26	29	1
Biotreated	3,100	220/460/590	25/46/29	27	0
Contam.at > criterion	6,900	160/410/600	29/42/29	29	3

The PHC-contaminated soil “age” was greater than 10 years. The relative composition, redefined as the PHC CWS fractions is as follows:

Table G.11: Percent composition of tested soils.

EC	Contam. at < criterion	Biotreated	Contam. at > criterion
CWS F1	*nd (0.0%)*	*nd (0.0%)*	*nd (0.0%)*
>C8-C10	nd	nd	nd
CWS F2	*20*	*5*	*18*
>C10-C12	5	nd	3
>C12-C16	15	5	15
CWS F3	*45*	*55*	*50*
>C16-C21	15	15	20
>C21-C35	30	40	30
CWS F4	*35*	*40*	*35*
>C35	35	40	35

The compositional data provides limited evidence of the possibility of a shift in the relative proportion of >C16 to C21 versus >C21 to C35 hydrocarbons with the CWS F3 fraction from the bioremediated versus original aged site soil that had a Mineral Oil and Grease (MOG) concentration in excess of MEF criteria.

For the soil type with an initial soil concentration of 6,900 mg/kg MOG, the toxicity test results were as follows:

Table G.12: Toxicity thresholds for former refinery site soil samples.

Organism	Endpoint	Toxicity Unit[A]	Effects Conc (% soil)	Effective MOG conc. (mg/kg)
Soil contaminated at > criterion (6,900 mg/kg MOG)				
Lettuce germination	5 day EC_{20}	**2.4**	**41%**	**2,800**
Cress germination	5 day EC_{20}	**1.0**	**100%**	**6,900**
Cress plant growth	16 day EC_{20}	<1.0	> 100%	>6,900
Barley germination	5 day EC_{20}	**2.0**	**50%**	**3,400**
Barley plant growth	17 day EC_{20}	<1.0	> 100%	>6,900
Earthworm	14 day LC_{50}	<1.0	>100%	>6,900
Soil contaminated at<> criterion (2,000 mg/kg MOG)				
Lettuce germination	5 day EC_{20}	<1.0	>100%	>2,000
Cress germination	5 day EC_{20}	<1.0	>100%	>2,000
Cress plant growth	16 day EC_{20}	<1.0	>100%	>2,000
Barley germination	5 day EC_{20}	<1.0	>100%	>2,000
Barley plant growth	17 day EC_{20}	<1.0	>100%	>2,000
Earthworm	14 day LC_{50}	<1.0	>100%	>2,000
Biotreated Soil (3,100 mg/kg MOG)				
Lettuce germination	5 day EC_{20}	**1.1**	**91%**	2,800
Cress germination	5 day EC_{20}	<1.0	>100%	> 2,800
Cress plant growth	16 day EC_{20}	<1.0	>100%	> 2,800
Barley germination	5 day EC_{20}	<1.0	>100%	> 2,800
Barley plant growth	17 day EC_{20}	<1.0	>100%	> 2,800
Earthworm	14 day LC_{50}	<1.0	>100%	> 2,800
Thermally treated Soil (<40 mg/kg MOG)				
Lettuce germination	5 day EC_{20}	<1.0	>100%	B
Cress germination	5 day EC_{20}	<1.0	>100%	B
Cress plant growth	16 day EC_{20}	**1.6**	**63%**	B
Barley germination	5 day EC_{20}	**1.4**	**71%**	B
Barley plant growth	17 day EC_{20}	<1.0	>100%	B
Earthworm	14 day LC_{50}	**1.4**	**71%**	B

Notes: A) Toxicity Unit , T.U. is defined as 1/[effects Conc (% soil)]; B) it is unlikely that the growth inhibition was attributable to the MOG content, as opposed to alteration of other soil properties during thermal treatment.

A longer term, follow-up study is presently underway. A more detailed chemical characterization of the soils is available, although the PHC constituents appear to have only been analyzed as MOG as well as individual PAHs. The lowest MOG concentration in toxicity test units associated with an effect was 2,800 mg/kg (Table G.12). It is difficult to convert this into an equivalent concentration for the PHC CWS four fractions, due to the highly disparate nature of the different underlying analytical methodologies. In fact, an assumption that MOG concentrations are directly equivalent to TPH measurements using GC-FID approaches as refined for the PHC CWS would not be justified. With this cautionary note in mind, a MOG concentration of 2,800 mg/kg would be divided among the CWS fractions – assuming a direct equivalence of the analytical techniques – as follows: F1 – nd; F2 - 504 mg/kg; F3 – 1,400 mg/kg; F4 – 980 mg/kg.

This can be compared, with some trepidation in the equivalence of the soil concentration data and toxicity endpoints, with the soil toxicity thresholds for fresh Federated Whole

Crude, as provided by Stephenson et al (1999). As shown in Figures 4.17 and 4.18, the 25th percentile for fresh Federated Whole Crude of the EC_{50} (or LC_{50}) soil concentrations for soil invertebrates or plants was 1,600 mg/kg and 5,500 mg/kg, respectively, when expressed as a nominal concentration. In general, this is within the range of thresholds for the higher concentration aged soil from the Montreal site.

G.5.0 Miscellaneous Studies

Figures G.3 through G.7 illustrate the range of toxicological responses encountered, based primarily on data from the primary peer-reviewed literature, including the previously discussed data from studies by Saterbak *et al.,* but excluding data discussed in Sections 4.2.4 to 4.2.6. The data base, which comprised more than a thousand individual toxicity endpoints, was broken down into the following subgroups for analysis:

- by type of whole product used or originally released;
- divided between soil invertebrates and plants
- further divided between fresh versus weathered product; and
- finally divided into the effects database (comprising all non-redundant LOEC, EC_x and LC_x endpoints) and the no-effects database (NOEC endpoints).

The plots show the challenges associated with the reconstruction of multi-species sensitivity curves from toxicity data that were collected for other purposes. The existing whole products database suggests the following:

> The effects and no-effects concentration distribution for soil invertebrates or plants overlapped substantially, in a way that is contrary to the underlying theoretical model for multi-species sensitivity curves.
> There was no evidence that weathered crude oil was less toxic to either soil invertebrates or plants. If anything, the existing data would suggest that fresh product tends to be less toxic to more sensitive species.
> The 25th percentile concentration for the effects endpoint data, if adjusted to reflect expected exposure concentration as opposed to nominal concentration, varied substantially, but were generally consistent with the equivalent 25th percentile estimates for the F3 and F2 distillates.

Figure G.7 shows the distribution of the available weathered and unweathered effects data for diesel or heating oil. The existing database is very limited. At face value, the data suggest that weathered diesel is substantially less toxic to plants than fresh diesel. It is important to note, however, that the diesel (nominal) exposure concentrations were expressed as TPH, generally encompassing >C9 to some upper boiling point limit depending on analytical conditions.

Fresh diesel would be roughly divisible as 50% F2 and 50% F3, as previously discussed. Weathered diesel, on the other hand, would undoubtedly exhibit a very different composition, possibly with a strong proportion of higher end F3 and lower end F4 constituents. Overall, the data do not allow a discrimination between toxicity changes

associated with compositional changes during weathering and other aspects such as the strength of soil sorption.

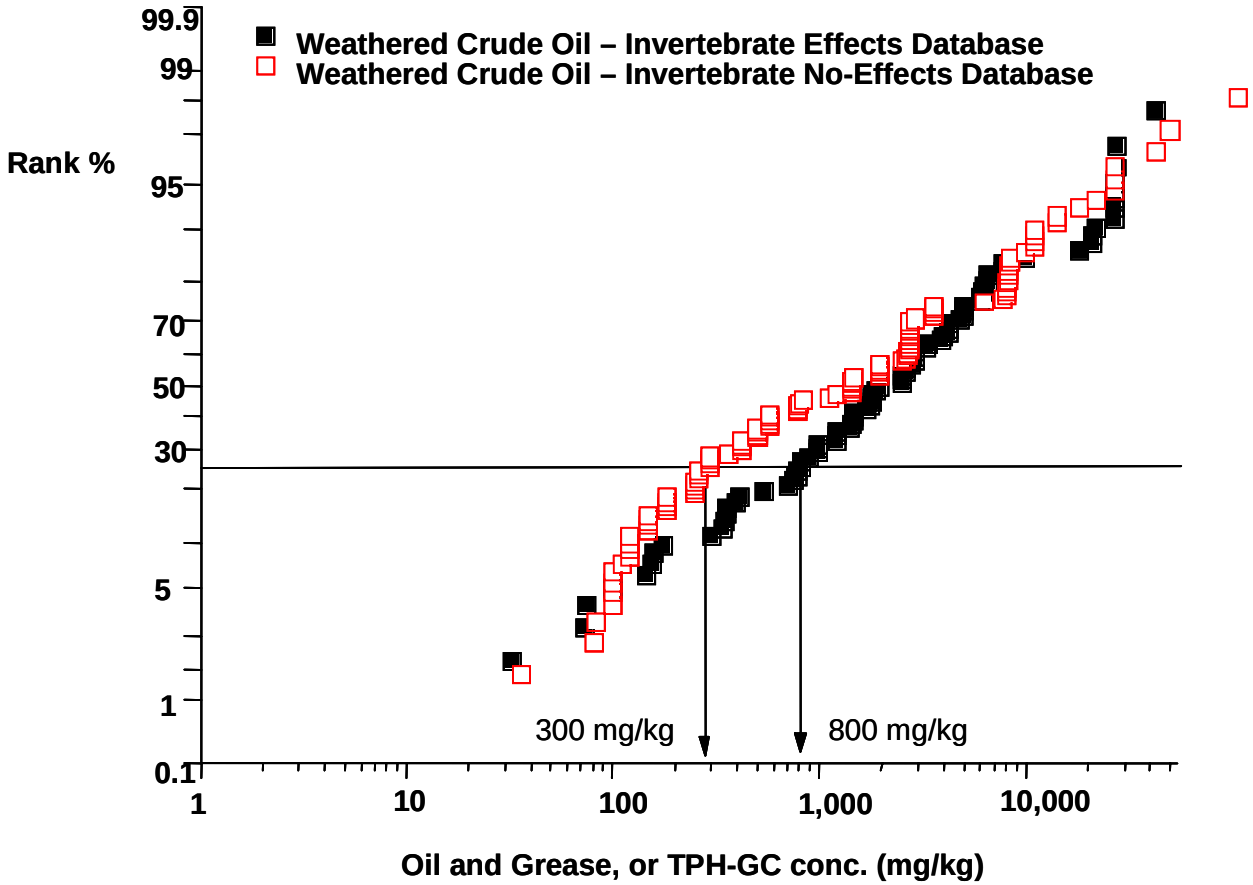


Figure G.3: Ranks data for toxicity of weathered crude oil to soil invertebrates (with comparison of effects and no-effects data distribution).

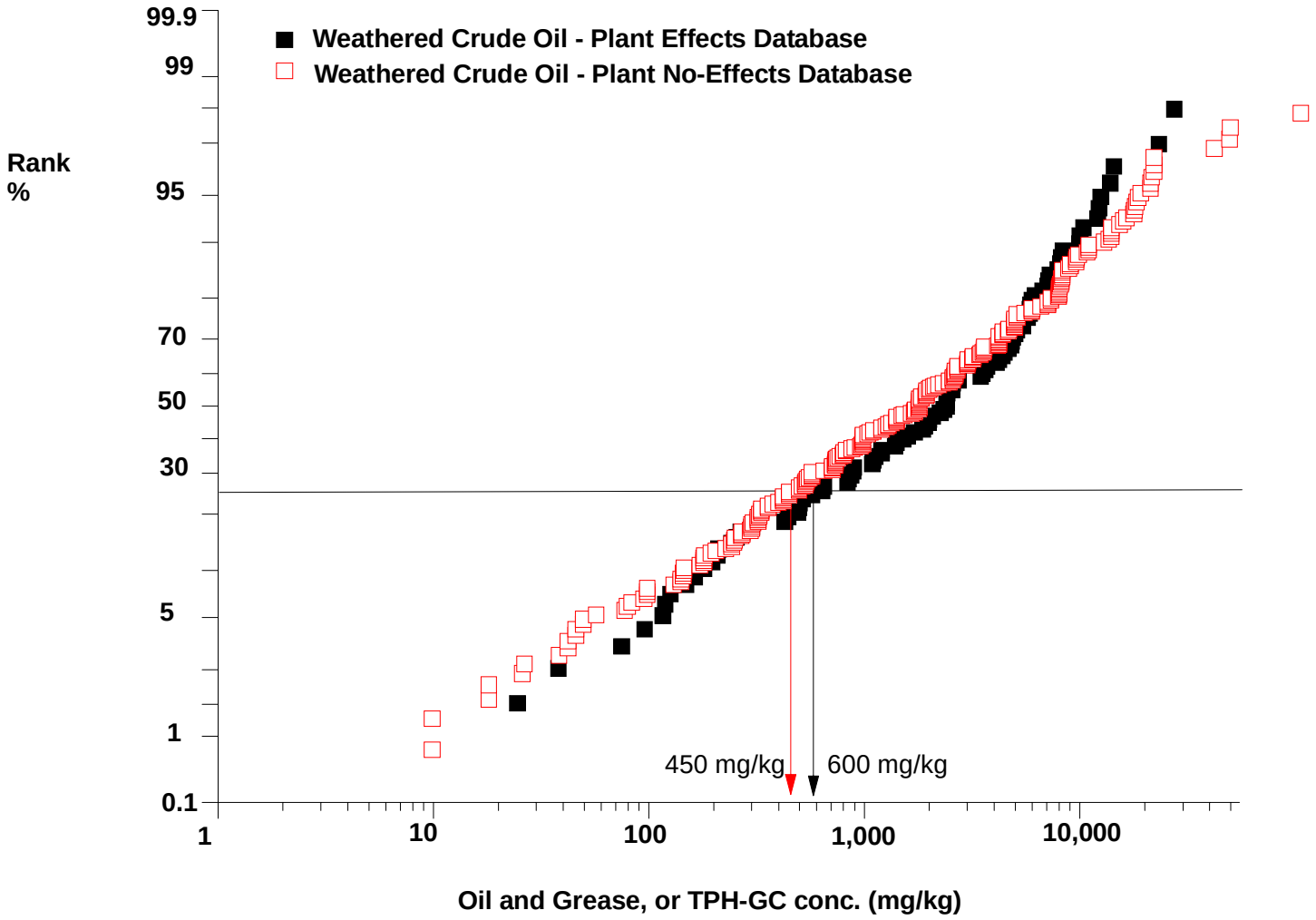


Figure G.4: Ranks data for toxicity of weathered crude oil to plants (with comparison of effects and no-effects data distribution).

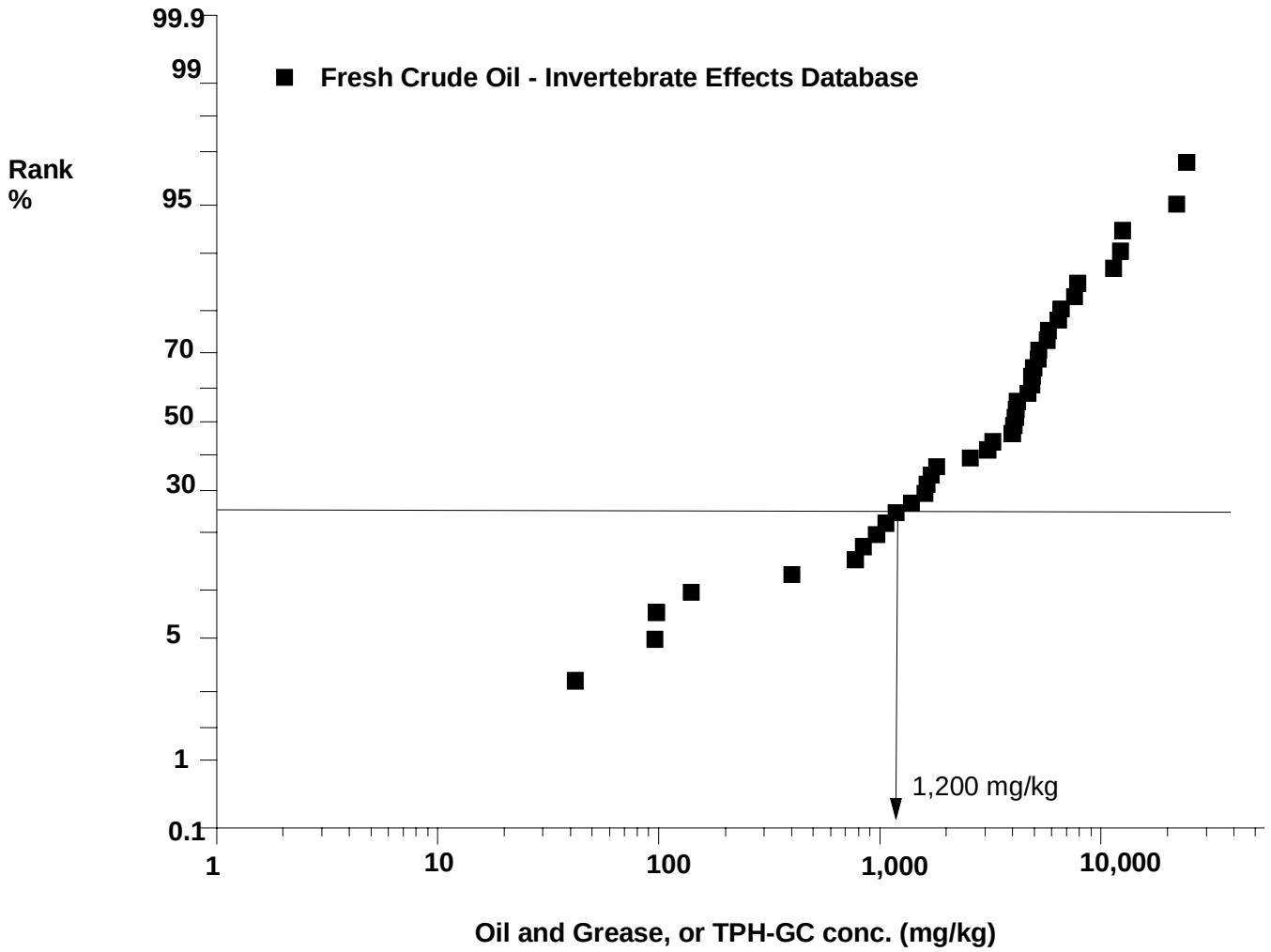


Figure G.5: Ranks data for toxicity of fresh crude oil to soil invertebrates.

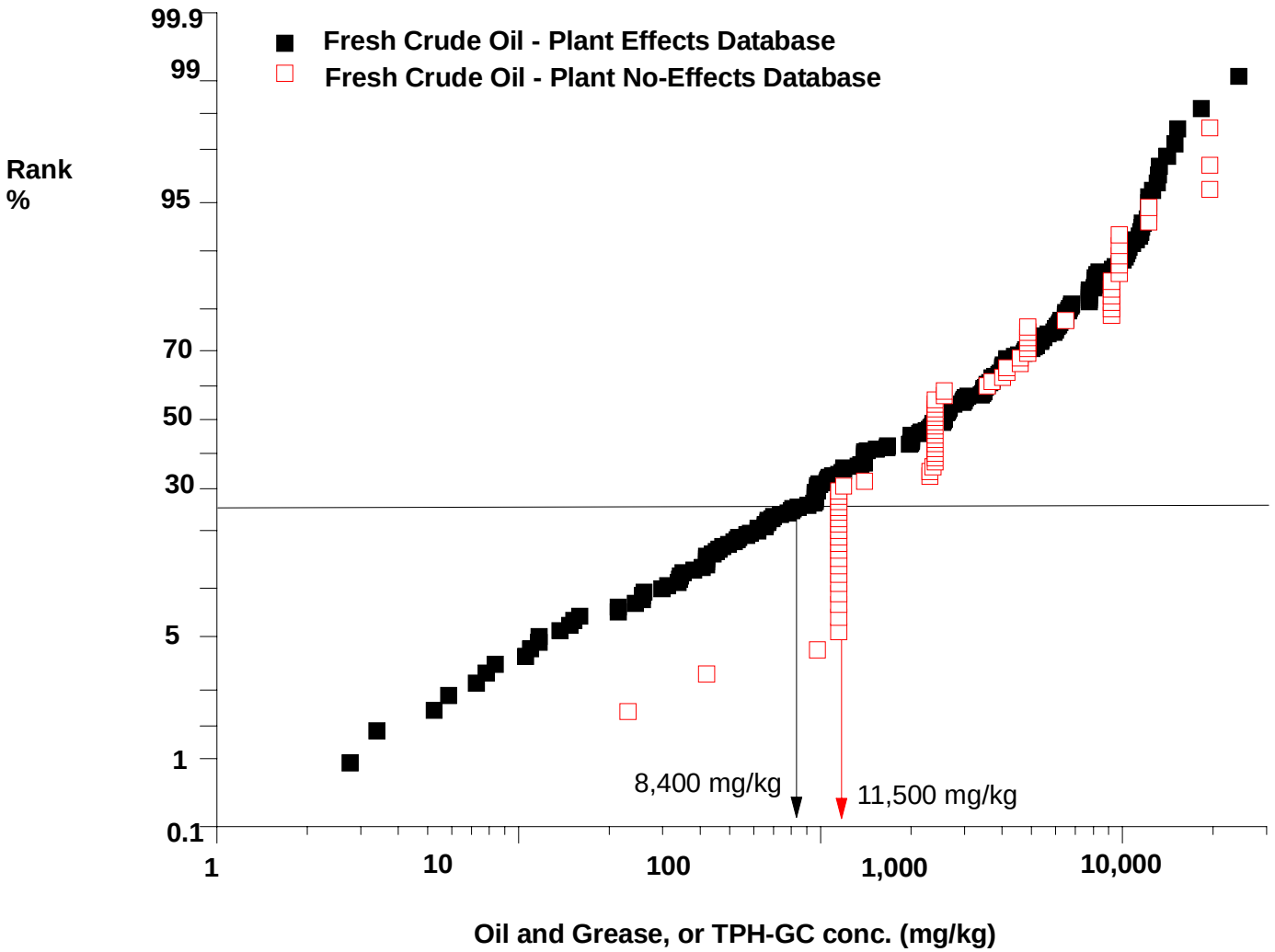


Figure G.6: Ranks data for toxicity of fresh crude oil to plants (with comparison of effects and no-effects data distribution).

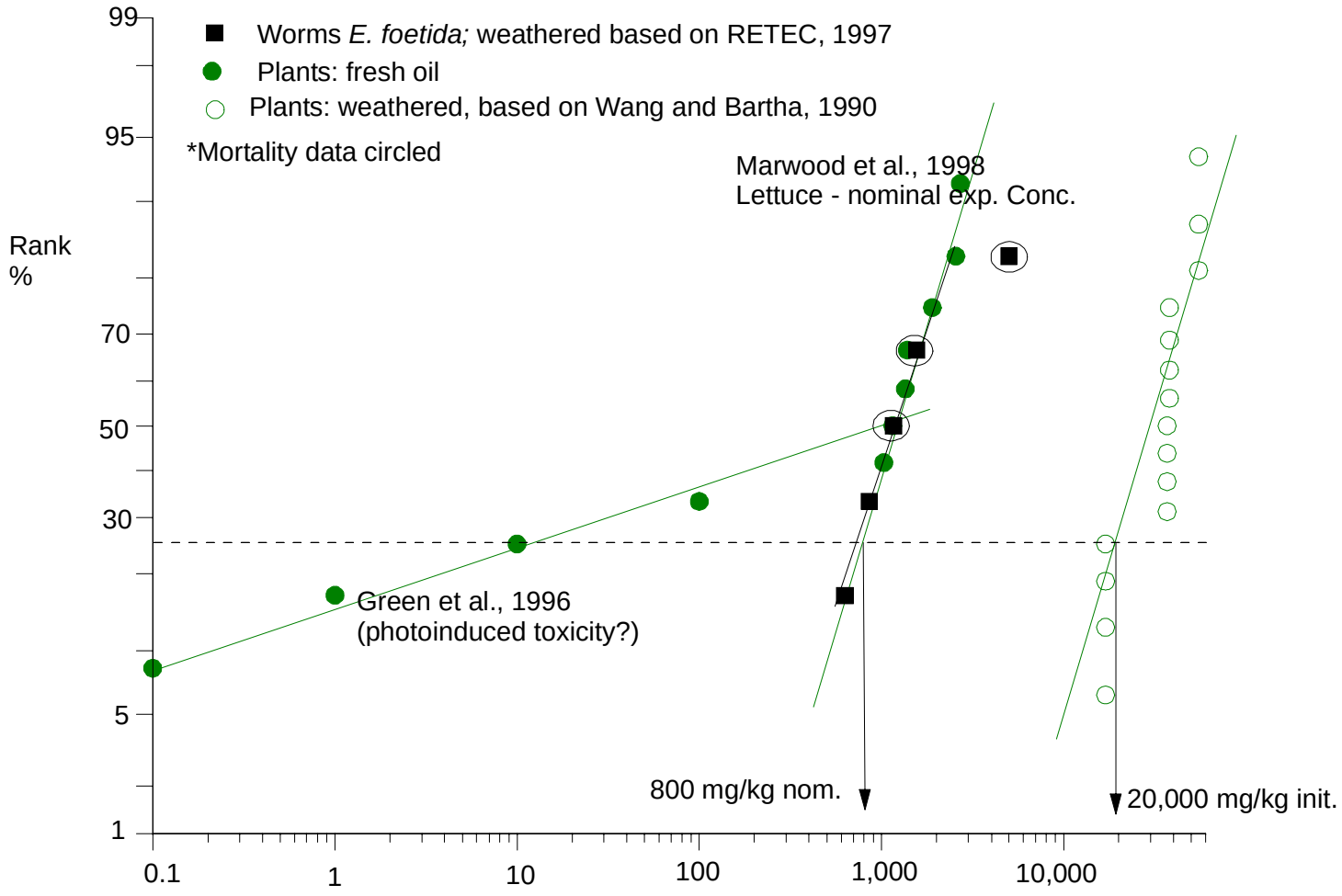


Figure G.7: Toxicity of diesel or heating oil to soil invertebrates and plants.

Appendix H: The B.C. Environment groundwater model.

H.1.0 The B.C. Environment Groundwater Model and Default Assumptions

The model presently used by the Pollution Prevention and Remediation Branch of the British Columbia Ministry of Environment, Lands and Parks (BCE) simulates contaminant partitioning from the soil to groundwater via the unsaturated zone, entry into the water table, and subsequent transport of contaminants in the saturated zone to a surface water body containing aquatic receptors. The model assumes one-dimensional groundwater flow, but may include transport mechanisms such as dispersion, biodegradation, adsorption-desorption, and dilution (between contaminated leachate and groundwater).

The CSST groundwater model includes four main components as follows:

i) Contaminant partitioning between soil particles, soil pore air, and soil pore water;

ii) Groundwater flow and contaminant leachate transport in the unsaturated zone;

iii) Mixing of unsaturated and saturated groundwater at the water table; and

iv) Groundwater flow and contaminant transport in the saturated zone to a receptor.

Numerous assumptions are incorporated into the model. They are as follows:

- the soil is physically and chemically homogeneous;
- the moisture content is uniform throughout the unsaturated zone;
- the infiltration rate is uniform throughout the unsaturated zone;
- decay of the contaminant source is not considered (i.e., infinite source mass);
- flow in the unsaturated zone is assumed to be one dimensional and downward only (vertical recharge) with dispersion, sorption-desorption, and biological degradation;
- the contaminant is not present as a free product phase;
- the maximum concentration in the leachate is equivalent to the solubility limit of the chemical in water under the defined site conditions;
- the groundwater aquifer is unconfined;
- groundwater flow is uniform and steady;

- co-solubility and oxidation/reduction effects are not considered;
- attenuation of the contaminant in the saturated zone is assumed to be one dimensional with respect to sorption-desorption, dispersion, and biological degradation;
- dispersion is assumed to occur in the longitudinal and transverse directions only and diffusion is not considered;
- mixing of the leachate with the groundwater is assumed to occur through mixing of leachate and groundwater mass fluxes; and
- dilution of the plume by groundwater recharge down-gradient of the source is not included.

The model is constructed by specifying the contaminant concentration in groundwater (saturated zone) at the source. The model then back-calculates the soil concentration at the source and forward calculates the groundwater concentration at the receptor. The model derives soil concentration standards to ensure that the contaminant concentrations in the groundwater discharging to the surface aquatic receptor are less than or equal to the Canadian Water Quality Guideline criteria for the receptor or some other suitably protective benchmark of groundwater quality.

H.2.0 Site Assumptions for Tier I Groundwater Fate Modeling

Table H.1 presents the default model input parameters adopted by CSST, based on a 'generic' site. Given the nature of Tier I guidance within Canadian jurisdictions, the default site parameters conservatively assume that conditions are optimal for the exposure of aquatic life from a mass of PHC contaminated soils on site, based on groundwater transport. No attempt was made to calibrate the model for PHCs; however, the model was originally developed for petroleum hydrocarbon spills, and there may be suitable validation studies available. The CSST default values are considered typical of the conditions for the lower Fraser River/Vancouver area of British Columbia.

Table H.1 also contains assumed generic site parameters for Tier I guidance, based on previous deliberations by the Human Health Fate and Transport Technical Advisory Committee (HHFT TAG) and the Protocol Implementation Working Group (PIWG), as well as discussions between Bright and Mah-Paulson, O'Connor Associates. The tabulated site parameter estimates were, to the extent possible, consistent with assumptions made for the derivation of human health protective PHC soil quality guidelines based on groundwater transport to potable water sources. In the case of potable water, however, it was assumed that the point of exposure - the drinking water well - was in the immediate vicinity of the contaminated soil mass.

In deriving modified estimates of site parameters, it is important to note that some of the properties are linked. The modification of one parameter in the suite must be carried out

in careful consideration of the values of the rest of the suite, otherwise the modeling predictions are invalid:

Suite 1			Suite 2		Suite 3	
source soil volume			climatic conditions		subsurface environ.	
X	source length	dimension	***P***	precipitation rate	**x**	distance from source to receptor
Y	source width	dimension	**(RO + EV)**	run-off and evaporation	**n**	contaminated soil porosity
Z	source depth	dimension	**D1/2US**	days when ground surface temp is below 0^{o} C.	**nu**	water-filled porosity
					ne	effective porosity
					foc	soil org. C. fraction
					V	Darcy velocity in saturated zone
					d	depth to unconfined aquifer
					da	depth of unconfined aquifer
					ρb	soil dry bulk density
					pH(s)	soil pH
					pH(gw)	groundwater pH

The default assumptions used herein are based on PHC-contaminated soils at a generic site with a biota-containing surface water body, or livestock watering dugout, that is within 10 m in a down-gradient direction. The site is assumed to have a 3 m unsaturated zone, which is contaminated throughout its entire depth at the source. As a worst case, the soil is assumed to have limited organic carbon content (0.5%) and the subsurface environment remains unfrozen throughout the year.

Table H.1: Default model input parameters and site-specific model calibration data.

Parameter	Units	Default CSST Value	PHC CWS Values, as recommended by PIWG and HHFT TAG[A]	
			coarse textured	fine textured
Contaminant Source Width	m	30		
Contaminant Source Depth	m	3	(3) [B]	(3) [B]
Contaminant Source Length	m	5	10 [C]	10 [C]
Distance to Receptor	m	10		
Precipitation	m/yr	1.000		
Runoff & Evaporation	m/yr	0.454	(0.72) [D]	(0.80) [D]
Precip. minus Runoff and Evap.	m/yr		0.28	0.20
Depth to Groundwater (water table)	m	3.0	(3) [E]	(3) [E]
Half-life in unsaturated zone	days	substance specific	infinite (set at 1E+09) [H]	infinite (set at 1E+09) [H]
Partition Coefficient, K_{oc}	mL/g	substance specific		
Weight fraction of organic carbon in soil, f_{oc}	[/]	0.006	0.005	0.005
H_2O-filled porosity (unsaturated)	[/]	0.1	0.119	0.168
Air filled porosity (unsaturated)	[/]	0.2	0.281	0.132
Henry's Constant = H*42.3	[/]	substance specific		
Days with surface temp. < 0 deg. C	days	0		
Darcy velocity in saturated zone	m/yr	12.6	16	1.6
Depth of unconfined aquifer	m	5	(5) [F]	(5) [F]
Total porosity (saturated)	[/]	0.3	0.4	0.3
Effective porosity (saturated)	[/]	0.2	(0.4) [G]	(0.3) [G]
Soil bulk density	g/cm^3	1.74	1.7	1.4
Maximum solubility of contaminant	mg/L	substance specific		
Half-life in saturated zone	days	substance specific	infinite (set at 1E+09) [H]	infinite (set at 1E+09) [H]

Shaded values indicate a chemical specific parameter for which CSST has not supplied default values.

Additional Notes: (A) Where no determination was made by HHFT TAG and/or PIWG, the CSST defaults were applied provided that they were reasonable estimates; (B) Not explicitly defined as part of HHFT modeling calculations; however, the model assumed intimate contact between the top of the groundwater table and the PHC contaminated soil mass. This is also consistent with CSST default assumptions; (C) Not required for HHFT modeling calculations. However, the original publication by Domenico on which the PIRI toolkit model is based makes mention of a 'width' of 10 m in the direction of groundwater flow; (D) Not set as part of human health-based calculations; however, "precip. minus runoff and evaporation" was set at 0.28 m/yr for coarse-grained soils and 0.20 m/yr for fine-grained soils; (E) 3 m based on discussions between Mah-Paulson and Bright, in recognition of the nature of the generic site scenario; (F) not defined by PIWG: Set at 5 m herein, since this was the minimum allowable distance within the BCE model; (G) For purpose of the PHC CWS, it was assumed that the effective porosity is 100% of the total porosity; (H) The issue of biodegradation in the subsurface environment was subsequently revisited. After extensive deliberations, the t1/2 for CWS F1 and F2, respectively was established as 712 d and 1,750 d for both the saturated and unsaturated zones. These were chosen as being highly conservative values.

H.3.0 Model Details

The groundwater model used for the PHC CWS Tier I calculations for ecological receptors is directly adopted from the model established by British Columbia Environment, Lands and Parks, in support of the B.C. Contaminated Sites Regulation.

BC Environment, with the assistance of Golder Associates Ltd., compiled a model in which flow is assumed to be essentially one dimensional, while still incorporating the major transport and attenuation processes affecting contaminant movement. The draft "Soil Screening Guidance, 1994" produced by the US Environment Protection Agency was used as the framework to develop the model (U.S. EPA 1994b). The mathematical code for the saturated groundwater transport is based on work by Domenico and Robbins, (Domenico and Robbins 1984). Model assumptions however, were based on work by BC Environment.

BC Environment recommended its four component model because:

- the major transport processes are represented,
- the major variables affecting each of the transport components are included, can be identified, and can be modified,
- physical and chemical affects are considered,
- model assumptions and criteria derivations are "transparent,"
- the model can be calibrated,
- the model performs with reasonable accuracy using a small set of input parameters,
- the accuracy and reliability of the model increases as site specific information increases,
- the model can be used with assumed site characteristics or use site specific data, and
- the model is scientifically based and defensible.

The BC Environment Transport Model as approved by the Contaminated Sites Soils Taskgroup (CSST) has been used to develop soil matrix standards for the protection of groundwater for both organic and inorganic contaminants. The model best simulates the transport of non-polar organic contaminants, and with modifications the model is used to simulate the transport of weakly ionizing substances. Metal transport modelling must be augmented by using an equilibrium geochemical speciation model, such as MINTEQ2.

In all transport models, the proportionment or partitioning of a chemical between soil, soil pore air, and soil pore water is critical. In the CSST approved model, the partitioning for non-polar organic contaminants is primarily a function of the organic carbon coefficient of the contaminant and the amount of organic carbon in the soil. For weakly ionizing substances, such as pentachlorophenols, partitioning in the model is additionally influenced by the pH of the soil. Partitioning of inorganics is considerably more complex, being additionally dependent on factors such as pH, sorption to clays, organic matter, iron oxides, oxidation/reduction conditions, major ion chemistry and the

chemical form of the metal. This model uses distribution coefficients (Kd) calculated as a function of pH, and as a function of an idealized soil with assigned physical and chemical characteristics. For inorganic contaminants modeling flexibility is limited in that distribution coefficients are only allowed to vary with respect to changes in soil pH. Soil pH, however, is only one of many geochemical parameters that actually can affect and change the distribution coefficient.

Attenuation within the model is essentially confined to adsorption-desorption reactions (partitioning), dilution (mixing between contaminated leachate and groundwater, biological degradation (for organics only) and dispersion.

The transport model derives soil concentration standards to ensure that the contaminant concentrations in the groundwater discharging and in contact with a receptor are less than or equal to established substance specific water quality criteria for the receptor (i.e. aquatic life) or water use (i.e. irrigation watering, livestock watering or drinking water) of concern. Thus, allowable concentrations in the groundwater at the point of contact with a receptor are based on either the aquatic life criteria, or for irrigation and livestock water uses. The respective irrigation or livestock watering criteria, presented in the CCME "Interim Canadian Environmental Quality Criteria for Contaminated Sites" (CCME 1991), or "Canadian Environmental Quality Guidelines" (CCME 1999) and/or BC Environment's "Approved and Working Criteria for Water Quality" (BC Ministry of Environment, Lands and Parks 1995b). Soil standards to protect groundwater for use as drinking water are based on the drinking water criteria presented in "Guidelines for Canadian Drinking Water Quality" (Health Canada 1993) and/or "Approved and Working Criteria for Water Quality" (BC Ministry of Environment, Lands and Parks 1995b) documents.

The Groundwater Protection Transport Model is based on assumptions generally typical of the climatic conditions of the lower Fraser River/ Vancouver area of British Columbia, and assumed groundwater characteristics typical of those found within the Fraser River sands of the Fraser River delta area. Other assumptions include:

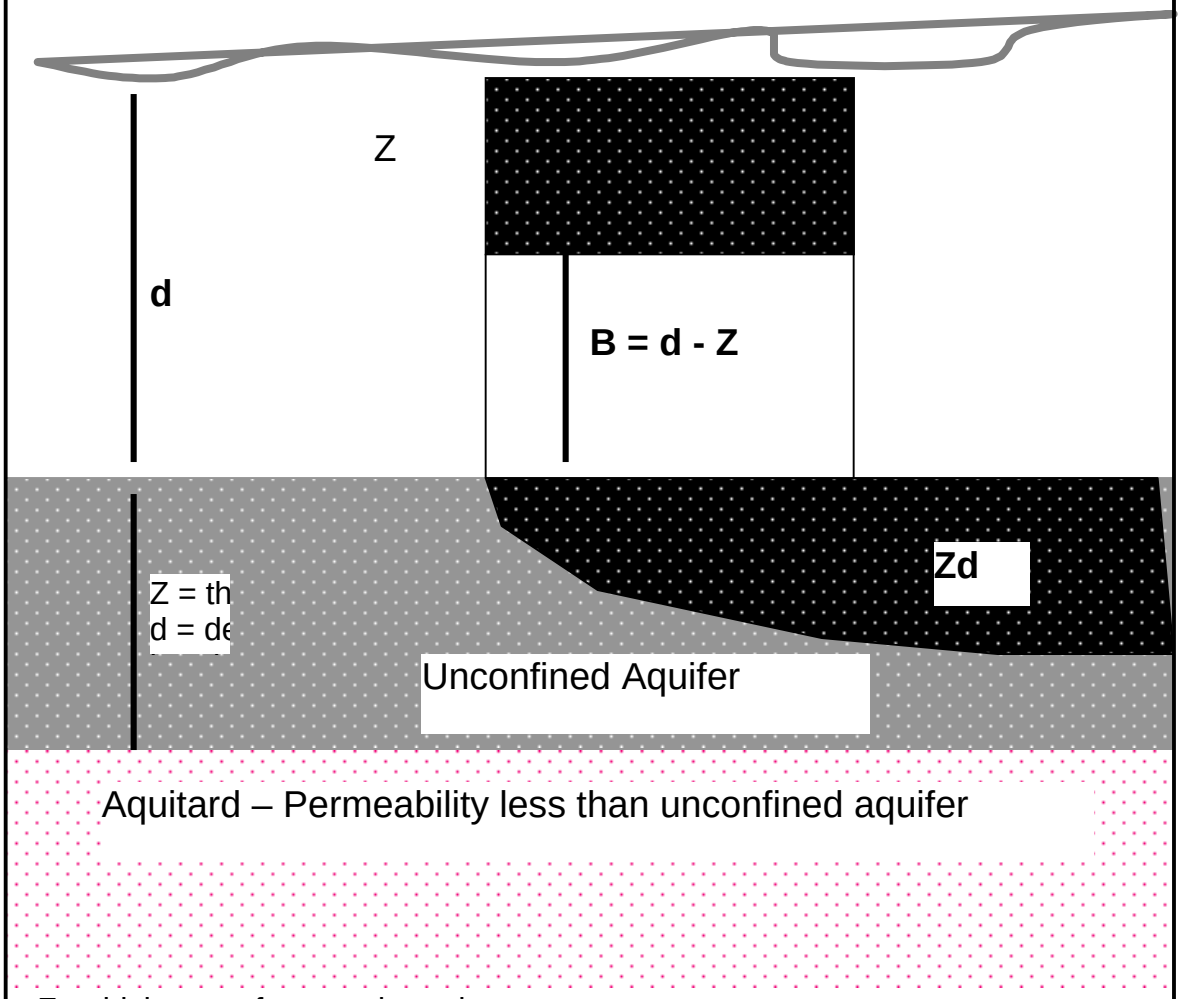
- the site is medium sized (between 1500 m^2 and 12,000 m^2),
- the total volume of contaminated soil is less than 450 cubic metres (5m x 30 m x 3 m),
- the depth to groundwater is not more than three (3) metres,
- the distance to the receptor is at least 10 metres,
- the soil is physically and chemically homogeneous,
- the organic content of the soil is at least 0.6 percent,
- the moisture content is uniform throughout the unsaturated zone,

- the porosity of the soil is 30 percent, and 10 percent of the pore volume is water filled,
- the infiltration rate is uniform throughout the unsaturated zone,
- flow in the unsaturated zone is assumed to be one dimensional and downward only, with dispersion, retardation and biological degradation,
- the contaminant is not present as a free product phase (i.e. a non-aqueous phase liquid),
- the maximum concentration in the leachate is equivalent to the solubility limit of the chemical in water under the defined site conditions,
- the groundwater aquifer is unconfined,
- the groundwater flow is uniform and steady,
- co-solubility and oxidation/reduction effects are not considered,
- attenuation in the saturated zone is assumed to be one dimensional with respect to retardation, dispersion and biodegradation,
- dispersion is assumed to occur in the longitudinal and horizontal transverse directions only, and diffusion is not considered,
- mixing of the leachate with the groundwater is assumed to occur through mixing of leachate and groundwater mass fluxes, and
- dilution by groundwater recharge down gradient of the source is not included.

Refer to Schematic drawing 1 for a typical transverse section through a contaminated source.

The mathematical equations for each of the four model components are presented below in Exhibits 1, 2, 3, 4 and 5. The soil/leachate partitioning component is presented in Exhibit 1. The flow component in the unsaturated soil zone is presented in Exhibit 2. The mixing of unsaturated and saturated zone waters is presented in Exhibit 3. The flow component in the saturated groundwater zone is presented in Exhibit 4. Conditions relating to the contaminant concentration in the saturated groundwater zone are provided in Exhibit 5.

Schematic drawing 1 – Transverse section of contaminated source in various layers of soil



Z = thickness of contaminated source
d = depth from ground surface to uncontaminated groundwater surface
b = thickness of the unsaturated zone
da = thickness of the unconfined groundwater aquifer
Zd = thickness of the mixing zone

Exhibit 6 provides definitions for parameters, and corresponding default values, used in modelling to produce matrix soil groundwater protective standards.

For each of the chemicals for which matrix soil-groundwater protection standards have been derived, the chemical characteristics used in the model are presented in Tables H.2 and H.3. Chemical characteristics provided include solubility, organic:water and other distribution coefficients, biological degradation rates, and Henry's Law constants.

Exhibit 1 - Soil/Leachate Partitioning Model

$$C_S = C_L \left\{ Kd + \frac{(n_u + H' n_a)}{P_b} \right\}$$

Parameter	Definition (units)	Default
C_S	= soil concentration at source (mg/kg)	
C_L	= leachate concentration at source (mg/L)	calculated value
Kd	= distribution coefficient for a chemical (cm^3/g)	chemical/physical specific[1]
n_u	= water filled porosity (dimensionless)	H x 42.3[2]
H'	= dimensionless Henry's Law constant for the chemical	
H	= Henry's Law constant (atm-m^3/mol)	chemical specific
n_a	= air filled porosity (dimensionless): $n_a = n - n_u$.	0.2
P_b	= dry bulk density of soil (g/cm^3)	
n	= total porosity (dimensionless)	

Notes:
1 = see Annex A
2 = where 42.3 is a units conversion factor for 15°C
3 = based on "Fraser River sand" characteristics

Exhibit 2 - Unsaturated Groundwater Zone

$$C_Z = C_L \; exp\left[\frac{b}{2\partial_u} - \frac{b}{2\partial_u}\left\{1 + \left(\frac{4\partial_u L_{US}}{V_u}\right)\right\}^{1/2}\right]$$

Parameter	Definition (units)	Default
C_Z	= chemical concentration of the leachate at the watertable (mg/L)	
C_L	= leachate concentration at the source (mg/L)	calculated value
b	= thickness of the unsaturated zone (m): b=d-Z	0
d	= depth from surface to uncontaminated groundwater surface (m)	3
Z	= depth of contaminated soil (m)	3
∂_u	= dispersivity in the unsaturated zone (m)	0.1 x b
L_{US}	= decay constant for chemical ($seconds^{-1}$) in unsaturated zone: $L_{US} = \frac{0.691}{t_{1/2US}} \times (e^{-0.07 \times d}) \times 1 - (\frac{D_{1/2US}}{365})$	calculated value
$t_{1/2US}$	= chemical half-life in unsaturated zone	chemical specific[1]
$D_{1/2US}$	= frost free days	365
V_u	= average linear leachate velocity (m/s)	calculated value
I	= infiltration rate (m/yr): I = P - (RO + EV)	0.55
P	= precipitation rate (m/yr)	1
(RO + EV)	= sum of runoff rate (R0) + surface evapotranspiration rate (EV) (m/yr)	0.45
n_u	= water-filled porosity (dimensionless)	0.1
R_u	= retardation factor in unsaturated zone (dimensionless)	calculated value
P_b	= dry bulk density of soil (kg/L)	1.75 [2]
K_d	= distribution coefficient for a chemical (cm^3/g): for organics - $K_d = K_{oc} \times f_{oc}$ for metals - K_d = function of soil organic carbon, pH, redox conditions, iron oxide content, cation exchange capacity, and major ion chemistry	chemical specific[1]
K_{oc}	= organic carbon partitioning coefficient (cm^3/g)	chemical specific[1]
f_{oc}	= weight fraction of organic carbon in soil (dimensionless)	0.006

Notes:
1 = see Annex A
2 = based on "Fraser River sand" characteristics

Exhibit 3 - Mixing Zone Unsaturated/Saturated

$$C_Z = C_{gw} \{1 + (\frac{Z_d \times V}{I \times X})\}$$

Parameter	Definition (units)	Default
C_Z	= chemical concentration of the leachate at the water table (mg/L)	
C_{gw}	= chemical concentration in the groundwater at source (mg/L)	calculated value
Z_d	= average thickness of mixing zone (m)	0.5[1]
V	= Darcy velocity in groundwater (m/year)	12.6
I	= infiltration rate (m/s)	2×10^{-8}
X	= length of contaminated soils (m) for point source	5

1 = Z_d is a function of mixing zone depths available due to dispersion/diffusion and due to infiltration and underground flow rates. See Exhibit 4.

Exhibit 4 - Calculation of Average Thickness of Mixing Zone, Z_d

$$Z_d = r + s$$

Parameter	Definition (units)	Default
Z_d	= average thickness of mixing zone (m)	
r	= mixing depth available due to dispersion and diffusion (m): $r = 0.01 \times X$	calculated value
X	= length of contaminated soils (m)	5
s	= mixing depth available due to infiltration rate and groundwater flow rate (m): $s = d_a \{1 - e^{-[2.178 \times (X \times 1)/Vxda]}\}$	calculated value
d_a	= unconfined groundwater aquifer (m) (used to calculate Z_d)	5
	= infiltration rate (m/yr): $I = P - (RO + EV)$	0.55
	= precipitation rate (m/yr)	1
(RO + EV)	= sum of runoff rate (R0) + surface evapotranspiration rate (EV) (m/yr)	0.45
V	= Darcy velocity (m/yr)	12.6

Exhibit 5 - Saturated Groundwater Zone

$$C_w(x,y,z,t) = \left(\frac{C_{gw}}{4}\right) \exp\left\{\left(\frac{x}{2\partial_x}\right)\left[1 - \left(1 + \frac{4L_s\partial_x}{\nu}\right)^{1/2}\right]\right\} \operatorname{erfc}\left[\frac{x - \nu t\left(1 + \frac{4L_s\partial_x}{\nu}\right)^{1/2}}{2(\partial_x \nu t)^{1/2}}\right]$$

$$\left\{\operatorname{erf}\left[\frac{y+Y/2}{2(\partial_y x)^{1/2}}\right] - \operatorname{erf}\left[\frac{y-Y/2}{2(\partial_y x)^{1/2}}\right]\right\}$$

$$V = Ki; \quad \nu = \frac{V}{n_e R_f}; \quad R_f = 1 + \left(\frac{P_b K_d}{n}\right); \quad K_d = K_{oc} f_{oc}$$

Parameter	Definition (units)	Default
C_w	= chemical concentration in groundwater flow at receptor (mg/L)	applicable water quality standard
x	= distance to source (m)	10
x,y,z	= Cartesian coordinates that coincide with principle directions of the dispersivity tensor (m)	x is site specific
t	= time since contaminant release (years)	100
C_{gw}	= chemical concentration in the groundwater at source (rng/L)	calculated value
$\partial_{xf}\partial_{yf}\partial_z$	= principle values of the dispersivity tensor (m): $\partial_x = O.1_X$ $\partial_y = O.1\partial_x$	calculated values
L_S	= decay constant (seconds^{-1}) in saturated zone: $L_S. = \frac{0.691}{t_{l/2S}} \times (e^{-0.07 \times d})$	chemical/depth specific
d	= depth from surface to uncontaminated groundwater surface (m)	3
$t_{1/2s}$	= decay (biodegradation) half-life (yr)	chemical specific[1]
ν	= velocity of the contaminant (m/s)	$v = V / n_e R_f$
V	= Darcy velocity or specific discharge (m/yr): $V = Ki$	12.6
K	= hydraulic conductivity (m/yr): $K = V/i$	calculated value
I	= groundwater gradient (dimensionless): $i = V/K$	calculated value
n	= porosity of contaminated soil	0.3
n_e	= effective porosity (dimensiordess)[l]	0.2
Y	= source's width (m), perpendicular to ground-water flow	30
R_f	= Retardation factor (dimensionless)	calculated value
P_b	= bulk density of soil (g/cm^3)	1.75

Exhibit 5 - Saturated Groundwater Zone (Con't.)

K_d	= distribution coefficient for chemical and soil (cm^3/g)	chemical/soil specific[1]

$$K_d = K_{oc} \times f_{oc}$$

K_{oc}	= distribution coefficient for chemicals between organic carbon and water (cm^3/g)	chemical specific[1]
f_{oc}	= weight fraction of organic carbon in soil (dimensionless)	0.006

Note: Above simplified solution based on the assumptions that there is no vertical dispersion, and effective molecular diffusion is relatively negligible,
Therefore –

$D_X = \partial_x \nu$ and $D_Y = \partial_x \nu$

D_X = longitudinal mechanical dispersion coefficient (m^2/s) $\partial_x \nu + D^*$
D_Y = lateral mechanical dispersion coefficient (m^2/s) $\partial_Y \nu + D^*$

Notes
1 = see Annex A

Exhibit 6 - Default Groundwater Model Parameters

Parameter	Definition (units)	Default
S	= maximum solubility	chemical specific[1]
n	= total porosity (dimensionless)	0.3
n_u	= water filled porosity	0.1
n_a	= air filled porosity (dimensionless):	calculated value
	$n_a = n - n_u$	0.2
P_b	= dry bulk density of soil (g/cm,)	1.75
H	= Henry's Law constant	chemical specific[1]
H’	= dimensionless Henry's Law constant	chemical specific[1]
∂_u	= dispersivity in unsaturated zone	0.1 x b
f_{oc}	= fraction of organic carbon in soil	0.006
V	= Darcy velocity in saturated zone (m/yr)	12.6
Z_d	= thickness of mixing zone (m)	0.5
K_d	= distribution coefficient for a chemical (cm^3 /g)	chemical specific[1]
Koc	= organic carbon partitioning coefficient (cm^3/g)	chemical specific[1]
∂_x	= dispersivity in x-direction	∂_x = 0.lx
∂_y	= dispersivity in y-direction	$\partial_Y = 0.1\partial_x$
d	= unconfined groundwater aquifer (m)	5
b	= thickness of the unsaturated zone	0
	note: b = d-Z	
d	= depth from surface to uncontaminated groundwater surface (m)	3
x	= distance from source to receptor (m)	10
n_e	= effective porosity (dimensionless)	0.2
$t_{1/2US}$	= decay (biodegradation) half-life at unsaturated sites	chemical specific[1]
$t_{1/2S}$	= decay (biodegradation) half-life at saturated sites	chemical specific[1]
I	= infiltration rate (m/yr)	0.55
	Note: 1 = P - (RO + EV)	(1 - 0.45)
P	= precipitation rate (m/yr) 1	
(RO-EV)	= runoff rate plus surface evapotranspiration rate (m/yr)	0.45
X	= source dimension length (m)	5
Y	= source dimension width (m)	30
Z	= source dimension thickness (m)	3
$D_{1/2US}$	= frost free days	365

Notes
1 =reference values provided in Annex A

Table H.2: Values for BCE Groundwater Model.

Substance	pH	RECEPTOR CRITERIA				Solubility	Koc	t ½ unsat (days)	t ½ sat (days)	H' [/] =H*42.3
	Range	AW (mg/L)	Irr (mg/L)	Lstk (mg/L)	DW (mg/L)	(mg/L)				
Benzene		0.3	-	-	0.005	1745	83.2	183	365	2.32E-01
Ethylbenzene		0.7	-	-	0.0024	152	1,096.5	114	114	3.67E-01
Toluene		0.3	-	-	0.024	515	302.0	56	105	2.85E-01
Xylenes		-	-	-	0.3	170	389.0	183	183	2.26E-01
Benzo(a)pyrene		0.00001	-	-	0.00001	0.004	891,250	529	1059	1.02E-04
Naphthalene		0.001	-	-	-	32	1,288.2	65	129	2.60E-02
Pyrene		0.00002	-	-	-	0.17	72,443.6	1898	3796	1.04E-03
Pentachlorophenol	<6.9	0.00002	-	0.03	0.03	5000	pH*	383	767	6.01E-04
	6.9 – 7.9	0.0001	-	0.03	0.03	5000	pH*	383	767	6.01E-04
	>7.9	0.0003	-	0.03	0.03	5000	pH*	383	767	6.01E-04
Tetrachloroethylene		0.11	-	-	-	150	158.5	411	821	7.61E-01
Trichloroethylene		0.02	-	0.05	0.05	1070	1,070	411	821	8.46E-01
PCBs		0.0000001	0.0005	-	-	-	-	-	-	-
Dioxins/Furans		-	-	-	-	-	-	-	-	-
Arsenic (As+3)		0.05	0.1	0.5	0.025	pH*	Kd**	-	-	-
Cadmium (Cd+2)		0.0018	0.01	0.02	0.005	pH*	Kd**	-	-	-
Chromium (Cr+3)		-	-	-	-	pH*		-	-	-
Chromium (Cr+6)		-	-	-	-	pH*	Kd**	-	-	-
Chromium (total)		0.002	0.1	1	0.05	pH*		-	-	-
Copper (Cu+2)		0.008	0.2	0.3	1	pH*	Kd**	-	-	-
Lead (Pb+2)		0.011	0.2	0.1	0.01	pH*		-	-	-
Zinc (Zn+2)		0.03	1.0-5.0	50	5	pH*	Kd**	-	-	-

Rule: t1/2 unsaturated (organics) - Greater of the anaerobic rate high (lowest number of days) and 25% of the anaerobic rate low (highest number of days). Unless t1/2 unsaturated > t1/2 saturated, then t1/2 unsaturated equals t1/2 saturated.
Rule: t1/2 saturated (organics) – Equals to 50 percent of anaerobic rate low (highest number of days).
*pH dependent
** Kd calculated

Table H.3: Koc and Kd values for BCE Groundwater Model.

pH	Koc PCP	Kd PCP foc = 0.006	Kd As(+3)	Kd Cd	Kd Cr(+6)	Kd Cu(2+)	Kd* Pb	Kd Zn(2+)
4.5	20,303	121.82	24.3		35.0			
4.6	18,454	110.73	24.4		34.0			
4.7	16,557	99.34	24.6		33.1			
4.8	14,659	87.95	24.8		32.2			
4.9	12,810	76.86	25.0	0.8	31.4	39.8	*	1.6
5.0	11,055	66.33	25.2	0.9	30	50.1	*	1.8
5.1	9,429	56.57	25.4	1.0	29.7	63.1	*	2.0
5.2	7,956	47.73	25.6	1.1	28.9	79.4	*	2.2
5.3	6,648	39.89	25.7	1.3	28.2	100	*	2.5
5.4	5,508	33.05	25.9	1.5	27.4	126	*	3.2
5.5	4,530	27.18	26-1	1.7	26.7	158	*	4.0
5.6	3,703	22.22	26.3	2.0	26.0	219	*	5.0
5.7	3,010	18.06	26.5	2.5	25.3	302	*	6.3
5.8	2,437	14.62	26.7	3.2	24.6	417	*	8.6
5.9	1,965	11.79	26.9	4.0	24.0	575	*	11.7
6.0	1,580	9.482	27.1	5.0	23.3	794	*	15.8
6.1	1,268	7.607	27.3	7.5	22.7	1,148	*	24.0
6.2	1,015	6.090	27.5	11.2	22.1	1,660	*	36.3
6.3	811	4.868	27.7	16.8	21.5	2,399	*	55.0
6.4	648	3.887	27.9	25.1	21.0	3,467	*	83.2
6.5	517	3.100	28.1	36.9	20.4	5,012	*	126
6.6	412	2.470	28.3	54.1	1@91.91	6,310	*	191
6.7	328	1.967	28.6	79.4	19.3	7,943	*	288
6.8	261	1.566	28.8	117	18.8	10,000	*	437
6.9	208	1.246	29.0	171	18.3	12,589	*	661
7.0	165	0.991	29.2	251	17.8	15,849	*	1,000
7.1	131	0.788	29.4	355	17.4	17,783	*	1,380
7.2	104	0.626	29.6	501	16.9	19,953	*	1,905
7.3	83.0	0.498	29.9	708	16.4	22,387	*	2,630
7.4	65.9	0.396	30.1	972	16.0	25,119	*	3,631
7.5	52.4	0.314	30.3	1,334	15.6	25,119	*	5,012
7.6	41.6	0.250	30.5	1,830	15.2	25,119	*	6,310
7.7	33.1	0.198	30.8	2,512	14.8	25,119	*	7,943
7.8	26.3	0.158	31.0	3,073	14.4	25,119	*	10,000
7.9	20.9	0.125	31.2	3,758	14.0	25,119	*	12,589
8.0	16.6	0.100	31.4	4,597	13.6	25,119	*	15,849
8.1	13.2	0.079	31.7	56,234	13.3			19,953
8.2	10.5	0.063	31.9		12.9			
8.3	8.3	0.050	32.2		12.6			
8.4	6.6	0.040	32.4		12.2			
8.5	5.2	0.031	32.6		11.9			

* Copper Kd values used as surrogates for lead Kd values.

Appendix I: PHC biodegradation in the subsurface environment.

I.1.0 Literature Review of PHC Biodegradation in the Subsurface Environment

In light of the sensitivity of the groundwater modeling predictions to estimated degradation half-life, especially in the often anaerobic saturated zone, a brief literature review was carried out on PHC persistence in the subsurface environment. Table I.1 provides a summary.

It should be noted that the major portion of studies cited have very limited applicability to the generic site scenario established for the PHC CWS. Several of the cited studies are based on bench-top or other studies that are of limited relevance to the prediction of PHC fate in *in situ* subsurface soils and groundwater.

Table I.1: Brief overview of literature values for the environmental persistence of various petroleum hydrocarbon constituents.

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
MONOAROMATICS				
Benzene	10 day – 2 year	groundwater	Piet and Smeenk, 1985	
	8.6 day	soil incubations study	Tabak *et al.*, 1981	
	120 day	soil slurry	Zoetman *et al.*, 1981	Static-culture flask biodegradation test
	68 day	field soils	Baker and Mayfield, 1980	
	24-248 day	soil incubation study	Baker and Mayfield, 1980	
	7 day	surface water	Heath *et al.*, 1993	
***eip*-isopropylbenzene**	2 day	surface water	Heath *et al.*, 1993	
1,2,4-trimethyl-benzene	7 day	surface water	Heath *et al.*, 1993	
Ethylbenzene	3 day	surface water	Heath *et al.*, 1993	
	37 day	groundwater		natural soil groundwater system
Toluene	4 day	surface water	Heath *et al.*, 1993	
	37 day		Swindoll *et al.*, 1987	
	1 day	groundwater	Zoeteman *et al.*, 1981	Field observation
	37 day	groundwater	Baker and Patrick, 1985	Field observation
	8 day	groundwater	Baker *et al.*, 1987	Field observation
	126 day	groundwater, anaerobic/ methanogenic env.	Wilson *et al.*, 1986	Microcosm study

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
	9.9 day	plowed plot with sewage-sludge amended soils	Wilson *et al*., 1997.	Field plots
	0.4 day	pasture plot with sewage sludge amended soils		
Xylenes	7 day	surface water	Heath *et al.*, 1993	
	5.8 to 7.6 day	plowed plot with sewage-sludge amended soils	Wilson *et al*., 1997.	Field plots
	0.3 to 0.7 day	pasture plot with sewage sludge amended soils		
(*o*-xylene)	11 day	groundwater	Zoeteman *et al.*, 1981	Field observation
	126 day	Soil incubation study	Wilson *et al.*, 1982	
	32 day	shallow subsurface soils and water	Baker and Patrick, 1985	
Phenol	2.7 h to 23 day	various soil types based on biodegradation	CEPA, 1999, and references therein	
	7 day	soil; volatilization/ partitioning only	Mackay *et al*., 1995	

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
	total biol. dissim-ilation (1-7 day)	soil at 20° C; aerobic	Prager, 1995.	Degradation slower under anaerobic conditions
	(5-19 day)	soil at 4° C; aerobic		
	3.7 day	water soluble fraction of soils	Loehr and Webster, 1997 (adapted from Dassapa and Loehr, 1991)	phenolics contaminated soils in a slurry bioreactor from a PCP treatment facility
	0.56 day	subsurface soils	Federle, 1988	
	23 day	acidic soil (pH 4.8)	**Loehr and Matthews, 1992**	In batch microcosms at 20° C.
	4.1 day	basic soils (pH 7.8)		
***p*-Cresol**	7 day	soils	ASTDR, 1992.	
	0.5 day	acidic soils (pH 4.8)	Loehr and Matthews, 1992	In batch microcosms at 20° C.
	< 1 day	basic soils (pH 7.8)		
POLYAROMATIC HYDROCARBONS				
Acenaphthene	25-204 day	groundwater (estimated)	Howard *et al.*, 1991	
Acenaphthylene	85-120 day	groundwater (estimated)	Howard *et al.*, 1991	
Anthracene	100 day – 2.5 year	groundwater (estimated)	Howard *et al.*, 1991	
Benzo(a)anthracene	204 day – 3.73 year	groundwater (estimated)	Howard *et al.*, 1991	

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
Benzo(b)fluoranthene	1.97-3.34 year	groundwater (estimated)	Howard *et al.*, 1991	
Benzo(k)fluoranthene	5 – 11.7 year	groundwater (estimated)	Howard *et al.*, 1991	
Benzo(a)pyrene	114 day – 2.9 year	groundwater (estimated)	Howard *et al.*, 1991	
Chrysene	2.04 – 5.48 year	groundwater (estimated)	Howard *et al.*, 1991	
Fluoranthene	0.8 – 2.4 year	groundwater (estimated)	Howard *et al.*, 1991	
Fluorene	64-120 day	groundwater (estimated)	Howard *et al.*, 1991	
Naphthalene	7-14 day	soils in slurry reactor	Loehr and Webster, 1997	soils from slurry reactor treatment of PAH contaminated wood-treatment site
	1-258 day	slurry	Tabak *et al.*, 1981	Static-culture flask biodegradation test
	0.9 day	Natural soil groundwater system	Zoeteman *et al.*, 1981	
	33 day	sludge-amended soils	Wild and Jones, 1993	
	15 day	spiked soils		
	1.1 day	soil - top 1 cm	Environment Canada, 1996b	soil with 1.25% org. C
	14 day	soil - top 10 cm (based on loss through volatilization)		
	2.1- 2.2 day	soil -microbial biodegradation	Park *et al.*, 1990, as cited in Environment Canada, 1996b	0.5% org. C, pH 7.9; sandy loams

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
Phenanthrene	28-46 day	soils in slurry reactor	Loehr and Webster, 1997	soils from slurry reactor treatment of PAH contaminated wood-treatment site
	108 day	sludge-amended soils	Wild and Jones, 1993	
	14 day	spiked soils		
	2.5 day to 5.7 year	soils	CEPA, 1993	
	32 day – 1.1 year	groundwater (estimated)	Howard *et al.*, 1991	
Pyrene	7-14 day	soils in slurry reactor	Loehr and Webster, 1997	soils from slurry reactor treatment of PAH contaminated wood-treatment site
	43 day	soils -batch study	Symon and Sims, 1988; as cited in	In “Kidman Sandy Loam”
	30 day	soils - soil column	Loehr and Webster, 1997	
	32 day	soils -batch study	Symon and Sims, 1988; as cited in	In “Nunn Clay Loam”
	33 day	soils - soil column	Loehr and Webster, 1997	
	285 day	sludge-amended soils	Wild and Jones, 1993	
	51 day	spiked soils		
	1.15 – 10.4 year	groundwater (estimated)	Howard *et al.*, 1991	

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
2-ring PAHs **3-ring PAHs** **4-ring PAHs**	17-48 day 31-176 day 206-1,003 day	hydrocarbon-contaminated soils (observed range)	Loehr and Webster, 1997 (Table 2-62: adapted from US EPA data as documented in Howard *et al.*., 1991)	
2-ring PAHs **3-ring PAHs** **4-ring PAHs**	1,746 day 856 day 1,144 day	hydrocarbon-contaminated soils (observed range)	Loehr and Webster, 1997 (Table 2-62)	based on six years of intrinsic/passive bioremediation of soils, **following** one year of active bioremediation.
ALIPHATICS				
Octadecane (C18)	66% in 20 day	aerobic soil suspension	Haines and Alexander, 1974	1% silt-loam suspension w mineral salts
Octacosane (C28)	3.2, 108 day 3-300 day	surface water groundwater, aerobic	Matsumoto, 1983 Zoeteman *et al.*, 1980	Tama R., Tokyo, aerobic estimate from field study
Dotriocontane(C36)	0.6 to 43% over 28 day	soil, aerobic	Moucawi *et al*., 1981	biodegradation rate dependent on soil type; France

It is evident from the tabulated values that estimates of degradation are highly variable either for a single compound, or across compounds within a narrow range of molecular weights. This is not surprising: The environmental persistence of a substance, while undoubtedly influenced by the inherent chemical properties, is likely to be more strongly influenced by site specific conditions, including microbial ecology and site-specific ecological history, microclimate, soil and groundwater properties, co-contaminants, and so on. Expected site-to-site variations notwithstanding, constituents of PHC mixtures that tend to be more persistent in the saturated zone include PAHs, alkyl-PAHs and alkyl-benzenes. In addition, it is clear from the published literature that microbial degradation of petroleum hydrocarbons occurs more rapidly in aerobic than anaerobic conditions.

In choosing biodegradation rates which are applicable to sites across Canada, and on a generic basis, worst-case estimates of degradation are appropriate: i.e.-likely underestimates of the rate at which PHCs degrade in the saturated zone.

For some of the more refractory polyaromatic compounds in the PHC CWS Fraction 2 boiling point range, aerobic degradation half-lives of up to approximately 1,750 days have been previously observed for two-ring PAHs (naphthalene) (Loehr and Webster 1997). This is based on a rather slower rate of degradation in soils passively remediated *in situ*, and following one year of active bioremediation, wherein initial loss rates were much higher. An upper estimate of around 1,750 days for the half-life of PAHs in the F2 fraction is generally consistent with estimates provided by Howard *et al.* (1991). On the other hand, the field experimental conditions used by Zoeteman *et al.* (1980) to calculate a half-life for naphthalene in groundwater of only 0.9 days were probably more representative of the ‘generic’ conditions of the conceptual model inherent in the PHC CWS.

For lighter PHCs in the CWS F1 fraction (C6 to nC10), estimated environmental half-lives as tabulated above ranges from 0.3 day to 2 years (for benzene; Piet and Smeenk 1985). Wilson *et al*. (1986) used soil microcosms to study the biodegration of toluene under methanogenic/anaerobic conditions. The estimated environmental half-life was 126 day.

Based on the consulted studies, conservatively low estimates of environmental biodegradation were established as follows:

1. **CWS F1: 2 years = 712 day**
2. **CWS F2: 1,750 day**

In light of the highly conservative nature of these environmental half-life estimates, it is recommended that they apply to fate calculations in both the saturated and unsaturated zone.