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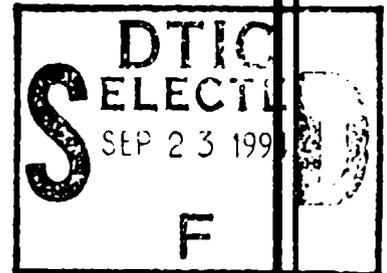


EVALUATION OF THE TOTAL
PETROLEUM HYDROCARBON STANDARD AT
JET FUEL CONTAMINATED AIR FORCE SITES

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13. ABSTRACT (Maximum 200 words) This document evaluates the scientific strength of chemicals other than total petroleum hydrocarbons (TPH) as a basis for establishing risk-based cleanup standards at fuel-contaminated sites. The appropriateness of using benzene, toluene, ethylbenzene, and xylenes (BTEX) as substitutes for TPH was evaluated, including examination of the basis for current federal and state TPH and BTEX cleanup levels. The suitability of specific components of jet-fuel as potential substitutes for TPH was evaluated. Benzene appears to be the most appropriate substitute for TPH based on its toxicity, weight-of-evidence cancer classification, motility in the environment, ubiquity at fuel-contaminated sites, and solubility in ground water. Finally, assumptions, constants, and risk-assessment methods critical to deriving site-specific cleanup concentrations were examined to establish a more scientifically justifiable and defensible basis for cleanup concentrations. Two major components were examined: 1) alternative cancer slope factor determinations for benzene (i.e., distributional analysis of dose-response relationships developed from cancer studies), and 2) site specific exposure reduction strategies (i.e., distributional analysis of exposure estimates). <p style="text-align: right;">DTIC QUALITY INSPECTED 7</p>			
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**Evaluation of the
Total Petroleum Hydrocarbon Standard
at
Jet Fuel Contaminated Air Force Sites**

Selection of Possible
Scientifically-Based Alternatives



Prepared by
EA[®] Engineering, Science, and Technology, Inc.
For
Armstrong Laboratory
Environmental Sciences Branch
Occupational and Environmental Health Directorate
Brooks AFB, Texas



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EXECUTIVE SUMMARY

A study was conducted to examine potential substitutions for total petroleum hydrocarbons (TPH) at JP-4 (jet fuel) contaminated Air Force installations. The objective of the study was to examine the scientific basis for potential use of compounds other than TPH in establishing cleanup standards at JP-4 sites. There were four steps to the study's analytical approach:

- (1) Examination of current bases for existing numerical soil cleanup levels for TPH and four major fuel constituents — BTEX (benzene, ethylbenzene, toluene, and xylene);
- (2) Identification of potential TPH substitutes for establishing soil cleanup concentrations;
- (3) Selection of the most appropriate TPH substitute; and,
- (4) Options for raising a risk-based soil cleanup concentration for the TPH substitute (*i.e.*, benzene).

(1) *Current bases for existing numerical soil cleanup levels*

There are four categories of methods being used by states to establish cleanup concentrations:

- A minimally scientifically-defensible approach, yielding semi-site-specific cleanup concentrations, based on ground water protection;
- A scientifically-defensible approach, yielding site-specific cleanup concentrations, protective of ground water;
- A risk assessment approach with varying degrees of scientific defensibility, typically yielding soil cleanup concentrations with variable extents of health protection from a soil ingestion route; and,
- Scientifically-defensible approaches, with site-dependent methodologies, yielding highly site-specific cleanup concentrations, ultimately protective of ground water.

The general categorization of the bases for BTEX and TPH cleanup concentrations showed that all state-specific approaches could be described as scientifically-based, technology-driven, or other (*e.g.*, "cleanup to background" policy). In summary,

- There are no federal soil cleanup criteria established by the USEPA for TPH, or for BTEX, *per se*.

- There are state-specific cleanup concentrations for TPH and BTEX.
- The majority of state-specific BTEX cleanup concentrations are human health-protective.
- The majority of human health-protective cleanup concentrations are designed to be protective of ground water for use as drinking water.

(2) *Identification of potential TPH substitutes for establishing soil cleanup concentrations*

A series of criteria were used to judge the viability of JP-4 constituents as TPH substitutes. These included chemical fate and transport¹, toxicity², and regulatory standards for relevant media of concern.³

Fate and transport. The fate and transport properties of principal candidates for TPH substitutes can be summarized in the following manner. In a new JP-4 spill, BTEX and lower molecular-weight alkane substitutes⁴ are the volatile constituents. Given their lower molecular-weights, relatively higher water solubilities, and greater soil mobilities, these constituents tend to leach into soil with surface water precipitation and migrate over greater vertical distances than the other potential substitutes.

The primary fate of PAHs, which do not volatilize and tend to remain associated with soils, appears to be biodegradation, although the nature and extent of this activity will vary widely with such factors as the size of the spill, the soil type, and soil microbial characteristics. Transport of higher molecular-weight PAHs associated with jet fuels⁵ is limited by their soil affinity and low water solubility. These compounds are increasingly hydrophobic in nature and tend to remain preferentially associated with the organic carbon fraction in soil, as opposed to the percolating water phase. Lower molecular-weight PAHs, such as fluorene, have been shown to exhibit faster migration rates than their higher molecular-weight counterparts and are most likely to reach the water table.

¹Relative proportions of potential substitutes in JP-4, physicochemical properties, temporal variations in soil-related distributions of potential substitutes, and implications for human routes of exposure.

²Substitute-specific toxic effects, availability of relevant toxicity information, and availability of established, recognized toxicity benchmark values.

³Identification of existing or anticipated media of concern and availability of established standards for media of concern in addition to soil (i.e., groundwater maximum contaminant levels (MCLs)).

⁴e.g., hexane, octane, and cyclohexane

⁵e.g., percolation or leaching of benzo(e)pyrene, chrysene, and fluoranthene

Naphthalene and substituted naphthalenes, by virtue of their smaller size and greater relative water solubility, are also expected to be transported further, although perhaps not as rapidly as the BTEX and alkanes.

Therefore, higher molecular-weight PAHs and possibly some naphthalene would appear to remain associated with the soils at the site of the spill for significantly longer periods of time than BTEX, while BTEX, naphthalene, and low molecular-weight PAHs would be anticipated to migrate further, thereby exhibiting a greater potential for ground water contamination.

Toxicity. A comparison of the magnitude of the toxicity values for the carcinogenic JP-4 constituents (oral slope factors for benzene and chrysene indicates that the marginally larger slope factor is associated with chrysene [(0.073 (mg/kg/day))⁻¹ for chrysene; 0.029 (mg/kg/day)⁻¹ for benzene]). However, at this time benzene is the only potential TPH substitute with an oral slope factor established by the USEPA.

Comparisons of the noncarcinogenic toxicity values for potential TPH substitutes indicate that the lowest chronic oral R_Ds and, hence, the greatest potential for producing adverse health effects under similar exposure conditions, are for naphthalene and several of the PAHs.

(3) *Selection of the most appropriate TPH substitute*

The physicochemical properties of benzene influencing its potential for ground water impact, the magnitude of and scientific understanding of its toxicity, and an established toxicity value, combine to support benzene as the TPH substitute of choice for JP-4. Chrysene, the sole carcinogenic PAH in JP-4, as a possible substitute is not as viable a substitute, given its less definitive toxicity benchmark concentration and lesser potential to impact ground water. Naphthalene is not a viable choice, given the lesser magnitude of the toxicity associated with naphthalene, the lack of an established toxicity benchmark concentration, and the lack of a maximum contaminant level (MCL). Coupled with the anticipated lack of carcinogenic PAHs in ground water, the inability to accurately extrapolate noncarcinogenic toxicity information, and the absence of additional MCLs for PAHs other than benzo(a)pyrene, *the TPH substitute of choice is benzene.*

(4) *Options for raising a risk-based soil cleanup concentration for the TPH substitute (i.e., benzene)*

Factors that affect the benzene cleanup level⁶ were explored. As benzene carcinogenicity is anticipated to drive the site risk estimates, the two major components specifically examined were alternative cancer slope factor (SF) determinations for benzene (i.e., distributional analysis of

⁶(1) The predetermined "acceptable" level of risk, (2) benchmark measures of toxicity, and (3) site-specific exposure parameters.

dose-response relationships developed from cancer studies), and site-specific exposure strategies (*i.e.*, distributional analysis of exposure estimates) that might be employed at Air Force JP-4 sites.

Alternative cancer slope factor (SF) determinations. Based on the current USEPA documentation on the derivation of the benzene SF (USEPA 1985), the potential for appreciably altering the benzene cancer SF is not anticipated to be significant, based on three strengths of the existing SF:

- Unlike the majority of chemicals for which SFs have been derived, the benzene cancer SF was estimated from existing human epidemiology data.
- The benzene cancer SF was estimated using two different lifetime cancer risk models (relative and absolute risk) and two different assumptions of the appropriate exposure parameters (cumulative and weighted-cumulative exposure).
- The benzene SF was presented as the geometric mean of the maximum likelihood estimates (MLEs), as opposed to the more standard approach used for the majority of SFs, which is to present the SF as the 95th percentile upper bound.

In addition, a recent study designed to quantitatively re-evaluate the USEPA estimate of the benzene SF proposed that the benzene cancer SF could effectively be decreased by an order of magnitude. However, the USEPA is indicating that there has been no study to substantially refute the currently established SF.

Site-specific exposure reduction strategies. The potential for exposure of humans who come in contact with the site of a former JP-4 spill can be influenced by identification of the current and future land uses at the site, identification of the human receptor of greatest concern, physical nature of the site, the size/volume of the spill, and the age of the spill. The need for site-specific considerations and the use of site-specific exposure parameters, whenever feasible, is crucial to this process.

With regard to values placed on the various exposure parameters, an alternative approach to the use of conservative assumptions is an exposure distributional analysis, in which ranges or distributions of individual exposure parameters (*e.g.*, the distribution of adult body weights) are considered to produce an overall distribution of potential exposure. In exposure assessment, Monte Carlo simulation can be used to estimate distributions for exposure assumptions, rather than point estimates. Use of this methodology does not alter the basic structure of the exposure estimate and further refines the way chemical intakes are calculated.

Conclusions

- There is no established USEPA regulatory policy for BTEX or TPH soil cleanup concentrations, to date. There are variable state-specific approaches to setting BTEX and/or TPH soil cleanup levels.
- State-specific soil cleanup concentrations for BTEX are based primarily on protection of human health via protection of ground water, and/or protection of health for the soil ingestion route.
- Among all potential substitutes for TPH at JP-4 spill sites, benzene appears to be the most appropriate substitute based on its toxicity (carcinogenicity), weight-of-evidence cancer classification (Category A carcinogen), motility in the environment, ubiquity at JP-4-contaminated sites, and potential for migration to ground water.
- Based on these parameters, risk-based soil cleanup concentrations based on BTEX tend to be driven by benzene. Risks associated with exposure to benzene in ground water used as a drinking water source is anticipated to dominate risks for benzene in other media.
- There is no scientific consensus on use of specific distributions. However, scientifically defensible, rationally chosen, site-specific distributions should be used to estimate exposure.

Recommendations

- Benzene should be adopted as the TPH substitute.
- Research and funding efforts should focus on formulating site-specific soil cleanup concentrations for benzene, based on protection of ground water.
- A cost-benefit analysis should be undertaken for soil remediation of benzene and TPH, using current, acceptable remediation methods, and applying a site-specific approach.
- Research and funding efforts should be directed towards characterizing TPH, including chemical characterization, health effects, fate and transport, and the utility of TPH in the risk assessment process.

SECTION SUMMARIES

Section 1: Background and Rationale for Seeking Alternatives to TPH at JP-4 Contaminated Sites

Section 1 of this report introduces the concept of replacing total petroleum hydrocarbons (TPH) as the basis for establishing cleanup concentrations of JP-4 chemical constituents in soil at individual Air Force bases. There are two reasons why replacing a TPH-based cleanup standard is desirable: (1) the chemical composition of TPH, as a class of chemicals, is poorly and inconsistently defined, and (2) the TPH-based cleanup standard is often based solely on the detection limit of current analytical equipment, so that there is no rational scientific basis, such as human health protection, for the standard. In this investigation, alternative JP-4 constituents are examined as potential TPH replacements in a sequential, stepwise fashion by: (1) surveying the different ways that governments (federal and state) use TPH to set standards, (2) identifying potential chemical candidates that are reasonable alternatives to TPH, (3) examining the most promising candidate substitutes in depth for their scientific merit, (4) selecting from among these chemicals the best TPH substitute, and (5) quantifying the impact of choosing this best substitute on the cleanup standard. Via this process, attention quickly turns to BTEX (benzene, toluene, ethylbenzene, and xylene) as the most promising chemical group, and finally to benzene as the most promising chemical substitute for TPH in establishing a cleanup standard.

Section 2: Current Bases for Existing Numerical Soil Cleanup Levels for TPH and BTEX

Section 2 of this report identifies, as the first step in examining substitutes for TPH, how federal and state governments are currently regulating soil cleanup of JP-4 chemicals — specifically what the soil cleanup requirements are and how they were derived. The purposes of this step are to: (1) determine the extent to which the governments rely on TPH to establish a cleanup standard, (2) what quantitative and qualitative criteria are used to set the TPH standard, (3) whether other chemicals, such as benzene, are considered at all (and if so in what way), (4) the consistencies among and differences between various governments in establishing cleanup standards, (5) identification of states that might be amenable to considering alternatives to TPH as a basis for establishing cleanup, and (6) the adaptability of government criteria to other chemicals that are promising TPH substitutes. The results of this survey were used to assist in selecting promising TPH substitutes.

Section 3: Potential TPH Substitutes for Establishing Soil Cleanup Concentrations

In Section 3 of this report, constituents in JP-4 are considered for their suitability as TPH substitutes as the basis for soil cleanup standards. Four classes of chemicals were short-listed because, as groups, they are present in JP-4 in greater proportions than other chemicals: BTEX, naphthalenes, alkanes, and PAHs. Chemicals in these four groups were examined in depth

according to their environmental fate and transport, toxicity, and existing regulatory standards. While other JP-4 constituents may have one or more desirable qualities as TPH substitutes, their lower proportions in JP-4 blends and lesser importance as soil contaminants removed them from in-depth consideration. **Section 3.0** presents and compares the comprehensive information available on JP-4 constituents without drawing conclusions about the most suitable TPH substitute. Conclusions about the most promising JP-4 substitutes and selection of the preferred substitute are deferred for detailed consideration in **Section 4.0**.

Section 4: Selection of the Appropriate TPH Substitute(s)

Section 4 uses all of the information compiled and assessed in **Sections 2.0 and 3.0** to select the preferred TPH substitute. As explained in **Section 1.0**, the desire is to select a standard that is both scientifically defensible and based on human health risk, rather than on best available technology. **Section 4.0** describes the health risk assessment process and how it leads to the development of a preliminary remediation goal (PRG) for soil cleanup. Specific chemicals in the four chemical groups identified in **Section 3.0** (BTEX, naphthalenes, PAHs, and alkanes) were then considered in the context of human health risk and the development of a soil PRG. To do this, the following criteria were considered: toxicity, availability of toxicity benchmark values, the calculated PRGs, anticipated environmental fate and transport, potential for contaminating other environmental media, and relevance of state-specific approaches to regulating soil contaminants. Based on these criteria, benzene was selected as the preferred TPH substitute.

Section 5: Options for Raising a Risk-Based Soil Cleanup Concentration for the TPH Substitute (Benzene)

Section 5 is focussed on how an appropriate preliminary remediation goal (PRG) is developed for benzene, the preferred TPH substitute in soil as determined in **Section 4.0**. The two key elements considered in establishing the benzene PRG are the same two key elements used to establish human health risk: benzene's cancer potency factor and, quantitative expression of the potential for human exposure to benzene. Various ways of expressing both of these elements were explored in this section, including the use of Monte Carlo simulation. PRGs are site-specific because many of the factors used to calculate them vary from site to site and are necessarily dependent on conditions at a particular site. Therefore, site-specific PRGs were not calculated in **Section 5.0**.

Section 6: Conclusions and Recommendations

Section 6 of this report presents the conclusions which constitute the results of analyses performed throughout this report. Additionally, Recommendations are also presented which are the outcome of the conclusions of these analyses as well as additional considerations.

1.0 BACKGROUND AND RATIONALE FOR SEEKING ALTERNATIVES TO TPH AT JP-4 CONTAMINATED SITES

Summary: Section 1.0 of this report introduces the concept of replacing total petroleum hydrocarbons (TPH) as the basis for establishing cleanup concentrations of JP-4 chemical constituents in soil at individual Air Force bases. There are two reasons why replacing a TPH-based cleanup standard is desirable: (1) the chemical composition of TPH, as a class of chemicals, is poorly and inconsistently defined, and (2) the TPH-based cleanup standard is often based solely on the detection limit of current analytical equipment, so that there is no rational scientific basis, such as human health protection, for the standard. In this investigation, alternative JP-4 constituents are examined as potential TPH replacements in a sequential, stepwise fashion by: (1) surveying the different ways that governments (federal and state) use TPH to set standards, (2) identifying potential chemical candidates that are reasonable alternatives to TPH, (3) examining the most promising candidate substitutes in depth for their scientific merit, (4) selecting from among these chemicals the best TPH substitute, and (5) quantifying the impact of choosing this best substitute on the cleanup standard. Via this process, attention quickly turns to BTEX (benzene, toluene, ethylbenzene, and xylene) as the most promising chemical group, and finally to benzene as the most promising chemical substitute for TPH in establishing a cleanup standard.

Historically, there are numerous sites on Air Force installations, at which jet fuel spills have occurred or can be anticipated to occur. As part of the Installation Restoration Program, military installations are required to delineate and remediate concentrations of fuel-related contaminants in site media whose concentrations exceed existing state and/or federal standards. Sources of controversy and uncertainty in the extent of remediation required stem from the lack of a scientific, credible basis for establishing the applicable standards or guidance criteria, real or perceived. This document contains an exploration of the scientific or technological basis for setting cleanup concentrations or guidance criteria for fuel spill-related compounds, in particular for JP-4 jet fuel contaminants.

Traditionally, the typical fuel spill-related indicator compounds for which cleanup concentrations have been established are the total petroleum hydrocarbons (TPH), and the four BTEX (benzene, toluene, ethylbenzene and xylene) compounds. The analytical progression followed in this exploration was based on six assumptions:

1. Anticipation that the federal and state regulatory contexts for these indicator chemicals can be characterized.
2. Specific approaches that the federal and state governments are using (or will use in the future) to formulate regulations on cleanup standards (TPH or otherwise) can be assessed.

3. The scientific rigor with which existing standards have been established can be assessed and characterized.
4. Individual JP-4 fuel-related chemicals, if carefully selected and justified, can serve as a basis for the development of cleanup standards that are alternatives to the TPH standard.
5. An opinion can be rendered on the relative merit of a benzene-based cleanup standard as an alternative to the TPH cleanup standard.
6. Uncertainty associated with a benzene-based cleanup concentration can be measured.

With these assumptions in mind, and recognizing that the TPH cleanup standard is technology-based, the overall objective of this study is:

To examine the scientific rationale for potential use of compounds OTHER than TPH, based on human health criteria rather than technology-based criteria, in establishing cleanup standards at JP-4 contaminated Air Force installations.

The scope of the analyses presented in this report can be summarized in five sequential stages contained in the following sections of this document:

- 2.0 Current Bases For Existing Numerical Cleanup Levels for TPH and BTEX
- 3.0 Potential TPH Substitutes for Establishing Soil Cleanup Concentrations
- 4.0 Selection of the Appropriate TPH Substitute(s)
- 5.0 Options For Raising a Risk-based Soil Cleanup Concentration For the TPH Substitute (Benzene)
- 6.0 Conclusions and Recommendations

2.0 CURRENT BASES FOR EXISTING NUMERICAL SOIL CLEANUP LEVELS FOR TPH AND BTEX

Summary: Section 2.0 of this report identifies, as the first step in examining substitutes for TPH, how federal and state governments are currently regulating soil cleanup of JP-4 chemicals — specifically what the soil cleanup requirements are and how they were derived. The purposes of this step are to: (1) determine the extent to which the governments rely on TPH to establish a cleanup standard, (2) what quantitative and qualitative criteria are used to set the TPH standard, (3) whether other chemicals, such as benzene, are considered at all (and if so in what way), (4) the consistencies among and differences between various governments in establishing cleanup standards, (5) identification of states that might be amenable to considering alternatives to TPH as a basis for establishing cleanup, and (6) the adaptability of government criteria to other chemicals that are promising TPH substitutes. The results of this survey were used to assist in selecting promising TPH substitutes.

The four BTEX compounds were chosen, in addition to TPH, for characterization of existing state and federal soil remediation concentrations because:

- They are associated with fuel spills;
- They are ubiquitous;
- Their environmental fate and transport is predictable;
- Their toxicology is relatively well-characterized; and,
- There is regulatory precedence at federal and state levels for establishing site-specific cleanups based on one or more component(s) of BTEX.

2.1 Regulatory Approaches for Soil Remediation of TPH and BTEX

The range of state and federal regulatory approaches for establishing site-specific cleanup concentrations was established in order to:

- Obtain a sense of the feasibility, locally and nationally, of moving individual states and the U.S. as a whole away from a technology-driven cleanup concentration for TPH to a more scientifically defensible risk-based cleanup concentration for BTEX;
- Identify reasonable criteria that can be used to justify replacing TPH with BTEX;

- Ascertain the proportion of states relying on TPH to establish cleanup concentrations and the proportion relying on additional or other criteria; and,
- Assume a broad reach in examining alternative cleanup bases for all Air Force installations, distributed throughout the entire U.S.

In an effort to determine the approaches that are being taken towards formulating and enforcing soil remediation levels for fuel spill-related contaminants such as TPH and BTEX, state-specific information was compiled from numerous sources in the literature, as well as via direct telephone conversations with state agency representatives. Information on the federal approach towards regulating these constituents was obtained via direct telephone contact with USEPA representatives involved in ongoing efforts.

2.1.1 Federal Approaches to Establishing Soil Remediation Concentrations for Fuel-Spill Related Contaminants

To date, the USEPA has not proposed standards for soil remediation of TPH or BTEX compounds. For example, the USEPA's Underground Storage Tank (UST) program has decided not to develop federal guidelines for the cleanup of soils contaminated with TPH/BTEX. Rather, UST is leaving the selection of TPH/BTEX soil cleanup levels at the discretion of individual states (John Heffelfinger, personal communication, 1993). For states desiring guidance, UST will provide information on other states' TPH/BTEX activities. In addition, UST is funding an effort to summarize all state activities in TPH/BTEX soil cleanup; study results will appear in Soils Magazine (Debbie Tremblay, personal communication, 1993).

The USEPA's Office of Solid Waste and Superfund Office have assembled a Work Group whose purpose is to develop a set of soil screening levels for 30 contaminants (including the BTEX compounds). The screening levels would be used by USEPA during investigation of NPL (National Priorities List) sites. If a contaminant soil level at a site exceeds the screening level, further investigation and characterization of the site would be recommended.

The Work Group is developing a tiered approach to deriving soil screening concentrations (Loren Henning, personal communication, 1993). The following information describes a tiering process proposed by the Work Group. It should be noted that this proposed method may be revised prior to the issuance of any Work Group guidance documents. A first tier, generic, conservative soil contaminant level would be calculated (this level would equate to a soil concentration that would not result in the exceedance of groundwater standards - either health-based National Primary Drinking Water Regulations (MCLs), or state-specific groundwater standards). The generic level may be determined using a partitioning/dilution/attenuation factor equation with default values. A second tier soil screening level may use the same equation, with site-specific data rather than default values. Third and fourth tiers might include a leach test and full site-specific characterization, respectively. It is assumed that screening levels based on

successively higher tiers will be progressively less conservative (*i.e.*, higher soil concentrations will result).

The Work Group's Draft Interim Guidance Document is currently undergoing internal review at the USEPA. The Document is not likely to be available until at least June, 1994 (Loren Henning, personal communication, 1993).

2.1.2 State Approaches to Establishing Soil Remediation Concentrations for Fuel Spill-Related Contaminants

Information pertaining to the existing regulations or guidance criteria for TPH and BTEX was sought for a subset of states perceived to be representative of the variation in remediation levels and approaches for all states. The bases for existing regulations were ascertained from relevant sources in the literature, state guidance documents, or personal contacts. Any information pertaining to proposed or ongoing approaches was solicited as well. The following sections discuss the strategy for identification and selection of target states, and the state-specific characterizations of regulatory standards and approaches.

2.1.2.1 Identification of Soil Cleanup Concentrations of BTEX and TPH for Targeted States

A national survey, conducted by Bell *et al.* (1991), was initially used to compile regulatory approaches used by states to clean up hydrocarbon-contaminated soils, particularly from leaking underground storage tanks. Based on these survey results, certain state-specific considerations in the establishment of numerical values for cleanup concentrations were identified, including background levels of TPH/BTEX, land use of the site, ground water proximity, and potential for ground water impacts. All parameters were subsequently compiled for each state, as presented for BTEX/TPH-specific data in Table 2-1. The information in Table 2-1 is based primarily on examination of the existing survey information (Bell *et al.* 1991) and preliminary personal communications with members of select state agencies.

2.1.2.1.1 Selection of Targeted States for Further Evaluation

From the compilation of state regulatory approaches based on the published Bell *et al.* (1991) survey, 26 states were identified as warranting further investigation to determine the bases for the BTEX/TPH cleanup levels, as illustrated in Figure 2-1. The following initial criteria were used to select the target states:

- States with the highest cleanup concentrations from the reported spectrum of levels (*e.g.*, Tennessee, Georgia);

- States with the midpoint cleanup concentrations from the reported spectrum of levels (*e.g.*, Idaho, Washington);
- States with the lowest cleanup concentrations (or cleanup to background) from the reported spectrum of levels (*e.g.*, Ohio, Minnesota, Illinois); and,
- States that historically have exhibited environmental leadership, innovation, or conservative environmental policy (*e.g.*, California's enactment of Proposition 65).

This approach to targeting states for more in-depth delineation of regulatory approaches was based on three assumptions:

- Inclusion of the complete range of numerical values would reflect the range of approaches being used by the states;
- All relevant parameters considered by the states in establishing values would also be encompassed; and,
- Inclusion of states with historically progressive environmental practices would "flag" any new trends or developments in establishing remediation criteria.

2.1.2.1.2 Compilation of Information from Targeted States

State-specific information for the final 26 targeted states was categorized as mentioned above. For each targeted state, additional or supplemental information was subsequently sought by contacting state regulatory agencies and soliciting verbal or written documentation for the numerical values for TPH/BTEX, as well as the bases for these values. State-specific categories reflect the parameters specifically considered by the states in their methods for deriving the numerical values. If current policy differed from prior survey information, or if clarification of state-specific parameters being considered in the establishment of numerical values was obtained, the state-specific information was adjusted accordingly. The updated and adjusted regulatory information for the 26 targeted states is presented for BTEX in Table 2-2 (and detailed in Appendix A). A similar table was generated for TPH concentrations and analytical method considerations. This information is presented in Table 2-3. States which allow development of site-specific cleanup concentrations were not listed with definitive cleanup concentrations in the tables. A comprehensive series of footnotes were compiled for each table. Readers should refer to them for more detail on the relevant categories and exceptions therein.

2.1.2.2 Characterization of State Approaches to Establishing Cleanup Concentrations for BTEX and TPH

There were four overriding, common themes observed on examination of the approaches and methodologies used by the 26 targeted states in establishing soil cleanup concentrations for BTEX:

- (1) Most states sought to protect the quality of ground water. Whether fate-and-transport models or "generic" attenuation factors were used, background levels applied, or technology-based cleanup plans utilized, soil standards were established such that ground water quality would be in compliance with some existing ground water quality standard.
- (2) The underlying goal of most state hydrocarbon cleanup policies is the protection of human health. The ground water standards mentioned above were almost without exception drinking water standards when potable water was impacted. Usually the standard invoked was the federal maximum contaminant level (MCL) under the National Primary Drinking Water Regulations (NPDWRs), but occasionally a state-specific drinking water standard was cited.
- (3) The overwhelming trend in establishing soil cleanup concentrations is to use quantitative, compound-specific, scientifically defensible methodologies. Quantitative human health risk assessment is playing an increasingly important role in the derivation of compound-specific cleanup levels.
- (4) States acknowledged the limitations of using a TPH cleanup level. Five states did not regulate TPH (Hawaii, Illinois, Michigan, New Jersey, and New York), two used TPH levels only as screening levels or to provide "rough" estimates of the degree of contamination (Massachusetts and Oregon), and one state alluded to plans to include phasing out use of TPH altogether (New Hampshire). This amounts to approximately 30 percent of the targeted states that do not rely on TPH measurements for soil cleanup.

There is considerable variation among the states with respect to approaches and methodologies. For instance, some states permit the use of different standards, applied on a site-by-site basis, based on site-specific information. Others apply fairly consistent criteria to most sites. Certain states advocate the use of very conservative assumptions in their risk-based approaches, while others allow or encourage the use of site-specific assumptions. Still other states allow the responsible party to select an approach for establishing a cleanup concentration, based on consideration of several available options and economic factors, provided that mutual accord is reached. Regardless of the exact nature of the methods, the overriding concerns were centered on human health protection, particularly by achieving relevant ground water standards.

In addition to variation in states' approaches and methodologies, there are varying degrees of scientific rigor employed by states in establishing cleanup standards.

- (1) *A minimally scientifically defensible approach, yielding semi-site-specific cleanup concentrations, based on ground water protection*

Typically, these states used methods that considered "typical" background concentrations and/or basic attenuation and migration assumptions to formulate semi-site-specific cleanup values. These values were to be protective of ground water quality, and usually included several levels of stringency in their derivation. The states surveyed employing this approach are Colorado, Georgia, Hawaii (for BTEX only), Idaho, Kansas (for BTEX only), Massachusetts (for TPH only), Missouri, Ohio, Oregon (for TPH only), South Dakota (for TPH only), and Tennessee.

- (2) *A scientifically defensible approach, yielding site-specific cleanup concentrations, protective of ground water*

This included states that apply fate and transport computer modeling methods and site-specific characteristics to determine levels of soil contamination corresponding to "acceptable" levels of hydrocarbons in ground water. States surveyed which adopted this approach are California, Illinois (for BTEX only), Massachusetts (for BTEX only), New Hampshire, Oregon (for BTEX only), and Texas.

- (3) *A risk assessment approach with varying degrees of scientific defensibility, typically yielding soil cleanup concentrations with variable extents of health protection from a soil ingestion route*

These states based cleanup concentrations on the availability of either a more conservative set of "generic" (nonsite-specific) cleanup levels or a "less conservative" (more site-specific) set of risk-based cleanup levels. Michigan (for BTEX only) and Washington were the only states surveyed using this approach.

- (4) *Scientifically defensible approaches, with site-dependent methodologies, yielding highly site-specific cleanup concentrations, ultimately protective of ground water.*

States included here derive site-specific remediation goals on a site-by-site basis, usually in conjunction with a ground water monitoring program in order to ascertain that the remediation goals are met. Surveyed states which implement this approach are Delaware, Louisiana, Maryland, Minnesota (for TPH only), Utah, and Wisconsin.

The general categorization of the bases for BTEX and TPH cleanup concentration showed that all state-specific approaches could be described as:

- Scientifically-based (*e.g.*, human health risk, fate-and-transport computer modeling)
- Technology-driven (*e.g.*, BAT remediation), and

- Other (e.g., comparison to other states, "cleanup to background" policy, use of generic migration and attenuation assumptions).

The relative proportions of the 26 targeted states that base their soil cleanup values on these three general categories, *scientific*, *technology*, and *other*, are presented graphically for BTEX and TPH in Figures 2-2 and 2-3, respectively. The categories corresponding to a *scientific* basis or approach included use of human health risk assessment procedures, the use of fate and transport modeling, and protection of ground water to health-based MCLs with fate and transport modeling. Scientific approaches for TPH were developed by deriving criteria for one or several of the BTEX compounds, and extrapolating them to TPH, on a fuel-specific (BTEX proportionality) basis. *Technology*-based categories included concentrations based on the limits of the relevant remediation technique or the method detection limit. The general category of *other* was applied to categories which encompassed cleanup to "background", aesthetic concerns, application of such attenuation factors as soil-to-ground water dilution factors, or use of cleanup concentrations established by another state, with or without scientific justification.

Of the 24 states that have developed soil cleanup concentrations for BTEX, 17 use scientifically-based approaches for their derivation (California, Delaware, Florida, Illinois, Louisiana, Massachusetts, Michigan, New Hampshire, New Jersey, New York, Ohio, Oregon, Tennessee, Texas, Utah, Washington, and Wisconsin); one (Maryland) uses technology-driven cleanup criteria; the remaining six states (Colorado, Georgia, Hawaii, Idaho, Kansas, and Missouri) fall into the category 'other'.

Of the 21 states that have developed soil cleanup concentrations for TPH, 12 use scientifically-based approaches for their derivation (California, Delaware, Louisiana, Massachusetts, Minnesota, New Hampshire, Ohio, Tennessee, Texas, Utah, Washington, and Wisconsin); one (Maryland) uses technology-driven cleanup criteria; the remaining eight states (Colorado, Florida, Georgia, Idaho, Kansas, Missouri, Oregon, and South Dakota) fall into the category 'other'.

2.2 Summary

- The USEPA has not established federal soil cleanup criteria for TPH or for BTEX.
- There are state-specific cleanup concentrations for TPH and BTEX.
- The majority (22 out of 24) of state-specific BTEX cleanup concentrations are human health-protective. The following states have human health-protective BTEX cleanup concentrations: California, Colorado, Delaware, Florida, Hawaii, Idaho, Illinois, Kansas, Louisiana, Maryland, Massachusetts, Michigan, Missouri, New Hampshire, New Jersey, New York, Ohio, Oregon, Tennessee, Texas, Utah, and Washington.

- The majority (12 out of 22) of human health-protective cleanup concentrations are designed to be protective of ground water drinking water standards. The following states have human health-protective cleanup concentrations protective of ground water drinking water: California, Colorado, Delaware, Hawaii, Idaho, Illinois, Minnesota, Missouri, New Hampshire, New York, Utah, and Washington.

Table 2-1. Characteristics of BTEX/TPH Cleanup Levels By State (Bell, Kostocki, and Calabrese, 1991)

State	Detection Limit	Blyd Levels	Appearance or Smell	HNu (VVA/PI)	GW Proximity or Impact	Lead Use	Nature of (p) (MW)	WQ Sids	Human Health	Air Site Specific	fiber	Nuc. Estimat	TPH	BTEX	Benzene	Toluene	Ethyl benzene	Xylene
AK													50 100	10				
AL					X					X			100					
AR																		
AZ								X	X				100		130	200	44	44
CA	X				X					X			10-10,000		0.3 1	3 50	1 50	1 50
CO																		
CT																		
DE													50 (gas)					
FL				X						X		X	100 (gas)	10 (gas)				
GA					X								50					
HI					X			X	X				100 500	20 100				
IA										X			50					
IL													100		1	1	1	1
IN													100 1000		16 025			
KS										X			100					
KY	X	X											100		1 4			
LA													Blyd	Blyd				
MA										X			100					
MD	X	X																
ME																		
MI	X	X																
MN																		
MO													20 50					
MS													Blyd	Blyd				
MT													50					
NC													10					
ND													100 (dij)	100 (gas)				
NE													100	10				
NH													10					
NJ										X								
NM																		
NV																		
NY																		
OH																		
OK																		
OR																		
PA																		
RI																		
SC																		
SD																		
TN																		
TX																		
UT																		
VA																		
VT																		
WA	X																	
WI	X																	
WV																		
WY																		

HNu, OVA/PI - HNu broad range vapor analyzer/pneumotransducer detector
MW = Molecular weight

Table 2-2. Derivation Methodologies for BTEX Cleanup Levels By State for 26 Target States

Asbestos	Remediation Technology	Analyzed Other States	Attenuation Factor	Bldg or Exact Limit	Fate/Transport Modeling	Human Health Risk	Completely Site-Specific	Regulatory Goal	Type of Level	Level (ppm)	Remarks
CA								GW/HH	RG	20-100 total BTEX	Use of SESOIL/AT123D
CO								GW/HH	RG		Importance of ground water potability
DE								GW/HH	RG		Consultants hired for derivation [1]
FL								HH	RG		Conservative residential exposure scenario used
GA								GW/SW	CS	100 total VOA	In-situ water quality drives cleanup levels
HI								GW/HSW	RG	20-100 total BTEX	State water quality criteria drives cleanup levels
IL								GW/HH	RG	1.7 B; 21 T; 1.4 X	Looked at Oregon's approach
IN								GW	CAL	1.8 T; 1.1 E; 1 X	Apply to LSTs only, not above ground spills
KS								GW/HH	CAL	10-025 BTEX; 0.25 B	Cleanup level is flexible
LA								GW	RG	1.4 B	Consultants hired for derivation [1]
MA								GW/HH	RG	B 10-200; T 90-2500; E 40-500; X 500-2500	Use of SESOIL/AT123D
MD								GW	RG		Site remediated until GW concentrations stabilize
MI								GW/HH	CAL		RP chooses bldg, detect, limit, or risk ast
MN											Regulate TPH only
MO								GW/HH	RG	1 total BTEX; 0.5 B	Importance of ground water potability
NH								GW/HH	RG		Method based on CA LIFT procedure
NJ								HH	RG	001-013 B; 5-1 T; 1-1 E; 01-1 X	Ground water impact important
NY								GW/HH	RG	001 B; 005 T; 005 E; 003 X	Must satisfy both GW and HH criteria
OH								GW/HH	RG	200-5 B; 4-12 T; 6-18 E; 28-85 X	Importance of drinking water quality
OK								GW/HH	CS	0.1 B; 40 T; 100 E; 800 X	Use of SESOIL/AT123D
SD											Regulate TPH only
TN								GW/HH	CS	10-500 total BTEX	RP may use state's levels or derive their own
TX								GW/HH	RG		Use of API computer model
UT								GW/HH	RG		Developed on a site-by-site basis
VA								HH	RG	5 B; 40 T; 20 E; 20 X	RP chooses state's levels or risk ast
WI								GW/HH	RG		Consultants hired for derivation [1]

[1] This method provides greater flexibility than choosing among risk assessment, background, or detection limit values, since the latter methods values tend to be conservative and must be approved by the state.

Asbestos Lack of adverse aesthetic qualities is an important consideration when considering soil to be "clean"

Remediation Technology Soil considered "clean" when ground water concentrations are below asymptotic levels

Analyzed Other States Cleanup levels were determined on the basis of the levels used by other states

Attenuation Factor Allowable concentrations to soil were determined by multiplying allowable ground water concentrations by an accepted attenuation factor (e.g., 20)

Bldg/Exact Limit Remediation goal equals background levels (in literature or via sampling) or designated MHL

Fate/Transp. Computer model was used to calculate soil concentrations which would leave ground water concentrations below a certain level

Human Health Risk Risk based remediation goals established through use of a structured risk assessment methodology

Site Spc Remediation goals established on a case-by-case basis, using virtually any scientifically-defensible method

Reg Goal GW is goal of cleanup level in protection of ground water, HHL = Human Health, SW = Surface Water

Type Level RG = Level in Remediation Goal, CS = Level in Cleanup Standard (Law), CAL = Level in Corrective Action Level

Table 2-3. Derivation Methodologies for TPH Cleanup Levels By State for 26 Target States

State	Asbestos	Radionuclides	Inorganic	Organic	Analyzed	Other Sites	Atmosphere	Soil	Detect Level	Fate/Transport	Human Health	Risk	Compliance	Regulatory	Goal	Type of	Level (ppm)	Remarks
CA																		Use of SESOB/A1131D, derived from BTEX levels
CO																	100-500	Importance of ground water potential
DE																		Consultant hired for derivations
FL																		Consultant hired for derivations
IL																		Atmos attenuation factor of 2
IA																		In stream water quality drives cleanup levels
IN																		Regulate BTEX only
ID																		Looked at Oregon's approach especially
IL																		Regulate BTEX only
KS																		Cleanup level is flexible
LA																		Consultant hired for derivations
MA																		Use of SESOB/A1131D, derived from BTEX levels
MD																		Site remediated until GW concentrations stabilize
MI																		Regulate BTEX only
MIN																		Consultant hired for derivations
MO																		Importance of ground water potential
NH																		Method based on CA LUFT procedure
NJ																		Regulate BTEX only
NY																		Regulate BTEX only
OH																		Importance of drinking water quality
OR																		Use of PPA attenuation factor of 100
SD																		Used conservative attenuation factor of 1:10
TN																		RP may use state's levels or derive their own
TX																		Use of API computer model
UT																		Established on a case-by-case basis
WA																		RP chooses state's levels or risk ass.
WI																		Consultant hired for derivations

* Values for Table 2-2 apply, except as MCLs apply for TPH so these will be as ** is Human Health Risk column

Figure 2-1. Selection of Targeted States

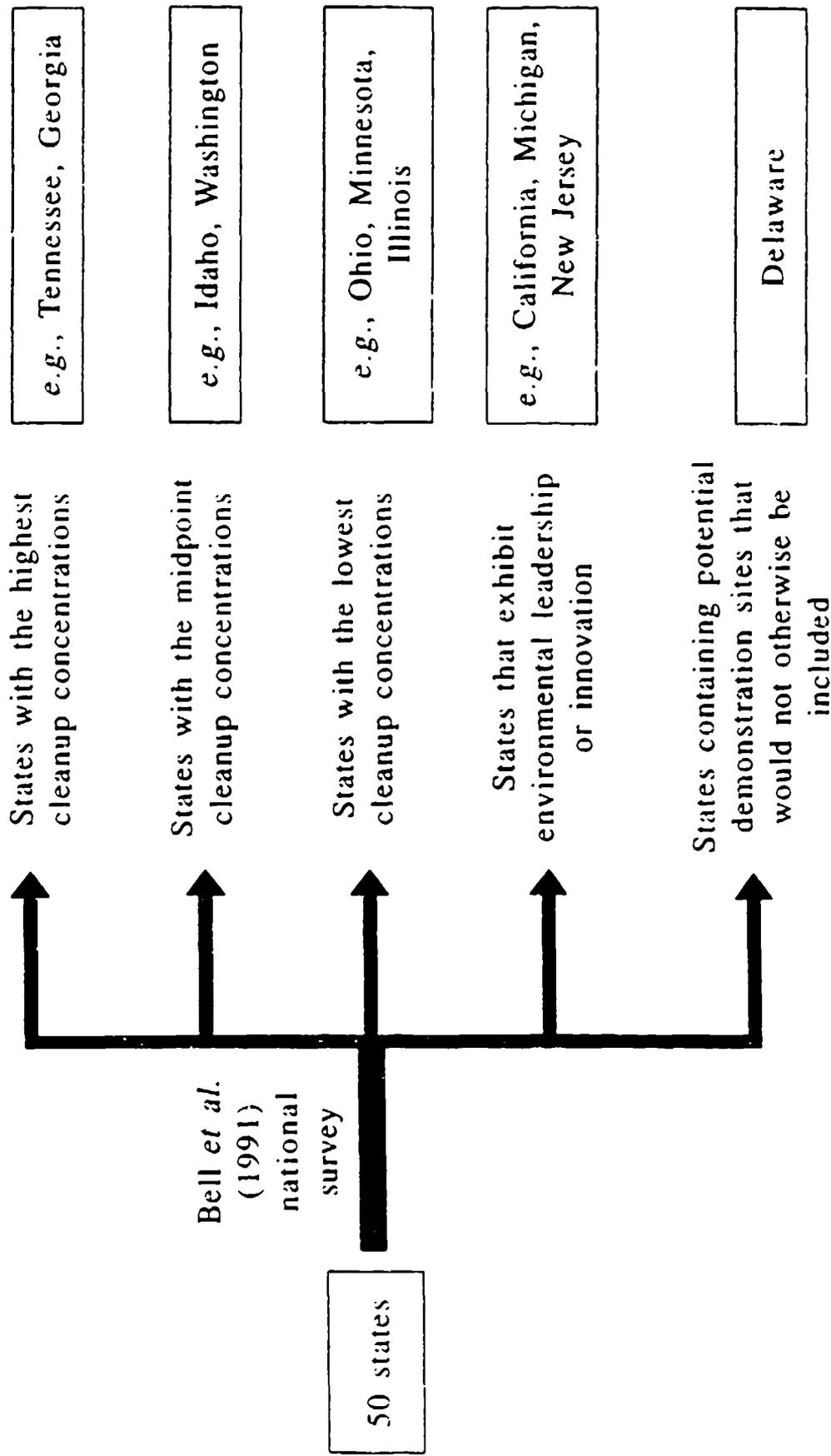
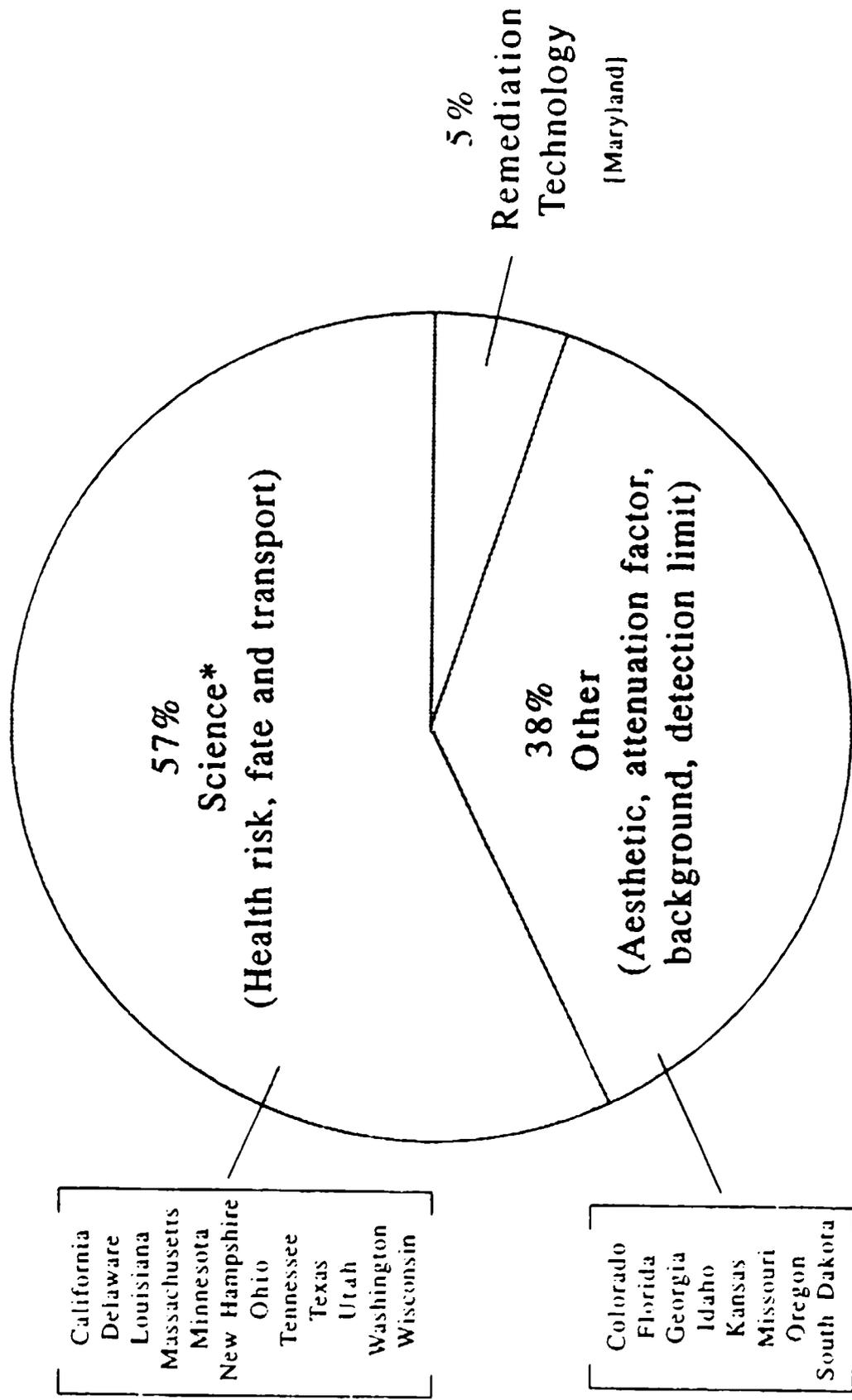
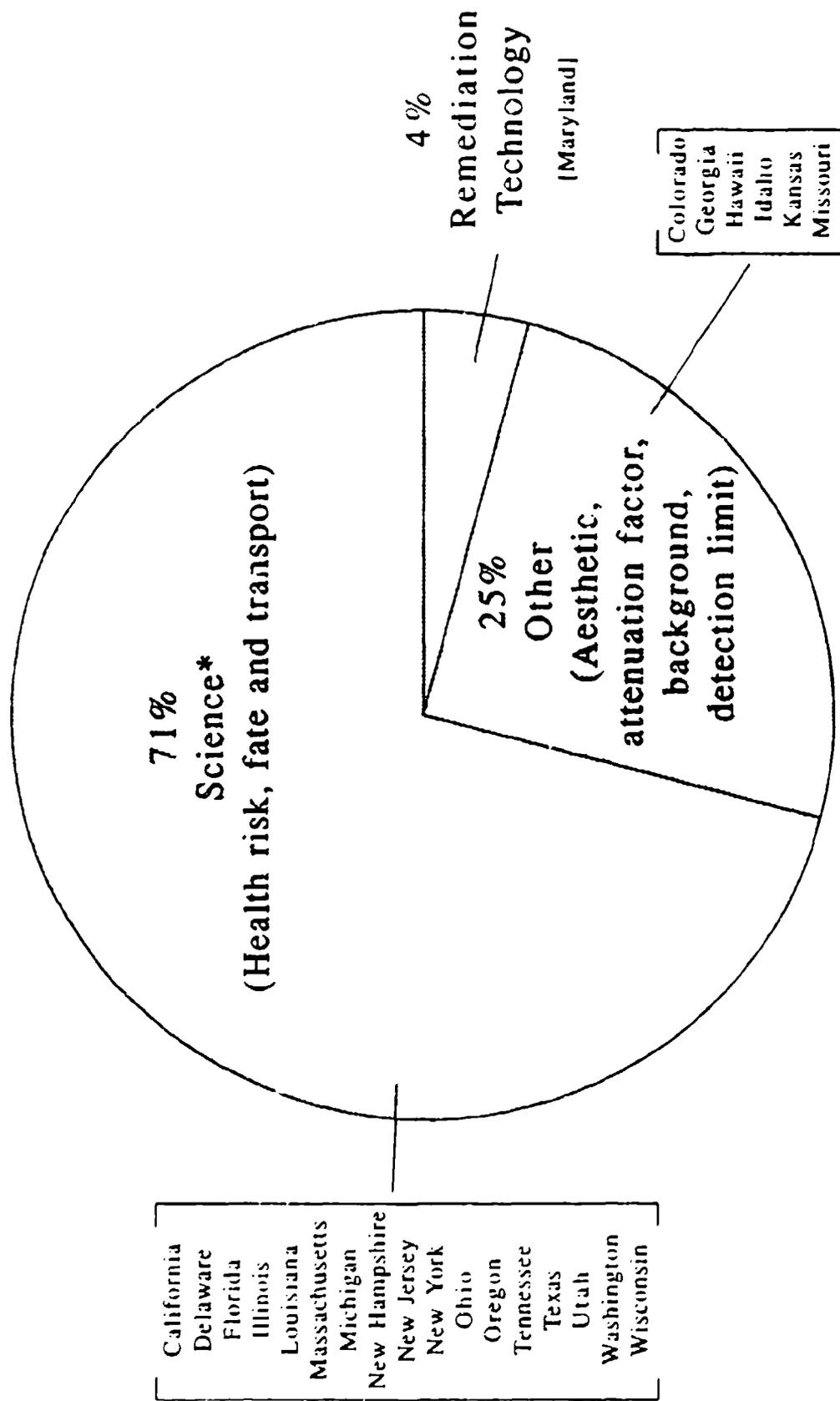


Figure 2-2. Target State-Specific Bases for TPH Soil Cleanup Concentrations



*Cleanup concentrations are not based on TPH-related science, per se. They tend to be based on BTEX, with extrapolation to TPH concentrations for specific fuels.

Figure 2-3. Target State-Specific Bases for BTEX Soil Cleanup Concentrations



*Of the 17 states using a science-based approach, 12 states have regulatory goals designed for groundwater protection.

3.0 POTENTIAL TPH SUBSTITUTES FOR ESTABLISHING SOIL CLEANUP CONCENTRATIONS

Summary: In Section 3.0, constituents in JP-4 are considered for their suitability as TPH substitutes as the basis for soil cleanup standards. Four classes of chemicals were short-listed because, as groups, they are present in JP-4 in greater proportions than other chemicals: BTEX, naphthalenes, alkanes, and PAHs. Chemicals in these four groups were examined in depth according to their environmental fate and transport, toxicity, and existing regulatory standards. While other JP-4 constituents may have one or more desirable qualities as TPH substitutes, their lower proportions in JP-4 blends and lesser importance as soil contaminants removed them from in-depth consideration. Section 3.0 presents and compares the comprehensive information available on JP-4 constituents without drawing conclusions about the most suitable TPH substitute. Conclusions about the most promising JP-4 substitutes and selection of the preferred substitute are deferred for detailed consideration in Section 4.0.

The potential for specific constituents of JP-4 fuel to serve as TPH substitutes was investigated, specifically for the purpose of exploring their usefulness in formulating JP-4 representative soil cleanup concentrations. The soil medium was used here because it is the medium of choice by regulators for TPH cleanup at most sites. The analysis was conducted using a three-step approach:

- (1) fate and transport considerations;
- (2) assessment of toxicity; and,
- (3) determination of the existence of regulatory standards for the media of concern.

These considerations can be used to assist in the identification of the appropriate TPH substitute.

3.1 Criteria for Assessing and Selecting TPH Substitutes

Multiple considerations are involved in identifying potential TPH substitutes and subsequently evaluating their relative utility in developing risk-based cleanup concentrations. The parameters considered within each of the three broad steps listed above are detailed below, and are discussed both generally and specifically for identified potential substitutes in the following sections.

Fate and transport

- Relative proportions of potential substitutes in JP-4
- Physicochemical properties

- Temporal variations in soil-related distributions of potential substitutes, and
- Implications for human routes of exposure

Toxicity

- Substitute-specific toxic effects
- Availability of relevant toxicity information, and
- Availability of established, recognized toxicity benchmark values

Regulatory standards for relevant media of concern

- Identification of existing or anticipated media of concern, and
- Availability of established standards for media of concern in addition to soil (*i.e.*, ground water MCLs).

3.1.1 Fate and Transport

There are two primary fate and transport parameters that influence the selection of a potential TPH substitute for determining soil cleanup levels. The substitute should: (1) be present in JP-4 fuels in detectable concentrations in environmental media, and (2) possess physicochemical properties that promote migration through the subsurface. Fate and transport processes are not only chemical-specific, but site-specific, as well (*i.e.*, surface and subsurface characteristics at a site influence how JP-4 constituents will segregate within and between site media over time). In this section, the chemical-specific parameters influencing fate and transport are presented.

3.1.1.1 Amounts of Potential TPH Substitutes in JP-4 or Related Fuels

JP-4 is a broad cut, naphtha jet fuel, similar to fuel oil no. 1 (kerosene), whose composition has been described as a mixture approximately 65% gasoline and 35% light petroleum distillates (Curl and O'Connell 1977). The blending of JP-4 fuel is designed to produce a product with a composition that broadly segregates (by weight) as: 32% *n*-alkanes, 31% branched alkanes, 16% cycloalkanes, 18% benzenes and alkylbenzenes, and 3% naphthalenes⁷ (ATSDR 1992a). Therefore, alkanes and cycloalkanes account for the substantial portion of JP-4 fuel, followed in priority order by benzene and alkylbenzenes, and naphthalenes. Given the imprecise nature and extent of characterization of the constituents of jet fuels, these weight percents are only representative estimates. The compositional variations of specific compounds within these broad classifications are augmented by the natural variations in the compositions of the crude oil precursors to the final refined fuel (namely, crude petroleum oils or crude shale oils), as well as the refining process operated by the individual fuel manufacturers (ATSDR 1992a). Therefore,

⁷For purposes of this report, naphthalenes are defined as group of compounds, substituted and unsubstituted, that have two fused rings. Naphthalenes fall within a larger class of compounds in JP-4, PAHs, that have multiple fused rings.

it is not possible to determine the exact concentrations of individual chemicals within JP-4 or related fuels. However, ranges of values have been generated based on available compositional information for various jet fuels or similar fuel types. In addition to these broadly grouped classes of components stated above, jet fuels such as JP-4 contain polyaromatic hydrocarbons (PAHs), although their combined weight fraction is typically less than the naphthalenes. PAHs in jet fuels tend to group within the lower molecular-weight range for these compounds (USEPA 1980).

Table 3-1 identifies the relative concentrations of the BTEX compounds within JP-4 or similar fuels. Similar information for other primary components of JP-4 and related fuels is shown in **Table 3-2**. Fuels chosen to approximate the constituents of JP-4 included low sulfur Jet fuel A, high sulfur Jet fuel A, and a more generic Jet fuel. The compositions of kerosene or fuel oil no. 1 were used only as sources of fallback information, where JP-4 or jet fuel-specific information for select compounds was not available.

As stated above, the greatest weighted proportion of JP-4 constituents includes alkanes, benzenes, and naphthalenes, with minimal amounts of low molecular-weight PAHs.

3.1.1.2 Physicochemical Properties of Potential TPH Substitutes

Certain compounds will preferentially remain associated with the site soils, while others will tend to migrate through soils with percolating surface water (*e.g.*, precipitation), and still others will fall somewhere between these two fate and transport trends. Physicochemical factors that can influence the fate and transport of compounds include:

- The potential for volatilization (*e.g.*, boiling point, vapor pressure, Henry's law constant)
- The potential to migrate through the soil column (*e.g.*, octanol-water partition coefficient (K_{ow}), molecular weight, water solubility, soil adsorption (K_d))

Compounds expected to have high soil mobility would typically include those with low boiling points, high vapor pressures, and high Henry's law constants, low octanol-water partition coefficients, low molecular weights, high water solubility, and low organic-carbon partition coefficients. Conversely, compounds with relatively low soil mobility would include those having higher boiling points, lower vapor pressures, Henry's law constants, high octanol-water partition coefficients, high molecular weights, low water solubility, and higher organic-carbon partition coefficients. Chemical-specific properties for TPH substitutes, BTEX and others, are listed in **Table 3-3**. The following subsections discuss substitute-specific characteristics.

3.1.1.3 Fate and Transport of Potential TPH Substitutes

BTEX, naphthalene, alkanes, and discrete PAHs have been found in association with one or more environmental media following JP-4 fuel spills or leaks (ATSDR 1992a). Quantitative estimates of site associations have not been made. Potential TPH substitutes fall into three categories: volatile, semivolatile, and nonvolatile. The potential TPH substitutes that are generally considered to be volatile in nature include the BTEX compounds, the low molecular-weight alkanes, and naphthalenes. After a JP-4 spill or leak, the primary fate of the volatile constituents, including potential substitutes such as BTEX and some of the lower molecular weight alkanes (e.g., hexane, heptane), is to evaporate. Although the majority of studies aimed at determining extent of JP-4 volatilization were conducted for JP-4 spills or leaks to water, high volatilization rates (ATSDR 1992a) after a fresh JP-4 spill on soil would also be expected for these components. These constituents of JP-4 are also typically very mobile in soils, a fact supported by the results of petroleum products and water partitioning studies (ATSDR 1992a; Coleman *et al.* 1984; Kramer and Hayes 1987) and borne out by the historical association of benzene, ethylbenzene, and toluene with ground water in the United States (ATSDR 1990a, 1992b, 1993; Coleman *et al.* 1984; USEPA 1990).

For the semivolatile to nonvolatile constituents, such as certain members of the PAH group, this is not the case. Of the PAHs, the lower molecular-weight compounds such as chrysene and fluorene have been shown to be the more mobile components. Higher molecular-weight PAHs are present in relatively small quantities compared to other constituents in JP-4 and similar fuels. In addition, as PAHs' molecular weights increase, there is a general corresponding increase in hydrophobicity. Therefore, higher molecular-weight PAHs would tend to remain associated with organic carbon fraction of soils near the site of contamination, as opposed to the percolating water phase. The combination of PAHs' physicochemical properties (low water solubility, low volatility, and high octanol-water and organic carbon partition coefficients) and relatively small quantities in fuel indicate that these compounds are not likely to be major contributors to human health risk. A synopsis of how potential TPH substitutes partition in environmental media is presented in Figure 3-1.

3.1.1.3.1 Temporal Alterations in Substitute Distributions

For the more volatile substitutes, such as BTEX, naphthalenes, and low molecular-weight alkanes, the portions of these JP-4 components not volatilized after the initial spill event(s) will enter the surficial and near-surficial soils. Continued emissions over time may continue, albeit at lower rates, given the dilution and percolation incurred by precipitation. The smaller, less hydrophobic compounds, with relatively greater water solubilities (*i.e.*, BTEX, naphthalene, and fluorene) will migrate with percolating water, and therefore have the greatest potential for existing in subsurface soils and for impacting ground water over time.

Temporal variations in soil concentrations for the relatively nonvolatile substitutes, such as higher molecular-weight PAHs or long-chain and branched alkanes will be much less pronounced.

These PAHs appear to remain preferentially associated with the soil at the site of a spill for significantly longer periods of time than the BTEX components. Although the primary fate of PAHs in soils appears to be biodegradation (ATSDR 1990b), the actual nature and extent of biodegradation will vary widely with such site-specific factors as the size of the spill, the soil type, and the microbes present. It is anticipated that the hydrophobic and bulky alkanes would exhibit similar characteristics in the soil matrix. As mentioned above, lower molecular-weight PAHs such as fluorene (ATSDR 1992a) have been shown to exhibit faster migration rates and greater migration distances than their high molecular-weight counterparts (ATSDR 1992a), and would be more likely to reach the watertable.

The anticipated progression of alterations in the media-specific distributions of potential substitutes, as a function of increasing age of the spill (*weathering*), is qualitatively described in **Table 3-4**.

3.1.1.4 Effects of Fate and Transport on Human Exposure Routes

Variations in the distribution of JP-4 constituents in site media will influence the relative concentrations of potential TPH substitutes present over time. Information on temporal variations can be used to predict the concentrations of JP-4 fuel constituents in various subsurface media. This information can be combined with constituent toxicity information in order to determine which compounds have the greatest risks associated with them. Such compounds can be expected to be the *risk drivers* for the site. While anticipated risk drivers can be identified based on consideration of exposure routes, temporal variations, and toxicity considerations, it is site-specific features which allow for definitive determination of the compounds driving risk. The extent to which temporal effects influence the final risk drivers associated with a spill site is *emphatically* site-specific; responsible remediation decisions should be based predominantly on site-specific, not generic, information. However, it is still possible to make scientifically informed and defensible predictions, based on applicable principles and chemical properties.

Soil-to-Ground Water Fate and Transport

Variation in soil concentrations of BTEX and other potential TPH substitutes over time (*e.g.*, with increasing time-from-spill) impact the potential for one or several compounds to be the pivotal risk-driver associated with JP-4 spills. Any factor causing temporal alteration in soil or air concentrations can influence which fuel constituent will become the risk driver for routes of exposure which may include ingestion of surface soil or inhalation of vapors. However, the emerging trend towards regulating soil levels based on ground water protection may supersede exposures via soil ingestion or vapor inhalation for those compounds which present greater soil mobility (*e.g.*, BTEX, naphthalene, low molecular-weight PAHs such as fluorene). For relatively non-mobile substitutes, or substitutes lacking established ground water protective concentrations, risks from exposures via soil ingestion or inhalation may still predominate at the site.

Given the comparatively higher soil mobility of the BTEX compounds, naphthalene, and low molecular-weight PAHs, these compounds could be expected to impact ground water to the

greatest extent, and within relatively shorter time spans. However, it is primarily site-specific characteristics that have the greatest potential to influence contaminant fate and transport from subsurface soil to ground water. Properties such as the magnitude of precipitation, permeability of the soil, type of soil (fraction of organic carbon present), geological strata, distance to ground water, and the physical and dynamic nature of the underlying ground water aquifer(s) will exert great influence on the subsequent fate and transport of any contaminant over time.

Illustrative Example. In a residential setting, a child playing in the surface soil at an older spill site will breathe air, and may ingest soil and ground water. The surface soil is not likely to contain volatiles, given their propensity to volatilize or migrate downward into soil over time. For the same reasons, inhalation of volatile compounds will probably not be a primary route of exposure at an older spill site. Ingestion of semivolatile, less mobile substitutes (*i.e.*, high molecular-weight alkanes or bulkier PAHs) in surface soil is more likely to occur, given their greater propensity to associate with soils. The potential risks from drinking site ground water may drive the risk for more volatile, mobile compounds. Even at a recent spill site, where migration of compounds to ground water may not yet have occurred, the typical future land use scenario involving drinking of site ground water should still address risks from this exposure route.

3.1.2 Toxicity

Criteria that must be considered in the selection of potential TPH substitutes, in addition to fate and transport properties, include an assessment of the toxicity, if any, associated with each potential substitute. The nature and magnitude of the toxic effects should be identified, and the weight-of-evidence in the literature supporting these effects verified. In order to apply a risk-based approach to formulating cleanup concentrations, the existence of any established, recognized, toxicity benchmark values for each compound must be verified as well.

3.1.2.1 Availability of Toxicity Information

The extent of information on the toxicities associated with the potential TPH substitutes (the BTEX compounds, naphthalene, PAHs, and alkanes) varies with the compound. Of the BTEX compounds, benzene has been studied most extensively. Toxicities associated with ethylbenzene, toluene, and xylene could be located, and critical studies have been identified and peer reviewed by the USEPA. Similarly, naphthalene has well-defined toxicity; the USEPA continues to critically review naphthalene toxicity papers. For the PAHs, the most extensively studied PAH is the higher molecular-weight benzo(*a*)pyrene (or B(*a*)P). This compound has been critically reviewed for its toxic effects, and the trend within the Agency has been to use this PAH as a measuring stick for assessing relative toxicities of other PAHs. The cyclic and straight chain alkanes have less toxicity information available, and do not typically have identified or peer reviewed critical studies. The general nature of the critical toxicities associated with the potential substitutes is discussed in the next section.

3.1.2.2 Toxic Effects

The toxic effects associated with chronic exposures (long term or lifetime) to potential substitutes are considered for these analyses, as being most representative of exposures associated with land use at spill sites, and being more conservative (*i.e.*, more protective) of human health.

The relative toxicities of the BTEX compounds, naphthalenes, PAHs, and alkanes can be categorized according to their carcinogenic and noncarcinogenic potential. Of the BTEX compounds, benzene has been classified as a human carcinogen. The PAH, B(a)P, has been classified as a probable human carcinogen. Certain other higher molecular-weight PAHs have also been classified as probable carcinogens, in addition to having noncarcinogenic toxic effects. The remainder of the BTEX compounds (*i.e.*, the alkylbenzenes toluene, ethylbenzene, and the xylenes), as well as naphthalene, exhibit only noncarcinogenic effects of varying severity. Normal and cyclic alkanes are not typically considered to cause significant adverse health effects, particularly for chronic exposures.

For purposes of these analyses, compounds exhibiting carcinogenic endpoints are viewed as being more prone to be risk drivers, from human health and a regulatory perspectives. However, for compounds with carcinogenic and noncarcinogenic potential (benzene and B(a)P), both toxicities are considered, where possible.

3.1.2.3 Availability of Benchmark Toxicity Values

As mentioned above, for purposes of this selection process, the most significant adverse effects (*e.g.*, carcinogenicity) were considered to be those exhibited from chronic exposures, followed by chronic noncarcinogenic effects. Most of the potential substitutes have toxicity values that have been established and peer reviewed by the USEPA (USEPA 1992, 1993). Potential substitutes with established toxicity values are shown in Table 3-5 (BTEX) and Table 3-6 (nonBTEX, potential TPH substitutes). A tentative approach for deriving carcinogenic toxicity values for several of the high molecular-weight PAHs (probable human carcinogens) has been proposed by the USEPA ("relative potency estimates", Schoeny 1993), although it is currently undergoing technical and policy reviews. The application and implications of these toxicity values will be discussed in subsequent sections.

3.1.3 Availability of Regulatory Standards for Relevant Media

Based on current state and federal trends in regulating BTEX and TPH concentrations in soil, the potential migration of contaminants to ground water is of primary concern for both present and future land use. The approach to determining the maximum soil concentration that corresponds to associated unacceptable ground water concentrations typically involves identification or establishment of health-based ground water concentrations, either federal or state-specific, and then modeling soil concentrations that will not cause an exceedance of the ground water

standards. To varying degrees of scientific rigor and extent, existing or emerging models are being used to derive soil concentrations that maintain ground water concentrations within federal or state standards. In some cases, site-specific contingencies are built into the "allowable" soil levels to accommodate site-specific conditions, such as potability of the ground water, distances to well heads, soil type, and soil permeability.⁸ Policies for establishing soil cleanup concentrations that allow for the use of site-specific parameters have greater flexibility than those which attempt to establish a generic soil cleanup concentration applicable to all sites. The nonhomogeneous nature of regional geological and hydrogeological properties at the sites of JP-4 spills often makes it impossible to apply a generic dilution factor or a chemical-specific mobility retardation factor. Soil compositions vary greatly, subsurface soil strata are nonhomogeneous, depths to ground water vary, precipitation rates can differ greatly, interactions between ground water and surface water can be complex and the actual nature of the ground water aquifers in question is bound to differ, even on a subregional scale. Ideally, all of these factors could be accounted for and their relative contributions factored into the estimation of the soil-ground water dynamics. Therefore, while attenuation factors can be applied to the transport of contaminants through the soil column, their generic application to every site under consideration can yield erroneous soil cleanup concentrations.

Establishing soil cleanup concentrations corresponding to *acceptable risks* adds a new level of complexity. In determining remediation goals protective of human health, risks associated with both ingestion of soil and ingestion of underlying ground water must be determined. Certainly, the potential for future contamination of any underlying ground water that may serve as a drinking water source should also be considered. The acceptable ground water concentrations for contaminants in drinking water sources are governed by the federally established National Primary Drinking Water Standards (NPDWS), which exist as enforceable standards termed Maximum Contaminant Levels (MCLs). Cleanup efforts for soils would have to ensure that future ground water concentrations not exceed any MCLs for the potential TPH substitutes. The available MCLs for all potential substitutes are listed in **Table 3-7**.

3.2 Application of Selection Criteria to Potential TPH Substitutes

Preliminary selection of potential TPH substitutes identified the following JP-4 constituents:

- BTEX compounds (*i.e.*, benzene, toluene, ethylbenzene, xylene);
- Polyaromatic hydrocarbons (select PAHs);
- Naphthalene(s); and,
- Normal alkanes (*e.g.*, hexanes, octanes) and cycloalkanes (*e.g.*, cyclohexane).

⁸ For example, Alaska, Idaho and Washington have developed matrices which allow for the adjustment of soil TPH/BTEX cleanup levels based on site specific-features including: depth to subsurface water, annual precipitation, volume of contaminated soil, and soil or rock type.

A substitute-specific analysis of the fate and transport properties and toxicological effects of these compounds that will influence the selection of the TPH substitute of choice is presented in the following sections.

3.2.1 TPH

There are two predominant factors that limit consideration of TPH characteristics:

- (1) product-specific variation, and
- (2) analytical method-specific variation.

The constituents and relative proportions of potential chemicals of concern can be expected to vary greatly with the type of fuel or petroleum product. In addition, the method of analysis and quantification of TPH in a given medium will greatly affect the types and proportions of constituents that ultimately become classed as "TPH". These complications stem from the fact that TPH represents a highly complex mixture of chemicals, extracted from an even more complex original mixture. The all-inclusive aspect implied by use of the acronym TPH ("Total Petroleum Hydrocarbons") is itself misleading for this very reason.

3.2.1.1 Fate and Transport

There are not likely to be TPH-specific fate and transport information that can consistently reflect the same contaminants, for a given medium, over time. While migration of certain constituents is bound to be influenced by the initial properties of the original petroleum product or fuel, over the course of weathering at the site, specific types of constituents should undergo transport in chemical- and site-specific manners. Measurements quantifying TPH over time, even within the same medium and location, will be indicators of a dynamically changing profile of constituents, with minimal intersample consistency. While temporal predictions could be made for the anticipated components of TPH in, for example, a surface soil sample, the lack of consistency in sample components over time would offer little useful information unless fairly extensive characterizations of the TPH constituent profile were made.

Qualitatively, it could be assumed that, for a very recent JP-4 spill, TPH in soils would reflect predominantly all constituents, with eventual loss of BTEX components first, lighter alkanes second, lighter PAHs third, followed by naphthalenes. For an aged spill, TPH might reflect predominantly trace amounts of high molecular-weight PAHs (*i.e.*, B(a)P). However, since these PAHs are not typically present in JP-4 fuel, it is more likely that the residuals would be higher molecular-weight and branched alkanes.

3.2.1.2 Toxicity

It is not anticipated that there would be any TPH-specific toxicity information, for the same reasoning applied to the fate and transport considerations. Measurements of TPH would be internally inconsistent over time with respect to the chemical components present. Given that the actual components of TPH will be highly site-specific, and analytical method-specific, the associated toxicity will vary as well. If the qualitative fate and transport considerations are applied, then the toxicity of TPH should vary over time based on the presence of the anticipated constituents.

There are no established or proposed TPH-specific toxicity values.

3.2.2 Examination of BTEX

Fate and transport parameters for the BTEX compounds, as well as the critical, predominant toxicities associated with these compounds are presented in the following two sections.

3.2.2.1 Fate and Transport

Based on their relatively high vapor pressures and moderate to high water solubilities, the BTEX compounds typically exhibit high mobility in soils. They volatilize extensively to air following a surface spill, and from surface water following a spill and subsequent transport processes. The relatively low K_{oc}'s indicate nonextensive to moderate association with organic carbon in soils, especially in light of their water solubilities. Trends towards decreased leaching (effectively, soil migration) with increasing soil organic carbon fraction have been observed for toluene and the xylenes. All BTEX compounds undergo biodegradation in soil or water, although benzene biodegradation in soil is minimal. The nature and extent of biodegradation appears to be highly influenced by the degree of oxygenation of the soils, as well as other site-specific parameters. BTEX compounds have been found in association with ground water, although toluene is not typically encountered to any significant extent.(ATSDR 1990a, 1990c, 1992b, 1993).

3.2.2.2 Toxicity

The chronic toxicities of the individual BTEX compounds are driven primarily by the toxic properties of benzene. Benzene is a known carcinogen in animals and humans, both orally and via inhalation. Increased risk of leukemia in occupationally exposed persons (Ott *et al.* 1978; Rinsky *et al.* 1981; Rinsky *et al.* 1987, Wong *et al.* 1983) and in animal studies (Cronkite *et al.* 1984, 1986, 1989; Maltoni *et al.* 1982) supports this conclusion. In addition, benzene has been shown to be harmful to the immune and hematopoietic systems (Snyder *et al.* 1980; Rozen and Snyder 1985; ATSDR 1992b). Ethylbenzene, toluene, and xylenes exhibit similar types of acute toxic effects, primarily manifested as depression of the central nervous system (CNS) and

respiratory impairment, with reported effects on the liver, kidneys, and hematopoietic system (ATSDR 1990a, 1990c, 1993). Some evidence of teratogenicity (adverse effects on fetuses) have been reported for xylenes (ATSDR 1990c) and ethylbenzene (Andrew *et al.* 1981; ATSDR 1990a) although there are complications in interpreting these studies.

The established benchmark toxicity concentrations for these compounds are shown in **Table 3-5**.

3.2.3 Examination of Other Potential TPH Substitutes

Potential TPH substitutes, in addition to the BTEX compounds, are discussed below, with respect to their specific fate and transport characteristics and their respective critical toxic effects.

3.2.3.1 Alkanes

The lower molecular-weight alkanes, such as hexane, heptane, and cyclohexane, are discussed in this section. There is a paucity of information on higher molecular-weight alkanes.

3.2.3.1.1 Fate and Transport

The physicochemical properties of the alkanes such as hexane, heptane, and cyclohexane indicate that they are fairly volatile compounds, and therefore will tend to vaporize following spills. However, unlike the BTEX compounds, their hydrophobic nature, and affinity for organic carbon does not indicate a great tendency to leach and migrate into subsurface soils or ground water (CRC 1986).

3.2.3.1.2 Toxicity

Alkanes such as hexane, heptane, octane, and cyclohexane exhibit related toxicity following acute exposure, such as CNS depression at fairly high levels. *n*-Hexane chronic toxicity includes peripheral nerve damage in workers exposed by inhalation (Iida and Yamamoto 1973; ACGIH 1990) and animals (Spencer 1980; ACGIH 1990a). Minimal negative evidence for heptane chronic toxicity was found (API 1980; Crespi *et al.* 1979). No information was found on octane toxicity in humans or animals. Chronic to subchronic cyclohexane exposures in animals indicate minimal-to-no observations of neural and other tissue toxicity (ACGIH 1990b; Patty 1981-2; Frontali *et al.* 1981) although it has been suggested that cyclohexane may function as a weak tumor promotor (Gupta and Mehrotra 1990). Additional information for these compounds is limited, as they have not been associated with particularly toxic endpoints.

There are no established toxicity values for these compounds.

3.2.3.2 Naphthalene

Naphthalene is a relatively low molecular weight, aromatic compound comprised of two fused rings.

3.2.3.2.1 Fate and Transport

Naphthalene is moderately volatile, and has a fairly low water solubility, a relatively high K_{ow} , and a moderate affinity for organic carbon. These characteristics do not indicate a great tendency to migrate into subsurface soil or ground water. Biodegradation has been noted for soil and water, although the nature and extent of these processes are site-specific (ATSDR 1990d).

3.2.3.2.2 Toxicity

Naphthalene carcinogenicity in animals has been studied by the National Toxicology Program (NTP 1991) and Adkins *et al.* (1986), with equivocal outcomes on carcinogenicity although it has caused hemolytic anemia following both chronic and acute exposures. Both the liver and the hematopoietic system have been indicated as sites of naphthalene toxicity (ATSDR 1990d).

The existing benchmark toxicity concentrations for naphthalene are shown in **Table 3-6**.

3.2.3.3 PAHs

The PAHs typically include those organic compounds with three or more fused aromatic rings in their structures. The vast majority of the high molecular-weight PAHs are not associated with JP-4 fuel. However, those PAHs that are associated with JP-4 fuel represent some of the fuel's heavier compounds.

3.2.3.3.2 Fate and Transport

Polyaromatic hydrocarbons are a broad class of compounds with respect to their molecular weights and properties. In general, lower molecular-weight PAHs (*e.g.*, fluorene) are more water soluble and exhibit greater soil mobility than higher molecular-weight PAHs. However, as a chemical group, these compounds are not considered particularly volatile or mobile in terms of their environmental fate and transport. Therefore, PAHs tend to remain associated with soils, rather than leaching into ground water. The higher molecular-weight PAHs have much less potential for migration into ground water. While the primary fate of these compounds in soils is biodegradation, the actual extent of biodegradation and reduction of soil levels cannot be established as a fixed variable, since site-specific microorganisms and spill conditions are the driving factors in the process.

3.2.3.3.1 Toxicity

The predominant toxicity associated with PAHs (primarily select high molecular-weight PAHs) is carcinogenicity. However, the PAHs that are classed by the USEPA as probable human carcinogens (*e.g.*, benzo(*a*)pyrene, benz(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, chrysene, and, dibenz(*ah*)anthracene) have not been detected in appreciable amounts in jet fuels, with the exception of chrysene (USEPA 1980; chrysene present at less than 4 ppb).⁹ The carcinogenic effects have been best defined for the PAH benzo(*a*)pyrene, a potent skin and lung carcinogen in animals. In addition, it has been demonstrated that benzo(*a*)pyrene (B(*a*)P) is a cause of adverse reproductive effects and is teratogenic (ATSDR 1990b). Noncarcinogenic PAHs that have been detected in jet fuels include phenanthrene, anthracene, fluoranthene, pyrene, benzo(*e*)pyrene, and fluorene, which exhibit variable to unknown degrees of toxicity.

As part of their efforts to develop PAH-specific carcinogenic toxicity values, the USEPA's proposed approach of "relative potency factors" was developed (USEPA 1993b). Past attempts to derive toxicity equivalency factors for PAHs based on their carcinogenicity relative to benzo(*a*)pyrene (ICF-Clement 1988) posed inherent problems. A more recent approach tentatively proposed by the USEPA (the Relative Potency Estimate approach, USEPA 1993b) is similar, and provides a means for deriving relative cancer slope factors for six other high molecular-weight carcinogenic PAHs (benz(*a*)anthracene, benz(*b*)fluoranthene, benz(*k*)fluoranthene, chrysene, dibenz(*ah*)anthracene, and indeno(1,2,3-*cd*)pyrene). With the exception of chrysene, these PAHs are not constituents of jet fuels (USEPA 1980). This approach cannot be applied to the PAHs in jet fuel most likely to migrate from soil to ground water, like fluorene, since these jet fuel PAHs are not carcinogenic. However, this approach could be applied to chrysene, a higher molecular-weight PAH in jet fuel that tends to remain associated with soils, since chrysene is a carcinogen. The basic approach compares the magnitude of the carcinogenic properties of six PAH carcinogens to that of B(*a*)P and normalizes them to B(*a*)P. A PAH-specific adjustment factor (an *order-of-magnitude* factor) is then applied to either known soil concentrations of these PAHs or to the B(*a*)P slope factor, to essentially express PAH-specific carcinogenicity in what equates to B(*a*)P equivalents. The order-of-magnitude adjustment factor for chrysene, the sole carcinogenic PAH present in trace amounts in jet fuels, is 0.01 (USEPA 1993b). When this adjustment factor is applied to the B(*a*)P oral slope factor of $7.3 \text{ (mg/kg/day)}^{-1}$ (USEPA 1993a), an oral slope factor of $0.073 \text{ (mg/kg/day)}^{-1}$ can be ascribed to chrysene. This toxicity value is shown in Table 3-6.

3.2.4 Summary

Substitute-specific fate and transport properties. In a new JP-4 spill, BTEX and lower molecular-weight alkane substitutes (*e.g.*, hexane, octane, and cyclohexane) are the volatile

⁹ The order of potencies for seven PAHs has been estimated as follows (USEPA 1993b): dibenz(*ah*)anthracene > benzo(*a*)pyrene > benzo(*b*)fluoranthene > benz(*a*)anthracene > indeno(1,2,3-*cd*)pyrene > benzo(*k*)fluoranthene > chrysene

constituents (ATSDR 1992a). Given their lower molecular-weights, relatively higher water solubilities, and greater soil mobilities, these constituents tend to leach into soil with surface water precipitation and migrate over greater vertical distances than the other potential substitutes.

The primary fate of PAHs that do not volatilize and tend to remain associated with soils, appears to be biodegradation (ATSDR 1990b, 1992a), although the nature and extent of this activity will vary widely with such factors as the size of the spill, the soil type, and soil microbial characteristics. Transport (*e.g.*, percolation or leaching) of higher molecular-weight PAHs associated with jet fuels (*e.g.*, benzo(e)pyrene, chrysene, and fluoranthene) is limited by their soil affinity and low water solubility. These compounds are hydrophobic in nature and tend to remain associated with the organic carbon fraction in soil, as opposed to the percolating water phase. Lower molecular-weight PAHs, such as fluorene, have been shown to exhibit faster migration rates than their higher molecular-weight counterparts (ATSDR 1990b, 1992a) and are most likely to reach the water table.

Naphthalene and substituted naphthalenes, by virtue of their smaller size and greater relative water solubility, are also expected to be transported further, although perhaps not as rapidly as the BTEX and alkanes.

Therefore, higher molecular-weight PAHs and possibly some naphthalene would appear to remain associated with the soils at the site of the spill for significantly longer periods of time than BTEX, while BTEX, naphthalene, and low molecular-weight PAHs would be anticipated to migrate further, thereby exhibiting a greater potential for ground water contamination.

Substitute-specific toxicity and established benchmark toxicity concentrations. A comparison of the magnitude of the toxicity values for the carcinogenic JP-4 constituents (oral slope factors for benzene and chrysene, **Tables 3-5 and 3-6**) indicates that the marginally larger slope factor is associated with chrysene ($0.073 \text{ (mg/kg/day)}^{-1}$ for chrysene; $0.029 \text{ (mg/kg/day)}^{-1}$ for benzene). However, at this time benzene is still the only potential TPH substitute with an oral slope factor established by the USEPA's Carcinogen Risk Assessment Verification Endeavor (CRAVE). In addition, since the concentration of chrysene in JP-4 fuel tends to be much lower than that of benzene, benzene is more likely to exhibit a greater potential for ground water contamination than chrysene.

Comparisons of the noncarcinogenic toxicity values for potential TPH substitutes (**Tables 3-5 and 3-6**) indicate that the lowest chronic oral R_f Ds and, hence, the greatest potential for producing adverse health effects under similar exposure conditions, are for naphthalene and several of the PAHs.

Table 3-1. Concentrations of BTEX Compounds in Fuels Similar to JP-4

Compound	Kerosene (ppm; mg/L) ^(a)	Jet A Fuel (ppm) ^(b)
Benzene	<1681	2521
Toluene	2773	11765
Ethylbenzene	3109	2521
Xylenes (total <i>o</i> -, <i>m</i> -, <i>p</i> -)	8067	7563

(a) In: *Development of a Standard Pure-Compound Base Gasoline Mixture for Use as a Reference in Field and Laboratory Experiments*. 1990. Kreamer and Stetzenbach. Values were converted from a range of weight percents to ppm (mg/L) by using the midpoint value of the weight percent range in combination with the midpoint value for the density of kerosene.

[weight percent (g/kg) × 1 kg kerosene/1.19 L × 1000 = ppm]

(b) In: *Soluble Hydrocarbons Analysis From Kerosene/Diesel Type Hydrocarbons*. Dunlap and Beckmann. Values were converted from weight percents in manner analogous to that described in footnote (a).

Table 3-2. Concentrations of Potential Substitutes in Fuels Similar to JP-4

Compound	Jet A Fuel (low sulfur) (ppb) ^(a)	Jet A Fuel (high sulfur) (ppb) ^(a)	Jet fuel (ppb) ^(b)	Fuel oil no. 1 (Kerosene) (ppm) ^(c)
Polyaromatic hydrocarbons (PAHs):				
Phenanthrene	1800	2200		210
Anthracene	140	200		0.84
Fluoranthene	12	48		
Pyrene	18	76		
Triphenylene	3.6	7.2		
Chrysene	2.8	3.2		
Benzo(e)pyrene	1.6	11.4		
Benzo(a)-anthracene	ND	ND		
Benzo(a)pyrene	ND	ND		
Benzo(g,h,i)-perylene	ND	ND		
Anthanthrene	ND	ND		
Corenene	ND	ND		
Flourene	ND	ND		
Total PAHs	1978	2546	150	151
Naphthalene	5882 ppm ^(d)			3781
Total Naphthalenes				
Alkanes:	NR	NR	NR	NR
n-Hexane				
Cyclohexane				
Total Alkanes				
Total Cycloalkanes				

(a) In: *Quantitative Analysis of Polynuclear Aromatic Hydrocarbons in Liquid Fuels*. 1980. USEPA, Environmental Sciences Research Laboratory, Research Triangle Park, NC. EPA-600/2-80-069. Values represent the average concentration for two samples.

(b) In: *Soil Cleanup Criteria For Selected Petroleum Products*. 1986. Stokman and Dime.

(c) In: *Development of a Standard Pure-Compound Base Gasoline Mixture for Use as a Reference in Field and Laboratory Experiments*. 1990. Kreamer and Stetzenbach. Values were converted from a range of weight percents to ppm (mg/L) by using the midpoint value of the weight percent range in combination with the midpoint value for the density of kerosene. [weight percent (g/kg) x 1 kg kerosene/1.19 L x 1000 = ppm]

(d) In: *Soluble Hydrocarbons Analysis From Kerosene/Diesel Type Hydrocarbons*. Dunlap and Beckmann. Values were converted from weight percents in manner analogous to that described in footnote (b).

NR = Not Reported

Table 3-3. Physical-Chemical Properties of Potential TPH Substitutes

Chemical	Molecular Weight	Boiling Point (°C)	Vapor Pressure (mm Hg)	Henry's Law Constant (atm-m ³ /mole)	Water Solubility (mg/L)	Organic Carbon Partition Coefficient (K _{oc})	Octanol Water Partition Coefficient (K _{ow})
Range of Values (Bold values indicate higher soil mobility)	78.1 to 252.3	69 to 448	5.6 × 10⁹ to 400	4.9 × 10⁻⁷ to 3.21	3.8 × 10⁹ to 1780	48 to 5.5 × 10 ⁶	135 to 1.55 × 10 ⁶
BTEX							
Benzene ^(a)	78.1	80.1	95	5.5 × 10 ⁻³	1780	63-79.4	135
Ethylbenzene ^(b)	106	136.3	9.5	8.7 × 10 ⁻³	160-208	165-254	1349-2200
Toluene ^(c)	92.1	110.6	22	6.7 × 10 ⁻³	448	395	617
Xylenes ^(d) (o-m-p-)	106.2	137-144	6.7-10	5.2-7.6 × 10 ⁻³	134-213	48-260	1202-1585
Potential Surrogates							
Alkanes:							
Heptane ^(e)	100.2	98.4	~40	2.06	2.4	2400-8100	10 ^{4.66}
Hexane ^(e)	86.2	69	100 < x < 400	1.81	9.5	1250-4100	10 ^{3.9} -10 ^{4.11}
Octane ^(e)	114.2	125.7	~10	3.21	7 × 10 ⁻⁴	5500-15,600	10 ⁶ -10 ^{3.18}
Cycloalkanes:							
Cyclohexane ^(e)	84.2	80.7	100	0.19	54.8	480	No data
Naphthalene ^(f)	128.2	218	0.087	4.6 × 10 ⁻⁴	31.7	933	1950

Table 3-3. Physical-Chemical Properties of Potential TPH Substitutes (continued)

Chemical	Molecular Weight	Boiling Point (°C)	Vapor Pressure (mm Hg)	Henry's Law Constant (atm-m ³ /mole)	Water Solubility (mg/L)	Organic Carbon Partition Coefficient (K _{oc})	Octanol Water Partition Coefficient (K _{ow})
PAHs:							
Anthracene ^(a)	178.2	340-342	1.7 × 10 ⁻⁵	8.6 × 10 ⁻⁵	No Data	1.4 × 10 ⁴	2.8 × 10 ⁴
Benzo(a)-pyrene ^(a)	252.3	310-312	5.6 × 10 ⁻⁹	4.9 × 10 ⁻⁷	3.8 × 10 ⁻⁹	5.5 × 10 ⁶	1.55 × 10 ⁶
Chrysene ^(a)	228.3	448	6.3 × 10 ⁻⁹	1.0 × 10 ⁻⁶	1.5 × 10 ⁻³	2.0 × 10 ⁵	4.1 × 10 ⁵
Flouranthene ^(a)	202.3	375	5.0 × 10 ⁻⁶	6.5 × 10 ⁻⁶	No Data	3.8 × 10 ⁴	7.9 × 10 ⁴
Flourene ^(a)	166.2	295	7.1 × 10 ⁻⁴	6.4 × 10 ⁻⁵	1.7-2.0	7.3 × 10 ³	1.5 × 10 ⁴
Pyrene ^(a)	202.3	393-404	2.5 × 10 ⁻⁶	5.1 × 10 ⁻⁶	0.13-0.17	3.8 × 10 ⁴	8.0 × 10 ⁴

- (a) Toxicological Profile for Benzene. ATSDR. 1992b.
 (b) Toxicological Profile for Ethylbenzene. ATSDR. 1990a.
 (c) Toxicological Profile for Toluene. ATSDR. 1993.
 (d) Toxicological Profile for Total Xylenes. ATSDR. 1990c.
 (e) CRC Handbook of Chemistry and Physics. 67th ed. 1986-87.
 (f) Toxicological Profile for Naphthalene, 2-Methylnaphthalene. ATSDR. 1990d.
 (g) Toxicological Profile for Polyaromatic Hydrocarbons. ATSDR. 1990b.

Table 3-4. Anticipated Temporal Variations in Relative Proportions of BTEX and High MWr PAH Substitutes

Relative Age of Spill	BTEX	PAHs
Recent, fresh spill	Surface Soil: High levels Groundwater: None	Surface Soil: High levels Groundwater: None
Older spill	Surface Soil: Low levels Groundwater: Low levels; typically benzene	Surface Soil: High to moderate Groundwater: None to traces of low MWr PAHs; e.g., flourene
Old Spill	Surface Soil: None to trace Groundwater: Low levels; BTEX	Surface Soil: Moderate levels of high MWr PAHs; e.g., B(a)P Groundwater: Trace to low levels of low MWr PAHs

Table 3-5. Toxicity Values For BTEX Compounds

Chemical	Chronic Oral R _d D (mg/kg/day)	Inhalation Reference Dose (mg/m ³)	Oral Slope Factor (mg/kg/day) ⁻¹	Inhalation Unit Risk (Risk/(mg/m ³))
Carcinogens:				
Benzene	Not Available	Not Available	2.9×10^2	8.3×10^{-6} per (µg/m ³) [unit risk]
Noncarcinogens:				
Toluene	2×10^{-1}	4×10^{-1}	Not Applicable	Not Applicable
Ethylbenzene	1×10^{-1}	1×10^0	Not Applicable	Not Applicable
Xylenes [<i>o-m-p</i> -]	2×10^0	Not Available	Not Applicable	Not Applicable

Table 3-6. Toxicity Values For Additional Potential TPH Substitutes

Chemical	Chronic Oral R ₁ D (mg/kg/day)	Inhalation Reference Dose (mg/m ³)	Oral Slope Factor (mg/kg/day) ⁻¹	Inhalation Unit Risk (Risk/(mg/m ³))
Polyaromatic Hydrocarbons:				
Anthracene	3×10^{-1}	---	Not Applicable ^(a)	Not Applicable
Benzo(e)-pyrene	---	---	Not Applicable ^(b)	Not Applicable
Chrysene	---	---	0.073 ^(c)	Not Available
Fluoranthene	4×10^{-2}	---	Not Applicable ^(a)	Not Applicable
Fluorene	4×10^{-2}	---	Not Applicable ^(a)	Not Applicable
Phenanthrene	---	---	Not Applicable ^(a)	Not Applicable
Pyrene	3×10^{-2}	---	Not Applicable ^(a)	Not Applicable
Alkanes:				
Hexane, Octane, or Cyclohexane	None Available	None Available	Not Applicable	Not Applicable
Naphthalene	$4 \times 10^{-2(d)}$	Not Available	Not Applicable	Not Applicable

(a) USEPA 1993. Integrated Risk Information System (IRIS), NLM on-line database was consulted.

(b) Benzo(a)pyrene has an oral slope factor of $7.3 \text{ (mg/kg/day)}^{-1}$, but benzo(e)pyrene is not currently considered a carcinogen.

(c) USEPA 1993b. Chrysene oral slope factor derived via "relative potency factor" approach. See text for detailed explanation.

(d) Naphthalene toxicity values are currently undergoing extensive review by the USEPA R₁D Work Group. These values are from the Health Effects Assessment Tables (HEAST) for 1991; as such, they are subject to potential alterations in the future.

Table 3-7. Maximum Contaminant Levels (MCLs or NPDWRs) for BTEX and Potential TPH Substitutes

Chemical	MCL (ppm) ^(a)
Alkanes (cyclohexane, hexane, octane)	Not Listed
Benzene	0.005
Ethylbenzene	0.7
Naphthalene	Not Listed
PAHs: Benzo(a)pyrene ^(b) Other PAHs	0.0002 None
Toluene	1.0
Xylene	10.0

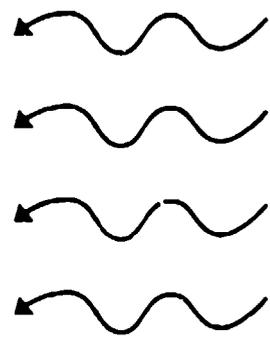
(a) MCLs are taken from the Final and Proposed Drinking Water Standards (40 CFR 141), July 1992.

(b) Benzo(a)pyrene is not present in jet fuels. It is listed here because it is the only PAH with an MCL.

Figure 3-1. Fate and Transport of Potential TPH Substitutes

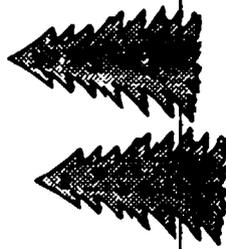
Potential Substitutes Released into the Air:

- Alkanes (butane, heptane, pentane)
- Aromatics (benzene, ethylbenzene, toluene, xylene)



Potential Substitutes Primarily in Soil:

- High molecular weight alkanes
- High molecular weight PAHs (chrysene)
- Aromatics (naphthalene)



SOIL

Potential Substitutes Released into Groundwater:

- Low molecular weight PAHs (fluorene)
- Aromatics (benzene, ethylbenzene, toluene, xylene)



GROUNDWATER



4.0 SELECTION OF THE APPROPRIATE TPH SUBSTITUTE(S)

Summary: Section 4.0 uses all of the information compiled and assessed in Sections 2.0 and 3.0 to select the preferred TPH substitute. As explained in Section 1.0, the desire is to select a standard that is both scientifically defensible and based on human health risk, rather than on best available technology. Section 4.0 describes the health risk assessment process and how it leads to the development of a preliminary remediation goal (PRG) for soil cleanup. Specific chemicals in the four chemical groups identified in Section 3.0 (BTEX, naphthalenes, PAHs, and alkanes) were then considered in the context of human health risk and the development of a soil PRG. To do this, the following criteria were considered: toxicity, availability of toxicity benchmark values, the calculated PRGs, anticipated environmental fate and transport, potential for contaminating other environmental media, and relevance of state-specific approaches to regulating soil contaminants. Based on these criteria, benzene was selected as the preferred TPH substitute.

The final selection of the appropriate TPH substitutes is made based on several considerations that will influence the magnitude of a health risk-based soil cleanup concentration. To this end, the current human health risk methodology is briefly discussed as it relates to the development of soil cleanup concentrations protective of human health for each potential substitute. The final selection of the substitute of choice is presented with additional supportive information.

4.1 Current Methodology for Establishing Health Risk-Based Soil Cleanup Concentrations

The human health risk assessment process and the potential to establish health risk-based cleanup concentrations for chemicals of concern in discrete media are discussed in the following sections.

4.1.1 The Human Health Risk Assessment Process

The USEPA approach to human health risk assessment for chemicals essentially follows the approach first articulated by the U.S. National Academy of Sciences (NRC 1983). The four elements of risk assessment include:

- **Hazard Identification** - establishes the relationship between exposure to a chemical and a specific adverse health effect. Chemicals of potential concern for all given media are identified, and their hazardous properties are defined.
- **Dose-Response Assessment** - describes the quantitative relationship between the amount of a chemical to which individuals come into contact, and the degree and severity of known toxic injury or disease. The outcome of the dose-response

assessment is a benchmark concentration that expresses a threshold, with a margin of safety, above which toxic injury or disease may occur. A compound-specific reference dose, R_fD , is the toxicity value generally used in evaluating the noncarcinogenic effects of substances. To evaluate the potential risk of carcinogens, USEPA uses a two-part evaluation in which the substance first is assigned a weight-of-evidence classification that describes the likelihood that the agent is a human carcinogen; and secondly, a toxicity value is calculated that defines quantitatively the relationship between dose and response (*i.e.*, the slope factor, SF).

- **Exposure Assessment** - describes the human population exposed to chemical agents, and the quantity and duration of individuals' exposures. Typically, land use, human receptors of potential concern, and exposure pathways and specific routes are identified. The final outcomes of the exposure assessment are chemical-specific estimates of chemical intakes associated with the exposure pathways for those receptor populations that could potentially be exposed.
- **Risk Characterization** - integrates the data and analyses from the first three steps of risk assessment. It is used to determine the likelihood that some members of the population of interest may experience any of the various forms of toxicity associated with a chemical under the existing conditions of exposure. In this step, the noncarcinogenic and carcinogenic toxicity benchmark values (*i.e.*, R_fDs and SFs, respectively) for the chemicals of concern are used in conjunction with the estimated chemical intakes for the modeled populations to quantitatively estimate carcinogenic and noncarcinogenic risk.

The risk assessment process has been described in a systematic method: USEPA guidance documents provide methods for organizing, analyzing, and presenting information on the nature and magnitude of risks to public health from potential exposure to chemicals (*e.g.*, USEPA 1989).

Standard equations and exposure parameters exist to ascertain the Lifetime Average Daily Intake (LADI) from ingesting a compound in soil (USEPA 1989). The LADI can then be used to calculate risk (USEPA 1989):

$$\text{Cancer risk}_{\text{Ingestion}} = \text{LADI} \times \text{Oral Slope Factor} \quad (1)$$

$$\text{Hazard Quotient}_{\text{Ingestion}} \text{ (HQ)} \text{ for Noncarcinogenic Effects} = \frac{\text{LADI}}{R_fD} \quad (2)$$

According to the National Oil and Hazardous Substances Contingency Plan (NCP) (40 CFR Part 300), carcinogenic risk greater than 1×10^{-6} is generally regarded to be unacceptable. In the context of hazardous waste cleanup, site-specific cancer risk between 1×10^{-4} and 1×10^{-6} may

be deemed acceptable by the appropriate regulatory authority, depending on site-specific conditions and variables. Noncarcinogenic effects are generally considered to be unacceptable when the HQ exceeds a value of one (1.0). Based on the two equations above, carcinogenic risk will increase with increasing oral SF and LADI (soil concentration-dependent). The HQ increases as the oral R_D decreases and the LADI increases.

The potential for an unacceptable cancer risk or adverse noncancer health effect is a function of chemical potency and concentration in the soil. It follows that a "threshold" soil concentration can be back-calculated from the "threshold" risk that is acceptable.

A complementary outgrowth of the risk assessment process has been the formulation of methodologies for determining the chemical concentrations corresponding to the upper limits for acceptable carcinogenic or noncarcinogenic "risks" in various media of concern. The USEPA has established a set of guidelines for this risk-based approach to formulating what they term *Preliminary Remediation Goals*, or PRGs (USEPA 1991a). The use of the human health risk assessment process in formulating PRGs, as well as the implications and assumptions inherent in this process, are discussed in the following section.

4.1.2 Preliminary Remediation Goals (PRGs)

PRGs are designed to assist in the analysis and selection of remedial alternatives. They should be in compliance with any ARARs (applicable or relevant and appropriate requirements) and result in acceptable health risks for the given medium at the site. Chemical-specific PRGs are the concentrations of the chemical for a given medium and land use combination. Therefore, two general sources of PRGs are: (1) concentrations based on ARARs; and (2) concentrations based on health risk assessment. ARARs that must be met include those for the medium as well as other media that could be impacted (*i.e.*, ground water). Risk-based calculations that set medium-specific concentration limits, using carcinogenic and/or noncarcinogenic toxicity benchmark values in conjunction with exposure assumptions, must satisfy the NCP (40 CFR Part 300) requirements for protection of human health.

The typical approach advocated by the USEPA in establishing PRGs is to identify PRGs at the site-scoping stage, modify them during and after the Remedial Investigation (RI) using site-specific information, and ultimately select site remediation levels in the Record of Decision (ROD). In the context of this report, this might initially involve identification of soil ARARs for potential chemicals of concern (*e.g.*, TPH, BTEX, other TPH substitutes) and development of PRGs for nonARAR chemicals of concern (*e.g.*, BTEX, or others). In general, chemical-specific soil ARARs may not be available, although this report has identified state-specific soil cleanup concentrations for BTEX compounds with varying degrees of "enforceability", ranging from screening or action levels, to guidelines, to goals or actual standards.

USEPA PRGs are based on definition of the *future* land use of the site and, in the absence of definitive evidence for a particular scenario, residential land use is typically the land use of

choice. According to USEPA PRG guidance, residential land use requires that PRGs be formulated for the soil ingestion route of exposure, where an individual has been living onsite from birth through 30 years of age. In this manner, human health risk calculations will encompass exposures for both a child and an adult — effectively the most conservative estimates of risk (*i.e.*, they will result in the lowest soil cleanup concentration, since exposure includes that of the most sensitive human receptor).

The approach for formulating a PRG for a single chemical in a single medium (*e.g.*, soil) is the derivation of the soil concentration that will yield either an "acceptable" carcinogenic risk level of 1×10^{-6} or an "acceptable" noncarcinogenic hazard quotient (HQ) of one (1.0), for the human receptor of primary concern. When the potential exists for risks to be generated from exposure to the same chemical in multiple media, an approach similar in rationale, yet slightly more complicated in application, is advocated. When risks to the human receptor of concern are associated with their concurrent exposure to more than one medium (*i.e.*, soil and air), and hence more than one route of exposure (*i.e.*, ingestion and inhalation), the risk is considered in an additive manner. For example, if an adult person ingests surficial soil from a given area on a site, while simultaneously inhaling volatile compounds emitted from the soil, the acceptable carcinogenic risk level for **both** exposure pathways would still be 1×10^{-6} , or the noncarcinogenic hazard quotient of 1.0 for both exposure pathways. The calculation of the corresponding acceptable soil concentration must now incorporate the exposure information for both routes of intake.

In summary, preliminary screening for assessing potential adverse health impacts attributable to the ingestion and/or inhalation of contaminated soils can be performed using either standard or refined risk-based PRG approaches. Standard equations and exposure parameters exist for ascertaining the soil PRG for either a noncarcinogenic or a carcinogenic compound obtained from ingestion of soil, or from ingestion of soil and inhalation of vapors and particulates (USEPA 1991a). In accordance with USEPA guidance, the land use for the site determines the routes of exposure that must be included in the PRG approach. Typically, for residential land use (either current or future), the route must involve soil ingestion for an adult who has been exposed since childhood for 30 years. For commercial/industrial land use, these routes must include soil ingestion, coupled with inhalation of soil vapor and soil particulates for an adult worker onsite. The approaches detailed in the USEPA guidance for PRGs were followed in the subsequent sections addressing the estimation of soil cleanup concentrations.

4.2 Soil Cleanup Concentrations for TPH Substitutes

As discussed in the previous sections, application of the PRG risk-based approach to formulating soil cleanup values was used to estimate relative soil cleanup concentrations for the potential TPH substitutes. These estimates were based on the assumption that exposure occurs primarily via ingestion of site soil under assumed future residential land use. The potential for estimating soil cleanup concentrations for soil ingestion and the inhalation exposure route is also discussed, along with its inherent limitations.

4.2.1 Soil Cleanup Concentrations Based on Soil Ingestion

Using the PRG health risk-based approach, soil cleanup concentrations can be formulated for all chemicals with established toxicity benchmark values, for both noncarcinogenic and carcinogenic effects. The equations and assumptions used to calculate the noncarcinogenic PRG for soil based on soil ingestion are shown in **Figure 4-1**. Similarly, equations and assumptions for estimating the carcinogenic PRG for soil based on soil ingestion are shown in **Figure 4-2**. The dependence of the noncarcinogenic and carcinogenic soil PRGs on either the noncarcinogenic R_fD or the carcinogenic SF are best illustrated in the reduced versions of each equation, shown at the bottom of each figure. The magnitude of the noncarcinogenic PRG is directly proportional to the established toxicity value (oral R_fD , R_fDo), while the carcinogenic PRG is inversely proportional to the magnitude of the carcinogenic toxicity value (oral SF, SFo). In other words, the greater the oral toxicity, either noncarcinogenic or carcinogenic, the lower the "acceptable" soil concentration.

The USEPA human health risk-based PRG approach has been applied to the estimation of soil cleanup concentrations for the potential TPH substitutes, using the PRG equations for the soil ingestion route of exposure. These cleanup concentrations are estimated primarily for purposes of comparison among the potential substitutes, as a preliminary indicator of the potential for each compound to drive a risk assessment or a remediation effort. Chemicals for which established toxicity values exist are included. Soil cleanup concentrations corresponding to "acceptable" risks are presented for both carcinogenic and noncarcinogenic toxic endpoints in **Table 4-1**. For carcinogenic and noncarcinogenic chemicals, the most conservative soil cleanup concentration is considered to drive the risk. The potential substitutes with the most conservative soil PRG estimates are chrysene and benzene, with PRGs of 8.8 ppm and 22 ppm, based on their carcinogenicity.

4.2.2 Soil Cleanup Concentrations for Soil Ingestion and Inhalation Exposure

For cases where compounds of concern may include volatiles, the inhalation pathway for vapors and soil particulates can be included along with soil ingestion in the estimation of the soil PRG. USEPA does not advocate this approach for residential land use, although for industrial land use, both of these pathways are considered for the onsite adult worker. It is not anticipated that risks associated with adult occupational exposure, even with the additional inhalation pathways, will exceed those risks calculated for the child/adult receptor under residential land use. The inclusion of exposure via vapor inhalation or inhalation of soil particulates requires knowledge of site-specific information on the nature and extent of the soil contamination with volatiles (e.g., area of the spill or distribution of volatile samples, depth to encounter of volatiles, air temperature, and regional wind speed, among others). However, for demonstrative purposes, this report will consider a hypothetical commercial/industrial exposure which includes soil ingestion, as well as vapor and particulate inhalation, and presents information on both the modified risk-based equations and the limitations in making risk-based calculations in the absence of site-specific information.

Modified equations for potential use in estimating noncarcinogenic and carcinogenic soil PRGs, respectively, based on ingestion and inhalation exposure routes are shown in **Figures 4-3 and 4-4**. For each set of equations, the site-specific parameters required for deriving the soil PRG are indicated by bold, italicized text. The parameters requiring site-specific information were indicated in this manner to highlight the crucial role of site-specific input, which is especially relevant when considering the inhalation route of exposure. The lack of site-specific information essentially negates the quantification of a soil cleanup criterion for the hypothetical commercial/industrial land-use scenario. An examination of the simplified versions of these equations, shown on the bottom of each figure, indicates the direct dependence of the soil PRGs on the magnitude of the oral and inhalation R_f Ds or the oral and inhalation SFs (*i.e.*, the greater the toxicity, the lower the PRG). The relationships between the PRGs and the site-specific parameters for the soil-to-air volatilization factor (VF) as well as on the particulate emission factor (PEF) are similar (the greater the volatilization and the emission from soil, the lower the soil PRG).

4.2.3 Soil Cleanup Concentrations for Inhalation Exposure Only

Because of the complexity of the issue, the ability to derive a soil cleanup concentration based solely on the inhalation exposure route will be demonstrated via illustration. Benzene is the only volatile compound which has an inhalation toxicity benchmark concentration. The unit cancer risk for benzene inhalation is 8.3×10^{-6} (corresponding to the risk associated with the inhalation of a unit dose of $1 \mu\text{g}/\text{m}^3$ of benzene). A simple proportionality equation allows the determination of the air concentrations corresponding to an acceptable benzene risk level of 10^{-6} (since $1 \mu\text{g}/\text{m}^3$ yields a risk of 8.3×10^{-6} , what benzene concentration yields a risk of 1×10^{-6} ?) An inhalation risk level of 10^{-6} corresponds to an air concentration of $0.12 \mu\text{g}/\text{m}^3$ of benzene, which can be converted to 0.037 ppb, using the benzene-specific conversion factor of $1 \text{ mg}/\text{m}^3 = 0.31 \text{ ppm}$ (ATSDR 1992b). This would be the air concentration associated with an "acceptable" risk level from benzene exposure (if exposure occurred for 24 hours/day for a lifetime of 70 years). This same value was calculated by the USEPA (1990) in *Leaking USTs and Health*. However, estimating the soil concentration corresponding to this "acceptable" air concentration could be modeled *only* for a site-specific exposure scenario, using site-specific input information (*e.g.*, a future exposure might be from emissions from an underground fuel spill into a residential basement).

4.2.4 Assumptions and Limitations

The estimation of soil cleanup concentrations based on the soil ingestion exposure pathway entails the use of several assumptions, and has limitations in usefulness, as well.

- The soil PRGs established in this report were estimated for the purposes of comparing their risk-based outcomes and determining which of the potential TPH substitutes were the predominant risk drivers.

- The actual soil cleanup concentrations generated using the PRG approach correspond to a residential future land use, and do not include the use of any exposure assumptions that are nonstandard from a risk assessment point of view (*i.e.*, all USEPA default values for exposure parameters were used, hence the PRG estimates are fairly conservative).
- The PRG approach has been established by the USEPA for application to CERCLA sites. As was discussed in **Section 2.1.1**, in the absence of USEPA-established soil cleanup concentrations for the BTEX compounds (or TPH), the primary regulatory agency with BTEX soil cleanup concentrations may be the particular state in which the site is located. Depending on the state-specific approach being used to estimate cleanup concentrations, the soil ingestion-based PRG may be a relevant consideration, but not necessarily the *final* consideration in setting a remediation standard in the Record of Decision.
- State-specific approaches for establishing soil cleanup concentrations for the BTEX compounds rely principally on human health protection, with the predominant trend toward the use of ground water standards. This approach is in variable stages of development and enforcement in many states; the use of somewhat more traditional health protective approaches, such as relying on soil ingestion as the primary exposure consideration, may receive variable weight in a risk management decision-making process.

4.3 Selection of Benzene as the TPH Substitute of Choice

Several factors must be considered in the final selection of the TPH substitute of choice, including toxicity, availability of an established toxicity benchmark concentration, the soil PRG, the anticipated fate and transport, the potential for contamination of other media, and the relevance to existing and emerging state-specific approaches to regulating soil contaminants. These points are considered in the following sections.

4.3.1 Relative Soil Cleanup Concentrations

When the relative toxicities of the potential TPH substitutes are considered, the compounds that have the most conservative toxicity concentrations are the carcinogens (**Tables 3-5 and 3-6**). The carcinogenic compounds, chrysene and benzene, are also those substitutes yielding the most conservative (*i.e.*, lowest) soil PRGs (**Table 4-1**). Substantially more toxicity information exists for benzene, and the carcinogenic endpoint has been studied extensively for multiple routes of exposure to benzene. Definitive carcinogenic toxicity benchmark values have been established for benzene (the oral SF and the inhalation unit risk). Chrysene, on the other hand, has substantially less supporting toxicity information. In addition, it has been assigned a relative potency factor as a means of *adjusting* its carcinogenicity relative to that of benzo(*a*)pyrene. To

date there is no definitive oral SF for chrysene. In short, from the human health perspective, the overall weight-of-evidence for benzene carcinogenicity and the existence of recognized cancer slope factor information makes benzene a better candidate for a TPH substitute than chrysene.

4.3.2 Protection of Ground Water Standards

Consideration of the remaining factors, such as the anticipated fate and transport of benzene and chrysene, and the potential for contamination of other media, also point to benzene as the TPH substitute of choice.

The lower molecular weight of benzene, coupled with its higher water solubility and lower affinity for soils, indicates that benzene is more mobile than chrysene and will tend to percolate into soils to a greater and more rapid extent. Over time, chrysene can be expected to be more tightly associated with soil, and to leach more slowly. Based on these physicochemical properties, the potential for impacts to ground water, given similar site conditions, appears to be much greater for benzene. Therefore, there is greater potential for risks associated with the site to encompass multiple media and to be quantifiable therein.

The USEPA guidance for formulating PRGs also indicates the importance of considering the potential for cross-media contamination, via secondary sources. It suggests that for instances where the medium of concern (*i.e.*, soil) may appear to pose acceptable risk at a site, but where the medium may have the potential to contaminate another medium (*i.e.*, ground water), a new method for deriving a health-based PRG may need to be developed, provided that fate and transport information exists and can adequately predict potential impacts. As discussed in Section 2.1.1, the USEPA is currently developing a series of guidelines for BTEX compounds based on fate and transport modeling from soil to ground water. As was also discussed in Section 2.1.1, state-specific approaches to deriving soil cleanup concentrations have incorporated these methods as well, with variable levels of effort and results.

The approach to deriving the soil concentration corresponding to achieving the protective ground water concentration involves fate and transport modeling from soil to ground water. In some cases, such site-specific contingencies as:

- Ground water potability, under current or future land use;
- Distances to aquifers and well heads;
- Soil type; and,
- Soil permeability.

are built into the "allowable" soil concentrations to accommodate site-specific conditions. Soil cleanup policies that allow for site-specific considerations have greater flexibility than those based on a universal soil cleanup concentration or on a generic modeling approach to "reverse transport". While so-called soil retardation factors or attenuation factors can be applied to the transport of contaminants through the soil column, their universal application to every site under

consideration would yield misrepresentative soil cleanup concentrations. Fate and transport modeling, provided site-specific information is incorporated, is a more reliable scientific tool.

Typically, the federal drinking water standards (Maximum Contaminant Levels (MCLs) or National Primary Drinking Water Regulations, (NPDWRs)), or state-specific drinking water or ground water quality criteria, are being used as the acceptable criteria for protecting drinking water sources. Chemical-specific MCLs are established to be protective of adverse human health effects for noncarcinogenic and carcinogenic effects for a lifetime via the oral drinking-water route of exposure. As such, the stringency of the MCL is driven by the stringency of the existing oral toxicities. All MCLs currently available for the potential TPH substitutes are listed in Table 3-7. Of the BTEX compounds, the MCL for benzene is lower (more stringent) than the MCLs for ethylbenzene, toluene, and xylenes by 140-, 200-, and 2000-fold factors, respectively. There are no MCLs for alkanes or PAHs associated with JP-4. There is no MCL for chrysene. The compound with the lowest MCL, and hence the most stringent ground water criterion, is benzene. A comparison of the relative potentials for migration to ground water of benzene and chrysene indicates that benzene, with its greater soil mobility, higher water solubility, and lower soil adsorption is the compound with the greatest potential to impact ground water.

4.3.3 Summary Information

There are insufficient bases for suggesting that any constituents of JP-4 other than benzene would serve as viable substitutes for TPH. This includes the three most promising candidate chemical groups--alkanes, naphthalene, and PAHs:

Alkanes. While alkanes are a primary component of JP-4 fuel, the spectrum of their toxicity, relative to the other potential candidates, does not represent the range of adverse toxicities exhibited by JP-4 or the known BTEX constituents. Also toxicity values and sufficient scientific information to support development of toxicity values have not been established. Alkanes are not considered to be carcinogenic compounds, and their primary acute noncarcinogenic effect (CNS depression) is not considered to have a significant potential for chronic adverse effects at anticipated chronic exposure levels. While these compounds are volatile and fairly mobile in soils (thereby increasing their potential to impact ground water via percolation, leaching, etc.), their potential for adverse toxic effects manifested through potential ingestion of ground water is not as significant as that of the other candidate substitutes or benzene.

Naphthalene. Naphthalene and substituted naphthalenes are present in lesser proportion than the alkanes in JP-4 fuel. However, naphthalene is a relatively low molecular-weight compound relatively mobile in soil and which has a fairly broad base of knowledge regarding its toxicity. The toxicity of naphthalene relative to the alkanes is more severe. The primary toxic effects are noncarcinogenic (e.g., effects on the hematopoietic system, liver, and kidneys). Toxicity values for naphthalene are currently under review, although a federal drinking water standard does not exist for this compound in ground water. Relative to the toxicities of benzene and the higher

molecular-weight PAHs, especially those exhibiting defined carcinogenic endpoints, naphthalene is not the best candidate to substitute for TPH.

Polyaromatic Hydrocarbons (PAHs), Chrysene. Polyaromatic hydrocarbons are a broad class of compounds with respect to their molecular weights and their toxic endpoints. In general, lower molecular-weight PAHs (e.g., fluorene) are more water soluble and exhibit greater soil mobility than higher molecular-weight PAHs. However, as a chemical group, these compounds are not considered particularly volatile or mobile in terms of their environmental fate and transport. Therefore, they tend to remain more associated with soils rather than leach into ground water. In addition, the PAHs that are probable human carcinogens (e.g., benzo(a)pyrene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, and dibenz(ah)anthracene) have not been detected in jet fuels, with the exception of chrysene (USEPA 1980). These PAHs are higher molecular-weight compounds with much less potential for migration into ground water. While the primary fate of PAHs in soils is biodegradation, the actual extent to which this occurs to effectively reduce soil levels cannot be established as a fixed variable, since site-specific microorganisms and spill conditions are the driving factors in the process. The low tendency for these compounds to impact ground water and the lack of adequate scientific justification for apportioning relative risks among PAHs limit their usefulness as potential TPH substitutes in JP-4.

Conclusion. The physicochemical properties of benzene influencing its potential for ground water impact, the magnitude of and scientific understanding of its toxicity, and the availability of an established toxicity value, point to benzene as the substitute of choice for JP-4. Chrysene, the sole carcinogenic PAH in JP-4 considered as a possible substitute, is not as viable a substitute, given its less definitive toxicity benchmark value and lesser potential to impact ground water. Naphthalene is not a viable choice, given the lesser magnitude of the toxicity associated with naphthalene, the lack of an established toxicity benchmark concentration, and the lack of an MCL. Combined with the anticipated lack of carcinogenic PAHs in ground water, the lack of sufficient data regarding noncarcinogenic health effects, and the absence of MCLs for PAHs other than benzo(a)pyrene, *the TPH substitute of choice is benzene.*

4.4 The Potential for Simultaneous Achievement of Benzene and TPH Soil Cleanup Concentrations - A Comparative Approach

The degree of health and environmental protection that could be provided by the use of TPH cleanup concentrations at hydrocarbon-contaminated sites was compared to the degree of protection provided by cleanup of benzene to the PRG, resulting in a residual risk of less than 10^{-4} to 10^{-6} . A direct health risk-based comparison was not possible because of the inability to assess health risks for TPH and the lack of historical health risk-based approaches to establishing TPH cleanup concentrations. The following two hypothetical illustrations demonstrate this point.

4.4.1 Remediation to a Conservative TPH Soil Cleanup Concentration

Hypothesis 1: Cleaning up site soil to the conservative TPH method detection limit (10 ppm) will simultaneously achieve acceptable benzene risk levels. Because, in reality, site-specific scenarios are complex, simplifying points and assumption need to be stated:

- The estimated soil cleanup concentration for BTEX is driven by benzene;
- Soil ingestion is the principal exposure route of interest;
- A risk level of 10^{-6} is conservatively estimated to be achieved at a benzene soil concentration of 22 ppm (soil PRG);
- The lowest soil cleanup level proposed by a state for TPH is 10 ppm based on the current method detection level for TPH in soils; and,
- 100 percent of the TPH concentration is conservatively assumed to be benzene.

Based on these assumptions, a TPH-based soil cleanup level of 10 ppm will allow simultaneous achievement of the "acceptable" risk-based benzene soil cleanup concentration of 22 ppm.

Weaknesses in this illustration:

- It represents the soil medium and ingestion pathway only. Factoring the ground water medium (or air) or a ground water-protective cleanup strategy into the illustration will impact the ability of cleanup to TPH background to allow achievement of benzene cleanup concentrations, in a site-specific manner.
- The assumption that all TPH is benzene is purposely erroneous, since jet fuel typically contains less than 18 percent of total benzenes (benzene and substituted benzenes), and typically there is extensive volatilization of these compounds following a spill.

4.4.2 Remediation to a Benzene Soil Cleanup Concentration

Hypothesis 2: Cleaning up a site to a benzene 10^{-6} risk level (22 ppm) also achieves TPH cleanup to the method detection level (10 ppm). If BTEX was considered to be 100 percent benzene and was cleaned up to the 10^{-6} risk level of 22 ppm in soil, the TPH method detection limit may or may not be achieved. The major components of JP-4, the alkanes, may still be present in soil at a concentration greater than 10 ppm. If contamination occurred substantially in the past, it is more likely that cleanup to a 10^{-6} benzene risk level would be protective of TPH, since fate and transport processes could result in reduction of the initial high TPH (alkane) levels. PAHs, the primary TPH components in soil possessing significant toxicity (*i.e.*, chrysene), are

present in relatively small concentrations in jet fuels, and are not expected to contribute extensively to TPH.

As an alternative to this approach, a simplified comparative analysis for one cubic yard of soil cleaned to a TPH cleanup level of 10 ppm or a BTEX (benzene) cleanup level of 22 ppm can be constructed.

In summary, the ability of an acceptable BTEX (benzene) soil cleanup level to result in an acceptable TPH soil level, and vice versa, is best presented at the site level with full consideration of individual site-specific factors.

Table 4-1. Soil Concentrations of Potential TPH Substitutes Associated With Maximum "Acceptable" Noncarcinogenic or Carcinogenic Human Health Effects From Soil Ingestion

Carcinogens:		
Chemical	Oral Slope Factor (mg/kg/day) ⁻¹	Soil Concentration (ppm)
Benzene	2.9×10^{-2}	22
Chrysene (PAH)	0.073	8.8
Noncarcinogens:		
Chemical	Oral R _d (mg/kg/day)	Soil Concentration (ppm)
Anthracene	3×10^{-1}	81,000
Ethylbenzene	1×10^{-1}	27,000
Fluoranthene	4×10^{-2}	10,800
Fluorene	4×10^{-2}	10,800
Naphthalene	4×10^{-2}	10,800
Pyrene	3×10^{-2}	8,100
Toluene	2×10^{-1}	54,000
Xylene	2×10^0	540,000

Figure 4-1. Residential PRG, Soil Ingestion
Noncarcinogenic Equation

$$THI = \frac{C \times 10^{-6} \text{ kg/mg} \times EF \times IF_{\text{soil/adj}}}{RD_o \times AT \times 365 \text{ days/year}}$$

$$C \text{ (mg/kg)} = \frac{THI \times AT \times 365 \text{ days/year}}{1/RD_o \times 10^{-6} \text{ kg/mg} \times EF \times IF_{\text{soil/adj}}}$$

where:

<u>Parameter</u>	<u>Definition</u>	<u>Default Value</u>
C	Chemical concentration (mg/kg)	None
THI	Target Hazard Index	1.0
RD _o	Oral chronic R _o D (mg/kg/day)	Chemical-specific
AT	Averaging time (years)	30 years (equal to exposure duration, which is incorporated in IF _{soil/adj})
EF	Exposure frequency (day/yr)	350
IF _{soil/adj}	Age-adjusted ingestion factor (mg-yr/kg-day)	14

Reduced Equation:

$$\text{Risk-based PRG (mg/kg soil)} = 2.7 \times 10^5 (RD_o)$$

Figure 4-2. Residential PRG, Soil Ingestion Carcinogenic Equation

$$TR = \frac{SF_o \times C \times 10^{-6} \text{ kg/mg} \times EF \times IF_{\text{soil/adj}}}{AT \times 365 \text{ days/year}}$$

$$C(\text{mg/kg}) = \frac{TR \times AT \times 365 \text{ days/year}}{SF_o \times 10^{-6} \text{ kg/mg} \times EF \times IF_{\text{soil/adj}}}$$

where:

<u>Parameter</u>	<u>Definition</u>	<u>Default Value</u>
C	Chemical concentration (mg/kg)	None
TR	Target excess lifetime cancer risk	10 ⁻⁶
SF _o	Oral slope factor (mg/kg/day) ⁻¹	Chemical-specific
AT	Averaging time (years)	70
EF	Exposure frequency (day/yr)	350
IF _{soil/adj}	Age-adjusted ingestion factor (mg-yr/kg-day)	114

Reduced equation:

$$\text{Risk-based PRG} = \frac{0.64}{SF_o}$$

Figure 4-3. Commercial/Industrial PRG, Ingestion and Inhalation
Noncarcinogenic Equation

$$THI = \frac{C \times 10^{-6} \text{ kg/mg} \times EF \times ED \times IR_{\text{soil}}}{RP_D \times BW \times AT \times 365 \text{ days/year}} + \frac{C \times EF \times ED \times IR_{\text{dr}} \times (1/VF) \times (1/PEF)}{RP_D \times BW \times AT \times 365 \text{ days/year}}$$

$$C (\text{mg/kg}) = \frac{THI \times BW \times AT \times 365 \text{ days/year}}{ED \times EF \times [(1/IR_D) \times 10^{-6} \text{ kg/mg} \times IR_{\text{soil}}] + ((1/IR_D) \times IR_{\text{dr}} \times (1/VF + 1/PEF))}$$

where:

<u>Parameter</u>	<u>Definition</u>	<u>Default Value</u>
C	Chemical concentration (mg/kg)	None
THI	Target Hazard Index	1.0
$R_1 P_{10}$	Oral chronic $R_1 D$ (mg/kg/day)	Chemical-specific
$R_1 D_1$	Inhalation chronic $R_1 D$ (mg/kg/day)	Chemical-specific
BW	Adult body weight (kg)	70
AT	Averaging time (year)	25 (equal to ED)
EF	Exposure frequency (day/yr)	250
ED	Exposure duration (year)	25
IR_{soil}	Soil ingestion rate (mg/day)	50
IR_{dr}	Inhalation rate (m ³ /day)	20
VF	Soil-to-air volatilization factor	Site, chemical-specific
PEF	Particulate emission factor (m ³ /kg)	Site-specific

Reduced Equation:

$$\text{Risk-based PRG} = \frac{102}{(5 \times 10^{-3} / IR_D) + ((1/IR_D) \times (20/VF)) + (1/PEF)}$$

Figure 4-4. Commercial/Industrial PRG, Ingestion and Inhalation Carcinogenic Equation

$$TR = \frac{(SF_o \times C \times 10^{-6} \text{ kg/mg} \times EF \times ED \times IR_{\text{soil}}) + SF_i \times C \times EF \times ED \times IR_{\text{air}} \times (1/VF + 1/PEF)}{BW \times AT \times 365 \text{ days/year}} + \frac{TR \times BW \times AT \times 365 \text{ days/year}}{EF \times ED \times [(SF_o \times 10^{-6} \text{ kg/mg} \times IR_{\text{soil}}) + (SF_i \times IR_{\text{air}} \times (1/VF + 1/PEF))]}$$

$$C(\text{mg/kg}) = \frac{TR \times BW \times AT \times 365 \text{ days/year}}{EF \times ED \times [(SF_o \times 10^{-6} \text{ kg/mg} \times IR_{\text{soil}}) + (SF_i \times IR_{\text{air}} \times (1/VF + 1/PEF))]}$$

where:

<u>Parameter</u>	<u>Definition</u>	<u>Default Value</u>
C	Chemical concentration (mg/kg)	None
TR	Target excess lifetime cancer risk	10 ⁻⁶
SF _o	Oral slope factor (mg/kg/day) ⁻¹	Chemical-specific
SF _i	Inhalation slope factor (mg/kg/day) ⁻¹	Chemical-specific
BW	Adult body weight (kg)	70
AT	Averaging time (year)	70
EF	Exposure frequency (day/yr)	250
ED	Exposure duration (years)	25
IR _{soil}	Ingestion rate (mg/day)	50
IR _{air}	Inhalation rate (m ³ /day)	20
VF	Soil-to-air volatilization factor	Site, chemical-specific
PEF	Particulate emission factor (m ³ /kg)	Site-specific

Reduced equation:

$$\text{Risk-based PRG} = \frac{2.9 \times 10^{-4}}{((5 \times 10^{-5}) \times SF_o) + (SF_i \times (20/VF) + (1/PEF))}$$

5.0 OPTIONS FOR RAISING A RISK-BASED SOIL CLEANUP CONCENTRATION FOR THE TPH SUBSTITUTE (BENZENE)

Summary: Section 5.0 is focussed on how an appropriate preliminary remediation goal (PRG) is developed for benzene, the preferred TPH substitute in soil as determined in Section 4.0. The two key elements considered in establishing the benzene PRG are the same two key elements used to establish human health risk: benzene's cancer potency factor and, quantitative expression of the potential for human exposure to benzene. Various ways of expressing both of these elements were explored in this section, including the use of Monte Carlo simulation. PRGs are site-specific because many of the factors used to calculate them vary from site to site and are necessarily dependent on conditions at a particular site. Therefore, site-specific PRGs were not calculated in Section 5.0.

Risk-based cleanup concentrations for a chemical of concern are derived from benchmark measures of toxicity (e.g., R_d) for the chemical and its site-specific exposure conditions. As discussed in Sections 4.1 and 4.2, the USEPA has developed methods for calculating "risk-based preliminary remediation goals" (PRGs) for Superfund sites (USEPA 1991a). This methodology involves solving the risk equation for the soil concentration term (i.e., by back-calculating an "acceptable" concentration based on a predetermined "acceptable" level of risk). Thus, the factors that affect the cleanup level are: (1) the predetermined "acceptable" level of risk; (2) benchmark measures of toxicity; and (3) site-specific exposure parameters.

As benzene carcinogenicity is anticipated to drive the site risk estimates, the two major components specifically examined were alternative cancer slope factor (SF) determinations for benzene (i.e., distributional analysis of dose-response relationships developed from cancer studies), and site-specific exposure reduction strategies (i.e., distributional analysis of exposure estimates) that might be employed at Air Force JP-4 sites. These elements are discussed in the sections below.

5.1 Establishing a Predetermined "Acceptable" Risk Level

The target risk level for Superfund sites for carcinogenic effects is usually 1×10^{-6} (based on the NCP's point of departure for analysis of remedial alternatives) (USEPA 1991a). However, the interpretation of this "point of departure" is based on the following:

"For known or suspected carcinogens, acceptable exposure levels are generally concentration levels that represent an excess upper bound lifetime cancer risk to an individual of between 10^{-4} and 10^{-6} ." (40 CFR Part 300)

Thus, depending on site-specific conditions (*e.g.*, severity of biological effect, potency of the chemical of concern, size of the potentially exposed population, degree of potential future exposure based on future land-use projections), 10^{-5} or 10^{-4} may be more appropriate predetermined levels of "acceptable" risk. In addition, state-specific interpretations of "acceptable" risk may vary as well (*i.e.*, California, where "acceptable" equates to 10^{-5} risk levels), although nonCERCLA sites would be the best candidate sites where state jurisdiction takes precedence.

5.2 The Cancer Slope Factor

The general approach to formulating a cancer slope factor is presented below, along with the inherent uncertainties in its estimation. In addition, a specific discussion of the basis for the existing benzene cancer slope factor is presented.

5.2.1 Derivation of a Cancer Slope Factor

The USEPA has developed cancer slope factors for specific compounds whose cancer weights-of-evidence classifications are Categories A, B1, or B2¹⁰. Cancer SFs reflect the dose-response relationship between the dose of the chemical and (typically) tumor frequency. The SF represents a numeric estimate of the lifetime probability of a particular response (cancer) for a given unit dose of a chemical, although procedurally this dose is typically estimated by the USEPA as the conservative 95th percentile upper confidence level (the "upper bound") on the probability. There are several components to the derivation of the SF that can significantly influence the value of the SF, such as:

- Selecting and interpreting an appropriate data set as the basis for the SF;
- Extrapolating a response obtained at the exposure levels in the data set to a response at the more typical low-dose exposures anticipated to occur;
- Determining equivalent human doses from animal studies; and,
- Generating the upper-bound on the point estimate of the cancer SF.

The procedure for deriving a cancer SF is discussed below in the context of use of best professional judgement in applying these four components and the potential for variation among the components.

¹⁰ Category A = Known human carcinogen
Category B1 = Probable human carcinogen with human evidence
Category B2 = Probable human carcinogen with animal evidence

5.2.2 Selecting Appropriate Data Sets as the Basis for the Slope Factor

In establishing an SF, human epidemiologic or experimental data of good quality are invariably preferred over animal data. Practically, animal studies are utilized more extensively to generate SFs because exposures are more controlled and quantifiable and because adverse health endpoints are easier to measure. Animal species with greatest metabolic, physiologic, and pharmacokinetic similarity to humans are preferred, although more typically, dose-response data obtained from the most sensitive animal species are used because other desired information is lacking. Study results are weighted according to the strength of their experimental design and the quality of their results.

The accuracy and representativeness of the benzene dose-response relationship is affected by the number of experimental dose levels used, the number of animals exposed at each dose level, the route of exposure, the duration of the study, and the health endpoints examined. Typically, the "best quality" study is identified and then used as the basis for the SF. If no single study is identified as most appropriate, several studies may be considered to ensure that all relevant and applicable data have been utilized. Variations in any of these study parameters and in their interpretation can affect the derived SF.

5.2.3 High-Dose to Low-Dose Extrapolation

Results from human occupational studies and experimental animal studies are based on human exposures or experimental doses that are higher than those to which humans are usually exposed. The advantages to using higher exposures/doses is that they elicit observable, measurable responses in relatively small sample sizes. While adverse biological effects may be noted at higher dose levels, the correct manner for extrapolating experimental high-dose information to environmental low-dose exposures remains at issue. High-to-low-dose extrapolation typically involves the use of one of several mathematical models to "fit" the available data and extend the dose-response curve into the lower dose regions. The bases for these models range from simple estimations of dose-related probabilities derived from general premises about the mechanism of cancer formation, to more biologically-based models involving more complex interpretations of cancer mechanisms and chemical-specific information.

Different models exhibit different degrees of fit with respect to the study data, and while the relative differences in fit may be scientifically acceptable, the resulting predicted response levels (cancer frequencies and their associated risks) at low doses may vary considerably.

The USEPA typically uses the linear multistage model (LMS), which incorporates current assumptions about the mechanism of cancer formation, in addition to a "goodness of fit"

approach to the study data.¹¹ LMS is used preferentially by the USEPA when there is limited information on the actual mechanism of cancer formation, because it derives a more conservative SF (*i.e.*, it predicts a higher SF), and yields correspondingly higher risk estimates.

5.2.4 Deriving the Equivalent Human Dose of Benzene

When animal data are used as the basis for the human SF, doses given to the animals must subsequently be mathematically converted for applicability to humans. This conversion is based on the premises that:

- Absorbed doses are the same from species to species within the same unit of body surface area; and,
- The approximate mathematical relationship between surface area and body weight is:

$$\text{Surface Area} = \text{Body Weight}^{\frac{2}{3}} \quad (1)$$

$$\text{Human Dose} = \text{Animal Dose} \times \left[\frac{\text{Human Body Weight}}{\text{Animal Body Weight}} \right]^{\frac{2}{3}} \quad (2)$$

Typically, for inhalation studies involving partially soluble/absorbed gases, the air concentration to which the animal is exposed (*i.e.*, ppm) is considered the equivalent human dose (given equal exposure times). For gases which are completely absorbed, the amount absorbed per unit of body surface area is considered equal.

Human equivalent-dose conversion is controversial. It has been proposed, for example, that equivalent doses be obtained using a direct body weight-based approach rather than a surface area-based approach (USEPA 1992), where

$$\text{Human Equivalent Dose} = \text{Animal Dose} \times \left[\frac{\text{Human Body Weight}}{\text{Animal Body Weight}} \right]^{\frac{3}{4}} \quad (3)$$

¹¹ The basic assumptions are that: (1) the mechanism of cancer involves a series of stages in a cell's progression toward becoming a tumor cell, and (2) the low-dose-response region of the dose-response curve is linear.

5.2.5 Presenting the "Upper Bound" Slope Factor

Once the dose-response data have been fit to the chosen model, the slope of the low-dose-response curve is estimated, and the upper 95th percentile confidence limit (upper bound) on this estimate is calculated. This upper-bound on the cancer SF represents a conservative 95 percent probability on the cancer dose-response relationship. In some cases, as with human data used for generating a cancer SF, the best estimate (*i.e.*, the maximum likelihood estimate, MLE) for the cancer SF is used, without its 95 percent upper bound, to reflect increased certainty in the cancer dose-response relationship derived from human data.

Use of the upper-bound estimate in lieu of the MLE can lead to an overestimation of risk. A single value for the cancer SF limits the interpretation of the risk estimate derived from the SF. An alternative procedure for crafting a SF that permits a broader inclusion of available scientific data involves calculating a *range or distribution* of cancer SFs. This approach permits the expression of variabilities in:

- Different dose-response data sets;
- Different assumptions about the mechanisms of cancer formation;
- Different methods for estimating human dose equivalence; and,
- Different low-dose extrapolation models.

The implications of applying these variabilities to the calculation of the benzene cancer SF are presented in the next section.

5.3 Distributional Analysis of Dose-Response Relationships Developed from Cancer Studies

The derivation of the benzene cancer slope factor is presented below, with its accompanying uncertainties. The potential for alternative procedures and estimates is also discussed.

5.3.1 Derivation of the Benzene Cancer Slope Factor

The USEPA's approach to deriving the cancer SF for benzene (USEPA 1985) is based on consideration of data obtained primarily from three epidemiology studies of workers exposed to benzene occupationally via inhalation (Ott *et al.* 1978; Rinsky *et al.* 1981; Wong *et al.* 1983). In all studies, the critical endpoint was cancer mortality attributable to leukemias. Information regarding the concentrations of benzene and durations of exposure were used to generate "dose groups" with benzene-related leukemia mortalities associated with each group, which were then

used to derive dose-response curves. Finally, different cancer risk models were combined with different exposure parameters to generate cancer unit risks.¹²

Six different combinations of exposure model and risk model were used to generate benzene unit risks, depending on the magnitude of exposure and the type of risk being modeled. The six combinations were based on:

- Three models of benzene exposure:
 - Cumulative exposure;
 - Weighted cumulative exposure; or
 - A window of exposure.

These exposure parameters were meant to encompass all potential permutations of cancer latency, where latency was defined as the time to onset of tumor or death. They allowed for the risk of benzene cancer mortality to rise or fall proportionally with benzene concentration and exposure duration.

- Two risk models:
 - A *relative* risk model, where risk values could be estimated relative to the background leukemia incidence or the leukemia incidence of a control population; or
 - An *absolute* risk model, where risk values were not expressed with respect to the background or control leukemia incidence.

The two risk models (and their associated risk estimates) were applied to each of the three exposure models, yielding six possible combinations of conditions/models under which to estimate benzene cancer SFs. For each one of the six combinations, several variations of the three data sets from the three epidemiology studies were used to calculate the slopes of the respective low-dose-response curves¹³, resulting in 21 dose-response combinations of models and data sets. From the 21 dose-response curves, 21 maximum likelihood estimates (MLEs)¹⁴ and upper and lower bounds on these MLEs were generated. MLEs were then presented for the risk at the unit dose of 1 ppm (unit cancer risks, ppm⁻¹). These MLE unit cancer risks ranged from 8.98×10^{-3} ppm⁻¹ to 1.04×10^{-1} ppm⁻¹, an 11-fold variation (over 1 order of magnitude). The actual distribution of these initial unit cancer risk estimates is shown in **Figure**

¹²The risk associated with a unit dose of benzene equal to 1 ppm.

¹³Typically the variations involved extending the length of followup time for the populations, thereby altering the frequencies of mortalities associated with each exposure group.

¹⁴The actual fitted data estimates.

5-1. In order to obtain a representative estimate of the MLE, four MLEs from the 21 MLEs were chosen, thought to be the best approximations based on:

- Use of the two best common data sets (Ott *et al.* 1978 and Rinsky *et al.* 1981),
- Excluding estimates for "window" doses, and
- Giving equal weight to each of the risk/exposure (dose) models:
 - Relative risk-cumulative dose
 - Absolute risk-cumulative dose
 - Relative risk-weighted cumulative dose, and
 - Absolute risk-weighted cumulative dose.

The four MLEs ranged from 1.04×10^{-2} to 2.89×10^{-2} , a two-fold variation. The geometric mean of these four unit cancer risks was estimated (2.11×10^{-2}), and subsequently modified by a factor (1.23) which reflected an adjustment for comparative consideration of the Wong study (1983), to yield a final unit risk estimate of $2.6 \times 10^{-2} \text{ ppm}^{-1}$. This unit cancer risk value was converted by USEPA to an oral SF of $2.9 \times 10^{-2} (\text{mg/kg/day})^{-1}$ (the value shown in Table 3-5), using standard conversion methods¹⁵ (USEPA 1989).

Animal data were considered to be a secondary and less germane source of information for estimating the benzene cancer SF. Several studies examined (Goldstein *et al.* 1980; Maltoni *et al.* 1983; NTP 1984) were based on inhalation or oral gavage routes. When endpoints from the animal inhalation studies related to leukemia were used to generate unit cancer risks, all unit risk values were less than those obtained from human epidemiology data (indicating less associated risk). Gavage studies generally yielded higher unit risk estimates, based on nonleukemia endpoints such as tumors of the preputial gland. However, preputial glands are only found in rats, and the exposure route was not similar to the epidemiology studies. Therefore, this endpoint was not considered to be directly applicable to estimates of human risks.

Sensitivity analysis¹⁶ was explored by the USEPA as a method for examining the inherent variation within the animal inhalation unit cancer risk estimates. Assumptions that were explored included:

- Using the LMS model or a second model, the LMS-Weibull model (to compensate for animal mortality prior to the end of the study);

¹⁵ Conversion assumes 1 ppm benzene = 3.26 mg/m^3 ; adult body weight = 70 kg; adult inhalation rate = $20 \text{ m}^3/\text{day}$.

¹⁶The effect produced on the final unit risk value when one variable or pair of variables (assumptions) are altered, while keeping all other parameters constant.

- Generating the MLEs of unit risks or the 95th percentile upper bound unit risk values; and
- Converting from animal to human equivalent dose using either a surface area proportionality or a body weight proportionality.

The results indicated that regardless of which dose equivalence method was used, use of one model versus the other model yielded a variation of only two-fold in the final unit cancer risks (for MLE or 95th percentile upper bound estimates). The greatest variation between unit cancer risks generated (an order of magnitude (12-fold) difference) occurred with each of the two risk models, using the same model with different human dose-equivalence methods.

5.3.2 Uncertainties Associated with the Benzene Cancer SF

- Human exposure groups were defined according to broad categories of exposure, based on duration and concentration of exposure (in contrast to animal studies, for example, where doses are discrete and precise). Each human exposure group (category) contained numerous combinations of exposure concentration and duration; individuals were placed within a given category. Individual group distributions and variabilities, as well as where on the distribution continuum most of the exposure occurred, were unknown.
- Exposures were known or grouped partially on the basis of the benzene air concentration to which an individual was exposed. Therefore, the benzene air concentration effectively acts as an *external* dose. There is no compensation for the percent of benzene absorption after inhalation, which yields an *internal or biological* dose.
- The estimation and use of the two categories of the exposure parameters¹⁷ also carries associated uncertainty. In cumulative exposure:

$$Risk \propto \sum [Exposure\ Duration \times Time] \quad (4)$$

In *weighted* cumulative exposure:

$$Risk \propto \sum [Exposure\ Duration \times Time \times Leukemia\ Latency] \quad (5)$$

¹⁷Either (1) Cumulative exposure (total lifetime exposure in ppm-years), or (2) weighted cumulative exposure (total lifetime exposure in ppm-years, but weighted for the relative prior duration of exposure).

Both proportionality assumptions were given equal weight in the final estimation of the cancer SF for benzene, given the uncertainty of the relative accuracy of either one.

- The use of models that estimate *relative* risk versus *absolute* risk also carries uncertainty:
 - *Relative* risk assumes that benzene leukemia occurs via the same mechanism as "other" (*i.e.*, nonbenzene-associated) leukemias observed in the background group (general population or control group). Therefore, the benzene-associated leukemia risk (or benzene-associated leukemia mortality rate) is proportional to the overall leukemia background rate and should follow the same trend (to increase over time/age) as the background leukemia rates.
 - *Absolute* risk is not based on the assumption of a similar mechanism or trend for benzene-associated leukemia mortalities.

Since it was not clear which of the two risk models is more appropriate, equal consideration was given to each model. Relative risk models were employed for two of the four unit cancer risk values used for the SF, while the other two used absolute risk as the model.

5.3.3 Alternate Methods for Characterizing the Benzene SF

Methods that are employed or suggested in presenting the uncertainty inherent in estimates of risk included sensitivity analysis and Monte Carlo simulation. These methods and a more novel approach, information analysis, are discussed in the following paragraphs.

A sensitivity analysis on the SF, the application of which was described in Section 5.3.1 (Derivation of the Benzene Cancer Slope Factor), is a method for detecting the relative effects of altering the assumptions or parameters used to derive the SF. The method involves altering one factor while holding all others constant. By systematically altering each variable separately, the variable that will result in the greatest magnitude of change in the SF can be identified as a sensitive parameter. This process defines the range over which the final SF can vary according to the variation in a single input parameter.

Applying this approach to the relative risk model for cumulative exposure in the benzene SF estimation (one of the six modeling approaches described above), the same data set is used three times, except that in each cycle the followup time for the population of interest has been increased by approximately ten years. In essence, this is a sensitivity analysis of the effect of modifying followup time (or latency time) on the MLE of the benzene SF.

While such an approach can be applied to the benzene SF, it yields limited information beyond the SF range attributable to one or two individual parameters.

Monte Carlo simulation is more sophisticated approach, in that it allows for some estimation or deduction of the variation in the cancer SF when multiple input variables are altered. For application to the benzene SF, the following parameters must be known:

- The "correct" combinatorial risk model to apply (absolute or relative; cumulative or weighted cumulative exposure), and
- Distributions or the lower and upper bounds on these and other parameters.

A distributional approach for a single model is very difficult unless the following information is present:

- Specific mechanistic information on benzene carcinogenesis;
- Understanding of the latency of benzene-induced leukemia from inhalation exposure; and,
- Epidemiologic trends in mortality rates.

Information analysis (Sielken 1991a,b) is a recently developed alternate weight-of-evidence technique for presenting the benzene SF distribution. This approach depicts the variation in the SF from the point-of-view of the "most likely" scenario(s), yet does not require knowledge of the specific mechanisms or distributions. The weight-of-evidence approach involves three major steps:

- Generating a series of options for input parameters;
- Applying weight-of-evidence to support the degree to which each input parameter is "correct" (*scientific truth*); and,
- Applying weight-of-evidence for each potential path used to model the unit risk value.

This is a means for adjusting individual MLEs that are generated by any one of several methods, so that each individual MLE reflects the best available knowledge on both the chemical and the SF methodology. The end result is a distribution of weighted SFs.

For example, the major parameters for the various stages in formulating the SF that require characterization in deriving an SF include:

- *The human carcinogenic response.* What is the carcinogenic weight-of-evidence for a specific route of exposure?
- *Mode of action.* What is the chemical-specific mechanistic information? Is the chemical genotoxic, a proliferation-inducer, or both?

- *Dose scale.* Are doses presented as administered, delivered, or biologically effective?
- *Dose-response model.* What model is being used: quantal (e.g., probit, logit, Weibull, multihit, multistage), time-to-tumor (e.g., multistage-Weibull, Weibull-Weibull, Hartley-Seilken, Armitage-Doll), or growth (e.g., two-stage MVK)?
- *Experimental data set.* What are the specific features of the data set on which the SF is based (e.g., study design, route, species, response)?
- *Interspecies extrapolation method.* Is the extrapolation from animals to humans according to body weight or surface area?

All possible permutations of the choices are represented, and are depicted as branches on a tree, where each fork is the next stage at which a choice is made. For each major input parameter (mode of action, dose scale, model type, etc.), all possible choices are considered for how well they reflect the current state of knowledge or "truth", with respect to the choices/inputs made prior to that point, and are given a proportional weight-of-evidence¹⁸. Each pathway then has a series of weights associated with each component, all of which are then multiplied together to yield the final weight for the particular pathway or final branch. The unit risk for each possible pathway is estimated as the MLE, with its associated weight-of-evidence that represents the probability that this MLE reflects a true risk estimate, yielding a distribution of weighted MLEs.

The potential for the application of the weight-of-evidence approach to substantially alter the benzene SF is questionable. This type of approach has the advantage of not requiring that any hypothesis be proven wrong (i.e., there is no need to know the "correct" model to use, since it assigns weights that are relative to one another for all permutations that yield unit-risk MLEs). However, this method does require expert knowledge of all stages in the SF derivation and benzene-specific applications therein, and expert judgments that are made may require rigorous substantiation at all stages in the decision tree process.

5.3.4 Lack of Anticipated Appreciable Alteration in Benzene SF

Based on the current USEPA documentation on the derivation of the benzene SF (USEPA 1985), the potential for appreciably altering the benzene cancer SF is not anticipated to be significant. The following points address aspects in SF development that have traditionally been sources of considerable variation in deriving and interpreting SFs, and particularly those associated with the benzene SF derivation. Reference to more recent studies that have examined the USEPA approach are made as well, within the context of their applicability to lowering the cancer SF for benzene.

¹⁸Note that the sum of these values equals one, since they are probabilities of being "correct".

- Unlike the majority of chemicals for which SFs have been derived, the benzene cancer SF was estimated from existing human epidemiology data. Hence, there is no variation associated with the interspecies extrapolation from animals to humans for which to account. In addition, peer review suggests that the studies used in setting the SF were the best available human studies.
- The benzene cancer SF was estimated using two different lifetime cancer risk models (relative and absolute risk) and two different assumptions of the appropriate exposure parameter (cumulative and weighted-cumulative exposure). While variation exists solely on the basis of the use of four estimates derived in four different manners, the extent of this variation is only two-fold, and the value is believed to encompass all potentially viable options. The traditional linear multistage model (LMS), with its inherent conservative estimation of cancer SFs relative to other models, was not used by the USEPA in the derivation of the benzene SF.
- The benzene SF was presented as the geometric mean of the maximum likelihood estimates (MLEs), as opposed to the more standard approach used for the majority of SFs, which is to present the SF as the 95th percentile upper bound. The use of the upper bound versus the MLE would yield a SF greater than the MLE, with the variation between the MLE and the upper bound being substantially greater than the variation between the four MLE estimates used to establish the benzene SF.
- In light of recent increased understanding of several parameters employed in the estimation of the benzene SF, a study was designed to quantitatively reevaluate the USEPA estimate of the benzene SF (Clement 1988). The study proposed that the benzene cancer SF could effectively be decreased by an order of magnitude (Clement 1988). At this time, the extent to which this report has been reviewed, either by external peer review or the USEPA, has not been directly ascertained, although USEPA personnel indicate that there has been no study to substantially refute the currently established SF.

5.4 Alternative Methods for Determining Exposure Estimates

The USEPA risk assessment methodology for exposure assessment suggests a series of standard default exposure routes and exposure assumptions/parameters for use in conjunction with discrete current and future land use scenarios. While the exposure routes themselves may be more or less applicable to a specific site, the majority of the standard exposure assumptions advocated for use in estimating chemical intakes are not site-specific, nor are they necessarily the most current, relevant numerical values. Historically, the use of alternate *standard* assumptions or the development of site-specific assumptions has been met with varying degrees of acceptance by regulatory agencies, although the existing guidelines for these assumptions (USEPA 1989, 1991b) and the guidelines regarding the formulation of site-specific PRGs (USEPA 1991a) advocate the use of site-specific information wherever possible. Site-specific information and

viable exposure routes will vary with the location, magnitude, and nature of the spill or leak, as well as the local human populations, regional topology and hydrogeology, and land use. Some practical, site-specific considerations are discussed below.

5.4.1 Use of Site-Specific Exposure Parameters

The potential for exposure of humans who come in contact with the site of a former JP-4 spill or leak can be influenced by factors, such as: *the identification of the current and future land uses at the site* (e.g., current land use which is active, inactive, industrial, residential, or agricultural; future land use which is similar to current, or involves conversion to industrial, residential, or agricultural); *the identification of the human receptor of greatest concern* under these land uses (e.g., a worker in an industrial setting, a child in a residential setting, a farmer in an agricultural setting); *the physical nature of the site* (e.g., heavily vegetated, bare topsoil, pavement, limited geographical access, fenced, distance to a potable aquifer; geological stratification); *the size/volume of the spill or leak*; and, *the age of the spill or leak*. Based on knowledge of such conditions, realistic assessments of potential routes for exposure can be made. Knowledge of the fate and transport of JP-4 constituents will assist in making educated and experienced exposure route assessments. The establishment of a realistic route of exposure for a site lends greater strength to any soil remediation criteria that may be developed using these exposure routes. This, in turn, ensures that the soil cleanup criteria will accurately reflect the risk at the site. Site-specific considerations and the use of site-specific exposure parameters, whenever feasible, are crucial to this process.

Most exposure estimates and risk calculations are a multiplicative combination of exposure assumptions resulting in a point estimate for the intake of a chemical. A "traditional" practice is to choose a combined variety of average, conservative, and worst-case standard assumptions. There are three disadvantages to this approach:

- There is no way of knowing the actual degree of conservatism in an assessment (*i.e.*, no realistic depiction of the variation can be presented for the exposure estimate, and hence for the ultimate risk level);
- By selecting upper limits on many exposure variables, the assessment generally considers scenarios that will rarely occur (*e.g.*, what is the likelihood of an individual ingesting the maximum soil amount per day, for every day of the maximum number of exposure days, for the maximum number of years the individual could live near site?); and,
- Sensitivity analyses are of limited value since many of the variables are at or near their maxima.

An alternative approach to the use of conservative assumptions is an exposure distributional analysis, in which ranges or distributions of individual exposure parameters (*e.g.*, the

distribution of adult body weights) are considered to produce an overall distribution of potential exposure. A Monte Carlo simulation¹⁹ is such an analysis.

5.4.2 The Monte Carlo Approach

Monte Carlo simulation is a procedure for solving problems involving random variation (chance or probability) where time does not play a major role (Law and Kelton 1982; Hillier and Lieberman 1986). It is widely used within the statistics community for certain types of problems that are not amenable to solution by experimentation (*e.g.*, estimating critical values, estimating the power of a new hypothesis test, estimating the effect of uncertainty on complex systems). Monte Carlo simulation has been used by statisticians, systems analysts, and engineers for many years, but its use in human health risk assessment is relatively recent (*e.g.*, Burmaster *et al.* 1990; ENVIRON 1991; Burmaster and von Stackelberg 1991; Hawkins 1991; RiskFocus 1990, 1991a,b).

Rather than using point estimates in exposure assessment, Monte Carlo simulation can be used to estimate distributions for exposure assumptions. Use of this methodology does not alter the basic structure of the exposure estimate as first described by the National Research Council (1983). However, it does refine the way chemical intakes are calculated in the exposure assessment.

In both the "traditional" and Monte Carlo approaches to exposure assessment, the analyst first constructs a model consisting of relationships between random variables [*e.g.*, the model for intake of a compound via ingestion of water (USEPA 1989, Exhibit 6-11, page 6-35)]:

$$Intake = \frac{CW \times IR \times EF \times ED}{BW \times AT} \quad (6)$$

where:

<i>Intake</i>	=	Intake (mg/kg/day)
<i>CW</i>	=	Chemical concentration in water (mg/L)
<i>IR</i>	=	Ingestion rate (L/day)
<i>EF</i>	=	Exposure frequency (days/year)
<i>ED</i>	=	Exposure durations (years)
<i>BW</i>	=	Body weight (kg)

¹⁹ There are three classes of methods generally used for simulating exposure under uncertainty: (1) sensitivity analysis; (2) probabilistic error propagation, and (3) fuzzy sets. Monte Carlo simulation is in the class of probabilistic error propagation (Lapton *et al.* 1992).

AT = Averaging time (days)

In the "traditional" approach to risk assessment, point estimates for each of the variables in the intake equation are chosen (e.g., the 95th percentile upper confidence limit on the mean of the ground water sample concentrations; the 90th percentile of the distribution of adult water consumption). This results in a point estimate for intake which, having used conservative estimates for each variable, suggest an intake quantity that is doubly indemnified by using 90th and 95th percentiles in its derivation. Because different percentiles were used²⁰, it is not possible to know what *combined* percentile to assign to the overall expression of intake.

In a Monte Carlo simulation model, the analyst determines a continuous or discrete distribution to describe each of the random variables in the model's equation. This distribution is defined in terms of the probability density function (PDF) or the cumulative distribution function (CDF). In the case of a normal distribution, the distribution is completely defined by specifying two parameters: the mean and variance. An entire family of normal distributions is generated by varying the mean and/or the variance. Other distributions are defined by one, two, or more parameters.

When running a Monte Carlo simulation model, the computer randomly "draws" one value from the appropriate distribution for each of the random variables in the model. For example, the computer randomly selects a chemical concentration from the chemical's distribution of concentrations, an ingestion rate from the distribution of ingestion rates, and other parameters necessary to solve Equation 6. The model then calculates a human daily intake according to Equation 6. This variable selection and computation process is repeated thousands of times to provide a distribution of daily intakes. The distribution is often bell-shaped (i.e., a normal distribution) or skewed to the right. From this distribution, a specific intake can be selected (e.g., the average or mean intake, median intake, or 95th percentile upper confidence limit on the intake) that, in combination with the appropriate toxicity benchmark concentration, is used to calculate risk.

In addition, a Monte Carlo simulation can include correlations between variables (Smith *et al.* 1992). For example, there is a correlation between body weight and ingestion rate. Using strongly correlated variables in deriving an estimate of exposure serves to strengthen the estimate by preventing nonsensical combinations of variables in its derivation.

In most cases, the daily human intake calculated using Monte Carlo simulation is less than that calculated using point estimates. This is not to suggest the use of Monte Carlo simulation because it produces lower estimates, but rather because its estimates can be associated with probabilities. This results in increased confidence in the estimate of intake, thus ensuring increased confidence in public health protection.

²⁰In some cases *no* distribution-based percentiles are used, such as an exposure frequency of 350 days per year based on the assumption that people are away from home two weeks per year.

5.5 Distributional Analysis of Exposure Estimates

The identification of the essential components of an exposure analysis and their application within a Monte Carlo-based approach are discussed in the following sections.

5.5.1 Critical Components of the Exposure Analysis

One means to deriving exposure estimates is to use a Monte Carlo simulation to yield a distributional analysis of exposure estimates. The objective of the exposure analysis in the risk assessment process is to estimate the magnitude, frequency, and duration of human exposures to a chemical present in the environment. A complete exposure estimate, then, would characterize the route, duration, and magnitude of exposure; the populations exposed, including sensitive populations; and the uncertainties associated with all estimates. The critical components of an exposure analysis have thereby been delineated as:

- Analysis of data,
- Evaluation of transport, migration and distribution of chemical constituents,
- Identification of all exposure routes and potentially exposed populations, and
- Estimation of exposure parameters (to include, but not be limited to: soil ingestion rates, dermal contact rates, inhalation rates, and bioavailability issues) (Michaud *et al.* 1991).

Each of these components is used in some manner in the resulting exposure estimate (*e.g.*, the analysis of data is used to estimate media-specific chemical concentrations; transport and migration are used to evaluate potential exposure points; the exposure parameters are used in the actual mathematical calculations). However, those components critical to the Monte Carlo simulation are the parameters used in the mathematical calculations.

A recent workshop cosponsored by USEPA and the University of Virginia attempted to: (1) assess the state of the art in selecting input distribution functions, with an emphasis on their applications to environmental risks; and (2) establish theoretically sound and defensible foundations upon which to generate future guidelines for USEPA use in the selection of probability distributions (UVA 1993). The issue papers and workshop participants concluded that the selection of the input distributions are critical and attempted to propose means to advance the state of the art. There was no consensus on the use of specific distributions, the exception being mutual agreement on the need for use of scientifically defensible, rationally chosen, site-specific distributions.

Thus, the selection of input distributions for exposure assessment at a JP-4-contaminated site must be made based on site-specific conditions. This need for site-specificity incorporates all of the critical components listed above, including choice of appropriate exposure pathways and sensitive subpopulations.

5.5.2 Application of the Monte Carlo Approach

For example, at a hypothetical site it is determined that ground water is the medium of concern and offsite residents are the population of concern based on their use of ground water as a drinking water source. Use of exposure estimation equations yields an estimation of intake for ground water. Typically this would result in a point estimate. Using a distributional analysis, a distribution of intakes would be estimated. **Figure 5-2** presents the input distribution variables used in a hypothetical estimation of intake for benzene in drinking water, while **Figure 5-3** presents the input for deriving the standard, point estimate. As can be seen from **Figure 5-4**, the resulting point estimate of the lifetime average daily dose (LADD), 4.11×10^{-2} mg/kg/day, corresponds to greater than the 95th percentile on the distributional analysis (offscale). If, instead, the 95th percentile was of interest, the resulting estimate from the distributional analysis would be 1.7×10^{-2} mg/kg/day, a lower exposure estimate. In addition, if the cancer risk estimate includes a simple distributional analysis of the slope factor, in this case assumed to be lognormal, the effect of the distributional analysis is even greater (**Figure 5-5**). The cancer risk estimated by use of the point estimate LADD and the benzene SF is 1.19×10^{-3} (essentially 1×10^{-3}) (**Figure 5-3**), while the 95th percentile for the cancer risk based on the distributional analysis (**Figure 5-5**) would predict 3.8×10^{-4} (essentially 4×10^{-4}).

In another example, Lloyd *et al.* (1992) used a Monte Carlo simulation to evaluate the New Jersey Department of Environmental Protection (NJDEP) approach for calculating surface soil cleanup standards for benzene. The authors considered only a soil ingestion pathway. The NJDEP point estimate for the benzene cleanup concentration is 3 mg/kg, which is well below the 1st percentile of the overall distribution determined by Lloyd *et al.*, and thus a very conservative value.

Figure 5-1. Benzene Unit Risks
Frequency Distribution (USEPA 1985)

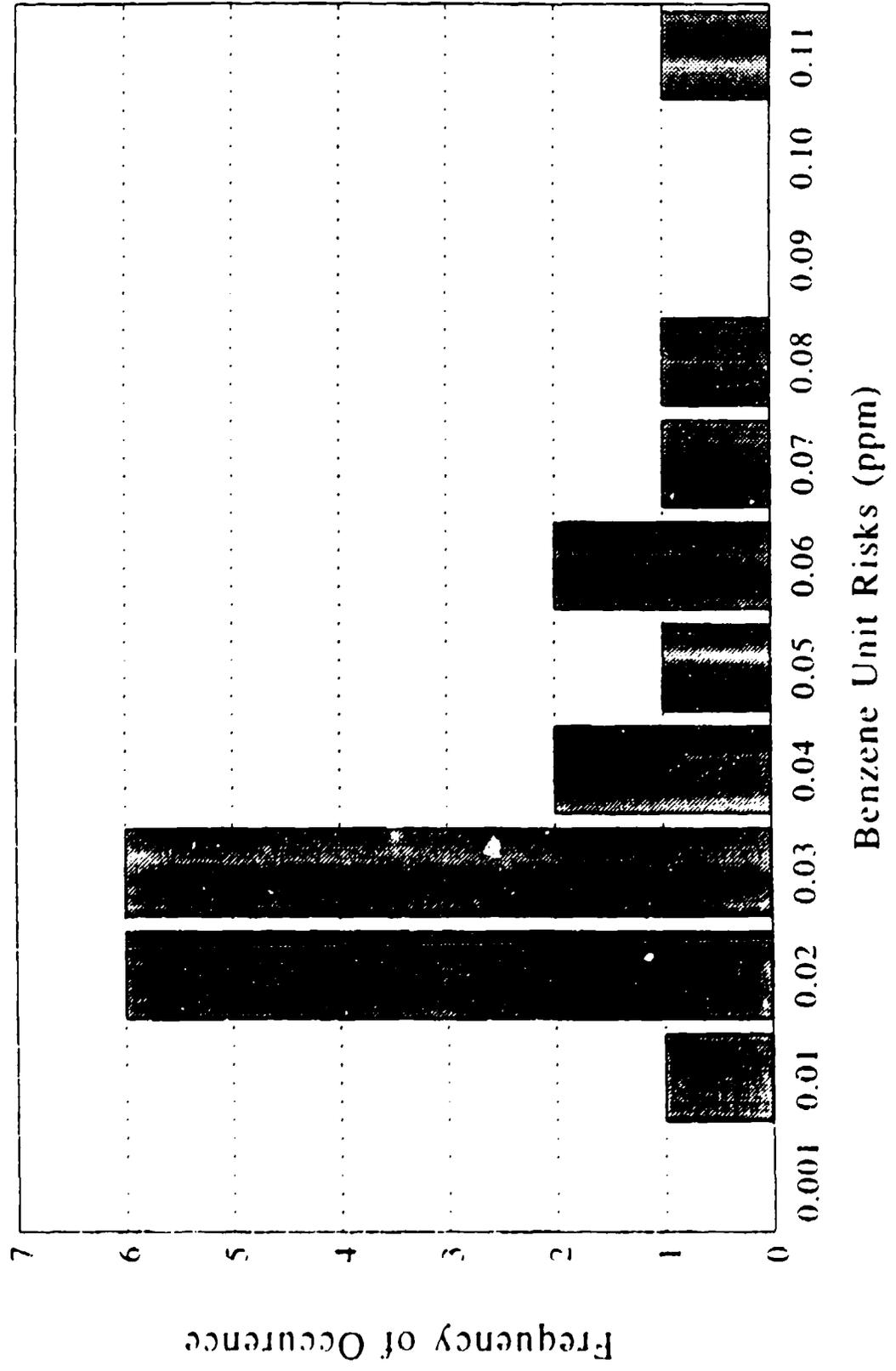


Figure 5-2. Estimating a Distribution of Human Daily Intakes

Scenario: Ingestion of benzene in water

$$LADD = \frac{C \times IR \times EF \times ED}{BW \times LS \times CF}$$

where:

- LADD = Lifetime Average Daily Dose (mg/kg/day)
- C = Concentration (mg/liter)
- IR = Ingestion rate (liters/day)
- EF = Exposure frequency (days/year)
- ED = Exposure duration (years)
- BW = Body weight (kg)
- LS = Life span (years)
- CF = Conversion factor (365 days/year)

$$\text{Cancer risk} = LADD \times CPF$$

where:

- LADD = Lifetime Average Daily Dose (mg/kg/day)
- CPF = Cancer potency factor (mg/kg/day)⁻¹

Input distributions:

- C Triangular (minimum = 0.25, most likely = 1.0, maximum = 1.5)
- IR Normal ($\mu = 1.3$, $\sigma = 0.25$)
- EF Triangular (minimum = 250, most likely = 350, maximum = 365)
- ED Triangular (minimum = 9, most likely = 30, maximum = 70)
- BW Equal chance of selecting male or female body weight
 - Male (ln lb): Lognormal ($\mu = 5.14$, $\sigma = 0.17$)
 - Female (ln lb): Lognormal ($\mu = 4.95$, $\sigma = 0.21$)
- CPF Lognormal ($\mu = -4.33$, $\sigma = 0.67$) of underlying normal

Figure 5-3. Calculating LADD and Cancer Risk
Using Point Estimates

Point estimate:

$$LADD = \frac{1.5 \text{ mg/l} \times 2.0 \text{ l/day} \times 350 \text{ days/year} \times 70 \text{ years}}{70 \text{ kg} \times 70 \text{ years} \times 365 \text{ days/year}} = 4.11 \times 10^{-2} \text{ mg/kg/day}$$

$$\text{Cancer risk} = 4.11 \times 10^{-2} \text{ mg/kg/day} \times 0.029 (\text{mg/kg/day})^{-1} = 1.19 \times 10^{-3}$$

Figure 5-4. Point Estimate and Distribution of a Groundwater to Drinking Water LADD

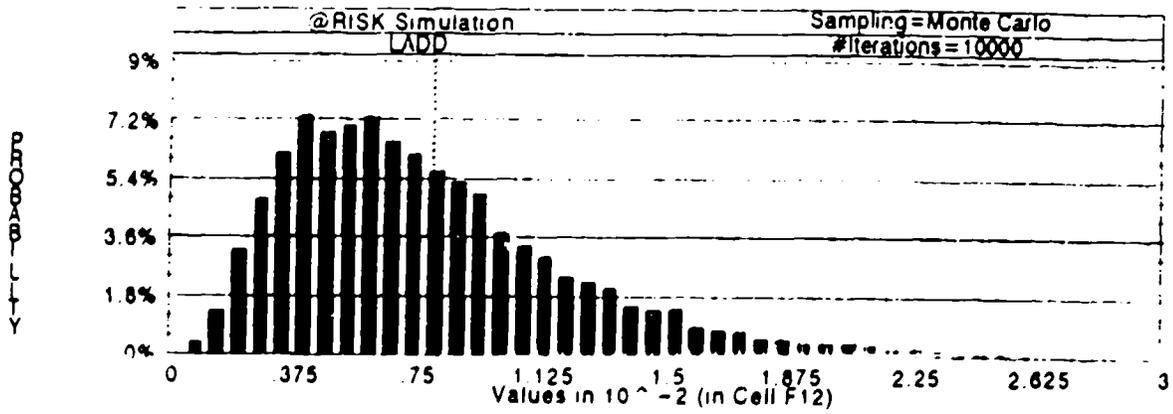
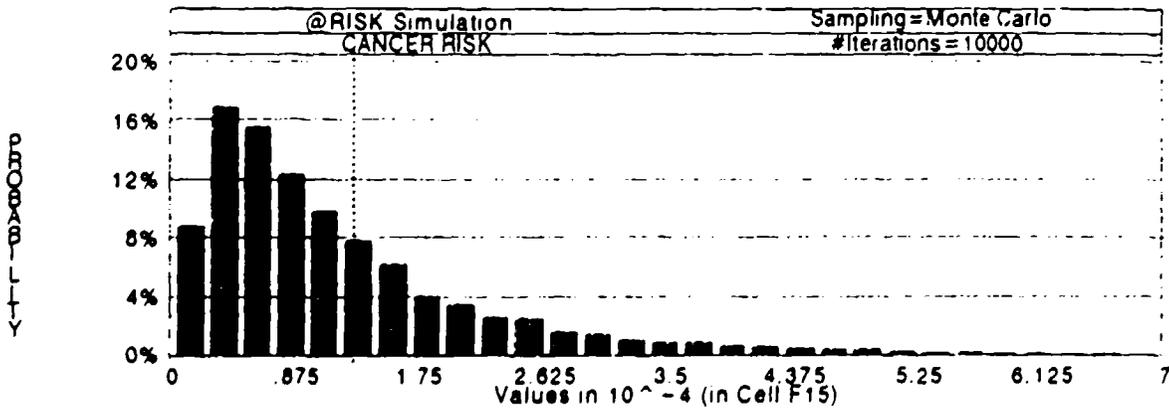


Figure 5-5. Point Estimate and Distribution of a Groundwater to Drinking Water Cancer Risk



6.0 CONCLUSIONS AND RECOMMENDATIONS

The following conclusions constitute the results of analyses performed throughout this report:

- There is no established USEPA regulatory policy for BTEX or TPH soil cleanup concentrations, to date.
- There is ongoing USEPA work towards establishing guidelines for soil cleanup concentrations based on protection of ground water.
- There are variable state-specific approaches to setting BTEX and/or TPH soil cleanup levels
- State-specific soil cleanup concentrations for BTEX are based primarily on protection of human health via protection of ground water, and/or protection of health for the soil ingestion route.
- State-specific soil cleanup concentrations for TPH are based primarily on consideration of one or more BTEX components in specific fuels, and extrapolation to TPH concentrations, as well as increasingly nonscientific approaches.
- Among all potential substitutes for TPH at JP-4 spill sites, benzene (BTEX) appears to be the most appropriate substitute based on its toxicity (carcinogenicity), weight-of-evidence cancer classification (Category A carcinogen), motility in the environment, ubiquity at JP-4-contaminated sites, and potential for migration to ground water.
- Based on these parameters, risk-based soil cleanup concentrations based on BTEX tend to be driven by benzene.
- Risks associated with exposure to benzene in ground water used as a drinking water source is anticipated to dominate risks for benzene in other media.
- Risk-specific concentrations for benzene (and other BTEX constituents) can be developed in soil, ground water, and other media.
- Remediation to a benzene soil cleanup concentration will not necessarily achieve simultaneous TPH soil cleanup.
- Benzene cancer risk is determined from the benzene slope factor and potential for exposure. Factors influencing the slope factor include the experimental data set used in its derivation, method of low-dose extrapolation, interspecies (animal to human) extrapolation, and use of the upper bound on the slope factor instead of the maximum likelihood estimate

- The potential for appreciably altering the benzene cancer slope factor is not anticipated to be significant.
- There is no scientific consensus on use of specific distributions. However, scientifically defensible, rationally chosen, site-specific distributions should be used to estimate exposure.

The following recommendations are the outcome of the conclusions of these analyses as well as additional considerations:

- Benzene should be adopted as the TPH substitute;
- Research and funding efforts should focus on formulating site-specific soil cleanup concentrations for benzene, based on protection of ground water;
- A cost-benefit analysis should be undertaken for soil remediation of benzene and TPH, using current, acceptable remediation methods, and applying a site-specific approach;
- Research and funding efforts should be directed towards characterizing TPH, including chemical characterization, health effects, fate and transport, and the utility of TPH in the risk assessment process.

APPENDIX A

Approaches Used By States to Regulate BTEX

APPENDIX A APPROACHES USED BY STATES TO REGULATE BTEX

California

The State of California develops site-specific remediation goals according to the procedure described in its LUFT Manual (State of California 1989). This approach begins with a "Leaching Potential Analysis," which is used for initial site screening. Tank and piping samples are analyzed for TPH and BTEX; geologic site characteristics, such as soil type and permeability, are taken into account. Detected concentrations are compared to allowable concentrations for a site with the same geologic attributes. The matrix of allowable concentrations for various geologic site conditions was developed using fate-and-transport computer modeling. If the detected concentrations exceed the allowable concentrations, further study is warranted and a "General Risk Appraisal" is performed. The "General Risk Appraisal" involves the development of a soil contamination profile, in which soil borings are done, boring logs made, and soil samples are taken every five feet and analyzed for TPH and BTEX. Depth-specific contaminant concentrations and geologic attributes of the site are incorporated into computer models SESOIL and AT123D to arrive at site-specific cleanup goals for BTEX which represent the amount of contaminants which may be present in the soil under a similar site scenario and not cause drinking water standards to be exceeded at a point ten meters down gradient at the top of the aquifer (Daugherty 1991). Acceptable TPH levels are estimated by dividing the acceptable BTEX soil levels by the composition percentage in fuel. After remediation has been completed and the cleanup goals met, a human health risk assessment may be performed to ensure that public health will not be threatened by the site in the future. If groundwater had been impacted, a groundwater monitoring program may be required to assess the long-term effectiveness of the remedial action.

Colorado

Colorado, like California, has only remediation goals for the remediation of petroleum-contaminated soils; no enforceable regulations exist (LaRoca 1993). For both TPH and BTEX, remediation goals were formulated for three different levels of stringency by analyzing cleanup levels other states have implemented and picking "reasonable" values. These three levels are called Remedial Action Categories (RACs): Level 1 (most stringent) is for groundwater which functions as a public water supply, present or future; Level 2 is for groundwater which functions as a private water supply, present or future; Level 3 (least stringent) is for groundwater which is either not part of a drinking supply or has little permeability or storativity (State of Colorado 1992). Specific values for the cleanup levels were derived by analyzing values used by other states. The objective of the cleanup levels is that soil be clean enough so that drinking water standards are met in groundwater aquifers; the State may be lenient when this is either technically or economically not feasible. Groundwater monitoring is done to ascertain the contamination present in groundwater after remediation.

Delaware

Due to varied site conditions and geology in Delaware, state regulators advocate a site-by-site approach and have not derived any state-wide soil cleanup requirements for TPH or BTEX (Lemer 1993). Delaware places sites in one of three categories: A (high risk), B (moderate risk), or C (low risk). A site is considered high risk if groundwater is impacted, moderate risk if the property use is commercial, and low risk if the property use is industrial. There is a set of generic "screening levels" for TPH and BTEX which are applied to determine if remediation is necessary. These screening levels are usually prescribed cleanup levels for moderate risk sites. Low risk sites are generally cleaned up to background levels. High risk sites are cleaned up such that groundwater contamination does not exceed an MCL or detection limit. No modeling or quantitative methods are used to determine cleanup levels in this case; a quarterly groundwater monitoring program is implemented and remediation continues until groundwater goals are met and groundwater concentrations are stable for one year. In all three categories the State is very flexible in establishing cleanup goals. Generally, the responsible party hires a consultant and they and the State work together to negotiate exact cleanup goals which are feasible and protective of the environment.

Florida

Florida has developed a guidance level for soil TPH concentrations. Soils with TPH levels exceeding the guidance level be remediated. Florida does not have cleanup criteria for TPH and BTEX as such, but does apply standards for total recoverable petroleum hydrocarbons (TRPH) and total volatile organic aromatics (VOAs) (State of Florida 1992). The remediation goals for VOAs in soil are risk-based and are derived using a very conservative residential scenario which allows for soil ingestion by children (Conrardy 1993). The remediation level for TRPH in soil has the protection of groundwater as its purpose and is much less rigorously derived. This level is twice the groundwater TRPH standard, and is based on the conservative assumption that at most half of the soil contamination will leach into groundwater.

Georgia

Georgia is concerned with both groundwater and surface water (State of Georgia 1989). Stated cleanup standards apply only for a contaminant plume with a boundary within three miles of a public water withdrawal point, or within one-half mile of a nonpublic water withdrawal point. The levels are driven by Georgia's in-stream state water quality standards: soil concentrations less than required cleanup standards ensure that contaminants leaching from soil into surface water are in concentrations sufficiently small that state surface water standards are met. The specific levels were derived by combining knowledge of other states' regulatory approaches with an accepted background level of 100 ppm TPH for industrial sites and a conservative estimate that gasoline is at most 5% benzene, 5% toluene, 5% ethylbenzene, and 5% total xylenes (20% BTEX) (Gottschalk 1993).

Hawaii

In Hawaii, two sets of remediation goals exist for hydrocarbon spills based on their location relative to a "line" running around the perimeter of each Hawaiian island delineating drinking water (on the mountain side of the line) from non-drinking water (on the ocean side of the line) (Seid 1993.) For drinking water, a remediation goal based on the MCL is used; for non-drinking water, the remediation goals are based on water quality standards (acute and chronic criteria.) In both cases, the appropriate water standard is multiplied by a very conservative attenuation factor dependent on the contaminant's mobility and toxicity. This factor is 10 for all BTEX compounds but benzene; a factor of 1 is used for benzene. TPH is not regulated because no water quality standards exist for TPH. If the contaminant of concern is other than benzene, ethylbenzene, toluene, acenaphthene, fluoranthene, or naphthalene, the responsible party may opt for one of the following two alternatives in place of applying the cleanup standards described above: (1) perform a human health/ecological risk assessment using EPA Superfund guidelines to derive alternative cleanup criteria, or (2) implement a monitoring program, provided there is no exposure pathway.

Idaho

The ultimate goal of Idaho's remediation goals is to ensure that groundwater hydrocarbon concentrations meet federal standards (Wicherski 1993). Benzene drives the soil remediation goals because it is the most carcinogenic and the most mobile of the petroleum hydrocarbons. Thus, the prescribed BTEX and TPH levels for soil are the concentrations that will allow the groundwater concentration of benzene to remain below the MCL of 5 ppb. Exact numerical values for cleanup levels were selected after analysis of other states' levels. Oregon's regulatory approach was of particular importance.

Illinois

Illinois has formulated corrective action levels for BTEX using groundwater protection as the primary objective (Potter and Tin 1993). However, these levels apply only to USTs and not to above-ground spills. Regulators consider a site's soil type, soil permeability, and contribution of impacted groundwater to a water supply, and assign one of two sets of corrective action levels based on these criteria. Modeling and simulation techniques were used to calculate the two sets of corrective action levels. The levels are based on the concentrations of BTEX in soil which will not result in exceedance of existing state groundwater quality standards. The State of Illinois chooses to regulate hydrocarbon contamination using only a BTEX level; no TPH level has been developed.

Kansas

Kansas developed corrective action levels for TPH and benzene with the goal of protecting the state's groundwater. These levels are flexible; State regulators' professional judgment plays a significant role in determining which levels are actually applied (Sexton 1993). The TPH level

was selected based on: the concentration where fumes are first noticeable; the concentration that can be easily detected by laboratory equipment; the concentration which exceeds background; TPH levels where leaching into groundwater occurs, and; the ability to quantify human health risk (Blackburn 1993). The benzene level is the concentration of benzene in soil which would result in a groundwater concentration of 0.07 ppm, assuming an attenuation factor of 20. The amount 0.07 ppm value was established as a "hazardous" quantity of benzene in groundwater many years ago by researchers developing the TCLP test. While more recent research indicates that this value could be increased, Kansas prefers to maintain the original value to assure the protection of human health and the environment.

Louisiana

Louisiana has no regulations or promulgated remediation goals for BTEX/TPH cleanups in soil (Mayeux 1993). Because of the state's diverse geology, each site must be considered individually. Typically, the responsible party hires a consultant to derive site-specific cleanup goals using techniques such as fate-and-transport computer simulation or human health risk assessment. The consultant meets with state regulators to propose the derived levels with appropriate scientific justification. The State accepts or rejects the proposal based on past experience cleaning up similar sites. Currently, Louisiana is formulating a risk-based computer model which will arrive at cleanup levels based on site-specific parameters. This model will not assume the role the consultants have always had; it will merely be used to give state regulators a set of site-specific cleanup objectives with which to compare the consultants' levels for a more objective assessment of the validity of the consultants' conclusions.

Maryland

Maryland's guidance level of 10 ppm TPH is based on best available technology for cleanup (Meade 1993). If contamination in excess of 10 ppm TPH is found, a site-specific risk characterization is performed to determine if remediation is warranted. Property use, groundwater usage, potential for contaminant migration, and human exposure pathways are considered when site-specific remediation goals are developed. The protection of groundwater is of primary importance. A groundwater monitoring program is implemented and remediation continues until groundwater contamination reaches asymptotic levels.

Massachusetts

Massachusetts' approach to regulating hydrocarbon contamination is almost identical to that of Oregon. The State has devised a numerical "matrix" of remediation goals for TPH by applying an attenuation factor to calculate soil concentrations which would result in groundwater contamination (Fitzgerald 1993; Locke 1993). Site characteristics, such as the frequency and intensity of human exposure to the contaminants of concern, accessibility of the contamination (*e.g.*, its depth below ground surface), and the potential of the contaminants to leach into the water table, are used to select the most relevant cleanup value from this matrix. Human health risk assessment equations and the fate-and-transport computer models SESOIL and AT123D were

used to derive a range of cleanup levels for benzene, toluene, ethylbenzene, and total xylenes. If the responsible party can prove that the State's leachability assumptions used in deriving this matrix are overly conservative for the particular site in question, the State will permit the applicable cleanup level to be raised appropriately. The responsible party may also elect to perform a site-specific risk characterization and derive site-specific cleanup levels.

Michigan

The State of Michigan employs a combination of techniques to arrive at its corrective action levels for BTEX; TPH is not regulated (Howard 1992; MEPA 1993). The objective of these levels is to protect both groundwater quality and human health. Three methods exist for the derivation of site-specific levels: Methods A, B, and C.

Method A is the most conservative and requires the use of either a method detection limit or the background level of petroleum hydrocarbons present at the site as the cleanup level. Establishment of a background level involves taking soil samples in areas of the site which are not impacted by petroleum contamination and determining an "average" level of petroleum hydrocarbons present in the unimpacted areas. Method B is considered moderately conservative. Under Method B, risk-based (but not site-specific) soil cleanup levels are applied; these levels were derived using a residential land-use exposure scenario which incorporates ingestion of soil, dermal contact with soil, and the ingestion of groundwater. Method C is also a risk-based soil cleanup level, but is not developed with a residential scenario. Instead, the site is characterized and a site-specific exposure scenario is developed. This Method is typically used at industrial sites, where a residential scenario is not appropriate. If a risk-based value for a compound is calculated to be less than its method detection limit, the method detection limit is used as the cleanup level (Howard 1993).

Michigan allows the responsible party to select one of these three methods based on current and proposed land use, but state regulators reserve the right to object if they believe that an inappropriate method is chosen. Method B is most frequently chosen because it provides the most conservative estimate without excessive cost. Method C, while generally less conservative an estimate than B, is often cost-prohibitive because of the extensive site characterization required. To lower the cost of Method C, the State of Michigan is currently developing a generic industrial exposure scenario analogous to its residential exposure scenario.

Minnesota

Minnesota's remediation goals for surface spills are based on protection of both groundwater and public health (Aho 1993). State regulators work with the responsible party and their consultant to arrive at site-specific cleanup levels. The consultant may use a variety of techniques for developing the cleanup goals; groundwater modeling and informal human health risk assessment are commonly used. Often a groundwater monitoring program is implemented to ensure that the remediation's objectives have been met. The State is flexible in accepting site-specific cleanup requirements but insists upon a thorough analysis of the site. It is important to consider the use

of the potentially affected aquifer (drinking water, potential drinking water, or other), the potential for vertical and horizontal migration, and the remediation cost. The goal of any cleanup levels is to ensure that both state drinking water standards and surface water standards are met. State drinking water standards are MCLs for public water supplies and values derived by the Minnesota Health Department for private wells. BTEX constituents are not usually monitored.

Missouri

Missouri's regulatory approach to soil cleanup levels BTEX and TPH is specifically for USTs (Schroeder 1993). Missouri regulators examined levels set by other states and selected an "average level" as their guidance level. Missouri applies a different set of soil cleanup levels for each of three soil types: excavated or remediated soil, undisturbed soil, and soil which has the potential to impact groundwater. Soil which may impact groundwater must be cleaned up to soil concentrations which ensure groundwater concentrations will be at or below a set of prescribed state groundwater levels. If the groundwater is potable, the state groundwater level for benzene is equal to the federal benzene MCL.

New Hampshire

New Hampshire's techniques for deriving soil remediation goals for TPH and BTEX are patterned after those of California (Lombardo 1993). The same groundwater models are used, but conditions specific to New Hampshire rather than California are used as input parameters. In the near future, New Hampshire will no longer regulate TPH concentrations in soil.

New Jersey

Three sets of guidance levels exist: for residential soil, non-residential soil, and soil which has the potential to impact to groundwater (Richter 1993). Land use determines whether a site is classified as residential or non-residential. The groundwater impact criteria are applied if the affected aquifer is classified as drinking water (as most aquifers in the state of New Jersey are), or is classified as an important natural resource by the State. If two sets of criteria are relevant, the most stringent one is applied. All three sets of guidance levels are risk-based, derived to be protective of human health. EPA policies and methodologies for human health risk assessment greatly influenced New Jersey's procedure for deriving these levels (State of New Jersey 1992).

New York

For concentrations of petroleum hydrocarbons in soil to be in compliance with New York State's guidance levels, groundwater, human health, and fish and wildlife must be protected, and nuisance characteristics (e.g., odor, taste) must be eliminated (State of New York 1992.) Groundwater is considered protected if petroleum-contaminated soil is leaching contaminants in low enough concentrations such that groundwater standards are met. In order to determine these concentrations, the Toxicity Characteristic Leaching Procedure (TCLP) is used to simulate site-specific conditions and measure how much contaminant is capable of migrating into the water

table. A cost-effective alternative to the TCLP is to measure the contaminant concentration in the soil and divide by 20 to calculate the maximum possible contaminant concentration which will leach into groundwater. Groundwater standards applied by the State of New York are the more stringent of either NYSDEC groundwater standards or NYSDOH drinking water standards. Human health is considered protected if contaminant concentrations in soil are less than Human Health Guidance Values (HHGV). HHGVs are derived from toxicity data contained in the Health Effects Assessment Summary Table (HEAST) Report using a soil ingestion scenario. If sediments are impacted, fish and wildlife are considered protected if the concentrations of hydrocarbons in sediment do not exceed New York State's Sediment Guidance Values. These values have not been derived for BTEX or TPH; only five PAH compounds have Sediment Guidance Values. Two different sets of levels have been developed: one set for gasoline, and another for fuel oil.

Ohio

Like many other states, Ohio has developed a matrix of remediation goals corresponding to varying site conditions (McClure 1993). Site conditions which play an important role in selecting values from the matrix are soil type, distance from drinking water source(s) or conduit(s), and proximity to utility lines. Sites are given a numerical score based on their attributes and the cleanup levels are selected from the matrix based on this score. Ohio used risk assessment procedures and principles of contaminant migration and attenuation to interpolate its matrix of remediation goals from "safe" soil contaminant levels derived by the Ohio EPA (Rowe 1993).

Oregon

Oregon has developed three sets of state soil cleanup standards corresponding to three levels of stringency. For each site, the State assigns a set based on the site's score from a numerical ranking procedure. Regulators evaluate the site and assign a numerical score in each of the following five areas: (1) depth to groundwater, (2) mean annual precipitation, (3) native soil or rock type and permeability, (4) contribution of the uppermost aquifer to a drinking water source, and (5) potential receptors, which are based on both the distance to the nearest well and the number of people at risk (Oregon 1990). A high potential impact to the water supply corresponds to a high score in each area; a high overall score warrants cleanup to a more stringent standard than if the score were low. If a score in any of the five areas cannot be ascertained, it is assigned the highest, most conservative possible score. The specific cleanup value for TPH was assigned assuming a dilution and attenuation factor of 100; the value for this factor was determined based on research conducted by EPA. Compound-specific cleanup levels for benzene, toluene, ethylbenzene, and total xylene were derived using EPA fate and transport computer models SESOIL and AT123D, and human health risk assessment procedures (Anderson 1993).

South Dakota

South Dakota set its soil remediation goals after examining other state's methods and cleanup levels (Miller 1993). State regulators selected the MCL for xylene to be the groundwater standard for TPH and established soil remediation goals which would ensure groundwater concentrations of TPH never exceed this level. The soil remediation goals cover a range of 10 to 100 ppm TPH. The lower bound of 10 ppm for TPH in soil was selected because the state groundwater quality standard for TPH is 10 ppm, and it was conservatively assumed that a 10 ppm concentration in soil would never result in a 10 ppm level in groundwater. The upper bound of 100 ppm TPH was based on levels used by other states. Regulators consider characteristics such as depth to groundwater, extent of vertical migration, and soil permeability when assigning a site-specific remediation goal within this range (State of South Dakota 1991). Remediation must result in a decrease in adverse aesthetic properties (appearance, smell) caused by the contamination.

Tennessee

Tennessee formulated state soil cleanup standards with the primary objective of protecting groundwater (Tennessee Department of Health and Environment 1989). According to regulations, cleanup levels for soil vary according to two site characteristics: soil permeability and whether or not the groundwater below the site contributes to a drinking water supply. The standards were developed using the EPA's derived attenuation factor of 100, combined with approaches used by other states, especially California (Head 1993). The responsible party may hire a consultant to derive site-specific standards and petition the State to apply these standards. The State may accept or reject the proposal, based on the adequacy of its defense. State regulators consider it important that the consultant include the following in the analysis: (1) physical/chemical characteristics of petroleum, including toxicity, persistence, and potential for migration, (2) hydrogeologic characteristics of the site, (3) proximity, quality, and current/future use(s) of the groundwater, (4) an exposure assessment, and (5) proximity, quality, and current/future use(s) of surface waters.

Texas

Texas has action levels for soil which, when exceeded, trigger a detailed site investigation. These action levels are based on soil grain size (Pena 1993). Upon completion of the site investigation, site-specific data are recorded on a questionnaire and used as input parameters for a site-specific risk assessment computer model developed by the American Petroleum Institute. The model yields site-specific soil cleanup levels for TPH and BTEX.

Utah

Utah formulated guidance levels after examination of the rationale of several other states, particularly Oregon and California (Stonestreet 1993). If TPH or BTEX are detected at concentrations above the guidance levels, a detailed site investigation is conducted. Specific

remediation goals are developed during the course of this investigation; the responsible party may or may not hire a consultant to assist in their derivation. The goal of soil cleanup is to achieve groundwater contaminant levels which are below MCLs. Groundwater monitoring programs are essential in determining what type of remediation is necessary and when remediation goals have been met (Jenkins 1993).

Washington

Washington's remediation goals were established to protect the state's groundwater (Wilhelm 1993). Washington has three approaches: (A) use of a "standard" set of levels for commonly encountered substances which are based on federal standards and cleanup levels used by other states; (B) use of a site-specific risk-based estimate based on a residential exposure scenario, and (C) use of a site-specific risk-based estimate based on an industrial exposure scenario. Method A is intended for sites that are either small or have only a few contaminants, such that a risk assessment would be cost-prohibitive (State of Washington 1991). Under Method A, soil hydrocarbon concentrations must be reduced such that groundwater concentrations of TPH do not exceed 1000 ppb, groundwater concentrations of the four BTEX constituents do not exceed their MCLs, and any "adverse aesthetic qualities" such as smell and taste are reduced. Under Methods B and C, total lifetime cancer risk must be less than 1 in 100,000. Of the three Methods, Method B is most frequently used.

Wisconsin

Wisconsin uses action levels for TPH and BTEX to trigger a site investigation. These action levels are method detection limits. If cleanup is prescribed by the state, site-specific cleanup levels must be derived (McCurry 1993). The State works with the responsible party and a consultant to derive the cleanup levels. Several approaches are acceptable, including fate and transport modeling and use of detection limits or remediation techniques. The State is flexible when considering allowable levels. Their objective is to arrive at cleanup levels which are technically and economically feasible and restore the environment to its natural state prior to the contamination. If at all possible, the State requires soil be cleaned up to the point that state groundwater quality regulations are met.

GLOSSARY OF TERMS

absorption. The process whereby toxicants cross body membranes and enter the bloodstream.

additive effect. A situation in which the combined effect of two chemicals is equal to the sum of the effect of each agent given alone.

average daily dose (ADD). The average dose received on any given day during a period of exposure, expressed in mg/kg body weight-day. Ordinarily used in assessing noncarcinogenic risks.

antagonistic effect. A situation in which the combined effect of two chemicals is less than the sum of the effect of each agent given alone.

carcinogen. A chemical or physical agent that causes an increase in tumors in exposed organisms or individuals.

chronic exposure. A persistent, recurring, or long-term exposure, as distinguished from acute. Chronic exposure may result in health effects (such as cancer) that are delayed in onset, occurring long after exposure has ceased.

chronic toxicity. An adverse effect (*e.g.*, liver damage, cancer) resulting from long-term exposure to a chemical.

dose. The amount of a chemical received by the target organism (*e.g.*, humans) or a target organ (*i.e.*, delivered dose); it is generally reported in units of weight of the substance (*e.g.*, mg or micrograms) per body weight of an individual (*e.g.*, in kg) per unit time (*e.g.*, hours or days).

dose-response assessment. The second step in the risk assessment process. This step describes the quantitative relationship between the amount of exposure to a chemical and the extent of toxic injury or disease. Data are derived from animal studies or, less frequently, from studies in exposed human populations. Many dose-response relationships can exist for a chemical agent, depending on conditions of exposure (*e.g.*, single versus repeated and prolonged exposures) and the type of response (*e.g.*, cancer, birth defects) being considered. This process is highly complex, taking into account diverse information about the body's ability to transform a chemical into more toxic metabolites up to a point where overload occurs, variations in sensitivity to doses of toxic substances, and differences between the mechanisms of toxicity in test organisms (*e.g.*, laboratory rodents) and in human target organs. In many cases, the features of a dose (*e.g.*, duration, frequency, and route) have a great impact on the degree of toxic

potency. Specialized procedures must be employed to assure that later characterization of toxic risk is as scientifically defensible as possible.

epidemiology. The study of the association of human disease with environmental factors, such as chemical exposure.

exposure. The amount of material ingested, inhaled, or otherwise contacted by an organism; generally reported in concentration units such as ppm, ppb, mg/m³, or in dose units of mg/kg-day.

exposure assessment. This is the third step of the risk assessment process. It describes the nature and size of the various populations exposed to a chemical agent, and the magnitude and duration of their exposures. The assessment might include current, and anticipated future exposures. This step also involves characterizing the nature of the populations likely to come into contact with the chemicals under evaluation. This includes determinations of not only the numbers of individuals potentially exposed, but also consideration of the distribution of age, gender, and unique conditions such as pregnancy, childhood, senescence, preexisting illness, and lifestyle.

exposure duration. The length of time an organism is in contact with a chemical.

exposure pathway. An exposure pathway describes a mechanism by which a population or individual can be exposed to chemicals present at or migrating from a site. An exposure pathway consists of the four following components:

- a source and mechanism of chemical release to the environment;
- an environmental transport medium for the released chemical;
- a point of potential human contact with the contaminated medium; and
- a human exposure route at the point of exposure.

exposure point. An exposure point is defined as the location of potential contact between a receptor population and a chemical of concern. The objective of determining exposure points is to identify specific locations where receptor populations may be potentially exposed to chemicals of concern contained within environmental transport media.

exposure route. An exposure route is defined as the mechanisms by which a chemical comes in contact with the receptor population, *e.g.*, ingestion or inhalation.

hazard identification. This is the first step in the risk assessment process. It is a determination of where there is a causal relationship between exposure to a chemical and an injurious effect on health. It involves gathering and evaluating toxicity data on the types of health injury or disease that may be produced by a chemical and on the conditions of exposure under which injury or disease is produced. It may also involve characterization of the behavior of a chemical within the body and the interactions it

undergoes with organs, cells, or even part of cells. Data of the latter types may be of values in answering the ultimate question of whether the forms of toxicity known to be produced by a chemical agent in one population group or in laboratory animals are also likely to be produced in the human population group of interest. Note that risk is not assessed at this stage; hazard identification is conducted to determine whether and to what degree it is scientifically correct to infer that toxic effects observed in one setting will occur in other settings (e.g., are chemicals that are found to be carcinogenic or teratogenic at high doses in experimental animals also likely to be so in humans exposed to high - or even low - doses?).

hazard quotient (HQ). An indicator of the degree of hazard for noncarcinogenic effects resulting from exposure to a single chemical. The hazard quotients are added together to calculate a hazard index (HI) to examine exposure from multiple chemicals.

hematopoietic. Describing the formation of blood in the body.

gavage. The introduction of material into the stomach by means of a tube.

interspecies extrapolation. A method to apply the results of experimental studies in animals to humans: also called cross-species extrapolation.

intraspecies extrapolation. The differences within a species (e.g., humans) that cause individuals to differ in susceptibility (and, thus, response) to a chemical or agent.

molecular weight. The sum of the atomic weights of all the atoms of a molecule.

no-observed-adverse-effect-level (NOAEL). A term used to describe the dose that elicits no toxicity in an animal bioassay or human study.

noncarcinogen. A chemical or physical agent that does not cause an increase in the tumor rate in exposed organisms or individuals.

nonthreshold effect. A response that is proportional to a level of exposure.

pharmacokinetic. The study of the absorption, metabolism, and action of drugs.

reference concentration (RfC). An estimate of daily exposure by inhalation (expressed as micrograms of substance per cubic meter of air per day) that is likely to be without appreciable risk of adverse noncarcinogenic health effects in the humans population over a lifetime; technically the NOAEL divided by the appropriate uncertainty or modifying factors.

reference dose (RfD). This is an estimate of a daily exposure by ingestion or dermal contact (expressed as milligrams of substance per kilogram of body weight per day) that is

likely to be without appreciable risk of adverse noncarcinogenic health effects in the human population over a lifetime; technically the NOAEL divided by the appropriate uncertainty factors.

USEPA has developed various types of RfDs depending on:

- the exposure route (*i.e.*, oral or inhalation);
- the critical effect (*i.e.*, developmental or other); and,
- the length of exposure being evaluated (*i.e.*, chronic, subchronic or single event).

The USEPA defines a chronic RfD as an estimate of a daily exposure level for the human population that is unlikely to result in deleterious effects during a lifetime. These chronic RfDs are used to evaluate the potential noncarcinogenic effects associated with exposure periods between 7 years and a lifetime.

Subchronic RfDs have been developed by the USEPA to characterize potential noncarcinogenic effects associated with shorter term exposures (*i.e.*, periods between two weeks and seven years). Where only a chronic RfD has been developed by USEPA, a subchronic RfD has been estimated by multiplying the chronic RfD by 10. A factor of 10 is generally used by USEPA as the uncertainty factor applied to subchronic toxicity data to derive a chronic RfD (USEPA, 1989).

risk assessment. The characterization of the potential adverse health effects of human exposure to environmental hazards. The basic risk assessment paradigm is made up of four elements: hazard identification, dose-response assessment, exposure assessment, and risk characterization.

risk characterization. This is the fourth, and final, step of the risk assessment process. It involves integration of the data and analyses from the other three steps of risk assessment (hazard identification, dose-response assessment, and exposure assessment) to determine the likelihood that the human population of concern will experience any of the various forms of toxicity associated with a chemical under its known or anticipated conditions of exposure. This step includes estimations of risk for individuals and population groups, and a full exposition of the uncertainties associated with the conclusions. Scientific knowledge is usually incomplete, so that inferences about risk are inevitable. A well-constructed risk assessment relies on inferences that are most strongly supported by general scientific understanding, and does not include blanket conservative assumptions derived for use in the absence of actual data simply for ease of risk management or public policy directives.

route-to-route extrapolation. A method to apply the results of a study involving one route of administration of a chemical (*e.g.*, ingestion) to predict the results via another route of administration (*e.g.*, inhalation).

synergistic effect. A situation in which the combined effect of two chemicals is much greater than the sum of each chemical when given alone.

systemic toxicity. A toxic effect of a chemical beyond its point of exposure.

target organ. The organ or organs that are the major site of toxicity of a chemical.

teratogenicity. The ability of a substance to cause fetal malformations.

threshold. A critical level of exposure below which a response attributable to the specific agent is not possible.

uncertainty factors. These factors, applied to NOAELs in calculations of RfDs, are intended to account for specific types of uncertainty inherent in extrapolation from the available data, including variations in the sensitivity of individuals in a population, extrapolation from animal data to humans, limitations in exposure duration, and other limitations in the experimental data. The use of these safety factors increases the health-protectiveness of the RfD.

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