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## Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites<sup>1</sup>

This standard is issued under the fixed designation E1739; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This is a guide to risk-based corrective action (RBCA), which is a consistent decision-making process for the assessment and response to a petroleum release, based on the protection of human health and the environment. Sites with petroleum release vary greatly in terms of complexity, physical and chemical characteristics, and in the risk that they may pose to human health and the environment. The RBCA process recognizes this diversity, and uses a tiered approach where corrective action activities are tailored to site-specific conditions and risks. While the RBCA process is not limited to a particular class of compounds, this guide emphasizes the application of RBCA to petroleum product releases through the use of the examples. Ecological risk assessment, as discussed in this guide, is a qualitative evaluation of the actual or potential impacts to environmental (nonhuman) receptors. *There may be circumstances under which a more detailed ecological risk assessment is necessary* (see Ref (1)).<sup>2</sup>

1.2 The decision process described in this guide integrates risk and exposure assessment practices, as suggested by the United States Environmental Protection Agency (USEPA), with site assessment activities and remedial measure selection to ensure that the chosen action is protective of human health and the environment. The following general sequence of events is prescribed in RBCA, once the process is triggered by the suspicion or confirmation of petroleum release:

1.2.1 Performance of a site assessment;

1.2.2 Classification of the site by the urgency of initial response;

1.2.3 Implementation of an initial response action appropriate for the selected site classification;

1.2.4 Comparison of concentrations of chemical(s) of concern at the site with Tier 1 Risk Based Screening Levels (RBSLs) given in a look-up table;

1.2.5 Deciding whether further tier evaluation is warranted, if implementation of interim remedial action is warranted or if RBSLs may be applied as remediation target levels;

1.2.6 Collection of additional site-specific information as necessary, if further tier evaluation is warranted;

1.2.7 Development of site-specific target levels (SSTLs) and point(s) of compliance (Tier 2 evaluation);

1.2.8 Comparison of the concentrations of chemical(s) of concern at the site with the Tier 2 evaluation SSTL at the determined point(s) of compliance or source area(s);

1.2.9 Deciding whether further tier evaluation is warranted, if implementation of interim remedial action is warranted, or if Tier 2 SSTLs may be applied as remediation target levels;

1.2.10 Collection of additional site-specific information as necessary, if further tier evaluation is warranted;

1.2.11 Development of SSTL and point(s) of compliance (Tier 3 evaluation);

1.2.12 Comparison of the concentrations of chemical(s) of concern at the site at the determined point(s) of compliance or source area(s) with the Tier 3 evaluation SSTL; and

1.2.13 Development of a remedial action plan to achieve the SSTL, as applicable.

1.3 The guide is organized as follows:

1.3.1 Section 2 lists referenced documents,

1.3.2 Section 3 defines terminology used in this guide,

1.3.3 Section 4 describes the significance and use of this guide,

1.3.4 Section 5 is a summary of the tiered approach,

1.3.5 Section 6 presents the RBCA procedures in a step-by-step process,

1.3.6 Appendix X1 details physical/chemical and toxicological characteristics of petroleum products,

1.3.7 Appendix X2 discusses the derivation of a Tier 1 RBSL Look-Up Table and provides an example,

1.3.8 Appendix X3 describes the uses of predictive modeling relative to the RBCA process,

1.3.9 Appendix X4 discusses considerations for institutional controls, and

1.3.10 Appendix X5 provides examples of RBCA applications.

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<sup>2</sup> The boldface numbers in parentheses refer to the list of references at the end of this guide.

1.4 This guide describes an approach for RBCA. It is intended to compliment but not supersede federal, state, and local regulations. Federal, state, or local agency approval may be required to implement the processes outlined in this guide.

1.5 The values stated in either inch-pound or SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.6 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

## 2. Referenced Documents

2.1 *ASTM Standards:*<sup>3</sup>

**E1599 Guide for Corrective Action for Petroleum Releases**<sup>4</sup>

2.2 *NFPA Standard:*

NFPA 329 Handling Underground Releases of Flammable and Combustible Liquids<sup>5</sup>

## 3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *active remediation*—actions taken to reduce the concentrations of chemical(s) of concern. Active remediation could be implemented when the no-further-action and passive remediation courses of action are not appropriate.

3.1.2 *attenuation*—the reduction in concentrations of chemical(s) of concern in the environment with distance and time due to processes such as diffusion, dispersion, absorption, chemical degradation, biodegradation, and so forth.

3.1.3 *chemical(s) of concern*—specific constituents that are identified for evaluation in the risk assessment process.

3.1.4 *corrective action*—the sequence of actions that include site assessment, interim remedial action, remedial action, operation and maintenance of equipment, monitoring of progress, and termination of the remedial action.

3.1.5 *direct exposure pathways*—an exposure pathway where the point of exposure is at the source, without a release to any other medium.

3.1.6 *ecological assessment*—a qualitative appraisal of the actual or potential effects of chemical(s) of concern on plants and animals other than people and domestic species.

3.1.7 *engineering controls*—modifications to a site or facility (for example, slurry walls, capping, and point of use water treatment) to reduce or eliminate the potential for exposure to a chemical(s) of concern.

3.1.8 *exposure*—contact of an organism with chemical(s) of concern at the exchange boundaries (for example, skin, lungs, and liver) and available for absorption.

3.1.9 *exposure assessment*—the determination or estimation (qualitative or quantitative) of the magnitude, frequency, duration, and route of exposure.

3.1.10 *exposure pathway*—the course a chemical(s) of concern takes from the source area(s) to an exposed organism. An exposure pathway describes a unique mechanism by which an individual or population is exposed to a chemical(s) of concern originating from a site. Each exposure pathway includes a source or release from a source, a point of exposure, and an exposure route. If the exposure point differs from the source, a transport/exposure medium (for example, air) or media also is included.

3.1.11 *exposure route*—the manner in which a chemical(s) of concern comes in contact with an organism (for example, ingestion, inhalation, and dermal contact).

3.1.12 *facility*—the property containing the source of the chemical(s) of concern where a release has occurred.

3.1.13 *hazard index*—the sum of two or more hazard quotients for multiple chemical(s) of concern or multiple exposure pathways, or both.

3.1.14 *hazard quotients*—the ratio of the level of exposure of a chemical(s) of concern over a specified time period to a reference dose for that chemical(s) of concern derived for a similar exposure period.

3.1.15 *incremental carcinogenic risk levels*—the potential for incremental carcinogenic human health effects due to exposure to the chemical(s) of concern.

3.1.16 *indirect exposure pathways*—an exposure pathway with at least one intermediate release to any media between the source and the point(s) of exposure (for example, chemicals of concern from soil through ground water to the point(s) of exposure).

3.1.17 *institutional controls*—the restriction on use or access (for example, fences, deed restrictions, restrictive zoning) to a site or facility to eliminate or minimize potential exposure to a chemical(s) of concern.

3.1.18 *interim remedial action*—the course of action to mitigate fire and safety hazards and to prevent further migration of hydrocarbons in their vapor, dissolved, or liquid phase.

3.1.19 *maximum contaminant level (MCL)*—a standard for drinking water established by USEPA under the Safe Drinking Water Act, which is the maximum permissible level of chemical(s) of concern in water that is delivered to any user of a public water supply.

3.1.20 *Monte Carlo simulation*—a procedure to estimate the value and uncertainty of the result of a calculation when the result depends on a number of factors, each of which is also uncertain.

3.1.21 *natural biodegradation*—the reduction in concentration of chemical(s) of concern through naturally occurring microbial activity.

3.1.22 *petroleum*—including crude oil or any fraction thereof that is liquid at standard conditions of temperature and pressure (60°F and 14.7 lb/in.<sup>2</sup> absolute; (15.5°C and 10 335.6 kg/m<sup>2</sup>)). The term includes petroleum-based substances comprised of a complex blend of hydrocarbons derived from crude oil through processes of separation, conversion, upgrading, and finishing, such as motor fuels, jet oils, lubricants, petroleum solvents, and used oils.

3.1.23 *point(s) of compliance*—a location(s) selected between the source area(s) and the potential point(s) of exposure

<sup>3</sup> Withdrawn.

<sup>4</sup> Withdrawn. The last approved version of this historical standard is referenced on [www.astm.org](http://www.astm.org).

<sup>5</sup> Available from National Fire Protection Association, 1 Batterymarch Park, P.O. Box 9101, Quincy, MA 02269.

where concentrations of chemical(s) of concern must be at or below the determined target levels in media (for example, ground water, soil, or air).

3.1.24 *point(s) of exposure*—the point(s) at which an individual or population may come in contact with a chemical(s) of concern originating from a site.

3.1.25 *qualitative risk analysis*—a nonnumeric evaluation of a site to determine potential exposure pathways and receptors based on known or readily available information.

3.1.26 *reasonable maximum exposure (RME)*—the highest exposure that is reasonably expected to occur at a site. RMEs are estimated for individual pathways or a combination of exposure pathways.

3.1.27 *reasonable potential exposure scenario*—a situation with a credible chance of occurrence where a receptor may become directly or indirectly exposed to the chemical(s) of concern without considering extreme or essentially impossible circumstances.

3.1.28 *reasonably anticipated future use*—future use of a site or facility that can be predicted with a high degree of certainty given current use, local government planning, and zoning.

3.1.29 *receptors*—persons, structures, utilities, surface waters, and water supply wells that are or may be adversely affected by a release.

3.1.30 *reference dose*—a preferred toxicity value for evaluating potential noncarcinogenic effects in humans resulting from exposure to a chemical(s) of concern.

3.1.31 *remediation/remedial action*—activities conducted to protect human health, safety, and the environment. These activities include evaluating risk, making no-further-action determinations, monitoring institutional controls, engineering controls, and designing and operating cleanup equipment.

3.1.32 *risk assessment*—an analysis of the potential for adverse health effects caused by a chemical(s) of concern from a site to determine the need for remedial action or the development of target levels where remedial action is required.

3.1.33 *risk reduction*—the lowering or elimination of the level of risk posed to human health or the environment through interim remedial action, remedial action, or institutional or engineering controls.

3.1.34 *risk-based screening level/screening levels (RBSLs)*—risk-based site-specific corrective action target levels for chemical(s) of concern developed under the Tier 1 evaluation.

3.1.35 *site*—the area(s) defined by the extent of migration of the chemical(s) of concern.

3.1.36 *site assessment*—an evaluation of subsurface geology, hydrology, and surface characteristics to determine if a release has occurred, the levels of the chemical(s) of concern, and the extent of the migration of the chemical(s) of concern. The site assessment collects data on ground water quality and potential receptors and generates information to support remedial action decisions.

3.1.37 *site classification*—a qualitative evaluation of a site based on known or readily available information to identify the need for interim remedial actions and further information gathering. Site classification is intended to specifically prioritize sites.

3.1.38 *site-specific target level (SSTL)*—risk-based remedial action target level for chemical(s) of concern developed for a particular site under the Tier 2 and Tier 3 evaluations.

3.1.39 *site-specific*—activities, information, and data unique to a particular site.

3.1.40 *source area(s)*—either the location of liquid hydrocarbons or the location of highest soil and ground water concentrations of the chemical(s) of concern.

3.1.41 *target levels*—numeric values or other performance criteria that are protective of human health, safety, and the environment.

3.1.42 *Tier 1 evaluation*—a risk-based analysis to develop non-site-specific values for direct and indirect exposure pathways utilizing conservative exposure factors and fate and transport for potential pathways and various property use categories (for example, residential, commercial, and industrial uses). Values established under Tier 1 will apply to all sites that fall into a particular category.

3.1.43 *Tier 2 evaluation*—a risk-based analysis applying the direct exposure values established under a Tier 1 evaluation at the point(s) of exposure developed for a specific site and development of values for potential indirect exposure pathways at the point(s) of exposure based on site-specific conditions.

3.1.44 *Tier 3 evaluation*—a risk-based analysis to develop values for potential direct and indirect exposure pathways at the point(s) of exposure based on site-specific conditions.

3.1.45 *user*—an individual or group involved in the RBCA process including owners, operators, regulators, underground storage tank (UST) fund managers, attorneys, consultants, legislators, and so forth.

## 4. Significance and Use

4.1 The allocation of limited resources (for example, time, money, regulatory oversight, qualified professionals) to any one petroleum release site necessarily influences corrective action decisions at other sites. This has spurred the search for innovative approaches to corrective action decision making, which still ensures that human health and the environment are protected.

4.2 The RBCA process presented in this guide is a consistent, streamlined decision process for selecting corrective actions at petroleum release sites. Advantages of the RBCA approach are as follows:

4.2.1 Decisions are based on reducing the risk of adverse human or environmental impacts,

4.2.2 Site assessment activities are focussed on collecting only that information that is necessary to making risk-based corrective action decisions,

4.2.3 Limited resources are focussed on those sites that pose the greatest risk to human health and the environment at any time,

4.2.4 The remedial action achieves an acceptable degree of exposure and risk reduction,



4.2.5 Compliance can be evaluated relative to site-specific standards applied at site-specific point(s) of compliance,

4.2.6 Higher quality, and in some cases faster, cleanups than are currently realized, and

4.2.7 A documentation and demonstration that the remedial action is protective of human health, safety, and the environment.

4.3 Risk assessment is a developing science. The scientific approach used to develop the RBSL and SSTL may vary by state and user due to regulatory requirements and the use of alternative scientifically based methods.

4.4 Activities described in this guide should be conducted by a person familiar with current risk and exposure assessment methodologies.

4.5 In order to properly apply the RBCA process, the user should avoid the following:

4.5.1 Use of Tier 1 RBSLs as mandated remediation standards rather than screening levels,

4.5.2 Restriction of the RBCA process to Tier 1 evaluation only and not allowing Tier 2 or Tier 3 analyses,

4.5.3 Placing arbitrary time constraints on the corrective action process; for example, requiring that Tiers 1, 2, and 3 be completed within 30-day time periods that do not reflect the actual urgency of and risks posed by the site,

4.5.4 Use of the RBCA process only when active remediation is not technically feasible, rather than a process that is applicable during all phases of corrective action,

4.5.5 Requiring the user to achieve technology-based remedial limits (for example, asymptotic levels) prior to requesting the approval for the RBSL or SSTL,

4.5.6 The use of predictive modelling that is not supported by available data or knowledge of site conditions,

4.5.7 Dictating that corrective action goals can only be achieved through source removal and treatment actions, thereby restricting the use of exposure reduction options, such as engineering and institutional controls,

4.5.8 The use of unjustified or inappropriate exposure factors,

4.5.9 The use of unjustified or inappropriate toxicity parameters,

4.5.10 Neglecting aesthetic and other criteria when determining RBSLs or SSTLs,

4.5.11 Not considering the effects of additivity when screening multiple chemicals,

4.5.12 Not evaluating options for engineering or institutional controls, exposure point(s), compliance point(s), and carcinogenic risk levels before submitting remedial action plans,

4.5.13 Not maintaining engineering or institutional controls, and

4.5.14 Requiring continuing monitoring or remedial action at sites that have achieved the RBSL or SSTL.

## 5. Tiered Approach to Risk-Based Corrective Action (RBCA) at Petroleum Release Sites

5.1 RBCA is the integration of site assessment, remedial action selection, and monitoring with USEPA-recommended risk and exposure assessment practices. This creates a process

by which corrective action decisions are made in a consistent manner that is protective of human health and the environment.

5.2 The RBCA process is implemented in a tiered approach, involving increasingly sophisticated levels of data collection and analysis. The assumptions of earlier tiers are replaced with site-specific data and information. Upon evaluation of each tier, the user reviews the results and recommendations and decides whether more site-specific analysis is warranted.

5.3 *Site Assessment*—The user is required to identify the sources of the chemical(s) of concern, obvious environmental impacts (if any), any potentially impacted humans and environmental receptors (for example, workers, residents, water bodies, and so forth), and potentially significant transport pathways (for example, ground water flow, utilities, atmospheric dispersion, and so forth). The site assessment will also include information collected from historical records and a visual inspection of the site.

5.4 *Site Classification*—Sites are classified by the urgency of need for initial response action, based on information collected during the site assessment. Associated with site classifications are initial response actions that are to be implemented simultaneously with the RBCA process. Sites should be reclassified as actions are taken to resolve concerns or as better information becomes available.

5.5 *Tier 1 Evaluation*—A look-up table containing screening level concentrations is used to determine whether site conditions satisfy the criteria for a quick regulatory closure or warrant a more site-specific evaluation. Ground water, soil, and vapor concentrations may be presented in this table for a range of site descriptions and types of petroleum products ((for example, gasoline, crude oil, and so forth). The look-up table of RBSL is developed in Tier 1 or, if a look-up table has been previously developed and determined to be applicable to the site by the user, then the existing RBSLs are used in the Tier 1 process. Tier 1 RBSLs are typically derived for standard exposure scenarios using current RME and toxicological parameters as recommended by the USEPA. These values may change as new methodologies and parameters are developed. Tier 1 RBSLs may be presented as a range of values, corresponding to a range of risks or property uses.

5.6 *Tier 2 Evaluation*—Tier 2 provides the user with an option to determine SSTLs and point(s) of compliance. It is important to note that both Tier 1 RBSL and Tier 2 SSTLs are based on achieving similar levels of protection of human health and the environment (for example,  $10^{-4}$  to  $10^{-6}$  risk levels). However, in Tier 2 the non-site-specific assumptions and point(s) of exposure used in Tier 1 are replaced with site-specific data and information. Additional site-assessment data may be needed. For example, the Tier 2 SSTL can be derived from the same equations used to calculate the Tier 1 RBSL, except that site-specific parameters are used in the calculations. The additional site-specific data may support alternate fate and transport analysis. At other sites, the Tier 2 analysis may involve applying Tier 1 RBSLs at more probable point(s) of exposure. Tier 2 SSTLs are consistent with USEPA-recommended practices.

5.7 *Tier 3 Evaluation*—Tier 3 provides the user with an option to determine SSTLs for both direct and indirect pathways using site-specific parameters and point(s) of exposure and compliance when it is judged that Tier 2 SSTLs should not be used as target levels. Tier 3, in general, can be a substantial incremental effort relative to Tiers 1 and 2, as the evaluation is much more complex and may include additional site assessment, probabilistic evaluations, and sophisticated chemical fate/transport models.

5.8 *Remedial Action*— If the concentrations of chemical(s) of concern at a site are above the RBSL or SSTL at the point(s) of compliance or source area, or both, and the user determines that the RBSL or SSTL should be used as remedial action target levels, the user develops a remedial action plan in order to reduce the potential for adverse impacts. The user may use remediation processes to reduce concentrations of the chemical(s) of concern to levels below or equal to the target levels or to achieve exposure reduction (or elimination) through institutional controls discussed in [Appendix X4](#), or through the use of engineering controls, such as capping and hydraulic control.

## 6. Risk-Based Corrective Action (RBCA) Procedures

6.1 The sequence of principal tasks and decisions associated with the RBCA process are outlined on the flowchart shown in [Fig. 1](#). Each of these actions and decisions is discussed as follows.

6.2 *Site Assessment*— Gather the information necessary for site classification, initial response action, comparison to the RBSL, and determining the SSTL. Site assessment may be conducted in accordance with [Guide E1599](#). Each successive tier will require additional site-specific data and information that must be collected as the RBCA process proceeds. The user may generate site-specific data and information or estimate reasonable values for key physical characteristics using soil survey data and other readily available information. The site characterization data should be summarized in a clear and concise format.

6.2.1 The site assessment information for Tier 1 evaluation may include the following:

6.2.1.1 A review of historical records of site activities and past releases;

6.2.1.2 Identification of chemical(s) of concern;

6.2.1.3 Location of major sources of the chemical(s) of concern;

6.2.1.4 Location of maximum concentrations of chemical(s) of concern in soil and ground water;

6.2.1.5 Location of humans and the environmental receptors that could be impacted (point(s) of exposure);

6.2.1.6 Identification of potential significant transport and exposure pathways (ground water transport, vapor migration through soils and utilities, and so forth);

6.2.1.7 Determination of current or potential future use of the site and surrounding land, ground water, surface water, and sensitive habitats;

6.2.1.8 Determination of regional hydrogeologic and geologic characteristics (for example, depth to ground water, aquifer thickness, flow direction, gradient, description of confining units, and ground water quality); and

6.2.1.9 A qualitative evaluation of impacts to environmental receptors.

6.2.2 In addition to the information gathered in [6.2.1](#), the site assessment information for Tier 2 evaluation may include the following:

6.2.2.1 Determination of site-specific hydrogeologic and geologic characteristics (for example, depth to ground water, aquifer thickness, flow direction, gradient, description of confining units, and ground water quality);

6.2.2.2 Determination of extent of chemical(s) of concern relative to the RBSL or SSTL, as appropriate;

6.2.2.3 Determination of changes in concentrations of chemical(s) of concern over time (for example, stable, increasing, and decreasing); and

6.2.2.4 Determination of concentrations of chemical(s) of concern measured at point(s) of exposure (for example, dissolved concentrations in nearby drinking water wells or vapor concentrations in nearby conduits or sewers).

6.2.3 In addition to the information gathered in [6.2.1](#) and [6.2.2](#), the site assessment information for Tier 3 evaluation includes additional information that is required for site-specific modeling efforts.

6.3 *Site Classification and Initial Response Action*—As the user gathers data, site conditions should be evaluated and an initial response action should be implemented, consistent with site conditions. This process is repeated when new data indicate a significant change in site conditions. Site urgency classifications are presented in [Table 1](#), along with example classification scenarios and potential initial responses. *Note that the initial response actions given in [Table 1](#) may not be applicable for all sites. The user should select an option that best addresses the short-term health and safety concerns of the site while implementing the RBCA process.*

6.3.1 The classification and initial response action scheme given in [Table 1](#) is an example. It is based on the current and projected degree of hazard to human health and the environment. This is a feature of the process that can be customized by the user. “Classification 1” sites are associated with immediate threats to human health and the environment; “Classification 2” sites are associated with short-term (0 to 2-year) threats to human health, safety, and the environment; “Classification 3” sites are associated with long-term (greater than 2-year) threats to human health, safety, and the environment; “Classification 4” sites are associated with no reasonable potential threat to human health or to the environment.

6.3.2 Associated with each classification scenario in [Table 1](#) is an initial response action; the initial response actions are implemented in order to eliminate any potential immediate impacts to human health and the environment as well as to minimize the potential for future impacts that may occur as the user proceeds with the RBCA process. Note that initial response actions do not always require active remediation; in many cases the initial response action is to monitor or further assess site conditions to ensure that risks posed by the site do not increase above acceptable levels over time. The initial response actions given in [Table 1](#) are examples, and the user is free to implement other alternatives.

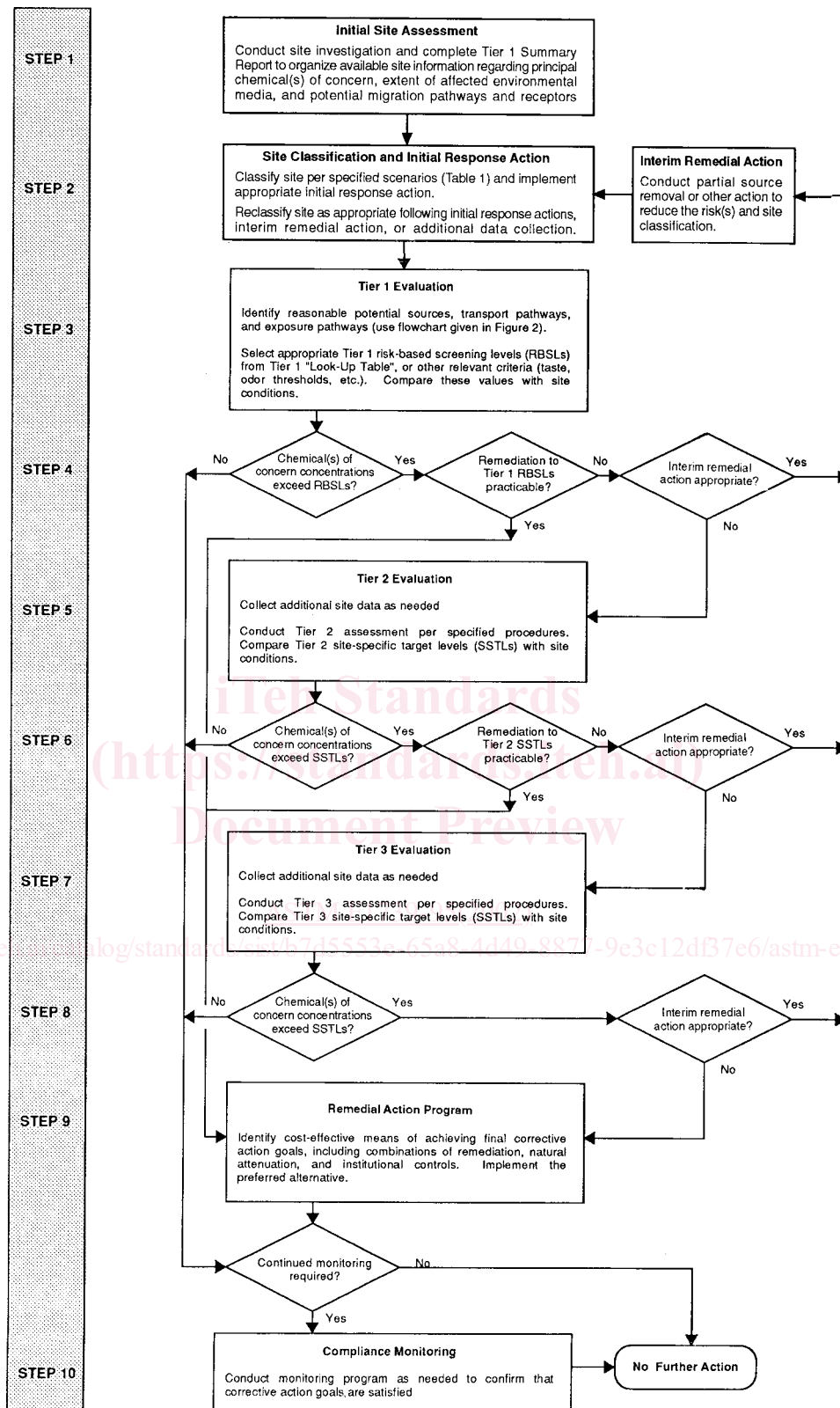


FIG. 1 Risk-Based Corrective Action Process Flowchart

**TABLE 1 Example Site Classification and Initial Response Actions<sup>A</sup>**

| Criteria and Prescribed Scenarios                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Example Initial Response Actions <sup>B</sup>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |
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| <p>1. Immediate threat to human health, safety, or sensitive environmental receptors</p> <ul style="list-style-type: none"> <li>• Explosive levels, or concentrations of vapors that could cause acute health effects, are present in a residence or other building.</li> <li>• Explosive levels of vapors are present in subsurface utility system(s), but no building or residences are impacted.</li> <li>• Free-product is present in significant quantities at ground surface, on surface water bodies, in utilities other than water supply lines, or in surface water runoff.</li> <li>• An active public water supply well, public water supply line, or public surface water intake is impacted or immediately threatened.</li> <li>• Ambient vapor/particulate concentrations exceed concentrations of concern from an acute exposure or safety viewpoint.</li> <li>• A sensitive habitat or sensitive resources (sport fish, economically important species, threatened and endangered species, and so forth) are impacted and affected.</li> </ul>                                                                                                                                                                                                                                                   | <p>Notify appropriate authorities, property owners, and potentially affected parties, and only evaluate the need to</p> <ul style="list-style-type: none"> <li>• Evacuate occupants and begin abatement measures such as subsurface ventilation or building pressurization.</li> <li>• Evacuate immediate vicinity and begin abatement measures such as ventilation.</li> <li>• Prevent further free-product migration by appropriate containment measures, institute free-product recovery, and restrict area access.</li> <li>• Notify user(s), provide alternate water supply, hydraulically control contaminated water, and treat water at point-of-use.</li> <li>• Install vapor barrier (capping, foams, and so forth), remove source, or restrict access to affected area.</li> <li>• Minimize extent of impact by containment measures and implement habitat management to minimize exposure.</li> </ul>                                                                                                                    |
| <p>2. Short-term (0 to 2 years) threat to human health, safety, or sensitive environmental receptors</p> <ul style="list-style-type: none"> <li>• There is potential for explosive levels, or concentrations of vapors that could cause acute effects, to accumulate in a residence or other building.</li> <li>• Shallow contaminated surface soils are open to public access, and dwellings, parks, playgrounds, day-care centers, schools, or similar use facilities are within 500 ft (152 m) of those soils.</li> <li>• A non-potable water supply well is impacted or immediately threatened.</li> <li>• Ground water is impacted, and a public or domestic water supply well producing from the impacted aquifer is located within two-years projected ground water travel distance down gradient of the known extent of chemical(s) concern.</li> <li>• Ground water is impacted, and a public or domestic water supply well producing from a different interval is located within the known extent of chemicals of concern.</li> <li>• Impacted surface water, storm water, or ground water discharges within 500 ft (152 m) of a sensitive habitat or surface water body used for human drinking water or contact recreation.</li> </ul>                                                               | <p>Notify appropriate authorities, property owners, and potentially affected parties, and only evaluate the need to</p> <ul style="list-style-type: none"> <li>• Assess the potential for vapor migration (through monitoring/modeling) and remove source (if necessary), or install vapor migration barrier.</li> <li>• Remove soils, cover soils, or restrict access.</li> <li>• Notify owner/user and evaluate the need to install point-of-use water treatment, hydraulic control, or alternate water supply.</li> <li>• Institute monitoring and then evaluate if natural attenuation is sufficient, or if hydraulic control is required.</li> <li>• Monitor ground water well quality and evaluate if control is necessary to prevent vertical migration to the supply well.</li> <li>• Institute containment measures, restrict access to areas near discharge, and evaluate the magnitude and impact of the discharge.</li> </ul>                                                                                           |
| <p>3. Long-term (&gt;2 years) threat to human health, safety, or sensitive environmental receptors</p> <ul style="list-style-type: none"> <li>• Subsurface soils (&gt;3 ft (0.9 m) BGS) are significantly impacted, and the depth between impacted soils and the first potable aquifer is less than 50 ft (15 m).</li> <li>• Ground water is impacted, and potable water supply wells producing from the impacted interval are located &gt;2 years ground water travel time from the dissolved plume.</li> <li>• Ground water is impacted, and non-potable water supply wells producing from the impacted interval are located &gt;2 years ground water travel time from the dissolved plume.</li> <li>• Ground water is impacted, and non-potable water supply wells that do not produce from the impacted interval are located within the known extent of chemical(s) of concern.</li> <li>• Impacted surface water, storm water, or ground water discharges within 1500 ft (457 m) of a sensitive habitat or surface water body used for human drinking water or contact recreation.</li> <li>• Shallow contaminated surface soils are open to public access, and dwellings, parks, playgrounds, day-care centers, schools, or similar use facilities are more than 500 ft (152 m) of those soils.</li> </ul> | <p>Notify appropriate authorities, property owners, and potentially affected parties, and only evaluate the need to</p> <ul style="list-style-type: none"> <li>• Monitor ground water and determine the potential for future migration of the chemical(s) concerns to the aquifer.</li> <li>• Monitor the dissolved plume and evaluate the potential for natural attenuation and the need for hydraulic control.</li> <li>• Identify water usage of well, assess the effect of potential impact, monitor the dissolved plume, and evaluate whether natural attenuation or hydraulic control are appropriate control measures.</li> <li>• Monitor the dissolved plume, determine the potential for vertical migration, notify the user, and determine if any impact is likely.</li> <li>• Investigate current impact on sensitive habitat or surface water body, restrict access to area of discharge (if necessary), and evaluate the need for containment/control measures.</li> <li>• Restrict access to impact soils.</li> </ul> |
| <p>4. No demonstrable long-term threat to human health or safety or sensitive environmental receptors</p> <p>Priority 4 scenarios encompass all other conditions not described in Priorities 1, 2, and 3 and that are consistent with the priority description given above. Some examples are as follows:</p> <ul style="list-style-type: none"> <li>• Non-potable aquifer with no existing local use impacted.</li> <li>• Impacted soils located more than 3 ft (0.9 m) BGS and greater than 50 ft (15 m) above nearest aquifer.</li> <li>• Ground water is impacted, and non-potable wells are located down gradient outside the known extent of the chemical(s) of concern, and they produce from a nonimpacted zone.</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | <p>Notify appropriate authorities, property owners, and potentially affected parties, and only evaluate the need to</p> <ul style="list-style-type: none"> <li>• Monitor ground water and evaluate effect of natural attenuation on dissolved plume migration.</li> <li>• Monitor ground water and evaluate effect of natural attenuation on leachate migration.</li> <li>• Monitor ground water and evaluate effect of natural attenuation on dissolved plume migration.</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                |

<sup>A</sup> Johnson, P. C., DeVuall, G. E., Ettinger, R. A., MacDonald, R. L. M., Stanley, C. C., Westby, T. S., and Conner, J., "Risk-Based Corrective Action: Tier 1 Guidance Manual," Shell Oil Co., July 1993.

<sup>B</sup> Note that these are potential initial response actions that may not be appropriate for all sites. The user is encouraged to select options that best address the short-term health and safety concerns of the site, while the RBCA process progresses.



6.3.3 The need to reclassify the site should be evaluated when additional site information is collected that indicates a significant change in site conditions or when implementation of an interim response action causes a significant change in site conditions.

6.4 *Development of a Tier 1 Look-Up Table of RBSL*—If a look-up table is not available, the user is responsible for developing the look-up table. If a look-up table is available, the user is responsible for determining that the RBSLs in the look-up table are based on currently acceptable methodologies and parameters. The look-up table is a tabulation for potential exposure pathways, media (for example, soil, water, and air), a range of incremental carcinogenic risk levels (10E-4 to 10E-6 are often evaluated as discussed in [Appendix X1](#) paragraph [X1.7](#), Discussion of Acceptable Risk) and hazard quotients equal to unity, and potential exposure scenarios (for example, residential, commercial, industrial, and agricultural) for each chemical(s) of concern.

6.4.1 The RBSLs are determined using typical, non-sitespecific values for exposure parameters and physical parameters for media. The RBSLs are calculated according to methodology suggested by the USEPA. For each exposure scenario, the RBSLs are based on current USEPA RME parameters and current toxicological information given in Refs ([2](#), [3](#)) or peer-reviewed source(s). Consequently, the RBSL look-up table is updated when new methodologies and parameters are developed. For indirect pathways, fate and transport models can be used to predict RBSLs at a source area that corresponds to exposure point concentrations. An example of the development of a Tier 1 Look-Up Table and RBSL is given in [Appendix X2](#). *Fig. 2 and Appendix X2 are presented solely for the purpose of providing an example development of the RBSL, and the values should not be viewed as proposed RBSLs.*

6.4.2 [Appendix X2](#) is an example of an abbreviated Tier 1 RBSL Look-Up Table for compounds of concern associated with petroleum releases. The exposure scenarios selected in the example case are for residential and industrial/commercial scenarios characterized by USEPA RME parameters for adult males. The assumptions and methodology used in deriving the example are discussed in [Appendix X2](#). Note that not all possible exposure pathways are considered in the derivation of the example. *The user should always review the assumptions and methodology used to derive values in a look-up table to make sure that they are consistent with reasonable exposure scenarios for the site being considered as well as currently accepted methodologies.* The value of creating a look-up table is that users do not have to repeat the exposure calculations for each site encountered. The look-up table is only altered when RME parameters, toxicological information, or recommended methodologies are updated. Some states have compiled such tables for direct exposure pathways that, for the most part, contain identical values (as they are based on the same assumptions). Values for the cross-media pathways (for example, volatilization and leaching), when available, often differ because these involve coupling exposure calculations with predictive equations for the fate and transport of chemicals in the environment. As yet, there is little agreement in the technical community concerning non-site-specific values for

the transport and fate model parameters, or the choice of the models themselves. *Again, the reader should note that the example is presented here only as an abbreviated example of a Tier 1 RBSL Look-Up Table for typical compounds of concern associated with petroleum products.*

6.4.3 *Use of Total Petroleum Hydrocarbon Measurements*—Various chemical analysis methods commonly referred to as total petroleum hydrocarbons (TPHs) are often used in site assessments. These methods usually determine the total amount of hydrocarbons present as a single number and give no information on the types of hydrocarbon present. The TPHs should not be used for risk assessment because the general measure of TPH provides insufficient information about the amounts of individual chemical(s) of concern present.

6.5 *Comparison of Site Conditions with Tier 1 Risk-Based Screening Levels (RBSL)*—In Tier 1, the point(s) of exposure and point(s) of compliance are assumed to be located within close proximity to the source area(s) or the area where the highest concentrations of the chemical(s) of concern have been identified. Concentrations of the chemical(s) of concern measured at the source area(s) identified at the site should be compared to the look-up table RBSL. If there is sufficient site assessment data, the user may opt to compare RBSLs with statistical limits (for example, upper confidence levels) rather than maximum values detected. Background concentrations should be considered when comparing the RBSLs, to the site concentrations as the RBSLs may sometimes be less than background concentrations. Note that additivity of risks is not explicitly considered in the Tier 1 evaluation, as it is expected that the RBSLs are typically for a limited number of chemical(s) of concern considered at most sites. Additivity may be addressed in Tier 2 and Tier 3 analyses. To accomplish the Tier 1 comparison:

6.5.1 Select the potential exposure scenario(s) (if any) for the site. Exposure scenarios are determined based on the site assessment information described in [6.2](#);

6.5.2 Based on the impacted media identified, determine the primary sources, secondary sources, transport mechanisms, and exposure pathways;

6.5.3 Select the receptors (if any) based on current and anticipated future use. Consider land use restrictions and surrounding land use when making this selection.

6.5.4 Identify the exposure scenarios where the measured concentrations of the chemical(s) of concern are above the RBSL.

6.6 *Exposure Evaluation Flowchart*—During a Tier 1 evaluation, the risk evaluation flowchart presented in [Fig. 2](#) may be used as a tool to guide the user in selecting appropriate exposure scenarios based on site assessment information. This worksheet may also be used in the evaluation of remedial action alternatives. To complete this flowchart:

6.6.1 Characterize site sources and exposure pathways, using the data summarized from Tier 1 to customize the risk evaluation flowchart for the site by checking the small checkbox for every relevant source, transport mechanism, and exposure pathway.

6.6.2 Identify receptors, and compare site conditions with Tier 1 levels: For each exposure pathway selected, check the



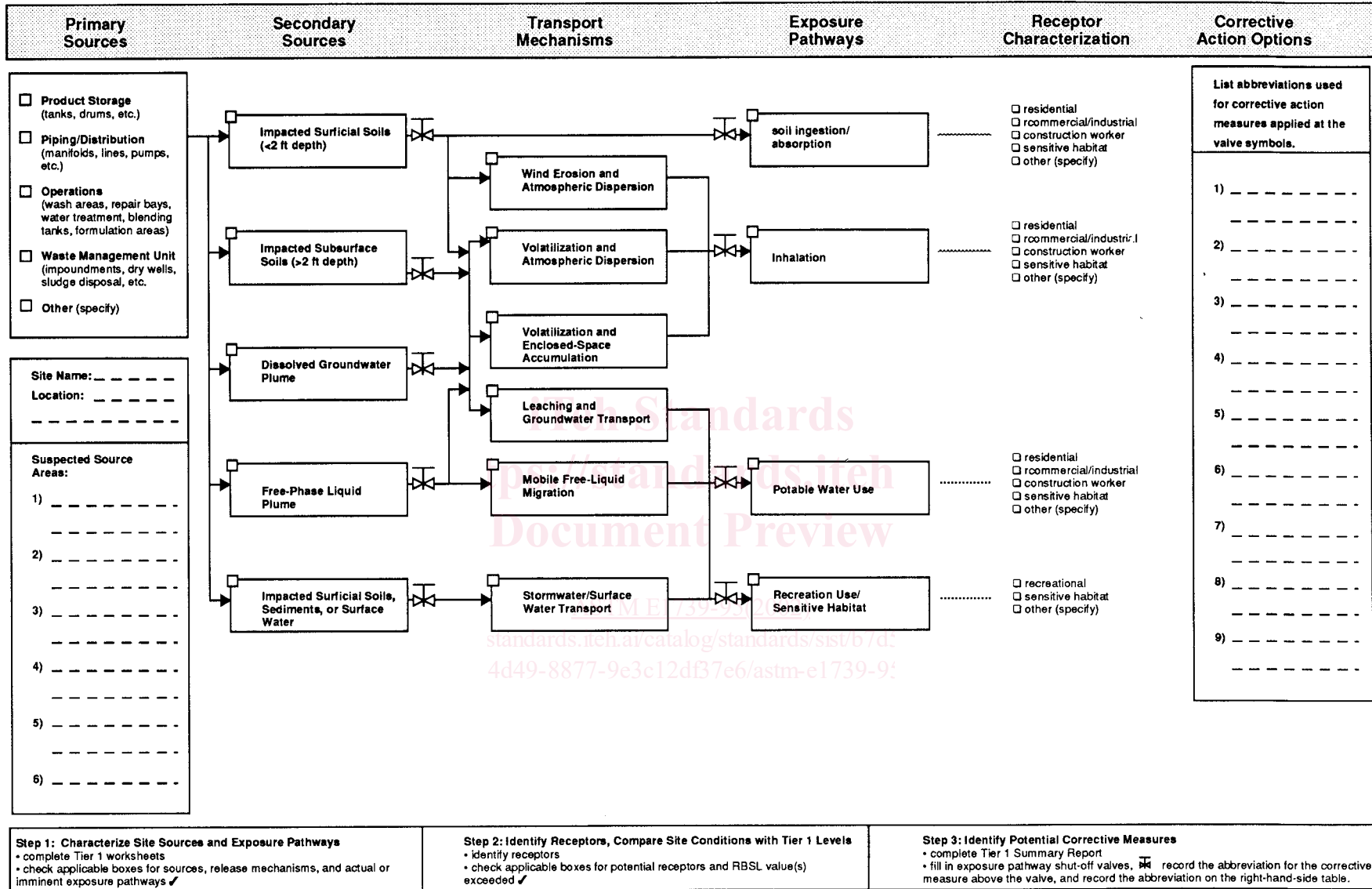


FIG. 2 Exposure Scenario Evaluation Flowchart

receptor characterization (residential, commercial, and so forth) where the concentrations of the chemical(s) of concern are above the RBSL. Consider land use restrictions and surrounding land use when making this selection. Do not check any boxes if there are no receptors present, or likely to be present, or if institutional controls prevent exposure from occurring and are likely to stay in place.

6.6.3 Identify potential remedial action measures. Select remedial action options to reduce or eliminate exposure to the chemical(s) of concern.

6.6.4 The exposure evaluation flowchart (Fig. 2) can be used to graphically portray the effect of the Tier 1 remedial action. Select the Tier 1 remedial action measure or measures (shown as valve symbols) that will break the lines linking sources, transport mechanisms, and pathways leading to the chemical(s) of concern above the RBSL. Adjust the mix of remedial action measures until no potential receptors have concentrations of chemical(s) of concerns above the RBSL with the remedial action measures in place. Show the most likely Tier 1 remedial action measure(s) selected for this site by marking the appropriate valve symbols on the flowchart and recording a remedial action measure on the right-hand-side of this figure.

6.7 *Evaluation of Tier Results*—At the conclusion of each tier evaluation, the user compares the target levels (RBSLs or SSTLs) to the concentrations of the chemical(s) of concern at the point(s) of compliance.

6.7.1 If the concentrations of the chemical(s) of concern exceed the target levels at the point(s) of compliance, then either remedial action, interim remedial action, or further tier evaluation should be conducted.

6.7.1.1 *Remedial Action*—A remedial action program is designed and implemented. This program may include some combination of source removal, treatment, and containment technologies, as well as engineering and institutional controls. Examples of these include the following: soil venting, bioventing, air sparging, pump and treat, and natural attenuation/passive remediation. When concentrations of chemical(s) of concern no longer exceed the target levels at the point of compliance, then the user may elect to move to 6.7.3.

6.7.1.2 *Interim Remedial Action*—If achieving the desired risk reduction is impracticable due to technology or resource limitations, an interim remedial action, such as removal or treatment of “hot spots,” may be conducted to address the most significant concerns, change the site classification, and facilitate reassessment of the tier evaluation.

6.7.1.3 *Further Tier Evaluation*—If further tier evaluation is warranted, additional site assessment information may be collected to develop SSTLs under a Tier 2 or Tier 3 evaluation. Further tier evaluation is warranted when:

- (1) The basis for the RBSL values (for example, geology, exposure parameters, point(s) of exposure, and so forth) are not representative of the site-specific conditions; or
- (2) The SSTL developed under further tier evaluation will be significantly different from the Tier 1 RBSL or will significantly modify the remedial action activities; or
- (3) Cost of remedial action to RBSLs will likely be greater than further tier evaluation and subsequent remedial action.

6.7.2 If the concentrations of chemicals of concern at the point of compliance are less than the target levels, but the user is not confident that data supports the conclusion that concentrations will not exceed target levels in the future, then the user institutes a monitoring plan to collect data sufficient to confidently conclude that concentrations will not exceed target levels in the future. When this data is collected, the user moves to 6.7.3.

6.7.3 If the concentrations of chemicals of concern at the point of compliance are less than target levels, and the user is confident that data supports the conclusion that concentrations will not exceed target levels in the future, then no additional corrective action activities are necessary, and the user has completed the RBCA process. In practice, this is often accompanied by the issuing of a no-further-action letter by the oversight regulatory agency.

6.8 *Tier 2*—Tier 2 provides the user with an option to determine the site-specific point(s) of compliance and corresponding SSTL for the chemical(s) of concern applicable at the point(s) of compliance and source area(s). Additional site assessment data may be required; however, the incremental effort is typically minimal relative to Tier 1. If the user completes a Tier 1 evaluation, in most cases, only a limited number of pathways, exposure scenarios, and chemical(s) of concern are considered in the Tier 2 evaluation since many are eliminated from consideration during the Tier 1 evaluation.

6.8.1 In Tier 2, the user:

6.8.1.1 Identifies the indirect exposure scenarios to be addressed and the appropriate site-specific point(s) of compliance. A combination of assessment data and predictive modeling results are used to determine the SSTL at the source area(s) or the point(s) of compliance, or both; or

6.8.1.2 Applies Tier 1 RBSL Look-Up Table values for the direct exposure scenarios at reasonable point(s) of exposure (as opposed to the source area(s) as is done in Tier 1). The SSTLs for source area(s) and point(s) of compliance can be determined based on the demonstrated and predicted attenuation (reduction in concentration with distance) of compounds that migrate away from the source area(s).

6.8.1.3 An example of a Tier 2 application is illustrated in Appendix X5.

6.8.2 Tier 2 of the RBCA process involves the development of SSTL based on the measured and predicted attenuation of the chemical(s) of concern away from the source area(s) using relatively simplistic mathematical models. The SSTLs for the source area(s) are generally not equal to the SSTL for the point(s) of compliance. The predictive equations are characterized by the following:

6.8.2.1 The models are relatively simplistic and are often algebraic or semianalytical expressions;

6.8.2.2 Model input is limited to practicably attainable site-specific data or easily estimated quantities (for example, total porosity, soil bulk density); and

6.8.2.3 The models are based on descriptions of relevant physical/chemical phenomena. Most mechanisms that are neglected result in predicted concentrations that are greater than those likely to occur (for example, assuming constant concentrations in source area(s)). Appendix X3 discusses the use of

predictive models and presents models that might be considered for Tier 2 evaluation.

6.8.3 *Tier 2 Evaluation*—Identify the exposure scenarios where the measured concentrations of the chemical(s) of concern are above the SSTL at the point(s) of compliance, and evaluate the tier results in accordance with 6.7.

6.9 *Tier 3*—In a Tier 3 evaluation, SSTLs for the source area(s) and the point(s) of compliance are developed on the basis of more sophisticated statistical and contaminant fate and transport analyses, using site-specific input parameters for both direct and indirect exposure scenarios. Source area(s) and the point(s) of compliance SSTLs are developed to correspond to concentrations of chemical(s) of concern at the point(s) of exposure that are protective of human health and the environment. Tier 3 evaluations commonly involve collection of significant additional site information and completion of more extensive modeling efforts than is required for either a Tier 1 or Tier 2 evaluation.

6.9.1 Examples of Tier 3 analyses include the following:

6.9.1.1 The use of numerical ground water modeling codes that predict time-dependent dissolved contaminant transport under conditions of spatially varying permeability fields to predict exposure point(s) of concentrations;

6.9.1.2 The use of site-specific data, mathematical models, and Monte Carlo analyses to predict a statistical distribution of exposures and risks for a given site; and

6.9.1.3 The gathering of sufficient data to refine site-specific parameter estimates (for example, biodegradation rates) and improve model accuracy in order to minimize future monitoring requirements.

6.9.2 *Tier 3 Evaluation*—Identify the exposure scenarios where the measured concentrations of the chemical(s) of concern are above the SSTL at the point(s) of compliance, and evaluate the tier results in accordance with 6.7 except that a tier upgrade (6.7.5) is not available.

6.10 *Implementing the Selected Remedial Action Program*—When it is judged by the user that no further assessment is necessary, or practicable, a remedial alternatives evaluation should be conducted to confirm the most cost-effective option for achieving the final remedial action target levels (RBSLs or SSTLs, as appropriate). Detailed design specifications may then be developed for installation and operation of the selected measure. The remedial action must continue until such time as monitoring indicates that concentrations of the chemical(s) of concern are not above the RBSL or SSTL, as appropriate, at the points of compliance or source area(s), or both.

6.11 *RBCA Report*—After completion of the RBCA activities, a RBCA report should be prepared and submitted to the

regulatory agency. The RBCA report should, at a minimum, include the following:

- 6.11.1 An executive summary;
- 6.11.2 A site description;
- 6.11.3 A summary of the site ownership and use;
- 6.11.4 A summary of past releases or potential source areas;
- 6.11.5 A summary of the current and completed site activities;
- 6.11.6 A description of regional hydrogeologic conditions;
- 6.11.7 A description of site-specific hydrogeologic conditions;
- 6.11.8 A summary of beneficial use;
- 6.11.9 A summary and discussion of the risk assessment (hazard identification, dose response assessment, exposure assessment, and risk characterization), including the methods and assumptions used to calculate the RBSL or SSTL, or both;
- 6.11.10 A summary of the tier evaluation;
- 6.11.11 A summary of the analytical data and the appropriate RBSL or SSTL used;
- 6.11.12 A summary of the ecological assessment;
- 6.11.13 A site map of the location;
- 6.11.14 An extended site map to include local land use and ground water supply wells;
- 6.11.15 Site plan view showing location of structures, aboveground storage tanks, underground storage tanks, buried utilities and conduits, suspected/confirmed sources, and so forth;
- 6.11.16 Site photos, if available;
- 6.11.17 A ground water elevation map;
- 6.11.18 Geologic cross section(s); and
- 6.11.19 Dissolved plume map(s) of the chemical(s) of concern.

6.12 *Monitoring and Site Maintenance*—In many cases, monitoring is necessary to demonstrate the effectiveness of implemented remedial action measures or to confirm that current conditions persist or improve with time. Upon completion of this monitoring effort (if required), no further action is required. In addition, some measures (for example, physical barriers such as capping, hydraulic control, and so forth) require maintenance to ensure integrity and continued performance.

6.13 *No Further Action and Remedial Action Closure*—When RBCA RBSLs or SSTLs have been demonstrated to be achieved at the point(s) of compliance or source area(s), or both, as appropriate, and monitoring and site maintenance are no longer required to ensure that conditions persist, then no further action is necessary, except to ensure that institutional controls (if any) remain in place.



**X1. PETROLEUM PRODUCTS CHARACTERISTICS: COMPOSITION, PHYSICAL AND CHEMICAL PROPERTIES, AND TOXICOLOGICAL ASSESSMENT SUMMARY**

*X1.1 Introduction:*

X1.1.1 Petroleum products originating from crude oil are complex mixtures of hundreds to thousands of chemicals; however, practical limitations allow us to focus only on a limited subset of key components when assessing the impact of petroleum fuel releases to the environment. Thus, it is important to have a basic understanding of petroleum properties, compositions, and the physical, chemical, and toxicological properties of some compounds most often identified as the key chemicals or chemicals of concern.

X1.1.2 This appendix provides a basic introduction to the physical, chemical, and toxicological characteristics of petroleum products (gasoline, diesel fuel, jet fuel, and so forth)<sup>6</sup> and other products focussed primarily towards that information which is most relevant to assessing potential impacts due to releases of these products into the subsurface. Much of the information presented is summarized from the references listed at the end of this guide. For specific topics, the reader is referred to the following sections of this appendix:

- X1.1.2.1 *Composition of Petroleum Fuels*—See X1.2.
- X1.1.2.2 *Physical, Chemical, and Toxicological Properties of Petroleum Fuels*—See X1.3.
- X1.1.2.3 *Chemical of Concern*—See X1.4.
- X1.1.2.4 *Toxicity of Petroleum Hydrocarbons*—See X1.5.
- X1.1.2.5 *Profiles of Select Compounds*—See X1.6.

*X1.2 Composition of Petroleum Products:*

X1.2.1 Most petroleum products are derived from crude oil by distillation, which is a process that separates compounds by volatility. Crude oils are variable mixtures of thousands of chemical compounds, primarily hydrocarbons; consequently, the petroleum products themselves are also variable mixtures of large numbers of components. The biggest variations in composition are from one type of product to another (for example, gasoline to motor oil); however, there are even significant variations within different samples of the same product type. For example, samples of gasoline taken from the same fuel dispenser on different days, or samples taken from different service stations, will have different compositions. These variations are the natural result of differing crude oil sources, refining processes and conditions, and kinds and amount of additives used.

X1.2.2 *Components of Petroleum Products*—The components of petroleum products can be generally classified as either hydrocarbons (organic compounds composed of hydrogen and carbon only) or as non-hydrocarbons (compounds containing other elements, such as oxygen, sulfur, or nitrogen).

Hydrocarbons make up the vast majority of the composition of petroleum products. The non-hydrocarbon compounds in petroleum products are mostly hydrocarbon-like compounds containing minor amounts of oxygen, sulfur, or nitrogen. Most of the trace levels of metals found in crude oil are removed by refining processes for the lighter petroleum products.

X1.2.3 *Descriptions and Physical Properties of Petroleum Products*—In order to simplify the description of various petroleum products, boiling point ranges and carbon number (number of carbon atoms per molecule) ranges are commonly used to describe and compare the compositions of various petroleum products. Table X1.1 summarizes these characteristics for a range of petroleum products. Moving down the list from gasoline, increases in carbon number range and boiling range and decreases in volatility (denoted by increasing flash point) indicate the transition to “heavier products.” Additional descriptions of each of these petroleum products are provided as follows.

X1.2.4 *Gasoline*—Gasoline is composed of hydrocarbons and “additives” that are blended with the fuel to improve fuel performance and engine longevity. The hydrocarbons fall primarily in the C4 to C12 range. The lightest of these are highly volatile and rapidly evaporate from spilled gasoline. The C4 and C5 aliphatic hydrocarbons rapidly evaporate from spilled gasoline (hours to months, depending primarily on the temperature and degree of contact with air). Substantial portions of the C6 and heavier hydrocarbons also evaporate, but at lower rates than for the lighter hydrocarbons.

X1.2.4.1 Fig. X1.1 shows gas chromatograms of a fresh gasoline and the same gasoline after simulated weathering; air was bubbled through the gasoline until 60 % of its initial volume was evaporated. In gas chromatography, the mixture is separated into its components, with each peak representing different compounds. Higher molecular weight components appear further to the right along the x-axis. For reference, positions of the *n*-aliphatic hydrocarbons are indicated in Fig.

**TABLE X1.1 Generalized Chemical and Physical Characterization of Petroleum Products**

|                                       | Predominant Carbon No. Range | Boiling Range, °C | Flash Point, <sup>A</sup> °C                              |
|---------------------------------------|------------------------------|-------------------|-----------------------------------------------------------|
| Gasoline                              | C4 to C12                    | 25 to 215         | -40                                                       |
| Kerosene and Jet Fuels                | C11 to C13                   | 150 to 250        | <21, <sup>B</sup> 21 to 55, <sup>C</sup> >55 <sup>D</sup> |
| Diesel Fuel and Light Fuel Oils       | C10 to C20                   | 160 to 400        | >35                                                       |
| Heavy Fuel Oils                       | C19 to C25                   | 315 to 540        | >50                                                       |
| Motor Oils and Other Lubricating Oils | C20 to C45                   | 425 to 540        | >175                                                      |

<sup>A</sup> Typical values.  
<sup>B</sup> Jet-B, AVTAG and JP-4.  
<sup>C</sup> Kerosene, Jet A, Jet A-1, JP-8 and AVTUR.  
<sup>D</sup> AVCAT and JP-5.

<sup>6</sup> “Alternative products,” or those products not based on petroleum hydrocarbons (or containing them in small amounts), such as methanol or M85, are beyond the scope of the discussion in this appendix.

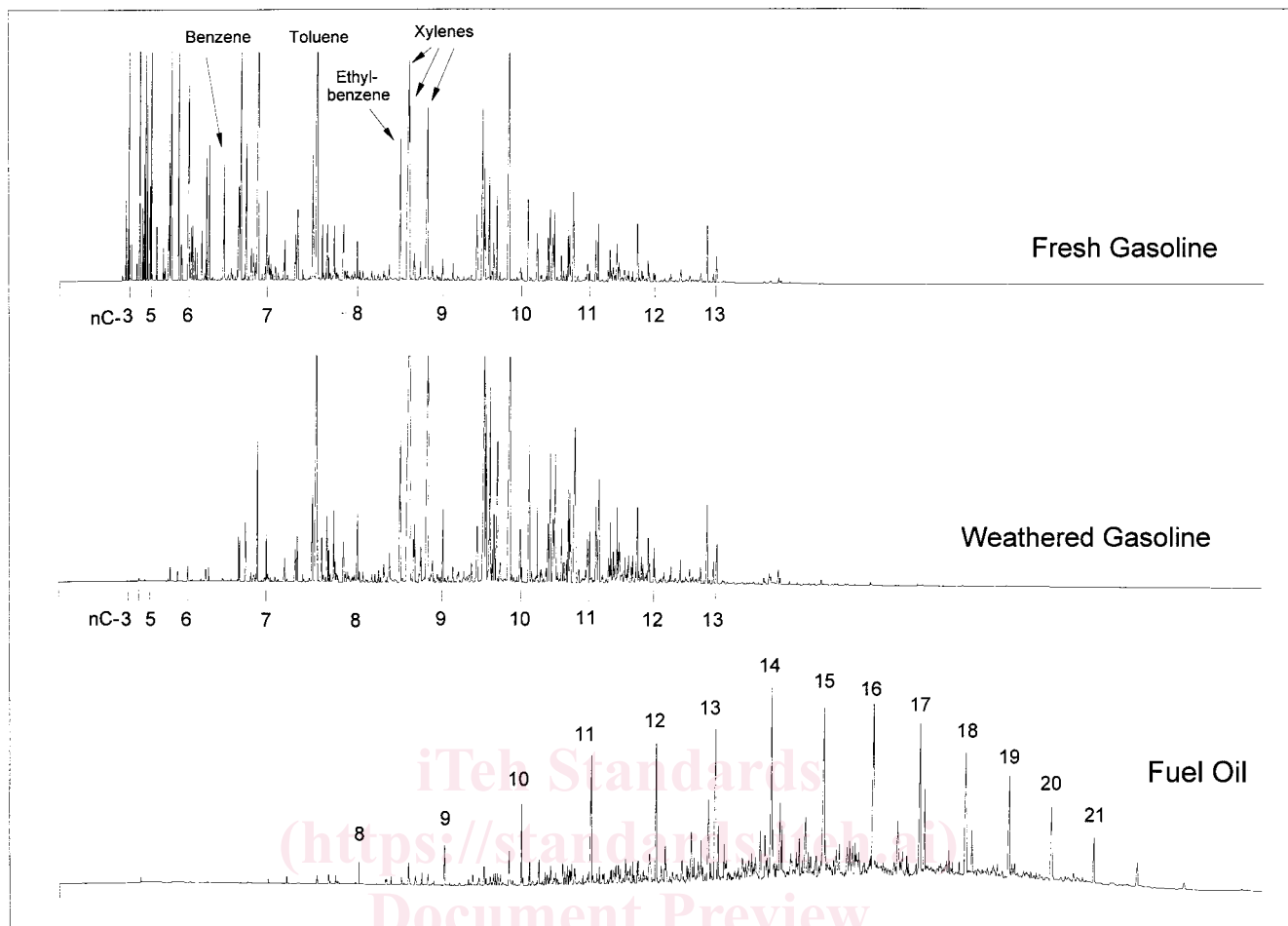


FIG. X1.1 Gas Chromatograms of Some Petroleum Fuels

X1.1. The height of, and area under, each peak are measures of how much of that component is present in the mixture. As would be expected by their higher volatilities, the lighter hydrocarbons (up to about C7) evaporate first and are greatly reduced in the weathered gasoline. The gas chromatogram of a fuel oil is also shown for comparison.

X1.2.4.2 The aromatic hydrocarbons in gasoline are primarily benzene ( $C_6H_6$ ), toluene ( $C_7H_8$ ), ethylbenzene ( $C_8H_{10}$ ), and xylenes ( $C_8H_{10}$ ); these are collectively referred to as “BTEX.” Some heavier aromatics are present also, including low amounts of polyaromatic hydrocarbons (PAHs). Aromatics typically comprise about 10 to 40 % of gasoline.

X1.2.4.3 Oxygenated compounds (“oxygenates”) such as alcohols (for example, methanol or ethanol) and ethers (for example, methyl tertiarybutyl ether—MTBE) are sometimes added to gasoline as octane boosters and to reduce carbon monoxide exhaust emissions. Methyl tertiarybutyl ether has been a common additive only since about 1980.

X1.2.4.4 Leaded gasoline, which was more common in the past, contained lead compounds added as octane boosters. Tetraethyl lead (TEL) is one lead compound that was commonly used as a gasoline additive. Other similar compounds were also used. Sometimes mixtures of several such compounds were added. Because of concerns over atmospheric emissions of lead from vehicle exhaust, the EPA has reduced

the use of leaded gasolines. Leaded gasolines were phased out of most markets by 1989.

X1.2.4.5 In order to reduce atmospheric emissions of lead, lead “scavengers” were sometimes added to leaded gasolines. Ethylene dibromide (EDB) and ethylene dichloride (EDC) were commonly used for this purpose.

X1.2.5 *Kerosene and Jet Fuel*—The hydrocarbons in kerosene commonly fall into the C11 to C13 range, and distill at approximately 150 to 250°C. Special wide-cut (that is, having broader boiling range) kerosenes and low-flash kerosenes are also marketed. Both aliphatic and aromatic hydrocarbons are present, including more multi-ring compounds and kerosene.

X1.2.5.1 Commercial jet fuels JP-8 and Jet A have similar compositions to kerosene. Jet fuels JP-4 and JP-5 are wider cuts used by the military. They contain lighter distillates and have some characteristics of both gasoline and kerosene.

X1.2.5.2 Aromatic hydrocarbons comprise about 10 to 20 % of kerosene and jet fuels.

X1.2.6 *Diesel Fuel and Light Fuel Oils*—Light fuel oils include No. 1 and No. 2 fuel oils, and boil in the range from 160 to 400°C. Hydrocarbons in light fuel oils and diesel fuel typically fall in the C10 to C20 range. Because of their higher molecular weights, constituents in these products are less volatile, less water soluble, and less mobile than gasoline- or kerosene-range hydrocarbons.

X1.2.6.1 About 25 to 35 % of No. 2 fuel oil is composed of aromatic hydrocarbons, primarily alkylated benzenes and naphthalenes. The BTEX concentrations are generally low.

X1.2.6.2 No. 1 fuel oil is typically a straight run distillate.

X1.2.6.3 No. 2 fuel oil can be either a straight run distillate, or else is produced by catalytic cracking (a process in which larger molecules are broken down into smaller ones). Straight run distillate No. 2 is commonly used for home heating fuel, while the cracked product is often used for industrial furnaces and boilers. Both No. 1 and No. 2 fuel oils are sometimes used as blending components for jet fuel or diesel fuel formulations.

X1.2.7 *Heavy Fuel Oils*—The heavy fuel oils include Nos. 4, 5, and 6 fuel oils. They are sometimes referred to as “gas oils” or “residual fuel oils.” These are composed of hydrocarbons ranging from about C19 to C25 and have a boiling range from about 315 to 540°C. They are dark in color and considerably more viscous than water. They typically contain 15 to 40 % aromatic hydrocarbons, dominated by alkylated phenanthrenes and naphthalenes. Polar compounds containing nitrogen, sulfur, or oxygen may comprise 15 to 30 % of the oil.

X1.2.7.1 No. 6 fuel oil, also called “Bunker Fuel” or “Bunker C,” is a gummy black product used in heavy industrial applications where high temperatures are available to fluidize the oil. Its density is greater than that of water.

X1.2.7.2 Nos. 4 and 5 fuel oils are commonly produced by blending No. 6 fuel oil with lighter distillates.

X1.2.8 *Motor Oils and Other Lubricating Oils*—Lubricating oils and motor oils are predominately comprised of compounds in the C20 to C45 range and boil at approximately 425 to 540°C. They are enriched in the most complex molecular fractions found in crude oil, such as cycloparaffins and PNAs having up to three rings or more. Aromatics may make up to 10 to 30 % of the oil. Molecules containing nitrogen, sulfur, or oxygen are also common. In addition, used automotive crankcase oils become enriched with PNAs and certain metals.

X1.2.8.1 These oils are relatively viscous and insoluble in ground water and relatively immobile in the subsurface.

X1.2.8.2 Waste oil compositions are even more difficult to predict. Depending on how they are managed, waste oils may contain some portion of the lighter products in addition to heavy oils. Used crankcase oil may contain wear metals from engines. Degreasing solvents (gasoline, naphtha, or light chlorinated solvents, or a combination thereof) may be present in some wastes.

### X1.3 *Physical, Chemical, and Toxicological Characteristics of Petroleum Products:*

X1.3.1 *Trends in Physical/Chemical Properties of Hydrocarbons*—In order to better understand the subsurface behavior of hydrocarbons it is helpful to be able to recognize trends in important physical properties with increasing number of carbon atoms. These trends are most closely followed by compounds with similar molecular structures, such as the straight-chained, single-bonded aliphatic hydrocarbons. In general, as the carbon number (or molecule size) increases, the following trends are observed:

X1.3.1.1 Higher boiling points (and melting points),

X1.3.1.2 Lower vapor pressure (volatility),

X1.3.1.3 Greater density,

X1.3.1.4 Lower water solubility, and

X1.3.1.5 Stronger adhesion to soils and less mobility in the subsurface.

X1.3.2 **Table X1.2** lists physical, chemical, and toxicological properties for a number of hydrocarbons found in petroleum products. In general:

X1.3.2.1 Aliphatic petroleum hydrocarbons with more than ten carbon atoms are expected to be immobile in the subsurface, except when dissolved in nonaqueous phase liquids (NAPLs), due to their low water solubilities, low vapor pressures, and strong tendency to adsorb to soil surfaces.

X1.3.2.2 Aromatic hydrocarbons are more water soluble and mobile in water than aliphatic hydrocarbons of similar molecular weight.

X1.3.2.3 Oxygenates generally have much greater water solubilities than hydrocarbons of similar molecular weight, and hence are likely to be the most mobile of petroleum fuel constituents in leachate and ground water. The light alcohols, including methanol and ethanol, are completely miscible with water in all proportions.

X1.3.3 *Properties of Mixtures*—It is important to note that the partitioning behavior of individual compounds is affected by the presence of other hydrocarbons in the subsurface. The maximum dissolved and vapor concentrations achieved in the subsurface are always less than that of any pure compound, when it is present as one of many constituents of a petroleum fuel. For example, dissolved benzene concentrations in ground water contacting gasoline-impacted soils rarely exceed 1 to 3 % of the ~1800-mg/L pure component solubility of benzene.

X1.3.4 *Trends in Toxicological Properties of Hydrocarbons*—A more detailed discussion of toxicological assessment is given in **X1.5** (see also **Appendix X3**), followed by profiles for select chemicals found in petroleum products given in **X1.6**. Of the large number of compounds present in petroleum products, aromatic hydrocarbons (BTEX, PAHs, and so forth) are the constituents that human and aquatic organisms tend to be most sensitive to (relative to producing adverse health impacts).

### X1.4 *Chemicals of Concern for Risk Assessments:*

X1.4.1 It is not practicable to evaluate every compound present in a petroleum product to assess the human health or environmental risk from a spill of that product. For this reason, risk management decisions are generally based on assessing the potential impacts from a select group of “indicator” compounds. It is inherently assumed in this approach that a significant fraction of the total potential impact from all chemicals is due to the chemicals of concern. The selection of chemicals of concern is based on the consideration of exposure routes, concentrations, mobilities, toxicological properties, and aesthetic characteristics (taste, odor, and so forth). Historically, the relatively low toxicities and dissolved-phase mobilities of aliphatic hydrocarbons have made these chemicals of concern of less concern relative to aromatic hydrocarbons. When additives are present in significant quantities, consideration should also be given to including these as chemicals of concern.