

CHARACTERISTICS OF DISSOLVED PETROLEUM HYDROCARBON PLUMES

RESULTS FROM FOUR STUDIES

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EXECUTIVE SUMMARY

Recent studies of over 600 groundwater contamination sites throughout the U.S. provide important information regarding the fate and transport of petroleum hydrocarbons in the subsurface. This API research summary examines the findings of four independent research studies and addresses several key technical issues regarding the assessment and remediation of BTEX (benzene, toluene, ethylbenzene, xylene) plumes. On-going research regarding MTBE plume characteristics will be addressed in a future bulletin as data become available.

Key Finding: Most BTEX groundwater plumes are less than 200 ft in length and are in a STABLE or SHRINKING condition.



THE FOUR STUDIES

This bulletin summarizes information from four separate multi-site plume studies. Each study involved detailed analysis of data from a large number of sites (primarily underground storage tank facilities) to identify the key characteristics of groundwater contaminant plumes caused by petroleum hydrocarbon releases. Two comprehensive studies (California and Texas) evaluated how dissolved petroleum hydrocarbon plumes change over time.

In all four studies, detailed technical information regarding groundwater flow parameters and plume characteristics for each site were compiled from technical reports or questionnaires completed by site hydrogeologists or engineers. In combination, the four studies define the typical features of a dissolved hydrocarbon plume based on a cumulative database of 604 sites.

This API bulletin reviews the general methodology and principal conclusions of each study and uses these findings to answer several important questions related to the assessment and remediation of groundwater impacts associated with petroleum releases.

Technical Issues Regarding Dissolved BTEX in Groundwater:

- Typical plume length
 Persistence over time
 - Effect of remediation Key factors in plume length
- Plume stability condition
- BTEX vs. other contaminants
- · Drinking water impacts



NFORNIA

Sites

California Leaking Underground Fuel Tank (LUFT) Historical Case Analysis

Rice, D.W., R.D. Grose, J.C. Michaelsen, B.P. Dooher, D.H. MacQueen, S.J. Cullen, W.E. Kastenberg, L.G. Everett, M.A. Marino. CA Environmental Protection Dept., Nov. 16, 1995.

APPROACH: This study, also referred to as the Lawrence Livermore National Laboratory (LLNL) Study, involved compilation and analysis of a detailed electronic database for 271 LUFT sites. Groundwater flow gradients and the average length and concentration of benzene plume were characterized on the basis of static water level data and groundwater time-series sampling records.

KEY RESULTS: Plume lengths "change slowly and stabilize at relatively short distances from the FHC (fuel hydrocarbon) release site" (90% of sites less than 255 ft). The median plume length was 101 ft for one of the two methods of calculation (see the following page). Plume lengths tend to change slowly with time, while average plume concentrations decline more rapidly. Hydrogeologic parameters (e.g., hydraulic conductivity, gradient) appear to have little relationship to plume length. Finally, "while active remediation may help reduce plume benzene concentrations, significant reductions in benzene concentrations can occur over time, even without active remediation."

Extent, Mass, and Duration of Hydrocarbon Plumes from Leaking Petroleum Storage Tank Sites in Texas

Mace, R.E., R.S. Fisher, D.M. Welch, and S.P. Parra. Bureau of Economic Geology, University of Texas at Austin, Austin, Texas. Geologic Circular 97-1, 1997.

APPROACH: The Texas Bureau of Economic Geology (BEG) evaluated groundwater impacts from fuel hydrocarbon releases at 217 sites in Texas. Groundwater plume lengths and concentration trends were analyzed in a manner similar to the California study (see Rice et al., above). In addition, hydraulic gradient and groundwater flow directions were characterized for various hydrogeologic and climatic regions of Texas.

KEY RESULTS: Most benzene plumes (75%) are less than 250 ft long and have either stabilized or are decreasing in length and concentration. The median plume length was 181 ft. Only 14% are increasing in concentration, and only 3% are increasing in length. The length of a benzene plume cannot be predicted on the basis of either site hydrogeology or previous remediation activities. Benzene plume characteristics are not statistically different between sites where groundwater remediation activities have or have not been implemented, although the authors state that these activities should "logically shorten the time required to decrease plume length and concentration."

Florida RBCA Planning Study

Groundwater Services, Inc. Prepared for Florida Partners in RBCA Implementation, Groundwater Services, Inc., Houston, Texas. 1997. www.GSI-net.com

APPROACH: The Florida RBCA (Risk-Based Corrective Action) Planning Study involved collection and analysis of groundwater data from 117 leaking underground storage tank (LUST) sites distributed throughout 33 counties in Florida. Using these data, the report addresses the cost significance of various policy decisions related to development of the Florida RBCA regulations. For use in this bulletin, the plume maps and detailed site questionnaires compiled for 74 sites were reanalyzed to define typical plume properties.

KEY RESULTS: The median plume length among these Florida LUST sites is 90 ft based on available benzene and BTEX data. The shorter plume lengths observed in this database may be related to the varying detection limits used for plume delineation. For plumes delineated to a 50 ppb benzene limit (51 sites), median plume length was 90 ft, compared to 120 ft for plumes delineated to 1 ppb benzene (21 sites). In addition, 51% of the Florida database sites are currently or had previously been subject to groundwater remediation efforts.

A Hydrogeologic Database for Ground-Water Modeling

Newell, C.J., L.P. Hopkins, and P.B. Bedient. Ground Water, Vol. 28, No. 5, Sept./Oct. 1990. pp. 703-714. API, 1989. Hydrogeologic Data Base for Groundwater Modeling, API Publication No. 4476, Washington, D.C.

APPROACH: Hydrogeologic and chemical information from 400 site investigations across the U.S. was obtained in a national survey of National Ground Water Association members conducted in 1990. This 400-site database (available in spreadsheet form from the API Information Specialist, ehs@api.org) includes groundwater plume dimensions for a broad range of groundwater contaminants, including 42 service station BTEX sites, 40 non-service station BTEX sites, 78 chlorinated ethene sites, 25 non-ethene solvent sites, and 21 inorganic sites. For use in this bulletin, these data were reanalyzed to define typical plume properties for each chemical class.

KEY RESULTS: The 42 service station sites show a median benzene/BTEX plume length of 213 ft. This database includes a higher percentage of longer plumes, with six BTEX plume lengths greater than 900 ft. On average, however, BTEX plumes are significantly smaller than the other chemical classes reported in this study, as discussed later in this Bulletin.







WHAT IS THE LIMIT OF MIGRATION OF DISSOLVED PETROLEUM HYDROCARBON PLUMES?

COMBINED RESULTS FROM FOUR STUDIES:



LOCATION OF SITES:	CALIFORNIA	TEXAS	FLORIDA	ENTIRE U.S.
• Plume constituent(s):	Benzene	Benzene	Benzene, BTEX	Mostly benzene, BTEX constituents
Plume Delineation Limit:	10 ppb	10 ppb	1 - 50 ppb	Not reported; probably analytical detection limit.
• Types of Sites:	UST sites with affected groundwater. No fractured rock sites.	UST sites with affected groundwater. Includes limestone aquifers.	UST sites with affected groundwater.	UST sites at service stations located in various hydrogeologic settings.
 Method For Determining Plume Length: 	Modeled: Length extrapolated from 2-D transport models fit to site monitoring data. Reported results for exponential and error-function equations (summary stats above from error function).	<i>Modeled</i> : Length extrapolated from 2-D GW transport model fit to site monitoring data. Used exponential equation only.	<i>Measured:</i> Length derived from site plume maps. Data analyzed as part of this bulletin.	Reported: Plume lengths reported by site consultants in survey questionnaires. Data analyzed as part of this bulletin.
 Sites w/ Soil Vapor Extract. Sites w/ GW Pump & Treat Sites w/ GW Sparging 	Not reported 53 of 208 sites (26 %) Not reported	105 of 479 (22%) 92 of 479 sites (19 %) 22 of 479 sites (5 %)	Not reported 32 of 74 sites (43 %) 6 of 74 sites (8 %)	Not reported Not reported Not reported

(note different #s of sites reported)

HOW MANY PETROLEUM PLUMES ARE SHRINKING? STABLE? EXPANDING?

APPROACH

Both the California and the Texas studies (Rice et al., 1995; Mace et al., 1997) analyzed changes over time in the length and average concentration of dissolved hydrocarbon plumes. For the California study, these evaluations were conducted on a subset of sites having at least 6 wells and 8 sampling episodes extending over multiple years. Typical monitoring records for the Texas study ranged from 4 to 7 years as shown in data from two typical sites to the right.

Plume stability trends were determined as follows:

Plume Length Trend: For each sampling episode, the plume length from the source to the 10 ppb concentration point was extrapolated using a 2-D groundwater transport model calibrated to the site monitoring data. Length vs. time was plotted for each site to define change over time.



Plume Concentration Trend: For each sampling episode, the average benzene concentration in the plume area was estimated using Delauney triangulation (Isaaks and Srivastava, 1989), an area-weighted averaging procedure involving subdivision of the plume area into triangular segments defined by adjacent wells. Average concentration vs. time was plotted for each site to define change over time.

These methods do not account for plume spreading beyond the area described by the monitoring well array. However, both studies found this approach to be sufficiently robust to accurately characterize plume trends over time.

KEY RESULTS

Based on the observed trends, the studies grouped the plumes into four categories:

- Expanding: Residual source present. Mass flux of contaminants exceeds assimilative capacity of aquifer.
- Stable: Insignificant changes. Active or passive remediation processes are controlling plume length.
- Shrinking: Residual source nearly exhausted, and active or passive remediation processes significantly reducing plume mass.
- Exhausted: Average plume concentration very low (e.g., 1 ppb) and unchanging over time. Final stages of source zone dissolution over a relatively small area at a site.

As shown in the conceptual plume lifecycle figures below, of the nearly 500 sites addressed by this analysis, nearly 75% were found to be in either a stable or shrinking condition, based on analyses of both plume length and concentration. Plume concentrations were predominantly shrinking (47 to 59%), whereas lengths were frequently stable (42 to 61%). These results suggest that dissolved hydrocarbon plumes tend to reduce more rapidly in concentration than in length. Similar results were observed in a plume study performed by Buscheck et al. (1996), where 67% of 119 plumes in northern California were found to be stable/shrinking in length, and 91% had stable/diminishing concentrations.



Figures adapted from Rice et al., 1996.

Texas BEG

Study

California

LLNL Study

HOW LONG WILL BTEX PLUMES PERSIST?

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SNTES

CALIFORNIA & TEXAS STUDIES: 90% Attenuation of <u>Average</u> Concentration of <u>Shrinking</u> Plumes

MEDIAN SITE

10th Percentile:

90th Percentile:

IN CALIFORNIA:

Time Required for 90% Attenuation in <u>Average</u> Concentration for <u>Shrinking</u> Plumes:

90

ITES

<u>3.2 vrs</u>

1.5 yrs

7 yrs

For those plumes characterized as shrinking (see page 4), both the California and Texas studies (Rice et al., 1995; Mace et al., 1997) included an evaluation of the time required for the average plume concentration to reduce by 90%. The rates of change calculated for each data set are shown in the table to the right.

Note that, in these analyses, the aver-

age concentration term corresponds to an area-weighted average BTEX concentration derived using the Delauney triangulation method for each groundwater sampling episode. Consequently, trends in this concentration term should be representative of the total plume mass. Data from the California and Texas studies show that, once a dissolved BTEX plume begins to shrink (a condition observed at roughly 50 - 60% of the LUST sites in these studies), the rate of decline in plume mass is relatively rapid. Based on the median rate of mass reduction reported in these studies, for a shrinking plume, only 5 to 10 years are required for the average plume BTEX concentration to drop from an initial level of 1 ppm down to 1 ppb. (This assumes a first order decay model applies over three orders of magnitude of concentration reduction.) At this point, the plume reaches an exhausted condition, which may represent low levels of BTEX persisting in source-area wells for an extended time period thereafter.

WHAT IS THE EFFECT OF REMEDIATION ON BTEX PLUMES?

Three of the four studies evaluated the performance of remediation efforts in reducing or controlling petroleum hydrocarbon plumes. Based on a review of large site populations, the studies consistently draw a conclusion that runs counter to expectations: soil and groundwater remediation efforts did not result in smaller BTEX plumes.

QUOTES



"While active remediation may help reduce plume benzene concentrations, significant reductions in benzene concentrations can occur with time, even without active remediation." (pg. EX-2)

"At low concentration sites, pump and treat increases the probability of having a negative average benzene concentration trend by roughly a factor of two, while it has essentially no impact on probability at high concentration sites." (pg. 13)

CONCENTRATION TREND*				
Pump & Treat Site?	Pump & Site Over- reat Site? Excavated?			
		52 %		
\checkmark	-	71%		
	V	64 %		
\checkmark	1	80 %		

% OF PLUMES THAT ARE:

Shrinking

61 %

52 %

Exhaus.

4%

10 %

Stable

35 %

38 %

67 Sites WITH

Pump & Treat

Pump & Treat

117 WITHOUT

MEDIAN SITE

IN TEXAS:

10th Percentile:

90th Percentile:

<u>1.4 yrs</u>

0.7 yrs

2.7 yrs

(Rice et. al. 1995)

"An analysis of plume length categories shows that none of the remediation treatment variables have a significant impact on the relative frequencies of the different categories." (pg. 13)



(Mace et. al, 1997)

remediation do not appear different from plume lengths at sites without remediation." (pg. 34) "This probably means that significant spills occur before being detected and that most plumes are in place and in equilibrium before active remediation takes effect." (pg. 34)

"The use of active ground-water remediation has not yet resulted in a

lower median plume length at LPST sites throughout the state where corrective action is under way. This does not mean that remediation does not improve ground-water conditions at individual sites, but that

when all LPST sites are reviewed, plume lengths at sites with

"We found no difference in plume length between different remediation techniques and sites with no remedial action." (pg. 33)



(GSI, 1997)

"Of the 117 sites included in this study, affected soils have been previously removed at 28 sites. For these 28 sites, the estimated median groundwater source mass is approximately 34% lower than the median groundwater source mass where overlying soils have not yet been removed. These data suggest that, while the soil removal actions have served to reduce groundwater impacts, a significant percentage of the contaminant source (66%) remains in place in the saturated, water-bearing unit." (pg. 21)



"...soil removal would not significantly affect groundwater remediation requirements." (pg. 21)

WHAT ARE THE FACTORS THAT CONTROL BTEX PLUME LENGTH?

TEXAS AND CALIFORNIA STUDIES

The California and Texas studies attempted to correlate plume length with various hydrogeologic factors. In both studies, plumes were segregated into two subsets (shallow vs. deep) and correlation coefficients were calculated for plume length vs. a range of site parameters. Results of these analyses are summarized below.



These studies suggest that the size of the release is probably one of the key variables that controls plume length. Larger sources (in terms of mass, width, and affected soil volume) mean that more dissolved-phase constituents are transferred to groundwater, creating longer dissolved phase plumes.

HOW MUCH GROUND WATER IS AFFECTED BY BTEX PLUMES?

An upper-range estimate of the total volume of groundwater resources impacted by releases from LUST sites can be obtained using a calculation method described in the California study (Rice et al., 1995). In this method, the 95th percentile BTEX plume volume observed in the California study (i.e., 0.7 acre ft. or 230,000 gallons) is multiplied by the total number of reported LUST sites to obtain a total affected groundwater volume. Dividing this value by the total groundwater basin storage capacity provides an estimate of the percentage of resources impacted by LUST sites. Results for both California and the U.S. are provided below. Note that LUST sites usually affect shallow water table aquifers not typically used for public supply.



HOW ARE BTEX PLUMES DIFFERENT FROM OTHER PLUMES?

The HGDB Study (Newell et al., 1990) provides plume length data for a variety of contaminants, including BTEX, chlorinated solvents, and brine releases. This chart shows plume widths and lengths as reported by HGDB respondents. As shown, BTEX plumes are much smaller than other types of plumes. Likely causes for this difference include: i) the smaller source zone area associated with BTEX releases from LUST sites, and ii) the more biodegradable nature of BTEX constituents relative to the other contaminants. Note that other studies are in progress to characterize other types of plumes (e.g., Happel et al., 1998; Mace, 1998; Newell et al., 1998).

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- U.S. EPA, 1998. Semi-Annual Corrective Action Activity Report, EPA Office of Underground Storage Tanks.

API Soil & Groundwater Research Publications

Publ 4668, Delineation and Characterization of the Borden MTBE Plume: An Evaluation of Eight Years of Natural Attenuation Processes, June 1998

In 1988, a natural gradient tracer test was performed in the shallow sand aquifer at Canada Forces Base (CFB) Borden to investigate the fate of a methyl-tertiary-butyl-ether (MTBE) plume introduced into the aquifer. Solutions of groundwater mixed with oxygenated gasoline were injected below the water table along with chloride (CI), a conservative tracer. The migration of benzene, toluene, ethylbenzene, the xylenes (BTEX); MTBE; and Cl⁻ was monitored in detail for about 16 months. The mass of BTEX in the plume diminished significantly with time due to intrinsic biodegradation. MTBE, however, was not measurably attenuated. In 1995-96, a comprehensive groundwater sampling program was undertaken to define the mass of MTBE still present in the aquifer. Only about 3 percent of the initial MTBE mass was found, and it is hypothesized that biodegradation played an important role in its attenuation. Additional evidence is necessary to confirm this possibility. Pages: 88.

Order Number: 146680, Price: \$30.00

Publ 4657, Effects of Sampling and Analytical Procedures on the Measurement of Geochemical Indicators of Intrinsic Bioremediation: Laboratory and Field Studies, November 1997 This study evaluates the effects of various sampling and analytical methods of collecting groundwater geochemical data for intrinsic bioremediation studies. Sampling and analytical methods were tested in the laboratory and in the field. Several groundwater sampling and analytical methods may be appropriate for measuring geochemical indicators of intrinsic bioremediation. The methods vary in accuracy, level of effort, and cost. Pages: 86.

Order Number: 146570, Price: \$30.00

Publ 4658, Methods for Measuring Indicators of Intrinsic Bioremediation: Guidance Manual, November 1997

This guidance manual is intended to be a resource for practitioners of intrinsic bioremediation in allowing selection of sampling and analytical methods that meet project-specific and site-specific needs in scoping field investigations, provides procedures that will improve the representative quality of the collected data, and considers potential biases introduced into data through the sampling and analytical techniques employed in the site investigation. Pages: 96. Order Number: I46580, Price: \$35.00

Publ 4654, Field Studies of BTEX and MTBE Intrinsic Bioremediation, October 1997

A gasoline release field site in the Coastal Plain of North Carolina was monitored for more than three years to allow calculation of in situ biodegradation rates. Laboratory microcosm experiments were performed to further characterize the biodegradation of BTEX and MTBE under ambient, in situ conditions. Finally, groundwater modeling studies were conducted to facilitate the interpretation of field data and to evaluate various approaches for predicting the fate and effects of these gasoline constituents in the subsurface. Pages: 244. Order Number: 146540, Price: \$40.00 Publ 4627, In Situ and On-Site Biodegradation of Refined and Fuel Oils: A Review of Technical Literature 1988-1991, June 1995 This report reviews more than 200 technical articles published between 1988 and 1991 in the area of on-site and in situ bioremediation of petroleum hydrocarbons. It focuses specifically on current field and laboratory research related to petroleum hydrocarbon biodegradation including biodegradation of crude oil and solvents. Recent work in fate and transport modeling that can be applied to petroleum hydrocarbon contamination in groundwater is also covered. The review is designed to complement an earlier (pre-1988) review published by the U.S. Navy. Pages: 146. Order Number: 146270, Price: \$30.00

DR 200, Modeling Aerobic Biodegradation of Dissolved Hydrocarbons in Groundwater, April 1995

This report describes a 3-D groundwater transport model that accurately characterizes the nature of aerobic biodegradation, i.e., the mixing of oxygen and dissolved hydrocarbons at plume edges of petroleum spills to the subsurface. The report also demonstrates the differences between spreading and mixing phenomena. The approaches in this report will be used to develop user-friendly biodegradation models which will be helpful in site-specific evaluations. The use of such models could lead to shorter and less expensive cleanups at some sites. Pages: 76. Order Number: 100200, Price: \$30.00

Publ 4593, Transport and Fate of Non-BTEX Petroleum Chemicals in Soils and Groundwater, September 1994 Order Number: 145930, Price: \$40.00

Publ 4601, Transport and Fate of Dissolved Methanol, MTBE and Monoaromatic Hydrocarbons in a Shallow Sand Aquifer, April 1994

Order Number: 146010, Price: \$65.00

Publ 4551, Treatment of Gasoline-Contaminated Groundwater Through Surface Application: Laboratory Experiments, July 1994 Order Number: 145510, Price: \$55.00

Publ 4552, Treatment of Gasoline-Contaminated Groundwater through Surface Application: A Prototype Field Study, July 1994 Order Number: 145520, Price: \$40.00

Publ 4415, Literature Survey: Unassisted Natural Mechanisms to Reduce Concentrations of Soluble Gasoline Components, August 1985

Order Number: 144150, Price: \$25.00

Publ 4476, Hydrogeologic Data Base for Groundwater Modeling, February 1989

Order Number: 144760, Price: \$25.00

NOTE: Prices are subject to change.

Copies of these publications are available from API's Publications Department, (202) 682-8375. For more information about the research, contact the Health, Environment, & Safety Information Specialist at the American Petroleum Institute by phone (202) 682-8319 or email <u>ehs@api.org</u>.