

Cleanup Standards for Petroleum Hydrocarbons. Part 1. Review of Methods and Recent Developments

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ABSTRACT: Many states across the U.S. use the total petroleum hydrocarbon (TPH) measurement as a regulatory tool for setting cleanup standards for underground storage tank sites and other petroleum-related sites requiring cleanup. In Part 1 of this article, alternative techniques for developing site-specific cleanup standards for petroleum hydrocarbons are reviewed, including the use of chemical fingerprinting, constituent analysis, and risk assessment methods that address hydrocarbons found in the environment. New developments in standard setting for petroleum hydrocarbons are described, including risk-based standards for hydrocarbon mixtures and ecological risk-based approaches. In Part 2 of this article, the cost-effectiveness and accuracy of the most commonly used of these approaches will be evaluated by comparing a generic TPH cleanup standards approach with site-specific cleanup standards approaches for two actual sites in Washington State, a neighborhood gas station and a former bulk fuel storage facility.

KEY WORDS: petroleum, cleanup standards, contaminated sites, risk assessment

I. INTRODUCTION

Many states, including Washington, Oregon, and California, use the total petroleum hydrocarbon (TPH) measurement as a regulatory tool for setting cleanup standards for petroleum-contaminated sites, such as gas stations and refineries (WDOE 1991a; ODEQ 1990; CWRCB 1988). The TPH measurement represents the total concentration of a broad spectrum of petroleum hydrocarbon constituents that can be detected by the TPH analysis. Generic cleanup standards are typically set for ranges of compounds detected by the TPH analysis, without identifying the specific chemicals or chemical classes present. In particular, petroleum hydrocarbons detected within specified ranges (as determined by the number of carbons present in the component chemicals) are labeled as “TPH-gasoline” or “TPH-diesel” and are often regulated by a single numerical standard.

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Such numerical standards, while offering some advantages, have several important limitations. For example, the toxicities and mobilities of the specific chemicals present within the detected range, and the corresponding hazards posed by those chemicals, may vary widely from site to site. Moreover, the mixture present at a specific site may not actually be gasoline or diesel, but another petroleum mixture whose constituents have a similar range of molecular weights. As a result, the actual risk associated with a reported TPH concentration may vary greatly from site to site.

A variety of analytical methods are used to measure TPH, and these methods must be calibrated to specific mixtures. In addition, petroleum mixtures such as diesel and gasoline undergo various physical, chemical, and biological processes in the environment that alter the composition, mobility, and toxicity of these mixtures. As a result, the actual TPH concentration may differ from the reported TPH concentration. TPH concentrations reported at different sites may not be comparable because of differences in the analytical method used, the specific petroleum compounds present, and the degree of weathering and/or transport the petroleum has undergone in the environment.

TPH standards have several advantages from a regulatory and compliance standpoint. They are simple and easy to use, and appear to promote consistency among cleanups by the use of a single numerical standard. In addition, the TPH measurement itself is inexpensive, potentially saving money in characterizing uncomplicated sites and evaluating compliance with cleanup standards (Dixon 1992). However, generic TPH standards may result in an inefficient allocation of cleanup resources, because they do not identify and address actual risks at a site, potentially resulting in an overprotective or underprotective cleanup. These deficiencies can be addressed through the use of alternative approaches to setting cleanup standards that take into account site- and chemical-specific factors.

This article addresses these issues, beginning with Part 1, a review of standard methods as well as newer, innovative methods that may be used to set cleanup standards for petroleum hydrocarbons. The cost-effectiveness and protectiveness of generic TPH-based standards for petroleum hydrocarbons relative to site-specific, health-based methods of setting standards are explored through the use of two case studies in Part 2 (to be published in the September 1993 issue of the *Journal of Soil Contamination*).

II. GENERIC STANDARDS BASED ON THE TOTAL PETROLEUM HYDROCARBON ANALYSIS

The TPH analysis typically uses infrared spectroscopy or gas chromatography (GC) with a flame ionization detector (FID) or a photoionization detector (PID) to provide a measurement of the bulk concentration of petroleum hydrocarbons present in a sample. These methods (EPA Methods 418.1 [U.S. EPA 1986] and

8015 modified [e.g., CWRCB 1988; WDOE 1991a]), when calibrated using an appropriate standard, can determine the concentration of a chemical or range of component chemicals with specific molecular weights. The GC trace can be used to a limited extent to identify specific chemicals or petroleum mixtures using a “fingerprint” analysis (see Section III, below). However, the results of the TPH analysis are usually reported simply as the concentration of “gasoline” or “diesel” TPH present.

Substantial error and analytical variabilities associated with these methods have been documented (Douglas *et al.* 1993). To standardize analytical and reporting procedures, several states (e.g., Washington and California) have published standard methods for use in analyzing samples from contaminated sites (CWRCB 1988; WDOE 1991a). However, the methods used by different states are not identical, and analysis of the same sample by different methods may produce widely varying results. For example, both Washington and California use Method 8015-M (modified) for TPH analyses, but the two states assign different ranges of molecular weights to the designations “gasoline” and “diesel” (CWRCB 1988; WDOE 1991a). Because only the concentrations of hydrocarbons detected within those ranges are reported, differences in the reported concentrations of TPH may arise.

At least 30 states have set specific cleanup levels or guidelines based on the TPH measurement (Oliver and Kostecki 1992), alone or in combination with standards for benzene, toluene, ethylbenzene, and xylenes (BTEX) and/or polynuclear aromatic hydrocarbons (PAHs). The most commonly used soil cleanup standard for TPH is 100 mg/kg, although the standards and guidelines range from background concentrations to 10,000 mg/kg TPH in soil. In at least 12 states, the cleanup level varies within a defined range depending on the type of hydrocarbons present (e.g., gasoline or diesel) or factors such as depth to groundwater, the proximity of human populations, and future use of the site.

The technical basis for these TPH standards is generally not presented in the regulations, and is often difficult to determine by contacting regulatory personnel. Many states have adopted numbers already in use by other states (the proliferation of the 100 mg/kg level is an example of this trend). Washington and California are notable exceptions to the rule in that the bases for the standards are described in the rule or in a technical guidance document. Washington State’s TPH standards are based on protection of taste and odor qualities of groundwater (assuming use of groundwater as drinking water), represented by a 1 mg/l guideline for groundwater. This guideline was multiplied by a factor of 100 to identify a target level of 100 mg/kg for gasoline in soil.

TPH concentrations derived in the California LUFT manual are stated to have been based on the concentrations of benzene and other toxic components expected to be present in the mixture. However, some of the basic assumptions used to derive these values have been questioned and the manual is currently under review to determine whether it should be revised. Although the reasoning behind these

standards is described, it should be noted that TPH standards are generally not based on health risk assessments or state-of-the-art fate and transport evaluations. Protection of aesthetic drinking water characteristics is more typically their foundation, when the purpose and assumptions of the standards are stated.

Most TPH standards were developed for the specific types of products assumed to be present at most sites. For some sites, these assumptions regarding the products present and their current composition do not hold true. For example, a TPH standard based on the health risks and mobility of BTEX compounds in gasoline would be overprotective for sites with other types of petroleum products that do not contain substantial amounts of BTEX (such as diesel fuels, mineral oils, and hydraulic fluids). In addition, there are several widely used products that fall within the same range as gasoline on a TPH scan, such as Stoddard Solvent, which is not enriched in BTEX (Bruya and Eng 1992). These products are indistinguishable from gasoline as reported by most laboratories, but are much less toxic.

In addition, BTEX compounds, which are primary contributors to the toxicity of gasoline, are easily weathered and highly mobile in the environment. Therefore, weathered gasoline and other petroleum products are not appropriately addressed by a cleanup standard that is based on the composition of fresh gasoline. Weathered products or hydrocarbons other than gasoline and diesel fuel present additional difficulties during analysis. Specifically, the TPH analysis must be carefully calibrated using standard mixtures of the product being analyzed. If the hydrocarbons in the sample are of unknown origin or composition, or if the hydrocarbons have been fractionated or weathered in the environment, the standard mixture used for calibration may not be appropriate and the reported concentration may be inaccurate. For example, a recent study conducted with spiked samples suggests that if the product in the soil is significantly weathered compared with the standard used for calibration, the concentration reported may be inaccurate by as much as $\pm 50\%$ (Bruya and Eng 1992).

By contrast, petroleum mixtures such as tank bottoms, coal tars, and creosote may contain up to 90% PAHs (Nestler 1974). A TPH cleanup standard developed for gasoline or diesel fuel, which contain much lower percentages of PAHs, might be underprotective for exposure to these types of mixtures. Most states have TPH standards only for gasoline, or for gasoline and diesel fuel. Washington State has a category for "other" TPH, but the cleanup standard is the same as that for diesel fuel.

Attempts have been made to incorporate site-specific factors into the cleanup levels set at each site, particularly on the west coast. Three examples of this approach are the California LUFT Manual (CWRCB 1988), the Oregon UST matrix for developing numerical soil cleanup standards (ODEQ 1990), and the Petroleum-Contaminated Soils Rating Matrix recently developed by Washington State (WDOE 1992). Each of these approaches uses a matrix system in which a cleanup standard is selected based on a scoring system. Scores take into account

the nature of the petroleum mixture (e.g., gasoline or diesel fuel), fate and transport considerations, and the potential for human exposure. The Washington matrix was developed using modeling data (obtained for the models B-LEACH and MULTIMED) for different soil types and data from leaking UST sites in Washington. Cleanup standards resulting from use of this matrix are summarized in Table 1.

While these matrices take some site-specific factors into account, their ability to reflect and incorporate the full range of petroleum hydrocarbons and site-specific conditions found in the environment is still somewhat limited. Even when BTEX measurements are used in combination with TPH measurements, the concentrations of carcinogenic PAHs are often not determined. These compounds may account for a significant percentage of the known risk associated with petroleum-contaminated sites in cases where products other than gasoline are present or when the hydrocarbons have been weathered significantly (i.e., the volatile and mobile constituents such as benzene are no longer present). Because these compounds are not highly mobile or easily leached into groundwater, they are typically found only in soil. Thus, risks associated with these chemicals would generally only occur in situations where children or other receptors come into direct contact with the soil or ingest it inadvertently while playing or working.

III. CHEMICAL FINGERPRINTING AND CONSTITUENT ANALYSIS

There are a variety of analytical techniques that may be used as alternatives to the TPH measurement that provide more detailed information on the mixtures and/or individual chemicals present in a sample. These methods are particularly useful when products other than fresh gasoline or diesel fuel are suspected to be present, or when a site-specific risk assessment or fate and transport evaluation are to be conducted.

At refineries, bulk storage facilities, loading racks, or other facilities that handle many products, specific identification of the product in the sample is frequently

TABLE 1
**Soil Cleanup Standards
 Resulting from Washington's
 Petroleum-Contaminated Soils Rating Matrix**

Substance	Minimum (mg/kg)	Maximum (mg/kg)
Benzene	0.5	2.5
Toluene	40	130
Ethylbenzene	20	250
Xylene	20	250
TPH-gasoline	100	600
TPH-diesel	200	800

desirable, as knowledge about the product that is present may assist in determining its toxicity and mobility in the environment. Such knowledge may also allow a specific source, such as a leaking tank or line, to be identified. Product identification may also be important for determining responsibility for cleanup in areas that may have multiple possible sources, such as localized groundwater contamination in an industrial area of a city.

Products and their chemical constituents may be identified using a variety of techniques. Although the results of a TPH-gasoline or TPH-diesel GC analysis are typically reported as a single concentration, the GC traces for the samples may be obtained from the laboratory and evaluated by a qualified chemist. These traces can be used as a “fingerprint” to determine the type of product that is present, the degree of weathering that has taken place, and, in some cases, the specific origin of the hydrocarbons. For example, crude oils originating from different parts of the world have widely different chemical fingerprints in GC analyses (Bruya and Eng 1992).

The information obtained from the fingerprint can be used for a variety of purposes. Although many of the chemicals that make up the GC trace for a given product cannot be individually identified, the presence or absence of BTEX compounds can be readily determined. This provides important information for risk assessment and assists in evaluating the degree of weathering of the mixture, and, consequently, its likely mobility in the environment. Identification of the product(s) present at a site may also assist a decision-maker in determining whether existing standards, intended for regulation of standard products such as gasoline or diesel, are appropriate for the site in question or whether site-specific approaches should be used to develop cleanup standards.

Chemical fingerprinting may also be conducted using a variety of other analytical procedures. Notable among these is thin-layer chromatography, which can be used in the field, and is capable of identifying a wide range of petroleum products, including higher-molecular-weight mixtures such as creosote or asphalt. The technique can also be used at sites with multiple types of contamination, as it is capable of detecting a number of other types of contaminants, such as chlorinated phenols, PCBs, and pesticides (Friedman and Bruya 1991).

Specific compounds of interest may be analyzed using a variety of methods, including EPA Method 8270 (high-resolution GC/MS) for semivolatile organic compounds such as PAHs and methyl-*tert*-butyl ether (MTBE, a gasoline additive), EPA Methods 8020 and 8240 for BTEX and other volatile organic compounds, and ICP/MS for organic lead additives (Baugh and Lovegreen 1990; Potter 1990). Quantitative analysis for individual constituents of petroleum mixtures may be used in chemical fingerprinting (e.g., to identify products with specific additives), to establish concentrations of indicator chemicals for human health risk assessment (discussed in greater detail in Section IV, below), or to assist in source identification.

Method 8270 can be used alone or in combination with measurement of total

aliphatic hydrocarbons (TAH) to determine the sources of PAHs in the environment. LPAH/HPAH and TAH/PAH ratios are particularly useful in determining the origin of PAHs in sediments and soils that are far from their original sources and that may have undergone degradation and fractionation through a variety of fate and transport processes (Clark and Brown 1977; Nestler 1974). For example, the ratios of LPAH/HPAH (low-molecular-weight PAH/high-molecular-weight PAH) and TAH/total PAHs were used successfully to differentiate between contamination arising from creosote, diesel fuels, and area-wide combustion sources at a wood treatment facility in Oregon (PTI 1992). These methods are especially useful in differentiating between low-level contamination from a site and area-wide or natural sources of PAHs in the environment (Barrick and Prahl 1987). In addition, the LPAH/HPAH ratio may be used to evaluate the degree of weathering and/or fractionation due to environmental transport of petroleum products, as the LPAH compounds are more soluble and biodegrade more quickly in the environment than the HPAH compounds.

IV. HUMAN HEALTH RISK ASSESSMENT

Evaluating potential human health risks associated with a site provides another approach for determining cleanup needs. Such evaluations consider both of the necessary components of risk — toxicity (the potential for a substance to cause adverse health effects) and exposure (the potential for an individual to come into contact with the substance of concern). The variable composition of TPH found in the environment presents particular challenges in assessing both toxicity and exposure. Moreover, exposure potential is influenced both by chemical characteristics (e.g., physical and chemical properties that influence chemical mobility in the environment) and site characteristics (e.g., factors influencing land use). Issues in assessing toxicity and exposure potential at petroleum sites are discussed below.

A. Toxicity Assessment Issues

Two types of toxicity information are available for petroleum hydrocarbons — toxicity information for individual toxic TPH constituents (e.g., benzene and benzo[*a*]pyrene) and toxicity information for specific petroleum product mixtures (e.g., unweathered gasoline). No toxicity data are available for the actual TPH mixtures found in the environment at petroleum sites. Available toxicity data can be combined with data and assumptions regarding potential human exposures to site-related substances in soil, groundwater, or other environmental media to calculate cleanup standards for petroleum sites based on protection of human health. In performing such calculations, each type of toxicity data offers advan-

tages and disadvantages as discussed below.

1. Chemical-Specific Standards for Individual Toxic Components

Where quantitative toxicity factors and physical and chemical property data are available for TPH components, cleanup standards for petroleum sites can be set based on the presence of individual known toxic TPH constituents. This approach parallels the risk assessment approach commonly used in evaluating hazardous waste sites under such programs as the federal Superfund program. Such cleanup standards can directly and quantitatively account for site differences in the presence of toxic constituents and site conditions that might influence exposure. Focusing only on those chemicals for which quantitative toxicity factors are available raises the concern of the potential hazards posed by other TPH components of unknown toxicity. This concern can be offset, however, by the numerous health-protective assumptions that are typically made in developing and applying toxicity factors in evaluating human health risks and establishing cleanup levels.

The primary constituents of petroleum fuels fall into several categories of hydrocarbon compounds. Many TPH components, such as paraffins and naphthenes, are generally not considered to be highly toxic (Amdur *et al.* 1991; Clayton and Clayton 1981) and are not typically included as chemicals of concern in standard risk assessments.

The constituents of primary concern for risk assessment are contained in the aromatic fraction. The most toxic known compounds found in the aromatic fraction are benzene and the carcinogenic PAH compounds. Noncarcinogenic compounds that may also be of concern include toluene, ethylbenzene, xylenes, naphthalene, and other noncarcinogenic PAH compounds. In addition to their potential toxic effects, BTEX compounds are of concern because of their volatility and mobility in the environment, properties that increase the likelihood of exposure. Naphthalene is also relatively mobile, but the higher-molecular-weight PAH compounds (including the carcinogenic PAH compounds) are much less volatile and mobile than the BTEX compounds.

BTEX and PAH compounds are frequently used in characterizing potential risks and cleanup requirements for petroleum sites because this group of chemicals includes the most toxic known TPH constituents and represents a broad range of physical and chemical properties influencing environmental mobility. Thus, these compounds can serve as indicators of overall site risk and cleanup needs. Moreover, cleanup methods addressing these compounds will also result in cleanup of other substances with similar environmental fate properties.

2. Toxicity Factors for Specific Petroleum Products

Another option for developing cleanup levels for a TPH-containing site is the use of toxicity factors developed for the original petroleum product mixtures. Such factors have been developed recently by the U.S. Environmental Protection Agency (U.S. EPA 1992b) and others (e.g., Millner *et al.* 1992). Toxicity factors based on complete petroleum product mixtures are advantageous because they can account for the toxicity of all components of the mixture and any additive or other effects resulting from simultaneous exposures to multiple chemicals. However, because the composition of the original petroleum product may become substantially altered after release into the environment, toxicity factors based on the original products may not be directly applicable to environmental settings, particularly where significant product weathering has occurred. In addition, the composition of different petroleum products (e.g., gasoline) is highly variable because of differences in the source petroleum composition and refining methods. Toxicity data are also much more limited for these mixtures than they are for some of the individual known toxic constituents (e.g., benzene). Thus, caution must be exercised when applying such toxicity factors to develop cleanup standards.

Among the toxicity factors currently available for petroleum products are provisional toxicity factors recently issued by EPA for several fuel mixtures, including gasoline, jet fuel (JP-4 and JP-5), and diesel fuel (U.S. EPA 1992b). These values are summarized in Table 2. In deriving these factors, EPA reviewed the toxicological literature and identified a limited number of toxicological studies using the pure fuel products that provided data relevant for developing toxicity factors. Although EPA acknowledges that the derivation of these factors has many uncertainties, these factors can provide an additional means of evaluating protective cleanup levels and potential residual risks present at sites.

TABLE 2
EPA Provisional Toxicity Factors

Substance	Toxicity value	Confidence level	Uncertainty factor
Gasoline	CSF: 0.0017 (mg/kg-day) ⁻¹	Class C ^a	NA
	RfD: 0.2 mg/kg-day	low	1,000
JP-4	RfD: 0.08 mg/kg-day	low	10,000
JP-5/diesel fuel	RfD: 0.02 mg/kg-day	low	10,000
Marine diesel fuel	RfD: 0.008 mg/kg-day	low	10,000

Source: U.S. EPA (1992)

Note: CSF, carcinogenic slope factor; EPA, U.S. Environmental Protection Agency; NA, not applicable; RfD, reference dose.

^a EPA carcinogenic weight-of-evidence classification; Class C — possible human carcinogen.

EPA notes several sources of uncertainty in developing and applying these provisional toxicity factors. First, the only data judged to be adequate for developing quantitative toxicity factors were data from inhalation studies. As a result, EPA chose to develop toxicity factors for ingestion exposures by extrapolating from the inhalation data. In the absence of pharmacokinetic data regarding relative absorption following inhalation or ingestion of fuel mixtures, EPA assumed that absorption following ingestion is equal to absorption following inhalation and that the dose-response relationship was the same for each exposure route. Both of these assumptions may result in an over- or underestimation of risks.

Second, as noted above, the composition of the original fuel materials used in the toxicity studies on which the toxicity factors are based will differ from the composition of the fuel mixtures in the environment. This issue is of particular concern at sites where the original fuel mixtures have undergone extensive weathering over several decades. In particular, where site data indicate that the volatile components of the original fuel mixture (e.g., BTEX) are present to only a limited extent, these toxicity factors for fuel mixtures are unlikely to accurately reflect the toxicity of fuel mixtures found in the environment. Because these chemicals can contribute significantly to the total toxicity of the mixtures that form the basis for the toxicity factors, product toxicity factors (particularly those for gasoline) are likely to overestimate the toxicity of weathered fuel products with reduced volatile concentrations.

The uncertainty in the provisional toxicity factors is reflected both in EPA's low overall confidence ratings for the values for noncarcinogenic health effects (i.e., "low" confidence) and in the Class C (i.e., possible human carcinogen) ranking given to the carcinogenic slope factor developed for gasoline. The large uncertainty factors that EPA applied in deriving the noncancer toxicity factors from the original studies (1000 for the gasoline reference dose [RfD] and 10,000 for the other RfDs) further reflect the substantial uncertainty in the available data. These factors are used to develop noncancer toxicity values by dividing either a no-observable-adverse-effect-level (NOAEL) or lowest-observed-adverse-effect-level (LOAEL) derived from a suitable study for each mixture by the specified uncertainty factor. These values were designed to account for intra- and interspecies extrapolation, extrapolations among exposure durations, and other deficiencies in the available toxicological database (including uncertainties regarding the composition of TPH mixtures that might be found in the environment). Use of such large uncertainty factors suggests that these values could substantially overestimate actual risks. Moreover, these uncertainties must be acknowledged if using these provisional toxicity factors to evaluate human health risks and potential cleanup needs at specific sites.

B. Exposure Assessment Issues

In addition to toxicity, exposure potential plays a necessary role in determining the risks associated with chemicals present at a site. Exposure assessment includes evaluation of human populations that could potentially come into contact with site-related chemicals as well as the magnitude, frequency, duration, route(s), and locations of potential exposure. Assessing the potential for human contacts with chemicals to occur at specific locations requires consideration both of activity patterns that might bring the receptor (i.e., the exposed individual) to the exposure point location as well as the potential for the chemical to be present now or in the future at the specific location of concern. Chemical presence can be assessed either through direct measurement at the location of concern or through modeling, which allows prediction of chemical concentrations at locations or times other than those at which sampling has occurred.

Of critical importance in performing an exposure assessment for any site (including petroleum sites) is determining reasonable exposure scenarios and pathways. In particular, the current and potential future use of the site will significantly influence the types and magnitude of exposures that might occur. Land use will also affect the cleanup levels that will be required to meet risk-based cleanup goals. For example, residential land use typically results in the lowest (i.e., most stringent) cleanup levels because a residential exposure scenario includes assumptions of daily, extensive contact with environmental media such as soil and groundwater over a long period of time. Where residential land use can be ruled out for a site, higher cleanup levels may be sufficient to achieve target risk levels. Similarly, the need for and level of groundwater cleanup goals depends on the use of site groundwater and the potential for site-related chemicals to affect the groundwater (e.g., as influenced by the depth to groundwater). In performing site-specific analyses, realistic exposure assessment assumptions should be used that accurately reflect current and potential future site conditions and use.

Chemical-specific characteristics also influence exposure potential and exposure assessment. The inherent mobility of chemicals determines the environmental media in which they are expected to be present as well as the degree to which they are expected to disperse in the environment. For example, the mobile and volatile BTEX chemicals would be more likely to enter groundwater or air and thus to present exposure potential via these media. By contrast, the carcinogenic PAH compounds tend to remain adsorbed to soils and thus are of greater concern for exposures to this medium. Moreover, just as no quantitative toxicity factors are available for the specific petroleum hydrocarbon mixtures found in the environment at petroleum sites, values for the physical and chemical properties necessary for predicting and modeling environmental transport and fate of petroleum hydrocarbons are only available for certain specific TPH constituents and not for TPH mixtures. Thus, exposure assessments tailored to site-specific conditions are most accurately assessed using data for specific constituents that can serve as indicator chemicals. As noted above, the individual constituents of TPH for

which quantitative toxicity factors are available possess a range of physical and chemical properties reflecting a corresponding spectrum of mobility in soil and groundwater. Thus, these chemicals can serve as indicators of a broad range of chemicals present in TPH for which chemical-specific toxicity and other data are not currently available.

V. ECOLOGICAL RISK ASSESSMENT

In contrast to methods used for human health risk assessment, ecological risk assessment often relies on the use of direct toxicity measurements, such as bioassays, to determine whether a mixture of chemicals is toxic to a variety of organisms. Bioassays are particularly useful tools for predicting the ecological risks associated with petroleum hydrocarbons, because the lack of complete information on the chemical constituents of the hydrocarbons complicates the use of indirect predictive tools, such as numerical chemical standards that are based on biological effects.

The use of bioassays as a regulatory tool is more developed for sediments than for soils, primarily because ecological effects have typically been the main focus in cleaning up contaminated sediments, whereas human health concerns have generally been foremost in cleanup of soils. The State of Washington's Department of Ecology has pioneered the use of bioassays as a means of regulating contaminated sediments. Washington's Sediment Management Standards provide two methods of evaluating the toxicity of sediments: a set of numerical chemical standards (based on the apparent effects threshold approach; WDOE 1991b), and an alternative method relying directly on bioassays and benthic infaunal analysis.

The U.S. Environmental Protection Agency is also in the process of developing cleanup standards for sediments. The draft standards are based on the equilibrium partitioning approach (an approach that is primarily valid for nonpolar organic chemicals), and have currently been developed for only a few PAHs and pesticides. For recent reviews of biological test methods and standard-setting approaches for sediments see Adams *et al.* (1992) and Burton (1991).

In Washington state, numerical standards have been set for 47 chemicals whose relationship to adverse biological effects have been studied extensively in Puget Sound. However, the vast majority of the chemical constituents of petroleum hydrocarbons are not included on the list. Therefore, biological tests are recommended to assess the risks associated with these and other chemical mixtures.

Washington State uses a suite of two acute and one chronic biological tests to evaluate marine sediment toxicity: an amphipod (*Rhepoxynius abronius*) mortality bioassay, one of several larval bioassays that combine the effects of mortality and abnormality, and a chronic test, which may be either the Microtox® bioassay (measuring reduction in photoluminescence), the *Neanthes* bioassay (measuring reduced biomass), or benthic infaunal analysis (WAC 173-204-315). This combi-

nation of tests has been shown to be sensitive to changes in chemical concentrations and to be an effective predictor of altered benthic assemblages found at contaminated sites (Pastorok and Becker 1990; Johns *et al.* 1991; Becker *et al.* 1990). An amphipod bioassay (*Hyaletta azteca*) and the Microtox[®] bioassay are also recommended for petroleum-contaminated freshwater sediments (Bennett and Cabbage 1992), although the specific biological tests to be included in the regulations have not yet been determined.

EPA and several state agencies are beginning to focus on developing similar tools for evaluating ecological risks associated with terrestrial sites, and bioassays are being considered as one method of evaluation. For example, the Washington Department of Ecology is evaluating a group of five biological tests for evaluating the ecological risks associated with contaminated soils (La Tier and Landis 1992a–e). These tests include earthworm and plant vigor toxicity tests for evaluating the direct effects of soil on terrestrial organisms, fathead minnow and *Daphnia* toxicity tests for evaluating the impacts of soil runoff to freshwater systems, and a frog embryo teratogenesis assay for evaluating the effects of soil contaminants in wetlands environments. These tests have not yet been approved by Ecology, but are currently being field-tested for a number of contaminants, including petroleum hydrocarbons. For a complete review of available biological test methods for terrestrial and wetland sites see U.S. EPA (1992a).

Biological tests such as those described above can be used to define areas requiring cleanup at hydrocarbon-contaminated aquatic sites without the need for numerical chemical cleanup standards (for examples see Athey *et al.* 1989 and PTI 1992). Areas to be capped or dredged can be defined solely on the basis of a selected level of biological effects, which may vary depending on the cleanup objectives for the site. For example, in Washington State, cleanup levels may range from a “no adverse effects” level to a “minor adverse effects” level, each of which is defined for specific biological tests in the rule. Confirmatory biological monitoring is required, as with chemical standards, to evaluate the success of cleanup.

Alternatively, if a statistical correlation between biological effects and petroleum concentrations in the environment can be derived for a large site, a site-specific set of cleanup standards may be derived. This approach was used recently to develop a site-specific chemical threshold for biological effects associated with PAHs offshore of a creosoting facility in Portland, Oregon (PTI 1992). However, development of site-specific standards requires the use of synoptic chemical and biological measurements, and a relatively large number of samples (30 to 50).

VI. CONCLUSIONS

Part 1 of this article has reviewed the methods available for setting cleanup standards for petroleum hydrocarbons. Although many states use the TPH measurement to set cleanup standards, the technical basis for these standards is not

strong. In addition, TPH standards also have implicit assumptions about the conditions and petroleum mixtures likely to be present at a site. Finally, most TPH standards for soil have been set to protect drinking water resources, a need that is not present at every site. The assumptions under which TPH standards were developed should be clearly stated in any regulation that uses them, and regulatory alternatives to the use of these standards should be provided for sites that are sufficiently different from these assumptions.

A variety of alternatives are available for characterizing sites and developing site-specific cleanup standards for petroleum hydrocarbons, ranging from traditional EPA health risk assessment techniques to the use of toxicity factors for mixtures and the use of bioassays to identify and protect against risk to biological resources. Use of these techniques usually requires additional resources (i.e., time and money) during the characterization of a site and requires a more sophisticated level of understanding of environmental processes and risk assessment on the part of both the regulators and the regulated community. However, because of the greater accuracy and technical foundation of these methods, use of site-specific cleanup standards is expected to result in a more equitable distribution of cleanup resources by directing them toward sites that pose greater potential for human health or ecological risk.

In Part 2 of this article, these conclusions will be tested through application to two case studies, selected from actual sites and expected to be representative of typical petroleum-contaminated sites. Generic TPH standards and site-specific cleanup standards are developed for each of the two sites, and the costs and benefits of each approach are evaluated. Based on the conclusions of these studies, recommendations will be provided on selecting cleanup standards for petroleum hydrocarbons in the environment.

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