CCME

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Canada-Wide Standard for Petroleum Hydrocarbons (PHC) 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 was endorsed by Ministers of Environment (with the exception of Quebec) in May 2001. A commitment was made to review additional scientific, technical and economic analysis to reduce information gaps and uncertainties after 5 years; the present version of the PHC CWS includes modifications and updates resulting from that review.

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.

PHC 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, PHC may create aesthetic problems such as offensive odour, taste or appearance in environmental media. Finally, under some conditions PHC 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 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, 2006) 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 (toddler)	Nutrient cycling Invertebrates Plants Human (toddler)	Nutrient cycling Invertebrates Plants Human (toddler)	Nutrient cycling Invertebrates Plants Human (adult)
Soil Ingestion	Herbivores Human (toddler)	(wildlife)* Human (toddler)	(wildlife)* Human (toddler)	(wildlife)* Human (adult)
Groundwater/ Surface Water	Aquatic Life/ Livestock Watering Human (toddler)	Aquatic Life Human (toddler)	Aquatic Life Human (toddler)	Aquatic Life Human (adult)
Vapour Inhalation (humans only)	Toddler, indoor	Toddler, indoor	Toddler, indoor	Adult, indoor
Produce, meat and milk produced on site (humans only)	Toddler**	Toddler** (produce only)		
Off-site migration of Soil/Dust				Human/Eco

* wildlife dermal contact and ingestion data may be particularly important for PHC (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

** in most cases PHC are not expected to bioaccumulate to high concentrations in produce, meat or milk, though some polycyclic aromatic hydrocarbons (PAH) may bioaccumulate to a limited extent; the available data are currently insufficient to evaluate this pathway on a generic basis

To address the diversity of PHC contamination types, including various crudes and product admixtures, PHC 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 management levels described below.

1.5 Human Health Protection

Direct contact with contaminated soil, including inadvertent ingestion of soil and dermal contact with 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 toddlers were assumed to ingest four times the amount of soil as an adult, consistent with Health Canada (2004) recommendations. Tier 1 levels were calculated using an algorithm adapted from CCME (2006a).

Ingestion of cross-contaminated groundwater is addressed through use of the analytical groundwater model from CCME (2006a). It is conservatively assumed that the PHC contamination is underlain by an unconfined aquifer, that a potable well is located at the downgradient boundary of the site, and that the potable well could be a person's sole source of drinking water. At the Tier 1 level, this pathway, where applicable, may govern remedial response for F1 and F2 on sites with fine-textured soils, and F1 only on coarse-textured soils with a commercial or industrial land use.

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). The vapour inhalation pathway governs remedial response at the Tier 1 level for F1 and F2 on coarse-textured sites with an agricultural or residential/parkland land use.

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 PHC on the biotic component of a terrestrial ecosystem. Specifically, it evaluates the potential for adverse effects to occur from exposures to soil-based PHC 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, and for F2 under some scenarios.

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 1985 as adapted by BC Environment and CCME, 2006a) is used for this purpose. Remedial response is not governed by the aquatic life protection pathway at the Tier 1 level. 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 and Incorporation of Management 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.

In the process of developing these features the Development Committee, and subsequently the Soil Quality Guidelines Task Group, 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;
- 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. 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 generally 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 from *PHC* (e.g. leaky underground storage tanks, overflow spills, etc.).

ecological receptor: 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 PHC 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 aliphatic 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 PHC). 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*). 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 rate of 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. Also referred to as the tolerable concentration (TC).

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. Also referred to as the tolerable daily intake (TDI).

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 of the total allowable exposure to a contaminant at a site (e.g. residual TDI) from various environmental pathways (air, soil, food, water, consumer products) which soil is allowed to comprise.

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 *PHC CWS* 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 by *PHC* (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
BC: British Columbia
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
DTED: daily threshold effects dose
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
IC_x: inhibitory concentration with x percent inhibition of parameter
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
LS: less stringent
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
Mogas: motor gasoline
MS: more stringent
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
RRD: Ranked Response Distributions
RRfC: residual reference concentration
RTDI: residual tolerable daily intake
SAF: soil allocation factor
SEA TAG: Socio-economic Analysis Technical Advisory Group
SQG: soil quality guideline
SQGTG: Soil Quality Guidelines Task Group
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
RRD: Ranked Response Distributions
UF: uncertainty factor
US EPA: United States Environmental Protection AgencyVF: 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. The PHC CWS was endorsed by Ministers of Environment (with the exception of Quebec) in May 2001. A commitment was made to review additional scientific, technical and economic analysis to reduce information gaps and uncertainties after 5 years; the present version of the PHC CWS includes modifications and updates resulting from that review.

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 2008).

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.

PHC 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, PHC may create aesthetic problems such as offensive odour, taste or appearance in environmental media. Finally, under some conditions PHC 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 PHC are released to soils and groundwater. A blend of generic guidelines and site-specific, risk-based approaches emerged across Canada during the 1990's, but there was 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 historically 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 2000 and implemented in 2001 in recognition of the above factors. The current version of this document incorporates the results of the 5-year technical review conducted in 2005.

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 PHC 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 PHC requires a systematic approach and a number of simplifying assumptions. The PHC CWS considers PHC 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 - agricultural, residential/parkland, commercial and industrial (Figure 1.1). Additional land uses may be defined by regulatory jurisdictions as part of the implementation of the standard. 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 (2008).

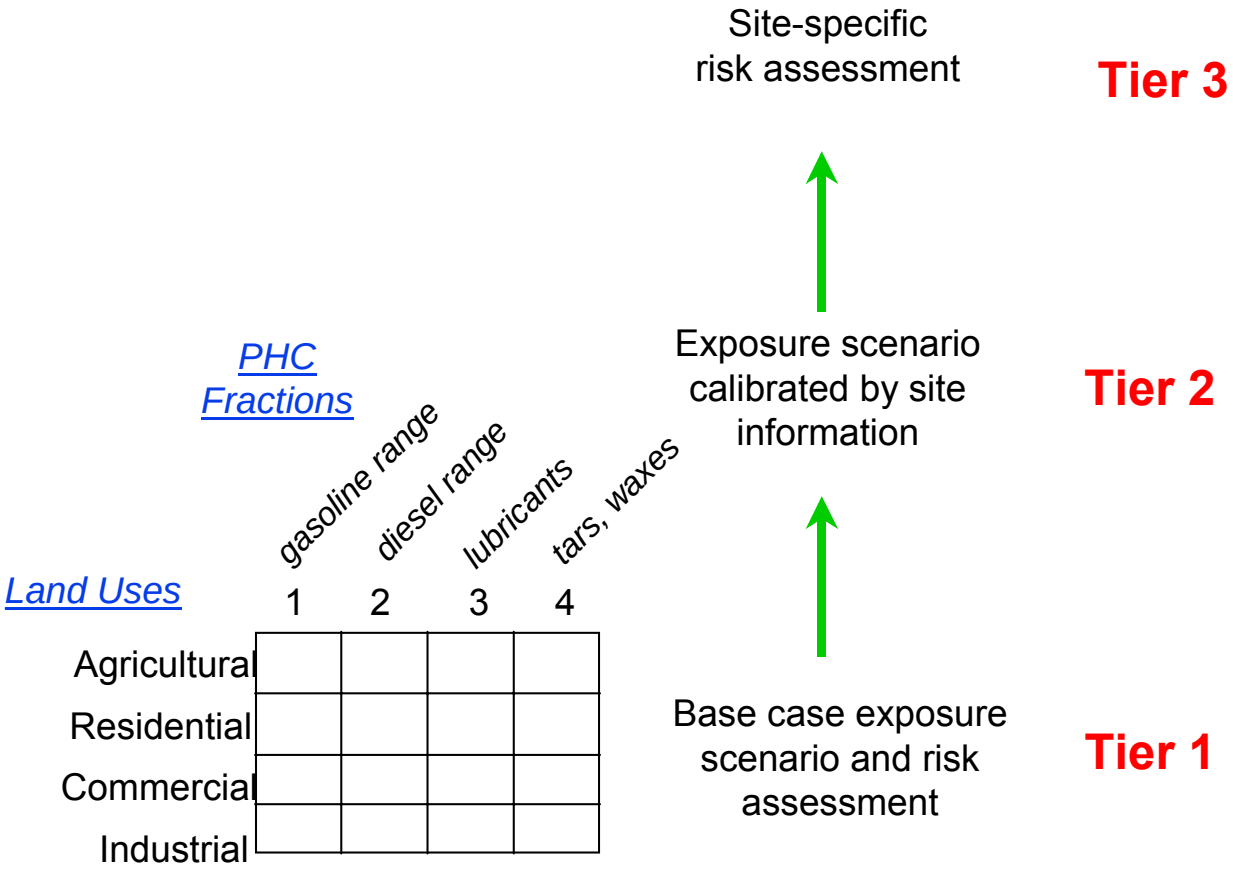


Figure 1.1: Tiered risk-based approach to managing PHC-contaminated soils.

1.4 Summary of Key Changes Since 2001

When the PHC CWS was implemented in 2001, a commitment was made to review new scientific information and experience with implementation, and update the standard after 5 years. Based on input from stakeholders, 3 technical advisory subgroups were struck to prepare a report and recommendations for updates to the standard. Reports from the 3 advisory subgroups are available under a separate cover. Based on these recommendations, the following key changes were made to the PHC CWS:

- The human soil ingestion and dermal contact pathways were combined, consistent with the current CCME (2006a) protocol.
- Modifications were made to several fate and transport model parameters to reflect current science.
- Ecological direct soil contact values were updated based on further toxicity testing and field studies conducted since the PHC CWS was implemented, as well as revisions to the

CCME (2006a) protocol for the development of guidelines based on the ecological direct soil contact pathway.

- Subsoil guidelines were removed from the standard due to difficulties with implementation, differences in approach between jurisdictions, and concerns about the scientific validity of the approaches for subsoils.
- Management considerations which had previously been incorporated into the ecological direct soil contact guidelines for subsoils have been separated and stated explicitly.

Minor adjustments and clarifications have been made throughout the PHC CWS supporting documents.

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* and the 2006a revised version of this document;
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 BC Ministry of Environment (Golder, 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 PHC, and following discussions with members of the PHC Development Committee and the Technical Advisory Groups (Appendix A). Based on a consideration of both physical-chemical properties and toxicological RfDs for the TPHCWG fractions, four 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 PHC rendered it necessary to generate ecotoxicological data on a carbon fraction-specific basis for the development of the standard. In the leadup to the 2001 criteria, ecotoxicity tests for F2, F3, mogas (motor gasoline) (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 BC Ministry of Environment.

Since 2001, several changes occurred that necessitated a review of toxicological information generated in 2001. This included;

1. Additional studies that have been performed since 2001. Additional work that was considered included Visser, 2003, 2005a, 2005b; Cermak *et al*., 2005; Cermak, unpublished; Axiom, 2005; ESG, unpublished.
2. The CCME (1996) protocol was revised and the details of the weight of evidence approach that was used in 2001 were no longer consistent with the revised protocol (CCME 2006a). Therefore, the data was reviewed with respect to evaluation methods used.

The results of this re-evaluation were incorporated into the toxicological evaluation of F1 through F4.

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.

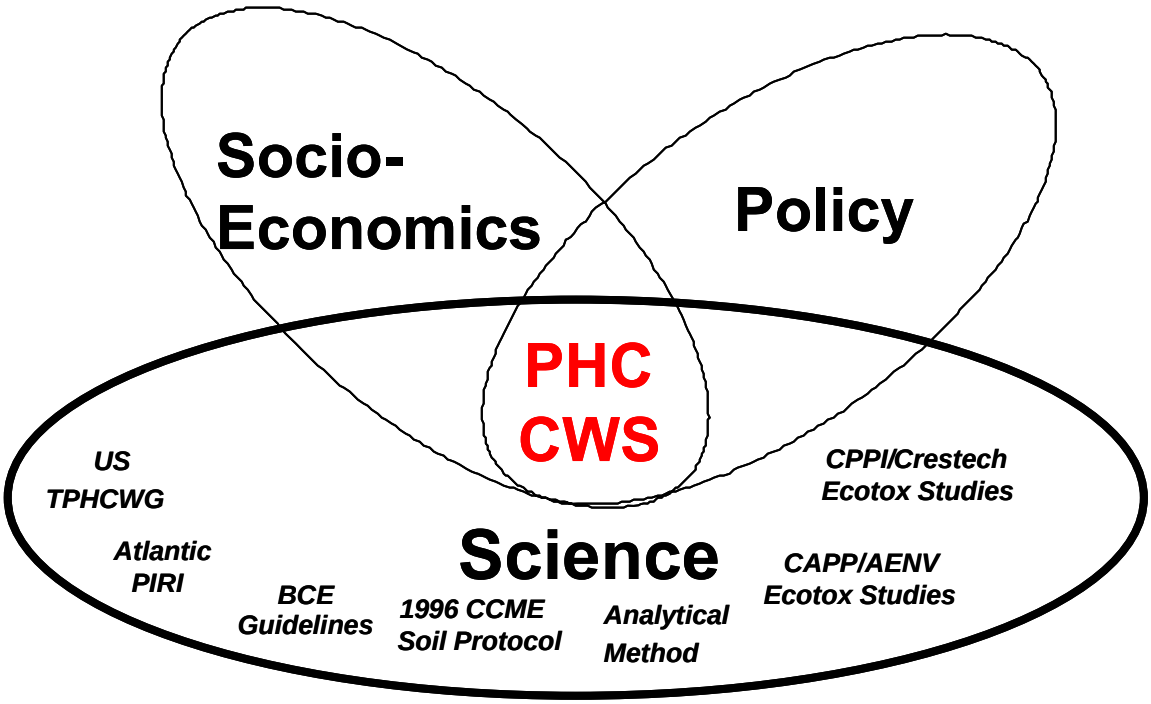


Figure 2.1: Scientific, socio-economic and policy based components of the PHC CWS.

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:

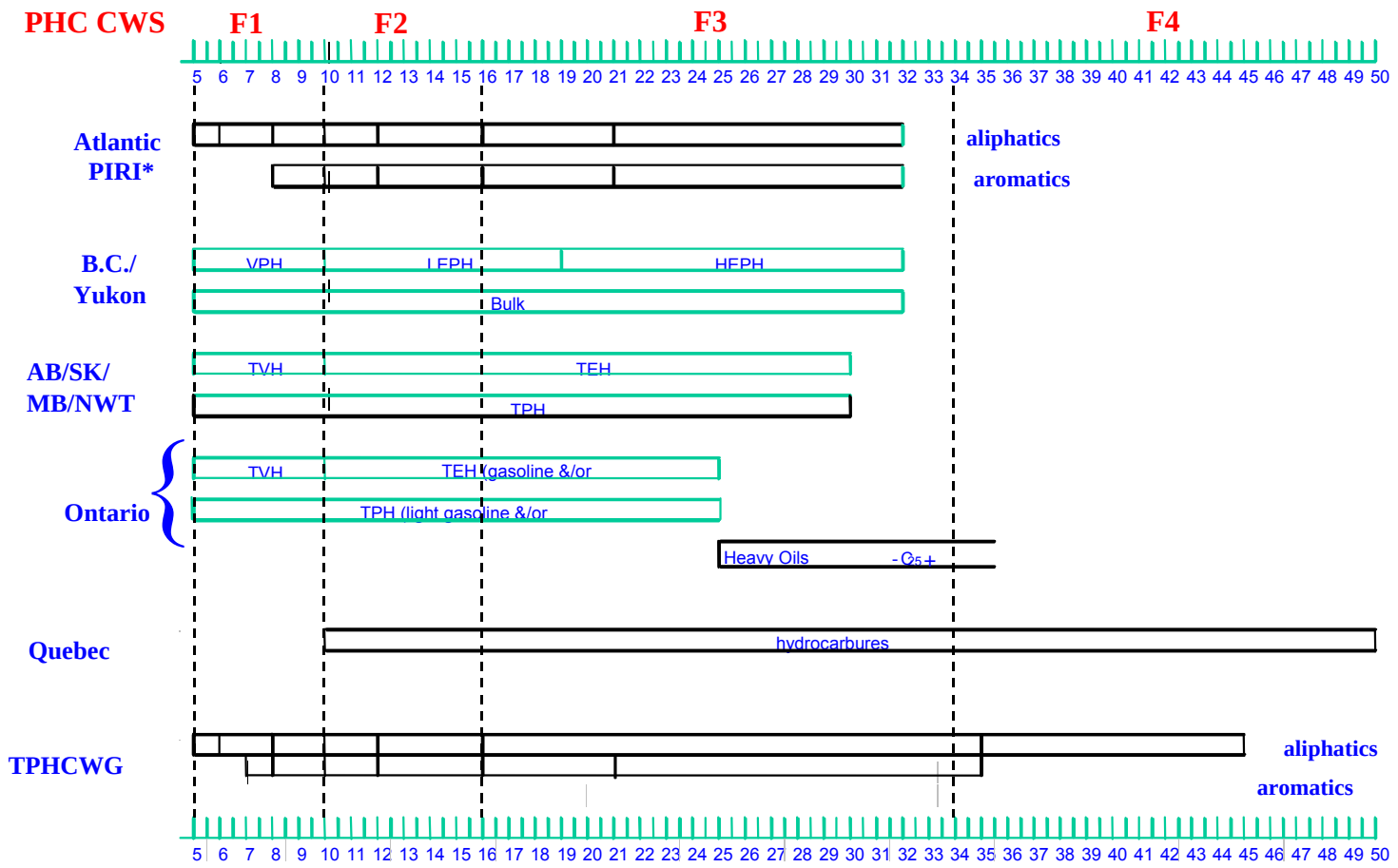
1. aromatics $C_{>7}$-C_8, $C_{>8}$-C_{10}
2. aliphatics C_6-C_8, $C_{>8}$-C_{10}

For aromatic hydrocarbons, the only aromatic hydrocarbons with ECN≤8 are benzene and toluene. Since it was recommended that both of these components be analyzed separately in PHC mixtures, the aromatic $C_{>7}$-C_8 was not used as a subfraction in the final evaluation.

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 a single RfD and RfC for 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: Historical carbon-fractions in relation to the PHC CWS fractions

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 PHC 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 PHC in soil is summarized in Table 3.7. Also included in Table 3.7 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 PHC at the contaminated site, thus requiring that BTEX be analyzed, assessed and managed separately from PHC.

2.3 Representing PHC Fractions: Whole Fraction Properties vs. Surrogates

TPHCWG Vol. 4 (Edwards *et al.*, 1997) 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 PHC 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 PHC, 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 - agricultural, 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 PHC and the pathways by which PHC 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 or natural areas). 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. Agricultural land may also include a farm residence.

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.

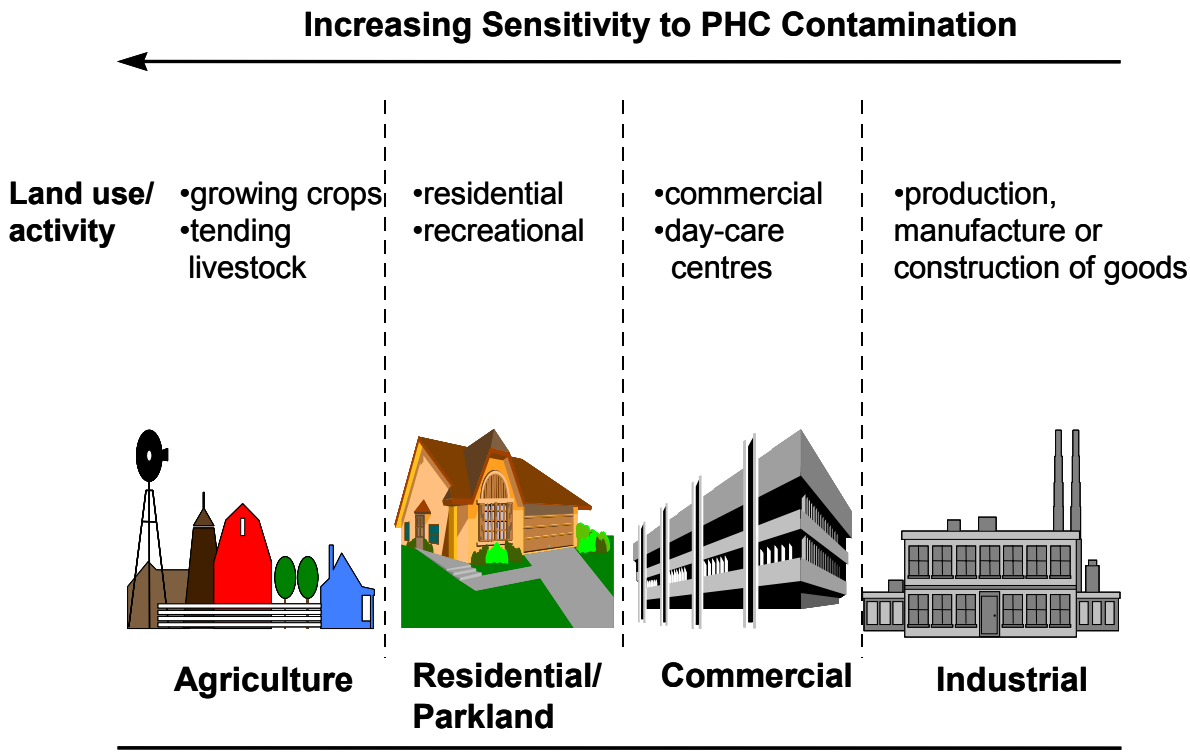


Figure 2.3: Generic land-use scenarios and their associated activities.

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 2008).

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

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

* wildlife dermal contact and ingestion data may be particularly important for PHC (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

** in most cases PHC are not expected to bioaccumulate to high concentrations in produce, meat or milk, though some polycyclic aromatic hydrocarbons (PAH) may bioaccumulate to a limited extent. The available data are currently insufficient to evaluate this pathway on a generic basis.

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 or livestock watering, it is assumed that use or potential use occurs on or immediately adjacent to the PHC-contaminated site. For the protection of aquatic life, it is assumed that a minimum lateral distance of 10 m exists between the contamination source in soil and a surface water body.

Details on the technical description of movement and attenuation of PHC in groundwater for potable use and aquatic life/livestock watering are provided in Chapters 3 and 4 respectively. In overview, potable groundwater and livestock watering 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 is described in CCME (2006a), and is similar to those used previously in CCME (1996), US EPA (1996) 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. Groundwater model parameters were chosen to be consistent with CCME (2006a).

An additional model component is required for the protection of aquatic life because it is assumed that a minimum lateral separation of 10 m 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 (1985) as adapted by CCME (2006a). Under this mathematical description attenuation of PHC includes:

- retardation by organic matter in the aquifer;
- a conservative, anaerobic biodegradation process;
- dispersion during transport.

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 cut-off 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 PHC

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 four 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 unity along four pathways – inhalation of vapours, direct contact with contaminated soil (incidental ingestion of soil and dermal contact with 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. Representative values for most parameters and characteristics are used which, when combined with conservative assumptions made about bioavailability and certain contaminant fate and transport processes, 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 PHC on the biotic component of a terrestrial ecosystem. Specifically, it evaluates the potential for adverse effects to occur from exposures to soil-based PHC 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 PHC in soils for the protection of ecological receptors is based on a 'weight of evidence' method as outlined in the CCME 2006a Protocol with some modifications. This approach facilitates the incorporation of disparate types of high quality information on the risks of PHC 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), bioavailability of PHC from exposure media, 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

During the initial development of the standard, 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 PHC 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.

An additional Socio-Economic analysis was undertaken as part of the 5-year review (Meridian, 2007). This socio-economic analysis was conducted on the basis of the proposed Tier 1 numerical values established as a result of the 5-year review of the Standard. While qualitative socio-economic factors, such as practical attainability and level of protection of human health and the environment, were considered in the assessment of uncertainties, a quantitative analysis was undertaken subsequently to assess the overall costs of complying with the standard, and the financial implications of moving from the original 2000 standard to the revised 2007 values.

The results of the 2007 analysis were not compared directly with those of the previous analysis, since different sources of data were used to estimate remediation requirements and costs for PHC contaminated sites. Many of the general socio-economic considerations discussed in the previous analysis remain valid. However, the major goals of the present analysis were to obtain an up-to-date estimate of the overall liability associated with PHC contaminated sites in various industry sectors across Canada, and to assess the effect of the proposed revisions to the numerical standard, in terms of differences in remediation costs, using actual, current site data representative of PHC conditions across a range of facilities and industries. While the results of the new analysis did indicate that there may be some specific circumstances that may be associated with a significantly higher or lower cost of remediation, the overall effects of the proposed 2007 revisions to the PHC CWS on remediation costs for PHC contaminated sites across Canada are relatively small.

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 Management Limits

In 2001, 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. In the 5 year review, it was determined that the subsoil levels created a lack of clarity relative to the derivation and implementation. Therefore, this approach was reviewed and the subsoil tables were removed. In their place, a management limit was developed to assess risks that may be associated with contaminant at depth and an option to remove the ecological direct contact pathway for contaminants at depth was incorporated. The rationale for, and details of the development of these 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, guidance on use of the management level is left to the discretion of the jurisdiction. 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 PHC have been developed for four general land uses (agricultural, residential/parkland, commercial, industrial) and two soil textures (coarse-grained and fine-grained).

3.1 Land Uses

The frequency, duration and intensity with which people contact pollutants at a contaminated site are related 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 and 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 the possible presence of an onsite residence (similar to those specified for residential/parkland sites, below) is considered in the default scenario. 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.

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 PHC 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 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. Intake via direct contact with soil (soil ingestion and dermal contact) is proportional to the days per week and weeks per year spent at the facility, but is not adjusted for hours per day since these exposures occur during discrete exposure events, and not at a continuous rate over 24 hours. 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 PHC 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 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. Intake via direct contact with soil (soil ingestion and dermal contact) is proportional to the days per week and weeks per year spent at the facility, but is not adjusted for hours per day since these exposures occur during discrete exposure events, and not at a continuous rate over 24 hours. 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 PHC penetrate the building envelope via foundation cracks and gaps.

3.2 Soil Texture

Tier 1 levels for PHC 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 PHC 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 PHC, the following pathways were considered (see Figure 3.1):

(a) direct contact with contaminated soil, including inadvertent ingestion of PHC contaminated soil and dermal absorption of PHC from contaminated soil deposited on the skin;
(b) inhalation of volatile PHC emanating from the soil following their infiltration to the indoor environment; and/or
(c) ingestion of soluble PHC 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 2006a), 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 pathways described in Section 3.3. Numerous models exist with which to assess these exposures. In selecting models to support Tier 1 and 2 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 PHC only).

Calculations performed for vapour intrusion and water ingestion pathways involve partitioning of PHC constituents among dissolved, sorbed and vapour phases. Tier 1 levels calculated for these pathways are based on the *total* (three phase) soil concentration as would be observed through the analytical method.

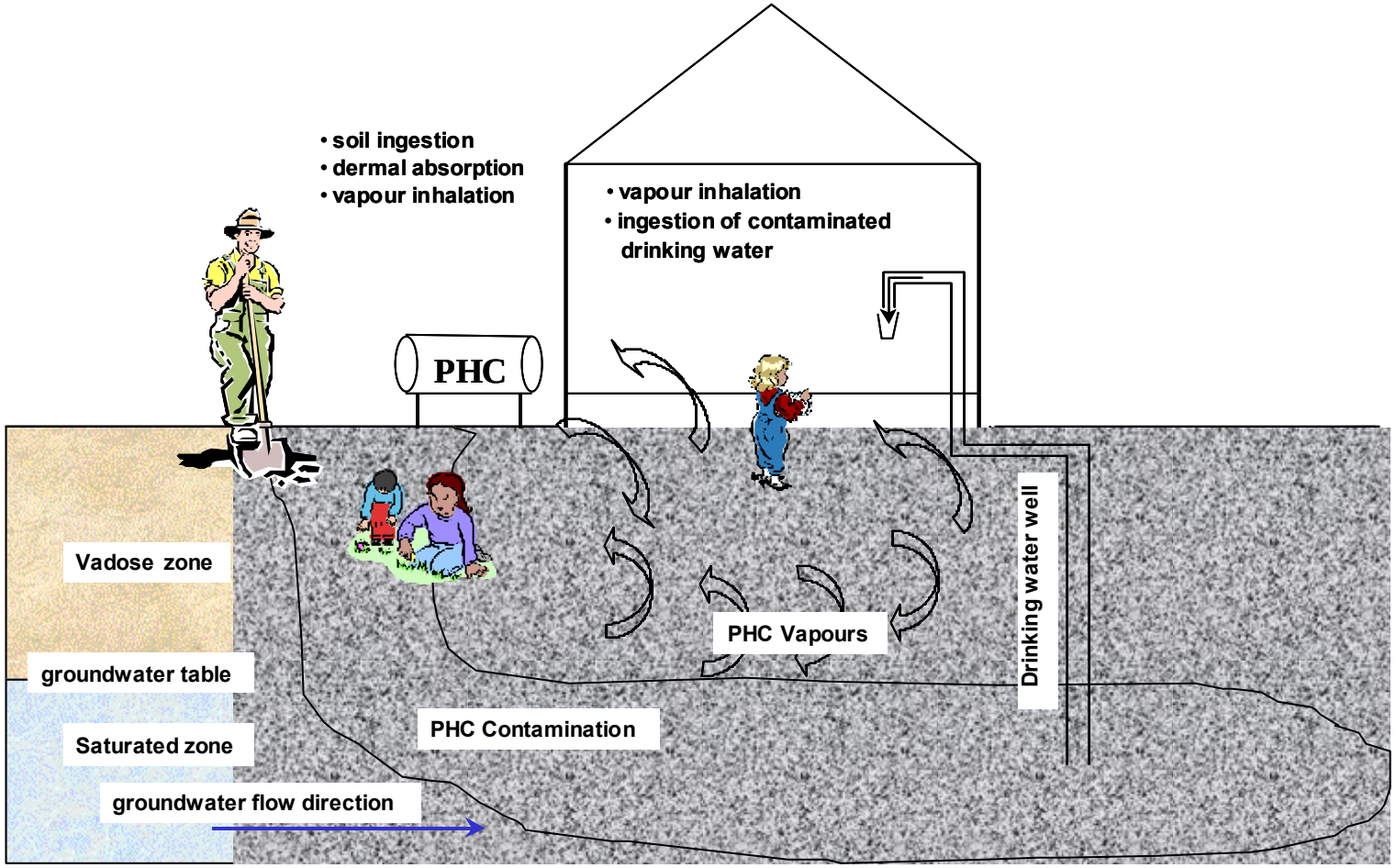


Figure 3.1: Human health exposure pathways to PHC contaminated soil.

3.4.1 Direct Contact with PHC-contaminated soil

Direct contact with contaminated soil (inadvertent ingestion of soil and dermal contact with soil) can be a significant pathway of human exposure to contaminated soil.

Studies indicate that children, and toddlers in particular, 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. 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.

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. Assumptions concerning exposed skin surface area and soil loading to skin are included in Table 3.1.

The equation used to estimate risk-based Tier 1 levels that prevent unacceptable exposure via inadvertent soil ingestion and dermal contact with soil is presented in Appendix C. This equation is based on that employed within the current CCME (2006a) protocol. It should be noted that the exposure term for direct soil contact does not include the number of hours per day exposed, since exposure via these mechanisms does not occur at a constant rate throughout the day, but is instead dominated by specific exposure events.

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)	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)	0.08	0.02
Surface Area - hands (SA_{HANDS})(m^2)	0.043	0.089
Surface Area - other (SA_{OTHER}) (m^2)	0.258	0.250
Dermal Loading to Skin (mg/m^2-event)		
Hands (DL_{HANDS})	1000	1000
Surfaces other than hands (DL_{OTHER})	100	100
Exposure Frequency (EF) (events/d)	1	1
Inhalation Rate (IR) (m^3/d)	9.3	15.8
Water Ingestion Rate (IR_W) (L/d)	0.6	1.5

(after CCME, 2006a, unless otherwise noted)
1 Toddlers are the critical receptors for agricultural, residential and commercial land uses.
2 Adults are the critical receptors for industrial land uses.
3 Exposure term for direct contact is (5/7)*(48/52) as discussed above

3.4.2 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 odour concerns at concentrations lower than the Tier 1 level concentrations derived to prevent health effects. Unfortunately guidelines for aesthetic factors, such as taste and odour, do not currently exist for broad PHC fractions as defined herein; guidelines for such aesthetic qualities may require future development. Aesthetic concerns must be addressed on a site-specific basis where they arise.

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 PHC distributed between the adsorbed, dissolved and vapour phases in soil were estimated using the linear partitioning methods described in CCME (2006a). 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 C of CCME (2006a). 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 potable water quality target 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 pore water concentration at the soil source. Linear partitioning constants are then applied to the pore water 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.

Site characteristics and soil parameters required for the modelling are summarized in Appendix C. The groundwater model is described in more detail in Appendix C.

Partitioning Relationship

Physico-chemical parameters (including log Koc) for TPHCWG sub-fractions are provided in Table B.1. Based on a review of the organic carbon 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 is calculated based on recharge rates, the groundwater Darcy velocity and aquifer depth, as described in Appendix C. Model parameters needed for the dilution expression are also listed in Appendix C.

Toxicological Benchmark

Toxicological endpoints and reference doses for TPHCWG sub-fractions are summarized in Appendix C. 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 3.7.

3.4.3 Indoor infiltration of Volatile PHC

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 Appendix C, along with assumptions concerning buildings into which the vapours might infiltrate and assumptions for chemical-specific variables.

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 US EPA (2003), 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. Available field data, primarily for chlorinated solvents, indicate that when correctly parameterized the model can be reasonably accurate for substances which do not undergo significant biodegradation (Golder, 2004).

3.4.3.1 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; US EPA 1997; Hers and Zapf-Gilje 1999; Little *et al*. 1992; and references therein). Therefore, advective flow must be considered and building characteristics and site features that influence advective flow must be defined.

Careful consideration of soil properties affecting both advective and diffusive flow was undertaken in preparation of the Tier 1 levels. For coarse-textured soils, measured soil gas flow rates have generally been found to be between 1 L/min to 10 L/min (US EPA, 2002; Golder, 2004). In addition, there are now identified ratios that have recommended ranges for coarse-textured sites. One such ratio is the Qsoil/Qbuilding ratio (ratio of the advective flow in the soil relative to the advective flow in the building (Johnson, 2002; Golder, 2004)). It is important to keep these principles in mind when developing default parameters for the coarse soil.

For fine soil, there is less available guidance relative to default soil parameters. However, concern was raised regarding the potential for fractured or macropore flow in fine soils that would potentially result in higher relative permeabilities than expected based on texture alone (e.g. McCarty et al., 1993, Jorgensen, 2004). Therefore, it was recommended that default permeability in fine soils be set at 10^{-9} cm^2 rather than 10^{-10} cm^2 recommended in CCME (2006a).

3.4.3.2 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 US 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 PHC 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. US EPA (2003) also recommends a default pressure differential of 4 Pa for residential buildings.

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.

Air exchange rates

- Residential buildings: 0.5 ACH
- Commercial buildings: 0.9 ACH
- Industrial buildings: 0.9 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 US 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.

Information does not appear to be substantially different than that available in 2001. However, generally this has led to a lower recommended default rate for air exchange than recommended in 2001 (Johnson, 2002, US EPA, 2003, Golder, 2004, Tindale, 2004). Based on the available data, an air exchange rate of 0.5 ACH was deemed appropriate to represent typical residential buildings.

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. However, mechanical ventilation often does not operate continuously. Based on more recent data reported by Persily and Gorfain (2004), an air exchange rate between 0.75 and 1 ACH per hour appears to be typical for commercial buildings; the midpoint of this range (0.875 ACH, or 0.9 ACH rounded to 1 significant figure) was therefore selected to represent commercial buildings.

Soil Vapour Permeability

The permeability of soil beneath a building foundation to vapours is one of the most sensitive parameters in the Johnson and Ettinger (1991) model. It is affected by the size and shape of soil pore openings as well as the water content of the soil.

US EPA (2003) suggests that typical soil vapour permeabilities are within the following ranges:

Soil Type	Vapour Permeability (cm^2)
Medium sand	$1.0x10^{-7}$ to $1.0x10^{-6}$
Fine sand	$1.0x10^{-8}$ to $1.0x10^{-7}$
Silty sand	$1.0x10^{-9}$ to $1.0x10^{-8}$
Clayey silt	$1.0x10^{-10}$ to $1.0x10^{-9}$

The Johnson and Ettinger (1991) model indicates that advective flow is the dominant process by which contaminants enter a building when the soil vapour permeability is high; as the soil vapour permeability becomes lower, diffusion begins to affect transport into the building. However, advection can still have a noticeable effect even at a soil vapour permeability of $1.0x10^{-10}$ cm^2.

Available empirical data (US EPA, 2003; Golder, 2004) indicate that soil gas flow rates into residences above coarse-textured soils are likely on the order of 5 L/min. Based on the other assumed site and building parameters, a soil vapour permeability of $5x10^{-8}$ cm^2 leads to soil gas flow rates of this magnitude (using the calculation method in Appendix C) and an appropriate ratio of soil gas flow rate to building air flow rate (based on Johnson, 2002); this value is also consistent with the anticipated vapour permeability of typical coarse-textured sites. A value of $1x10^{-9}$ cm^2, expected to reflect silty soils, was selected as representative of fine-textured sites. The upper end of the range was chosen based on the potential for fractured flow in fine medium, as described in the previous section.

Soil Temperature

Soil temperature influences the amount of a volatile chemical entering the vapour phase. Some regulatory guidance documents allow the Henry's Law constant of chemicals to be adjusted for temperature to reflect this. However, the Henry's Law constants developed by TPHCWG and applied for the PHC CWS are based on correlations of data reflecting a range of temperatures from 10°C to 25°C (Gustafson *et al.*, 1997), making it difficult to justify a temperature adjustment. Furthermore, theoretical modelling conducted by the University of Alberta in support of the PHC CWS 5-year review indicated that temperatures within 1 m of a building slab are generally within approximately 1°C of temperatures in the overlying buildings; this observation is also supported by a Greek study (Mihalakakou *et al*., 1995) of soil temperatures beneath buildings. Therefore, a soil temperature of 294 K is used for vapour intrusion modelling, and Henry's Law constants are not adjusted for temperature.

Diffusional path length for volatile PHC

For Tier 1, 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 site specific, Tier 3 analysis is required because the performance of the vapour intrusion model is uncertain in this parameter range; seasonal fluctuations in the water table, sumps connected to the basement, and other factors may affect the migration of vapours when contamination is very close to the building (Golder, 2004). It is also assumed that the building includes a concrete foundation. 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 3.2. The vapour intrusion pathway is not considered to be operative beyond a distance of approximately 30 m (US EPA, 2003; Golder, 2004).

Table 3.2: 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 basement		Residential, slab-on-grade		Commercial/Industrial, slab-on-grade	
	f/g	c/g	f/g	c/g	f/g	c/g
30	35671	1889	30524	1438	62935	4605
100	36137	2469	31360	2480	64190	6167
200	36802	3297	32556	3968	65983	8399
300	37468	4125	33751	5456	67777	10630
500	38798	5781	36142	8431	71363	15094
1000	42124	9922	42119	15871	80328	26252
2000	48778	18202	54073	30749	98259	48570
3000	55430	26483	66026	45627	116189	70887

* - adjustment factor (below) not included in DF

Adjustment Factor for Biodegradation and Partitioning

Modifications to several model input parameters have been made since the 2001 PHC CWS, supported by recent scientific literature. Although the objective of these modifications is to increase the degree of realism and defensibility of the model assumptions, the modifications in fact result in less attenuation of PHC vapours than is observed from site data at actual PHC-contaminated sites.

While, as noted above, the Johnson and Ettinger (1991) model has been shown to predict indoor air concentrations relatively well for chemicals which do not undergo significant biodegradation, such as chlorinated solvents, the model predictions are considered less reliable for substances which undergo significant biodegradation in the vadose zone, such as PHC.

The extent of biodegradation is highly variable and dependent on site-specific factors. Roggemans *et al*. (2001) found that steady-state equations not accounting for biodegradation did not reasonably predict hydrocarbon profiles in soil vapours at most sites, and indicated that not accounting for biodegradation could result in risks being over-predicted by a factor of 10 to 10,000 at some sites; however, the observed biodegradation at the studied sites could not be correlated with site characteristics. Numerical modelling conducted by Abreu and Johnson (2006) showed that even limited biodegradation would result in significant attenuation of hydrocarbon vapours, and that sufficient oxygen for aerobic biodegradation of PHC would be expected beneath slab-on-grade foundations. Golder (2004) suggested that a conservative factor of 10 to account for biodegradation of PHC during transport from the PHC source to the building would be reasonable if the vapour contamination is located at least 4 m below the building and there is no significant capping effect which would prevent oxygen from migrating below the building. NJDEP (2005) applied a biodegradation factor of 10 to groundwater guidelines for BTEX based on the vapour inhalation pathway, without any specific site conditions being required.

Furthermore, empirical data and a literature review indicate that the equilibrium partitioning relationship may significantly over-predict soil vapour concentrations of PHC. US EPA (1993) noted order of magnitude differences between observed and predicted sorption of volatile organic compounds to soils. Hartman (2002) stated that observed petroleum hydrocarbon soil vapour concentrations were 10 to 1000 times lower than those predicted based on soil concentrations, while Viellenave and Fontana (undated) stated that measured vapour concentrations were often 3 to 5 orders of magnitude lower than those predicted by modelling; these authors did not provide actual data to support these assertions, however.

There are several potential factors which may affect the partitioning relationship (US EPA, 1993; US EPA, 2005; Viellenave and Fontana, undated; Shih and Wu, 2005):

- contaminants adsorb to soil minerals as well as organic carbon
- the degree of adsorption to organic carbon is affected by the form of the organic matter
- contaminants may be adsorbed by anthropogenic carbon sources, including residual hydrocarbons in the soil
- secondary soil structures such as aggregates, fractures and bedding affect adsorption
- organic compound residues form in occluded soil pores; the amount of these residues increases over time

- organic compounds may adsorb to the air-water interface in the unsaturated zone
- where a residual organic phase or occluded organic compounds are present, the presence of the organic phase may influence sorption of the compound of interest.

US EPA (1993) indicated that non-equilibrium soil adsorption occurring over time is much greater than equilibrium adsorption. Eventually, the soluble, volatile and easily desorbed phases dissipate, and the non-equilibrium sorbed fraction becomes the dominant form of soil contamination. Additionally, Shih and Wu (2005) found that, under laboratory conditions, sorption of toluene to soil was related to soil surface area as well as organic carbon content.

The Henry's Law constant, used to predict the partitioning of chemicals between the dissolved and vapour phases, assumes that equilibrium conditions are present. Volatilization may be rate-limited, with diffusion of contaminants through pore water and across the water-air interface being much slower than diffusion of contaminants away from the source through the soil air.

A review of matched soil and soil vapour data for F1 in coarse soils undertaken for the PHC CWS revision found that predicted to observed concentration ratios for F1 were consistently greater than 100.

Despite the data suggesting that the equilibrium partitioning relationship does not accurately reflect actual PHC concentrations in the vapour phase, no suitable alternative relationship was identified.

Based on the available empirical data, an adjustment factor of 10 has been applied to the vapour inhalation modelling results. The adjustment factor only applies to soil guidelines for PHC (not to soil vapour guidelines at this time, or to chemicals other than PHC). The adjustment factor can be used in Tier 2 modifications of Tier 1 values. If site-specific conditions such as low oxygen (which would result in lower aerobic biodegradation) may be present, the appropriateness of the adjustment factor should be assessed on a site-specific basis, and a Tier 2 or Tier 3 approach applied if necessary.

3.5 Receptor Characteristics

The critical human receptor, that may experience the hypothetical (modeled) exposure to PHC, is dependent on the prescribed land use. For residential land use, the critical receptor is assumed to be a toddler, which 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 PHC 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 guidelines for PHC 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 US 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); these values have also been adopted by Health Canada (2004) and CCME (2006a). In cases where empirical Canadian data do not exist for receptor characteristics (soil ingestion rate, for example), alternate sources for assumptions were used by Health Canada (2004) and CCME (2006a); these values are adopted herein.

3.5.1 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, 2004) recommended deterministic assumptions for risk assessments. These body weight values have also been adopted for use by the Atlantic provinces within the Atlantic RBCA Tool Kit and are now widely employed throughout Canada for contaminated site risk assessments.

3.5.2 Inhalation rate

Recommended values:

- Adult: 15.8 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 Health Canada (2004) for preliminary quantitative risk assessments and are widely used in contaminated site

risk assessments in Canada. It should be noted that inhalation rates are not directly used in the Tier 1 calculations for the PHC CWS, since toxicity reference values for F1 and F2 for the inhalation pathway were expressed as RfCs, and are provided only for completeness and extension of the methodology to other chemicals.

3.5.3 Water ingestion rate

Recommended values:

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

Recommended water ingestion rates were proposed by 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 Atlantic RBCA Tool Kit and are now widely employed throughout Canada for contaminated site risk assessments.

3.5.4 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 oesophagus 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 (US EPA 1997a). 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, 2006a) have been adopted for derivation of the PHC CWS. These values have also been adopted by Health Canada (2004), and a recent review of soil ingestion rates conducted on behalf of Health Canada concluded that they remain appropriate for deterministic risk assessments (Wilson and Meridian, 2006).

3.5.5 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 US 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 the Atlantic RBCA Tool Kit, and are now routinely employed for site-specific risk assessments across Canada (Health Canada, 2004).

3.5.6 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.

3.5.7 Exposure frequency

Recommended values are:

- Agricultural land use: 1 (24 h/d, 365 days/year)
- Residential land use: 1 (24 h/d, 365 days/year)
- Commercial land use: 0.275 (inhalation) or 0.66 (direct contact)
  - (10 h/d) x 5 d/wk x 48 wk/yr
- Industrial land use: 0.275 (inhalation) or 0.66 (direct contact)
  - (10 h/d) x 5 d/wk x 48 wk/yr

Note: hours per day exposed are not considered for direct contact (soil ingestion and dermal contact), since these exposures do not occur at a constant rate over the day, but rather from specific exposure episodes (Health Canada, 2004).

Recommendations concerning exposure frequency, for derivation of the PHC CWS, were adopted from CCME (2006a) to maintain consistency with previous methods and assumptions regarding exposure frequency for soil quality guidelines derivation and site-specific risk assessment in Canada.

3.5.8 Exposure duration

For purposes of deriving the PHC CWS, shorter-than-lifetime exposures were not amortized (averaged) over a lifetime (70 years), consistent with Health Canada and CCME protocols for non-carcinogens. Therefore, explicit definition of a default exposure duration is not required for derivation of Tier 1 soil quality levels.

3.5.9 Route-specific absorption rates

3.5.9.1 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 PHC is 100%.

3.5.9.2 Inhalation. Tolerable air concentrations (TCs) (RfCs) for volatile environmental contaminants are normally derived based on the exposure concentration for test subjects or animals, rather than the absorbed dose. For those PHC 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 PHC is 100%.

3.5.9.3 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 relative 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; CCME, 1996, 2006a). 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, US EPA 1992a).

For the purpose of prescribing soil quality levels for the CWS PHC initiative, it is recommended that a relative 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 ethylbenzene 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 (US 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 (US 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 3.3. 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 a relative 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 3.3: 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)

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

3.6.1 Application of RfCs Versus TDIs

The PHC CWS development process considered non-carcinogenic PHC only. Soil quality guidelines for carcinogenic PHC (benzene, various PAH) have been published elsewhere (CCME 1999 and updates). 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 PHC has opted to employ route-specific toxicity reference values (TRVs) for the derivation of soil quality levels for those PHC. For the purposes of Tier 1 level development, reference concentrations RfCs (similar to the Health Canada term "tolerable concentration") were identified for evaluation of PHC via the inhalation route, while tolerable daily intakes (TDIs) (similar to the US EPA term "reference dose" or RfD) were identified for evaluation of PHC via the oral and dermal routes of exposure. 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, residential, commercial, industrial). For PHC fractions considered non-volatile (F3 and F4) or for those pathways involving exposure routes other than inhalation (i.e., direct soil ingestion, ingestion of contaminated groundwater, dermal absorption), TDIs were applied.

RfCs are defined by the US Environmental Protection Agency (US EPA 2006) 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 essentially analogous to TDIs from a protection goal perspective except that the units are expressed as air concentrations rather than dose rates. 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 (as well as Health Canada and the US EPA) considers RfCs to provide adequate human health protection for all age groups.

The usual approach for identifying RfCs and TDIs for use in Canadian soil quality guidelines development (and for human health risk assessment) is to rely on information provided by regulatory agencies in the following order of preference (see Health Canada 2004 for additional details):

- Health Canada;
- US EPA;
- World Health Organization (WHO);

- Netherlands National Institute of Public Health and the Environment (RIVM); and,
- US Agency for Toxic Substances and Disease Registry (ATSDR).

If none of the above agencies have a stated position on a particular chemical or chemical group, other agencies and expert organizations are typically reviewed. Finally, if no information is identified from recognized organizations, the scientific literature can be reviewed to determine if a *de novo* toxicity reference value can be developed.

In the case of PHC as a group of chemicals, the review failed to identify any major regulatory agency that has developed a specific toxicity reference value rationale for the evaluation of human health effects from PHC mixtures (as opposed to distinct chemicals, for which toxicity reference values are quite common), though RIVM has provided a rationale for adopting the TPHCWG approach. Consequently, RfCs for PHC groups derived by the TPHCWG, following methods delineated by the US EPA (1994), for aromatic and aliphatic sub-fractions spanning C_6 to C_{16} (Edwards *et al*. 1997) were recommended for use by the Development Committee for the PHC CWS. The basis and rationale for this recommendation is provided in the sections that follow.

3.6.2 Toxicology of PHC

An extensive review of the toxicity of components and fractions of PHC has been presented by Edwards *et al*. (1997), along with the derivation of TDIs and RfCs for the petroleum hydrocarbon sub-fractions defined by the TPHCWG. Edwards *et al*. (1997) reviewed the 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 3.4 were established by the TPHCWG. Those toxicity reference 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 unacceptable risks from arising in the vast majority of the population throughout lifelong exposure. It should be noted that the toxicity 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.

As part of the 5-year review process, the TRV Advisory Subgroup was convened in 2005; this group completed a review and analysis of the toxicological data to determine if more recent data and information had become available since the release of Edwards *et al*. (1997). Overall, it was the opinion of the TRV Advisory Subgroup and the CCME Soil Quality Guidelines Task Group (SQGTG) that, although various uncertainties remain with the Edwards *et al*. (1997) analysis, the toxicity reference values provided by the TPHCWG remain valid at the current time and represent the most reasonable published approach for addressing risk from PHC. There were some concerns raised and therefore certain provisions made relative to the distribution of compounds in the fractions. These are noted in the subsequent sections below. As part of these provisions, it has been recommended that the concentration of n-hexane be assessed in the F1 fraction. Further discussion on this is noted in section 3.6.2.2.

3.6.2.1 **Aromatics**

Overview of the TPHCWG Approach for Aromatics

While TPHCWG presented toxicity reference values for aromatic PHC in the $C_{>6}$ to C_8 range, this subfraction is not considered herein, since benzene and toluene are the only aromatic hydrocarbons with an equivalent carbon number in this range, and these are managed separately at PHC-contaminated sites. Edwards *et al*. (1997) included data for ethylbenzene, xylenes and styrene for this range as well, but all of these compounds have equivalent carbon numbers greater than C_8 (Gustafson *et al*., 1997).

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 US EPA. In addition, unpublished data on the effects of oral exposure of rats to a mixture of naphthalene and methylnaphthalenes 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 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 PHC 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 PHC with $C_{>16}$ are insufficiently volatile to pose an inhalation risk.

Re-Evaluation of the TPHCWG Approach for Aromatics:

At the current time, there does not appear to be specific information that suggests that the TPHCWG approach will not be protective of adverse health effects from aromatics. Although various new toxicological data have been published and regulatory positions have been amended on individual chemicals, it appears that the TPHCWG approach should still be protective of human health risks on aromatics as a group.

It is noted that a report prepared for Health Canada by Equilibrium Environmental Inc. (Equilibrium, 2005a) identified that new inhalation toxicity studies and regulatory reference values have been developed for naphthalene and methylnaphthalenes since the original release of the PHC CWS. In addition, Equilibrium (2005a) identified that new inhalation toxicity studies and preliminary reference values have been developed for 1,2-diethylbenzene and 1,2,4-triethylbenzene since the original release of the PHC CWS. The TRV Advisory Subgroup (CCME 2006d) assessed the potential for these substances to be present in sufficient quantities to pose a risk to human health via indoor air exposure and drive the existing F2 TRV. In brief, the maximum estimated vapour phase concentrations of naphthalene, methylnaphthalenes, 1,2-diethylbenzene, and 1,2,4-triethylbenzene were estimated to be relatively low (i.e., less than the

corresponding screening concentration derived for protection of indoor air quality) and, therefore, it was concluded from a preliminary analysis perspective that these substances were unlikely to pose a risk to indoor air quality at petroleum-contaminated sites remediated based on the TPHCWG RfCs.

Consequently, although additional information has become available since the publication of Edwards *et al*. (1997), modification of the TPHCWG toxicity reference values for aromatics was not considered to be warranted on the basis of the information reviewed. However, as more data become available on both the composition of the aromatic sub-fractions in vapours at contaminated sites and on toxicity of the compounds and mixtures in this range, further re-evaluation may be required.

3.6.2.2 Aliphatics

Overview of the TPHCWG Approach for Aliphatics

As described by Edwards *et al*. (1997), within the aliphatic sub-fraction C_6 to C_8, n-hexane is the only compound for which the US EPA has established a TDI (or RfD), At the time of preparation of the TPHCWG report, that value was 0.06 mg/kg-d. This value has subsequently been revised, as discussed in the following section. In addition to the regulatory agency positions, toxicity data for a variety of other hydrocarbons exists, which were reviewed by Edwards *et al*. (1997). These hydrocarbons include cyclohexane, methylpentanes and methylcyclohexane. Also, data exist on commercial hexanes, and mixtures 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_8 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, was selected by Edwards *et al*. (1997) 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 PHC 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 PHC 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 PHC in this range.

Re-Evaluation of the TPHCWG Approach for Aliphatics:

At the current time, and assuming that n-hexane does not comprise a major component of the F1 fraction or is addressed separately as a distinct chemical entity (similar to BTEX chemicals), there does not appear to be any specific information that suggests that the TPHCWG approach will not be protective of adverse health effects from aliphatics. Various new toxicological data have been published and regulatory positions have been amended for various aliphatic chemicals. However, at the current time, no information is available that indicate adverse health effects from aliphatics will occur at the RfCs used by TPHCWG and summarized in Table 3.4.

Since the time of preparation of the TPHCWG, US EPA (2006) has re-evaluated n-hexane and currently recommends an RfC of 0.7 mg/m^3 (at the time of publication of Edwards *et al*. [1997], the US EPA recommended a TDI of 0.06 mg/kg bw/day which was essentially equivalent to a RfC of 0.2 mg/m^3). The revised RfC was based on a re-analysis of the data that suggested that the study previously used to determine a toxicity reference value may have overstated the toxic potency of n-hexane due to concomitant exposures with other chemicals.

It is noted that a report prepared for Health Canada by Equilibrium Environmental Inc. (Equilibrium 2005b) identified possible irritant effects in laboratory animals that may be associated with the C_6-C_8 aliphatics at an exposure concentration of approximately 3100 mg/m^3, which is lower than the NOAEL used to derive the commercial hexane RfC. This information dominantly seems to originate from an American Petroleum Institute two-year rat inhalation exposure study (API, 1995 as cited in MDEP, 2003) that indicated evidence of irritation and mucosal lining inflammation in rats. These end points occurred at a dose of ~3100 mg/m3. However, as a follow-up to this study, a preliminary review of the toxicological data on the irritancy of aliphatics did not identify any specific human studies that demonstrated irritancy at the TPHCWG RfC for the C_6-C_8 aliphatics (Equilibrium 2006).

TRV Advisory Subgroup (CCME 2006d) did note that if n-hexane existed at appreciable concentrations within the C_6-C_8 aliphatic fraction, it may be possible that the US EPA n-hexane RfC could be exceeded without exceeding the C_6-C_8 aliphatic fraction RfC. However, provided that n-hexane is evaluated as a specific chemical entity, there would be no unacceptable health risks expected from this RfC.

Finally, Equilibrium (2005b) indicated that n-heptane, 3-methyl hexane, 3,4-dimethyl hexane and n-nonane could potentially form neurotoxic metabolites. TRV Advisory Subgroup (CCME 2006d) concluded that limited available data for n-heptane, 3-methyl hexane and n-nonane suggested that these compounds likely have significantly lower neurotoxic potential than n-hexane (from a preliminary analysis perspective). In addition, the concentrations of these specific chemicals are largely unknown.

Although some uncertainties exist, at the current time, modification of the TPHCWG toxicity reference values for aliphatics was not considered to be warranted on the basis of the information reviewed (provided that n-hexane is evaluated as a distinct chemical). Similar to that described

for aromatics, however, further re-evaluation may be required as more data become available on both the composition of the aliphatic sub-fractions in vapours at contaminated sites and on toxicity of the compounds and mixtures in this range.

Table 3.4: Toxicological endpoints for tolerable daily intakes (reference doses) and reference concentrations developed by the Total Petroleum Hydrocarbon Criteria Working Group.

TPH Sub-fraction	TDI mg/kg/d	RfC mg/m^3	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 PHC is not sufficiently volatile to present air-borne exposure.

3.6.3 Background Exposures, Residual TDIs and Residual RfCs

Excluding PAH, no reports of generalized background contamination of air, water, food or soil (unrelated to contaminated sites) were located for component PHC in fractions 2, 3 and 4 (i.e., $C_{>10}$). This likely stems from their generally low or negligible solubility and volatility. PAH are evaluated separately from PHC 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 PHC in fractions 2, 3 and 4, the estimated daily intakes (EDI) of PHC in fractions 2, 3 and 4 from background sources are considered to be zero.

PHC 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 PHC. Therefore, it was concluded that the occurrence of these PHC 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 PAH in grilled and barbecued foods, for example).

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

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 3.5.

3.7 Soil Allocation Factors and EDIs to be Employed for Tier 1 Levels

People can receive exposure to contamination from five different media – 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). This has subsequently been updated in CCME, 2006a.

Table 3.5: 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]				
	µg/m^3	µg/m^3	µg/kg-d	µg/kg-d	µg/kg-d	µg/m^3	µg/m^3	µg/kg-d	µg/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 PHC, 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 3.6 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. In 2001, CCME used a SAF of 1 for the water ingestion pathway and this was not changed in the review.

It should be noted that in using the SAF to account for each of the contaminated soil pathways, the Development Committee has assumed that there is an imbalance in exposure from 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.

3.8 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. Necessary assumptions for input variables are presented in Appendix C. Default characteristics for critical receptors are presented in Table 3.1. Calculations for individual TPHCWG sub-fractions are combined into the four CCME fractions on a weight-percent basis, employing the formula for combining fractions presented in Appendix C and the weight percents (also presented in Appendix C).

Table 3.6: Soil allocation factors (SAF) for deriving soil quality levels for PHC*.

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 3.7)

Table 3.7: 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 1; 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.

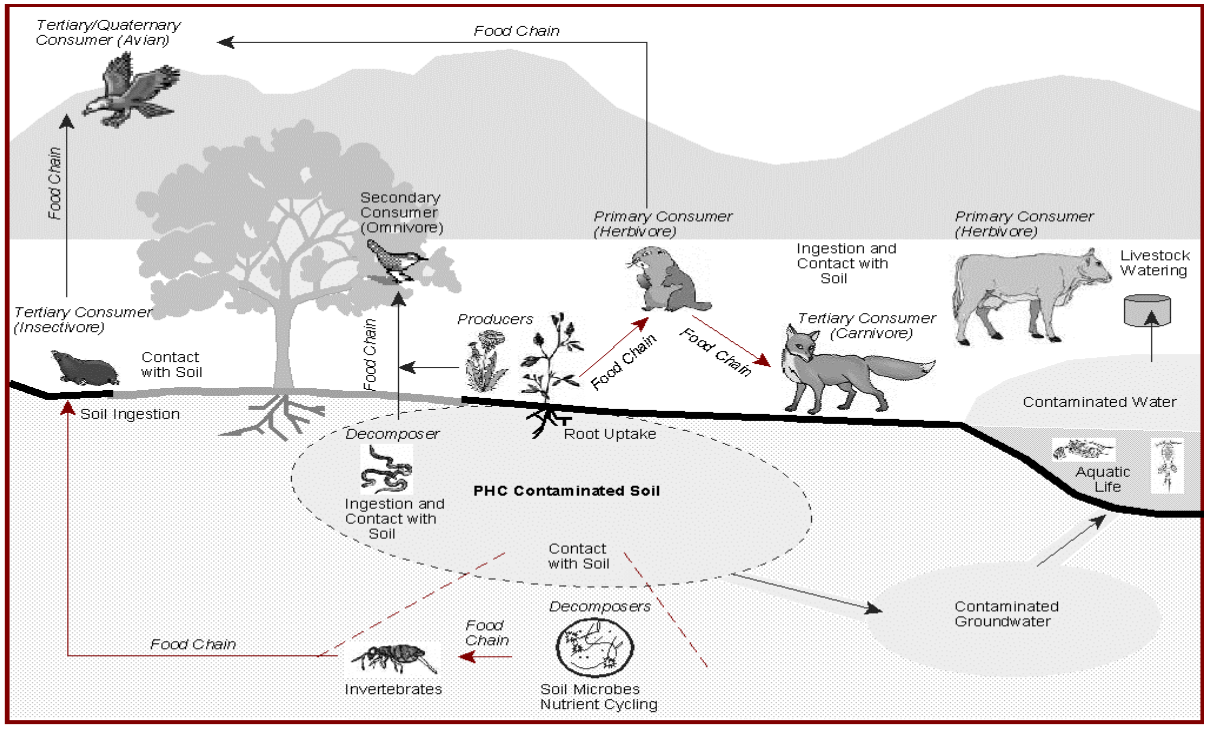


Figure 4.1: Key ecological receptors and exposure pathways of PHC contaminated soils.

The PHC CWS Tier 1 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 fulfill critical ecological roles under each land use 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.

Specifics of the scientific rationale for the guideline values developed 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 · Aquatic life in adjacent water bodies

In some non-Canadian jurisdictions, as well as in detailed ecological risk assessments, the development of soil screening or remediation guidance for PHC 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 PHC 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 PHC are readily metabolized by vertebrates, modified into a more readily excretable form, and thus do not tend to accumulate in tissues. In addition, PHC 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 PHC 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 PHC from anthropogenic releases to the environment is unacceptable and that remedial activities are necessary wherever free-phase PHC are observed.

The derivation of the PHC CWS 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 PHC 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.

A range of different data types was available as the toxicological basis of the various ecological soil quality guidelines. The way in which the available data were used to derive the ecological soil quality guideline for each exposure pathway and hydrocarbon fraction are described in the following sections. The overall principles applied were to consider all of the available data, and then to evaluate each dataset on its merits, taking into consideration the most recent available draft of the CCME protocol for developing soil quality guidelines (CCME, 2006a).

4.2 Direct Soil Contact – Protection of Soil Invertebrates and Plants

This section builds on work done in the 2001 development of the PHC CWS, and considers existing and new (post-2001) toxicological data and the latest CCME (2006a) protocol, Pertinent sections of the 2001 PHC CWS scientific rational document are preserved in this document as Appendix D. These are provided as background information and to retain an understanding of how the ecological direct soil contact guidelines in the 2001 PHC CWS were developed.

4.2.1 Protocols Used, and Departures from Existing Protocols

There are challenges inherent in selecting a single guideline value to protect plants and soil invertebrates based on a disparate dataset of toxicological information for a wide range of species and endpoints. The 2001 PHC CWS approached this challenge by developing a protocol where redundant data were combined or eliminated, and the response of each non-redundant species/endpoint were expressed, wherever possible, as the 50th percentile effect level (IC50, EC50, or LC50). The non-redundant data were ranked, and the 25th percentile of the distribution was adopted as the guideline for agricultural and residential/parkland use, while the 50th percentile of this same distribution was used as the commercial/industrial guideline.

Since 2001, further consideration has been given to the protocols for developing soil quality guidelines for this exposure pathway. These deliberations have been brought together in the updated CCME (2006a) protocol. The most significant change from the 2001 PHC CWS protocol is additional guidance around application of the weight of evidence method. In particular, in the CCME (2006a) protocol toxicological data are standardized at the 25th percentile (IC25, EC25, or LC25) and additional guidance is given on response of individual species within the weighting process that was not available in 1996.

The weight of evidence CCME (2006a) protocol for developing soil quality guidelines for the ecological direct soil contact exposure pathway may be summarized as follows.

- Available data are standardized at, or as close as possible to the 25th percent effects level (EC25, IC25, or LC25).
- If tests are available which differ only in exposure duration, then only the results from the longest duration test are used.
- Redundant data are combined (as a geometric mean) or removed.
- The remaining data are ranked as a "species sensitivity distribution" (SSD), and the 25th percentile of the SSD is used as the guideline for agricultural and residential land use, while the 50th percentile of the SSD is used as the guideline for commercial and industrial land use.
- Final check to ensure both invertebrates and plants are sufficiently protected by the ranked percentile.

In the analysis which follows (Sections 4.2.4 to 4.2.7), existing and new data for each of the four PHC fractions were considered on their respective merits. Data analysis followed the CCME (2006a) guidance as closely as possible, however, as indicated in the following sections, there

were certain areas where it was necessary and desirable to diverge from CCME (2006a), based on the types of available data and other issues.

An important point to note with all weight-of-evidence protocols, including the protocols used to generate the 2001 PHC CWS guideline values, the CCME (2006a) protocols, and the protocols used to develop guidelines in this document is that they set guideline values within the effects range. This means that at the guideline level, effects may be seen in sensitive species/endpoints. For instance earthworm reproduction may be affected at the guideline level. This is inherent in the approach taken, and reflects the objective of retaining overall soil ecosystem function while considering the socio-economic costs of remediating soil to a particular level.

4.2.2 Available Data

All of the data that were used to develop the ecological direct soil contact guideline in the 2001 PHC CWS were generated explicitly for that project by ESG International Inc. (ESG, 2000,2003). These data are summarized in Appendix D. Since the 2001 PHC CWS, a number of related projects have been completed that have information relevant to the toxicity of one or more of the PHC fractions. Relevant existing and new studies are summarized in Table 4.2.

None of the new (i.e., subsequent to 2001 PHC CWS) studies in Table 4.2 were conducted with the sole purpose of generating toxicity data for developing soil quality guidelines. Thus, while each study has data that are relevant to the current endeavour, care must be taken to evaluate each study critically on its individual merits. In particular, three of the studies are designated as "single concentration studies", where a single (or a very limited number of) concentration(s) was used in a field study, rather than the normal battery of concentrations used in a serial dilution laboratory study. Another issue requiring careful consideration is the analytical basis for the hydrocarbon concentrations that are reported. Both these issues will be discussed in further detail in Sections 4.2.4 to 4.2.7 below.

Table 4.2: Summary of PHC Ecotoxicity Data Sources

	Study	Type[1]	Applicable to Guideline for F1	F2	F3	F4	Comments
Studies Used in the 2001 PHC CWS							
Canada-Wide Standard for Petroleum Hydrocarbons (PHC) in Soil: Scientific Rationale	CCME (2000)	multi	✓	✓	✓	✓	Analysis of ESG (2003) data
Final Report on the Acute Screening and Definitive, Chronic Toxicity Tests with Motor Gasoline	ESG (2000)	multi	✓				Source for original PHC CWS derivations for F1
New Studies and Data							
Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase 2: Field Studies	Visser (2003)	single		✓	✓		Mostly acute data
Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase 3: Long-term Field Studies	Visser (2005a)	single			✓		Mostly definitive/chronic data
Summary of the soil toxicity and soil chemical analysis data for petroleum hydrocarbon fractions 2 and 3	Cermak *et al*. (2005)	multi		✓	✓		Used same soil as ESG (2003)
Environmentally Acceptable Endpoints of CCME Canada-Wide Standards (CWS) Petroleum Hydrocarbons Fraction F3 for Weathered Petroleum Hydrocarbons in Soil	Axiom (2005)	single			✓		
Ecotoxicity of Hydrocarbon Residuals in Bioremediated Oil-Contaminated Clay Soils	Visser (2005b)	multi			✓		Toxicity tests in 70% clay soil
Unpublished dataset on 64 day earthworm "pseudo-reproduction" effects for F4	Cermak (unpublished)	multi				✓	
Unpublished dataset on toxicity of mogas to barley in chernozem soil	Cermak (unpublished)	multi	✓				
ESG F1 Toxicity Data	ESG (unpublished)	multi	✓				

1. Type:
"single" refers to single concentration studies where field soils were spiked at one (or two) concentrations, or existing contaminated soils were used.
"multi" refers to studies using multiple concentrations (i.e., a serial dilution format test).

4.2.3 Weathered and Fresh Hydrocarbons

It is acknowledged that the toxicity of PHC may decrease for hydrocarbons in soil as weathering and aging processes progress. However, this has not always been inherently the case as weathered hydrocarbons have sometimes been associated with higher toxic responses than unweathered hydrocarbons. The toxic implications of weathering may be dependant on a number of factors including hydrocarbon type, soil condition, and weathering process. Information from the 2001 review is contained in Appendix G.

Tier 1 guidelines for the ecological direct soil contact pathway are intended to be generally applicable, and, as such, need to apply to both weathered and fresh hydrocarbons. There are provisions at Tier 2/3 for taking account of potentially reduced toxicity due to weathering on a site-specific basis by using a combination of site-specific ecotoxicological testing and chemical analysis. The reader is referred to the PHC CWS user guide for further information.

In general, the Tier 1 soil quality guidelines developed in this document are based on toxicity tests with fresh hydrocarbons. However, for F3, data from weathered hydrocarbons figure prominently in the derivation. This is considered a special case, and the rationale for considering the F3 guidelines to be protective for both fresh and weathered F3 is provided in Section 4.2.6.

4.2.4 Fraction 1 (C6-nC10)

Approach/Protocol

The existing 2001 PHC CWS guidelines for F1 were based on the data from the ESG (2000) study of the toxicity of Mogas (motor gasoline) to plants and soil invertebrates. Existing guideline values are provided in Table 4.3. The guidelines were derived using the protocol that was valid at the time, based on EC/IC/LC50 values. Full details of the 2001 guideline derivation can be found in Appendix D.

Since the 2001 PHC CWS, some additional, unpublished F1 data has become available (Table 4.2). This includes unpublished data on Mogas toxicity, and also some unpublished data on the toxicity of F1. The composition of Mogas is primarily F1, but also contains approximately 18% F2 (ESG, 2000). Thus, fresh Mogas is a reasonable approximation for F1. However, F1 is lost much more rapidly from soil than F2, and chemical analysis indicates that even immediately after spiking into soil, F2 accounted for 30%-50% of the remaining hydrocarbon in the soil (ESG, 2000). After 7 days, the F2 comprised 50%-80% of the total petroleum hydrocarbons (ESG, 2000). This raised the possibility that some of the Mogas toxicity tests reflected the toxicity of F2 more than that of F1.

In light of the above discussion, the approach taken in the current document was to use the F1 data in preference where available, and only to use Mogas data for species/endpoints where F1 data were not available.

The existing and new data were all expressed on the basis of measured, analytical concentrations, and were treated as a single dataset.

Data Analysis

F1 guidelines for agricultural/residential and commercial/industrial guidelines were calculated using the CCME (2006a) protocol. Details are available in Appendix E.

Revised Guideline Values

Existing and revised guideline values for F1 are summarized in Table 4.3. The majority of the available data for F1 and/or Mogas were for coarse textured soil. The limited data available for fine soil were insufficient to develop a separate guideline value for fine soil with confidence. Accordingly, the same guideline values are applied to both coarse and fine soil. The available F1 and Mogas source data, together with details of the guideline derivation process for F1, are provided in Appendix E.

Table 4.3: Existing and Revised Guideline Values for F1

	Fine Soil		Coarse Soil	
	Ag/Res (mg/kg)	**Com/Ind** (mg/kg)	**Ag/Res** (mg/kg)	**Com/Ind** (mg/kg)
2001 PHC CWS	260	660	130	330
Revised guidelines based on new data	nd	nd	210	320
2008 PHC CWS Guideline Values	210	320	210	320

notes:
nd = not determined
ag/res = agricultural/residential
com/ind = commercial/industrial

Difference From Existing Guidelines

The revised guidelines for fine soil are somewhat lower than the existing values, while the revised values for coarse soil are somewhat higher. This is the result of a number of factors. Replacing Mogas data with F1 values where available has resulted in an increase in guideline values, since plants and soil invertebrates appear to be more sensitive to Mogas than they are to F1. One factor that has caused guideline values to drop is changing from the 2001 PHC CWS protocol which used a distribution of EC/IC/LC50 data to the CCME (2006a) protocol that uses a distribution of EC/IC/LC25 data. As well, in the new guideline the protocol for commercial and industrial land use was updated to include both plant and invertebrate effects whereas the 2001 protocol only considered plant effects. In addition, a factor of 2 was erroneously applied to previous guideline values to extrapolate from coarse to fine soils, when in reality the test soils on which the guideline was based were fine. This erroneous factor was removed in the current analysis, resulting in a decrease in the F1 guidelines for fine soil. Together, these factors account for much of the difference between current and previous guideline values.

4.2.5 Fraction 2 (>nC10-nC16)

Approach/Protocol

The original 2001 PHC CWS guidelines for F2 were based on data from the ESG (2003) study of the toxicity of F2 and other PHC fractions to plants and soil invertebrates. Existing guideline values are provided in Table 4.4. The existing guidelines were derived using the protocol that was valid at the time, based on EC/IC/LC50 values. Full details of the 2001 guideline derivation can be found in Appendix D.

Since the 2001 PHC CWS, some additional, unpublished data relevant to F2 toxicity have become available (Table 4.2). This includes some data available in Cermak *et al*. (2005) and also some unpublished ESG data.

The existing and new data were all expressed on the basis of measured, analytical concentrations, and were treated as a single dataset.

Data Analysis

F2 guidelines for agricultural/residential and commercial/industrial guidelines were calculated using the CCME (2006a) protocol. Details are available in Appendix E.

Revised Guideline Values

Existing and revised guideline values for F2 are summarized in Table 4.4. The majority of the available data for F2 were for fine textured soil. The limited data available for coarse soil were insufficient to develop a separate guideline value for coarse soil with confidence. Accordingly, the same guideline values are applied to both coarse and fine soil. The available F2 source data, together with details of the guideline derivation process for F2, are provided in Appendix E.

Table 4.4: Existing and Revised Guideline Values for F2

	Fine Soil		Coarse Soil	
	Ag/Res (mg/kg)	**Com/Ind** (mg/kg)	**Ag/Res** (mg/kg)	**Com/Ind** (mg/kg)
2001 PHC CWS	900	1,500	450	760
Revised guidelines based on new data	150	260	nd	nd
2008 PHC CWS Guideline Values	**150**	**260**	**150**	**260**

notes:
nd = not determined
ag/res = agricultural/residential
com/ind = commercial/industrial

Difference From Existing Guidelines

There is a significant difference between the 2006 PHC CWS guideline values for F2 and the previous values. Little of this difference is due to the new data that have become available since 2001. The two main reasons for the difference are i) a factor of 2 was erroneously applied to

previous guideline values to extrapolate from coarse to fine soils, when in reality the test soils on which the guideline was based were fine, and ii) The CCME (2006a) protocol uses a distribution of EC/IC/LC25 data, rather than the EC/IC/LC50 data used in the 2001 PHC CWS derivation. In addition for commercial and industrial land uses, the 2001 criteria was based on a plant effects only data base whereas this was updated in 2007 to a plant an invertebrate data set to be consistent with the CCME (2006a) protocol.

4.2.6 Fraction 3 (>nC16-nC34)

Approach/Protocol

Data relevant to setting guideline values for F3 were available from one existing and five new studies (Table 4.2). Based on the CCME (2006a) protocol, the preferred approach to data analysis would be to treat all of the available data as a single dataset, remove/combine redundant data, and generate a distribution of non-redundant 25th percentile effect level data. This approach was not adopted in the analysis of the available F3 data for the following reasons:

- Three of the five new studies are "single concentration studies", (Table 4.2) and are not amenable to being combined with the other data under the CCME (2006a) protocol. Direct adoption of CCME (2006a) would exclude these new studies, including much of the potentially most relevant data.

- The calculation of the F3 guideline in the 2001 PHC CWS was based on an analytical recovery of 31% (i.e., only 31% of the spiked concentration of F3 was recovered analytically from samples collected at time 0). Subsequent work has indicated that it is likely that organisms in soil freshly spiked with F3 are exposed to significantly greater than 31% of the nominal F3 concentration (typically 65%-100%). It was not possible to make a realistic re-assessment of the actual exposure concentration in the data from the 2001 PHC CWS. Without reasonable confidence in the analytical basis of the CCME (2000) derivations, there was a reluctance to combine this data with the data from other studies.

- The dataset was a mixture of results from studies using freshly spiked hydrocarbons fractions (ESG, 2003; Cermak *et al*, 2005) with the results from studies using weathered hydrocarbons (Visser, 2003,2005a,b; Axiom 2005). It was not felt appropriate to combine the results of fresh and weathered studies.

Each of the five new studies noted above has points that make it relevant to refining the ecological direct soil contact guidelines for F3, but other issues which make interpretation of the data challenging. It was felt that the most appropriate way forward for F3 was not to attempt to combine all the data in a single distribution, but rather to calculate guideline values for each dataset individually using the substance and spirit of the CCME (2006a) protocols as closely as was feasible.

Data Analysis

Of the five new studies, two were multiple concentration studies (Cermak 2005, Visser, 2005b), and three (Visser 2003, 2005a, Axiom 2005) were single concentration. A different approach to data analysis was required for each of these study types.

The multiple concentration studies were analyzed following the weight of evidence method from the CCME (2006a) protocol. Details are provided in Appendix F.

The single concentration studies were not amenable to analysis using the standard CCME (2006a) protocol. This was because the CCME protocol is based on combining EC25/IC50/LC25 data, and these values cannot normally be calculated with confidence from a single (or two) concentration study. Accordingly, an alternative way to use these data was developed. Data from the single concentration studies are presented as the response relative to controls for a range of species/endpoints. For each exposure concentration, the non-redundant data were ranked and presented as "Ranked Response Distributions" (RRDs).

RRDs were interpreted as follows:

- Under the CCME (2006a) approach, an RRD was deemed to meet guideline requirements for agricultural/residential land use if the 25th percentile of the RRD showed a response of at least 75% of the control response. Similarly, the level of adverse effects was deemed to be within the level implicit in the definition of the guideline for commercial/industrial land use if the 50th percentile of the RRD showed a response of at least 75% of the control response.

Details of the available data from each study, the process used to eliminate redundant data, and the methodology used to calculate guideline values are provided in Appendix F. Guideline values calculated from each study are summarized in Table 4.5. It should be noted that no attempt was made to recalculate the CCME 2001 PHC CWS guidelines. Thus the guideline values for the 2001 PHC CWS are based on the 2001 PHC CWS protocols, while the guideline values for all the new studies are based either on the CCME (2006a) protocol, or on a RRD approach intended to approximate the goals of the CCME (2006a) approach.

Revised Guideline Values

The guideline values presented in Table 4.5 cover a range of values, reflecting in some cases the relative sensitivity of organisms to F3 in varying soil types, but also the actual range of species and endpoints available in each study.

Particular attention was paid to the results of the Visser (2005a) field study, reflecting i) the greater number of species considered in this study, ii) the fact that this study measured actual crop yields and invertebrate populations in the field; iii) the chronic duration of most of the tests; and iv) the fact that measured analytical concentrations were available that could be tied to results from the CCME reference method with a good degree of confidence. Less confidence was placed on the Cermak *et al*. (2005) data due to the difficulty in linking the results from the analytical methodology required for that work to results that might have been obtained using the standard CCME reference method analysis (See Appendix F for details).

Analysis of Visser (2005a) data suggests that a guideline value of 1,300 mg/kg is protective of plants and soil invertebrates in fine soils. Data in Visser (2005a) also suggest that the current guideline for F3 in coarse soils for agricultural/residential land use (400 mg/kg) is protective of plant growth, but may not be protective of all soil invertebrates. It should be noted that the current guideline (400 mg/kg) is protective of both plants and soil invertebrates based on the CCME (2000) approach. However, the guideline would need to be less than 330 mg/kg to be protective of both plants and soil invertebrates under the more stringent CCME (2006a) approach.

Based on the above, the soil quality guideline for F3 in fine soil under agricultural/ residential land use is revised from 800 mg/kg to 1,300 mg/kg, and the soil quality guideline for F3 in coarse soil under agricultural and residential land use is revised from 400 mg/kg to 300 mg/kg. Further details of the rationale for these changes are available in Appendix F.

There were no data that supported changing the commercial/industrial guideline for either fine or coarse soil from the default values (Table 4.5). The F3 guidelines for these land uses are unchanged at 2,500 mg/kg and 1,700 mg/kg for fine and coarse soil, respectively (Table 4.5).

Table 4.5: Existing and Revised Guideline Values for F3

	Guideline Values Indicated from Each Study			
	Fine Soil		**Coarse Soil**	
Study	**Ag/Res** (mg/kg)	**Com/Ind** (mg/kg)	**Ag/Res** (mg/kg)	**Com/Ind** (mg/kg)
2001 PHC CWS [1]	800	2,500	400	1,700
Visser *et al*. (2003) (Phase 2 Field Studies) [2]	>3,100	>3,100	<1,100	>1,100
Visser (2005a) (Phase 3 Field Studies) [3]	**>1,300**	**>2,500**	**<330**	**>390**
Axiom (2005) [3]	>2,500	>2,500	nd	nd
Cermak (2005) [2]	1,000	3,200	nd	nd
Visser (2005b) (Clay Study) [2]	2,300	2,900	nd	nd
Revised Guideline Values [4]	***1,300***	**2,500**	***300***	**1,700**

notes:
nd = no data
ag/res = agricultural/residential
com/ind = commercial/industrial
1. based on 2001 PHC CWS approach (using EC/LC/IC_{50} values)
2. based on CCME (2005) approach (using EC/LC/$IC_{25/20}$ values)
3. based on the ranked response distribution procedure.
4. italic = new value is different from 2001 PHC CWS value.

5. note uncertainty in extrapolating measured hydrocarbon concentrations compatible with the CCME reference method.

Comments on the Non-Standard Approach Used

It is noted that the methodology used above to derive revised F3 guidelines is a non-standard approach, however it represents the best use of the limited F3 data currently on hand. It is acknowledged that the revised guidelines are based on a study where soils had been weathered for 1-4 years. It would be preferable to use a study on freshly-spiked hydrocarbons to set guideline values. The rationale for not using the available data from fresh studies includes the following points:

- There were concerns with using the F3 data from the 2001 PHC CWS, based on uncertainty in the ratio of nominal to measured F3, and hence the actual exposure concentrations in those experiments.
- Data provided by Cermak *et al*. (2005) were for freshly-spiked F3 in soil, but were limited in the number of species/endpoints available, and there were concerns with correlating the results from the specialised analytical methodology employed in that study (to determine separately the concentrations of aliphatic and aromatic hydrocarbons) with the results that might have been obtained using the PHC CWS standard analytical method.

There are several lines of evidence that suggest that a guideline based on the weathered Visser (2005a) study is still reliable:

- The ecological receptors studied by Visser (2005a) are more detailed than those encompassed in any toxicity study available to date. This includes much more detail on different soil invertebrates that have proven to be more sensitive to hydrocarbon contamination than specific plant species. This leads to some additional credibility as to the applicability of results from this study relative to the entire ecosystem response.
- All ecotoxicity studies, including the initial verification studies in the PHC CWS, include some level of weathering by the very nature of toxicity testing.
- In many cases, F3 contaminated soil in the field will be weathered, either because the spill occurred several years in the past, and/or because active bioremediation has been undertaken at the site. Fresh releases of hydrocarbon will become weathered over the period of a few years.
- Information provided by Cermak *et al*. (2005) was used to determine an ecological value for fresh product of 1,000 mg/kg in fine soil. Although no information was available for coarse soil and there was a more limited range of toxicity tests available in this experiment, it does appear to support the appropriateness of the new values being proposed in general terms.
- Questions regarding recovery in the original experiment would suggest that reliance on this data set is problematic if we are trying to balance the need for conservative guidance with the need for realistic and achievable standards.
- The protocol does allow for use of field data in determining relevant ecological standards. Although it is recognized that in the case of hydrocarbons, this introduces

influences related to biological weathering and bioavailability relative to fresh spills, other lines of evidence suggest that the values recommended remain conservative.

Overall, it is suggested that the revised guidelines in Table 4.5 represent the best use of all the available F3 data to balance the need for conservative guidance with the need for realistic and achievable standards. It needs to be remembered, however, that the method employed does rely heavily on results from hydrocarbon materials that would have been weathered in the field for at least a minimal amount of time. In this instance, there may be some concerns that can be raised, particularly with respect to response of sensitive species (e.g. earthworms) in fresh products. At the same time, it does appear that these guidelines may represent a better estimate with respect to biotreatability endpoints related to the hydrocarbon. It is recommended that the final guidelines present a balance between economic, policy and scientific considerations and are in keeping with recommended ecological endpoints given the uncertainty associated with the data.

4.2.7 Fraction 4 (>nC34)

The existing soil quality guidelines for F4 are summarized in Table 4.6. These values were developed in the 2001 PHC CWS by analyzing the toxicity of whole crude oil to plants and soil invertebrates, and considering: i) possible volatile losses of whole crude from spiked soils, ii) the potential apportionment of toxicity from whole crude oil between the 4 fractions, and iii) levels of F4 unlikely to result in soil hydrophobicity. Further details of the methodology used to develop these guideline values can be found in Appendix D.

Table 4.6: Existing Guideline Values for F4

	Fine Soil		Coarse Soil	
	Ag/Res (mg/kg)	**Com/Ind** (mg/kg)	**Ag/Res** (mg/kg)	**Com/Ind** (mg/kg)
2001 PHC CWS	5,600	6,600	2,800	3,300
Analysis of new F4 data	4,900	8,300	nd	nd
2008 PHC CWS Guideline Values (Retained from 2001 PHC CWS)	**5,600**	**6,600**	**2,800**	**3,300**

notes:
nd = no data
ag/res = agricultural/residential
com/ind = commercial/industrial

Ecotoxicological data for F4 in fine soil have become available since the 2001 PHC CWS values were developed. These data are presented and analyzed in Appendix F. Using CCME (2006a) methodology, guideline values of 4,900 mg/kg and 8,300 mg/kg were calculated for fine soils for agricultural/residential and commercial/industrial land uses, respectively. No data for F4 ecotoxicity in coarse soil were available.

In consideration of the fact that the new F4 guidelines for fine soil, calculated using the CCME (2006a) protocol, were relatively consistent with the existing values, that no new F4 guideline

values were available for coarse soil, and that site remediation is rarely driven by F4 guidelines, it was decided to retain the existing F4 guideline values.

4.2.8 Subsoil Considerations

In the 2001 PHC CWS, subsoil guidelines were calculated for soils deeper than 1.5 m. Implementation of these subsoil guidelines has varied based on the legislative framework in each individual jurisdiction.

The ecological direct soil contact subsoil guidelines in the 2001 PHC CWS included some consideration of potential limited plant root and soil invertebrate contact, but also included judgement- and policy-based considerations.

In the current document, the policy-based considerations have been extracted and are now presented as "management limits". Considering the application of the ecological direct soil contact pathway to subsoils, the guideline for this pathway is applicable to all soils above 1.5 m. The pathway need not be applied to soils deeper than 3 m. For soils at intermediate depths (between 1.5 and 3 m), each jurisdiction will make a ruling as to how to proceed. The reader is referred to the PHC CWS user guide for further details on the application of PHC soil quality guidelines to subsoils.

4.3 Exposure Scenarios for Ecological Receptors Based on PHC 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 well, 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.

4.3.1 Modelling Approach and Assumptions for Tier 1 Groundwater Protection Values

The modelling approach used herein is adapted from CCME (2006a), which in turn is based on an approach developed by the British Columbia Contaminated Sites Soil Task Group (CSST). The protection of aquatic life pathway includes lateral transport with a default distance of 10 m, since the locations of surface water bodies can normally be considered fixed. The livestock watering pathway assumes that a dugout or well could be installed at the downgradient edge of the site, consistent with the potable water scenario evaluated for human health. The mathematical equations incorporated in the model are provided in Appendix C. Relative chemical properties used for each of the subfractions are contained in Appendix B, table B.1.

The model includes descriptions of contaminant partitioning between the adsorbed, dissolved and vapour phases, and mixing of dissolved leachate at the water table. Groundwater flow and contaminant transport in the saturated zone is also modelled for the aquatic life pathway to account for the assumed offset distance. The model also includes a component for groundwater flow and contaminant leachate transport in the unsaturated zone, but this component is not used at Tier 1 where the contamination is assumed to be in contact with the groundwater. The model equations and the basis of the model are presented in Appendix C.

Consistent with the human health pathways, modelling was undertaken for both coarse soils (D_{50} > 75 μm) and fine soils (D_{50} < 75 μm), using the same default soil and hydrogeological characteristics as the human health pathways. The default model parameters, including chemical properties, are summarized in Appendix C. Representative or typical values were used for most model parameters, with the exception of the hydraulic conductivity for fine soils which was set at 32 m/y to reflect the high end of the range normally encountered in fine soils. The higher hydraulic conductivity is conservative for the protection of aquatic life, and represents the minimum hydraulic conductivity expected to result in sufficient yield for a livestock watering source without dilution from surface runoff.

4.3.2 PHC Toxicity to Aquatic Receptors

One of the challenges for the development of the 2001 PHC CWS was the absence of appropriate water quality benchmarks for the protection of aquatic life for the PHC fractions or subfractions. An extensive literature review and evaluation of potential approaches was undertaken; this review is detailed in Appendix H and only briefly summarized in this section.

Two approaches for estimating the toxicity of PHC to aquatic receptors were evaluated: the use of individual surrogates to represent the toxicity of PHC fractions to aquatic receptors, and the use of a “Critical Body Residue” (CBR) approach using narcosis-type thresholds based on the internalized dose of lipophilic substances. The toxicity estimates derived using these approaches were also compared to data available for whole products, including fuel oil #2 and gasoline.

As detailed in Appendix H, the surrogate and CBR approaches yielded similar results. The CBR approach was selected since it more readily accounts for varying PHC compositions and differential partitioning/transport of different PHC components. This approach was used to develop a toxicity-based aquatic life benchmark for each PHC subfraction:

Table 4.7: Toxicity Aquatic Life benchmarks for the CCME subfractions

Subfraction	Toxicity Benchmark (µg/L)
F1	
Aliphatics $C_6 – C_8$	46.5
Aliphatics $C_{>8} – C_{10}$	7.6
Aromatics $C_{>8} – C_{10}$	140
F2	
Aliphatics $C_{>10} – C_{12}$	1.18
Aliphatics $C_{>12} – C_{16}$	0.074
Aromatics $C_{>10} – C_{12}$	96
Aromatics $C_{>12} – C_{16}$	55.4

Please see Appendix H for further information regarding process and information that was used to develop benchmark reference concentrations.

4.3.3 PHC Toxicity to Livestock Based on Drinking Water Uptake

The toxicity of PHC to livestock via drinking water uptake is also needed for the PHC CWS, although this pathway is rarely expected to govern. The analysis of PHC toxicity to livestock undertaken for the 2001 PHC CWS is detailed in Appendix I and summarized briefly in this section.

Very limited data on the toxicity of PHC to livestock were identified during the development of the PHC CWS. Most of the available data were based on consumption of oil by cattle. The lowest identified exposure dose exhibiting an effect in cattle (2.1 g unweathered crude oil per day) was used as the basis for a daily threshold effects dose (DTED) for livestock drinking water of 210 mg/kg-bw/d. Using an assumed body weight and drinking water ingestion rate for cattle, this is equivalent to a fresh crude concentration of 230[1] mg/L in water, which is established as the reference concentration (RfC) in water for livestock. It is anticipated that toxicity of weathered crude oil would be lower (i.e. the DTED and RfC would be higher).

In the absence of appropriate data on the toxicity of different PHC fractions, the above RfC was apportioned between the fractions based on the composition of fresh crude oil. The resulting fraction-specific water RfCs for cattle are:

[1] This value was revised from 23mg/L to the correct value of 230 mg/L on May 1, 2008.

Table 4.8: Reference concentrations for livestock watering

Fraction	RfC_{LDW} (mg/L)
F1	53
F2	49
F3	79
F4	42

Fractions F3 and F4 were not considered in the calculation of soil guidelines for the protection of livestock watering, since the RfCs calculated for these fractions substantially exceeded the solubility limits of the fractions.

4.3.4 Model Predictions and Calculation of Tier 1 Levels

Tier 1 levels were calculated for all F1 and F2 subfractions for both the protection of aquatic life and the protection of livestock watering. The subfraction Tier 1 levels were combined to determine final Tier 1 levels for F1 and F2 using the inverse mass-weighted average calculation detailed in Appendix C. Sensitivity analyses conducted for the protection of aquatic life during the derivation of the 2001 PHC CWS are included in Appendix J for reference.

Based on results of the groundwater modelling with an assumed separation distance of 10 m between the contamination and a surface water body, the following Tier 1 levels are calculated for the protection of freshwater life:

coarse soils F1 – 970 mg/kg
F2 – 380 mg/kg

fine soils F1 - >30 000 mg/kg (RES)
F2 - >30 000 mg/kg (RES)

Tier 1 levels calculated for the protection of livestock watering, based on a potential well or dugout at the downgradient edge of the contaminated area, are:

coarse soils F1 – 5300 mg/kg
F2 – 14 000 mg/kg

fine soils F1 – 4200 mg/kg
F2 – 10 000 mg/kg

Values calculated for fine soils for the protection of livestock watering are lower than those calculated for coarse soils, consistent with the lower aquifer dilution encountered in less permeable soils.

5 Integration of Ecological and Human Health Levels and Incorporation of Management Limits

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 management limits which are applied to address various scientific, technical and socio-economic factors other than chronic toxicity of PHC to human and ecological receptors; these management limits are considered to apply at all sites.

In developing management limits, there was an effort to stay true to the original process described in CCME (2001). Therefore, it was necessary to consider several factors that were investigated in the original CCME subsoil guidelines but not easily accommodated in explicit, quantitative exposure and risk estimates. Factors identified in 2001 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.

5.2 Ecological Soil Contact Pathway – Role of Soil Texture Offsite Migration Check

In addition to direct impacts to human and ecological receptors at a contaminated site, the potential for contamination to be transported to a more sensitive site must also be considered.

The offsite migration check from the CCME (1996, 2006a) protocol accounts for the migration of surficial soils to neighbouring properties via wind and water erosion and subsequent deposition. This check applies to non-volatile PHC fractions (F3 and F4) for the commercial and industrial land uses.

As detailed in CCME (2006a), the offsite migration check value can be calculated as:

$SQG_{OM} = 14.3 \times SQG_A - 13.3 \times BSC$

where:

SQG_{OM} = soil quality guideline for offsite migration (mg/kg)
SQG_A = governing Tier 1 level for the agricultural land use (mg/kg)
BSC = background soil concentration (mg/kg)

The offsite migration check may be excluded on a site-specific basis if there are no agricultural or residential properties in the vicinity of the contaminated commercial or industrial site.

The transport of the more volatile PHC fractions (F1 and F2) via groundwater or soil vapour to nearby more sensitive properties may also be of concern. However, due to the site-specific nature of this transport and the variations in policies between different jurisdictions, this mechanism is not evaluated quantitatively at this time. Some jurisdictions may apply offset distances (e.g. land within 30 m of a residential property being treated as residential) to address offsite transport, and transport of PHC to more sensitive neighbouring properties should be considered during Tier 2 and Tier 3 evaluations.

5.3 Management Limits and Risk Management Decisions

The effects of PHC are not limited to chronic toxicity to human and ecological receptors. In order to ensure that the PHC CWS is protective of other potential effects and to incorporate consideration of additional scientific, technical and socio-economic factors, management limits have been established. The management considerations were previously incorporated into the ecological direct soil contact values in the 2001 PHC CWS, but have now been separated and explicitly stated consistent with the CCME (2006a) protocol.

Factors currently considered in the management limits include:

- Free phase formation;
- Exposure of workers in trenches to PHC vapours;
- Fire and explosive hazards;
- Effects on buried infrastructure;
- Aesthetic considerations; and,
- Technological factors

5.3.1 Development of Management Limits

Free Phase Formation

The presence of free phase hydrocarbons, particularly mobile free phase, is generally considered to be undesirable at sites, since a free phase acts as a source of future contamination and may result in effects on indoor air quality or water quality not accounted for by the three-phase partitioning models used in the calculation of Tier 1 levels.

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, mobile free phase formation (which occurs when the residual saturation limit is reached) is often observed when 10% to 20% of the soil pore space contains hydrocarbons (Mercer & Cohen, 1990). This observation is affected by depth to water table with values in the unsaturated zone generally being lower than that of the saturated zone. For most petroleum products and soil types, the residual saturation limit occurs with total PHC concentrations on the order of 20,000 mg/kg to 30,000 mg/kg, though it may occur at lower concentrations for light-end products such as gasoline. Therefore, a limit of 2% total PHC in soil, of which not more than 1% should be in the sum of F1 to F3 and 1% in F4, has been established to protect against the formation of a mobile free phase.

Due to the relatively high mobility and solubility of F1, this fraction may become mobile at lower concentrations than the other fractions, and even residual hydrocarbons may recontaminate groundwater to unacceptable levels. Therefore, it was decided that the guideline for the F1 fraction should consider the potential presence of a free phase. Based on this, F1 limits of 700 mg/kg in coarse soils and 800 mg/kg in fine soils have been established, based on the concentrations at which all F1 subfractions are predicted to be present at their saturation limits. This value is consistent with subsoil decisions in 2000, where due to mobility and flammability limits posed by the presence of F1 hydrocarbons, a maximum limit of 1000 mg/kg was proposed for the F1 fraction, with risks predicted to be present to workers in a trench (following section), and is consistent with decisions in most jurisdictions that require the free phase to be addressed if present.

Free phase may in some cases be observed at lower concentrations than predicted here, and should be addressed on a site-specific basis as necessary.

Effects on Workers in Trenches

While outdoor exposure to PHC vapours volatilizing from soil is normally considered to be a relatively insignificant pathway due to the dilution that occurs in outdoor air, PHC vapour concentrations may be higher in trenches and excavations due to more limited airflow and hence lower dilution. While air exchange in trenches and excavations is expected to be higher than in buildings in most cases, the lack of a concrete foundation slab may result in higher rates of vapour infiltration into trenches.

A model predicting the influx of contaminant vapours into trenches was developed by Virginia Department of Environmental Quality (VDEQ, 2005). This model was applied using the PHC and soil characteristics summarized in Appendix C and default model parameters recommended by VDEQ (2005) for additional parameters such as trench air exchange rate. Modelling was conducted for a variety of trench scenarios, including trenches with width greater than depth, which would reflect excavations with 45^{o} sloped sidewalls in which workers might spend

extended periods of time, and trenches with depth greater than width, which workers would normally be expected to enter only for short periods of time with proper structural supports. The human health reference concentrations for PHC subfractions were applied for longer duration exposure scenarios. In the absence of relevant acute toxicity endpoints for PHC fractions, occupational exposure limits for gasoline and jet fuel were respectively applied to represent F1 and F2 for screening purposes, although it is acknowledged that these are not appropriate endpoints for human health risk assessment. Contamination was assumed to be in direct contact with the trenches.

Based on the modelling evaluation, limits of 1000 mg/kg each for F1 and F2 were deemed protective for both coarse and fine soils.

Fire and Explosive Hazards

When PHC vapour concentrations exceed the lower explosive limit, combined with sufficient oxygen and an ignition source, a fire or explosive hazard exists. The lower explosive limit for gasoline is 14,000 ppm, or approximately 41,500 mg/m^3 if an average molecular weight of 72 g/mol is assumed for the vapours (ACGIH, 2001).

Equilibrium partitioning calculations indicate that F1 concentrations exceeding the gasoline explosive limit in soil pore space could occur with soil concentrations as low as 30 mg/kg in coarse soils. However, vapour concentrations in soil pores exceeding the lower explosive limit are not considered to be a realistic explosive hazard, due to the absence of adequate oxygen sources and limited pore connectivity.

Vapour concentrations exceeding the explosive limit in larger enclosed spaces are considered to be of concern. While many underground enclosed spaces such as sanitary sewers may have relatively high air exchange rates due to drag from moving fluids (Edwini-Bonsu & Steffler, 2004) or openings to the surface, others may have lower air exchange and therefore a high potential to accumulate PHC vapours.

Modelling was conducted using both the Johnson & Ettinger (1991) model, to represent situations where contamination was at least 30 cm from the enclosed space, and with the VDEQ (2005) trench model for contamination in contact with the enclosed space. In both cases, an air exchange rate of 0.05 exchanges/hour (i.e. 10% of the default residential air exchange rate) was assumed. Based on the modelling, limits of 1400 mg/kg and 1700 mg/kg have been established for F1 in coarse and fine soils, respectively, and a limit of 5200 mg/kg has been established for F2 in both coarse and fine soils.

Underground enclosed spaces with very low air exchange rates that are in contact with or close to PHC contamination may require evaluation on a site-specific basis.

Effects on Buried Infrastructure

PHC have been known to affect buried infrastructure, including underground utilities. Of particular concern is the potential for PHC to enter water distribution systems, though impacts on other utilities are undesirable as well. The potential effects of PHC on buried infrastructure were reviewed by Stantec (2003). While some jurisdictions have proposed threshold levels for specific chemicals to protect buried infrastructure, at this time the available data do not appear to be adequate to derive meaningful thresholds for the PHC fractions on a generic basis. However, potential effects of PHC on buried infrastructure should be addressed on a site-specific basis where utilities or other infrastructure are in contact with contaminated soils.

Aesthetic Considerations

High concentrations of PHC can adversely affect aesthetics. Specific effects may include odours, visible impacts on soils, or effects on the taste of potable water. Secondary effects may include visible plant damage. Aesthetic effects are often somewhat subjective and may be highly dependent on site-specific factors.

It is expected that the Tier 1 guidelines for the vapour intrusion pathway will be protective of odours in buildings in most cases. While the concentrations of PHC subfractions in potable water leading to adverse tastes have not been quantified, it is similarly anticipated that soils meeting the Tier 1 levels for the protection of potable groundwater will not generally result in adverse effects to the taste of potable water. Likewise, the ecological direct soil contact guidelines are expected to protect against visible plant damage at most sites. However, any odour or taste concerns or observed effects on vegetation identified at individual sites should be addressed.

Visible effects on soils and outdoor odours resulting from high PHC concentrations have not been explicitly evaluated, and are dependent on various site-specific factors. It is expected that other considerations evaluated herein, such as free phase formation and exposure of workers in trenches, will be protective of major aesthetic impacts. However, aesthetic impacts should be addressed on a site-specific basis when they occur.

Technological Factors

Bioremediation is presently the preferred technology for dealing with percent range PHC contamination of soils, 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). In 2001, the following upset limits were established for F3 in subsoils in consideration of toxic risk, aesthetics, effects on infrastructure and bioremedial capabilities. Due to the lack of additional information, these numbers were adopted in 2007 without review.

- Coarse textured subsoil, agricultural and residential uses: 2,500 mg/kg
- Coarse textured subsoil, commercial and industrial uses: 3,500 mg/kg
- Fine textured subsoil, agricultural and residential uses: 3,500 mg/kg
- Fine textured subsoil, commercial and industrial uses: 5,000 mg/kg

5.3.2 Final Management Limits

Based on the considerations outlined in Section 5.3.1 above, the following management limits have been established:

Table 5.1: Recommended Management Limits for each fraction.

	Coarse soils	Fine soils
Fraction 1	700 mg/kg	800 mg/kg
Fraction 2	1000 mg/kg	1000 mg/kg
Fraction 3	2500 mg/kg (ag/res) 3500 mg/kg (com/ind)	3500 mg/kg (ag/res) 5000 mg/kg (com/ind)
Fraction 4	10 000 mg/kg	10 000 mg/kg

The management limits are considered applicable at all sites, and are not subject to Tier 2 adjustment procedures.

5.4 Review of Pathways

Human Health

(a) Direct Contact with Contaminated Soil (soil ingestion and dermal contact) – While the direct contact pathway can be managed through physical barriers or depth to contamination, it is normally always employed when obtaining regulatory closure on a site to account for future changes in land use and the potential for contaminated soils to be brought to the surface, and it is not normally subject to Tier 2 modification procedures. This pathway does not normally govern for PHC.

(b) 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. This pathway is only considered to be of concern for F1 and F2, and is operative for all sites which may have buildings within 30 m of the contamination. It cannot normally be excluded when obtaining unconditional closure due to the possibility of future buildings at most sites. The vapour inhalation pathway can be modified at Tier 2 with appropriate supporting data.

(c) Potable groundwater protection – Tier 1 values for the protection of potable groundwater can be excluded if there is no potential for potable water use (no aquifer which may be affected by the PHC contamination, or the aquifer is not suitable for use as a potable water source). The potable groundwater protection pathway can be modified at Tier 2 with appropriate supporting data.

Ecological Health

(a) Direct soil contact – The ecological direct soil contact pathway is applied for all soils with a depth of less than 1.5 m below surface. Between 1.5 and 3 meters, direct soil contact may be required depending on the jurisdiction. This pathway is not subject to Tier 2 adjustments at this time, although research is underway related to bioavailability indices and alternate extraction methods (e.g. cyclodextrin extraction) which may eventually yield Tier 2 approaches.

(b) Soil and food ingestion/bioaccumulation – Tier 1 levels for this pathway are not calculated at this time.

(c) Protection of groundwater for aquatic life – This pathway can be excluded if there are no surface water bodies in the vicinity of the site; it can also be adjusted at Tier 2 with adequate supporting data.

(d) Protection of groundwater for livestock watering – This pathway is only considered for the agricultural land use, and can be excluded if there is no suitable aquifer for use as a livestock watering source. The pathway can be adjusted at Tier 2 with adequate supporting data.

Miscellaneous

(a) Off-site migration of Soil/Dust – The offsite migration check can be excluded if there are no agricultural or residential properties in the vicinity of the commercial/industrial site. This pathway is not normally adjusted at Tier 2, but also does not normally govern.

(b) Management Limits – The management limits are applied to all soils and cannot normally be excluded or adjusted at Tier 2.

5.5 Tabular Presentation of Generic PHC CWS Levels

Tables 5.2 and 5.3 on the following pages summarize the outcomes of the risk assessment and risk management procedures discussed in detail in Chapters 1 through 5. Two tables are presented:

- Table 5.2: Tier 1 levels for fine-grained surface soil.
- Table 5.3: Tier 1 levels for coarse-grained surface soil.

Table 5.2: Tier 1 levels (mg/kg soil) for PHC for fine-grained surface soils.

Land Use	Exposure Pathways	F1 (C6-C10)	F2 (>C10-C16)	F3 (>C16-C34)	F4 (>C34)
Agricultural	Direct Contact (Ingestion + Dermal Contact)	12 000	6800	15 000	21 000
	Vapour Inhalation (indoor, basement)	710	3600	NA	NA
	Vapour Inhalation (indoor, slab-on-grade)	610	3100	NA	NA
	Protection of Potable GW[1]	170	230	NA	NA
	Protection of GW for Aquatic Life[2]	RES	RES	NA	NA
	Protection of GW for Livestock Watering[3]	4200	10 000	NA	NA
	Nutrient Cycling	NC	NC	NC	NC
	Ecological Direct Soil Contact	210	150	1300	5600
	Ecological Soil Ingestion	NC	NC	NC	NC
	Produce, Meat and Milk	NC	NC	NC	NC
	Management Limit[4]	800	1000	3500	10 000
Residential	Direct Contact (Ingestion + Dermal Contact)	12 000	6800	15 000	21 000
	Vapour Inhalation (indoor, basement)	710	3600	NA	NA
	Vapour Inhalation (indoor, slab-on-grade)	610	3100	NA	NA
	Protection of Potable GW[1]	170	230	NA	NA
	Protection of GW for Aquatic Life[2]	RES	RES	NA	NA
	Nutrient Cycling	NC	NC	NC	NC
	Ecological Direct Soil Contact	210	150	1300	5600
	Produce	NC	NC	NC	NC
	Management Limit[4]	800	1000	3500	10 000
Commercial	Direct Contact (Ingestion + Dermal Contact)	19 000	10 000	23 000	RES
	Vapour Inhalation (indoor)	4600	23 000	NA	NA
	Protection of Potable GW[1]	170	230	NA	NA
	Protection of GW for Aquatic Life[2]	RES	RES	NA	NA
	Nutrient Cycling	NC	NC	NC	NC
	Ecological Direct Soil Contact	320	260	2500	6600
	Offsite Migration	NA	NA	19 000	RES
	Management Limit[4]	800	1000	5000	10 000
Industrial	Direct Contact (Ingestion + Dermal Contact)	RES	RES	RES	RES
	Vapour Inhalation (indoor)	4600	23 000	NA	NA
	Protection of Potable GW[1]	170	230	NA	NA
	Protection of GW for Aquatic Life[2]	RES	RES	NA	NA
	Nutrient Cycling	NC	NC	NC	NC
	Ecological Direct Soil Contact	320	260	2500	6600
	Offsite Migration	NA	NA	19,000	RES
	Management Limit[4]	800	1000	5000	10 000

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.
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.= A management limit has been developed that may be used in place of the ecological criteria below 3 meters depth.

Table 5.3: Tier 1 levels (mg/kg soil) for PHC for coarse-grained surface soils.

Land Use	Exposure Pathways	F1 (C6-C10)	F2 (>C10-C16)	F3 (>C16-C34)	F4 (>C34)
Agricultural	Direct Contact (Ingestion + Dermal Contact)	12 000	6800	15 000	21 000
	Vapour Inhalation (indoor, basement)	40	190	NA	NA
	Vapour Inhalation (indoor, slab-on-grade)	30	150	NA	NA
	Protection of Potable GW	240	320	NA	NA
	Protection of GW for Aquatic Life[1]	970	380	NA	NA
	Protection of GW for Livestock Watering[2]	5300	14 000	NA	NA
	Nutrient Cycling	NC	NC	NC	NC
	Ecological Direct Soil Contact	210	150	300	2800
	Ecological Soil Ingestion	NC	NC	NC	NC
	Produce, Meat and Milk	NC	NC	NC	NC
	Management Limit[3]	700	1000	2500	10 000
Residential	Direct Contact (Ingestion + Dermal Contact)	12 000	6800	15 000	21 000
	Vapour Inhalation (indoor, basement)	40	190	NA	NA
	Vapour Inhalation (indoor, slab-on-grade)	30	150	NA	NA
	Protection of Potable GW	240	320	NA	NA
	Protection of GW for Aquatic Life[1]	970	380	NA	NA
	Nutrient Cycling	NC	NC	NC	NC
	Ecological Direct Soil Contact	210	150	300	2800
	Produce	NC	NC	NC	NC
	Management Limit[3]	700	1000	2500	10 000
Commercial	Direct Contact (Ingestion + Dermal Contact)	19 000	10 000	23 000	RES
	Vapour Inhalation (indoor)	320	1700	NA	NA
	Protection of Potable GW	240	320	NA	NA
	Protection of GW for Aquatic Life[1]	970	380	NA	NA
	Nutrient Cycling	NC	NC	NC	NC
	Ecological Direct Soil Contact	320	260	1700	3300
	Offsite Migration	NA	NA	4300	RES
	Management Limit[3]	700	1000	3500	10 000
Industrial	Direct Contact (Ingestion + Dermal Contact)	RES	RES	RES	RES
	Vapour Inhalation (indoor)	320	1700	NA	NA
	Protection of Potable GW	240	320	NA	NA
	Protection of GW for Aquatic Life[1]	970	380	NA	NA
	Nutrient Cycling	NC	NC	NC	NC
	Ecological Direct Soil Contact	320	260	1700	3300
	Offsite Migration	NA	NA	4300	RES
	Management Limit[3]	700	1000	3500	10 000

NA = Not applicable
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.
1 = Assumes surface water body at 10 m from site.
2 = Includes use of dugouts and wells for supply of livestock water.
3 = A management limit has been developed that may be used in place of the ecological criteria below 3 meters depth.

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 PHC. 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 PHC. 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 2007).

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 (2007).

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**, 2007). The CWS PHC method does not

address in detail sampling of PHC contaminated sites. It does provide general guidance using CCME and US 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 accredited laboratories. 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

PHC are divided into two practical categories that differ in analytical procedures: (1) volatile PHC (F1), and (2) extractable PHC (F2-F4). Depending on the amount of F4 material in the sample and user/analyst preferences, extractable PHC may be further sub-divided on the basis of detection method (chromatographic/gravimetric).

Volatile PHC are recovered by extracting the sample with methanol in a sealed container. Volatile PHC 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 PHC are recovered by Soxhlet extraction in 50:50 hexane-acetone. The extract is dried over sodium sulphate 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 PHC greater than nC50 are present in appreciable quantities, residual PHC may be determined gravimetrically or through extended, high temperature chromatography. If determinations of target PAH (e.g., naphthalene,

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 PHC:

There is an incredible diversity of methods for analyzing PHC. This meant that compromises had to be struck. For example, considerable debate was held by the AM TAG 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 PHC.

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, in order for laboratories to be accredited to run the reference method, they are required to participate in a regular Proficiency Testing program with an appropriate accreditation agency. This program would allow Canadian laboratories accredited by accrediting bodies recognized through the jurisdictional authority to include PHC by this method in their scope of accreditation. The requirements for the accreditation agency may be dependant on jurisdictional requirements. The appropriate jurisdictional authority should be consulted regarding the accreditation process.

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 PAH if they are present in sufficient quantity to affect the PHC result. Sites showing considerable quantities of PAH 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, and are discussed further in CCME (2007).

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

PHC 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, PHC 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, updated in 2006 by the CCME Soil Quality Guidelines Task Group. These Tier 1 standards for soil 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 (2007).

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 and cross-contaminated groundwater. Knowledge of receptor response to PHC contamination was used to calculate or estimate environmentally acceptable concentrations in the soil.

Because environmental behaviour and effects of PHC in the geo-environment are related to chemical properties (e.g., size, geometry and extent of oxidation) it was advantageous to consider these substances in 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 soil-dwelling 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 livestock watering) or at a nominal 10 m offset (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 in Canada. Coupled to the tiered assessment framework (CCME 2007), 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 levels were designed to be attainable. A socio-economic analysis was undertaken that confirmed that liabilities for remediation of PHC-contaminated sites in Canada are in the multi-billion dollar range and remediation will take many years to accomplish, given the size of the remediation industry. While the analysis was based on costs associated with remediation by excavation and disposal or ex situ treatment, it was noted that a number of other active remedial technologies in common use for PHC-contaminated sites exhibit similar overall unit costs when long tem operating and monitoring costs are considered. It was recognized in the development of the standard, however, that in situ bioremediation technologies are increasingly used and offer potential cost savings over conventional methods. The performance capabilities of bioremediation technologies were therefore considered in the interpretation of scientific uncertainties in development of the Tier 1 standards.

Socio-economic factors were a major consideration in many of the risk management decisions taken during the original development and subsequent review of the PHC CWS. An example is the decision to base ecological protection for commercial and industrial soils solely on the response of plants and soil invertebrates. Many of the socio-economic impacts of achieving a

certain level of human health or environmental protection cannot be readily quantified and are typically evaluated in a qualitative sense. The general objective of the standard, therefore, is that soils remediated to the Tier 1 standards should pose no adverse effects to human health or the environment within the conservative exposure scenarios used. The PHC CWS is intended to be a practical standard, a fact that is considered along with scientific uncertainty around the definition of acceptable environmental quality.
The principal benefits expected from implementation of the PHC CWS include:

- Documented scientific basis for risk management decisions for PHC-contaminated sites;
- Protection of human and environmental health;
- Clear land and water use decisions at PHC-contaminated sites;
- A consistent approach to measurement, assessment and remediation which levels the playing field for responsible parties and stakeholders;
- Attainable standards, which encourage responsible action and bring affected areas back into productive use at a faster rate;
- A tiered assessment framework, which allows efficient use of remedial resources while ensuring protection, and avoids over- and under-management of 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 PHC 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

- Partitioning of PHC between adsorbed, dissolved and vapour phases. Empirical data indicate that the standard three-phase equilibrium partitioning model appears to over-predict vapour-phase concentrations; however, a suitable generic alternative has not been identified.

- 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 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.

Effects of Different PHC Mixtures in Cold Climates

- A broader understanding of the implications of cold climates, particularly conditions where permafrost is present on toxic response is still desirable.

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 PHC 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.

- Guidance on sampling, storage and handling of PHC-contaminated soil, subsoil and groundwater is also required.

- Guidance on fate and transport in cold climates, particularly where transport of contaminants may be influenced by permafrost conditions in Arctic environments is desirable.

8 REFERENCES

Abernathy, S.G., D. Mackay, and L.S. McCarty. (1988). "Volume Fraction" Correlation for Narcosis in Aquatic Organisms: The Key Role of Partitioning. Environmental Toxicology and Chemistry 7:469-481.

Abreu, L.D.V. and P.C. Johnson. 2006. Simulating the effect of aerobic biodegradation on soil vapour intrusion into buildings: influence of degradation rate, source concentration and depth. *Environ. Sci. Technol.* 40: 2304-2315.

American Conference of Governmental Industrial Hygienists (ACGIH). 2001. Gasoline: TLV® Chemical Substances 7th Edition Documentation.

American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE). 1989. Ventilation for Acceptable Indoor Air Quality. ASHRAE 62-1989.

Agency for Toxic Substances and Disease Registry (ATSDR). 1992. *Toxicological Profile for Cresols: o-cresol, p-cresol and m-cresol*. US Department of Health and Human Services, Public Health Service: Atlanta, GA.

Agency for Toxic Substances and Disease Registry (ATSDR). 1995a. *Toxicological Profile for Xylenes (Update)*. US Department of Health and Human Services, Public Health Service, Atlanta, GA

Agency for Toxic Substances and Disease Registry (ATSDR). 1995b. *Toxicological Profile for polycyclic aromatic hydrocarbons (PAHS) (Update*). US Department of Health and Human Services, Public Health Service, Atlanta, GA

Agency for Toxic Substances and Disease Registry (ATSDR). 1997. *Toxicological Profile for Benzene (Update)*. US Department of Health and Human Services, Public Health Service, Atlanta, GA

Agency for Toxic Substances and Disease Registry (ATSDR). 1998. *Toxicological Profile for Ethylbenzene (Update)*. US Department of Health and Human Services, Public Health Service, Atlanta, GA

Agency for Toxic Substances and Disease Registry (ATSDR). 1999a. *Toxicological Profile for Total Petroleum Hydrocarbons (TPH) (Draft for Public Comment)*. US Department of Health and Human Services, Public Health Service, Atlanta, GA

Agency for Toxic Substances and Disease Registry (ATSDR). 1999b. *Toxicological Profile for Toluene (Update*). US Department of Health and Human Services, Public Health Service, Atlanta, GA.

Alberta Environment Protection (AEP). 1994. Remediation Guidelines for Petroleum Storage Tanks - Draft. 68 pp.

Allan, M. and Richardson, G.M. 1998. Probability Density Functions Describing 24-hour Inhalation Rates for Use in Human Health Risk Assessments. *Human and Ecological Risk Assessment*, Vol. 4(2), 379-408.

American Society for Testing and Materials (ASTM) 2000. Standard Classification of soils for engineering purposes(Unified soil classification system). D2487-00. ASTM, West Conshohocken, PA.

American Society for Testing and Materials (ASTM). 1995. Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites. Standard E 1739-95. ASTM, West Conshohocken, PA.

Anonymous. 1997. State summaries of soil and groundwater clean up standards. Journal of Soil Contamination, 6(1): 113-146.

Atlantic Partnership in RBCA (Risk-Based Corrective Action) Implementation (Atlantic PIRI). 1999. Reference Documentation for Petroleum Impacted Sites. Version 1.0, April 1999.

Axiom (Axiom Environmental Inc.) 2005. Environmentally Acceptable Endpoints for Weathered/Aged Petroleum Hydrocarbon Fraction F3 in Soil – Development of a Bioavailability Index. Interim report prepared for Petroleum Technology Alliance Canada (PTAC), September 22, 2005.

Baker, J.F., and G.C. Patrick, 1985. Natural attenuation of aromatic hydrocarbons in shallow and aquifer. Proc. NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater - Prevention, Detection, and Restoration., November 13-15, 1985., Houston, TX., Dublin, OH: National Water Well Association.

Baker, J.F., G.C. Patrick, and D. Major, 1987. Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer. Ground Water Monitor. Review, 64-71.

Baker, M.D., and C.I. Mayfield, 1980. Microbial and non-biological decomposition of chlorophenols and phenols in soil. Water Air Soil Poll. 13, 411.

Bobra, A.M., W.Y. Shiu, and D. Mackay. (1983). Quantitative Structure-Activity Relationships for the Acute Toxicity of Chlorobenzenes in Daphnia magna - Review. Environ. Toxicol. Chem. 4:297-306.

Borgmann, U., W.P. Norwood and K.M. Ralph. (1990). Chronic Toxicity and Bioaccumulation of 2,5,2',5'- and 3,4,3',4'-Tetrachlorobiphenyl and Araclor 1242 in the Amphipod Hyalella azteca. Arch. Environ. Contam. Toxicol. 19:558-564.

British Columbia Ministry of Environment, Lands and Parks (BC MELP). 1993. Waste Management Amendment Act, 1993. Assented to June 18, 1993.

British Columbia Ministry of Environment, Lands and Parks (BC MELP). 1995a. "Draft 3.0 Contaminated Sites Regulation". Industrial Waste and Hazardous Contaminants Branch.

British Columbia Ministry of Environment, Lands and Parks (BC MELP). 1995b. "Approved and Working Criteria for Water Quality - 1995". Water Quality Branch. Environmental Protection Department. Victoria, British Columbia.

British Columbia Ministry of Environment, Lands and Parks (BC MELP). 1996. Overview of CSST Procedures for the Derivation of Soil Quality Matrix Standards for Contaminated Sites. Report prepared by the Risk Assessment Unit, Environmental Protection Department, BC Environment. 51 pp.

British Columbia Ministry of Environment, Lands and Parks (BC MELP). 1998. *Calculation of Volatile Petroleum Hydrocarbons in Solids or Water*. BC Ministry of Environment, Lands and Parks, Data Standards Group, Waste Management Branch.

Call, D.J., L.T. Brooke, M.L. Knuth, S.H. Poirier, and M.D. Hoglund. (1985). Fish Subchronic Toxicity Prediction Model for Industrial Organic Chemicals that Produce Narcosis. Environ. Toxicol. Chem. 4:335-341.

Canada Mortgage and Housing Corporation (CMHC). 1997. Estimating the Concentrations of Soil Gas Pollutants in Housing: A Step-by-Step Method. July.

Canadian Council of Ministers of the Environment (CCME). 1991. "Interim Canadian Environmental Quality Criteria for Contaminated Sites". Report CCME EPC-CS34. National Contaminated Sites Remediation Program. September, 1991.

Canadian Council of Ministers of Environment (CCME) 1993. Guidance Manual on Sampling, Analysis and Data Management for Contaminated Sites. CCME-EPC-NCS 62E. ISBN 0-919074-21-9

Canadian Council of Ministers of Environment (CCME). 1999. Canadian Environmental Quality Guidelines. Canadian Council of Ministers of Environment, Winnipeg. ISBN#: 1-896997-34-1, Pub. No. 1299.

Canadian Council of Ministers of Environment (CCME). 1996. A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines. Winnipeg, MB, CCME-EPC-101E. En 108-4/8-1996E. ISBN 0-662-24344-7.

Canadian Council of Ministers of Environment (CCME). 2001. Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil – Tier 1 Method. ISBN 1-896997-01-5. Publication No. 1310.

Canadian Council of Ministers of Environment (CCME). 2006a. A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines. Winnipeg, MB,

Canadian Council of Ministers of the Environment (CCME), 2006b. Five-year review of the Canada-Wide Standards for Petroleum Hydrocarbons (PHC CWS): Ecological, Direct Soil Contact Guidance. Report to the Canadian Council of Ministers of Environment (CCME) Soil Quality Guidelines Task Group (SQGTG) by the Ecological Criteria Advisory Subgroup. Dated March, 2006.

Canadian Council Ministers of the Environment (CCME), 2006c. 2005 Review of Canada-Wide Standards for Petroleum Hydrocarbons in Soil: Report of the Model Parameter Advisory (MPA) Sub Group. Dated February, 2006.

Canadian Council Ministers of the Environment (CCME), 2006d. 2005 Review of Canada-Wide Standards for Petroleum Hydrocarbons in Soil: Report of the Toxicity Reference Value (TRV) Advisory Sub Group. Dated February, 2006.

Canadian Council of Ministers of Environment (CCME). 2008. Canada Wide Standards for Petroleum Hydrocarbons in Soils: User Guidance. ISBN 978-1-896997-78-0 PDF. Publication Number 1398

CCME (Canadian Council of Ministers of the Environment), 2000. Canada-Wide Standards for Petroleum Hydrocarbons (PHCs) In Soil: Scientific Rationale Supporting Technical Document. December 2000.

Canadian Environmental Protection Act (CEPA), 1993. *Priority Substances List Assessment Report: Polycyclic Aromatic Hydrocarbons*. 61 pp.

Canadian Environmental Protection Act (CEPA), 1999. *Priority Substances List Assessment Report: Phenol* (Draft Report, February 1999). 85 pp plus appendices.

Canadian Fitness and Lifestyle Research Institute (CFLRI). 1981. Unpublished data. CFLRI, Ottawa, ON.

Canadian Fitness and Lifestyle Research Institute (CFLRI). 1988. Unpublished data. CFLRI, Ottawa, ON.

CanTOX Inc. 1997. Summary of the CanTOX Health-Based TPH Method: Development and Application to Risk Assessment of Petroleum-Contaminated Sites. Personal communication from E. Sigal, CanTOX Inc., Mississauga, Ontario. 9p.

Carlson, A.W. and P.A. Kosian. (1987). Toxicity of Chlorinated Benzenes to Fathead Minnows (Pimephales promelas). Arch. Environ. Contam. Toxicol. 16:129-135.

Cermak, J.H., Stephenson, G.L., Birkholz, D, and Dixon, D.G., 2005. Summary of the Soil Toxicity and Soil Chemical Analysis Data for Petroleum Fractions 2 and 3. Interim report prepared for the CCME CWS Ecotoxicological Criteria Advisory Sub-Group, October 31, 2005.

Chalmers, G.E. 1997. A literature review and discussion of the toxicological hazards of oilfield pollutants in cattle. Alberta Research Council, Vegreville, AB.

ChemInfo Services. 1998. Petroleum Hydrocarbons in Soil. IN: Socio-Economic Assessment of Canada-wide Standards: Scoping Phase, Final Report, April 1998, CHEMinfo Services Inc.

Chung, N. and M. Alexander. 1998. Differences in sequestration and bioavailability of organic compounds aged in dissimilar soils. Environ. Sci. Technol. 32: 855-860.

Coppock, R.W and C.A.J. Campbell, 1997. Risk Assessment, Chapter 16, in G.E.Chalmers, ed. A Literature Review and Discussion of the Toxicological Hazards of Oilfield Pollutants In Cattle. Alberta Research Council, Vegreville. pg. 363 -381.

Demirjian, A. 1980. Anthropometry Report: Height, Weight and Body Dimensions. A report from Nutrition Canada. Health Promotion Directorate, Bureau of Nutritional Sciences, Health and Welfare Canada, Ottawa, ON. 133 pages + unpublished data of the Nutrition Canada Survey.

Deneer, J.W., T.L. Sinnege, W. Seinen, and J.L.M. Hermens. (1988). The Joint Acute Toxicity to Daphnia magna of Industrial Organic Chemicals at Low Concentrations. Aquat. Toxicol. 12:33-38.

Di Toro, D.M., J.A. McGrath and D.J. Hansen, 2000. Technical Basis for Narcotic Chemicals and Polycyclic Aromatic Hydrocarbon Criteria. I. Water and Tissue. Environ Toxicol. Chem. 19: 1951-1970.

Didyk, B.M. and B.R.T. Simoneit, 1989. Hydrothermal oil of Guaymas Basin the implications for petroleum formation mechanisms. Nature, 342: 65-69.

Domenico,P.A. and B.A. Robbins. 1985. A new model of contaminated plume analysis. Groundwater. 23:476-485.

Donkin, P., J. Widdows, S.V. Evans, C.M. Worrall, and M. Carr. (1989). Quantitative Structure-Activity Relationships for the Effect of Hydrophobic Organic Chemicals on Rate of Feeding by Mussels (Mytilus edulis). Aquat. Toxicol. 14:277-294.

EcoTAG, 2000a. *Overview of Methods for the Derivation of Soil Quality Guidelines based on Direct Soil Contact Exposure Pathways and Ecological Receptors*. Report to the Petroleum Hydrocarbons Canada Wide Standards Development Committee, Jan 16, 2000. 24 pp plus annexes.

Edwards, D.A., M.D. Androit, M.A. Amoruso, A.C. Tummey, C.J. Bevan, A. Tveit, L.A. Hayes, SlH. Yongren and D.V. Nakles. 1997. Development of Fraction Specific Reference Doses (RfDs) and Reference Concentrations (RfCs) for Total Petroleum Hydrocarbons (TPH). Volume 4 of the Total Petroleum Hydrocarbon Criteria Working Group Series, Amherst Scientific Publishers, Amherst, MA. 137 p.

Edwini-Bonsu, S. and P.M. Steffler. 2004. Air flow in sanitary sewer conduits due to wastewater drag: a computation fluid dynamics approach. *J. Environ. Eng. Sci.* 3: 331-342.

Environment Canada, 1996a. *Canadian Soil Quality Guidelines for Benzo(a)pyrene: Environmental. Support Document - Final Draft, December 1996*. Guidelines Division, Science Policy and Environment Branch, Environment Canada, Ottawa.

Environment Canada, 1996b. *Canadian Soil Quality Guidelines for Naphthalene: Environmental. Support Document - Final Draft, December 1996*. Guidelines Division, Science Policy and Environment Branch, Environment Canada, Ottawa.

Environment Canada, 1996c. *Canadian Soil Quality Guidelines for Benzene: Environmental. Support Document - Final Draft, December 1996*. Guidelines Division, Science Policy and Environment Branch, Environment Canada, Ottawa.

Environment Canada, 1996d. *Canadian Soil Quality Guidelines for Toluene, Ethylbenzene and Xylene(TEX): Environmental. Support Document - Final Draft, December 1996*. Guidelines Division, Science Policy and Environment Branch, Environment Canada, Ottawa.

Environmental Protection Department. Victoria, British Columbia.

EPA. (1988). Estimating Toxicity of Industrial Chemicals to Aquatic Organisms Using Structure Activity Relationships. R.G. Clements, Ed. US Environmental Protection Agency, Washington DC. EPA-560-6-88-001.

Equilibrium Environmental Inc. (Equilibrium). 2005a. Critical Review and Evaluation of Toxicological Reference Values for Petroleum Hydrocarbon Sub-fractions within Fractions F2, F3 and F4. Report prepared for Environmental Protection Branch, Health Canada, Burnaby, BC. March 29.

Equilibrium Environmental Inc. (Equilibrium). 2005b. Evaluation of Issues Related to the Development of Updated Petroleum Hydrocarbon Constituent Toxicity Reference Values and Development of an Updated Toxicity Reference Value for C_6 to C_8 Aliphatic Hydrocarbons. Report prepared in association with GlobalTox Toxicology Focused Solutions and Wilson Scientific Consulting Inc. for Environmental Protection Branch, Health Canada, Burnaby BC. April 25.

Equilibrium Environmental Inc. (Equilibrium). 2006. Preliminary examination of vapour concentration thresholds for adverse effects on the human respiratory system and/or mucosal irritation, and comparison with the existing CCME TRV of 18.4 mg/m^3 for the F1 C_6 to C_8 aliphatic hydrocarbons. Memorandum prepared for CCME Soil Quality Guidelines Task Group Toxicity Reference Value Subgroup. Prepared by A. Knafla (Equilibrium Environmental Inc.) and R. WIlson (Wilson Scientific Inc.). February 7, 2006.

Erickson, R.J., G.T. Ankley, D.L. DeFoe, P. A. Kosian and E.L. Makynen, 1999. Additive toxicity of binary mixtures of phototoxic polycyclic aromatic hydrocarbons to the oligochaete *Lumbriculus variegatus*. Toxicol. Appl. Pharmamacol. 154: 97-105

Ershow, A.G. and K.P. Cantor. 1989. *Total water and tap water intake in the United States: population-based estimates of quantiles and sources.* Life Sciences Research Office, Federation of American Societies for Experimental Biology.

ESG (ESG International Inc.) 2000. Final Report on the Acute Screening and Definitive, Chronic Toxicity Tests with Motor Gasoline. Report prepared by G.L. Stephenson and J. Princz, ESG International Inc. March 2000. 32 pp. plus appendices.

ESG (ESG International Inc.) 2003. Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase I – Fraction Specific Toxicity of Crude Oil. Report prepared for the Petroleum Technology Alliance of Canada. 238 pages.

Federle, T.W., 1988. Mineralization of monosubstituted aromatic compounds in unsaturated and saturated subsurface soils. *Can. J. Microbiol*. 34: 1037-1042.

Ferguson, J. (1939). The Use of Chemical Potentials as Indices of Toxicity. Proc. Royal Society of London 127B:387-404.

Gas Research Institute, 2000. Environmentally Acceptable Endpoints for Hydrocarbon-Contaminated Soils. PERF Project 94-06.

Gerry, P.A., L.L. Green, and D.O. Moses. 1986. A Comparison of the Effects of Ventilation and Other Factors for Residential Combustion Sources of Indoor Air Pollution. For presentation at the 79th Annual Meeting of the Air Pollution Control Association, Minneapolis, MN, June 22-27.

Golder Associates Ltd. 1995. Working Document - Recommendations to BC Environment for Development of Remediation Criteria for Petroleum Hydrocarbons in Soil and Groundwater: Volume 1, Text. Prepared for BC Ministry of Environment, Land and Parks, Victoria, BC June 16, 1995.

Golder Associates. 2004 (draft). Soil Vapour Intrusion Guidance for Health Canada Screening Level Risk Assessment (SLRA). Contractor report prepared for Health Canada. Burnaby, BC.

Grimsrud, D.T., M.H. Sherman, and R.C. Sonderegger. 1983. Calculating Infiltration: Implications for a Construction Quality Standard. In: *Thermal Performance of the Exterior Envelopes of Buildings II*, SP 38, ASHRAE, Atlanta,GA. pp. 422-454. LBL-9416.

Gustafson, J.G., J. G. Tell and D. Orem. 1997. Selection of Representative TPH Fractions Based on Fate and Transport Considerations. Volume 3 of the Total Petroleum Hydrocarbon Criteria Working Group Series, Amherst Scientific Publishers, Amherst, MA. 102 p.

Haines,J.R. and Alexander,M. 1974. Microbial degradation of high molecular weight alkanes. Appl. Microbiol. 28: 1084-1085.

Hartman, B. 2002. Reevaluating the Upward Vapor Migration Risk Pathway. LUSTLine Bulletin 41.

Health and Welfare Canada. 1993. Fifth Edition. "Guidelines for Canadian Drinking Water Quality". Federal-Provincial Subcommittee on Drinking Water. Ottawa, Ontario.

Health Canada (HC). 1994. *Human Health Risk Assessment for Priority Substances.* Canadian Environmental Protection Act Assessment Report, Health Canada, Ottawa. 36 p.

Health Canada. 2004. Federal Contaminated Site Risk Assessment in Canada – Part I: Guidance on Human Health Preliminary Quantitative Risk Assessment. Ottawa.

Heath,J.S., K. Koblis and S.L. Sager, 1993. Review of chemical, physical and toxicological properties of components of total petroleum hydrocarbons. J. Soil Contam. 2: 1-27.

Hermens, J., E. Brockhuyzen, H. Canton, and R. Wegman. (1985a). Quantitative Structure Activity Relationships and Mixture Toxicity Studies of Alcohols and Chlorohydrocarbons: Effects on Growth of Daphnia magna. Environ. Toxicol. Chem. 4:273-279.

Hermens, J., H. Canton, P. Janssen, and R. de Jong. (1984). Quantitative Structure-Activity Relationships and Toxicity Studies of Mixtures of Chemicals with Anaesthetic Potency: Acute Lethal and Sublethal Toxicity to Daphnia magna. Aquat. Toxicol. 5:143-154.

Hermens, J., P. Leeuwangh, and A. Musch. (1985b). Joint Toxicity of Mixtures of Groups of Organic Aquatic Pollutants to the Guppy (Poecilia reticulata). Ecotox. Environ. Safety 9:321-326.

Hers, I. and R. Zapf-Gilje. 1999. Canadian consortium research project – field validation of soil gas transport to indoor air pathway.

Howard, P.H., R.S. Boethling, W.F. Jarvis, W.M. Meylan, and E.M. Michalenko, 1991. Handbook of Environmental Degradation Rates, Chelsea, MI: Lewis Publishers, p. 725.

Irwin, R.J., M. VanMouwerik, L. Stevens, M.D., Seese, and W. Basham. 1997. Environmental Contaminants Encyclopedia:TPH National Park Service, Water Resources Division, Fort Collins, Colorado. Distributed within the Federal Government as an Electronic Document

Joergensen, P.R., L.D. McKay, and J.P. Kistrup, 2004. Aquifer Vulnerability to Pesticide Migration Through Till Aquitards. Ground Water, 42,6: 841-855.

Johnson, P.C. 2002. Identification of Critical Parameters for the Johnson and Ettinger (1991) Vapor Intrusion Model. API Bulletin No. 17. American Petroleum Institute, Washington, DC.

Johnson, P.C. and R.A. Ettinger. 1991. Heuristic model for predicting the intrusion rate of contaminant vapors into buildings. Environ. Sci. Tech., 25: 1445-1452.

Kailing, S.H. 1984. Building Air Exchange in Cold Regions. Proceedings: Cold Regions Engineering Specialty Conference, April 4-6, Canadian Society for Civil Engineering, Montreal, QB.

Kelsey, J.W. and M. Alexander. 1997. Declining bioavailability and inappropriate estimation of risk for persistent compounds. Environ. Tox. Chem. 16: 582-585.

King, T.A., L.L. Green and D.O. Moses. 1986. Estimating Concentrations and Health Risks of Nitrogen Dioxide in Residences. Presented at the Air Pollution Control Association, June 22-27, Minneapolis, MN.

Kissel, J.C., J.H. Shirai, K.Y. Richter and R.A. Fenske. 1998. Investigation of dermal contact with soil in controlled trials. *J. Soil Contam.,* 7(6): 737-752.

Kissel, J.C., K.Y. Richter and R.A. Fenske. 1996. Field measurement of dermal soil loading attributable to various activities: implications for exposure assessment. *Risk Anal.*, 16(1): 115-125.

Komex International Inc. 2000. Socio-Economic Analysis of Canada-Wide Standards for Petroleum Hydrocarbons in Soil. Prepared for the CCME Socio-Economic Analysis Technical Advisory Group.

Lamb, B., H. Westberg, P. Bryant, J. Dean, and S. Mullins. 1985. Air Infiltration Rates in Pre- and Post-Weatherized Houses. *J. Air Pollu. Cont. Assoc.,* (35): 545-551.

Layton, D.W. 1993. Metabolically consistent breathing rates for use in dose assessments. *Health Physics* 64: 23-36.

Little, John C., Daisey, Joan M. and Nazaroff, William W. 1992. Transport of Subsurface Contaminants Into Buildings: An Exposure Pathway for Volatile Organics. Environ. Sci. Technol., Vol. 26, No. 11.

Loehr, R. and J. Matthews. 1992. Loss of Organic Chemicals in Soil: Pure Compound Treatability Studies. US Environmental Protection Agency, Washington, D.C., EPA/600/J-93/037 (NTIS PB93158913)

Loehr, R.C. and M.T. Webster. 1996. Performance of long-term, field-scale bioremediation processes. J. Haz. Materials 50: 105-128.

Loehr, R.C. and Webster, M.T., 1997. Effect of treatment on contaminant availability, mobility and toxicity, Chapter 2 in "Environmentally Acceptable Endpoints in Soil: Risk-Based Approach to Contaminated Site Management Based on Availability of Chemicals in Soil". D.G.Linz and D.V. Nakles, *eds*. American Academy of Environmental Engineers Publication. pp. 136-223.

MacFarlane and Fox 2000

Mackay, D., W.-Y. Shiu and K.-C. Ma, 1995. *Illustrated handbook of physical-chemical properties and environmental fate of organic chemicals. Vol. IV*. Lewis Publishers/CRC Press Inc., Boca Raton, Fla.

McKay, Larry D., J.A. Cherry and R.W. Gillham. 1993. Field Experiments in a Fractured Clay Till 1. Hydraulic Conductivity and Fracture Aperture. Wat. Res. Res. 29:4, 1149-1163.

Massachusetts Department of Environmental Protection (MADEP). 1989. Guidance for Disposal Site Risk Characterization and Related Phase II Activities - In Support of the Massachusetts Contingency Plan. Massachusetts Department of Environmental Quality Engineering. [Policy No. WSC/ORS-141-89] (1989).

Massachusetts Department of Environmental Protection (MADEP). 1991. Development of Soil Advisory Levels, Technical Support Document. Massachusetts Department of Environmental Protection, Office of Research and Standards, DRAFT (October 1991).

Massachusetts Department of Environmental Protection (MADEP). 1994. Interim Final Petroleum Report: Development of Health-Based Alternatives to the Total Petroleum Hydrocarbon (TPH) Parameter. MADEP, Boston, MA.

Massachusetts Department of Environmental Protection (MADEP). 1994. Background Documentation for the Development of MCP Numerical Standards.

Massachusetts Department of Environmental Protection (MADEP). 1996. Revisions to the Massachusetts Contingency Plan, 310 CMR 40.0000 - Public Hearing Document. November 1, 1996. MADEP, Boston, MA.

Massachusetts Department of Environmental Protection (MADEP). 1997. Revisions to the Massachusetts Contingency Plan, 310 CMR 40.0000 - Public Hearing Document. January 17, 1997. MADEP, Boston, MA. (Includes cover letter and Notice of Public Hearings).

Massachusetts Department of Environmental Protection (MDEP) (2003) Updated Petroleum Hydrocarbon Fraction Toxicity Values for the VPH/EPH/APH Methodology. MDEP Bureau of Waste Site Cleanup, Boston, MA. November 2003. 65 pp. Available at: www.mass.gov/dep/cleanup/tphtox03.pdf (accessed 1 February 2006).

Matsumoto,G. 1983. Changes in organic constituents in river water during incubation. Wat. Res. 17: 1803-1810.

Mauck, W.L., P.M. Mehrle and F.L. Mayer. (1978). Effects of the Polychlorinated Biphenyl Araclor 1254 on Growth, Survival and bone Development in Brook Trout (Salvelinus fontinalis). J. Fish Res. Board Can. 35:1084-1088.

Mayer, F.L., P.M. Mehrle and H.O. Sanders. (1977). Residue Dynamics and Biological Effects of Polychlorinated Biphenyls in Aquatic Organisms. Arch. Environ. Contam. Toxicol. 5:501-511.

McCarthy, L.S. and D. Mackay, 1993. Enhancing ecotoxicological modeling and assessment. Body residues and modes of toxic action. Environ. Sci. Technol. 27: 1719-1728.

McCarty, L.S. (1986). The Relationship Between Aquatic Toxicity QSARs and Bioconcentration for some Organic Chemicals. Environ. Toxicol. Chem. 5:1071-1080.

McCarty, L.S. (1991). Toxicant Body Residues: Implications for Aquatic Bioassays with Some Organic Chemicals. In: Aquatic Toxicology and Risk Assessment, 14th Volume. M.A. Mayes and M.G. Barron, Eds. American Society for Testing and Materials, ASTM STP 1124, Philadelphia, PA.

McCarty, L.S. and D. Mackay. (1993). Enhancing Ecotoxicological Modeling and Assessment. Environmental Science and Technology 27(9):1718-1729.

McKim, J.M. and P.K. Schmieder. (1991). Bioaccumulation: Does it Reflect Toxicity? In: Bioaccumulation in Aquatic Systems, Contributions to the Assessment. R. Nagel and R. Loskill, Eds. VCH Publishers, Weinheim, Germany.

Mercer, J.W., and R.M. Cohen, 1990. A review of immiscible fluids in the subsurface: Properties, models, characterization, and remediation, Journal of Contaminant Hydrology, 6:107-163.

Meridian Environmental, 2007. Socio-Economic Analysis of the Proposed Updated Criteria Canada-Wide Standard for Petroleum Hydrocarbons in Soil. Prepared for CCME Soil Quality Guidelines Task Group, August, 2007.

Michelsen, T. (1997) The Narcosis Model for Predicting the Toxicity of Dissolved Petroleum Constituents in Groundwater to Surface Water Receptors. MTCA TECHNICAL SUPPORT DOCUMENT, Washington Department of Ecology, Toxics Cleanup Program, 42 pp.

Ministère de L'Environnement et de la Faune Québec (MEFQ). 1996. Projet de politique de protection des sols et de réhabilitation des terrains contaminés - Document de consultation. MEFQ, Service des lieux contaminés. March, 1996.

Mitchell. L.H., R.G. Brown, and J.W. Dent. The effect of gasoline contamination of the water supply on the growth and consumption of pigs. Rev. Vet. Can. 19: 10-12.

Mihalakakou, G., Santamouris, M., Asimakopoulos, D. and Argiriou, A. 1995. On the ground temperature below buildings. *Solar Energy* 55(5): 355-362.

Moucawi,J., Fustec,E., Jambu,P., Ambles,A., and Jacques,Y.R. 1981. Bio-oxidation of added and natural hyrocarbons in soils: Effect of iron. Soil Biol. Biochem. 13: 335-342.

Nakles, D.V., J.W. Lynch, D. Edwards, J.G. Tell, T.L. Potter, R.P. Andes and C.P.L. Barkan. 1996. Risk-Based Management of Diesel-Contaminated Soil. Association of American Railroads, Washington, D.C..

National Health and Welfare (NHW). 1981. *Tapwater consumption in Canada*. Department of National Health and Welfare, Environmental Health Directorate, Ottawa, ON. 83p + unpublished detailed frequency counts for various categories including sex, age, season, and activity level.

NJ DEP (New Jersey Department of Environmental Protection). 2005. Vapor Intrusion Guidance. Draft. Division of Science, Research and Technology.

Nazaroff, W.W., H. Feustel, A.V. Nero, K.L. Revzan, D.T. Grimsrud, M.A. Essling, and R.E. Toohey. 1985. *Environ. Sci. Technol.*, 19: 31-46.

Nazaroff, W.W., S.R. Lewis, S.M. Doyle, B.A. Moed and A.Nero. 1987. *Environ. Sci. Technol*., 19: 31-46.

O'Connor Associates Environmental Inc. (OAEI). 1996. [Final Report] Development of Remediation Guidelines for Petroleum Storage Tank Sites. Submitted to Alberta Environmental Protection, Edmonton. September, 1996.

Ontario Ministry of Environment and Energy (MOEE). 1997. *Guideline for Use at Contaminated Sites in Ontario (Revised February 1997*). OMEE, Toronto, ON.

Ontario Ministry of Environment and Energy (OMEE). 1993. Interim Guidelines for the Assessment and Management of Petroleum Contaminated Sites in Ontario. MOEE, Hazardous Contaminants Branch, Toronto.

Ontario Ministry of Environment and Energy (OMEE). 1996. *Guideline for Use at Contaminated Sites in Ontario*. OMEE, Toronto, ON.

Opperhuizen, A. and S.M. Schrap. (1988). Uptake Efficiencies of Two Polychlorobiphenyls in Fish after Dietary Exposure to Five Different Concentrations. Chemosphere 17:253-262.

Otson, R., D.T. Williams and P. Fellin. 1998. Relationship Between Air Exchange Rate and Indoor VOC Levels. For presentation at the Air & Waste Management Association's 91st Annual Meeting & Exhibition, June 14-18, 1998, San Diego, CA.

Pandian, M.D., W.R. Ott and J.V. Behar. 1993. Residential Air Exchange Rates for Use in Indoor Air and Exposure Modeling Studies. *J. Exp. Anal. Environ. Epidem.*, 3: 407-416.

Parkerton, T.F. and M.A. Stone, in press. Ecotoxicity on a stick: A novel analytical method for assessing the ecotoxicity of hydrocarbon contaminated samples.

Persily, A. and J. Gorfain. 2004. Analysis of Ventilation Data from the US Environmental Protection Agency Building Assessment Survey and Evaluation (BASE) Study. National Institute of Standards and Technology (NIST), Technology Administration, US Department of Commerce. NISTIR 7145.

Piet, G.J., and J.G.M.M. Smeenk, 1985. Behavior of organic pollutants in pretreated Rhine water during dune infiltration. Ground Water Quality, eds. By C.H. Ward *et al*., New York: Wiley, pp. 122-144.

Potter, T.L. and K. E. Simmons. 1998. Composition of Petroleum Mixtures. Volume 2 of the Total Petroleum Hydrocarbon Criteria Working Group Series, Amherst Scientific Publishers, Amherst, MA. 102 p.

Prager, J.C., 1995. *Environmental Contaminant Reference Databook. Vol. 1*. Van Nostrand Reinhold.

Protocol Improvement Working Group (PIWG). 2000. Canada wide standard on petroleum hydrocarbons (PHCs): Improved protocol for derivationof human health-based soil quality guidelines. Final report submitted to the CCME PHC CWS development committee. July 2000.

Puls, R., 1988. Mineral Levels in Animal Health - Diagnostic Data. Clearbrook, British Columbia: Sherpa.

Richardson, G. M. 1997. *Compendium of Canadian Human Exposure Factors for Risk Assessment.* Published by O'Connor Associates Environmental Inc., Ottawa, Ontario. 74p.

Roggemans, S., Bruce, C.L., Johnson, P.C. and Johnson, R.L. 2001. Vadose Zone Natural Attenuation of Hydrocarbon Vapors: An Emperical Assessment of Soil Gas Vertical Profile Data. American Petroleum Institute Technical Bulletin No. 15.

Rogues, D.E., E.B. Overton and C.B. Henry, 1994. Using GC/MS fingerprint analyses to document progress and process of oil degradation. J. Environ. Qual., 23: 851-855.

Rowe, L.D., J.W. Dollahite and B.J. Camp, 1973. Toxicity of two crude oils and of kerosine to cattle. J. Am. Vet. Med. Assoc. 162(1): 61-66.

Ryan, E.A., E.T. Hawkins, B. Magee and S.L. Santos. 1987. Assessing risk from dermal exposure at hazardous waste sites. In: Superfund '87: Proceedings of the 8th National Conference, Washington, DC, November 16-18, 1987.

Salanitro, J.P., P.B. Dorn, H.H. Huesemann, K.O. Moore, I.A. Rhodes, L.M.R. Jackson, T.E. Vipond, M.M. Western and H.L. Wisniewski. 1997. Crude oil hydrocarbon bioremediation and soil ecotoxicity assessment. Environ. Sci. Technol. 31: 1769-1776.

Saterbak, A., R.J. Toy, B.J. McMain, M.P. Williams, and P.B. Dorn, in press. Ecotoxicological and analytical assessment of the effects of bioremediation of hydrocarbon-containing soils.

Saterbak, A., R.J. Toy, D.C.L. Wong, B.J. McMain, M.P. Williams, P.B. Dorn, L.P. Brzuzy, E.Y. Chai and J.P. Salanitro, 1999. Ecotoxicological and analytical assessments of hydrocarbon-contaminated soils and application to ecological risk assessment. Environ. Toxicol. Chem. 18: 1591-1607.

Sawatsky, N. and X. Li, 1999. Land Disposal of Bioremediated Hydrocarbon Contaminated Soils/Wastes. Alberta Research Council Final Report – August, 1999. 63 pp.

Sedman, R.M. and R.J. Mahmood. 1994. Soil ingestion by children and adults reconsidered using the results of recent tracer studies. *J. Air & Waste Manage. Assoc*., 44: 141-144.

Sherman, M. and D. Dickerhoff. 1994. Monitoring Ventilation and Air Leakage in a Low-Rise Commercial Building. Presented at the 1994 ASME/JSME/JSES International Solar Energy Conference, San Francisco, CA, March 27-30, 1994.

Shih, Y and S Wu. 2005. Distinctive sorption mechanisms of soil organic matter and mineral components as elucidated by organic vapour uptake kinetics. Environmental Toxicology and Chemistry 24(11):2827-2832.

Slaski, J.J., N. Sawatski and X. Li, 1999. Ecotoxicity of Bioremediated Hydrocarbon Contaminated Soils/Wastes. Alberta Research Council Final Report – June, 1999. 21 pp.

Smith, J.H., Bird, M.G., Lewis, S.C., Freeman, J.J., Hogan, C.K. and Scala, R.A. 1995. Subchronic feeding study of four white mineral oils in dogs and rats. *Drug and Chem. Tox.* 18:83-103.

Smith, J.H., Mallet, A.K., Priston, R.A.J., Brantom, P.G. and Worrel, N.R. 1996. Ninety-day feeding study in Fischer 344 rats of highly refined petroleum-derived food-grade white oils and waxes. *Toxicol. Pathol.* 24:214-230.

Soil Classification Working Group. 1998. The Canadian System of Soil Classification. 3rd Ed. NRC Research Press. Ottawa 1998.

Stanek, E.J. III and E.J. Calabrese. 1994a. Limits in soil ingestion data: the potential for imputing data when soil ingestion estimates are below the detection limit. *J. Soil Contam*., 3(3): 265-270.

Stanek, E.J. III and E.J. Calabrese. 1994b. Bias and the detection limit model for soil ingestion. *J. Soil Contam*., 3(2): 183-189.

Stanek, E.J. III and E.J. Calabrese. 1995. Soil ingestion estimates for use in site evaluations based on the best tracer method. *Human and Ecolog. Risk Assess.,* 1(2): 133-157.

Stanek, E.J. III, E.J. Calabrese and R.M. Barnes. 1999. Soil ingestion estimates for children in Anaconda using trace element concentrations in different particle size fractions. *Human and Ecolog. Risk Assess.*, 5(3): 547-558.

Stanek, E.J. III, E.J. Calabrese, K. Mundt, P. Pekow and K.B. Yeatts. 1998. Prevalence of soil mouthing/ingestion among healthy children aged 1 to 6. *J. Soil Contam*., 7(2): 227-242.

Stantec Consulting Ltd. 2003 (draft). Research for Utility Criteria Development. Contractor report prepared for Alberta Environment.

Stephenson, G.L. 2000. CCME Canada-wide Standards for Petroleum Hydrocarbons: Assessment of motor gasoline and surrogate toxicity data for derivation of SQGs. Final report prepared by ESG International for Alberta Environmental Protection, Edmonton, Alberta. 30 p. (Appendices).

Stephenson, G.L., J. McCann, P. Jokuty, Z. Wang. 2000a. Draft report on the acute screening and definitive, chronic toxicity tests with Fraction 2 derived from Federated crude oil. A report prepared by ESG International for the Petroleum Technology Alliance of Canada and the Canadian Association of Petroleum Producers, Calgary, Alberta, 33 p. (Appendices).

Stephenson, G.L., J. McCann, P. Jokuty, Z. Wang. 2000b. Draft report on the acute screening and definitive, chronic toxicity tests with Fraction 3 derived from Federated crude oil. Prepared by ESG International for the Petroleum Technology Alliance of Canada and the Canadian Association of Petroleum Producers, Calgary, Alberta, 47 p.

Stephenson, G.L., N.Koper, Janet McCann,Zhendi Wang. 1999. Draft report on the acute screening and definitive, chronic toxicity tests with Whole Federated crude oil. ESG International. Prepared by ESG International for the Petroleum Technology Alliance of Canada and the Canadian Association of Petroleum Producers, Calgary, Alberta, 52 p.

Stevenson, F.J. 1983. Humus Chemistry. Academic Press, NY.

Swindoll, C.M., C.M. Aelion, and F.K. Pfaender, 1987. Inorganic and organic amendments effects of the biodegradation of organic pollutants by groundwater microorganisms. Amer. Soc. Microb. Abstr., 87th Annl. Mtg., Atlanta, GA., p. 298.

Tabak, H.H., S.A. Quave, C.I. Mashni, and E.F. Barth, 1981. Biodegradability studies with organic priority pollutant compounds. *J.Water Poll. Control Fed*. 53, 1503-1518.

Tindale, Miles and D.A. Bright, 2004. Literature and Information Review for the Canada-Wide Standard for Petroleum Hydrocarbons. CCME. Contract 314-2004. 55pp.

Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). 1997 - 1999. Total Petroleum Hydrocarbon Criteria Working Group Series Vols. 1 - 5. Amherst Scientific Publishers, USA.

Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). 1999. Human Health Risk-Based Evaluation of Petroleum Release Sites: Implementing the Working Group Approach. Amherst Scientific Publishers, Amherst, MA.

Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). 1997. Volume 3: Selection of Representative TPH Fractions Based on Fate and Transport Considerations. Final Draft. Total Petroleum Hydrocarbon Criteria Working Group and Association of American Railroads. Amherst Scientific Publishing.

Tsuruta, H. 1982. Percutaneous absorption of organic solvents, III. On the penetration rates of hydrophobic solvents through the excised rat skin. *Industrial Health*, 20: 335-345.

US EPA. 1992. *Dermal exposure assessment: principles and applications*. Report EPA/600/8-91/001B, US EPA, Washington, D.C.

US EPA. 1992b. Estimating Potential for Occurrence of DNAPL at Superfund Sites. US EPA Publ. No. 9355.4-07FS. Washington, DC.

US EPA. 1993. Behavior and Determination of Volatile Organic Compounds in Soil: A Literature Review. Office of Research and Development, Washington, DC. EPA/600/R-93/140.

US EPA. 1994. Methods for Derivation of Inhalation Reference Concentrations and Application of Inhalation Dosimetry. EPA/600/8-90/066F October 1994.

US EPA. 1996. Soil Screening Guidance: Technical Background Document. Office of Solid Waste and Emergency Response. US Environmental Protection Agency. Washington D.C..20460. Publication 9355.4-17A.

US EPA. 1997. User's guide for the Johnson and Ettinger (1991) model for subsurface vapor intrusion into buildings. US EPA, Washington, D.C.

US EPA. 1997a. *Exposure Factors Handbook*. Update to EPA/600/8-89/043. Washington, D.C.

US EPA. 2002. Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils.

US EPA. 2003. User's Guide for Evaluating Subsurface Vapor Intrusion Into Buildings. Prepared by Environmental Quality Management Inc. Office of Emergency and Remedial Response, Washington, DC.

US EPA. 2005. Review of Recent Research on Vapor Intrusion. National Exposure Research Laboratory, Athens, Georgia. EPA/600/R-05-106.

US EPA. 2006. Glossary of terms. www.epa.gov/iris/gloss8.htm

van Hoogan, G. and A. Opperhuizen. (1988). Toxicokinetics of Chlorobenzenes in Fish. Environ. Toxicol. Chem. 7:213-219.

Van Wenzel, A.P., G. Cornelissen, J.K. Miltenburg and A Oppenhuizer, 1996. Membrane burdens of chlorinated benzenes lower the main transition temperature in dipalmitoyl-phosphathdycholine vesicle: Implications for the toxicity of narcotic chemicals. Environ. Toxicol. Chem. 15: 203-212.

van Wezel, A.P., D.A.M. de Vries, S. Kostense, D.T.H.M. Sijm, and A. Opperhuizen. (1995). Intraspecies variation in lethal body burdens of narcotic compounds. Aquatic Toxicology 33:325-342.

Veith, G.D., D.J. Call, and L.T. Brooke. (1983). Structure-Toxicity Relationships for the Fathead Minnow, Pimephales promelas: Narcotic Industrial Chemicals. Can. J. Fish. Aquat. Sci. 40:743-748.

Viellenave, J.H. and J.V. Fontana. undated. Vapor Risks: If Done Right, it's Not as Bad as You Think. ESN Rocky Mountain, Golden, CO. Online: http://www.esn-rm.com/pdf/vaporrisk.pdf

VDEQ (Virginia Department of Environmental Quality). 2005. Voluntary Remediation Program – Risk Assessment Guidance. Online: http://www.deq.virginia.gov/vrprisk.raguide.html

Visser, S. 2005a. Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality Phase 3: Long-term Field Studies. Report prepared for Petroleum Technology Alliance Canada (PTAC). February 2005.

Visser, S. 2005b. Ecotoxicity Risk Assessment of PHC Residuals in Bioremediated Oil-Contaminated Clay Soils. PowerPoint presentation prepared for Petroleum Technology Alliance Canada (PTAC). November 2005.

Visser, S., Leggett, S., and Lee, K. 2003. Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality Phase 2: Field Studies. Report prepared for Petroleum Technology Alliance Canada (PTAC). April 2003.

Vogel, T. and D. Grbic-Galic.1986. “Incorporation of Oxygen from Water into Toluene and Benzene During Anaerobic Fermentative Transformation”. *Applied and Environmental Microbiology*. Vol 52, No 1. pp 200-202.

Vouk, V. B., Butler, G.C., Upton, A.C., Park, D.V., Asher, S.C., 1987. *Methods For Assessing the Effects of Mixtures of Chemicals Scope 30, SGOMSEC 3.* UNEP/ILO/WHO International Programme on Chemical Safety IPCS Joint Symposia 6.

Wang, Z. Fingas, M., and G. Sergy, 1995. Chemical characterization fo crude oil residues from an Arctic bbeach by GC/MS and GC/FID. Environ. Sci. Technol. 29, 2622-2631.

Water Environment Federation. 1997. WEF/US EPA Biosolids Fact Sheet Project. Water Environment Web. 04/29/99.

Weisman, W. (Ed.). 1998. Analysis of Petroleum Hydrocarbons in Environmental Media. Volume 1 of the Total Petroleum Hydrocarbon Criteria Working Group Series, Amherst Scientific Publishers, Amherst, MA. 98 p.

Weschler, C.J., H.C. Shields and B.M. Shah. 1996. Understanding and Reducing the Indoor Concentration of Submicron Particles at a Commercial Building in Southern California. *J. Air & Waste Manag. Assoc.*, 46: 291-299.

Wild, S.R. and K.C. Jones, 1993. Biological and abiotic losses of polynuclar aromatic hydrocarbons (PAHs) from soils freshly amended with sewage sludge. *Environmental Toxicology and Chemistry*, 12: 5-12.

Williams, D.R., J.C. Paslawski and G.M. Richardson. 1996. Development of a screening relationship to describe migration of contaminant vapours into buildings. *J. Soil Contam.*, 5(2): 141-156.

Wilson, B.H., G.B. Smith, and J.F. Rees, 1986. Biotransformations of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer materials: A microcosm study. Environ. Sci. Technol. 20, 997-1002.

Wilson, J.T., J.F. McNabb, B.H. Wilson, and M.J. Noonan, 1982. Biotransformation of selected organic pollutants in groundwater. Dev. Indust. Microb. 24. 225-233.

Wilson, S.C., R.E. Alcock, A.P. Sewart and K.C. Jones, 1997. Organic chemicals in the environment: Persistence of organic contaminants in sewage sludge-amended soil: a field experiment. *J. Environ. Qual*. 26: 1467-1477.

Wilson Scientific Consulting Inc. and Meridian Environmental Inc. 2006. Critical Review of Soil Ingestion Rates for Use in Contaminated Site Human Health Risk Assessments in Canada. Contractor report prepared for Health Canada Safe Environments Program.

Wong, D.C.L., E.Y. Chai, K.K. Chu and P.B. Dorn, 1999. Prediction of ecotoxicity of hydrocarbon-contaminated soils using physicochemical parameters. Environ. Toxicol. Chem. 18: 2611-2621.

Zoeteman, B.C., Harmsen, K, Linders, J.B.H.J., Morra, C.F.H and Slooff, W., 1980. Persistent organic pollutants in river water and ground water of the Netherlands. Chemosphere; 9:231-49.; 1980

Zoeteman, B.C., J.E. DeGreef, and F.J.J. Brinkmann, 1981. Persistency of organic contaminants in groundwater, lessons from soil pollution incidents in the Netherlands. Sci. Total Environ. 21, 187-202.

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.

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

[1] Nunavut Signed on to the Harmonization Accord and Subagreements when it joined the Council in November 1999.

[2] CCME is the major intergovernmental 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. CCME undertakes activities associated with environmental protection and sustainable development through coordinated action, which includes the development of Canada-wide Standards.

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 (AM TAG), Human Health Fate and Transport TAG (HHFT TAG), Ecological TAG (EcoTAG), and Socioeconomic Analysis TAG (SEA TAG). 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.1.2 Review and Update of the PHC CWS in 2005

When the PHC CWS was implemented, a formal commitment was made to review additional scientific, technical and economic data after 5 years in order to address outstanding data gaps and incorporate experience with the implementation of the standard.

After submissions from stakeholders were invited and compiled, an initial scoping study was conducted in 2004 (Tindal and Bright, 2004) to identify relevant new scientific research and key areas requiring further evaluation. The CCME Soil Quality Guidelines Task Group (SQGTG) then formalized the scope of the 5 year review and struck 3 advisory subgroups in 2005: the Toxicity Reference Value (TRV) Advisory Subgroup, the Model Parameters Advisory Subgroup and the Ecological Criteria Advisory Subgroup. Each of these groups, comprising members of government regulatory agencies and industry groups as well as technical experts, reviewed the available scientific and technical data within their respective scopes and made recommendations to SQGTG for updates to the PHC CWS.

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)	Canada

Connie Gaudet, Kathie Adare	
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 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 (EcoTAG)

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 (AM TAG) of CCME contributed to the establishment and validation of this method.

Name	Affiliation
Richard Turle	Environment Canada (AM TAG 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

A.2.7 CCME Soil Quality Guidelines Task Group (2006)

SQGTG coordinated the 5-year revision of the PHC CWS. Its activities included defining the scope of the review, establishing the advisory subgroups, arriving at decisions based on the recommendations of the subgroups, and coordinating contracts related to the review and update of the PHC CWS.

Name	Affiliation
Mike Zemanek	Alberta Environment
Norman Sawatsky (alternate)	
Glenn Harris	BC Ministry of Environment
Doug Spry (Chair)	Environment Canada
Joan La Rue-van Es	Manitoba Conservation
Raymond Morin	New Brunswick Department of Environment
Harvey Gaukel	NWT Environment and Natural Resources
Dan Hemsworth	Nova Scotia Environment and Labour
Robert Eno	Nunavut Department of Environment
Marius Marsh	Ontario Ministry of Environment
Danny MacInnis	PEI Department of Environment, Energy and Forestry
Hugues Ouellette	Ministère du Développement durable, de l'Environnement et des Parcs du Québec
Pritam Jain	Saskatchewan Environment
Ruth Hall	Yukon Department of Environment
Kelly Potter	Environment Canada, Technical Secratariat
Sarah Davarbakhsh	CCME Secratariat

A.2.8 Toxicity Reference Values (TRV) Advisory Subgroup

The mandate of the TRV Advisory Subgroup was to develop recommendations and advise SQGTG with respect to human health toxicity reference values for PHC in soil. Their activities included:

- Reviewing relevant information submitted to CCME with respect to human health toxicity reference values for the PHC sub-fractions.

- Evaluating the additive nature of direct soil exposure pathways (soil ingestion and dermal contact).
- Comparing the fraction approach used in the PHC CWS with the whole-product approach applied by Atlantic PIRI.
- Obtaining and reviewing additional information directly relevant to submissions made to CCME with respect to human health TRVs.
- Examining relevant policy and protocol decisions developed since the original PHC CWS derivation.
- Determining if technical or policy changes since the development of the PHC CWS may result in substantial changes to the current human health TRVs.
- Developing updated recommendations and rationale for human health TRVs consistent with relevant CCME policies and the current state of science.

Name	Affiliation
Christopher Rowat	Health Canada
Shairoz Ramji	Health Canada
Heather Valsangkar	New Brunswick Department of Environment and Local Government
Asish Mohapatra	Calgary Health Region
Roger Keefe	Imperial Oil Limited
Carol Drury	Shell Canada Limited
Geoffrey Granville	Shell Canada Limited
Bryan Leece	Dillon Consulting Ltd.
Tony Knafla	Equilibrium Environmental Inc.
Ross Wilson	Wilson Scientific Consulting Inc.
Ian Mitchell	Meridian Environmental Inc.
David Williams	Meridian Environmental Inc.
Joelle Hatton (recorder)	Alberta Environment
Mike Zemanek (SQGTG rep.)	Alberta Environment
Warren Kindzierski (chair)	WBK & Associates Inc.

A.2.9 Model Parameter Advisory Subgroup

The Model Parameter Advisory Subgroup was tasked to develop recommendations and advise SQGTG with respect to model parameters and methods applied in the soil vapour and groundwater transport models for the PHC CWS, as well as to review information and make recommendations with respect to explosive hazards and effects of PHC on buried utilities. Their activities included:

- Reviewing relevant information submitted to CCME with respect to contaminant transport model parameters, explosive hazards, and effects on buried infrastructure.
- Obtaining and reviewing additional information directly relevant to submissions that were made to CCME.
- Examining relevant policy and protocol decisions implemented by SQGTG since the PHC CWS was developed.

- Determining if there were relevant and significant technical or policy changes since the development of the PHC CWS that may result in substantial changes to the current guidelines.
- Developing recommendations and rationale for vapour intrusion, groundwater, explosive hazards and effects to buried infrastructure.
- Investigating the potential for use of soil vapour screening levels in the vapour intrusion pathway and appropriate mechanisms for implementation in keeping with defined protocol and policy decisions.

Name	Affiliation
Christopher Rowat	Health Canada
Meghan Roushorne	Health Canada
Joan La Rue-van Es	Manitoba Conservation
Raymond Morin	New Brunswick Department of Environment and Local Government
Heather Valsangkar	New Brunswick Department of Environment and Local Government
Dennis Stefani	Calgary Health Region
Andrea Walter	Petro-Canada
John Czechowski	Shell Canada Ltd.
Ian Hers	Golder Associates Ltd.
Debra Hopkins	Golder Associates Ltd.
Miles Tindal	Axiom Environmental Inc.
Ian Mitchell	Meridian Environmental Inc.
David Williams	Meridian Environmental Inc.
Norman Sawatsky (SQGTG rep.)	Alberta Environment
Joelle Hatton (recorder)	Alberta Environment
Warren Kindzierski (chair)	WBK & Associates Inc.

A.2.10 Ecological Criteria Advisory Subgroup

The Ecological Criteria Advisory Subgroup was tasked with reviewing the ecological direct soil contact levels established for the PHC CWS based on further toxicity testing and field studies, and advise SQGTG with respect to this pathway. Specific activities included:

- Undertaking scientific reviews of critical issues of relevance to understanding and managing risks to soil invertebrates and plants exposed to petroleum hydrocarbon mixtures in soil;
- In light of the best available scientific information, reviewing the existing PHC CWS Tier 1 ecological direct soil contact levels in terms of their derivation particulars as well as the realized level of biological effects, especially in field studies, relative to narrative protection goals;
- Proposing changes to the existing generic soil quality guidelines, as appropriate, and provide a clear and unequivocal scientific rationale;
- Identifying those critical components of the soil quality guideline development that may require policy decisions from the SQGTG; and,

- Assisting with the development of further site-specific approaches to addressing petroleum hydrocarbon risks to soil systems.

Name	Affiliation
Beverly Hale (chair)	University of Guelph
Chris Meloche	Husky Energy Inc.
Doug Bright	UMA Engineering Ltd.
Rick Scroggins	Environment Canada
Gordon Dinwoodie	Alberta Environment
Doug Spry	Environment Canada
Kelly Potter	Environment Canada
Anne-Marie Lafortune	Ministère du Développement durable, de l'Environnement et des Parcs du Québec
Gladys Stephenson	Stantec Consulting Ltd.
Marius Marsh	Ontario Ministry of Environment
Miles Tindal	Axiom Environmental Inc.
Janet McCann	University of Waterloo
Suzanne Visser	University of Calgary
Peter Miasek	Imperial Oil Ltd.

Appendix B: Brief historical review of soil quality guidelines for PHC

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) (BC);
- 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

During the 1990's, there were 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 were 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 BC 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 US 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 US 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 US 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 US 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 US 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 USA, 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 US 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 BC MOE - Working Document: Recommendations to BC Environment for Development of Remediation Criteria for Petroleum Hydrocarbons in Soil and Groundwater

On behalf of BC 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 BC MOE policy, and current BC MOE guidelines for PHCs

in soil and groundwater were based largely on professional judgement rather than quantitative risk assessment (G. Fox, BC 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 (^oC)	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 BC 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.
	Kerosene	C10-C32	AZ 8015	(2)		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
	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
Delaware	Gasoline	TPH GRO	(1)	100	Deleware Department of Natural Resources & Environmental Control	Note: Contact Delaware'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		

STATE	PRODUCT	PARAMETER/ CONSTITUENT	ANALYTICAL METHOD	NUMERIC CRITERION (mg/kg)	DEPARTMENT	COMMENTS
West Virginia	Gasoline	TPH	EPA 5015 M(1)	Site Specific	West Virginia Department of Environmental Protection	(1) Report GRO and DRO separately.
	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, default model parameters, 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*

Direct Contact Pathway:

Consistent with the CCME (2006a) protocol, the soil ingestion and dermal contact pathways are combined to calculate a single guideline value. Both of these exposure pathways are based on direct contact with contaminated soil, and both are evaluated using oral toxicity reference values in the absence of relevant dermal toxicity reference values.

$$SQG_{DC} = \frac{(TDI - EDI)\times SAF \times BW}{\left[(AF_G \times SIR) + (AF_D \times \{SA_H DL_H + SA_O DL_O\} EF)\right]\times ET} + BSC$$

Where: SQG_{DC} = soil quality guideline by direct contact (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 (kg/d)
AF_G = gastrointestinal absorption factor (unitless)
AF_D = dermal absorption factor (unitless)
SA_H = surface area of hands (m^2)
SA_O = surface area of exposed body surfaces other than hands (m^2)
DL_H = dermal loading of soil to hands (mg/m^2-event)
DL_O = dermal loading of soil to other skin surfaces (mg/m^2-event)

EF = exposure frequency (events/d)
ET = exposure term (unitless) (based on days/week and weeks/year at site; hours/day not considered)
BSC = background soil concentration (mg/kg)

Indoor Infiltration and Inhalation Pathway:

Tier 1 levels for the indoor infiltration and inhalation pathway are calculated based on modelled dilution between soil vapours and indoor air, and a partitioning relationship between adsorbed, dissolved and vapour phases.

$$SQG_I = [(RfC - C_a)\{\theta_w + (K_{OC})(f_{OC})(\rho_b) + (H')(\theta_a)\}(SAF)(AF)(DFi)(10^3 g/kg)]/[(H')(\rho_b)(ET)(10^6 cm^3/m^3)] + BSC$$

Where:
SQG_I = 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)
AF = Adjustment Factor (unitless)
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' = unitless Henry's Law Constant = H/RT
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 (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)

The attenuation coefficient is calculated using the model developed by Johnson and Ettinger (1991). Both advective and diffusive flow into the building are considered for both coarse and fine soils; based on the default parameter values, flow into the building is dominated by advective flow for coarse soils, while both advection and diffusion affect the attenuation factor for fine soils.

$$\alpha = \frac{\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right) \exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right)}{\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right) + \left(\frac{D_T^{eff} A_B}{Q_B L_T}\right) + \left(\frac{D_T^{eff} A_B}{Q_{soil} L_T}\right)\left[\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right) - 1\right]}$$

D_T^{eff} = effective porous media diffusion coefficient (cm^2/s) – calculated below
A_B = building area exposed to soil, including basement wall area (cm^2)
Q_B = building ventilation rate (cm^3/s) – calculated below
L_T = distance from contaminant source to foundation (cm)
Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s) – calculated below
L_{crack} = thickness of the foundation (cm)
D^{crack} = effective vapour-pressure diffusion coefficient through the crack (cm^2/s) - calculated below
A_{crack} = area of cracks through which contaminant vapours enter the building (cm^2)

$$D_T^{eff} \approx D_a \left(\frac{\theta_a^{10/3}}{n^2}\right)$$

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)

$$D^{crack} \approx D_a \left(\frac{\theta_{a\_c}^{10/3}}{n_c^{\,2}} \right)$$

D^{crack} = effective diffusion coefficient through foundation crack (cm^2/s)
D_a = pure component molecular diffusivities in air (cm^2/s)
θ_{a_c} = air-filled porosity of soil-filled foundation crack (unitless)
n_C = total soil porosity in foundation crack (unitless)

Note: soil in foundation cracks is assumed to be dry, so the air-filled porosity is equal to the total porosity in this case.

$$Q_B = L_B W_B H_B (ACH) \big/ \left(3600\, s/h\right)$$

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})

$$Q_{soil} = \frac{2\pi\ \Delta P\ k_v\ X_{crack}}{\mu \ln\left[\dfrac{2\left(Z_{crack}\right)}{r_{crack}}\right]}$$

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)

Protection of Groundwater (Potable Groundwater, Aquatic Life and Livestock Watering)

The groundwater model specified in the CCME (2006a) protocol (adapted from the BC CSST groundwater model) includes four components:

- Soil/leachate partitioning (DF1)
- Unsaturated zone transport of leachate (DF2)
- Mixing and dilution of leachate at the water table (DF3)
- Lateral groundwater advective/dispersive transport (DF4)

It should be noted that not all of these components will apply in every scenario. Specifically, the unsaturated zone transport (DF2) only applies if the contamination is not in contact with

groundwater, and is therefore not applied in generic guideline development. Also, the saturated-zone transport (DF4) only applies if there is a lateral separation between the remediated site and the groundwater receptor; for the development of Tier 1 levels it is assumed that a water well or livestock dugout could be installed at the edge of the contaminant source area (i.e. no offset distance), while a 10 m offset distance to a surface water body is assume for the protection of aquatic life.

Several assumptions are incorporated into the model:

- the soil is physically and chemically homogeneous;
- the groundwater aquifer is present in unconsolidated mineral soils (not fractured bedrock);
- 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 (non-aqueous phase liquid);
- 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 (no vertical dispersion) 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.

Soil/Leachate Partitioning (DF1)

Partitioning of the contaminant to leachate is evaluated using the standard three-phase equilibrium partitioning model as detailed in Appendix A of CCME (2006a).

$$SQG_{GW} = C_L \left\{ K_d + \left(\frac{\theta_w + H'\theta_a}{\rho_b} \right) \right\}$$

SQG_{GW}	=	soil quality guideline for the protection of groundwater (mg/kg) (i.e. potable water, aquatic life or livestock watering)
C_L	=	allowable leachate concentration at source (mg/L) – calculated below
K_d	=	distribution coefficient (cm^3/g) = K_{oc} x f_{oc}
K_{OC}	=	organic carbon partition coefficient (mL/g)
f_{OC}	=	fraction organic carbon (g/g)
θ_w	=	water filled porosity (unitless)

H'	=	dimensionless Henry's Law constant = H/RT
H	=	Henry's Law constant (atm-m^3/mol)
R	=	gas constant (8.2 x 10^{-5} atm-m^2/mol-^{O}K)
T	=	absolute temperature (K)
θ_a	=	air-filled porosity (unitless)
ρ_b	=	soil bulk density in contaminant partitioning zone (g/cm^3)

Unsaturated Zone Transport (DF2)

Note – for generic guideline development, contamination is assumed to be in contact with groundwater, and DF2 = 1 ($C_L = C_z$); this equation is provided for completeness only

$$C_L = \frac{C_z}{\exp\left[\frac{b}{2\partial_u} - \frac{b}{2\partial_u}\left(1 + \frac{4\partial_u L_{US}}{v_u}\right)^{1/2}\right]}$$

$$v_u = \frac{I}{\theta_w R_u}; \quad R_u = 1 + \frac{\rho_b}{\theta_w} K_d$$

C_L	=	allowable chemical concentration in leachate at the source (mg/L)
C_z	=	allowable chemical concentration in leachate at the water table (mg/L) calculated below
b	=	thickness of unsaturated zone below the source (m) = d – Z
d	=	depth from surface to groundwater surface (m)
Z	=	depth to bottom of contaminated soil (m)
∂_u	=	dispersivity in the unsaturated zone (m) = 0.1b
L_{US}	=	decay constant for chemical (y^{-1}) in unsaturated zone:

$$L_{US} = \frac{0.6931}{t_{1/2US}}\left(e^{-0.07d}\right)$$

$t_{1/2US}$	=	chemical half-life in unsaturated zone (years)
v_u	=	average linear leachate velocity (m/y)
I	=	infiltration rate (m/y) = precipitation minus runoff and evapotranspiration
θ_w	=	water-filled porosity (unitless)
R_u	=	retardation factor in unsaturated zone (unitless)
ρ_b	=	soil bulk density in unsaturated zone (g/cm^3)
K_d	=	distribution coefficient (cm^3/g) = K_{oc} x f_{oc}
K_{OC}	=	organic carbon partition coefficient (mL/g)
f_{OC}	=	fraction organic carbon (g/g)

Mixing and Dilution at the Water Table (DF3)

The mixing zone unsaturated/saturated equation (below), used to represent dilution of the leachate into groundwater, is based on a mass-balance approach considering movement of the chemical into the groundwater beneath the source (via infiltration of leachate) and away from the source area (via aquifer flow).

The equation is based on the assumption that the chemical is distributed evenly throughout a "mixing zone". While in reality the concentration of the chemical would not be constant throughout this zone, further vertical mixing would be expected to occur at the point of exposure (water well, dugout or surface water body). Therefore, the mixing zone approach is considered to be a reasonable approximation for purposes of generic guideline development.

$$C_z = C_{gw}\left\{1+\left(\frac{Z_d K_H i}{IX}\right)\right\}$$

C_z = allowable chemical concentration in leachate at the water table (mg/L)
C_{gw} = allowable chemical concentration in groundwater at the source (mg/L) – calculated below
Z_d = average thickness of mixing zone (m) – calculated below
K_H = hydraulic conductivity in the saturated zone (m/y)
i = hydraulic gradient (unitless)
I = infiltration rate (m/y) = precipitation minus runoff and evapotranspiration
X = length of source parallel to groundwater flow (m)

Calculation of average thickness of mixing zone:

$Z_d = r + s$; Z_d cannot exceed d_a

r = mixing depth available due to dispersion and diffusion (m)
= 0.01 X
X = length of source parallel to groundwater flow (m)
s = mixing depth available due to infiltration rate and groundwater flow rate (m)

$$s = d_a\left\{1-e^{-\frac{2.178XI}{K_H i d_a}}\right\}$$

d_a = depth of unconfined aquifer (m)
I = infiltration rate (m/y) = precipitation minus runoff and evapotranspiration
K_H = hydraulic conductivity in the saturated zone (m/y)
i = hydraulic gradient (unitless)

Lateral Groundwater Transport (DF4)
Note: for a receptor located at the edge of the contaminant source, DF4 = 1 ($C_{gw} = C_w$)

The groundwater model includes the Domenico and Robbins (1985) analytical equation to evaluate lateral transport to a downgradient receptor. The implementation of this model presented below assumes no vertical dispersion downgradient of the source area. This

assumption is "realistic" (doesn't significantly affect model results) for situations where the contaminant has mixed through the entire thickness of the aquifer or where there is a relatively large mixing depth and relatively short distance to the receptor, such as the default fine-grained soil scenario, and is conservative in other situations.

The below version of the equation is the steady-state version of the model (i.e. time since release does not need to be considered).

$$C_w(x,y,z,t) = \left(\frac{C_{gw}}{2}\right)\exp\left\{\left(\frac{x}{2\partial_x}\right)\left[1-\left(1+\frac{4L_s\partial_x}{v}\right)^{1/2}\right]\right\}\left\{erf\left[\frac{(y+Y/2)}{2(\partial_y x)^{1/2}}\right]-erf\left[\frac{y-Y/2}{2(\partial_y x)^{1/2}}\right]\right\}$$

$$v = \frac{K_H i}{n_e R_f}; \quad R_f = 1 + \frac{\rho_b}{n} K_d$$

C_w	=	allowable chemical concentration in water at receptor (mg/L) (i.e. aquatic life guideline, livestock watering RfC); for potable water pathway, calculated as (TDI – EDI)(BW)/IR_W
TDI	=	tolerable daily intake (mg/kg/d)
EDI	=	estimated daily intake (mg/kg/d)
BW	=	body weight (kg)
IR_W	=	water ingestion rate (L/d)
x	=	distance from source to receptor (m)
x,y,z	=	Cartesian coordinates relating source and receptor (m); y, z assumed to be 0
C_{gw}	=	allowable chemical concentration in groundwater at source (mg/L)
∂_x	=	longitudinal dispersivity tensor = 0.1x
∂_y	=	lateral dispersivity tensor = 0.1∂_x
L_s	=	decay constant (y^{-1}) in saturated zone:

$$L_s = \frac{0.6931}{t_{1/2US}}\left(e^{-0.07d}\right)$$

d	=	depth from surface to groundwater surface (m)
$t_{1/2S}$	=	biodegradation half-life (y)
v	=	velocity of contaminant (m/y)
K_H	=	hydraulic conductivity in the saturated zone (m/y)
i	=	hydraulic gradient (unitless)
n	=	total porosity of soil = 1 - ρ_b/2.65 (unitless)
n_e	=	effective soil porosity (unitless)
Y	=	source width (m) perpendicular to groundwater flow
R_f	=	retardation factor (unitless)
ρ_b	=	soil bulk density in saturated zone (g/cm^3)
K_d	=	distribution coefficient (cm^3/g)

Offsite Migration Check

The offsite migration check is applied for commercial and industrial sites which may have more sensitive land uses nearby (CCME, 2006a).

$SQG_{OM} = 14.3 \times SQG_A - 13.3 \times BSC$

where:

SQG_{OM}	= soil quality guideline for offsite migration (mg/kg)
SQG_A	= governing Tier 1 level for the agricultural land use (mg/kg)
BSC	= background soil concentration (mg/kg)

Part B: Default Model Parameters

Table C.1: Soil and Hydrogeological Parameters[a]

Parameter	Symbol	Soil Type	
		Coarse	Fine
Saturated Hydraulic Conductivity (m/y)	K_H	320	32[a]
Hydraulic Gradient	i	0.028	0.028
Recharge (Infiltration rate) (m/y)	I	0.28	0.20
Organic Carbon Fraction (g/g)	foc	0.005	0.005
Soil Bulk Density (g/cm^3)	ρ_b	1.7	1.4
Water Content (Mw/Ms)	M_W/M_S	0.07	0.12
Total Soil Porosity[b]	n	0.36	0.47
Soil Vapour-Filled Porosity[b]	θ_a	0.241	0.302
Soil Moisture-Filled Porosity[b]	θ_w	0.119	0.168
Vapour-Filled Porosity in Foundation Cracks	θ_{a_c}	0.36	0.47
Moisture-Filled Porosity in Foundation Cracks	θ_{w_c}	0	0
Soil Vapour Permeability (cm^2)	k_v	$5x10^{-8}$ [c]	$1x10^{-9}$ [d]

a – all values based on CCME (2006a) unless otherwise specified
b – calculated based on soil bulk density and water content
c – based on empirical data on soil gas flow rates into buildings over coarse soils
d – based on expected vapour permeability of silt or clay loam soils

Table C.2: Site Characteristics[a]

Parameter	SYMBOL	VALUE
Contaminant Source Width (m)	Y	10
Contaminant Source Depth (m)	Z	3
Contaminant Source Length (m)	X	10
Distance to Surface Water (m)	x	10
Distance to Potable Water User (m)	x	0
Distance to Livestock Watering (m)	x	0
Distance from Contamination to Building Slab (cm)	L_T	30
Depth to Groundwater (water table) (m)	d	3
Thickness of Unsaturated Soils Beneath Contamination (m)	b	0
Depth of unconfined aquifer (m)	d_a	5
Soil Temperature (K)	T	294
Vapour viscosity (g/cm-s)[c]	μ	0.000173
Adjustment Factor for Vapour Intrusion	AF	10[b]

a – all values based on CCME (2006a) unless otherwise specified
b – see discussion in section 3.4.3.2
c – based on the viscosity of air at 1 atmosphere pressure and 5^0 C.

Table C.3: Building Characteristics[a]

Parameter	Symbol	Residential Basement	Residential Slab-On-Grade	Commercial Slab-On-Grade
Building Length (cm)	L_B	1225	1225	2000
Building Width (cm)	W_B	1225	1225	1500
Building Area (cm^2)[b]	A_B	$2.7x10^6$	$1.5x10^6$	$3.0x10^6$
Building Height (cm)[c]	H_B	360	360	300
Thickness of Building Foundation (cm)	L_{crack}	11.25	11.25	11.25
Depth Below Grade of Foundation (cm)	Z_{crack}	244	11.25	11.25
Crack Radius (cm)	r_{crack}	0.2	0.2	0.26
Area of Crack (cm^2)	A_{crack}	994.5	994.5	1846
Length of Idealized Cylinder (cm)	X_{crack}	4900	4900	7000
Air Exchanges per Hour (1/h)[d]	ACH	0.5	0.5	0.9
Pressure Differential ($g/cm\text{-}s^2$)[d]	ΔP	40	40	20

a –all values based on CCME (2006a) unless otherwise specified

b – includes basement wall area

c – including basement; height of a 2-storey building reduced to account for incomplete mixing of contaminant between storeys (based on US EPA, 2003)

d – see Section 3.4.3.2

Table C.4: Chemical Properties

	F1			F2			
	Aliphatic C>6-C8	**Aliphatic C>8-C10**	**Aromatic C>8-C10**	**Aliphatic C>10-C12**	**Aliphatic C>12-C16**	**Aromatic C>10-C12**	**Aromatic C>12-C16**
Tolerable Daily Intake (TDI) (mg/kg/d)[a]	5	0.1	0.04	0.1	0.1	0.04	0.04
Estimated Daily Intake (EDI) (mg/kg/d)[b]	0.02334	0.0103	0.00938	0	0	0	0
Reference Concentration (RfC) (mg/m^3)[a]	18.4	1	0.2	1	1	0.2	0.2
Background Air Conc. (C_a) (mg/m^3)[b]	0.09111	0.03881	0.03745	0	0	0	0
Water Solubility (mg/L)[c]	5.4	0.43	65	0.034	0.00076	25	5.8
Henry's Law Constant (atm-m^3/mol)[c]	1.2	1.9	$1.20x10^{-2}$	2.9	12.5	$3.40x10^{-3}$	$1.30x10^{-3}$
Henry's Law Constant (unitless)[c]	50	80	0.48	120	520	0.14	0.053
Organic Carbon Partition Coefficient (K_{oc}) (mL/g)[c]	$10^{3.6}$	$10^{4.5}$	$10^{3.2}$	$10^{5.4}$	$10^{6.7}$	$10^{3.4}$	$10^{3.7}$
Diffusion Coefficient in Air (cm^2/s)[d]	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Absorption Factor for GI Tract (AF_G)[e]	1	1	1	1	1	1	1
Absorption Factor for Skin (AF_D)[e]	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Aquatic Life Benchmark (mg/L)[f]	0.0465	0.0076	0.14	0.00118	0.000074	0.096	0.0554
Livestock Water Reference Conc. (mg/L)[g]	53	53	53	49	49	49	49
Half Life in Saturated & Unsaturated Zone (days)[h]	712	712	712	1750	1750	1750	1750
Mass Fraction in Soil[i]	0.55	0.36	0.09	0.36	0.44	0.09	0.11

a – see Section 3.6
b – see Section 3.7
c – adapted from TPHCWG (Gustafson *et al.*, 1997)
d – recommended by PIWG
e – see Section 3.5.9
f – see Section 4.3.2
g – see Section 4.3.3
h – see Appendices H and I
i – based on typical petroleum product compositions
NS – not specified

Table C.4: Chemical Properties (page 2 of 2)

	F3				F4	
	Aliphatic C>16-21	**Aliphatic C>21-C34**	**Aromatic C>16-C21**	**Aromatic C>21-C34**	**Aliphatic C>34**	**Aromatic C>34**
Tolerable Daily Intake (TDI) (mg/kg/d)[a]	2	2	0.03	0.03	20	0.03
Estimated Daily Intake (EDI) (mg/kg/d)[b]	0	0	0	0	0	0
Reference Concentration (RfC) (mg/m^3)[a]	NA	NA	NA	NA	NA	NA
Background Air Conc. (C_a) (mg/m^3)[b]	0	0	0	0	0	0
Water Solubility (mg/L)[c]	$2.5x10^{-6}$	NS	0.65	0.0066	NS	NS
Henry's Law Constant ($atm\text{-}m^3/mol$)[c]	118	13500	$3.10x10^{-4}$	$1.61x10^{-5}$	$2.90x10^{6}$	$4.40x10^{-7}$
Henry's Law Constant (unitless)[c]	4900	$5.60x10^{5}$	0.012	$6.7x10^{-4}$	$1.20x10^{8}$	$1.8x10^{-5}$
Organic Carbon Partition Coefficient (K_{oc}) (mL/g)[c]	$10^{8.8}$	10^{13}	$10^{4.2}$	$10^{5.1}$	$10^{18.2}$	$10^{6.25}$
Diffusion Coefficient in Air (cm^2/s)[d]	0.05	0.05	0.05	0.05	0.05	0.05
Absorption Factor for GI Tract (AF_G)[e]	1	1	1	1	1	1
Absorption Factor for Skin (AF_D)[e]	0.2	0.2	0.2	0.2	0.2	0.2
Aquatic Life Benchmark (mg/L)[f]	NS	NS	NS	NS	NS	NS
Livestock Water Reference Conc. (mg/L)[g]	79	79	79	79	42	42
Half Life in Saturated & Unsaturated Zone (days)[h]	NS	NS	NS	NS	NS	NS
Mass Fraction in Soil[i]	0.56	0.24	0.14	0.06	0.8	0.2

a – see Section 3.6
b – see Section 3.7
c – adapted from TPHCWG (Gustafson *et al.*, 1997)
d – recommended by PIWG
e – see Section 3.5.9
f – see Section 4.3.2
g – see Section 4.3.3
h – see Appendices H and I
i – based on typical petroleum product compositions
NS – not specified

Part C: Example Derivation

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

Direct Contact Pathway:

$$SQG_{DC} = \frac{(TDI - EDI) \times SAF \times BW}{\left[(AF_G \times SIR) + (AF_D \times \{SA_H DL_H + SA_O DL_O\} EF)\right] \times ET} + BSC$$

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 (kg/d) = 0.00008
AF_G = gastrointestinal absorption factor (unitless) = 1
AF_D = dermal absorption factor (unitless) = 0.2
SA_H = surface area of hands (m^2) = 430
SA_O = surface area of other exposed body surfaces (m^2) = 2580
DL_H = dermal loading of soil to hands (kg/m^2-event) = $1x10^{-7}$
DL_O = dermal loading of soil to other skin surfaces (mg/m2-event) = $1x10^{-8}$
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)
= 437 899 mg/kg

Indoor Infiltration and Inhalation Pathway:

$$D_T^{eff} \approx D_a \left(\frac{\theta_a^{10/3}}{n^2} \right)$$

D_a = pure component molecular diffusivity in air (cm^2/s) = 0.05
θ_a = air-filled porosity (unitless) = 0.241
n = total soil porosity (unitless) = 0.36

D_T^{eff} = overall effective porous media diffusion coefficient (cm^2/s) = 0.00336

$$D^{crack} \approx D_a \left(\frac{\theta_{a\_c}^{10/3}}{n_c^2} \right)$$

D_{a_c} = pure component molecular diffusivity in air (cm^2/s) = 0.05
θ_a = air-filled porosity of soil-filled foundation crack (unitless) = 0.36
n_C = total soil porosity in foundation crack (unitless) = 0.36

D^{crack} = effective diffusion coefficient through foundation crack (cm^2/s) = 0.0128

$$Q_B = L_B W_B H_B (ACH) \big/ \left(3600\ s/h\right)$$

L_B = building length (cm) = 1225
W_B = building width (cm) = 1225
H_B = building height, including basement (cm) = 360
ACH = air exchanges per hour (h^{-1}) = 0.5

Q_B = building ventilation rate (cm^3/s) = 7.50×10^4

$$Q_{soil} = \frac{2\pi\ \Delta P\ k_v\ X_{crack}}{\mu \ln\left[\frac{2\left(Z_{crack}\right)}{r_{crack}}\right]}$$

ΔP = pressure differential ($g/cm \cdot s^2$) = 40
k_v = soil vapour permeability to vapour flow (cm^2) = 5×10^{-8}
X_{crack} = length of idealized cylinder (cm) = 4900
μ = vapour viscosity ($g/cm \cdot s$) = 0.000173
Z_{crack} = distance below grade to idealized cylinder (cm) = 244
r_{crack} = radius of idealized cylinder (cm) = 0.203

Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s) = 45.7

$$\alpha = \frac{\left(\frac{D_T^{eff} A_B}{Q_B L_T}\right) \exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right)}{\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right) + \left(\frac{D_T^{eff} A_B}{Q_B L_T}\right) + \left(\frac{D_T^{eff} A_B}{Q_{soil} L_T}\right)\left[\exp\left(\frac{Q_{soil} L_{crack}}{D^{crack} A_{crack}}\right) - 1\right]}$$

D_T^{eff} = effective porous media diffusion coefficient (cm^2/s) = 0.00336
A_B = building area exposed to soil, including basement wall area (cm^2)
Q_B = building ventilation rate (cm^3/s) = 0.0128
L_T = distance from contaminant source to foundation (cm) = 30
Q_{soil} = volumetric flow rate of soil gas into the building (cm^3/s) = 45.7
L_{crack} = thickness of the foundation (cm) = 11.25
D^{crack} = effective vapour-pressure diffusion coefficient through the crack (cm^2/s) = 7.50×10^{4}
A_{crack} = area of cracks through which contaminant vapours enter the building (cm^2) = 994.5

α = attenuation coefficient = 0.000695

$$DF_i = \frac{1}{\alpha}$$

DF_i = dilution factor from soil gas concentration to indoor air concentration (unitless) = 1439

$$SQG_I = [(RfC - C_a)\{\theta_w + (K_{OC})(f_{OC})(\rho_b) + (H')(\theta_a)\}(SAF)(AF)(DFi)(10^3 g/kg)]/[(H')(\rho_b)(ET)(10^6 cm^3/m^3)] + BSC$$

RfC = reference air concentration (mg/m^3) = 18.4
C_a = background indoor/outdoor air concentration (mg/m^3) = 0.02334
SAF = Soil Allocation Factor (unitless) = 0.5
AF = Adjustment Factor (unitless) = 10
θ_w = moisture-filled porosity (unitless) = 0.119
θ_a = vapour-filled porosity (unitless) = 0.241
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' = unitless Henry's Law Constant = H/RT = 50
H = Henry's Law Constant (atm-m^2/mol) = 1.2
R = gas constant (8.2×10^{-5} atm-m^2/mol-^{O}K)

T = absolute temperature (K) = 294
DF_i = dilution factor from soil gas to indoor air (unitless) = 1439
ET = exposure term (unitless) = 1
BSC = background soil concentration (mg/kg) = 0

SQG_I = soil quality guideline by indoor infiltration for volatile PHCs using RfC (mg/kg) = 93.9

Protection of Groundwater (Potable Groundwater, Aquatic Life and Livestock Watering)

Lateral Groundwater Transport (DF4)

$$C_w(x,y,z,t) = \left(\frac{C_{gw}}{2}\right)\exp\left\{\left(\frac{x}{2\partial_x}\right)\left[1-\left(1+\frac{4L_s\partial_x}{v}\right)^{1/2}\right]\right\}\left\{erf\left[\frac{(y+Y/2)}{2(\partial_y x)^{1/2}}\right]-erf\left[\frac{y-Y/2}{2(\partial_y x)^{1/2}}\right]\right\}$$

$$v=\frac{K_H i}{n_e R_f};\quad R_f=1+\frac{\rho_b}{n}K_d$$

C_w = allowable chemical concentration in water at receptor (mg/L)
(i.e. aquatic life guideline, livestock watering RfC); for potable water pathway, calculated as (TDI – EDI)(BW)/IR_W
aquatic life: 0.0465 mg/L
livestock watering: 53 mg/L
potable water: (5-0.02334)*70.7/1.5 = 139 mg/L
x = distance from source to receptor (m) = 10 for aquatic life, 0 for others
x,y,z = Cartesian coordinates relating source and receptor (m); y, z assumed to be 0
∂_x = longitudinal dispersivity tensor = 0.1x = 1 (aquatic life only)
∂_y = lateral dispersivity tensor = 0.1∂_x = 0.1 (aquatic life only)
d = depth from surface to groundwater surface (m) = 3
$t_{1/2S}$ = biodegradation half-life (y) = 712/365 = 1.95
L_s = decay constant (y^{-1}) in saturated zone = 0.00158

$$L_s=\frac{0.6931}{t_{1/2US}}\left(e^{-0.07d}\right)$$

K_H = hydraulic conductivity in the saturated zone (m/y) = 320
i = hydraulic gradient (unitless) = 0.028
n = total porosity of soil = 1 - ρ_b/2.65 (unitless) = 0.36
n_e = effective soil porosity (unitless) = total porosity = 0.36
Y = source width (m) perpendicular to groundwater flow = 10
R_f = retardation factor (unitless) = 95
ρ_b = soil bulk density in saturated zone (g/cm^3) = 1.7
K_d = distribution coefficient (cm^3/g) = K_{oc}xf_{oc} = $10^{3.6}$x0.005 = 19.9

v = velocity of contaminant (m/y) = 0.262

C_{gw} = allowable chemical concentration in groundwater at the source (mg/L)
aquatic life: 34.7 mg/L
livestock watering: $C_{gw} = C_w = 53$ mg/L
potable water: $C_{gw} = C_w = = 139$ mg/L

Mixing and Dilution at the Water Table (DF3)

$$C_z = C_{gw}\left\{1+\left(\frac{Z_d K_H i}{IX}\right)\right\}$$

K_H = hydraulic conductivity in the saturated zone (m/y) = 320
i = hydraulic gradient (unitless) = 0.028
I = infiltration rate (m/y) = precipitation minus runoff and evapotranspiration = 0.28
X = length of source parallel to groundwater flow (m) = 10

Calculation of average thickness of mixing zone:

$Z_d = r + s$; Z_d cannot exceed d_a

r = mixing depth available due to dispersion and diffusion (m)
= 0.01 X = 0.1
s = mixing depth available due to infiltration rate and groundwater flow rate (m) = 0.64 (calculated below)

$$s = d_a\left\{1-e^{-\frac{2.178XI}{K_H i d_a}}\right\}$$

d_a = depth of unconfined aquifer (m) = 5
Z_d = average thickness of mixing zone (m) = 0.74

C_z = allowable chemical concentration in leachate at the water table (mg/L) = C_{gw} x 3.36
aquatic life = 117 mg/L
livestock watering = 178 mg/L
potable water = 467 mg/L

Unsaturated Zone Transport (DF2)

At Tier 1, $C_L = C_z$

C_L = allowable leachate concentration at source (mg/L)

Soil/Leachate Partitioning (DF1)

Partitioning of the contaminant to leachate is evaluated using the standard three-phase equilibrium partitioning model as detailed in Appendix A of CCME (2006a).

$$SQG_{GW} = C_L \left\{ K_d + \left(\frac{\theta_w + H'\theta_a}{\rho_b} \right) \right\}$$

C_L	=	allowable leachate concentration at source (mg/L) aquatic life = 117 mg/L livestock watering = 178 mg/L potable water = 467 mg/L
K_d	=	distribution coefficient (cm^3/g) = K_{oc} x f_{oc} = 19.9
θ_w	=	water filled porosity (unitless) = 0.119
H'	=	dimensionless Henry's Law constant = H/RT = 50
H	=	Henry's Law constant (atm-m^3/mol) = 1.2
R	=	gas constant (8.2 x 10^{-5} atm-m^2/mol-^{O}K)
T	=	absolute temperature (K) = 294
θ_a	=	air-filled porosity (unitless) = 0.241
ρ_b	=	soil bulk density in contaminant partitioning zone (g/cm^3) = 1.7
SQG_{GW}	=	soil quality guideline for the protection of groundwater (mg/kg)
	=	27.17 x C_L aquatic life = 3170 mg/L livestock watering = 4830 mg/L potable water = 12500 mg/L

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:

$SQG_{sub\text{-}fraction\ C>6\ to\ C8\ aliphatics}$ = 437 899 mg/kg
(as shown in calculations above)

$SQG_{sub\text{-}fraction\ C>8\ to\ C10\ aliphatics}$ = 7 893 mg/kg

$SQG_{sub\text{-}fraction\ C>8\ to\ C10\ aromatics}$ = 2 694 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 / { [0.55/437899] + [0.36/7893] + [0.09/2694]}

= 12 500 mg/kg

Offsite Migration Check (F3, coarse soils, residential)

$SQG_{OM} = 14.3 \times SQG_A - 13.3 \times BSC$

where:

SQG_A	= governing Tier 1 level for agricultural land use (mg/kg) = 300
BSC	= background soil concentration (mg/kg) = 0
SQG_{OM}	= soil quality guideline for offsite migration (mg/kg) = 4300

APPENDIX D: BACKGROUND INFORMATION – ECOTOXICOLOGICAL DATA AND ANALYSIS USED IN THE 2001 PHC CWS

D.1 Introduction

Significant effort was expended in the collection and analysis of ecotoxicological data to develop the direct contact ecological soil quality guidelines that were included in the 2001 PHC CWS. The current document used these calculations as a starting point, but incorporated new data from several studies and used updated CCME protocols to develop the current PHC CWS soil quality guidelines for this exposure pathway, as described in the main text and Appendixes E and F of this document. The methodology and data used to derive the ecological direct soil contact guideline have diverged from the 2001 PHC CWS, but key elements relevant to the development of the ecological direct soil contact guidelines from the previous scientific rational document are preserved here as background information.

Section D.2 of this appendix reproduces the relevant part of the main text of the 2001 PHC CWS scientific rationale document. Section D.3 reproduces Appendix D from the 2001 PHC CWS scientific rationale document, and provides some of the deliberations that were held within EcoTAG – the ecological technical advisory group - that went into the development of the ecological direct contact guideline values. Section D.4 reproduces Appendix E from the 2001 PHC CWS scientific rationale document, and tabulates all the ecotoxicological data that were generated for that project. Section D.5 reproduces Appendix F from the 2001 PHC CWS scientific rationale document, and provides a tabulated comparison of the toxicity of the individual PHC fractions relative to the toxicity of whole crude oil.

D.2 Derivation of the 2001 PHC CWS Ecological Soil Contact Guidelines (From 2001 PHC CWS Main Text)

D.2.1 Methods

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 D.1.

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 D.1) 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.

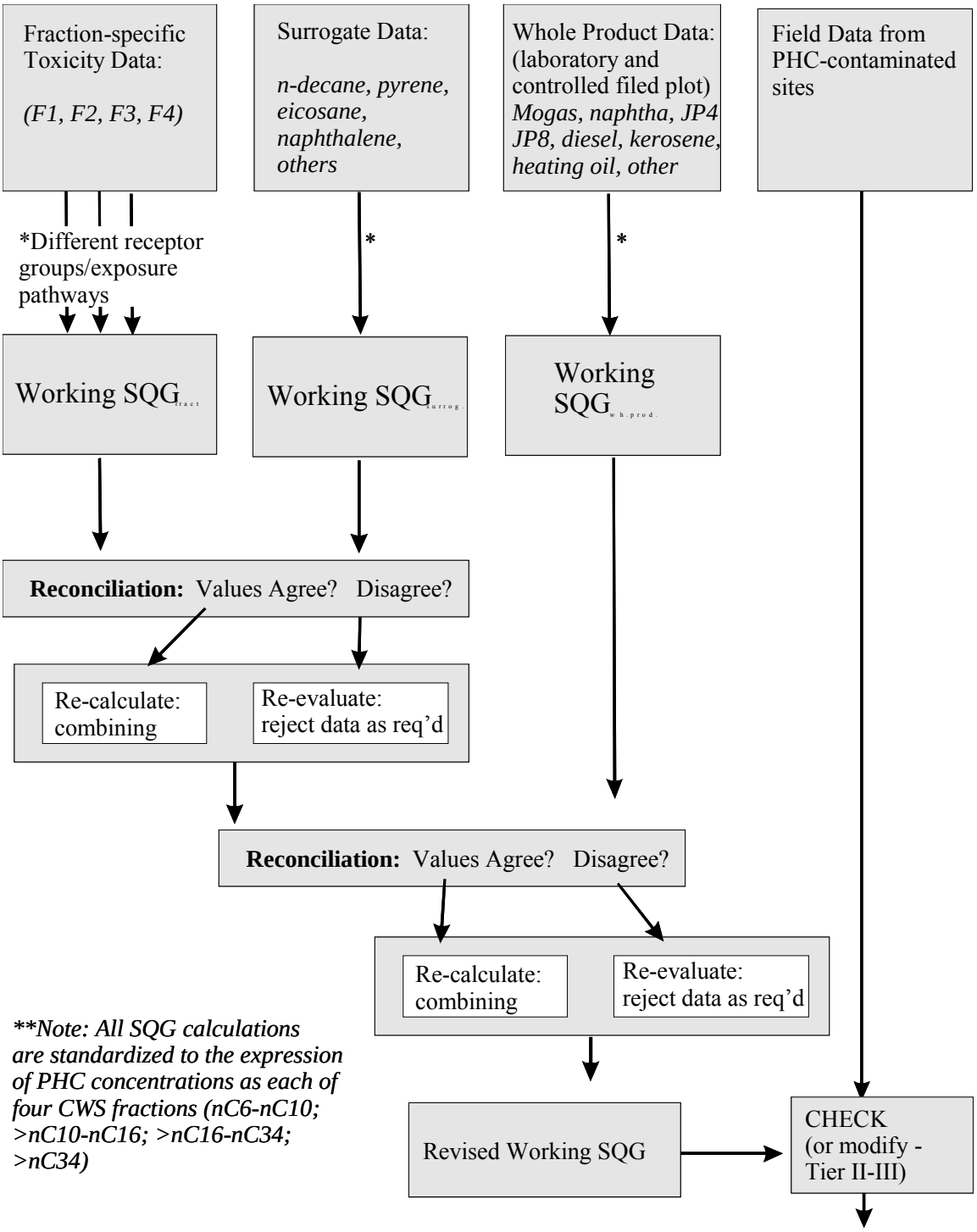


Figure D.1: Summary of framework used for reconciling disparate data types when developing PHC Soil Quality Tier levels.

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 BC 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.

D.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;
- Separate analyses 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 25^{th}, 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)[2];
- 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

[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.

[2] 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.

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 25^{th} percentile 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.

D.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 D.2.9, and illustrated in Figures D.16 and D.17. 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 D.2.4 through D.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).

D.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 D1 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 D.1: 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
barley	EC20	shoot length	39400	as above	4	as above		as above

[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	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
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

Organism	Endpoint	Parameter[1]	Value (mg/kg nominal)	# conc. in test series	# Reps. for ea. conc.	Soil	pH	Comment
northern wheat grass	EC50	shoot length	42100	7 (0, 15, 30, 50, 60, 70, 80 mg/g)	4	as above		8 day test. n = 5
northern wheat grass	EC50	root length	51100	as above	4	as above		as above
northern wheat grass	EC20	root length	20400	as above	4	as above		as above
northern wheat grass	EC50	whole ww	26700	as above	4	as above		as above
northern wheat grass	EC20	whole ww	13700	as above	4	as above		as above
northern wheat grass	EC50	whole dw	24800	as above	4	as above		as above
northern wheat grass	EC20	whole dw	12100	as above	4	as above		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		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		as above
northern wheat grass	EC50	root length	7300	as above	3-6	as above		as above
northern wheat grass	EC20	root length	4300	as above	3-6	as above		as above
northern wheat grass	EC50	shoot ww	610	as above	3-6	as above		as above
northern wheat grass	EC20	shoot ww	13	as above	3-6	as above		as above
northern wheat grass	EC50	shoot dw	1400	as above	3-6	as above		as above
northern wheat grass	EC20	shoot dw	50	as above	3-6	as above		as above
northern wheat grass	EC50	root ww	890	as above	3-6	as above		as above
northern wheat grass	EC20	root ww	180	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
northern wheat grass	EC50	root dw	1100	as above	3-6	as above		as above
northern wheat grass	EC20	root dw	210	as above	3-6	as above		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		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		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		as above
springtail (*O.folsomi*)	EC50	# juvenile	1490	as above	10	as above		as above
springtail (*O.folsomi*)	EC20	# juvenile	910	as above	10	as above		as above
springtail (*O.folsomi*)	EC50	adult fecundity	1410	as above	10	as above		as above
springtail (*O.folsomi*)	EC20	adult fecundity	620	as above	10	as above		as above
springtail (*O.folsomi*)	NOEC	adult mortality	3000	as above	10	as above		as above
springtail (*O.folsomi*)	LOEC	adult mortality	4000	as above	10	as above		as above
springtail (*O.folsomi*)	NOEC	# juvenile	1000	as above	10	as above		as above
springtail (*O.folsomi*)	LOEC	# juvenile	2000	as above	10	as above		as above
springtail (*O.folsomi*)	NOEC	adult fecundity	1000	as above	10	as above		as above
springtail (*O.folsomi*)	LOEC	adult fecundity	2000	as above	10	as above		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		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		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		as above
worm (*E. foetida*)	EC50	juvenile ww	854	as above	10	as above		as above
worm (*E. foetida*)	EC20	juvenile ww	272	as above	10	as above		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 dw	809	as above	10	as above		as above
worm (*E. foetida*)	EC20	juvenile dw	213	as above	10	as above		as above
worm (*E. foetida*)	NOEC	# juveniles	0	as above	10	as above		as above
worm (*E. foetida*)	LOEC	# juveniles	500	as above	10	as above		as above
worm (*E. foetida*)	NOEC	juvenile ww	0	as above	10	as above		as above
worm (*E. foetida*)	LOEC	juvenile ww	500	as above	10	as above		as above
worm (*E. foetida*)	NOEC	juvenile dw	0	as above	10	as above		as above
worm (*E. foetida*)	LOEC	juvenile dw	500	as above	10	as above		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		as above

(from Stephenson *et al*. 2000b)

Figure D.2 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 25th percentile of the ranked data (around 3,000 mg/kg PHCs as F3 in Figure D.2). 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 D.2 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 D.2 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 D.3 shows the data distribution, and corresponding 25th 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 25th 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 D1). 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 D.3, 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 D.2 (approx. 3,000 mg/kg). The data also approximate a bimodal log-normal sensitivity distribution.

Figure D.4 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 D.4. 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 D.4 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 D.5 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 D.5 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 D.4. 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 D.6 and D.7 provide a parallel analysis for the F3 soil invertebrate data set. The entire invertebrate toxicity endpoint data set is shown in Figure D.6. 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 D.7 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 25th percentile nominal concentration of around 800 mg/kg, based on the combined mortality-type and non-lethal endpoints.

Figure D.8 compares the underlying data distributions and 25th 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 D2 provides an excerpt of the data on F3 losses during toxicity testing.

Table D.2: 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.

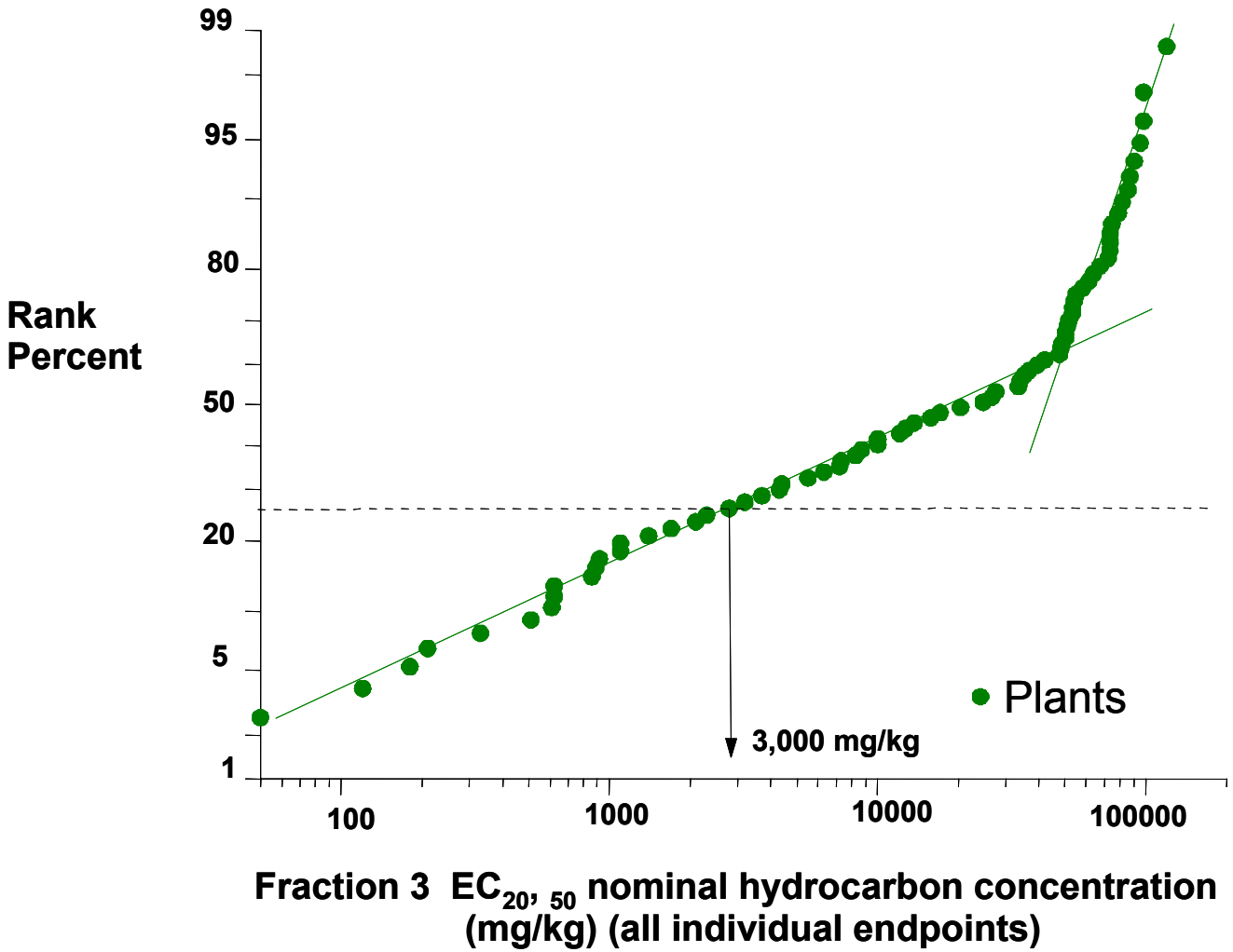


Figure D.2: Distribution of plant toxicological endpoints for studies on F3 PHCs based on all data provided in Table D1.

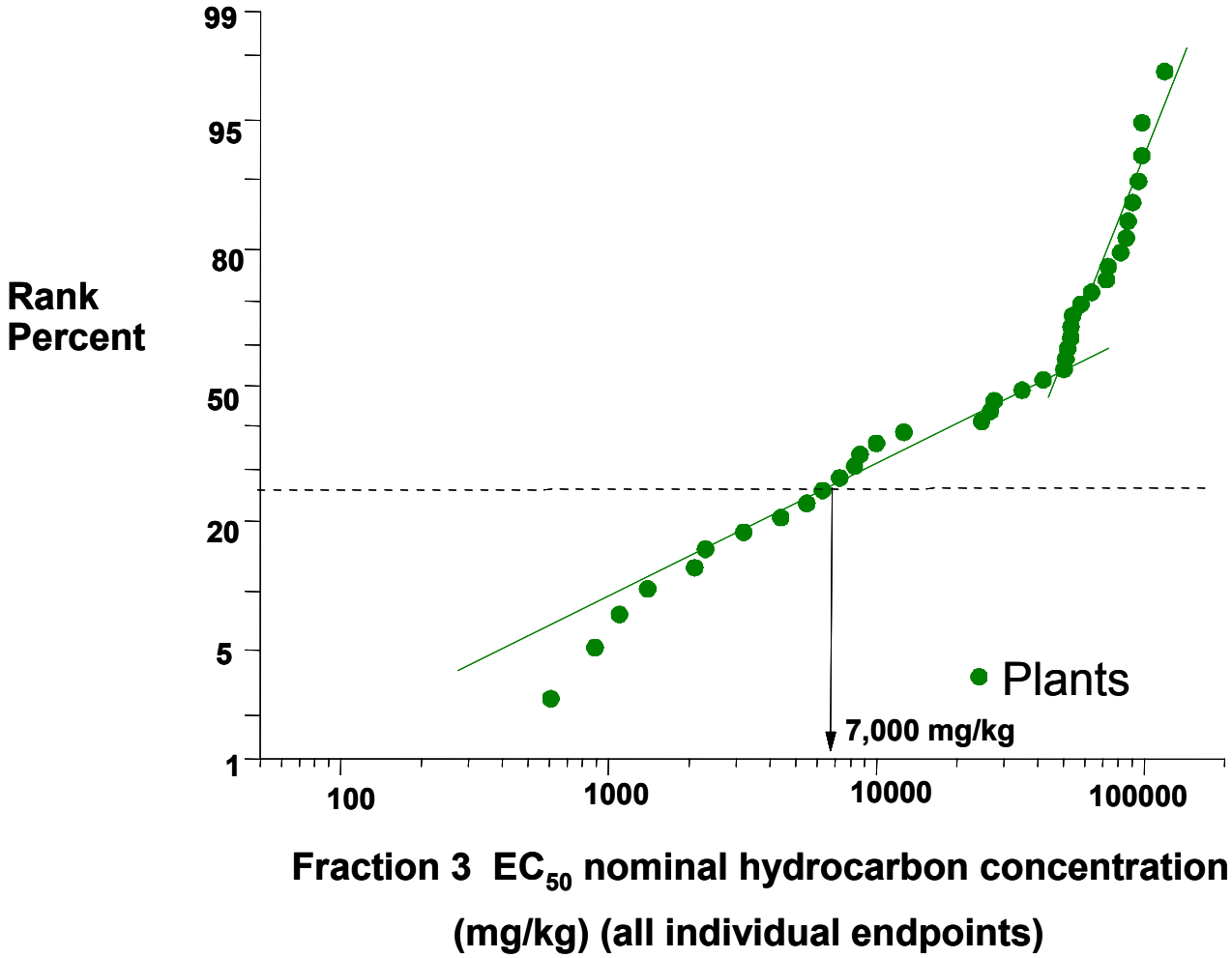


Figure D.3: Distribution of plant toxicological endpoints for studies on F3 PHCs based on EC_{50} data.

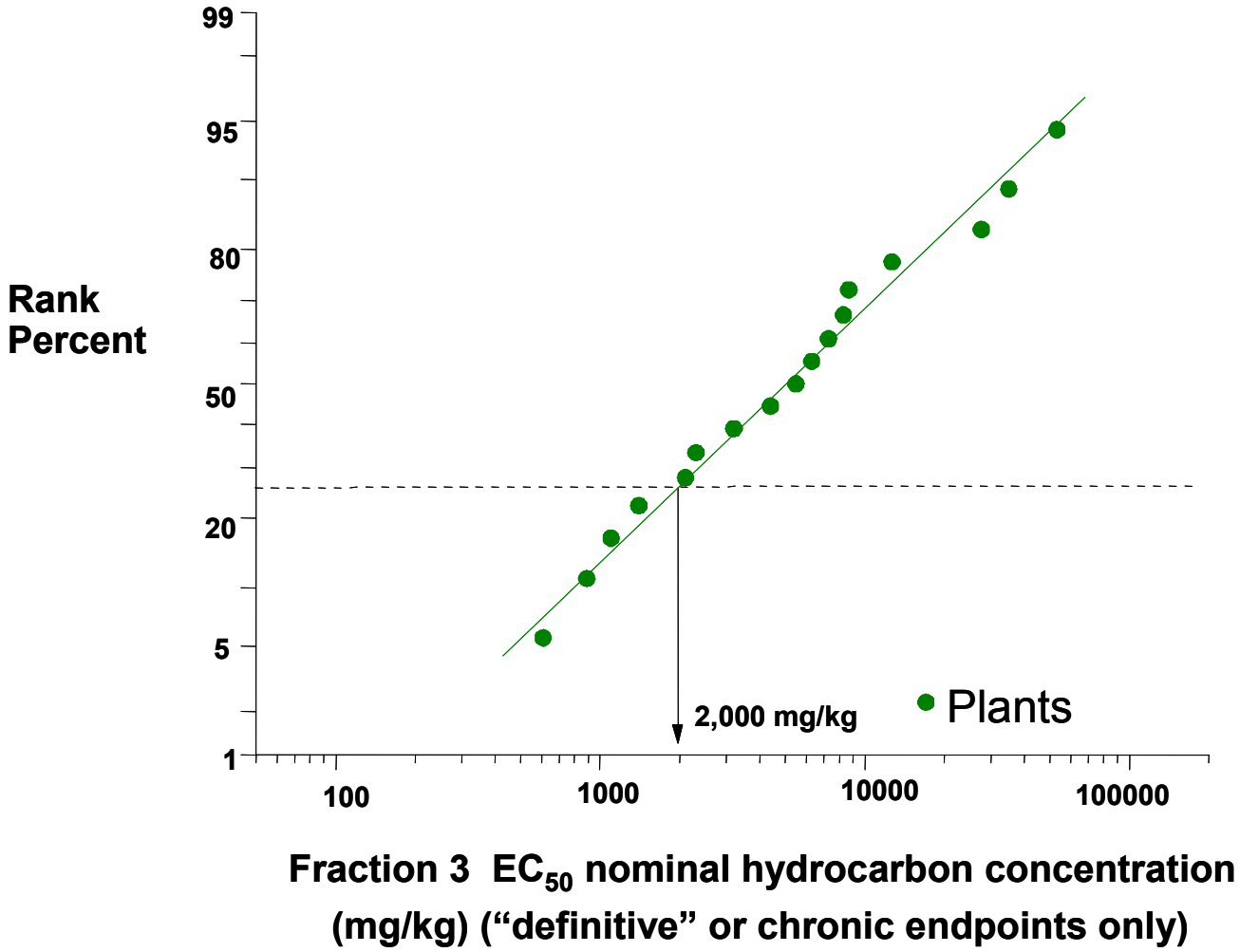


Figure D.4: Distribution of plant toxicological endpoints for studies on F3 PHCs based on EC_{50} data and chronic ("definitive") exposure periods only.

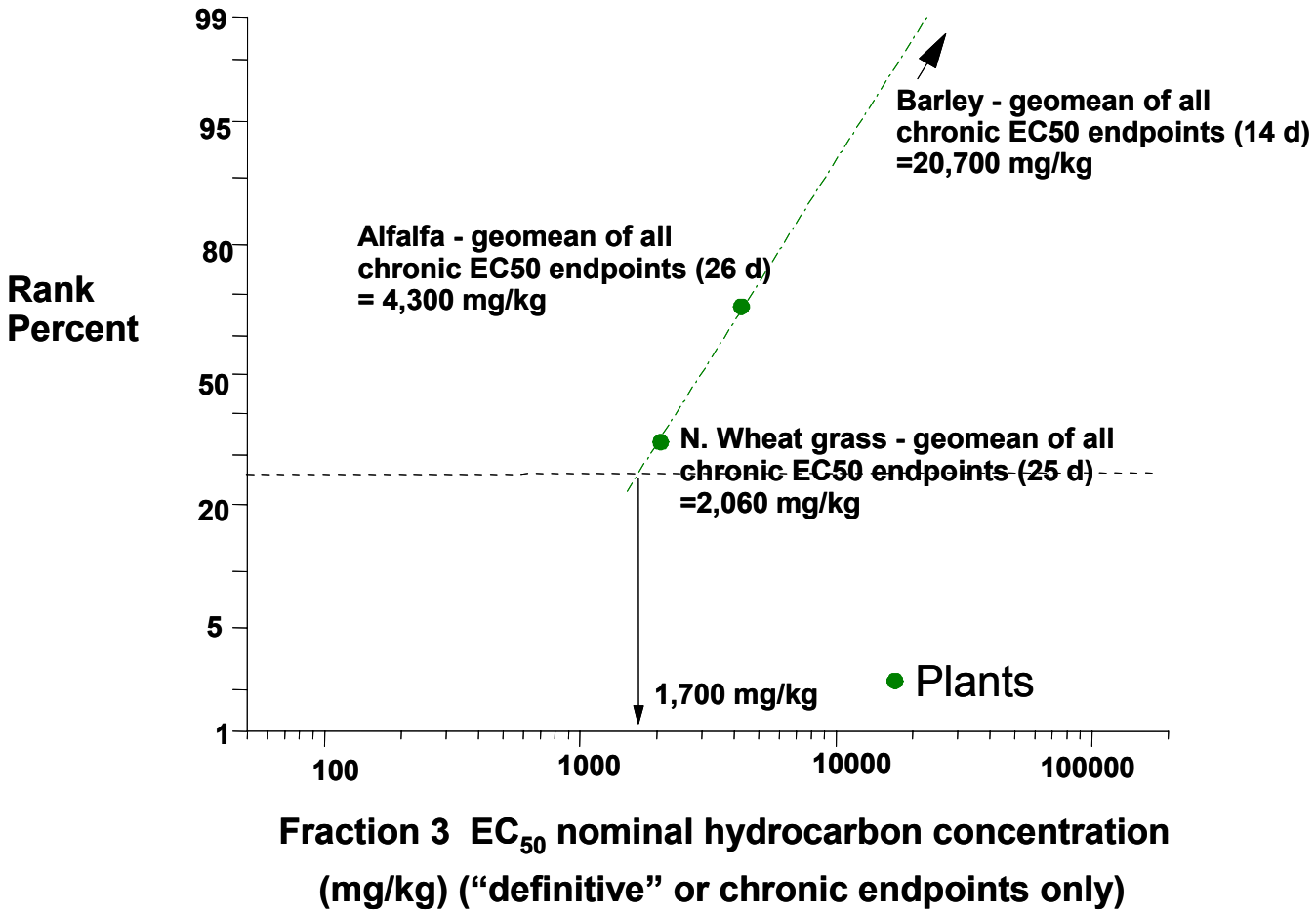


Figure D.5: Distribution of plant toxicological endpoints for studies on F3 PHCs - consolidated EC_{50} estimates for three plant species for chronic ("definitive") exposure periods only.

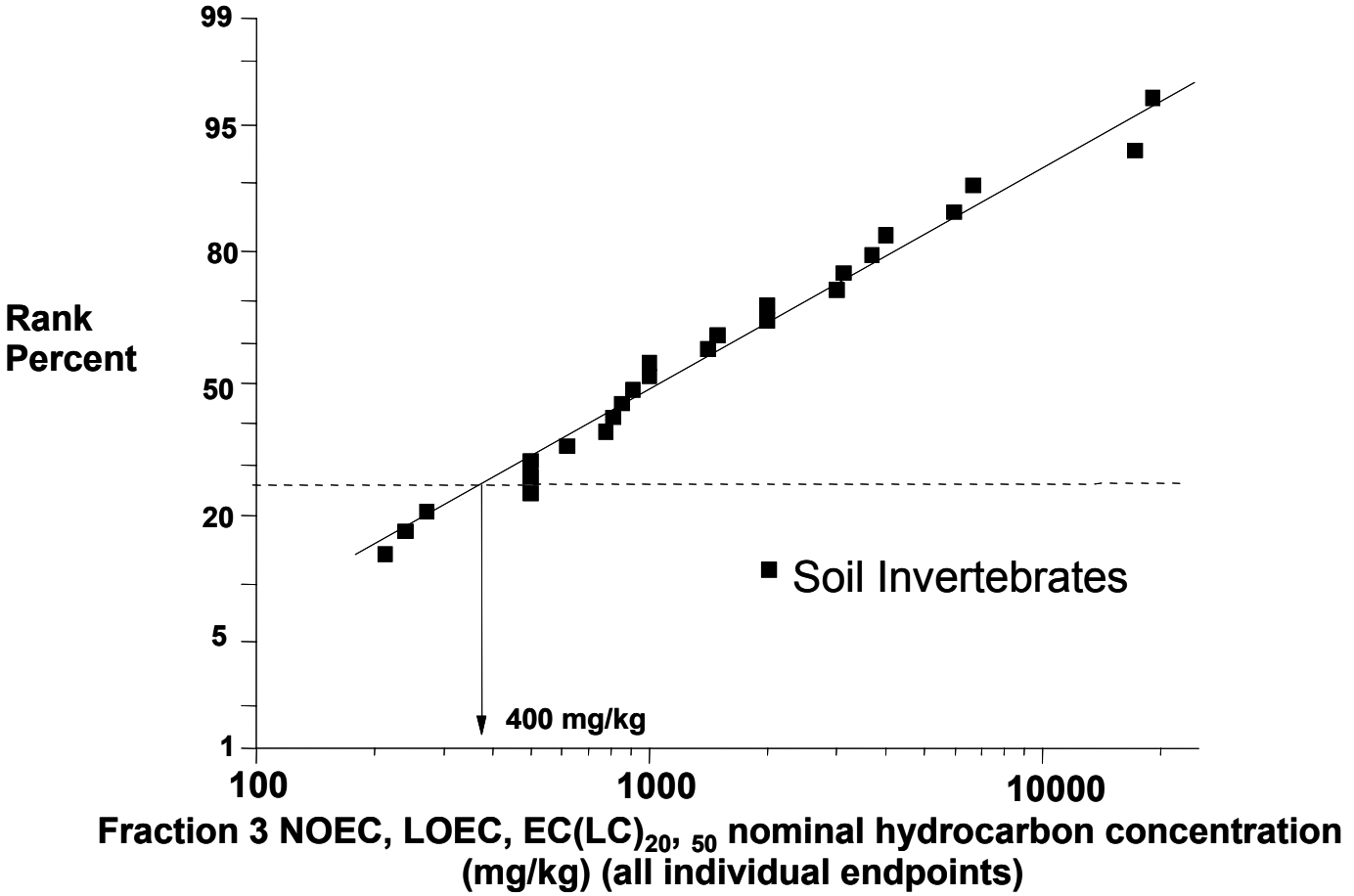


Figure D.6: Distribution of soil invertebrate toxicological endpoints for studies on F3 PHCs based on LOEC, NOEC, $EC(LC)_{20}$ and $EC(LC)_{50}$ data across two different soil types and acute and chronic ("definitive") exposure periods.

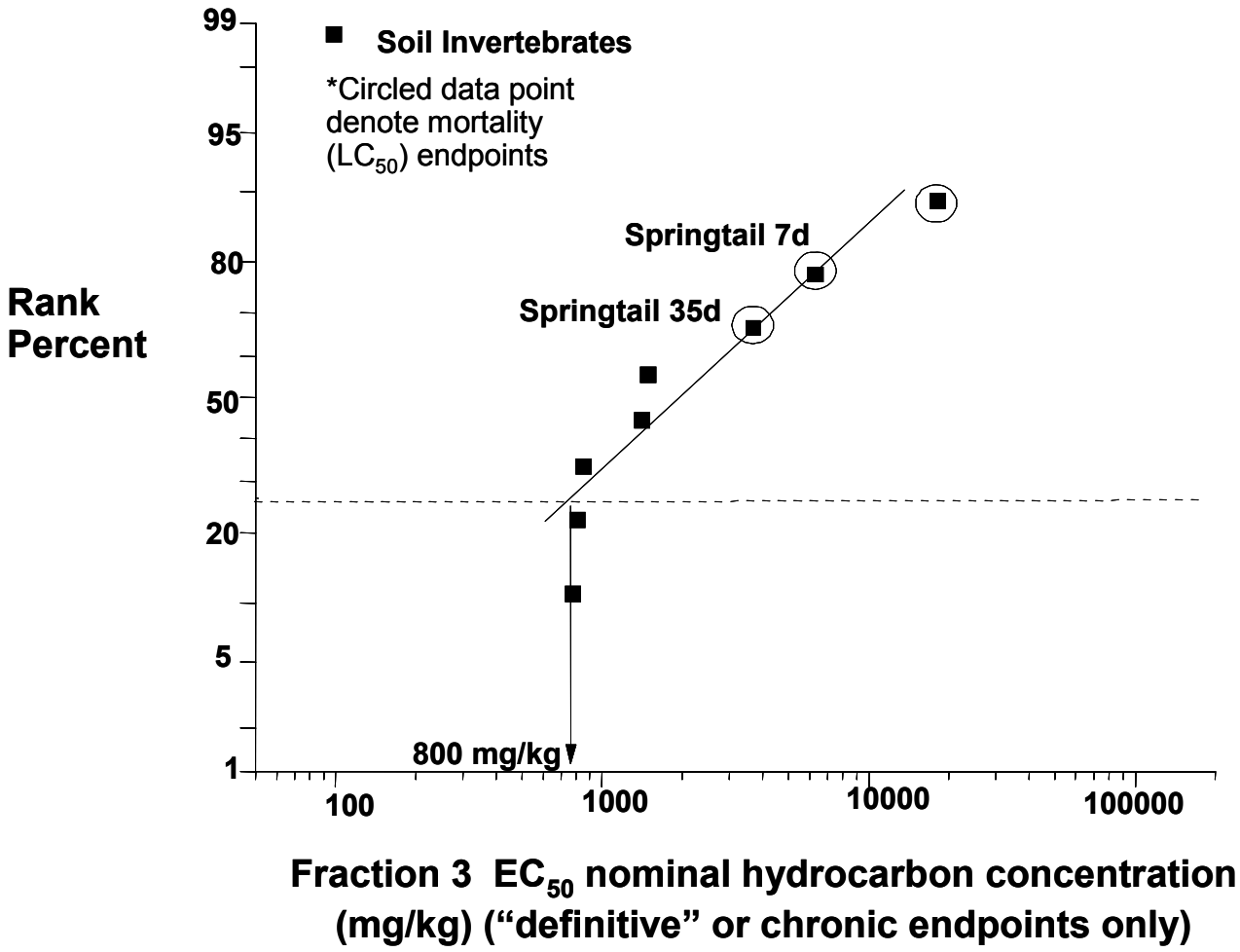


Figure D.7: Distribution of soil invertebrate toxicological endpoints for studies on F3 PHCs based on $EC(LC)_{50}$ and primarily chronic ("definitive") exposure periods.

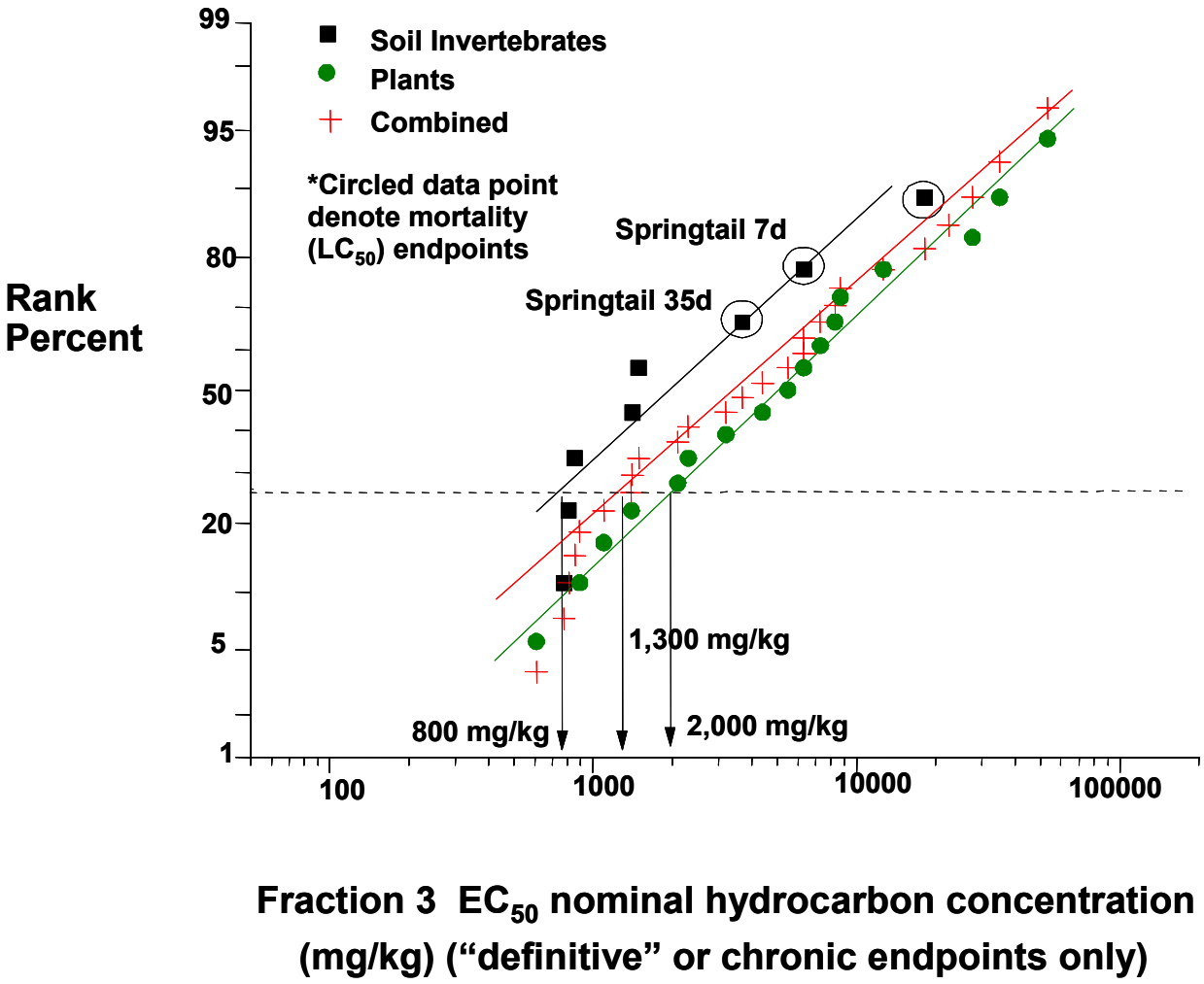


Figure D.8: Comparison of data distributions for soil invertebrate and plant toxicological endpoints for studies on F3 PHCs.

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 D3. The 50th percentile of the $EC(LC)_{50}$ data distribution, as illustrated in Figure D.8 is also shown. This shows the effect of the defined ranks level on the resulting soil concentration.

Table D.3: Threshold effects concentrations for PHC CWS fraction F3.

	Soil Invertebrates Only	Plants Only	Soil Invertebrates and Plants Combined
Est. 25th 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 D2, above)	31%	31%	31%
Est. 25th percentile of effects data based on "initial" realized exposure levels: F3	**250 mg/kg**	**620 mg/kg**	**400 mg/kg**
Est. 50th percentile of effects data based on "nominal" exposure levels: F3	2,000 mg/kg	5,500 mg/kg	4,000 mg/kg
Est. 50th 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 25th percentile of the effects database (EC_{50}s and LC_{50}s) are lower than might have been initially anticipated. Referring back to Table D1, 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

D.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 D.9 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)**.**

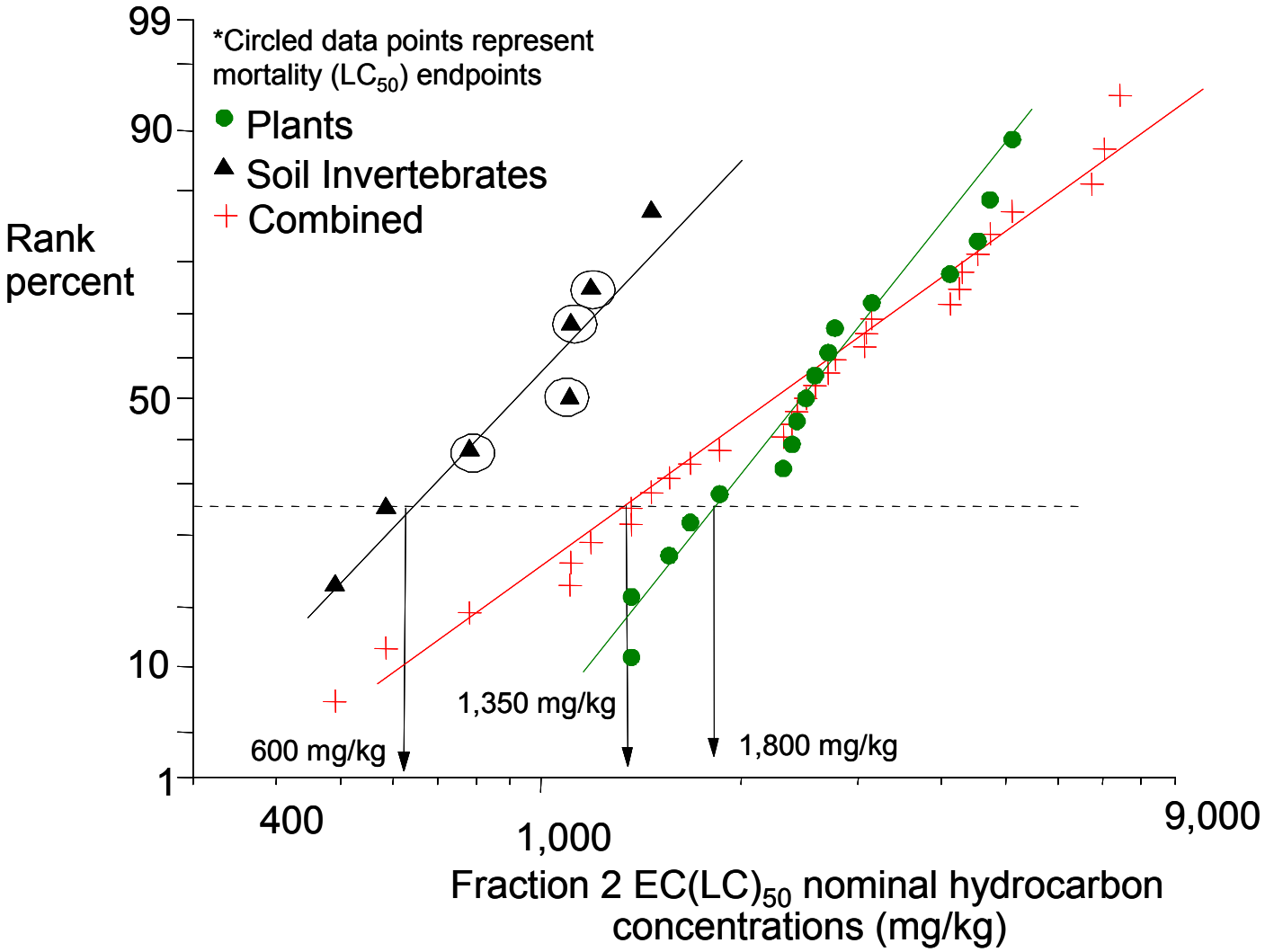


Figure D.9: Comparison of data distributions for soil invertebrate and plant toxicological endpoints for studies on F2 PHCs.

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 D4 provides an excerpt of the F2 losses during toxicity testing:

Table D.4: 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 D5.

Table D.5: 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 D4, 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**

D.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 D.10 illustrates the plant and soil invertebrate $EC(LC)_{50}$ data distributions.

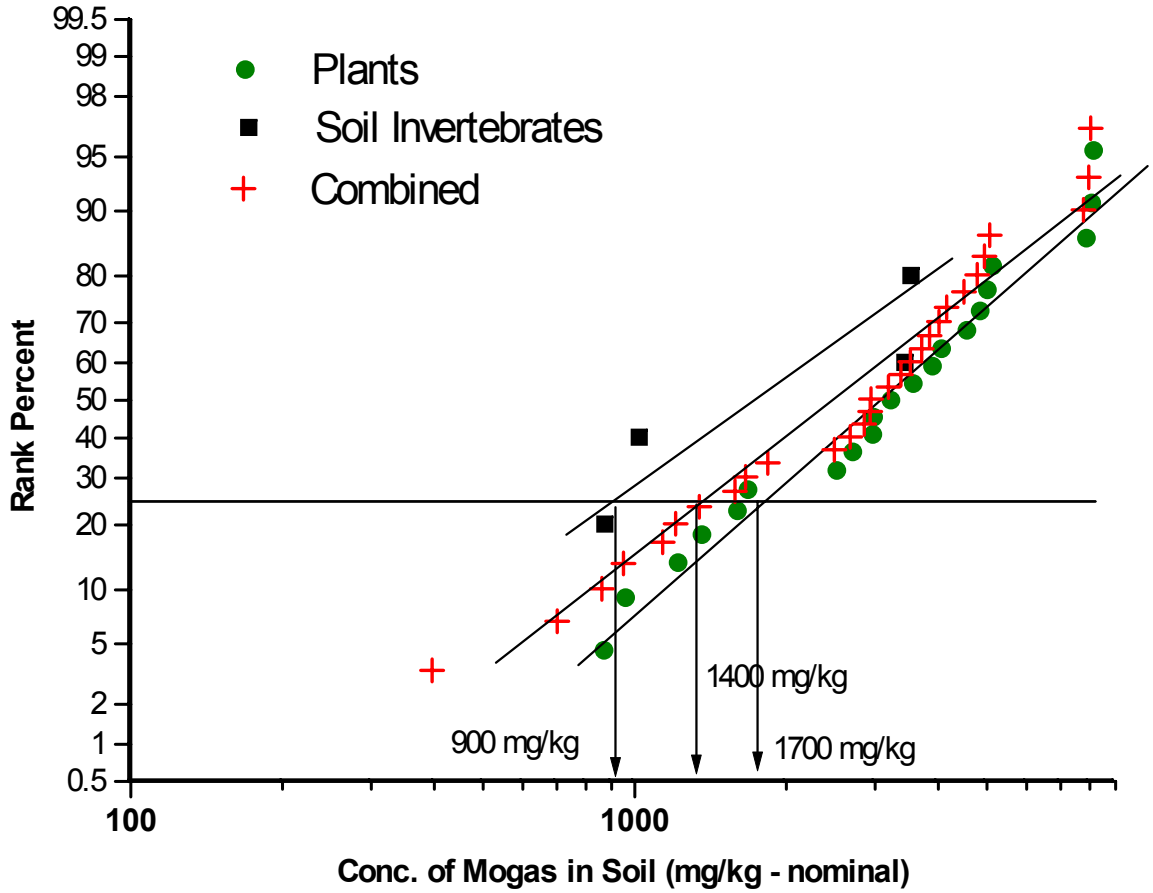


Figure D.10: Comparison of data distributions for soil invertebrate and plant toxicological endpoints for studies on mogas.

Table D6 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 D.6: 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.

Table D.7: 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**

D.2.7 Surrogate PHC Data

D.2.7.1 F4 Surrogate Ecotoxicity.

No surrogates have been identified to the present time for the F4 fraction.

D.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 D8).

Table D.8: 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 scepticism, pending a more detailed analysis of the methodological details.

The toxicological response concentrations for benzo(a)pyrene in Table D8 are much higher in general than for the F3 fraction for soil invertebrates or plants (estimated 25th 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 D.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 x 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.

D.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 D.9: 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 D.11 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 D.11. 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 D5, 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 D.11) 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 D8 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).

D.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 D.12 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.

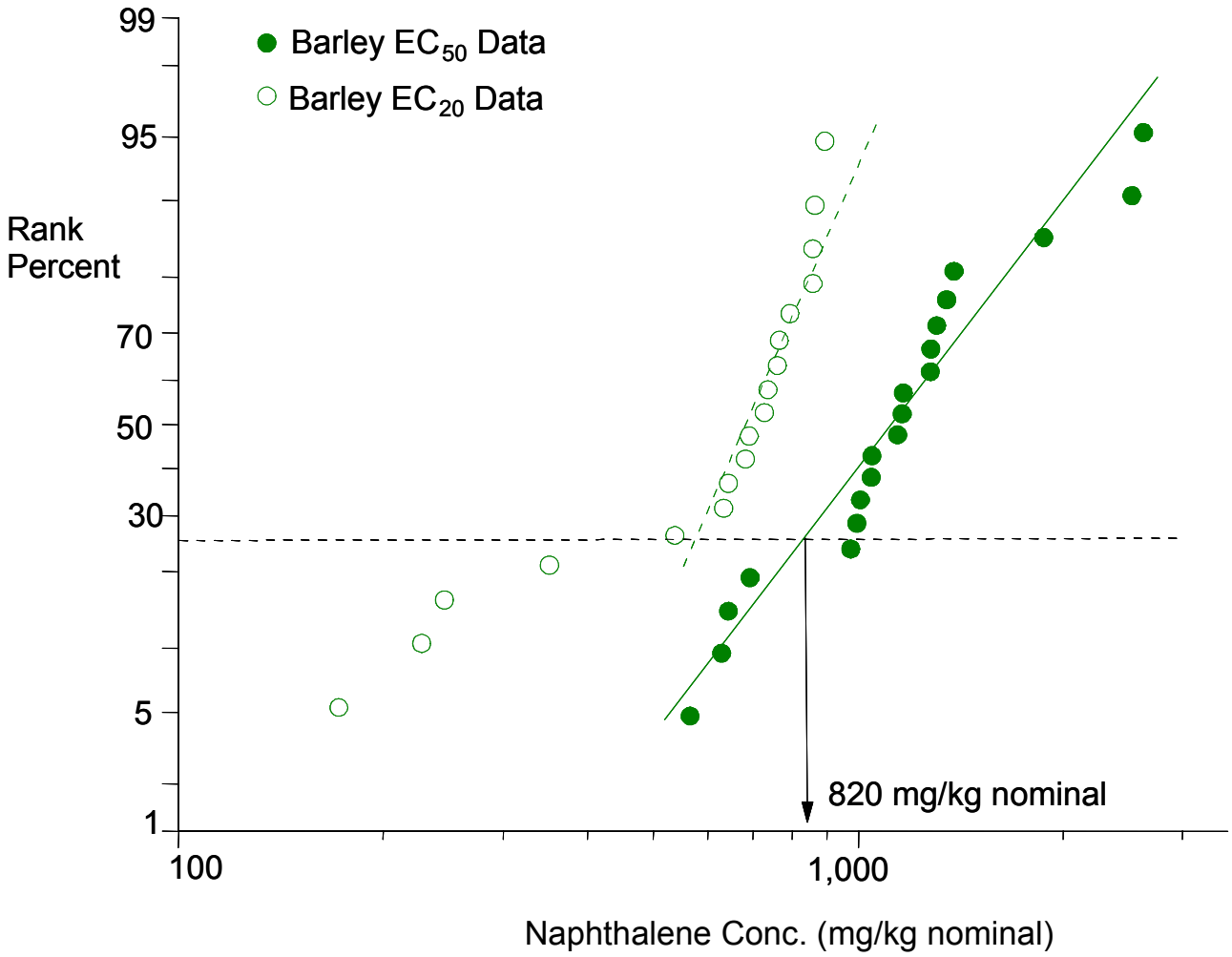


Figure D.11: Distribution of barley ecotoxicological endpoints for studies on naphthalene based on EC_{50} and EC_{20} endpoints from four different laboratories.

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.

D.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 D10.

Table D.10: 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 (?)

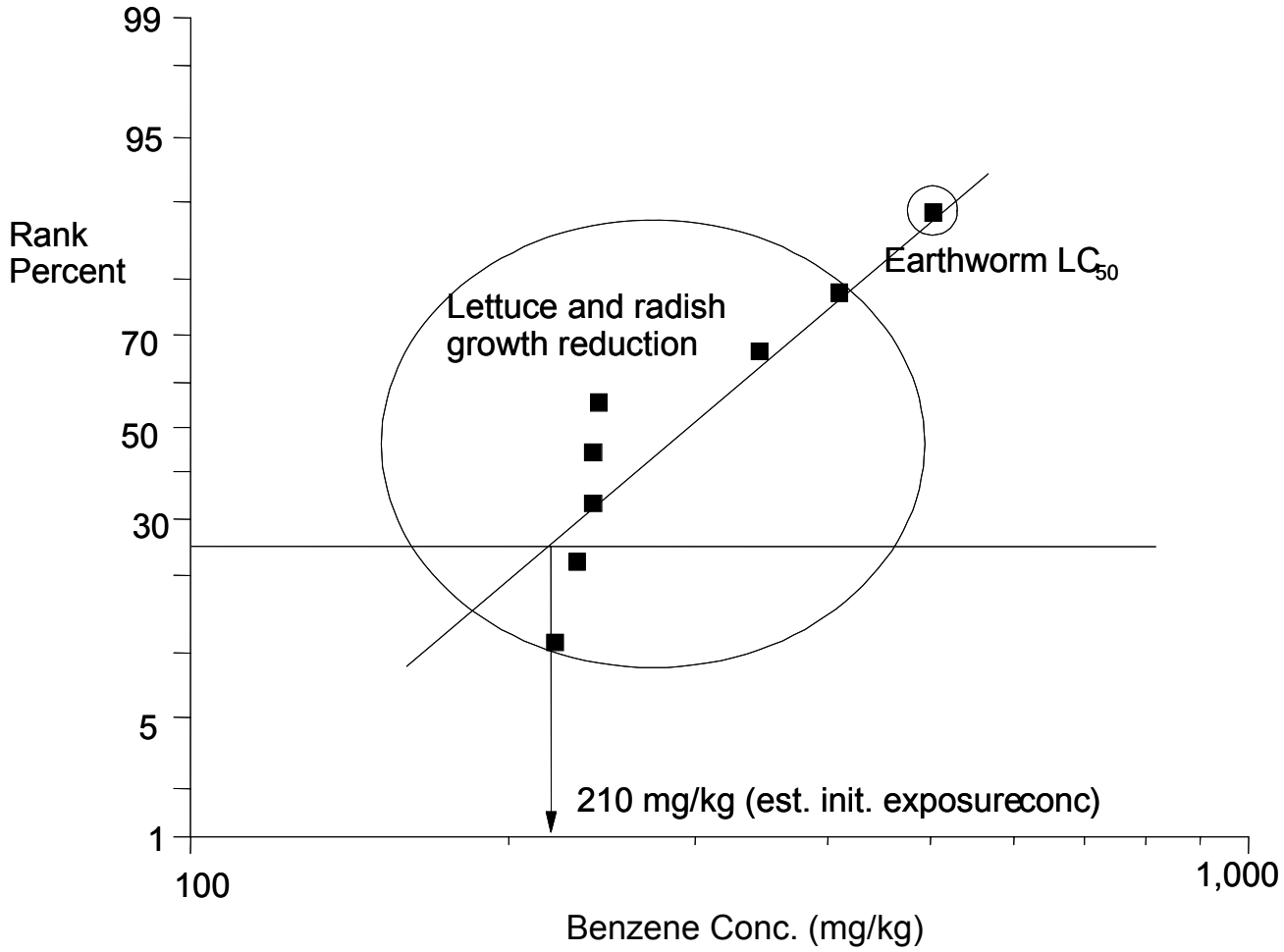


Figure D.12: Distribution of plant and soil invertebrate ecotoxicological endpoints for benzene based on EC_{50} and LC_{50} endpoints.

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 D10). 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.

D.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 D.13 to D.15.

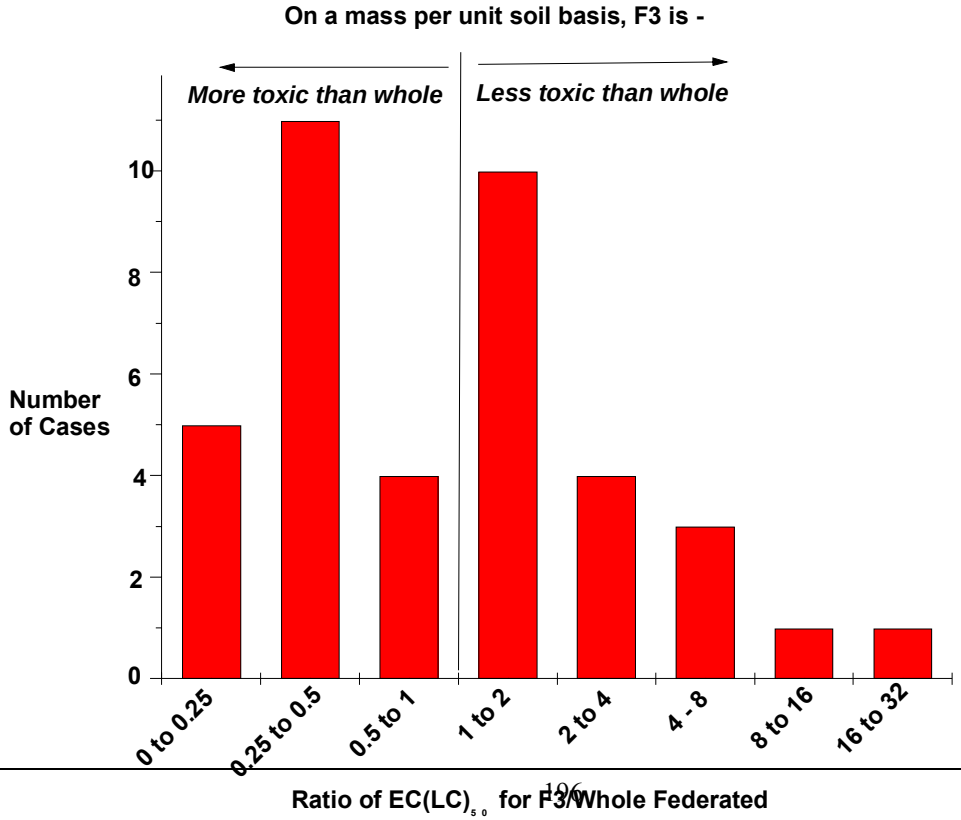


Figure D.13: Frequency histogram of the relative toxicity of F3 to Federated Whole Crude, based on EC(LC)$_{50}$ endpoints.

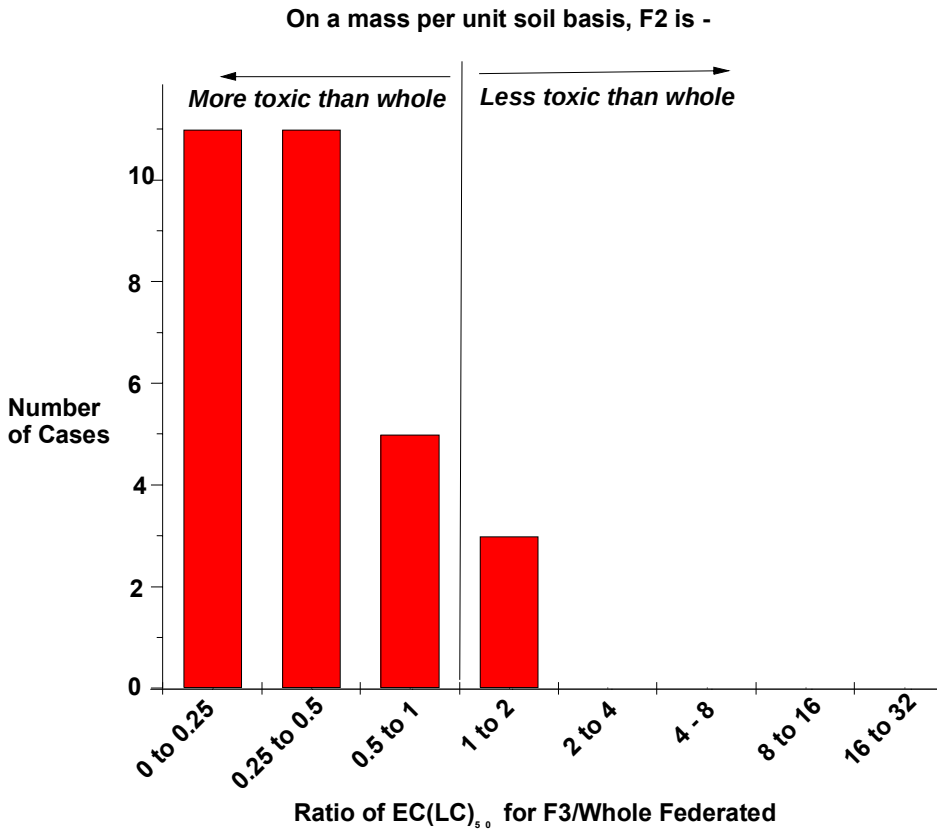


Figure D.14: Frequency histogram of the relative toxicity of F2 to Federated Whole Crude, based on $EC(LC)_{50}$ endpoints.

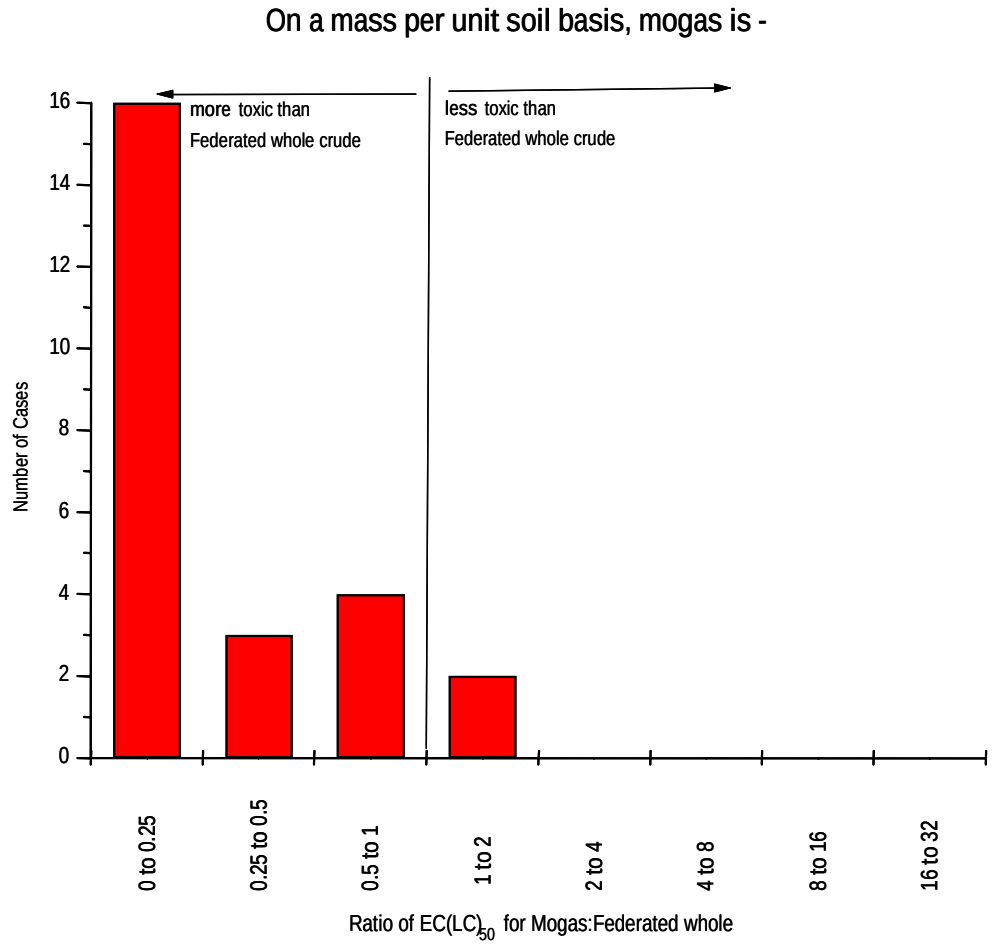


Figure D.15: Frequency histogram of the relative toxicity of Mogas to Federated Whole Crude, based on $EC(LC)_{50}$ endpoints.

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 D.14 and D.15 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 D.16 and D.17 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.

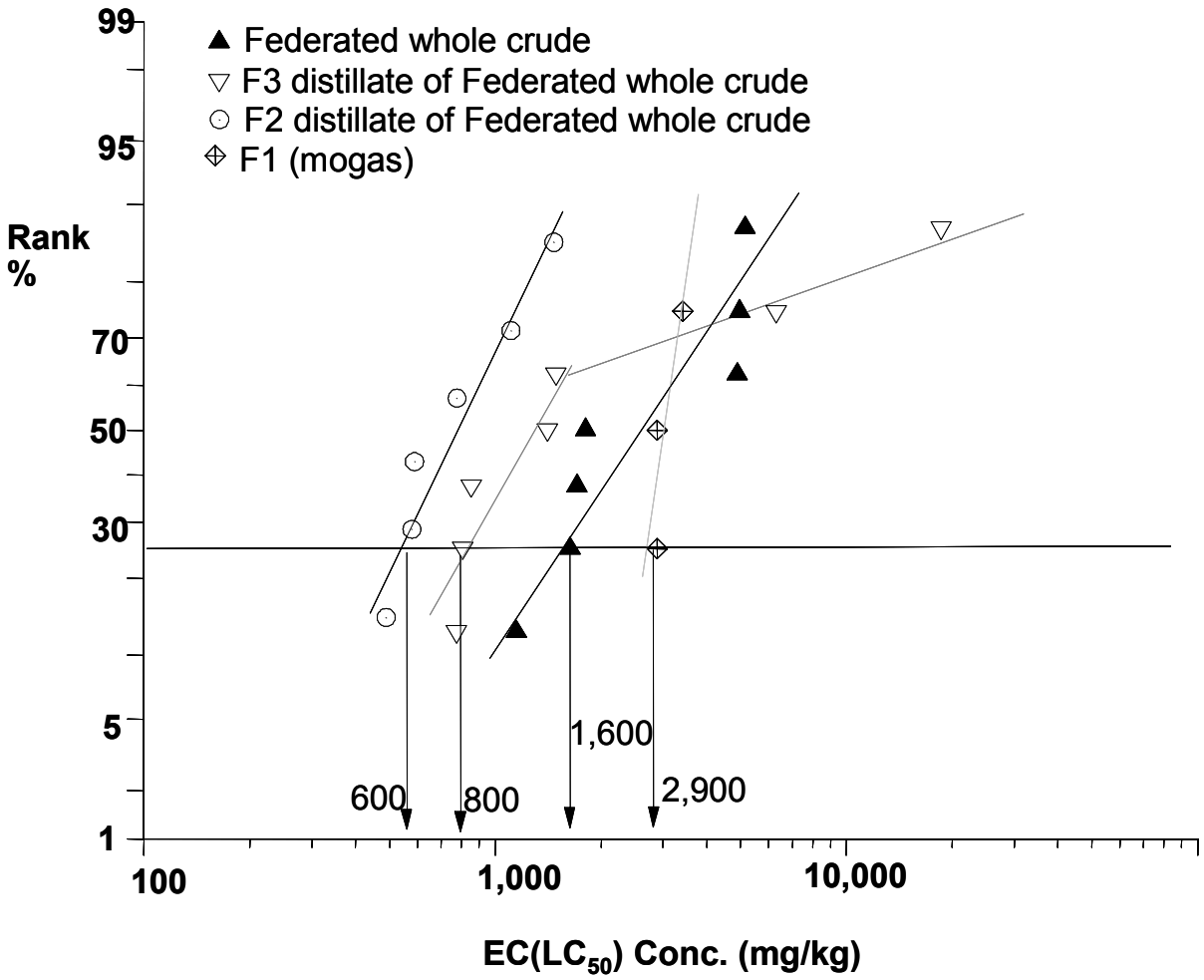


Figure D.16: Comparison of ranked data for soil invertebrate toxicity effects.

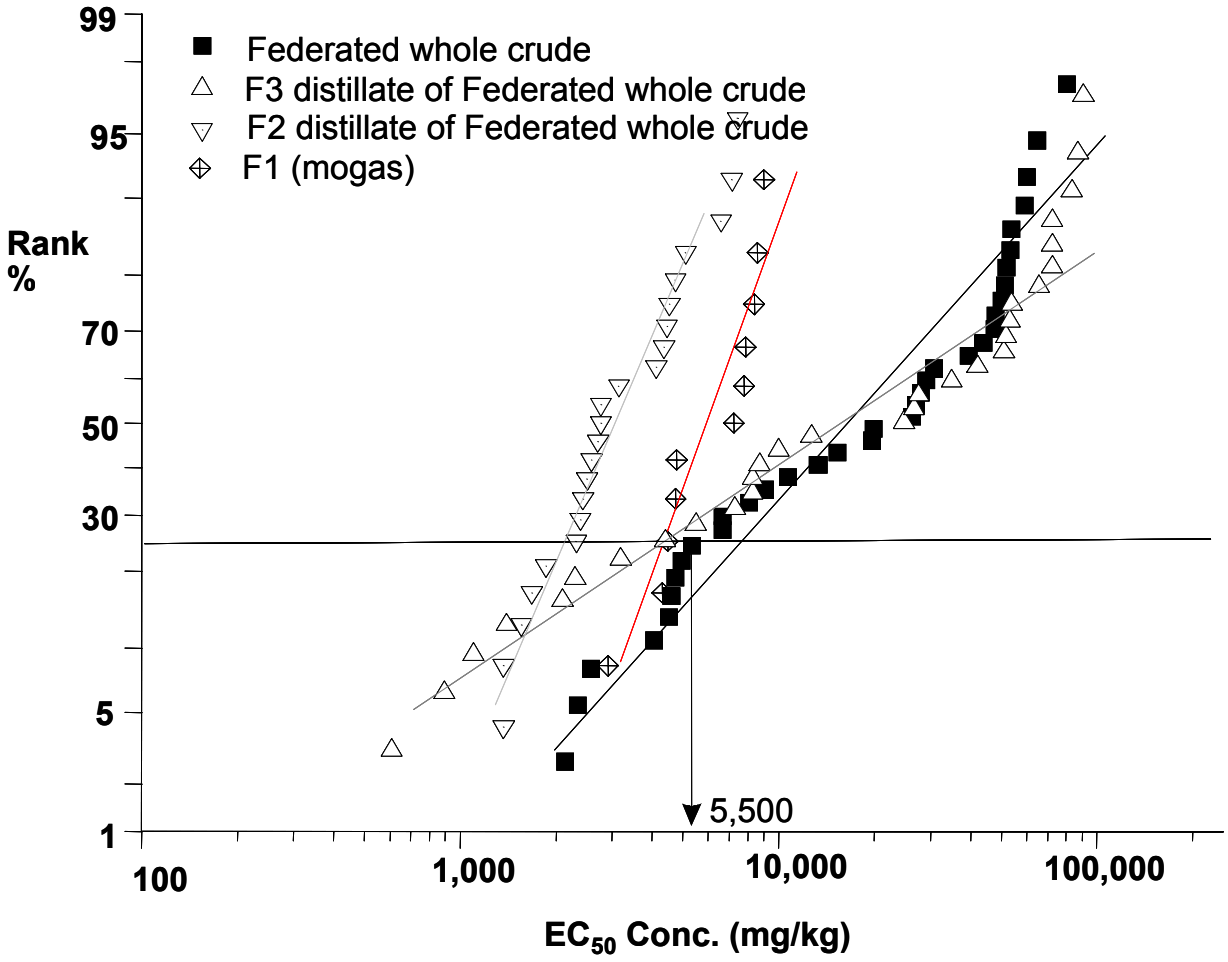


Figure D.17: Comparison of ranked data for plant toxicity effects endpoints [EC_{50} estimates].

D.2.9.1 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 direct 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 D.2.4 through D.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.

D.2.10 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 D11.

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 D.11: 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.

D.3 Application of the CCME 1996 Soil Protocol to the Derivation of Tier 1 Ecological Values (Appendix D from 2001 PHC CWS).

This section reproduces Appendix D from the 2001 PHC CWS, and is reproduced as background information.

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). Commercial/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 25^{th} 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 D12, below)

Table D.12: 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 artefact of (i) the experimental protocol (specific concentrations to which the test organism is exposed), and (ii) shortcomings of the Analysis 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 (BC 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.

D.4 Summary of Ecotoxicity Data Developed for the 2001 PHC CWS (Appendix E from 2001 PHC CWS)

Table D.13: 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					
Barley	shoot length	EC20	74800	7 (0,15,30,50, 60,70, 80 mg/g)	4	nominal	Artificial - 70%	7d test. n=5

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	root length	EC20	79000				silica sand, 20%	
	shoot ww	EC20	73800				kaolinite 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 clear lids kept on till plants 3cm in height
	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 clear lids kept on till plants 3cm in height
	root length	EC50	3200				- Delacour Orthic	
	shoot ww	EC50	54100				Black Chernozem	

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	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, 70,80 mg/g)	4	nominal	Artificial - 70%	12d test. n=5
	root length	EC20	54900				silica sand, 20%	
	whole ww	EC20	34000				kaolinite clay	

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
	whole dw	EC20	33500				10% sphagnum peat	
	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, 10,12.5,15,20,2 5 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% kaolinite clay, 10% sphagnum peat	14d test. n=3 perforated lids
	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

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Springtail (*O. folsomi*)	mortality	LC50	6670	6 (0,2,4,8,12,15 mg/g)	3-4	nominal	artificial 70% silica sand 20% kaolinite clay 10 % sphagnum peat	7d test. n=10 covered loosely
	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					
	adult mortality	EC50	3695-4280					

(after Stephenson *et al*., 2000b)

Table D.14: 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					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
Northern wheatgrass	shoot length	EC50	7440	11 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20, 30 mg/g)	3-6	nominal	field soil – Delacour, Orthic Black Chernozem	14d test. n=5
	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 D.15: 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 mech mix open plastic test units.
	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 mech mix closed plastic test units.
	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 mech mix closed plastic test units.
	shoot ww	EC20	**1210**					
	shoot dw	EC20	**1210**					
	root length	EC20	**1380**					
	root ww	EC20	**1130**					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
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 first 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 first 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**					
	root dw	EC20	**5470**					

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
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 tumble mixing closed glass jars.
	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 mixing closed glass jars. mech.
	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 mixing closed glass jars. mech.
	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 mixing closed glass jars. mech.
	shoot ww	EC50	**6960**					
	shoot dw	EC50	**7100**					
	root length	EC50	**3960**					
	root ww	EC50	**6910**					
	root dw	EC50	**6650**					
Red fescue	shoot	EC20	**2790**	10 (0,1,2,3,5,	3	nominal	artificial	9 d. acute test. n=5 closed glass jars.

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
	length			6,8,12,15, 25 mg/g)				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**					
	mortality	LC50	**4720**	8 (0,0.5,1,2, 3,5,8,10 mg/g)	3	nominal	artificial 76.4% sand 8.9% silt	7d test. n=? closed units

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
							14.8% clay	
	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 response!
	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 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	mech. mixing. 7d test. closed test container

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. (mg/g)	# reps.	Conc. type nom./init./final	Soil type	Comments
							11.4% clay	
	mortality	LC50	**1230**		2	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	mech. mixing. 7d test. closed test container
	mortality	LC50	**710**		2	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	mech. mixing. 7d test. open test container
	mortality	LC50	**2080**		2	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	mech. mixing. 7d test. open test container
	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. 14d test. closed test container
	mortality	LC50	**400**		2	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	mech. mixing. 14d test. closed test container
	mortality	LC50	**1860**		2	nominal	artificial 76.4% sand 8.9% silt 14.8% clay	mech. mixing. 14d test. open test container
	mortality	LC50	**710**		2	nominal	sandy loam 60.8% sand 27.8% silt 11.4% clay	mech. mixing. 14d test. open test container

(after Stephenson 2000)

Table D.16: 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% kaolinite 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% kaolinite 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% kaolinite 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% kaolinite 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% kaolinite 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 provided	initial measures are
	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 provided	initial measures are
	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% kaolinite 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% kaolinite 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					
Springtails (***O.***	mortality	LC50	7588	9 (0, 0.5, 1, 2, 4, 8, 15, 25, 50	6 control 3 trt	nominal	Artificial: 70% silica sand; 20% kaolinite	7d test. n=10 loosely sealed lids

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
***folsomi*)**				mg/g)			clay;10% sphagnum peat	
	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% kaolinite 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% kaolinite 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% kaolinite 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
	juvenile ww	EC50	1807	10 (0, 0.075, 0.125, 0.25, 0.5, 0.8, 1,	10	nominal	Field soil Delacour Orthic Black	61d test. n=2 adults removed D33 & cocoons allowed to hatch. perforated lids.

Organism	Parameter	Endpoint	Value (mg/kg)	Exposure conc. # (conc.)	# reps.	Conc. type nom./init./final	Soil type	Comments
				2, 3, 4 mg/g)			Chernozem	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% kaolinite clay;10% sphagnum peat	14d test. n=3 perforated lids
	mortality	LC50	64158	(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)

D.5 Comparison of the Toxicity of PHC Fractions and Whole Federated Crude Oil (Appendix F from 2001 PHC CWS)

Table D.17: 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 E: NEW ECOTOXICOLOGICAL DATA AND ANALYSIS FOR PHC FRACTIONS F1 AND F2

E.1 Introduction

Appendix E provides the rationale for the revised soil quality guidelines for the ecological direct contact exposure pathway for F1 and F2 that were summarized and discussed in Sections D.2.4 and D.2.5 of the main text. The information in this Appendix is presented to achieve two objectives:

- to record the ecotoxicological data that were available for F1 and F2; and,
- to indicate how the available data were used to calculate the F1 and F2 guidelines.

Potential ecological direct soil contact guideline values were calculated for F1 and F2 by two reports which used a range of methodologies proposed by members of the Ecological Criteria Advisory Sub-Group ("the Sub-Group") of the CCME Soil Quality Guidelines Task Group.

The first of the two reports is a contract report whose principal author was Janet Cermak (Cermak and Tindal, 2006), and which is the source of much of the data and analysis in this appendix. This report was commissioned by the Sub-Group to summarize all the available F1 and F2 data, to develop revised F1 and F2 guidelines based on i) the 2001 PHC CWS methodology; ii) the revised CCME (2006a) methodology; and, iii) a hybrid method, and to provide the rationale for the values derived. Data relevant to F1 considered in this report included data on motor gasoline ("Mogas") and limited data for F1 itself.

The second of the two reports is a memorandum from Dr. Doug Bright to the Sub-Group (Bright, 2006a). This memorandum provided two alternatives to the derivation of F1 soil quality guidelines provided in the Cermak and Tindal (2006) report, including a weight of evidence method in which F1 data were used wherever they were available for a given species and endpoint, and Mogas data were only used if F1 data were not available.

In the report generated by the sub-group ("the Sub-Group Report", CCME, 2006b), potential guideline values were presented based on all three methodologies (2001 PHC CWS, CCME, 2006a, and hybrid), using the F2 guidelines calculated in Cermak and Tindal (2006) and the F1 guidelines from Bright (2006). The CCME Soil Quality Guidelines Task Group elected to use the guidelines developed using the CCME (2006a) methodology. The remainder of this appendix provides the data and methodology used to calculate the F1 and F2 guideline values adopted in the 2006 PHC CWS.

The majority of this appendix is taken from or adapted from Cermak and Tindal (2006) and Bright (2006).

E.2 DATA SOURCES AND APPROACH

Available sources of ecotoxicological data relevant to developing soil quality guidelines for F1 and F2 are summarized below.

Study	Citation	Notes
Canada-Wide Standards for Petroleum Hydrocarbons (PHCs) in Soil: Scientific Rationale	CCME (2000)	Provides method for the determination of PHC CWS. Ecological soil contact values derived using data from ESG (2003)
Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase 1: Fraction-specific Toxicity of Crude Oil	ESG (2003)	Source of data for the derivation of Fraction 2 and 3 ecological soil contact values in CCME (2000). Contains some additional data not available at the time of the CCME derivation process.
Summary of the Soil Toxicity and Soil Chemical Analysis Data for Petroleum Hydrocarbon Fractions 2 and 3	Cermak *et al.* (2005)	Ecotoxicity data for Fractions 2 and 3 for soil organisms.
Final Report on the Acute Screening and Definitive, Chronic Toxicity Tests with Motor Gasoline	ESG (2000)	Ecotoxicity data for Mogas, a surrogate for Fraction 1
Unpublished dataset on the toxicity of Mogas to barley in a Chernozem soil	Cermak (unpublished)	Ecotoxicity data for Mogas, a surrogate for Fraction 1
Unpublished Fraction 1 toxicity data	ESG (unpublished)	Raw data from toxicity tests with Fraction 1 were obtained in order to statistically determine toxicity values.

The overall approach to developing the guidelines for F1 and F2 was as follows.

All relevant toxicity data for Fractions 1 and 2 were collected and summarized, listing both the median (50%) and 25% effect levels, as well as general information regarding the testing protocol and key notes on the results (see Tables E.1 to 4, located at the end of this appendix). In many cases, only 20% effect levels were available from the studies. These were considered to be close approximations of the 25% effect levels and were used in place of them. In cases where both 20% and 25% effect levels were available, the 25% effect levels were used.

Based on the CCME (2006a) protocols, the data carried forward for each species/endpoint were the values that represented an effect as close as possible to the 25th percentile (normally IC/EC25 or IC/EC20).

Fraction-specific data were analyzed based on the protocols for the weight of evidence method in CCME (2006a). First, the data were assessed for redundancy following the redundancy reduction strategy outlined in CCME (2006a). To summarize, redundancy was reduced during data analysis in the following manner:

1. Redundant data points for the same species were combined by taking the geometric mean of the individual values. Individual data points were considered

redundant if they were based on different endpoints that are directly, causally connected (i.e., wet and dry biomass measurements).

2. If data were available for different exposure periods, but for the same species, endpoint, response level and exposure conditions, the value from the longest exposure period was used.

Insufficient data were available to analyze the data for fine and coarse soils separately. Accordingly, data for both soil textures were combined and analyzed together. Some data were screened out as being unsuitable. NOEC and LOEC data were excluded since they can include a wide-range of response levels. In addition, the collembolan reproductive endpoint "fecundity" reported by ESG (ESG 2000, 2003) was omitted for two reasons. First, this endpoint is redundant with the number of progeny produced. Second, the inability to determine the sex of the adult collembola precludes the determination of fecundity as generally understood in biology (i.e., as the number of progeny/female).

Following redundancy reduction, a ranked species sensitivity plot was constructed by plotting the rank sensitivity against the logarithm of the concentration. To determine the rank sensitivity, the toxicity data were listed from the lowest to highest value, each data point was assigned a rank number (one for the lowest value, two for the second lowest value, etc.), and the rank sensitivity was calculated as:

Rank sensitivity = (rank number/(total number of data points + 1))*100

The agricultural/residential and commercial/industrial criteria were then determined from the plot, by taking the 25^{th} and 50^{th} percentiles, respectively, of the combined plant and invertebrate LC/IC25 dataset.

E.3 CCME Fraction F1

E.3.1 Available Data for Fraction 1

The following reports included data on the toxicity of Fraction 1 and/or Mogas:

- ESG (2003). *Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase I Fraction-specific Toxicity of Crude Oil.* Report prepared for the Petroleum Technology Alliance Canada. January 2003.
- ESG Unpublished data on the toxicity of Fraction 1 to Eisenia andrei and barley and the toxicity of Mogas to earthworms.
- ESG (2000). *Final Report on the Acute Screening and Definitive, Chronic Toxicity Tests with Motor Gasoline.* Report prepared by G.L. Stephenson and J. Princz. March 2000.
- Cermak Unpublished data on the toxicity of Mogas to barley.

Table E.1 lists some of the information from each of these studies and summarizes key points relevant to the review of Fraction 1 toxicity to soil organisms. The relationship between the measured concentration ("y") and the nominal concentration ("x") for the ESG data (ESG 2003, ESG unpublished data), as listed in Table E.1, was derived from the relationships for Fraction 1 found in Appendix F of ESG (2003). These relationships were "y = 0.3213x - 0.028" and "y = 0.2066x - 0.0118". From the slope parameter, it is noted that the measured concentration was

approximately 32.1% of the nominal concentration in one test and 20.7% of the nominal concentration in the other. Therefore, on average, the measured concentration was estimated to be 26.4% of nominal.

Table E.2 lists all of the available Fraction 1 and Mogas ecotoxicity data. Mogas is used as a surrogate for Fraction 1. The majority of the data are Mogas values from ESG (2000); these data were used exclusively in the determination of the 2001 PHC CWS for Fraction 1 (CCME 2000). Additional Mogas data were found for two species from two studies, both unpublished (ESG unpublished data, Cermak unpublished data). Unlike the tests conducted by ESG (2000), which used only coarse-textured soils, these tests were conducted in a fine-textured, Chernozem soil. The data from the fine-textured soil were very similar to those from the coarse-textured soils; therefore the results for the two soil-textural classes were combined for analysis.

One Mogas data point from ESG (2000) was discarded (number of progeny produced by *O. folsomi* in the sandy-loam reference soil). The natural logarithm of the data was used in the non-linear regression analysis. Data transformation was recently found to result in erroneous inhibition concentration estimates when the non-linear regression models given in EC (2005) and used in ESG (2000) are applied (B. Zajdlik, Zajdlik & Associates Inc., *personal communication*).

Very few toxicity data specific to Fraction 1 were found. Acute earthworm lethality and definitive plant growth assays were conducted by ESG International Inc. Some of the results are provided in Tables F.5 and F.6 of Appendix F of ESG (2003). However, not all of the endpoint data were analyzed; therefore, the raw data were obtained and statistically analyzed following the recommendations of Environment Canada (EC, 2005). This resulted, in some cases, in slightly different toxicity values from those reported in ESG (2003). When this occurred, the values derived following the new Environment Canada protocol (EC, 2005) were used (Table E.2).

It should be noted, that one IC50 value for Fraction 1 was excluded as it was below the lowest concentration tested and significantly lower than the results from similar tests. The accuracy of estimates below the lowest test concentration is questionable. As well, 13 of the calculated IC20s were below the lowest concentration tested. Two of these values were considered to be unreasonably low (over two orders of magnitude lower than the lowest test concentration) and were excluded from the dataset.

E.3.2 Estimation of Ecological Soil Contact Values for Fraction 2

Data in Table E.2 indicate that the toxicity of Mogas is generally greater than that of F1. Mogas is primarily F1, but includes a proportion of F2. Due to the relative volatility of F1 and F2, the relative proportion of F2 in the soil of a toxicity test will increase as the test progresses. Accordingly, the Mogas toxicity data for longer duration tests may be controlled by the toxicity of F2 as much or more than the toxicity of F1. For this reason, where available, the F1 data were preferred to the Mogas data. The approach chosen was to employ the weight of evidence method to derive guidelines, using F1 data where available, and using Mogas data only in those instances where similar quality toxicity data for F1 did not exist. Available data for F1 and Mogas are summarized below.

Species	CWS F1 (Whole Federated Crude)		Mogas	
	Acute	Sub-Acute to Chronic	Acute	Sub-Acute to Chronic
Barley		✓14 d	✓7 d	✓13 d
Alfalfa			✓7 d	✓21 d
Corn			✓ ?	
Red Fescue			✓9 d	
E. andraei		✓14 d	✓7 d	✓14 d
O. folsomi			✓7 d	✓35-36 d

Green shading indicates selected endpoint.

Taking the selected endpoints, as indicated above, from the data in Table E.2, and removing redundancy as indicated in Section E.2 results in the following dataset, which was used to develop the soil quality guidelines for F1.

Species	Test type	Endpoint	Product	Measured LC/IC20(25) mg/kg d.w.
alfalfa	definitive	shoot length	Mogas	280
alfalfa	definitive	root length	Mogas	230
alfalfa	definitive	shoot weight	Mogas	190
alfalfa	definitive	root weight	Mogas	230
barley	definitive	shoot length	F1	610
barley	definitive	root length	F1	500
barley	definitive	shoot weight	F1	490
barley	definitive	root weight	F1	610
corn	acute	shoot length	Mogas	380
corn	acute	root length	Mogas	160
corn	acute	shoot weight	Mogas	740
corn	acute	root weight	Mogas	830
red fescue	acute	shoot length	Mogas	300
red fescue	acute	root length	Mogas	190
red fescue	acute	total weight	Mogas	400
O. folsomi	definitive	adult mortality	Mogas	230
O. folsomi	definitive	#progeny	Mogas	220
E. andrei	14 d	mortality	F1	510

Some data points represent the geometric mean of the results of more than one test

Arguably, this data set meets the minimum requirements for a WOE determination (≥ 10 data points; ≥ 2 plant + 2 invertebrate taxa; ≥ 3 studies). The data include six species (4 plant and 2 invertebrate spp.), from three separate studies, albeit by the same group of researchers, with > 10 data points overall.

The corresponding 25th and 50th percentile of the data distribution is illustrated in Figure E.1:

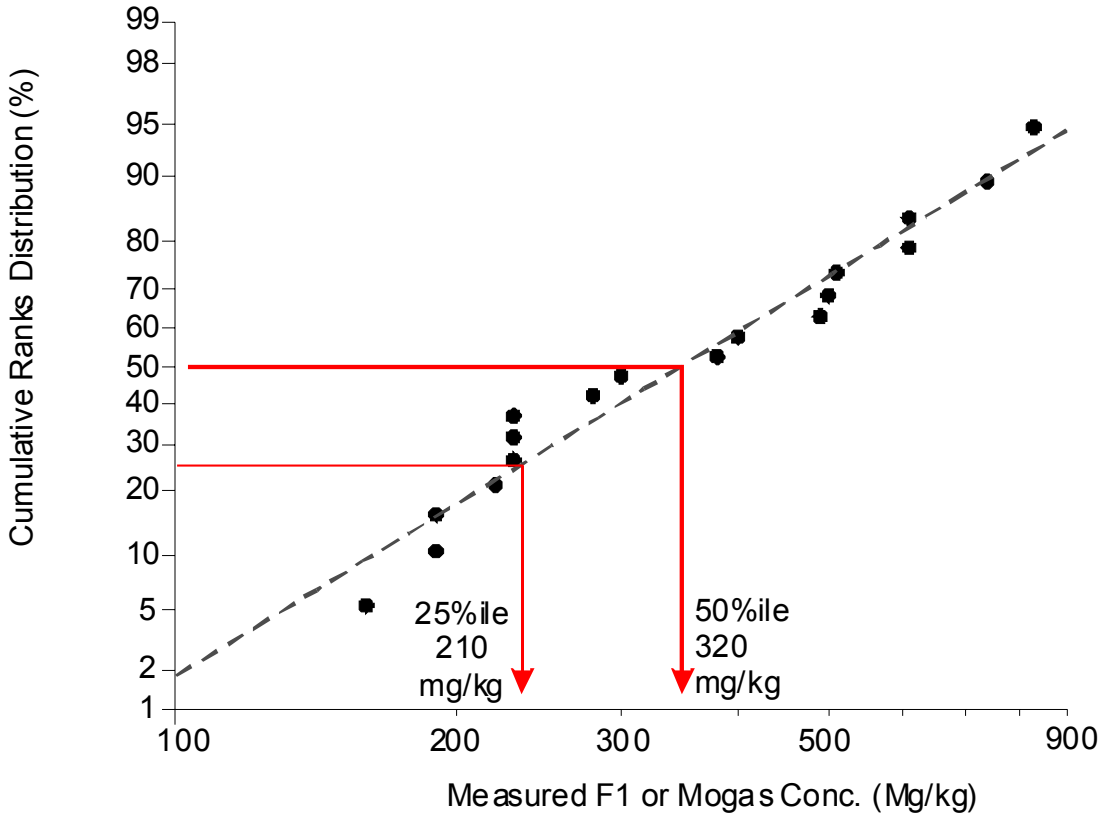


Figure E.1: Approximated Species Sensitivity to F1 PHCs – Soil Invertebrates and Plants

As noted above, insufficient data were available to develop separate guidelines for coarse and fine soils, and the combined dataset of coarse and fine soils was considered together to develop the above species sensitivity distribution. The guideline values calculated are applied to both coarse and fine soils. Existing and new guideline values are summarized below.

	Existing (mg/kg)	New (mg/kg)
Fine-textured soils		
Agricultural/Residential	260	210
Commercial/Industrial	660	320
Coarse-textured soils		
Agricultural/Residential	130	210
Commercial/Industrial	330	320

E.4 CCME Fraction 2

E.4.1 Available Data for Fraction 2

The following reports included data on the ecotoxicity of CCME Fraction 2:

- ESG (2003). *Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase I Fraction-specific Toxicity of Crude Oil*. Report prepared for the Petroleum Technology Alliance Canada. January 2003.
- Cermak, J.H., G.L. Stephensen, D. Birkholz, and D.G. Dixon (2005). *Summary of the Soil Toxicity and Soil Chemical Analysis for Petroleum Fractions 2 and 3.* A report prepared for the CCME CWS Ecological Criteria Advisory Sub-group, October 31, 2005.
- ESG. Unpublished data on the toxicity of Fraction 2 to *E. andrei* and barley.

Table E.3 lists selected information from each of these studies, and summarizes key points relevant to the review of Fraction 2 toxicity to soil organisms.

Field and lab studies on the toxicity of crude oil-contaminated soil to plant and soil invertebrate receptors were also found. The following documents contained data on the toxicity of the crude oil reported as the concentration of petroleum hydrocarbons in each of the PHC CWS fraction ranges:

- Visser, S. (2005a). *Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality. Phase 3: Long-term Field Studies.* Report prepared for the Petroleum Technology Alliance Canada. February 2005.
- Visser, S. (2005b). *Ecotoxicity Risk Assessment of PHC Residuals in Bioremediated Oil-Contaminated Clay Soils.* PowerPoint presentation prepared for the Petroleum Technology Alliance Canada. November 2005.
- Visser, S. (2003). *Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality. Phase 2: Field Studies.* Report prepared for the Petroleum Technology Alliance Canada. April 2003.

In the studies conducted by Visser (2003, 2005a, and 2005b), no instances occurred where the toxicity of the soil could be attributed solely to Fraction 2. Generally, the concentration of Fraction 2 was less than the PHC CWS criteria (CCME 2000) while the concentrations of Fraction 3 was greater. In those instances where the concentration of Fraction 2 was greater than the criteria, so were the concentrations of other fractions and any effect caused by Fraction 2 could not be separated from effects due to other fractions. Thus, the data from these studies could not be analyzed further.

Table E.4 lists all of the available Fraction 2-specific toxicity data for ecological receptors. The majority of the data are from ESG 2003 and were used in the derivation of the PHC CWS Fraction 2 criteria. Very few new fraction-specific data were found.

Since 2001, further testing with Fraction 2 was conducted by ESG International Inc. Specifically, toxicity tests were conducted with individual fractions concurrent with tests

investigating the toxicity of binary combinations of fractions to earthworms and plants. Some of these results are provide in Tables F.5 and F.6 in Appendix F of ESG (2003). However, not all of the endpoint data were analyzed and provided in ESG (2003); therefore, the raw data were obtained and statistically analyzed following the recommendations of Environment Canada (EC, 2006). This resulted in slightly different toxicity values from those reported in Tables F.5 and F.6 for Fraction 2. The values from the analyses following the new Environment Canada protocol (EC, 2006) were used (Table E.4). In general, the new F2 data for plants (barley) and the earthworm, *Eisenia andrei* were similar to those from previous tests.

New data were also provided by Cermak *et al*. (2005), who conducted acute toxicity tests with *E. andrei*. These data were similar to those obtained by ESG (2003 and unpublished data) on a nominal concentration basis, but were slightly greater when expressed as measured concentrations.

ESG (2003, unpublished data) and Cermak *et al.* (2005) used different analytical methods to determine the measured concentration of petroleum hydrocarbons in the soil. The relationship between the nominal and measured concentration therefore differs between the studies. Because of this, criteria derivations were conducted using toxicity values adjusted to the measured concentrations using the relationships indicated in Table E.3.

E.4.2 Estimation of Ecological Soil Contact Values for Fraction 2

Insufficient data were available to analyze coarse and fine soils separately, and accordingly, the combined dataset of fine and coarse data was considered together. Preferred data were selected, and redundant data were removed or combined using the techniques described in Section E.2. The resultant dataset, which was used to develop the soil quality guidelines for F1, is summarized below.

Species	Test Type	Endpoint	Product	Measured LC/IC20/25 mg/kg d.w.
alfalfa	definitive	root length	F2	221
alfalfa	definitive	root weight	F2	764
alfalfa	definitive	shoot length	F2	455
alfalfa	definitive	shoot weight	F2	167
northern wheatgrass	definitive	root length	F2	86
northern wheatgrass	definitive	root weight	F2	79
northern wheatgrass	definitive	shoot length	F2	1092
northern wheatgrass	definitive	shoot weight	F2	308
barley	definitive	root length	F2	381
barley	definitive	root weight	F2	311
barley	definitive	shoot length	F2	494
barley	definitive	shoot weight	F2	284
E. andrei	definitive	mortality	F2	305
E. andrei	definitive	# progeny	F2	116
E. andrei	definitive	progeny biomass	F2	135
O. folsomi	definitive	# progeny	F2	211

Arguably, this data set meets the minimum requirements for a WOE determination (≥ 10 data points; ≥ 2 plant + 2 invertebrate taxa; ≥ 3 studies). The data include five species (3 plant and 2 invertebrate spp.), from three separate studies, albeit by the same group of researchers, with > 10 data points overall.

The corresponding 25th and 50th percentile of the data distribution is illustrated in Figure E.2:

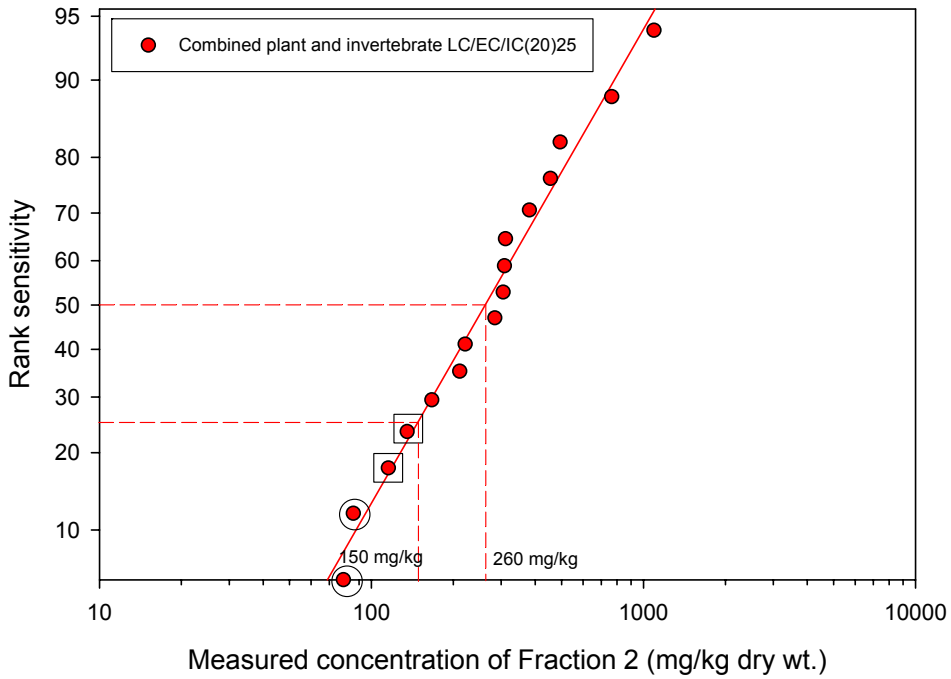


Figure E.2: Approximated Species Sensitivity to F2 PHCs – Soil Invertebrates and Plants

Note: Plant (circle) and earthworm reproduction (square) data points that fall below the 25th percentile are indicated.

As noted above, the combined dataset of coarse and fine soils was considered together to develop the above species sensitivity distribution. However, all the data actually selected were for chernozem (fine) soil. Insufficient data were available to develop a separate coarse soil guideline, however, the coarse soil data that were available did not support a difference in the toxicity of F2 in coarse or fine soil, and accordingly, the guideline values calculated are applied to both coarse and fine soils. Existing and new guideline values are summarized below.

	Existing	New
Fine-textured soils		
Agricultural/Residential	900	150
Commercial/Industrial	1,500	260
Coarse-textured soils		
Agricultural/Residential	450	150
Commercial/Industrial	760	260

E.5 References

Bright, D., 2006. Proposed Method for Utilizing F1 Soil Toxicity Data for Updating the CWS F1 SQG. Memorandum to the Ecological Criteria Advisory Sub-Group dated 16 January 2006.

CCME (Canadian Council of Ministers of the Environment), 2000. Canada-wide standards for petroleum hydrocarbons (PHCs) in soil: scientific rationale. Supporting technical document. Canadian Council of Ministers of the Environment, Winnipeg, Manitoba, December 2000.

CCME (Canadian Council of Ministers of the Environment), 2006a. A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines. Canadian Council of Ministers of the Environment, Winnipeg, Manitoba. 2006.

CCME (Canadian Council of Ministers of the Environment), 2006b. Five-year review of the Canada-Wide Standards for Petroleum Hydrocarbons (PHC CWS): Ecological, Direct Soil Contact Guidance. Report to the Canadian Council of Ministers of Environment (CCME) Soil Quality Guidelines Task Group (SQGTG) by the Ecological Criteria Advisory Subgroup. Dated March, 2006.

Cermak, J, and Tindal, M., 2006. Data Compilation of Recent Projects on PHC F1-F2 Ecotoxicity, and their Implications for PHC CWS Guideline Values. Report prepared on behalf of the Ecological Criteria Advisory Sub-Group dated 20 February 2006.

Cermak, J.H., G.L. Stephenson, D. Birkholz, and D.G. Dixon. 2005. Summary of the Soil Toxicity and Soil Chemical Analysis Data for Petroleum Fractions 2 and 3. Interim report prepared for the CCME CWS Ecotoxicological Criteria Advisory Sub-Group, October 31, 2005.

EC (Environment Canada), 2005. Guidance Document on Statistical Methods for Environmental Toxicity Tests. Report No. EPS 1/RM/46. Method Development and Application Section, Environmental Technology Centre, Environment Canada. March 2005. 170 pp. plus appendices.

ESG (ESG International Ltd.), 2000. Final Report on the Acute Screening and Definitive, Chronic Toxicity Tests with Motor Gasoline. Report prepared by G.L. Stephenson and J. Princz, ESG International Inc. March 2000. 32 pp. plus appendices.

ESG (ESG International Ltd.), 2003. Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase 1: Fraction-specific Toxicity of Crude Oil. Report prepared by ESG International Inc. for the Petroleum Technology Alliance Canada. January 2003. 238 pp.

Visser, S. 2003. Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase 2: Field Studies. Report prepared for the Petroleum Technology Alliance Canada. April 2003.

Visser, S. 2005a. Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase 3: Long-term Field Studies. Report prepared for the Petroleum Technology Alliance Canada. February 2005.

Visser, S. 2005b. Ecotoxicity Risk Assessment of PHC Residuals in Bioremediated Oil-Contaminated Clay Soils. PowerPoint presentation prepared for the Petroleum Technology Alliance Canada. November 2005.

Table E.1: Summary of F1 and Mogas Toxicity Studies

Document	Product	Contaminant Source	Soil Type(s)	Test Species	Test Type	Analytical Method	Analytical Recovery	Key Points
ESG 2003	Fraction 1 (>nC10-nC16)	Federated crude oil, distilled using a modified ASTM D1160	Chernozem (fine) soil	Plants earthworms	Laboratory assays; acute invertebrate lethality, definitive plant growth	CCME method (CCME 2001)	On average measured was 24.6% of nominal	•Fraction 1 was tested during studies on the toxicity of binary combinations of fractions. Only median effect levels were provided. Obtained most of the raw data to reanalyze (see ESG unpublished). Used one data point from ESG (2003) for which the raw data was not obtained (acute earthworm lethality). •Linear relationship between nominal and measured concentrations •Only one plant and one invertebrate species tested in a fine-textured soil
ESG (unpublished data)	Fraction 1 (>nC10-nC16)	Federated crude oil, distilled using a modified ASTM D1160	Chernozem (fine) soil	Plants earthworms	Laboratory assays; acute invertebrate lethality, definitive plant growth	CCME method (CCME 2001)	On average measured was 24.6% of nominal	•ESG raw data reanlyzed following EC (2005) guidance to obtain LC/IC50 and LC/IC20(25) estimates. •Earthworms were the most sensitive species. •One plant IC50 estimate was below the lowest test concentration. Did not use this data point as it was much less than estimates for the same endpoint. •Thirteen plant IC20s were below the lowest test concentration. Two were discarded, as they were unreasonably low (over two orders of magnitude less than the lowest concentration tested).
ESG 2000	Mogas	Composite blend of additive-free motor gasoline from five Ontario refineries	Artificial soil (coarse) and a sandy-loam field soil (coarse)	Plants earthworms collembola	Laboratory assays; acute invertebrate lethality, acute and definitive plant growth, invertebrate reproduction	Canadian General Standards Board procedure CAN/CGSB-3.0 No. 14.3-94 "Standard Test Method for the Identification of Hydrocarbon Components in Automotive Gasoline Using Gas Chromatography "	Log(initial measured conc.) = 1.232 log(nominal conc) - 1.762	•Tested different spiking methodologies and test conditions. Significant loss of Mogas observed with all tests, •Conducted acute tests with four plant species and longer-duration definitive tests with only two plant species. Mogas toxicity was always less (e.g., higher LC/IC50s) for the shorter-duration tests. •The rate of loss of Mogas over time from soil was concentration-dependent. Most of the Mogas was lost within 14 days. •No effect was observed on E. andrei reproduction. Hypothesized that Mogas was lost quickly and organisms that survived the initial exposure could reproduce. •For the plant tests, four acute IC50s, 12 acute IC20s, and two definitive IC20s were below the lowest test concentration. •One data point for O. folsomi reproduction was not used as an inappropriate transformation was used in the statistical determination of the toxicity estimate.

Cermak (unpublished data)	Mogas	Composite blend of additive-free motor gasoline from five Ontario refineries	Chernozem (fine) soil	Barley	Laboratory assays; definitive plant growth.	As above	Log(initial measured conc.) = 1.232 log(nominal conc) - 1.762	•Conducted definitive tests with barley.

Adapted from: Cermak and Tindal (2006)

Table E.2: Available F1 and Mogas Toxicity Data Used

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.	Notes
Fraction 1 Data																	
ESG unpublished data	chernozem	definitive	14 days	barley	shoot length	8 (0, 3, 4, 5, 7, 9, 12, 15 mg/g)	3-6	ICPIN	8170	1270		CCME 2001	26.40%	2157	335.28		
ESG unpublished data	chernozem	definitive	14 days	barley	shoot ww	8 (0, 3, 4, 5, 7, 9, 12, 15 mg/g)	3-6	gompertz	5110	2170		CCME 2001	26.40%	1349	572.88		
ESG unpublished data	chernozem	definitive	14 days	barley	shoot dw	8 (0, 3, 4, 5, 7, 9, 12, 15 mg/g)	3-6	gompertz	4570	1880		CCME 2001	26.40%	1206	496.32		
ESG unpublished data	chernozem	definitive	14 days	barley	root length	8 (0, 3, 4, 5, 7, 9, 12, 15 mg/g)	3-6	gompertz	7190	2050		CCME 2001	26.40%	1898	541.2		
ESG unpublished data	chernozem	definitive	14 days	barley	root ww	8 (0, 3, 4, 5, 7, 9, 12, 15 mg/g)	3-6	gompertz	5280	2640		CCME 2001	26.40%	1394	696.96		
ESG unpublished data	chernozem	definitive	14 days	barley	root dw	8 (0, 3, 4, 5, 7, 9, 12, 15 mg/g)	3-6	gompertz	5050	2230		CCME 2001	26.40%	1333	588.72		
ESG unpublished data	chernozem	definitive	14 days	barley	shoot length	7 (0, 3, 5, 7, 8, 10, 11 mg/g)	3-6	logistic weighted	6550	4200		CCME 2001	26.40%	1729	1108.8		
ESG unpublished data	chernozem	definitive	14 days	barley	shoot dw	7 (0, 3, 5, 7, 8, 10, 11 mg/g)	3-6	logistic	3360	1710		CCME 2001	26.40%	887	451.44		
ESG unpublished data	chernozem	definitive	14 days	barley	root length	7 (0, 3, 5, 7, 8, 10, 11 mg/g)	3-6	gompertz	4300	1630		CCME 2001	26.40%	1135	430.32		
ESG unpublished data	chernozem	definitive	14 days	barley	root dw	7 (0, 3, 5, 7, 8, 10, 11 mg/g)	3-6	logistic	3940	2480		CCME 2001	26.40%	1040	654.72		
ESG unpublished data	chernozem	definitive	14 days	barley	shoot length	7 (0, 3, 5, 7, 8, 10, 11 mg/g)	3-6	ICPIN	4060	90		CCME 2001	26.40%	1072			
ESG unpublished data	chernozem	definitive	14 days	barley	shoot dw	7 (0, 3, 5, 7, 8, 10, 11 mg/g)	3-6	ICPIN	1060	20		CCME 2001	26.40%				
ESG unpublished data	chernozem	definitive	14 days	barley	root length	7 (0, 3, 5, 7, 8, 10, 11 mg/g)	3-6	gompertz	4280	1880		CCME 2001	26.40%	1130	496.32		
ESG unpublished data	chernozem	definitive	14 days	barley	root dw	7 (0, 3, 5, 7, 8, 10, 11 mg/g)	3-6	logistic	3150	1940		CCME 2001	26.40%	832	512.16		
ESG 2003	chernozem	lethality	14 days	E. andrei	mortality				1800			CCME 2001	26.40%	475			
ESG unpublished data	chernozem	lethality	14 days	E. andrei	mortality	8 (0, 0.5, 1, 1.5, 2, 2.5, 3, 5)		probit	1780	1460	1520	CCME 2001	26.40%	470	385.44	401.28	

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.	Notes
ESG unpublished data	chernozem	lethality	14 days	E. andrei	mortality	8 (0, 0.5, 1, 1.5, 2, 2.5, 3, 5)		probit	2850	2330	2430	CCME 2001	26.40%	752	615.12	641.52	
Mogas Data																	
ESG 2000	artificial	acute	11 days	alfalfa	shoot length	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	exponential	5450	3210		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	694	361		closed test units, mech mixing
ESG 2000	artificial	acute	11 days	alfalfa	root length	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	logistic	5010	3310		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	625	375		closed test units, mech mixing
ESG 2000	artificial	acute	11 days	alfalfa	total ww	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	logistic	5320	3390		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	673	387		closed test units, mech mixing
ESG 2000	artificial	acute	11 days	alfalfa	total dw	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	logistic	4910	3400		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal)-1.762	610	388		closed test units, mech mixing
ESG 2000	SLR	acute	11 days	alfalfa	shoot length	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	logistic	6600	2410		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	878	254		closed test units, mech mixing
ESG 2000	SLR	acute	11 days	alfalfa	root length	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	hormesis	4580	3080		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	560	343		closed test units, mech mixing
ESG 2000	SLR	acute	11 days	alfalfa	total ww	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	hormesis	8220	5900		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	1151	765		closed test units, mech mixing
ESG 2000	SLR	acute	11 days	alfalfa	total dw	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	hormesis	6750	5100		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	903	639		closed test units, mech mixing
ESG 2000	SLR	definitive	21 days	alfalfa	shoot length	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	logistic	5130	2570		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	644	275		closed test unit first 7 days
ESG 2000	SLR	definitive	21 days	alfalfa	root length	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	logistic	3900	2240		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal)	459	232		closed test unit first 7 days

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.	Notes
													1.762				
ESG 2000	SLR	definitive	21 days	alfalfa	shoot ww	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	hormesis	2710	1890		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	293	188		closed test unit first 7 days
ESG 2000	SLR	definitive	21 days	alfalfa	shoot dw	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	hormesis	2520	1850		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	268	183		closed test unit first 7 days
ESG 2000	SLR	definitive	21 days	alfalfa	root ww	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	logistic	2980	2310		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	330	241		closed test unit first 7 days
ESG 2000	SLR	definitive	21 days	alfalfa	root dw	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	hormesis	2970	2120		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	328	217		closed test unit first 7 days
ESG 2000	artificial	acute	7 days	barley	shoot length	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	gompertz	7240	4430		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	984	537		open plastic test units, mech mix
ESG 2000	artificial	acute	7 days	barley	shoot ww	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	gompertz	7860	5530		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	1089	706		open plastic test units, mech mix
ESG 2000	artificial	acute	7 days	barley	shoot dw	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	gompertz	7790	5740		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	1077	740		open plastic test units, mech mix
ESG 2000	artificial	acute	7 days	barley	root length	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	gompertz	4480	2310		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	545	241		open plastic test units, mech mix
ESG 2000	artificial	acute	7 days	barley	root ww	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	gompertz	4310	2180		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	520	224		open plastic test units, mech mix
ESG 2000	artificial	acute	7 days	barley	root dw	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	gompertz	4780	2320		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	590	242		open plastic test units, mech mix

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.	Notes
ESG 2000	artificial	acute	7 days	barley	shoot length	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	logistic	5000	2850		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	624	312		closed plastic test units, mech mix
ESG 2000	artificial	acute	7 days	barley	shoot ww	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	gompertz	5500	4390		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	702	532		closed plastic test units, mech mix
ESG 2000	artificial	acute	7 days	barley	shoot dw	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	logistic	5440	3560		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	692	411		closed plastic test units, mech mix
ESG 2000	artificial	acute	7 days	barley	root length	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	logistic	2760	1590		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	300	152		closed plastic test units, mech mix
ESG 2000	artificial	acute	7 days	barley	root ww	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	gompertz	3660	1930		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	425	193		closed plastic test units, mech mix
ESG 2000	artificial	acute	7 days	barley	root dw	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	gompertz	3590	1620		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	415	156		closed plastic test units, mech mix
ESG 2000	SLR	acute	7 days	barley	shoot length	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	logistic	3100	1900		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	346	189		closed plastic test units, mech mix
ESG 2000	SLR	acute	7 days	barley	shoot ww	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	logistic	2320	1210		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	242	109		closed plastic test units, mech mix
ESG 2000	SLR	acute	7 days	barley	shoot dw	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	gompertz	2520	1210		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	268	109		closed plastic test units, mech mix
ESG 2000	SLR	acute	7 days	barley	root length	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	gompertz	2220	1380		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	229	128		closed plastic test units, mech mix
ESG 2000	SLR	acute	7 days	barley	root ww	7 (0, 2.5, 5, 10, 25, 50,	3	logistic	1770	1130		CAN/CGSB-3.0	log(initial meas)	174	100		closed plastic test units,

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.	Notes
						100 mg/g)						No. 14.3-94	1.232 log(nominal) 1.762				mech mix
ESG 2000	SLR	acute	7 days	barley	root dw	7 (0, 2.5, 5, 10, 25, 50, 100 mg/g)	3	gompertz	1950	910		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	196	76		closed plastic test units, mech mix
ESG 2000	SLR	definitive	13 days	barley	shoot length	10 (0, 0.25, 0.5, 0.75, 1, 1.5, 2, 4, 6, 10 mg/g)	3	logistic	1680	890		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	163	74		closed plastic test units for 7 days, mech mixing
ESG 2000	SLR	definitive	13 days	barley	shoot ww	10 (0, 0.25, 0.5, 0.75, 1, 1.5, 2, 4, 6, 10 mg/g)	3	logistic	1360	770		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	125	62		closed plastic test units for 7 days, mech mixing
ESG 2000	SLR	definitive	13 days	barley	shoot dw	10 (0, 0.25, 0.5, 0.75, 1, 1.5, 2, 4, 6, 10 mg/g)	3	logistic	1220	680		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	110	53		closed plastic test units for 7 days, mech mixing
ESG 2000	SLR	definitive	13 days	barley	root length	10 (0, 0.25, 0.5, 0.75, 1, 1.5, 2, 4, 6, 10 mg/g)	3	linear	1600	640		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	153	50		closed plastic test units for 7 days, mech mixing
ESG 2000	SLR	definitive	13 days	barley	root ww	10 (0, 0.25, 0.5, 0.75, 1, 1.5, 2, 4, 6, 10 mg/g)	3	hormesis	870	580		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	72	44		closed plastic test units for 7 days, mech mixing
ESG 2000	SLR	definitive	13 days	barley	root dw	10 (0, 0.25, 0.5, 0.75, 1, 1.5, 2, 4, 6, 10 mg/g)	3	hormesis	960	590		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	82	45		closed plastic test units for 7 days, mech mixing
ESG 2000	artificial	acute		corn	shoot length	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	hormesis	4880	3230		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	606	364		closed glass jars, tumble mixing
ESG 2000	artificial	acute		corn	shoot ww	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	logistic	7590	5260		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	1043	664		closed glass jars, tumble mixing
ESG 2000	artificial	acute		corn	shoot dw	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	gompertz	7710	4230		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal)	1064	508		closed glass jars, tumble mixing

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.	Notes
													1.762				
ESG 2000	artificial	acute		corn	root length	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	logistic	3140	1920		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	352	192		closed glass jars, tumble mixing
ESG 2000	artificial	acute		corn	root ww	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	hormesis	9090	6830		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	1303	916		closed glass jars, tumble mixing
ESG 2000	artificial	acute		corn	root dw	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	hormesis	9610	6730		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	1395	900		closed glass jars, tumble mixing
ESG 2000	artificial	acute		corn	shoot length	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	logistic	4650	3080		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	571	343		closed glass jars, mech mixing
ESG 2000	artificial	acute		corn	shoot ww	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	logistic	9250	6670		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	1331	890		closed glass jars, mech mixing
ESG 2000	artificial	acute		corn	shoot dw	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	gompertz	9620	6250		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	1397	821		closed glass jars, mech mixing
ESG 2000	artificial	acute		corn	root length	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	exponential	2700	1000		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	292	86		closed glass jars, mech mixing
ESG 2000	artificial	acute		corn	root ww	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	logistic	8930	6750		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	1275	903		closed glass jars, mech mixing
ESG 2000	artificial	acute		corn	root dw	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	gompertz	8440	5470		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	1189	697		closed glass jars, mech mixing
ESG 2000	SLR	acute		corn	shoot length	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	hormesis	5020	3840		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	627	451		closed glass jars, mech mixing

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.	Notes
ESG 2000	SLR	acute		corn	shoot ww	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	hormesis	6960	6270		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	938	825		closed glass jars, mech mixing
ESG 2000	SLR	acute		corn	shoot dw	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	hormesis	7100	6240		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	961	820		closed glass jars, mech mixing
ESG 2000	SLR	acute		corn	root length	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	logistic	3960	2290		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	468	238		closed glass jars, mech mixing
ESG 2000	SLR	acute		corn	root ww	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	hormesis	6910	6260		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	929	823		closed glass jars, mech mixing
ESG 2000	SLR	acute		corn	root dw	11 (0, 1, 2, 3, 5, 6, 8, 15, 25, 50, 100 mg/g)	3	hormesis	6650	6020		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	887	784		closed glass jars, mech mixing
ESG 2000	artificial	acute	9 days	red fescue	shoot length	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	logistic	5070	2790		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	635	304		closed glass jars, mech mixing
ESG 2000	artificial	acute	9 days	red fescue	root length	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	logistic	4350	2440		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	526	258		closed glass jars, mech mixing
ESG 2000	artificial	acute	9 days	red fescue	total ww	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	hormesis	5790	4240		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	748	509		closed glass jars, mech mixing
ESG 2000	artificial	acute	9 days	red fescue	total dw	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	hormesis	4250	3370		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	511	384		closed glass jars, mech mixing
ESG 2000	SLR	acute	9 days	red fescue	shoot length	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	logistic	4110	2680		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	490	289		closed glass jars, mech mixing
ESG 2000	SLR	acute	9 days	red fescue	root length	10 (0, 1, 2, 3, 5, 6, 8, 12, 15,	3	gompertz	2930	1430		CAN/CGSB-3.0	log(initial meas)	323	133		closed glass jars, mech

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.	Notes
						25 mg/g)						No. 14.3-94	1.232 log(nominal) 1.762				mixing
ESG 2000	SLR	acute	9 days	red fescue	total ww	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	logistic	4330	3400		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	523	388		closed glass jars, mech mixing
ESG 2000	SLR	acute	9 days	red fescue	total dw	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3	logistic	3890	2970		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	458	328		closed glass jars, mech mixing
ESG 2000	artificial	reproduction	35-36 days	O. folsomi	adult mortality	10 (0, 0.025, 0.05, 0.1, 0.5, 1, 2, 3, 5, 8 mg/g	10	logistic	3420	1940		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	391	194		closed units for 7 d, then loosely closed, mech mixing, questionable results due to low reproduction in control
ESG 2000	artificial	reproduction	35-36 days	O. folsomi	adult mortality	10 (0, 0.025, 0.05, 0.1, 0.5, 1, 2, 3, 5, 8 mg/g	10	NOAEC = 2000, LOAEC = 3000				CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762				
ESG 2000	artificial	reproduction	35-36 days	O. folsomi	# progeny	10 (0, 0.025, 0.05, 0.1, 0.5, 1, 2, 3, 5, 8 mg/g	10	hormesis	2890	2170		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	318	223		closed units for 7 d, then loosely closed, mech mixing, questionable results due to low reproduction in control
ESG 2000	artificial	reproduction	35-36 days	O. folsomi	# progeny	10 (0, 0.025, 0.05, 0.1, 0.5, 1, 2, 3, 5, 8 mg/g	10	NOAEC = 0, LOAEC (sig at 25, but not at 5000 and 8000)				CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762				
ESG 2000	SLR	reproduction	35-36 days	O. folsomi	adult mortality	11 (0, 0.05, 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 4, 5 mg/g	10	logistic	3760	2630		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	439	283		closed units for 7 d, then loosely closed, mech mixing
ESG 2000	SLR	reproduction	35-36 days	O. folsomi	adult mortality	11 (0, 0.05, 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 4, 5 mg/g	10	NOAEC=2000, LOAEC = 3000				CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762				

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.	Notes
ESG 2000	SLR	reproduction	35-36 days	O. folsomi	# progeny	11 (0, 0.05, 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 4, 5 mg/g	10	ln transformed data, logistic	4210	2350		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	505	246		closed units for 7 d, then loosely closed, mech mixing
ESG 2000	SLR	reproduction	35-36 days	O. folsomi	# progeny	11 (0, 0.05, 0.1, 0.2, 0.3, 0.5, 1, 2, 3, 4, 5 mg/g	10	NOAEC=2000, LOAEC = 3000				CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762				
ESG 2000	artificial	lethality	7 days	O. folsomi	mortality	8 (0, 0.5, 1, 2, 3, 5, 8, 10 mg/g)	3	Spearman-Karber	5960	ND		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	775	ND		closed test units
ESG 2000	SLR	lethality	7 days	O. folsomi	mortality	8 (0, 0.5, 1, 2, 3, 5, 8, 10 mg/g)	3	Spearman-Karber	4190	ND		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	502	ND		closed test units
ESG 2000	artificial	lethality	7 days	E. andrei	mortality	7 (0, 0.1, 0.5, 1, 2, 3, 5 mg/g)	2	Spearman-Karber	1230	ND		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	111	ND		closed test units, mech mixing,
ESG 2000	artificial	lethality	7 days	E. andrei	mortality	7 (0, 0.1, 0.5, 1, 2, 3, 5 mg/g)	2	Spearman-Karber	2080	ND		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	212	ND		open test units, mech mixing
ESG 2000	artificial	lethality	14 days	E. andrei	mortality	7 (0, 0.1, 0.5, 1, 2, 3, 5 mg/g)	2	Spearman-Karber	1150	ND		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	102	ND		closed test units, mech mixing,
ESG 2000	artificial	lethality	14 days	E. andrei	mortality	7 (0, 0.1, 0.5, 1, 2, 3, 5 mg/g)	2	Spearman-Karber	1860	ND		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	185	ND		open test units, mech mixing
ESG 2000	SLR	lethality	7 days	E. andrei	mortality	7 (0, 0.1, 0.5, 1, 2, 3, 5 mg/g)	2	Spearman-Karber	630	ND		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	49	ND		closed test units, mech mixing,
ESG 2000	SLR	lethality	7 days	E. andrei	mortality	7 (0, 0.1, 0.5, 1, 2, 3, 5 mg/g)	2	Spearman-Karber	710	ND		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	56	ND		open test units, mech mixing
ESG 2000	SLR	lethality	14 days	E. andrei	mortality	7 (0, 0.1, 0.5, 1, 2, 3, 5	2	Spearman-Karber	400	ND		CAN/CGSB-3.0	log(initial meas)	28	ND		closed test units, mech

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.	Notes
						mg/g)						No. 14.3-94	1.232 log(nominal) 1.762				mixing,
ESG 2000	SLR	lethality	14 days	E. andrei	mortality	7 (0, 0.1, 0.5, 1, 2, 3, 5 mg/g)	2	Spearman-Karber	710	ND		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	56	ND		open test units, mech mixing
Stephenson unpublished data	Chernozem	lethality	7 days	E. andrei	mortality			Spearman-Karber	1072	ND		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	94	ND		
Stephenson unpublished data	Chernozem	lethality	14 days	E. andrei	mortality			Spearman-Karber	1072	ND		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	94	ND		
Cermak unpublished data	chernozem	definitive	14 days	barley	shoot length	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3-6	gompertz	1950	1130		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	196	100		
Cermak unpublished data	chernozem	definitive	14 days	barley	shoot dw	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3-6	gompertz	1610	970		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	154	83		
Cermak unpublished data	chernozem	definitive	14 days	barley	root length	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3-6	gompertz	2080	1260		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	212	114		
Cermak unpublished data	chernozem	definitive	14 days	barley	root dw	10 (0, 1, 2, 3, 5, 6, 8, 12, 15, 25 mg/g)	3-6	gompertz	1330	700		CAN/CGSB-3.0 No. 14.3-94	log(initial meas) 1.232 log(nominal) 1.762	122	55		

Source: Cermak and Tindal (2006)
Data used in deriving the F2 guideline are presented in red
*Test species were:
Eisenia andrei (earthworm)
Orthoonychiurus folsomi (collembola, formerly *Onychiurus folsomil*)
Medicago sativa (alfalfa)
Hordeum vulgare (barley)
Zea mays (corn)
Festuca rubra (red fescue)

Table E.3: Summary of F2 Toxicity Studies

Document	Product	Contaminant Source	Soil Types	Test Species	Test Type	Analytical Method	Analytical Recovery	Key Points
ESG 2003	Fraction 2 (>nC10-nC16)	Federated crude oil, distilled using a modified ASTM D1160	Artificial (coarse) and Chernozem (fine) soils	Plants Earthworms collembola	Laboratory assays; acute lethality, definitive plant growth and invertebrate reproductio n	Environment Canada method: soils sonicated in 1:1 DCM:hexane, analyzed by GC-FID	Within the concentration range for toxicity, the measured concentration was on average 33% of nominal	•Values from this report used to calculate the PHC CWS ecological soil contact values for Fraction 2 •Concentration-dependent loss of F2 observed during treatment preparation •Results similar for tests in artificial and Chernozem soils •Results similar between acute and longer duration tests •Earthworms most sensitive •Four IC20 data points occur below the lowest test concentration. All were included in the analysis.
Cermak et al. 2005	Fraction 2 (>nC10-nC16)	Federated crude oil, distilled using ASTM D2892	Chernozem soil (fine)	Earthworms	Laboratory assays; acute lethality	EnviroTest Laboratories method: soxhlet extracted using 1:1 DCM:hexane, silica gel clean-up, separation into aliphatics and aromatics on alumina column, analysis of aliphatics and aromatics by GC-FID	Measured conc. = 0.772(nominal conc.) - 161	•Data amenable to the determination of LC25s •Earthworm acute lethality results were similar to those from other tests on a nominal basis, but slightly greater than those from other tests on a measured concentration basis •A loss of F2 from the soil was observed during treatment preparation, but it was not concentration-dependent
ESG unpublishe d data	Fraction 2 (>nC10-nC16)	Federated crude oil, distilled using a modified ASTM D1160	Chernozem soil (fine)	Plants (barley) earthworms	Laboratory assays; definitive plant growth and earthworm acute lethality	Environment Canada method: soils sonicated in 1:1 DCM:hexane, analyzed by GC-FID	Within the concentration range for toxicity, the measured concentration was on average 33% of nominal	•Plant results similar to those observed in ESG 2003 for barley •Earthworm acute lethality (LC50) values were similar to those from ESG 2003 •Six LC/IC20 data points occur below the lowest test concentration. All were included in the analysis.

Source: Cermak and Tindal (2006)

Table E.4: Available Data for F2

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.
Cermak et al. 2005	Chernozem	lethality	7 days	*E. andrei*	mortality	8 (0, 0.2, 0.4, 0.6, 0.8, 1, 2, 4 mg/g)	3	logit	960	750	790	soxhlet extraction 1:1 hexane:DCM, silica gel, alumina separation into aliphatics/aromatics, GC-FID	F2 meas = 0.772 (nominal) =161	580	420	448.88
Cermak et al. 2005	Chernozem	lethality	7 days	*E. andrei*	mortality	6 (0, 0.5, 0.7, 1, 1.4, 1.9 mg/g)	3	Spearman-Karber	680	ND		soxhlet extraction 1:1 hexane:DCM, silica gel, alumina separation into aliphatics/aromatics, GC-FID	F2 meas = 0.772 (nominal) =161	360	ND	ND
Cermak et al. 2005	Chernozem	lethality	7 days	*E. andrei*	mortality	6 (0, 0.4, 0.6, 0.8, 1, 1.2) mg/g	4	logit	800	720	740	soxhlet extraction 1:1 hexane:DCM, silica gel, alumina separation into aliphatics/aromatics, GC-FID	F2 meas = 0.772 (nominal) =161	460	390	410.28
Cermak et al. 2005	Chernozem	lethality	14 days	*E. andrei*	mortality	8 (0, 0.2, 0.4, 0.6, 0.8, 1, 2, 4 mg/g)	3	logit	960	750	790	soxhlet extraction 1:1 hexane:DCM, silica gel, alumina separation into aliphatics/aromatics, GC-FID	F2 meas = 0.772 (nominal) =161	580	420	**448.88**
Cermak et al. 2005	Chernozem	lethality	14 days	*E. andrei*	mortality	6 (0, 0.5, 0.7, 1, 1.4, 1.9 mg/g)	3	Spearman-Karber	680	ND		soxhlet extraction 1:1 hexane:DCM, silica gel, alumina separation into aliphatics/aromatics, GC-FID	F2 meas = 0.772 (nominal) =161	360	ND	ND
Cermak et al. 2005	Chernozem	lethality	14 days	*E. andrei*	mortality	6 (0, 0.4, 0.6, 0.8, 1, 1.2) mg/g	4	logit	790	720	730	soxhlet extraction 1:1 hexane:DCM, silica gel, alumina separation into aliphatics/aromatics, GC-FID	F2 meas = 0.772 (nominal) =161	450	390	**402.56**
ESG 2003	Chernozem	definitive	21 days	alfalfa	root length	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	logistic	1860	670		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	613.8	**221.1**	
ESG 2003	Chernozem	definitive	21 days	alfalfa	root wet weight	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	logistic	4740	2310		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1564.2	**762.3**	
ESG 2003	Chernozem	definitive	21 days	alfalfa	root dry weight	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20	3-7	logistic	5120	2320		extraction by sonication with 1:1 hexane:DCM, GC-	average 33% of nominal over range of 500 -	1689.6	**765.6**	

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.
						mg/g)						FID	6000 mg/kg nominal			
ESG 2003	Chernozem	definitive	21 days	alfalfa	shoot length	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	exponential	2710	1380		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	894.3	**455.4**	
ESG 2003	Chernozem	definitive	21 days	alfalfa	shoot wet weight	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	logistic	1680	580		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	554.4	**191.4**	
ESG 2003	Chernozem	definitive	21 days	alfalfa	shoot dry weight	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	logistic	1370	440		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	452.1	**145.2**	
ESG 2003	Chernozem	definitive	21 days	alfalfa	emergence	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	anova	NOEC = 8000			extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	NOEC = 2640		
ESG 2003	Chernozem	definitive	21 days	alfalfa	emergence	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	anova	LOEC = 12000			extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	LOEC = 3960		
ESG 2003	Artificial soil	acute	8 days	barley	shoot length	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	logistic	6370	1930		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	2102.1	636.9	
ESG 2003	Artificial soil	acute	8 days	barley	root length	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	logistic	3440	2300		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1135.2	759	
ESG 2003	Artificial soil	acute	8 days	barley	shoot wet weight	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	logistic	7510	4150		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	2478.3	1369.5	
ESG 2003	Artificial soil	acute	8 days	barley	shoot dry weight	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	logistic	7830	4290		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	2583.9	1415.7	
ESG 2003	Artificial soil	acute	8 days	barley	root wet weight	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	logistic	4760	2770		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1570.8	914.1	

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.
ESG 2003	Artificial soil	acute	8 days	barley	root dry weight	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	logistic	4180	2710		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1379.4	894.3	
ESG 2003	Artificial soil	acute	8 days	barley	emergence	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	anova	NOEC = 6000			extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	NOEC = 1980		
ESG 2003	Artificial soil	acute	8 days	barley	emergence	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	anova	LOEC = 8000			extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	LOEC = 2640		
ESG 2003	Chernozem	acute	8 days	barley	root length	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	logistic	2770	1150		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	914.1	379.5	
ESG 2003	Chernozem	acute	8 days	barley	root wet weight	1 0 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	logistic	4460	1990		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1471.8	656.7	
ESG 2003	Chernozem	acute	8 days	barley	root dry weight	1 0 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	logistic	4370	1860		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1442.1	613.8	
ESG 2003	Chernozem	acute	8 days	barley	shoot length	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	logistic	7150	2460		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	2359.5	811.8	
ESG 2003	Chernozem	acute	8 days	barley	shoot wet weight	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	logistic	6610	2830		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	2181.3	933.9	
ESG 2003	Chernozem	acute	8 days	barley	shoot dry weight	1 0 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 25 mg/g)	4	logistic	8240	4350		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	2719.2	1435.5	
ESG 2003	Chernozem	definitive	13 days	barley	root length	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	logistic	4550	1910		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1501.5	**630.3**	
ESG 2003	Chernozem	definitive	13 days	barley	root wet weight	10 (0, 0.5, 1, 3, 5,	3-6	logistic	2390	1620		extraction by sonication with 1:1	average 33% of nominal over	788.7	**534.6**	

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.
						6, 8, 12, 15, 20 mg/g)						hexane:DCM, GC-FID	range of 500 - 6000 mg/kg nominal			
ESG 2003	Chernozem	definitive	13 days	barley	root dry weight	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	logistic	2510	1190		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	828.3	**392.7**	
ESG 2003	Chernozem	definitive	13 days	barley	shoot length	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	logistic	4130	1350		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1362.9	**445.5**	
ESG 2003	Chernozem	definitive	13 days	barley	shoot wet weight	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	logistic	2430	1060		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	801.9	**349.8**	
ESG 2003	Chernozem	definitive	13 days	barley	shoot dry weight	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	logistic	2590	970		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	854.7	320.1	
ESG 2003	Chernozem	definitive	13 days	barley	emergence	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	anova	NOEC = 8000			extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	NOEC = 2640		
ESG 2003	Chernozem	definitive	13 days	barley	emergence	10 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20 mg/g)	3-6	anova	LOEC = 12000			extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	LOEC = 3960		
ESG 2003	Chernozem	definitive	14 days	northern wheatgrass	root length	11 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20, 30 mg/g)	3-6	Gompertz	2320	260		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	765.6	**85.8**	
ESG 2003	Chernozem	definitive	14 days	northern wheatgrass	root wet weight	11 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20, 30 mg/g)	3-6	Gompertz	1560	300		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	514.8	**99**	
ESG 2003	Chernozem	definitive	14 days	northern wheatgrass	root dry weight	11 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20, 30 mg/g)	3-6	Gompertz	1370	190		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	452.1	**62.7**	
ESG 2003	Chernozem	definitive	14 days	northern wheatgrass	shoot length	11 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20, 30 mg/g)	3-6	logistic	7440	3310		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg	2455.2	**1092.3**	

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.
													nominal			
ESG 2003	Chernozem	definitive	14 days	northern wheatgrass	shoot wet weight	11 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20, 30 mg/g)	3-6	logistic	2770	960		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	914.1	**316.8**	
ESG 2003	Chernozem	definitive	14 days	northern wheatgrass	shoot dry weight	11 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20, 30 mg/g)	3-6	Gompertz	3150	910		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1039.5	**300.3**	
ESG 2003	Chernozem	definitive	14 days	northern wheatgrass	emergence	11 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20, 30 mg/g)	3-6	anova	NOEC non-monotonic			extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	NOEC non-monotonic		
ESG 2003	Chernozem	definitive	14 days	northern wheatgrass	emergence	11 (0, 0.5, 1, 3, 5, 6, 8, 12, 15, 20, 30 mg/g)	3-6	anova	LOEC = 8000			extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	LOEC = 2640		
ESG 2003	Artificial soil	Lethality	7 days	*E. andrei*	Mortality	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	Spearman-Karber	1190	ND		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	392.7	ND	
ESG 2003	Chernozem	Lethality	7 days	*E. andrei*	Mortality	8 (0, 0.1, 0.3, 0.5, 1, 2, 3, 6 mg/g)	3	Spearman-Karber	1030	ND		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	339.9	ND	
ESG 2003	Artificial soil	Lethality	14 days	*E. andrei*	Mortality	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	Spearman-Karber	1150	ND		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	379.5	ND	
ESG 2003	Chernozem	Lethality	14 days	*E. andrei*	Mortality	8 (0, 0.1, 0.3, 0.5, 1, 2, 3, 6 mg/g)	3	Spearman-Karber	530	ND		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	174.9	ND	
ESG 2003	Chernozem	reproduction	62-63 days	*E. andrei*	adult survival	10 (0, 0.029, 0.041, 0.059, 0.084, 0.12, 0.17, 0.245, 0.35, 0.5, mg/g)	10		No sig effect at 500			extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal			
ESG 2003	Chernozem	reproduction	62-63 days	*E. andrei*	# progeny	10 (0, 0.029, 0.041, 0.059, 0.084, 0.12, 0.17, 0.245,	10	hormesis	490	350		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg	161.7	**115.5**	

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.
						0.35, 0.5, mg/g)							nominal			
ESG 2003	Chernozem	reproduction	62-63 days	*E. andrei*	progeny ww	10 (0, 0.029, 0.041, 0.059, 0.084, 0.12, 0.17, 0.245, 0.35, 0.5, mg/g)	10	logistic	590	420		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	194.7	**138.6**	
ESG 2003	Chernozem	reproduction	62-63 days	*E. andrei*	progeny dw	10 (0, 0.029, 0.041, 0.059, 0.084, 0.12, 0.17, 0.245, 0.35, 0.5, mg/g)	10	logistic	580	400		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	191.4	**132**	
ESG 2003	Artificial soil	Lethality	14 days	*L. terrestris*	Mortality	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	Spearman -Karber	1100	ND		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	363	ND	
ESG 2003	Chernozem	Lethality	14 days	*L. terrestris*	Mortality	8 (0, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	3	Spearman -Karber	1120	ND		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	369.6	ND	
ESG 2003	Artificial soil	Lethality	7 days	*O. folsomi*	Mortality	9 (0, 0.5, 1, 2, 3, 5, 8, 10, 25 mg/g)	3	Spearman -Karber	2920	ND		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	963.6	ND	
ESG 2003	Chernozem	Lethality	7 days	*O. folsomi*	Mortality	9 (0, 0.5, 1, 2, 3, 5, 8, 10, 25 mg/g)	3	Spearman -Karber	3230	ND		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1065.9	ND	
ESG 2003	Chernozem	reproduction	35-36 days	*O. folsomi*	adult survival	10 (0, 0.025, 0.05, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	10		no sig effect at 3000			extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal			
ESG 2003	Chernozem	reproduction	35-36 days	*O. folsomi*	adult fecundity	10 (0, 0.025, 0.05, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	10		1310	500		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	432.3	165	
ESG 2003	Chernozem	reproduction	35-36 days	*O. folsomi*	# progeny	10 (0, 0.025, 0.05, 0.1, 0.3, 0.5, 0.8, 1, 2, 3 mg/g)	10	Gompertz	1470	640		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	485.1	**211.2**	
ESG unpublished data	Chernozem	Lethality	14 days	*E. andrei*	Mortality	7 (0, 0.2, 0.4, 0.6, 0.8, 1, 1.5 mg/g)	3	probit	720	620	640	extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	237.6	204.6	**211.2**

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.
ESG unpublished data	Chernozem	Lethality	14 days	*E. andrei*	Mortality	7 (0, 0.2, 0.4, 0.6, 0.8, 1, 1.5 mg/g)	3	probit	820	710	730	extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	270.6	234.3	**240.9**
ESG unpublished data	Chernozem	Lethality	14 days	*E. andrei*	Mortality	7 (0, 0.2, 0.4, 0.6, 0.8, 1, 1.5 mg/g)	3	probit	920	850	870	extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	303.6	280.5	**287.1**
ESG unpublished data	Chernozem	definitive	14 days	barley	shoot length	8 (0, 1, 3, 5, 8, 12, 15, 20 mg/g)	3-6	logistic	4150	1160		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1369.5	**382.8**	
ESG unpublished data	Chernozem	definitive	14 days	barley	shoot dry weight	8 (0, 1, 3, 5, 8, 12, 15, 20 mg/g)	3-6	logistic	2010	760		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	663.3	**250.8**	
ESG unpublished data	Chernozem	definitive	14 days	barley	root length	8 (0, 1, 3, 5, 8, 12, 15, 20 mg/g)	3-6	ICPIN	4000	1980		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1320	**653.4**	
ESG unpublished data	Chernozem	definitive	14 days	barley	root dry weight	8 (0, 1, 3, 5, 8, 12, 15, 20 mg/g)	3-6	ICPIN	2600	1080		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	858	**356.4**	
ESG unpublished data	Chernozem	definitive	14 days	barley	shoot length	7 (0, 1, 3, 5, 8, 12, 15 mg/g)	3-6	logistic	4500	1380		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1485	**455.4**	
ESG unpublished data	Chernozem	definitive	14 days	barley	shoot dry weight	7 (0, 1, 3, 5, 8, 12, 15 mg/g)	3-6	logistic	1500	600		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	495	**198**	
ESG unpublished data	Chernozem	definitive	14 days	barley	root length	7 (0, 1, 3, 5, 8, 12, 15 mg/g)	3-6	logistic	2620	900		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	864.6	**297**	
ESG unpublished data	Chernozem	definitive	14 days	barley	root dry weight	7 (0, 1, 3, 5, 8, 12, 15 mg/g)	3-6	logistic	1750	910		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	577.5	**300.3**	
ESG unpubli	Chernozem	definitive	14 days	barley	shoot length	7 (0, 1, 3, 5, 8, 12, 15 mg/g)	3-6	logistic	5690	2320		extraction by sonication with 1:1	average 33% of nominal over	1877.7	**765.6**	

Study	Soil	Test type	Duration	Species *	Endpoint	Nominal test concentrations	Rep	Model	Nominal LC/IC50 (mg/kg dw)	Nominal LC/IC20 (mg/kg dw)	Nominal LC/IC25 (mg/kg dw)	Chemical analysis method	Relationship for measured to nominal concentration	Measured LC/IC50 mg/kg d.w.	Measured LC/IC20 mg/kg d.w.	Measured LC/IC25 mg/kg d.w.
shed data												hexane:DCM, GC-FID	range of 500 - 6000 mg/kg nominal			
ESG unpublished data	Chernozem	definitive	14 days	barley	shoot dry weight	7 (0, 1, 3, 5, 8, 12, 15 mg/g)	3-6	logistic	2490	1010		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	821.7	333.3	
ESG unpublished data	Chernozem	definitive	14 days	barley	root length	7 (0, 1, 3, 5, 8, 12, 15 mg/g)	3-6	Gompertz	2110	520		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	696.3	171.6	
ESG unpublished data	Chernozem	definitive	14 days	barley	root dry weight	7 (0, 1, 3, 5, 8, 12, 15 mg/g)	3-6	ICPIN	3050	390		extraction by sonication with 1:1 hexane:DCM, GC-FID	average 33% of nominal over range of 500 - 6000 mg/kg nominal	1006.5	128.7	

Source: Cermak and Tindal (2006)
Data used in deriving the F2 guideline are presented in red
*Test species were:
Eisenia andrei (earthworm)
Lumbricus terrestris (earthworm)
Orthoonychiurus folsomi (collembola, formerly *Onychiurus folsomil*)
Medicago sativa (alfalfa)
Hordeum vulgare (barley)
Elymus lanceolatus (northern wheatgrass, formerly *Elytrigia dasystachyum* and *Agropyron dasystachyum*)

APPENDIX F: NEW ECOTOXICOLOGICAL DATA AND ANALYSIS FOR PHC FRACTIONS F3 AND F4

F.1 Introduction

This Appendix is a stand-alone report that was undertaken on behalf of the CCME Ecological Criteria Advisory Sub-Group (the Eco Sub-Group) to provide a solid scientific basis for revisions to the ecological direct soil contact guidelines for F3 and F4. Numbering and tables have been reformatted but all other content reflects the original report, submitted to the Eco Sub-Group.

F.1.1 Objective and Scope of Work

The objective of the work described in this Appendix was to identify whether ecotoxicological work conducted since the release of the 2001 PHC CWS supports the existing ecological soil contact guidelines for PHCs or whether these new data suggest that a higher or lower guideline would be appropriate.

The scope of work for the project included the following tasks:

1. Review all relevant data sources, as summarized in Table F.1.
2. Compile relevant ecotoxicological data from each project, with particular attention to measured analytical hydrocarbon concentrations and the methodology used to obtain those measurements.
3. For "single" concentration studies (see Table F.1):
    a. organize the data into a "Ranked Response Distribution" i.e., express the non-redundant data for each endpoint as a percentage of control response and rank the data; and,
    b. where possible, determine whether each dataset supports existing guideline values, or higher or lower values.
4. For "multiple" concentration studies (see Table F.1):
    a. where possible, determine whether each dataset supports existing guideline values, or higher or lower values by considering the following 3 scenarios:
        i. using the existing guideline derivation methodology in the PHC CWS (based on EC_{50}/LC_{50} data);
        ii. using the CCME (2006a) proposed methodology (based on EC_{25}/LC_{25} data);
        iii. using a hybrid method proposed at the November 21 meeting (based on EC_{25} plant data and EC_{50}/LC_{50} invertebrate data.
5. Based on the weight of evidence of all the available data, and in consultation with the rest of the Eco Sub-Group, make overall recommendations for each existing ecological direct soil contact guideline value to retain or change the existing value, with detailed rationale.

6. Generate a brief summary report, and present the findings to the PHC CWS Eco Sub-Group.

This report covers the above tasks for hydrocarbon fractions F3 and F4. A parallel project is being undertaken for fractions F1 and F2 (See Appendix E).

F.1.2 Background

F.1.2.1 Available Studies

Available studies on the ecotoxicity of petroleum hydrocarbon fractions F1 to F4 are summarized in Table F.1. For the studies that have data relevant to F3 or F4, Table F.2 summarizes the organisms considered by each study. As can be seen, the Visser *et al*. (2003), and Visser (2005a) field studies consider a much wider range of species than any of the other studies, and for this reason, these studies are considered of key importance in setting guideline values.

F.1.2.2 Methodology

Protocol and Guideline Basis

The original PHC CWS guideline values were generated using a series of protocols that were developed in parallel with that project. Current CCME (2006a) protocols are largely based on the PHC CWS protocols, but have evolved in some aspects.

The original PHC CWS guidelines were calculated based on a distribution of IC/LC_{50} data ("the CCME (2000) Approach"). More recent guidance from CCME (2006a) proposed basing guidelines on a distribution of IC/LC_{25} data ("the CCME (2006a) Approach"). A third approach was proposed in the Eco Sub-Group ("the Hybrid Approach") in which IC_{25} data was used for plants and IC/LC_{50} data for invertebrates. All three of these approaches were evaluated in this report.

Ranked Response Distribution

The PHC CWS calculated guidelines using a species sensitivity distribution of 50^{th} percentile effect level data, which is a ranked distribution of IC/LC_{50} data for non-redundant endpoints. Guidelines were calculated as the 25^{th} or 50^{th} percentiles of this distribution.

The field-based studies discussed in this report investigate either one or two treatment rates, and do not lend themselves to calculating IC/LC_{50} or IC/LC_{25} values. An alternative way to use these data is proposed here. Data from the field-based studies are presented as the response relative to controls for a range of species/endpoints. For each exposure concentration, the non-redundant data were ranked and presented as "Ranked Response Distributions" (RRDs).

RRDs were interpreted as follows.

- Under the CCME (2000) Approach, an RRD was deemed to meet guideline requirements for agricultural/residential land use if the 25^{th} percentile of the RRD showed a response of at least 50% of the control response. Similarly, the level of adverse effects was deemed to be within the level implicit in the definition of the guideline for

commercial/industrial land use if the 50th percentile of the RRD showed a response of at least 50% of the control response.

- Under the CCME (2006a) Approach, an RRD was deemed to meet guideline requirements for agricultural/residential land use if the 25th percentile of the RRD showed a response of at least 75% of the control response. Similarly, the level of adverse effects was deemed to be within the level implicit in the definition of the guideline for commercial/industrial land use if the 50th percentile of the RRD showed a response of at least 75% of the control response.
- The Hybrid Approach did not lend itself to analysis of RRDs.

Calculation of Percentiles

The guideline calculation protocols call for the calculation of 25th and 50th percentiles of various distributions. In this report, all percentiles were calculated using the "PERCENTILE" function in Microsoft Excel.

F1.2.3 Data Redundancy

The strategy adopted in this report for reducing the reliance on redundant data points was based on that provided in CCME (2008):

1. *Data points for the same species that are redundant should be combined into a single composite response concentration calculated as the geometric mean of the individual values. Individual toxicity data points are considered redundant if they:*
    a. *represent different response levels for the same type of response under the same or highly similar exposure conditions; or,*
    b. *were based on different response data which are known to be directly, causally connected (e.g., plant wet weight and dry weight).*
2. *If toxicity data are available for the same species, response type, response level and exposure conditions, based on different exposure periods, then the data for the longer exposure period should be given preference.*
3. *In some cases, data points may also be combined if the data are for the same species and response type but for different soil types, particularly if including all of the data points will result in a significant bias of the EC_{25} distribution towards a single species, though it should be noted that variations in toxicity due to the effects of exposure conditions are a valid part of the overall sensitivity distribution. Professional judgement should be used in these cases.*

Based on the above, it is clear that wet mass and dry mass for the same endpoint should be considered redundant. Based on precedent from the existing PHC CWS derivations, plant shoot length, shoot mass, root length and root mass were considered non-redundant, and invertebrate number of juveniles and mass of juveniles were also considered non-redundant. However, invertebrate adult fecundity was considered redundant with number of juveniles produced, and fecundity was not used in the derivation of guideline values.

F1.3 Report Organization

Data for PHC Fraction F3 for fine soil are discussed in Section F.2. Data for PHC Fraction F3 for coarse soil are discussed in Section F.3. Data for PHC Fraction F4 are discussed in Section F.4. A summary is provide in Section F.5, and report closure and references are provided in Sections F.6 and F.7, respectively.

F2 PHC Fraction F3 in Fine Soil

F2.1 Approach

The existing guideline for ecological direct soil contact for F3 in fine soil and agricultural land use is 800 mg/kg. This value was calculated as follows. The 25th percentile of the species sensitivity distribution of EC_{50}/LC_{50} values (combined plants and soil invertebrates) was 1,300 mg/kg, based on nominal exposure. This value was multiplied by a factor of 0.31 to give 400 mg/kg reflecting what was believed to be the analytical recovery of F3. Finally the resulting value was multiplied by 2 to reflect the perceived difference in toxicity between fine and coarse soils.

A exhaustive study on the recovery of F3 hydrocarbons from chernozem soil using the CCME reference method and including over 70 separate analyses has suggested that the recovery of F3 from chernozem soil may be close to 100%, which would suggest that the F3 guideline for fine agricultural/residential soil should be closer to the nominal value of 1,300 mg/kg than the current 800 mg/kg. However, the Eco Sub-Group was not able to resolve the discrepancy between this finding, and the recovery of 31% found in the CCME (2000) work. The Eco Sub-Group did note, however, that the chemical analysis conducted in CCME (2000) was conducted using a non-standard method, and that full QA/QC data have not been made available for this work.

Based on the above uncertainty in the 31% analytical recovery value that was used in the PHC CWS, it was decided to take a weight of evidence approach to the guideline for F3 in fine soil by evaluating each relevant study separately, and making no attempt to combine the data from all the available studies into a single guideline value.

Particular attention was paid to the Visser (2005a) field study, reflecting i) the greater number of species considered in this study, ii) the fact that this study measured actual crop yields and invertebrate populations in the field; iii) the chronic duration of most of the tests; and iv) the fact that measured analytical concentrations were available that could be tied to results from the CCME reference method with a good degree of confidence.

Less confidence was placed on the Cermak *et al*. (2005) data due to the difficulty in linking the analytical methodology required for that work to standard CCME reference method analyses.

F2.2 Single Concentration Studies

In Visser *et al*. (2003) and Visser (2005a), Dr. Suzanne Visser of the University of Calgary presented data from a long-term field study that was initiated in 1999. The degradation and ecotoxicity of fresh Alberta Federated crude oil, applied to sandy loam field plots at 1.2% (w/w)

(discussed in Section F.3) and to clay loam field plots at 1.7% and 3.7% (w/w) (discussed in this Section), were monitored with the following objectives:

- to determine the degradation patterns of crude oil petroleum hydrocarbons (PHCs) in fine- and coarse-textured soils using analytical and soil respiration methods.
- to identify the length of time required for crude oil PHCs to achieve a stable degradation endpoint, and to determine the concentrations of PHC residuals in each of the two soil types when a stable endpoint was achieved.
- to monitor changes in ecotoxicity as fresh crude oil degrades in coarse- and fine-textured surface soils using standardized laboratory bioassays and field assessments for measuring the effects of PHCs on plants, macrofauna, mesofauna and microbial processes.
- to evaluate the environmental risks associated with PHC residuals remaining in coarse- and fine-textured surface soils following an extended period (three to four years) of weathering.

Analytical data from these studies indicate that, for periods 12 months and greater following application of Federated crude, only PHC fraction F3 exceeded guidelines, and accordingly, adverse effects observed at 12 months or greater were assumed to be related to F3 toxicity.

F2.2.1 Visser et al. (2003)

Selected ecotoxicity data from Visser *et al*. (2003) are presented in Table F.3, expressed as the response in the 1.7% or 3.7% contaminated soils as a percentage of the response in the corresponding control. Data presented are for plots in which a crop had not been seeded, assessed at 12 months after the soil was spiked with Federated crude oil. Data were also provided in Visser *et al*. (2003) for 0, 1, 3, 9 months after spiking. These earlier data had both F2 and F3 above the current agricultural/residential guideline, and hence it was unclear whether any toxicity was due to F2, F3, or a combination of the two.

Analytical Basis

All data in this study are presented on the basis of measured PHC concentrations. PHC analyses in this study were conducted using the Alberta G108 methodology (AENV 1992). Subsequent parallel analyses for F3 using both this method and the CCME method indicated that the recovery of F3 with the CCME method was lower than with the Alberta G108 (AENV 1992). Available data were regressed in Figure F.1, which yielded the following relationship:

$$CCME\ F3 = (0.6327 \times G108\ F3) + 87.178$$

The correlation coefficient (R^2) was 0.86. For consistency, this relationship was used to convert all the G108 F3 concentrations to equivalent CCME F3 concentrations.

Laboratory data presented in Table F.1 include acute (6-8 day) seed emergence and root elongation for barley, canola, and alfalfa, and acute (7 and 14 day) mortality for springtail (*Folsomia candida*) and earthworm (*Eisenia andrei*), respectively. These analyses were not

included in the guideline derivation process on account of the known lower sensitivity of these acute tests relative to longer duration chronic or definitive tests.

Non-redundant data are shaded in Table F.3 for the 1.7% and 3.7% treatments, respectively. The 25th percentile of the RRD for the 3.7% treatment is 79% which is greater than the 75% criterion, and hence suggests that the appropriate guideline level for F3 is above 3,100 mg/kg, based on this study alone (Table F.17).

F2.2.2 Visser (2005a)

This report is particularly relevant to assessing appropriate guideline values for F3 based on the large number of species considered, and also because it assessed actual effects on crop growth and invertebrate communities in a field setting, rather than relying solely on laboratory bioassays.

Analytical Basis

PHC concentrations measured using the Alberta G108 (AENV 1992) methodology were converted to CCME equivalent values in the same way as described in Section F.2.2.1 above.

Summary of Report Findings

In the clay loam soil, after 36 months weathering, the concentration of F2 and F4 had dropped below PHC CWS guideline levels for fine soil. However, F3 at 1,161 and 2,371 mg/kg in the 1.7% and 3.7% treatments, respectively, was still above guideline levels. Accordingly, any residual toxic effects from these treatments were assumed to be associated with the residual F3 concentrations. At these levels of residual hydrocarbon, there was no toxicity to plant growth, springtail survival or reproduction in laboratory tests. However, there was a significant decrease in earthworm reproduction in laboratory tests and significantly lower abundance of harvestmen and possibly springtails and mites in the field plots.

Data Summary and Comments

Data for the Turner Valley (fine soil) plots from Visser (2005a) are summarized in Tables F.4 (Plants) and F.5 (Invertebrates). Data are presented as the response for each endpoint for oiled soils (1.7% or 3.7%) as a percentage of the response in the control plots. The calculated CCME F3 concentration is presented for each plot. Data are presented for 24, 32, and 36 months after oil application.

Data were available for six different concentrations of F3 (three time points for each of 2 application rates). However, clear dose-response relationships did not exist for the majority of endpoints. Without a dose-response relationship, it was not possible to calculate effect concentration values such as EC_{25} and EC_{50}, and therefore it was not possible to define a species sensitivity distribution. Accordingly, the Ranked Response Distribution approach (introduced in Section F.1.2.2) is used here.

Ranked Response Distributions (RRDs) for the 1.7% and 3.7% treatments are presented in Figures F.2 and F.3. Data from 24, 32, and 36 months were considered to have essentially the same concentration of F3, represented by the arithmetic mean of the three concentrations (1,251 mg/kg and 2,458 mg/kg for the 1.7% and 3.7% treatments, respectively, Tables F.4 and F.5)..

Data from endpoints that are considered non-redundant are shaded in Tables F.4 and F.5. The shaded values for the different time periods were combined as their geometric mean, and these values were used to generate the RRDs in Figures F.2 and F.3.

Conclusions

Figure F.2 indicates that the 25th percentile of the RRD is an 79% response relative to controls for the 1.7% application between months 24 and 36 (mean F3 concentration = 1,251 mg/kg). At this concentration, therefore, 75% of the species/endpoints tested showed a reduction of less than 25% from the response in control values. This meets the criterion for acceptability that is implicit in the CCME (2000) Approach. It would also meet the criterion for the CCME (2006a) Approach.

Figure F.3 indicates that the 25th percentile of the RRD is a 58% response relative to controls for the 3.7% application between months 24 and 36 (mean F3 concentration = 2,458 mg/kg). At this concentration, therefore, 75% of the species/endpoints tested showed a reduction of more than 25% from the response in control values. This meets the criterion for acceptability that is implicit in the CCME (2000) Approach. However, it would not meet the criterion for the CCME (2006a) Approach.

Based on this analysis, therefore, and taken in isolation, the data in Visser (2005a) would appear to support an F3 guideline for fine soil of approximately 2,500 mg/kg under the CCME (2000) Approach, or an F3 guideline of more than 1,300 mg/kg under the CCME (2000) Approach (Table F.17).

F2.2.3 Axiom (2005)

This project was a collaborative effort between four research providers, with project direction being overseen by an eleven-member technical steering committee, chaired by Chris Meloche of Husky Energy. The primary objective of the project was to look for an empirical correlation between cyclodextrin-extractable F3 and ecotoxicity, and hence to develop a guideline for weathered/aged F3 based on analysis of cyclodextrin-extractable F3. The experimental phase of this project is now complete, and a final report is expected late 2005.

The primary focus of this project was to implement the following:

- identify a range of field-weathered F3-contaminated soils;
- analyze these soils for bioavailable hydrocarbon, using a cyclodextrin extraction methodology;
- conduct ecotoxicity tests to determine which of these soils would be considered toxic, based on criteria analogous to those used to develop the PHC CWS guidelines:
    - the Turner Valley 1.7% and 3.7% soils (Visser, 2005a) were submitted for the full battery of PHC CWS toxicity tests (definitive/chronic tests for 3 plant and 2 invertebrate species); and,

- a further 13 soils (11 fine, 2 coarse) were submitted for chronic earthworm testing only (earthworm reproduction was found to be the most sensitive species/endpoint to F3 in the PHC CWS).
- relate bioavailability to toxicity, and hence, if possible, develop a guideline for weathered F3 based on cyclodextrin-extractable F3.

Analytical Basis

All analytical data for PHCs reported in this project were obtained using the CCME reference method.

Data Summary and Comments

Relevant ecotoxicological data collected for this project are compiled here. All of the ecotoxicological work in this project was undertaken by Stantec Consulting Ltd., and is reported in detail in Stantec (2005).

Year 5 data for the Turner Valley (fine soil) plots from Axiom (2005) are summarized in Table F.6, with the non-redundant data being highlighted in red.

As with the Turner Valley 24-36 month data, clear dose-response relationships were not evident for many endpoints. Accordingly the "Ranked Response Distribution" (RRD) approach was also adopted for these data. RRDs for the Turner Valley year 5 soils are provided in Figures F.4 and F.5 for the 1.7% and 3.7% treatments, respectively.

Conclusions

Figure F.4 indicates that the 25th percentile of the RRD is an 86% response relative to controls for the 1.7% application at year 5 (F3 concentration = 1,362 mg/kg). Figure F.5 indicates that the 25th percentile of the RRD is an 80% response relative to controls for the 3.7% application at year 5 (F3 concentration = 2,545 mg/kg).

Based on this analysis, therefore, and taken in isolation, the data discussed in this Section would appear to support an F3 guideline for agricultural/residential land use and fine soil of greater than 2,500 mg/kg using either the CCM E(2000) or CCME (2006a) Approaches (Table F.17).

F2.3 Multi-Concentration Studies

Ecotoxicological data for multi-concentration studies relevant to guideline derivation for F3 in fine soil are summarized in Table F.7.

F2.3.1 Cermak et al. (2005)

The primary research provider for this project was Janet Cermak, a doctoral student at the University of Waterloo. The project had three main phases:

1. To determine the toxicity of sub-Fractions of CCME Fraction 3 (F3a: >nC16-nC23; F3b: >nC23-nC34) to an earthworm, collembolan and plant species.
2. To determine the acute toxicity of binary combinations of Fractions 2, 3a and 3b (F2/F3a, F3a/F3b) to earthworms.

3. To determine the uptake and elimination of the aliphatic and aromatic portions of individual and binary combinations of Fractions 2, 3a and 3b by earthworms.

This project has made and is making a significant advance in our understanding of the mechanisms of toxicity for Fractions F2 and F3. It also provides additional toxicity testing data for F3 spiked into an orthic black chernozem, which is texturally a fine soil. Interim results are presented in Cermak *et al*. (2005).

Analytical Basis

The extraction of soils did not follow CCME protocol. Instead, soil samples were extracted and analyzed in the following manner. An aliquot of soil was mixed with anhydrous sodium sulphate and subjected to Soxhlet extraction overnight using a dichloromethane:hexane (1:1) solvent mixture. The resulting extract was concentrated and cleaned up via gel permeation chromatography. This extract was further concentrated, exchanged into pentane and then separated into saturate/monoaromatic and PAH/PASH chemical class fractions via calibrated neutral alumina column fractionation. During fractionation, the extract was placed on the column and first eluted with pentane to obtain the saturate/monoaromatic fraction, and then with benzene to obtain the PAH/PASH fraction. The saturate/monoaromatic and PAH/PASH fractions were each concentrated to 1.0 mL and analyzed by gas chromatography-flame ionization detection following the CCME protocol (CCME, 2001) with the following exception: an additional standard (*n*C23) was used to allow separate reporting of Fraction 3 as Sub-Fractions F3a and F3b. The relationship between measurements using this extraction, and measurements made using the standard CCME method is not currently known.

Measured analytical concentrations of F3 were corrected for "analytical recovery", which in this case was 67%. This correction involved increasing all the measured concentrations by a factor of approximately 1.5. This correction is justified in this study because the alumina fractionation technique typically results in some sample mass loss, and the analytical recovery correction allows for this.

Data Summary and Comments

Ecotoxicity data for F3 in fine soil for *Eisenia andrei, Orthoonychiurus folsomi*, and northern wheatgrass are summarized in Table F.8. A species sensitivity distribution of these data is provided in Figure F.6. Where multiple IC_{25}/IC_{50} values were provided for the same endpoints in Cermak *et al*. (2005), Table F.8 presents only a single value for each endpoint. Methods that did not appear to yield a valid result were not included; if there were multiple apparently valid results, they were combined by using their geometric mean.

Conclusions

The 25^{th} and 50^{th} percentile values included in Table F.8 indicate that:

1. for agricultural/residential land use the Cermak *et al*. (2005) data would support a guideline value of approximately 2,500 mg/kg based on the CCME (2000) Approach, or approximately 1,000 mg/kg based on the CCME (2005) Approach (Table F.17).

2. for commercial/industrial land use the Cermak *et al.* (2005) data would support a guideline value of approximately 8,400 mg/kg based on the CCME (2000) Approach, or approximately 3,200 mg/kg based on the CCME (2005) Approach (Table F.17).

It should be noted that the interpretation of the Cermak *et al*. (2005) data in the current report is somewhat compromised by the uncertainty in extrapolating the measured analytical concentrations to the equivalent values that might have been obtained using the CCME reference method.

F2.3.2 Visser (2005b)

The research provider for this project was Dr. Suzanne Visser of the University of Calgary. The primary objectives of this study were i) to evaluate the toxicity associated with clay soils containing weathered, stable PHCs in excess of the CCME guideline for F3 (800 mg/kg); and ii) to submit the data as part of a "weight of evidence" argument for use in the reconsideration of the PHC CWS ecological direct soil contact guidelines.

A heavy clay (71% clay) was spiked with Federated Crude at 0 – 50,000 mg/kg, and bioremediated in the lab for 12 months. The F3 residuals following 12 months bioremediation/weathering ranged from 230 mg/kg to 6,600 mg/kg. F2 and F4 were below guidelines in all samples. Ecotoxicity tests were conducted with barley (growth, 14 days), northern wheatgrass (growth, 21 days), earthworm (reproduction, 56 days), and springtail (reproduction, 28 days).

Analytical Basis

All analytical data for PHCs reported in this project were obtained using the CCME reference method.

Data Summary and Comments

Data for various definitive/chronic endpoints for barley and northern wheatgrass growth, and for springtail and earthworm reproduction are summarized in Table F.9. A species sensitivity distribution of these data is provided in Figure F.7. $IC/LC_{50/20}$ values were not available in the interim summary of this work provided in Visser (2005b), but were calculated for the current report based on curves of the format

$$y = \frac{a}{1 + exp\left(\frac{-(x - x_0)}{b}\right)}$$

fit to the data by Dr. Beverley Hale of the University of Guelph. It is understood that data from additional endpoints (e.g., root mass, root length) will become available once the final report is issued. Since PHC F2 and F4 concentrations were below guideline values in all treatments, the ecotoxicological responses were conservatively assumed to be due to the residual F3 hydrocarbons.

Conclusions

The 25th and 50th percentile values included in Table F.9 indicate that:

1. for agricultural/residential land use the Visser (2005b) data would support a guideline value of approximately 3,400 mg/kg based on the CCME (2000) Approach, or approximately 2,300 mg/kg based on the CCME (2006a) Approach (Table F.17).
2. for commercial/industrial land use the Visser (2005b) data would support a guideline value of approximately 4,200 mg/kg based on the CCME (2000) Approach, or approximately 2,900 mg/kg based on the CCME (2006a) Approach (Table F.17).

However, it should be noted that the six datapoints available in the interim report on this study would not be sufficient on their own to fulfill the data requirement for the weight of evidence method (minimum of 10 datapoints).

F3 PHC Fraction F3 in COARSE Soil

The existing guideline for ecological direct soil contact for F3 in coarse soil and agricultural land use is 400 mg/kg. This value differs from the guideline for fine soil by a factor of 2, deemed to represent the difference in sensitivity between coarse and fine soils.

F3.1 Single Concentration Studies

Three studies in this category have become available since the PHC CWS was published. Visser *et al*. (2003), Visser (2005a) and Axiom (2005) were described in Section F.2.1. In addition to the studies on the fine textured Turner Valley plots described in Section F.2.1, the Visser studies also investigated the toxicity of PHCs at the Richmound site in a coarse soil oiled with Federated Crude at an initial rate of 1.2%.

F3.1.1 Visser et al. (2003)

Selected ecotoxicity data from Visser *et al*. (2003) are presented in Table F.10, expressed as the response in the 1.2% contaminated soil as a percentage of the response in the corresponding control. Data presented are for plots in which a crop had not been seeded, assessed at 12 months after the soil was spiked with Federated crude oil. Data were also provided in Visser *et al*. (2003) for 0, 1, 3, 9 months after spiking. These earlier data had both F2 and F3 above the current agricultural/residential guideline, and hence it was unclear whether any toxicity was due to F2, F3, or a combination of the two.

Analytical Basis

As noted in Section F.2.2.2, all hydrocarbon concentrations were converted from Alberta G108 (AENV 1992) F3 concentrations to equivalent CCME F3 concentrations. The relationship for coarse soils is illustrated in Figure F.8 and the equation used was:

$$CCME\ F3 = (0.4062 \times G108\ F3) + 106.64$$

Comments and Conclusions

Non-redundant data are shaded in Table F.10. The 25th and 50th percentile values included in Table F.10 indicate that:

1. for agricultural/residential land use the Visser *et al*. (2003) data would support a guideline value of less than 1,100 mg/kg based on either the CCME (2000) or CCME (2006a) Approaches (Table F.10).
2. for commercial/industrial land use the Visser *et al*. (2003) data would support a guideline value of greater than 1,100 mg/kg based on either the CCME (2000) or the CCME (2006a) Approach (Table F.10).

F3.1.2 Visser (2005a)

Analytical Basis

As noted in Section F.2.2.2, all hydrocarbon concentrations were converted from Alberta G108 (AENV 1992) F3 concentrations to equivalent CCME F3 concentrations. The relationship for coarse soils is illustrated in Figure F.8 and the equation used was:

$$CCME\ F3 = (0.4062 \times G108\ F3) + 106.64$$

Data Summary and Comments

Data for the Richmound (coarse soil) plots from Visser (2005a) are summarized in Tables F.11 (Plants) and F.12 (Invertebrates). Data are presented as the response for each endpoint for oiled soils as a percentage of the response in the control plots. Non-redundant data from the 32 month measurements are presented in red. Non-redundant data from the 36 month measurements are presented in blue. The calculated CCME F3 concentration is presented with the data.

As with the Visser (2005a) studies at the Turner Valley plots (Section F.2.2.2), these data were not amenable to generating dose response relationships, and accordingly the Ranked Response Distribution approach was used. Ranked Response Distributions for these data for 32 months and 36 months are provided in Figures F.11 and F.12.

Conclusions

Figure F.9 indicates that the 25th percentile of the RRD is a 56% response relative to controls for the 32 month sampling event (F3 = 391 mg/kg). Taken in isolation, this dataset would meet the criterion for the CCME (2000) Approach, but not that for the CCME (2006a) Approach.

Figure F.10 indicates that the 25th percentile of the RRD is a 65% response relative to controls for the 36 month sampling event (F3 concentration = 334 mg/kg). Taken in isolation, this dataset would meet the criterion for the CCME (2000) Approach, but not that for the CCME (2006a) Approach.

Based on this analysis, therefore, and taken in isolation, the data in Visser (2005a) would appear to suggest that the existing F3 guideline for coarse soil (400 mg/kg) may be sufficiently conservative to achieve the desired level of protection based on the CCME (2000) Approach, but may not be sufficiently conservative to achieve the desired level of protection based on the

CCME (2006a) Approach, and under the CCME (2006a) Approach a lower guideline value, perhaps in the range of 300 mg/kg would be indicated (Table F.17).

F3.1.3 Axiom (2005)

Axiom (2005) reports *Eisenia* reproduction data from previous work conducted by Dr. Suzanne Visser for two coarse soils. These data are summarized in Table F.13. All analytical data were obtained using the CCME reference method.

F3.2 Multi-Concentration Studies

Ecotoxicity data for coarse (artificial) soil were provided in ESG (2003), and these data are summarized in Table F.14. However, these data were not used as a basis for guideline derivation based on the preponderance of data for acute endpoints. Chronic/definitive endpoints are typically much more sensitive than acute endpoints, and form a better basis for guideline derivation.

F4 PHC Fraction F4

Ecotoxicity studies on F4 were included in ESG (2003) and are summarized in Table F.15. However these data were apparently not available at the time of the original derivation of the PHC CWS F4 guidelines, and so the existing F4 guidelines were calculated based on extrapolating the toxicity of whole crude oil. The guideline derivation is illustrated in Table F.16 for all three Approaches (CCME (2000), Hybrid, and CCME (2006a)). The species sensitivity distribution for this dataset is illustrated in Figure F.11.

Guideline values for F4 calculated using the CCME (2006a) method were 4,900 mg/kg, and 8,300 mg/kg for agricultural/residential and commercial/industrial, respectively. These guidelines are essentially consistent with the existing guidelines for F4.

F5 Summary

Table F.17 presents the guideline values that can be calculated for F3 from each of the relevant studies. Guideline calculations are presented both on the basis of both the CCME (2000) and CCME (2006a) Approaches.

F5.1 F3 in Fine Soil

Five studies, conducted since 2000, which included ecotoxicity data on F3 for fine soils were available. Their implications for the F3 guideline value for fine soil were assessed against the CCME (2000) and CCME (2006a) Approaches. These two Approaches are equivalent to setting a guideline based on the species sensitivity distribution of IC/LC/EC_{50} values or IC/LC/EC_{25} values, respectively.

Among the available studies, the greatest weight was given to the Visser (2005a) phase 3 field studies. This was done because the study considered a greater number of species (14, compared to 4 or 5 in most other studies), and assessed crop growth and invertebrate populations in an actual field setting, rather than extrapolating exclusively from laboratory studies. Using the CCME (2006a) (EC_{25}) methodology, the F3 guidelines calculated for fine soil would be >1,300

mg/kg, and >2,500 mg/kg, for agricultural/residential and commercial/industrial land uses, respectively (Table F.17).

Less weight was given to the Cermak (2005) data, based on the uncertainty in extrapolating the measured analytical concentrations to the equivalent values that might have been obtained using the CCME reference method.

The other studies listed in Table F.17 provide additional support for guideline values in a similar range.

Overall, therefore, the Eco Sub-Group recommends updating the F3 guideline for fine soil from 800 mg/kg to 1,300 mg/kg for agricultural/residential land use, and retaining the existing F3 fine soil guideline of 2,500 mg/kg for commercial/industrial land use (Table F.17).

F5.2 F3 in Coarse Soil

Data in Visser (2005a) suggest that the current guideline for F3 in coarse soils for agricultural/residential land use (400 mg/kg) is protective of plant growth, but may not be protective of all soil invertebrates. The current guideline is protective based on the CCME (2000) Approach, but the guideline would need to be less than 330 mg/kg to be protective under the CCME (2006a) Approach.

Overall, therefore, the Eco Sub-Group recommends updating the F3 guideline in coarse soil for agricultural/residential land use from 400 mg/kg to 300 mg/kg. Insufficient new data are available to recommend updating the corresponding commercial/industrial guideline of 1,700 mg/kg (Table F.17).

F5.3 F4

Existing PHC CWS guidelines for F4 were calculated by extrapolation from the toxicity of whole crude oil. In this report, guideline values are calculated for F4 in fine soil (Table F.18), based on F4 ecotoxicity data that were not available at the time of the original derivation. The values calculated using the CCME (2006a) method were 4,900 mg/kg, and 8,300 mg/kg for agricultural/residential and commercial/industrial, respectively. These guidelines are essentially consistent with the existing guidelines for F4, and no changes to the existing guidelines for F4 are recommended (Table F.18).

F6 References

Alberta Environment. 1992. Methods manual for chemical analysis of trace organics and pesticides in environmental samples. AECV 92-M2.

Axiom (Axiom Environmental Inc.) 2005. Environmentally Acceptable Endpoints for Weathered/Aged Petroleum Hydrocarbon Fraction F3 in Soil – Development of a Bioavailability Index. Interim report prepared for Petroleum Technology Alliance Canada (PTAC), September 22, 2005.

CCME (Canadian Council of Ministers of the Environment), 2000. Canada-Wide Standards for Petroleum Hydrocarbons (PHCs) In Soil: Scientific Rationale Supporting Technical Document. December 2000.

CCME (Canadian Council of Ministers of the Environment), 2001. Reference Method for The Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method. ISBN 1-896997-01-5. Publication No. 1310.

CCME (Canadian Council of Ministers of the Environment), 2006a. A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines. 2006.

Cermak, J.H., Stephenson, G.L., Birkholz, D, and Dixon, D.G., 2005. Summary of the Soil Toxicity and Soil Chemical Analysis Data for Petroleum Fractions 2 and 3. Interim report prepared for the CCME CWS Ecotoxicological Criteria Advisory Sub-Group, October 31, 2005.

ESG, 2003. Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase I – Fraction Specific Toxicity of Crude Oil. Report prepared for the Petroleum Technology Alliance of Canada. 238 pages.

Stantec (Stantec Consulting Ltd.), 2005. Summary of chronic screening toxicity tests results with reference soils and soils contaminated with petroleum hydrocarbon residuals. Draft Final report, dated October 28, 2005, prepared for Petroleum Technology Alliance Canada.

Visser, S. 2005a. Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality Phase 3: Long-term Field Studies. Report prepared for Petroleum Technology Alliance Canada (PTAC). February 2005.

Visser, S. 2005b. Ecotoxicity Risk Assessment of PHC Residuals in Bioremediated Oil-Contaminated Clay Soils. PowerPoint presentation prepared for Petroleum Technology Alliance Canada (PTAC). November 2005.

Visser, S., Leggett, S., and Lee, K. 2003. Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality Phase 2: Field Studies. Report prepared for Petroleum Technology Alliance Canada (PTAC). April 2003.

Table F.1: Summary of PHC ecotoxicity data sources

	Study	Type[1]	Applicable to Guideline for F1	F2	F3	F4	Comments
Canada-Wide Standards for Petroleum Hydrocarbons (PHCs) in Soil: Scientific Rationale	CCME (2000)	multi	✓	✓	✓	✓	Analysis of ESG (2003) data
Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase I Fraction-Specific Toxicity of Crude Oil.	ESG (2003)	multi	✓	✓	✓	✓	Source for original PHC CWS derivations for F2-F4
Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase 2: Field Studies	Visser (2003)	single		✓	✓		Mostly acute data
Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase 3: Long-term Field Studies	Visser (2005a)	single			✓		Mostly definitive/chronic data
Summary of the soil toxicity and soil chemical analysis data for petroleum hydrocarbon fractions 2 and 3	Cermak et al. (2005)	multi		✓	✓		Used same soil as ESG (2003)
Environmentally Acceptable Endpoints of CCME Canada-Wide Standards (CWS) Petroleum Hydrocarbons Fraction F3 for Weathered Petroleum Hydrocarbons in Soil	Axiom (2005)	single			✓		
Ecotoxicity of Hydrocarbon Residuals in Bioremediated Oil-Contaminated Clay Soils	Visser (2005b)	multi			✓		Toxicity tests in 70% clay soil
Unpublished dataset on 64 day earthworm “pseudo-reproduction” effects for F4	Cermak (unpublished)	multi				✓	
Unpublished dataset on toxicity of mogas to barley in chernozem soil	Cermak (unpublished)	multi	✓				
Final Report on the Acute Screening and Definitive, Chronic Toxicity Tests with Motor Gasoline	ESG (2000)	multi	✓				Source for original PHC CWS derivations for F1
ESG F1 Toxicity Data	ESG (unpublished)	multi	✓				

1. Type:
“single” refers to single concentration studies where field soils were spiked at one (or two) concentrations, or existing contaminated soils were used.
“multi” refers to studies using multiple concentrations (i.e., a serial dilution format test).

Table F.2: Test species used in ecotoxicity studies that have been used in the F3 and F4 analysis.

	Organisms Grown in Lab								Organisms Grown or Observed in Field													
	Northern wheatgrass	Barley	Alfalfa	Canola	*Eisenia andrei*	*Onychiurus folsomii*	*Folsomia candida*	*Lumbricus terrestris*	Barley	Wheat	Weeds	Grashoppers	Crickets	Carabid beetles	Other beetles	Spiders	Harvestmen	Ants	Other macrofauna	Total macrofauna	Total mites	Total collembola
ESG (2003)	✓	✓	✓		✓	✓		✓														
Visser (2003)		✓	✓	✓	✓		✓		✓	✓	✓	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓
Visser (2005a)	✓	✓	✓		✓		✓		✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
Cermak (2005)	✓	✓	✓		✓	✓																
Visser (2005b)	✓	✓			✓		✓															
Axiom (2005)	✓	✓	✓		✓		✓															

Table F.3: Turner Valley plant and invertebrate data, Year 1.

Treatment	Months	CCME F3 (calculated)	emergence, %	root length, cm	emergence, %	root length, cm	emergence, %	root length, cm	shoot	seed	total biomass	total biomass	total biomass	adult survival	adult survival	abundance	abundance	abundance	abundance	abundance	abundance	25th percentile of non-redundant field data	50th percentile of non-redundant field data
Species			barley	barley	canola	canola	alfalfa	alfalfa	barley	barley	barley	weeds	all plants	springtail	earthworm	beetles	spiders	ants	other macrofauna	total mites	total collembola		
Lab/Field		(mg/kg)	lab	lab	lab	lab	lab	lab	field	field	field	field	field	lab	lab	field	field	field	field	field	field		
1.7%	12	1,521	**100%**	**90%**	**106%**	**128%**	**96%**	**100%**	**377%**	**645%**	463%	**96%**	199%	**100%**	**100%**	**65%**	**48%**	**133%**	**72%**	**74%**	**31%**	**82%**	**100%**
3.7%	12	3,131	**100%**	**101%**	**104%**	**132%**	**96%**	**124%**	**501%**	**1024%**	666%	**23%**	203%	**100%**	**100%**	**59%**	**53%**	**133%**	**104%**	**62%**	**25%**	**79%**	**101%**

Notes:
all data relate to plots 12 months after oil application
all laboratory invertebrate toxicity tests are of acute duration: barley = 5 days, canola = 6 days, alfalfa = 7 days
all laboratory plant toxicity tests are of acute duration: springtail = 7 days; earthworm = 14 days
non-redundant field data are shaded

Table F.4: Turner Valley Plant Data Year 2 and 3

Treatment	Months	CCME F3 (calculated)	shoot height, cm	root length, cm	shoot weight, mg dwt/plant	root weight, mg dwt/plant	total weight, mg dwt/plant	shoot height, cm	root length, cm	shoot weight, mg dwt/plant	root weight, mg dwt/plant	total weight, mg dwt/plant	shoot	seed	total biomass	total biomass	total biomass
Species			barley	barley	barley	barley	barley	NWG	NWG	NWG	NWG	NWG	barley	barley	barley	weeds	all plants
Lab/Field			lab	lab	lab	lab	lab	lab	lab	lab	lab	lab	field	field	field	field	field
	24	1,114	100%	100%	91%	76%	86%	-	-	-	-	-	-	-	-	-	-
1.7%	32	1,390	100%	108%	107%	100%	105%	103%	92%	108%	90%	103%	130%	179%	142%	92%	135%
	36	1,250	91%	102%	92%	98%	94%	99%	106%	93%	114%	98%	-	-	-	-	-
Mean of 1.7% Data		**1,251**	**97%**	**103%**	**96%**	**91%**	-	**101%**	**99%**	**100%**	**101%**	-	**130%**	**179%**	-	**92%**	-
	24	2,557	104%	95%	86%	70%	80%	-	-	-	-	-	-	-	-	-	-
3.7%	32	2,536	98%	114%	93%	89%	92%	98%	101%	93%	63%	86%	-	-	-	-	-
	36	2,282	96%	106%	83%	96%	87%	97%	103%	101%	105%	102%	134%	200%	150%	40%	136%
Mean of 3.7% Data		**2,458**	**96%**	**106%**	**83%**	**96%**	-	**97%**	**103%**	**101%**	**105%**	-	**134%**	**200%**	-	**40%**	-

Notes:
- = not measured/not calculated
barley tests are 14 days duration
NWG = northern wheatgrass, tests are 28 days duration
Shaded values are the arithmetic mean of the three CCME F3 concentrations

Table F.5: Turner Valley Invertebrate data year 2 and 3

Treatment	Months	CCME F3 (calculated)	adult survival	juvenile production	adult survival	adult mass	juvenile production	abundance	abundance	abundance	abundance	abundance	abundance	abundance	abundance	abundance	abundance	abundance
Species			springtail	springtail	earthworm	earthworm	earthworm	grashoppers	carabid beetles	other beetles	spiders	harvestmen	ants	other macrofauna	total macrofauna	total mtes	total collembola	total mesofauna
Lab/Field			lab	lab	lab	lab	lab	field	field	field	field	field	field	field	field	field	field	field
	24	1,114	-	-	-	-	-	-	-	-	-	-	-	-	-	80%	45%	68%
1.7%	32	1,390	111%	113%	100%	80%	73%	108%	61%	58%	96%	43%	113%	53%	76%	77%	82%	78%
	36	1,250	81%	104%	100%	104%	63%	-	-	-	-	-	-	-	-	47%	131%	66%
Mean of 1.7% Data		**1,251**	**95%**	**108%**	**100%**	**91%**	**68%**	**108%**	**61%**	**58%**	**96%**	**43%**	**113%**	**53%**	142%	**66%**	**79%**	-
	24	2,557	-	-	-	-	-	-	-	-	-	-	-	-	-	35%	24%	32%
3.7%	32	2,536	103%	137%	100%	81%	32%	81%	56%	78%	100%	33%	127%	58%	79%	43%	51%	45%
	36	2,282	74%	87%	100%	92%	58%	-	-	-	-	-	-	-	-	36%	6%	29%
Mean of 3.7% Data		**2,458**	**88%**	**109%**	**100%**	**87%**	**43%**	**81%**	**56%**	**78%**	**100%**	**33%**	**127%**	**58%**	-	**38%**	**20%**	-

Notes:
- = not measured
Shaded values are the arithmetic mean of the three CCME F3 concentrations

Table F.6 Turner Valley plant and invertebrate data, year 5.

Test	Measured Data			% of Control	
	Control	1.70%	3.70%	1.70%	3.70%
CCME F3 (mg/kg)				**1,362**	**2,545**
Eisenia andrei					
63 day reproduction					
Number of juveniles	13.7	11.9	10.20	87%	74%
Wet mass of juveniles (mg)	15.12	12.8	12.07	85%	80%
Dry mass of juveniles (mg)	3.04	2.4	2.44	77%	80%
Folsomia candida					
28 day survival and reproduction					
Adult survival	6.7	7.0	6.40	nd	96%
Number of juveniles produced	263.8	280.3	285.40	106%	108%
Adult fecundity	44.2	40.2	49.30	91%	112%
Northern wheatgrass					
Definitive growth test					
Shoot length (mm)	144.4	150.4	137.20	104%	95%
Shoot wet mass (g)	0.4	nv	0.27	73%	68%
Shoot dry mass (mg)	93.34	58.3	57.14	62%	61%
Root length (mm)	165.2	138.6	172.20	84%	104%
Root wet mass (g)	0.53	0.3	0.36	53%	68%
Root dry mass (mg)	39.48	20.9	26.36	53%	67%
Alfalfa					
Definitive growth test					
Shoot length (mm)	59.4	nv	54.30	105%	91%
Shoot wet mass (g)	1.27	1.3	0.92	104%	72%
Shoot dry mass (mg)	225.38	253.4	177.10	112%	79%
Root length (mm)	167.4	185.1	172.30	111%	103%
Root wet mass (g)	1.65	1.7	1.13	104%	68%
Root dry mass (mg)	104.38	nv	88.24	107%	85%
Barley					
Definitive growth test					
Shoot length (mm)	165.2	173.4	173.80	105%	105%
Shoot wet mass (g)	2.52	nv	2.45	106%	97%
Shoot dry mass (mg)	395.2	442.7	411.42	112%	104%
Root length (mm)	234.9	234.5	202.40	100%	86%
Root wet mass (g)	3.96	4.0	3.04	100%	77%
Root dry mass (mg)	320.78	328.9	281.58	103%	88%

Notes:
Data source Axiom (2005)

	1.70%	3.70%
	1,362	**2,545**
	53%	61%
	62%	67%
	77%	74%
	84%	79%
	87%	80%
	100%	85%
	103%	86%
	104%	88%
	104%	91%
	105%	95%
	105%	96%
	106%	103%
	107%	104%
	111%	104%
	112%	105%
	112%	108%
25 th percentile	86%	80%
50th percentile	104%	90%

Table F.7: Available Ecotoxicity data for F3 in fine soils (multi concentration studies)

Organism	Parameter	LC/IC20 (mg/kg)	wet (mg/kg)	dry (mg/kg)	LC/IC50 (mg/kg)	wet (mg/kg)	dry (mg/kg)	Exposure conc (mg/g) # (conc.)	# reps.	Conc. Type	Test Duration (d)	Organisms /Unit (d)	Soil Type
Study: ESG (2003) (Fine Soils)													
Alfalfa	shoot length	2,800			51,900			0,15,30,50,60,70,80	4	nom	8	10	RS
	root length	7,200			10,000			(n=7)					
	plant mass	28,163	15,800	50,200	84,261	72,300	98,200						
	shoot length	620			**8,300**			0,1,3,6,12,15,20,40,60,80,100,120	3-6	nom	26	10	RS
	root length	920			**6,300**			(n=12)					
	shoot mass	562	510	620	**2,198**	2,100	2,300						
	root mass	973	860	1,100	**4,919**	4,400	5,500						
Barley	shoot length	39,400			53,400			0,4,10,30,50,80	4	nom	6	5	RS
	root length	47,600			58,200			(n=6)					
	shoot mass	36,700	36,700	nd	50,300	50,300	nd						
	shoot length	3,700			**27,600**			0,10,20,30,40,50,60,70,80,100	3-6	nom	14	5	RS
	root length	120			3,200			(n=10)					
	shoot mass	**48,449**	48,200	48,700	**53,699**	54,100	53,300						
	root mass	4,123	1,700	10,000	**17,475**	8,700	35,100						
Northern wheatgrass	shoot length	nv			42,100			0,15,30,50,60,70,80	4	nom	8	5	RS
	root length	20,400			51,100			(n=7)					
	plant mass	12,875	13,700	12,100	25,732	26,700	24,800						
	shoot length	330			**12,700**			0,5,10,15,20,30,40,50,60,70,80	3-6	nom	25	5	RS
	root length	4,300			**7,300**			(n=11)					
	shoot mass	25	13	50	924	610	1,400						
	root mass	194	180	210	989	890	1,100						
Eisenia andrei	adult survival	nv			**22,362**			0,4,8,12,15,20,50 (n=7)	3-4	nom	14	5	RS
	number of juveniles	240			**776**			0,0.5,1,3,5,7,10,12.5,15,20,25	10	nom	57	2	RS
	mass of juveniles	241	272	213	**831**	854	809	(n=11)					
Onychiurus folsomi	adult survival	nv			**5,969**			0,1,2,4,8,15 (n=6)	3-4	nom	7	10	RS
	adult survival	**3,120**			**3,977**			0,0.5,1,2,3,4,5,5.5,6,7	10	nom	35-36	10	RS
	number of juveniles	**910**			**1,490**			(n=10)		nom			RS
	adult fecundity	**620**			**1,410**								
Lumbricus terrestris	adult survival	nv			**17,218**			0,4,8,12,15,20,50 (n=7)	3-4	nom	14	3	RS

Table F.7: (cont'd)

Organism	Parameter	LC/IC20 (mg/kg)	wet (mg/kg)	dry (mg/kg)	LC/IC50 (mg/kg)	wet (mg/kg)	dry (mg/kg)	Exposure conc (mg/g) # (conc.)	# reps.	Conc. Type	Test Duration (d)	Organisms /Unit (d)	Soil Type
Study: Cermak (2005) (Fine Soils)													
Barley	shoot length	5,650			41,770			0,1,5,10,20,40,60,80,100	3-6	ar	14	5	RS
	root length	4,960			45,120			(n=9)					
	shoot dry mass	4,900			16,290								
	root dry mass	3,280			12,470								
Barley	shoot length	6,470			27,480			0,5,10,20,30,40,60	3-6	ar	14	5	RS
	root length	9,930			41,210			(n=7)					
	shoot dry mass	5,560			17,100								
	root dry mass	9,290			20,320								
Barley	shoot length	**6,046**			**33,880**				3-6	ar	14	5	RS
(geometric mean	root length	**7,018**			**43,121**								
of above tests)	shoot dry mass	**5,220**			**16,690**								
	root dry mass	**5,520**			**15,918**								
Northern wheatgrass	shoot length	nv			15,630			0,5,10,15,20,25,30,40,50,60	3-6	ar	25	5	RS
	root length	17,020			41,500			(n=10)					
	shoot dry mass	na			na								
	root dry mass	na			na								
Northern wheatgrass	shoot length	3,450			13,150			0,0.26,0.53,1.1,2.1,4.2,8.4,15.8,31.6,52	3-6	ar	25	5	RS
	root length	4,550			32,660			(n=10)					
	shoot dry mass	1,180			3,140								
	root dry mass	1,280			4,580								
Northern wheatgrass	shoot length	**3,450**			**14,336**			na	3-6	ar	25	5	RS
	root length	**8,800**			**36,816**								
	shoot dry mass	**1,180**			**3,140**								
	root dry mass	**1,280**			**4,580**								
Eisenia andrei	adult survival	**7,435**	(LC25)		**9,005**			na	3-4	ar	28	5	RS
	number of juveniles	**540**			**890**			na	10	ar	56-63	2	RS
	mass of juveniles	**730**			**1,230**								
Onychiurus folsomi	adult survival	**3,490**			**8,660**			na	3	ar	7	10	RS
	adult survival	nv			**2,570**			na	10	ar	35	10	RS
	number of juveniles	**510**			**1,080**			na	10	ar	35	10	RS

Table F.7 (cont'd)

Organism	Parameter	LC/IC20 (mg/kg)	wet (mg/kg)	dry (mg/kg)	LC/IC50 (mg/kg)	wet (mg/kg)	dry (mg/kg)	Exposure conc (mg/g) # (conc.)	# reps.	Conc. Type	Test Duration (d)	Organisms /Unit (d)	Soil Type
Study: Visser (2005) (Clay Soil)													
Barley	shoot length	**2,956**			**6,600**			0,0.23,0.35,0.65,1,1.4,3.1,6,6.6 (n=9)	na	meas	14	na	CS
Northern wheatgrass	shoot length	**2,750**			**5,379**			0,0.23,0.35,0.65,1,1.4,3.1,6,6.6 (n=9)	na	meas	21	na	CS
	shoot dry mass	**2,141**			**3,527**								
Eisenia andrei	adult survival	**4,006**			**4,913**			0,0.23,0.35,0.65,1,1.4,3.1,6,6.6 (n=9)	na	meas	56	na	CS
	number of juveniles	**754**			**1,192**								
Folsomia candida	number of juveniles	**3,572**			**4,753**			0,0.23,0.35,0.65,1,1.4,3.1,6,6.6 (n=9)	na	meas	28	na	CS

Notes:
wet = calculated ona wet weight basis
dry = calculated ona dry weight basis
Where IC20/50 data are available on both a wet and a dry weight basis, the two values were combined as the geometric mean
nom = nominal concentrations basis
ar = nominal values have been corrected for analytical recovery
(analytical method used involves separation of aliphatic and aromatic fractions on an alumina column; the correction for analytical recovery accounts for losses on the column)
meas = measured concentrations basis
na =not available
nd = not determined
nv = no value - not amenable to analysis

Table F.8: Analysis of Cermak et. al (2005) Chernozem data

Data based on Nominal Concentra

Organism	Parameter	Guideline Calculation Basis [a] LC/IC20 (mg/kg)	Hybrid (mg/kg)	LC/IC50 (mg/kg)	Measured IC20, F
Barley	shoot length	**5,727**	**5,727**	**32,893**	**324**
	root length	**6,676**	**6,676**	**41,912**	**353**
	shoot dry mass	**4,920**	**4,920**	**16,116**	**538**
	root dry mass	**5,214**	**5,214**	**15,362**	**978**
					1,075
Northern wheatgrass	shoot length	**3,193**	**3,193**	**12,660**	**3,193**
	root length	**8,415**	**8,415**	**35,758**	**3,232**
	shoot dry mass	**978**	**978**	**2,891**	**4,920**
	root dry mass	**1,075**	**1,075**	**4,296**	**5,214**
					5,727
Eisenia andrei	adult survival	**7,082**	**8,615**	**8,615**	**6,676**
				nd	**7,082**
	number of juveniles	**353**	**695**	**695**	**8,415**
	mass of juveniles	**538**	**1,026**	**1,026**	
Onychiurus folsomi	adult survival	**3,232**	**8,278**	**8,278**	
	adult survival	**nv**	**2,334**	**2,334**	
	number of juveniles	**324**	**880**	**880**	
		nv			
25th Percentile (Ag/Res Land Use)		**978**	**1,039**	**2,473**	
50th Percentile (Com/Ind Land Use)		**3,232**	**4,057**	**8,446**	

Notes:
nv = no value - not amenable to analysis
all values based on measured concentrations
a. Guidelines were calculated on the basis of 3 alternative approaches, described below:
1. CCME (2000) is the method used in the original PHC CWS work:
The ag/res guideline is calculated as the 25th percentile of the combined plant and invertebrate EC50 dataset.
The com/ind guideline is calculated as the 50th percentile of the EC50 plant only dataset.
2. The Hybrid method uses a dataset consisting of EC25(20) plant data and EC50 invertebrate data
3. The CCME (2005) method uses a dataset consisting of the combined EC25(20) plant and invertebrate data
For the hybrid and CCME (2005) methods, the ag/res and com/ind guidelines are calculated as the 25th and 50th percentiles, respectively, of the applicable distribution.

Organism	Parameter	LC/IC20 (mg/kg)
Barley	shoot length	**6,046**
	root length	**7,018**
	shoot dry mass	**5,220**
	root dry mass	**5,520**
Northern wheatgrass	shoot length	**3,450**
	root length	**8,800**
	shoot dry mass	**1,180**
	root dry mass	**1,280**
Eisenia andrei	adult survival	**7,435**
nd		
	number of juveniles	**540**
	mass of juveniles	**730**
Onychiurus folsomi	adult survival	**3,490**
	adult survival	**nv**
	number of juveniles	**510**
25th Percentile (Ag/Res Land Use)		**1,180**
50th Percentile (Com/Ind Land Use)		**3,490**

Notes:
nv = no value - not amenable to analysis

Table F.9: Analysis of Visser (2005b) clay soil data.

		LC/IC20 (mg/kg)	Hybrid (mg/kg)	LC/IC50 (mg/kg)	
Barley	shoot length	**2,866**	**2,866**	**6,600**	(SigmaPlot)
Northern wheatgrass	shoot length	**3,002**	**3,002**	**3,586**	(SigmaPlot)
	shoot dry mass	**2,126**	**2,126**	**3,306**	(SigmaPlot)
Eisenia andrei	adult survival	**4,006**	**4,913**	**4,913**	(Linear Interp)
	number of juveniles	**754**	**1,192**	**1,192**	(SigmaPlot)
Folsomia candida	number of juveniles	**3,572**	**4,753**	**4,753**	(SigmaPlot)
25th Percentile (Ag/Res Land Use)		**2,311**	**2,311**	**3,376**	
50th Percentile (Com/Ind Land Use)		**2,934**	**2,934**	**4,170**	

Table F.10: Richmound Plant and Invertebrate Data, year 1

Treatment	Months	CCME F3 (calculated)	emergence, %	root length, cm	emergence, %	root length, cm	emergence, %	root length, cm	shoot	seedhead	total biomass	total biomass	total biomass	adult survival	adult survival	abundance	abundance	abundance	abundance	abundance	abundance	abundance
Species			barley	barley	canola	canola	alfalfa	alfalfa	wheat	wheat	wheat	weeds	all plants	springtail	earthworm	grashoppers	crickets	carabids	other beatles	other fauna	total fauna	total mtes
Lab/Field		(mg/kg)	lab	lab	lab	lab	lab	lab	field	field	field	field	field	lab	lab	field	field	field	field	field	field	field
1.2%	12	1,114	**100%**	**114%**	**110%**	**146%**	**104%**	**157%**	**48%**	**53%**	50%	**3%**	28%	**100%**	**100%**	**90%**	**47%**	**51%**	**72%**	**69%**	67%	**4%**

Notes:
all data relate to plots 12 months after oil application
all laboratory invertebrate toxicity tests are of acute duration: barley = 5 days, canola = 6 days, alfalfa = 7 days
all laboratory plant toxicity tests are of acute duration: springtail = 7 days; earthworm = 14 days
non-redundant data are shaded

Table F.11: Richmound plant data year 2 to 4.

Treatment	Months	AENV G108 F3	CCME F3 (calculated)	shoot height, cm	root length, cm	shoot weight, mg dwt/plant	root weight, mg dwt/plant	total weight, mg dwt/plant	shoot height, cm	root length, cm	shoot weight, mg dwt/plant	root weight, mg dwt/plant	total weight, mg dwt/plant	shoot height, cm	root length, cm	shoot weight, mg dwt/plant	root weight, mg dwt/plant	total weight, mg dwt/plant	shoot	seed	total biomass	total biomass	total biomass
Species				Wheat	Wheat	Wheat	Wheat	Wheat	Barley	Barley	Barley	Barley	Barley	NWG	NWG	NWG	NWG	NWG	Wheat	Wheat	Wheat	weeds	all plants
Lab/Field		(mg/kg)	(mg/kg)	lab	lab	lab	lab	lab	lab	lab	lab	lab	lab	lab	lab	lab	lab	lab	field	field	field	field	field
1.2%	24	890	468	88%	85%	70%	57%	66%	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	32	701	**391**	**78%**	**99%**	**36%**	**34%**	36%	**87%**	**102%**	**86%**	**93%**	88%	**88%**	**94%**	**69%**	**67%**	67%	-	-	-	-	-
	36	560	**334**	**99%**	**91%**	**81%**	**61%**	75%	**107%**	**114%**	**101%**	**103%**	101%	**93%**	**101%**	**95%**	**88%**	89%	**53%**	**54%**	53%	**53%**	53%
	48	461	294	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	91%	73%	82%	61%	77%

Notes:
data incorporated into figures F.9 and F.10 are shaded.

Table F.12: Richmound Invertebrate data, years 0 to 4.

Treatment	Months	AENV G108 F3	CCME F3 (calculated)	adult survival	juvenile production	adult survival	adult mass	juvenile production	abundance	abundance	abundance	abundance	abundance	abundance	abundance	abundance	abundance
Species				springtail	springtail	earthworm	earthworm	earthworm	grashoppers	crickets	carabid beetles	other beetles	other macrofauna	total macrofauna	total mites	total collembola	total mesofauna
Lab/Field		(mg/kg)	(mg/kg)	lab	lab	lab	lab	lab	field	field	field	field	field	field	field	field	field
	0	4792	2053						124%	42%	37%	180%	146%	80%			
	12	1076	544						90%	47%	51%	72%	69%	67%			
	24	890	468												18%	17%	17%
1.2%	**32**	701	**391**	**107%**	**50%**	**100%**	**62%**	**10%**							**30%**	**188%**	33%
	36	560	**334**	**104%**	**100%**	**100%**	**72%**	**27%**	**91%**	**42%**	**94%**	**92%**	**82%**	85%	**69%**	**32%**	59%
	48	461	294												56%	17%	54%

Notes:
data incorporated into figures F.9 and F.10 are shaded

Table F.13: Chronic Eisenia andrei Ecotoxicity Data from Two Coarse Soils

Site	CCME F3 (mg/kg)	Juvenile Worms	
		#	Dry Mass (mg)
Site 9	1,200	57%	87%
Site 10	690	11%	57%

Notes:
Data source: Axiom (2005)

Table F.14: Available Ecotoxicity Data for F3 in Coarse Soils (Multi-Concentration Studies)

Organism	Parameter	LC/IC20 (mg/kg)	wet (mg/kg)	dry (mg/kg)	LC/IC50 (mg/kg)	wet (mg/kg)	dry (mg/kg)	Exposure conc (mg/g) # (conc.)	# reps.	Conc. Type	Test Duration (d)	Organisms /Unit (d)	Soil Type	Study
Study: ESG (2003)														
Barley	shoot length	74,800			98,200			0,15,30,50,60,70,80	4	nom	7	5	AS	ESG (2003)
	root length	79,000			119,600			(n=7)						
	shoot mass	73,700	73,800	73,600	86,548	85,900	87,200							
	root mass	93,023	90,800	95,300	64,225	61,200	67,400							
Northern wheatgrass	shoot length	17,100			81,900			0,15,30,50,60,70,80	4	nom	12	5	AS	ESG (2003)
	root length	54,900			121,000			(n=7)						
	plant mass	33,749	34,000	33,500	68,485	73,400	63,900							
Eisenia andrei	adult survival	nv			22,362			0,4,8,12,15,20 (n=6)	3-4	nom	14	5	AS	ESG (2003)
Lumbricus terrestris	adult survival	nv			17,218			0,8,12,15,20,50 (n=6)	3-4	nom	14	3	AS	ESG (2003)
Onychiurus folsomii	adult survival	nv			5,969			0,2,4,8,12,15 (n=6)	3-4	nom	7	10	AS	ESG (2003)

Notes:
wet = calculated ona wet weight basis
dry = calculated ona dry weight basis
Where IC20/50 data are available on both a wet and a dry weight basis, the two values were combined as the geometric mean
nom = nominal concentrations basis
na =not available
nd = not determined
nv = no value - not amenable to analysis

Table F.15: F4 Ecotoxicity Data

Organism	Parameter	IC20 (mg/kg)	wet (mg/kg)	dry (mg/kg)	IC50 (mg/kg)	wet (mg/kg)	dry (mg/kg)	Exposure conc (mg/g) # (conc.)	# reps.	Conc. type nom./init./final	Test Duration (d)	Soil type
Study: ESG (2003)												
Alfalfa	shoot length	**10,030**			**16,210**			0,10,20,30,40,50,60,80,100 (n=9)	3-6	nom	21	RS
	root length	**3,760**			**11,570**							
	shoot mass	**2,214**	3,500	1,400	**16,696**	9,310	29,940					
	root mass	**12,633**	14,470	11,030	**39,216**	36,810	41,780					
Barley	shoot length	**16,500**			**115,010**			0,10,20,30,40,50,60,80,100 (n=9)	3-6	nom	14	RS
	root length	**41,360**			**18,120**							
	shoot mass	**5,282**	9,720	2,870	**72,689**	35,380	149,340					
	root mass	**13,614**	12,250	15,130	**29,037**	23,240	36,280					
Northern wheatgrass	shoot length	**65,240**			**75,830**			0,10,20,30,40,50,60,80,100 (n=9)	3-6	nom	17	RS
	root length	**6,020**			**12,240**							
	shoot mass	**6,611**	5,030	8,690	**26,626**	16,820	42,150					
	root mass	**2,239**	2,410	2,080	**13,881**	12,250	15,730					
Eisenia andrei	number of juveniles	nc			**4,400**			0, 0.5, 1,2,5,10,20,30,40,50,60,80,100 (n=12)	10	nom	62-63	RS
	juvenile mass	nc	nc	nc	**4,694**	2,850	7,730					
	adult survival	nc			**80,000**						35	
Lumbricus terrestris	adult survival	nc			**100,000**			0,10,20,40,80,100 (n=6)		nom	14	RS

Notes:
RS = reference soil, a Delacour Orthic Black Chernozem from Alberta
wet = calculated on a wet weight basis
dry = calculated on a dry weight basis
where wet and dry weight basis measurements were available, these values were treated as redundant, and combined as the geometric mean
Conc. Type: concentration type. Endpoints calculated on the basis of nominal or measured initial or final concentration.
Data used in guideline derivation are shaded

Table F.16: F4 Guideline Calculation

Organism	Parameter	Guideline Calculation Basis [a] CCME (2000) (mg/kg)	Hybrid (mg/kg)	CCME (2006) (mg/kg)
Data				
Alfalfa	shoot length	16,210	10,030	10,030
	root length	11,570	3,760	3,760
	shoot mass	16,696	2,214	2,214
	root mass	39,216	12,633	12,633
Barley	shoot length	115,010	16,500	16,500
	root length	18,120	41,360	41,360
	shoot mass	72,689	5,282	5,282
	root mass	29,037	13,614	13,614
Northern wheatgrass	shoot length	75,830	65,240	65,240
	root length	12,240	6,020	6,020
	shoot mass	26,626	6,611	6,611
	root mass	13,881	2,239	2,239
Eisenia andrei	number of juveniles	4,400	4,400	nc
	juvenile mass	4,694	4,694	nc
	adult survival	80,000	80,000	nc
Lumbricus terrestris	adult survival	100,000	100,000	nc
Guideline Calculation				
Agricultural/Residential		**13,471**	**4,620**	**4,901**
Commercial/Industrial		**22,373**	**8,321**	**8,321**

Notes:
All data presented and guidelines galculated on the basis of nominal concentrations
Hydrocarbon concentrations were not measured. It is assumed that volatile losses would be minimal for this fraction
a. Guidelines were calculated on the basis of 3 alternative approaches, described below:
1. CCME (2000) is the method used in the original PHC CWS work:
The ag/res guideline is calculated as the 25th percentile of the combined plant and invertebrate EC50 dataset.
The com/ind guideline is calculated as the 50th percentile of the EC50 plant only dataset.
2. The Hybrid method uses a dataset consisting of EC25(20) plant data and EC50 invertebrate data
3. The CCME (2005) method uses a dataset consisting of the combined EC25(20) plant and invertebrate data
For the hybrid and CCME (2005) methods, the ag/res and com/ind guidelines are calculated as the 25th and 50th percentiles, respectively, of the applicable distribution.

Table F.17: Summary of Revised F3 Guideline Values

Study	Guideline Values Indicated from Each Study			
	Fine Soil		Coarse Soil	
	Ag/Res (mg/kg)	Com/Ind (mg/kg)	Ag/Res (mg/kg)	Com/Ind (mg/kg)
Guidelines Derived based on IC/LC50 Values or Equivalent				
CCME (2000) (Original PHC CWS Derivation)	800	2,500	400	1,700
Visser et al. (2003) (Phase 2 Field Studies)	>3,100	>3,100	<1,100	1,100
Visser (2005a) (Phase 3 Field Studies)	>2,500	>2,500	>390	>390
Axiom (2005)	>2,500	>2,500	na	na
Cermak (2005)	2,500	8,400	na	na
Visser (2005b) (Clay Study)	3,400	4,200	na	na
Guidelines Derived based on IC/LC25(20) Values or Equivalent				
Visser et al. (2003) (Phase 2 Field Studies)	>3,100	>3,100	<1,100	>1,100
Visser (2005a) (Phase 3 Field Studies)	**>1,300**	**>2,500**	**<330**	**>390**
Axiom (2005)	>2,500	>2,500	na	na
Cermak (2005)	1,000	3,200	na	na
Visser (2005b) (Clay Study)	2,300	2,900	na	na
Guideline Value Recommended in this Report	**1,300**	**2,500**	**300**	**1,700**

Notes:
na = not assessed
values above 500 rounded to the nearest 100
values below 500 rounded to the nearest 10
Proposed changes to existing Guideline Values are shaded.

Table F.18: Summary of Revised F4 Guideline Values

Study	Guideline Values Indicated from Each Study			
	Fine Soil		Coarse Soil	
	Ag/Res (mg/kg)	**Com/Ind** (mg/kg)	**Ag/Res** (mg/kg)	**Com/Ind** (mg/kg)
CCME (2000) (Original PHC CWS Derivation)	5,600	6,600	2,800	3,300
ESG (2003)	4,900	8,300	na	na
Guideline Value Recommended in this Report	**5,600**	**6,600**	**2,800**	**3,300**

Notes:
CCME (2000) values were calculated on the basis of a distribution of EC/IC/LC50 data
Values derived from ESG (2003) ere calculated on the basis of a distribution of EC/IC/LC25(20) data
na = not assessed
values rounded down to the nearest 100
Guideline values calculated in this report are essentially consistent with existing guidelines and no change is proposed to existing guideline values for F4

Figure F.1. Turner Valley - Correlation of CCME vs. G108 F3 Analysis

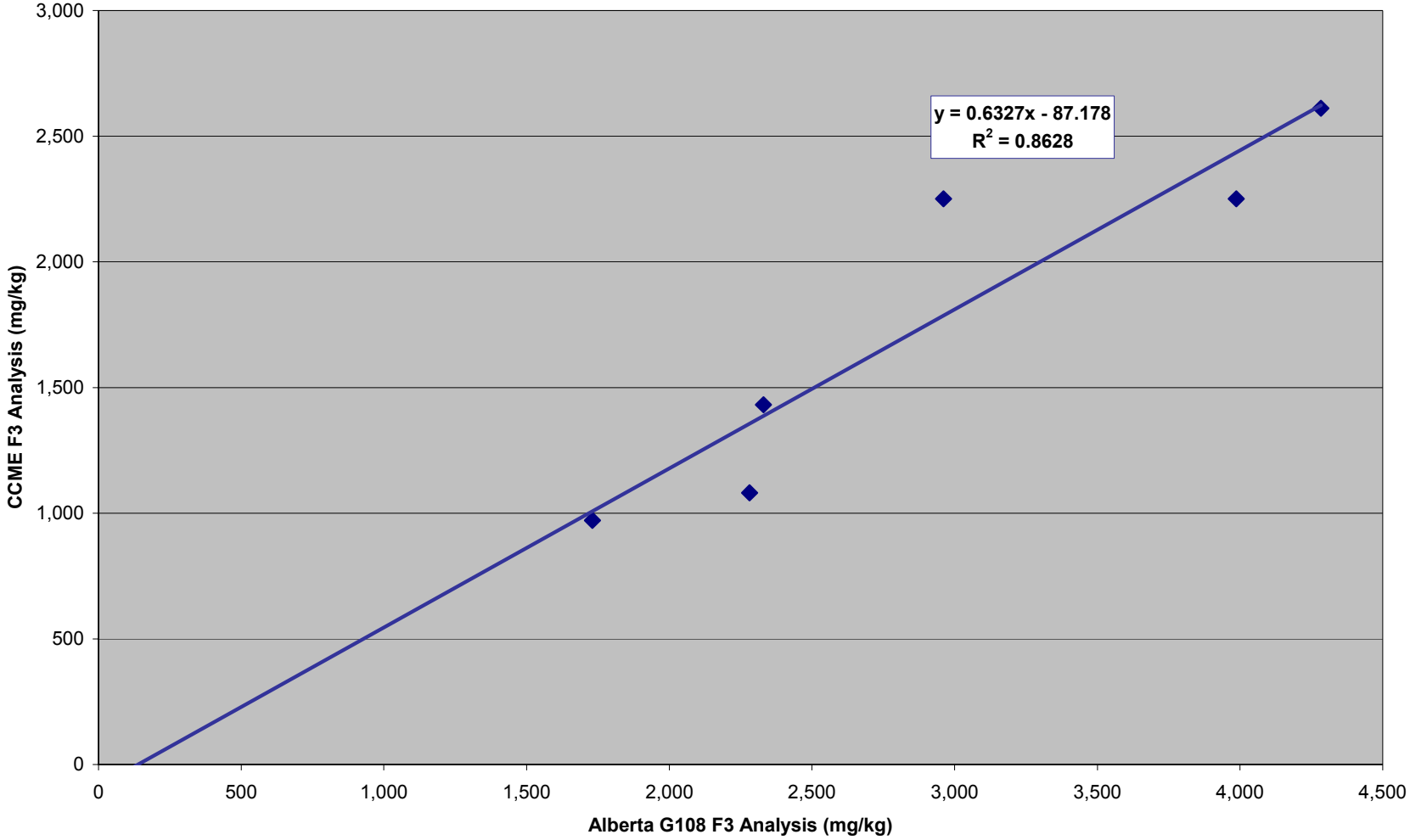


Figure F.2. "Ranked Response Distribution" for Turner Valley 1.7% Soils, Years 2-3 (Mean F3 = 1,251 mg/kg)

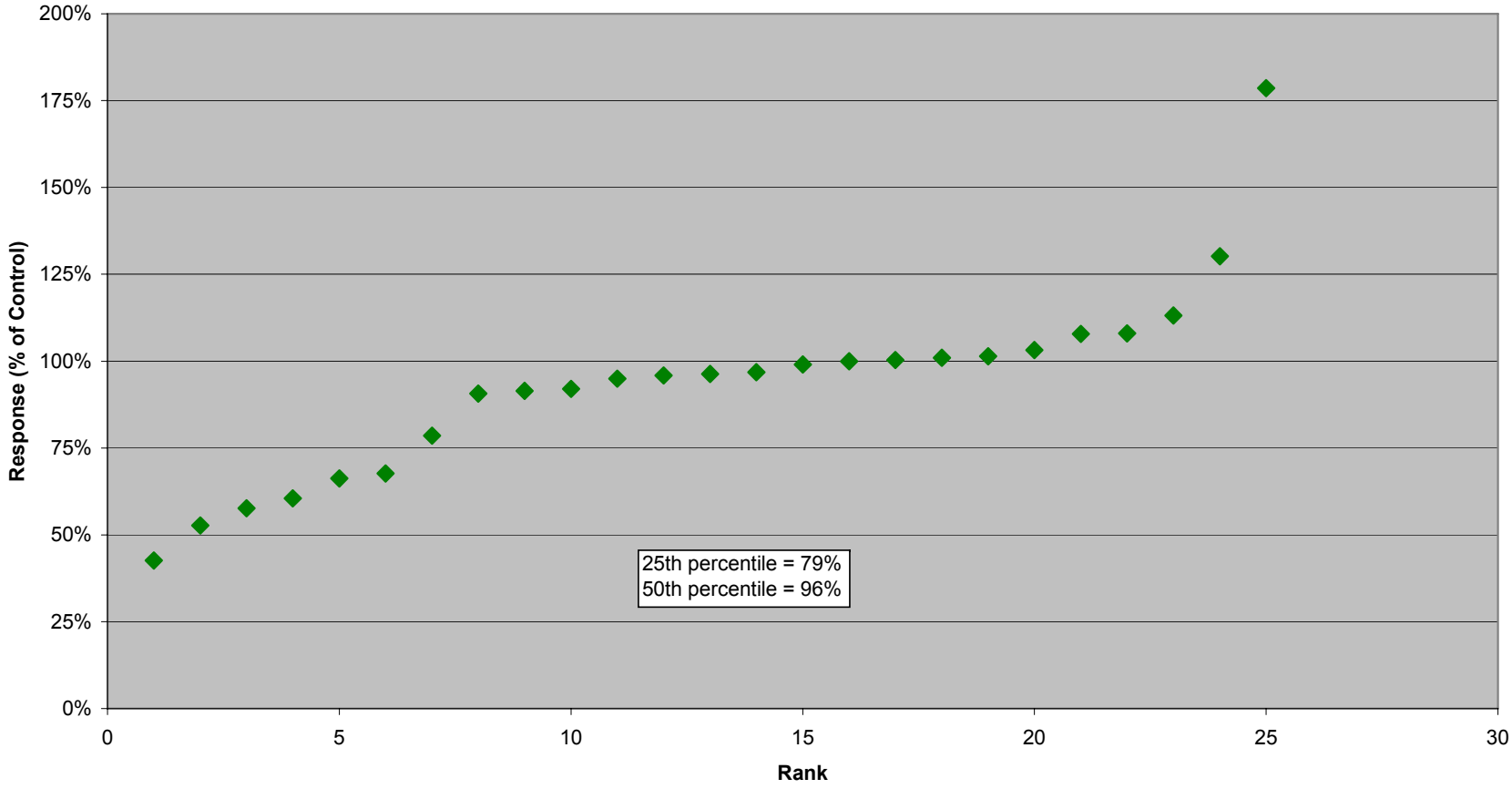


Figure F.3. "Ranked Response Distribution" for Turner Valley 3.7% Soils, Years 2-3 (Mean F3 = 2,458 mg/kg)

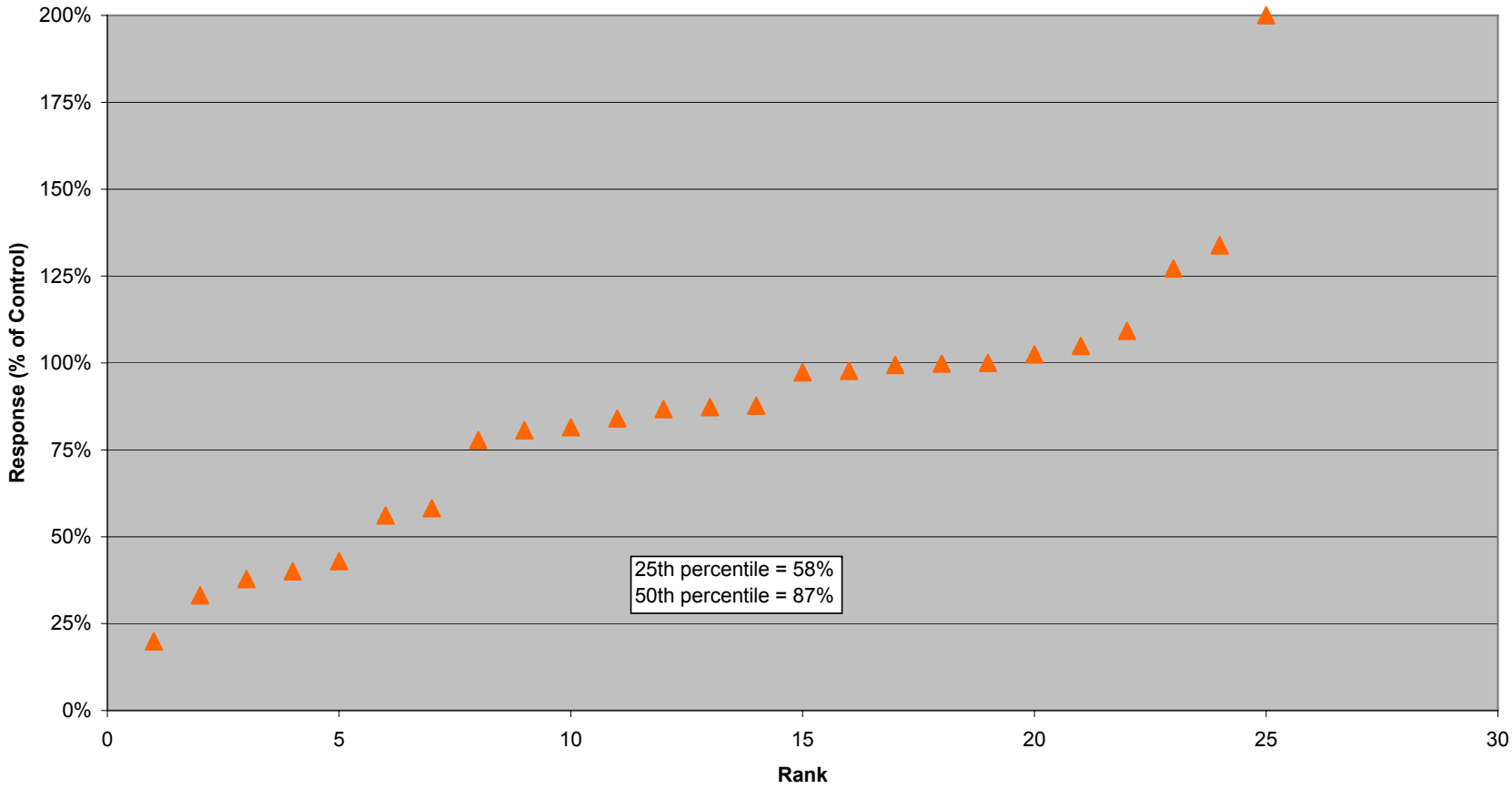


Figure F.4: "Ranked Response Distribution" for Turner Valley 1.7% Soils, Year 5 (Mean F3 = 1,362 mg/kg)

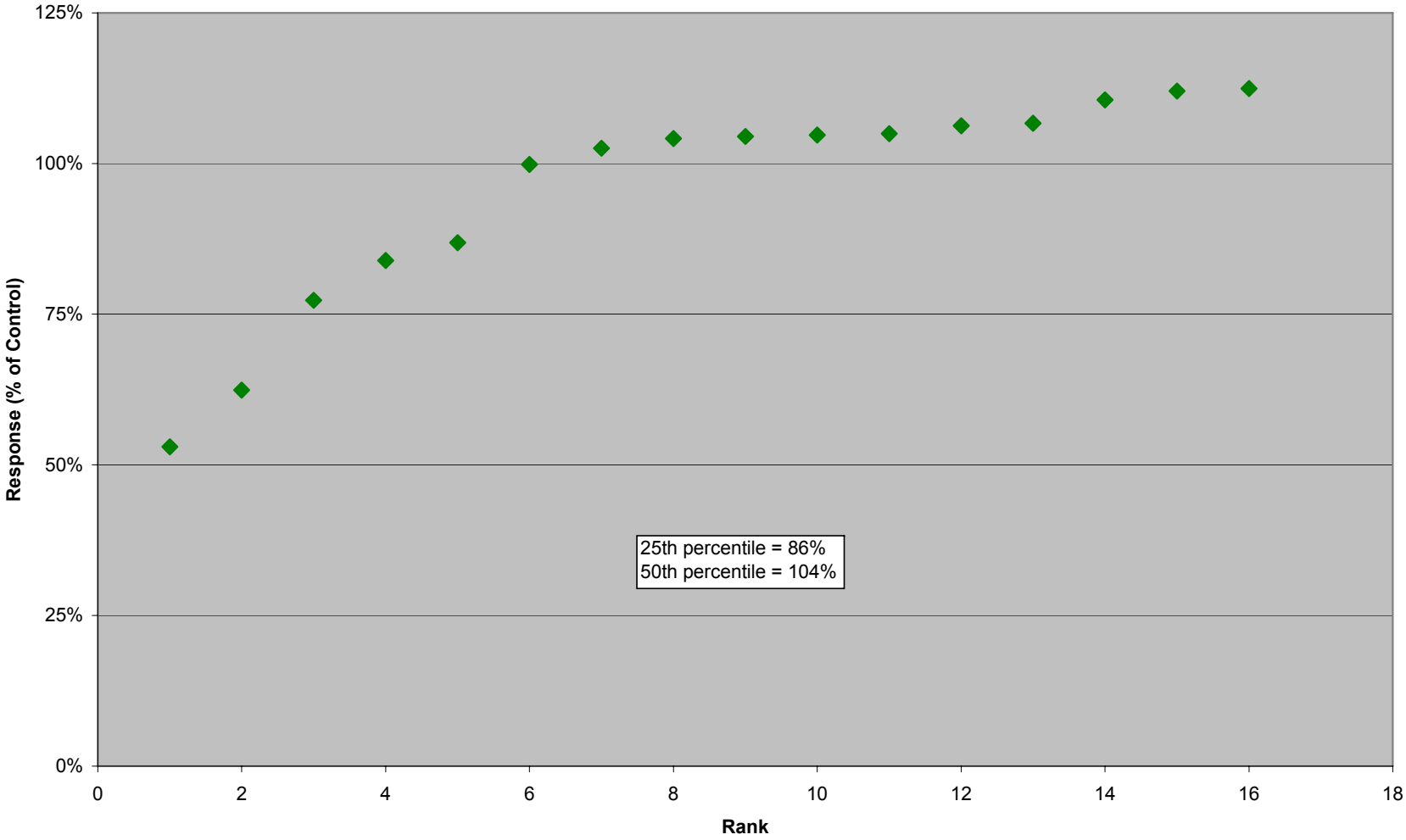


Figure F.5: "Ranked Response Distribution" for Turner Valley 3.7% Soils, Year 5 (Mean F3 = 2,545 mg/kg)

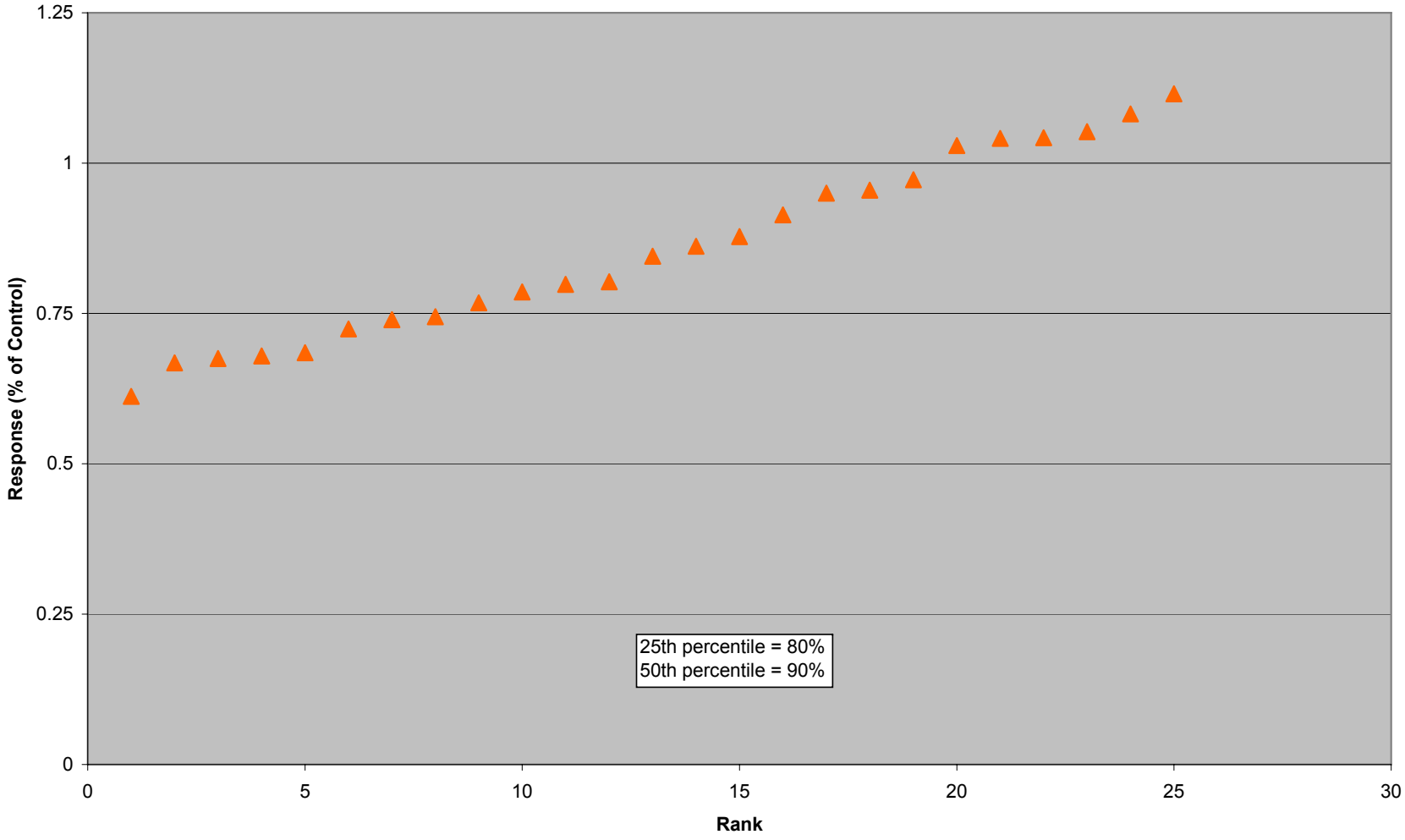


Figure F.6: Species Sensitivity Distribution for Cermak (2005) Data

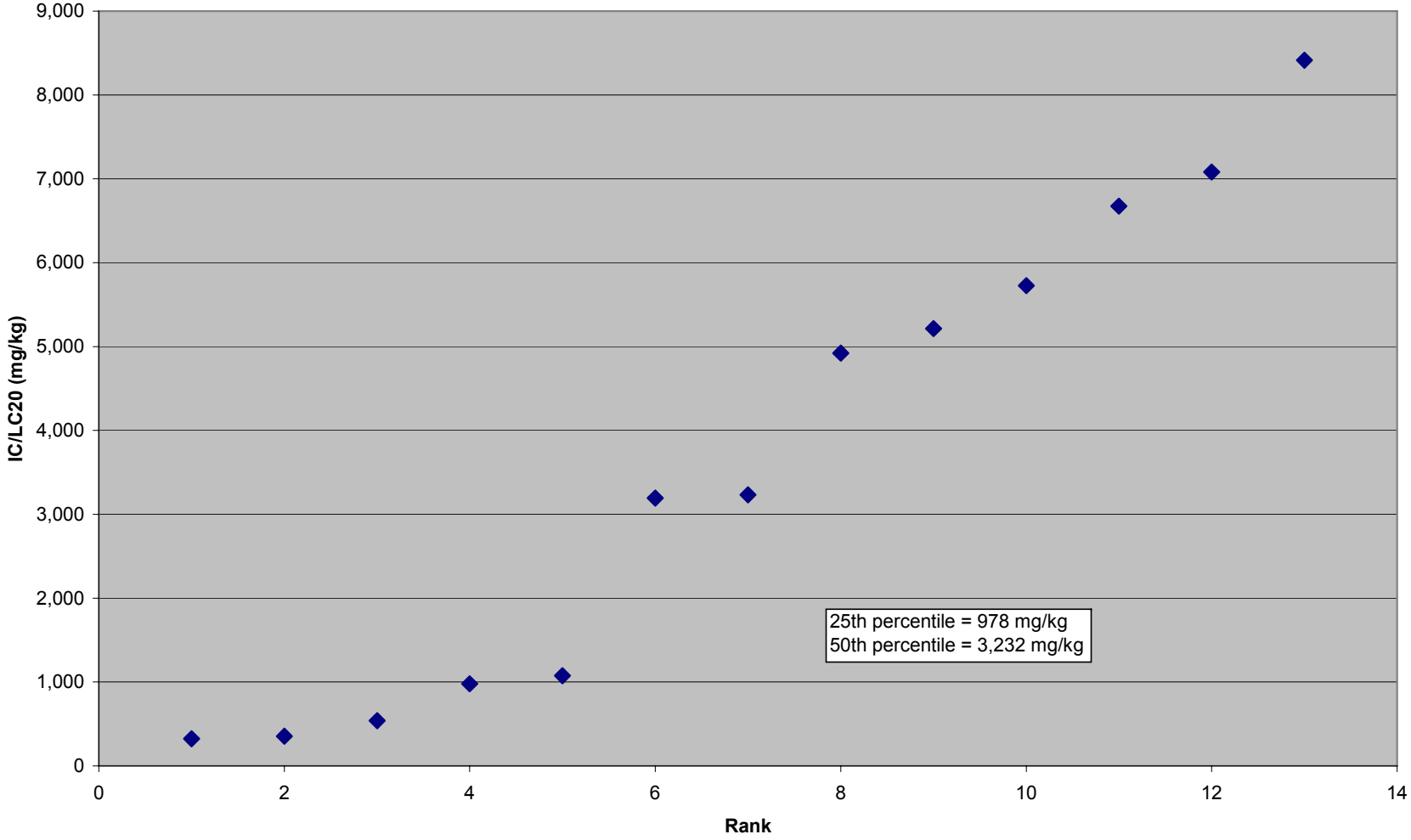


Figure F.7: Species Sensitivity Distribution for Visser (2005b) Data

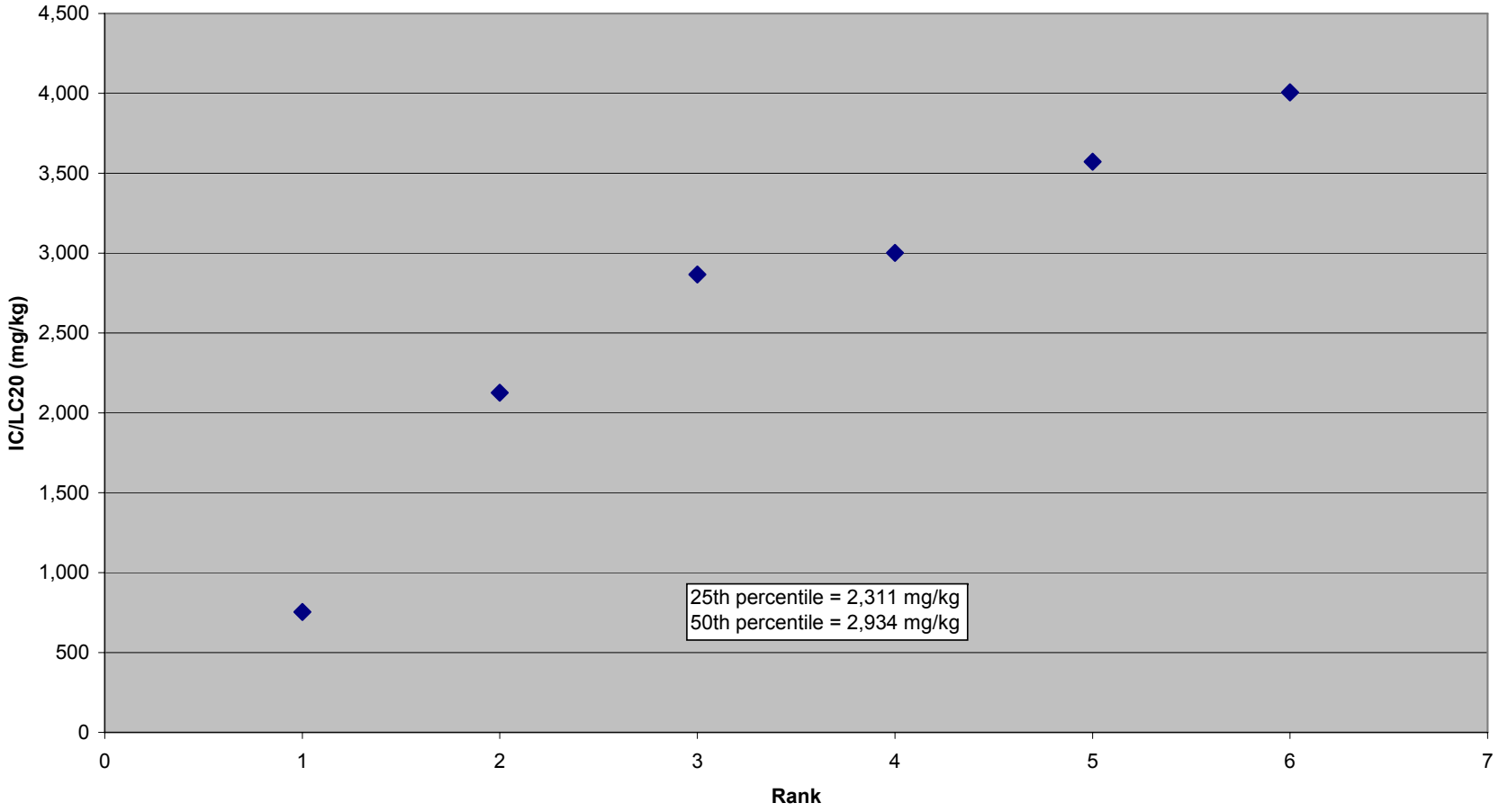


Figure F.8: Richmound - Correlation of CCME vs. G108 F3 Analysis

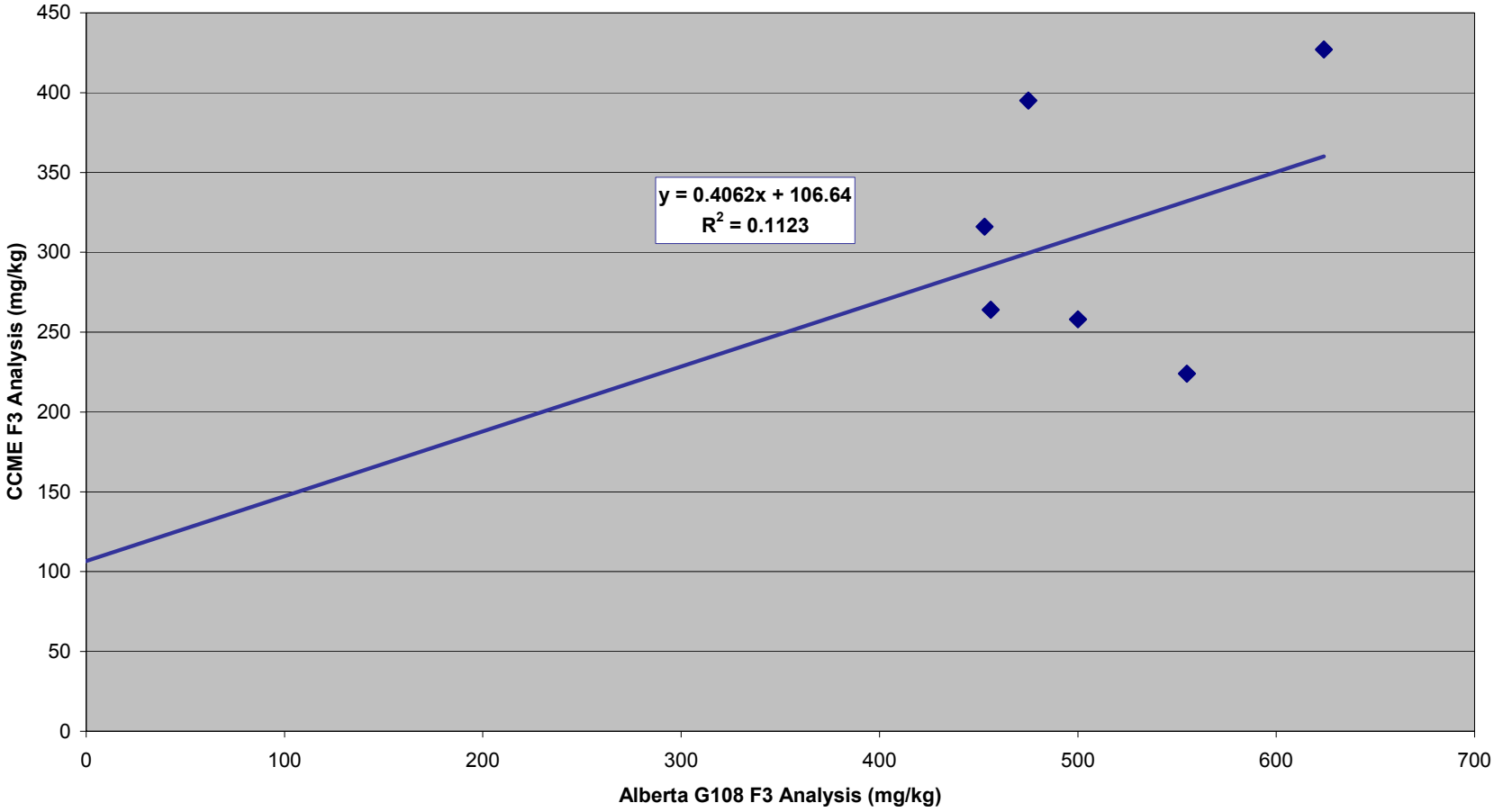


Figure F.9: "Ranked Response Distribution" for Richmound 1.2% Soils, 32 Months (Mean F3 = 390 mg/kg)

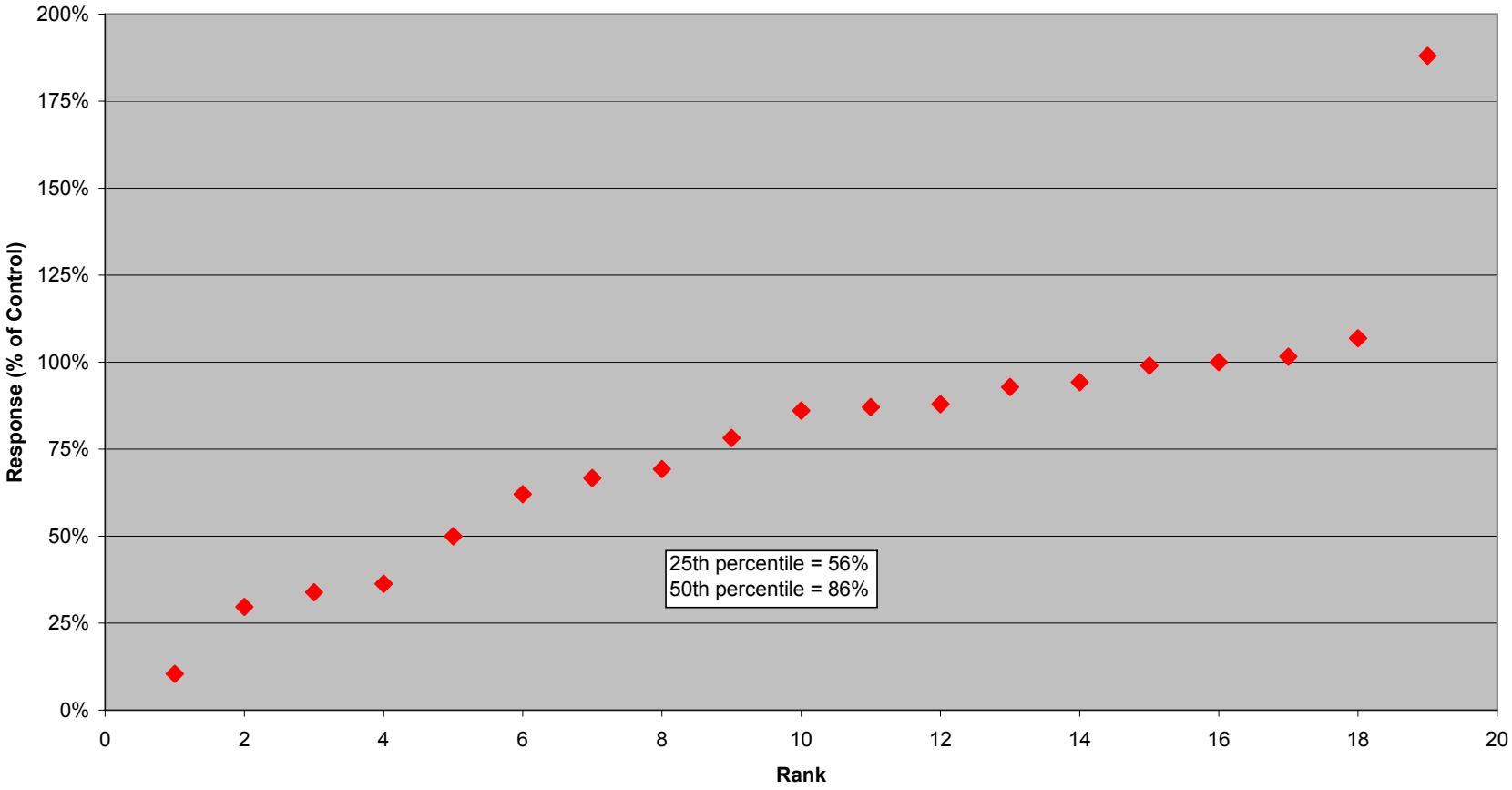


Figure F.10: "Ranked Response Distribution" for Richmound 1.2% Soils, 36 Months (Mean F3 = 330 mg/kg)

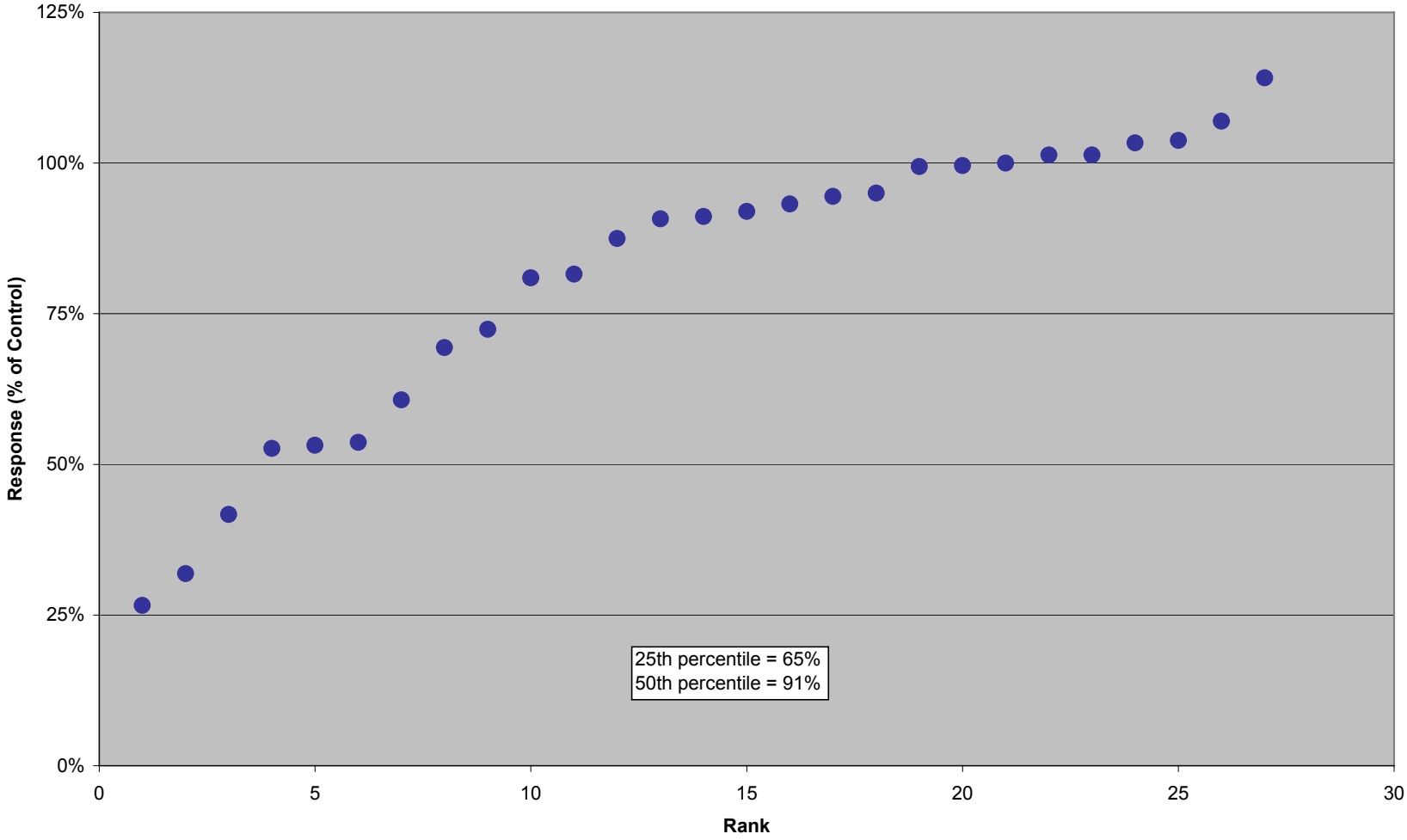
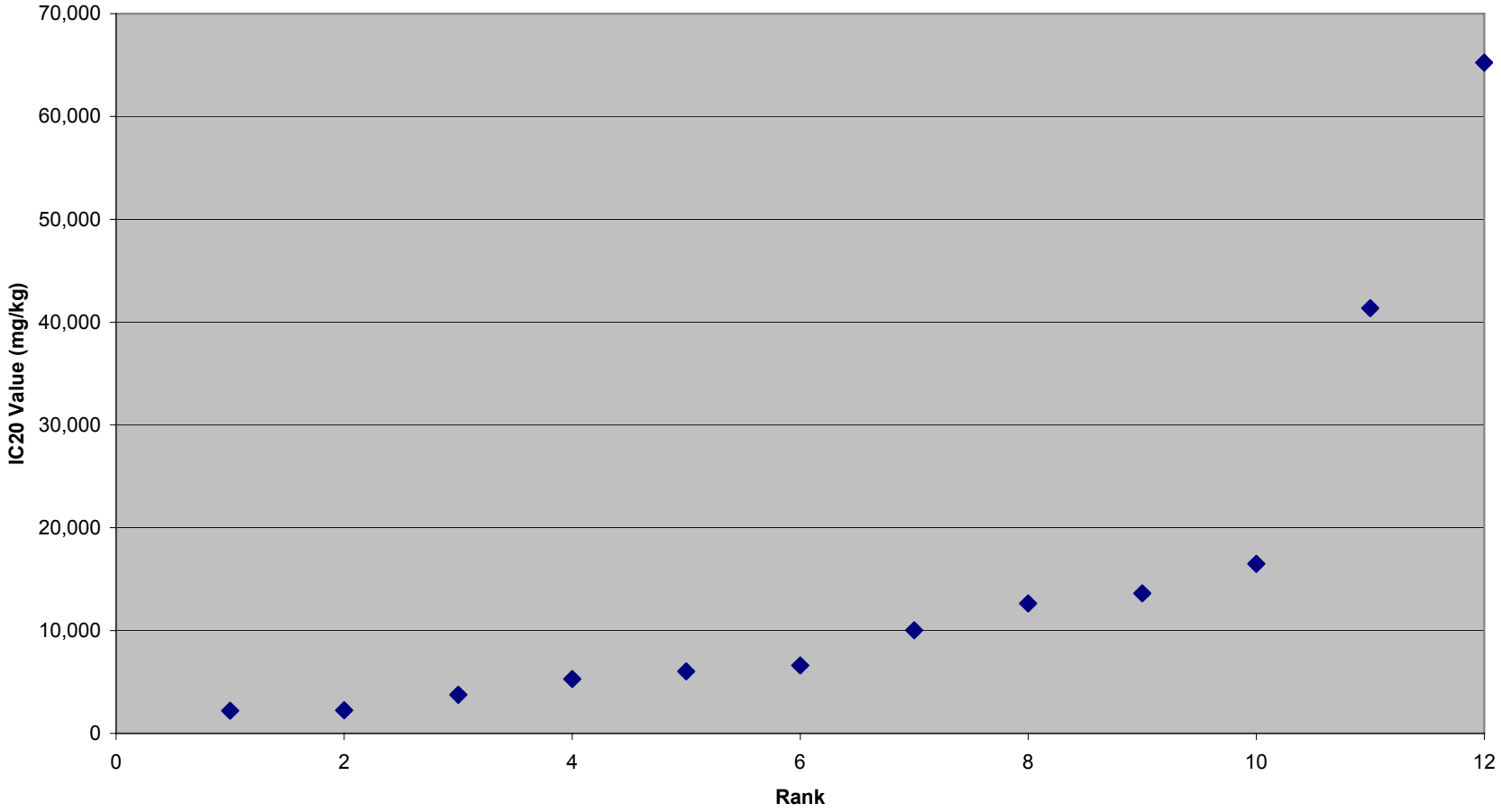


Figure F.11: Species Sensitivity Distribution for F4 in Fine Soil



APPENDIX G: Toxicity of PHCs in Weathered Soil

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 Studies by Visser *et al*.

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 D.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 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.

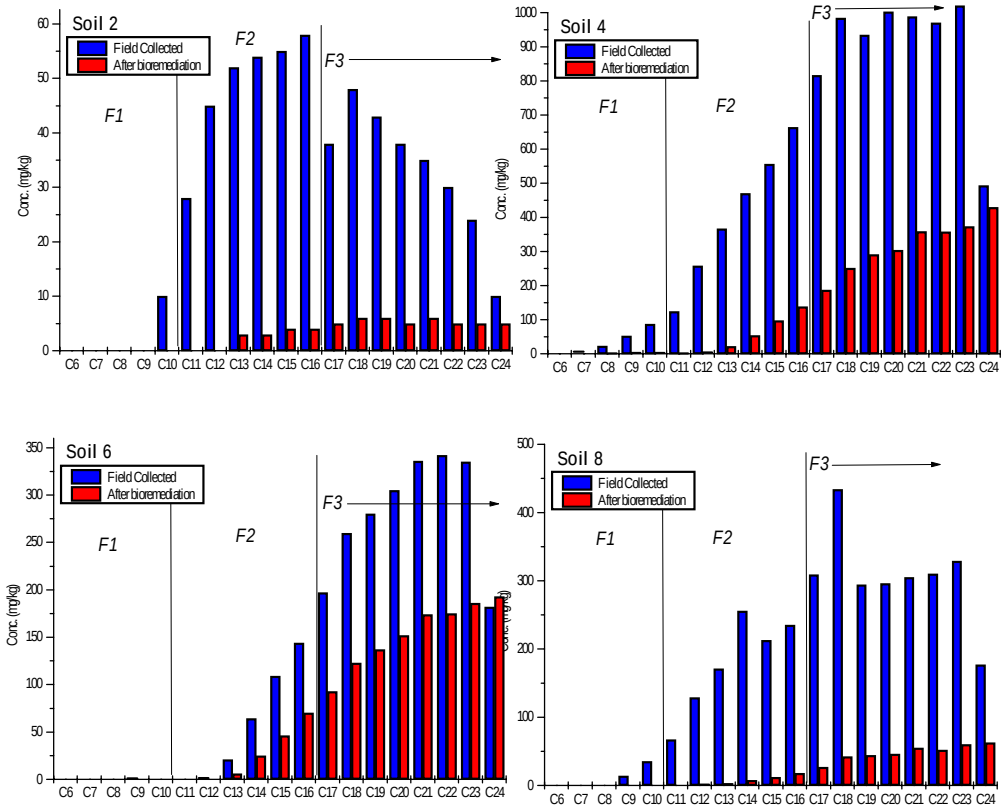


Figure G.1: C6 to C24 PHC carbon profiles for field collected and subsequently bioremediated soils.

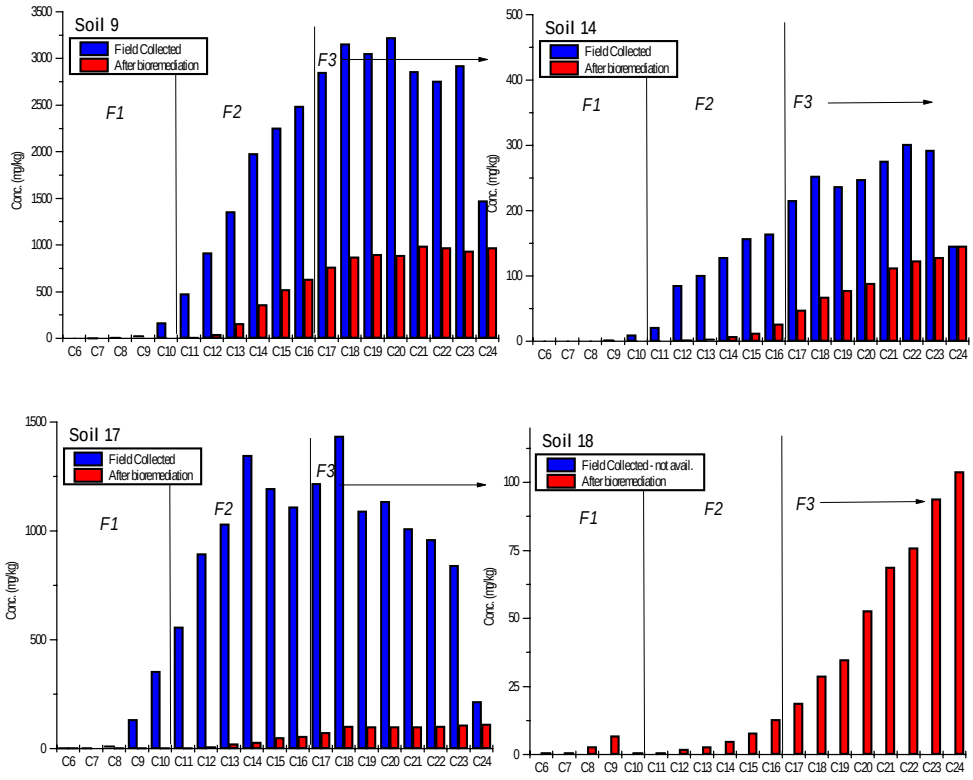


Figure G.2: C6 to C24 PHC carbon profiles for field collected and subsequently bioremediated soils.

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.

In 1999 in a project funded through PERF (GRI, 2000), it was concluded that–

> "…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, the report 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 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 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 D.16 and D.17, 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 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 D.2.4 to D.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.

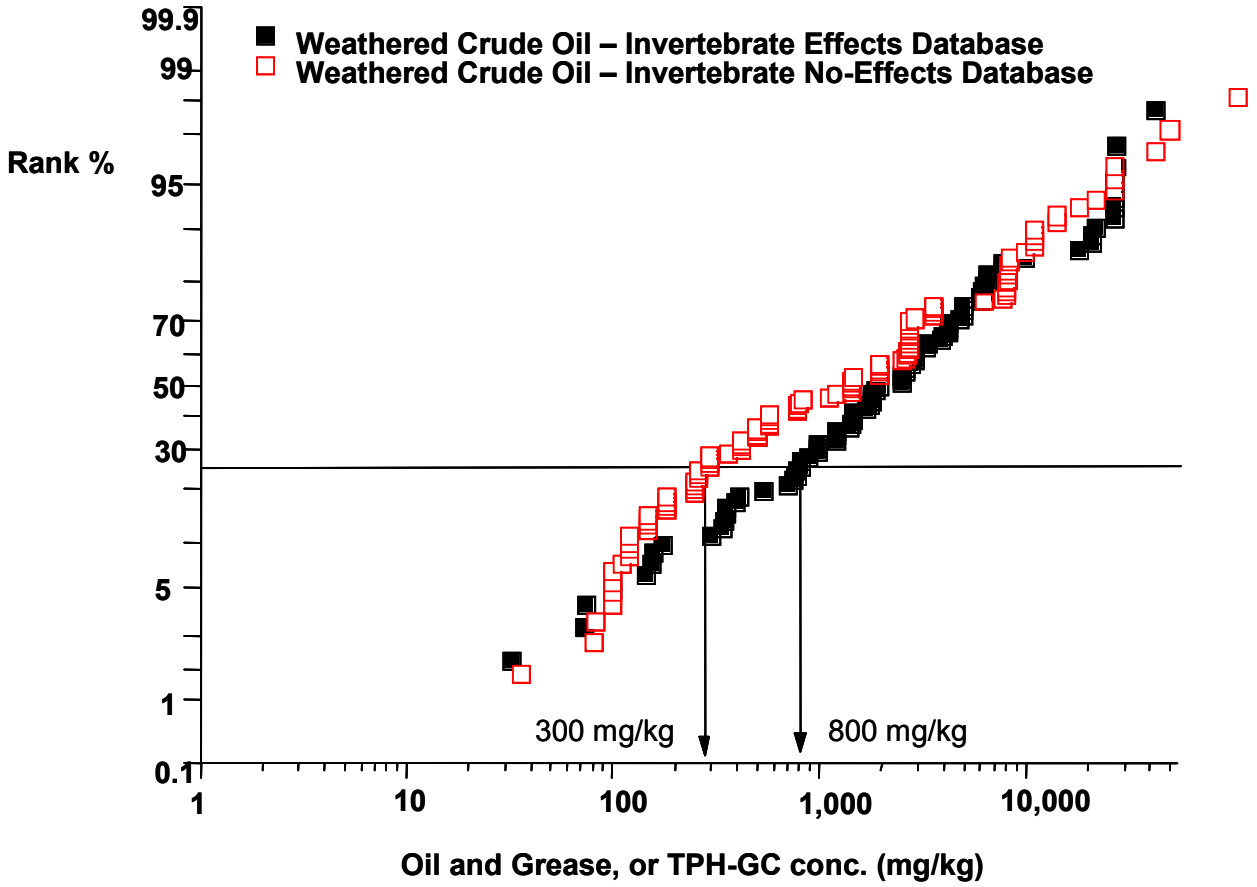


Figure G.3: Ranks data for toxicity of weathered crude oil to soil invertebrates (with comparison of effects and no-effects data distribution).

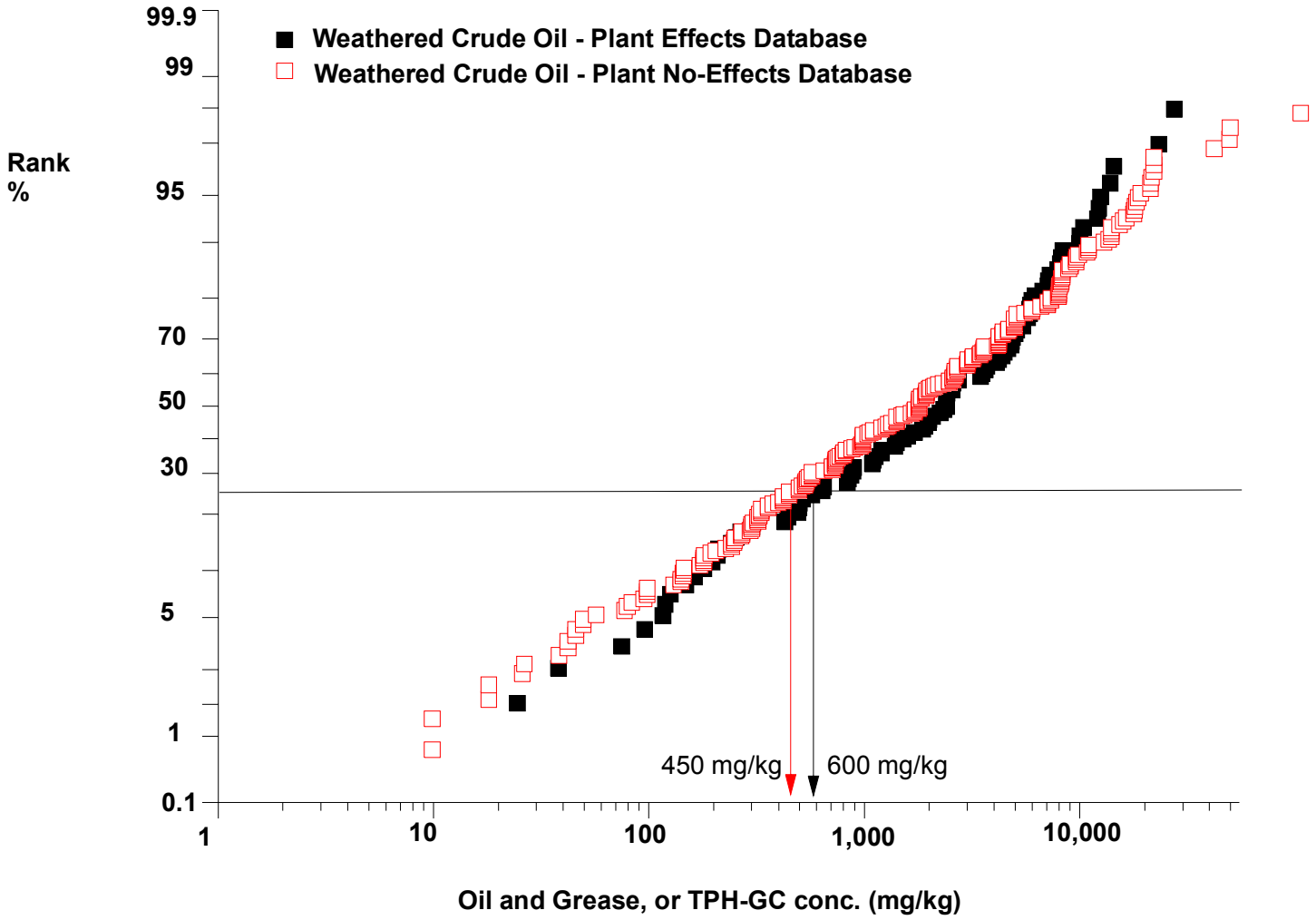


Figure G.4: Ranks data for toxicity of weathered crude oil to plants (with comparison of effects and no-effects data distribution).

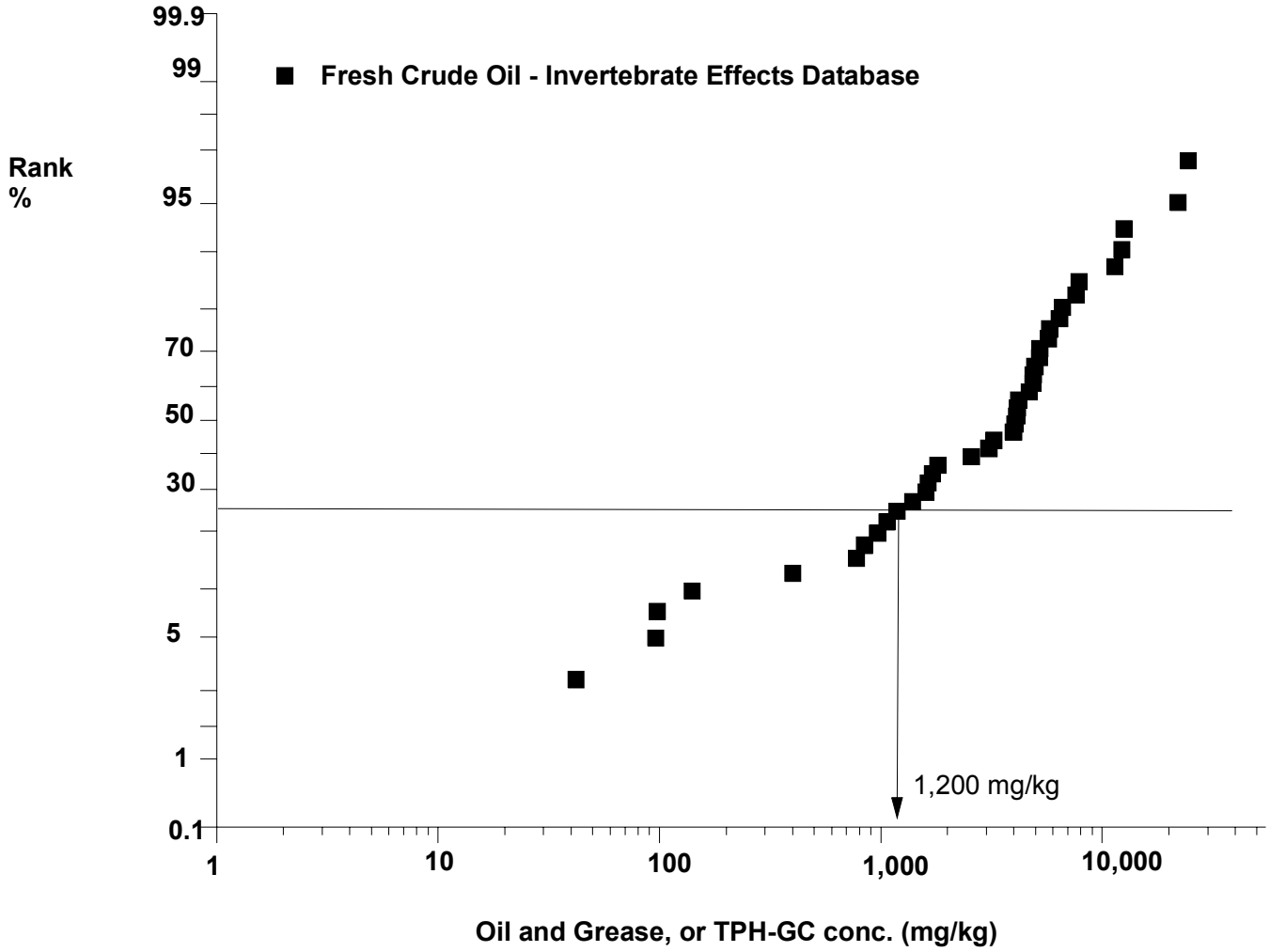


Figure G.5: Ranks data for toxicity of fresh crude oil to soil invertebrates.

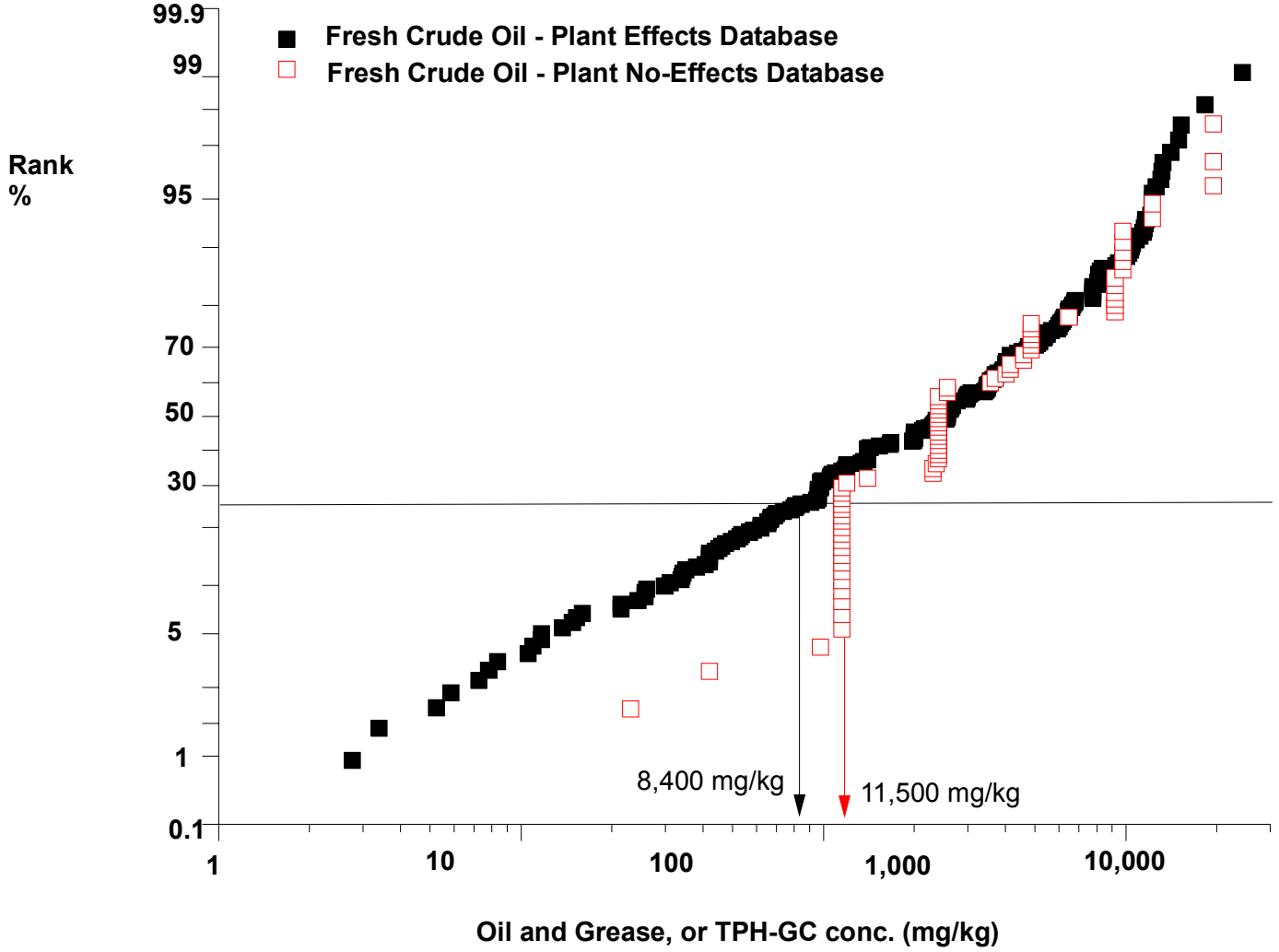


Figure G.6: Ranks data for toxicity of fresh crude oil to plants (with comparison of effects and no-effects data distribution).

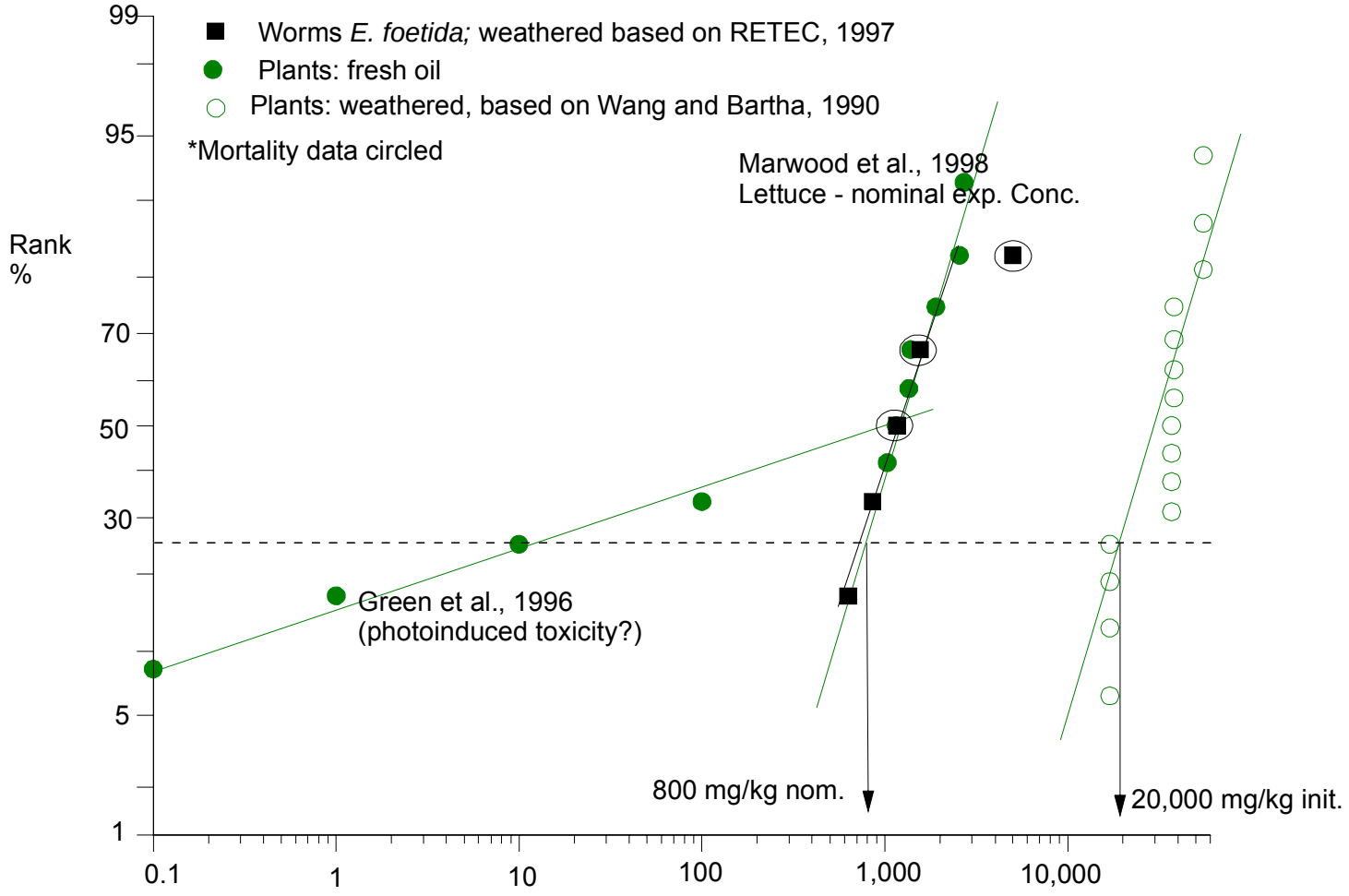


Figure G.7: Toxicity of diesel or heating oil to soil invertebrates and plants.

APPENDIX H: Estimation of Toxicity of PHC to Aquatic Receptors

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 B.1, Appendix B) 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 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 H.1):

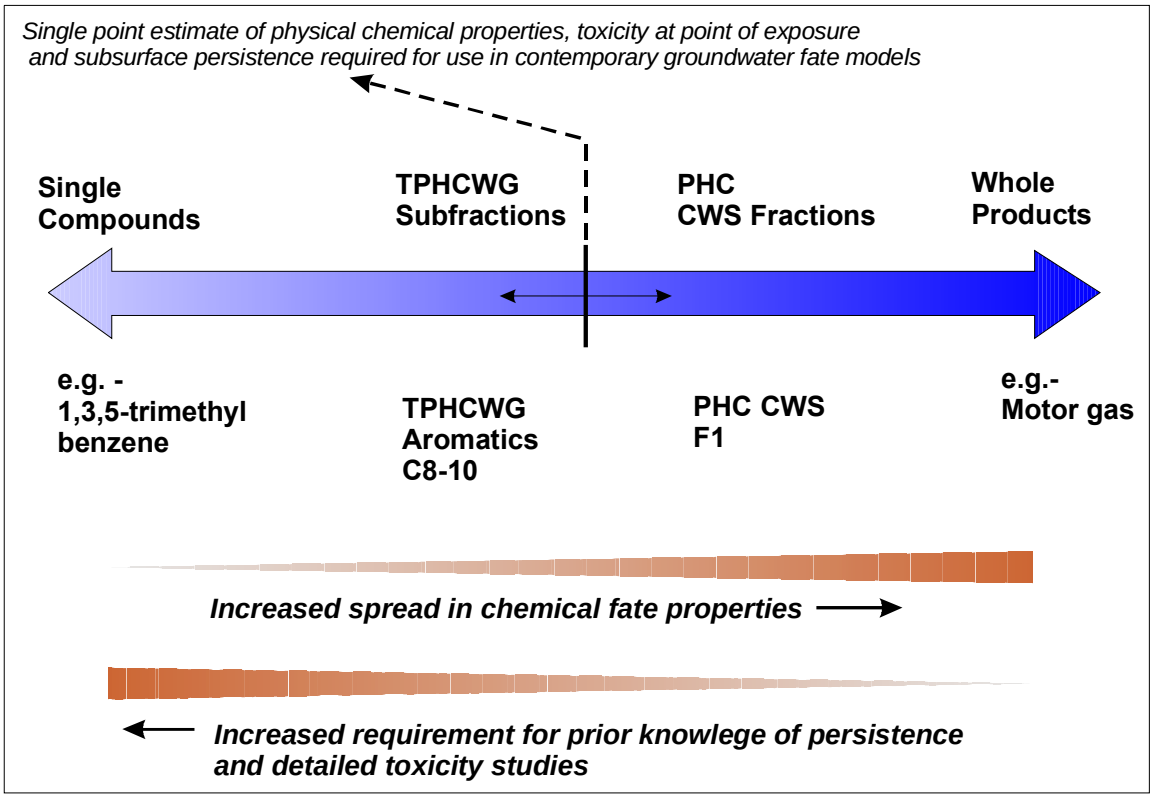


Figure H.1: Compromise between precision of estimates and level of detailed knowledge of chemical-specific toxicity.

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.

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*

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 PHC 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 PHC 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 PHC 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 PHC present in either fraction F1 or F2.

The two approaches are described in more detail below.

Use of a Surrogates-Based Approach to Define Acceptable Ambient Water Concentrations

BC 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 fraction 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 LEPH 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 LEPH 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:

Fraction 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.

Fraction 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

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

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. –

$$\textit{Toxicity Reference Value (CWS Fraction)} = \frac{1}{\Sigma \left[MF_{sub\text{-}fj}/TRV_{sub\text{-}fj}\right\}}$$

where –

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

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

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

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

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

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

$$\textit{Toxicity Reference Value (CWS F2-draft)} = \frac{1}{[(0.8/\ 130\ \mu g/L.)+(0.2\ /\ 11\ \mu g/L)]}$$

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

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 H.1, 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% <nC6 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

The expected relative contribution of individual non-BTEX aromatics to F1 is also shown in Figure H.2: 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 H.2, and summarized in Figures H.3 through H.5. 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 H.2), 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.

Table H.1: 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.

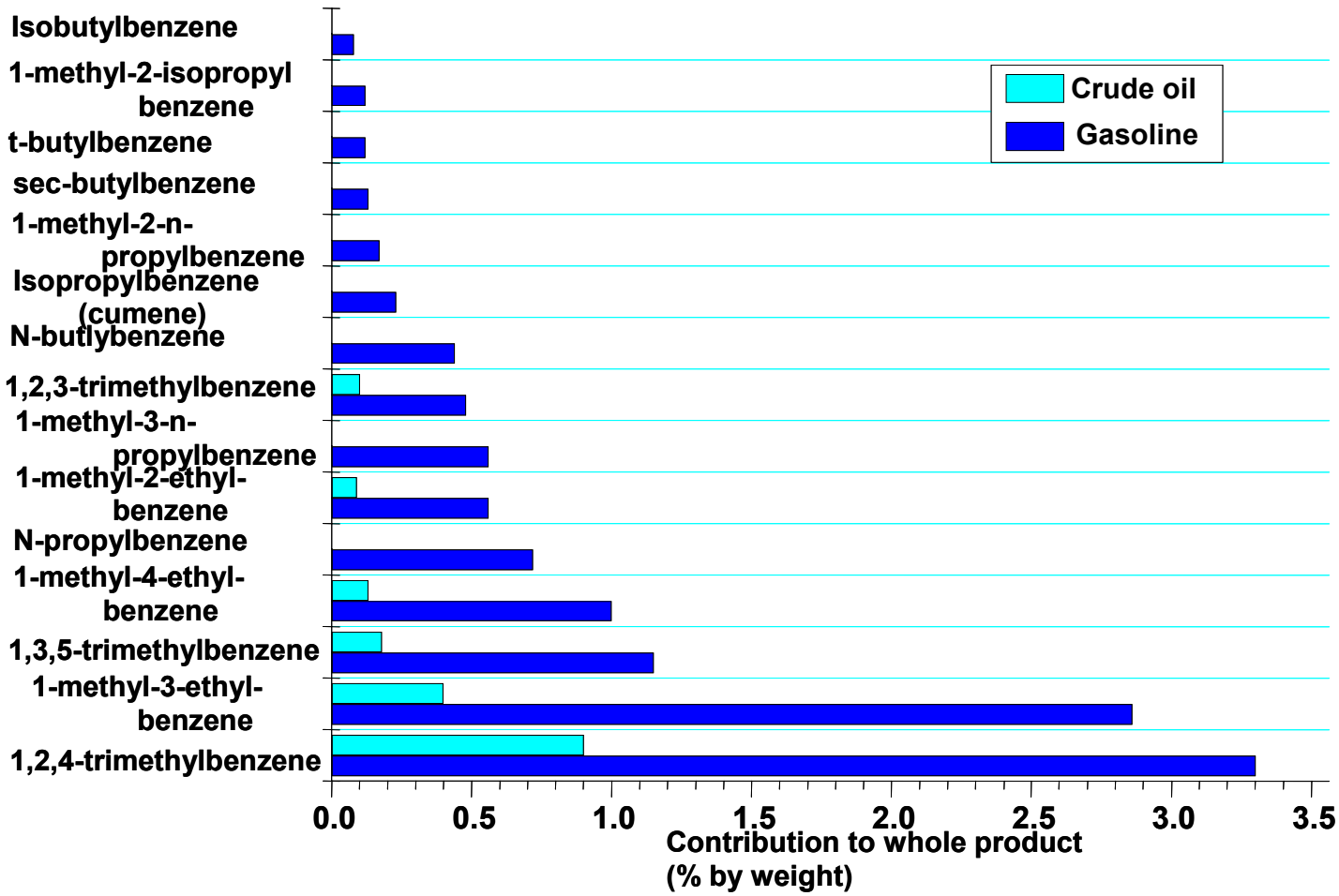


Figure H.2: Relative abundance of different non-BTEX aromatics in F1.

Table H.2: 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.
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.

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	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.
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.

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	*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.
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.

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	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.

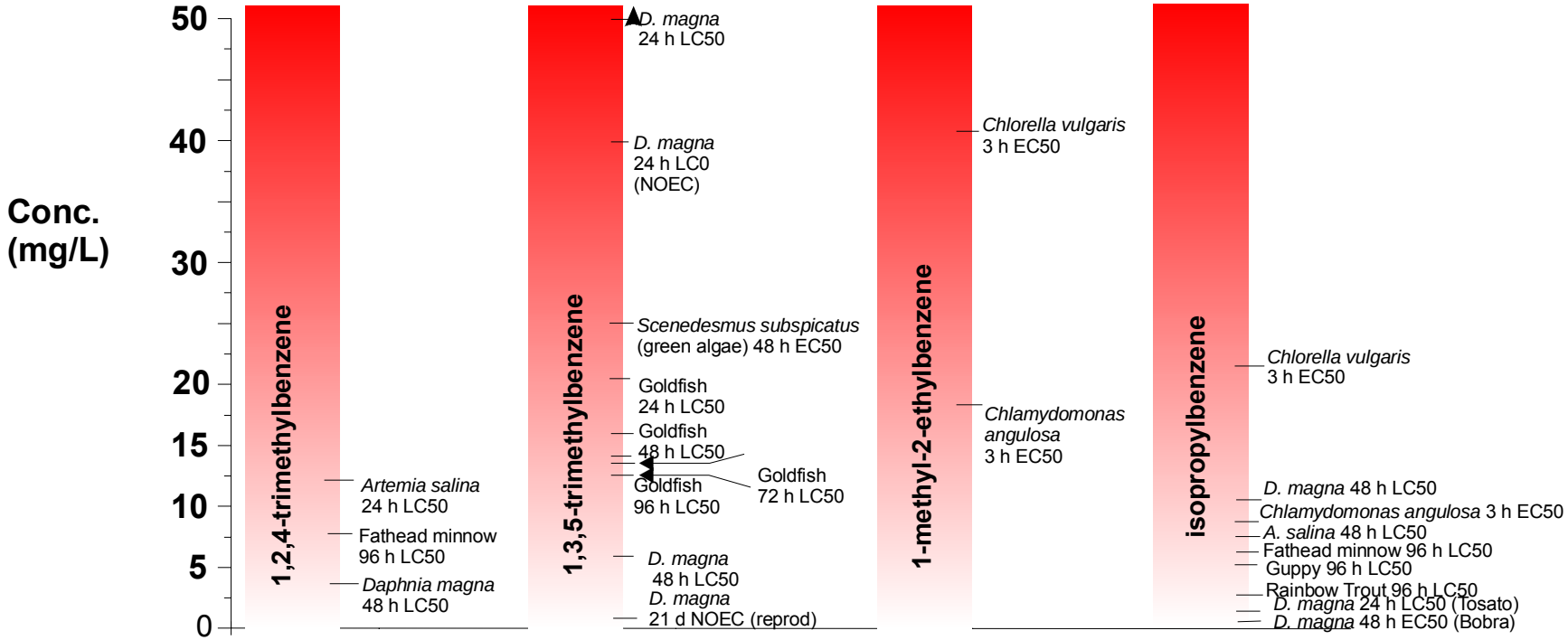


Figure H.3: Illustration of the aquatic toxicity of alkylbenzenes.

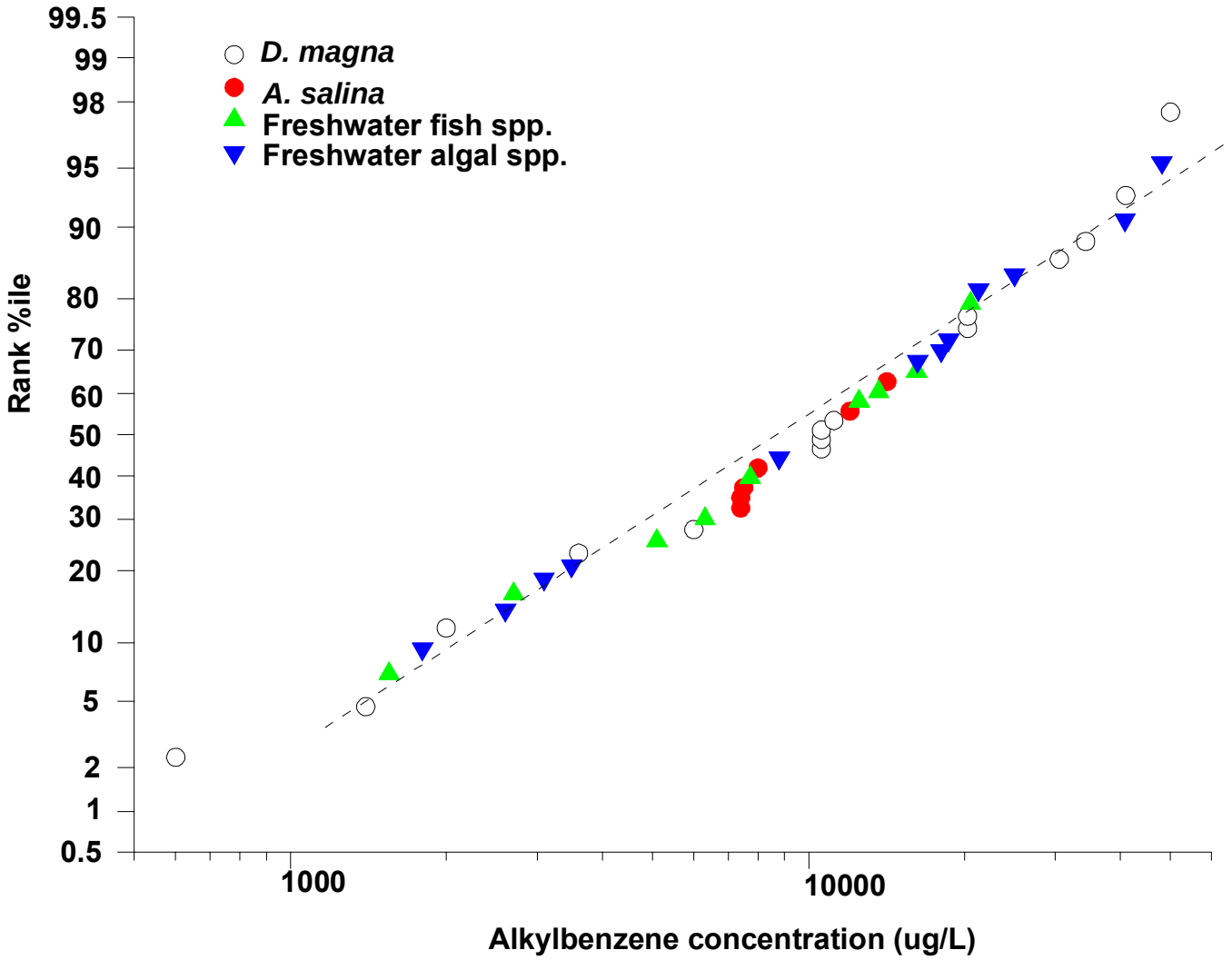


Figure H.4: Re-constructed aquatic species sensitivity distribution based on the available toxicity data for alkylbenzenes.

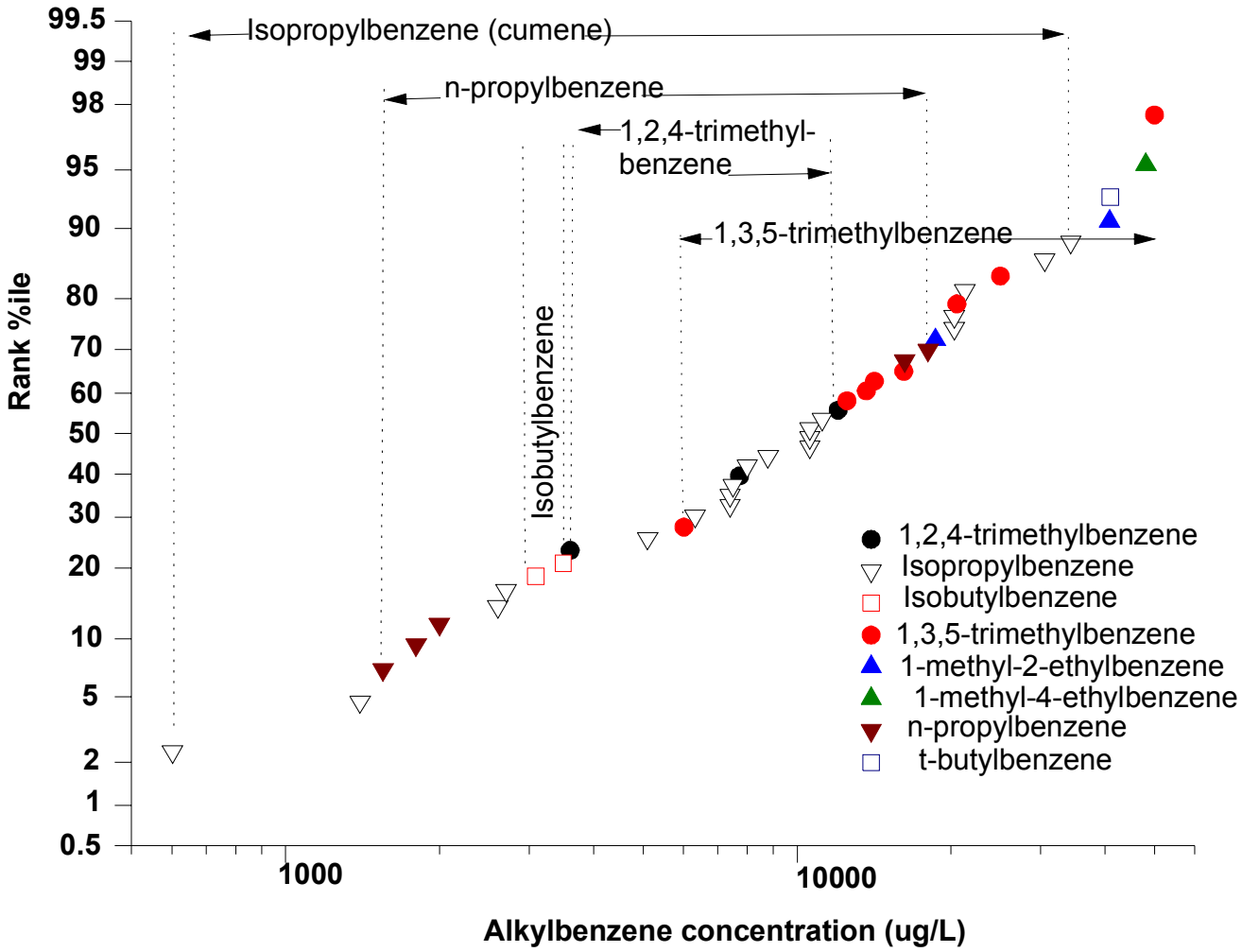


Figure H.5: Re-constructed aquatic species sensitivity distribution based on the available toxicity data for alkylbenzenes – Relative toxicity of different alkylbenzenes.

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.

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 PHC 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 PHC relative to the previously described approach. Hence, the available aquatic toxicity data for alkylbenzenes (Table H.2) 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 H.4 was re-plotted (Figure H.6), 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 PHC 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 PHC, 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 previously, *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. Under the previous approach, the uncertainty factor applied in extrapolating from a sub-chronic to chronic endpoint was adjusted in light of this.

Di Toro *et al.* (2000) applied the critical body residue approach to develop water quality criteria for narcotic contaminants in general, and PAH 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 predictable, however, and Di Toro *et al*. (2000) 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 5^{th} %ile of the ranked data (as specified in the USEPA guidelines for establishing water quality criteria), and provide a universal acute-chronic ratio adjustment.

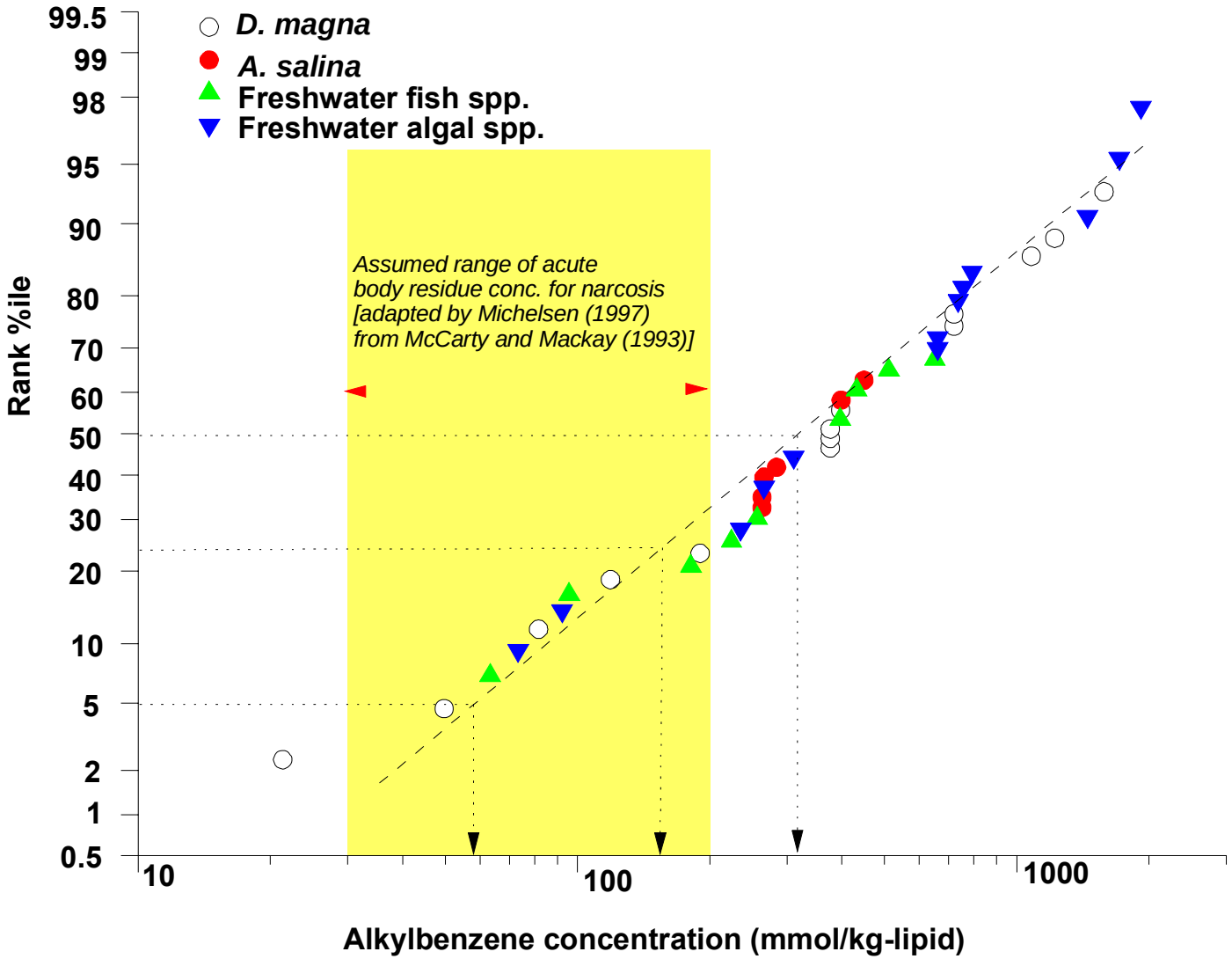


Figure H.6: Range of critical body residues calculated from experimentally derived acute toxicity (primarily LC_{50}) endpoints for alkylbenzenes. [NB: plant endpoints were acute impairment of photosynthetic pigments (absorbance) and cell division (culture turbidity)].

Table H.3 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 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 H.3: 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 -

$$C_W = \frac{BR_{LB} x\ K}{K_{ow}}$$

Table H.4: 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 (Gustafson *et al.*, 1997)
B: Based on empirical relationship between Koc and Kow developed by Karickhoff *et al*. (1979).

Final Reconciliation of Approaches

The F1 (167 μg/L) and F2 (42 μg/L) toxicity reference values developed previously 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 H.5).

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 PHC 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 LC_{50}) the value derived is 150 μg/L - not far different from 167 ug/L.

Table H.5: 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 LC_{50} 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 4.7). This compares favourably with a threshold toxicity reference value of alkylbenzenes as discussed previously 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 4.7 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

APPENDIX I: Toxicity of PHC in Water to Livestock

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 PHC 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 ingestion 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 major contributors to the internalized dose. For PHC, 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 PHC 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 I.1). Unweathered oil (with a specific gravity of 0.843) exhibited a threshold dose of 2.5 mL/kg (adapted from Stober, 1962).

Table I.1: 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) $\mathbf{RfC_{LDW}} = (DTED_{LDW} \times AF \times BW)/WIR,$

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 Puls (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) $\mathbf{RfC_W} = (210 \text{ mg/kg bw/d} \times 0.2 \times 550 \text{ kg bw})/100 \text{ L/d}$

$= \mathbf{230 \text{ mg/L fresh crude}}$

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 230 mg/L	=	**53 mg/L;**
PHC CWS F2:	= 0.213 x 230 mg/L	=	**49 mg/L;**
PHC CWS F3:	= 0.345 x 230 mg/L	=	79 mg/L;
PHC CWS F4:	= 0.182 x 230 mg/L	=	42 mg/L.

Fractions F3 and F4 were removed from further consideration since (i) the bioavailability and gastrointestinal absorption of petroleum hydrocarbons >C16 is expected to be limited, and (ii) the water solubilities of these fractions are much lower than the provisional RfC_{LDW} estimates.

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 kerosene. 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. Kerosene 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 kerosene 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).

APPENDIX J: Groundwater Model Sensitivity Analysis

The following analyses were conducted during the derivation of the 2001 PHC CWS. While certain model parameters have changed, the sensitivity analyses have value and are therefore retained in this appendix.

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 K 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 Appendix H,, 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).

TPHCWG Aliphatics C6-C8. Table J.1 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 and chemical property assumptions as documented in Appendix C.

Table J.1: 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

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.

TPHCWG Aromatics C8-C10. Table J.2 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 Appendix C.

Table J.2: 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				

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 J.3: 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

TPHCWG Aromatics C10-C12. Table J.4 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 and chemical property assumptions as documented in Appendix C.

Table J.4: 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					

TPHCWG Aromatics C12-C16. Table J.5 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 and chemical property assumptions as documented in Appendix C.

Table J.5: 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					

Associated Issues: The Influence of Soil Organic Carbon Content (Foc).
The calculated sub-fraction soil quality guidelines presented in Tables J.1 to J.5 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 J.1-J.5, 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 J.1:

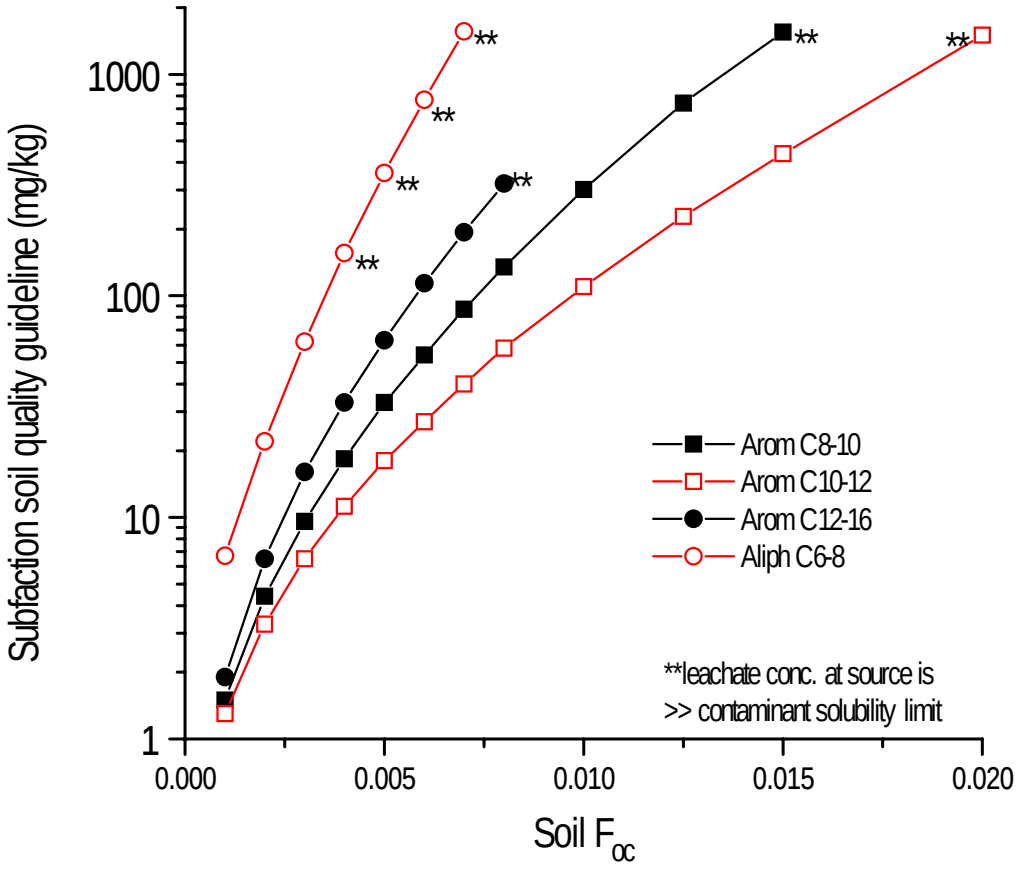


Figure J.1: Change in modeled PHC soil quality benchmarks based on changes in soil organic carbon content.

APPENDIX K: 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 K.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 K.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	
Benzo(b)fluoranthene	1.97-3.34 year	groundwater (estimated)	Howard *et al.*, 1991	

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
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
Phenanthrene	28-46 day	soils in slurry reactor	Loehr and Webster, 1997	soils from slurry reactor treatment of PAH contaminated wood-treatment site

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
	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	
2-ring PAHs	17-48 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)	
3-ring PAHs	31-176 day			
4-ring PAHs	206-1,003 day			

Substance	Estimated Environ-mental Half-Life	Medium/ Conditions	Reference	Notes
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. High concentrations or presence separate or occluded phases that limit contaminant exposure to microbial processes will be important in determining rates of contaminant degradation. Similarly, low redox conditions resulting from either natural conditions or from biological and chemical reactions occurring in zones of high PHC concentration may also be strongly influential in determining expected half lives.

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 biodegradation 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 days**
2. **CWS F2: 1,750 days**

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.