## NATURAL ATTENUATION STUDY IN WISCONSIN AND ILLINOIS

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**ABSTRACT:** A natural attenuation field study has been conducted jointly by the U. S. Environmental Protection Agency (U. S. EPA) Region 5, Wisconsin Department of Natural Resources (WDNR), the Illinois Environmental Protection Agency (IEPA), and Amoco Corporation (Amoco) since October 1994. Project goals included determining the effectiveness of natural attenuation and developing a cost-effective way to evaluate it. Four leaking underground storage tank (LUST) sites in Wisconsin and three in Illinois were selected, and petroleum hydrocarbon compounds, such as benzene, toluene, ethylbenzene, and total xylenes (BTEX)), as well as selected bioparameters, were measured at these sites for two or more years. Methyl tertiary butyl ether (MTBE) was also measured at the Wisconsin sites. Data obtained from this field study indicate, with the exception of one site which appears to have been impacted by a release from up-gradient of the site, that the plumes have been stable or shrinking and there is strong evidence that natural biodegradation has been occurring. Although several bioparameters could be used to demonstrate biodegradation, the trend of the BTEX compounds over time or distance was found to be the best indicator for demonstrating the appropriateness and effectiveness of natural attenuation.

## **INTRODUCTION**

In 1988, when the Federal LUST program took effect, few state programs anticipated the large numbers of LUST sites generated as a result of the rules. In many ways, the increased demand for oversight created innovative approaches to environmental regulatory management. For example, traditional risk assessment and evaluation approaches have been modified and streamlined into what is now known as risk-based corrective action (RBCA) programs. RBCA programs allow states and responsible parties to manage the large workloads so those sites posing the greatest risk to the human health and the environment are addressed first and with the necessary resources.

In the past decade, significant advancements have been noted in the areas of site investigation methods and corrective action technologies. Early on, some studies seemed to indicate that certain LUST sites were undergoing constituent concentration reduction without the use of active technologies. Eventually, the use of natural attenuation, which is the process where naturally occurring physical, chemical, and biological processes will effectively achieve remedial goals and can be demonstrated through monitoring, was being considered by state regulatory programs as a viable remediation alternative.

Many states were unfamiliar with and, therefore, unwilling to consider approving corrective action plans in which natural attenuation was being proposed as an alternative. Although several environmental consultants had conducted similar types of studies, some state regulators suggested that results could be viewed as more credible if the states and the U. S. EPA had participated in the study. If a regulatory agency had participated and supported the results of a study, state LUST programs might be more willing to modify existing or create new policies with respect to natural attenuation.

Early in 1994, U. S. EPA Region 5 approached LUST managers within the WDNR and scientists within Amoco to determine the feasibility of conducting a natural attenuation field study at a number of LUST sites in Wisconsin. At the time, Wisconsin had completed a natural attenuation policy guidance document and was evaluating the concept further. Soon after, staff with the IEPA agreed to participate, and additional sites in Illinois were included in the study.

The goal of this project was to gain a better understanding of natural attenuation at several petroleum impacted sites, to determine effectiveness and cost effective monitoring strategies. Another goal of the project was to select sites with varied lithology instead of only focusing on homogeneous sandy soils which most other studies were based on.

The basic premise was to conduct a site selection process, agree on specific natural attenuation indicator parameters to be studied, establish a monitoring schedule, and monitor the sites over time. The purpose of monitoring the sites over time was to determine if any contaminant reduction trends could be established, and if so, could the trends be attributed to natural attenuation processes. The study of these particular sites would be conducted outside of the formal LUST oversight process state regulators often follow. In general, the effectiveness of natural attenuation was determined on the basis of whether the

individual plumes were expanding, stable, or shrinking, and whether or not the data collected from the sites adequately made the case for any of those scenarios. Personnel from the Regulatory agencies, Amoco, and consultants (mainly from Delta Environmental) met at least twice a year to evaluate progress and monitoring strategies.

#### MATERIALS AND METHODS

#### Site Geology and Hydrogeology

Following the site selection process, four LUST sites from Wisconsin and three from Illinois were chosen to participate in the study. The selected sites in Wisconsin were located in Concord, Milwaukee, Hales Corners, and Marshfield. The selected sites in Illinois were located in Highland Park, Broadview, and Chicago (Table 1 summarizes the geology, hydrogeology, and background information of the selected study sites).

The near surface geology beneath the Concord, Wisconsin site is predominantly silty- and sandyclay underlain by bedrock. The depth to water at the site ranges from 8 to 11 feet below ground surface (bgs) with a calculated hydraulic conductivity of  $3.1 \times 10^{-3}$  centimeters per second (cm/sec). The ground water velocity is estimated to be approximately 10 feet per year (ft/yr).

Beneath the Milwaukee, Wisconsin site, the near surface geology is predominantly clay and silty-clay. The depth to water at the site ranges from 11 to 16 feet bgs with a calculated hydraulic conductivity of  $9.5 \times 10^{-5}$  cm/sec. The ground water velocity is calculated to be approximately 3 ft/yr.

The geology beneath the Hales Corners, Wisconsin site is predominantly clay underlain by bedrock at approximately 12 feet bgs. The site appears to have three separate hydrogeologic systems with a perched water table (upper aquifer), underlain by a another shallow aquifer (lower aquifer), and a bedrock aquifer. The depths to water range from 5 to 7, 13 to 16, and 39 to 43 feet bgs, in the respective hydrogeologic systems. A calculated hydraulic conductivity of 8.2 x  $10^{-5}$  cm/sec was

established for the upper aquifer. The ground water velocity for the upper aquifer is calculated to be approximately 1.5 ft/yr.

The geology beneath the Marshfield, Wisconsin site is predominantly sandy-clay. The depth to water at the site ranges from 24 to 29 feet bgs with a calculated hydraulic conductivity of 7.9 x  $10^{-5}$  cm/sec. The ground water velocity is calculated to be approximately 7.5 ft/yr.

Beneath the Highland Park, Illinois site, the near surface geology consists of predominantly clay and silty-clay. The depth to water at the site ranges from 2 to 6 feet bgs with a calculated hydraulic conductivity of  $1.4 \times 10^{-6}$  cm/sec. The ground water velocity is calculated to be approximately 0.2 ft/yr.

The near surface geology beneath the Broadview, Illinois site is also silty-clay with traces of sand and gravel. The depth to water at the site ranges from 3 to 6 feet bgs with a calculated hydraulic conductivity of  $5.2 \times 10^{-5}$  cm/sec. The ground water velocity is calculated to be approximately 1.2 ft/yr.

The near surface geology beneath the Chicago, Illinois site is predominantly backfill to approximately 7 feet bgs, underlain by sand to 12 feet bgs, and then silty-clay. The depth to water at the site ranges from 5 to 9 feet bgs with a calculated hydraulic conductivity of  $5.2 \times 10^4$  cm/sec. The ground water velocity is calculated to be approximately 7 ft/yr.

A summary of the geology and hydrogeology for the selected sites is presented on Table 1.

## **Ground Water Sampling and Analytical Methods**

To measure petroleum hydrocarbon constituents in ground water, wells were purged of five well volumes or until dry using a submersible pump. Ground water samples were collected with a disposable bailer and containerized in 40 milliliter vials containing hydrochloric acid (HCl) preservative. Ground water samples from the Wisconsin sites were submitted to Pace Analytical Services, Inc. (Pace) and analyzed for petroleum volatile organic compounds (PVOCs) by EPA Method 8020 and gasoline range organics (GRO) by the WDNR Modified GRO Method 8015. Ground water samples from the Illinois sites were submitted to Industrial & Environmental Analysts, Inc. (IEA) and analyzed for BTEX by EPA Method 8020.

#### **Biodegradation Parameters in Ground Water**

To evaluate the occurrence and rate of natural biodegradation, the measurement of site-specific environmental parameters is essential. During the study, various ground water parameters were measured, including petroleum hydrocarbon constituents, dissolved oxygen (DO), oxidation-reduction potential (ORP), pH, temperature, and conductivity. Following collection of the ground water sample that were sent for laboratory analysis, bioparameters were measured directly in the wells. DO and temperature were measured by a YSI MODEL 57 meter with MODEL 5739 probes, pH by a COLE-PARMER DIGISENSE meter, ORP by an ORION ORP probe, or an OAKTON MODEL 35650 tester, and conductivity by a YSI MODEL 33 meter.

#### Soil Gas Bioparameters

Other bioparameters such as oxygen ( $O_2$ ) and carbon dioxide ( $CO_2$ ) in soil were also measured for all seven sites. In addition, vapor phase methane ( $CH_4$ ) and volatile organic compounds (VOCs) were measured for the three sites in Illinois and for one site in Wisconsin (Marshfield) during several sampling events. Similar to measurement of bioparameters in groundwater, soil gas bioparameters were measured directly in the wells., soil gases  $O_2$ ,  $CO_2$ ,  $CH_4$ , and VOCs were measured for selected sites. A polyvinyl chloride (PVC) cap with an attached sampling tube was placed on a monitoring well, a low volume pneumatic diaphragm pump was used to purge the headspace for approximately five minutes, and soil gas was then collected into a tedlar bag which was later measured for  $O_2$  and  $CO_2$  by using a GASTECH 32500X. If  $O_2$  was depleted, a 10:1 air to sample dilution was used for the total VOCs (including  $CH_4$ ) reading. Soil gases  $CH_4$ and VOCs were measured by a FOXBORO OVA 128 meter. The actual VOCs were calculated by the difference between the total VOCs and  $CH_4$ . For  $CH_4$  analysis, a carbon filter was used to adsorb all hydrocarbons except  $CH_4$ .

## SITE SELECTION CRITERIA FOR USING NATURAL ATTENUATION

To determine whether these seven sites were appropriate for natural attenuation, a work plan was developed based on literature information <sup>(3,4,5,6,9,10,12,&14)</sup> as well as field screening experiences. Sites were selected based on (1) past history of BTEX compounds, (2) potential risk to receptors, and (3) availability of dissolved oxygen in background.

The data on the BTEX concentrations addresses the question of whether these sites had a potential for natural attenuation. According to the ASTM Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Sites<sup>2</sup> and U.S. EPA Directive 9200.4-17<sup>13</sup>, trends established from historical data are the primary line of evidence for natural attenuation, and measured petroleum hydrocarbon concentrations over time form the basis for defining the plume as shrinking, stable or expanding. For the purpose of this study, an initial pool of potential sites was established which met additional criteria such as whether the site was an inactive or active service station (a mixture was preferred), if dissolved BTEX concentrations were at a sufficient baseline level to track any decrease and whether any of the sites were undergoing regulatory enforcement action. Several sites in the available pool were considered suitable for natural attenuation because plumes were reasonably expected to continue to remain "low risk" sites and not adversely impact sensitive receptors. Background information on the selected sites is summarized in Table 1.

Remediation by natural attenuation depends upon not only biodegradation but also natural processes such as dilution, dispersion, sorption, volatilization, and so on. Due to the numerous processes involved, it was not practical to quantify the relative contribution of biodegradation with respect to other natural attenuation processes. The primary concern for site selection was the attenuation status and behavior of plume and the secondary concern was whether or not favorable

attenuation conditions existed at the sites. Nevertheless, natural attenuation is looked upon more favorably if the appropriate conditions for biodegradation exist in the subsurface.

Availability of dissolved oxygen in background was considered as one of the most important conditions for rapid biodegradation of compounds of concern. The stabilization and eventual shrinking of the plume edge can be anticipated due to relatively fast biodegradation rates under aerobic conditions as compared to anaerobic conditions. Since DO in background wells was above 0.7 milligrams per liter (mg/L) at all seven selected sites, an aerobic condition around the edge of the plumes was indicated. An oxygen level of above 0.7 mg/L has been selected as an indicator of aerobic condition, based on the study by Barker *et al.* <sup>(3)</sup>, in which benzene, toluene, and xylenes were observed to biodegrade at an initial DO of 0.5 mg/L or higher. The level of DO in the center of the plume was not considered to be as critical since anaerobic biodegradation will take place via other available electron acceptors, such as nitrate, sulfate, ferrous iron, and carbonates, when oxygen is absent <sup>(14)</sup>.

The results from the DO readings indicated that bioremediation was already occurring since the DO levels observed in the impacted wells were much lower than those in background, upgradient, or non-impacted wells<sup>(5)</sup>. Figure 1 indicates the relationship between average DO readings in ground water and a well's location to the plume center. Except at the Marshfield, Wisconsin site where there may be an off-site impact, a consistent correlation between DO and well location exists.

Other terminal electron acceptors or degradation indicators such as nitrate, sulfate, and iron, were not analyzed since the DO levels in background wells were above 0.7 mg/L, suggesting an aerobic zone around the edge of the plumes which aid in stabilizing and eventually shrinking the plumes. Nutrients such as nitrogen and phosphorus were not measured since addition of nutrients would not be expected to increase *in situ* biodegradation rates <sup>(1,7,8,9,&11)</sup>. Although bacterial counts were initially performed, this parameter is viewed as unnecessary for future sites because almost all petroleum release sites exhibit adequate bacterial counts. The pH measurement was performed at

these sites but is considered as an optional parameter since pH in a petroleum release site is generally between 5.5 and 8.5 which is considered as the optimal pH range <sup>(9)</sup>.

In short, the selected seven study sites were determined to be suitable for natural attenuation mainly based on receptor surveys, historic data trends on the compounds of concern, the availability of DO in background wells, and the fact that the primary sources of impact (tanks, dispensers, and/or lines) were removed and free product, if present, continued to be recovered until it was no longer present.

## PARAMETERS USED TO MONITOR NATURAL ATTENUATION

To determine a long-term cost-effective monitoring plan for natural attenuation, various bioparameters (in addition to compounds of concern and DO) were measured to evaluate their added benefits for demonstrating natural attenuation. The ground water bioparameters measured for selected sites included pH, ORP, temperature, and conductivity, and the soil bioparameters measured for selected sites included bacterial counts, soil gas O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub>, and VOCs. It should also be noted that additional site characterization took place at several sites during the course of the project to better define the extent of contamination. This included the advancement of soil borings, installation of monitoring wells and performance of vapor surveys in nearby utilities.

Analysis of bacterial counts was established initially and subsequently dropped as a routine parameter since other researchers in the field began to discount the usefulness of routine measurements due to abundance of bacteria observed at petroleum hydrocarbon sites. As far as soil gas data ( $O_2$ ,  $CO_2$ ,  $CH_4$ , and VOCs) are concerned, the results did establish consistent trends, and it was determined by the project team that further collection of these data was not warranted. Similarly, other parameters (such as pH, temperature, conductivity, and redox potential.) discussed above, although informative, did not provide significant insight to the effectiveness of natural attenuation at these sites. The important learning from this project was that a number of parameters measured initially did not prove to be much value added.

The best evidence that natural attenuation was appropriate and sufficient at these sites and that biodegradation was occurring was provided by an evaluation of the difference of the DO levels between impacted and background wells, change in the concentrations of chemicals of concern over time, decrease in the concentration of chemicals of concern along the groundwater direction, and the location of the plume edge in relation to receptors. Consistent with the ASTM Standard Guide for Remediation of Ground Water by Natural Attenuation at Petroleum Sites<sup>2</sup> and U.S. EPA Directive 9200.4-17<sup>13</sup>, this natural attenuation study results suggest that plume status is the primary line of evidence for reduction of constituents.

Over the years, other research has indicated that other terminal electron acceptors (TEAs) such as nitrate, iron, sulfate, manganese, etc. contribute to the biodegradation process and at some sites these other TEAs may be more significant than DO. Users of this report should determine if only measuring DO is adequate or if they need to also sample and analyze for other TEAs or other biological indicators.

#### TRENDS AND CORRELATION

Concord, Wisconsin site has been an inactive service station since 1988 with the USTs excavated in May 1989. At that time, approximately 300 cubic yards (yds<sup>3</sup>) of petroleum impacted soil was excavated and treated on-site by thin spreading. The occurrence of natural attenuation at the Concord, Wisconsin site (Appendix A, Figure A-1) was evident as the plume was reduced to the acceptable levels within three years. To illustrate this, estimated benzene isoconcentration maps for May 1993 and April 1996 sample events are presented on Figure A-2. In addition, benzene concentrations vs. time were plotted on a semi-log graph and the result is presented as Figure A-3. Historical data indicates that benzene concentrations have not been detected since February 1995. Offsite monitoring wells and a piezometer well were installed and monitored. The results indicated that plume adequately attenuated and did not migrate off-site and/or vertically. Closure of the site has been approved by the WDNR (July 17, 1996). A summary of the ground water analytical results and bioparameter measurements is presented in Table A-1.

At the Milwaukee, Wisconsin site (Appendix B, Figure B-1), the service station discontinued operations in 1992 after the removal of the USTs. At that time, no petroleum impacted soil was excavated. Historical data indicates the benzene concentrations have decreased over time. Monitoring well OW-4, located adjacent to the former tank basin, is the only well of significant concern with relatively high concentrations of benzene (Figure B-4). An MTBE plume has proceeded ahead of the BTEX plume as indicated by the analytical data from down-gradient monitoring wells MW-13 and MW-14. Since MTBE levels are only slightly above Wisconsin Ground Water Standards, additional wells were not installed to assess plume migration. Estimated benzene isoconcentration maps are presented as Figure B-2 and an estimated MTBE isoconcentration map is presented as Figure B-3. Ground water analytical results and bioparameter measurements are summarized in Table B-1.

Before starting the use of natural remediation at the active Hales Corners, Wisconsin site (Appendix C, Figure C-1), the site had undergone active remediation with soil vapor extraction and ground water recovery and treatment. However, because of the complex geology of the site, the system proved to be ineffective and was discontinued. The natural attenuation progress after shutting down soil vapor extraction was most evident by the benzene concentration change over time, indicating a stable or shrinking plume (Figure C-2). The plume is concentrated predominantly in the upper aquifer which is composed of clay and will greatly limit migration of ground water impacts to potential receptors. Figure C-3 illustrates benzene concentration change over time at the site. A summary of ground water analytical and bioparameter results are in Table C-1.

At the Marshfield, Wisconsin site (Appendix D, Figure D-1), the effectiveness of natural attenuation could not be adequately assessed due to the possibility of impact by an off-site source. The service station discontinued operations in December 1988 and the removal of the USTs occurred in June 1989. At that time, approximately 400 yds<sup>3</sup> of petroleum impacted soil was excavated and

treated on-site by thin spreading. Negotiations have occurred between the WDNR and the neighboring responsible party to allow Amoco access to the off-site property to collect indicator data. Ground water analytical results and bioparameter measurements are summarized in Table D-1 and Table D-2.

The effectiveness of natural attenuation at the active Highland Park, Illinois site (Appendix E, Figure E-1) was apparent by the benzene concentration change over time (Figure E-2). A stabilized plume is evident at the site. A down-gradient, off-site monitoring well (MW-17) verifies that the plume stabilizes due to natural attenuation and not off-site and/or vertical migration. To illustrate this, estimated benzene isoconcentration maps are presented on Figure E-3. Bioparameter results and ground water analytical results are summarized in Table E-1 and Table E-2, respectively.

A stable plume is also evident at the Broadview, Illinois site (Appendix F, Figures F-1 and F-2) which discontinued operation as a service station in November 1987. The USTs were excavated in February 1988. Since January 1993, benzene concentrations have remained stable or slightly decreased. However, a minor impact appeared off-site. To locate and assess the potential of petroleum hydrocarbons in off-site utilities, manholes, and grates, a receptor survey was performed. Hydrocarbons were not detected in any of the utilities surrounding the site. Figure F-3 illustrates benzene concentration change over time at the site. Bioparameter measurements and ground water analytical results are summarized in Table F-1 and Table F-2, respectively.

At the Chicago, Illinois site (Appendix G, Figure G-1), benzene has been stable at low concentrations. Minor impacts exist adjacent to the former and existing UST basins, as indicated on Figure G-2. Semi-log plots of benzene concentrations over time are presented on Figure G-3. The trend of BTEX compounds over time was found to be the best evidence for demonstrating the appropriateness and effectiveness of natural attenuation. Bioparameter measurements and ground water analytical results and bioparameter measurements are summarized in Table G-1 and Table G-2. This site was somewhat complicated by the fact that it is an active service station and some of the concentration fluctuations could be attributed to small spills near the dispenser islands from motorists

refueling their vehicles. At other sites where natural attenuation is being considered in the future, this aspect should be considered.

To further assess the occurrence and appropriateness of natural attenuation, a number of correlation were attempted to derive possible connections between bioparameters (such as DO, ORP, pH etc.) and BTEX concentrations (Appendix H). Bioparameters were also plotted against other bioparameters (e.g. DO vs. ORP). In addition, water elevations and the effect they may have on BTEX concentrations or bioparameter measurements was analyzed.

No significant trends or correlations were derived when comparing bioparameters DO, ORP, and pH with BTEX concentrations (See Figures in Appendix H). Further, nothing significant was derived from ORP and DO comparison.

As previously mentioned, the trend of BTEX compounds over time was found to be the best evidence for demonstrating the appropriateness and effectiveness of natural attenuation. Table 2 is a summary of whether benzene concentrations in individual monitoring wells are increasing, decreasing, or stable. As seen from the table, the benzene concentration in down-gradient and side wells stabled or decreasing while the benzene concentration in the impacted wells declined. In general, it can be concluded that the benzene plumes in all seven sites are either stable or shrinking, providing evidence of natural attenuation.

Table 3 is a summary of the first-order benzene natural attenuation rates estimated using analytical data from selected monitoring wells. As seen from the table, the first-order benzene attenuation rates ranged from 0.05% to 0.82%.

The Wisconsin DNR has had ground water standards for MTBE for several years and has required that this parameter be measured. Since MTBE has not been added to petroleum based fuels at high levels in Wisconsin, MTBE in ground water has not been a serious issue in the state. For example, the Milwaukee site may have a low level MTBE plume extending off site. Since the MTBE level are only slightly above Wisconsin Standards in downgradient wells, benzene concentrations in the source area at that site is a much greater concern than low level MTBE that may migrate off site. MTBE's natural attenuation characteristics may be quite different than natural attenuation characteristics for other BTEX compounds. Therefore the conclusions in this report may not be applicable to sites in other state where MTBE is present at high levels.

## CONCLUSIONS

Without any effective active remedial systems, petroleum hydrocarbon plumes at the selected service stations have decreased, stabilized, or dissipated due to natural attenuation processes. As indicated by the different values of biological parameters found in the impacted area compared to background measurements, the plume's shrinking, stabilizing, or disappearing could be attributed in part to biological degradation.

One way to demonstrate the occurrence and appropriateness of natural attenuation with respect to the adequate protection to human health and the environment is to examine the plume status combined with a receptor survey. Among various biological indicators, the dissolved oxygen measurement alone may be sufficient at most sites since the purpose of monitoring is not to identify and quantify all the biological mechanisms underneath a site, but rather to verify that biological degradation is contributing to the overall natural attenuation of a plume. As indicated above, when the number of the bioparameters measured increases, cost effectiveness of natural attenuation may be reduced.

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#### DISCLAIMER

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Site No.	Location	Reported Release Date	Geology	Depth to Water	Average Hydraulic Conductivity	Average Hydraulic Gradient	Ground Water Velocity	LPH Presen t	Highest Historic Benzene Concentration	Highest Benzene Concentratio n (1996)	Potential Receptors
1*	Concord, WI	2/89	Silty and sandy clay	8 to 11 feet bgs	3.1 x 10 <sup>-3</sup> cm/sec	0.0014 ft/ft	10 ft/yr	No	300 µg/L (9/93)	<1.0 µg/L (4/96)	No
2	Milwaukee, WI	2/92	Clay and silty clay	11 to 16 feet bgs	9.5 x 10 <sup>-5</sup> cm/sec	0.03 ft/ft	3 ft/yr	No	24,000 µg/L (11/94)	17,000 μg/L (3/96)	No
3	Hales Corners, WI	11/89	Clay underlain by bedrock at approx. 12 feet bgs	Upper aquifer: 5-7 ft bgs Lower aquifer:13-16 ft bgs Bedrock aquifer: 39-43 ft bgs	8.2 x 10 <sup>-5</sup> cm/sec (upper aquifer)	0.017 ft/ft (upper aquifer)	1.5 ft/yr (upper aquifer)	See notes**	8,600 µg/L (2/91)	1,800 µg/L (3/96)	No
4	Marshfield, WI	6/89	Sandy clay	24 to 29 feet bgs	7.9 x 10 <sup>-5</sup> cm/sec	0.03 ft/ft	7.5 ft/yr	No	12,000 µg/L (5/94)	10,000 µg/L (6/96)	No
5	Highland Park, IL	9/89	Clay and silty clay	2 to 6 feet bgs	1.4 x 10 <sup>-6</sup> cm/sec	0.10 ft/ft	0.2 ft/yr	No	4,070 µg/L (1/90)	3,200 μg/L (12/96)	No
6	Broadview, IL	6/91	Silty clay with traces of sand and gravel	3 to 6 feet bgs	5.2 x 10 <sup>-5</sup> cm/sec	0.08 ft/ft	1.2 ft/yr	No	5,600 μg/L (10/93)	3,600 μg/L (12/96)	No
7	Chicago, IL	6/92	0-7 ft: backfill 7-12 ft: sand 12-14 ft: silty clay	5 to 9 feet bgs	5.2 x 10 <sup>-4</sup> cm/sec	0.004 ft/ft	7 ft/yr	No	2,000 μg/L (11/92)	96 µg/L (3/96)	No

# Table 1.Geology, Hydrogeology, and background Information of the Selected Study Sites.

Notes:

bgs = below ground surface

cm/sec = centimeter p	er second
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ft/ft = feet per foot

ft/yr = feet per year

LPH = liquid-phase hydrocarbons

µg/L = micrograms per liter

\* = Site closed by State of Wisconsin

\*\* = Liquid-phase hydrocarbons present in GMOW-1S on 6/8/95 and 9/14/95.

 Table 2. Stability of Benzene Concentrations in Individual Monitoring Wells.

	Up-gradient Wells	Side-gradient Wells	Impacted Wells	Down-gradient Wells
Concord, WI	MW-1 (0), MW-9 (0), MW-13 (0)	MW-5 (0), MW-8 (0), MW-11 (0), MW-12 (0)	MW-3 (0), MW-4 (-), MW-6 (0)	MW-7 (0), MW-10 (0), MW-14 (0)
Milwaukee, WI	OW-1 (0), OW-5 (0), GMOW-12 (0)	OW-10 (0)	OW-4 (0)	OW-6 (0), OW-7 (0), GMOW-8 (0), GMOW-9 (0), GMOW-11 (0), MW-13 (0), MW-14 (0)
Hales Corners, WI	OW-1 (0), OW-6 (0), GMOW-2S (0), GMOW-6D (0)	OW-5 (0), GMOW- 2S (0), GMOW-5D (0)	GMOW-1S (-), GMOW-1D (-)	OW-2 (-), GMOW-3S (-), GMOW-3D (0), GMOW-4D (0), GMOW-8D (0)

Marshfield, WI	MW-10 (0)	MW-4 (0)	MW-8 (0), MW-9 (0), MW-12 (0), MW-13 (0)	MW-6 (0), MW-14*
Highland Park, IL	MW-7 (0), MW-9 (0), MW-10 (0),	MW-16 (0)	MW-1 (0), MW-3 (-), MW-14 (0), MW-15 (-), SVE (-)	MW-4 (0), MW-17 (0)
Broadview, IL	MW-6 (0), MW-8 (0), MW-9 (0)	MW-3 (0), MW-10 (- ), MW-11 (0)	MW-2 (0), MW-5 (-), MW-7 (0)	MW-12 (0)
Chicago, IL	MW-1 (0), MW-2 (-), MW-6 (0)	MW-5 (0), RW-2 (-), RW-3 (-)	MW-3 (-), RW-1 (0)	MW-4 (0)

# Notes:

- + = increasing
- = decreasing
- 0 = no change
- \* = only 1 sampling event

Source of Data	First-Order Rate	Half Lives	R-square of Fit	
	Constant Estimated	(days)		
MW-3 in Concord WI	0.16%	430	65.0%	
MW-4 in Concord WI *	0.20%	350	44.6%	
GMOW-1S in Hales Corners WI *	0.11%	630	30.0%	
GMOW-3S in Hales Corners WI	0.13%	580	24.3%	
OW-6 in Hales Corners WI	0.16%	430	23.0%	
MW-3 in Broadview IL	0.17%	410	36.5%	
MW-5 in Broadview IL	0.28%	250	40.0%	
MW-10 in Broadview IL	0.12%	560	16.1%	
MW-2 in Chicago IL	0.82%	85	53.2%	
MW-3 in Chicago IL *	0.20%	350	61.8%	
RW-3 in Chicago IL	0.17%	410	46.2%	
MW-14 in Highland Park IL	0.27%	260	33.9%	
MW-15 in Highland Park IL *	0.05%	1390	35.9%	
MW-16 in Highland Park IL	0.13%	530	49.4%	

## Table 3. Summary of First-Order Natural Attenuation Rate Estimate for Benzene

Note:

(1). Wells marked with an asterisk (\*) are source area wells.

(2). No data are included in the above table for wells that indicated negative degradation rates.

(3). Graphs that illustrate the estimation for these first-order rates are included in Appendix I.