



## Project Summary

# Monitoring and Assessment of In-Situ Biocontainment of Petroleum Contaminated Ground-Water Plumes

R. Ryan Dupont, Darwin L. Sorensen, Marian Kemblowski, Mark Bertleson, Dietrick McGinnis, Idris Kamil, and Yang Ma

### Abstract

This two-year field research project was conducted to assess the potential for natural attenuation of gasoline-contaminated ground-water plumes at two underground storage tank (UST) sites in northern Utah. An evaluation of rapid site-assessment techniques for plume delineation and subsurface site characterization was carried out using cone penetrometer and ambient temperature headspace (ATH) analysis techniques. An approach was developed for the collection and evaluation of soil and ground-water monitoring data for determining the efficacy of in-situ biocontainment and to identify "stabilized" fuel-impacted ground-water plumes. A decision framework was developed to guide the user in data collection, data reduction, data interpretation, and decision making efforts to evaluate the nature and potential extent of intrinsic plume bioattenuation taking place under a given set of site conditions. Data collected from the two field sites are presented and evaluated in detail, the rate and extent of the natural attenuation of ground-water plumes are quantified, and recommendations regarding source removal action are made for these two field sites.

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under CR 818835-01 to the Utah Water Research Laboratory, Utah State University. It has been subjected to the

Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

*This Project Summary was developed by the National Exposure Research Laboratory's Characterization Research Division, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

Ground-water quality impacts resulting from leaking underground petroleum storage tanks are a significant environmental concern due to the sheer number of such tanks and the extent of possible environmental contamination when they leak. Many of these tanks are being removed and replaced or upgraded to eliminate the source of possible petroleum contamination to underlying aquifers. However, there remains a large number of sites with ground-water contamination above existing water quality limits (300,000 confirmed releases as of June 1995, with an additional 100,000 releases expected by 2000 (e.g., personal communication, Hal White, U.S. EPA, OUST, 1995). While contamination from petroleum storage tank releases can have a significant impact on public health and the environment, active remediation of these contaminated sites can be difficult and expensive. Expectations of having to apply

active remediation at all sites has generally not allowed the focusing of resources on those sites representing the greatest threat to public health and the environment.

When gasoline is released into the subsurface, it distributes among the soil, gas, and aqueous phases that make up this environment. As it moves through the unsaturated zone, it leaves behind vapors containing volatile gasoline components and residual liquid hydrocarbons retained within the soil matrix. A large fraction of gasoline is water soluble and migrates to underlying aquifer with infiltrating water. Plumes of ground-water hydrocarbon contamination spread within the soil environment by ground-water advection and diffusion. Many gasoline components are biodegradable, and a primary mechanism for their transformation in the subsurface is via biodegradation. Biotransformation takes place under a variety of soil pH and oxidation-reduction potential (redox) conditions, and involves various terminal electron acceptors (oxygen, nitrate, manganese, iron, sulfate, carbon dioxide, carbon). If biodegradation of a contaminant proceeds at a rate greater than or equal to the rate of advance of the contaminant front, the plume will be effectively contained, and can eventually be completely remediated if the source of contamination is removed.

The only costs associated with site clean-up under these intrinsic biocontainment conditions are related to the costs for source removal and for the necessary, on-going monitoring of contaminant distribution and movement over the lifetime of the dissolved contaminant plume. Without reliable containment information, contamination may continue to spread, worsening existing conditions, posing increased public health risk, and increasing final clean-up costs. To obtain intrinsic degradation process rates for contaminants at fuel release sites, chemical/biological parameters indicative of in-situ biodegradation processes taking place in these environments must be well understood and documented. Once this is accomplished, routine measurements of these parameters, or a subset of these parameters, would allow identification of conditions under which in-situ biodegradation could be relied upon to provide natural attenuation of a contaminant plume.

The goal of this project was to identify and validate field monitoring techniques, and data reduction and reporting methods that can be utilized to rapidly and conclusively demonstrate the existence of intrinsic biodegradation reactions at leaking UST sites. With this demonstration of the natural containment of a hydrocarbon plume, rational decisions can be made regarding the need to actively remediate it to ensure the

protection of public health and the environment. Based on an evaluation of field and laboratory water quality determinations, soil core measurements, and companion modeling results, recommendations have been made regarding the selection of process variables, monitoring procedures, and data reduction and reporting methods that should be implemented at hydrocarbon contaminated sites to document intrinsic bioremediation of ground-water plumes.

## Procedure

The research was conducted in four phases. The first was a site assessment/characterization phase in which contaminant distribution and site hydraulic characteristics were determined using rapid field characterization methods. The second phase involved process monitoring, in which field techniques were used to monitor ground-water and soil gas characteristics that reflect in-situ biodegradation reactions taking place throughout the field sites. The third phase was the reduction of field data to yield estimates of total dissolved plume contaminant mass, center of mass, mass center trajectory, contaminant degradation rates, and estimated source lifetime. The final phase involved the use of a three-dimensional analytical model to provide in-situ biodegradation process verification and long-term predictions of fate of the plume as attenuated by natural biodegradation reactions.

Two field sites with known contamination from gasoline storage tanks were selected for this study: the Hill AFB site and the Layton, Utah site. Both sites were "aged" with initially "constant" source terms where it was reasonable to hypothesize that natural biodegradation reactions, and subsequent plume containment, had developed and were quantifiable. Single and multi-level ground-water monitoring probes were placed within and around the area of the contaminant plume at both sites. These wells included upgradient "background" wells, and wells within the area of contamination, allowing the definition of the boundaries of the plumes with some certainty. A gradient of chemical and biological conditions was observed throughout each plume so that transformation/degradation rates, mass transfer rates, etc., could be estimated. Plume characterization was carried out using cone penetrometry and 5/8-in diameter piezometer ground-water sampling wells to rapidly and inexpensively collect soil textural information and ground-water data from sampling locations throughout each plume. During long-term monitoring, site characterization information was collected using all of the ground-water sampling points.

The following data were collected throughout the site during the initial site characterization phase and six times during the process monitoring phase of the project: in ground water - pH, O<sub>2</sub>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>; in soil gas—O<sub>2</sub>, CO<sub>2</sub>; and in both soil gas and ground water - aromatic hydrocarbons and total petroleum hydrocarbons (TPH).

Field data were reduced to generate estimates of total dissolved mass of contaminant using the Thiessen area method (Chow et al., 1988) to assign a specific plume area to each ground-water monitoring point. Total dissolved plume mass was estimated for each sampling event, while the center of the total dissolved plume mass was estimated by taking the first moment about a defined axis of the masses represented at each sampling location within the contaminant plumes. The movement of the plume centroid over time was described based on the changes in its absolute position, and contaminant plume velocities were calculated between each sampling interval. Contaminant degradation rates were estimated based on the change in total dissolved plume mass between each sampling interval. Aquifer assimilation capacity was estimated based on the change in terminal electron acceptor concentration and mass inside versus outside of the plume.

Finally, an analytical, three-dimensional ground-water fate-and-transport model, which accounts for advection, dispersion, contaminant sorption and contaminant degradation, was applied to both field sites to validate intrinsic biodegradation reactions observed at these sites. Hydraulic properties were selected based on measured field data and information regarding the nature of soil below each site. A source configuration was established for each site. Model input variables for measured source concentrations, contaminant properties, and time since the release were varied to assess the sensitivity of the model to these parameters and to determine those combinations of parameters producing the best model fit of centerline contaminant concentrations for a tester data set. The effects of source removal on the lifetime of the plume and the maximum plume travel distance were assessed using the site-specific, field-data calibrated model.

## Results and Discussion

### *Site Assessment/Monitoring Techniques*

#### Cone Penetrometer Testing (CPT) Methods

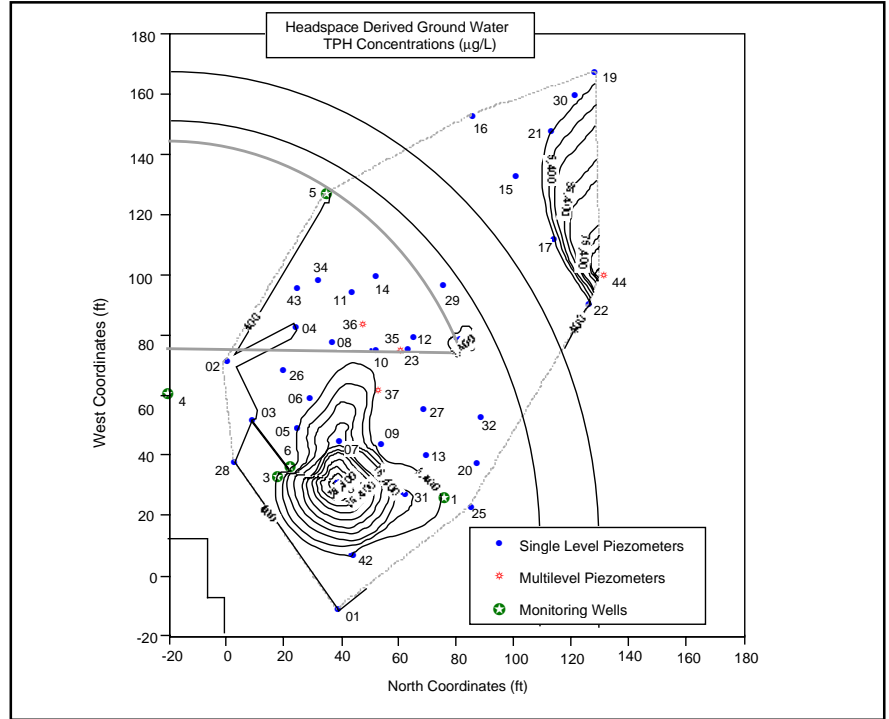
The application of cone penetrometer testing (CPT) for soil textural data collec-

tion coupled to piezometer well placement is appropriate for initial site investigation activities at sites where no prior data regarding ground-water plume characterization are available. These techniques can also be effectively applied at sites where existing data are limited in scope and detail, as was exemplified from the results obtained from CPT and ground-water probe data collected at the Hill AFB site.

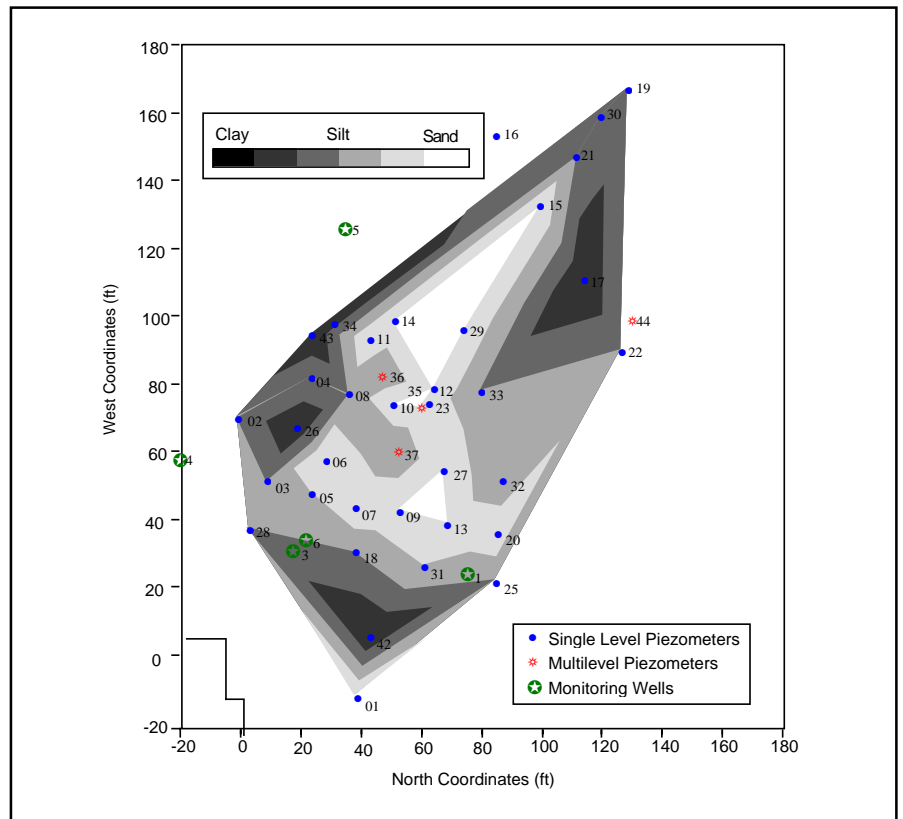
The Hill AFB site was the location of a former 18,000-gallon UST that was excavated in 1989. At the time of excavation, holes were observed in the tank and petroleum odors were detected in the tank pit. Five conventional ground-water monitoring wells were installed at the site and soil gas. Soil boring and limited ground-water monitoring data collected from the site from 1989 to 1991 led to the conceptual site model suggesting a plume migrating to the south-west.

Soon after site investigation activities began, it became apparent that the initial conceptual model of contaminant distribution and plume migration at the Hill AFB site was significantly flawed. Ground probe samples that were collected near the source of contamination within the plume boundaries showed hydrocarbon levels at background concentrations. CPT analysis and ground-water piezometer sampling were moved into the north and northwest regions of the site in an attempt to locate the contaminant plume. Field hydrocarbon screening data collected from these piezometers were successful in identifying the true north-westerly direction of the hydrocarbon plume as indicated by the ground-water concentration data shown in Figure 1. CPT measurements collected in this study also provided insight into ground-water flow conditions existing below the Hill site. Figure 2 clearly indicates a distribution of high and low permeability deposits that correspond to what appears to be an old stream bed resulting in channeling of the regional westerly flow to the northwest direction beneath the Hill site.

It is not known how widespread the findings for the Hill AFB site are in terms of the development of a less than complete picture of actual plume distribution and transport using limited, conventional site investigation data. It was found, however, that the use of CPT methods facilitated the rapid collection of soil textural information and the placement and sampling of ground-water probes that allowed a much more comprehensive picture of both structural and chemical features of the subsurface than was possible using soil core sampling and laboratory analysis procedures routinely applied at UST sites. This added information is combined with the complete elimination of soil



**Figure 1.** Initial ground-water plume hydrocarbon data developed from field screening headspace analyses conducted at the Hill AFB site, July 1992.



**Figure 2.** Textural map for soils at the ground-water table generated from CPT data collected at the Hill AFB site in July 1992.

cuttings and large volumes of contaminated ground water that are often costly and regulatorily challenging to manage, making the screening techniques used in this study ideal for application at many sites. The importance of additional insights into local ground-water flow conditions that can be provided by these CPT techniques is also unquestionable, especially when considering an intrinsic remediation management option at a site.

## Ambient Temperature Headspace (ATH) Results

Two data sets (July and December 1992) were collected from each field site to evaluate the representativeness of ATH field screening techniques compared to results generated from standard laboratory-generated purge-and-trap hydrocarbon measurements. This comparison between field- and laboratory-generated results was based on total hydrocarbon determinations using serial dilutions of a gasoline-saturated water standard in the field and hexane-equivalent concentrations for laboratory results.

The ratio of field- and laboratory-determined ground-water hydrocarbon concentrations was quite variable, ranging from a low of 0.0 to a high of 446. This ratio was generally consistent for a given sampling location between the two sampling times; however, some ratios varied by one to two orders of magnitude. The average ratio of field- to laboratory-determined ground-water hydrocarbon concentrations was greater than 1 for both sampling events at both sites, and ranged from 4.9 to 32.1. This result suggests that the field ATH procedures used in this study provided a conservative estimate of contaminant concentration from most sampling locations by a factor of 5 to 30.

A statistically significant relationship was found between laboratory and field data for both sites. A background field concentration of 279 µg/L was found when laboratory results indicated a zero TPH concentration at the Hill AFB site, while at the Layton site, a ground-water concentration of 3,680 µg/L was indicated from ATH readings before laboratory purge-and-trap methods detected TPH contamination. The slope of the field versus laboratory hydrocarbon concentration relationship was less than one for the Hill AFB site, indicating that when true ground-water concentrations (as defined by laboratory purge-and-trap results) exceed 842 µg/L, field ATH values under-predict actual ground-water TPH concentrations. The slope of the Layton relationship was greater than one, however, indicating that unlike the Hill AFB data, field ATH measurements consistently over-predicted laboratory purge-

and-trap ground-water concentrations by nearly a factor of two.

These findings suggest that there is a general relationship between laboratory and field ATH determined hydrocarbon concentrations, but this relationship is very much site-specific. The utility of these field ATH measurements appears then to be in the initial site assessment phase where rapid, semi-quantitative results are used for detailed plume delineation efforts. Field ATH measurements can be used to effectively guide initial ground-water quality investigations and to optimize ground-water monitoring probe and monitoring well placement for long-term site monitoring. Once this initial screening is completed, however, laboratory analyses are necessary to provide accurate ground-water quality data for further site fate-and-transport and intrinsic remediation evaluation.

## Hill AFB Site Intrinsic Remediation Results

### Site Background Data

This site is located in the west area of Hill AFB south of the city of Ogden, Utah. The site is immediately north of Building 1141 that was used by the Air Force for small vehicle maintenance. Generally, the regional shallow and deep ground-water flow direction through the fluvial and lacustrine deposits underlying the base is from the mountains on the east toward the Great Salt Lake on the west. Hydraulic conductivity of the shallow soils at the Building 1141 site, as determined by slug tests performed on selected wells by Engineering Science, were found to range between  $1.0 \times 10^{-5}$  and  $7.7 \times 10^{-5}$  cm/s.

In December 1989, an 18,000-gallon bare steel gasoline UST was excavated and no free-phase hydrocarbons were observed at this time, although observations of odors and holes in the UST indicated that a release may have occurred. Two soil samples and a ground-water sample were collected and analyzed for benzene, toluene, ethylbenzene, xylenes (BTEX), and total petroleum hydrocarbons (TPH). Data from this sampling event indicated that residual and dissolved BTEX and TPH contaminants were present in the soil and shallow ground water. Field investigative activities conducted in October and November 1990 included a soil-gas survey, soil borings, installation of ground-water monitoring wells, collection of soil and ground-water samples for laboratory analyses, slug tests, and a site survey. From these analyses, limited residual-phase and dissolved hydrocarbons were documented in the soil and the upper portion of the shallow aquifer immediately

downgradient and adjacent to the former UST.

In March 1991, levels of dissolved contaminants in the ground water were similar to those documented in November 1990. No free-phase product was observed, indicating that the bulk of the released product was bound in capillary pore spaces of the shallow soils. In July and August 1992, CPT data were collected at 44 locations throughout the Hill AFB site to augment the existing five-well monitoring network. CPT data successfully identified a subsurface stream channel (Figure 2) at the ground-water table, producing a significant northerly flow component to the regional, westerly ground-water flow.

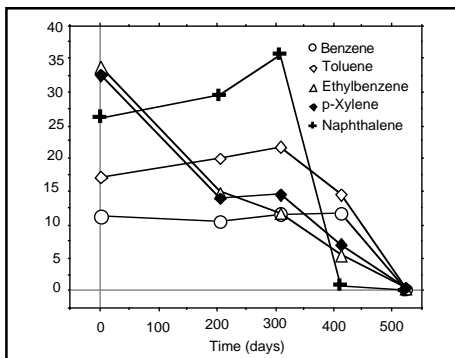
Seven sampling events were used at the Hill AFB site to describe the distribution and movement of contaminants and electron acceptors occurring at the site between April 1992 and January 1994. These data were used to determine steady-state plume conditions and to estimate total mass and mass center values for various analytes at the site over time.

## Intrinsic Remediation Assessment

### Determination of Steady-State Plume Conditions

Based on centerline concentration data observed at the Hill AFB site over time, the concentration profile for BTEX and TPH constituents remained at pseudo-steady-state after December 1992. To further evaluate plume stability conditions, total dissolved plume mass was estimated over time.

To determine dissolved plume mass, Thiessen areas were generated for each sampling event using a fixed outer plume boundary and individual areas determined based on the actual sampling locations used in a given sampling event. Specific compound mass data shown in Figure 3 suggest that steady-state conditions existed for some of the compounds (benzene, toluene, naphthalene) during a portion of the study period, while a continuously declining mass was seen for ethylbenzene and p-xylene during the entire study period. All of the specific compounds of interest did show a significant decline at the end of the study, however. Dissolved plume TPH mass confirmed the non-steady-state conditions existing at the Hill AFB site, as its mass was found to exponentially decay over time. Center of mass analyses showed migration of the mass center downgradient from its location in August 1992, although the total downgradient distance traveled was small, ranging from a maximum of 106 ft for TPH, to a low of only 17 ft for naphthalene. This



**Figure 3.** Time course of total dissolved plume mass estimates for BTEX and naphthalene contaminants at the Hill AFB site over the course of the study.

decreasing contaminant mass and center of mass moving downgradient suggest that the source was finite, and despite plume migration, the reductions in contaminant mass indicated assimilation was taking place.

### Estimation of Parent Compound Degradation Rate

Because the mass of contaminants in the dissolved plume at the Hill site were found to be decreasing over time, the plume appeared to originate from a pulse source. With a pulse source, contaminant degradation rates can be estimated by linear regression of total dissolved contaminant mass data versus time. The results of these regressions are shown in Table 1.

### Estimation of Source Mass/Lifetime

The projected lifetimes of the BTEX ground-water plumes using this mass versus time regression approach were quite short, being less than 2 weeks from the last sampling event. This was due to the low mass of contaminant remaining in the plume as of January 1994. The naphthalene and TPH plumes could persist for a much longer time but were estimated to last only slightly longer than 2 years at the current rate of degradation. The TPH plume mass center was projected to move the farthest of the compounds analyzed in the study, a total of 156 ft downgradient from its position in January 1994. This puts the mass center approximately 50 ft downgradient of the existing monitoring network, still within the boundaries of Hill AFB, and without impact to a downgradient receptor.

### Predicting Long-Term Behavior

Consideration of a source removal scenario for this site is not relevant as data indicate that the initial contaminant mass has

been depleted from the original source area through intrinsic processes of contaminant dissolution, dispersion, and degradation. The long-term behavior of the plume is modeled using the degradation rates of the contaminants within the "detached" dissolved plume and the rate at which the contaminants are migrating within the aquifer. The results of this analysis are shown in Table 1.

## Decision Making Regarding Intrinsic Remediation

### Impacted Receptors

The long-term behavior of the contaminant plumes existing at the Hill AFB site projected from contaminant degradation and transport data suggests that the maximum extent of any plume of interest will only be 50 ft downgradient of the existing ground-water monitoring network. This limited extent of potential contaminant migration ensures that no downgradient receptors will be impacted by contamination at the Hill AFB site over the projected lifetime of the ground-water plumes that exists there.

### Potential Aquifer Assimilative Capacity

When the mass of electron acceptor moving onto a site equals or exceeds the stoichiometric equivalent of dissolved contaminant in the plume, then it can be assumed that the availability of the electron acceptor will not limit future contaminant degradation and plume attenuation. The electron acceptor concentrations quantified throughout the

contaminated portion of the Hill AFB site were used along with the electron acceptor concentrations measured in background ground water to estimate the potential assimilative capacity existing within the aquifer. The hydrocarbon (HC) assimilative capacities related to dissolved oxygen (0.66 mg HC/L), nitrate (5.4 mg HC/L) and sulfate (10.7 mg HC/L) utilization were based on the lowest observed concentration in the background well. For iron (0.06 mg HC/L) and manganese (0.02 mg HC/L), their assimilative capacities were estimated based on the smallest increase in the soluble concentrations of these solid phase electron acceptors observed within the center of the plume during the study.

Sulfate was the most significant electron acceptor, accounting for more than 60 percent of the potential assimilative capacity at the site. The potential assimilative capacity projected for the site was more than 90 times greater than that required to assimilate the TPH remaining there. This result provides additional evidence that an intrinsic remediation management option for the Hill site would be protective of public health and the environment.

## Layton Utah Site Intrinsic Remediation Results

### Site Background Data

The Blaine Jensen R.V. facility, Layton, UT, was used as a recreational vehicle (RV) sales and service facility during the study and consisted of a service shop, an RV sales building, and associated sales and display

**Table 1.** Contaminant center of mass velocities and degradation rates based on ground-water data collected at the Hill AFB site from March 1992 to January 1994

	Benzene	Toluene	Ethylbenzene	p-Xylene	Naphthalene	TPH
Distance Traveled (ft)	25.7	53.3	42.9	55.6	17.2	106
Contaminant Velocity (ft/d)	0.05	0.1	0.08	0.11	0.03	0.2
Contaminant Velocity (ft/yr)	18	37.4	30.1	39	12.1	74.2
Zero Order						
Degradation Rate (g/d)	≈0.10	≈0.099	0.063	0.058		
Zero Order						
Degradation Rate (g/yr)	≈36.9	≈28.5	23.4	22.3		
First Order						
Degradation Rate (1/d)					≈0.026	0.009
First Order						
Degradation Rate (1/yr)					≈9.5	3.285
Remaining Mass in 1/94 (g)	0.41	0.66	0.53	0.8	0.13	28.8
Time to Degrade						
Remaining Mass -						
Zero Order (d)	≈4.1	≈6.7	8.4	13.8		
Time to Degrade 99.9% Mass -						
First Order (d)					≈266	768
Travel Distance in						
Degradation Time (ft)	≈0.20	≈0.67	0.67	1.5	≈8	156



lots. The majority of the site is covered by asphalt, and several underground utilities are present. The ground surface slopes gently toward the southwest and toward U.S. Interstate Highway 15 which borders the site directly to the west. The property was in agricultural production until approximately 1958, at which time it was leased to Sinclair Oil for retail gasoline sales from a newly constructed gasoline station building (the present service shop). The fuel storage and dispensing system consisted at that time of four USTs (2,000 gallons each) with suction pumps located to the west of the tanks. The property was subsequently utilized for camper sales between 1968 and 1974, followed by use for retail gasoline sales until 1984. The site was upgraded in 1974 with three additional 6,000-, 8,000-, and 10,000-gallon USTs equipped with pressurized dispenser systems. The tanks were removed in 1984, and the property was subsequently used for the recreational vehicle sales and service facility that occupied the site during the study. The area surrounding the site is characterized as mixed residential and agricultural use.

Soils encountered at the site are primarily sands in the southern portion of the site and silts and clays in the northern half of the site. Ground water is encountered at approximately 8 to 10 ft below grade. The direction of shallow ground-water flow is predominantly southwest, although westerly and northwesterly flows were observed at the site during the study. Hydraulic conductivity values of the shallow aquifer at the Layton site, determined by slug tests performed during this study, indicated values ranging from 0.78 to 3.1 ft/d, with an average of 1.5 ft/day.

A soil-gas survey was performed in 1990 at a depth of approximately 4 ft below ground surface using a portable organic vapor monitor (OVM) equipped with a photoionization detector (PID). A total of 36 locations were surveyed for volatile organic vapors. The highest vapor concentrations (250 to 1,975 ppmv) were found in the two tank excavations and in the dispenser island area between the former tanks. An outer area of lower vapor concentrations (0 to 250 ppmv) extended to the west and southwest. Overall, an area of elevated vapor concentrations of approximately 18,400 ft<sup>2</sup> was identified. In January 1991, soil borings were collected and three ground-water monitoring wells were installed and screened across the water table from 7 to 17 ft below ground surface.

In July and August 1992, CPT data were collected at 27 locations to augment the existing monitoring network. This detailed

site investigation effort provided analysis of soil textural features from the surface to a depth of 22 ft. This CPT information suggested a finer grained material than was indicated from soil boring data, and identified a clay to silty clay lens 2 to 6 ft thick covering most of the site 12 to 14 ft below ground surface.

Seven sampling events were conducted at the Layton site to describe the distribution and movement of contaminants and electron acceptors taking place there between April 1992 and January 1994. These data were used to determine steady-state plume conditions and to estimate total mass and mass center values for these various analytes, and to model contaminant transport and degradation occurring there over time.

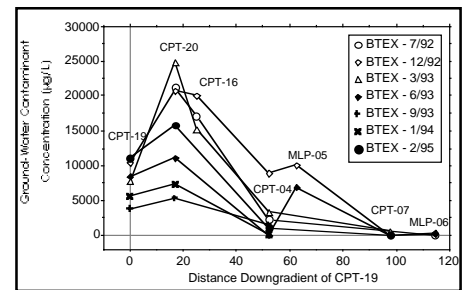
### ***Intrinsic Remediation Assessment***

#### **Determination of Steady-State Plume Conditions**

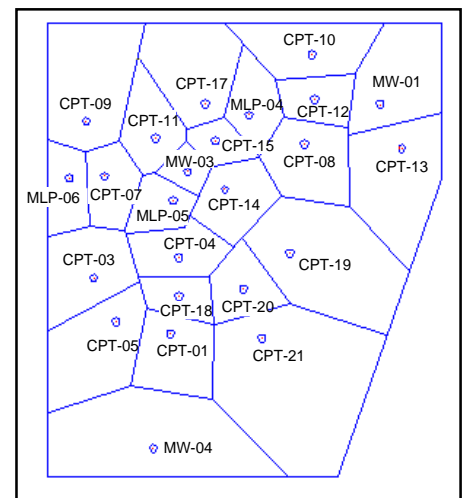
A westerly centerline transect was used to make a determination regarding steady-state plume conditions. Figure 4 shows plume centerline data for combined BTEX concentrations at the Layton site from July 1992 to February 1995. A pseudo-steady-state was found to occur for both BTEX components and TPH. Both BTEX and TPH concentrations increased and decreased along the plume centerline transect over time, but no consistent pattern downgradient of the source was evident.

Thiessen areas generated for each sampling event using a fixed outer plume boundary for the Layton site are shown in Figure 5. Based on the Thiessen areas associated with each monitoring point at each sampling time, estimates of the total dissolved plume mass and center of mass of BTEX, naphthalene, and TPH were made.

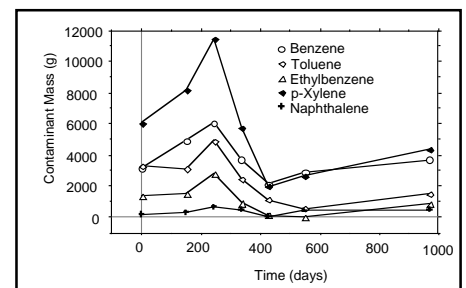
Despite a decline in dissolved contaminant mass observed at the Layton site between July 1992 and September 1993, further sampling in January 1994 and February 1995 indicated that the dissolved mass of the contaminants has remained essentially constant over the two and one-half year project period (Figure 6). The mobility of the center of mass of all of BTEX, naphthalene and TPH was limited, with a maximum of only a 10-ft movement of TPH mass over the two and one-half year field study. The pseudo-steady-state contaminant mass levels and limited center of mass movement downgradient suggest that a continuous source exists at the Layton site which reflects a plume stabilized by continuing intrinsic attenuation mechanisms.



**Figure 4.** Combined BTEX plume centerline concentration data collected at the Layton, UT, site from July 1992 to February 1995.



**Figure 5.** Outer plume boundary used for Layton site plume total mass and mass center calculations. Thiessen areas for the July 1993 sampling event are shown.



**Figure 6.** Time course of total dissolved plume mass estimates for BTEX and naphthalene contaminants at the Layton site during the study, July 1992 through February 1995.

## Estimation of Contaminant Degradation Rate

Using the intrinsic remediation protocol developed in this study, the estimation of contaminant degradation rates with a steady-state plume mass is carried out either from an analysis of plume centerline concentration data or through the calibration of a fate-and-transport model using field data.

### Plume centerline concentration data

A steady-state, time-averaged concentration profile was used to estimate first order degradation rates, the results of which are summarized in Table 2. Naphthalene had the slowest degradation rate, while benzene was found to be the most degradable of the compounds investigated. These degradation rates do not explicitly account for reductions in concentration due to dispersion and dilution (i.e., non-degradative) processes taking place within the Layton aquifer. The more preferred approach to estimate contaminant degradation involves the use of a ground-water fate-and-transport model that is calibrated to field-generated data.

### Ground-Water Model Calibration

An analytical solution for the advection-dispersion equation with degradation (assuming a continuous source with one-dimensional ground-water flow) was applied, along with site-specific physical/chemical input parameters, to model the fate and transport of contaminants under actual field conditions. Aquifer pore water velocities were calculated based on measured values of hydraulic gradient (0.01 ft/ft) and hydraulic conductivity (1.5 ft/d) and estimated values of total aquifer porosity (0.38) using Darcy's Law. An average pore water velocity of approximately 0.037 ft/d resulted. Transverse dispersivity was assumed to be 1/20th of the longitudinal dispersivity while vertical dispersivity was assumed to be negligible (0.001 m). Based on current practice, a longitudinal dispersivity of 0.1 times the plume length was used, resulting in longitudinal and transverse dispersivity values of 14 and 0.7 ft, respectively. Contaminant retardation factors were estimated from compound-specific organic carbon normalized soil/water partition coefficients ( $K_{oc,s}$ ). The soil organic carbon content, bulk density, and porosity values assumed for the Layton aquifer were 0.3%, 1.15 g/cm<sup>3</sup>, and 0.38, respectively.

The analytical solution used in this intrinsic remediation protocol assumes a constant plane source perpendicular to the direction of ground-water flow. The Layton site vertical source dimension was set equal to

**Table 2.** Contaminant degradation rates estimated from time-averaged centerline concentrations measured at the Layton site from July 1992 to February 1995

Compound	First Order Rate (1/d)	95 Percent Confidence Interval (1/d)	r <sup>2</sup>	p Value
Benzene	0.00087	0.00057	0.8204	0.0129
Toluene	0.00044	0.00010	0.9742	0.0003
Ethylbenzene	0.00026	0.00010	0.9263	0.0021
p-Xylene	0.00024	0.00013	0.8737	0.0063
Naphthalene	0.00014	0.00008	0.8243	0.0123

10 ft, the approximate maximum thickness of the contaminated ground-water column observed in monitoring wells. The lateral source dimension was based on an inspection of contaminant concentration profiles perpendicular to ground-water flow near the source area, approximately 100 ft.

From the site history, a range of simulation times from 10 to 25 years was used for model calibration. Contaminant degradation rate and simulation time were varied to evaluate the sensitivity of model output to these parameters, and to determine those combinations of parameters producing the best model fit. From model calibration, a source simulation lifetime of 25 years resulted in the best overall model fit. Benzene results are shown in Figure 7, while Table 3 summarizes model-calibrated degradation rates for all contaminants of interest.

### Estimation of Source Mass/Lifetime

When a continuous source is identified at a site, the estimation of source mass and source lifetime is based on the total mass of contaminant existing both above and below the ground-water table. This mass is generally estimated based on soil core concentration data collected from within the source area. The estimated source area mass at the Layton site appeared to be greatly underpredicted by soil core results based on the dissolved plume masses measured in February 1995. Source area mass was then estimated based on typical residual hydrocarbon saturation within a smear zone at and below the ground-water table for a given soil texture. It was assumed that approximately 10 percent of the subsurface porosity could be expected to be occupied by product material in the clay to silty clay soils below the Layton site, resulting in an estimated 241,000 lb of TPH remaining in the source area.

Because of the large mass of contaminant remaining within the source area, without source removal, site management requirements could be in excess of 100 years based on an ethylbenzene maximum contaminant level (MCL) of 700 µg/L and a

source area ethylbenzene ground-water concentration of ≈ 1,900 µg/L measured in February 1995. With source removal, the time to reach the ethylbenzene MCL is reduced to slightly more than 10 years, with benzene becoming the contaminant taking the longest to assimilate, requiring approximately 20 years before reaching its MCL. Source removal greatly reduces the length of time for assimilation of the mass of all contaminants at the Layton site, strongly suggesting the need for source removal so that the duration of site management becomes acceptable.

### Predicting Long-Term Behavior

The time to reach the MCL following source depletion can be predicted for each component using the calibrated fate-and-transport model described in this report by the superposition of a continuous source plume, with a source concentration equal to the negative of the original source concentration, -C<sub>0</sub>, on top of the steady-state plume concentration profile, at a point in time corresponding to the time of source removal. A benzene plume of greater than the MCL of 5 µg/L is projected to persist for 18 years, while all other contaminants of concern are projected to reach their MCL values everywhere within the plume in less than 7.5 years following source removal.

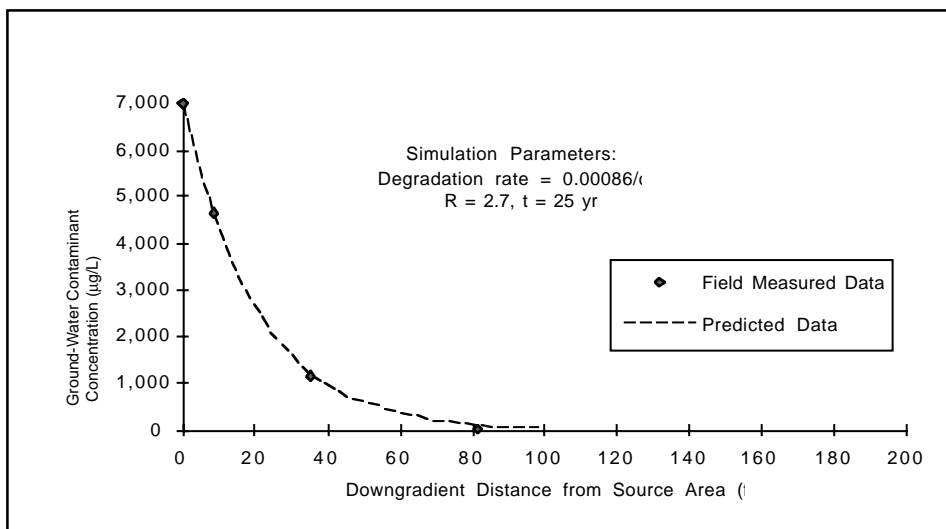
### Decision Making Regarding Intrinsic Remediation

#### Impacted Receptors

The projected long-term behavior of the contaminant plumes existing at the Layton site suggests that they have stabilized and are not expected to migrate from the site as long as existing site hydraulic conditions persist. This limited extent of potential contaminant migration ensures that no

#### Potential Aquifer Assimilative Capacity

The aquifer assimilative capacities related to dissolved oxygen (0.76 mg HC/L), nitrate (19.6 mg HC/L), sulfate (30 mg HC/L), iron (0.06 mg HC/L), and manganese



**Figure 7.** Results of benzene plume centerline calibration at the Layton site using data collected in March 1993.

(0.03 mg HC/L) amounted to approximately 50.5 mg HC/L. With a maximum TPH concentration of nearly 100 mg/L and a maximum BTEX concentration of nearly 25 mg/L observed during the study, this potential assimilative capacity is marginal. This result provides additional evidence that some form of source removal to reduce contaminant mass flux into the impacted ground water is the preferred approach for the Layton site. Without additional contaminant source removal, intrinsic remediation appears marginally protective of public health and the environment.

## CONCLUSIONS AND RECOMMENDATIONS

The research was conducted in four phases: 1) site assessment and characterization; 2) process monitoring; 3) field data reduction; and 4) three-dimensional analytical modeling. Based on the results of the study, the following conclusions can be made.

1. Conventional site assessment techniques using a small number of large diameter ground-water monitoring wells and limited soil core and shallow soil gas survey data can be severely limited in their ability to provide a detailed understanding of subsurface soil conditions at a site. CPT techniques can be used to improve delineation of subsurface conditions that may greatly impact local ground-water flow and contaminant transport. Coupled with placement of small diameter ground-water monitoring probes and field ATH measurements, CPT measurements enabled the col-

lection of cost-effective data for accurate plume delineation on nearly a real-time basis in this study.

2. The field ATH method used in this study appears more sensitive in situations with free product or high levels of residual saturation, than at those sites where weathered fuel contamination exists. Field ATH measurements can be used to effectively guide initial ground-water quality investigations and to optimize ground-water monitoring probe and monitoring well placement for long-term site monitoring. However, field screening data should not be used as a substitute for laboratory determined, long-term ground-water monitoring data.
3. Centerline concentration profile and dissolved contaminant mass analyses indicated that a significant decline in all contaminant mass levels took place at the Hill AFB site over the course of the study. Center of mass calculations suggested that the plume was responding to a pulse source with con-

taminant attenuation. Dissolved plume mass changes over time were used to estimate zero and first order degradation rates for BTEX, naphthalene, and TPH contaminants.

4. The lifetime of the BTEX compounds within the Hill AFB plume were short. Approximately 270 days was predicted for 99.9 percent naphthalene removal. More than 2 years was estimated for the same removal efficiency of TPH components under existing site conditions. The decision to apply intrinsic remediation at the Hill AFB site is warranted based on: a) the contaminant degradation rates and plume attenuation observed; b) the absence of an impacted downgradient receptor; and c) the potential aquifer assimilative capacity that is more than 90 times greater than that required for the assimilation of the TPH and BTEX remaining in the dissolved plume. A long-term monitoring scheme for both compliance and process monitoring purposes can be carried out using the existing monitoring network. Annual monitoring until 1997 should provide adequate data to validate complete plume assimilation to permit site closure.
5. Centerline concentration profile, dissolved contaminant mass and center of mass analyses for the Layton site indicated that the plume appeared to be at steady-state through February 1995. Results suggest that the Layton plume was acting as a continuous source which was stabilized by on-going intrinsic attenuation mechanisms. Changes in contaminant plume centerline concentrations with distance from the source area and a contaminant fate-and-transport model described in this study were also used to estimate contaminant degradation rates using measured March 1993 field data. Comparison of results from the centerline concentration and model calibration methods for degradation rate estimates suggest that the

**Table 3.** Contaminant degradation rates estimated from model calibration of the Layton site data collected March 1993

Compound	Calibrated Degradation Rate (1/d)	Retardation Factor, R
Benzene	0.00086	2.7
Toluene	0.00062	4.4
Ethylbenzene	0.00020	7.2
p-Xylene	0.00037	7.5
Naphthalene	0.00012	12.8



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simpler degradation rate approach can be used to provide representative contaminant degradation rates when a plume has reached steady-state conditions.

6. The soil core data available from the Layton site were limited, and residual product volume estimates based on gasoline residual saturation values reported in the literature for silty clay soils were used to estimate the mass remaining in the Layton site source area. From these residual mass estimates, the lifetime of the total mass of BTEX and naphthalene at the Layton site, based on reaching their MCL values in the plume, ranged from approximately 30 years for toluene to over 100 years for ethylbenzene. With 100 percent source removal, the required site management timeframe, based on the ethylbenzene MCL, was reduced to approximately 8 to 14 years. Under these site conditions, however, benzene becomes the contaminant with the greatest duration of concern, requiring approximately 18 to 22 years to reach its MCL value of 5 µg/L.
7. The decision to apply only an intrinsic remediation plume management approach at the Layton site should be made with caution. Despite apparent plume stabilization and the absence of an impacted downgradient recep-

tor, the low contaminant degradation rates (approximately one order of magnitude lower than at the Hill AFB site), large residual masses of contaminant within the source area and marginal potential aquifer assimilative capacity observed at the site will require long-term monitoring and site management (>30 years). Active source removal and residual mass remediation are warranted at the Layton site to accelerate the rate of contaminant removal from the site, and shorten the length of time required for plume management.

Based on the findings in this study, the following recommendations can be made:

1. The combined CPT/ATH procedures used for initial plume delineation proved to be rapid and cost-effective, leading to a significantly improved understanding of subsurface conditions at both of the field sites. This approach should be refined and evaluated for general application for site assessment activities at UST sites.
2. The intrinsic remediation protocol developed in this study provides a logical, quantitative approach for evaluating the presence and rates of contaminant assimilation within an aquifer system. The protocol provides improvements over conventional plume containment assessment methods. Plume centerline concentration analy-

sis is used, along with plume mass and center of mass determinations, to incorporate the aerial aspects of plume containment that have not normally been included in other field evaluations of intrinsic remediation processes. Its application should be evaluated for routine use at UST sites.

3. The modeling approach used to describe intrinsic remediation processes occurring at the two UST field sites allowed the quantitative assessment of contaminant migration and degradation using actual field data. The model was easy to implement in a spreadsheet environment and appeared to provide a quantitative description of contaminant plume profiles that were observed at the two distinctly different field sites evaluated in this study. The model provided independent verification of plume steady-state conditions, and allowed the rapid assessment of the impact of various source removal options on the duration of contaminant plumes produced from hydrocarbon releases at these sites. Its application should be evaluated for routine use at UST sites.

## REFERENCES

Chow, V.T, D.R. Maidment, and L.W. Mays. Applied Hydrology. New York: McGraw Hill Book Co., 1988.

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*R. Ryan Dupont, Darwin L. Sorensen, Marian Kemblowski, Mark Bertleson, Dietrick McGinnis, Idris Kamil and Yang Ma are with Utah Water Research Laboratory, Utah State University, Logan, UT 84322-8200*

**Charlita Rosal** is the EPA Project Officer (see below).

The complete report, entitled "Monitoring and Assessment of In-Situ Biocontainment of Petroleum Contaminated Ground-Water Plumes," (Order No. PB98-145329; Cost: \$47.00, subject to change) will be available only from:

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The EPA Project Officer can be contacted at:

Characterization Research Division  
National Risk Management Research Laboratory  
U.S. Environmental Protection Agency  
Las Vegas, NV 89193-3478

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