FINAL PAPER: Development of Site-Specific Remedial Objectives (SSRO) for Weathered Petroleum Hydrocarbons in Peat Soils. Harris, C.S. and R. Jackson. AMEC Earth & Environmental, Edmonton, Alberta.

Introduction and Scope

AENV September 2001 guidelines do not apply to organic, peat rich soils. In the absence of specific guidelines, AENV applies *de minimis* coarse grained criteria to peat soil environments. Consequently, the objective of the recent AMEC site characterization and toxicological work is to develop a SSRO under the AENV September 2002 Tier 3A approach. The Tier 3A approach allows proponents who remediate their sites to the SSRO to obtain "closure" for the sites. The Tier 3A approach still includes all applicable land use receptors included with Tier 1, and assumes protection of those receptors is achieved without the need for engineered or institutional controls. The Tier 3A approach involves more detailed site-specific information, including site-specific toxicity information, and rigorous, defensible scientific rationale.

The overall work program for the remote, northern boreal hydrocarbon spill was to fully characterize and delineate the nature of the hydrocarbon contamination and to develop a risk based, site specific remedial objective (SSRO). The SSRO will provide Tier 1 equivalent environmental protection without the need for any land use restrictions or engineered barriers. Secondly, the SSRO was expected to provide a soil hydrocarbon numerical remedial target that would be technically and economically achievable.

This paper highlights that component of the overall scope focusing on the selection, and use, of the site-specific soils in a battery of terrestrial soil toxicological bioassays supporting the numerical SSRO. The provincial regulatory framework is outlined in AENV September 2001 and the development of the soil quality guidelines followed the protocols set forth in the CCME[1], 1996 and CCME[2] December 2000 guidance and scientific rational documents.

For natural land use areas, AENV September 2001 lists several receptor pathways that require protection. These include protection of groundwater for human/wildlife ingestion and aquatic life. The development of the SSRO only evaluated the hydrocarbons in the residual range (F2 + F3 + F4), with organisms representative of the direct ecological soil contact pathway. Therefore, AENV September 2001 Tier 1 *de minimis* criteria for the light end aromatics (BTEX) and aliphatics (F1) shall apply as the remedial targets for these fractions. Additionally, where a water body exists within 300 m downgradient of the site, the F2 remedial soil criteria defaults to that designed to be protective of aquatic life.

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[1] CCME, March 1996. A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines.

[2] CCME, December 2000. Canada-Wide Standards for Petroleum Hydrocarbons (PHC's) in Soil: Scientific Rationale, Supporting Technical Document.

Ecological Setting

Regionally, the undisturbed land surrounding the site lies within the Boreal Mixed Wood Ecological area and in the Central Mixed Wood Natural subregion. Well drained reference sites of this region are vegetated by aspen, balsam poplar, white birch, white spruce, and balsam fir with mixtures being common. The understory vegetation consists of an assortment of shrubs and forbs[3]. Using field observations and air photo interpretation, a total of four ecosite phases have been selected to classify the native vegetation in the area: treed bog, treed poor fen, low bush cranberry and shrubby rich fen. In disturbed ecosites a variety of grass and weed species, either deliberately seeded or natural migrants, predominate.

Site Assessment Work

The delineation approach was very thorough with samples collected on a grid pattern at surface, 0.5 m , 1.0 m and 1.5 m depths. All surface and 0.5 m depth samples were analysed for CCME Petroleum Hydrocarbons (PHC) with gravimetric heavy hydrocarbon (GHH) analysis conducted as required by the CCME method. Subsequently, deeper soil hydrocarbon data was collected from those few locations that failed the AENV September 2001 *de minimis* coarse grained criteria at the 0.5 m depth. The results from this comprehensive delineation indicate the majority of the soil hydrocarbons are contained within a shallow peat layer which lies atop the native clay till. Spatially, the soil hydrocarbons show little detectable patterns, with the possible exception of the immediate location of the historical crude oil spill. Lighter end hydrocarbons (BTEX + F1) above *de minimis* criteria are found randomly situated within the general spill area. The results from the GHH analysis often did not compare well with the cumulative CCME fractions and it was suspected that this analytical technique was capturing both natural and anthropogenic hydrocarbons in the peat soils. Additionally, toxicological responses were poorly correlated to the GHH fraction. As a result, the quantitative statistical evaluation and subsequent SSRO development did not consider the GHH parameter.

The rigorous analytical program resulted in over 120 sample locations with a data set comprised of 87, 150 and 111 detections of F2, F3 and F4 CCME PHC in the shallow soils. This extensive data set allowed for a parametric statistical evaluation which revealed a lognormal distribution of hydrocarbons (Figure 1)

[3] Beckingham, J.D. and Archibald. J.H. 1996. Field Guide to Ecosites of Northern Alberta, Special Report 5. Canadian Forest Service Northwest Region Northern Forestry Centre.

Additional polycyclic aromatic hydrocarbon (PAH) and inorganic analysis was conducted on a limited number of samples. The trace metal and soil salinity analysis did not detect any parameters that exceeded the published CCME or AENV criteria. The limited PAH analysis detected primarily naphthalene with it's methylated form and phenanthrene. Any additive or synergistic toxicological effects experienced as a results of these PAH compounds are captured within the site-specific bioassays conducted on the peat soils. Therefore, the SSRO generated is considered protective for the expected residual PAH compounds associated with this crude oil. The most important soil parameter linked to the bioavailability and mobility of organic contaminants, in general, is the soil organic content. The upper peat soils contain between 19 – 21% organic carbon. This percentage drops to 0.6 – 0.7% within the clay till which directly underlies the peat.

Selection of Candidate "Residual" Soils

The hydrocarbon results from the site assessment work were reviewed to select candidate locations to collect bulk soil samples for toxicological testing. Twenty locations were selected with two control locations (total of 22 bulk soil samples). The selection of locations ensured a broad aerial representation and the soil chemistry had to meet the following criteria:

- hydrocarbon fractions in the residual range (F2 and greater) which exceeded the Tier 1 criteria for eco-soil contact pathway; and
- no detectable F1 or BTEX constituents.

The bulk samples were manually collected in 4 L pails. Composite soil samples were collected from each pail and submitted for CCME PHC analysis to confirm hydrocarbon concentrations. Of the 22 samples analyzed, two controls and ten bulk samples containing PHC were selected to undergo the toxicological testing. The range of hydrocarbon concentrations within the bulk samples submitted for toxicity testing are presented below and illustrated in box plots (Figure 2).

F2:	< 50 mg/kg to 760 mg/kg
F3:	860 mg/kg to 7,500 mg/kg
F4	420 mg/kg to 4,200 mg/kg
F4 (GHH):	< 100 mg/kg to 10,000 mg/kg

The F2, F3 and CCME F4 maximum ranges included for toxicity testing capture more than 75%, 90% and 85% of the hydrocarbon distributions present on the spill site. Hydrocarbon concentrations above this range, were not considered good candidate "residual" soils – they would require further remedial efforts.

Selection of Test Species

The following plant and invertebrate species selected in this study have either been identified on the site (trees) or are familiar and comparable species used in the development of the CCME December 2000 Canada Wide Standards for Petroleum Hydrocarbons in Soil :

- black spruce (*Picea mariana*);
- tamarack (*Larix laricina*);
- lettuce*(Lactuca sativa)*;
- springtail (*Folsomia candida)*;and
- earthworm *(Eisenia foetida)*.

Twelve samples (including two field controls) formed the substrate for the following tests:

- 2 tree seed emergence and root elongation tests;
- 1 crop seed emergence and root elongation test;
- 1 acute earthworm survival and growth test; and
- 1 chronic springtail survival and reproduction test.

This selection of tests and organisms includes a minimum of two soil invertebrates, and a minimum of two crop/plants with both lethal and sub-lethal effects evaluated. Therefore, the minimum data requirements stipulated for the CCME, 1996 weight of evidence approach for soil quality guideline development was met.

Toxicity Testing and Data Analysis

All twelve bulk soil samples were tested, initially with the acute earthworm and lettuce seed emergence test in the undiluted state. Following the results of these preliminary tests, the chronic springtail bioassay and tree seed emergence tests were conducted. The raw bioassay results from undiluted samples are reported as number of survivors, offspring, emergent seeds or growth responses such as root length and wet weight. The results are reported as percentage mortality or sub lethal response, relative to the artificial control response.

Only those samples that displayed significant toxicity in the undiluted state were subjected to definitive dilution bioassays to estimate threshold effects concentrations (TECs) and percentile inhibition concentrations (IC*p*). Because of the lengthy duration required for tree seed emergence, no definitive dilution testing was conducted with these site specific organisms. All definitive test soils were diluted with artificial soil, consequently, the bioassays included artificial soil controls.

The median lethality statistic (LC50 or EC50) for each of the definitive bioassays was estimated using a modified US EPA Probit analysis[4]. The lower range TEC estimates arose through the application of a more definitive parametric probit program[5] capable of estimating confidence limits. These parametric probit programs work on the premise that the data are binomially distributed (success vs. failure).

Sub-lethal effects of growth and reproduction were treated with a non-parametric Bootstrapping statistical technique to estimate various inhibition concentrations (IC*p*). The bootstrap technique does not rely on parametric assumptions regarding the data distribution and implements random re-sampling to generate a data set of 80 observations. Newman[6] et al. 2000 recently compared traditional parametric lognormal techniques against non-parametric bootstrapping for the generation of species sensitivity distributions. The authors found that the techniques produced comparable results. Additionally, Environment Canada[7], December 1999 states that IC*p* values generated by these non-parametric techniques are more meaningful and preferable to the restrictions imposed with the no observable and lowest observable effect concentrations (NOEC, LOEC) endpoints.

Dose - Response

The various endpoints from these laboratory dilution tests were reported as percentage dilution from the original sample. For the purpose of generating a numerical site specific remedial objective (SSRO), the various endpoint responses must be expressed as an appropriate hydrocarbon concentration: individually F2, F3, F4, or cumulative GHH or a sum of all individual fractions, omitting GHH.

The GHH concentrations appeared to be influenced by naturally occurring organic matter and often varied significantly from the sum of all hydrocarbons quantified by gas chromatography. Additionally, toxicological responses were poorly correlated to the GHH fraction. Thus the GHH values were not used to

4 TOXDAT program (1988) developed by Charles Stephan, United States Environmental Protection Agency, Duluth, Minnesota.

5 Gulley, D., A.M. Boelter, and H. L. Bergman. TOXSTAT v4.0

6 Newman, M.C., D.R. Ownby, L.C.A. Mezin, D.C. Powell, T.R.L. Christensen, S.B. Lerberg and BA Anderson. 2000. Applying species-sensitivity distributions in ecological risk assessment: Assumptions of distribution type and sufficient numbers of species. *Environmental Toxicology and Chemistry*. vol **19**:No. 2: 508-515.

7 Environment Canada. December 1999. Guidance document on application and interpretation of single-species tests in environmental toxicology. EPS 1/RM/34.

develop the SSRO. Following a qualitative evaluation of the toxicological percent response against each CCME fraction individually and cumulatively, it appeared clear that the cumulative hydrocarbon concentrations (F2+F3+F4) best captured the observed toxicological response data. Additionally, the soils are complicated mixtures containing undifferentiated hydrocarbon fractions, which include polycylic aromatic hydrocarbons (PAH). Consequently, AMEC considered it appropriate to standardize all the toxicological responses to the cumulative CCME F2, F3 and F4 hydrocarbons.

The site specific soils are only acutely toxic to earthworms where the total hydrocarbons exceed approximately 10,000 mg/kg (Figure 3). Although no significant adult mortality was observed in the springtails, significant inhibition of reproductive success was observed in several samples (Figure 4). Close to 90% inhibition was observed in the sample with the highest F2 concentration (760 mg/kg). In contrast to all other biological responses, the inhibition in springtail reproduction was better explained by the F2 fraction, rather than the cumulative hydrocarbon value (Figure 4A). With the exception of the response to the highest F2 (760 mg/kg), the lettuce seeds appeared to be tolerant to relatively high concentrations of total hydrocarbons (Figure 5). The black spruce seed emergence test produced a wide range of responses including 11% failure rate in one of the field control soils (Figure 6). The tamarack seed showed the greatest adverse effects from the site specific soils. Seed emergence failure rates in the two field control soils were 25% and 29% (Figure 7).

In summary, The most sensitive biological response was observed in the reproductive success of the springtail invertebrates and the least sensitive response was the mortality of the soil invertebrates. The site-specific tree species displayed a greater sensitivity to the hydrocarbons than did the standard lettuce seeds.

Data Analysis of Undiluted Samples

The range of cumulative hydrocarbons (F2 through F4) in the 12 bulk samples ranged from non-detect in the control soil to > 12,000 mg/kg, essentially mimicking a multiple range toxicity trial. The lethality response variables were in a binomial (success or failure), whole number format; therefore, were treated with a parametric probit statistical analysis. A dose response was generated for lethality of the two invertebrates, seed emergence success in the lettuce, black spruce and tamarack. In order to estimate sub-lethal response percentiles, the growth data was rounded to the nearest whole number and subjected to the same parametric probit statistical analysis. A success was considered a root length or weight wet equal, or greater, than those measured in the field controls.

Species Sensitivity Distribution and SSRO

Ultimately, the battery of toxicological testing returned over 30 response endpoints used to generate a species sensitivity distribution (SSD) portrayed in Figure 8. The CCME 1996 minimum data requirements for the derivation of soil quality guidelines were exceeded, thus eliminating the need to apply arbitrary safety factors. Individual response endpoints were generated based on acceptable statistical analysis and a rigorous data quality assessment eliminated 3 response outliers prior to generating the SSRO from the lower 25th percentile of the SSD.

The toxicological endpoints within the SSD enclose a hydrocarbon range between 1,500 mg/kg to 10,500 mg/kg. The SSRO is expected to provide suitable environmental protection for the soil ecological contact pathway at 5,560 mg/kg of cumulative F2 + F3 + F4 fraction hydrocarbons. The final soil remediation targets are tabulated in below.

Final soil remedial numerical criteria (aquatic receptor)

Parameter	*de minimis* Pathway	Remedial Target (mg/kg)
Benzene	Groundwater Potability	0.13
Toluene	Groundwater Aquatic Life	0.16
Ethylbenzene	Groundwater Potability	0.36
Xylene	Groundwater Potability	49
F1	Eco- Soil Contact	130
F2	Groundwater Aquatic Life	230
F2 + F3 + F4	Eco- Soil Contact	SSRO - 5560

Note: pathways and numerical values based on AENV September 2001, natural land use area in coarse grained surface soils with the presence of a water body within 300 m downgradient.

Final soil remedial numerical criteria (terrestrial only)

Parameter	*de minimis* Pathway	Remedial Target (mg/kg)
Benzene	Groundwater Potability	0.13
Toluene	Groundwater Potability	1.6
Ethylbenzene	Groundwater Potability	0.36
Xylene	Groundwater Potability	49
F1	Eco- Soil Contact	130
F2 + F3 + F4	Eco- Soil Contact	SSRO - 5560

Note: Pathways and numerical values based on AENV September 2001, natural land use area in coarse grained surface soils with no water body in the vicinity.

Conclusion

The calculated SSRO captures 75% of the residual heavy end hydrocarbons present at the spill location (Figure 9). The bulk samples that fail the SSRO are those that also displayed repeated adverse effects in the bioassay tests. Therefore, the SSRO appears to be suitably protective and would identify soils with hydrocarbon concentrations that are most likely to cause adverse ecological effects. The SSRO of 5,560 mg/kg for the cumulative F2 + F3 + F4 fractions represents an 18% increase over the *de-minimis* cumulative value of 3,750 mg/kg.