

TRABASO 13 T0501

LOW COST REMEDIATION: STRATEGIES FOR COST EFFECTIVE

RISK-BASED REMEDIATION OF HYDROCARBON CONTAMINATED

SOIL AND GROUNDWATER

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1.0 INTRODUCTION

Petroleum Hydrocarbon releases are a common problem, to some extent they are the inevitable result of oil exploration, refining, transportation, and marketing. Although recent awareness of the potential environmental impact of hydrocarbon releases have resulted in improved storage and handling practices, as long as we continue to use hydrocarbon based products some release into the environment is unavoidable. In addition, existing contamination of soil and groundwater resulting from past practice has not been fully discovered, and will persist for many years to come. For these reasons it is important that we gain an understanding of the risks to human health and the environment posed by these hydrocarbons and implement effective remediation where and when necessary.

In the U.S., and most of the world, prior to the 1980's hydrocarbon releases were only discovered when some obvious impact was discovered. This was usually either contamination of a drinking water well with sufficient hydrocarbon to cause a taste or odor problem or direct discharge of oil from groundwater to a surface water. In the 1980's the U.S. EPA and others became aware that hydrocarbon releases to groundwater were much more common than had been understood. This in turn lead to a concern that much of our groundwater was threatened by these hydrocarbon releases. The perception was that we had literally millions of releases, many resulting in groundwater contamination plumes that were growing and spreading with time. This lead to a regulatory environment which called for immediate action to remediate these sites. In the late 1980's and early 1990's hundreds of thousands of sites in the U.S. were investigated and remediation was instigated. In the earlier years remediation generally consisted of excavation with off-site treatment or disposal or some form of pump and treat or soil vapor extraction. Over time bioventing, air sparging, and vacuum enhanced oil recovery became more popular.

Several things have been learned as the result of this widespread remediation effort. Probably most importantly we became aware that most of these plumes were in fact not increasing in size but many were shrinking. For example, in a study published in 1995 (Rice et al.) the Lawrence Livermore National Laboratory studied over 1200 hydrocarbon plumes in California and came to the conclusion that 90 percent of the time dissolved benzene migrated no farther than about 80 meters in groundwater, and that most plumes were stable or shrinking, not expanding. They also observed that very few of these plumes posed any risk to human health or the environment. At about the same time it was becoming apparent that most of the remediation efforts have limited effect. It appeared that although at times it was possible to extract some mass of hydrocarbon it was not feasible at most sites to remediate to levels such as drinking water standards in groundwater.

The combined realization that complete remediation was not usually feasible, and that most hydrocarbon releases did not result in significant risk to human health or the environment has led to development and growing acceptance of the Risk-Based Remediation process. This approach recognizes the potential for hydrocarbons to have an impact and results in appropriate remedial action when and where necessary without needlessly expending resources.

2.0 RISK-BASED SITE ANALYSIS

Based on conservative toxicological studies, safe exposures to many chemical compounds such as the BTEX (benzene, toluene, ethyl benzene and xylenes) found in petroleum hydrocarbon have been determined. Chemical exposure is generally based on the average intake of a certain mass of chemical per day. The U.S. EPA has established different human exposure scenarios for different land uses. For example, the residential scenario generally assumes a 24-hour-per-day exposure, while the industrial scenario assumes an 8-hour-per-day exposure for each worker. From these exposure scenarios, generic screening levels have been established to provide safe exposure concentrations for a variety of different chemicals. For any chemical risk to exist three elements must exist at the site (see Figure 1):

- A chemical source that exceeds the safe exposure concentration;
- A completed pathway for the chemical to enter the receptor; and
- A human or ecological receptor available for chemical contact.

2.1 Review of Available Site Data

At most sites, data from past investigations is available and very useful in completing an initial risk-based screening. Historical data are particularly valuable in establishing evidence of natural attenuation processes which may be limiting contaminant migration and reducing long-term risks. Site contaminant data should be organized by environmental medium (e.g., soil, soil gas, groundwater, etc.) and

arranged in a tabular format. A site map should be available showing sampling locations, historical BTEX plumes, other contaminants of concern, if appropriate, and key land use and natural features. Existing data should be sufficient to address the following key questions:

- Where is the primary source of the contamination and has it been removed or the leak stopped?
- Is the date of release known or was it a long-term leak?
- What media have been impacted (soil, groundwater, soil gas, surface water)?
- Are there any immediate obvious risks to human health or the environment?
- Are there any potential risks due to soil vapors, excavation, or groundwater migration to drinking water wells or surface water?
- Does free product remain at the site?
- Has the geology and soil stratigraphy been adequately defined?
- Have the groundwater flow direction and gradient been defined?
- Has the extent of soil and groundwater contamination been adequately defined?
- Does the groundwater plume appear to be migrating or stable based on historical data?
- Have basic geochemical parameters (dissolved oxygen, ferrous iron, sulfate, and methane) been collected and plume migration estimated?

If any of these questions cannot be adequately addressed, additional site characterization may be required before a risk-based site closure can be pursued. It should be noted that conducting a risk analysis does not necessarily require extensive data collection. Data collection needs are always site-specific and are limited to sufficient data to assess potential pathways. For example, on a site with groundwater at a depth of 50 meters in a location where local groundwater is not used there may be no need to address the free product question.

2.2 Determining Current and Future Land Use

An equally important aspect of the initial site evaluation is an understanding of current and future land use at the site. A site walk may be conducted to determine land use and the proximity and type of buildings constructed near the site, as well as the frequency and type of human activity. An understanding of planned or potential future land use is also important. Because risk-based remediation methods rely on a clear understanding of how humans could be exposed to chemicals (exposure pathways), it is essential to have a complete knowledge of the current land use and potential land use changes.

2.3 Developing a Conceptual Site Model (CSM)

The next step of the process is to develop a CSM which combines available information on-site contamination with information on potential human receptors based on current and future land use. Potential ecological receptors such as wildlife living in or near drainage ditches should also be included in the conceptual site model. Although the complexity of risk-based analysis will vary from one site to another and one regulatory environment to another, there are three common elements of all risk-based evaluations: a source, pathways, and receptors.

If any one of these elements is absent at a site, there is no current risk. The reduction or removal of risk can be accomplished by limiting or removing any one of these three elements from the site. The goal of risk-based remediation is to find the most cost-effective method of reducing present and future risk by combining three risk reduction techniques:

1. **Chemical Source Reduction** - Achieved by natural attenuation processes over time or by engineered removals such as limited excavation, soil vapor extraction, or bioventing.
2. **Chemical Pathway Elimination** - Examples include the natural attenuation of a groundwater plume and restrictions on excavation or groundwater use to prevent on-site or off-site receptors from contacting chemicals of concern.
3. **Restrict Receptors** - Land use controls and site fencing can eliminate chemical exposure until natural attenuation or engineered remediation reduces the chemical source.

A CSM consists of three primary components that were addressed at the beginning of this section. A source of contamination, a contaminant migration pathway or pathways from the source to receptors, and potential receptors. Figure 2 illustrates a CSM for a typical underground storage tank (UST) leak in an industrial area. The primary contaminant source is the UST; the secondary source is the soil contaminated with hydrocarbon residuals (with no remaining free product). Potential exposure pathways include soil contact, soil-vapor inhalation, or dermal contact with impacted shallow groundwater. The only potential receptor in this industrial scenario are intrusive construction or utility workers who will have a limited exposure time frame resulting in limited risk.

Figure 3 illustrates a CSM for a leaking UST located in a more accessible commercial area such as a service station. Potential exposure pathways include soil contact or ingestion, soil vapor migration to the atmosphere, incidental contact with shallow groundwater, and direct contact or incidental ingestion of impacted surface waters. Potential receptors include both on-site workers and ecological receptors in the nearby surface water. This CSM indicates a greater risk may be present at this site due to greater potential for receptors to be exposed through multiple pathways.

The preliminary CSM should account for all possible pathways and receptors given the current and likely future land uses.

In the risk-based remediation process, site characterization is used to first determine if a completed pathway exists. Existing site data should be reviewed to identify which potential pathways cannot be evaluated due to a lack of quantitative chemical data for that environmental medium. For example, one pathway that is frequently overlooked is the exposure of site workers to soil vapors during excavation activities. One common data gap is the lack of soil gas data to quantify the concentration of specific hydrocarbons (usually BTEX). A complete CSM will help ensure that all the data required for risk evaluation are gathered in one field mobilization.

2.4 Estimating Natural Attenuation

2.4.1 Natural Attenuation in Soil

To accurately assess the potential for soil contaminants to attenuate, many fate and transport processes must be accounted for. For example, it is important to understand the relationship between fuel residuals in the soil (sorbed, trapped, and free product) and soil gas and groundwater contamination. A number of predictive models are available to estimate contaminant fate and transport. If possible, soil gas samples should be collected from near the center of the spill area and at several points around the perimeter of the spill. If site soil gas data indicate an abundance of oxygen (>5 percent) in contaminated soils, it generally can be assumed that atmospheric oxygen is available to soil bacteria and these bacteria are biodegrading residual hydrocarbons. Site-specific biodegradation rates can be estimated by conducting in situ respiration tests as described in Hinchee, et al. (1992). Natural biodegradation rates generally range from 1 to 10 mg TPH/kg soil/day with 4 mg/kg soil/day as an average value based on over 135 test sites (Leeson and Hinchee, 1995). At sites where soil gas oxygen is below 5 percent natural attenuation still occurs in soils, but at a lower rate. The rates of this attenuation can be estimated through oxygen diffusion modeling or other means.

For natural biodegradation to proceed in soil, the soil must be naturally aerated through simple atmospheric oxygen diffusion and barometric pressure changes. Oxygen will first be consumed at the outer circumference of the fuel spill. As the fuel is degraded over time, the replenished oxygen supply will be available to support biodegradation closer and closer to the center of the spill. Almost any fuel contamination with a constant supply of oxygen will eventually biodegrade to carbon dioxide and water. Complete attenuation is more likely to occur in shallow and sandy soils, but less likely in asphalt or concrete covered areas, and in fine-grained or layered soils which will impede the supply of oxygen to subsurface microorganisms. Evidence of natural attenuation in soil, or the need for supplied oxygen (bioventing), should be established during the site screening process.

2.4.2 Natural Attenuation in Groundwater

A useful approach to documenting natural attenuation in groundwater is described in the *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (Weidemeier 1995). This document describes three lines of evidence that can be used to support remediation by natural attenuation:

- Documented loss of contaminants at the field scale;
- Contaminant and geochemical analytical data; and
- Direct microbiological plate counts or "microcosm" studies.

The first line of evidence involves using historical trends in contaminant concentrations to show that a plume is stable or receding and that a reduction in the total mass of contaminants is occurring at the site. This is by far the most persuasive argument for natural attenuation and one of the easiest to prove if quality historical data is available. If historical data for several wells indicate that concentrations are decreasing without any significant forward migration of the plume, the rate of natural biodegradation at the site must exceed or equal the rate at which BTEX and other dissolved contaminants are partitioning out of the source. In many states natural attenuation alone is an accepted site remedy if historical data indicates plume stability and land use controls will prevent pathway completion. If historical data is the use of simple fate and transport models such as BIOSCREEN (Newell et al., 1996) to predict the time required for plume stability maybe appropriate.

The second line of evidence involves the use of geochemical data to show that decreases in contaminant concentrations are the result of biological destruction. When biodegradation is occurring, electron acceptor concentrations (oxygen, nitrate, sulfate, carbon dioxide, etc.) are depleted in the BTEX plume. Similarly, metabolic by-products (ferrous iron, methane, etc.) increase in areas of highest BTEX concentration and highest biological activity. This evidence can be used to show that electron acceptor concentrations in groundwater are sufficient to support continued biodegradation of dissolved contaminants. The strong positive correlation between electron acceptor, electron donor, and by-product data proves that the historical disappearance of contaminants is due to biodegradation and not adsorption or dilution. Although a complete geochemical analysis will not be required for initial site screening, this data is inexpensive to collect and can be useful in convincing skeptics that contaminant loss is permanent. Methods of geochemical analysis are described more fully in Weidemeier (1995).

Although seldom required for hydrocarbon sites, laboratory "microcosm studies" or "bacteria plate counts" provide a third line of evidence that indigenous microbes are

available and capable of degrading site contaminants. These studies are generally reserved for unique sites where the first two lines of evidence cannot be demonstrated and for sites with non-petroleum or more toxic compounds that may be difficult to degrade.

2.5 Developing a Site Closure Approach

Two primary site closure approaches are discussed in this section: a risk management strategy based on land use controls and plume stability, and a strategy which relies on cleaning up a site to numerical risk-based goals. Although other approaches are available, they are generally variations of these two primary approaches.

The first risk management strategy uses a combination of demonstrated natural attenuation and land use control to ensure that no current or future exposure pathway is complete. These sites are placed in a long-term monitoring status or can be closed without long-term monitoring requirements if land use controls remain in place. This closure strategy is recommended for sites with well-defined limits of contamination and stable or receding plumes. For hydrocarbon sites this is the most common approach, in the U.S. as many as 80 to 90 percent of hydrocarbon sites are now closed with natural attenuation alone, sometimes, but not always, with long-term monitoring.

The second closure approach relies on more traditional risk assessment techniques to determine appropriate cleanup goals that are based on conservative exposure scenarios for the site (generally an industrial scenario). This approach focuses on specific contaminants of concern, such as benzene, and then uses a combination of monitored natural attenuation and source reduction to decrease contaminant concentrations to acceptable exposure concentrations which become the risk-based cleanup goal. Once the goal is achieved, industrial workers could theoretically be exposed to contaminated soil or groundwater without a significant health risk. This approach is described in the American Society for Testing and Materials (ASTM) Risk-Based Corrective Action (RBCA) Standard E1739-95 (ASTM 1994) that has been adapted by most states in the U.S. This site closure method is appropriate for larger sites where future exposures cannot be prevented with simple land use controls. Figure 4 illustrates several key decision points for achieving risk-based site closures using these two approaches.

3.0 MANAGING RISK THROUGH PATHWAY ELIMINATION

The underlying principle of this approach is that risk can be minimized through the use of land use controls if the contamination is stable and the long-term monitoring requirement is not excessive. Eliminating the pathway between the contamination and the receptor is one approach for eliminating risk. A combination of

land/groundwater use control, source reduction, and natural attenuation can provide both a short-term and long-term pathway elimination.

3.1 Completing a Pathway Analysis

A pathway analysis can begin once the full extent of soil and groundwater contamination has been defined and a CSM has been developed. Beginning with the soil, soil gas, and groundwater contamination, trace the potential pathways that could exist to site workers, nearby residents, and ecological receptors. For each potential pathway available site data is used to determine if exposure to the contaminant is occurring and under what circumstances future exposure could reasonably occur. Particular attention is given to the soil gas pathway and any potential groundwater discharge to surface waters. Confined spaces such as utility vaults and buildings can accumulate fuel vapors. The air in these confined spaces should be analyzed for volatile organics, particularly benzene, to insure that this pathway is fully defined. The most common pathways to ecological receptors is through groundwater discharging to a nearby surface water or to a drainage ditch. Surface waters located downgradient of the site should be sampled to determine if the pathway is complete. Two or three surface water samples are generally required: a sample that is upstream of the potential discharge point, a sample in the middle of the discharge pathway, and a sample downstream of the discharge area.

3.2 Establishing Institutional Controls

Pathway elimination is often feasible depending on the degree of control possible. For example, if possible restriction on future excavation would prevent human contact with contaminated soil with proper safety precautions. A restriction on well drilling and deep excavation could prevent human contact with contaminated groundwater. The use and future use of land and/or groundwater controls can be complicated by ownership and local issues. Long-term land use control can often be insured by recorded deed restrictions or similar legal means. Even with deed restrictions in place, local government must have the authority to enforce these deed restrictions. The process of establishing institutional controls is quite site-specific and often driven by local issues.

3.3 Source Reduction

At some point a level of source remediation may be required. For example, in the U.S. for regulatory reasons some attempt at product recovery is often "mandatory" before site closure can be granted. Even under optimum site conditions, a 30 percent recovery of the free product is difficult to achieve (Freeze and McWhorter, 1997). In fact, most product recovery efforts will yield little reduction in groundwater contamination and natural dissolution, smearing, and product dispersion are more effective in reducing dissolved BTEX levels. Sites where the actual free product migration is creating a problem, such as a site where there is an oily discharge to a

surface water, may require some free product recovery to eliminate this pathway. In such a case the remedial objective should be to stop the discharge, not to fully remediate the free product.

Other more cost-effective methods of source reduction such as limited excavation, bioventing, and soil vapor extraction will be more effective at reducing BTEX residuals in soils and the capillary fringe. Potential benefits of source reduction include a rapid reduction in soil and soil gas risk, and a reduction in the leaching of BTEX compounds to groundwater shortening long-term monitoring requirements. Based on results from the bioventing initiative reported in Hinchee and Leeson (1995) a 95 percent BTEX reduction can be expected at most sites after one year of bioventing.

3.4 Natural Attenuation for Plume Containment

A second and equally important element of the risk management approach to site closure is providing evidence to demonstrate that any groundwater plume emanating from a hydrocarbon release is stable or receding with no danger of migrating off-site or towards a receptor. In the U.S. local regulations vary, for example, Texas typically requires a series of 4 to 8 groundwater monitoring events to demonstrate plume stability. While other states, such as California, may not require any monitoring for sites where no immediate threat to a receptor is present. Often plume stability can be proven by using historical sampling data and plume maps to demonstrate that concentrations are decreasing over time and that the plume is not migrating. The BIOSCREEN model (Newell et al., 1996) is a useful tool for demonstrating the potential for plume stability when adequate historical data is not available.

Long-Term Monitoring - In the U.S. regulatory agencies may require some level of groundwater monitoring to confirm that groundwater contaminants are decreasing in concentration and are not migrating from the site. The number of monitoring wells required will vary with site size and complexity. Figure 5 illustrates a simple long-term monitoring network. One upgradient well, one source area well, and one well at the leading edge of the plume are required at a small site where the groundwater direction is known. More wells may be needed if the plume direction is not well defined or exhibits seasonal shifts. In the U.S. some states will require one or more "point-of-action" well downgradient of the existing plume. Unexpected migration of contaminants to these wells can trigger the need for additional action. If this is the case, point-of-action wells should be located downgradient of the plume's leading edge.

Monitoring Frequency and Duration - If long term monitoring is required, both the frequency of sampling and the number of years of sampling should be determined on a site-specific basis. Annual monitoring is recommended for stable

plumes and plumes with limited migration potential (low permeability/flat gradients). Monitoring should be conducted during the same month each year to minimize seasonal effects. Quarterly monitoring is usually not required unless significant seasonal changes are known to occur in the groundwater velocity or direction. Three to five years of annual monitoring should generally be sufficient to illustrate decreasing plume concentrations and plume stability.

4.0 REMEDIATION TO RISK-BASED CLEANUP GOALS

At many sites remediation will be required to achieve some numerical cleanup goals before final site closure can be granted. As illustrated in Figure 4, there are several specific circumstances where risk-based cleanup goals may be needed to move the site closure process forward:

- Sites for which local regulations require cleanup to specific numerical criteria;
- Sites with completed exposure pathways which require more immediate reductions in soil or groundwater contamination; or
- Sites where future land/groundwater use controls and excavation restrictions cannot be guaranteed

In each of these situations, the establishment and application of risk-based cleanup goals to the site remediation process may result in a more reasonable closure agreement and limited long-term monitoring requirements. This section describes the key steps in selecting and establishing risk-based cleanup goals.

4.1 Fundamentals of Risk-Based Corrective Actions (RBCA)

The RBCA process involves a tiered approach in which assessment and resultant remediation activities can be tailored to site-specific conditions and risks (ASTM, 1994). Increasingly complex levels of data collection and risk evaluation may be performed to establish the type and magnitude of remediation required to reduce or eliminate unacceptable risks at a particular site. The tiered approach provides the flexibility to replace potentially overly conservative, generic exposure assumptions with site-specific information, while still providing the same level of human health and environmental resource protection. Three basic tiers of site evaluation (e.g., data analysis) have been established in the RBCA process:

- Tier 1 or screening-level evaluations;
- Tier 2 or site-specific evaluations; and
- Tier 3 or advanced site-specific evaluations.

4.1.1 Using Tier 1 Generic Screening Levels

Tier 1 risk-based screening levels (RBSLs) are conservative (health protective), generic cleanup criteria that define the amount of a contaminant that can remain on-

site and not present an unacceptable risk to potential receptors. In the U.S. many states have developed land-use-based RBSLs derived using reasonable maximum exposure (RME) assumptions for industrial site workers. Industrial RBSLs represent the concentrations at which there should be no unacceptable threat to industrial site workers including excavation workers. Because industrial RBSLs are often based on 25 years of adult exposure to contaminated soil and groundwater, they are less stringent than residential RBSLs which assume child and adult exposure over a 30-year timeframe. For example, the state of South Carolina has established an industrial RBSL for direct contact with benzene in soil of 200 mg/kg, significantly greater than the 22 mg/kg standard for residential land use.

Because industrial RBSLs represent worst case exposure scenarios, in the U.S. many states have streamlined the approval process for sites which have contaminant concentrations below these standards. Preparation of closure documents based on generic RBSLs are easy to prepare and do not require specialized risk assessment skills.

On many sites, maximum contaminant concentrations are less or very near to industrial RBSLs. Site closure agreements for these sites normally require some guarantee that land use will remain industrial and that soil or groundwater will be monitored until RBSLs are achieved through natural attenuation or engineered source reduction. Sites where contaminant concentrations significantly exceed RBSLs and the cost or timeframe to attain RBSLs is excessive, the development of site-specific cleanup goals may be beneficial.

4.1.2 Developing Tier 2 Site-Specific Cleanup Goals

Site-specific cleanup goals can be developed when generic RBSLs are unreasonably conservative and will result in a requirement for expensive engineered remediation or extended long-term monitoring. Site-specific cleanup goals will differ from RBSLs in several ways:

- These goals incorporate site-specific data rather than generic assumptions about land and groundwater use restrictions;
- They are based on more reasonable exposure routes given the likelihood that reliable and enforceable exposure controls will limit/prevent certain types of receptor exposures to contaminated media;
- They account for the positive impacts of natural chemical attenuation processes on interrupting potential exposure pathways and/or minimizing exposure-point concentrations; and
- They may sometimes be based on higher target risk levels than RBSLs, once the decreased probability of actual exposure is documented.

Some U.S. states have specified the types of modifications, equations, and/or predictive models that can be used to develop site-specific cleanup goals (Kosteki, 1997). On most hydrocarbon contaminated sites the most likely exposure scenario involves short-term excavation with human contact with contaminated soil, soil gas, and groundwater. This limited exposure (90 days or less) will result in cleanup criteria that are often an order of magnitude higher than RBSLs.

Before proceeding to Tier 2, it is wise to evaluate the additional cost of developing and negotiating these site-specific goals versus the cost of compliance with generic RBSLs. For example, if the site is small and RBSLs can be achieved by removing and treating contaminated soil, it may be more cost effective to actively remediate rather than fund the development of site-specific cleanup goals. Sites where less than 100 cubic meters of soil are contaminated at levels above RBSLs can generally be remediated more cost-effectively using excavation and off-site treatment rather than pursuing site-specific cleanup goals.

Development of site-specific cleanup goals can create significant savings on large sites such as fuel storage and transfer facilities with thousands of cubic yards of contaminated soil and large undefined groundwater plumes. The timeframe required to achieve site-specific cleanup goals will be significantly less and result in lower long-term monitoring costs.

4.2 Cleanup Goals Based on Natural Attenuation

If existing contaminant concentrations exceed risk-based cleanup goals, the impact of natural chemical attenuation processes should be fully documented and factored into the evaluation. In addition to proving that the plume is stable, the rate of biodegradation must be estimated to determine an approximate timeframe for long-term monitoring. Because the potential for exposure is greater if more contamination is left in place, more advanced models may be required to predict the effect of natural chemical attenuation processes on exposure pathway completion and exposure-point concentrations over time. Predictions about chemical fate over time and health-protective cleanup goals must be based on verifiable field evidence of natural chemical attenuation. The timeframe for achieving risk-based cleanup goals (levels of risk reduction) can be estimated and factored into long-term land use decisions. If the timeframe and cost of long-term monitoring is excessive, source reduction options should be considered.

4.3 Cleanup Goals Based on Source Reduction

There are several situations when source reduction should be used to more rapidly or efficiently attain risk-based cleanup goals:

- There is an immediate risk to site workers due to explosive fuel vapors or vapors which are migrating into an occupied work space;

- There is a high probability that soil excavation will take place in soils which exceed risk-based cleanup goals;
- The groundwater plume is expanding and moving toward an important water resource (drinking water well or surface water); or
- The timeframe for natural attenuation alone to decrease soil and groundwater contamination below risk-based cleanup goals is excessive.

In each of these situations, protection of human health should be the primary concern with cost the secondary concern.

4.3.1 Identifying the Remediation Target

It is important to identify where the greatest mass of contamination contributing to risk is located in the subsurface. For example, in many hydrocarbon releases the benzene in groundwater may represent the chemical and receptor exposure pathway of greatest concern. Due to the relatively low solubility of benzene in water the mass of dissolved benzene typically is quite small. It is not uncommon to find that less than 1 percent of the mass of benzene at a site is dissolved in groundwater. In contrast, over 95 percent of the benzene mass is often retained in free product or fuel residuals trapped in soils near the source of the spill. *The most cost effective source reduction technology will be the one that can remove the greatest mass of contaminant risk at the lowest overall cost.*

Hydrocarbon contamination may be present in several forms:

Continuous free phase - Free product or recoverable (mobile) LNAPL. This is the free-phase product present in sufficiently high concentrations to form continuous streams and will flow into a monitoring well. This form normally represents less than 10 percent of the LNAPL mass present at most sites, and rarely exceeds 30 percent.

Residual Oil - In soils, the LNAPL often exists at concentrations that are less than a mobile concentration. This hydrocarbon LNAPL is present as small oil droplets trapped between soil particles. This is the form that represents the majority of the contaminant mass at most sites.

Sorbed - This is contamination reversibly bound to the surface of soil particles and may represent a more significant mass at many sites than dissolved contaminant, but usually less than trapped oil droplets.

Soil gas - The fraction of contamination in this phase depends upon vapor pressure of the fuel and site-specific conditions. A highly volatile fuel such as gasoline may generate 1 or 2 percent of the total hydrocarbon mass in the soil gas.

Dissolved - This fraction of the fuel generally represents less than 1 percent of the total mass.

While groundwater and soil gas are the media through which contaminants most readily migrate, the source of risk is generally concentrated in the soil or free product. It is also important to determine the position of the contaminant mass relative to the water table. Contamination can be found in the vadose zone and/or the saturated zone depending on the depth at which the fuel release occurred. Generally, a major fraction of the LNAPL contaminant mass is above the seasonally low water table. At most sites the only mechanism for transport downward into the water table is the leaching of dissolved hydrocarbons. Leaching is minimized when soils are covered with concrete or asphalt and in low precipitation regions. Two exceptions occur, when the regional water table has been lower in the past than it currently is, and when fuel leaks from tanks that are installed below the seasonal low groundwater level.

The "smear zone" is defined as the layer between the permanent vadose and saturated zones. This is the zone within which the water table fluctuates seasonally, where capillary forces maintain near-saturated conditions. The thickness of the smear zone is site-specific and is based on soil characteristics and seasonal water table fluctuations. At most sites the water table fluctuates only a few feet. The thickness of the capillary fringe will also depend on site-specific conditions. In a coarse sandy soil, the capillary fringe may be quite thin, a few inches at most; in a clay soil, the capillary fringe may extend several feet above the water table. Before entering the technology selection process it is important to estimate the relative distribution of fuel contaminants among the various media and subsurface zones at the site.

4.3.2 Source Reduction Technology Selection Process

Considerable guidance has been published on the process for identifying and screening remedial technologies (see for example U.S. EPA, 1988, Environmental Services Directory, 1993). Detailed screening of technologies is seldom required for petroleum contaminated sites. A simplified process for selecting the most cost-effective technology for achieving specific risk-reduction or other remedial objectives is usually adequate. In many cases it will be more cost effective to abbreviate the technology evaluation process and simply apply a proven remedy. For example, if a small quantity of surface soils (<100 yd³) is contaminated with diesel fuel, it usually will be more cost-effective to excavate and properly dispose of the soils (landfarm, landfill, or off-site thermal treatment) rather than to go through a formal technology evaluation, selection, and implementation. Throughout the remediation planning process, the following question should be frequently asked: Could the remedial objectives be achieved for less cost by going straight to a preferred remedy rather than by continuing to study the problem? If the source area

is large and the cost of active remediation is high, the selection process outlined in this section should be applied to achieve remedial objectives at the lowest cost.

4.3.3 Appropriate Remedial

Many technologies are widely accepted and have proven to be cost-effective remedies for a variety of source reduction applications. Examples include soil vapor extraction (SVE) for treatment of volatile hydrocarbons (e.g., gasoline) and bioventing for treatment of diesel or jet fuel in the vadose zone, and excavation and off-site treatment for small quantities of contaminated soils. The selection of a preferred remedy requires minimum evaluation of alternatives or pilot testing. If the estimated cost of applying a preferred remedy is lower than the cost of continuing to study a contamination problem, the preferred remedy should be applied.

Table 1 provides a listing of technologies with widespread application for treating the environmental media contaminated by petroleum hydrocarbons.

Table 1
Technologies for Remediation of Petroleum-Contaminated Sites

Treatment Technology	Soils-Vadose	Soils-Smear	Soils-Saturated	Ground-water	Soil Gas
In Situ					
Natural Attenuation	1	1	1	1	1
Bioventing	2	2	6	6	3
Soil Vapor Extraction	3	3	6	6	2
In Situ Heating Methods	3	3	6	6	4
Air Sparging/Bioventing	3	3	4	4,5	4
Biological Enhancements	4	4	4	4	6
In-Well Aeration/Recirculation	8	4	4	4	6
Barrier/Treatment Walls	8	8	6	4	8
Pump and Treat	8	8	7	4, 5	8
Free Product Recovery					
Skimming	8	4	6	6	8
Groundwater Depression	8	4	6	5	8
Vacuum Enhanced Recovery	4	4	6	5	3
Excavation and Ex Situ Treatment/Disposal					
Biopile	3	3	3	6	3
Low-Temperature Thermal Desorption	3	3	3	6	6
Off-site Disposal	3	3	3	6	6

1. Technology of first choice, usually lowest cost and effective; a preferred remedy.
2. Technology of choice if natural attenuation cannot be applied; usually a preferred remedy.
3. Technology that may be selected if 1 or 2 cannot be applied; may be a preferred remedy.

4. Technology that will provide some treatment, effectiveness uncertain; not a preferred remedy.
5. Technology that may be effective for containment; not a preferred remedy.
6. Technology may provide limited treatment, but is not designed for this purpose, and the effectiveness is uncertain; not a preferred remedy.
7. No immediate impact is expected, long-term improvement may occur as a result of application; not a preferred remedy.
8. No impact anticipated; not a preferred remedy.

If it is protective of human health and the environment, natural attenuation is the technical approach of choice for all environmental media.

The technologies presented here are routinely applied at fuel-contaminated sites. No effort was made to present the multitude of emerging technologies or those technologies that have produced questionable results. For example, bioaugmentation (the process of adding microorganisms to enhance biodegradation at a site) has been marketed for many years by numerous vendors, but peer-reviewed literature shows little advantage of bioaugmentation over biodegradation by native bacteria. A brief summary of several of the more cost-effective technologies is presented below.

Bioventing is the process of injecting or extracting air from the vadose zone to supply oxygen for aerobic biodegradation of fuel residuals. Bioventing is related to SVE; the significant difference is in the design objectives. SVE is designed to maximize volatilization of contaminants, and bioventing is designed to maximize biodegradation of these chemicals. Bioventing systems usually employ a much lower air-flow rate than SVE systems. Bioventing systems with air-flow rates in the range of 0 to 40 cubic meters per hour are not uncommon. Bioventing usually does not result in a air emissions requiring permitting or treatment. Bioventing has been less successful in desert environments where moisture may be limiting. Bioventing will not work if soil air permeability is too low to allow gas flow. This is rare, and in practice bioventing is usually successful even in low permeability soils. Bioventing can also be used to effectively treat the smear zone, which is particularly important if the fuel mass is concentrated in this zone. To the extent that the water table fluctuates, the deeper portion of the smear zone will be aerated during the seasonal low water table. Bioventing will also aerate the vadose zone immediately above the smear zone, allowing some limited treatment by diffusion. Air injection bioventing may depress the water table somewhat, resulting in additional smear zone treatment. Bioventing probably has minimum effect on groundwater contaminants. Any reports of bioventing contributing to decreased groundwater contaminant concentrations are probably attributable to source removal rather than to oxygen transfer into the saturated zone.

Soil Vapor Extraction (SVE) is the process of extracting soil gas from the vadose zone to enhance the volatilization of contaminants and remove the vapor-phase

contaminants for atmospheric discharge or aboveground treatment. SVE is a proven and widely applied technology for treatment of volatile contaminants such as gasoline and chlorinated solvents in the vadose zone. SVE air flow rates tend to be higher than those for bioventing, often as much as 10 to 20 times greater. SVE results in a contaminated air stream that may require an air emissions permit and frequently requires off-gas treatment. SVE has been applied successfully at thousands of fuel- (and solvent-) contaminated sites. In contrast to bioventing, low-permeability soils can be a serious limitation for SVE due to the higher required air flow rates. The impact of SVE on contaminants in the smear zone and saturated zone are similar to those discussed for bioventing, except that when air is extracted the applied vacuum may cause the water table near the extraction wells to rise, resulting in less effective treatment of the smear zone at some sites.

The primary reasons for not using SVE are cost and feasibility. If air injection can be safely performed, bioventing is almost always less expensive than SVE. SVE is not feasible for removing heavier hydrocarbons and for treatment of fuels in some tight soils.

Free Product Recovery in planning free product recovery, remember that the fraction of recoverable hydrocarbon contamination at most sites is small (i.e., rarely more than 30 percent of the total NAPL and usually much less). For example, if the initial TPH concentration in the smear zone is 60,000 milligrams per kilogram (mg/kg), then after a very successful free product recovery program, the concentration could still be over 40,000 mg/kg. Although frequently required in the U.S. without regard to risk considerations, free product recovery is usually only necessary for risk reduction where the migration of the product itself will result in a risk. Because of the difficulty in predicting performance, only after careful pilot testing should any product recovery technology requiring expensive aboveground treatment be recommended for full-scale installation. There are a number of technologies in use for free product recovery that can be grouped into three categories:

- **Passive skimming**, where only product, and minimal groundwater or soil gas is extracted and no gradient is induced;
- **Groundwater depression**, where both product and groundwater are pumped, a cone of depression is produced resulting in a gravity gradient driving product flow; and
- **Vacuum enhanced recovery** (aka bioslurping and dual phase extraction), where product, groundwater, and soil gas are extracted, and a vacuum is induced to drive product flow.

Passive recovery impacts only the continuous free phase in the smear zone. Groundwater depression relies on gravity flow and requires a pump-and-treat system

to create the gravity flow that recovers mobile LNAPL from the smear zone. Vacuum enhanced recovery has a similar impact below the water table as groundwater depression, but also extracts soil gas from the vadose zone, resulting in some biodegradation (hence the term "bioslurping") and some volatilization. The dual-phase extraction system also may induce additional flow of LNAPL from the capillary fringe that neither skimming nor groundwater depression will effect. The drawback of groundwater depression and dual-phase systems is the high cost of treating extracted groundwater and soil vapor. Determination of recoverable product at any given site is more of an art than a science. The past standard practice of estimating product thickness in wells and trying to extrapolate a recoverable product volume has resulted in large investments in free product recovery systems that have failed to recover even 1 percent of the estimated product. The best approach is to conduct a series of simple baildown tests, limited pump down tests, and vacuum enhanced recovery tests to determine the likelihood of successful free product removal.

Excavation and Treatment or Disposal, soils can be excavated and treated on-site or treated and disposed of off-site. Excavation is normally the preferred remedy for small volumes of easily accessible, contaminated soil. The feasibility of excavation is a function of depth, soil structure, and surface structures at the site. Off-site disposal is frequently an option, but depends on the availability of facilities willing to accept fuel-contaminated soil. In some localities it is possible to dispose of hydrocarbon-contaminated soil at no cost where a landfill is short of daily cover and needs the soil. In other areas, fuel-contaminated soils can be disposed of as nonhazardous waste in a landfill for \$10 to \$100 per cubic meter. If the soil must be disposed of at a hazardous waste landfill, transport and disposal fees will be much higher. Other off-site options include regional treatment facilities that may treat the soil thermally or biologically. In some locations it may be possible to use a predominantly sandy soil as feed material in an asphalt plant.

Low-temperature thermal desorption heats soils (and the fuel contaminants) to a temperature below ignition and above the vapor pressure. This desorbs the contamination from the soil and into the vapor phase. The hydrocarbons in the air stream are then incinerated at a high temperature. Low-temperature thermal desorbers are available in mobile or may operate at fixed facilities near some sites. Mobile units that have relatively high mobilization costs and are only cost effective for sites with larger quantities of soil (usually more than 1,000 cubic meters). On-site treatment costs of \$30 to \$60 per cubic meter are common for this technology. At some bases the soils from several small sites have been treated during a single mobilization, making the process more cost effective.

Landfarming is the spreading and mixing of contaminated soils at an aboveground facility to stimulate biodegradation; frequently volatilization is also an important

treatment mechanism. It is an effective technology for treating a variety of petroleum hydrocarbons, and is in widespread use. The cost of landfarming is reduced as the soil volume increases, but generally falls in the \$20 to \$50 per cubic meter range. Drawbacks to this technology include the relatively large land area requirements, and in some climates, the seasonal nature of operations due to precipitation or cold temperatures.

Biopiles are piles of soil into which oxygen is introduced through ventilation pipes. Moisture and nutrients may or may not be added, and temperature may or may not be controlled. Piles may be covered with plastic when leachate formation is a concern. Costs tend to be higher than for landfarming, but less land is required, the process can be better controlled, and year-round operation is possible. The Navy has constructed centralized biopiles at several bases to treat soils from multiple sites.

5.0 SUMMARY AND CONCLUSIONS

Based upon nearly 20 years of significant experience in the evaluation and remediation of hydrocarbon contaminated sites a reasonable Risk-Based Remediation approach has evolved. This risk-based approach couples a determination of real risk to appropriate and achievable remedial action insuring protection of human health and the environment at a reasonable cost. This approach allows the focusing of remediation resources on hydrocarbon contamination which has the greatest risk, while allowing natural attenuation processes to treat contamination which will not present a risk left in place. The process has been developed and applied to many sites in the U.S. and elsewhere and the process continues to evolve. As new technologies arise, the cost and effectiveness of existing technologies change, or as our understanding of the toxicology and environmental behavior improve the process can be expected to improve.

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Figure 1
BASIC RISK EVALUATION MODEL

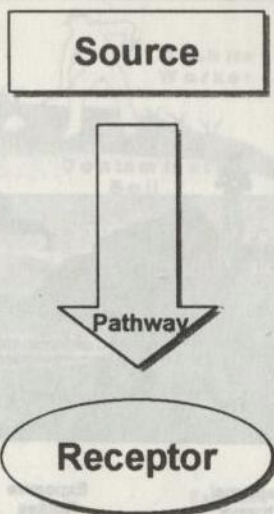
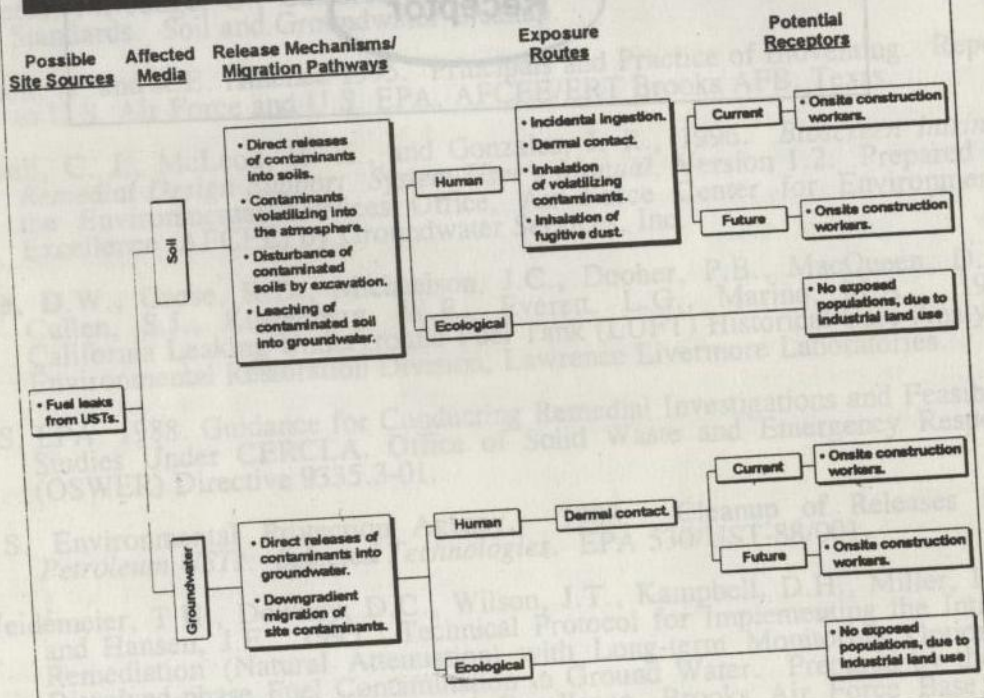
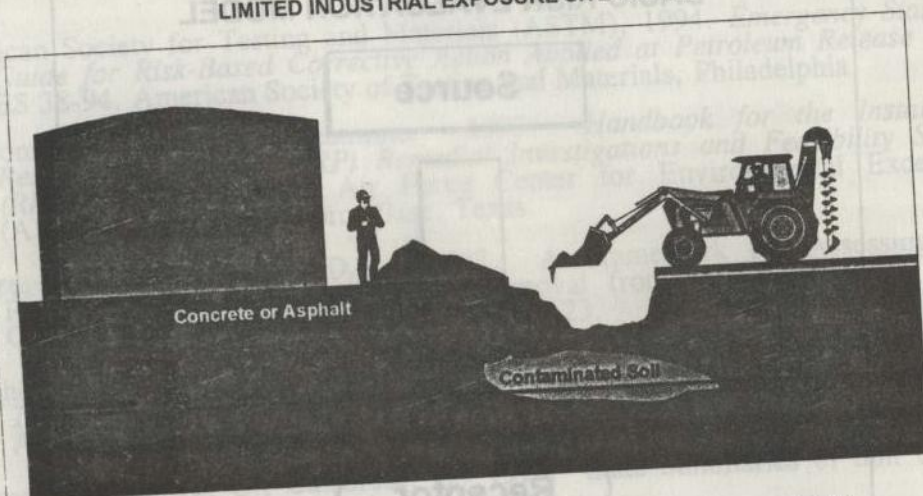
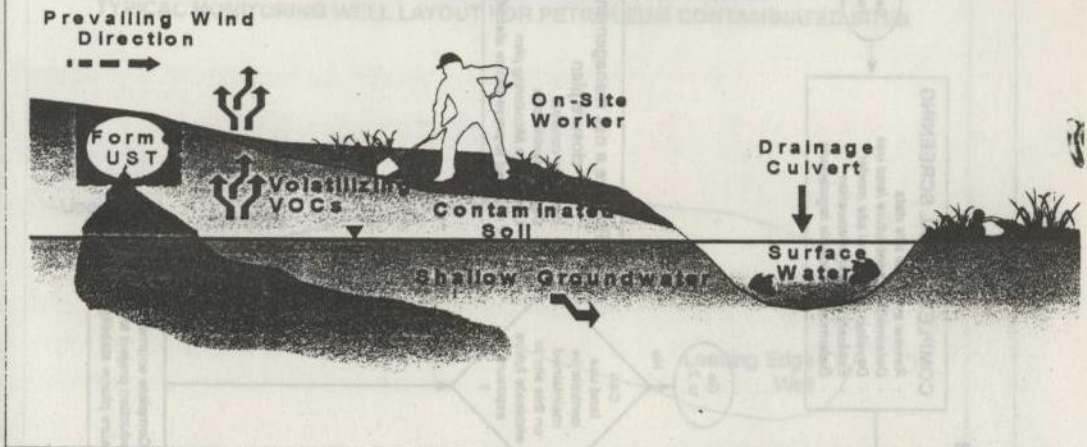


FIGURE 2
LIMITED INDUSTRIAL EXPOSURE SITE MODEL



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FIGURE 3
EXAMPLE CONCEPTUAL SITE MODEL



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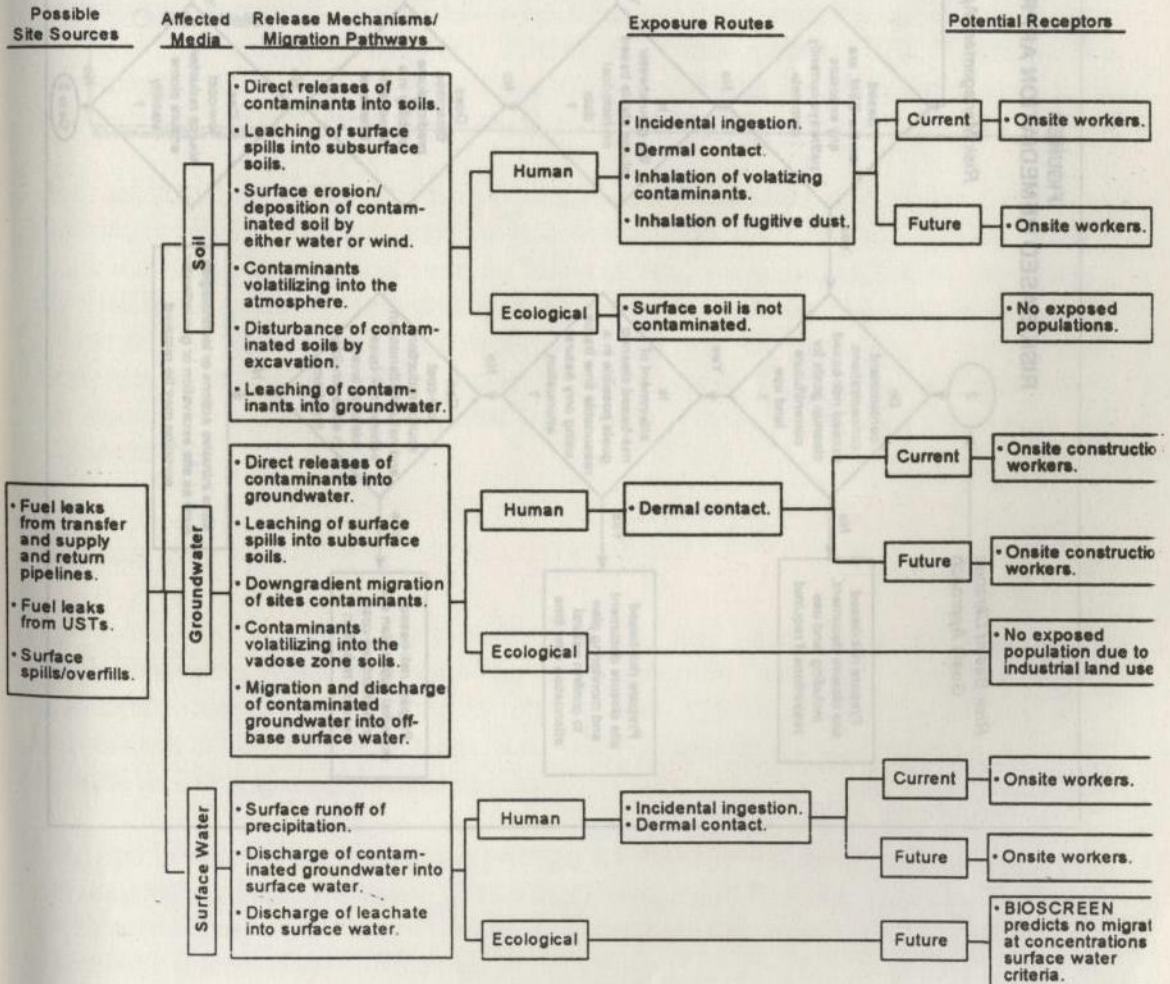


FIGURE 4
RISK-BASED REMEDIATION APPROACH

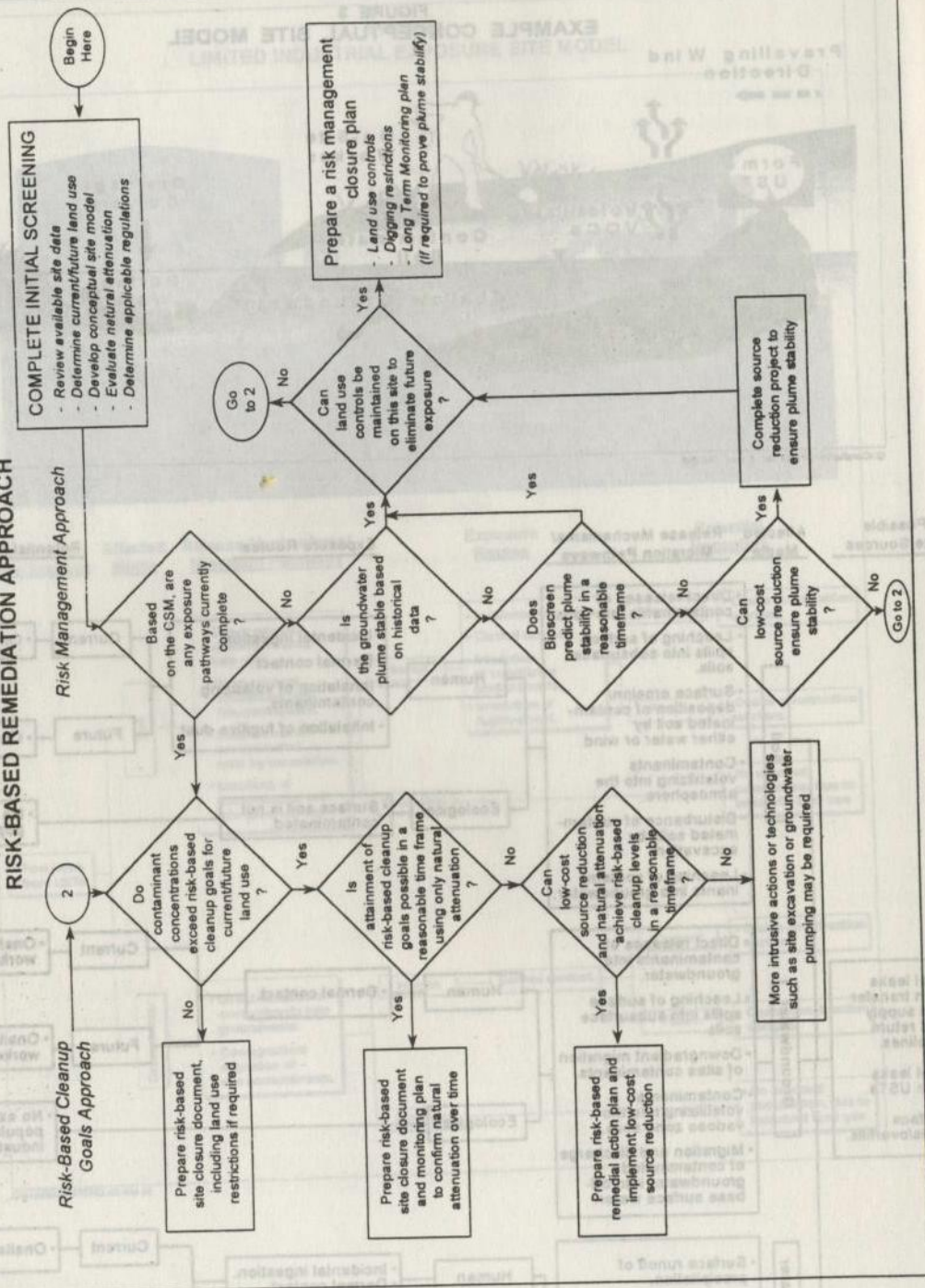
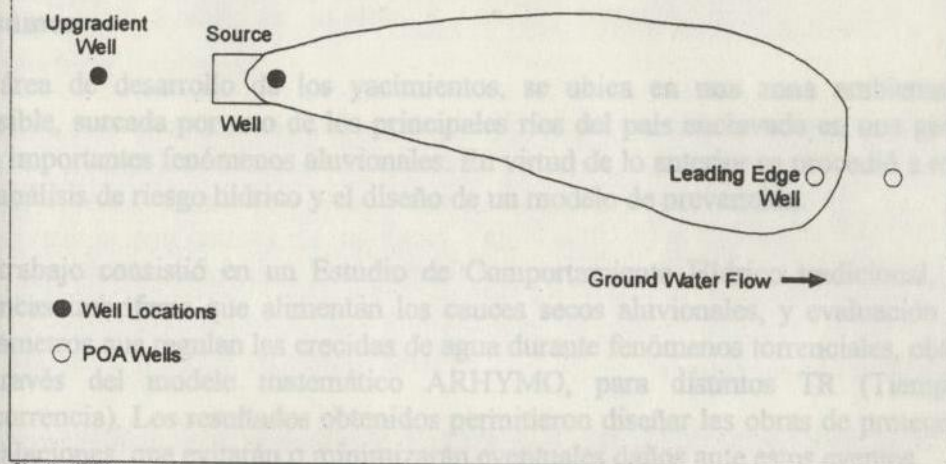


FIGURE 5
TYPICAL MONITORING WELL LAYOUT FOR PETROLEUM CONTAMINATED SITES



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Con los datos obtenidos, se efectuó además una simulación matemática basada en algoritmos usuales, determinando velocidades de avance y tiempos de aviso. En el caso del Río Colorado de un eventual derrame de hidrocarburo, sin participación de los fenómenos aluvionales. A partir de estos antecedentes, se confeccionó un plano de Escurrimiento para un volumen máximo operado en los yacimientos, para poder implementar un plan de medidas preventivas que incluye: válvulas de cierre en ductos y pozos, embalsamientos en cauces, etc., y un sistema de alerta de contingencias.

Introducción

En virtud de la sensibilidad ambiental del área que como se mencionó precedentemente, está enclavada en una geografía compuesta por los fenómenos aluvionales y surcada por el Río Colorado, ARTSA, en el año 1991, encomendó a Geólogos Asociados S.A. (GEA) realizar, en una primera etapa, un Estudio de Contingencias Meteorológicas.

Este tipo de estudio fue orientado a proteger las instalaciones petrolíferas de los fenómenos aluvionales y la implementación de una metodología para la determinación de los tiempos de escurrimiento de crisis (isocronas de Escurrimiento), en condiciones de flujo vinculados a fenómenos aluvionales.

Por último, el objetivo fundamental del trabajo fue proteger a la zona de estudio de los