WEATHERED PHC F2 - PROPOSED GUIDELINES FOR THE ECO-CONTACT PATHWAY FINAL REPORT

Report Prepared for:
Petroleum Technology Alliance Canada (PTAC)
Suite 400, Chevron Plaza
500 – Fifth Avenue S.W.
Calgary, Alberta T2P 3L5

With Funding from:
Environmental Research Advisory Council (ERAC)
Alberta Upstream Petroleum Research Fund (AUPRF)

Prepared by:

Miles J. Tindal, M.Sc.
Principal
Axiom Environmental Inc.
438 Eagle Heights
Canmore, Alberta T1W 3C9
Phone: (403) 678-4790
mtindal@axiomenvironmental.ca

July 2012

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

EXECUTIVE SUMMARY

Introduction

The latest version of the CCME Petroleum Hydrocarbon Canada-Wide Standard revised the guideline for the ecological contact with plants and soil invertebrates pathway (the "eco-contact pathway") for PHC fraction F2 down from 900 mg/kg to 150 mg/kg (natural area, agricultural, and residential land use) and from 1,500 mg/kg to 260 mg/kg (commercial and industrial land use). This is the limiting pathway for F2 at the vast majority of sites. Current Alberta Environment Tier 1 Guidelines adopt this same value. This change to the F2 guideline value has significant implications for the management of hydrocarbons at upstream and downstream petroleum hydrocarbon sites.

Various work has indicated that plant and invertebrate toxicity in soil can be lower for weathered than fresh F3 PHCs. However, very little corresponding work on the toxicity of weathered F2 appears to have been conducted. The current project collects and analyzes data to support a possible future revision to the F2 eco-contact guideline. Work on the project consisted of a rangefinding exercise followed by two phases of ecotoxicity testing, with Phase 1 considering fine-grained soils, and Phase 2 using coarse-grained soils.

Methodology

In overview, the methodology used in this project included the following steps:

- Conduct a rangefinding test to investigate the kinetics of F2 degradation in soil.
- Based on the rangefinding test, spike an F2 distillate into soil (fine-grained for Phase 1 and coarse-grained for Phase 2) to generate two concentration series.
- Age/weather these samples for six months.
- Conduct triplicate chemical analysis on each sample
- Conduct ecotoxicity testing using standard Environment Canada protocols and a standard battery of three plant and two invertebrate species.
- Derive soil remediation guidelines for the eco-contact pathway for weathered F2 using standard CCME protocols.

Results and Guideline Development

The soil remediation guidelines calculated for the ecological direct contact exposure pathway for weathered F2 in soil, for both coarse and fine-grained soils are:

- 300 mg/kg – natural area, agricultural, and residential land use.
- 500 mg/kg – commercial and industrial land use.

This report will be submitted to Alberta Environment and Sustainable Resource Development (AESRD) for their consideration.

1. INTRODUCTION

The current version of the Canadian Council of Ministers of the Environment (CCME, 2008) Petroleum Hydrocarbon Canada-Wide Standard (PHC CWS) revised the guideline for the ecological contact with plants and soil invertebrates pathway (the "eco-contact pathway") for PHC fraction F2 from 900 mg/kg to 150 mg/kg (natural area, agricultural, and residential land use) and from 1,500 mg/kg to 260 mg/kg (commercial and industrial land use). This is the limiting pathway for F2 at the vast majority of sites. Current Alberta Environment Tier 1 Guidelines (AENV, 2010) adopt this same value.

This change to the F2 guideline value has significant implications for the management of hydrocarbons at upstream and downstream petroleum hydrocarbon sites. Little of the difference between old and new F2 guideline values was due to new data that had become available between 2001 and 2008. The two main reasons for the changed guideline values were i) a factor of 2 had been 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 (2008) guidelines were developed using a new (CCME, 2006) soil quality guideline protocol which uses a distribution of 25th percentile effect data, rather than the 50th percentile effect data used in the 2001 PHC CWS derivation. Based on current protocols and currently-available data, the revised F2 guideline of 150 mg/kg may be appropriate for fresh F2 hydrocarbon.

Various work, including several former PTAC studies (e.g., Axiom, 2005; Visser, 2005a,b) have indicated that plant and invertebrate toxicity in soil can be lower for weathered than fresh F3 PHCs. It has been theorized (e.g., Alexander, 1997) that this lowering of toxicity may be due to sequestering of hydrocarbon in soil leading to lower bioavailability and/or the preferential removal of more toxic components of a hydrocarbon fraction. However, very little work on the toxicity of weathered F2 appears to have been conducted.

The former PTAC studies on the ecotoxicity of weathered PHC F3 were some of the key data considered by the CCME in revising the eco-contact guideline for F3 upward from 800 mg/kg to 1,300 mg/kg in 2008. The current project is intended to collect data to support a possible future revision to the F2 eco-contact guideline. Work on the project consisted of a rangefinding exercise followed by two phases of ecotoxicity testing. Phase 1 of the ecotoxicity testing was completed in 2009/2010 and considered the ecotoxicity of weathered F2 in a fine-grained Orthic Black Chernozem soil. Phase 2 of the ecotoxicity testing was completed in 2011/2012 and expanded the scope of Phase 1 to additionally consider a coarse-grained artificial soil. The current document reports on both phases of this work.

1.1 Objective

The overall objective of the work presented in this report was to collect data to support a possible future revision to the F2 eco-contact guideline, and to develop recommended soil remediation guidelines for the ecological direct contact exposure pathway applicable to weathered PHC fraction F2.

1.2 Scope of Work

As noted in the introduction, this project was divided into two phases, which addressed the ecotoxicity of weathered F2 in fine soil (Phase 1) and coarse soil (Phase 2).

The scope of work for Phase 1 was:

1. Develop a workplan for the project.
2. Conduct a rangefinding test with F2 spiked into Orthic Black Chernozem soil and regularly aerated and mixed, to investigate F2 degradation kinetics over a 12 month period.
3. Identify a series of initial F2 concentrations that are anticipated to generate an appropriate series of weathered F2 concentrations for ecotoxicity testing.
4. Spike F2 into Orthic Black Chernozem soil and simulate an aging/weathering process with regular aeration, mixing, and management of moisture content.
5. Conduct sufficient analytical testing to determine when an appropriate level of aging/weathering has been achieved (this turned out to be 6 months).
6. At this point, initiate the following battery of ecotoxicity tests, using Environment Canada test protocols, on the concentration series of weathered F2 spiked soils:
    a. Definitive plant growth tests with northern wheatgrass, alfalfa and barley.
    b. Invertebrate survival and reproduction tests with earthworm and springtail species.
7. Use CCME (2008) methodology to calculate a draft guideline value for weathered F2 in a fine-grained soil.
8. Generate a report summarizing key elements of the program.

The scope for Phase 2 was the same as steps 3 through 8 of Phase 1 with the following exceptions and notes:

- A coarse-grained artificial soil was used in place of the fine-grained Phase 1 soil.
- The duration of the weathering was set at 6 months to be consistent with the duration used in Phase 1.

1.3 Acknowledgements

This project was a collaborative effort among many parties, and we would like to acknowledge the following:

Funding

- Phase 1 funding: Environmental Research Advisory Council (ERAC Project # 907951).
- Phase 2 funding: Alberta Upstream Petroleum Research Fund (AUPRF Project # 913551).
- Bodycote Laboratories, now Exova Laboratories (in kind).

Technical Steering Committee

- Steve Kullman, Husky Energy Inc., CAPP Project Manager
- Gordon Dinwoodie, Alberta Environment and Sustainable Resource Development
- Miles Tindal, Axiom Environmental Inc.

PTAC Coordinators

- Tannis Such
- Lorie Frei

Research Providers

- Axiom Environmental Inc. – Miles Tindal (project scope, data analysis, reporting).
- Exova Laboratories – Darlene Lintott (rangefinding testing).
- Stantec Consulting Ltd. – Gladys Stephenson et al. (ecotoxicological testing).

In addition, we are grateful to Stantec for making available F2 distillate and Orthic Black Chernozem soil that had been obtained for previous projects.

2. AGING AND WEATHERING

When hydrocarbon mixtures are added to soil, a number of processes can occur over time. Processes which reduce the bioavailability of the hydrocarbons to biota are referred to as aging. Processes which preferentially remove some components from the mixture and hence change its composition are collectively termed weathering processes.

Aging of hydrocarbons in soil involves a number of processes including sorption and sequestration, all of which make hydrocarbons less available or unavailable to plants and soil invertebrates. ESG (2003b) includes a detailed review of these processes, and the details are not repeated in this summary report. Aggressive solvent extraction (such as the hexane/acetone Soxhlet extraction used in the PHC CWS reference method, CCME, 2001) may still be able to recover much of the hydrocarbon sorbed or sequestered to soil components, and may not, therefore, be a particularly good indication of how much hydrocarbon is biologically available to plants or soil invertebrates.

Weathering refers to compositional changes in hydrocarbon mixtures over time as a result of various processes (e.g., biodegradation, volatilization, leaching) occurring at different rates for different hydrocarbon components. For instance, n-alkanes may be biodegraded more rapidly than aromatic hydrocarbons, resulting in compositional changes in the hydrocarbon mixture in the soil.

Both aging and weathering can occur concurrently, and both can potentially contribute to changes in the ecotoxicity of hydrocarbon mixtures in soil over time. No attempt is made in the current work to separate the effects of these two processes, and, for convenience, the term “weathered” is used in this report to refer to the aggregate effect of the two processes on soil ecotoxicity.

3. METHODOLOGY

Some of the previous work on weathered F3 was based on weathered soils that had previously been spiked with a whole hydrocarbon mixture (e.g., crude oil, diesel), or were the product of a spill (release) of a whole hydrocarbon mixture. Once thoroughly weathered, these data could generally be interpreted in terms of the toxicity of the residual F3, since typically the F1 and F2 F2 components had been degraded more rapidly than the F3, and F4 is known to have relatively low availability/ecotoxicity. Such a method, however, cannot be used to determine the toxicity of weathered F2, since any results would be confounded by residual F3 toxicity.

Thus, the work in this project to determine the toxicity of weathered F2 was undertaken by spiking a distilled F2 cut into soil, conducting an accelerated weathering treatment, and then performing eco-toxicity tests on the weathered soils.

3.1 Overview

In overview, the methodology used in this project included the following steps:

- Identify a source of a PHC F2 cut, Orthic Black Chernozem soil, and an artificial coarse-grained soil.
- Conduct a rangefinding test to determine the rate of degradation of F2 under lab conditions.
- Based on the results of the rangefinding test, generate and weather a spiked F2 soil series in fine- (Phase 1) and coarse- (Phase 2) grained soils to produce a suitable series of weathered F2 concentrations for ecotoxicity testing.
- Conduct ecotoxicity testing with three plant and two invertebrate species on the weathered concentration series for each of the soil textures.
- Use the data from the ecotoxicity testing to calculate draft guideline values for weathered F2 in fine- and coarse-grained grained soils.

This report only summarizes key elements of the ecotoxicity testing. Full technical reports on the Phase 1 and Phase 2 ecotoxicity testing are available in Stantec (2009) and Stantec (2012), respectively, and these reports are available on the PTAC website http://www.ptac.org/.

3.2 Source of Test Materials

Fraction F2 refers to hydrocarbons in the range equivalent to straight chain alkanes with a carbon chain length greater than 10 and up to 16. In this sense, “equivalent” refers to “eluting through a gas chromatography column in the same time as”. The F2 used for this work was originally generated for an earlier ecotoxicity project which was part of the process to develop

the original PHC CWS guidelines (ESG, 2003a). The F2 used in the rangefinding test was from a distillation of Federated Crude Oil made by Environment Canada. The F2 used for the ecotoxicity tests was distilled in 2002 by Imperial Oil Ltd. at their Sarnia, Ontario facility from Federated Crude Oil. The F2 had been stored at low temperature by Stantec (previously ESG), and was kindly made available by Stantec for the current work.

The Orthic Black Chernozem soil was also kindly made available by Stantec from supplies remaining from the original PHC CWS work. It was considered important to use the same soil and F2 distillate for this weathered F2 project that were used to generate the fresh F2 ecotoxicity data for the original and current PHC CWS.

The artificial coarse-grained soil was a standard test soil mixed by Stantec and again was the same soil used for the original PHC CWS work.

3.3 Rangefinding Test

Key parameters of the experimental design for the rangefinding test are summarized below.

- F2 was spiked into Orthic Black Chernozem at the following initial concentrations:
    - 3,000 mg/kg;
    - 10,000 mg/kg; and,
    - 30,000 mg/kg.
- An additional sample with 10,000 mg/kg F2 was brought to an electrical conductivity (EC) of 40 dS/m with the intention of sterilizing the sample.
- Once a week, soils were spread out, mixed and returned to the sample container. If necessary, water was added to maintain moisture content.
- Samples were analyzed for F2 to F4 hydrocarbons at the time of spiking (time zero) and after 1, 2, and 3 weeks, than at 1, 2, 3, 4, 5, 6, 7, 10, and 12 months. The time zero analysis was performed in triplicate for each concentration, subsequent analyses were single samples only.
- Four different analytical techniques were used to determine the F2 to F4 hydrocarbons. Either the standard Soxhlet extraction (CCME, 2001) or a shake flask procedure was used. Each extraction was used with and without the silica gel clean-up step.
- Other analyses performed included benzene, toluene, ethylbenzene and xylenes (BTEX) and F1, heterotrophic place count and hydrocarbon utilizing bacteria.

3.4 Ecotoxicity Testing – Phase 1

The results of the rangefinding test were used to estimate a series of initial F2 concentrations that would, after aging/weathering, become a suitable series of concentrations for conducting

ecotoxicity tests. Details of the methodology for spiking and aging/weathering the soils, and of the ecotoxicity tests themselves are provided in Stantec (2009), which is available on the PTAC website. Key points are summarized here.

- F2 was spiked into Orthic Black Chernozem at the following initial concentrations:
  - 0 mg/kg (control)
  - 100 mg/kg;
  - 250 mg/kg;
  - 500 mg/kg;
  - 1,000 mg/kg;
  - 2,000 mg/kg;
  - 4,000 mg/kg;
  - 8,000 mg/kg;
  - 16,000 mg/kg;
  - 32,000 mg/kg; and,
  - 64,000 mg/kg.
- Each sample was hydrated to 35% water holding capacity, mixed vigorously and returned to its bucket on a biweekly basis for the first month, and weekly thereafter.
- After six months of this aging/weathering procedure, ecotoxicity testing was initiated.
- The battery of ecotoxicity tests conducted with the weathered F2 soils was the same as that used with fresh F2 for the PHC CWS (ESG, 2003a), and included the following species/endpoints:
  - Earthworm (*Eisenia andrei)* – 35 day adult survival.
  - Earthworm (*Eisenia andrei)* – 63 day reproduction endpoints.
  - Springtail (*Folsomia candida)* – 28 day adult survival.
  - Springtail (*Folsomia candida)* – 28 day reproduction endpoints.
  - Northern wheatgrass (*Agropyron dasystachyum)* – 21 day growth endpoints.
  - Alfalfa (*Medicago sativa)* – 21 day growth endpoints.
  - Barley (*Hordeum vulgare)* – 14 day growth endpoints.
- Ecotoxicity tests were conducted according to Environment Canada protocols (Environment Canada, 2004, 2005a,b).
- Chemical analysis for F2 was performed at various intervals throughout the aging/weathering process and in triplicate at the time of spiking and at the start of the ecotoxicity tests.

3.5 Ecotoxicity Testing – Phase 2

The results of Phase 1 were used to estimate a series of initial F2 concentrations that would, after aging/weathering in a coarse-grained artificial soil, become a suitable series of concentrations for conducting ecotoxicity tests. The artificial soil was mixed from 70% silica

sand, 20% kaolinite clay, 10% Sphagnum peat, and sufficient calcium carbonate to adjust the soil pH to 6.0-7.5. Details of the methodology for spiking and aging/weathering the soils, and of the ecotoxicity tests themselves are provided in Stantec (2012), which is available on the PTAC website. Key points are summarized here.

- F2 was spiked into a coarse-grained artificial soil m at the following initial concentrations:
  - 0 mg/kg (control)
  - 1,000 mg/kg;
  - 1,500 mg/kg;
  - 2,250 mg/kg;
  - 3,500 mg/kg;
  - 5,000 mg/kg;
  - 7,500 mg/kg;
  - 10,000 mg/kg;
  - 15,000 mg/kg;
  - 22,500 mg/kg; and,
  - 35,000 mg/kg.
- Each sample was hydrated to 35% water holding capacity, mixed vigorously and returned to its bucket on a biweekly basis for the first month, and weekly thereafter.
- After six months of this aging/weathering procedure, ecotoxicity testing was initiated.
- The battery of ecotoxicity tests conducted with the weathered F2 soils was the same as that used in Phase 1 and also the same as was used with fresh F2 for the PHC CWS (ESG, 2003a), and included the following species/endpoints:
  - Earthworm (*Eisenia andrei)* – 35 day adult survival.
  - Earthworm (*Eisenia andrei)* – 63 day reproduction endpoints.
  - Springtail (*Folsomia candida)* – 28 day adult survival.
  - Springtail (*Folsomia candida)* – 28 day reproduction endpoints.
  - Northern wheatgrass (*Agropyron dasystachyum)* – 21 day growth endpoints.
  - Alfalfa (*Medicago sativa)* – 21 day growth endpoints.
  - Barley (*Hordeum vulgare)* – 14 day growth endpoints.
- Ecotoxicity tests were conducted according to Environment Canada protocols (Environment Canada, 2004, 2005a,b).
- Chemical analysis for F2 was performed at various intervals throughout the aging/weathering process and in triplicate at the time of spiking and at the start of the ecotoxicity tests.

4. RESULTS AND ANALYSIS

4.1 Degradation Kinetics

The measured F2 concentrations from the rangefinding test, Phase 1 weathering and Phase 2 weathering, as a function of time, are summarized in Tables 1 through 3, respectively, and illustrated in Figures 1 through 3, respectively. Note that the y axis on Figures 1 through 3 is on a logarithmic scale.

In all cases, as expected, the F2 concentration in each test unit showed a general decrease with time, related to biodegradation, volatilization and other losses. Trend lines are shown on Figures 1 through 3 for all datasets where the correlation coefficient (R^2) was greater than 0.8. The straight line relationship on these log-linear charts confirms that F2 degradation closely follows first order degradation (exponential decay) in these tests.

The slope of the trend lines in Figures 1 through 3 were interpreted to calculate half-life values for each test wherever R^2 was greater than 0.8. These half-life values are provided in Table 4 and the relationship between initial concentration and half-life is illustrated in Figure 4. While there appears to be little difference between the degradation rates observed in coarse and fine soil, it is clear from Figure 4 that the F2 half-life gets increasingly long at higher initial F2 concentrations. For example, at an initial F2 concentration of 10,000 mg/kg, Figure 4 indicates a half-life of approximately 140 days, 3.5 times longer than the half-life expected at an initial concentration of 1,000 mg/kg. This suggests that there may be increasing inhibition of biodegradation at increasing F2 concentrations.

While degradation half-lives in the field are likely to be significantly slower that those measured in the favourable conditions of moisture and temperature in this laboratory study, it might be reasonable to anticipate a similar trend of increasing half-life with increasing initial concentration under field conditions.

4.2 Other Data from Rangefinding Test

Analysis of bacterial parameters conducted as part of the rangefinding test (heterotrophic plate counts and hydrocarbon utilizing bacteria) were quite variable from measurement to measurement, did not appear to add useful data, and are not reported here. Bacterial counts did not seem to be significantly different for the “sterilized” and unsterilized 10,000 mg/kg tests, indicating that using a salinity of EC = 40 dS/m does not appear to have been effective for bacterial sterilization.

The different extraction and clean-up methodologies used for F2 to F4 analysis (soxhlet and shake flask extraction, with and without silica gel cleanup) showed significant variability. In most case the relative percent difference between corresponding values was less than 50%, but in a few cases was as high a 100%. The "shake flask" analytical technique with no silica gel cleanup was generally the closest to the nominal value for time zero data, and accordingly, this is the value presented in Table 1 and Figure 1.

4.3 Quality of F2 Distillation

As noted in Section 3.2, the F2 used in the rangefinding test was from a distillation of Federated Crude Oil made by Environment Canada. The F2 used for the ecotoxicity tests (both Phases) was distilled in 2002 by Imperial Oil Ltd. at their Sarnia, Ontario facility from Federated Crude Oil, and has been kept refrigerated since that time).

Analysis of the Environment Canada F2 cut indicated that F2 was approximately 89% of the cut by weight, with approximately 10% F3, and 1% F1. Analysis of the Imperial Oil F2 cut (mean of 3 vials) indicated that F2 was approximately 89% of the cut by weight, with approximately 7% F3, and 4% F1.

4.4 Phase 1 Ecotoxicity Testing (Fine-grained Soils)

The results of the Phase 1 study to generate the concentration series of F2 spiked fine-grained soils and the results of the ecotoxicity testing are provided in detail in Stantec (2009). Data analysis is provided in Section 5. Triplicate samples were collected from each concentration at the start of the ecotoxicity tests, and the last row in Table 2 (highlighted in orange) summarizes the mean measured concentration for each nominal (initial) concentration. The original laboratory reports for these data are available in Stantec (2009).

4.5 Phase 2 Ecotoxicity Testing (Coarse-grained Soils)

The results of the Phase 2 study to generate the concentration series of F2 spiked coarse-grained soils and the results of the ecotoxicity testing are provided in detail in Stantec (2012). Data analysis is provided in Section 5. Triplicate samples were collected from each concentration at the start of the ecotoxicity tests, and the last row in Table 3 (highlighted in orange) summarizes the mean measured concentration for each nominal (initial) concentration. The original laboratory reports for these data are available in Stantec (2012).

5. DATA ANALYSIS AND GUIDELINE CALCULATION

Based on the latest protocol developed by CCME (2008) and adopted by AENV (2010), soil remediation guidelines for the protection of ecological direct contact are preferably developed from a species sensitivity distribution. Available data are standardized at, or as close as possible to the 25th percent effects level (IC25). A minimum of 10 independent data points are required.

The data analysis conducted for this report consisted of the following steps.

1. IC25 data were selected for all endpoints. All IC25 data discussed in this report are those calculated on the basis of concentrations measured at the start of the test, unless otherwise indicated.
2. For plants, shoot and root length and mass endpoints were selected, but emergence endpoints were rejected as being relatively insensitive to soil toxicants.
3. For invertebrates, adult survival and progeny production endpoints were selected, while progeny wet and dry mass were considered redundant, and were combined, using an arithmetic mean to give an endpoint called progeny mass.
4. For all data, the IC25 value calculated from statistical analysis in the Stantec reports was compared against the actual data in a "reality check" step to make sure that the computed IC25 value was approximately consistent with the point at which the measured parameter (shoot length, etc.) actually dropped below 75% of its value in controls.

Based on steps 1 to 3 above, and following the convention in CCME (2008), the list of included data was the IC25 value for:

- For each of the three plant species (northern wheatgrass, alfalfa, barley):
    - Shoot length
    - Root length
    - Shoot dry mass
    - Root dry mass
- For Folsomia candida:
    - Adult survival
    - Progeny production
- For Eisenia andrei:
    - Adult survival
    - Progeny production
    - Progeny mass

Thus, 17 data points were considered for each soil, or 34 data points in total.

The raw IC25 values from the Stantec (2009, 2012) reports for Phase 1 and Phase 2 are summarized in Tables 5 and 6.

In step 4 of the data analysis process, the Stantec IC25 values were cross checked with the actual data presented in the appendices of Stantec (2009, 2012). In the majority of cases the data were consistent with the IC25 value calculated. However, in a few cases, there were values that were not calculated or apparent discrepancies, as indicated in Tables 5 and 6 and discussed in more detail below.

Phase 1

- Folsomia candida adult survival. Stantec (2009) provided adult survival data, but did not calculate an IC25 for this endpoint. An IC25 was interpreted from the data in Table C2 of Stantec (2009) as follows. Mean adult survival was 103.75% of control survival for the 715 mg/kg measured F2 concentration (corresponding to 4,000 mg/kg nominal F2). Mean adult survival was 28.75% of control survival for the 1,557 mg/kg measured F2 concentration (corresponding to 8,000 mg/kg nominal F2). Linear interpolation between these two points for the concentration corresponding to 75% of control survival gives a concentration of 1,038 mg/kg, which is used as the IC25 in this analysis (Table 5).
- Eisenia andrei adult survival. Stantec (2009) provided adult survival data, but did not calculate an IC25 for this endpoint. An IC25 was interpreted from the data in Table B2 of Stantec (2009) as follows. Mean adult survival was 100% of control survival for the 715 mg/kg measured F2 concentration (corresponding to 4,000 mg/kg nominal F2). Mean adult survival was 15% of control survival for the 1,557 mg/kg measured F2 concentration (corresponding to 8,000 mg/kg nominal F2). Linear interpolation between these two points for the concentration corresponding to 75% of control survival gives a concentration of 963 mg/kg, which is used as the IC25 in this analysis (Table 5).

Phase 2

- Eisenia andrei progeny production. Stantec (2012) calculated an IC25 of 77 mg/kg by ICPIN (measured basis, Table 5). On a nominal basis, this is very close to the 2,250 mg/kg concentration reported in Table E2 of Stantec (2012). However, the next concentration up, 3,500 mg/kg nominal, has a progeny production greater than controls, and a monotonic decrease occurs through all higher concentrations. This suggests strongly that the IC25 of 77 mg/kg is a result of noise in the data. With this in mind, a revised IC25 was calculated for this endpoint as follows. Mean progeny production was 105.7% of control survival for the 431 mg/kg measured F2 concentration (corresponding to 5,000 mg/kg nominal F2). Mean progeny production was 48.6% of control survival for the 245 mg/kg measured F2 concentration (corresponding to 3,500 mg/kg nominal F2). Linear interpolation between these two points for the concentration corresponding to

75% of control survival gives a concentration of 345 mg/kg, which is used as the IC25 in this analysis (Table 5).

The CCME (2006, 2008) and AENV (2010) protocols, taken together, indicate that the soil remediation guidelines for ecological direct contact are preferably calculated based on a species sensitivity distribution of 25th percent effects concentrations ranked in order. The soil remediation guidelines for ecological direct contact for natural area, agricultural and residential land use are evaluated at the 25th percentile of this species sensitivity distribution and the soil remediation guidelines for ecological direct contact for commercial and industrial land use are evaluated at the 50th percentile.

The species sensitivity distributions for coarse and fine soils are illustrated in Figure 5. Given the similarity of the two distributions, it was decided to combine the two datasets and benefit from the greater statistical power of a larger dataset. Accordingly, the guidelines calculated apply to both coarse and fine-grained soils.

The combined dataset of IC25 values, adjusted as noted above, and ordered by rank is provided in Table 7. Rank percentiles are also included in Table 7, calculated using the formula recommended in CCME (2006):

$$j = \frac{i}{(n+1)} \times 100$$

where,

j = rank percentile
i = rank of the data point in the data set
n = total number of data points in the data set.

The concentrations corresponding to the 25th percentile and 50th percentile of the dataset are 294 mg/kg and 484 mg/kg, respectively (Table 7). These values, rounded to 1.5 significant figures (i.e., 1 significant figure with 5 or 0 in the second place) give soil remediation guideline values for the ecological direct contact exposure pathway for weathered F2 hydrocarbons as follows:

- 300 mg/kg – natural area, agricultural, and residential land use.
- 500 mg/kg – commercial and industrial land use.

6. SUMMARY

The guideline values calculated in this report follow exactly the same procedures, and use the same soils, species, endpoints and test methods as those used to calculate the corresponding F2 guidelines in the Petroleum Hydrocarbon Canada-Wide Standard and the Alberta Tier 1 Guidelines. The sole difference is that the F2 hydrocarbons spiked into the test soils were "weathered" by weekly aeration, mixing and moisture control for a period of 6 months prior to the start of ecotoxicity testing. The values calculated for weathered F2 are approximately twice the current Tier 1 guidelines, reflecting the reduced toxicity of weathered F2 relative to fresh, possibly as a result of F2 becoming sequestered into soil over time and becoming less available.

It is hoped that the new data collected as part of this project and the analysis provided in this report will support ongoing discussions with Alberta Environment and Sustainable Resource Development to continue to strengthen the scientific basis of environmental guidelines in Alberta.

7. CLOSURE

The information presented in this report was compiled and interpreted exclusively for the purposes stated in Section 1 of this document. Axiom Environmental Inc. (Axiom) provided this report for the Petroleum Technology Alliance of Canada (PTAC) solely for the purpose noted above.

Axiom has exercised reasonable skill, care and diligence to assess the information acquired during the preparation of this report, but makes no guarantees or warranties as to the accuracy or completeness of this information. The information contained in this report is based upon, and limited by, the circumstances and conditions acknowledged herein, and upon information available at the time of its preparation. Guidelines developed in this report are based on current regulatory protocols. The information provided by others is believed to be accurate but cannot be guaranteed.

Axiom does not accept any responsibility for the use of this report for any purpose other than that stated in Section 1 and does not accept responsibility to any third party for the use in whole or in part of the contents of this report. Any alternative use, including that by a third party, or any reliance on, or decisions based on this document, is the responsibility of the alternative user or third party.

8. REFERENCES

AENV (Alberta Environment), 2010. Alberta Tier 1 Soil and Groundwater Remediation Guidelines. February 2009.

Alexander M. 1997. Sequestration and bioavailability of organic compounds in soil. In: Environmentally Acceptable Endpoints in Soil: Risk-Based Approach to Contaminated Site Management Based on Availability of Chemicals in Soil (Eds) DG. Linz and DV. Nakles. United Book Press, Inc., United States. pp. 44-136.

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), 2001. Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method. PN 1310. Canadian Council of Ministers of the Environment, Winnipeg, Manitoba.

CCME (Canadian Council of Ministers of the Environment), 2006. A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines. PN 1332.

CCME (Canadian Council of Ministers of the Environment), 2008. Canada-Wide Standard for Petroleum Hydrocarbons (PHCs) in Soil: Scientific Rationale. Supporting Technical Document, January 2008.

Environment Canada, 2004. Biological Test Method: Tests for Toxicity of Contaminated Soil to Earthworms (*Eisenia andrei*, *Eisenia fetida*, or *Lumbricus terrestris*). Method Development and Applications Section, Environmental Science and Technology Centre, Environment Canada, Ottawa, Ontario. EPS 1/RM/43 – June 2004.

Environment Canada, 2005. Biological Test Method: Test for Measuring Emergence and Growth of Terrestrial Plants Exposed to Contaminants in Soil. Method Development and Applications Section, Environmental Science and Technology Centre, Environment Canada, Ottawa, Ontario. EPS 1/RM/45 – February 2005.

Environment Canada, 2007. Biological Test Method: Test for Measuring Survival and Reproduction of Springtails Exposed to Contaminants in Soil. Method Development and Applications Section, Environmental Science and Technology Centre, Environment Canada, Ottawa, Ontario. EPS 1/RM/47 – September, 2007.

ESG (ESG International Inc.), 2003a. Toxicity of Petroleum Hydrocarbons to Soil Organisms and The Effects on Soil Quality: Phase 1, Fraction-Specific Toxicity of Crude Oil. Report dated January 30, 2003, prepared for Petroleum Technology Alliance Canada.

ESG (ESG International Inc.), 2003b. Framework Foundation and Guidance for Tier 2 Site-Specific Development of Soil Contact Standards for PHC-Contaminated sites: Literature Review. Report dated May 15, 2003, prepared for Petroleum Technology Alliance Canada.

Stantec (Stantec Consulting Ltd.), 2009. Weathered F2 Ecotoxicity Assessment. Report dated October, 2009, File # 160960435, prepared for Petroleum Technology Alliance Canada.

Stantec (Stantec Consulting Ltd.), 2012. Ecotoxicity of Weathered PHC F2 – Phase 2. Report dated January 2012, File #122160048, 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.

TABLES

Table 1. F2 Concentrations vs. Time - Rangefinding Test

Time	Nominal Initial F2 Concentration (mg/kg)			
Days	3,000	10,000	10,000ST	30,000
0	2,323	8,653	8,157	26,133
7		7,070		
14		8,810		
21		6,780		
28	1,710	5,690	6,140	16,100
42		6,640		
56	1,420	5,620	4,750	19,400
70		6,450		
84	1,120	5,490	4,440	12,900
98		5,100		
112	1,470	4,710	5,300	19,900
126		5,772		
140	870	3,900	4,260	15,900
154		4,010		
168	750	4,160	3,620	13,300
182		3,140		
196	670	3,350	3,240	8,960
210		2,510		
280	370	2,190	4,340	13,900
336	300	1,120	1,770	4,280

Table 2. F2 Concentrations vs. Time - Phase 1

Sample Date	Time Days	Rep	Nominal Initial F2 Concentration (mg/kg)										
			0	100	250	500	1,000	2,000	4,000	8,000	16,000	32,000	64,000
9-Dec-08	0	rep 1	<10	35	126	361	638	1,290	2,840	6,270	13,600	25,000	33,100
		rep 2	<10	22	150	305	621	1,260	3,400	6,000	12,400	24,800	32,800
		rep 3	<10	69	164	321	627	1,290	3,230	6,100	12,400	24,500	34,800
		mean	<10	42	147	329	629	1,280	3,157	6,123	12,800	24,767	33,567
5-Mar-09	86		<10	<10	<10	46	136	481	1,580	2,830	7,440	19,200	18,800
2-Apr-09	114		<10	<10	30	61	240	396	1,080	2,520	7,520	19,700	29,200
1-May-09	143		<10	<10	<10	32	35	281	818	1,970	6,760	17,700	29,800
10-Jun-09	183	rep 1	<10	<10	<10	<10	67	209	749	1,490	5,910	17,900	26,100
		rep 2	<10	<10	<10	<10	74	272	724	1,570	6,240	18,400	27,700
		rep 3	<10	<10	<10	<10	93	266	671	1,610	5,870	18,400	26,600
		mean	<10	<10	<10	<10	78	249	715	1,557	6,007	18,233	26,800

Note:
Concentrations in last row (highlighted orange) represent starting concentrations for Phase 1 ecotoxicity testing.

Table 3. F2 Concentrations vs. Time - Phase 2

Sample Date	Time Days	Rep	Nominal Initial F2 Concentration (mg/kg)										
			0	1,000	1,500	2,250	3,500	5,000	7,500	10,000	15,000	22,500	35,000
28-Apr-11	0	rep 1	<10	742	1,230	1,860	2,860	4,380	6,450	7,400	13,400	18,900	31,000
		rep 2	<10	846	1,170	1,650	3,130	4,860	6,870	5,330	13,000	20,400	30,400
		rep 3	<10	976	1,050	1,630	2,790	4,480	6,990	8,310	13,200	19,900	29,500
		mean	<10	855	1,150	1,713	2,927	4,573	6,770	7,013	13,200	19,733	30,300
26-May-11	28	1			401				4,350			15,500	
23-Jun-11	56	2			190				3,870			17,300	
21-Jul-11	84	3			103				2,770			15,500	
19-Aug-11	113	4			78				2,420			13,000	
15-Sep-11	140	5			52				1,620			17,200	
13-Oct-11	168	rep 1	<10	39	51	77	227	449	1,100	2,100	9,830	9,970	18,700
		rep 2	<10	41	59	69	259	461	1,160	2,380	4,990	10,700	18,900
		rep 3	<10	34	46	89	248	383	1,190	2,180	5,020	9,910	2,100
		mean	<10	38	52	78	245	431	1,150	2,220	6,613	10,193	13,233

Note:
Concentrations in last row (highlighted orange) represent starting concentrations for Phase 1 ecotoxicity testing.

Table 4. Calculated F2 Half-Lives

Test	Soil Type	Initial Concentration (mg/kg)	Half-Life (Days)
Rangefinding Test	Fine	3,000	116
Rangefinding Test	Fine	10,000	133
Phase 1	Fine	500	39
Phase 1	Fine	2,000	75
Phase 1	Fine	4,000	81
Phase 1	Fine	8,000	92
Phase 1	Fine	16,000	170
Phase 1	Fine	32,000	391
Phase 2	Coarse	1,500	38
Phase 2	Coarse	7,500	70

Note:

Half-lives only calculated where correlation coefficient (R^2) is greater than 0.8

Table 5. Ecotoxicity Test Results - Phase 1

Species	Endpoint	IC25 Stantec (2009) (mg/kg)	IC25 Adjusted (mg/kg)	Adjustment Rationale [a]
Nothern Wheatgrass	Shoot Length	647	647	
Nothern Wheatgrass	Root Length	295	295	
Nothern Wheatgrass	Shoot Dry Mass	199	199	
Nothern Wheatgrass	Root Dry Mass	290	290	
Alfalfa	Shoot Length	355	355	
Alfalfa	Root Length	258	258	
Alfalfa	Shoot Dry Mass	265	265	
Alfalfa	Root Dry Mass	403	403	
Barley	Shoot Length	1200	1200	
Barley	Root Length	522	522	
Barley	Shoot Dry Mass	418	418	
Barley	Root Dry Mass	493	493	
Folsomia candida	Adult Survival	nc	1038	IC 25 not calculated by Stantec (2009)
Folsomia candida	Progeny Production	533	533	
Eisenia andrei	Adult Survival	nc	963	IC 25 not calculated by Stantec (2009)
Eisenia andrei	Progeny Production	139	139	
Eisenia andrei	Progeny Mass [b]	297	297	

Notes:

a. see text for detailed explantion of adjustments to IC25 values

b. Arithmetic mean of IC25 values for dry and wet mass

nc = not calculated

Table 6. Ecotoxicity Test Results - Phase 2

Species	Endpoint	IC25 Stantec (2009) (mg/kg)	IC25 Adjusted (mg/kg)	Adjustment Rationale [a]
Nothern Wheatgrass	Shoot Length	1455	1455	
Nothern Wheatgrass	Root Length	533	533	
Nothern Wheatgrass	Shoot Dry Mass	644	644	
Nothern Wheatgrass	Root Dry Mass	508	508	
Alfalfa	Shoot Length	298	298	
Alfalfa	Root Length	58	58	
Alfalfa	Shoot Dry Mass	96	278	
Alfalfa	Root Dry Mass	278	96	
Barley	Shoot Length	5618	5618	
Barley	Root Length	474	474	
Barley	Shoot Dry Mass	2552	2552	
Barley	Root Dry Mass	312	312	
Folsomia candida	Adult Survival	1508	1508	
Folsomia candida	Progeny Production	2784	2784	
Eisenia andrei	Adult Survival	6324	6324	
Eisenia andrei	Progeny Production	77	345	Statistical anomaly
Eisenia andrei	Progeny Mass [b]	574	574	

Notes:

a. see text for detailed explantion of adjustments to IC25 values

b. Arithmetic mean of IC25 values for dry and wet mass

Table 7. Ecotoxicity Test Results - Combined, Adjusted and Ranked IC25 Concentrations

Species	Endpoint	IC25 Adjusted (mg/kg)	Rank	Rank Percentile
Alfalfa	Root Length	58	1	2.86%
Alfalfa	Root Dry Mass	96	2	5.71%
Eisenia andrei	Progeny Production	139	3	8.57%
Nothern Wheatgrass	Shoot Dry Mass	199	4	11.43%
Alfalfa	Root Length	258	5	14.29%
Alfalfa	Shoot Dry Mass	265	6	17.14%
Alfalfa	Shoot Dry Mass	278	7	20.00%
Nothern Wheatgrass	Root Dry Mass	290	8	22.86%
Nothern Wheatgrass	Root Length	295	9	25.71%
Eisenia andrei	Progeny Mass [b]	297	10	28.57%
Alfalfa	Shoot Length	298	11	31.43%
Barley	Root Dry Mass	312	12	34.29%
Eisenia andrei	Progeny Production	345	13	37.14%
Alfalfa	Shoot Length	355	14	40.00%
Alfalfa	Root Dry Mass	403	15	42.86%
Barley	Shoot Dry Mass	418	16	45.71%
Barley	Root Length	474	17	48.57%
Barley	Root Dry Mass	493	18	51.43%
Nothern Wheatgrass	Root Dry Mass	508	19	54.29%
Barley	Root Length	522	20	57.14%
Nothern Wheatgrass	Root Length	533	21	60.00%
Folsomia candida	Progeny Production	533	22	62.86%
Eisenia andrei	Progeny Mass [b]	574	23	65.71%
Nothern Wheatgrass	Shoot Dry Mass	644	24	68.57%
Nothern Wheatgrass	Shoot Length	647	25	71.43%
Eisenia andrei	Adult Survival	963	26	74.29%
Folsomia candida	Adult Survival	1,038	27	77.14%
Barley	Shoot Length	1,200	28	80.00%
Nothern Wheatgrass	Shoot Length	1,455	29	82.86%
Folsomia candida	Adult Survival	1,508	30	85.71%
Barley	Shoot Dry Mass	2,552	31	88.57%
Folsomia candida	Progeny Production	2,784	32	91.43%
Barley	Shoot Length	5,618	33	94.29%
Eisenia andrei	Adult Survival	6,324	34	97.14%
25th Percentile		**294**	**8.75**	**25.00%**
50th Percentile		**484**	**17.5**	**50.00%**

FIGURES

Figure 1. F2 Concentration vs. Time - Rangefinding Test

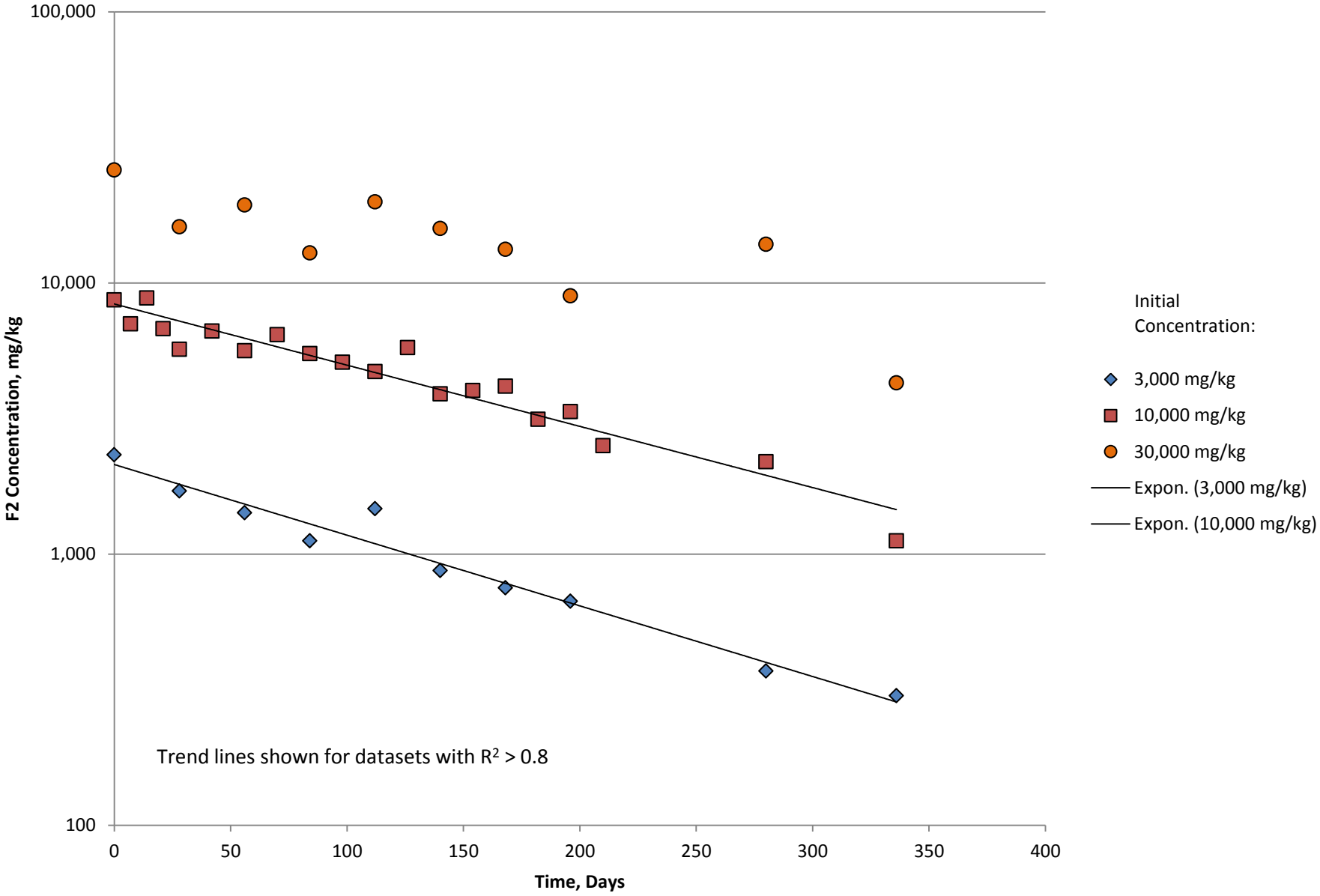

Figure 2. F2 Concentration vs. Time - Phase 1

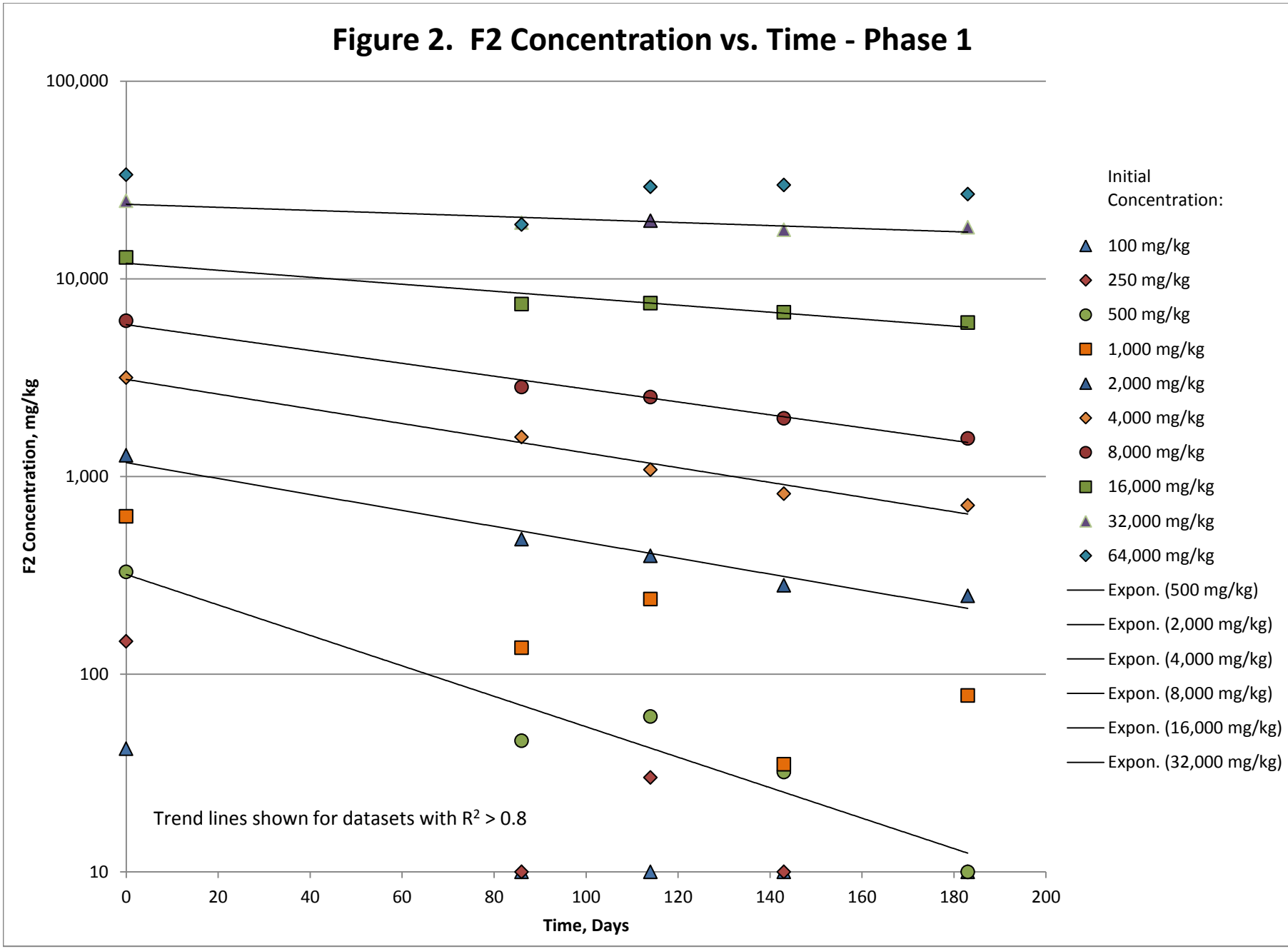

Figure 3. F2 Concentration vs. Time - Phase 2

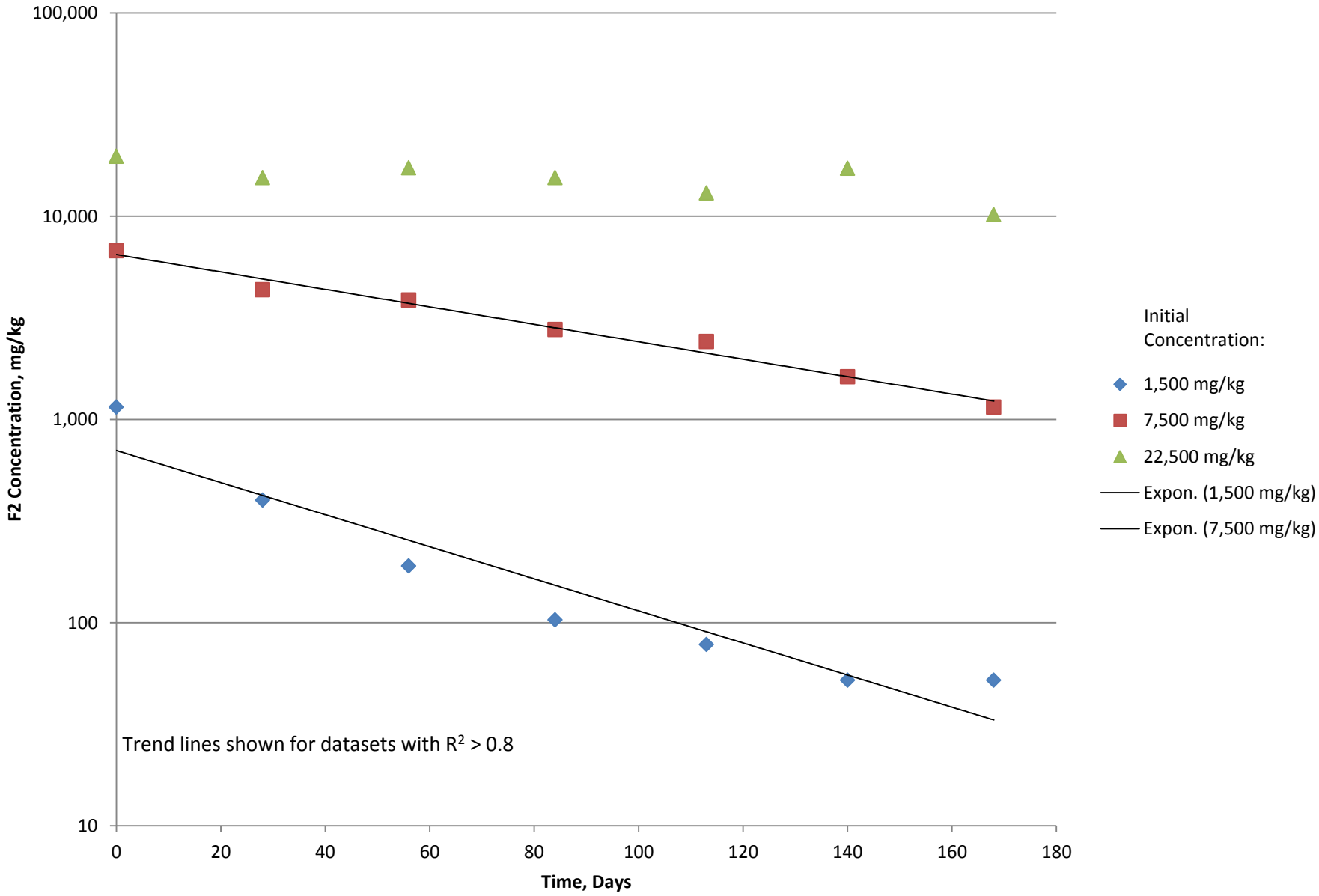

Figure 4. Half-Life of F2 in Soil vs. Initial Concentration

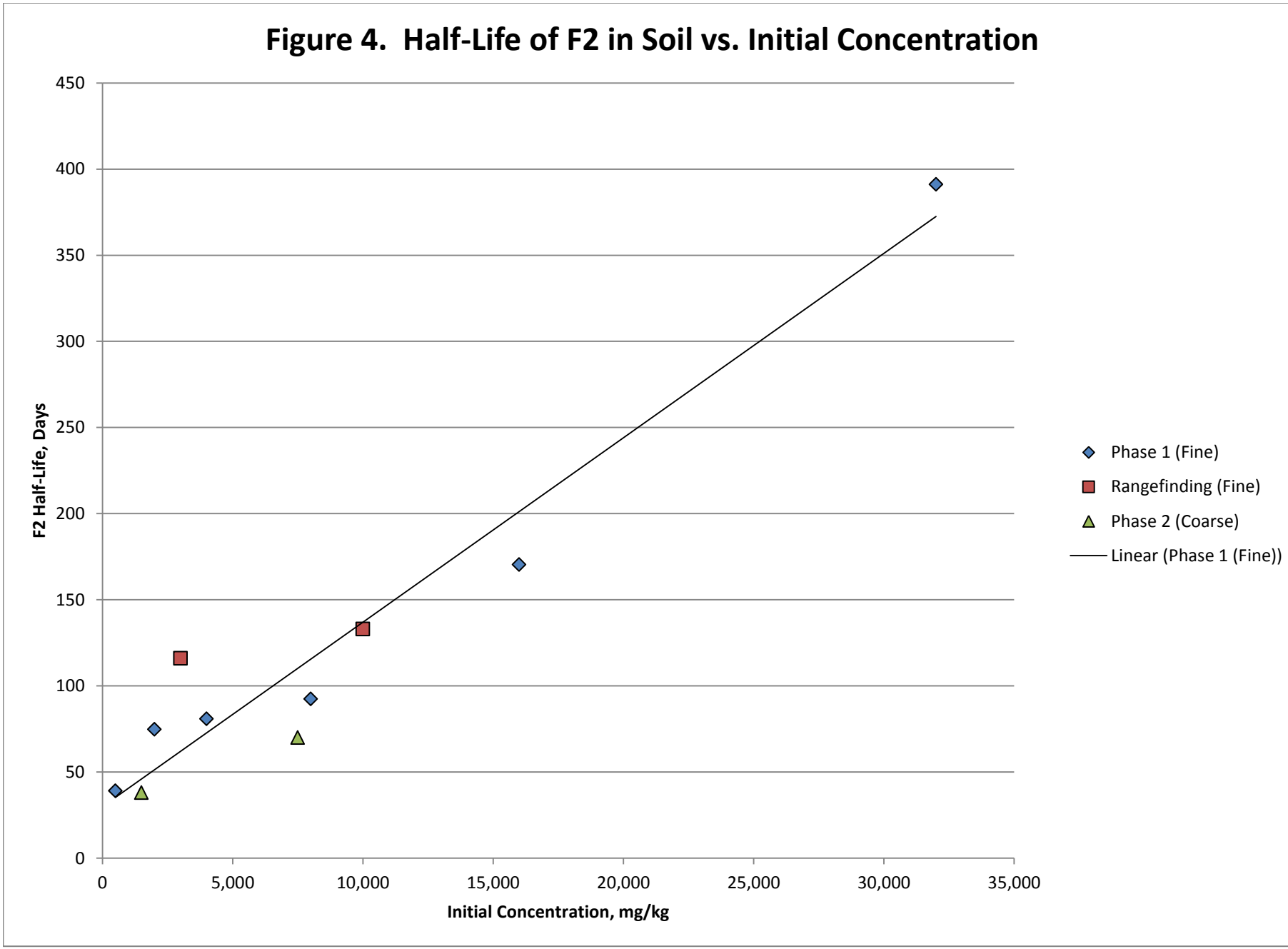

Figure 5. Species Sensitivity Distribution