UNITED STATES AIR FORCE GUIDELINES FOR SUCCESSFULLY SUPPORTING INTRINSIC REMEDIATION WITH AN EXAMPLE FROM HILL AIR FORCE BASE

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ABSTRACT

Based on work performed at numerous hydrocarbon-contaminated sites across the United States, a methodology and protocol for scientifically supporting and documenting intrinsic remediation was developed. Intrinsic remediation is a risk management strategy that uses natural attenuation to control exposure to hazards associated with contaminants in the subsurface. Intrinsic remediation is achieved when naturally occurring degradation mechanisms work to bring about the *in situ* destruction of contaminants. Mechanisms of natural attenuation can be classified as destructive and nondestructive. Destructive processes include biodegradation, abiotic oxidation, and hydrolysis. Biodegradation (both aerobic and anaerobic) is generally the most important natural attenuation mechanism. Nondestructive attenuation mechanisms include sorption, dilution, and volatilization. The first part of this paper presents a brief overview of the technical protocol for data collection and analysis, ground water modeling, and exposure assessment in support of the intrinsic remediation with long-term monitoring remedial option for restoration of fuel-hydrocarbon-contaminated ground water. This protocol is currently under development by the Air Force Center for Environmental Excellence (AFCEE) - Technology Transfer Division (Wiedemeier *et al.*, 1994a) and is being prepared through the joint effort of AFCEE, the Bioremediation Research Team at the United States Environmental Protection Agency (USEPA) Robert S. Kerr Environmental Research Laboratory (RSKRL) in Ada, Oklahoma, and Engineering-Science, Inc. (ES) to facilitate implementation of intrinsic remediation at fuel-hydrocarbon-contaminated sites. Specifically, this protocol is designed to evaluate the fate of dissolved-phase fuel hydrocarbons having regulatory maximum contaminant levels (MCLs). Included is a discussion of recommended site characterization activities and a laboratory analytical protocol. Also discussed are the geochemical parameters indicative of aerobic and anaerobic biodegradation, the numerical fate and transport modeling of intrinsic remediation, and the documentation necessary to successfully support this remedial option. This guidance was developed in cooperation with USEPA researchers but was not issued by the USEPA and does not represent USEPA guidance.

The potential for intrinsic remediation of fuel hydrocarbons was studied using the protocol outlined herein at Hill Air Force Base (AFB), Utah. Petroleum, oil, and lubricant facility operations at this base resulted in the formation of both light nonaqueous-phase liquid (JP-4) and dissolved-phase hydrocarbon plumes. Available data suggest that biodegradation of fuel hydrocarbons at Hill AFB is occurring through a combination of aerobic and anaerobic microbiological processes with aerobic respiration, denitrification, iron reduction, sulfanogenesis, and methanogenesis all being important degradation mechanisms.

OVERVIEW OF THE TECHNICAL PROTOCOL FOR IMPLEMENTING INTRINSIC REMEDIATION

Intrinsic remediation is achieved when naturally occurring attenuation mechanisms, such as biodegradation (aerobic and anaerobic), bring about a reduction in the total mass of a contaminant dissolved in ground water. During intrinsic remediation, contaminants are ultimately transformed to innocuous byproducts (e.g., carbon dioxide and water), not just transferred to another phase or location within the environment. Intrinsic remediation results from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Destructive processes include biodegradation, abiotic oxidation, and hydrolysis. Nondestructive attenuation mechanisms include sorption, dilution (caused by dispersion and infiltration), and volatilization.

In some cases, intrinsic remediation will reduce dissolved-phase contaminant concentrations to below maximum contaminant levels (MCLs) before the contaminant plume reaches potential receptors, even if little or no source removal/reduction takes place. In situations where intrinsic remediation will not reduce contaminant concentrations to below regulatory MCLs in an acceptable timeframe, less stringent cleanup goals may be implemented. This is especially likely if it can be demonstrated that intrinsic remediation will result in a continual reduction in contaminant concentrations over time such that calculated risk values are reduced. Intrinsic remediation is gaining regulatory acceptance and has been implemented at several sites over the past few years (e.g., Downey and Gier, 1991; Wiedemeier *et al.*, 1993; Wiedemeier *et al.*, 1994b). In addition to bringing about complete mineralization of contaminants, intrinsic remediation is nonintrusive and allows continuing use of

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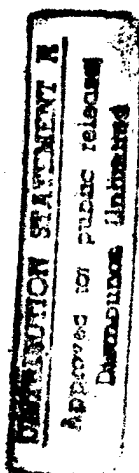
infrastructure during remediation. The main limitation of intrinsic remediation is that it is subject to natural and institutionally induced changes in local hydrogeologic conditions. In addition, aquifer heterogeneity may complicate site characterization as it will with any remedial technology.
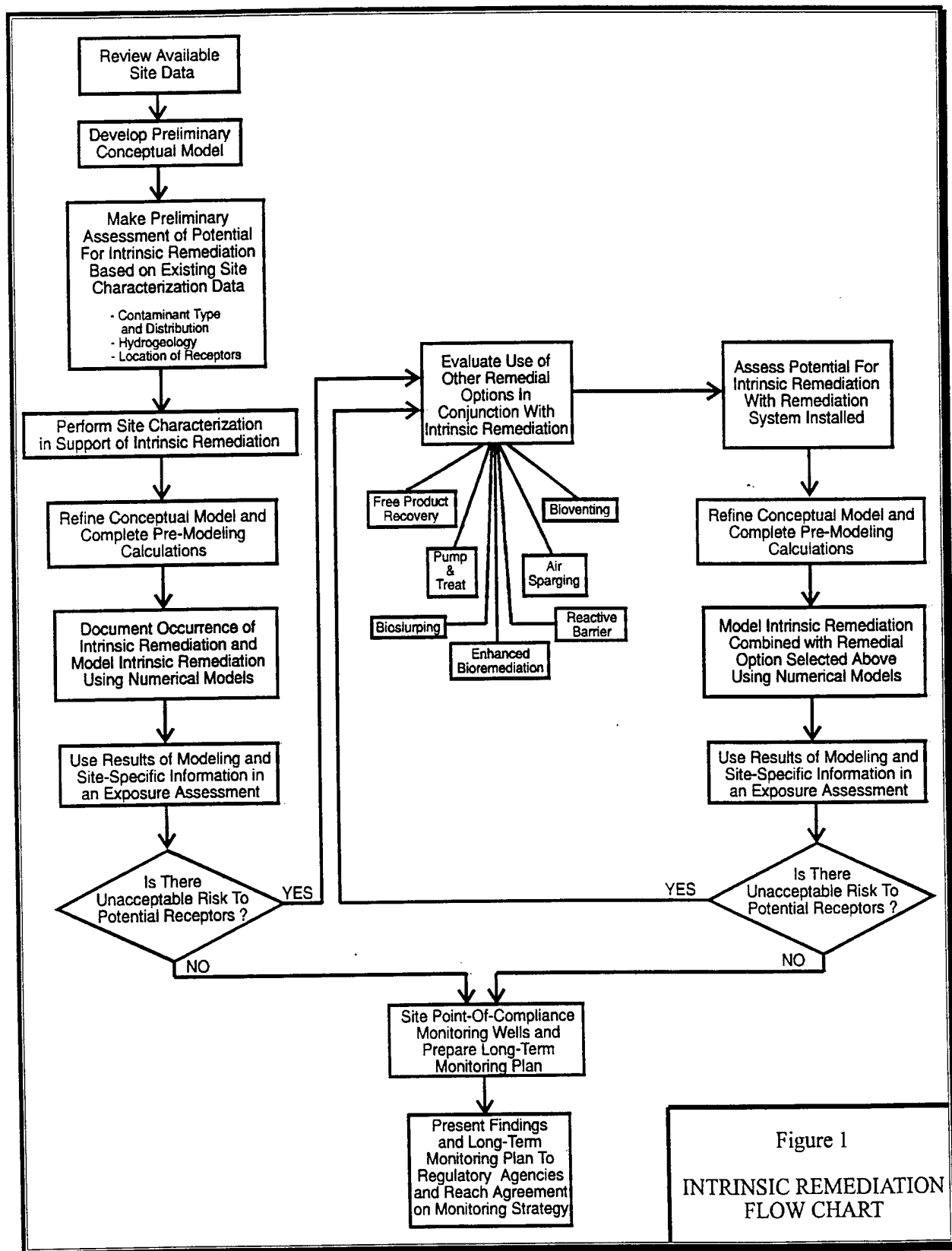
Evaluating the effectiveness of intrinsic remediation requires the quantification of ground water flow and solute transport and transformation processes, including rates of natural attenuation. Quantification of contaminant migration and attenuation rates, and successful implementation of the intrinsic remediation option, require completion of the following steps, each of which is discussed below and outlined in Figure 1:

1) Review existing site data;

2) Develop preliminary conceptual model for the site and assess potential significance of intrinsic remediation;

3) Perform site characterization in support of intrinsic remediation;

4) Refine conceptual model based on site characterization data, complete pre-modeling calculations, and document indicators of intrinsic remediation;

5) Model intrinsic remediation using numerical fate and transport models that allow incorporation of a biodegradation term (e.g., Bioplume II or Bioplume III);

6) Conduct an exposure assessment;

7) Prepare long-term monitoring plan and site long-term monitoring wells and point-of-compliance monitoring wells; and

8) Present findings to regulatory agencies and obtain approval for the intrinsic remediation with long-term monitoring remedial option.

Collection of an adequate database during the iterative site characterization process is an important step in the documentation of intrinsic remediation. At a minimum, the site characterization phase should provide data on the location and extent of contaminant sources; the location, extent, and concentration of dissolved-phase contamination; ground water geochemical data; geologic information on the type and distribution of subsurface materials; and hydrogeologic parameters such as hydraulic conductivity, hydraulic gradients, and potential contaminant migration pathways to human or ecological receptors. Contaminant sources include nonaqueous phase-liquid (NAPL) hydrocarbons present as mobile NAPLs (NAPLs occurring at sufficiently high saturations to drain to a well under the influence of gravity) or residual NAPLs (NAPLs occurring at immobile residual saturations that are unable to drain to a well by gravity).

The following analytical protocol should be used for analysis of soil and ground water samples. This analytical protocol includes all of the parameters necessary to document intrinsic remediation of fuel hydrocarbons, including the effects of sorption and biodegradation (aerobic and anaerobic). Soil samples should be analyzed for total volatile and extractable hydrocarbons, aromatic hydrocarbons, and total organic carbon. Ground water samples should be analyzed for dissolved oxygen (DO), oxidation-reduction potential, pH, temperature, conductivity, alkalinity, nitrate, sulfate, sulfide, ferrous iron, carbon dioxide, methane, chloride, total petroleum hydrocarbons, and aromatic hydrocarbons. The extent and distribution (vertical and horizontal) of contamination and electron acceptor and metabolic byproduct concentrations are of paramount importance in documenting the occurrence of biodegradation of fuel hydrocarbons and in numerical model implementation. Dissolved oxygen concentrations below background levels in an area with fuel hydrocarbon contamination are indicative of aerobic hydrocarbon biodegradation. Similarly, nitrate and sulfate concentrations below background in an area with fuel hydrocarbon contamination are indicative of anaerobic biodegradation through denitrification and sulfanogenesis. Elevated concentrations of metabolic byproducts such as ferrous iron and methane in areas with fuel hydrocarbon contamination are indicative of hydrocarbon biodegradation by the processes of ferric hydroxide reduction and methanogenesis. Contour maps can be used to provide visible evidence of these relationships.

To successfully implement the intrinsic remediation with long-term monitoring remedial option, the property owner must scientifically demonstrate that degradation of site contaminants is occurring at rates sufficient to be protective of human health and the environment.

Figure 1

INTRINSIC REMEDIATION
FLOW CHART

The flow chart contains the following elements:

- Review Available Site Data
- Develop Preliminary Conceptual Model
- Make Preliminary Assessment of Potential For Intrinsic Remediation Based on Existing Site Characterization Data
  - Contaminant Type and Distribution
  - Hydrogeology
  - Location of Receptors
- Perform Site Characterization in Support of Intrinsic Remediation
- Refine Conceptual Model and Complete Pre-Modeling Calculations
- Document Occurrence of Intrinsic Remediation and Model Intrinsic Remediation Using Numerical Models
- Use Results of Modeling and Site-Specific Information in an Exposure Assessment
- Is There Unacceptable Risk To Potential Receptors ?

- Evaluate Use of Other Remedial Options In Conjunction With Intrinsic Remediation
  - Free Product Recovery
  - Bioventing
  - Pump & Treat
  - Air Sparging
  - Bioslurping
  - Reactive Barrier
  - Enhanced Bioremediation

- Assess Potential For Intrinsic Remediation With Remediation System Installed
- Refine Conceptual Model and Complete Pre-Modeling Calculations
- Model Intrinsic Remediation Combined with Remedial Option Selected Above Using Numerical Models
- Use Results of Modeling and Site-Specific Information in an Exposure Assessment
- Is There Unacceptable Risk To Potential Receptors ?

YES / NO

- Site Point-Of-Compliance Monitoring Wells and Prepare Long-Term Monitoring Plan
- Present Findings and Long-Term Monitoring Plan To Regulatory Agencies and Reach Agreement on Monitoring Strategy

Three lines of evidence can be used to support intrinsic remediation including:

1) Documented loss of contaminants at the field scale,

2) The use of chemical analytical data in mass-balance calculations of microbial metabolism, and

3) Laboratory microcosm studies using aquifer samples collected from the site.

The first line of evidence involves using measured dissolved-phase concentrations of biologically recalcitrant tracers found in fuels in conjunction with aquifer hydrogeologic parameters such as seepage velocity and dilution to show that a reduction in the total mass of contaminants is occurring at the site. The second line of evidence involves the use of chemical analytical data in mass balance calculations to show that a decrease in contaminant and electron acceptor concentrations can be directly correlated to increases in metabolic byproduct concentrations. This evidence can be used to show that electron acceptor concentrations are sufficient to degrade dissolved-phase contaminants. Numerical models can be used to aid mass-balance calculations and collate information on degradation. The third line of evidence, the microcosm study, is optional and involves studying site aquifer materials under controlled conditions in the laboratory to show that indigenous biota are capable of degrading site contaminants and to confirm rates of contaminant degradation measured at the field scale. This option is necessary only when there is considerable skepticism concerning the universal biodegradation of fuel hydrocarbons.

The primary objective of the intrinsic remediation investigation is to determine if natural processes of degradation will reduce contaminant concentrations in ground water to below regulatory standards before potential exposure pathways are completed. This requires that a projection of the potential extent and concentration of the contaminant plume in time and space be made based on governing physical, chemical, and biological processes. This projection should be based on historic variations in, and the current extent and concentration of, the contaminant plume as well as the measured rates of contaminant attenuation. The data collected during site characterization can be used to model the fate and transport of contaminants in the subsurface. Such modeling allows an estimate of the future extent and concentration of the dissolved-phase plume to be made. Several models, including Bioplume II (Rifai *et al.*, 1988), have been used successfully to model dissolved-phase contaminant transport and attenuation. Additionally, a new version of the Bioplume model, Bioplume III, is under development by AFCEE. The intrinsic remediation modeling effort has three primary objectives: 1) to estimate the future extent and concentration of a dissolved-phase contaminant plume by modeling the combined effects of advection, dispersion, sorption, and biodegradation; 2) to assess the possible risk to potential downgradient receptors; and 3) to provide technical support for the natural attenuation remedial option at post-modeling regulatory negotiations.

Microorganisms generally utilize DO and nitrate in areas with dissolved-phase fuel-hydrocarbon contamination at rates that are instantaneous relative to the average advective transport velocity (seepage velocity) of ground water. This results in the consumption of these compounds at a rate approximately equal to the rate at which they are replenished by advective flow processes. For this reason, the use of these compounds as electron acceptors in the biodegradation of dissolved-phase fuel-hydrocarbons is a mass-transport-limited process (Borden and Bedient, 1986; Wilson *et al.*, 1985). The use of DO and nitrate in the biodegradation of dissolved-phase fuel-hydrocarbons can be modeled using Bioplume II. Microorganisms generally utilize sulfate, iron III, and carbon dioxide (used during methanogenesis) in areas with dissolved-phase fuel-hydrocarbon contamination at rates that are slow relative to the advective transport velocity of ground water. This results in the consumption of these compounds at a rate slower than the rate at which they are replenished by advective flow processes. Therefore, the use of these compounds as electron acceptors in the biodegradation of dissolved-phase fuel-hydrocarbons is a reaction-limited process that can be approximated by first-order kinetics. The Bioplume II model utilizes a first-order rate constant to model such biodegradation. First-order decay constants can be determined by simple calculations based on ground water chemistry or through the use of laboratory microcosm studies. In addition, the use of radiolabeled materials in a microcosm study can be used to provide evidence of the ultimate fate of the contaminants.

The results of the modeling effort are not in themselves sufficient proof that intrinsic remediation is occurring at a given site. The results of the modeling effort are only as good as the original data input into the model and the model itself. Because of the inherent uncertainty associated with such predictions, it is the responsibility of the proponent to provide sufficient evidence to demonstrate that the mechanisms of intrinsic remediation will reduce contaminant concentrations to acceptable levels before potential receptors are reached. This requires the use of conservative input parameters and numerous sensitivity analyses so that consideration is given to all plausible

contaminant migration scenarios. When possible, both historical data and modeling should be used to provide information that collectively and consistently supports the natural reduction and removal of the dissolved-phase contaminant plume. In some cases, simple calculations of contaminant attenuation rates are all that is required to successfully support intrinsic remediation.

Upon completion of the fate and transport modeling effort, model predictions can be used in an exposure assessment. If intrinsic remediation is sufficiently active to mitigate risks to potential receptors, the proponent of intrinsic remediation has a reasonable basis for negotiating this option with regulators. The exposure assessment allows the proponent to show that potential exposure pathways will not be completed.

The long-term monitoring plan consists of locating ground water monitoring wells and developing a ground water sampling and analysis strategy. This plan is used to monitor plume migration over time and to verify that intrinsic remediation is occurring at rates sufficient to protect potential downgradient receptors. The long-term monitoring plan should be developed based on the results of a numerical model such as Bioplume II.

Point-of-compliance (POC) monitoring wells are wells that are installed at locations downgradient of the contaminant plume and upgradient of potential receptors. POC monitoring wells are generally installed along a downgradient property boundary or at a location approximately 5 years downgradient of the current plume at the seepage velocity of the ground water, or 1 to 2 years upgradient of the nearest downgradient receptor, whichever is more protective. The final number and locations of POC monitoring wells will depend on regulatory considerations. Long-term monitoring wells are wells that are placed upgradient of, within, and immediately downgradient of the contaminant plume. These wells are used to monitor the effectiveness of intrinsic remediation in reducing the total mass of contaminant within the plume. Required are, one well upgradient of the contaminant plume, one well within the anaerobic treatment zone, one well in the aerobic treatment zone, and one well immediately downgradient of the contaminant plume. The final number and locations of long-term monitoring wells will depend on regulatory considerations. Figure 2 shows a hypothetical long-term monitoring scenario. The results of a numerical model such as Bioplume II can be used to help site both the long-term and POC monitoring wells.

Figure 2
HYPOTHETICAL LONG-TERM MONITORING STRATEGY

LEGEND

⊠ Point-of-Compliance Monitoring Well

O Long-Term Monitoring Well

Not To Scale
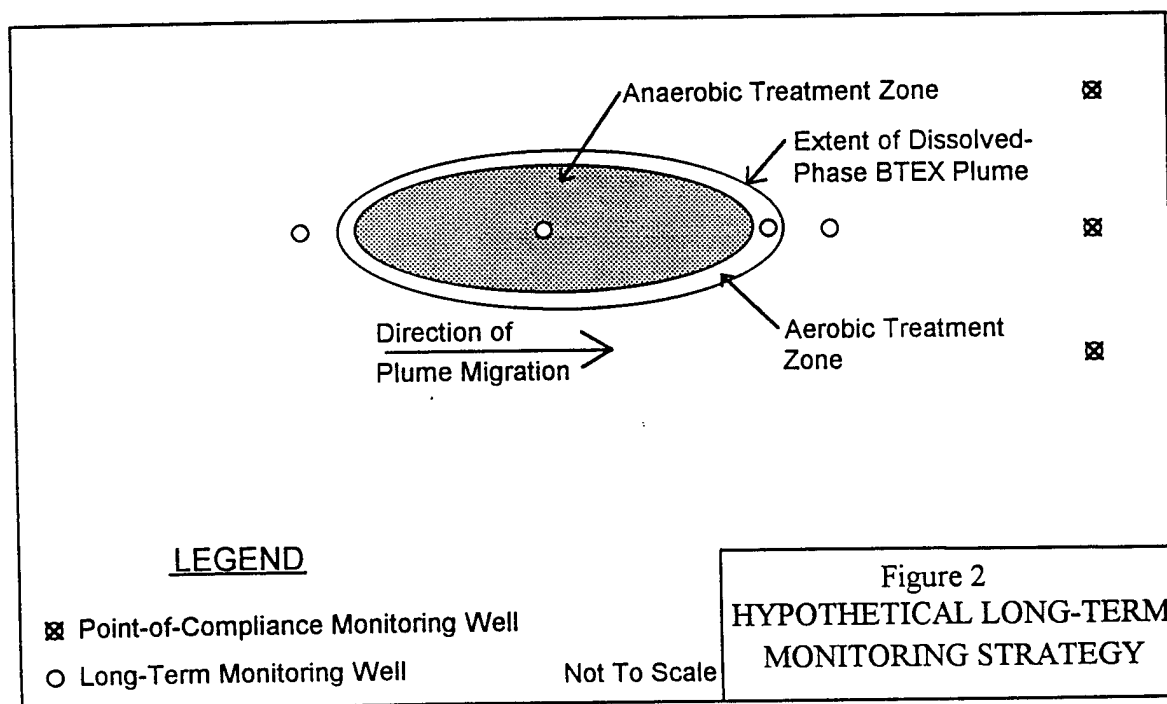
INTRINSIC REMEDIATION DEMONSTRATION AT HILL AFB, UTAH

Facility Background

ES, in conjunction with researchers from the USEPA RSKRL, was retained by AFCEE to implement the technical protocol for intrinsic remediation described herein at Hill AFB, Utah. Petroleum, oil, and lubricant (POL) facility operations at this base resulted in the formation of both light nonaqueous-phase (LNAPL) and dissolved-phase hydrocarbon plumes. Hill AFB is located at 41°07'N latitude, 111°58'W longitude on a bench of the Wasatch Mountains. The POL facility that is the focus of this study is located in the southwestern corner of the base. Figure 3 is a site map showing the POL area and the immediately adjacent area in detail. The POL site comprises the base fuel tank farm and consists of nine aboveground storage tanks (ASTs) used to store JP-4 and diesel fuel. A portion of the Patriot Hills base housing area, located southwest of the AST farm, is also included in

Figure 3

SITE MAP
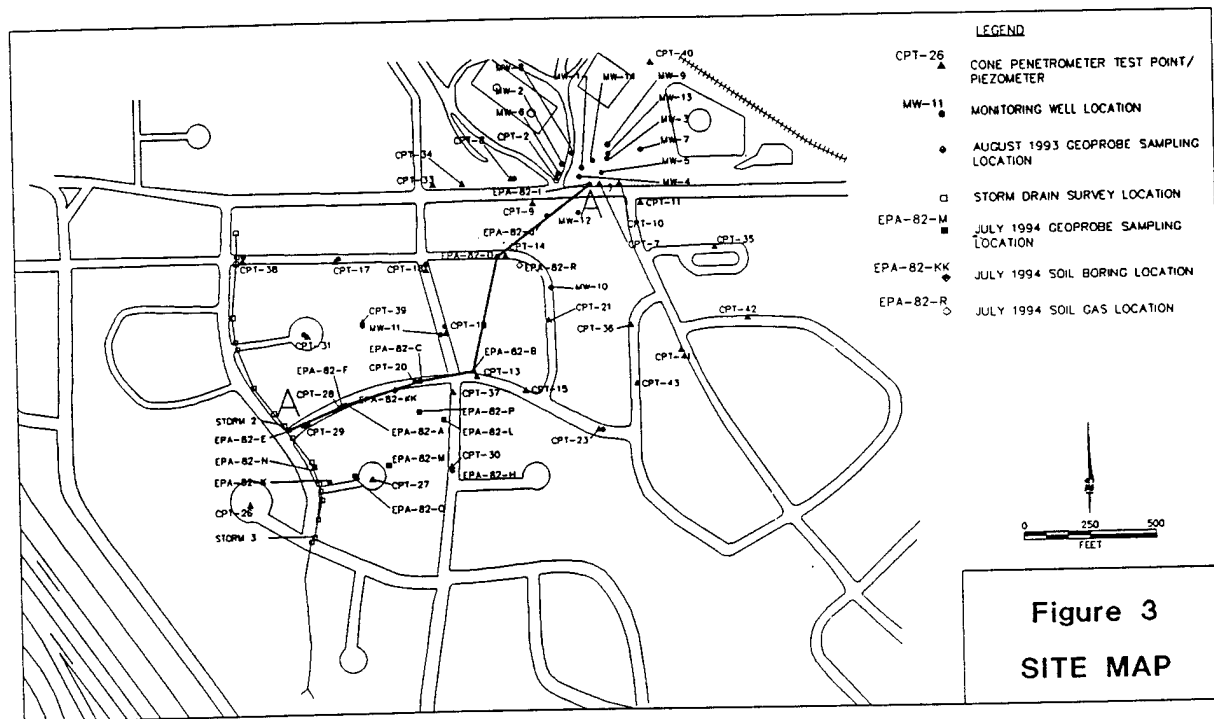
this area. Current remedial activities at the POL site include active and passive LNAPL recovery and bioventing. To date, about 650 gallons of LNAPL has been recovered from the LNAPL recovery systems.

Site Characterization Activities

To meet the requirements of the intrinsic remediation demonstration, several investigative techniques, including soil and ground water sampling and aquifer testing, were utilized. Soil sampling was accomplished during this investigation using modified hollow-stem auger (HSA) drilling in conjunction with continuous solid-barrel sampling. Previous investigations conducted at the site utilized standard HSA drilling and soil sampling as well as cone penetrometer testing (CPT). Ground water samples were collected during this investigation using Geoprobe® sampling apparatus and at newly installed and previously existing monitoring wells. Previous investigations utilized monitoring wells installed in HSA boreholes and monitoring points installed in CPT holes to sample ground water. Aquifer tests conducted at the site included pumping and slug testing.

## Physical Characteristics of the Study Area

This section incorporates data collected during previous investigations and during more recent investigations by ES and researchers from the USEPA RSKRL in August of 1993 and July of 1994, to describe the physical characteristics of the POL site.

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Topography and Surface Water Hydrology

The POL site is located on a plateau-like bench formed by the paleodelta of the ancient Weber River. This delta was formed as the Weber River deposited its sediment load when it entered ancient Lake Bonneville. Surface topography at the site slopes to the southwest. There are no naturally occurring surface water bodies in the immediate vicinity of the POL facility. There are, however, several manmade features at or near the site that influence surface water runoff. Surface cover at the POL facility and adjacent areas consists of asphalt paving, grass, residential housing, and concrete overlays. Precipitation either infiltrates into the ground surface or is collected in gutters along the numerous roads in the area and diverted into several storm water sewers.

Geology

The shallow sediments underlying the POL facility are composed of light reddish-brown to dark gray, cohesive clayey silts to silty clays. This clayey silt to silty clay interval ranges in thickness from approximately 4 to 15 feet and is abruptly underlain by poorly- to moderately-sorted, yellowish- to reddish-brown, silty, fine-grained sands that coarsen downward into moderately sorted medium- to coarse-grained quartzo-feldspathic sands. These sands range in thickness from approximately 3 to 22 feet and comprise the shallow saturated zone at the site. Underlying these sands is a sequence of competent, thinly interbedded clay to silty clay and fine- to very-fine-grained clayey sand and silt of unknown thickness. This sequence of interbedded clay and fine-grained sand and silt appears to act as an effective barrier to the vertical migration of water and contaminants. These stratigraphic relationships are illustrated by hydrogeologic section A-A' (Figure 4). This section is oriented approximately parallel to the direction of ground water flow. Figure 3 shows the location of this section.

Figure 4

HYDROGEOLOGIC SECTION A-A'
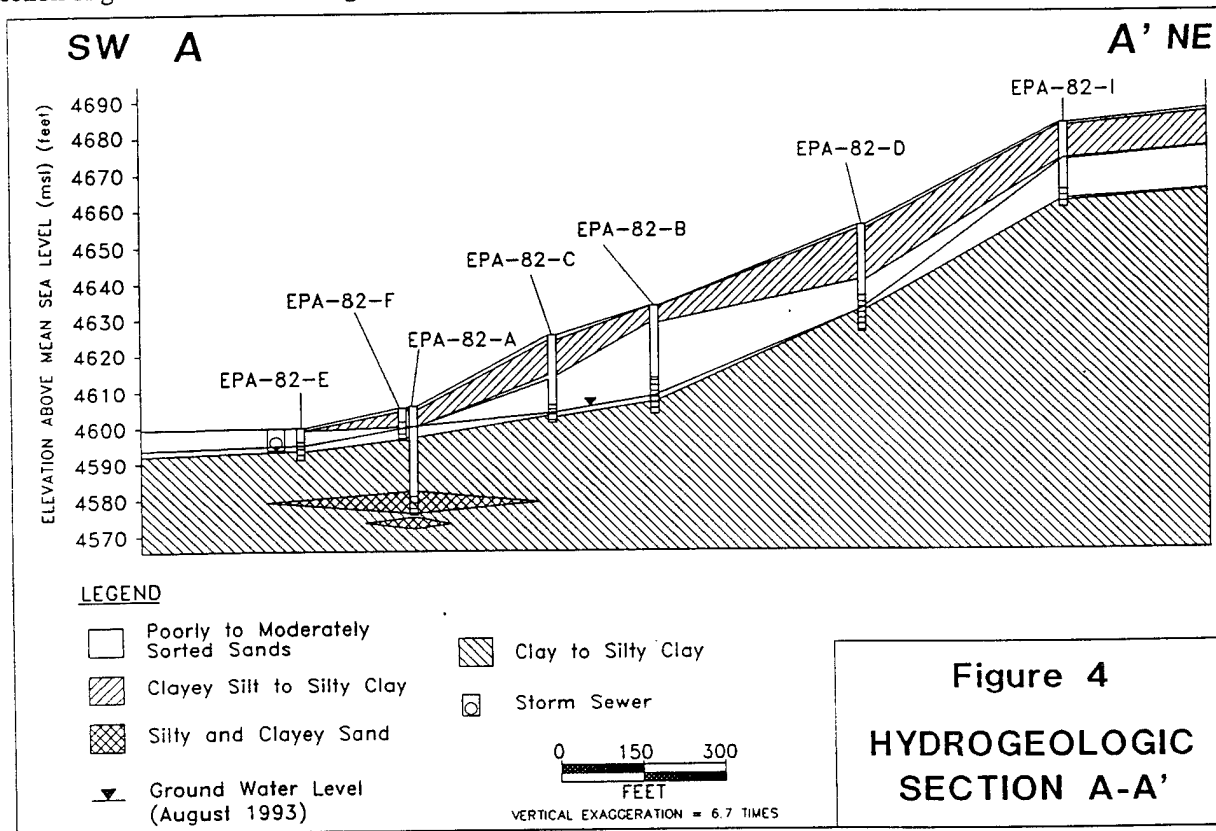
Grain size analyses were performed on soil samples from the deep interbedded clay to silty clay and fine- to very-fine-grained clayey sand and silt described earlier. Seventy to 90 percent of the sediment from both samples passed through the #200 US Standard Sieve. This sieve size represents the break between fine sand and silt.

Ground Water Hydraulics

Ground water flow in the vicinity of the POL site is to the southwest, with an average gradient of approximately 0.048 foot per foot (ft/ft) (Figure 5). Shallow ground water flow occurs under unconfined conditions and appears to be limited to a relatively thin zone in the medium- to coarse-grained sands located immediately above the lower thinly interbedded clay to silty clay and fine- to very-fine-grained clayey sand and silt horizon (Figure 4). Available site data show that there is almost no seasonal variation in ground water flow direction or gradient at the site. Vertical gradients at the site are strongly upward, as is characteristic of the entire Great Salt Lake Basin. However, based on vastly different geochemical data from the shallow saturated zone and the deeper, clayey zone, and the impermeable nature of the lower sediments, it is suspected that ground water upwelling has minimal impact on contaminant migration and attenuation at the site.
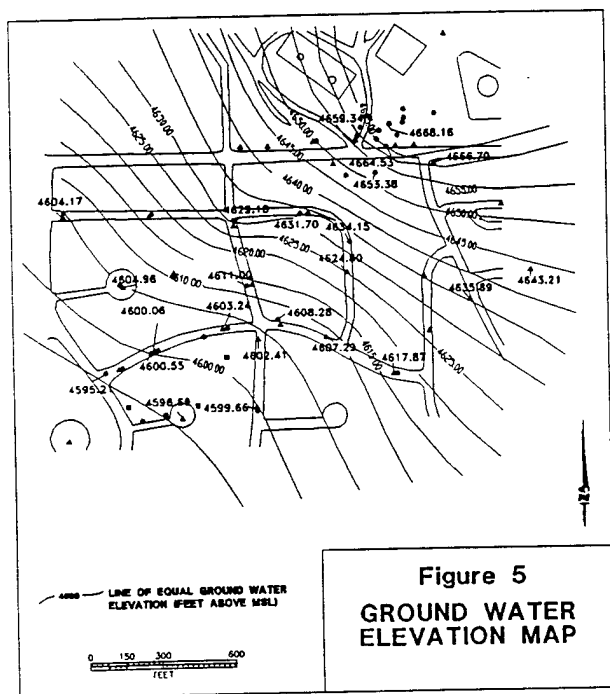
Figure 5

GROUND WATER ELEVATION MAP

Hydraulic conductivity, K, in the medium- to coarse-grained sands of the shallow saturated zone was estimated using slug tests. Slug tests were performed in five monitoring wells completed in this zone. The average hydraulic conductivity for the shallow saturated zone as determined from these tests is 0.0159 foot per minute or 0.0085 centimeter per second (cm/sec).

Because of the difficulty involved in accurately determining effective porosity, accepted literature values for the type of soil comprising the shallow saturated zone were used. Freeze and Cherry (1979) give a range of effective porosity for sand of 0.25 to 0.50. To be conservative (lower effective porosity results in greater ground water velocity), the effective porosity for sediments of the shallow saturated zone was assumed to be 0.25.

The advective velocity of ground water in the direction parallel to ground water flow is given by:

$$\bar{v} = \frac{-K}{n_e}\frac{dH}{dL}$$

Where: $\bar{v}$ = Average advective ground water velocity (seepage velocity) [L/T]
K = Hydraulic conductivity [L/T] (0.0159 ft/min)
dH/dL = Gradient [L/L] (0.048)
n_e = Effective porosity (0.25).

Using this relationship in conjunction with the data presented above, the average advective ground water velocity (seepage velocity) at the site is 4.4 feet per day (ft/day) or approximately 1,600 feet/year.

Soil Chemistry

LNAPL Contamination

Mobile LNAPL is defined as the LNAPL that is free to flow in the aquifer and that will flow from the aquifer matrix into a well under the influence of gravity. Mobile LNAPL is present in several monitoring wells and piezometers at the site. The greatest measured thickness of LNAPL observed at the site was 4 feet at CPT-14 in April and May of 1993. Figure 6 is an isopach map showing the distribution and measured thickness of mobile LNAPL at the site. The LNAPL plume is composed of weathered JP-4 that emanates from the POL facility. With the exception of the isolated LNAPL observed at CPT-37 in April 1994, the mobile LNAPL plume appears to extend approximately 900 feet downgradient from the source area (Figure 6). The areal extent of suspected free product contamination is approximately 270,000 square feet, or 6.2 acres. Concentrations of benzene, toluene, ethylbenzene, and the xylenes (BTEX) and trimethylbenzene (TMB) constituents in the mobile LNAPL were measured using a sample of LNAPL. Concentrations of BTEX and TMBs in this sample indicate that the JP-4
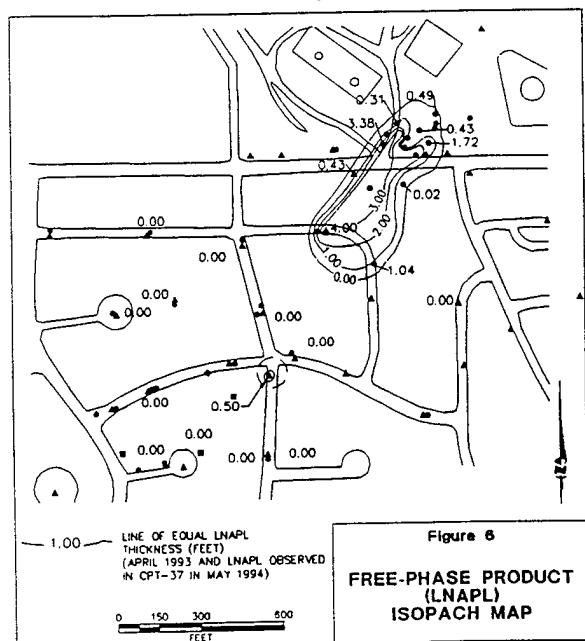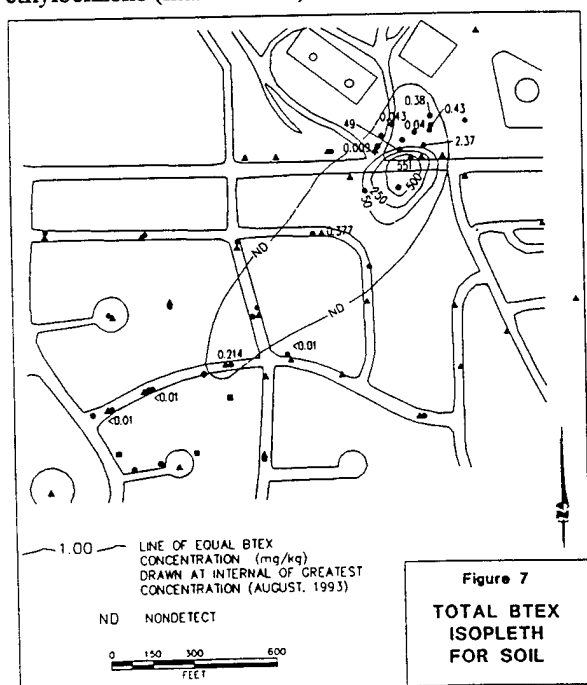
comprising the LNAPL plume is significantly weathered. Toluene and benzene concentrations in the LNAPL are reduced by 1 to 2 orders of magnitude compared to fresh JP-4, respectively, and ethylbenzene and total xylene concentrations are reduced by about one-half.

LINE OF EQUAL LNAPL THICKNESS (FEET) (APRIL 1993 AND LNAPL OBSERVED IN CPT-37 IN MAY 1994)

0   150   300   600
FEET

Figure 6

FREE-PHASE PRODUCT (LNAPL) ISOPACH MAP

Residual-phase LNAPL is defined as the LNAPL that is trapped in the aquifer by the processes of cohesion and capillarity and therefore will not flow within the aquifer and will not flow from the aquifer matrix into a well under the influence of gravity. Residual-phase BTEX contamination resulting from vertically and laterally migrating LNAPL is found over a wide area at the site (Figure 7). Soil BTEX contamination appears to extend approximately 1,600 feet downgradient from the source area and is approximately 500 feet wide at the widest point. The highest observed concentration of residual-phase BTEX was 551.25 milligrams per kilogram (mg/kg) in soil core samples taken in the suspected source area of JP-4 contamination. Compare this with the highest measured TPH concentration of 28,300 mg/kg in the same sample. Measured total BTEX concentrations decrease rapidly in areas devoid of mobile-phase LNAPL contamination and the majority of the area shown in Figure 7 is characterized by total BTEX concentrations of less than 50 mg/kg.

Total Organic Carbon

Total organic carbon (TOC) concentrations are used to estimate the amount of organic matter sorbed on soil particles or trapped in the interstitial passages of a soil matrix. The TOC concentration in the saturated zone is an important parameter used to estimate the amount of contaminant that could potentially be sorbed to the aquifer matrix. Sorption results in retardation of the contaminant plume relative to the average advective ground water velocity. Background TOC in the soil at this site ranges from 0.069 to 0.094 percent. This gives a range of coefficient of retardation (R) values from between 1.3 and 1.4 for benzene (minimum R) and between 2.7 to 3.4 for ethylbenzene (maximum R).
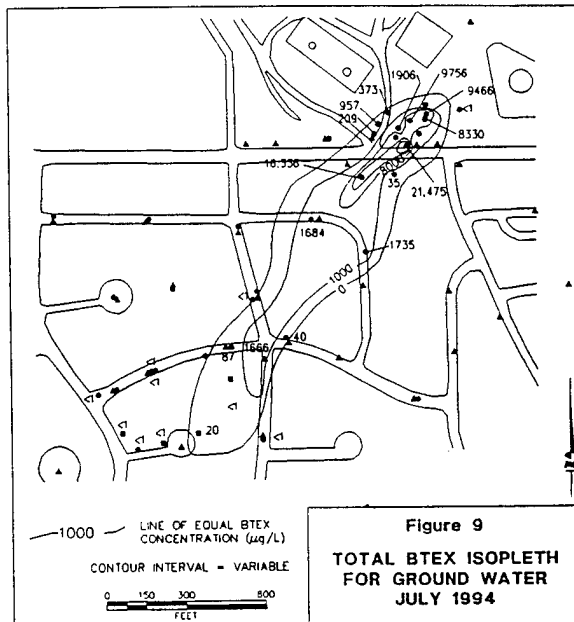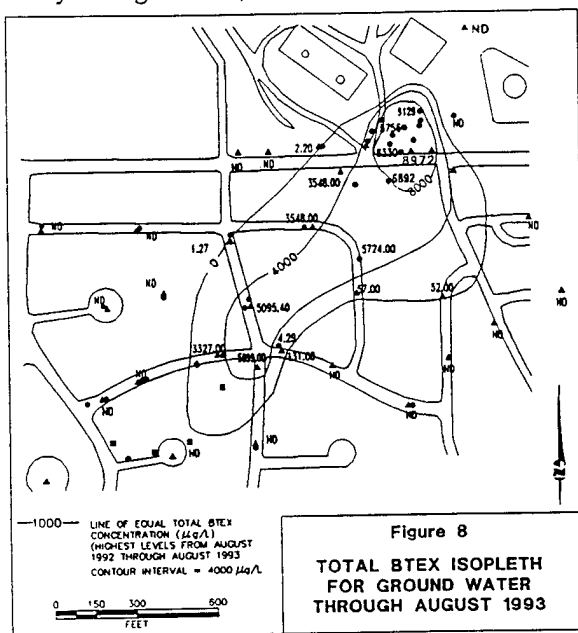

LINE OF EQUAL BTEX CONCENTRATION (mg/kg) DRAWN AT INTERNAL OF GREATEST CONCENTRATION (AUGUST, 1993)

ND   NONDETECT

0   150   300   600
FEET

Figure 7

TOTAL BTEX ISOPLETH FOR SOIL

Ground Water Chemistry

Dissolved-Phase BTEX Contamination

Figure 8 is an isopleth map that shows the distribution of total BTEX dissolved in ground water through August 1993. This figure also includes data collected in monitoring wells in the source area in December 1993/January 1994. BTEX contamination is migrating to the southwest in the direction of ground water flow. During the period through August 1993, the BTEX plume was approximately 1,650 feet long and 750 feet wide at the widest point. Figure 9 is an isopleth map that shows the distribution of total BTEX dissolved in ground water in July 1994. Comparison of Figures 8 and 9 shows that a substantial reduction in the areal extent and concentration of the BTEX plume occurred between August of 1993 and July of 1994. Based on data collected during the July 1994 sampling event, the BTEX plume had been reduced in areal extent and is currently 1,650 feet long and only 420 feet wide at the widest point (330 feet narrower than in August 1993). Figure 8 shows that in August 1993, the

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majority of the dissolved-phase BTEX plume had concentrations in excess of 5,000 micrograms per liter (μg/L) whereas Figure 9 shows that in July 1994, the majority of the dissolved-phase BTEX plume had concentrations below 2,000 μg/L. These reductions in the areal extent and concentration of the total BTEX plume were probably caused by biodegradation, as discussed in the following paragraphs.


Figure 8

TOTAL BTEX ISOPLETH
FOR GROUND WATER
THROUGH AUGUST 1993

Figure 9

TOTAL BTEX ISOPLETH
FOR GROUND WATER
JULY 1994

Dissolved Oxygen

Figure 10 shows the distribution of DO in ground water through August 1993. This figure also shows the dissolved-phase BTEX plume for this same period. Areas with elevated total BTEX concentrations have depleted DO concentrations, and the region in the center of the plume is anaerobic. This is a strong indication that aerobic biodegradation of the BTEX compounds is occurring at the site, and based on the high background DO levels measured at the site (up to 6.3 mg/L), it is likely that DO is an important electron acceptor at this site.

TOTAL BTEX ISOPLETH
FOR GROUND WATER

DISSOLVED OXYGEN
ISOPLETH FOR GROUND WATER

Figure 10
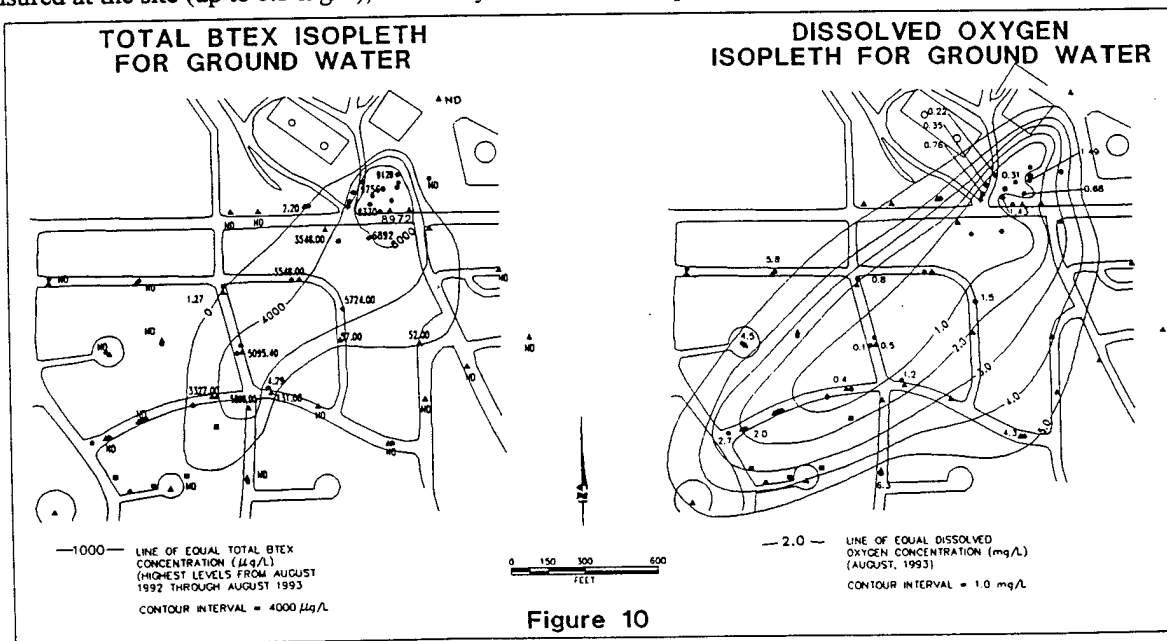
The following equations describe the overall stoichiometry of BTEX degradation caused by aerobic biodegradation. In the absence of microbial cell production, the oxidation (biodegradation) of benzene to carbon dioxide and water is given by:

$$C_6H_6 + 7.5O_2 \rightarrow 6CO_2 + 3H_2O$$
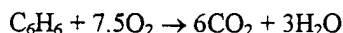
Therefore, 7.5 moles of oxygen are required to metabolize 1 mole of benzene. On a mass basis, the ratio of oxygen to benzene is given by:

Molecular weights: Benzene $6(12) + 6(1) = 78$ gm

Oxygen $7.5(32) = 240$ gm

Mass Ratio of Oxygen to Benzene = 240/78 = 3.08:1

In the absence of microbial cell production, 3.08 mg of oxygen are required to completely metabolize 1 mg of benzene. Similar calculations can be completed for toluene (3.13 mg oxygen to 1 mg toluene), ethylbenzene (3.17 mg oxygen to 1 mg ethylbenzene) and the xylenes (3.17 mg oxygen to 1 mg xylene). The average mass ratio of oxygen consumed to total BTEX degraded is thus 3.14:1. This means that approximately 0.32 mg of BTEX are biodegraded to carbon dioxide and water for every 1.0 mg of DO consumed. With a background DO concentration of approximately 6.0 mg/L, the shallow ground water at this site has the capacity to assimilate 1.92 mg/L (1,920 µg/L) of total BTEX.

Nitrate

Figure 11 shows the distribution of nitrate in ground water through August 1993. This figure also shows the dissolved-phase BTEX plume for this same period. Areas with elevated total BTEX concentrations have depleted nitrate concentrations, and the region in the center of the plume is devoid of nitrate. This is a strong indication that anaerobic biodegradation of the BTEX compounds is occurring at the site through the microbially mediated process of denitrification. Based on the high background nitrate concentrations measured at the site (up to 17 mg/L), it is likely that nitrate is also an important electron acceptor at this site.
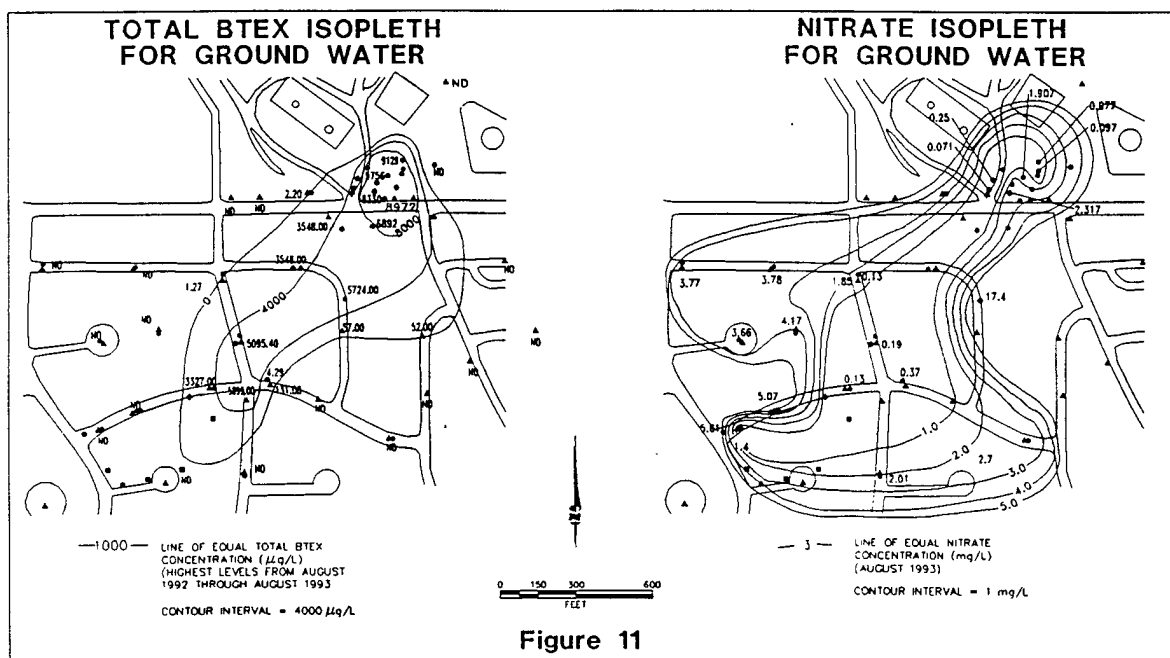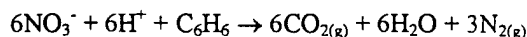

Figure 11

The following equations describe the overall stoichiometry of benzene oxidation by the anaerobic microbial process of denitrification. In the absence of microbial cell production, the biodegradation of benzene to carbon dioxide and water is given by:

$$6NO_3^- + 6H^+ + C_6H_6 \rightarrow 6CO_{2(g)} + 6H_2O + 3N_{2(g)}$$

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Therefore, 6 moles of nitrate are required to metabolize 1 mole of benzene. On a mass basis, the ratio of nitrate to benzene is given by:

Molecular weights: Benzene $6(12) + 6(1) = 78$ gm
Nitrate $6(62) = 372$ gm
Mass ratio of nitrate to benzene $= 372/78 = 4.77{:}1$

In the absence of microbial cell production, 4.77 mg of nitrate are required to completely metabolize 1 mg of benzene. Similar calculations can be completed for toluene (4.85 mg nitrate to 1 mg toluene), ethylbenzene (4.92 mg nitrate to 1 mg ethylbenzene) and the xylenes (4.92 mg nitrate to 1 mg xylene). The average mass ratio of nitrate consumed to total BTEX degraded is thus 4.9:1. This means that approximately 0.21 mg of BTEX are biodegraded for every 1.0 mg of nitrate consumed. With a background nitrate concentration of approximately 17 mg/L, the shallow ground water at this site has the capacity to assimilate 3.57 mg/L (3,570 µg/L) of total BTEX during denitrification.

Ferrous Iron

Figure 12 shows the distribution of ferrous iron in ground water through August 1993. This figure also shows the dissolved-phase BTEX plume for this same period. Areas with elevated total BTEX concentrations have elevated ferrous iron concentrations. This is an indication that ferric iron is potentially being reduced to ferrous iron during biodegradation of BTEX compounds. However, it is possible that sulfate reduction at the site is reducing the redox potential of the ground water to sufficiently low levels to cause the dissolution of iron-bearing minerals in the shallow saturated sediments at the site, thus elevating ferrous iron concentrations through nonbiological processes. The highest measured ferrous iron concentration was 50.5 mg/L. Background levels of ferrous iron are at or below 0.05 mg/L, as measured at wells located outside the area of known BTEX contamination.
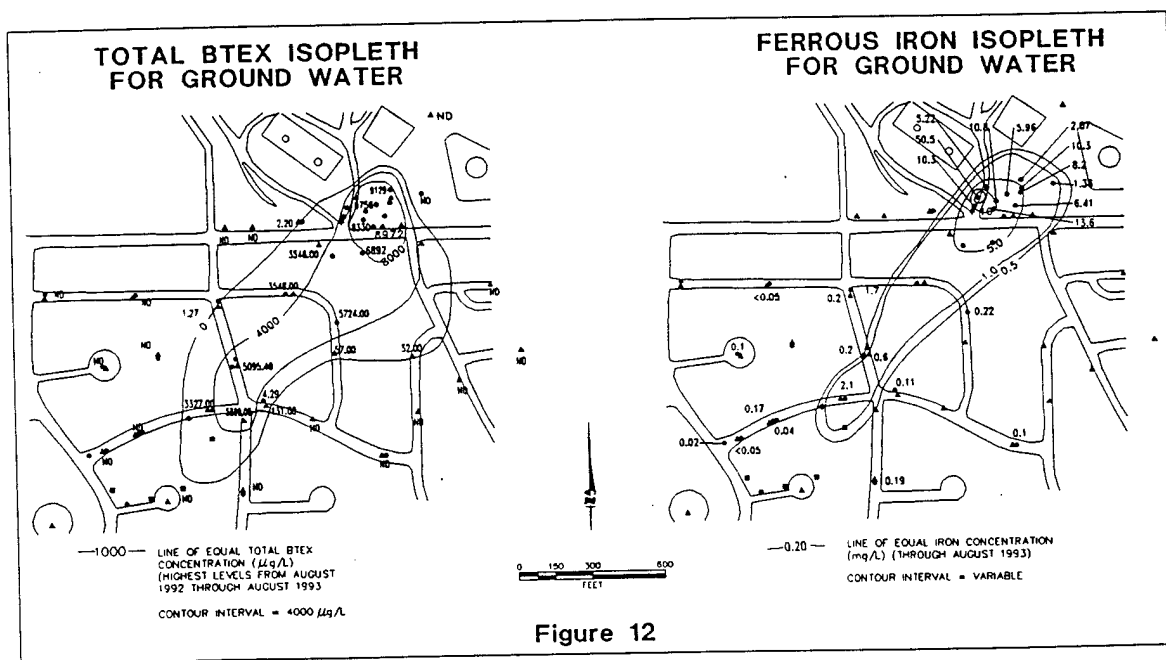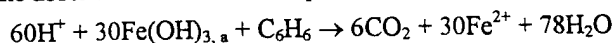

Figure 12

The following equations describe the overall stoichiometry of benzene biodegradation by iron reduction through microbial biodegradation. In the absence of microbial cell production, the biodegradation of benzene is given by:

$$60H^+ + 30Fe(OH)_{3,a} + C_6H_6 \rightarrow 6CO_2 + 30Fe^{2+} + 78H_2O$$

Therefore, 30 moles of $Fe(OH)_3$ are required to metabolize 1 mole of benzene. On a mass basis, the ratio of $Fe(OH)_3$ to benzene is given by:

Molecular weights: Benzene $6(12) + 6(1) = 78$ gm
$Fe(OH)_3$ $30(106.85) = 3205.41$ gm

12

Mass ratio of $Fe(OH)_3$ to benzene = 3205.41/78 = 41:1

In the absence of microbial cell production, 41 mg of $Fe(OH)_3$ are required to completely metabolize 1 mg of benzene. Alternatively, the mass ratio of ferrous iron produced during respiration to benzene degraded can be calculated and is given by:

Molecular weights: Benzene $6(12) + 6(1) = 78$ gm
                        Fe^{2+} $30(55.85) = 1675.5$ gm

Mass ratio of Fe^{2+} to benzene = 1675.5/78 = 21.5:1

Therefore, 21.5 mg of Fe^{2+} are produced during biodegradation of 1 mg of benzene. Similar calculations can be completed for toluene (21.86 mg of Fe^{2+} produced during biodegradation of 1 mg of toluene), ethylbenzene (22.0 mg of Fe^{2+} are produced during biodegradation of 1 mg of ethylbenzene), and the xylenes (22.0 of Fe^{2+} are produced during biodegradation of 1 mg of xylene). The average mass ratio of Fe^{2+} produced during total BTEX biodegradation is thus 21.8:1. This means that approximately 1 mg of BTEX is biodegraded for every 21.8 mg of Fe^{2+} produced. The highest measured Fe^{2+} concentration was 50.5 mg/L. This suggests that the shallow ground water at this site has assimilated at least 2.3 mg/L (2,300 μg/L) total BTEX by the process of iron reduction. This is based on observed ferrous iron concentrations and not on the amount of ferric hydroxide available in the aquifer. Therefore, iron assimilative capacity could be much higher.

Sulfate

Figure 13 shows the distribution of sulfate in ground water through August 1993. This figure also shows the dissolved-phase BTEX plume for this same period. Areas with elevated total BTEX concentrations have depleted sulfate concentrations. This is a strong indication that anaerobic biodegradation of the BTEX compounds is occurring at the site through the microbially mediated process of sulfanogenesis.
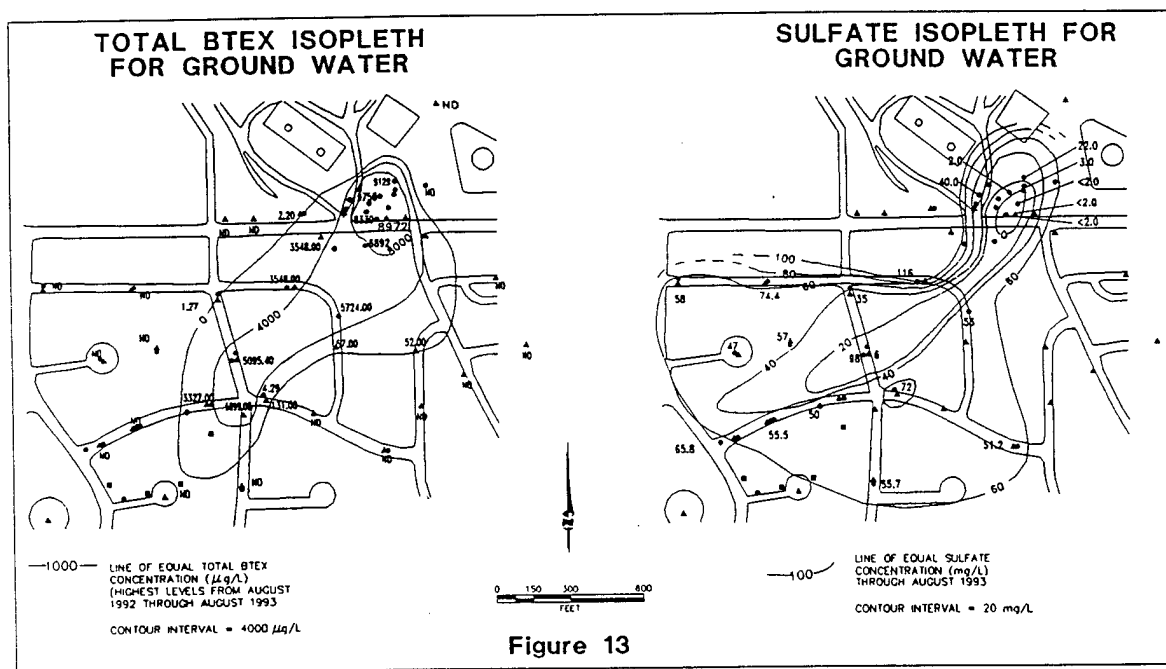

TOTAL BTEX ISOPLETH FOR GROUND WATER

—1000— LINE OF EQUAL TOTAL BTEX CONCENTRATION (μg/L) (HIGHEST LEVELS FROM AUGUST 1992 THROUGH AUGUST 1993)

CONTOUR INTERVAL = 4000 μg/L

SULFATE ISOPLETH FOR GROUND WATER

—100— LINE OF EQUAL SULFATE CONCENTRATION (mg/L) THROUGH AUGUST 1993

CONTOUR INTERVAL = 20 mg/L

Figure 13

The following equations describe the overall stoichiometry of BTEX oxidation by sulfate reduction caused by anaerobic microbial biodegradation. In the absence of microbial cell production, the biodegradation of benzene is given by:

$$7.5H^+ + 3.75SO_4^{2-} + C_6H_6 \rightarrow 6CO_{2(g)} + 3.75H_2S^\circ + 3H_2O$$
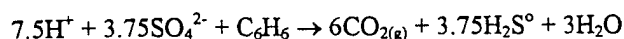
Therefore, 3.75 moles of sulfate are required to metabolize 1 mole of benzene. On a mass basis, the ratio of sulfate to benzene is given by:

Molecular weights: Benzene $6(12) + 6(1) = 78$ gm
                        Sulfate $3.75(96) = 360$ gm

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CH_4 produced. The highest measured CH_4 concentration was 2.04 mg/L. This suggests that the shallow ground water at this site has assimilated at least 2.6 mg/L (2,600 µg/L) total BTEX during methanogenesis. This is based on observed methane concentrations and not on the amount of carbon dioxide available in the aquifer. Therefore, methanogenic assimilative capacity could be much higher.

Alkalinity and pH

Alkalinity is a measure of the ability of ground water to buffer changes in pH caused by the addition of biologically generated acids. Total alkalinity at the POL site is fairly high, and varies from 959 mg/L at well EPA-82-D to 349 mg/L at well EPA-82-E. This amount of alkalinity should be sufficient to buffer potential changes in pH caused by biologically mediated BTEX oxidation reactions.

The pH of a solution is the negative logarithm of the hydrogen ion concentration [H^+]. Ground water pH at this site ranges from slightly acidic (6.3) to slightly basic (8.3). The majority of ground water has a pH of between 7.1 and 7.4. This range of pH is optimal for BTEX-degrading microbes.

Total Assimilative Capacity

Based on the stoichiometry presented in the preceding sections, the expressed BTEX assimilative capacity of ground water at the POL site is at least 30,890 µg/L (Table 1). The calculations presented in these earlier sections are extremely conservative because they do not account for microbial cell mass production. In addition, the measured concentrations of ferrous iron and methane may not be the maximum achievable. The highest observed total BTEX concentration at the site is 21,475 µg/L. Based on the work of Smith *et al.* (1981), this concentration is close to the theoretical maximum dissolved-phase BTEX concentration that can result from the equilibrium partitioning of BTEX compounds from JP-4 into ground water. Based on these calculations and on site observations, ground water at the POL site has enough assimilative capacity to degrade dissolved-phase BTEX that partitions from the LNAPL plume into the ground water before the plume migrates 1600 feet downgradient from the source area.

TABLE 1
EXPRESSED ASSIMILATIVE CAPACITY OF SITE GROUND WATER

Electron Acceptor or Process	Expressed BTEX (µg/L) Assimilative Capacity
Dissolved Oxygen	1,920
Nitrate	3,570
Ferric Hydroxide	2,300
Sulfate	20,500
Methanogenesis	2,600
Expressed Assimilative Capacity	30,890
Highest observed Total BTEX Concentration	21,475

Modeling

The Bioplume II model was used to help estimate the future migration and attenuation of the total BTEX plume at the POL site. This modeling effort aided ES in the accurate placement of long-term monitoring wells and POC monitoring wells and aided in sampling strategy development. Actual total BTEX concentrations observed between August 1993 and July 1994 were used to help calibrate the BTEX plume. The Bioplume II model was originally developed by researchers at Rice University to simulate the degradation of BTEX compounds by assuming an instantaneous reaction between DO and BTEX. The model also allows a first order rate constant to be input to account for the presence of additional degradation mechanisms, including anaerobic biodegradation using nitrate, iron III, sulfate, and carbon dioxide as electron acceptors. Based on observed patterns of contaminant migration and attenuation at the POL site, and on observations made by other researchers in the field, this approach vastly underestimates the assimilative capacity of the ground water. To more accurately simulate the migration of BTEX at the POL site, observed nitrate concentrations were converted to oxygen-equivalent nitrate concentrations and combined with observed oxygen concentrations. This allowed the reaction between nitrate and BTEX to be simulated as an instantaneous reaction relative to the advective flow velocity of the ground water.

$$\text{Mass ratio of sulfate to benzene} = 360/78 = 4.6:1$$

In the absence of microbial cell production, 4.6 mg of sulfate are required to completely metabolize 1 mg of benzene. Similar calculations can be completed for toluene (4.7 mg sulfate to 1 mg toluene), ethylbenzene (4.75 mg sulfate to 1 mg ethylbenzene) and the xylenes (4.75 mg sulfate to 1 mg xylene). The average mass ratio of sulfate to total BTEX is thus 4.7:1. This means that approximately 0.21 mg of BTEX are biodegraded for every 1.0 mg of sulfate consumed. With a background sulfate concentration of at least 97.6 mg/L, the shallow ground water at this site has the capacity to assimilate at least 20.5 mg/L (20,500 µg/L) of total BTEX during sulfanogenesis.

Methane

Figure 14 shows the distribution of methane in ground water through August 1993. This figure also shows the dissolved-phase BTEX plume for this same period. Areas with elevated total BTEX concentrations have elevated methane concentrations. Background levels of methane are below 0.001 mg/L. Only samples collected from monitoring wells located in the contaminant source area contain methane concentrations significantly above background. The highest methane concentration observed at the site was 2.04 mg/L. This is a strong indication that anaerobic biodegradation of the BTEX compounds is occurring at the site through the microbially mediated process of methanogenesis.
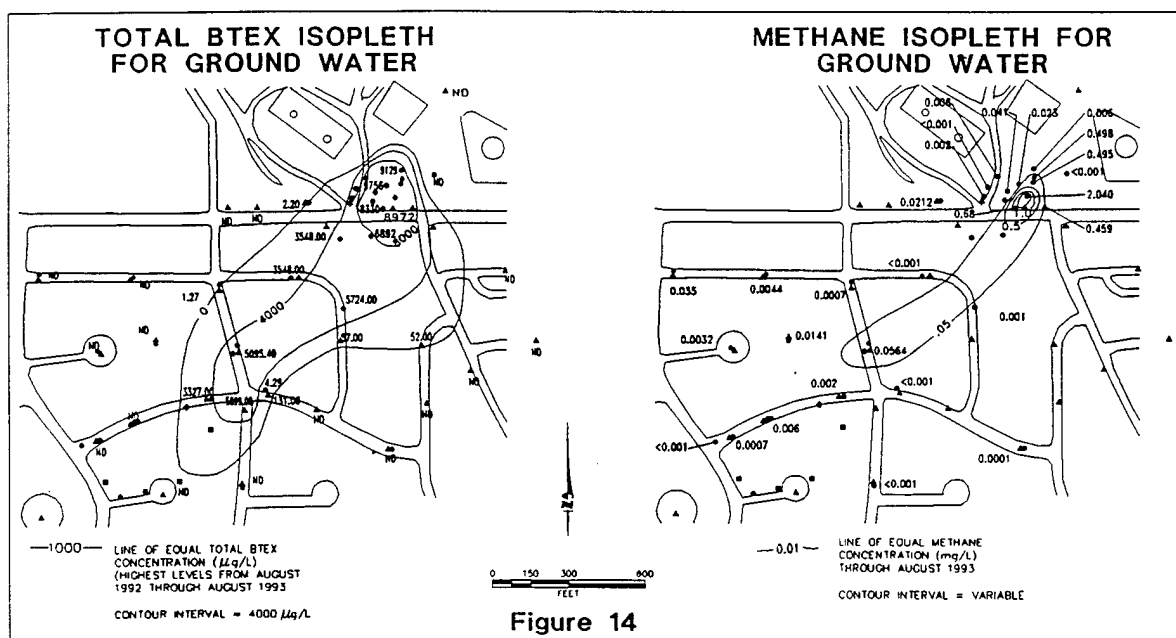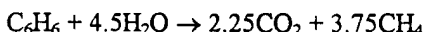

Figure 14

The following equations describe the overall stoichiometry of benzene biodegradation by methanogenesis. In the absence of microbial cell production, the biodegradation of benzene is given by:

$$C_6H_6 + 4.5H_2O \rightarrow 2.25CO_2 + 3.75CH_4$$

The mass ratio of methane produced during respiration to benzene degraded can be calculated and is given by:

Molecular weights: Benzene $6(12) + 6(1) = 78$ gm

CH_4 $3.75(16) = 60$ gm

$$\text{Mass ratio of } CH_4 \text{ to benzene} = 60/78 = 0.77:1$$

Therefore, 0.77 mg of CH_4 are produced during biodegradation of 1 mg of benzene. Similar calculations can be completed for toluene (0.78 mg of CH_4 produced during biodegradation of 1 mg of toluene), ethylbenzene (0.79 mg of CH_4 are produced during biodegradation of 1 mg of ethylbenzene) and the xylenes (0.79 mg of CH_4 are produced during biodegradation of 1 mg of xylene). The average mass ratio of CH_4 produced during total BTEX biodegradation is thus 0.78:1. This means that approximately 1 mg of BTEX is biodegraded for every 0.78 mg of

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Using this approach, in conjunction with a first order rate constant to describe biodegradation under iron reducing, sulfate reducing, and methanogenic conditions, the migration and attenuation of the total BTEX plume was accurately simulated. The rate constant used in this model was a very conservative 0.003/day compared to published rates ranging from 0.003/day to 0.06/day (Wilson et al., 1994; Chapelle, 1994). Figure 15 compares observed and simulated BTEX plume migration with a continuing source of constant BTEX contamination. This model predicts that a steady-state BTEX plume will develop after 1 year. This corresponds with observations made at the site between August 1993 and July 1994.

Exposure Assessment

An exposure assessment identifies the human and ecological receptors that could come into contact with site-related contamination and the pathways through which these receptors might be exposed. To have a complete exposure pathway there must be a source of contamination, a potential mechanism(s) of release, a pathway of transport to an exposure point, an exposure point, and a receptor. If any of these conditions are not met, the exposure pathway is considered incomplete, and receptors cannot come into contact with site-related contamination.
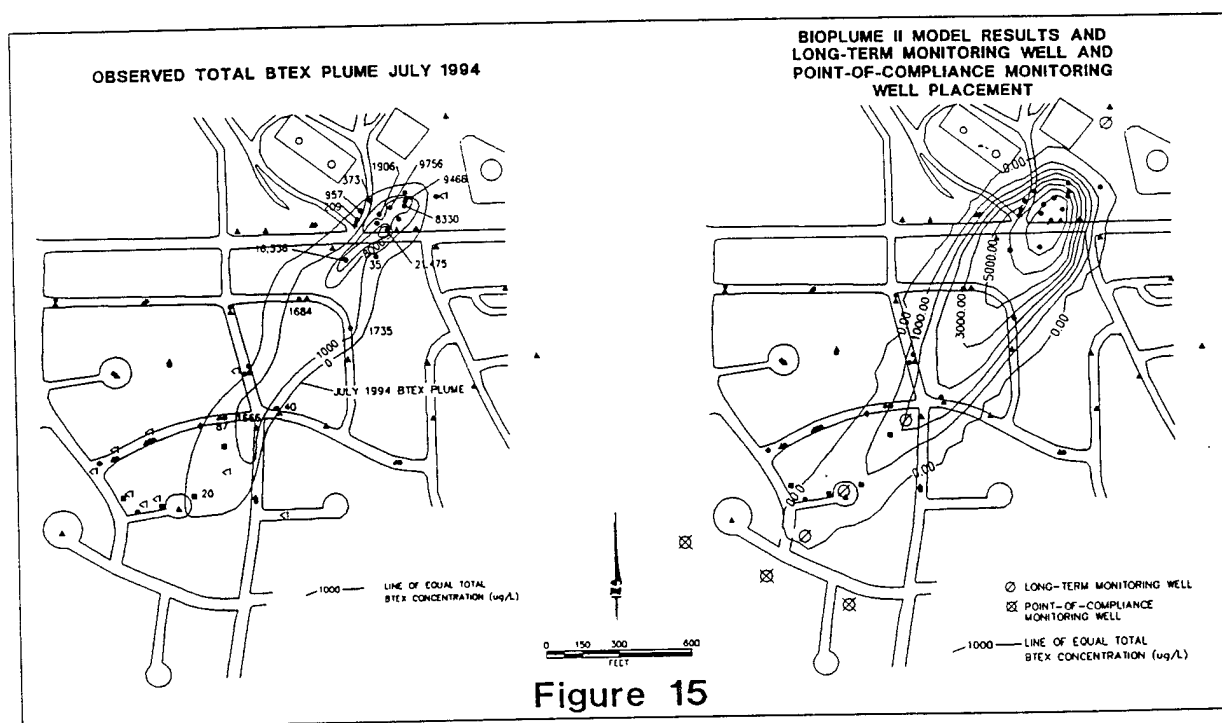

Figure 15

The results of numerical ground water modeling at the site suggest that no potential exposure pathways will be completed. However, to ensure that this is the case, long-term-monitoring wells and POC monitoring well locations were selected. This monitoring well network will allow the BTEX plume to be monitored over time so that the actual attenuation rates versus the predicted attenuation rates can be compared and the numerical ground water model for the site can be recalibrated. Based on the estimated migration potential of the dissolved-phase total BTEX plume, these wells were placed as shown in Figure 15.

Long-Term Monitoring Plan

Based on the results of the intrinsic remediation demonstration, long-term monitoring wells and POC monitoring well locations were determined (Figure 15). Based on the calculated advective ground water velocity for the site, and observed and predicted contaminant migration rates, a quarterly sampling frequency was recommended for this site. Ground water samples collected from long-term monitoring wells will be analyzed for BTEX, DO, nitrate, ferrous iron, sulfate, and methane. Ground water samples from POC monitoring wells will be analyzed for BTEX.

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CONCLUSIONS

This paper presents a brief synopsis of the technical protocol for implementation of the intrinsic remediation remedial option at fuel-hydrocarbon-contaminated sites. To illustrate how this protocol can be utilized, a case study from the POL site at Hill AFB, Utah is included. The material presented herein shows that the intrinsic remediation with long-term monitoring remedial option can be scientifically supported if the necessary data are collected.

Available hydrogeologic data from Hill AFB suggest that ground water is migrating at the rate of about 1,600 feet per year. Based on this, the total dissolved BTEX plume should have migrated about 1,450 feet between August 1993 and July 1994. However, contaminant data collected during this period indicate that the plume has reached a steady-state condition and is not migrating downgradient. Insofar as the maximum TOC concentration observed in uncontaminated portions of the aquifer is 0.094 percent, sorption alone cannot account for the discrepancy between the predicted and actual distance of contaminant plume migration. Available geochemical data as shown by isopleth maps suggest that biodegradation of fuel hydrocarbons at this site is occurring through the combined processes of aerobic respiration, denitrification, iron reduction, sulfanogenesis, and methanogenesis. By assuming an instantaneous reaction (relative to advective ground water flow velocity) between DO, nitrate, and the dissolved BTEX plume, and a first order rate constant to account for iron reduction, sulfanogenesis, and methanogenesis, the Bioplume II model accurately predicted the migration and attenuation of the BTEX plume during this period. A new model, Bioplume III is currently under development by AFCEE. This model will allow DO, nitrate, iron, sulfate, and methane data to be directly input into the model. This will greatly improve the predictive capacity of the intrinsic remediation numerical modeling effort.

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