Evaluating Petroleum Hydrocarbon-Contaminated Soil – 11557

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ABSTRACT

At many remediation sites contaminated by petroleum products, concentrations of total petroleum hydrocarbons (TPH) or concentrations of subsets of TPH are used to evaluate the need for corrective actions. Regardless of the type of petroleum product that is present in the soil, the petroleum products start out as an inconsistent mixture of many chemical compounds and then change with time as the individual constituents degrade at different rates to form other compounds. As such, it is not possible to accurately determine the inventory of related potentially hazardous chemical contaminants or their concentrations based only on knowing the type of product or the TPH concentrations. This issue is related to the lack of reliable toxicity information based only on types of petroleum products or fractions of TPH. Thus, it is not possible to reliably assign toxicity information (or risk-based action levels) to petroleum-contaminated soils. However, toxicity information is available for the individual potentially hazardous chemical compounds that may be present in petroleum products. If the concentrations of these potentially hazardous chemical compounds are known, the risk to receptors can be evaluated using conventional risk assessment methodologies. The potentially hazardous chemical compounds that may be present in petroleum products have been identified through numerous analyses of petroleum products. These analyses show significant variation in the chemical composition of petroleum products and identify the range of chemicals and concentrations that may be present in the products. An assessment was performed to (1) identify the chemical constituents in these products that have been identified as hazardous constituents by EPA, (2) determine whether there is a potential for these hazardous constituents to exceed EPA screening levels in soil, and (3) determine analytical methods available to detect these constituents at concentrations below their respective screening levels. At the Nevada National Security Site (NNSS) (formerly the Nevada Test Site), many remediation sites have been closed using a TPH criterion of 100 milligrams per kilogram (mg/kg). These sites were either cleaned up to this criterion or closed in place with use restrictions. The risk-based strategy described in this paper led to the removal of TPH-based use restrictions at 59 sites and the elimination or reduction of the need for corrective actions at many other sites. This represents significant savings in remediation and maintenance/monitoring costs.

INTRODUCTION

Due to the pervasive use of petroleum-based products (e.g., gasoline, diesel, fuel oil, and lubricating oil), inadvertent spills and releases of these products to soil is widespread. Although no federal regulations are in place for petroleum-contaminated soils, nearly all states have cleanup standards that are in some way linked to a general measurement of petroleum contamination in soil called total petroleum hydrocarbons (TPH) [1]. The presence of TPH in soil test results may require corrective action to remove or reduce the risk posed by petroleum contamination to receptors. The TPH soil cleanup standards range from 100 to 20,000 milligrams per kilogram (mg/kg) [2].

The definition of TPH depends on the analytical method used because the TPH measurement is the total concentration of the hydrocarbons extracted and measured by a particular method [3]. Many analytical techniques are available to measure TPH concentrations in the environment, and each may vary in the way hydrocarbons are extracted, cleaned up, and detected. Thus, they each measure slightly different subsets of the petroleum-derived hydrocarbons present in a sample. Variations in reporting TPH include the following:

- Total recoverable petroleum hydrocarbons (TRPH)
- Total petroleum hydrocarbons–diesel-range organics (TPH-DRO)
- Total petroleum hydrocarbons–gasoline-range organics (TPH-GRO)
- Total petroleum hydrocarbons–oil-range organics (TPH-ORO)
- Volatile petroleum hydrocarbons (VPH)
- Extractable petroleum hydrocarbons (EPH)

The term “gasoline” or “diesel” in the above analytical reporting does not necessarily imply that gasoline or diesel is present but simply reflects different categories of TPH based on carbon ranges.

The term TPH may include a broad family of compounds that would require a large undertaking to assess the risk from all the individual chemical constituents. As it is not practical to measure each one of these potential contaminants, several simplifying approaches have been developed and implemented. The major approaches to deal with petroleum product contamination include the following:

- The Massachusetts Department of Environmental Protection (MADEP) approach [4]
- The Total Petroleum Hydrocarbons Criteria Working Group (TPHCWG) approach [3]
- The Agency for Toxic Substances and Disease Registry (ATSDR) approach [5]
- The California State Water Resources Control Board approach [6]
- The American Society for Testing and Materials (ASTM) approach [7]

All of these approaches reduce the comprehensive list of potential petroleum contaminant constituents to a manageable size. These approaches (except for the ASTM approach) accomplish this purpose through some combination of TPH fractionization and indicator compounds. The TPH fractionization is a categorization of the petroleum constituents into a small number of groups (fractions) that have similar properties (based on similarity of chemical composition or physical properties such as mobility). The use of indicator compounds is a conservative simplification based on using a compound that has established risk information to represent the entire contaminant mixture.

The MADEP approach to characterize and evaluate risks posed by petroleum-contaminated sites was developed based on the following observations and conclusions:

- Petroleum products are composed mainly of aliphatic/alicyclic and aromatic hydrocarbon compounds.
- Aromatic hydrocarbons appear to be more toxic than aliphatic compounds.
- The toxicity of aliphatic compounds appears to be related to their carbon numbers/molecular weights.

This approach breaks down TPH into collective aliphatic and aromatic fractions. To support and implement this approach, MADEP developed VPH and EPH analytical methods that differentiate and quantify collective concentrations of aliphatic and aromatic hydrocarbons in soil and water. Specifically, under this approach, the non-cancer toxicity of petroleum-contaminated media is established by (1) determining the collective concentrations of specified ranges of aliphatic and aromatic hydrocarbons, and (2) assigning a toxicity value (e.g., Reference Dose) to each range. Toxicity values are determined based on a review and/or extrapolation of available toxicological data on hydrocarbon mixtures and specific hydrocarbon compounds. Cancer effects are evaluated separately by the identification and quantification of specific hydrocarbon compounds that are designated carcinogens, such as benzene and certain polycyclic aromatic hydrocarbons (PAHs) [4].

The TPHCWG approach was developed to address the large disparity among cleanup requirements used by states at sites contaminated with hydrocarbon materials such as fuels, lubricating oils, and crude oils. These requirements usually focus on TPH with numerical standards ranging from tens to tens of thousands of milligrams of TPH per kilogram of soil. Recognizing that these standards are not based on a scientific assessment of human health risk, TPHCWG members set out to develop scientifically defensible information for establishing soil cleanup levels that are protective of human health at petroleum-contaminated sites. The TPHCWG approach is a combined indicator and grouping or fraction approach. The carcinogenic risk is evaluated using indicator compounds, and the non-carcinogenic risk using fractions. The fractions of TPH are defined based on the potential mobility of the hydrocarbons [3].

The ATSDR approach is generally consistent with the TPHCWG approach, but ATSDR has developed its own set of TPH fraction representatives, many of which overlap those of the TPHCWG [5]. The California Leaking Underground Fuel Tank (LUFT) Program also assesses risk using a modified version of the MADEP fractionated approach as well as screening levels for individual constituents [6]. The ASTM approach relies on the direct analysis of petroleum constituents to evaluate risk to receptors [7].

PROBLEMS WITH THE ASSESSMENT OF TPH RISK

The ASTM approach states that TPH should not be used for risk assessment because the general measure of TPH provides insufficient information about the amounts of individual chemical(s) of concern present [7]. The amount of TPH found in a sample may provide a general indicator of petroleum contamination at that site, but does not directly provide useful information about the risk it may pose to a receptor. The TPHCWG states:

> TPH concentration data cannot be used to quantitatively estimate human health risk. The same concentration of TPH may represent very different compositions and very different risks to human health and the environment. For example, two sites may have TPH measurements of 500 ppm [parts per million] but constituents at one site may include carcinogenic compounds while these compounds may be absent at the other site. The risk at a specific site will change with time as contaminants evaporate, dissolve, biodegrade, and become sequestered. A valid correlation between TPH and risk would have to be site- and time-specific, related to a single spill, and, even then, the correlation might not be the same around the periphery of a plume where the rate of compositional change accelerates [3].

The difficulty of assigning risk to petroleum contamination that starts out as an inconsistent mixture of many chemical constituents is compounded by the fact that the constituents change with time as the individual constituents degrade at different rates to form other compounds. As such, it is not possible to accurately determine the inventory of related potentially hazardous chemical contaminants or their concentrations based only on knowing the type of product or the TPH concentrations. Therefore, the risk associated with fractions of TPH will be specific to the type of petroleum product released and the amount of “weathering” that has taken place.

The TPH fractionization approaches do not take into account the impacts of weathering. Weathering changes the composition of petroleum hydrocarbon soil contamination due to biodegradation, chemical reactions in the soil, the preferential loss of soluble constituents in percolating water, and volatilization of high vapor pressure constituents in the air. The rate of weathering is controlled by site-specific parameters such as temperature, precipitation, infiltration, soil density, depth of contamination, soil chemical composition, and biota present. If the contamination is on the soil surface, photodegradation also can be a significant weathering factor. Another complication in assigning risk to weathered petroleum contamination in soil is that very few data were identified that characterized the composition of weathered petroleum fuel mixtures [3].

NEVADA NATIONAL SECURITY SITE APPROACH

The Industrial Sites and Soils Projects within the Environmental Restoration Project at the Nevada National Security Site (NNSS) implement a risk-based corrective action (RBCA) process as defined in the *Industrial Sites Project Establishment of Final Action Levels* [8]. This process conforms with *Nevada Administrative Code* (NAC) Section 445A.227 [9], which lists the requirements for sites with soil contamination. For the evaluation of corrective actions, NAC Section 445A.22705 [10] requires the use of ASTM Method E1739 [7]. Based on Sections X1.5.4 and X1.42 of Method E1739 [7], potentially hazardous constituents in TPH are individually compared to their corresponding action levels to determine the need for corrective action. This approach eliminates assumptions about contaminants that are present in the various TPH fractions, assumptions about the risk associated with the TPH fractions, and any assumptions about the amount of weathering (or lack thereof) by directly measuring contaminants that are present in the soil. The difficulty of this approach is in the ability to measure all of the individual chemical contaminants contained in petroleum products that may have been released to the soil. As it is not practical to measure each one of these potential contaminants, a potential contaminant list was developed for each of the following four petroleum products: (A) diesel, (B) gasoline, (C) motor oil, and (D) fuel oil.

DETERMINATION OF THE POTENTIAL CONTAMINANT LIST

The potential contaminant list for each of the four petroleum products was developed from comprehensive lists of constituents in petroleum products that were compiled by the TPHCWG. The TPHCWG contacted government and private sector laboratories involved in petroleum hydrocarbon mixture analysis and searched the published technical literature. Individuals at the U.S. Environmental Protection Agency (EPA), U.S. Air Force, U.S. Navy, U.S. Department of Energy, and the oil industry research centers were contacted, and a comprehensive search of the technical literature was performed to identify all available composition data for the most common petroleum-based fuels, crude oil, and lubricating oils [3].

From these comprehensive lists of constituents, the potential contaminant lists were developed to include the constituents that met the following criteria:

1. They were listed as being of environmental concern by EPA in Appendix IX to Title 40 of the *Code of Federal Regulations* (CFR) Part 264 [11] (Note: Appendix IX to 40 CFR 264 comprises those compounds listed in Appendix VIII to 40 CFR 261 [12] for which it is feasible to analyze in groundwater samples, plus 17 chemicals that are routinely monitored for in the Superfund program).
2. They were listed on the EPA Regions 3, 6, and 9 Screening Levels for Chemical Contaminants list [13].
3. The concentration of the constituent in the petroleum product was sufficient to exceed the EPA Regions 3, 6, and 9 Screening Level when released to the soil.

The constituents of gasoline, diesel, fuel oil, and motor oil are listed in Table I. Table I also identifies those petroleum product constituents that were identified as being potentially hazardous constituents based on being listed in either Appendix IX to 40 CFR 264 [11] or the EPA regional screening level table [13]. Also presented is a conservative estimate of the concentration of each constituent within each of the petroleum products.

Table I. Constituents of Selected Petroleum Products.

Compound	Product (mg/kg)	40 CFR 264 Appendix IX?	EPA Region 9 Screening Levels?
A. DIESEL FUEL NO. 2			
1,2-Dimethylcarbazole	8.37[a]	No	No
1,3,5-Trimethylbenzene	3,115[a]	No	Yes
1,3-Dimethylcarbazole	5.21[a]	No	No
1,3-Dimethylnaphthalene	11,536[a]	No	No
1,4-Dimethylcarbazole	17.2[a]	No	No
1,4-Dimethylnaphthalene	2,108[a]	No	No
1,5-Dimethylnaphthalene	3,407[a]	No	No
1,6-Dimethyldibenzothiophene	105[a]	No	No
1-Methyl-4-isopropylbenzene	260[b]	No	No
1-Methyl-7-isopropylphenanthrene	16.0[a]	No	No
1-Methylcarbazole	21.7[a]	No	No
1-Methylnaphthalene	6,542[a]	No	Yes
1-Methylphenanthrene	105[a]	No	No
1-Methylpyrene	6.05[a]	No	No
2,6-Dimethyldibenzothiophene and 2-Ethyldibenzothiophene	273[a]	No	No
2-Aminoanthracene	5.62[a]	No	No
2-Aminophenanthrene	3.45[a]	No	No
2-Azapyrene	1.92[a]	No	No
2-Ethyldibenzothiophene	275[a]	No	No
2-Methylanthracene	95.2[a]	No	No
2-Methylcarbazole	7.09[a]	No	No
2-Methyldodecane	3,608[a]	No	No
2-Methylnaphthalene	11,981[a]	Yes	Yes
2-Methylphenanthrene	1,707[a]	No	No
2-Methylpyrene	5.35[a]	No	No
2-Methyltetradecane	5,608[a]	No	No
2-Phenylindole	5.04[a]	No	No
3-Aminophenanthrene	2.68[a]	No	No
3-Methylcarbazole	5.61[a]	No	No
3-Methylphenanthrene	67.5[a]	No	No
3-Methyltridecane	2,326[a]	No	No
3-Methylundecane	2,218[a]	No	No
4- & 9-Methylphenanthrene	141[a]	No	No
4-Aminophenanthrene	5.21[a]	No	No
4-Methylcarbazole	10.8[a]	No	No
6-Phenylquinoline	9.38[a]	No	No
9-Cyanoanthracene	9.07[a]	No	No
9-Cyanophenanthrene	9.47[a]	No	No
9-Phenylcarbazole	5.32[a]	No	No
Anthracene	93.5[a]	Yes	Yes
Arsenic	0.071[c]	Yes	Yes
Benz(a)anthracene	2.32[a]	Yes	Yes
Benzene	843[a]	Yes	Yes
Benzo(a)fluorene	5.68[a]	No	No
Benzo(a)pyrene	5.54[a]	Yes	Yes
Benzo(b+k)fluoranthene	0.759[a]	Yes	Yes
Benzo(e)pyrene	0.851[a]	No	No
Benzo(g,h,i)fluoranthene	1.80[a]	No	No

Compound	Product (mg/kg)	40 CFR 264 Appendix IX?	EPA Region 9 Screening Levels?
Benzo(g,h,i)perylene	0.227[a]	Yes	No
Benzo[def]carbazole	4.33[a]	No	No
Biphenyl	1,200[b]	No	Yes
Cadmium	0.490[c]	Yes	Yes
Chromium	1.70[c]	Yes	Yes
Chrysene	0.450[c]	Yes	Yes
Chrysene and Triphenylene	2.34[a]	No	No
Cyclopenta(cd)pyrene	1.48[a]	No	No
Dibenzothiophene	170[a]	No	No
Ethylbenzene	1,272[a]	Yes	Yes
Ethylhexyl nitrate	2,000[c]	No	No
Fluoranthene	95.4[a]	Yes	Yes
Fluorene	1,073[a]	Yes	Yes
Indeno(1,2,3-cd)pyrene	0.381[a]	Yes	Yes
Iron	37.0[c]	No	Yes
m+p-Xylenes	3,916[a]	No	No
Manganese	3.20[c]	No	Yes
Molybdenum	0.140[c]	No	Yes
Naphthalene	3,169[a]	Yes	Yes
n-Butylbenzene	460[b]	No	No
n-Decane	10,224[a]	No	No
n-Docosane	4,630[a]	No	No
n-Dodecane	20,819[a]	No	No
n-Eicosane	7,889[a]	No	No
n-Heneicosane	6,310[a]	No	No
n-Heptadecane	25,378[a]	No	No
n-Hexadecane	26,378[a]	No	No
n-Nonadecane	11,910[a]	No	No
n-Nonane	4,482[a]	No	Yes
n-Octadecane	18,277[a]	No	No
n-Octane	1,300[b]	No	No
n-Pentadecane	28,864[a]	No	No
n-Propylbenzene	542[a]	No	Yes
n-Tetracosane	3,500[c]	No	No
n-Tetradecane	23,091[a]	No	No
n-Tridecane	24,158[a]	No	No
n-Undecane	18,039[a]	No	No
o-Xylene	792[a]	No	Yes
Phenanthrene	1,236[a]	Yes	No
Phytane	5,654[a]	No	No
Picene	0.370[a]	No	No
Pristane	7,175[a]	No	No
Pyrene	73.3[a]	Yes	Yes
Toluene	4,021[a]	Yes	Yes
Triphenylene	3.30[c]	No	No
Zinc	3.10[c]	Yes	Yes
B. GASOLINE			
1,2,4-Trimethylbenzene	30,967[a]	No	Yes
1,3,5-Trimethylbenzene	10,113[a]	No	Yes
1,3-Butadiene	38.3[a]	No	Yes
1-Methyl-2-ethylbenzene	7,338[a]	No	No
1-Methyl-3-ethylbenzene	18,595[a]	No	No

Compound	Product (mg/kg)	40 CFR 264 Appendix IX?	EPA Region 9 Screening Levels?
1-Methyl-4-ethylbenzene	8,268[a]	No	No
1-Methylnaphthalene	724[a]	No	Yes
2,2,4-Trimethylpentane	24,878[a]	No	No
2,2-Dimethylbutane	5,064[a]	No	No
2,3,3-Trimethylpentane	6,853[a]	No	No
2,3,4-Trimethylpentane	10,057[a]	No	No
2,3-Dimethylbutane	10,327[a]	No	No
2,3-Dimethylhexane	4,032[a]	No	No
2,4-Dimethylhexane	4,544[a]	No	No
2,4-Dimethylpentane	8,583[a]	No	No
2-Methyl-1-butene	5,564[a]	No	No
2-Methyl-2-butene	11,327[a]	No	No
2-Methylhexane	30,967[a]	No	No
2-Methylnaphthalene	1,864[a]	Yes	Yes
2-Methylpentane	40,250[a]	No	No
3-Methylheptane	7,738[a]	No	No
3-Methylhexane	17,551[a]	No	No
3-Methylpentane	25,804[a]	No	No
Benzene	19,610[a]	Yes	Yes
cis-2-Butene	3,201[a]	No	No
cis-2-Pentene	4,019[a]	No	No
Cyclohexane	4,038[a]	No	Yes
Cyclopentane	4,864[a]	No	No
Ethylbenzene	17,551[a]	Yes	Yes
Isobutane	17,610[a]	No	No
Isopentane	81,530[a]	No	No
Methylcyclohexane	5,993[a]	No	No
Methylcyclopentane	18,595[a]	No	No
Methyl-tert-butylether	3,449[a]	No	Yes
m-Xylene	47,488[a]	No	Yes
Naphthalene	2,585[a]	Yes	Yes
n-Butane	48,637[a]	No	No
n-Heptane	11,357[a]	No	No
n-Hexane	24,789[a]	No	Yes
n-Pentane	40,280[a]	No	Yes
o-Xylene	25,833[a]	No	Yes
p-Xylene	19,610[a]	No	Yes
Toluene	83,679[a]	Yes	Yes
trans-2-Butene	3,718[a]	No	No
trans-2-Pentene	7,423[a]	No	No
C. MOTOR OIL			
1,1,1-Trichloroethane	2,800[b]	Yes	Yes
1,3,5-Trimethylnaphthalene	37.0[b]	No	No
1,5-Dimethylnaphthalene	56.0[b]	No	No
1-Methylnaphthalene	57.0[b]	No	Yes
1-Methylpyrene	1.30[c]	No	No
2-Ethylnaphthalene	58.0[b]	No	No
4-Methylpyrene	1.90[c]	No	No
4-Phenyltoluene	6.00[b]	No	No
Anthracene	46.7[a]	Yes	Yes
Arsenic	17.0[b]	Yes	Yes
Barium	210[b]	Yes	Yes

Compound	Product (mg/kg)	40 CFR 264 Appendix IX?	EPA Region 9 Screening Levels?
Benz(a)anthracene	69.6[a]	Yes	Yes
Benzene	960[b]	Yes	Yes
Benzo(a)fluorene	2.70[b]	No	No
Benzo(a)pyrene	18.0[a]	Yes	Yes
Benzo(b)fluoranthene	0.430[b]	Yes	Yes
Benzo(b)fluorene	1.60[c]	No	No
Benzo(b)naptho (2,1-d) thiophene	3.96[a]	No	No
Benzo(c)fluorene	0.500[c]	No	No
Benzo(c)phenanthrene	0.140[c]	No	No
Benzo(e)pyrene	19.4[a]	No	No
Benzo(g,h,i)perylene	31.1[a]	Yes	No
Benzo(k)fluoranthene	2.06[a]	Yes	Yes
Benzonaphthothiophene	0.390[c]	No	No
Biphenyl	83.0[b]	No	Yes
Cadmium	3.10[b]	Yes	Yes
Chromium	28.0[b]	Yes	Yes
Chrysene	82.1[a]	Yes	Yes
Chrysene and Triphenylene	26.4[a]	No	No
Coronene	3.06[a]	No	No
Cyclopenta(cd)pyrene	0.890[c]	No	No
Dibenz(a,c)anthracene	0.080[c]	No	No
Dibenzothiophene	0.900[c]	No	No
Dichlorodifluoromethane	370[c]	Yes	Yes
Ethylbenz(a)anthracene	0.740[c]	No	No
Fluoranthene	43.9[a]	Yes	Yes
Fluorene	95.5[a]	Yes	Yes
Indeno(1,2,3-cd)pyrene	40.6[a]	Yes	Yes
Lead	2,600[b]	Yes	Yes
Methylbenzo(mno)fluoranthene	0.340[c]	No	No
Naphthalene	1,001[a]	Yes	Yes
n-Dodecane	140[c]	No	No
n-Eicosane	2,200[b]	No	No
n-Heptadecane	530[b]	No	No
n-Hexadecane	280[b]	No	No
n-Nonadecane	820[b]	No	No
n-Octadecane	640[b]	No	No
Nonylcyclohexane	22.0[b]	No	No
n-Pentadecane	140[b]	No	No
n-Tetradecane	150[b]	No	No
n-Tridecane	230[b]	No	No
Octylcyclohexane	11.0[b]	No	No
Other Benzonaphthothiophenes	1.40[c]	No	No
Perylene	3.87[a]	No	No
Phenanthrene	151[a]	Yes	No
Phenanthro(4,4a,4b,5-bcd)thiophene	0.410[c]	No	No
Phenylnaphthalene	1.00[c]	No	No
Phytane	370[b]	No	No
Pristane	280[b]	No	No
Pyrene	107[a]	Yes	Yes
Terphenyl	0.140[c]	No	No
Tetrachloroethylene (PCE)	1,400[b]	Yes	Yes
Tetralin	24.0[b]	No	No

Compound	Product (mg/kg)	40 CFR 264 Appendix IX?	EPA Region 9 Screening Levels?
Toluene	2,200[b]	Yes	Yes
trans-Decalin	10.0[c]	No	No
Trichloroethylene (TCE)	1,400[b]	Yes	Yes
Trichlorotrifluoroethane	63,000[c]	No	No
Triphenylene	2.50[c]	No	No
Triphenylene(4,4a,4b,5-bcd)thiophene	0.120[c]	No	No
Zinc	980[b]	Yes	Yes
D. FUEL OIL NO. 6			
1-Methylphenanthrene	43.0[c]	No	No
2-Methylphenanthrene	830[c]	No	No
Anthracene	50.0[c]	Yes	Yes
Benz(a)anthracene	1,966[a]	Yes	Yes
Benzo(a)pyrene	44.0[c]	Yes	Yes
Benzo(b+k)fluoranthene	440[c]	No	No
Benzo(e)pyrene	10.0[c]	No	No
Chrysene	1,929[a]	Yes	Yes
Fluoranthene	240[c]	Yes	Yes
Indeno(1,2,3-cd)pyrene	100[c]	Yes	Yes
Naphthalene	124[a]	Yes	Yes
n-Decane	150[b]	No	No
n-Docosane	1,573[a]	No	No
n-Dodecane	340[b]	No	No
n-Dotriacontane	510[b]	No	No
n-Eicosane	1,573[a]	No	No
n-Heneicosane	1,573[a]	No	No
n-Hentricontane	662[a]	No	No
n-Heptacosane	1,166[a]	No	No
n-Heptadecane	1,792[a]	No	No
n-Heptatriacontane	99.0[b]	No	No
n-Hexacosane	1,199[a]	No	No
n-Hexadecane	1,709[a]	No	No
n-Hexatriacontane	110[b]	No	No
Nickel	89.0[c]	Yes	Yes
n-Nonacosane	968[a]	No	No
n-Nonadecane	1,725[a]	No	No
n-Nonane	59.0[b]	No	Yes
n-Nonatriacontane	76.0[b]	No	No
n-Octacosane	1,048[a]	No	No
n-Octadecane	1,588[a]	No	No
n-Octatriacontane	87.0[b]	No	No
n-Pentacosane	1,292[a]	No	No
n-Pentadecane	1,489[a]	No	No
n-Pentatriacontane	150[b]	No	No
n-Tetracontane	55.0[b]	No	No
n-Tetracosane	1,503[a]	No	No
n-Tetradecane	1,372[a]	No	No
n-Tetratriacontane	300[b]	No	No
n-Triacontane	867[a]	No	No
n-Tricosane	1,516[a]	No	No
n-Tridecane	885[a]	No	No
n-Tritriacontane	360[b]	No	No
n-Undecane	250[b]	No	No

Compound	Product (mg/kg)	40 CFR 264 Appendix IX?	EPA Region 9 Screening Levels?
Perylene	22.0[c]	No	No
Phenanthrene	439[a]	Yes	No
Phytane	710[b]	No	No
Pristane	620[b]	No	No
Pyrene	23.0[c]	Yes	Yes
Triphenylene	31.0[c]	No	No
Vanadium	73.0[c]	Yes	Yes

[a]Based on the 95% upper confidence limit (UCL) of measurements
[b]Based on the maximum measurement
[c]Based on the average measurement

As demonstrated by the TPHCWG's Composition of Petroleum Mixtures tables, the petroleum products are variable mixtures of large numbers of components with significant variations within different samples of the same product type. As such, these tables listed the number of samples from which compositional data were derived as well as the statistics of the datasets (e.g., average, minimum, maximum, and variability) for each of the petroleum products and their individual constituents. The concentration of each constituent for each of the petroleum products listed in Table I was conservatively estimated based on the following hierarchy:

- The 95th upper confidence limit (UCL) of the average concentration for those constituents with available statistical information
- The maximum concentration if statistical information was not available
- The average concentration if a maximum was not listed

All of the petroleum product constituents of diesel, gasoline, motor oil, and fuel oil that are listed in either Appendix IX to 40 CFR 264 [11] or the EPA regional screening level table [13] are defined as the constituents of potential environmental concern and listed in Table II.

POTENTIAL CONTAMINANTS OF CONCERN AT SOIL RELEASE SITES

The constituents of potential environmental concern in the petroleum products that are present in sufficient concentrations to result in a soil concentration exceeding the EPA screening levels are identified and shown in boldface in Table II. The potential concentration of each constituent in soil (i.e., soil contaminant) was calculated based on the concentration of the constituent in the petroleum product and the concentration of the petroleum product in soil using the following equation:

$$C_{cs} = C_{ps} \times C_{cp}, \quad \text{(Eq. 1)}$$

where C_{cs} is the resulting potential concentration of the constituent in soil at saturation (milligrams of constituent per kilogram of soil), C_{ps} is the saturated concentration of the petroleum product in soil (kilograms of petroleum product per kilogram of soil), and C_{cp} is the concentration of the constituent in the petroleum product (milligrams of constituent per kilogram of petroleum product).

Table II. Constituents of Potential Environmental Concern.

Compound	Action Level (mg/kg)	Sat. Soil (mg/kg)	Compound	Action Level (mg/kg)	Sat. Soil (mg/kg)
A. DIESEL FUEL NO. 2					
1,3,5-Trimethylbenzene	10,200	576	Fluoranthene	22,000	17.7
1-Methylnaphthalene	**98.7**	**1,210**	Fluorene	22,000	199
2-Methylnaphthalene	4,090	2,220	Indeno(1,2,3-cd)pyrene	2.11	0.0705
Anthracene	165,000	17.3	Iron	715,000	6.85
Arsenic	1.59	0.0131	Manganese	22,700	0.592

Compound	Action Level (mg/kg)	Sat. Soil (mg/kg)	Compound	Action Level (mg/kg)	Sat. Soil (mg/kg)
Benz(a)anthracene	2.11	0.429	Molybdenum	5,110	0.0259
Benzene	**5.37**	**156**	**Naphthalene**	**18**	**586**
Benzo(a)pyrene	**0.211**	**1.03**	**n-Nonane**	**234**	**829**
Benzo(b)fluoranthene	2.11	0.14	n-Propylbenzene	21,500	100
Benzo(g,h,i)perylene	16,500	0.042	o-Xylene	19,300	147
Biphenyl	51,100	222	Phenanthrene	165,000	229
Cadmium	798	0.0907	Pyrene	16,500	13.6
Chromium	45.5	0.315	Toluene	45,200	744
Chrysene	211	0.0833	Zinc	307,000	0.574
Ethylbenzene	**26.8**	**235**			
B. GASOLINE					
1,2,4-Trimethylbenzene	**261**	**5,060**	**Methyl-tert-butylether**	**215**	**563**
1,3,5-Trimethylbenzene	10,200	1,650	m-Xylene	16,600	7,750
1,3-Butadiene	**0.262**	**6.25**	**Naphthalene**	**18**	**422**
1-Methylnaphthalene	**98.7**	**118**	**n-Hexane**	**2,620**	**4,050**
2-Methylnaphthalene	4,090	304	**n-Pentane**	**3,670**	**6,580**
Benzene	**5.37**	**3,200**	o-Xylene	19,300	4,220
Cyclohexane	29,500	659	p-Xylene	16,900	3,200
Ethylbenzene	**26.8**	**2,870**	Toluene	45,200	13,700
C. Motor Oil					
1,1,1-Trichloroethane	38,100	549	Chrysene	211	16.1
1-Methylnaphthalene	98.7	11.2	Dichlorodifluoromethane	781	72.5
Anthracene	165,000	9.15	Fluoranthene	22,000	8.6
Arsenic	**1.59**	**3.33**	Fluorene	22,000	18.7
Barium	191,000	41.1	**Indeno(1,2,3-cd)pyrene**	**2.11**	**7.95**
Benz(a)anthracene	**2.11**	**13.6**	Lead	800	509
Benzene	**5.37**	**188**	**Naphthalene**	**18**	**196**
Benzo(a)pyrene	**0.211**	**3.53**	Phenanthrene	165,000	29.6
Benzo(b)fluoranthene	2.11	0.0842	Pyrene	16,500	21
Benzo(g,h,i)perylene	16,500	6.09	**Tetrachloroethylene (PCE)**	**2.64**	**274**
Benzo(k)fluoranthene	21.1	0.404	Toluene	45,200	431
Biphenyl	51,100	16.3	**Trichloroethylene (TCE)**	**14.2**	**274**
Cadmium	798	0.607	Zinc	307,000	192
Chromium	45.5	5.49			
D. Fuel Oil No. 6					
Anthracene	165,000	9.25	**Naphthalene**	**18**	**22.9**
Benz(a)anthracene	**2.11**	**364**	Nickel	19,700	16.5
Benzo(a)pyrene	**0.211**	**8.14**	n-Nonane	234	10.9
Chrysene	**211**	**357**	Phenanthrene	165,000	81.2
Fluoranthene	22,000	44.4	Pyrene	16,500	4.26
Indeno(1,2,3-cd)pyrene	**2.11**	**18.5**	Vanadium	71.5	13.5

The concentrations of each constituent in each of the petroleum products are listed in Table I. The concentration of the petroleum product in soil will depend on physical properties of the soil (i.e., soil texture and porosity), the petroleum product (e.g., viscosity, density, surface tension), and the amount of saturation. However, to identify potential petroleum contaminants in soil, the potential concentration of the petroleum product in soil was conservatively estimated based on a saturation of the available soil pore space by the petroleum product.

$$C_{ps} = \theta_{mo},$$

$$\theta_{mo} = \theta_{vo} \times \rho_o / \rho_b, \quad \text{(Eq. 2)}$$

where θ_{mo} is the mass petroleum product concentration in soil (kilograms of petroleum product per kilogram of soil), θ_{vo} is the residual petroleum product volume fraction (cubic meters of petroleum product per cubic meter of soil), ρ_o is the density of the petroleum product (kilograms of petroleum product per cubic meter), and ρ_b is the bulk density of soil (kilograms of soil per cubic meter).

Typical soil physical properties and the potential soil content of petroleum products at saturation are listed in Table III. The volumetric fraction of soil occupied by petroleum product was calculated based on the total amount of soil pore space available to be occupied by a petroleum product infiltrating into the soil and the fraction of the available pore space that is filled by the petroleum product [14].

$$\theta_{vo} = p_a \times s_r, \quad \text{(Eq. 3)}$$

where p_a is the available porosity of soil (cubic centimeters of available pore space per cubic centimeter of soil), and s_r is the volumetric fraction of available pore space occupied by petroleum product (cubic meters of petroleum product per cubic meter of pore space). For the purposes of this paper, it was assumed that 100% of available pore space was filled with petroleum product (i.e., $s_r = 1$).

The available soil pore space was estimated as the soil pore space not occupied by air, water, or organic material. The amount of total pore space was calculated based on typical estimates of soil bulk density. When more than one fluid exists in a porous media, the fluids compete for pore space [17]. Therefore, higher soil water contents would retain less of the spilled liquid hydrocarbons. The amount of pore space occupied by soil water was conservatively estimated at the permanent wilting point. The permanent wilting point is defined as the volumetric water content at which plants can no longer extract water from the soil (and thus permanently wilt and die). The volumetric water content of soil was converted from reported typical mass water contents at the permanent wilting point using soil bulk density and the density of water. Fractions of soil pore space occupied by organic matter and other biota were conservatively ignored (i.e., a larger fraction of soil pore space is then available to contain the petroleum product). This parameter was calculated using the following equation:

$$p_a = 1 - \left(\rho_b / \rho_p\right) - \theta_v,$$

$$\theta_v = \theta_{mwp} \times \rho_b / \rho_w, \quad \text{(Eq. 4)}$$

where p_a is the available porosity of soil (cubic meters of available pore space per cubic meter of soil), ρ_p is the particle density of soil (kilograms of solids per cubic meter), θ_{mwp} is the mass water content of soil at the permanent wilting point (kilograms of water per kilogram of soil), and ρ_w is the bulk density of water (kilograms of water per cubic meter).

The calculation of the potential concentrations in the soil of each constituent for each petroleum product as reported in Table III was conservatively based on saturation of the available pore space by the petroleum product. This may be a reasonable assumption if the spill is fresh and the soil is saturated by the product. For sites contaminated from historical releases, saturation is not a reasonable assumption. Petroleum products in the vadose zone tend to infiltrate through the soil in a period of days or weeks, which leads to the conclusion that nonaqueous phase liquid (NAPL) present in a vadose-zone soil months or years after a spill event is by definition immobile residual [18]. For these types of release sites, the saturation values listed in Table III should be adjusted using reported residual saturation values. Residual saturation values represent the amount of petroleum product retained in the soil after the soil was initially saturated with the product and allowed to drain. Residual saturation is expressed as the ratio of the soil

void space occupied by the petroleum product to the total pore space (volume of product divided by the total soil pore volume) [17]. It can also be influenced by the amount of pore space occupied by soil water that is not displaced by the petroleum product. Residual saturation values are generally higher for fine-grained soils, for dry soils, and for more viscous fluids.

Table III. Typical Soil Physical Properties and Potential Soil Content of Petroleum Products

Texture	Average Soil Bulk Density[a]	Total Porosity[b] (%)	Mass Water Content Wilting Point[c] (%)	Volumetric Water Content[d] (%)	Residual Available Porosity[e] (%)	Gasoline (% mass in soil)g	Diesel Fuel No. 2 (% mass in soil)[f]	Fuel Oil No. 6 (% mass in soil)[i]	Motor Oil (% mass in soil)[h]
Sand	1.71	35.5	1	1.4	34.1	15.0	17.0	17.0	17.9
Loamy Sand	1.66	37.4	2	2.5	34.9	15.8	17.9	17.9	18.9
Sandy Loam	1.53	42.3	5	6.9	35.4	17.3	19.7	19.7	20.8
Silt	1.45	45.3	8	10.9	34.4	17.8	20.2	20.2	21.4
Silt Loam	1.41	46.8	10	13.8	33.0	17.5	19.9	19.9	21.0
Loam	1.42	46.4	11	15.1	31.4	16.6	18.8	18.8	19.9
Sandy Clay Loam	1.4	47.2	14	20.0	27.1	14.5	16.5	16.5	17.5
Silty Clay Loam	1.27	52.1	17	21.1	31.0	18.3	20.7	20.7	22.0
Clay Loam	1.31	50.6	17	22.8	27.8	15.9	18.0	18.0	19.1
Sandy Clay	1.32	50.2	20	26.9	23.3	13.2	15.0	15.0	15.9
Silty Clay	1.22	54.0	20	24.9	29.1	17.9	20.3	20.3	21.4
Clay	1.21	54.3	23	28.3	26.0	16.1	18.3	18.3	19.4

[a]Calculated using the Soil Bulk Density Calculator (U.S. Texture Triangle) available on the Pedosphere.com website [15].
[b]Calculated using bulk density and a particle density of 2.65 grams per cubic centimeter (g/cm^3).
[c]Source: Campbell [16].
[d]Calculated from mass water content and bulk density.
[e]Total porosity minus volumetric water content.
[f]Calculated using available porosity volume, bulk density, and density of fuel oils (0.85 g/cm^3) [5].
[g]Calculated using available porosity volume, bulk density, and density of gasoline (0.75 g/cm^3) [5].
[h]Calculated using available porosity volume, bulk density, and density of mineral oil (0.9 g/cm^3) [5].
[i]Calculated using available porosity volume, bulk density, and density of fuel oils (0.85 g/cm^3) [5].

Based on these results, the potential contaminants of concern for each of the petroleum products are listed in Table IV for soil that is saturated with the petroleum product. This table also lists the EPA analytical method that can be used to detect soil concentrations of each of these potential contaminants [19]. Except for n-nonane, n-pentane, and arsenic, these potential contaminants can be evaluated using only EPA methods 8260 and 8270. For historical releases, n-nonane and n-pentane can be eliminated from consideration based on their volatility, solubility, and rapid biodegradation [20]. Arsenic can be removed

from consideration if background concentrations in soil are greater than the 1.59 mg/kg screening level (as is the case at NNSS, where background concentrations of arsenic are approximately 23 mg/kg).

Table IV. Petroleum Soil Contaminants of Potential Concern.

Compound	Analytical Method[a]	Diesel Fuel No. 2	Gasoline	Motor Oil	Fuel Oil No.6
1,2,4-Trimethylbenzene	8260		x		
1,3-Butadiene	8260		x		
1-Methylnaphthalene	8270	x	x		
Arsenic	6010			x	
Benz(a)anthracene	8270			x	x
Benzene	8260	x	x	x	
Benzo(a)pyrene	8270	x		x	x
Chrysene	8270				x
Ethylbenzene	8260	x	x		
Indeno(1,2,3-cd)pyrene	8270			x	x
Methyl-tert-butylether	8260		x		
Naphthalene	8270	x	x	x	x
n-Hexane	8260		x		
n-Nonane	EPA TO-15	x			
n-Pentane	ASTM 5134		x		
Tetrachloroethylene (PCE)	8260			x	
Trichloroethylene (TCE)	8260			x	

[a]See the EPA publication SW-846 [19].

Although these data were generated from the analysis of fresh products, identifying the constituents that have the potential to exceed EPA screening levels based on these concentrations is conservative because the overall environmental hazard posed by weathered petroleum mixtures is considered less than that posed by fresh mixtures [3]. This is due to the depletion of the more water soluble, more volatile, and more easily biodegradable compounds.

APPLICATION TO HISTORICAL AND CURRENT RELEASES

At the NNSS, many remediation sites were closed using a TPH criterion of 100 mg/kg. These sites were either cleaned up to this criterion or closed in place with use restrictions. The risk-based strategy described in this paper led to the removal of use restrictions at 59 sites and the elimination or reduction of the need for corrective actions at many other sites. This represents significant savings in remediation and future maintenance/monitoring costs.

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