GUIDANCE ON THE HUMAN HEALTH BASED AND ECOLOGICALLY BASED SOIL REMEDIATION CRITERIA FOR NUMBER 2 FUEL OIL AND DIESEL FUEL OIL

New Jersey Department of Environmental Protection

Site Remediation Program

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Primary Authors:

Chairpersons
Teruo Sugihara
David Haymes

Committee Members
Gary Buchanan
Ann Charles
Linda Cullen
Edward Demarest
Barry Frasco
Diane Groth
Nancy Hamill
William Hanrahan
William Lindner
Paul Sanders
Kevin Schick
Gregory Toffoli
Swati Toppin

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Executive Summary

The New Jersey Department of Environmental Protection (Department) is establishing a human health based remediation criterion and an ecological screening value for petroleum hydrocarbons in soil.

Direct Contact Human Health Based Criterion

The Department is establishing a direct contact human health based criterion of 4,800 mg/kg, which replaces the historical 10,000 mg/kg organic compound cap value. The 4,800 mg/kg value is based on protection from noncarcinogenic health effects at a hazard index of 1 and only applies to discharges of number 2 (no. 2) fuel oil and diesel fuel oil. This value is based solely on effects via the ingestion-dermal exposure pathway. The Department determined that the inhalation exposure pathway is not of regulatory concern.

The Department also determined that the establishment of a criterion for the impact to groundwater pathway is not applicable. However, this does not preclude the relevance of any other Site Remediation Program policies, including the sheen policy (http://www.nj.gov/dep/srp/guidance/sheen/), as well as the requirements to conduct an appropriate ground water investigation and remove and/or treat free and/or residual product pursuant to the Technical Requirements for Site Remediation (N.J.A.C. 7:26E; http://www.nj.gov/dep/srp/regs/techrule/).

Soil sampling will be in conformance with the latest versions of the Technical Requirements for Site Remediation and the Department's Field Sampling Procedures Manual (http://www.nj.gov/dep/srp/guidance/fspm/). Acceptable analytical methods for no. 2 fuel oil and/or diesel fuel oil are SW-846 Method 8015B - Diesel Range Organics, the Department's OQA-QAM-025, and/or their latest versions or equivalents (http://www.nj.gov/dep/srp/guidance/tph/). For sample results above 1,000 mg/kg, the current requirement to analyze for volatile organic compounds plus 10 tentatively identified compounds (VO+10) is to be discontinued. Instead, the Department will require base neutral compounds plus 15 tentatively identified compounds (BN+15) analysis of 25 percent of the samples exceeding 1,000 mg/kg. Of particular concern to no. 2 fuel oil and diesel fuel oil are the base neutral compounds naphthalene and 2-methylnaphthalene. Table 2.1 of the Technical Requirements for Site Remediation remains in effect for all other petroleum hydrocarbon analyses.

Because the human health based criterion is derived from the ingestion/dermal exposure pathway, single point compliance will be required, pursuant to the guidance established for the ingestion-dermal exposure pathway soil remediation standards (http://www.nj.gov/dep/srp/guidance/rs/ing_derm_guidance.pdf). Any value exceeding the 4,800 mg/kg human health based criterion will require further evaluation to determine the need for additional delineation and potential remedial action.

The Department intends to replace the 4,800 mg/kg value with a site-specific approach using an Extractable Petroleum Hydrocarbon (EPH) method that is currently under development by the

Department. Once the EPH Method is approved and certified, the EPH Method results will be used to determine if a hazard index of 1 is exceeded at the site. The Department is considering applying this protocol to discharges of other petroleum hydrocarbon compounds as well as no. 2 fuel oil and diesel fuel oil. The public and regulated community will be notified via the Department's website when the EPH Method becomes available and the site-specific approach implemented.

Ecological Based Screening Value

The Department is establishing an ecological screening value of 1,700 mg/kg that is applicable to all petroleum hydrocarbon discharges if and only if a sensitive environmental receptor is potentially impacted by petroleum hydrocarbon contamination as determined by a baseline ecological evaluation (N.J.A.C. 7:26E-3.11). In these situations, an ecological risk assessment will be conducted pursuant N.J.A.C. 7:26E-4.7 in order to establish a site-specific ecological criterion. The maximum allowable site-specific ecological criterion is 4,800 mg/kg. This ecological maximum is not related to the direct contact human health criterion.

Sampling will again be in conformance with the latest versions of the Technical Requirements for Site Remediation and the Department's Field Sampling Procedures Manual. The primary compliance mechanism will be on a single point basis.

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I. Introduction

This New Jersey Department of Environmental Protection (Department or NJDEP) Site Remediation Program (SRP) guidance document establishes the generic soil cleanup criteria for no. 2 fuel oil and diesel fuel oil. Two criteria are presented in this document: one human health based and the other ecologically based. The human health criterion will serve as the replacement for the previously used total organic cap value of 10,000 milligrams per kilogram dry weight soil (mg/kg).

The Department is legislatively mandated to establish human health based remediation criteria in accordance with the Brownfield Act (N.J.S.A. 58:10B-12). The human health criterion presented in this document is based on the ingestion/dermal exposure pathway, rather than either the inhalation exposure pathway or the impact to ground water pathway. The reasons for this are discussed in Sections V, VI, and VII of this document.

The previously used 10,000 mg/kg total organic cap value was particularly relevant at those locations where petroleum hydrocarbon discharges had occurred. As the vast majority of non-gasoline petroleum hydrocarbon discharges in New Jersey are from number 2 home heating oil (no. 2 fuel oil) and diesel fuel oil (diesel), this document will address no. 2 fuel oil and/or diesel discharges. These are the cases at which the SRP anticipates the greatest need for these new soil remediation criteria. The SRP recognizes that there are other types of non-gasoline petroleum hydrocarbon discharges in New Jersey (i.e., no. 4 fuel oil, no. 6 fuel oil, waste oil, etc.). The SRP intends to address these contaminants by expanding the application of the analytical method and to use this method to develop soil remediation criterion on a site-specific basis. It is important to emphasize that the effort to expand the use of this analytical method is still in the developmental stage.

Unlike the 10,000 mg/kg total organic cap value, the criterion described in this document is solely human health based, specifically based on the non-carcinogenic effects of no. 2 fuel oil and/or diesel. As such, the criterion applies only to no. 2 fuel oil and/or diesel discharges. The SRP has elected to address the carcinogenic effects of semi-volatile organic compounds that are found in no. 2 fuel oil and/or diesel on a compound-specific basis. This will be accomplished through a required base neutral (BN) analysis and a comparison of results on a compound-specific basis to the respective adopted soil remediation standards (N.J.A.C. 7:26D).

The Technical Requirements for Site Remediation requires the analysis of specific volatile organic compounds in soil samples associated with no. 2 fuel oil and diesel discharges that have a TPH concentration greater than 1,000 mg/kg (see N.J.A.C. 7:26E-2.1(d) Table 2.1). However, the results of such testing have shown that volatile organic compounds are not major components of no. 2 fuel oil and/or diesel fuel. Therefore, this guidance document recommends that the required volatile organic compound analysis be replaced with base neutral compound analysis on soils that have no. 2 fuel oil and diesel discharges with EPH concentrations over 1,000 mg/kg.

The second criterion covered by this guidance is ecological in nature. The Brownfield Act precludes the Department from developing generic ecological-based soil remediation standards until recommendations are made by the Environment Advisory Task Force. Until such recommendations are made, the Department may to continue to develop ecological-based soil

remediation criteria on a case-by-case basis (N.J.S.A. 58:10B-12a). This guidance document establishes a soil screening value for sites where ecological receptors are being impacted by petroleum hydrocarbons. A site-specific ecological-based soil remediation criterion will be developed at those sites where this screening value is exceeded and where a potential ecological impact has been identified in a baseline ecological evaluation (BEE).

The SRP intends to initially employ the two cited values as interim guidance. Following an evaluation period, administrative rule making procedures will be undertaken with the intent of adopting as a remediation standard, the procedures for calculating a site-specific human health based soil remediation standard for no. 2 fuel oil and diesel as well as other types of petroleum hydrocarbons. Upon adoption, this procedure will supersede the interim human health criterion.

There were several issues in developing these soil remediation criteria. The primary difficulties were that the composition of no. 2 fuel oil and/or diesel is variable, and toxicity information is limited. Additionally, the standard analytical method for petroleum hydrocarbons was United States Environmental Protection Agency (USEPA) Method 418.1. When the USEPA withdrew the use of Method 418.1 because it utilized Freon as an extractant, a replacement for that method became necessary. To assist in addressing all of these issues, the SRP has proposed the use of a new analytical method. Upon its certification as an acceptable analytical method by the Department's Office of Quality Assurance, this method, designated the EPH Method, will be the primary replacement for Method 418.1 in investigating and remediating sites contaminated with petroleum hydrocarbons. As stated previously, modification of the EPH Method is being considered to widen the applicability of its use beyond no. 2 fuel oil and diesel. If this option is exercised, the expanded version of the EPH Method would be evaluated with the goal of eventual certification as an acceptable analytical method.

II. Composition of Total Petroleum Hydrocarbons (TPH)

Although the term "Total Petroleum Hydrocarbon" (TPH) has been widely used, it has been rarely well defined. TPH is actually defined by the analytical method used to measure it. Petroleum products include hundreds of compounds with varying molecular weights and toxicities.

While the toxicity of the individual target analytes is sometimes available, the public health implications associated with TPH as a composite are far more difficult to establish. The difficulty with developing a remediation criterion for petroleum products lies in the very nature of the product. A petroleum product is not a single compound but rather a complex mixture. The compositions of these products may be made up from over 250 hydrocarbon compounds in varying amounts. Of these hundreds of compounds, toxicological information is available for only approximately 25. These issues make it difficult to determine the health risk posed by petroleum products.

In order to focus specifically on the composition of no. 2 fuel oil and/or diesel, the SRP reviewed the literature regarding compositional information for no. 2 fuel oil and/or diesel. Sources included Massachusetts (Massachusetts Department of Environmental Protection, 2002), Washington (Washington State Department of Ecology, 1997), Canada (Irwin et al., 1997), and

the efforts of the Total Petroleum Hydrocarbons Criteria Work Group (TPHCWG) (Potter and Simmons, 1998). The SRP concluded that there is no universally applicable composition for no. 2 fuel oil and/or diesel. Consequently, the SRP found it necessary to conduct a field study to obtain New Jersey specific composition data. Details of this study are presented in Section IV.

III. Analytical Methods

The existing options for analyzing no. 2 fuel oil and/or diesel contaminated soil samples are SW-846 Methods 8015B -Diesel Range Organics (DRO) (USEPA, 1996a) and NJDEP OQA-QAM-025 (NJDEP, 2008a). Both the DRO and the NJDEP OQA-QAM-025 methods generate a single result representing the total of all petroleum contaminants present and do not account for the varying characteristics of the mixture components. Although these methods are acceptable for determining compliance with a criterion, neither is suitable for initially establishing the actual human health based criterion.

The SRP investigated other states' and scientific groups' approaches to determine if an existing, suitable analytical framework was available or appropriate with modification. Particular attention was again given to Massachusetts (Massachusetts Department of Environmental Protection, 2004), Washington (Washington State Department of Ecology, 1997), Canada (Canadian Council of Ministers of the Environment, 2001), and the efforts of the TPHCWG (Weisman, 1998).

The SRP decided to modify and adopt the petroleum method from the Massachusetts Department of Environmental Protection and incorporate the method into the structure of OQA-QAM-025. This decision was largely based on the fact that the Massachusetts method has been part of a successful petroleum hydrocarbon regulation program for a number of years. The details of the approach follow.

The TPHCWG and Massachusetts took a fractionation approach. This approach addresses the issues by dividing the petroleum product into several carbon ranges based on the number of carbon atoms in conjunction with general structure, i.e., carbon ranges that are homogeneous with respect to physical and chemical properties.

In order to accomplish this, the SRP is proposing to use the Extractable Petroleum Hydrocarbon (EPH) Method. In the EPH Method, the sample is extracted with solvent and the extract is subsequently separated into two fractions, aliphatic and aromatic that are analyzed separately via two distinct analytical analyses. For each fraction, quantitation is performed over five defined equivalent carbon (EC) ranges (i.e., the "components" noted above). The sum of all of the EC ranges is used to determine a total concentration. The compounds used to define each equivalent carbon range for each fraction are further described in the method in Appendix A, Extractable Petroleum Hydrocarbon (EPH) Methodology. The EPH Method in Appendix A is the version used in the EPH-TPH Field Study. It is included in this guidance document to allow a more complete evaluation of what the Department did during the EPH-TPH Field Study as well as to be indicative of what the Department intends to do in the future.

The EC number is related to the boiling point of a compound and its retention time on a gas chromatography column normalized to the boiling point and actual carbon numbers of n-alkanes. For example, even though naphthalene has ten carbons, the EC number of naphthalene is 11.7 because the boiling point and gas chromatograph retention time are between those of n-Undecane and n-Dodecane. The EC numbers are used because they are more closely related to environmental mobility. This approach is also consistent with how the petroleum industry approaches petroleum hydrocarbon analysis.

The equivalent carbon ranges chosen by the SRP were per the recommendations of the TPHCWG. The TPHCWG based the equivalent carbon ranges on physical and chemical properties and also on data from partitioning models. Hydrocarbon mixtures separate and partition based on these properties. There are differences in both the levels of adsorption and mobility, resulting in the separation of the mixture. It is considered reasonable to assume that compounds chemically similar and of similar boiling point will behave the same. The TPHCWG delineated the different equivalent carbon ranges on the basis of an order of magnitude differentiation in the partitioning properties. There are five equivalent carbon ranges for each fraction. Each equivalent carbon range approximately corresponds to an order of magnitude range of the octanol-water partition coefficient (K_{oc}) value which directly affects compound mobility in soil. Fewer carbon ranges would have resulted in a variability in the mobility of compounds greater than an order of magnitude, which was decided to be excessive and unacceptable. The listing of the constituents of a typical no. 2 fuel, their carbon ranges, and their corresponding equivalent carbon numbers for the fractions are included in Appendix B.

IV. Extractable Petroleum Hydrocarbons (EPH)-TPH Field Study

There were several objectives to the EPH-TPH Field Study. The first objective was to empirically generate no. 2 fuel oil composition information. Specifically, this includes the percent contribution of each equivalent carbon range toward the total makeup of no. 2 fuel oil. The second objective was to determine the ability of the EPH Method to analyze actual soil samples contaminated with no. 2 fuel oil. Furthermore, the analysis of standardized samples of known contaminant concentration allowed for the evaluation of method accuracy. The third objective was to determine whether the two methods (EPH and 418.1) yielded comparable results; if so, the new criterion could be used to evaluate historical TPH data generated by Method 418.1. Based on the findings of these objectives, the Department would then determine whether the EPH Method is suitable to determine no. 2 fuel oil and/or diesel contaminant concentrations. The fourth objective was to determine whether there is a compositional difference between samples collected close to the point of discharge and those collected farther from the point of discharge.

A. Study methodology

The EPH-TPH Field Study was conducted between July and August 2007. The SRP coordinated its own sampling efforts with those of several private contractors (a list of the participating contractors is included as Appendix C) at 14 different sites located throughout New Jersey. The sites were selected based on the following criteria: known discharge of no. 2 fuel oil, availability for sample collection, and geographic and geologic variability. All sites were residential and the sole contaminant source at each site was a leaking underground no. 2 fuel oil tank. In addition to

petroleum hydrocarbons, BNs were also targeted by this study. Of particular interest was determining the concentration of 2-methylnaphthalene due to its relatively high mobility and toxicity.

At each site the SRP collected one sample near the underground storage tank (UST) in an area with free or residual product and one sample from the perimeter of the excavation. The perimeter sample was generally collected some distance away from the UST at a location with indications of contamination (odors and sheen) but no free product. The SRP split the near sample and analyzed the samples using both Method 418.1 and the EPH Method. The perimeter sample was collected by the SRP and split; one half was sent to the SRP contract laboratory for EPH Method analysis and the other half was sent to the contractor laboratory for Method 418.1 analysis.

In some instances samples were collected from direct push cores that were driven into the ground around a release. The majority of samples were collected from the open tank excavation. If the tank had been removed prior to the date of sample collection, the samples were collected from newly exposed soils, rather than the previously exposed excavation surface. Soils in the sample core or backhoe bucket were field screened with a photo-ionization detector prior to sample collection to gauge relative contaminant concentrations within the bucket or core. Samples were then processed according to the *New Jersey Department of Environmental Protection Field Sampling Procedures Manual* (NJDEP, 2005).

B. <u>Compositional determination</u>
All 14 of the near samples had detectable concentrations of no. 2 fuel oil using both Method 418.1 and the EPH Method; 12 of the 14 perimeter samples had detectable concentrations of no. 2 fuel oil using Method 4181.1; 11 of the 14 perimeter samples had detectable concentrations of no. 2 fuel oil using the EPH Method. Detectable Method 418.1 concentrations ranged from 67 mg/kg to 19,104 mg/kg. Detectable EPH Method concentrations ranged from 28 mg/kg to 29,299 mg/kg. Table 1 contains results in tabular form.

Table 1. EPH and TPH results for field study (all results in mg/kg)

SAMPLE ID	LOCATION	EPH	TPH
M66148-1	NEAR	4,302	3,420
M66149-1	NEAR	6,547	8,090
M66334-1	NEAR	8,521	7,680
M66554-1	NEAR	1,604	239
M66591-1	NEAR	1,444	923
M66592-2	NEAR	29,299	12,400
M66620-1	NEAR	1,485	571
M66621-1	NEAR	1,966	186
M66705-1	NEAR	1,675	3,690
M66706-1	NEAR	9,388	12,600
M66836-1	NEAR	5,832	4,340
M67046-3	NEAR	2,816	3,130

SAMPLE ID	LOCATION	EPH	TPH
M67047-2	NEAR	1,218	1,390
M67048-1	NEAR	537	521
M66148-2	PERIMETER	3,723	7,420
M66149-2	PERIMETER	0 *	67
M66334-3	PERIMETER	0 *	0 *
M66554-3	PERIMETER	791	928
M66591-3	PERIMETER	136	303
M66592-1	PERIMETER	1,392	1,080
M66620-3	PERIMETER	6,267	13,357
M66621-3	PERIMETER	193	138
M66705-3	PERIMETER	454	464
M66706-3	PERIMETER	28	0 *
M66836-3	PERIMETER	1,354	3,093
M67046-2	PERIMETER	128	68
M67047-1	PERIMETER	8,145	19,104
M67048-3	PERIMETER	0 *	197

* = "non detect" values are represented by zero (0).

An analysis of just the raw EPH data set in Table 1 using the Univariate Mahalanobis Distance Based (Grubb Test) Outlier Analysis indicated that the 29,299 mg/kg EPH value was an outlier. Removing that value, the percent composition was empirically determined and is presented in Table 2.

Table 2. Percent composition based on averaging EPH Field Study results

Fraction	Equivalent Carbon Range	Percent Composition
Aliphatic	8-10	0.6
	10-12	4.0
	12-16	25.6
	16-21	31.8
	21-34	4.8
Aromatic	8-10	0.1
	10-12	0.7
	12-16	7.5
	16-21	21.6
	21-34	3.4

C. EPH Method performance results

The laboratory extracted and analyzed four quality control (QC) samples as part of the research project. The certified values and corresponding quality control acceptance limits were provided for the compounds in the QC samples: naphthalene, 2-methylnaphthalene, fluorene, phenanthrene and summed values for the equivalent carbon ranges of EC 8-18 Aliphatics, EC

19-36 Aliphatics and Total Aromatics. All the reported values for the individual compounds and summed equivalent carbon ranges from the four QC samples were within the QC Performance Acceptance Limits, thereby demonstrating acceptable accuracy for the EPH Method.

D. Comparability of methods 418.1 and EPH results
To evaluate the comparability of the Method 418.1 and EPH Method data, data pairings were established. An analysis of the raw data set in Table 1 using the Classical Sequential Outlier Test Based Upon Maximum Mahalanobis Distance indicated that there were three pairs of data that were considered outliers. These were (EPH and TPH in mg/kg), respectively: (29,299 and 12,400); (6,267 and 13,357); and (8,145 and 19,104).

Removing the outlier values and performing an Ordinary Least Squares Regression Analysis yielded the equation:

$Y = 1.1257X - 79.091$ with a regression coefficient (R^2) of 0.8473

Where:
X = EPH
Y = TPH

Based on this analysis, the SRP is concluding that the EPH and TPH values are comparable at a ratio of roughly 1:1. Therefore, Method 418.1 results can be directly applied to the findings in this document that were derived using EPH data. Alternatively, findings based on Method 418.1 results can be extended to situations where EPH analyses are employed.

Results of the EPH-TPH Field Study indicate that the EPH Method shows promise as a suitable method for analyzing soil samples for no. 2 fuel oil and/or diesel. Minor modifications were made to the initial analytical method based on observations and recommendations from the laboratory performing the analyses as well as editorial issues recognized by the Department. The SRP is investigating the possible expansion of the method to have the capability of analyzing other petroleum hydrocarbons. As was indicated previously, the Department intends to evaluate the modified EPH Method by conducting a multi-laboratory method evaluation study in the future. These study results will hopefully then serve as the basis for requesting certification of the method from the Department's Office of Quality Assurance.

V. Ingestion/Dermal Pathway Based Criterion

A. Toxicology
Because no. 2 fuel oil and/or diesel is a mixture, a single toxicity factor calculation equation is not appropriate. The SRP decided to take the conceptual approach of the TPHCWG and Massachusetts which evaluated no. 2 fuel oil and/or diesel as a mixture of individual components, each with an assigned toxicity factor. Surrogate compounds were selected to represent the toxicological properties of each component (five equivalent carbon ranges in each of the two fractions). A health-based criterion was then derived using standard USEPA exposure models, by calculating a weighted average based on the composition and the assigned toxicity values, such that the hazard index does not exceed one (1).

A surrogate compound was assigned to represent the non-cancer toxicity (oral reference dose) associated with each equivalent carbon range. Due to the lack of toxicity information, several equivalent carbon ranges were assigned the same surrogate. The sum of the individual equivalent carbon range risks represents the overall risk of the petroleum fuel oil from a noncarcinogenic perspective. The effects of various carcinogenic compounds (benzene, carcinogenic polycyclic aromatic hydrocarbons [PAHs]) are evaluated on a chemical specific basis at a 10^{-6} risk level using existing standards. Table 3 lists the equivalent carbon ranges, surrogates, and toxicological/exposure information.

B. Surrogate identification

Surrogates for each equivalent carbon range were chosen considering both the available toxicity information for chemicals within the equivalent carbon range and the percentage of the chemical actually found in that range.

1. Aliphatics

For the aliphatic EC 8-10, EC 10-12, and EC 12-16 ranges, the SRP adopted an RfD based on oral data of petroleum hydrocarbon (PHC) mixtures from studies from Canada (Canadian Council of Ministers of the Environment, 2000) and Massachusetts (Massachusetts Department of Environmental Protection, 2003). While this toxicity information is not available on the Integrated Risk Information System (IRIS) (USEPA, 2008), these data are more recent and were determined to be sufficiently valid to use.

For the aliphatic EC 16-21 and EC 21-34 ranges, similar to Massachusetts and Canada, the SRP used white mineral oil as a surrogate. The specific toxicity factor used was from the TPHCWG study (Edwards et al., 1997).

2. Aromatics

For the aromatic EC 8-10 range, the surrogate chosen was ethylbenzene. Ethylbenzene was chosen because it represents a mid-range toxicity value for chemicals in this equivalent carbon range. The source of the toxicity value was IRIS (USEPA, 2008).

For the aromatic ranges EC 10-12, EC 12-16, EC 16-21, and EC 21-34, the respective surrogates chosen were naphthalene, acenaphthene, fluorene, and fluoranthene. These surrogates were chosen because they are the primary constituent for their respective equivalent carbon range that has known toxicological information. The source of the toxicity values was again IRIS (USEPA, 2008).

Table 3. Equivalent carbon fractions, surrogates, and toxicity/exposure information

Fraction	Equivalent Carbon Range	RfD (mg/kg-day)	Surrogate	Composition (%)	Ingestion/Dermal Pathway (mg/kg)
Aliphatics	8-10	0.10	PHC mixture	0.6	7,800
	10-12	0.10	PHC mixture	4.0	7,800
	12-16	0.10	PHC mixture	25.6	7,800
	16-21	2.0	White mineral oil	31.8	15,600

Fraction	Equivalent Carbon Range	RfD (mg/kg-day)	Surrogate	Composition (%)	Ingestion/Dermal Pathway (mg/kg)
	21-34	2.0	White mineral oil	4.8	15,600
Aromatics	8-10	0.10	Ethyl benzene	0.1	7,800
	10-12	0.02	Naphthalene	0.7	1,150
	12-16	0.06	Acenaphthene	7.5	3,440
	16-21	0.04	Fluorene	21.6	2,290
	21-34	0.04	Fluoranthene	3.4	2,290

C. Ingestion/Dermal Exposure Pathway

The Department developed the soil remediation standards (N.J.A.C. 7:26D) using the current soil screening level equations from USEPA to calculate the combined direct ingestion and dermal absorption pathways (USEPA, 2002). This approach acknowledges that exposure occurs through children's outdoor play and through gardening, landscaping, and excavation by adults. To be consistent with the soil remediation standards, this approach was also used to develop the EPH criterion.

1. Ingestion component

The ingestion component of the ingestion-dermal exposure pathway addresses the potential for human exposure to chemicals through direct ingestion of contaminated soil and dust. Inadvertent soil ingestion among children may occur through mouthing of objects or unintentional hand-to-mouth activity, which is considered a normal phase of childhood development. Children have a greater potential than adults for exposure to soil through ingestion as a result of these behavioral patterns that are present throughout early childhood. Adults may also ingest soil or dust particles that adhere to objects, food, cigarettes, or their hands.

Calculation of remediation standards for the direct ingestion of soil is based on USEPA risk assessment methodology. The procedure for calculating the residential exposure scenario is presented in *Risk Assessment Guidance for Superfund Human Health Evaluation Manual, Part B* (RAGS HHEM, Part B; USEPA, 1991), *Soil Screening Guidance: Technical Background Document* (USEPA, 1996b), and *Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites* (USEPA, 2002).

Under a residential scenario, the SRP has adopted USEPA *Soil Screening Guidance's* approach for noncarcinogenic contaminants that uses a protective "childhood only" exposure. The equation includes an averaging time based on exposure during a 6-year childhood period, a 15-kg body weight, and a soil ingestion rate of 200 mg/day (as shown in the ingestion portion of Equation 1 below).

2. Dermal absorption component

The dermal absorption component of this pathway is derived from risk assessment methodology outlined in USEPA *Risk Assessment Guidance for Superfund: (Part E, Supplemental Guidance for Dermal Risk Assessment) Final (*USEPA, 2004). Currently, soil compounds evaluated for dermal exposure are limited to several individual compounds and two chemical classes (Table 4). USEPA has not developed default dermal absorption values for volatile organic compounds

because they tend to volatilize from the soil adhered to skin, and exposure should be accounted for via the inhalation route of exposure.

The residential noncarcinogenic dermal endpoint focuses on a "childhood only" exposure scenario defaulting to a receptor between the ages of one through six years and incorporating a child's soil adherence factor (AF = 0.2 mg/cm^2-event) and skin surface area (SA = 2,800 cm^2). The skin surface area default values represent the 50th percentile for children (USEPA, 1997).

Other default values include an event frequency of one and the chemical-specific dermal absorption fraction (ABS_d) of 0.13 presented in Table 4. For compounds classified as both semi-volatile and as a PAH, the ABS_d for PAHs is used.

Equation 1. Combined ingestion and dermal absorption exposure to non-carcinogenic contaminants in soil residential scenario

Source: USEPA. 2002. Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites, Final.

$$Remediation\ Standard\ (mg/kg) = \frac{THQ * BW * AT * 365d/yr}{\left(EF * ED * 10^{-6}\ kg/mg\right)\left[\left(\frac{1}{RfD_o} * IR\right) + \left(\frac{1}{RfD_{ABS}} * AF * ABS_d * EV * SA\right)\right]}$$

Parameter/Definition (units)	Default
THQ = target hazard quotient (unitless)	1
BW = body weight (kg)	15
AT = averaging time (years)	6
EF = exposure frequency (days/year)	350
ED = exposure duration (years)	6
RfD_o = oral reference dose (mg/kg-d)	chemical-specific
IR = soil ingestion rate (mg/d)	200
RfD_{ABS} = dermally adjusted reference dose (mg/kg-d)	chemical-specific
AF = skin-soil adherence factor (mg/cm^2-event)	0.2
ABS_d = dermal absorption factor (unitless)	chemical-specific
EV = event frequency (events/day)	1
SA = skin surface area exposed-child (cm^2)	2,800

Table 4. Compounds and recommended dermal absorption fractions

Source: USEPA. 2002. Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites, Final.	
Compound	Dermal Absorption Fraction (ABS_d)
Arsenic	0.03
Benzo(a)pyrene	0.13
Cadmium	0.001
Chlordane	0.04
DDT	0.03
Lindane	0.04
PAHs	0.13
Pentachlorophenol	0.25
Semi-volatile organic compounds	0.1

D. Derivation of equation used to calculate the EPH Risk-Based Screening Level (RBSL)

The following is adapted from Vorhees et al., 1999.

The Hazard Quotient (HQ) for each component is defined as:

$$HQ_{(i)} = \frac{C_{(i)}}{RBSL_{(i)}}$$

where $C_{(i)}$ is the concentration of the component in the soil, and $RBSL_{(i)}$ is the risk-based screening level for fraction i (the total allowable concentration if the component comprises 100 percent of the EPH observed). Each component RBSL is calculated using Equation 1, in combination with the appropriate surrogate toxicity.

It is given that:

$$C_{(i)} = C_{total} * f_{(i)}$$

where C_{total} is the total EPH concentration, and $f_{(i)}$ is the weight fraction of component i.

Therefore, combining the above, the risk of each component is

$$HQ_{(i)} = \frac{C_{total} * f_{(i)}}{RBSL_{(i)}}$$

If there are 10 total components, the Hazard Index (HI) is the sum of all the HQs for the 10 components:

$$HI = \sum_{i=1}^{10} \frac{C_{total} * f_{(i)}}{RBSL_{(i)}}$$

C_{total} is constant for each component, so simplifying the equation yields:

$$HI = C_{total} \sum_{i=1}^{10} \frac{f_{(i)}}{RBSL_{(i)}}$$

Rearranging the equation by dividing both sides by the sum of all components to isolate C_{total} by itself yields:

$$C_{total} = \frac{HI}{\sum_{i=1}^{10} \frac{f_{(i)}}{RBSL_{(i)}}}$$

Expanding this last equation yields:

$$C_{total} = \frac{HI}{\frac{f_{(1)}}{RBSL_{(1)}} + \frac{f_{(2)}}{RBSL_{(2)}} + \frac{f_{(3)}}{RBSL_{(3)}} + \frac{f_{(4)}}{RBSL_{(4)}} + \frac{f_{(5)}}{RBSL_{(5)}} + \frac{f_{(6)}}{RBSL_{(6)}} + \frac{f_{(7)}}{RBSL_{(7)}} + \frac{f_{(8)}}{RBSL_{(8)}} + \frac{f_{(9)}}{RBSL_{(9)}} + \frac{f_{(10)}}{RBSL_{(10)}}}$$

When HI equals 1, C_{total} corresponds to the risk-based screening level for total EPH for the composition established by the specific 10 components being evaluated.

E. <u>Results</u>

The entire EPH-TPH Field Study data set was evaluated for use in calculating the RBSL for no. 2 fuel oil and/or diesel. As indicated in Section II, it was determined for the EPH data alone that the 29,299 mg/kg EPH value was an outlier. In addition, because it is not possible to derive compositional information from the non-detect values, these three values were excluded. The resulting data set of 24 EPH-TPH Field Study samples was used to generate 24 individual human health based no. 2 fuel oil and/or diesel criteria using the EPH concentrations only. For each sample, each equivalent carbon range concentration was paired with the appropriate toxicity factor for that equivalent carbon range. After adjusting for the presence of each equivalent carbon range by taking into account their measured concentration, these individual ranges were then summed to calculate the risk-based screening level (RBSL) which is the total allowable concentration of EPH for each individual sample. Table 5 shows the results of the RBSL calculations.

The resulting 24 RBSLs were initially grouped into three categories, the near samples, the perimeter samples, and all samples combined. The desired objective was to evaluate no. 2 fuel oil as product, as well as in a weathered condition. A statistical test was run that indicated no significant difference between the near and perimeter data sets. However, the power of the statistical test was extremely low because of the limited amount of data available. Therefore, the

SRP decided to pool all of the EPH data (still excluding the outlier and the three non-detect values) to enhance the robustness of the results.

The arithmetic mean of the combined data set is 5,108 mg/kg, with a minimum of 4,128 mg/kg and a maximum of 7,248 mg/kg. Because of the concern about the limited amount of data, the SRP decided to act conservatively and use the 95% lower confidence limit of the mean to determine the criterion. For this lognormally distributed dataset, the calculated 95% lower confidence limit is 4,816 mg/kg, which rounds to 4,800 mg/kg. Therefore, for human health concerns, the Department will regulate no. 2 fuel oil and/or diesel discharges using an EPH concentration of 4,800 mg/kg.

Table 5. RBSL calculation results

SAMPLE ID	Location	RBSL (mg/kg)
M66148-1	NEAR	4,468
M66149-1	NEAR	4,791
M66334-1	NEAR	4,367
M66554-1	NEAR	4,710
M66591-1	NEAR	4,128
M66620-1	NEAR	4,860
M66621-1	NEAR	4,616
M66705-1	NEAR	4,727
M66706-1	NEAR	5,522
M66836-1	NEAR	5,082
M67046-3	NEAR	6,513
M67047-2	NEAR	6,311
M67048-1	NEAR	7,248
M66148-2	PERIMETER	4,630
M66554-3	PERIMETER	4,754
M66591-3	PERIMETER	4,341
M66592-1	PERIMETER	4,317
M66620-3	PERIMETER	5,040
M66621-3	PERIMETER	4,886
M66705-3	PERIMETER	5,300
M66706-3	PERIMETER	5,625
M66836-3	PERIMETER	4,700
M67046-2	PERIMETER	5,805
M67047-1	PERIMETER	5,855
AVERAGE	**ALL**	**5,108**

VI. Inhalation Exposure Pathway Based Criterion

For the compounds being used as surrogates, the known inhalation exposure pathway soil remediation standards are generally not of concern. The one exception is naphthalene. However, because this surrogate represents only 0.7 percent of the EPH composition, the impact

is minimal. Using the RBSL equation from above, the calculated inhalation exposure pathway RBSLs for both the residential and non-residential exposure scenarios are greater than 1,000,000 mg/kg for EPH. Consequently, SRP has determined that for no. 2 fuel oil and diesel, there is no need to evaluate EPH discharges with respect to the inhalation exposure pathway.

VII. Impact to Ground Water Pathway Based Criterion

A. Effect of composition on the impact to ground water criterion

The impact to ground water (IGW) criteria for no. 2 fuel oil and/or diesel were calculated using the procedures described below. The criteria were calculated using Washington State, ExxonMobil and a SRP-estimated composition. Evaluation of the resulting criteria indicates that the IGW criteria are very sensitive to the composition of the fuel. The ingestion-dermal exposure pathway criteria were less sensitive (Table 6).

Table 6. Sensitivity of EPH criteria to composition and calculation procedure

EPH Criterion, mg/kg			
Pathway	SRP composition based on specific compound analysis (actual carbon number)	ExxonMobil heating oil (equivalent carbon number)	Washington State fresh diesel (equivalent carbon number)
IGW	80	960	No limit
Ingestion/Dermal	4,459	5,299	6,103

The SRP composition in Table 6 was based on a suggested composition from the TPHCWG (Potter and Simmons, 1998) and the National Park Service (Irwin et al., 1997). The ExxonMobil composition was obtained from a personal communication (ExxonMobil Corporation, 2006). The Washington State composition was from Park and San Juan (2000). As shown, the composition of fuel oil affects the IGW criteria by orders of magnitude.

B. Chemical properties

In addition to the toxicity information noted above in Table 3, each of the equivalent carbon ranges in Table 3 was assigned representative chemical properties, as shown in Table 7. The chemical properties shown in Table 7 were taken from the Washington State spreadsheet for calculating the impact of petroleum hydrocarbons (Washington, 2007), and found to be appropriate by the SRP. Note that these equivalent carbon range-specific values are essentially the same as those published by the TPHCWG (Gustafson et al., 1996).

Table 7. Chemical properties used in assessment of the impact to ground water pathway for no. 2 fuel oil

Fraction	RfD (mg/kg/day)	Water Solubility (mg/L)	Henry's Law Constant (dimensionless)	Soil Water-Carbon Partition Coefficient (L/kg)	Liquid Density (mg/L)
Aliphatic					
EC 8-10	0.1	4.30E-01	8.00E+01	3.02E+04	7.30E+05
EC 10-12	0.1	3.40E-02	1.20E+02	2.34E+05	7.50E+05
EC 12-16	0.1	7.60E-04	5.20E+02	5.37E+06	7.70E+05
EC 16-21	2	1.30E-06	4.90E+03	9.55E+09	7.80E+05
EC 21-34	2	1.50E-11	1.00E+05	1.07E+10	7.90E+05
Aromatic					
EC 8-10	0.10	6.50E+01	4.80E-01	1.58E+03	8.70E+05
EC 10-12	0.02	2.50E+01	1.40E-01	2.51E+03	9.00E+05
EC 12-16	0.06	5.80E+00	5.30E-02	5.01E+03	1.00E+06
EC 16-21	0.04	5.10E-01	1.30E-02	1.58E+04	1.16E+06
EC 21-34	0.04	6.60E-03	6.70E-04	1.26E+05	1.30E+06

C. Model and calculations

A human health based noncarcinogenic impact-to-groundwater value was developed for each EPH-TPH Field Study sample using Washington State's Excel Workbook for Calculating Cleanup Levels for Petroleum Contaminated Sites (Washington State Department of Ecology, 2007). The modeling approach is the same as that used by the SRP to assess the impact-to-groundwater pathway, which in turn is based on the USEPA Soil Screening Level (SSL) document (USEPA, 1996b). The primary equation is the soil-water partition equation coupled with the dilution-attenuation factor, which is applied to each carbon fraction. However, the model was modified in order to be useful for relatively high concentrations of petroleum hydrocarbons. It includes the nonaqueous phase, in addition to the sorbed, aqueous, and vapor phases. This four-phase model, in contrast to the standard three-phase partitioning model, allows the calculation of a human health based criterion when TPH concentrations exceed solubility limits and residual saturation or non aqueous phase liquid (NAPL) is present. The exposure pathway modeled is health-based and assumes ingestion of groundwater, with 80 percent of contaminant exposure occurring from other sources, as per Department policy. The maximum allowed total hazard index (the sum of all the hazard quotient values from each equivalent carbon range) was set to be equal to one. All other input parameters (soil properties, dilution-attenuation factor) were set to the default values used in the Department's impact to ground water soil remediation standards guidance document, "Development of Site Specific Impact to Ground Water Soil Remediation Standards Using Soil-Water Partition Equation" (NJDEP, 2008b).

D. Results

Ignoring the complicating issue of 2-methylnaphthalene (see below), none of the samples with detectable EPH concentrations ranging from 28 mg/kg to 29,299 mg/kg, resulted in a total hazard index greater than one. Therefore, the impact-to-groundwater pathway was not of concern for these samples. There are three reasons for this. First, aqueous concentrations of the EPH

constituents are limited by their solubility from NAPL source contamination. Once the NAPL concentration is reached, higher EPH concentrations do not result in increased aqueous concentrations of the EPH constituents (which are regulated by the Department); rather it simply increases the amount of NAPL present. Second, the bulk of the EPH constituents consists of chemicals with equivalent carbon number 12 or higher (see Table 3), and these compounds are relatively immobile even in aqueous solution (see partition coefficients in Table 7). Finally, the EPH fractions have relatively low toxicity (see RfD values in Table 7). Note that the absence of an IGW criterion for EPH does not preclude any other Site Remediation Policies, including the Sheen Policy and the removal of free product as well as any appropriate ground water investigation.

There is remaining concern for 2-methylnaphthalene, which is known to be present in petroleum hydrocarbon contaminated soil. This compound is relatively toxic for a noncarcinogen, with a RfD of 0.004 mg/kg/day. Additionally, 2-methylnaphthalene is relatively mobile (partition coefficient of 6,820 L/kg) compared to values in Table 7.

2-methylnaphthalene is a member of the aromatic equivalent carbon 12-16 range. The SRP did not select 2-methylnaphthalene as the surrogate for this equivalent carbon range because, as the most toxic compound identified for this equivalent carbon range, it would be overly conservative. However, because of concerns regarding the toxicity of 2-methylnaphthalene, its presence, and its ability to leach to ground water, the SRP determined that 2-methylnaphthalene potentially needed to be evaluated separately.

An assessment was conducted in which the 2-methylnaphthalene concentration for each of the samples from the research study was included as its own component in the sample composition (i.e., 11 components rather than 10). The 2-methylnaphthalene concentration was subtracted from the equivalent carbon 12-16 range concentration and its chemical-specific toxicity factor and chemical properties applied. The percent composition for each component was then calculated, and these values were evaluated using the model described in Section VII.C. As part of this assessment, the SRP calculated an IGW value for 2-methylnaphthalene using as a basis the USEPA soil water partition equation model (USEPA, 1996b). This resulted in an IGW value of 5 mg/kg.

The results of this assessment indicated that at higher EPH concentrations the Hazard Index sometimes exceeded 1 and/or the 2-methylnaphthalene concentration sometimes exceeded 5 mg/kg (Table 8). This occurred for 11 of the 24 samples. It was observed that EPH concentrations less than 1,700 mg/kg always yielded hazard indices less than 1, even when 2-methylnaphthalene was included in the analysis. Furthermore, EPH concentrations less than approximately 1,200 mg/kg resulted in 2-methylnaphthalene concentrations in soil less than 5 mg/kg. Therefore, concentrations less than 1,200 mg/kg meet both criteria. The TRSR currently have a trigger of 1,000 mg TPH/kg for requiring volatile organic compound analysis. Based on previous SRP experience with no. 2 fuel oil and/or diesel, volatile organic compounds typically are not a problem. Therefore, BN+15 analysis will be used as a substitute for the volatile organic compound analysis. It is SRP's intention to use 1,000 mg EPH/kg as the trigger for the BN+15 analysis. Doing so will allow for the specific evaluation of 2-methylnaphthalene at an EPH concentration that is protective of no. 2 fuel oil and/or diesel discharges.

Table 8. Correlation of EPH with 2-methylnaphthalene in 24 home heating oil samples

Sample	EPH (mg/kg)	Hazard Index > 1?	2-methylnaphthalene (mg/kg)
M66706-3	28	No	0.0
M67046-2	128	No	0.0
M66591-3	136	No	0.0
M66621-3	193	No	0.7
M66705-3	454	No	2.0
M67048-1	537	No	0.0
M66554-3	791	No	0.7
M67047-2	1,218	No	5.4
M66836-3	1,354	No	1.8
M66592-1	1,392	No	1.3
M66591-1	1,444	No	5.9
M66620-1	1,485	No	4.1
M66554-1	1,604	No	3.4
M66705-1	1,675	No	10.8
M66621-1	1,966	**YES**	14.1
M67046-3	2,816	No	1.3
M66148-2	3,723	No	2.3
M66148-1	4,302	**YES**	24.9
M66836-1	5,832	No	24.7
M66620-3	6,267	No	36.9
M66149-1	6,547	No	16.3
M67047-1	8,145	**YES**	54.9
M66334-1	8,521	**YES**	85.5
M66706-1	9,388	No	34.7

VIII. Base Neutral Concerns

A review of the SRP EPH-TPH Field Study analytical data (Table 9) indicates that, in general, BN parameters (inclusive of PAHs) that are typically targeted do not appear to be of concern for soil samples collected from sites with EPH concentrations below 1,000 mg/kg. While the study demonstrates that all samples (including those associated with EPH concentrations above 1,000 mg/kg) are in compliance with the historical BN/PAH Direct Contact Soil Cleanup Criteria (DCSCC), the study does not conclusively demonstrate that the samples would comply with the adopted soil remediation standards for benzo(a)pyrene (BaP) and dibenz(a,h)anthracene (DBahA). This is due to the Reporting Limits (RL) for the above compounds exceeding their respective adopted standard of 0.2 mg/kg. However, BaP and DBahA were not detected in any of the available EPH-TPH Field Study samples irrespective of the EPH concentration. This included EPH concentrations up to 9,388 mg/kg. This would suggest that BaP and DBahA are not present and that the reporting limit being above the adopted standard is not a relevant issue.

Table 9. Comparison of EPH and Base Neutral/PAH concentrations
(all results in mg/kg)

Sample ID	An	Any	Ant	BaA	BaP	BbF	BghiP	BkF	Chr	DBahA	FA	FL	IP	2MN	Naph	PA	Pyr	Total EPH (mg/kg)
M66149-2 Per	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.58	0	0	0
M66334-3 Per	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1.48	0	0	0
M67048-3 Per	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
M66706-3 Per	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.554	0	0	28
M67046-2 Per	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	128
M66591-3 Per	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	136
M66621-3 Per	0	0	0	0	0	0	0	0	0	0	0	0	0	0.657	0.661	0	0	193
M66705-3 Per	0.729	0	0	0	0	0	0	0	0	0	0	0	0	2	0.978	0	0	454
M67048-1 Near	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	537
M66554-3 Per	0	0	0	0	0	0	0	0	0	0	0	0.747	0	0.694	0	0	0	791
M67047-2 Near	1.12	0	0	0	0	0	0	0	0	0	0	0.956	0	5.41	1.04	0.935	0	1218
M66836-3 Per	1.68	0	0	0	0	0	0	0	0	0	0.776	1.73	0	1.8	0	1.91	0.707	1,354
M66592-1 Per	1.63	0.621	0	0	0	0	0	0	0	0	0	2.39	0	1.3	0	2.13	0	1,392
M66591-1 Near	2.27	0	0	0	0	0	0	0	0	0	0	2.15	0	5.9	0.837	2.31	0	1,444
M66620-1 Near	1.78	0	0	0	0	0	0	0	0	0	0	1.78	0	4.14	1.05	1.24	0	1,485
M66554-1 Near	0.922	0	0	0	0	0	0	0	0	0	0	1.75	0	3.36	0	1.71	0	1,604
M66705-1 Near	2.93	0.689	0	0	0	0	0	0	0	0	0	1.67	0	10.8	2.06	1.81	0	1,675
M66621-1 Near	3.25	0.693	0	0	0	0	0	0	0	0	0	2.36	0	14.1	2.99	2.48	0	1,966
M67046-3 Near	1.36	0	0	0	0	0	0	0	0	0	0	1.98	0	1.27	0	0.706	0	2,816
M66148-2 Per	3.73	0.999	0	0	0	0	0	0	0	0	1.15	3.74	0	2.29	1.22	3.29	0	3,723
M66148-1 Near	8.57	1.47	0	0	0	0	0	0	0	0	0	5.63	0	24.9	3.99	7.95	0	4,302
M66836-1 Near	5.93	1.36	0.882	0	0	0	0	0	0	0	1.12	6.16	0	24.7	2.86	6.24	1.21	5,832
M66620-3 Per	9.87	1.51	0	0	0	0	0	0	0	0	0.831	6.07	0	36.9	4.64	8.87	0.92	6,267
M66149-1 Near	7.01	1.82	0	0	0	0	0	0	0	0	1.18	7.4	0	16.3	3.24	7.78	1.67	6,547
M67047-1 Per	10.4	1.44	0.824	0	0	0	0	0	0	0	0.753	8.31	0	54.9	8.75	8.79	0	8,145
M66334-1 Near	0	0	0	0	0	0	0	0	0	0	0	0	0	85.5	11.1	20.6	2.45	8,521
M66706-1 Near	0	8.02	10.5	0	0	0	0	0	0	0	2.92	8.05	0	34.7	4.71	0	0	9,388
M66592-2 Near	7.35	26.9	0	0	0	0	0	0	1.04	0	33.8	44.8	0	18.9	2.76	10.7	0	29,299

Where: Near = Near samples; Per = Perimeter samples

Compound	Abbrev.	Compound	Abbrev.	Compound	Abbrev.
Acenaphthene	An	Benzo(g,h,i)perylene	BghiP	Indeno(1,2,3-cd)pyrene	IP
Acenaphthylene	Any	Benzo(k)fluoranthene	BkF	2-Methylnaphthalene	2MN
Anthracene	Ant	Chrysene	Chr	Naphthalene	Naph
Benzo(a)anthracene	BaA	Dibenz(a,h)anthracene	DBahA	Phenanthrene	PA
Benzo(a)pyrene	BaP	Fluoranthene	FA	Pyrene	Pyr
Benzo(b)fluoranthene	BbF	Fluorene	FL		

A more inclusive analysis of the PAHs yields the following results. The five PAHs with the lowest ingestion/dermal exposure pathway soil remediation standards are: benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene. In the EPH-TPH Field Study, these were not detected above their various reporting limits (which ranged from 0.490 to 0.640 mg/kg) in any of the samples. This is consistent with SRP's previous experience with no. 2 fuel oil and diesel. Other PAHs, benzo(g,h,i)perylene and benzo(k)fluoranthene, were similarly not detected. Anthracene, chrysene, and pyrene were only detected in five or less of all the samples and well below concentrations of regulatory concern. Acenaphthene, fluoranthene, and fluorene, were detected relatively frequently. These three compounds are not expected to be of regulatory concern because of the magnitude of their applicable soil remediation standard. Acenaphthylene and phenanthrene were also frequently detected, but are not of regulatory concern. However, naphthalene and 2-methylnaphthalene are also frequently observed, and are of regulatory concern, and will be discussed below. Overall, this evaluation indicates that PAHs, other than naphthalene and 2-methylnaphthalene, are not a significant component of no. 2 fuel oil and/or diesel. Again it is acknowledged that for BaP and DBahA the reporting limit was above the recently adopted soil remediation standard of 0.2 mg/kg.

The most stringent soil remediation standard for naphthalene is six (6) mg/kg, and is derived from the inhalation exposure pathway. Elevated naphthalene concentrations were detected in two of the 28 samples (Table 10). One of these elevated naphthalene concentrations was from a sample with an EPH concentration of 8,521 mg/kg. The other was from a sample with an EPH concentration of 8,145 mg/kg. Excluding the three non-detect samples and one outlier, there were 15 other samples (17 total) where EPH was detected above 1,000 mg/kg. These values ranged from 1,218 to 9,388 mg/kg, with no exceedances of the naphthalene soil remediation standard. The remaining seven samples below 1,000 mg EPH/kg did not exceed the naphthalene soil remediation standard. Therefore, requiring BN analysis including 15 non-targeted semivolatile organic compounds if present (BN+15) at sites with EPH and/or TPH concentrations above 1,000 mg/kg is reasonable. Requiring these BN+15 analyses will also address concerns regarding petroleum hydrocarbons of unknown composition.

Table 10. Comparison of EPH and Naphthalene concentrations (all results in mg/kg)

SAMPLE ID	LOCATION	EPH	Naphthalene
M66148-1	NEAR	4,302	3.99
M66149-1	NEAR	6,547	3.24
M66334-1	NEAR	8,521	11.1 *
M66554-1	NEAR	1,604	0
M66591-1	NEAR	1,444	0.837
M66592-2	NEAR	29,299	2.76
M66620-1	NEAR	1,485	1.05
M66621-1	NEAR	1,966	2.99
M66705-1	NEAR	1,675	2.06
M66706-1	NEAR	9,388	4.71
M66836-1	NEAR	5,832	2.86

SAMPLE ID	LOCATION	EPH	Naphthalene
M67046-3	NEAR	2,816	0
M67047-2	NEAR	1,218	1.04
M67048-1	NEAR	537	0
M66148-2	PERIMETER	3,723	1.22
M66149-2	PERIMETER	0	1.58
M66334-3	PERIMETER	0	1.48
M66554-3	PERIMETER	791	0
M66591-3	PERIMETER	136	0
M66592-1	PERIMETER	1,392	0
M66620-3	PERIMETER	6,267	4.64
M66621-3	PERIMETER	193	0.661
M66705-3	PERIMETER	454	0.978
M66706-3	PERIMETER	28	0.554
M66836-3	PERIMETER	1,354	0
M67046-2	PERIMETER	128	0
M67047-1	PERIMETER	8,145	8.75 *
M67048-3	PERIMETER	0	0

* Values are above the residential soil remediation standard of six (6) mg/kg for naphthalene, but below the non-residential soil remediation standard of 16 mg/kg.

ND = Non-detect

IX. Ecological Pathway Based Criterion

Following a literature search and a review of the pertinent documents, the SRP recommends 1,700 mg/kg TPH, measured by a Department certified analytical method for TPH and/or EPH given the field study findings, as the ecological screening criteria applicable to environmentally sensitive areas. There are clear adverse effects on soil organisms above this TPH concentration. Below 1,700 mg/kg TPH, adverse effects to ecological receptors are possible but not likely and further ecological evaluation in most cases is not warranted. If data from contaminated site soil are above 1,700 mg/kg and a sensitive ecological receptor is potentially impacted, the soils must be either remediated to 1,700 mg/kg or a site-specific risk-based remedial goal must be determined from more rigorous biological testing. Based on the additional likelihood of adverse effects to soil organisms including the soil microbial ecosystem, there are concerns when TPH concentrations are in the 4,000 mg/kg range in environmentally sensitive areas. However, the 4,800 mg/kg EPH value derived for human health purposes was deemed by the Department to be sufficiently protective of this concern.

The complete basis and background document is included in Appendix D.

X. Conclusions

The Department through this guidance is establishing a human health based replacement for the 10,000 mg/kg organic compound cap value. This value will be 4,800 mg/kg and is applicable to number 2 fuel oil and diesel fuel oil. For soil sample results above 1,000 mg/kg, BN+15 analysis (rather than VO+10) of 25 percent of the samples exceeding is required. Sampling will be in conformance with the latest versions of the Technical Requirements for Site Remediation and the Field Sampling Procedures Manual (NJDEP, 2005). Because the human health based criterion is derived from the ingestion/dermal exposure pathway, compliance will be accomplished as per the guidance established for the ingestion/dermal exposure pathway soil remediation standards (single point compliance). Any value exceeding the human health based criterion will require further evaluation for potential remediation.

As noted, the composition of no. 2 fuel oil and/or diesel can vary considerably. As opposed to the ingestion-dermal exposure pathway criterion, variations in composition significantly affect the IGW pathway criterion. As the composition of no. 2 fuel oil and/or diesel (as well as other fuel oils) in New Jersey could potentially change in the future, possibly to one where the IGW pathway becomes a concern, it is recommended that equivalent carbon range analysis using the EPH Method be continued, as it involves little increase in time and cost. This will allow a reassessment of the exposure pathway in the future, if needed. Note that the absence of an IGW criterion for EPH does not preclude any other Site Remediation Policies, including the Sheen Policy and the removal of free product as well as any appropriate ground water investigation.

Because the Method 418.1 has been withdrawn, there is a need to find a substitute method. Based on the above, the SRP is proposing a replacement method designated the EPH Method for future work once method certification is obtained. Until such time that this proposed method is certified and commercially available, the DRO and OQA-QAM-25 methods are acceptable alternatives. The SRP further intends to address number 4 and number 6 fuel oil through an expansion of the EPH Method to include larger range hydrocarbons. When the EPH Method is approved for use, the SRP intends to use the EPH based methodology to develop site-specific criterion for number 2, 4, and 6 fuel oil as well as diesel. The application of the EPH Method may, at that time, be expanded to include waste oil and other petroleum hydrocarbon contamination.

An evaluation of the values used by other states to regulate TPH was conducted. Differing approaches and goals of the criteria and/or standards make comparison somewhat difficult. However, the human health based criterion presented in this guidance is within the range of the values used by other states.

The Department is also establishing an ecological screening value of 1,700 mg/kg. If a sensitive environmental receptor is potentially impacted by petroleum hydrocarbon contamination above this concentration, a site-specific ecological criterion will need to be established. If site-specific determinations cause the human health based criterion to change from 4,800 mg/kg, the maximum ecologically allowed concentration will remain at 4,800 mg/kg. This is because the ecological maximum is based on a soil function end point and not human health. Sampling will be in conformance with the latest versions of the Technical Requirements for Site Remediation

and the Field Sampling Procedures Manual (NJDEP, 2005). The primary compliance mechanism will be on a single point basis.

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Appendix A. Extractable Petroleum Hydrocarbon (EPH) Methodology

NOTE: The following methodology is the one used by the contract laboratory that performed the EPH analyses for the EPH-TPH Field Study. It is provided here for informational purposes only. This is <u>not</u> a methodology officially certified by the state of New Jersey, and should not be used to perform EPH analyses. The Department currently is developing a methodology and once certified, will notify the public of its availability.

1.0 SCOPE OF APPLICATION

1.1. Scope

This method utilizes a gas chromatograph (GC) fitted with a flame ionization detector (FID). The following petroleum analyses are included in the method:

1.1.1. Quantitative analysis of environmental samples (water, soil, sediment, and sludge) for residues from commercial petroleum products such as crude oil, diesel fuel, waste oil, fuels oils Nos. 2-6, lubricating oil, processed oils and bunker fuel.

The method determines the collective concentrations of extractable aliphatic and aromatic petroleum hydrocarbons in water and soil/sediment matrices).

The method must not be used for gasoline contaminated sites.

1.2. Applicable Program

1.2.1. Underground Storage Tanks (UST), New Jersey Spill Fund, Comprehensive Environmental Response Compensation and Liability Act (CERCLA), Industrial Site Recovery Act (ISRA), Sludge Residuals, and Resource Conservation and Recovery Act (RCRA).

1.3. Method Advantages

1.3.1. The method replaces the TPHC method based on Freon 113 extraction and analysis by infrared spectroscopy.

1.3.2. The FID response produces extractable petroleum hydrocarbon (EPH) chromatograms that can be used to calculate concentrations of specified carbon ranges for both aliphatic and aromatic fractions.

1.4. Method Limitations

1.4.1. Quantitative Studies

1.4.1.1. The EPH is quantitatively restricted to the semi-volatile components as partial loss of volatiles (b.p. < 60°C) occurs during the extraction and/or concentration process.

1.4.1.2. The gas chromatographic conditions are not designed for compounds with carbon numbers greater than C44.

1.4.1.3. Benzene and hydrocarbons that elute from the column before heptane co-elute with the extraction solvent methylene chloride.

1.4.2. Identification Studies

1.4.2.1. The method is most successful in quantitating #2 fuel oil.

1.4.2.2. Absorption, adsorption, biological reactions, and chemical reactions occur in soil, changing the chromatographic profile which reduces the ability to make positive identifications. Method OQA-QAM-018 can be used for more detailed product analysis.

1.5. Matrix

1.5.1. Surface water, ground water, and wastewater.

1.5.2. Soil, sediments or high solids sludge (>50%).

2.0 SUMMARY OF METHOD

2.1. This quantitative EPH method is adopted from Method for the Determination of Extractable Petroleum Hydrocarbons (EPH), Massachusetts Department of Environmental Protection; the Method for the Determination of Extractable Petroleum Hydrocarbons (EPH) Fractions, Washington State Department of Ecology; the "Leaking Underground Fuel Tanks Field Manual" of the California State Water Resources Control Board (3); "Test Methods for Evaluating Solid Waste" USEPA Method 8015B and the Florida Department of Environmental Protection, "Method for the Determination of Total Petroleum Range Organics"(4, 25).

2.2. This petroleum method is adapted with modifications from ASTM Method D3328-82, and the US Coast Guard Oil Spill Identification Procedure for Total Petroleum (1,2).

2.3. Petroleum residues are extracted from sample matrices with methylene chloride,

dried over sodium sulfate, solvent exchanged to hexane and concentrated in a Kuderna-Danish apparatus. Extract separation into aliphatic and aromatic fractions is accomplished using silica gel columns, either commercially available or lab prepared. The two individual fraction extracts are re-concentrated and subsequently analyzed separately by capillary column GC/FID. The resultant chromatograms of the aliphatic compounds are collectively quantitated from several carbon ranges. The resultant chromatograms of the aromatic compounds are collectively quantitated from several carbon ranges. The carbon ranges used throughout this method are presented as equivalent carbon numbers (EC). The EC is related to the boiling point of a chemical normalized to the boiling point of the n-alkanes or its retention time in a boiling point gas chromatic column. The carbon ranges for the aromatic fractions are: C8 to C10, C10 to C12, C12 to C16, C16 to C21 and C21 to C34. The carbon ranges for the aliphatic fractions are: C8 to C10, C10 to C12, C12 to C16, C16 to C21 and C21 to C34. Surrogate compounds are added to all samples before extraction.

2.3.1. The EPH is determined by integration of the FID chromatogram. Average calibration factors or response factors using the aliphatic standard mixture are used to calculate the concentration of each carbon range. Average calibration factors or response factors using the aromatic standard mixture are used to calculate the concentration of each carbon range. Concentrations of each carbon range from both fractions are summed for a total EPH concentration.

2.3.2. The sensitivity of the method may be dependent on the level of interference rather than on instrumental limitations. The quantitation limit for EPH (total) in soil is approximately 10 mg/kg and in water 100 ug/L.

2.3.3. Dynamic Range

2.3.3.1. EPH

Soil 250-10,000 mg/kg
Aqueous 2.5-1,500 mg/L

2.3.3.2. Individual Carbon Ranges

Soil 10-2,000 mg/kg
Aqueous 0.10-20 mg/L

3.0 INTERFERENCES

3.1. Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with tap water, distilled water, methanol, and methylene chloride.

3.2. High purity reagents such as Burdick and Jackson GC2 methylene chloride, Baker

capillary grade methylene chloride or equivalent must be used to minimize interference problems.

3.3. Before processing any sample, the analyst should demonstrate daily, through the analysis of a method blank, that the entire system is interference-free.

3.4. Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference will vary considerably from source to source (e.g. fatty acids, biogenic materials, oxidized biodegradation products), depending upon the nature and diversity of the site being sampled. The silica gel cleanup procedure, EPA Method 3630B can be use to overcome many of these interferences, but unique samples may require additional cleanup approaches such as SW-846 Methods 3610B, 3620B and 3660B to achieve the necessary analytical sensitivity.

3.5. Naturally occurring alkanes may be detected by this method and may interfere with product identification. Naturally occurring plant waxes include odd carbon number alkanes from n-C25 through n-C35, and exhibit a dominant odd/even chain length distribution. Leaf hydrocarbons also may be detected.

3.6. A vial septum should be penetrated and extracted with methylene chloride to evaluate the potential alkane distribution that could occur in re-analyzed extracts. Vial septa should be changed after each analysis.

4.0 SAFETY

4.1. The toxicity or carcinogenicity of each reagent used in this method has not been defined precisely. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified for use by the analyst (8,9).

5.0 APPARATUS AND EQUIPMENT

5.1. Sampling Containers

5.1.1. Prior to use, wash bottles and cap liners with aqueous detergent solutions and rinse with tap water, distilled water, and methylene chloride. Allow the bottles and containers to air dry at room temperature, place in a 150°C oven for one hour, then remove and allow to cool in an area known to be free of organic analytes.

5.1.2. Screw cap bottle - 40 mL PTFE-faced silicone cap liners.

5.1.3. Narrow mouth bottles - 1 liter, amber, PTFE faced silicone cap liners.

5.1.4. Wide-mouth glass jar-four ounce, amber, PTFE faced silicone cap liners

5.2. Glassware

5.2.1. Serum bottles - 100 mL, 10 mL, 2 mL crimp-top, PTFE-faced silicone cap liners.

5.2.2. Pasteur pipettes

5.2.3. Screw-cap Erlenmeyer flasks - 250 mL, with PTFE faced silicone cap liners.

5.2.4. Volumetric flasks - 10 mL, 25 mL, 100 mL

5.2.5. Kuderna-Danish apparatus (KD)

5.2.6. Separatory funnels - 2 L Pyrex, Teflon stopcoat

5.2.7. Soxhlet Extractor

5.2.8. 1 cm I.D. by 10 to 20 cm glass column with glass or Teflon stopcock

5.3. Apparatus

5.3.1. Rotary shaker table, 350 rpm minimum

5.3.2. Analytical balance capable of accurately weighing 0.0001 g.

5.3.3. A gas chromatograph with split/splitless injector, equipped with a capillary column, capable of temperature programming. The analytical column chosen must adequately resolve the n-C8 to n-C34 aliphatic standard compounds and the aromatic standard compounds listed in 6.8.1 and 6.8.2 below. The recommended column is:

5.3.3.1. Column - 30m long x 0.32mm ID, 0.25um film thickness, 95% dimethyl-5% diphenyl polysiloxane (Restek RTX-5 or equivalent).

Recommended Conditions:
Oven Temperature: 60°C; hold for 1 minute; 8°/minute to 290°C, hold for 7 minutes

Injection size: 1 – 4 uL
Gas Flow Rates: Carrier Gas – Helium @ 2 –3 mL/minute;
Oxidizer – Air @ 400 mL/minute;
Fuel – Hydrogen @ 35 mL/minute;
Make up – Air @ 30 mL/minute.
Injection Port Temperature: 285°C
Column Inlet Pressure 15 p.s.i.
Detector Temperature: FID @ 315°C
Linear Velocity: 50 cm/sec

5.3.3.2. An alternative column is:

a. Column-30m long x .53mm ID, .5um film thickness dimethyl polysiloxane coating (Restek, J&W Scientific or equivalent). This column will allow for the resolution of alkanes from nC8 to nC40, as well as the resolution of phytane/nCl8 and pristane/nCl7. This column will also allow for the resolution of the petroleum products listed in Section 1.1 (21). Low bleed columns must be used. Equivalent columns maybe used.

Recommended Conditions:
Oven Temperature: 40°C; hold for 2 minutes; 12°/minute to 320°C, hold for 10 minutes
Injection size: 1 – 4 uL
Gas Flow Rates: Carrier Gas – Helium @ 2 –3 mL/minute;
Oxidizer – Air @ 400 mL/minute;
Fuel – Hydrogen @ 35 mL/minute;
Make up – Air @ 30 mL/minute.
Injection Port Temperature: 330°C
Column Inlet Pressure 15 p.s.i.
Detector Temperature: FID @ 330°C
Linear Velocity: 50 cm/sec

5.3.3.3. Detector - Flame Ionization Detector is required

5.3.4. An autosampler is recommended.

5.3.5. Boiling chips - Solvent extracted approximately 10/40 mesh.

5.3.6. Water bath - Top, with concentric ring cover, capable of temperature control. The bath should be used in a hood.

5.3.7. Gas-tight syringe - One milliliter (mL) with chromatographic needles.

5.3.8. Microsyringes – l0uL, 100uL, 200uL

5.3.9. Continuous liquid-liquid extraction apparatus.

5.3.10. Liquid chromatographic column - 400 x 20mm with course frit, Teflon stopcock.

5.3.11. Magnetic stirrer and 2-inch Teflon coated stirring bars.

5.3.12. Nitrogen concentration system composed of a precleaned pasteur pipette, with a small plug of glass wool loaded at the tip end, and filled with approximately 1-2 cm of precleaned alumina. The top of the pipette is attached to a hydrocarbon free nitrogen gas source using precleaned Teflon tubing. This concentration step should be performed at room temperature or lower to retain light end compounds.

6.0 REAGENTS

6.1. Purity of Reagents - Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee and Analytical Reagents of the American Chemical Society.

6.2. Reagent water - Reagent water is defined as a water in which an interference is not observed at the MDL of each parameter of interest. (ASTM Specification D1193, Type ii).

6.3. Methylene chloride, methanol, carbon, disulfide and hexane - pesticide grade, Burdick and Jackson GC2, Baker Capillary Grade or equivalent.

6.4. Sodium sulfate - (ACS) granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray, cool in a desiccator and store in a sealed glass bottle.

6.5. Silica gel (for fractionation)- Grade 923 (100/200) desiccant. Before use, activate for at least 16 hours at 130°C in a shallow glass tray that is loosely covered in foil. Cool and store as in Section 6.4. Commercially available Solid Phase Extraction (SPE) cartridges (20 ml tube volume/5 g bed weight) may be used. (Please note: Silica gel is hydroscopic. Unused cartridges must be stored in properly maintained desiccators prior to use to prevent absorption of moisture from air.)

6.6. Silica granular, fine (60-120 mesh) Fisher 5151-10. Purify by Soxhlet extraction with methylene chloride for four hours. Dry at 80°C. Store in glass bottle.

6.7. Hydrochloric acid, 1:1 - Mix equal volumes of (ACS) concentrated HCl and distilled water.

6.8. Stock Standards

6.8.1. Normal Aliphatic Hydrocarbons - Prepare a Methylene chloride solution containing, at a minimum, a mixture of the following:

n-Octane (C8)
n-Decane (C10)
n-Dodecane C12)
n-Tetradecane (C14)
n-Hexadecane (C16)
n-Octadecane (C18)
n-Eicosane (C20)
n-Heneicosane (C21)
n-Docosane (C22)
n-Tetracosane (C24)
n-Hexacosane (C26)
n-Octacosane (C28)
n-Triacontane (C30)
n-Tetratriacontane (C34)

at a concentration of 1 mg/ml each in hexane. (Mixtures are available from Supelco, Restek (31266), NSI Solutions and Ultrex (Note: Due to the commercial availability of standards, it may be necessary to combine two standard mixtures which may result in the addition of n-Nonane (C9), n-Nonadecane (C19) and n-Hexatriacontane (C36) to the aliphatic hydrocarbon standard.)

6.8.2. Aromatic Hydrocarbons - Prepare a Methylene chloride solution containing a mixture of the following:

Acenaphthene (C15.5)
Acenaphthylene (C15.06)
Anthracene (C19.43)
Benzo[a]anthracene (C26.37)
Benzo[a]pyrene (C31.34)
Benzo[b]fluoranthene (C30.14)
Benzo[g,h,i]perylene (C34.01)
Benzo[k]fluoranthene (C30.14)
Chrysene (C27.41)
Dibenz[a,h]anthracene (C30.36)
Fluoranthene (C21.85)
Fluorene (C16.55)
Indeno[1,2,3-cd]pyrene (C35.01)
2-Methylnaphthalene (C12.89)
Naphthalene (C11.7)
Phenanthrene (C19.36)
Pyrene (C20.8)
Toluene (C7.6)

1,2,3-Trimethylbenzene (C10.1)

at a concentration of 1 mg/ml each in methylene chloride. (Mixtures are available from Supelco, Restek (31266), NSI Solutions and Ultrex).

6.8.3. Surrogates (SS) - The surrogate ortho-terphenyl (OTP) is prepared by weighing 0.01000 g of pure material in a 10 mL volumetric flask. Dissolve the material to volume in methylene chloride. The surrogate 1-chlorooctadecane (COD) is prepared by carefully weighing 0.0100 g of pure material in a in a 10 mL volumetric flask. Dissolve the material to volume with hexane. (Standards are available from Restek Inc.)

6.8.4. Surrogate Spiking Solution – Prepare a surrogate spiking solution containing OTP and COD at a concentration of 100 ng/uL in acetone. Each sample, blank, and matrix spike is fortified with 1.0 ml of the surrogate spiking solution.

6.8.5. Laboratory Control Sample (LCS) (Blank Spike) – Prepare the LCS containing all the aliphatic and aromatic compounds defined in sections 6.8.1 and 6.8.2 each at a concentration of 100 ng/uL. A 1 mL aliquot is added to the sample designated as the LCS. The source of the standards shall be different than those from which the calibration standards are made.

6.8.6. Matrix spiking standard (MSS) - Prepare the MSS as described in 6.8.5 immediately above. A 1 mL aliquot is added to the sample designated as the matrix spike.

6.8.7. Fractionating Surrogates: The fractionating surrogates (2-Bromonaphthalene and 2-Fluorobiphenyl) are prepared by weighing 0.0100 g of pure material in a 10-ml volumetric flask and dissolving the material in Methylene Chloride. (Surrogates are available from Restek Inc.)

6.8.8. Fractionating Surrogate Spiking Solution – Prepare the solution containing 2-Bromonaphthalene and 2-Fluorobiphenyl at concentrations of 100 ng/ul each in hexane. An aliquot of 1 ml of the fractionating surrogate spiking solution is added to the 1 ml EPH sample extract prepared in accordance with sections 10.1 and 10.2 just prior to fraction separation with silica gel.

6.8.9. Fractionating Check Solution – This solution is used to monitor the fractionation efficiency of the silica gel cartridge/column and establish the optimum hexane volume required to efficiently elute the aliphatic fraction without significant aromatic breakthrough.

Prepare the solution containing 200 ng/uL of the aliphatic hydrocarbon standard and 200 ng/uL of the aromatic hydrocarbon standard in hexane. (Standards are available from Supelco, Restek or Ultrex.)

6.8.10. Quality Control Samples. The quality control samples, obtained from a vendor, may be submitted by the Department to determine if the laboratory can achieve satisfactory analytical precision. Multiple analyses may be required.

7.0 CALIBRATION

7.1. Initial Calibration

7.1.1. Retention time windows

a. Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of the Aromatic Hydrocarbon and Aliphatic Hydrocarbon standard mixtures. Serial injections over less than a 72 hr period result in retention time windows that are too restrictive.

b. Calculate the mean and the standard deviation of the three retention times (use any function of retention time; including absolute retention time, or relative retention time) for each individual compound in the aromatic standard, each individual compound in the aliphatic standard and all surrogates.

c. Plus or minus three times the standard deviation of the mean retention times for each compound in the aromatic and aliphatic standards will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. The default value for the retention time shall be a minimum of +/- 0.1 minutes, if the standard deviation is zero or close to zero.

d. Establish the midpoint of the retention time window for each surrogate by using the absolute retention for each surrogate from the mid-concentration standard of the initial calibration. The absolute retention time window equals the midpoint + 3 SD, where the standard deviation is determined as described in Section b.

e. The laboratory must calculate retention time windows for each aromatic standard compound, each aliphatic standard compound and each surrogate on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

7.1.2. FID External Standard Calibration for Quantitation of EPC. Calibrate the GC-FID with an initial five-point calibration. The concentrations of each individual component are to be at 40ng/uL, 100ng/ul, 250 ng/uL, 500 ng/uL and 1000ng/uL) Separate calibrations are to be conducted for each fraction (Sections 6.8.1 and 6.8.2). (Only if requested, the lowest concentration point in the calibration curve should be near the MDL.) The highest concentration point should be twice the expected sample concentration and within the linear range of the instrument. To maintain the standards in solution, a 10% carbon disulfide / 90% methylene chloride solvent may be required. Standards with concentrations greater than 20 mg/L may need to be equilibrated to room temperature prior to analysis. Prepare the calibration standards to contain 100 ng/uL of each surrogate. The surrogate OTP and the fractionating surrogates are included in the Aromatic Hydrocarbon Standard. The surrogate COD is included in the Aliphatic Hydrocarbon Standard.

A calibration factor must be established for each carbon range of interest. Calculate CFs for C8-C10, C10-C12, C12-C16, C16-C-21 and C21-C34 Aliphatic Hydrocarbons from the appropriate chromatogram . Calculate CFs for C8-C10, C10-C12, C12-C16, C16-C-21 and C21-C34 Aromatic Hydrocarbons from the appropriate chromatogram.

For the aromatic fraction, use the following compounds as carbon range markers:

Range	Compound	EC
C8-C10	Toluene	7.6
	1,2,3-Trimethylbenzene	10.1
C10-C12	1,2,3-Trimethylbenzene + 0.1 min.	
	Naphthalene	11.7
C12-C16	Naphthalene + 0.1 min	
	Acenaphthene	15.5
C16-C21	Acenaphthene + 0.1 min	
	Pyrene	20.8
C21-C34	Pyrene + 0.1min	
	Benzo(g,h,i)perylene	34.01

For the aliphatic fraction, use the following compounds as carbon range markers:

Range	Compound	EC
C8-C10	n-Octane	8.0
	n-Decane	10.0
C10-C12	n-Decane + 0.1 min.	
	n-Dodecane	12.0
C12-C16	n-Dodecane + 0.1 min	
	n-Hexadecane	16.0
C16-C21	n-Hexadecane + 0.1 min	

	n-Heneicosane	21.0
C21-C34	n-Heneicosane + 0.1min	
	n-Tetratriacontane	34.0

(Please note: The "+ 0.1 minutes" noted above in both the aromatic and aliphatic fractions are maximums. The laboratory should use less than the "compound + 0.1 minute" as the carbon range marker if peak shape and chromatographic resolution are favorable.)

Tabulate the summation of the peak areas of all the compounds in each carbon range against the total concentration injected for that carbon range. The Calibration Factor (CF), defined as the ratio of the summed peak area to the concentration injected, is calculated for each carbon range using the following equation. (Individual calibration factors may have to be calculated for naphthalene and 2-methylnaphthalene as these compounds are observed in the aliphatic fraction and the determination of their concentration is necessary.)

$$Carbon\ Range\ CF = \frac{Summed\ Area\ of\ Peaks\ in\ the Range}{Total\ Concentration\ Injected\ (ng\ /\ uL)}$$

Note that the areas for the surrogates must be subtracted out from the area summation of the range in which they elute. Also, any areas associated with naphthalene and 2-methylnaphthalene in the aliphatic fraction must be subtracted out from the appropriate carbon range.

The percent relative standard deviation (%RSD) of the calibration factors for each carbon range for the compounds and surrogates must be ≤ 25% over the working calibration range.

$$\%\ RSD = \frac{Standard\ Deviation\ of\ 5\ Range\ CFs}{Mean\ of\ 5\ Range\ CFs}$$

If %RSD is >25%, the source of the problem should be identified and the instrument re-calibrated.

7.2. Daily Calibration

7.2.1. At a minimum, the working calibration factors for each fractional carbon ranges must be verified on each working day, after every 20 samples or every 24 hours (whichever is more frequent) and at the end of the analytical sequence by the injection of the mid-level calibration standards (both aliphatic and aromatic). Calculate the percent differences (D%) between the continuing calibration factors and the average calibration from the initial calibrations for each carbon range for each fraction and for

the surrogates. If the %D of any carbon range is >25% (>30% for any single compound in a range) then a new calibration curve has to be generated for that range. (%Ds >25% are permissible for compounds whose equivalent carbon numbers are C8 or less. The non-compliance shall be noted in the nonconformance summary.) Any sample associated with a non-compliant calibration shall be reanalyzed.

$$\%D = \frac{CF_{AVG} - CF_{cc}}{CF_{AVG}}$$

Where :

CF_{AVG} = Average Calibration Factor calculated from initial calibration

CF_{CC} = Calibration Factor calculated from continuing calibration standard

7.2.2. The retention times of surrogates in the calibration verification standard analyzed at the beginning of the analytical shift must fall within the absolute retention time windows calculated in Sec. 7.1.1b. The purpose of this check is to ensure that retention times do not continually drift further from those used to establish the widths of the retention time windows. If the retention time of any surrogate at the beginning of the analytical shift does not fall within the + 3 SD window (minimum +/- 0.10 min.), then a new initial calibration is necessary unless system maintenance (Sec. 7.11) corrects the problem.

In addition, the retention times of all surrogates in the subsequent calibration verification standards analyzed during the analytical shift must fall within the absolute retention time windows established in Sec. 7.1.1d.

7.2.3. Surrogate Standards (SS) - The SS responses and retention times in the calibration check standard must be evaluated during or immediately after data acquisition. If the retention time(s) for the SS is outside the determined RT window, the chromatographic system must be inspected for malfunctions and corrections must be made. If the area(s) for the SS changes by +/- 50% from the last daily calibration standard check, the GC must be inspected for malfunctions and corrections must be made.

7.3. Mass Discrimination

7.3.1. Mass discrimination can take place in the injection port. The heavier molecules do not enter the column as a defined plug of vapor with the lighter molecules.

7.3.2. Mass discrimination is minimized by placing a small plug of silanized glass wool one centimeter from the base of the glass injection liner. The

end of the capillary column is placed just below the glass wool.

8.0 QUALITY CONTROL

8.1. Each laboratory that uses this method is required to operate a formal quality control program which conforms with New Jersey Regulation N.J.A.C. 7:18-4.7 (13). The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of QC samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with laboratory established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

8.1.1. The analyst must make an initial, one-time demonstration of the ability to generate acceptable accuracy and precision with this method (Section 8.2).

8.1.2. In recognition of advances that are occurring in chromatography, the analyst is permitted to improve the separations by changing the GC conditions or column. Each time such a modification is made to the method, the analyst is required to repeat and document the procedure in Section 8.2.

8.1.3. Each day before calibration and after the calibration, the analyst should analyze a reagent blank (instrument blank) to demonstrate that interferences from the analytical system are under control. Peaks should not be detected above the quantitation limit within the retention time window of any carbon range of interest. If so, re-extraction of all associated samples my be warranted.

8.1.4. With each sample batch, the analyst must analyze a method blank to demonstrate that interferences from sample extraction are under control. Target compounds' concentrations in the blank should be no more than 5x MDL. If blank levels for any component are above 5x MDL and the sample concentrations present in the samples are greater than 10X then the samples may be quantified and qualified. If the blank concentration is greater than 5X MDL and the sample concentrations present in the samples are less than 10 X the blank level, the affected samples should be re-extracted and re-analyzed. If a sample cannot be re-extracted or re-analyzed, the data should be qualified as such. Samples should not be blank corrected.

8.1.5. The laboratory must, on an ongoing basis, demonstrate through the analyses of a Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD) that the operation of the measurement system is in control. This procedure is described in Section 8.3. The frequency of

the LCCS/LCSD pair is one every 20 samples of similar matrix.

8.1.6. The laboratory must spike all samples with the surrogates to monitor recovery. This procedure is described in Section 8.4.

8.1.7. The laboratory must spike a minimum of five percent or one per batch, which ever is more frequent of all samples in each matrix, with the MSS (Section 6.8.5) to monitor and evaluate laboratory data quality. This procedure is described in Section 8.5.

8.2. To initially establish the ability to generate acceptable precision and accuracy, the laboratory must perform the following operations. A LCS containing aliphatic and aromatic compounds described in sections 6.8.1 and 6.8.2 at a concentration of 100 ng/uL in methylene chloride (Section 6.8.5) is required. The LCS concentrates must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.1. Aqueous

Analyze four 1 L aliquots of the well-mixed reagent water spiked with 1.0 mL LCS concentrate and 100 ug of each surrogate according to the method beginning in Section 10.1.

8.2.2. Soil and Sediment

Analyze four 10 g aliquots of reagent sodium sulfate spiked with 1.0 mL LCS concentrate and 100 ug of each surrogate according to the method beginning in Section 10.1.

8.2.3. For each matrix calculate the average recovery (X) and the standard deviation of the recovery (s) for the aliphatic and aromatic compounds using the four results. The average percent recovery must be between 40-140%. The laboratory is to establish the criteria for the standard deviations as described in USEPA Method 8000 A (4).

8.2.4. For each matrix, the FID retention times of the surrogates must match the calibration standard as described in 7.2.3.

8.3. For each analytical batch (up to 20 samples of a similar matrix) the laboratory must analyze a LCS. The LCS shall be prepared as directed in Section 8.2. The recovery of the LCS must be between 40% - 140%. Lower recoveries are permissible for compounds whose equivalent carbon numbers are C8 or less but must be noted in the case narrative. The FID retention times of the surrogates must match the previous calibration as described in 7.2.3.

8.4. For each analytical batch (up to 20 samples of a similar matrix) the laboratory

must analyze a LCSD. The LCS is separately prepared, processed and analyzed in the same manner as the LCS. The recovery of the LCSD must be between 40% - 140%. Lower recoveries are permissible for compounds whose equivalent carbon numbers are C8 or less but must be noted in the case narrative. The Analytical batch precision is determined from the Relative Percent Difference (RPD) of the concentrations (not the recoveries) of the LCS/LCSD pair. The RPDs for the aliphatic and aromatic carbon range concentrations (the sum of the individual compounds' concentrations within a carbon range) must be ≤25%. The FID retention times of the surrogates must match the previous calibration as described in 7.2.3.

8.5. As a quality control check, the laboratory must spike all samples with the surrogates chosen in Section 6.8.3 and calculate the percent recovery (%P) of the Surrogate based on the FID response.

$$\%P = \frac{A_x}{A_s} * 100$$

A_x = Area response of SS in check sample
A_s = Average area response of SS in standard

8.5.1. For the surrogate standards, the laboratory must develop separate accuracy statements of laboratory performance for each matrix. An accuracy statement for the method is defined as Percent Recovery + Standard Deviation (P + s). The accuracy statement should be developed by the analysis of four aliquots as described in Section 8.2, followed by the calculation of P and s. Alternatively, the analyst may use four data points gathered through the requirement for continuing quality control in Section 8.3. The accuracy statements should be updated regularly. The recovery must be within 40% – 140%.

8.5.2. Calculate upper and lower control limits for %R for the surrogate standard in each matrix.

Upper Control Limit (UCL) = P +3s
Lower Control Limit (LCL) = P - 3s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance (14).

8.5.3. The following corrective actions can be taken when the percent recovery of OTP and COD are outside of the recovery range:

8.5.3.1. Check calculations to assure there are no errors.

8.5.3.2. Check instrument performance. Check the sample preparation

procedure for loses due to temperature control and surrogate solutions for degradation contamination, etc.

8.5.3.3. Reanalyze the extract if the steps above fail to reveal a problem. If reanalysis yields surrogate recoveries within the stated limits, the reanalysis data should be used.

8.5.3.4. If COD recovery is below the acceptance range and is observed in the aromatic fraction and/or OTP recovery is below the acceptance range and is observed in the aliphatic fraction, then re-fractionate the extract with the remaining 1 mL aliquot of extract and analyze the new extracts.

8.5.3.5. If the surrogate could not be measured because the sample was diluted prior to analysis, qualify the surrogate recovery. Qualify the out of range surrogate on the data table. No additional corrective action is required.

8.5.3.6. If the steps above fail to reveal a problem, it may be necessary to re-extract and re-analyze the sample.

8.6. Matrix Spike Analysis - The laboratory must, on an ongoing basis, spike and analyze at least 5% of the samples for each matrix being monitored to assess accuracy with the MS. It may be necessary, at the request of the Department, to perform a matrix spike for each matrix from each site even though the frequency may be greater than 5%. The spike is the matrix spiking standard (MSS) defined is Section 6.8.7. (If a Matrix Spike Duplicate is required, the Relative Percent Difference (RPD) should be ≤50.)

8.6.1. Report the recoveries for each of the carbon ranges for each fraction.

8.6.2. The laboratory should establish their own acceptance criteria for % recovery (R) as in Section 8.2.4. However, recoveries of 40-140% should be achieved.

8.7. Sample Duplicate - The laboratory must, on an ongoing basis, analyze 5% of the samples for each matrix in duplicate. Both results are to be reported. (No specific criteria concerning the relative percent difference (RPD) exist at this time. However, results should not differ by more than 50%.) The laboratory should establish their own acceptance criteria for RPD based on control charts. A matrix spike duplicate may be used if no positive EPH samples are in the batch.

8.8. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

8.9. The laboratory shall determine the method detection limits (MDLs) for the fuels

of interest using the methods of 40 CFR 136 Appendix B (7). The MDLs must be confirmed by analyzing a low level standard (2-3XMDL). If the MDL can not be confirmed, then the laboratory shall re-calculate their MDLs per 40 CFR 136.

9.0 SAMPLE COLLECTION PRESERVATION

9.1. Aqueous Matrix

9.1.1. Collect a representative water sample in a 1L narrow mouth bottle. A delay between sampling and analysis of greater than four hours requires sample preservation by the addition of 5ml HCl (Section 6.7). Confirmation of a pH < 2 must be obtained in the field.

9.1.2. Sample must be chilled to 4+/-2°C on the day of collection and stored at 4+/-2°C until received at the laboratory.

9.1.3. The laboratory must determine the pH of all water samples s soon as possible after sample receipt and prior to extraction. Any sample found to contain a pH>2 must be noted in a laboratory notebook and the pH must be adjusted as soon as possible. Samples are to be stored at 4+/-2° until extraction.

9.1.4. Samples must be extracted within fourteen days from the time of collection. Extracts must be analyzed within 40 days of extraction.

9.2. Solid Matrix

9.2.1. Collect a representative soil-sediment sample in a four-ounce, wide-mouth jar with a minimum of air space.

9.2.2. Samples must be chilled at 4+/-2° on the day of collection and stored at 4+/-2°C until analyzed.

9.2.3. Samples must be extracted within fourteen days from the time of. Extracts must be analyzed within 40 days of extraction.

10.0 PROCEDURES

10.1. Dissolved Product (Aqueous Samples):

Separatory Funnel Extraction (7)

a. Aqueous samples are extracted using separatory funnel techniques. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When a sample volume of 2 L is to be extracted, use 250, 100 and 100-mL volumes of methylene chloride for the serial extraction.

b. Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2 L separatory funnel. Measure/adjust pH to 2 with 6N HCL. Add 100 ug of surrogates (1 ml of the surrogate spiking solution) into the separatory funnel and mix well (Section 6.8.3) .

c. Add 60 mL of methylene chloride to the sample bottle, seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 5 min.

   If the analyst must employ mechanical techniques to the complete phase separation, the optimum technique depends upon the sample. The techniques may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250 mL Erlenmeyer flask with a glass stopper.

   If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the extract to the chamber of a continuous extractor and proceed as described in Section 10.2.3.

d. Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract. Screen the extract (Section 10.4) before concentrating.

e. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask.

f. Pour the combined extract through a solvent rinsed drying column (Section 5.3.10) containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

g. Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Pre-wet each Snyder column by adding about 1 mL of methylene chloride to the top. Position the K-D apparatus in a hot water bath (60°C to 65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the

concentration in 15 to 20 minutes. At the proper rate of the distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

h. Exchange the methylene chloride with hexane by adding 50 ml of hexane to the top of the Snyder column. Concentrate the extract to less than 10 mL as described in g directly above, raising the temperature of the water bath, if necessary, to maintain proper distillation.

i. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of hexane. Place the concentrator tube containing the hexane extract onto a nitrogen blowdown apparatus. Adjust the final volume to 1.0 mL with the solvent under a gentle stream of nitrogen. (Note: Caution must be exercised during blowdown to prevent the loss of the lower boiling EPC constituents. The fraction extract volume should never be reduced below 1 mL.)

j. Add 1 mL of the concentrated fractionation surrogate spiking solution to the 1mL hexane extract. The two mL extract is ready to be cleaned and fractionated using either commercially available or self-packed silica gel SPE cartridges. If cleanup will not be performed immediately, transfer the extract to a Teflon lined screw cap vial and refrigerate.

k. Determine the original sample volume by refilling the sample bottle to the mark with water and transferring the liquid to a 1000 mL graduated cylinder. Record sample volume to the nearest five mL.

10.2. Sample preparation, soils and sediments (1,12): Soxhlet Extraction

10.2.1. Homogenize the soil sample with a solvent-rinsed stainless steel spatula. Weigh about five grams of the sample to +.01g into a tared aluminum pan. Dry at 105 degrees Celsius for 12 hours and calculate the percent solids content (Section 11.3.4).

10.2.2. The EPA soxhlet extraction method 3540 is recommended. Method 3540 may be used for all sample types.

a. Quickly blend 10-30g of the solid sample with 10-30g of anhydrous sodium sulfate and place in an extraction thimble. (The weight used should be such that, after correction for %moisture, the dry weight of the sample approximates 10 g.) The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the

thimble. Add 40 ug of the surrogate standard spiking solution onto the sample.

b. Place 300 mL of the extraction solvent into a 500-mL round-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract sample for 16-24 hours at 4-6 cycles/hr.

c. Allow the extract to cool after the extraction is complete. Screen the extract before continuing (Section 10.4). Dry and concentrate the extract as in Section 10.1.e through 10.1.i.

10.3. Extract fractionation

10.3.1. The silica gel cleanup and fractionation step is a critical and sensitive procedure. Small changes in the volumes of eluting solvents, fractionation equipment including the preparation of the silica gel columns and fractionation technique can impact the proportion of the hydrocarbons separated into their respective aliphatic and aromatic fractions. Care and attention is required to ensure acceptable results.

Each sample fractionation requires 1 mL of sample extract. As the final volume of the extract prior to fractionation is 2 mL, an additional fractionation is available should it be required. For example, if the original fractionation yields unacceptable breakthrough of naphthalene and/or unacceptable recoveries for the fractionation surrogate standards, the remaining 1 mL extract may have to undergo fractionation.

A commercially available 5g/20mL SPE cartridge may be used. Alternatively, columns packed with activated silica gel by the laboratory may be used. The use of activated silica gel is described in USEPA SW-846 Method 3630C.

Silica gel columns/cartridges must never be overloaded. Overloading may result in the premature breakthrough of the aromatic fraction. It is recommended that for a 1mL extract fractionated on a 5g cartridge, the extract should contain no more than 5mg total EPH. (This equates to 25,000ug/mL.)

10.3.2. Demonstrate Fractionation Capability

Every new lot of silica gel/SPE cartridges must be evaluated with the Fractionating Check Solution (Section 6.8.9) to establish the optimum volume of hexane to efficiently elute aliphatic hydrocarbons while not allowing significant aromatic hydrocarbon breakthrough. The amount of hexane used is critical. Excessive hexane can cause the elution of lighter aromatics into the aliphatic fraction. Insufficient hexane could result in

low recoveries of the aliphatics. The volume of hexane used should not exceed 20 mL. A fractionation check solution (FCS) is prepared in hexane containing all the aliphatics and aromatics listed in sections 6.8.1 and 6.8.2. at a nominal concentration of 200 ng/uL each component. To demonstrate proper fractionating capability, at least four replicate FCSs should be fractionated using the procedures detailed below and analyzed. The mean measured concentration (C x mean) of the individual fractionation compounds are determined using the following equation:

$$\%\,Mean\,Recovery = \frac{C_{x\,mean} - True\,Concentration}{True\,Concentration} * 100$$

Where $C_{x\,mean} = \frac{C_1 + C_2 + C_3 + ... + C_n}{n}$

For each analyte included in the FCS, with the exception of the compounds whose equivalent carbon number is C8 or less, the % mean recovery must be between 40% and 140%. Lower recoveries are permissible for compounds whose equivalent carbon numbers are C8 or less. However, if recovery is <25% for those compounds, the problem should be found and the fractionation check repeated.

10.3.3. Fractionate the extract into separate aromatic and aliphatic components.

a. Prepare the column by placing about 1 cm of glass wool (moderately packed) at the bottom of the column. Make sure the stopcock turns smoothly.

b. Fill the column with a slurry of 5 g activated silica gel in about 10 ml methylene chloride. Tap the side of the column to assure uniform packing. Top the column with approximately 1 to 2 cm sodium sulfate.

c. Rinse the column/SPE cartridge with 30 ml methylene chloride if there are concerns of contaminants in the silica gel. Let the solvent flow through the column until the head of the solvent is just above the top of the column packing. Discard the eluted methylene chloride.

d. Rinse the column with 30 mL of hexane (60 mL if pre-rinsed with methylene chloride). Let the hexane flow through the column until the head of the column is just above the frit. Close the stopcock to stop flow. Discard the hexane.

e. Load 1 mL of the combined sample extract/fractionation surrogate solution onto the column. Open the stopcock and start collecting the elutant immediately in a 25 mL flask labeled "aliphatics".

f. Just prior to the exposure of the column frit to air, elute the column with an additional 19 mL of hexane so a total of 20 mL of hexane has passed through the column. (It is essential that "plug flow" of the extract be achieved through the silica gel column/cartridge. Hexane should be added in 1 to 2 mL increments with additions occurring when the level of solvent drops to a point just prior to exposing the column frit to air. The use of a stopcock is required. Ensure that the silica gel is uniformly packed in the column. The technician must be aware of any channeling, streaking or changes in the silica gel matrix during fractionation. If any occurs, it is probable that procedure shall have to be repeated with another 1 mL aliquot.

g. Following the recovery of the aliphatic fraction, elute the column with 20 mL methylene chloride. Collect the elutant in a 25 mL volumetric flask. Label this fraction aromatics.

h. Transfer the contents of the aliphatic and aromatic volumetric flasks into separate, labeled graduated concentrator tubes. Concentrate each of the extracts to a final volume of 1 mL under a gentle stream of nitrogen. Analyze each of the extracts separately.

i. Analyze the extracts separately.

j. The recoveries of the fractionation surrogates must be within 40% – 140%.

k. Each field and QC sample must be evaluated for potential breakthrough on a sample-specific basis by evaluating the %recovery of the fractionation surrogate(s) and on a batch-specific basis by quantifying the concentrations of naphthalene and 2-methylnaphthalene in both the aliphatic and aromatic fractions of the LCS and LCSD. If either concentration of naphthalene and 2-methylnaphthalene in the aliphatic fraction exceeds 5% of the total concentration for naphthalene or 2-methylnaphthalene in the LCS or LCS duplicate, fractionation must be repeated on all stored affected sample extracts.(Note the total concentration for naphthalene or 2-methylnaphthalene in the LCS/LCS duplicate pair includes the summation of the concentration detected in the aliphatic and aromatic fractions.) If the fractionation surrogate recovery is outside 40%-140% then fractionation must be repeated

on the affected sample.

10.4. Preliminary Analysis of Extracts (Screening)

To minimize the frequency of sample extract dilution, screening of the extract prior to fractionation is recommended.

10.4.1. Adjust the chromatograph for maximum sensitivity.

10.4.2. Inject 1 uL of the sample extract using an auto sampler.

10.4.3. A complete profile of the extract should be obtained without saturating the detectors. The largest peak should be within the linearity of the instrument for that compound. If the response is too high, the extract should be diluted.

10.5. Chromatographic Analysis

10.5.1. One milliliter of extract ready for analysis should be transferred to a one mL GC auto sampler vial.

10.5.2. Inject 1 - 4 uL of extract using an autosampler device or the solvent plug method.

10.5.3. Instrument Performance

a. All of the peaks contained in the standard chromatograms must be sharp and symmetrical. Peak tailing must be corrected.

b. Check the precision between consecutive QC check samples. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks.

c. Monitor the retention time for each analyte using data generated from calibration standards. If individual retention times vary by more than ±3 standard deviations (7.1.1) over a twelve hour period, the source of retention data variance must be corrected before acceptable data can be generated.

d. The instrument sensitivity must be maximized. Injection of 2ul of a 1ng/ul hydrocarbon standard should yield a detector signal-to-noise ratio of between 5:1 and 15:1 for the individual alkanes.

10.6. Analysis Sequence

10.6.1. This method uses a 24 hour clock or 20 sample analytical batch, whichever is more frequent. The time sequence begins with the analysis of the first initial calibration standard. Continuing calibrations must be verified every 24 hours or 20 samples, whichever is more frequent.

10.6.2. Sequence (for each fraction)

1. Instrument Blank
2. Initial Calibration or mid range Continuing Calibration (required)
3. Method Blanks (required)
4. Extraction Batch LCS (required)
5. Extraction Batch LCS Duplicate (required)
6. Samples (up to 20)
7. Matrix Spike (required)
8. (Matrix Spike Duplicate)
9. Continuing Calibration (every 24hrs/20 samples) (required)
10. Samples (up to 20)
11. Closing mid-range Continuing Calibration Standard after 20 samples and at the end of an analytical batch.

11.0 CALCULATIONS

11.1. Concentration of Petroleum Hydrocarbons

11.1.1. To calculate the concentration of carbon ranges in the sample, the area response attributed to the petroleum must first be determined. This area includes all of the resolved peaks and the unresolved "envelope". This total area must be adjusted to remove area response of the solvent, surrogates and the GC column bleed.

11.1.2. Establishing the baseline

a. Column bleed is defined as the reproducible baseline shift that occurs during temperature programming of the GC column oven. The instrument baseline must be established by the direct injection of a system solvent blank. The injection of an air blank or activation of a temperature programmed chromatographic run without the injection of any material would be used to verify that the system noise is not attributable to solvent contamination. The instrument must be run at the actual operating conditions used to analyze all standards and samples. A system solvent blank injection should be analyzed at the beginning of the day and at a minimum after every 24 hours to determine the baseline response. The baseline is then set at a stable reproducible point just before the solvent peak. This baseline should be extended horizontally to

the end of the run. When quantifying on peak areas, collective peak area integration for the fractional ranges must be from baseline (i.e. must include the unresolved complex mixture "hump" areas). However, the unresolved "hump" areas are not to be included in the integration of individual compounds such as surrogates.

b. The baseline for the sample should be set in the same manner. The area in the sample will contain the area attributed to petroleum and that attributable to the baseline. Aliphatic and aromatic hydrocarbon carbon range data for the area between C8 and C34 may be corrected by the automatic or manual subtraction of the baseline area from the system solvent blank. Correction in this manner is not recommended or preferred but permissible in cases where reasonable steps have been taken to minimize or eliminate excessive baseline bias associated with analytical system noise.

c. If baseline correction is used, then the baseline must be re-established for every analytical batch by the analysis of a system solvent blank.

d. As the concentration of any carbon range in the sample approaches the quantitation limit, the baseline correction becomes more critical.

11.1.3. Mass discrimination must be kept to a minimum by placing a small plug of silanized glass wool approximately ½ the way up the liner (≈4 cm) from the base of the glass injection liner. The capillary column should be placed flush with the surface of the gold seal. A full range alkane standard should be run to test the degree a mass discrimination before performing any actual sample analyses. The response factor ratio of C30/C20 should be greater than 0.8. If less than 0.8, reposition the column until the mass discrimination is minimized.

11.2. External standard calibration - The concentration of each carbon range for each fraction in the sample may be determined by calculating the amount of analyte injected, from the peak response, using the calibration curve or the calibration factor. The concentration of a specific carbon range is calculated as follows:

(1) Aqueous samples

$$C(ug/L) = \frac{(A)(D)(V_e)}{CF(V_s)}$$

Where:

C = Concentration of each Hydrocarbon Carbon Range (or EPH), ug/L

A = Area response of each Carbon Range (or EPH) to be measured.

D = Dilution Factor

V_s = Volume of sample, L

V_e = Final volume of the extract

CF = Calibration Factor of each carbon range for each fraction (Section 7.1.2)

Where:

$$CF = \frac{Summed\ area\ of\ peaks\ in\ carbon\ range}{Total\ concentration\ injected\ (ng / L)}$$

(2) Nonaqueous

$$C(ug / g) = \frac{(A)(D)(V_e)}{CF(S)}$$

Where:

C = Concentration of each Hydrocarbon Carbon Range (or EPH) ug/L

A = Area response of each Carbon Range or EPH to be measured.

D = Dilution Factor

Ve = Final volume of the extract

CF = Calibration Factor of each carbon range for each fraction (Section 7.1.2).

Where:

$$CF = \frac{Summed\ area\ of\ peaks\ in\ carbon\ range}{Total\ concentration\ injected\ (ng / uL)}$$

S =Dry sample weight, grams

(3) Total Aromatics Concentration = $C_{C8-C10} + C_{C10-C12} + C_{C12-C16} + C_{C16-C21} + C_{C21-C34}$ (for compounds detected in the aromatic analysis)

(4) Total Aliphatics Concentration = $C_{C8-C10} + C_{C10-C12} + C_{C12-C16} + C_{C16-C21} + C_{C21-C34}$ (for compounds detected in the aromatic analysis)

(5) Total EPH Concentration = Total Aromatics Concentration + Total Aliphatics Concentration

11.3. Percent Recovery of Surrogate Standard (s)

Percent recovery based on External Calibration

$$\% SS\ Recovery = \frac{C_{of}}{C_{ot}} * 100$$

Where: C_{of} = Concentration of surrogate found

11.4. Percent Solids (P)

$$P = \frac{D_s}{T_s} * 100$$

D_s = Weight dry Sample, g

T_s = Weight wet Sample, g

11.5. Dry Weight (S)

$$S = \frac{Wet\ Weight\ x\ P}{100}$$

12.0 REPORTING REQUIREMENTS AND DELIVERABLES

The following minimal information must be provided to the Department on request. The Laboratory must keep this information on file and available for inspection by the Department as per N.J.A.C. 7:18 (16).

12.1. Chain of custody documents. For every sample submitted to the laboratory, both field and laboratory chain of custody documents MUST be provided at the end of the final data report. The chain of custody must show the signatures of the sample custodian, extraction supervisors and any other personnel who handled the sample. It must clearly track the movement of the sample through the laboratory by showing the relinquishing and acceptance of the sample by each person.

Tracking may be accomplished electronically if laboratory personnel have user specific password-protected access to their respective LIM systems that track sample movement through the laboratory.

12.2. Methodology Review

The laboratory shall provide a brief narrative outlining the essential points of each method actually employed in the analysis of the samples submitted to the laboratory.

12.3. Non-Conformance Summary Report

The laboratory shall describe in narrative and/or tabular from any item which does not conform to the requirements of this method. This shall include but is not limited to a discussion of missed holding times, of failed Quality Assurance/Quality Control criteria, sample matrix effects on the analysis, sample dilutions, re-analyses, corrective actions taken and deviations from the analytical method specified on the analytical request form or the preparative methods permitted.

12.4. Sample Data Package - must contain the following information. The information should be provided in the following sequence.

12.4.1. Quantitative Sample Results Summary (uncorrected for blank), Blank Results and Method Detection Limits.

12.4.2. Quantitation Reports. All samples and blanks must have the following information provided:

a. date collected
b. date received
c. date extracted
d. date analyzed
e. time analyzed
f. dilution factor
g. % Moisture

12.4.3. Sample Chromatograms

The chromatograms must be clearly labeled with the following information:

a. Sample identification number.
b. Volume injected.
c. Date and time of injection.
d. GC Column identification.
e. GC instrument identification - exact instrument employed.

f. f . Carbon ranges identified, either directly above the peak or on a printout of retention times, if the retention times are printed on chromatograms.
g. Surrogates labeled
h. Fractionation Surrogates labeled.
i. Analyst signature.

12.5. Quality Control Summary - must contain the following items:

a. Surrogate Recoveries (for all field samples and QC samples) including fractionation and extraction surrogates
b. QC Check Sample Results (if analyzed)
c. LCS Results
d. LCSD Results
e. Method Blank Summary
f. Matrix Spike Summary
g. Matrix Spike Duplicate Summary (if requested)
h. Duplicate Summary
i. Percentage of total naphthalene and 2-methylnaphthalene concentrations detected in the aliphatic fractions of the LCS/LCSD
j. Fractionation Check Solution results

12.6. Standard Data Packages - must contain the following items:

a. Initial Calibration Data Summary
b. Continuing Calibration Data Summary
c. Chromatograms of Standards and Quantitation Reports
d. Summary of retention times of each identified marker compound used to define the beginning and end of each carbon range for each fraction.

12.7. Raw QC Data Package - additionally must contain the following items:

a. Blank Chromatograms
b. QC Check Sample Chromatograms
c. LCS/LCSD Chromatograms.

12.8. Qualitative Sample Result Summary (At a later date, this method may be modified and used to determine the identity of petroleum product contamination by comparison of the sample chromatograms to the chromatograms of known petroleum products such as #2 fuel oil, #4 fuel oil, etc.).

12.9. Qualitative Sample Results Summary - List Sample Fingerprint matches (ASTM D3328(l)) (Same as 12.8 above).

a. Based upon the visual comparison of source chromatograms, and after considering weathering, report the sample of unknown origin as belonging

to one of the categories below:

1. Match - The chromatogram is identical to one, or more, of the samples submitted for comparison.

2. Probable Match - The chromatogram is similar to one, or more, of the samples submitted for comparison, except: (a) for changes which can be attributed to weathering, or (b) differences attributable to specific contamination.

3. Indeterminate - The chromatogram is similar to one, or more, of the samples submitted for comparison, except for certain differences as in 2, of such magnitude that it is impossible to determine whether the unknown is the same petroleum oil heavily weathered, or a totally different oil.

4. Mismatch - Unlike the samples submitted for comparison.

b. Compare unknowns to a library of the products listed in Section 1.1.

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Appendix B. Carbon ranges and numbers for no. 2 fuel oil constituents

Carbon Fraction / Equivalent Carbon Number Identification of No. 2 Fuel

	Carbon Range	Compound	C #	E.C.#
Aliphatics	C8 - C10	n-Octane	8	8
		n-Nonane	9	9
		n-Decane	10	10
		Monocycloalkanes		
	C10 -C12	n-Decane + 0.1 min.		
		n-Undecane	11	11
		n-Dodecane	12	12
		Monocycloalkanes		
		Dicycloalkanes		
	C12 - C16	n-Dodecane + 0.1 min.		
		n-Tridecane	13	13
		n-Tetradecane	14	14
		n-Pentadecane	15	15
		n-Hexadecane	16	16
		Dicycloalkanes		
		Tricycloalkanes		
	C16 - C21	n-Hexadecane + 0.1		
		n-Heptadecane	17	17
		n-Octadecane	18	18
		n-Nonadecane	19	19
		n-Eicosane	20	20
		n-Heneicosane	21	21
		Tricycloalkanes		
	C21 - C34	n-Heneicosane + 0.1 min.		
		n-Docosane	22	22
		n-Tetracosane	24	24
		n-Hexaxosane	26	26
		n-Octacosane	28	28
		n-Triacontane	30	30
		n-Tetratriacontane	34	34

Carbon Fraction / Equivalent Carbon Number Identification of No. 2 Fuel

	Carbon Range	Compound	C #	E.C.#
Aromatics	C8 - C10	Toluene	7	7.6
		Ethylbenzene	8	8.5
		Total Xylenes		8.6, 8.8
		remaining Total Alkyl-monoaromatics		
		1,2,3-Trimethylbenzene	9	10.1
	C10 - C12	1,2,3-Trimethylbenzene + 0.1 min.		
		Indene	9	
		Total Indans & Tetralins		11.3-11.7
		Total Trimethylnaphthalenes	13	
		remaining Total Alkyl-monoaromatics		
		Naphthalene	10	11.69
	C12 - C16	Naphthalene + 0.1 min.		
		Total Methylnaphthalenes	11	12.8-13
		Total Dimethylnaphthalenes	12	13.9-15
		Dibenzothiophene		
		Acenaphthylene		15.06
		Biphenyl		14.26
		Total Methyldibenzothiophenes	13	
		Total Tetramethylnaphthalenes	14	
		Acenaphthenes		
		Acenaphthalenes		
		Acenaphthene		15.5
	C16 - C21	C16 - C21		
		Acenaphthene + 0.1 min.		
		Fluorene	13	16.55
		Total Dimethylbenzothiophenes	14	
		Anthracene		19.43
		Phenanthrene		19.36
		Total Methylfluorenes		17.99
		Total Trimethyldibenzothiophenes	15	
		Total Methylphenanthrenes		20.73
		2-Methylanthracene		20.73
		Methylanthracene		20.45
		Total Dimethylfluorenes		
		Total Trimethylfluorenes		
		Acenaphthenes		
		Acenaphthalenes		
		Dinapthenobenzenes		

Carbon Fraction / Equivalent Carbon Number Identification of No. 2 Fuel

Carbon Range	Compound	C #	E.C.#
	Pyrene	16	20.8
C21 - C34	Pyrene + 0.1 min.		
	9,10-Dimethylanthracene	16	
	Fluoranthene		21.85
	Total Dimethylphenanthrenes		
	Total Trimethylphenanthrenes	17	
	Benz(a)anthracene	18	26.34
	Chrysene		27.41
	Total Tetramethylphenanthrenes		
	Triphenylene		26.61
	Total Methylchrysenes	19	28
	Benzo(a)pyrene	20	31.34
	Benzo(e)pyrene		31.17
	Total Dimethylchrysenes		29
	Total Trimethylchrysenes	21	
	Benzo(g,h,i)perylene	22	34.01

Appendix C. EPH-TPH Field Study Participants

Water Resource Technologies Inc. (WRT) of Newfoundland, NJ

Brilliant Lewis Environmental Services, Inc of Lakewood, NJ

Enviro-Tech Services, Inc of Jackson, NJ

Applied Service Corporation of Lafayette, NJ

Custom Environmental Management Co., Inc. (CEMCO) of Hainesport, NJ

Calmar Associates, LLC of Dorothy, NJ

Northstar Environmental Services of Clermont, NJ

Appendix D. Development of Ecological Screening Criterion and "Cap" Value for Total Petroleum Hydrocarbons in Contaminated Site Soils

Site Remediation Program
Total Petroleum Hydrocarbon Cap Value Committee
Ecological Subcommittee Report:

Development of Ecological Screening Criterion and "Cap" Value for Total Petroleum Hydrocarbons in Contaminated Site Soils

Prepared by

Gary Buchanan, Ph.D. - DSRT
Edward Demarest, Ph.D. - DRMR
Nancy Hamill, MS - DRMR

August 7, 2008

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I. Background

The Site Remediation and Waste Management Program (SRWMP) has established a Total Petroleum Hydrocarbon (TPH) Cap Value Committee to evaluate the feasibility of establishing human health risk-based remediation standards, an ecological screening criterion, and a "cap" value for total petroleum hydrocarbon residues in soils associated with contaminated sites. The Ecological Subcommittee, comprised of Environmental Toxicology and Risk Assessment Section (ETRA) and Division of Science, Research, and Technology (DSRT) staff, has conducted a literature review and prepared this report to support the development of ecological screening criteria and an ecological cap value for TPH applicable to environmentally sensitive areas as defined in N.J.A.C. 7:26E–3.11. This report is supplemented by *Ecotoxic Effects of Total Petroleum Hydrocarbon Residues in Soil: A Literature Review and Examination of the 10,000 mg/kg Maximum Allowable Level for the Protection of Ecological Receptors*, October 1996, which assessed the appropriateness of the 10,000 mg/kg total organic cap in NJDEP's *Soil Cleanup Criteria* for the protection of ecological receptors (Appendix I).

II. Scope and Objective

The conclusion of the 1996 report supported the use of 10,000 mg/kg weathered TPH in soil as an ecological cap value, based on phytotoxic effects and toxic effects on the soil invertebrate community above that concentration. The current effort seeks to develop an ecological screening criterion below which risk to wildlife receptors is not likely. It also examines the validity of the 10,000 mg/kg generic cap benchmark in terms of ecotoxicological studies published since 1996.

III. Methods

A Dialog Database search for literature on the ecotoxicity of TPH in soils for the years 1996 – 2004 was conducted in December 2004 by NJDEP's Information Resource Center; an additional run was conducted in June 2005 in order to obtain the most up-to-date references. Eighty-three (83) citations were provided to the Ecological Subcommittee; a preliminary review identified 20 that appropriately focused on the topic. The full text was obtained for these references and divided among committee members for a detailed review. Fourteen studies were reviewed in depth and written summaries were prepared (Appendix II); nine of these fourteen were retained for the final report because the majority of certain criteria were met: study focused on plant and/or invertebrate toxicity; soil was preferred to be from a documented contaminated site; the sample was of known depth; soil texture and chemical parameters were reported, the TPH was weathered; and TPH was analyzed via a defined method.

IV. Microbial/Microalgae Studies

Ecotoxic effects to the soil microbial ecosystem were not evaluated for the 1996 report, and their consideration herein addresses that data gap. Microalgae are ubiquitous and form an important component of the soil ecosystem, maintaining soil fertility and oxygen production. Soil enzymes

released by a wide variety of biota play an important role in organic matter degradation and nutrient cycling. Therefore any interference of petroleum hydrocarbons with normal microbial and microalgal activities and soil enzymes would be expected to have adverse effects on the overall functioning of soil ecosystems. In a study by Megharaj et al. (2000), the effect of weathered petroleum hydrocarbon on soil microbial biomass, microalgal population size, composition, and growth, and soil enzyme activity (dehydrogenase and urease) was evaluated in soils from a long-term TPH–contaminated site. TPH contamination ranges were identified as low (< 4,000 mg/kg), medium low (4,000 - 8,000 mg/kg), medium (8,000 – 12,000 mg/kg), medium high (12,000 –16,000 mg/kg) and high (> 16,000 mg/kg). This study indicates long-term total petroleum hydrocarbon contamination adversely affects soil microbial biomass, microalgae population size and composition, growth and morphology of two microalgal species, and soil enzyme activity (dehydrogenase and urease). The adverse effects begin at approximately 4,000 mg/kg soil TPH; severe/lethal effects are observed above 16,000 mg/kg. The reduction in microbial and microalgal biomass, biodiversity, and enzyme activity limits normal and necessary ecological functions of the soil ecosystem, such as dinitrogen fixation, degradation of organic matter, oxygen production, nutrient cycling, and polysaccharide production, the latter which determines soil structure.

V. Phytotoxicity Studies

Phytotoxic effects of TPH are evaluated via an array of techniques, including whole plant bioassays and tests for seed germination, root elongation, shoot weight, and plant height. Much of the literature available for the 1996 report originated from bioremediation studies for TPH-contaminated soils, since revegetation with higher plants is often a remediation goal. However, the final TPH concentrations remained elevated in those studies. Also, many of these older studies focused on phytotoxicity from freshly spilled petroleum products. It is noteworthy that the studies since 1996 focused specifically on phytotoxicity of weathered TPH over a lower range of concentrations.

Data from 62 field, greenhouse, and laboratory studies evaluating the toxicity of TPH to plants (mainly agricultural taxa) were reviewed by Efroymson et al. (2004) for possible application to soil benchmark development; ranges of toxicity values were presented and key sources of variability and uncertainty in the toxicity values were provided. The studies evaluated different petroleum hydrocarbon materials, treatments/soil amendments, soil type and characteristics, test species, and endpoint effects. While the authors concluded the data reviewed are not adequate for generating soil toxicity benchmarks for petroleum mixtures that would be applicable to a broad range of taxa, soils, and chemical compositions associated with aging, 11 individual studies met criteria established by the Ecological Subcommittee and were appropriate to consider and report toxicity ranges. No observed adverse effects concentrations (NOAECs) ranged from 26 – 12,100 mg/kg. Effects concentrations (EC25; EC≥20) ranged from 46-8,590 mg/kg.

Wilson et al. (2002) conducted a multi-trophic level soil ecotoxicity assessment on soil contaminated with weathered crude oil distilled into five different fractions based on hydrocarbon chain lengths. Seedling emergence showed marginal effects in lighter, paraffinic crude at 0.5% (5,000 mg/kg). At 5% (50,000 mg/kg), paraffinic and naphthenic crudes were toxic, but asphaltic crude was not. The toxic effect of the crudes was most likely not chemical,

but physical because the soils became hydrophobic, indicated by water not readily infiltrating the soil.

Saterbak et al. (1999) assessed phytotoxicity of crude oil-contaminated field soils to plants and correlated results with soil physical, chemical and hydrocarbon analyses. Endpoints included seed germination, root length, and plant growth. For plant germination, the hydrocarbon parameters evaluated were polar compounds, asphaltenes, and TPH by GC (C6-C25). Asphaltene concentrations best correlated with seed germination success (recommended test method). Mustard seed germination was reduced at asphaltene concentrations of 200 mg/kg to 1,000 mg/kg while wheat germination was reduced between 4,000 and 7,000 mg/kg. However, the study supports that different taxa respond differently to hydrocarbons and that a "universal" hydrocarbon parameter to predict toxic effects on soil communities has not been identified.

Research was conducted by Wong et al. (1999) in response to perceived inadequacy of arbitrary chemical cleanup levels." This study assessed if biological responses could be correlated to petroleum concentrations. The plant germination study found threshold concentrations above which phytotoxic effects are manifested. Germination was negatively correlated to most hydrocarbon parameters (asphaltenes > polar organic compounds > TPH measured via gas chromatography), whereas root growth was less well correlated. Effects on seed germination were species-specific, with mustard being affected at TPHgc concentrations $\geq$ 2,000 mg/kg. Toxic effects on wheat germination were observed at $\geq$ 10,000 mg/kg in most soils, whereas corn germination was substantially affected in only one soil, which had a concentration of 34,000 mg/kg. Based on the study, screening-levels are suggested which generally cluster around 10,000 mg/kg soil TPH.

Contrary to the general findings on phytotoxicity of TPH, Launo et al. (2002) observed minimal phytotoxicity from TPH up to approximately 13,250 mg/kg. These studies were directed toward determining an ecological soil screening criteria and used TPH (weathered crude oil) concentrations ranging from 1,278 to 13,250 mg/kg. BPH (bioavailable petroleum hydrocarbons) ranged from 83 µg hydrocarbon/g soil (reference) to 3,620 µg/kg. Reduced mustard germination occurred at 31,000 mg/kg TPH in another soil. The authors state these results reinforce the assertion that measuring the TPH levels is not a reliable measure of ecotoxicity.

Bioremediation studies were also considered by the Ecological Subcommittee. A bioremediation study was performed by Salanitro et al. (1997) on two soils with differing percent organics, to which was added light, medium, and heavy crude oils. Multiple oil concentrations were used to estimate EC_{50}s for percent seed germination and plant growth. Artificially weathered oily soils (TPH from 4,000 mg/kg to 27,000 mg/kg) caused reduced seed germination and plant growth (except corn); phytotoxicity was not observed after 3-4 months of bioremediation, when TPH levels were 10,800 mg/kg (heavy crude), 8,600 mg/kg (medium crude) and 1,200 mg/kg (light crude). After 8-11 months of bioremediation, some plant growth inhibition was apparent in both soil types with the heavy, medium and light oils. These results indicate that undegraded petroleum (other than BTEX) or metabolites may adversely affect plant growth.

In a phytoremediation study to determine appropriate plant species for growth, 29 species were examined by Kulakow et al., (2000). It was found plant species have different sensitivities to TPH in soil with initial TPH concentration ~25,000 mg/kg. In general, plant growth was stunted in TPH contaminated soil. TPH above approximately 18,000 mg/kg was toxic to three legume species. Grass species survived, but in general had stunted growth relative to controls in uncontaminated soils at these concentrations. This study is generally useful to indicate acute/chronic phytotoxicity of TPH contaminated soil at these relatively elevated concentrations.

VI. Earthworm Toxicity Studies

Earthworms are valuable bioindicators of soil contamination due to their intimate contact with soil, ubiquity in a wide array of soil types, and function as a principal vector for contaminant exposure to higher trophic level wildlife. Earthworms are associated with healthy soil and their absence is an indication of poor soil health.

A laboratory investigation was undertaken to determine the concentrations of weathered crude oil in soil that leads to reduced survival of *Eisenia fetida* (Shakir-Hanna and Weaver, 2002). *E. fetida* was exposed to soils containing a range of five weathered crude oil concentrations between 0.5 to 2.5% (5,000 – 25,000 mg/kg, dry weight); the number of viable earthworms was determined after 5, 7, 10, and 15 days. At 0.5% TPH, survival was 100% and 90% at the 10 and 15-day point, respectively. Reduction in 10-day survival was evident beginning at 1.0%, with no 10-day earthworm survival at 2.0% TPH.

The earthworm (*Eisenia foetida*) was tested for long-term survival (7 and 14 days) by Wilson et al. (2002), using dilutions of soil contaminated with weathered crude oil distilled into five different fractions based on hydrocarbon chain length. At 2.5% (25, 000 mg/kg), both paraffinic and naphthenic crude was toxic (0% survival) in 14 days. The heavier asphaltic crude (above C_{26}) was not toxic. The lighter, more soluble fractions likely had a solvent-effect on worm membranes.

Saterbak et al. (1999) assessed toxicity of hydrocarbon-contaminated field soils to earthworms, and correlated results with soil physical, chemical, and hydrocarbon analyses. Earthworm avoidance and survival and chronic assays were each significantly correlated with hydrocarbon measurements. The highest ranking parameters for earthworm avoidance and survival were TPH by GC, polar compounds and *n*- and *iso*-saturates. Worm reproduction was correlated most closely with soil texture and metals constituents. One of the clearest concentration-response curves was earthworm 14-day survival as a function of TPH by GC <4,000 mg/kg (not likely acutely toxic), 4,000 – 10,000 mg/kg (some mortality expected), >10,000 mg/kg (survival expected to be low). The more common Freon-extractable TPH and oil and grease (O&G) concentrations did not correlate strongly with 14-d earthworm survival. The 14-day survival test predicted chronic survival whereas the 7-day survival and avoidance tests did not.

In the work by Efroymson (2004), 51 studies were evaluated for toxicity to soil invertebrates. Of these, eight (8) met criteria established by the Ecological Subcommittee. NOAECs ranged from 15 mg/kg - 9830 mg/kg TPH. EC_{25} and $EC_{\geq 20}$ ranged from 15 mg/kg to 2,662 mg/kg.

The study by Salanitro et al. (1997) evaluated earthworm toxicity before, during and after bioremediation of artificially weathered light, medium and heavy crude oil contaminated soils. Before biotreatment, the weathered soils (TPH from 4,000 to 27,000 mg/kg) were acutely toxic to earthworms in a 2 week exposure. After 3-4 months, bioremediated soils with TPH concentrations ranging from 1,000 to 10,800 mg/kg (measured via gravimetric procedures) were not toxic.

The Wong et al. (1999) study to assess if biological responses could be correlated to petroleum concentrations also examined earthworm avoidance, survival, and reproduction. Earthworm avoidance and survival were correlated (negatively) only to chemical parameters (TPHgc > polars > *n*- and iso-saturates) whereas reproduction (cocoons, juvenile production) was correlated primarily with physical parameters (positive to clay and metals). The relationships found suggest possible threshold concentrations above which toxic effects are manifested. Earthworm avoidance and survival were apparent at TPHgc concentrations $\geq$ 10,000 mg/kg, whereas little or no acute effects were observed at < 4,000 mg/kg. Because TPHgc was identified as a common predictor of worm avoidance and survival, its measurement and use as an initial parameter in waste-site assessment to screen soil quality and toxicity are recommended. Based on the study, screening-levels are suggested which generally cluster around NJDEP's 10,000 mg/kg soil TPH ecological screening criterion.

Launo et al. (2002) concluded that earthworm cocoon production was the most sensitive ecological receptor used to date in ecotoxicological assessments of petroleum-contaminated soil. Earthworm reproduction testing indicated an EC_{50} of 2,118 mg/kg TPH.

VII. Canada-Wide Standards (CWS) for Petroleum Hydrocarbons

Canadian Council of Ministers of the Environment (CCME) has developed "Tier 1" soil standards for petroleum hydrocarbons that focus, as do the studies cited above, on phytotoxicity and invertebrate exposure pathways (*Canada-Wide Standards for Petroleum Hydrocarbons (PHC) in Soil,* 2000*)*. The primary goal of the standards is to have no substantial decrease in primary productivity or impairment of nutrient and energy recycling, which are essential for short and long-term ecological sustainability. The standard values were developed using a large body of toxicity studies, but emphasized data from new plant and soil invertebrate toxicity studies specifically designed by CCME for TPH standard development for four pre-determined carbon-number fractions and four types of land uses for coarse-textured surface soils. The 25th percentile of the combined effects data set for soil invertebrates (reduced growth or fecundity) and plants (reduced growth, yield, seed germination or productivity) was used to derive the soil quality benchmarks for agricultural and residential/parkland sites; the 50th percentile of the plant effects was used to derive a soil quality benchmark for commercial and industrial land uses. The CCME ecological standards for TPH are as follows; values are in mg/kg:

Fraction	Agricultural and Residential/Parkland	Commercial/Industrial
C_6 - C_{10}	130	330
C_{10} - C_{16}	450	760
C_{16} - C_{34}	400	1,700
C_{35+}	2,800	3,300

While these standards were developed primarily from toxicological studies that used fresh crude oil, the carbon numbers in Fraction 3 and Fraction 4 are representative of those expected to remain in weathered petroleum products.

VIII. Results

The literature survey results are summarized in Table 1.

The phytotoxic effects ranges noted in this report are generally lower than those in the 1996 NJDEP report, in which the majority of studies reviewed, indicated phytotoxicity in the TPH range between 5,000 and 15,000 mg/kg. More recent studies indicate phytotoxic effects are observed from TPH concentrations as low as 26 mg/kg up to 4,000 mg/kg with additional studies showing adverse effects at higher concentrations.

Only one study that evaluated earthworm toxicity to weathered TPH was available for the 1996 NJDEP report, and this evaluated relatively high TPH concentrations; that study indicated 100% earthworm mortality at 28,000 mg/kg. Additional studies were available for this report and adverse effects to earthworms were observed at concentrations ranging from 15 mg/kg up to 4,000 mg/kg, with toxicity also observed in the 4,000 mg/kg – 25,000 mg/kg range. Notable among earthworm toxicity studies was the work by Launo et al. (2002) regarding adverse effects to earthworm cocoon production, with an EC_{50} of 2118 mg/kg TPH.

The soil microbial ecosystem was not evaluated for the 1996 NJDEP report. The study by Megharaj et al. (2000) served to fill this data gap. Reduction in soil microbial and microalgal biomass, biodiversity, and enzyme activity, which begins at approximately 4,000 mg/kg TPH, will limit normal and necessary ecological functions of the soil ecosystem, such as dinitrogen fixation, degradation of organic matter, oxygen production, nutrient cycling, and polysaccharide production.

Table 1. Summary of Literature Studies on Effect Concentrations of Total Petroleum Hydrocarbons in Soil

Reference	Receptors	Endpoint, mg/kg TPH
Megharaj et al., 2000	Soil Microbes	4,000 EC[a]

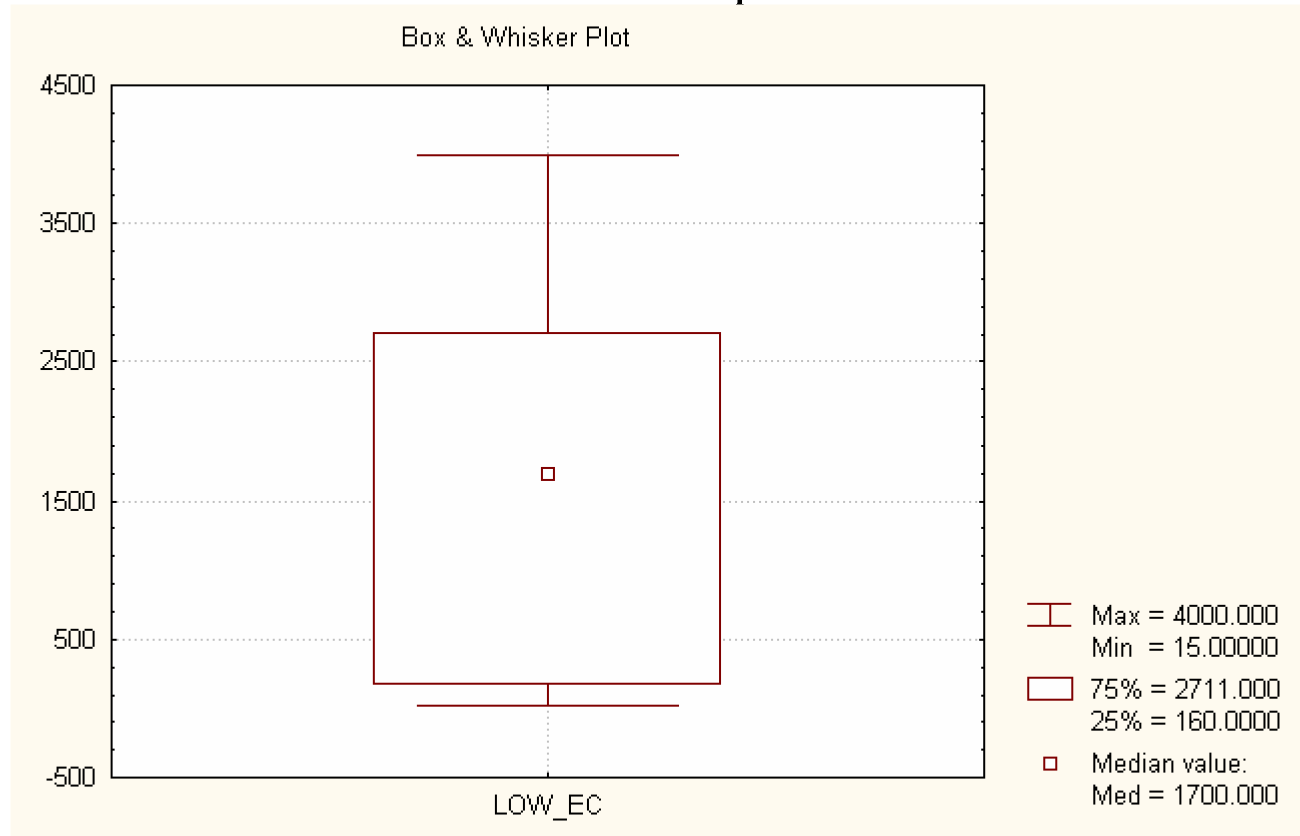
Reference	Receptors	Endpoint, mg/kg TPH
Efroymson et al., 2004	Plants	Individual Studies [b] 26-9,830: NOAEC 280-900: NOAEC 770-12,100: NOAEC 969-1,490: NOAEC 1,200: NOAEC 2,300-3,300: LOAEC 46-8,590: EC[a] 1,140 – 1,290: EC[a] 1,700-2,400: EC[a] 2,070-7,302: EC[a] 2,711: EC
Saterbak et al., 1999	Plants	200 – 1,000: NOAEC
Wong et al., 1999	Plants	2,000: EC[a]
Salanitro et al., 1997	Plants	4,000: EC[a]
Wilson et al., 2002	Plants	5,000: EC[a]
Launo et al., 2002	Plants	>13,000: EC[a]
Kulakow et al., 2000	Plants	18,000: EC[a,c]
Efroymson et al., 2004	Earthworm	Individual Studies [b] 15-1,490: NOAEC 98-9,830: NOAEC 146-1,460: NOAEC 15-149: EC[a] 25-60: EC[a] 160-2,010: EC[a] 570-2,580: EC[a] 1,037- 2,662: EC[a]
Launo et al., 2002	Earthworm cocoon	2,118: EC[a]
Saterbak et al., 1999	Earthworm	4,000: NOAEC
Salanitro et al., 1997	Earthworm	4,000: LC_{50}
Wong et al., 1999	Earthworm	4,000: EC[a]
Shakir-Hanna and Weaver, 2002	Earthworm	10,000: EC[a]
Wilson et al., 2002	Earthworm	25,000: EC[a,c]

a. EC – Effects Concentration, general (concentration at which effects were observed)
b. 11 of 62 plant studies and 8 of 62 earthworm studies met Ecological Subcommittee criteria
c. Lowest concentration studied

The Ecological Subcommittee examined the effect concentration (EC) data for the phytotoxicity and earthworm studies listed on Table 1. The "low" EC values (individual ECs or the low value when a range was given) were analyzed and the median concentration (1,700 mg/kg) was used to estimate a screening criterion for environmentally sensitive areas (Figure 1). This value is above

most of the observed NOAEC values, and the 50th percentile of the range of EC concentrations examined.

Figure 1. Box & Whisker Plot of "Low" Effect Concentrations for TPH Phytotoxicity and Earthworm Endpoints



IX. Ecological Subcommittee Recommendations

The subcommittee recommends 1,700 mg/kg TPH, measured by a NJDEP-certified analytical method for TPH, as the ecological screening criteria applicable to environmentally sensitive areas. There are clear adverse effects on soil organisms (e.g., earthworm cocoon production) at TPH concentrations above this level. Below 1,700 mg/kg TPH, adverse effects to ecological receptors are possible but not likely and further ecological evaluation in most cases is not warranted. If data from contaminated site soil are above 1,700 mg/kg, the soils must either be remediated to 1,700 mg/kg or a site-specific risk-based remedial goal must be determined from more rigorous biological testing. The maximum allowable concentration in an environmentally sensitive area is 4,800 mg/kg, based on the additional likelihood of adverse effects to soil organisms including the soil microbial ecosystem. The CCME standards are consistent with the literature-based screening values cited above.

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Appendix I: Ecotoxic Effects of Total Petroleum Hydrocarbon Residues in Soil: A Literature Review and Examination of the 10,000 mg/kg Maximum Allowable Level for the Protection of Ecological Receptors

ECOTOXIC EFFECTS OF TOTAL PETROLEUM HYDROCARBON RESIDUES IN SOIL:

A Literature Review and Examination of the 10,000 mg/kg Maximum Allowable Level for the Protection of Ecological Receptors

New Jersey Department of Environmental Protection
Site Remediation Program
Hazardous Site Science Element
Bureau of Environmental Evaluation and Risk Assessment

October, 1996

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I. SCOPE AND OBJECTIVES

The Site Remediation Program's (SRP) Soil Cleanup Criteria (2/3/94) set a maximum allowable soil level of total organic contaminants, including total petroleum hydrocarbons (TPHC), at 10,000 mg/kg. This value for TPHC was developed by selecting approximately 10% of the lower end of the typical range of soil field moisture capacities as a point above which movement of free product in soil could occur. The derivation of the 10,000 mg/kg cap value is presented in Attachment I.

A literature search has been performed to evaluate ecotoxic effects on wildlife (plants and animals) from exposure to total petroleum hydrocarbon residues in soil media in order to assess the appropriateness of the 10,000 mg/kg cap value for protection of ecological receptors.

The scope of this literature review is limited to scientific studies that consider ecotoxic effects of known concentrations of weathered petroleum products in the terrestrial environment; direct adverse effects on organisms from TPHC products freshly spilled or added to soils or diet are considered qualitatively as additional information.

II. BACKGROUND

Petroleum fuels are mixtures of thousands of chemical compounds, primarily hydrocarbons, which are derived from crude oil by distillation, a process that separates compounds based upon volatility. Petroleum products can be organized into one of three general classes based on ascending distillation temperatures and carbon number, and descending volatility (ASTM, 1994). They are described below according to distillation temperature:

1. Low-boiling distillates

Gasoline: consists mainly of hydrocarbons in the C4 to C12 range that distill from approximately 25°C to 215°C. Straight chain alkanes and isoalkanes predominate, with aromatics composing approximately 10% to 40% (primarily benzene, toluene, xylene, and ethylbenzene).

2. Medium-boiling distillates

a. Jet fuel and Kerosene: consist mainly of hydrocarbons in the C11 to C13 range that distill from approximately 150°C to 250°C. Aromatic hydrocarbons compose about 10% to 20% of these fuels.

b. Diesel Fuel, No.1 and No. 2 Fuel Oils: consist mainly of hydrocarbons in the C10 to C20 range that distill from

approximately 160°C to 400°C. Approximately 25% to 30% of these fuels are aromatics, primarily alkylated benzenes and naphthalenes.

3. High-boiling distillates

Heavy fuel oils, i.e., Nos. 4, 5, and 6 (Bunker C): consist mainly of hydrocarbons in the C19 to C25 range that distill from approximately 315°C to 540° C. They contain 15% to 40% aromatics, mainly condensed polycyclic aromatic hydrocarbons (PAHs).

It is generally recognized that the toxicity of a particular crude oil depends on its content of aromatic compounds, oxygenated or nitrogen-containing derivatives of aromatics, and to a lesser extent, aliphatic compounds. While low-boiling distillates are toxic to various organisms, the lighter petroleum fractions, with short straight-chain alkane components (volatile organics and volatile acidic compounds), are susceptible to microbial degradation and abiotic losses (e.g., volatilization). Higher boiling distillates composed of heavier oils with more complex hydrocarbon structure and greater aromatic content are less volatile and less water soluble, thus more resistant to degradation and abiotic losses, less mobile, and more persistent in the environment. The high molecular weight compounds present in weathered crude oil pose a threat especially from the polycyclic aromatic fraction (Hutchinson and Hellebust, 1974, in Emerson, 1983). Individual petroleum constituents in a contaminated soil medium vary, depending on the type of crude oil, the refining process used to derive the petroleum products, additives blended with the fuel, degree of weathering, etc.

Thus, while certain toxic components of petroleum products decrease with aging (due to abiotic losses, sorption, or sequestration), the body of literature from laboratory and field studies attributes significant toxicity to terrestrial plants and animals from weathered petroleum residues.

III. METHODS

References on the ecotoxicity of petroleum-derived compounds were obtained from conventional literature searches as well as on-line computer searches of the following databases performed by the Division of Science and Research's Information Resource Center: NTIS, Enviroline, Pollution Abstracts, Environmental Bibliography, Energy Science and Technology, PHYTOTOX, Biosis, GeoRef, and the U.S. National Library of Medicine Hazardous Substance Database. The literature searches targeted terrestrial plant and animal toxicological studies using total petroleum hydrocarbons or polycyclic aromatic hydrocarbons (PAHs) as indicators of petroleum contamination. Studies on PAHs are prevalent in the literature and PAHs are the preferred indicator compounds for kerosene, jet fuels, diesel fuel, light fuel oils, and heavy fuel oils (ASTM, 1994).

Field studies utilizing standard toxicity tests (plants and animal) were considered primary, since they are reflective of actual field conditions; soil extract tests or laboratory-based animal feeding studies or other in vitro studies are considered for supporting information. Results of single substance laboratory studies on higher animals, while available in the literature, are extremely difficult to apply to TPHC in field situations and are considered in this document only for informational purposes.

IV. PHYTOTOXICOLOGICAL STUDIES

Phytotoxic effects of petroleum hydrocarbons have been recognized since the early 1900s and have been assessed by increasingly refined measurement techniques, including whole plant bioassays and tests for seed germination, root elongation, shoot weight, and plant height. Much of the current literature on the phytoxicity of petroleum hydrocarbons in soils originates from bioremediation studies for petroleum-contaminated sites, since revegetation of contaminated soils with higher plants is often a desirable remediation goal.

The effects of oil on plants are functions of the composition and amount of oil involved, degree of weathering, soil characteristics, seasonal and climatic conditions (e.g., temperature, humidity, wind conditions), and plant species, age, and physiological state, e.g., flowering (Baker, 1978). The phytotoxic effects of petroleum hydrocarbons include effects on plant photosynthesis, respiration and transpiration, and effects on plant cells after penetration of the leaf's epidermis. During the 1950s, several studies indicated that applied oil can penetrate the plant's cell walls and plasma membranes, causing the permeability of the membranes to increase and allowing cell sap to leak into intracellular spaces. Typical symptoms of this damage were darkening of the leaf, loss of turgor, and an odor of macerated plant tissue (Young, 1935; Van Overbeek and Blondeau, 1954; Currier, 1951 in Baker, 1978). Plant roots can be affected by oil in soil. Plants with petroleum-coated roots can exhibit symptoms of water and nutrient stress, such as wilting, stunted growth, and chlorotic leaves. Root injury can also be related to the formation of intermediate petroleum breakdown products such as alkanoic acids, phenols and aromatic acids, depletion of nutrients by soil microorganisms, or increased solubilities of iron and manganese by creation of reducing soil conditions (Emerson, 1983).

The effects of oil spills on plant communities are also noted in the literature. Sensitive species may become locally extinct with tolerant species becoming dominant. Overall plant cover can be reduced and some areas may remain barren. Oil spills also contribute to habitat destruction by increasing soil erosion due to

lack of vegetative cover, disrupted soil structure, and reduced moisture holding capacity (Emerson, 1983).

While available literature describing the direct relationship between known total petroleum hydrocarbon concentrations in soil and phytotoxic effects is somewhat limited, the toxic effects of petroleum oils on plants have been studied quantitatively since the early 1900s. In 1919, toxic effects on soybean growth were reported in soil amended with varying amounts of crude oil. Concentrations of four percent (40,000 mg/kg) resulted in severe plant damage, with markedly reduced growth above 1% (Carr, 1919 in Baker, 1978). Field studies and greenhouse experiments were used during the 1970s to test the effect of applying a waste oil emulsion to various test plants, including Clinton oats, red clover, Golden Cross Bantum sweet corn, and Kentucky 31 fescue. Statistically significant reduced height, weight, and grain yield were observed with increasing application rates; chlorosis, leaf deformities, and weakening of stems resulting in a lodging effect were also observed (Baker, 1978). Several other studies conducted prior to 1980 on weathered crude oils indicate that seed germination was not affected by soil concentrations under approximately 3%. However, the oil concentrations they suggested as being inhibitory to seed growth cannot be considered safe levels for plant growth since adverse effects may have been observed had the test plants been grown to maturity. These studies did indicate that no seed germination was observed in the test species in soils with TPHC concentrations between 8% and 13% (Rowell, 1975, Mitchell et al., 1979, and Schendinger, 1968 in Emerson, 1983).

A body of literature that includes more recent studies suggests that oil levels in soils much lower than the 3% level can adversely affect plant growth. In the most comprehensive study highlighted by the literature search, phytotoxic effects were observed at known petroleum hydrocarbon concentrations nine months after the application of six selected petroleum products. The test media were neutral soils at three locations across the United States with differing soil types (Raymond, et al., 1976). It was demonstrated that, with the exception of home heating oil No. 2, approximately 30% of the applied oils remained in the top 20 cm of soil after one year. The plant study results indicate that, while most seeds germinated, few survived and developed into normal plants at the reported residual TPHC concentrations. In one test, growth occurred but plants exhibited deformed leaves and severe stunting. The following table summarizes the findings of this study. The concentrations in the original report were presented in g/kg.

9-month Oil Concentration Causing Phytoxicity (mg/kg dry wt)

Oil Type*	Soil Type Marcus Hook, PA (Glenville silt loam; radish)	Tulsa, OK (sandy loam; turnip)	Corpus Christi,TX (black clay loam; bean and turnip)
CC-car	15,600	5700	14,600
CC-car+f	10,900	5300	8100
CC-truck	12,800	6600	15,500
CC-truck+f	10,000	3800	10,700
HAC	12,400	4600	9500
HAC+f	9600	2100	8500
CMC	19,800	4400	12,300
CMC+f	11,600	4500	10,700
No.2 Fuel	5000	500	2800
No.2 fuel+f	1900	2600	1600
No.6 fuel	24,000	16,000	12,400
No.6 fuel+f	17,000	6500	8,900

* CC: Crank case oil; HAC: Heavy Arabian Crude oil; CMC: Coastal Mix Crude oil
* +f: fertilizer added

While this work indicates that TPHC concentrations in soil as low as 500 mg/kg may exhibit toxicity to plants, the majority of concentrations adversely affecting plant growth fall in a range between 5000 mg/kg and 15,000 mg/kg.

Phytotoxicity studies conducted since the time of Raymond's work further support the effects range noted above. In a study used as guidance by the SRP during the development of the 10,000 mg/kg total organic cap value, Wang and Bartha (1990) simulated spills of three hydrocarbon fuels (jet fuel, heating oil, and diesel fuel) and measured changes in hydrocarbon concentration and phytotoxicity with and without bioremediation at 4 and 14 weeks. No seed germination retardation or plant growth inhibition were observed in

the monocotyledonous ryegrass (Secale cereale) and the dicotyledonous soybean (Glycine max) when hydrocarbon residues were reduced from the initial 50,000 to 70,000 mg/kg to concentrations less than 15,000 mg/kg. Work conducted by McGill (1978, in Emerson, 1983) concluded that less than 1% (10,000 mg/kg) petroleum hydrocarbons in soil did not cause a toxic effect to plants, whereas severe effects began to develop above 2% (20,000 mg/kg). Mortality to the mangrove species Avicennia intermedia was shown to occur at concentrations of diesel oil above 10,000 ppm (Mathias, 1977).

A whole-plant bioassay test, specifically designed to obtain baseline phytotoxicity data, found spilled jet aviation fuel significantly ($P<0.01$) affected the growth of sorghum (monocotyledon) and pinto beans (dicotyledon) at concentrations ranging from 6000 to 50,000 mg/kg (Lillie and Bartine, 1990). Noted in this report were the results of approximately 20 other whole plant bioassays conducted between 1980 and 1989 by the US Air Force Occupational and Environmental Health Laboratory, which indicated concentrations of aviation fuel as low as 1000 mg/kg adversely affected plants.

Total PAHs as indicator compounds have been used in two recent studies and are presented here as additional information. In a bioremediation study using a fungal inoculum on soil from a hazardous waste site containing 5878 mg/kg total weathered PAHs, seed germination tests for lettuce, millet, and oat seeds produced an LC50 of 10% of contaminated soil, or approximately 600 mg/kg; root elongation studies determined the NOAEL to be approximately 700 mg/kg (Baud-Grasset, et al., 1993). The contaminated soil before treatment, at 5878 mg/kg total PAH, was highly toxic, with no germination occurring in the soil without dilution.

Several ecotoxicological strategies for measuring soil bioremediation effectiveness were evaluated at a contaminated site on soils containing 4500 mg/kg total PAH (Hund and Traunspurger,1994). Plant growth tests on Avena sativa and Brassica rapa showed a strong repression of growth during the first four months of the study, with growth repressed by about 96% for Brassica rapa and by approximately 49% for Avena sativa when compared with the control.

V. ANIMAL TOXICITY STUDIES

While a substantial body of literature exists regarding the effects of crude oil spills on marine wildlife (especially waterfowl and marine mammals), to date few oil remediation, land farming, and oil spill studies have produced quantitative data relating soil concentrations of weathered petroleum hydrocarbons to toxic effects on terrestrial animals. The primary route of exposure to

terrestrial animals from weathered petroleum products is through ingestion of contaminated food supply, incidental soil ingestion, and ingestion via preening. In general, the limited number of studies reviewed indicate definite impacts to the soil invertebrate community and low or no acute toxicity to higher birds and mammals, with reproductive effects the primary effects observed on avian species at high doses.

A. Soil Invertebrates

In soils with moderate pH values, nematodes are the main representatives of the mesofauna (e.g. about 80% in grassland soils), exhibiting the greatest number of individuals and species, with reported frequencies of 1-2 X 10^6 individuals/m^2. Since nematodes play an important role in the nutrient cycle and changes at the species and community levels as the result of environmental stresses are easily measurable, nematodes are desirable as environmental indicators (Hund and Traunspurger).

The study by Raymond, et al., (1976) discussed in the Phytotoxicity section, also comprehensively demonstrated the effect of waste oil biodegradation on soil nematode populations six and twelve months after oil application. At the Marcus Hook facility, reductions of 60 - 80% of the nematode population twelve months after treatment were typical for most of the oils tested; the most severe effect was caused by No. 2 home heating oil, reducing the nematode counts of the test soil by 98% and 90% six and twelve months after oil application, respectively. The concentrations causing deleterious effects range from 1500 mg/kg (No. 2 fuel oil) to 20,000 mg/kg (No.6 fuel oil); excluding No. 2 fuel oil, the range begins at 7000 mg/kg. At the Tulsa location, the nematode population recovered between three and six months, with the exception of the No. 2 fuel oil treatment. The low numbers observed for all treatments at the Corpus Christi location, including controls, were attributed to an unusually dry year.

The most frequently used animal in terrestrial toxicity tests is the earthworm, Eisenia foetida. Use of this organism allows for evaluation of direct exposure of soil contaminants of concern. In toxicity tests performed on surface soils from an oil disposal site in Florida, 100% mortality to earthworms (Eisenia foetida) was observed at 28,000 mg/kg TPHC (Roka, 1995).

Toxicity to soil invertebrates from the PAH component of petroleum hydrocarbons is exemplified by two studies. In a bioremediation study conducted by Hund and Traunspurger (1994) using an initial soil concentration of 4500 mg/kg total PAH, the tests using 100% contaminated soil demonstrated 100% mortality to earthworms (Eisenia foetida) at test initiation and at the four-month point. No nematodes were observed until ten months into the bioremediation. In another study cited in the draft Gas Research

Institute report entitled Environmentally Acceptable Endpoints (Loehr, et al., 1995), earthworm toxicity tests were conducted on PAH-contaminated soils from four manufactured gas plants. LC50 values ranged from 129 to 3700 mg/kg total PAH.

B. Amphibians and Reptiles

Limited data are available on the toxicological effects of PAHs on amphibians and reptiles (Eisler, 1987). Several studies cited describe direct implantation of PAH crystals or intraperitoneal injection of PAHs resulting in tumors. One study cites a single dose of 40 mg/kg body weight of 3-methylcholanthrene that caused the induction of mixed-function oxidase activity for several weeks in the leopard frog. In general, Eisler considers amphibians and reptiles to be more resistant to PAH carcinogenesis than mammals.

C. Birds and Mammals

Only two research studies were identified that assess the acute and subchronic toxicity of naturally weathered petroleum hydrocarbons in avian and mammalian wildlife. Laboratory feeding studies conducted by Stubblefield, et al., (1995, a.) evaluated the toxic effects of naturally weathered Alaskan Exxon Valdez crude oil in mallards and ferrets. The tests were designed to evaluate the effects resulting from short-term (acute) oral exposures to large quantities of weathered crude oil. The test sample was recovered crude oil obtained from an oil-holding barge taken 98 days after the March, 1989, spill.

Toxicity tests conducted on mallards (Anas platyrhynchos) included acute oral toxicity tests, a subacute dietary toxicity test, a food avoidance study, and a 14-day dietary study that evaluated subchronic effects. These results provided data on the toxicity of the crude when ingested directly (as in preening) or the affect of ingesting oil-contaminated food. The exposure concentrations used are within the range of doses likely to be encountered by oiled wildlife after a spill. Results indicate little potential for acute , subacute or subchronic toxicity to avian wildlife from oral ingestion. The LD50 and NOAEL for the acute oral toxicity tests were in excess of the maximum dose tested, i.e., greater than 5000 mg weathered crude oil/kg body weight. The subacute dietary toxicity study resulted in the LC50 and NOAEL greater than 50,000 mg weathered crude oil/kg diet. Mallard ducklings did not avoid food treated with up to 20,000 mg weathered crude /kg diet. The avian 14-day dietary feeding study indicated no mortalities or observable signs of toxicity with dietary concentrations up to 100,000 mg weathered crude oil/kg diet. There were no significant differences between test and control group mallards with respect to clinical chemistry parameters, hematological parameters, organ weight differences, or histological parameters. However, spleens of high-dose mallards contained slightly higher amounts of

lymphoblastic white pulp than did the spleens of control mallards; high-dose birds' livers contained fewer lymphocyte foci than did control birds' livers. It is noted that the concentration of total PAHs in the weathered crude was 8568 mg/kg test sample vs 11,362 mg/kg obtained in the unweathered crude. Analytical testing demonstrated that the weathering caused an appreciable loss <C-17 saturated hydrocarbons and 2-ring aromatics.

The effects of this same weathered crude oil on mallard reproductive capabilities were also assessed (Stubblefield, et al., 1995, b). A one-generation reproductive toxicity study was conducted using a diet of up to 20,000 mg of crude oil/kg diet. Also a direct eggshell-application toxicity test was conducted to evaluate the effects of the weathered crude on developing embryos and to characterize the potential for reduced gas exchange and the effect on embryo hatchability. For the reproductive study, the parameters measured were adult breeder parameters (body weight, growth, feed consumption, feed wastage, clinical chemistry parameters, hematological parameters, organ weights) and reproductive parameters (egg production, number of eggs cracked, number of eggs set, number of eggs fertile, number of eggs viable, number of eggs hatched, and measurements for eggshell thickness and strength). The observable effects were a decrease in certain clinical chemistry parameters in high-dose group females, trends towards increased liver weights and decreased spleen weights in both sexes, and reduced eggshell thickness and strength compared to controls. With regard to the direct eggshell application toxicity study, hatchling parameters were measured and included the number of 14-day survivors, hatchling body weights, and 14-day survivor body weights. Doses covering up to one-third of the shell area resulted in no effects on developing embryos, hatchling survival or growth. This study concludes that the weathering process substantially reduces the toxicity of the Exxon Valdez crude to developing bird embryos.

With regard to mammalian toxicity, Stubblefield, et al. (1995 a.) also evaluated the subacute oral toxicity on ferrets (<u>Mustela putorius</u>). Daily oral doses of up to 5000 mg weathered Exxon Valdez crude oil/kg body weight for five days resulted in minimal effects on ferrets. No mortalities or observable signs of toxicity were noted. Increased serum albumin concentrations and decreased spleen weights were noted in females.

To aid in meeting the intent of this review effort, it was desirable to approximate the soil concentrations associated with the mammalian NOAEL of 5000 mg/kg bw-day and avian LOAEL of 20,000 mg/kg dietary concentration referenced above in order to compare the results with the 10,000 mg/kg TPHC cap value. A "desk-top" model was employed using these reference doses with exposure variables for the short-tailed shrew and woodcock (USEPA, 1993). The basis for this model is that a high percentage of both animals' diets consist of earthworms, and solving for the dietary

concentration in the dose equation approximates earthworm tissue concentration; knowledge of earthworm tissue concentration affords easy approximation of soil concentration. The calculations are presented in Attachment II. The results for the shrew indicate that a TPHC soil concentration of 339,450 mg/kg causes no adverse effects. For the woodcock, a soil concentration of approximately 4100 mg/kg TPHC is indicated at the NOAEL.

Laboratory studies using fresh, pure PAHs have caused subchronic toxicity to mallards when dosages were administered via diet or applied externally to the mallard egg surface (Eisler, 1987). In a study by Patton and Dieter (1980, in Eisler, 1987), mallards (Anas platyrhynchos) were fed diets that contained 4000 mg PAHs/kg (mostly naphthalenes, naphthenes, and phenanthrene) for seven months. While no mortality or visible signs of toxicity were evident, sublethal effects on the liver were observed. A second study described by Eisler addresses the embryotoxic effects of various PAHs applied externally in a petroleum hydrocarbon mixture. 7,12-dimethylbenz(a)anthracene was the most embryotoxic PAH tested, where .002 ug/egg caused 26% mortality in 18 days, with significant anomalies in surviving embryos. Eisler notes that various investigators have suggested that the presence of certain PAHs in petroleum significantly enhances the overall embryotoxicity in avian species and that while PAHs make up a relatively low percent of the aromatic portion of petroleum hydrocarbons, they may be responsible for much of the adverse biological effects reported after eggs have been exposed to relatively small quantities of unweathered oils. This is potentially due to microsomal enzymes that avian embryos contain, which can metabolize PAHs into more highly toxic intermediates than can adults; avian embryos apparently have a greater capacity to metabolize PAHs in this manner than do mammalian embryos and fetuses.

PAHs are known for their ability to produce malignant tumors in skin and most epithelial tissues of many mammal species. Eisler (1987) extensively reports on latency periods, target organs and tissues, and cellular transformations for specific PAHs. He indicates, however, that results from single-substance laboratory studies are very difficult to apply to field situations and that little data exist on the toxicological properties of non-carcinogenic PAHs. He notes that malignancies can be induced by acute exposures to microgram quantities with latency periods as short as four to eight weeks. Certain carcinogenic PAHs are capable of passage across skin, lungs, and intestine and can enter the fetus following intragastric or intravenous administration to pregnant rats. The tissue affected is determined by numerous variables, including the route of administration and species under investigation. Examples of dietary doses causing acute oral toxicity include LD-50 values ranging from 50 - 2000 mg/kg body weight for various PAHs. Carcinogenic effects are caused by dietary concentrations ranging from 0.00004 - 3300 mg/kg body weight.

Biomagnification of petroleum related hydrocarbons, including PAHs, is not generally of concern for animal toxicity, hence food chain effects were not considered in this literature review. Studies show that unsubstituted PAHs do not accumulate in mammalian adipose tissue despite their high lipid solubility, probably because they tend to be rapidly and extensively metabolized (Eisler, 1980).

VI. CONCLUSIONS AND RECOMMENDATIONS

It is concluded that 10,000 mg/kg total petroleum hydrocarbon in soils is appropriate for use as an ecological screening value by the SRP based on the weight of evidence for phytotoxic effects, the demonstrated effects on earthworms and nematodes above this level, and the potential for adverse effects to soil invertebrate-consuming avian species as indicated via the "desk top" exposure model. This value should be used as guidance for weathered fuel products and is applicable to the 0-2' soil interval. Since the ecotoxicity of petroleum related compounds depends to a large extent on site-specific conditions such as soil properties, contaminant properties, and degree of weathering, deviations from this guideline should be based on more rigorous biological testing for bioavailability pursuant to SRP guidance (Gimello, 1995). Field studies to evaluate the effects on terrestrial animals from petroleum hydrocarbons residues in differing soil types appear to be a neglected aspect of research, and future quantitative studies in this area are encouraged. It is also recommended that this guideline be reevaluated on a regular basis to consider of findings of the extensive petroleum hydrocarbon research initiative entitled the "Environmentally Acceptable Endpoints Project" of the Gas Research Institute and Petroleum Environmental Research Forum.

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ATTACHMENT I

Derivation of the 10,000 mg/kg Total Organic Contaminant Cap Value used in SRP's Soil Cleanup Criteria, February 3, 1994

The 10,000 mg/kg total organic contaminant Soil Cleanup Criterion, which includes TPHC, was originally developed for inclusion in the formerly proposed Cleanup Standards for Contaminated Sites, N.J.A.C. 7:26D, February 3, 1992. The policy for using this cap value was based on two lines of reasoning:

1. 10,000 mg/kg approximates 10% of the lower end of the range typical field moisture capacities; the "lower end of the range" is assumed to be 8-30% (Brady, 1974). "Field moisture capacity" is defined as the minimum amount of water retained by adsorption and film forces when the water is free to move downward through a mass of soil (Kittredge, 1948). It is ordinarily expressed as a percentage of the oven-dried weight, which provides a standard through which different determinations are comparable. Conservatively assuming that free product moves analogously to water, 10,000 mg/kg represents a concentration beyond which movement of free product could occur.

Assumptions:
- a. For the 8-30% range, assume 10% is low end of field capacity range:
- b. Assume behavior of organic contaminant is analogous to behavior of water

Low end of Field Capacity = 100,000 mg moisture/ kg soil

Total organic cap value = (.10) (100,000 mg/kg)

= 10,000 mg contaminant/kg soil

2. During literature reviews conducted for the development of the formerly proposed regulations, a bioremediation study was used as supporting justification for the 10,000 mg/kg cap value (Wang and Bartha, 1990). In this study, spills of three hydrocarbons fuels were simulated and the changes in hydrocarbon concentrations and phytotoxicity were measured. No phytotoxic effects to monocotyledons or dicotyledons were observed when hydrocarbons residues were reduced to below 15,000 mg/kg.

ATTACHMENT II.

Estimation of TPHC Soil Screening Concentration from Literature-Derived Dietary NOAEL and LOAEL for Two Routinely Modeled Potential Receptor Species

A. Short-tailed shrew (Blarina brevicaudа)

Shrew Exposure variables (USEPA, 1993): Mean Body Weight: .015 kg
Ingestion Rate: .008 kg/day

Assumptions:
a. shrew diet consisting of 100% earthworms
b. earthworm tissue concentration is 10% of soil concentration (USEPA, 1993)

NOAEL: 5000 mg/kg bw-day, based on ferret dietary dose (Stubblefield, 1995)

NOAEL for shrew (based on Suter, 1994):

$d_a = d_b\ (bw_b/bw_a)^{1/3}$

$= 5000$ mg/kg bw-day $(.712\ \text{kg}/.015\ \text{kg})^{1/3}$

$= 18{,}104$ mg/kg bw-day

where .712 kg is ferret mean female body weight (Stubblefield, 1995)

Dose = (Conc)(IR) / BW

TPHC Soil Concentration at NOAEL:

Dietary concentration, mg/kg (Shrew) $= \dfrac{(\text{BW, kg})(\text{Dose, mg/kg bw-day})}{\text{IR, kg/day}}$

$= \dfrac{(.015)(18{,}104)}{.008}$

= 33,945 mg TPHC/kg diet (100% diet is earthworm)

TPHC SOIL CONCENTRATION AT NOAEL: 339,450 mg TPHC/kg soil (based on 10% of soil concentration in earthworm tissue, USEPA, 1993)

B. **Woodcock** (Scolopax minor)

Woodcock Exposure Variables (USEPA, 1993): Mean Female Body Weight: .176kg Ingestion Rate: .136 kg/day

Assumptions: a. woodcock diet composed of 100% earthworms
b. earthworm tissue concentration is 10% of soil concentration (USEPA, 1993)

LOAEL: 20,000 mg/kg diet, based on mallard reproductive effects (Stubblefield, 1995)

$$\text{Dose} = \frac{(\text{Dietary concentration, mg/kg})(\text{IR, kg/day})}{\text{BW (kg)}}$$

$$= \frac{(20{,}000 \text{ mg/kg})(.100 \text{ kg/day})}{1.2 \text{ kg}}$$

$$= 1670 \text{ mg/kg bw-day}$$

where .100 kg/day and 1.2 kg are the ingestion rate and mean female body weight, respectively, for mallard

NOAEL: NOAEL for mallard = LOAEL X.1 (based on USEPA, 1994)
= 167 mg/kg bw-day

NOAEL for woodcock (based on Suter, 1994)

$$d_a = d_b \ (bw_b/bw_a)^{1/3}$$

$$= 167 \text{ mg/kg bw-day } (1.2 \text{ kg}/.176 \text{ kg})^{1/3}$$

$$= 317.3 \text{ mg/kg bw-day}$$

TPHC soil concentration at NOAEL:

$$\text{Dietary Concentration, mg/kg (Woodcock)} = \frac{(\text{BW, kg})(\text{Dose, mg/kg-day})}{\text{IR, kg/day}}$$

$$= \frac{(.176 \text{ kg})(317.3 \text{ mg/kg bw-day})}{.136 \text{ kg/day}}$$

$$= 410 \text{ mg TPHC/kg diet}$$

TPHC SOIL CONCENTRATION AT NOAEL: 4100 mg TPHC/kg soil (based on 10% of soil concentration in earthworm tissue, USEPA, 1993)

Appendix II: Literature Review Summaries

Dialog Database Search for Literature on Ecological Impacts/Criteria for Total Petroleum Hydrocarbons

A Dialog Database search for literature on the ecotoxicity of total petroleum hydrocarbons (TPH) in soils for the years 1996 – 2004 was conducted in December 2004 by NJDEP's Information Resource Center; an additional run was conducted in June 2005 in order to obtain the most up-to-date references. Eighty-three (83) citations were provided to the Ecological Subcommittee; a preliminary review identified twenty that appropriately focused on the topic. The full text was obtained for these references and divided among committee members for a detailed review. Fourteen studies were reviewed in depth, and those written summaries are provided herein. Nine of these fourteen were retained for the final report because the majority of certain criteria were met: study focused on plant and/or invertebrate toxicity; soil was preferred to be from a documented contaminated site; the sample was of known depth; soil texture and chemical parameters were reported, the TPH was weathered; and TPH was analyzed via a defined method.

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Cuypers, C., R. Clemens, T. Grotenhuis, and W. Rulkens. 2001. *Prediction of Petroleum Hydrocarbon Bioavailability in Contaminated Soils and Sediments*. Soil and Sediment Contamination. 10(5):459-482

Summary: This article describes bioavailability as the rate at which hydrocarbon-degrading microorganisms can convert chemicals, which depends on the rate of transfer to the cell and the rate of uptake and metabolism by microorganisms; it is controlled by a number of physico-chemical processes such as sorption/desorption, diffusion and dissolution. Contaminant transfer in soil and sediments can be described in terms of desorption kinetics; desorption of hydrocarbons is biphasic, whereby a short period of rapid desorption is followed by a longer period of slow desorption. The poorly bioavailable fraction of hydrocarbon contamination is formed by the hydrocarbons that desorb slowly in the second phase of bioremediation.

Two laboratory methods for the prediction of total petroleum hydrocarbon (TPH) bioavailability, based on removal of readily bioavailable hydrocarbons, were evaluated for soils and sediments: solid phase extraction (SPE) and persulfate oxidation. SPE is based on the extraction of readily bioavailable hydrocarbons with water, enhanced with the solid sorbent Tenax -TA. The affinity of organic contaminants for Tenax is approximately similar to the affinity for organic carbon. The persulfate oxidation method is based on the removal of readily bioavailable hydrocarbons by means of oxidation, via a complex sulfate radical chain mechanism.

TPH bioavailability was studied in one weathered sediment sample (TPH = 15, 000 mg/kg) and two soil samples (one weathered, TPH = 8500 mg/kg, one fresh, TPH = 33,000 mg/kg) from TPH-contaminated field sites. Samples were subjected to microbial biodegradation, SPE, and persulfate oxidation; the removal of TPH by SPE and persulfate oxidation was then compared with the removal of TPH by biodegradation.

Results:

Biodegradation exhibited biphasic behavior, whereby TPH concentrations dropped rapidly in the first period of biodegradation (2-3 week for weathered media), after which concentrations leveled off. The C_{10}-C_{12} range was almost completely degraded, whereas a large portion of the C_{24}-C_{40} range was recalcitrant.

SPE also exhibited biphasic behavior, in that TPH concentrations dropped rapidly in the first 24-100 hours, after which they decreased only slowly. Comparisons of the residual TPH concentrations after SPE with residual concentrations after biodegradation showed that the extent of TPH degradation could be well-predicted by a short-term (@ 168 hr) SPE. Low molecular weight hydrocarbons were extracted more rapidly than high molecular weight hydrocarbons; in weathered media, hydrocarbons desorbed more slowly compared to freshly-contaminated media. This decreased bioavailability of weathered contaminants is likely caused by progressive sequestration during aging. A comparison of hydrocarbon desorption via SPE with microbial biodegradation showed the pattern of hydrocarbons after SPE were largely similar to the hydrocarbon pattern after biodegradation. SPE provided a rapid method for the prediction of residual TPH concentrations after biodegradation. It was observed that TPH degradation was affected by both bioavailability and biodegradability and it was concluded that bioavailability was the principal factor governing the extent of biodegradation in aged soil and sediment. SPE can successfully be used to predict TPH bioavailability in a wide range of soils and sediment with various compositional properties.

Persulfate oxidation appeared to unfit for the prediction of TPH bioavailability because it was unable to oxidize hydrocarbons with a high ionization potential.

Reviewer Conclusions: This article is directed at soil bioremediation efforts, where a rapid laboratory method is proposed to predict residual TPH concentration following bioremediation. It is assumed by this reader the test would be useful for treatability or pilot studies, prior to finalizing a decision to use bioremediation as a remedy for contaminated soil. The study is of limited direct use to the ecological subcommittee for the development of a toxicity reference concentration/cap value.

Recommendation: This study may be useful to the broader TPH Cap Value committee, for consideration during development of the laboratory analytical scheme. For example, it may be appropriate to perform the SPE test, followed by protocol-level TPH analyses for the bioavailable hydrocarbon ranges. This study will be summarized at a future full committee meeting; further investigation may be warranted.

Reviewed by: N. Hamill

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Efroymson, R.A., B.E. Sample, and M.J. Peterson. 2004. *Ecotoxicity Test Data for Total Petroleum Hydrocarbons in Soil: Plants and Soil-Dwelling Invertebrates*. Human and Ecological Risk Assessment, 10: 207-231.

Summary: Data from field, greenhouse, and laboratory studies evaluating the toxicity of total petroleum hydrocarbons (TPH) to plant and soil invertebrates were reviewed for possible application to soil benchmark development; ranges of toxicity values were presented and key sources of variability and uncertainty in the toxicity values were provided. The studies evaluated different petroleum hydrocarbon materials, treatments/soil amendments, soil type and characteristics, test species, and endpoint effects. Sixty-two (62) studies were evaluated for phytotoxicity; 51 for toxicity to soil invertebrates. The authors conclude the data reviewed are not adequate for generating soil toxicity benchmarks for petroleum mixtures that would be applicable to a broad range of taxa, soils, and chemical compositions associated with aging. When data were disaggregated according to petroleum material, nutrient addition, age of petroleum-soil contact, and measurement methods, sufficient data to present large, multi-study distributions were not available in any category. However, this reviewer determined that several individual studies met certain criteria established by the Ecological Subcommittee and were appropriate to consider and report toxicity ranges.

Results:

Of the 62 studies reviewed by the authors for phytotoxicity (mainly on agricultural taxa), eight (8) were retained by this reviewer. No observed adverse effects concentrations (NOAECs) ranged from 26 - 12, 1000 mg/kg. Effects concentrations (EC25; EC$\geq$20) ranged from 46-8590 mg/kg.

Of the 51 studies reviewed by the authors for toxicity to soil invertebrates, eight (8) were retained by this reviewer. NOAECs ranged from 15-9830 mg/kg. EC25 and EC$\geq$20 ranged from 15-40,000 mg/kg.

Criteria Evaluation:

Since this article presents summary results of a total of 113 studies, and individual studies were not reviewed, only several of the seven criteria established by this subcommittee were available in the summary data: TPH-soil contact time, analytical method, and soil texture. This reviewer evaluated studies where the soil-TPH contact time was greater than or equal to one year, samples were analyzed by gas chromatography or IR methodology (stated by authors to be consistent with EPA protocol level methods), and TPH identified as heavy, medium, and light crude, unspecified crude oil, and lube oil.

Reviewer Conclusions: While some phytotoxicity studies selected by this reviewer indicated NOAECs up to 12,000 mg/kg, adverse effects were observed as low as 46 mg/kg. For the soil invertebrate toxicity studies, the maximum NOAEC was 9830 mg/kg, with adverse effects observed as low as a 15 mg/kg.

Recommendation: Retain this citation for final report.

Reviewed by: N. Hamill

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Heath, J.S., K. Koblis, and C. Day. 1993. *Chapter 16: Risk Assessment for Total Petroleum Hydrocarbons*. Hydrocarbon Contaminated Soils. Boca Raton, FL: Lewis Publishers. Volume 3.

Summary: This chapter provides the following information:

1. The composition of TPH from various sources (gasoline, diesel, jet fuel),
2. Physical and chemical properties of these components to aid in evaluating mobility and weathering characteristics: water solubility, specific gravity, vapor pressure, Henry's law constant, diffusivity, K_{oc}, log K_{ow}, fish bioconcentration factor, and surface water half-life, and
3. Toxicity information (for human carcinogens/noncarcinogens, from IRIS and HEAST).

This information is then applied to select surrogate compounds for TPH risk assessments. This chapter considers human receptors only.

Results:

Steps in the selection process of surrogates are:

1. Estimate the initial composition of TPH released.

2. Using chemical and physical properties information (Tables 16.1 - 16.3), consider effects of weathering, fate, and transport on the ultimate composition of TPH

3. Select surrogate compounds to predict movement of TPH (or fractions of TPH) in the environment; use toxicity information (Table 16.4) to identify one or more surrogates to represent the toxicity of TPH associated with a particular release.

Six surrogates/surrogate combinations are selected by the authors as appropriate, since they represent the range of properties possessed by components present in TPH. Since the availability of verified toxicity information is the primary constraint on surrogate selection and it is difficult to ensure that surrogates represent the range of toxic effects, conservative simplifications are made:

1. TPH as 100% hexane (hexane represents toxicologic properties of straight-chain alkanes; considered conservative because longer chain alkanes are less toxic and move more slowly in the environment than those with shorter chains)

2. TPH as 100% benzo(a) pyrene (B(a)P represents carcinogenic PAHs)

3. TPH as 100% pyrene (pyrene represents non-carcinogenic PAHs; has lowest reference dose of PAHs, making it a conservative surrogate)

4. TPH (from gasoline) as 0.00028% benzo(a) pyrene, 35% n-hexane, and 0.49% pyrene

5. TPH from diesel as 7×10^{-9} % benzo(a) pyrene, and 1.04% pyrene

6. TPH from gasoline with BTEX, where BTEX is not analyzed separately, as 3.5% benzene, 0.00028% benzo(a) pyrene, 35% n-hexane, 0.49% pyrene, and 36.6 % toluene

This chapter provides three examples where surrogates for TPH are used to assess risk from 100 mg/kg TPH in soil: leaching to groundwater through the soil column, risk to excavation workers (nonresidential), and residential risk to adults; leachate concentrations for comparison with groundwater quality standards, hazard indices for non-carcinogenic compounds, and excess lifetime cancer risk, are determined. The choice of surrogates substantially affected the risk estimates.

Reviewer Conclusions: The approach to TPH risk assessment developed in this chapter is simplistic and conservative, and considers only human receptors. Similar concepts could be applied to ecological receptors, whereby surrogates could be assumed and adjusted soil concentrations could be used in standard food chain models to predict contaminant doses to upper trophic level receptors; hazard quotients could be calculated via comparison with toxicity reference values.

Recommendation: This reference should be used by the ecological subcommittee of the TPH Cap Value work group only for background information on TPH components and chemical and physical properties. ETRA will refer the reference to the human health subcommittee for consideration. If this or a similar approach is adopted by the full work group in the future, the chapter will be reevaluated for inclusion in the ecological subcommittee's report.

Reviewed by: N. Hamill

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Holman, H., R. Goth-Goldstein, D. Aston, M. Yun, and J. Kengsoontra. 2002. ***Evaluation of Gastrointestinal Solubilization of Petroleum Hydrocarbon Residues in Soil Using an In Vitro Physiologically Based Model.*** **Environ. Sci. Technol., 36: 11281-1286.**

Summary: This study used a model small intestine to examine the solubility of diesel- and crude-oil contaminated soil under different digestive regimes by comparing the TPH concentrations in the filtrate vs. the concentration in the soil. The physiologically based extraction model showed that a portion of (tightly bound) TPH residues on soil particles can be solubilized in the human gastrointestinal tract (GI) and become available for absorption. The data suggests there could be a relationship between the concentration of TPH and GI solubility. The most heavily-contaminated soil had the highest TPH solubility. GI solubility of TPH is "profoundly influenced by the digestion state, the type, and the concentration of petroleum

hydrocarbons present and modified by other site-specific conditions such as relative abundance of soil organic carbon."

Results:

- TPH residues from diesel-contaminated soils are more GI soluble than those from soils contaminated with crude oil.
- During fat digestion: Average in vitro GI solubility was 4.5% (2 - 7.8%) for crude oil soils and 16% (7.7 - 31%) for diesel contaminated soils.
- During the gallbladder empty phase of fasting: Average in vitro GI solubility was 1.2% (0.5 - 2%) for crude oil soils and 8% (4 - 11%) for diesel contaminated soils.
- For diesel-contaminated soils, GI solubility decreased with increasing soil organic carbon for both fat digestion and fasted states. Similar behavior was observed for crude oil-contaminated soils.
- Soil organic carbon ranged from 0.7 to 10.8%
- TPH ranged from 5.0 to 35.3 g/kg; diesel: 5,000 to 11,700 mg/kg; crude oil: 9,800 to 35,300 mg/kg

Criteria Evaluation:

1. Soil from documented contaminated site - yes
2. Weathered (long term) TPH contamination- yes
3. Soil texture identified - yes
4. Soil chemistry parameters - yes (clay/silt fraction, organic carbon)
5. Soil sample depth reported - no
6. TPH analysis via defined method - yes
7. PAH analysis via defined level method - no

Reviewer Conclusions: This was primarily a study on human health that has relevance to ecological effects. This study shows that petroleum hydrocarbons are soluble and available for absorption by the mammalian digestive system. The data suggests there could be a relationship between the concentration of TPH and GI solubility (i.e., higher TPH concentrations in soil could lead to higher absorption due to greater solubility).

Recommendation: Retain for background information for final report

Reviewed by: G. Buchanan

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Kulakow, P., A. P. Schwab, and M.K. Banks. 2000. ***Screening Plant Species for Growth on Weathered Petroleum Hydrocarbon-Contaminated Sediments.*** **International Journal of Phytoremediation, 2/4: 297-317.**

Summary: This was a phytoremediation study to determine appropriate plant species for growth (29 species examined). Initial TPH concentration was ~25,000 mg/kg (weathered

sediments were air dried and ground to pass a 6-mm screen to form a soil). Results show plant species have different sensitivities to TPH in soil. In general plant growth was stunted in TPH contaminated soil.

Results:

- All species grew less than control for root-length density test in TPH contaminated soils.
- No variation in TPH degradation by plant species, all the same.
- Mean TPH at 180 days of bioremediation was 18,119 mg/kg; mean for abiotic control was 25,356 mg/kg. Mean percentage degradation was 25%.
- No significant correlation between % TPH degradation and plant growth variables.
- No plant species enhanced the degradation of petroleum hydrocarbons.
- Three legume species did not survive for 180 days; all 26 grass species survived.

Criteria Evaluation:

1. Soil from documented contaminated site - yes (oil refinery wastewater stream sediments)
2. Weathered (long term) TPH contamination- yes (several decades)
3. Soil texture identified - yes
4. Soil chemistry parameters - yes (full characteristics)
5. Soil sample depth reported - yes (1.5m)
6. TPH analysis via defined method - yes GC-FID (C16-C34)
7. PAH analysis via defined method - NA

Reviewer Conclusions: TPH above approximately 18,000 mg/kg were toxic to 3 legume species. Grass species survived, but in general had stunted growth relative to controls in uncontaminated soils at these concentrations. Somewhat useful to indicate acute/chronic phytotoxicity of TPH contaminated soil at these relatively elevated concentrations.

Recommendation: Retain for final report**.**

Reviewed by: G. Buchanan

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Launo, R., W. Focht, A. Cross, and K. Duncan. 2002. Development of Relevant Ecological Screening Criteria (RESC) for Petroleum Hydrocarbon-Contaminated Exploration and Production Sites - Final Report. EPA Grant Number: R827015-01-0. Online at http://ipec.utulsa.edu/lpec/11.d/11_final.pdf.

Summary: This baseline laboratory study examined crude oil contaminated soils, which were tested on enchytraeids, Collembola, prairie plant species, earthworms, and plant species (e.g., lettuce, and mustard). Study examined 13 endpoints consisting of 7 soil macroorganism tests and 4 microbial measurements. Petroleum exposure was determined by measuring TPH and BPH (bioavailable petroleum hydrocarbon using solid-phase microextraction fibers). The

objective was to define a relevant ecological screening criterion (RESC) for petroleum contaminated sites.

Results:

- TPH concentrations ranged from 1,278 to 13,250 mg/kg oil in soil; BPH ranged from 83 µg hydrocarbon/kg soil (reference soil) to 3,620 µg/kg in a contaminated soil.
- Minimal ecological risk was found for the site, even at TPH levels higher than 13,000 mg/kg. The authors state that this reinforces the assertion that TPH is not a reliable measure of ecotoxicity.
- Concluded that earthworm cocoon production was the most sensitive ecological receptor used to date in ecotoxicological assessments of petroleum-contaminated soil. **Earthworm reproduction testing indicated an EC_{50} of 2,118 mg/kg TPH.** A generic RESC was not derived from the data, however the 2,118 mg/kg value was recommended at the site specific ecological criterion (SSEC)
- The paper references a value of 100 mmol hydrocarbon/kg of fiber **C** on SPME as a level at which earthworm toxicity occurs (Parkerton & Stone, 1996).
- Preliminary testing observed earthworm mortality and reduced mustard germination at 31,000 mg/kg TPH.
- Recommended the development of a standard measure of bioavailability.

Criteria Evaluation:

1. Soil from documented contaminated site - yes
2. Weathered (long term) TPH contamination- yes (spill in 1999, tests in 2000)
3. Soil texture identified - Yes
4. Soil chemistry parameters - Yes (full)
5. Soil sample depth reported - Yes (30 cm)
6. TPH analysis via defined method - 418.1 (IR) and 8015-B (GC)
7. PAH analysis via defined method - no

Reviewer Conclusions: Consider earthworm reproduction value as potential criteria.

Recommendation: Retain for final report

Reviewed by: G. Buchanan

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Marwood, T.M., K. Knoke, K. Yau, H. Lee, and J. Trevors. 1998. ***Comparison of Toxicity Detected by Five Bioassays during Bioremediation of Diesel Fuel-Spiked Soils.*** **Environ. Toxicology & Water Quality, 13/2: 117-126.**

Summary: Primarily looked at soil toxicity during bioremediation using multiple tests in four different types of soil spiked with diesel fuel. PAHs were approximately 10,000 mg/kg at start

of test; acclimation was defined as 10% recovery of spiked ^{14}C-octodecane (9-20 days) and mineralization as 25% cumulative recovery of CO2 (18-51 days).

Results:

- Reductions in TPH/PAH were not always predictive of reductions in soil toxicity. Seed germination and seedling emergence tests indicated that bioremediation increased soil toxicity; probably due to the formation of intermediate products more toxic than parent compounds.
- In all four soils, more than 25% of the TPH had been degraded at time of sampling. (Indicates that TPH <7500 mg/kg was still toxic in some tests.)
- Toxi-chromotest detected little toxicity in any of the four soils tested.

Criteria Evaluation:

1. Soil from documented contaminated site - no
2. Weathered (long term) TPH contamination- no
3. Soil texture identified - yes
4. Soil chemistry parameters - yes (pH, N, P, K, Mg)
5. Soil sample depth reported - no
6. TPH analysis via defined method - yes GC-FID
7. PAH analysis via defined method - unknown

Reviewer Conclusions: This was primarily a study on toxicity of diesel contaminated soils using five different tests. The soils would probably not be considered weathered since the tests were conducted for varying lengths between 0 and 51 days after spiking.

Recommendation: Reject for final report**.**

Reviewed by: G. Buchanan

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Megharaj, M., I. Singleton, N.C. McClure, and R. Naidu. 2000. *Influence of Petroleum Hydrocarbon contamination on Microalgae and Microbial Activities in a Long-Term Contaminated Soil.* Archives of Environmental Contamination and Toxicology. 38: 439-445.

Summary: Microalgae are ubiquitous and form an important component of the soil ecosystem, maintaining soil fertility and oxygen production. Soil enzymes released by a wide variety of biota play an important role in organic matter degradation and nutrient cycling. Therefore any interference of petroleum hydrocarbons with normal microbial and microalgal activities and soil enzymes would be expected to have adverse effects on the overall functioning of soil ecosystems. In this study, the effect of weathered petroleum hydrocarbon on soil microbial biomass, microalgal population size, composition, and growth, and soil enzyme activity

(dehydrogenase and urease) was evaluated in soils from a long-term petroleum hydrocarbon (TPH) –contaminated site.

Surficial soil samples (0-8 cm; five subsamples per location; sieved) were collected from areas known to cover a range of TPH concentrations and an uncontaminated on-site reference location. Soil was analyzed for TPH and PAHs by USEPA Method 8015B, TOC, nitrogen, and particle grain size. TPH contamination ranges in soil were identified as low (<4000 mg/kg), medium low (4000-8000 mg/kg), medium (8000 – 12,000 mg/kg, medium high (12,000 – 16,000 mg/kg), and high (16,000 mg/kg).

Results:

- Microbial biomass carbon – decreased in all contaminated soils, ranging from 43 % to 60% reduction; biomass reduction was most pronounced in the 4000-8000 mg/kg (medium – low level) soil.

- Microalgal population size – increased threefold over control soil in the low-level contaminated soil, followed by a large reduction in population size as soil TPH levels increased, beginning at the 4000 – 8000 mg/kg range.

- Species composition of microalgae – sensitive species were replaced by resistant species as TPH concentrations increased (nine genera were present in control and low level soils; only two were identified at high levels; almost all cyanobacteria were eliminated above medium-low TPH levels).

- Microalgal growth (determined vial algal growth inhibition tests on two species conducted with aqueous soil eluates) – cell growth was severely affected by eluates above low level soils contamination (i.e. above 4000 mg/kg); eluates from soils in the high range were lethal to both species. Microscopic observation showed alteration in morphology (enlarged, giant cells with irregular shapes).

- Activity of dehydrogenase and urease – generally decreased with increasing TPH soil concentrations.

Criteria Evaluation:

1. Soil from documented contaminated site - yes
2. Weathered (long term) TPH contamination- yes
3. Soil texture identified - yes
4. Soil chemistry parameters - yes (pH, total carbon, total nitrogen)
5. Soil sample depth reported - yes
6. TPH analysis via defined method - yes
7. PAH analysis via defined method - yes

Reviewer Conclusions:

This study indicates long-term total petroleum hydrocarbon contamination adversely effects soil microbial biomass, microalgae population size and composition, growth and morphology of two microalgal species, and soil enzyme activity (dehydrogenase and urease). The adverse effects begin at approximately 4000 mg/kg soil TPH; severe/lethal effects are observed above 16,000 mg/kg. The reduction in microbial and microalgal biomass, biodiversity, and enzyme activity will limit normal and necessary ecological functions of the soil ecosystem, such as dinitrogen fixation, degradation of organic matter, oxygen production, nutrient cycling, and polysaccharide production, which determines soil structure.

Recommendation: Retain for final report

Reviewed by: N. Hamill

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Salanitro, J.P., P. B. Dorn, M.H. Huesemann, K.O. Moore, I.A. Rhodes, L.M. Rice Jackson, T.E. Vipond, M.M. Western, and H.L Wisniewski. *Crude Oil Hydrocarbon Bioremediation and Soil Ecotoxicity Assessment.* 1997. Environ. Sci. Technol. 31, 1769-1776.

Summary: Bioremediation was performed on 2 soils with differing percent organics (4.6%, Norwood/Baccto and 0.3%, Norwood) to which was added light, medium and heavy crude oils. Multiple oil concentrations were used to estimate LC50s for earthworms (*Eisenia foetida*), EC50s for Microtox testing, percent seed germination and plant growth. Toxicity was not observed after 3-4 months of bioremediation resulting in TPH levels to 10,800 mg/kg (heavy crude), 8,600 mg/kg (medium crude) and 1,200 mg/kg (light crude).

Results:

- Pretreated oily soils (TPH from 4,000 to 27,000 mg/kg) were acutely toxic to earthworms (2 week exposure), reduced seed germination and plant growth (except corn) and were inhibitory in Microtox tests (results < EC50).
- 50-75% and 10-90% of the TPH were degraded in 3-4 months in the low and high organic soils respectively. Bioremediated soils contained 1,000 - 10,800 mg/kg residual hydrocarbons as gravimetric TPH (TPH-Gr). The greatest degradation occurred with light and medium weight oil in the high organic soil. Bioremediation did not reduce TPH after 4 months.
- Bioremediated soils were not toxic and most aromatics were not leachable (no metals and $\leq$ 50 ppb BTEX leached from treated soils).
- Earthworm bioassays were more sensitive than Microtox tests.
- After 8-11 months bioremediation, some plant growth inhibition was still apparent in both soil types with the heavy, medium and light oils. These results indicate that undegraded petroleum (other than BTEX) or metabolites may be affecting plant growth.

Criteria Evaluation:

1. Soil from documented contaminated site - no
2. Weathered (long-term) TPH contamination - (spiked + artificially weathered: 2-3 day aeration, mechanical breaking of soil clumps)
3. Soil texture identified - yes
4. Soil chemistry parameters - (grain size, moisture, pH, inorganic N and P, organic N)
5. Soil sample depth recorded - 0-6"
6. TPH analysis via defined method - yes (-Gr, -IR)
7. PAH analysis via defined method - yes
8. Other analyses (saturated/aromatic/polar fractions in oils, O&G, BTEX, metals in soils)
9. Biotic receptors evaluated (bioassay endpoints): earthworm survival, seed germination and plant growth (wheat, oat, corn), Microtox

Reviewer Conclusions: Uncertainty remains regarding toxicity of soil TPH $\geq$ 10,000 mg/kg since final soil TPH concentrations were $\leq$ 10,600 mg/kg. Some plant growth inhibition was noted (0-40%) after 8-11 months of biotreatment. This may be due to unremediated petroleum or metabolites (author comment).

Recommendation: Retain for final report

Reviewed by: E. Demarest

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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 Assessment of Hydrocarbon-Contaminated Soils and Application to Ecological Risk Assessment.* Environmental Toxicology and Chemistry, Vol. 18, No. 7, pp. 1591-1607.

Summary: Study objectives included evaluating acute and chronic assays for earthworms and plants in field soils, comparing the sensitivity and predictability of different ecotoxicity tests, assessing toxicity of hydrocarbon-contaminated field soils to plants and earthworms and correlating results with soil physical, chemical and hydrocarbon analyses. Testing was performed primarily on crude oil contaminated soils. Dilutions of each test soil were made. Endpoints included earthworm avoidance, survival and reproduction, seed germination, root length, and plant growth. No observed effects concentrations (NOECs) were calculated for all endpoints.

Results:

- Earthworm avoidance and survival and chronic assays were each significantly correlated with hydrocarbon measurements. The highest ranking parameters for earthworm avoidance and survival were TPH by GC, polar compounds and *n*- and *iso*-saturates. Worm reproduction was correlated most closely with soil texture and metals constituents.
- For plant germination, the identified hydrocarbon parameters were polar compounds, asphaltenes, and TPH by GC (C6-C25).

- One of the clearest concentration-response curves was earthworm 14-day survival as a function of TPH by GC <4,000 mg/kg (not likely acutely toxic), 4,000 - 10,000 mg/kg (some mortality expected), >10,000 (survival expected to be low). The more common Freon-extractable TPH and oil and grease (O&G) concentrations did not correlate strongly with 14-day earthworm survival.
- The 14-day survival test predicted chronic survival whereas the 7-day survival and avoidance tests did not.
- Asphaltene concentrations best correlated with seed germination success (recommended test method): Mustard seed germination was reduced at asphaltene concentrations of 200 mg/kg to 1,000 mg/kg while wheat germination was reduced between 4,000 and 7,000 mg/kg. However, the study supports that different taxa respond differently to hydrocarbons and that a "universal" hydrocarbon parameter to predict toxic effects on soil communities has not been identified.

Criteria Evaluation:

1. Soil from documented contaminated site - yes
2. Weathered (long-term) TPH contamination - yes (3 mo. - >5 yr.)
3. Soil texture identified - yes
4. Soil chemistry parameters - yes (O&G, N, P, metals, TOC, pH, bulk density, particle density, porosity)
5. Soil sample depth recorded - no ("field soils")
6. TPH analysis via defined - (most analyses)
7. PAH analysis via defined method - yes
8. Biotic receptors evaluated (bioassay endpoints) - earthworms (*Eisenia fetida*), corn, lettuce, mustard, wheat

Reviewer Conclusions: The majority of evaluation criteria were met; results of the earthworm avoidance, survival/reproduction, and phytotoxic studies are appropriate for inclusion in sections V and VI of the Ecological Subcommittee's report.

Recommendation: Retain for final report

Reviewed by: E. Demarest

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Shakir-Hanna, S. H. and R.W. Weaver. 2002. *Earthworm Survival in Oil Contaminated Soil.* Plant and Soil. 240: 127-132.

Summary: Earthworms are associated with healthy soil and their absence is an indication of poor soil health. Three laboratory investigations were undertaken to determine the concentrations of crude oil in soil that leads to reduced survival of *Lumbricus terrestris* and *Eisenia fetida* and one investigation to determine the propensity of *L. terrestris* to move away from contaminated soil. This review focused on the one out of the four investigations evaluating weathered crude oil.

Results:

E. fetida was exposed to soils containing a range of five weathered crude oil concentrations between 0.5 to 2.5% (5000 - 25,000 mg/kg, dry weight); the number of viable earthworms was determined after 5, 7, 10, and 15 days. At 0.5% TPH, survival was 100% and 90% at the 10 and 15-day point, respectively. Reduction in 10-day survival was evident beginning at 1.0%, with no 10-day earthworm survival at 2.0% TPH. Poorer survival was indicated for the weathered oil than unweathered.

Criteria Evaluation:

1. Soil from documented contaminated site - no
2. Weathered TPH contamination - yes (artificially)
3. Soil texture identified - yes
4. Soil Chemistry parameters - yes (pH, TOC, % saturation)
5. Soil sample depth reported - yes (surficial)
6. TPH analysis via defined method - yes (USEPA 418.1)
7. PAH analysis via defined method - no

Reviewer Conclusions: An allowable regulatory level of 1 % weathered TPH (10,000 mg/kg, dry weight) may not allow for survival of earthworms.

Recommendation: Retain for final report.

Reviewed by: N. Hamill

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Stewart, A.J., G.E. Napolitano, and B.E. Sample. 1996. *Biological Quality of Soils Containing Hydrocarbons and Efficacy of Ecological Risk Reduction by Bioremediation Alternatives.* Fossil Energy Program Annual Progress Report for April 1995 through March 1996. R.R. Judkins, Program Manager. Prepared by Lockheed Martin Energy Research Corp. for Oak Ridge National Laboratory. P. 223-230.

Summary: This is a progress report for initial work on: Task 1) the development of ecological risk assessment methods and tools, Task 2) testing of TPH-contaminated soils for toxicity to earthworms, and Task 3) development of chemical analysis methods for rapid and quantitative assessment of TPH constituents in soils. Toxicity testing on earthworms for 21 days on 100 g of contaminated soil with added food (fermented alfalfa); two worms per replicate. Soils diluted with a "reference" soil at "various" concentrations. Examined TPH, survival, growth and reproduction (cocoons).

Results:

- Only conducted preliminary work on two contaminated soils; expected to be conducted on up to 14 soils.
- No consistent relationship between observed testing parameters and TPH concentration. Growth increased with increasing TPH in one test soil (highest concentration ~ 350 mg/kg).
- Used thin-layer chromatography with flame ionization detection to analyze hydrocarbon class composition. No identification of individual compounds.

Criteria Evaluation:

1. Soil from documented contaminated site - yes
2. Weathered (long term) TPH contamination- yes
3. Soil texture identified - No
4. Soil chemistry parameters - No (clay/silt fraction, organic carbon)
5. Soil sample depth reported - no
6. TPH analysis via defined method - unknown
7. PAH analysis via defined method - no

Reviewer Conclusions: Inadequate amount of data in this progress report to use for consideration of a TPH soil number. Feeding the test organisms as well as not knowing the quality of the reference soil confounds any accurate interpretation of the data.

Recommendation: Reject for final report

Reviewed by: G. Buchanan

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Wilson, J.J., J. F. Hatcher, and J. S. Goudey. *Ecotoxicological Endpoints for Contaminated Site Remediation*. 2002. Ann. 1st Sanita, Vol. 38, No. 2, pp. 143-147.

Summary: Ecotoxicity testing provides a more direct assessment of adverse environmental impacts than chemical criteria. A multi-trophic level soil ecotoxicity assessment was done on soil contaminated with crude oil distilled into five different fractions based on hydrocarbon chain lengths. Results indicate that the fraction above C26 was not toxic to microbes, plants, and earthworms when present at concentrations far above the 1,000 mg/kg TPH Canadian criterion. Weathered heavy crude oils can be much less toxic than lighter, freshly spilled diesel oils, yet using a gross measure of TPH would not detect this difference.

Results:

- The earthworm (*Eisenia foetida*) was tested for long-term survival (7 and 14 days) using soil dilutions. At 2.5%, both paraffinic and naphthenic crude was toxic (0% survival) in 14 days. The heavier asphaltic crude was not toxic. The lighter, more soluble fractions likely had a solvent-effect on worm membranes.
- Seedling emergence showed marginal effects in paraffinic crude at 0.5%. At 5%, paraffinic and naphthenic crudes were toxic, but asphaltic crude was not. The toxic effect of the crudes

was most likely not chemical, but physical because the **soils became hydrophobic indicated by water not readily infiltrating the soil.**

- The heavy fractions of paraffinic and asphaltic crudes could not be tested because they were solid at room temperature and could not be adequately dispersed throughout the loam soil.
- C26 fractions were significantly less toxic than the lighter fractions for all trophic levels tested and supports raising the crude oil criterion above 1,000 mg/kg for sites where the C26+ represents the majority of the residual soil TPH.

Criteria Evaluation:

1. Soil from documented contaminated site - no (clean soil spiked)
2. Weathered (long-term) TPH contamination - prepared distillates (minus toxic volatile fractions) added to soil (50,000 mg/kg) crude and weathered 1 year at room temperature
3. Soil texture identified - yes (loam)
4. Soil chemistry parameters - moisture content, bulk density, organic carbon content
5. Soil sample depth recorded - no (topsoil)
6. TPH analysis via defined method - saturates, aromatics, polars, and asphaltenes via silica gel column chromatography
7. PAH analysis via defined method - no
8. Biotic receptors evaluated (bioassay endpoints) - earthworm (survival), lettuce seed (emergence).

Reviewer Conclusions: Lighter crude fractions are toxic for seed germination and earthworm survival in the 1,000 mg/kg to 25,000 mg/kg range.

Recommendation: Some value for assessing crude oil contaminant effects in acute tests; retain for final report.

Reviewed by: E. Demarest

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Wong, D.C.L., E.Y. Chai, K.K. Chu, and P.B. Dorn. *Prediction of Ecotoxicity of Hydrocarbon-Contaminated Soils Using Physicochemical Parameters.* 1999. Environmental Toxicology and Chemistry. Vol. 18, No. 11, pp. 2611-2621.

Summary: Study objectives included earthworm avoidance, survival and reproduction and plant germination and root growth. Univariate and multivariate statistical methods were used to examine relationships between physical and chemical properties and biological endpoints. TPH by GC (TPHgc) and polars were identified as predictors of earthworm avoidance and survival and seed germination. Asphaltenes also explained most variation in seed germination. Gravimetric TPH (TPHgr) explained 40% of the variation in earthworm reproduction and asphaltenes 43% of plant)root growth. The authors conclude that the TPHgc concentrations at which effects on earthworm avoidance ands survival and seed germination were observed in this study can provide initial screening-levels for the various biological endpoints in a tier-1 risk assessment.

Results:

- Earthworm avoidance and survival were correlated (negatively) only to chemical parameters (TPHgc > polars > *n*- and iso-saturates) whereas reproduction (cocoons, juvenile production) was correlated primarily with physical parameters (positive to clay and metals).
- Germination was negatively correlated to most hydrocarbon parameters (asphaltenes > polars > TPHgc), whereas root growth was less well correlated. Sensitivity between plant species was noted.
- Because TPHgc was identified as a common predictor of worm avoidance and survival and seed germination, its measurement and use as an initial parameter in waste-site assessment to screen soil quality and toxicity are recommended.
- The relationships found suggest possible threshold concentrations above which toxic effects are manifested. Earthworm avoidance and survival were apparent at TPHgc concentrations ≥ 10,000 mg/kg, whereas little or no acute effects were observed at < 4,000 mg/kg. Effects on seed germination were species specific, with mustard being affected at TPHgc concentrations ≥ 2,000 mg/kg. Toxic effects on wheat germination were observed at ≥ 10,000 mg/kg in most soils, whereas corn germination was substantially affected in only one soil, which had a concentration of 34,000 mg/kg.

Criteria Evaluation:

1. Soil from documented contaminated site - yes
2. Weathered (long-term) TPH contamination - yes (3 mo. - >5 yr.)
3. Soil texture identified - yes
4. Soil chemistry parameters - (TOC by gravimetric procedure and GC, pH, N, P, bulk density, metals, particle density, porosity)
5. Soil sample depth recorded - no ("field soils")
6. TPH analysis via defined method - yes
7. PAH analysis via defined-level method - yes
8. Other analyses (oil and grease, GC boiling-point distribution, BTEX)
9. Biotic receptors evaluated (bioassay endpoints) - earthworms (*Eisenia foetida*), corn, lettuce, mustard, wheat

Reviewer Conclusions: Research was conducted in response to perceived inadequacy of “arbitrary chemical cleanup levels". Study assessed if biological responses could be correlated to petroleum concentrations. Based on the study, screening-levels are suggested which generally cluster around our 10,000 mg/kg soil TPH ecological screening criterion.

Recommendation: Good study; retain for final report.

Reviewed by: E. Demarest

Addendum 1: Update on the Dialog Database Search for Literature on Ecological Impacts/Criteria of Total Petroleum Hydrocarbons

A third Dialog Database search for literature on the ecotoxicity of TPH in soils for the years 2005 –2007 was conducted by NJDEP's Information Resource Center on December 13, 2007 to update the prior searches for the years 1996 – June 2005. Sixty-three (63) new citations were provided to the Ecological Subcommittee; a preliminary review identified ten (10) that appropriately focused on the topic. The full text was obtained for these references. Further review indicated that only five (5) studies warranted in-depth review and preparation of written summaries. In addition to the requirement that the research had to focus on ecotoxicology of TPH in soils, the articles were considered for the final report only if the majority of certain criteria were met: soil was preferred to be from a documented contaminated site, the sample was of known depth, soil texture and chemical parameters were reported, the TPH was weathered, and TPH was analyzed via a defined method. The summaries of accepted studies are included herein. The Ecological Subcommittee determined that no change to the recommended ecological soil screening criteria is warranted based on the new literature reviews.

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Coulon, F., E. Pelletier, L. Gourhant, and D. Delille. 2005. Effects of nutrient and temperature on degradation of petroleum hydrocarbons in contaminated sub-Antarctic soil. Chemosphere 58: 1439-1448.

Summary: Used Microtox test (bioluminescent bacteria) to examine toxicity over 180 days of degradation of crude and diesel spiked natural sediment in a microcosm setting. Toxicity slightly decreased in all tests over the degradation period.

Results:
- Crude was 22.6 mg/g TPH dry wt; diesel was 21.4 mg/g TPH dry wt at beginning of experiment
- After 180 days, total alkanes losses were >77% (untreated) to >90% (treated)
- Total PAH losses ranged from 43% - 76% (untreated) to <65% (10°C) and <80% (20°C) in treated.

Criteria Evaluation:

1. Soil from documented contaminated site – no
2. Weathered (long term) TPH contamination– no (fresh crude and diesel)
3. Soil texture identified – yes
4. Soil chemistry parameters – yes (clay/silt fraction, organic carbon)
5. Soil sample depth reported – yes
6. TPH analysis via defined method – yes (MS)
7. PAH analysis via defined method – yes (GC-MS)

Reviewer Conclusions: Contamination not weathered, only used Microtox, so limited value.

Recommendation: Reject for final report.

Reviewed by: G. Buchanan

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Hubalek, T., S. Vosahlova, V. Mateju, N. Kovacova & C. Novotny. 2007 *Ecotoxicity Monitoring of Hydrocarbon-Contaminated Soil During Bioremediation: A Case Study.* Arch. Environ. Contam. Toxicol. 52: 1-7.

Summary: Study used several ecotoxicity tests to look at toxicity of a hydrocarbon-contaminated soil during bioremediation. Used bioluminescent test, inhibition of root growth for three plant species, growth inhibition of duckweed, earthworm acute and chronic tests, and freshwater ostracod.

Results:

- TPH residues (weathered mineral oil, hydraulic fluids and grease) were 6380 ug/g dry wt to start and ended at 2200 ug/g dry wt (17 months). Loss of ignition of 5.7% of dry weight.
- Most effective bioassays were the contact tests (with soil) in which the plants L. sativa (lettuce), L. minor (duckweed), crustacean *H. incongruens*, and earthworm *Eisenia fetida* were used.
- Inhibition of growth evident in several tests throughout the study (up to 17 months).
- Reproduction by the earthworm was only reduced ~20% by month 3, but inhibition increased until the end of the study (inhibition of ~70-100%)

Criteria Evaluation:

1. Soil from documented contaminated site – yes
2. Weathered (long term) TPH contamination– yes
3. Soil texture identified - no
4. Soil chemistry parameters – some (clay/silt fraction, organic carbon)
5. Soil sample depth reported - no
6. TPH analysis via defined method – yes (TPH by infrared spectrometric method
7. PAH analysis via defined method – no

Reviewer Conclusions: This was a study using several ecotoxicity tests during bioremediation. This study shows that toxicity persisted throughout the bioremediation process and hinted that intermediary metabolites may be responsible for observed increases in toxicity.

Recommendation: retain for additional information – no changes to report recommended.

Reviewed by: G. Buchanan

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Schaefer, M. and F. Juliane. 2007. The influence of earthworms and organic additives on the biodegradation of oil contaminated soil. Applied Soil Ecology 36: 53-62.

Summary: Two experiments were conducted. In exp 1, three species of earthworms were tested *E. fetida, A. chlorotica, L. terrestris* for 28 days to determine their influence on the degradation of crude oil contaminated soil @ 9500 mg TPH/kg dry wt. In exp 2, the influence of soil additives and/or earthworms on TPH degradation in crude oil polluted soil (5000 mg/kg) was examined for 28 days.

Results:

- Soil was a silty sand with soil organic matter concentration of 5.34%
- Exp 1: Concentrations of TPH were significantly reduced in soils with earthworms; varied by species
- TPH reduced by 30-42% with L. terrestris; 31-37% with E. fetida; and 17-18% w/A. chlorotica.
- Exp 2: mixed results
- Soil respiration measurements revealed higher microbial activity in the earthworm treatments compared to the treatments without worms.
- TPH concentrations of 5000-9500 mg/kg were lethal after 28 days. *E. fetida* and *A. chlorotica* were more resistant than *L. terrestris.* "However, other experiments have shown that lower concentration levels (TPH , 4000 mg/kg) cause hardly any mortality in earthworms (Saterbak et al., 1999; Dorn and Salanitro, 2000; Schaefer, 2001; Van Gestel et al., 2001)."

Criteria Evaluation:

- Soil from documented contaminated site – yes
- Weathered (long term) TPH contamination– yes (refinery soil ~30 years)
- Soil texture identified – yes
- Soil chemistry parameters – yes (clay/silt fraction, organic carbon)
- Soil sample depth reported – no
- TPH analysis via defined method – yes (GC/FID)
- PAH analysis via defined method – no

Reviewer Conclusions: Data shows that TPH were lethal to several earthworm species at levels >5000 mg/kg after 28 days.

Recommendation: Use as a reference.

Reviewed by: G. Buchanan

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Shin, K., H. Jung, P. Chang, H. Choi, and K. Kim. 2005. Earthworm Toxicity During Chemical Oxidation of Diesel-Contaminated Sand. Envir. Tox and Chem. 24: 1924-1929.

Summary: Objectives were to monitor toxicity variation during the chemical oxidation process using earthworm tests. The toxicity of earthworms to the TPH-contaminated sand/artificial soil was significantly decreased at the end of ozonation. Lethality observed in TPH >12,000 mg/kg. No mortality in TPH soil <5200 mg/kg. Growth affected at ~ 10,000 mg/kg.

Results:

- Measured survival and growth of earthworms up to 14 days; food added to the soil; weight taken with no apparent depuration.
- Used sand; Soil organic matter = 0.77%; particle size = 300-106 μm for ozonation test cell; used artificial soil composite for earthworm tests = 70% sand; 20% kaolin clay and 10% commercial peat with the sand portion representing the contaminated soil.
- Overall 90% removal rate of TPH mass during ozonation; high rate probably due to use of sand and low organic matter.

Criteria Evaluation:

1. Soil from documented contaminated site – no
2. Weathered (long term) TPH contamination– no (diesel weathered for two weeks)
3. Soil texture identified – yes (sand for ozonation; artificial soil for toxicity tests)
4. Soil chemistry parameters – yes (clay/silt fraction, organic carbon)
5. Soil sample depth reported - no
6. TPH analysis via defined method – yes (TPH by GC-FID)
7. PAH analysis via defined method – no

Reviewer Conclusions: This was a study that examined acute and chronic (growth) toxicity of earthworms to TPH contaminated sand in an artificial soil. Only exposed up to 14 days; 28 days or longer with cocoon (reproduction) measurements would have been more sensitive. Does not help with determining a lowest observed adverse effects level (LOAEL) or no observed adverse effects level (NOAEL) due to the short exposure and testing methods.

Recommendation: Retain for additional information – no changes to report recommended.

Reviewed by: G. Buchanan

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Soukup, D.A., A.I. Ulery, and S. Jones. 2007. *Distribution of Petroleum and Aromatic Hydrocarbons at a Former Crude Oil and Natural Gas Production Facility*. Soil & Sediment Contamination, 16:143-158.

Summary: This article describes subsurface site characterization sampling, analysis, and data evaluation for BTEX, diesel range, and heavier hydrocarbons at a 145 ha former crude oil and natural gas production facility in the greater Los Angeles area. The objective of the investigation was to estimate the horizontal and vertical extent of TPH-contaminated soil and to determine the variation in petroleum hydrocarbon chain lengths with depth. Site specific cleanup values for

TPH compounds have been established by the California State Regional Water Quality Control Board (RWQCB) are based on hydrocarbon chain length and relative mobility of the compounds occurring within each of the carbon chain ranges in the subsurface. Chain length is also used in the remedial method selection process. The RWQCB cleanup values for TPH are:

Condensate/gasoline ranges (C_1 to C_{12})) – 1000 mg/kg

Diesel range (C_{12} to C_{22}) – 10,000 mg/kg

Heavy TPH ($\geq C_{23}$) – 50,000 mg/kg

More than 10,000 samples were analyzed (from trenching, soil borings, and post-excavation).

Results:
Results from the trenching investigation indicated petroleum hydrocarbons ranging from C_6 to C_{35} as well as condensate (the volatile portion of crude oil) ranging from C_1-C_9; Concentrations ranged from 1000 – 81,000 mg/kg TPH. 44 samples exceeded the RWQCB cleanup values for gasoline, diesel, and heavy TPH ranges. Seven samples also exceeded the cleanup values for BTEX.

Results from the soil boring investigation indicated that 34 samples exceeded the RWQCB clean up values for TPH within the gasoline, diesel, and heavy TPH ranges; the maximum concentration was 92, 000 mg/kg TPH. 96 soil samples also exceeded the cleanup values for BTEX.

The results of the statistical analysis indicated the mean percentage of TPH compounds in the gasoline range (C4 – C12) was significantly greater in samples collected at depths ranging from 4.6 to 18 m than at shallower depths (i.e., the predominance of gasoline range hydrocarbons increased with increasing depth). These results are expected given the molecular weight, volatility, water solubility, and adsorption characteristics of condensate and TPH compounds within the gasoline range. The mean percentage of diesel range TPH compounds (C13 – C23) and in the heaviest hydrocarbons (>C24) was less in samples collected at depths between 4.6 and 18 m and depths greater than 18 m than in shallow samples. The highest mean concentrations of BTEX were reported in samples collected at depths ranging from 4.6 – 18 m.

The occurrence of BTEX, diesel range, and heavier hydrocarbons at depth may result in preferential pathways for downward migration, e.g., surface soil cracking, abandoned wellbores, blown out wells, and faults.

Criteria Evaluation:

1. Soil from documented contaminated site – yes
2. Weathered (long-term) TPH contamination – yes
3. Soil texture identified – yes
4. Soil chemistry parameters – yes
5. Soil sample depth recorded – yes

6. TPH analysis via defined method – yes
7. PAH analysis via defined level method – no

<u>Reviewer Conclusions</u>: This investigation is mainly concerned with identifying the depth intervals for several TPH fractions; the evaluation of ecological risk was not within the scope of the study.

<u>Recommendation</u>: This reference should be used by the ecological subcommittee of the TPHC Cap Value work group only for background information on the depth profiles of various TPH fractions from light crude oil at former industrial/petroleum sites. This investigation is helpful in that, since diesel range TPH compounds (C13 – C23) and heavier hydrocarbons (>C24) were the dominate carbon ranges in the shallow biotic zone (i.e., <4.6 m), ecological evaluations should focus on risk from these fractions. No changes to report recommended.

Reviewed by: N. Hamill