



Guidance for Assessing Petroleum Hydrocarbons in Soil

This guidance is for use in assisting regulators and responsible parties in assessing risk from soil impacted by petroleum hydrocarbons at remedial response sites.

Key Words

Petroleum hydrocarbons; soil; Total Petroleum hydrocarbons (TPH); gasoline; diesel; oil; light petroleum fractions; middle petroleum fractions; heavy petroleum fractions

Background

Ohio EPA-DERR addresses sites contaminated by petroleum hydrocarbons as a result of spills (emergency response and post-response activities), as co-contaminants at hazardous waste and CERCLA sites, as water pollution abatement actions under ORC 6111, and as Voluntary Actions under ORC 3746 and OAC 3745-300. Evaluation and remediation of petroleum hydrocarbon sites is difficult, owing to the complex regulatory and technical challenges associated with evaluating such sites.

This guidance document was developed to assist both the regulators and responsible parties in assessing the risk from soil impacted by petroleum hydrocarbons. The guidance document is part of the overall assessment of risk at the site, and is meant to be used in conjunction with the available regulations and other appropriate risk assessment guidance.

This guidance presents a risk-based approach for the assessment of soil impacted by petroleum hydrocarbons. This approach includes the evaluation of indicator chemicals and residual petroleum constituents. Necessary inputs to calculate human health risk-based numerical standards, such as physicochemical and toxicity data, are provided. Analytical sampling requirements necessary for site assessment are also provided to ensure that sample results are compatible with the proposed risk assessment process.

The guidance does not address petroleum hydrocarbons leaching to ground water. If leaching from soil impacted by petroleum hydrocarbons to ground water is a concern at the site, refer to the DERR Total Petroleum Hydrocarbons (TPH) leaching guidance. Also, in a spill situation where an immediate response is needed to address the release, it is expected that the [Petroleum Contaminated Sites Guidance Document for Emergency Response Actions](#) (ER-013, March 2005) will be the protocol followed.

Discussion

In Ohio, as in many other areas of the country, petroleum hydrocarbon contamination is widespread. Contamination results from mishandling, spilling, or leaking products, including gasoline, motor and lubricating oils, diesel fuel, heating oils and aircraft fuels. Each of these petroleum products are complex mixtures containing hundreds to thousands of different chemical compounds. Various petroleum products may also contain additives. The diverse chemical compounds exhibit a large range of behavior in environmental media governed by their physicochemical properties. As a result of these characteristics, the assessment of risk from exposure to petroleum hydrocarbon mixtures is difficult.

In the environment these mixtures can change through weathering (that may include volatilization, biodegradation, partitioning, oxidation, photo-degradation, etc.), further complicating the determination of risk from exposure. The more soluble or volatile compounds will migrate to other locations. The mostly non-mobile components are left behind at the release site. As a result, the receptors can be exposed to a different mixture than that originally released to the environment. Factors including location of release, length of time between the release and exposure, media of exposure, etc. can all contribute to these differences.

Ohio EPA-DERR has developed a tiered approach to assess the risk presented by petroleum contamination in soils as discussed below. Information from the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG), as well as that available from states, including Massachusetts and Louisiana, were used to develop this guidance. The TPHCWG is a national workgroup comprised of representatives from federal and state agencies, industry and academia. The group was formed to address the disparity among cleanup requirements at sites contaminated with hydrocarbon materials, and develop scientifically defensible soil clean up levels.

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If leaching from soil impacted by petroleum hydrocarbons is a concern at a site, reference should also be made to the DERR [Soil Leaching to Ground water Evaluation for Total Petroleum Hydrocarbons \(TPH\) Guidance](#) (RR-036, January 14, 2004).

- **Tier 1:**
 - (1) The analysis and assessment of individual petroleum-related compounds (indicator compounds) using chemical-specific toxicity criteria and physicochemical properties and
 - (2) the analysis for total petroleum hydrocarbons (TPH) oil, gasoline and diesel ranges and
 - (3) Total TPH should not exceed soil saturation concentrations.

- **Tier 2:**
 - (1) The analysis and assessment of individual petroleum-related compounds (indicator compounds) using chemical-specific toxicity criteria and physicochemical properties and
 - (2) TPH fractions using fraction-specific toxicity criteria and physio-chemical properties and
 - (3) Total TPH should not exceed soil saturation concentrations. It should be noted that the decision to assess petroleum contamination by the methods provided in Tier 2 is not a requirement of the proposed process.

Tier 2 is optional and it is provided for those situations where greater site-specific study is desired and warranted.

Each Tier documents the assessment process, determination of human health effects of chemicals of concern, and relevant physicochemical and toxicity values. Once the inputs to the risk assessment have been developed per these guidelines, these petroleum constituents are to be taken through the human health risk assessment procedures. The [DERR Ecological Risk Assessment guidance document](#) should be consulted for appropriate ecological-specific assessment procedures.

Tier I: Analysis of Indicator Compounds in TPH

In Tier 1, the evaluation of petroleum-impacted soil includes the assessment of:

- (1) Individual petroleum-related compounds (indicators) using chemical-specific toxicity criteria and physicochemical properties, and
- (2) Total petroleum hydrocarbons (TPH) (TPH-gasoline range organics (G), TPH-diesel range organics (D), and/or TPH-oil range organics (O)) and
- (3) Evaluate TPH soil saturation concentrations. The indicator compounds required for analysis are dependent on the source of the petroleum product and are summarized in Table 1. (note: if additional additives or oxygenates are found, these should be assessed as additional individual contaminants) The appropriate carbon ranges for the TPH determination (e.g., gasoline, diesel or oil ranges) are also dependent upon the source of the petroleum product and are summarized in Table 1. The physicochemical properties and appropriate composite surrogate toxicity criteria (chronic reference doses) are provided in Tables 2 and 3, respectively. Table 6 contains the TPH soil saturation concentrations.

If the source of petroleum hydrocarbons in soil is light petroleum fractions, such as gasoline, gasohol and naphtha solvents, the soil needs to be analyzed and assessed for benzene, toluene, ethylbenzene, total xylenes, lead, methyl tertiary-butyl ether (MTBE), and TPH.

If the source of petroleum hydrocarbons in soil comes from middle petroleum fractions, such as kerosene, diesel fuel and jet fuel, the soil needs to be analyzed for benzene, toluene, ethylbenzene, total xylenes, MTBE, naphthalene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, acenaphthene, anthracene, fluoranthene, fluorene, pyrene, and TPH.

If the source of petroleum hydrocarbons in soil is from heavy petroleum fractions, such as hydraulic oil, lube oil, and residual fuel oils, the soil needs to be analyzed for benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, acenaphthene, anthracene, fluoranthene, fluorene, pyrene, and TPH. Where petroleum hydrocarbons come from products of heavy petroleum fractions that have been used in a process such as used motor oil, used cutting oil, or hydraulic oil, additional chemicals of concern that may be typical impurities of the used heavy petroleum fractions product should be identified and included in the analysis as appropriate.

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If the source of petroleum hydrocarbons in soils is unknown the soil needs to be analyzed for benzene, toluene, ethylbenzene, total xylenes, MTBE, lead, naphthalene, benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenzo[a,h]anthracene, indeno[1,2,3-cd]pyrene, acenaphthene, anthracene, fluoranthene, fluorene, pyrene, methyl ethyl ketone, methyl isobutyl ketone, and TPH. If the source of petroleum hydrocarbons is across two or more fractions, as in the case of quench oils, the relevant indicator compounds need to be assessed. Also, all associated impurities will need to be assessed.

The identified human health chemicals of concern, including indicator compounds for the TPH, oil, gasoline and diesel ranges, should then be taken through the human health risk assessment process.

In addition to the indicator compounds listed above, the soil saturation concentrations for TPH should also be evaluated to address free-phase product. These have been determined based on the vertical hydraulic conductivity of the unsaturated soil and the specific source of petroleum hydrocarbons in the soil, and are provided in Table 6.

Tier II: Analysis of TPH Fractions and Indicator Compounds

The TPH Fraction and Indicator Method as described in the TPH Criteria Working Group (TPHCWG) Series Volumes 1-5 provides an alternative method for the risk assessment of TPH. The TPH Fraction and Indicator Method is based on the assessment of:

- (1) Individual petroleum-related compounds (indicators) using compound-specific toxicity criteria and physical/chemical properties (as is done in Tier 1);
- (2) TPH fractions using fraction-specific toxicity criteria and physical/chemical properties, followed by the cumulative assessment of the TPH fractions; and
- (3) Evaluate TPH soil saturation concentrations.

The hydrocarbon fractions for the TPH Fraction and Indicator Method were defined by the TPHCWG based on: (1) environmental behavior and (2) equivalent carbon number. Fractions were defined separately for aliphatics and aromatics due to the great variation in environmental behavior between these two chemical groups. To define the TPH fractions, the potential for individual TPH compounds to leach from soil to ground water and to volatilize from soil to air was modeled using equations from the ASTM (1995). The individual constituents were grouped into fractions based on their modeled environmental behavior. Fractions of these TPH constituents were then defined such that the difference in modeled environmental behavior between the fractions was no greater than an order of magnitude.

Each of these TPH constituents was then further subdivided based on the equivalent carbon number index. The equivalent carbon number index is related to: (1) boiling points and (2) retention times in a gas chromatographic column of individual TPH constituents, normalized to the n-alkanes. Fate and transport parameter values were assigned to each fraction based on the average values of the individual constituents comprising the fraction (TPHCWG Series, 1997a). These values are presented in Table 4 (For additional information on how these fractions were defined refer to TPHCWG 1997a).

The indicator compounds and hydrocarbon fractions are identified for different types of petroleum mixtures in Table 1. (Again, if additional oxygenates or additives are found, these should also be evaluated as indicator compounds. The physicochemical properties and fraction-specific chronic surrogate Reference Dose values (RfDs) and surrogate Reference Concentration values (RfCs) are listed in Table 5, respectively. For additional information on the derivation of these values, refer to the TPHCWG 1997b. Fraction-specific analytical data must be obtained to apply this approach. The laboratory requirements are discussed in more detail below.

As in the case of Tier 1, in addition to the indicator compounds listed above, the TPH soil saturation concentrations provided in Table 6 should also be evaluated to address free phase product.

Toxicity Criteria

Ohio EPA's TPH subgroup encountered the same types of problems determining toxicity criteria such as reference doses (RfDs) and slope factors for petroleum products as U.S. EPA. Ohio EPA researched the methods proposed by the TPHCWG, the Massachusetts Department of Environmental Protection and the Louisiana Department of Environmental Quality. It was found that some toxicity data and a few U.S. EPA-derived provisional reference doses (RfDs), reference concentrations (RfCs), and cancer assessments and Agency for Toxic Substances and Disease Registry (ATSDR)-derived

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Minimal Risk Levels are available for whole, un-weathered petroleum products. However, toxicity data for whole petroleum products, that are relatively heterogeneous, are not necessarily applicable to the fractions the receptor is exposed to in the environment.

Limitations exist to using the whole product data including that the type of each petroleum product is variable and depends on the crude oil from which it was refined, differences in the refining processes, and differences in formulation of the final product. The number of individual identified hydrocarbon components of various petroleum products has been estimated to be at least 250. Toxicity data are available for about 95 of these compounds. However, only about 25 were found by the TPHCWG to have U.S. EPA toxicity values or sufficient data to develop toxicity criteria.

For Tier 1 TPH toxicity values in Table 3, the methodology used by the Louisiana Dept. of Environmental Quality (1998) was followed. A conservative surrogate RfD for the TPH fractions comprising the hydrocarbon mixtures was selected to represent the total petroleum hydrocarbon mixture for gasoline (TPH-G), diesel (TPH-D) and oil (TPH-O). TPH-G is represented by the RfDs for Aromatics C>8-C10 and C>10-C12. TPH-D is represented by the RfDs for Aromatics C>8-C10, C>10-C12 and C>12-C16. TPH-O is represented by the RfD for Aromatics C>16-C21 and C>21-C35. Note that the TPH fraction ranges in Table 3 are different from the range of surrogate toxicity values used to address the three main petroleum fractions described in Tier 1; this is a function of the availability and appropriateness of the surrogate toxicity values.

The toxicity criteria recommended here for the TPH fractions in Tier 2 are those recommended through the extensive research conducted by the TPHCWG. Toxicity criteria were derived for each TPH fraction based on the best available toxicity data for individual constituents, well defined petroleum mixtures, and whole petroleum products. Some fractions have the same toxicity criterion due to similarity in toxicity or limitations in the available toxicity data. The toxicity criteria were developed in accordance with U.S. EPA methodologies and provide a representative and conservative estimate of each fraction's toxicity. These values are equivalent to chronic oral Reference Dose values (RfD) and chronic inhalation Reference Concentration values (RfC) (TPHCWG, 1997c). The surrogate RfDs and RfCs for the TPH fractions are presented in Table 5. For additional information on how these toxicity criteria were derived for the TPH fractions refer to the TPHCWG 1997b. In addition, TPHCWG 1999 provides specific guidance on applying this methodology and should be consulted. Toxicity criteria for the individual indicator compounds, including oxygenates and additives, can be obtained via IRIS, or see Ohio EPA DERR Technical Decision Compendium (TDC): [Assessing Compounds Without Formal Toxicity Values Available for Use in Human Health Risk Assessment](#) (April 14, 2004, with April 2, 2010 updates).

Requirement to Cap Standards at Residual Saturation Concentrations

The total petroleum hydrocarbon concentration in the soils should not exceed the soil saturation concentrations to address free-phase product as listed in Table 6.

Laboratory Analytical Requirements

Ohio EPA recommends that the following analytical methods from the most recent edition of the U.S. EPA's [Test Methods for Evaluating Solid Waste \(SW-846\)](#) be applied. These methods were chosen on the basis of their universal availability and acceptability. Other methods may be available for the quantification of these compounds, *e.g.*, ASTM methods. Ohio EPA concurrence on the acceptability of alternative methods should be sought on a case by case basis:

- a. The indicator compounds benzene, toluene, ethyl benzene, *o,m,p* - xylenes should be quantified by Method 8021B or by Method 8260B;
- b. Polycyclic aromatic hydrocarbon indicator compounds should be quantified by Method 8100, Method 8270C, or by Method 8310;
- c. Gasoline range organics, diesel range organics, and oil range organics should be quantified by Method 8015B.
- d. The analysis of the aliphatic and aromatic TPH fractions as required by the Tier 2 Approach should be determined using the [Method for the Determination of Extractable Petroleum Hydrocarbons \(EPH\)](#). Commonwealth of Massachusetts, Department of Environmental Protection (May 2004, Revision 1.1). This method was chosen by Ohio EPA's TPH subgroup because it appears to offer a functional analytical approach to quantifying the fractions in question, and it has been formally validated. It is recognized that this method may not yet be available through certain laboratories, and the ability of the laboratory to conduct the analysis may need to be verified prior to sending out the samples for analyses.

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Additivity

These procedures should be employed assuming that the cumulative risk of a mixture is additive. Risks from indicator compounds, if present, are added to those the TPH fractions. If a mixture of fractions is present, as is often the case, simple additivity of the risks should be assumed.

Weathering

A common view for petroleum is that the weathering which occurs over time will shift the components toward the heavier fractions. Because the heavy end components are generally less toxic, the soil standards initially generated by these procedures will be protective, and may be overly conservative. Weathering should be considered as part of the uncertainty analysis, and overall risk management decisions for the site.

References

[Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites](#), American Society for Testing and Materials, Designation ASTM E 1739-95 (2002).

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