



## Evaluation of natural attenuation rate at a gasoline spill site

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### Abstract

Contamination of groundwater by gasoline and other petroleum-derived hydrocarbons released from underground storage tanks (USTs) is a serious and widespread environmental problem. Natural attenuation is a passive remedial approach that depends upon natural processes to degrade and dissipate contaminants in soil and groundwater. Currently, in situ column technique, microcosm, and computer modeling have been applied for the natural attenuation rate calculation. However, the subsurface heterogeneity reduces the applicability of these techniques. In this study, a mass flux approach was used to calculate the contaminant mass reduction and field-scale decay rate at a gasoline spill site. The mass flux technique is a simplified mass balance procedure, which is accomplished using the differences in total contaminant mass flux across two cross-sections of the contaminant plume. The mass flux calculation shows that up to 87% of the dissolved total benzene, toluene, ethylbenzene, and xylene (BTEX) isomers removal was observed via natural attenuation at this site. The efficiency of natural biodegradation was evaluated by the in situ tracer method, and the first-order decay model was applied for the natural attenuation/biodegradation rate calculation. Results reveal that natural biodegradation was the major cause of the BTEX mass reduction among the natural attenuation processes, and approximately 88% of the BTEX removal was due to the natural biodegradation process. The calculated total BTEX first-order attenuation and biodegradation rates were 0.036 and 0.025% per day, respectively. Results suggest that the natural attenuation mechanisms can effectively contain the plume, and the mass flux method is useful in assessing the occurrence and efficiency of the natural attenuation process. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Natural attenuation; Groundwater contamination; Natural biodegradation; Mass flux

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## 1. Introduction

Accidental releases of petroleum products from underground storage tanks (USTs) are one of the most common causes of groundwater contamination. There are currently about 3 million USTs storing petroleum products in US, and as many as 500,000 may be leaking petroleum into the ground [1]. Current attention is focused on human and environmental safety, concerning the release of hydrocarbons to the environment. Petroleum hydrocarbons contain benzene, toluene, ethylbenzene, and xylene (BTEX) isomers, the major components of fuel oils (especially gasoline), which are hazardous substances regulated by many nations. In addition to BTEX, other gasoline constituents such as methyl-*t*-butyl ether (MTBE), naphthalene, 1,3,5-trimethylbenzene (1,3,5-TMB), and 1,2,4-trimethylbenzene (1,2,4-TMB) are also toxic to humans.

Field investigation suggests that many of these spills naturally biodegrade before contaminants reach a drinking water receptor [2,3]. Natural attenuation is a passive remedial approach that depends upon natural processes to degrade and dissipate contaminants in soil and groundwater. Natural attenuation processes include physical, chemical, and biological transformation (e.g. aerobic/anaerobic biodegradation, cometabolism, dispersion, volatilization, oxidation, reduction, and adsorption) [2,4–6]. Aerobic and anaerobic biodegradation are believed to be the major processes that account for both containment of the petroleum–hydrocarbon plume and reduction of the contaminant concentrations. Aerobic biodegradation relies on dissolved oxygen (DO) as the electron acceptor used by the subsurface microorganisms. Anaerobic processes refer to a variety of biodegradation mechanisms that use nitrate, ferric iron [Fe(III)], sulfate, and carbon dioxide (CO<sub>2</sub>) as terminal electron acceptors [7–11].

Currently, mathematical model application, in situ column technique, microcosm study, and contaminant concentration analysis are the commonly used tools to assess the occurrence and rates of natural attenuation. However, those techniques are unreliable and site-specific. At some UST sites, the attenuation rates estimated by laboratory techniques were one to two orders of magnitude greater than the field rates [9,10]. Therefore, incorporation of natural attenuation in mathematical model and its use in regulatory decision-making are still difficult, because there are no accepted methods to quantitatively estimate the petroleum–hydrocarbon degradation rate via natural attenuation process. To increase the ability to understand and predict contaminant fate and transport during natural attenuation processes, a more reliable and appropriate method for natural attenuation rate calculation is required.

In this study, a gasoline spill site was selected to fulfill the following objectives: (1) assess the feasibility of applying the in situ mass flux technique to study the occurrence of natural attenuation and its effects on plume contaminant; (2) calculate the BTEX mass flux and field-scale decay rate; (3) calculate natural biodegradation rate using the in situ tracer technique and (4) evaluate the effects of using natural attenuation as a remedial option.

## 2. Study site

A gasoline spill site (UST site) located in Wagram, NC, USA was selected for this natural attenuation rate study. At this site, the Cretaceous Middendorf formation occurs

beneath a thin veneer of Holocene sands and humic soils. Middendorf formation consists of intercalating, lensing, thick-bedded, light-colored sands and clays with local concentrations of clay–clast conglomerates [12]. In 1994, Geopex Ltd. started a site characterization at this UST site. Soil and groundwater samples were collected using the push technology (Geoprobe™ Technique). The contaminant plume was determined using the analytical results (data not shown). The boring log data show that the surficial aquifer sediments are a relatively uniform sand to sandy loam (silty sand) from water table to a depth of approximately 10 m. Depth to the seasonal high water table is approximately 1.2 m, and the groundwater flow direction is southeast. According to the results from hydrogeologic tests, the average hydraulic conductivity of the host geologic material was 0.48 m per day, and the calculated groundwater flow velocity was 6.2 m per year. Fig. 1 presents the site map showing the former UST pit, groundwater flow direction, and the monitoring system.

### 3. Materials and methods

For this gasoline spill site, the following activities were conducted: (1) installation of four monitor wells (MW1, MW2, MW3, and MW4) along the contaminant transport path and one monitor well (MW5) at the uncontaminated area for groundwater sampling and analysis; (2) mass flux calculation for three cross-sections perpendicular to the BTEX plume and (3) natural attenuation/biodegradation rate calculation for each BTEX component.

#### 3.1. Monitor well installation and groundwater analysis

Monitor wells MW1, MW2, MW3, MW4, and MW5 were located at the spill location (source area), mid-plume area, downgradient area, plume edge, and background area, respectively. All wells were screened approximately from 1.5 to 4.6 m below land surface (bls). Locations of the monitor wells are shown on the site map (Fig. 1).

Groundwater samples from monitor wells were collected and analyzed quarterly during the 2-year study period. Collected groundwater samples were analyzed for organic compounds and geochemical indicators including BTEX, methane (CH<sub>4</sub>), CO<sub>2</sub>, inorganic nutrients, anions, ferrous iron [Fe(II)], pH, redox potential (Eh), DO, and total organic carbon (TOC). Organic compound analyses were performed in accordance with US EPA method 602, using a Tekmer purge-and-trap model LSC 2000 with a Perkin-Elmer model 9000 auto system gas chromatograph (GC). Methane was analyzed on a Shimadzu GC-9A GC using headspace techniques. Ion chromatography (Dionex) was used for inorganic nutrients and anions (NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>) analyses. Perkin-Elmer plasma II inductively coupled plasma–argon emission spectrometer (ICP–AES) was used for Fe(II) analyses following standard methods [13]. TOC was analyzed by a total carbon analyzer (Shimadzu). DO, Eh, pH, CO<sub>2</sub>, and temperature were measured in the field. An Accumet 1003 pH/Eh meter (Fisher Scientific) was used for pH and Eh measurements, an Orion DO meter (model 840) was used for DO and temperature measurements, and a Hach digital titrator cartridge was used for CO<sub>2</sub> measurements [2,3,10].

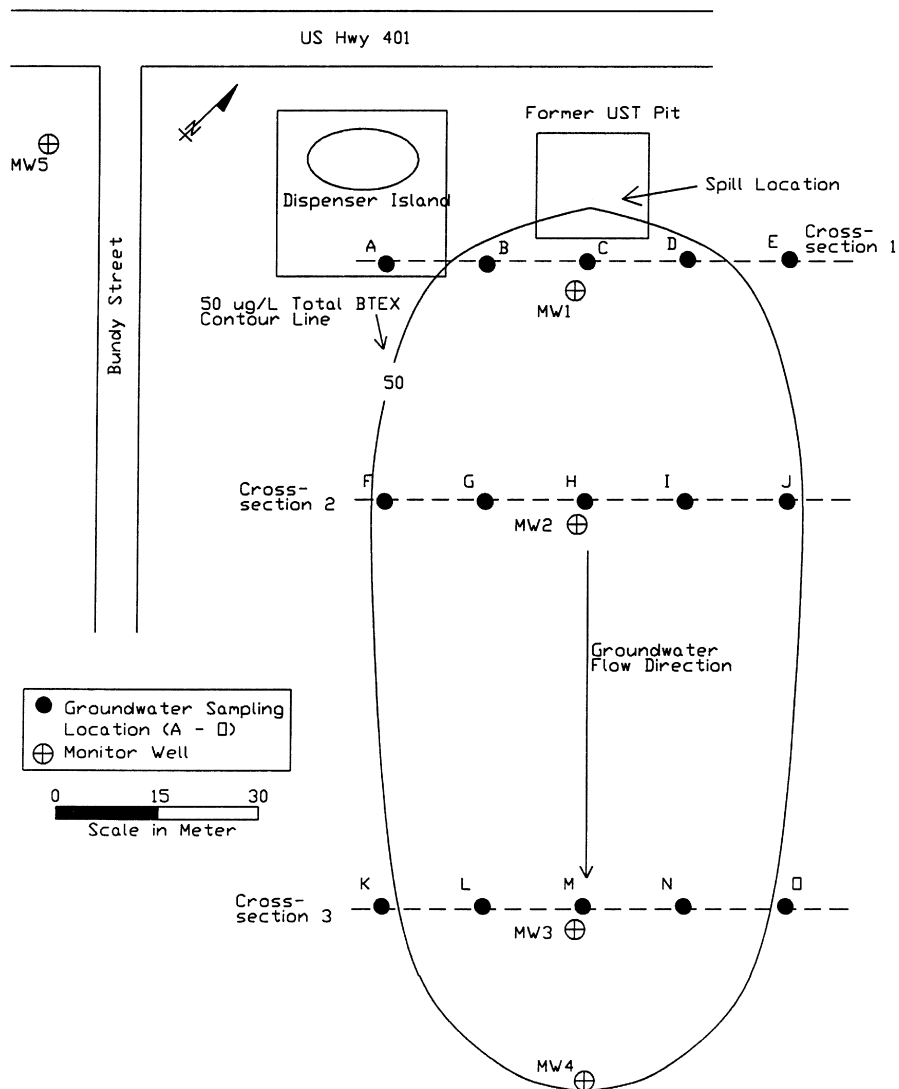


Fig. 1. Site map showing the former UST pit, groundwater flow direction, and monitoring system.

### 3.2. Mass flux and natural attenuation rate calculation

A simplified mass balance procedure was accomplished using the differences in total contaminant mass flux across two cross-sections of the contaminant plume. The total mass flux of contaminant through a cross-section of the plume can be defined by the following equation.

$$F_i = 1000C_i A_i v \quad (1)$$

where  $F_i$  is the total contaminant mass flux ( $\mu\text{g}$  per day) at cross-section  $i$ ;  $C_i$  the contaminant concentration ( $\mu\text{g/l}$ ) at cross-section  $i$ ;  $A_i$  the effective concentration area ( $\text{m}^2$ ) at cross-section  $i$ ;  $v$  the groundwater flow velocity (m per day).

Mass flux equation was also applied to the first-order decay model. The following relationship describes contaminant decay (natural attenuation) in terms of the difference in total mass flux across two cross-sections of the contaminant plume.

$$F_x = F_0 \exp(-Kt) \quad (2)$$

where  $F_x$  is the total mass flux ( $\mu\text{g}$  per day) for a cross-section at distance  $x$  (m);  $F_0$  the total mass flux ( $\mu\text{g}$  per day) at source;  $K$  the first-order decay rate (natural attenuation rate) (per day);  $t$  the hydraulic residence time (day) distance between two cross-sections/ $v = x/v$ .

A simple method of measuring the distribution of mass over an area is given by the Thiessen polygon technique commonly used in hydrologic studies [2,14,15]. In this study, three cross-sections perpendicular to the groundwater flow direction were selected along the plume (cross-sections 1, 2, and 3) (Fig. 1). These three cross-sections were located at the source area (cross-section 1, A–E), 35 m downgradient from the cross-section 1 (cross-section 2, F–J), and 95 m downgradient from the cross-section 1 (cross-section 3, K–O). Sampling locations at each cross-section were advanced at a distance of 15 m interval. For cross-sections 1–3, sampling locations were A–E, F–J, and K–O, respectively (Fig. 1). Therefore, a total of 15 sampling locations were determined. Sampling locations C, H, and M were located along the longitudinal centerline of the BTEX plume.

For each sampling location, groundwater samples from four designated depths were collected at 1.8–2.4, 3.6–4.2, 5.4–6, and 7.2–7.8 m bls to represent the contaminant distribution vertically. Instead of installing monitor wells or multilevel samplers for discrete groundwater sampling, groundwater samples from designated depths (1.8–2.4, 3.6–4.2, 5.4–6, and 7.2–7.8 m bls) at each location were collected using the push technology (Geoprobe™ Technique). A total of 60 discrete groundwater samples (from 15 sampling locations and 60 sampling points) were collected in 2 consecutive days.

Fig. 2 presents the schematic diagram showing the five sampling locations (A, B, C, D, and E), discrete sampling points, and the 20 designated polygons for cross-section 1. The discrete sampling point was the midpoint of each defined polygon. The sample collected from each point gave the average contaminant concentration passing through the polygon. Therefore, the mass flux for each sampling location was the sum of the four polygons. For example, sampling location A represented the sum for A1, A2, A3, and A4. The mass flux for each individual polygon was calculated, and the total mass flux for the cross-section was given from the sum of the 20 polygons. Fig. 3 presents the cross-section along the longitudinal transect through the BTEX plume. Results from the preliminary site assessment study indicate that the subsurface formation is relatively homogeneous although some micro-scale heterogeneity might occur. Thus, a homogeneous site was assumed in this study.

### 3.3. Biodegradation rate calculation

To determine what percentage of observed decrease in BTEX concentrations was attributed to biodegradation, measured BTEX concentrations must be corrected for the

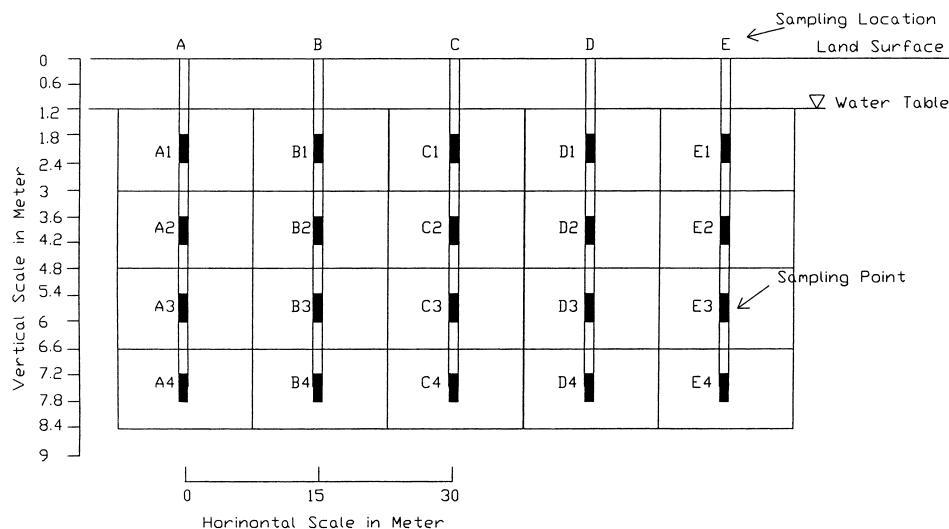


Fig. 2. Schematic diagram showing the sampling locations, discrete sampling points, and the designated polygon for cross-section 1.

effects of dispersion, dilution from the recharge, volatilization, and sorption. In this study, 1,2,4-TMB was used as a tracer to calculate the loss of BTEX through biodegradation because: (1) it has similar physical and chemical characteristics to BTEX and (2) it is recalcitrant to biodegradation [16,17].

BTEX concentrations from two cross-sections were applied in the calculation. The following equation (Eq. (3)) was used to calculate the corrected BTEX mass flux that would be expected at cross-section 2, located downgradient of cross-section 1, after correcting for the effects of dispersion, dilution, volatilization, and sorption between two cross-sections.

$$C_{2,\text{corr}} = C_2 \frac{\text{TMB}_1}{\text{TMB}_2} \quad (3)$$

where  $C_{2,\text{corr}}$  is the corrected BTEX mass flux ( $\mu\text{g}$  per day) at cross-section 2 due to biodegradation only;  $C_2$  the measured BTEX mass flux ( $\mu\text{g}$  per day) at cross-section 2 due to the effects of biodegradation and physical/chemical processes;  $\text{TMB}_1$  the measured 1,2,4-TMB mass flux ( $\mu\text{g}$  per day) at cross-section 1;  $\text{TMB}_2$  the measured 1,2,4-TMB mass flux ( $\mu\text{g}$  per day) at cross-section 2 due to the effects of physical/chemical processes.

Theoretically,  $C_1$  (measured BTEX mass flux at cross-section 1) dropped to  $C_{2,\text{corr}}$  due to the biodegradation process between cross-sections 1 and 2.  $C_{2,\text{corr}}$  dropped to  $C_2$  due to the effects of physical and chemical processes (e.g. dispersion, dilution, volatilization, and sorption). Thus, the following simplified equation can be developed to describe the relationship between  $C_{2,\text{corr}}$  and  $C_2$ .

$$\frac{C_2}{R} = C_{2,\text{corr}} \quad (4)$$

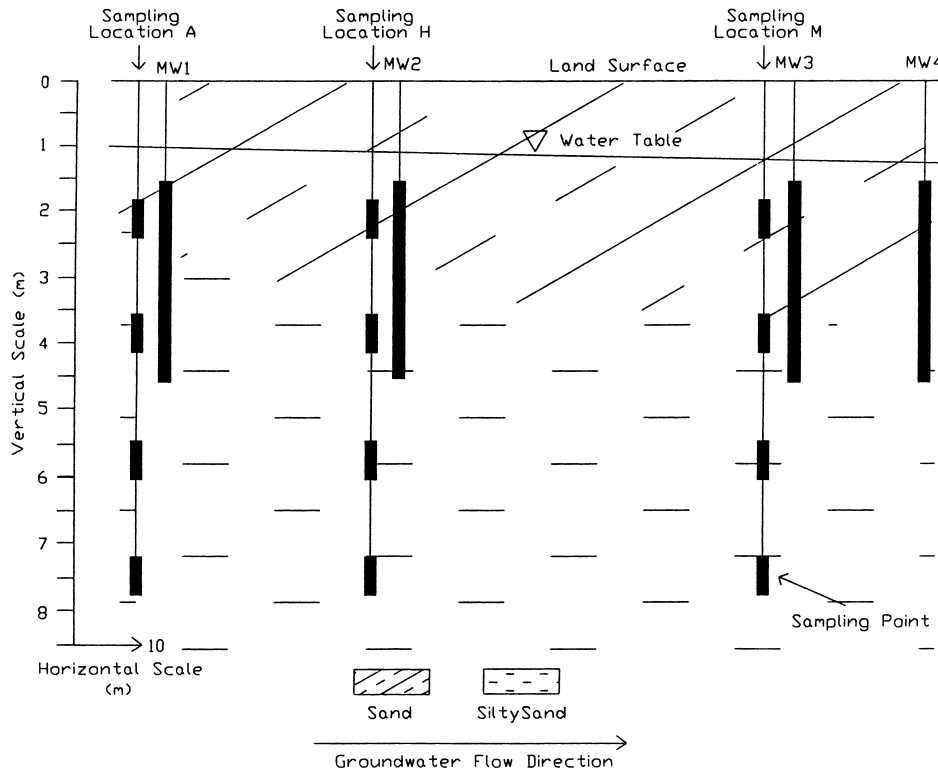


Fig. 3. Cross-section along the longitudinal transect through the BTEX plume.

where  $R$  is the residual ratio due to the physical/chemical processes, and  $R = 1 - \text{percentage of BTEX removal via physical/chemical processes}$ .

In this study, the residual ratio  $R$  was assumed to be  $TMB_2/TMB_1$ . Therefore, Eq. (3) was developed to calculate the corrected BTEX mass flux that would be expected at cross-section 2. The percent lost due to biodegradation can be calculated by the following equation.

$$\% = \frac{C_1 - C_{2,corr}}{C_1 - C_2} \times 100 \tag{5}$$

where  $C_1$  is the measured BTEX mass flux ( $\mu\text{g}$  per day) at cross-section 1.

Based on the calculated percent loss due to biodegradation, the order of preferential removal of certain BTEX components can be determined. Moreover, Eq. (2) can be applied to estimate the first-order biodegradation rate using the corrected BTEX mass flux. Therefore

$$C_{2,corr} = C_1 \exp(-K_b t) \tag{6}$$

where  $K_b$  is the first-order biodegradation rate (natural biodegradation rate) (per day). Therefore,  $K$  and  $K_b$  obtained from Eqs. (2) and (5), respectively, can be used to describe the effects and correlations between natural attenuation and natural biodegradation.

## 4. Results and discussion

### 4.1. Groundwater analysis from monitor wells

Based on the groundwater analytical results, the dissolved petroleum hydrocarbons are being transported from the spill location to the downgradient area. The front edge of the plume was approximately at 115 m downgradient from MW1 (Fig. 1). BTEX results indicate the existence of nonaqueous phase liquid (NAPL) hydrocarbons beneath the former spill location. The dissolved BTEX are being continuously released from NAPL into the groundwater, causing the stable BTEX concentrations in MW1 within the investigation period.

Table 1 presents the averaged analytical results for groundwater samples collected from five monitor wells. Investigation results indicate the occurrence of the anaerobic conditions within the plume. Compared to MW1 and MW2, the downgradient monitor wells MW3 and MW4 contained higher O<sub>2</sub> concentrations (up to 2 mg/l). This indicates that the downgradient edge of the plume was under the oxidized stage and aerobic biodegradation was the dominant biodegradation process within that area.

The decline in Eh within the plume reflects the change from oxidizing to reducing conditions. The increased CH<sub>4</sub> (up to 158 mg/l) and CO<sub>2</sub> (up to 311 mg/l) concentrations and decreased pH (pH = 5.2 in MW1) suggest that the methanogenesis was the dominant biodegradation process within the most contaminated zone. Nitrite and sulfide were not detected, and only trace level of nitrate, sulfate, and Fe(II) concentrations were detected (0–8 mg/l). The low nitrate, nitrite, sulfate, sulfide, and Fe(II) concentrations reveal that

Table 1  
Laboratory analytical results for five monitor wells

	MW1	MW2	MW3	MW4	MW5
Location	Source zone	Mid-plume	Downgradient	Plume edge	Background
Distance to MW1 (m)	0	35	95	115	NA <sup>a</sup>
Benzene (μg/l)	5892 ± 722	4498 ± 641	351 ± 129	22 ± 15	<0.5
Toluene (μg/l)	3201 ± 298	2091 ± 228	86 ± 23	5 ± 1	<0.5
Ethylbenzene (μg/l)	989 ± 177	785 ± 86	92 ± 27	15 ± 5	<0.5
<i>m</i> + <i>p</i> -Xylene (μg/l)	1344 ± 321	974 ± 144	43 ± 25	8 ± 2	<0.5
<i>o</i> -Xylene (μg/l)	1036 ± 226	841 ± 154	102 ± 31	11 ± 3	<0.5
TOC (mg/l)	16 ± 2	15 ± 2	6 ± 1	6 ± 1	2 ± 1
BTEX as C/TOC	0.7	0.56	0.1	0.09	NA
pH	5.2 ± 0.6	5.3 ± 0.5	5.5 ± 0.6	5.6 ± 0.7	6.1 ± 0.4
DO (mg/l)	0	0.1 ± 0.1	0.9 ± 0.2	2 ± 0.8	3.5 ± 1.1
Eh (mV)	−132 ± 22	−76 ± 17	82 ± 21	128 ± 34	347 ± 41
Nitrate as N (mg/l)	<0.1	<0.1	<0.1	<0.1	3 ± 1
Nitrite as N (mg/l)	<0.1	<0.1	<0.1	<0.1	<0.1
Ferrous iron (mg/l)	6 ± 2	8 ± 2	5 ± 1	2 ± 1	<0.01
Sulfide as S (mg/l)	<0.1	<0.1	<0.1	<0.1	<0.1
Sulfate as S (mg/l)	<0.1	<0.1	2 ± 1	2 ± 1	4 ± 2
CO <sub>2</sub> (mg/l)	311 ± 54	209 ± 38	165 ± 26	93 ± 37	43 ± 15
Methane (mg/l)	158 ± 37	127 ± 23	69 ± 17	16 ± 5	<0.2

<sup>a</sup> NA, not available.



Table 2

Calculated mass flux and percentage of mass removal for each compound through different cross-sections via natural attenuation process

Cross-section	Benzene (mg per day)	Toluene (mg per day)	Ethyl-benzene (mg per day)	<i>m + p</i> -Xylene (mg per day)	<i>o</i> -Xylene (mg per day)	1,2,4-TMB (mg per day)	Total BTEX (mg per day)
1	15263	7558	2146	2566	2350	1607	29883
2	8769	3258	1463	1392	1812	1398	16694
3	1970	257	378	218	486	888	3309
(1–2)/1% <sup>a</sup>	43	57	32	46	23	13	44
(2–3)/1%	45	40	51	46	56	32	45
(1–3)/1%	87	97	82	91	79	45	89

<sup>a</sup> [(Mass in cross-section 1 – mass in cross-section 2)/(mass in cross-section 1)] × 100%.

denitrification, sulfate reduction, and iron reduction were not the dominant biodegradation patterns within the plume. The declined BTEX as carbon to TOC ratio along the transport path reveals that total BTEX caused the high TOC measurements near the source area (Table 1). The decrease in the BTEX to TOC ratio suggests an increase of BTEX degradation by-products along the transport path, and also suggests the occurrence of natural biodegradation.

#### 4.2. Mass flux and natural attenuation rate calculation along the BTEX plume

Discrete groundwater samples were collected from a total of 15 sampling locations (locations A–O) for the mass flux calculation, and each sampling location composed of four sampling points (1–4). The total contaminant mass flux across each cross-section was computed as the sum of the mass flux for all polygons in that cross-section (Figs. 1 and 2). Table 2 presents the calculated total mass flux of individual BTEX and 1,2,4-TMB in cross-sections through the plume. Based on the mass flux results, 43% of the total BTEX was removed between cross-sections 1 and 2, and 44% of the BTEX was removed between cross-sections 2 and 3. This suggests that natural attenuation played an important role on contaminant removal.

The calculated first-order decay rates (natural attenuation rates) for BTEX between cross-sections 1–2, 2–3, and 1–3 are presented in Table 3. The total BTEX decay rate was 0.036% per day between cross-sections 1 and 3. Results show that toluene was the most quickly degraded compound in BTEX (up to 0.072% per day between cross-sections 2 and 3), followed by *m + p*-xylene, benzene, ethylbenzene, and *o*-xylene (Table 3). Compared to BTEX, 1,2,4-TMB had lower decay rates.

Table 3

Calculated first-order natural attenuation rate for each compound between cross-sections

Cross-section	Benzene (% per day)	Toluene (% per day)	Ethyl-benzene (% per day)	<i>m + p</i> -Xylene (% per day)	<i>o</i> -Xylene (% per day)	1,2,4-TMB (% per day)	Total BTEX (% per day)
1–2	0.027	0.041	0.019	0.03	0.013	0.007	0.028
2–3	0.042	0.072	0.038	0.053	0.037	0.013	0.046
1–3	0.037	0.061	0.031	0.044	0.028	0.011	0.039

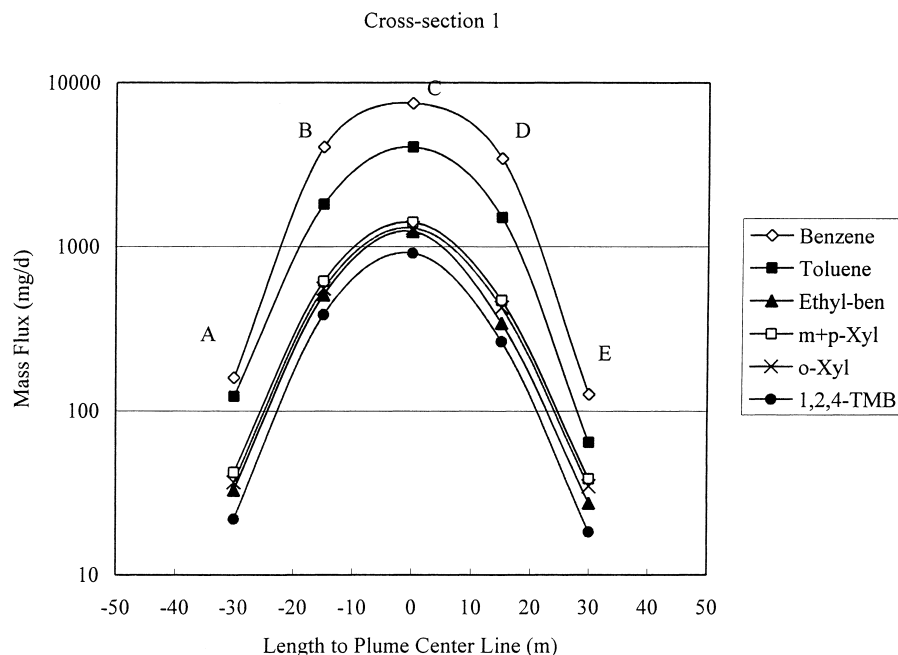


Fig. 4. Calculated mass flux results for five sampling locations along cross-section 1.

Figs. 4–6 present BTEX mass flux in cross-sections 1–3 through the plume at the source area (A–E), 35 m downgradient (F–J), and 95 m downgradient (K–O), respectively (Fig. 1). Results reveal that the sampling locations C, H, and M were located along the plume center-line. If dilution and dispersion were the only causes for the BTEX mass reduction, the width of the plume would increase, while the sum of the mass flux in three cross-sections should be constant. However, over the distances, significant drops of the BTEX mass were observed. The limited spreading of the plume was attributed to the natural attenuation, and aerobic biodegradation was the major cause of the BTEX mass reduction at the sides of the plume. As the plume spread in width due to dispersion, oxygen in the uncontaminated groundwater mixed with BTEX at the plume sides, enhancing biodegradation. This caused the elongated shape of the plume (Fig. 1). Results indicate that natural attenuation significantly reduces the contaminant mass causing the decrease in BTEX mass flux.

#### 4.3. Biodegradation rate calculation

Using 1,2,4-TMB as the tracer compound, the calculated mass flux removal due to biodegradation for the total BTEX and each BTEX component is listed in Table 4. Up to 80, 76, and 88% of the total BTEX was removed via natural biodegradation between cross-sections 1–2, 2–3, and 1–3, respectively. Results show that toluene (97% biodegradation between cross-sections 1 and 3) was the most biodegradable compound among BTEX components, and *o*-xylene (79% biodegradation between cross-sections 1 and 3) was the

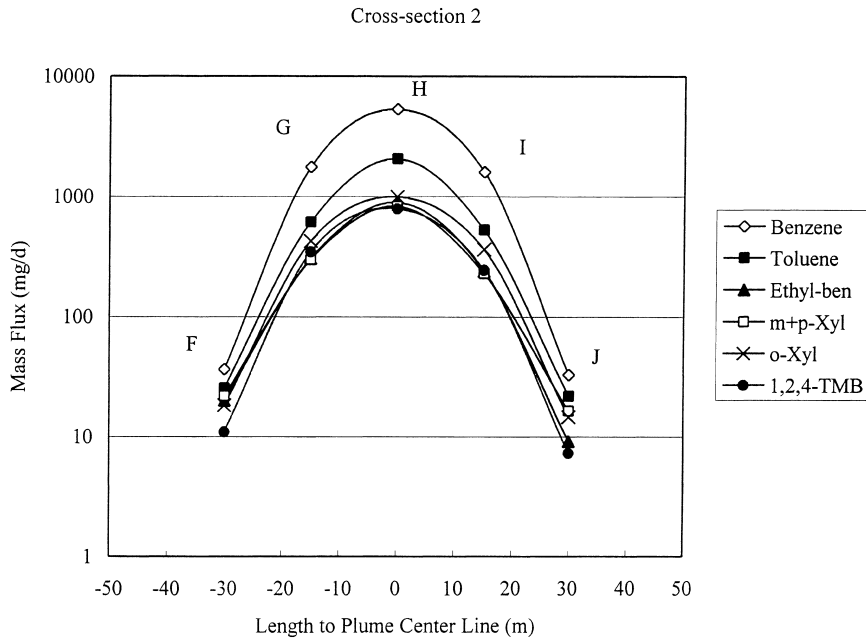


Fig. 5. Calculated mass flux results for five sampling locations along cross-section 2.

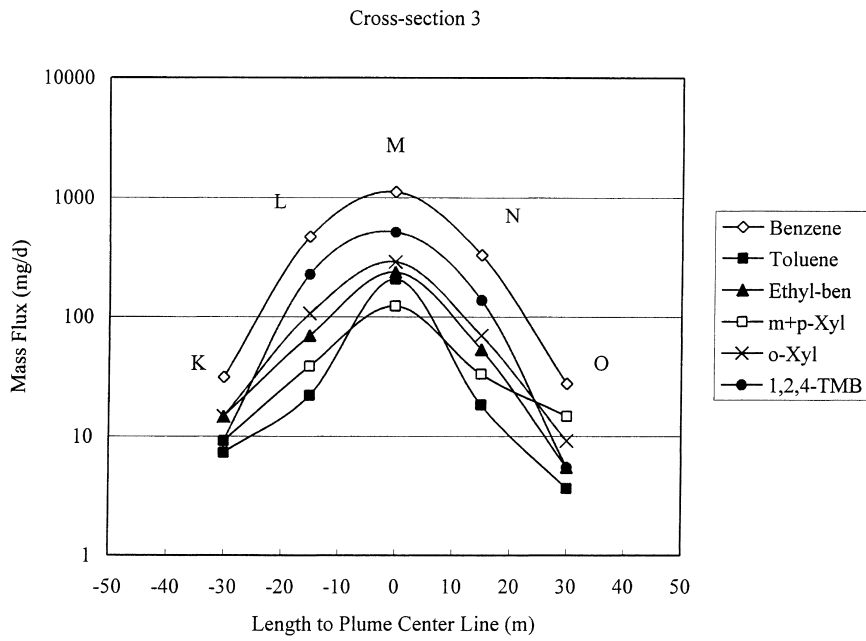


Fig. 6. Calculated mass flux results for five sampling locations along cross-section 3.

Table 4

Corrected mass flux and percentage of mass removal for each compound through different cross-sections via natural biodegradation

Cross-section	Benzene (mg per day)	Toluene (mg per day)	Ethyl-benzene (mg per day)	<i>m + p</i> -Xylene (mg per day)	<i>o</i> -Xylene (mg per day)	1,2,4-TMB (mg per day)	Total BTEX (mg per day)
Corrected 2 <sup>a</sup>	10081	3746	1683	1601	2084	1607	19195
Corrected 3	3566	465	684	395	880	1607	5990
(1–2)% <sup>b</sup>	80	89	68	83	50	0	81
(2–3)%	77	93	72	85	70	0	80
(1–3)%	88	97	83	92	79	0	90

<sup>a</sup> Corrected mass in cross-section 2.

<sup>b</sup> [(Measured mass in cross-section 1 – corrected mass in cross-section 2)/(measured mass in cross-section 1 – measured mass in cross-section 2)] × 100%.

Table 5

Calculated first-order biodegradation rate for each compound between cross-sections

Cross-section	Benzene (% per day)	Toluene (% per day)	Ethyl-benzene (% per day)	<i>m + p</i> -Xylene (% per day)	<i>o</i> -Xylene (% per day)	1,2,4-TMB (% per day)	Total BTEX (% per day)
1–2	0.02	0.034	0.012	0.023	0.006	0	0.02
2–3	0.029	0.059	0.025	0.04	0.024	0	0.033
1–3	0.026	0.05	0.02	0.033	0.018	0	0.029

least biodegradable component. Results reveal that biodegradation was the major cause of BTEX mass reduction.

The calculated first-order biodegradation rates using the corrected BTEX mass flux are shown in Table 5. Results indicate that the preferential removal trends for BTEX matched with the trends of natural attenuation. Toluene had the highest biodegradation rate (up to 0.059% per day between cross-sections 2 and 3), followed by *m + p*-xylene, benzene, ethylbenzene, and *o*-xylene. Rifai et al. [6] compiled the biodegradation results from field and laboratory studies. They observed a wide range in reported BTEX biodegradation rates. Reported first-order biodegradation rates for benzene ranged from non-detectable to approximately 1% per day, with an average of approximately 0.2% per day. Degradation rates for other hydrocarbons were typically somewhat in the same general range. Thus, the calculated BTEX first-order biodegradation rates using the corrected BTEX mass flux technique in this study were also in the reasonable range compared to other studies.

## 5. Conclusions

Natural attenuation is an important process for contaminant mass reduction and plume containment. Therefore, techniques for natural attenuation rate calculation are required to increase the ability to understand and predict the contaminant fate and transport during natural attenuation processes. In this study, mass flux and the first-order decay rate

calculations were applied to evaluate the occurrence and efficiency of the natural attenuation at a gasoline spill site. Moreover, natural biodegradation rate was also estimated using the in situ tracer technique.

The 2-year investigation results show that the natural attenuation and natural biodegradation mechanisms are occurring causing BTEX removal through mixed mass reduction processes. Evidence for the occurrence of natural attenuation was the decreased contaminant mass flux through the plume cross-sections along the transport path. Evidences for the BTEX biodegradation include: (1) depletion of DO within the plume; (2) CH<sub>4</sub> and CO<sub>2</sub> production within the plume; (3) decreased pH within the plume; (4) decreased BTEX as carbon to TOC ratio along the transport path; (5) decreased BTEX mass based on the results from the in situ tracer test and (6) preferential removal of certain BTEX components along the transport path.

Except for the observed evidences, other conclusions from the investigations contain the following points.

1. Based on the evaluation results, methanogenesis was the dominant biodegradation process within the plume, and aerobic biodegradation contributed on the edges and downgradient side of the plume.
2. Correlations between natural attenuation and natural biodegradation were observed. Natural attenuation rates for BTEX were only slightly higher than natural biodegradation rates (Tables 3 and 5). This indicates that natural biodegradation process was the major cause of BTEX removal. Without the occurrence of natural biodegradation, other natural attenuation processes cannot contain the plume effectively.
3. Under the methanogenic biodegradation process, toluene had the highest decay rate among BTEX, and *o*-xylene had the lowest rate. The degradation trend for BTEX was toluene → *m* + *p*-xylene → benzene → ethylbenzene → *o*-xylene. Results from other studies have shown that the BTEX degradation trend varied from site to site [2–4,9,17,18]. Environmental factors and status of biodegradation processes (e.g. methanogenesis, iron reduction, denitrification, sulfate reduction, aerobic biodegradation) would cause the variation in BTEX degradation order.
4. Up to 89% of BTEX was removed between cross-sections 1 and 3 (from the spill location to the 95 m downgradient line) via the natural attenuation processes. Results also show that the BTEX plume is not growing and has reached a pseudo-steady-state. This suggests that natural attenuation can be used as the remedial option at the gasoline spill site to solve the contaminated groundwater.
5. Lower natural attenuation and biodegradation rates were observed between cross-sections 1 and 2. Higher BTEX concentrations within this area might inhibit the microbial biotransformation processes, which caused the decrease in degradation efficiency. However, other environmental factors (e.g. local subsurface heterogeneities, microbial populations, variation in DO concentrations, status of oxidation/reduction) might also affect the natural attenuation and biodegradation rates.
6. Compared to other techniques (e.g. microcosm test, in situ column study, fate and transport model application), mass flux and first-order decay calculations are straightforward for natural attenuation and biodegradation rate/efficiency evaluations.

7. The drawbacks of this method includes the following: (a) site heterogeneity might influence the mass flux calculation; (b) it is fairly sampling intensive, thus several cross-section samplings are required; (c) this method is a “point in time measurement”, and thus it does not show the potential change in plume versus time.

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