

2003 Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effect on Soil Quality, Fraction-Specific Toxicity of Crude Oil, Phase 1

The Canada-wide standards (CWS) for petroleum hydrocarbons (PHCs) are currently being developed pursuant to the 1998 Canada-wide Accord on Environmental Harmonization of the Canadian Council of Ministers of the Environment (CCME) and its Canada-wide Environmental Standards Sub-agreement. The goal for the development of the Canada-wide standards for PHCs is to provide a consistent approach to managing PHC-contaminated sites across the country and to protect human health and the environment by determining the acceptable risk associated with exposure to these substances in soils and other environmental media.

A number of research programs were initiated to provide supporting documentation in the form of toxicity data to aid in the CWS development process.

To this end, participants of the Petroleum Technology Alliance Canada (PTAC) and the Canadian Association of Petroleum Producers partnered with the Program of Energy Research and Development (PERD) and Alberta Environment to support a multi-year, two-phase research program to determine the fraction-specific hydrocarbon toxicity of crude oil for the derivation of soil quality guidelines for the soil contact exposure pathway.

This initiative was divided into two phases. The aim of Phase I, comprising this report titled "Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality: Phase I Fraction-specific Toxicity of Crude Oil", was to develop a fraction-based approach to support ecologically-relevant, risk-based, PHC soil quality criteria for the protection of environmental health. The aim of Phase II, comprising a companion report titled "Toxicity of Petroleum Hydrocarbons to Soil Organisms and the Effects on Soil Quality, Phase II: Field Studies", was to examine the ecotoxicological properties and risks, if any, of weathered hydrocarbon residuals exceeding 1000 µg/g in agricultural soils.

Phase I was divided into two parts. Part 1 involved assessing the toxicity of a crude oil mixture and three hydrocarbon fractions (Fraction 2 or F2, Fraction 3 or F3, and Fraction 4 or F4) to a battery of terrestrial test species comprising plants (barley- *Hordeum vulgare* L., corn- *Zea mays* L., alfalfa-

Medicago sativa, northern wheatgrass- *Agropyron dasystachyum* [Hook.] (Scribn.)) and soil invertebrates (earthworms- *E. andrei* [Bouché], *Lumbricus terrestris* L. and springtail- *Onychiurus folsomi* [Schäffer, 1900]) using standardized toxicity tests (acute and definitive or chronic). Measurement endpoints for the acute tests were survivorship and/or growth (i.e., shoot and root length, shoot and root wet and dry mass); endpoints for the longer tests included survivorship, growth and/or reproduction parameters such as fecundity, number of offspring or juveniles produced per treatment, and number of hatched or unhatched cocoons produced per treatment.

Part 2 involved assessing the toxic interactions of three fractions of crude oil (F1, F2, and F3), the fractions responsible for a significant proportion of the toxicity. One species of earthworm (*E. andrei*) and one species of plant (*H. vulgare*) were used to determine the toxic interactions using a "toxic unit" approach.

The crude oil was a typical light, sweet, Alberta crude from the Federated fields near Swan Hills, Alberta. It was distilled to generate four hydrocarbon fractions. Fractions 1, 2, 3, and 4 comprised both aromatic and aliphatic constituents with carbon numbers ranging from n-C6 to n-C10, >n-C10 to n-C16, >n-C16 to n-C34, and >C34, respectively. The expected mass percentages of the four pre-selected fractions of the crude oil were 25, 25, 35, and 15% for Fractions

1, 2, 3, and 4, respectively. Two separate batches were distilled to generate sufficient material for testing. For Phase I, the material comprising Fractions 2 and 3 originated from the first batch, whereas F4 originated from the second batch. F2 and F3 used in tests to evaluate the toxic interactions were also from the second batch; F1 was from the first batch. The boiling point ranges for the fractionation method were 50-173EC, 174-287EC, 288-481EC, >481EC for F1, F2, F3, and F4, respectively.

The hydrocarbon fractions and the crude oil mixture were characterized using GC/FID (gas chromatography with flame ionization detection) and GC/MS (gas chromatography mass spectrometry) analyses. A gravimetric technique was used to determine the weight of the saturates, aromatics and total petroleum hydrocarbons (i.e., those hydrocarbons >C40) in Fraction 4 and the crude oil.

Two types of toxicity tests were performed: 1) acute (e.g., 5-14 d) screening toxicity tests whereby test organisms were exposed to relatively high concentrations of the petroleum products in soil for relatively short periods of time; and, 2) chronic or definitive (e.g., 14-72 d) tests whereby test organisms were exposed to relatively low concentrations of the petroleum products in the soil for relatively prolonged periods of time. Acute toxicity or screening tests were performed primarily to identify the "effective" concentrations that result

in a particular response or range of responses in the test organisms. The results of the acute toxicity tests were used to determine the optimal range of exposure concentrations that would best describe the concentration-response relationship for organisms exposed to sub-lethal levels of petroleum hydrocarbons in soil for the longer definitive or chronic tests. The test procedures, conditions and methods for the terrestrial plants and soil invertebrates closely followed those developed for the new terrestrial test methods being written by Environment Canada.

The petroleum products were evaluated in two types of media or test substrate, an artificial soil that was formulated in the laboratory and a field-collected soil that was representative of a prairie soil from Alberta. The artificial soil (AS) represented a coarse-textured soil similar to that of Fox Sand, an agricultural soil from Ontario. The field-collected reference soil (RS) was a clay loam, Black Chernozem representative of a moderate- to fine-textured agricultural soil typically found in Alberta prairie lands. All definitive and chronic tests were conducted with the reference soil only.

Final Report