



## Control of petroleum-hydrocarbon contaminated groundwater by intrinsic and enhanced bioremediation

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### Abstract

In the first phase of this study, the effectiveness of intrinsic bioremediation on the containment of petroleum hydrocarbons was evaluated at a gasoline spill site. Evidences of the occurrence of intrinsic bioremediation within the BTEX (benzene, toluene, ethylbenzene, and xylenes) plume included (1) decreased BTEX concentrations; (2) depletion of dissolved oxygen (DO), nitrate, and sulfate; (3) production of dissolved ferrous iron, methane, and CO<sub>2</sub>; (4) decreased pH and redox potential; and (5) increased methanogens, total heterotrophs, and total anaerobes, especially within the highly contaminated areas. In the second phase of this study, enhanced aerobic bioremediation process was applied at site to enhance the BTEX decay rates. Air was injected into the subsurface near the mid-plume area to biostimulate the naturally occurring microorganisms for BTEX biodegradation. Field results showed that enhanced bioremediation process caused the change of BTEX removal mechanisms from anaerobic biodegradation inside the plume to aerobic biodegradation. This variation could be confirmed by the following field observations inside the plume due to the enhanced aerobic bioremediation process: (1) increased in DO, CO<sub>2</sub>, redox potential, nitrate, and sulfate, (2) decreased in dissolved ferrous iron, sulfide, and methane, (3) increased total heterotrophs and decreased total anaerobes. Field results also showed that the percentage of total BTEX removal increased from 92% to 99%, and the calculated total BTEX first-order natural attenuation rates increased from 0.0092% to 0.0188% per day, respectively, after the application of enhanced bioremediation system from the spill area to the downgradient area (located approximately 300 m from the source area).

**Key words:** petroleum hydrocarbon; groundwater; natural attenuation; intrinsic bioremediation

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### Introduction

Releases of petroleum products (e.g., gasoline, diesel, fuel oil) from above ground and underground storage tanks or transport pipelines are the major causes of the groundwater pollution. Benzene, toluene, ethylbenzene, and xylene isomers (BTEX), the major components of petroleum products, are toxic chemicals. The slow dissolution of residual BTEX from the spill location or source area usually causes in a BTEX plume in the subsurface. To protect the subsurface receptors including drinking water wells, the plume control action must be taken and operated for a long period of time.

The field investigation results revealed that many of these subsurface contaminants naturally degrade before they reach a drinking water receptor (Brar et al., 2006; Chen et al., 2006; Lai et al., 2007; Fraser et al., 2008). Monitored natural attenuation (MNA) is an *in situ* and inactive treatment system using natural occurring processes

to remove pollutants in the subsurface. Among those natural occurring processes, intrinsic bioremediation or natural bioremediation is one of the most important processes for contaminant removal (Sutherland et al., 2004; Chen et al., 2006; Maier et al., 2007). The contaminants (e.g., BTEX) can be biodegradable under both aerobic and anaerobic conditions. Moreover, the aerobic degradation rates for BTEX are higher than those under anaerobic conditions (Atteia and Guillot, 2007). The biodegradation processes are believed to be the major mechanisms that cause the reduction of the contaminant concentrations.

Among commonly used groundwater remediation methods, bioremediation is a more cost-effective technology (Devlin et al., 2004; Sutherland et al., 2004; Chen et al., 2006; Neuhauser et al., 2009). Intrinsic bioremediation and natural bioremediation have been considered as the potential methods for the cleanup of petroleum-hydrocarbon contaminated sites. Because the intrinsic bioremediation rate is limited by *in situ* environmental factors, enhanced *in situ* bioremediation can be applied to stimulate pollutants

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biodegradation. Moreover, microbiological investigations of aquifer sediments have revealed the presence of microbial communities capable of degrading a broad range of naturally occurring and xenobiotic compounds under a broad range of environmental conditions (Kao et al., 2003, 2005). Thus, *in situ* aerobic bioremediation is a feasible technology to cleanup BTEX contaminated sites if aquifer oxygen can be supplied into the aquifer economically.

Enhanced aerobic bioremediation, such as injecting air at a low rate into the aquifer below the zone of contamination, is an effective mechanism for the removal of petroleum hydrocarbons including BTEX (Wu et al., 2005; Brar et al., 2006; Abu, 2008). At a relatively close well spacing, the injected air promotes oxygenation of the aquifer and thus promotes aerobic biodegradation (Ling and Rifai, 2007; Balcke et al., 2009). In this study, the enhanced aerobic bioremediation system is located to focus upon BTEX for the purpose of stimulating aerobic biodegradation of contaminants. In this study, a petroleum-hydrocarbon spill site was selected to fulfill the following objectives: (1) to assess the occurrence and mechanisms of intrinsic bioremediation, (2) to calculate the BTEX field-scale decay rates; and (3) to evaluate the effectiveness of enhanced aerobic bioremediation as a method for BTEX control.

## 1 Study site

A government owned tank farm facility site located in southern Taiwan was selected for this MNA study. In early 2000, leakage from a fuel-oil pipeline resulted in the groundwater contamination by petroleum hydrocarbons (mainly BTEX). During the following four-year investigation period, more than 100 soil gas and soil samples were collected, and 18 monitor wells were installed for the site characterization and contaminated-groundwater extraction. On-site borings encountered up to 25 m of mostly brown to gray, fine to medium sand to silty sand. The average groundwater elevation within the shallow aquifer is approximately 1.5 to 2.5 m below land surface. Groundwater in the unconfined aquifer, according to the groundwater elevation in site monitor wells, flows southwest. The measured effective porosity is 0.27, and the average hydraulic conductivity for the surficial, unconfined aquifer is  $1.15 \times 10^{-3}$  m/sec (99 m/day). The calculated site groundwater flow velocity is  $1.32 \times 10^{-5}$  m/sec (1.14 m/day). The measured groundwater temperature in the surficial aquifer varies from 17 to 29°C. The preliminary site investigation results indicated that the BTEX plume is approximately 480 m in length (along the groundwater flow direction) and 220 m in width (data not shown). Figure 1 presents the site map showing the estimated plume boundary, locations of representative monitor wells and soil sampling, and groundwater flow direction.

Since 2005, MNA has been applied to remediate contaminated groundwater. In 2007, enhanced aerobic bioremediation system was installed in the mid-plume area to evaluate the effectiveness of enhanced aerobic bioremediation system on BTEX removal. In the first part

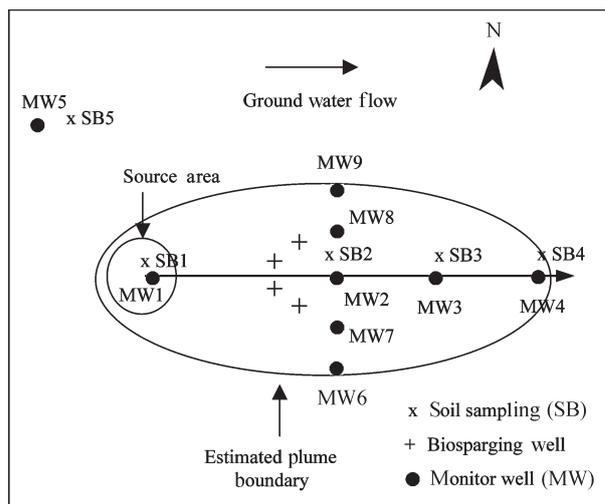


Fig. 1 Site map showing the groundwater flow direction, estimated plume boundary, and soil and groundwater sampling locations.

of this study, the effectivenesses of MNA and intrinsic bioremediation on the containment of petroleum hydrocarbons was evaluated. In the second part of this study, enhanced BTEX decay rates and evidences of enhanced BTEX biodegradation through the enhanced aerobic bioremediation process were evaluated.

## 2 Materials and methods

For simplicity and ease of identification, the studied site was divided into five different areas (1 to 5), which represented the highly contaminated area (Area 1), mid-plume area (Area 2), downgradient area (Area 3), plume edge area (Area 4), and background area (Area 5), respectively. Five monitor wells, which were labeled as MW1, MW2, MW3, MW4, and MW5 were located inside the five representative areas (Areas 1 to 5) and used for groundwater sampling and analysis. All wells were screened from 2 to 5.1 m below land surface (bls). Groundwater samples were collected quarterly and analyzed for organic compounds and geochemical indicators including BTEX, CH<sub>4</sub>, CO<sub>2</sub>, inorganic nutrients, anions, Fe(II), pH, redox potential (Eh), and DO during the two-year investigation period (first part of this study). Organic compound analyses were performed in accordance with U.S. 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>, SO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>) analyses. Sulfide was analyzed by Methylene-Blue method (APHA, 2001) using Hach technique (Hach Co., USA). Perkin-Elmer Plasma II Inductively Coupled Plasma-Argon Emission Spectrometer (ICP-AES) was used for Fe(II) analyses following Standard Methods (APHA, 2001). DO, Eh, pH, CO<sub>2</sub>, and temperature were measured in the field. A pH/Eh meter (Accumet 1003, Fisher Scientific, USA) was used for pH and Eh measurement, a DO meter (Orion Model 840, Thermo Scientific, USA) was used for DO and temperature

measurement, and a Hach digital titrator cartridge was used for CO<sub>2</sub> measurement.

To further confirm the occurrence of intrinsic bioremediation and evaluate the trend of the degradation processes, aquifer sediments were collected from the soil borings SB1, SB2, SB3, SB4, and SB5, which were adjacent to MW1, MW2, MW3, MW4, and MW5, respectively. Each soil core was analyzed for microbial enumeration to define the distribution of methanogens, total heterotrophs, and total anaerobes. Total anaerobes and methanogens were enumerated using a five-tube MPN assay. The total anaerobe tubes contained media described by Kao et al. (2001) and were scored positive based on optical density. Total plate counts were conducted using plate count agar (Difco) to assess the approximate size of the total heterotrophic bacterial using the spread plate method (APHA, 2001). The methanogen tubes contained 20% H<sub>2</sub> and 80% CO<sub>2</sub> in the headspace, and were scored positive based on the production of methane (Kao et al., 2001). In this study, monitor wells (MW6, MW7, MW2, MW8, and MW9) located in the cross-section line of MW6 to MW9 were selected to compare to total BTEX flux through the cross section before and after the operation of enhanced aerobic bioremediation system.

The first-order decay model (Eq. (1)) was applied to estimate the natural attenuation rate between upgradient well (MW1) and downgradient wells (MW2 and MW3) using the measured contaminant (BTEX) concentrations in MW1 and MW2.

$$C_2 = C_1 e^{-K_{na}t} \quad (1)$$

where,  $C_2$  ( $\mu\text{g/L}$ ) is the measured contaminant concentration at MW2 (or MW3);  $C_1$  ( $\mu\text{g/L}$ ) is the measured

contaminant concentration at MW1;  $K_{na}$  ( $\text{day}^{-1}$ ) is the first-order decay rate (natural attenuation rate);  $t$  (day) is the ratio of distance between MW1 and MW2 (or MW3)/groundwater flow velocity.

The enhanced aerobic bioremediation system consisted of two air injection wells (injection points) (well screen at 4.7 to 5 m bls), air compressors, flow indicators, inline regulators, and pressure gauges. The air flow was approximately 0.06 to 0.17 m<sup>3</sup>/min (2 to 6 cfm) for each air injection well. The four air injection wells were located upgradient of MW2 (Fig. 1). Preliminary results indicated that the radius of influence for the air injection well was approximately 5.5 m (data not shown). All selected wells were sampled bimonthly during the eight-month investigation period. Groundwater samples from the monitor wells were collected and analyzed for organic compounds and geochemical indicators described above.

### 3 Results and discussion

Groundwater samples were collected from monitor wells MW1, MW2, MW3, MW4, and MW5. Table 1 shows the averaged results of eight groundwater sampling events during the two-year investigation period before enhanced aerobic bioremediation process. Figure 2 presents the variations in BTEX concentrations in monitor wells (MW1 to MW4) before the operation of the enhanced aerobic bioremediation system along the groundwater transport direction. Table 2 shows the percentage of contaminant removal for each compound between monitor wells (MW1 to MW2 and MW1 to MW3) before enhanced aerobic bioremediation process. Aquifer sediments collected from soil borings S1 to S5 was used for microbial enumeration.

**Table 1** Concentrations of BTEX and indicating parameters in monitor wells before the operation of enhanced aerobic bioremediation system

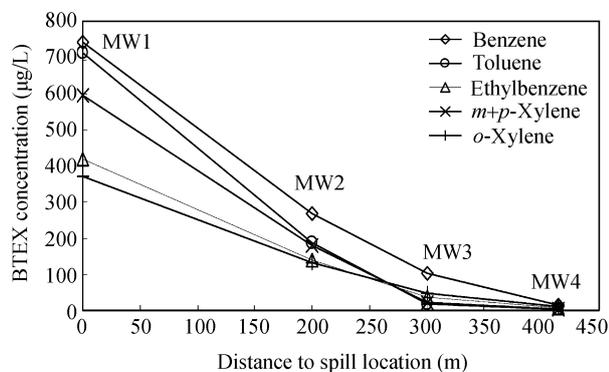
	MW1	MW2	MW3	MW4	MW5
Location	High	Mid	Down	Edge	BK
Distance from MW1 (m)	0	200	300	415	–
Benzene ( $\mu\text{g/L}$ )	743	269	102	15	BDL
Toluene ( $\mu\text{g/L}$ )	712	187	19	2	BDL
Ethylbenzene ( $\mu\text{g/L}$ )	419	141	36	6	BDL
<i>m+p</i> -Xylene ( $\mu\text{g/L}$ )	593	179	21	5	BDL
<i>o</i> -Xylene ( $\mu\text{g/L}$ )	371	131	46	11	BDL
Total BTEX ( $\mu\text{g/L}$ )	2838	907	224	39	BDL
DO (mg/L)	0	0.1	1.2	1.7	3.2
Nitrate (mg/L)	0.1	0.7	3.5	3.9	6.2
Total iron (mg/L)	14.3	4.6	0.5	0.7	0.9
Ferrous iron (mg/L)	15.5	7.2	0.2	0.2	0.1
Sulfate (mg/L)	3	9	12	14	18
Sulfide ( $\mu\text{g/L}$ )	14	11	3	2	2
Carbon dioxide (mg/L)	136	112	67	54	43
Methane (mg/L)	11	5.3	0.1	0.05	0.05
pH	6.6	6.7	6.8	6.9	7.0
Redox potential (mV)	–159	–98	78	126	206
Ammonia nitrogen (mg/L)	1.9	2.2	2.8	2.9	3.1
Phosphate (mg/L)	1.1	0.9	1.3	1.4	1.9
Temperature ( $^{\circ}\text{C}$ )	24.2	24.1	23.9	24.1	24.2
Methanogen (cells/g)	$5.4 \times 10^3$ (SB1)	$4.6 \times 10^2$ (SB2)	BDL (SB3)	BDL (SB4)	BDL (SB5)
Total heterotrophs (cells/g)	$1.2 \times 10^5$ (SB1)	$2.8 \times 10^5$ (SB2)	$6.2 \times 10^5$ (SB3)	$5.1 \times 10^4$ (SB4)	$2.7 \times 10^4$ (SB5)
Total anaerobes (cells/g)	$6.3 \times 10^4$ (SB1)	$1.2 \times 10^4$ (SB2)	$2.7 \times 10^2$ (SB3)	$1.5 \times 10^2$ (SB4)	$1.1 \times 10^2$ (SB5)

High: sample collected from the highly contaminated area; Mid: sample collected from the mid-plume area; Down: sample collected at the downgradient area; Edge: sample collected from the edge of the plume; BK: sample collected at the background area.

–: not available; BDL: below detection limit; SB: microbial enumeration was performed using soil sediments.

**Table 2** Percentage of contaminant removal for each compound between monitor wells before enhanced aerobic bioremediation process

	Benzene (%)	Toluene (%)	Ethylbenzene (%)	<i>m+p</i> -Xylene (%)	<i>o</i> -Xylene (%)	Total BTEX (%)
MW1–MW2	63.8	73.7	66.4	69.8	64.7	68.0
MW1–MW3	86.3	97.3	91.4	96.5	87.6	92.1

**Fig. 2** Variations in BTEX concentrations in monitor wells (MW1 to MW4) before the operation of the enhanced aerobic bioremediation system along the groundwater transport direction.

Results of the bacterial population assessment are also shown in Table 1. Results show that BTEX concentrations in the monitor wells reached a relatively stable condition, and no significant decrease or increase in BTEX concentrations was observed during the investigation period. This indicates that the presence of residual hydrocarbons beneath the former spill location is possible.

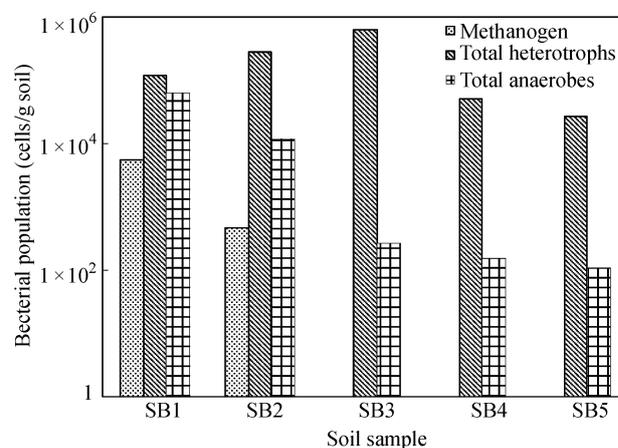
The dissolved BTEX are being continuously released from residual fuel globules into the groundwater, causing the stable BTEX concentrations in monitor wells within the investigation period. Investigation results indicate the occurrence of the anaerobic conditions within the plume. Compared to MW1 and MW2, the downgradient and plume edge monitor wells (MW3 and MW4) contained higher  $O_2$  concentrations (up to 1.2 mg/L). This indicates that the downgradient or edge of the plume was under the oxidized stage and aerobic biodegradation was the dominant biodegradation process in the area. The declines in Eh and DO near the source area reflect the change from oxidizing to reducing conditions. The increased  $CH_4$  (up to 11 mg/L in MW1) and  $CO_2$  (up to 136 mg/L in MW1) concentrations, and decreased pH (pH = 6.6 in MW1) (Table 1) in MW1 and MW2 suggest that the methanogenesis was the dominant biodegradation process within the most of contaminated zone. This indicates that significant microbial activity and intrinsic bioremediation occurred in this area.

The lower nitrate and sulfate concentrations within the plume reveal that both nitrate and sulfate acted as electron acceptors after the depletion of oxygen. High ferrous concentrations were detected in MW1 (15.5 mg/L) and MW2 (7.2 mg/L) (Table 1). This indicates that ferric iron might also act as the electron acceptor around the source area. The decrease in BTEX concentrations from MW1 to MW4 suggests the occurrence of natural attenuation of BTEX. Table 2 presents the percentage of concentration drop for each compound through MW1 to MW2 or MW3

along the transport path via natural attenuation process. Results indicate that 68% and 92.1% of the total BTEX were removed from MW1 to MW2 and from MW1 to MW3, respectively.

The observed bacterial populations are presented in Table 1. Figure 3 shows the microbial enumeration analyses for five soil samples before the operation of the enhanced aerobic bioremediation system. Results show that significant amount of methanogens ( $>10^2$  cells/g soil), total heterotrophs and total anaerobes ( $>10^4$  cells/g soil) were detected in SB1 and SB2 soil samples collected from the highly and mid plume areas, respectively. This indicates that an increased petroleum hydrocarbons concentrations and reduced conditions caused an increase in methanogenic and anaerobic bacterial population. However, only  $2.7 \times 10^2$  and  $1.5 \times 10^2$  cells of total anaerobes/g soil were observed in SB3 and SB4, respectively. This indicates that anaerobic bacteria were not the dominant microbial population under anaerobic conditions. Field results also indicate that the anaerobic biodegradation patterns were the dominant intrinsic biodegradation processes in the source and mid-plume areas.

The calculated first-order decay rates (natural attenuation rates) for BTEX between MW 1 to MW2 and MW1 to MW3 are presented in Table 3. The total BTEX decay rate was  $0.0092 \text{ day}^{-1}$  from MW1 to MW3. Results show that toluene was the most quickly degraded compound in BTEX (up to  $0.0131 \text{ day}^{-1}$ ), followed by *m+p*-xylene ( $0.0121 \text{ day}^{-1}$ ), ethylbenzene ( $0.0089 \text{ day}^{-1}$ ), *o*-xylene ( $0.0076 \text{ day}^{-1}$ ), and benzene ( $0.0072 \text{ day}^{-1}$ ) between MW1 to MW3 (Table 3). The observed decay rates for BTEX were similar to the rates obtained from other investigations (US EPA, 2004; Chen et al., 2005). This indicates that the natural attenuation mechanisms were under acceptable ranges, and caused the removal of

**Fig. 3** Microbial enumeration analyses for five soil samples before the operation of the enhanced aerobic bioremediation system.

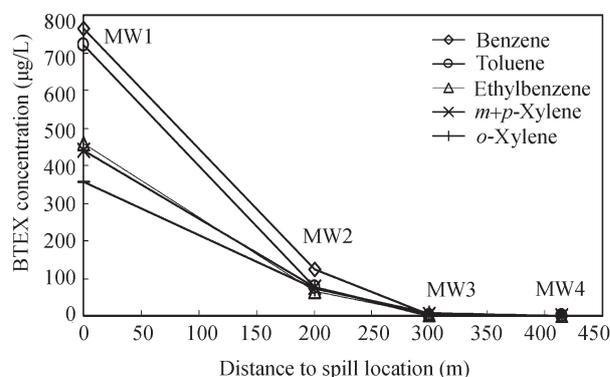
**Table 3** Calculated first-order natural attenuation rates for each compound between monitor wells before enhanced aerobic bioremediation process

	Benzene (day <sup>-1</sup> )	Toluene (day <sup>-1</sup> )	Ethylbenzene (day <sup>-1</sup> )	<i>m+p</i> -Xylene (day <sup>-1</sup> )	<i>o</i> -Xylene (day <sup>-1</sup> )	Total BTEX (day <sup>-1</sup> )
MW1–MW2	0.0056	0.0074	0.0061	0.0067	0.0058	0.0063
MW1–MW3	0.0072	0.0131	0.0089	0.0121	0.0076	0.0092

BTEX at studied site.

In the second part of this study, air injection wells were installed for air supplement to the groundwater. Table 4 shows the groundwater average results in MW1 to MW5 of four groundwater sampling events during a eight-month investigation after enhanced aerobic bioremediation process. Figure 4 presents the variations in BTEX concentrations in monitor wells (MW1 to MW4) after the operation of the enhanced aerobic bioremediation system along the groundwater transport direction. The significant decrease in BTEX concentrations was observed after the operation of enhanced aerobic bioremediation, which mainly due to the enhanced aerobic biodegradation. The part of BTEX loss might be also due to the vaporization. Because the measured soil gas results from nine soil gas sampling wells were insignificant (< 68 ppm) (data not shown) before and after the enhanced aerobic bioremediation process, the amount of BTEX loss due to volatilization would be insignificant. Table 5 shows the percentage of contaminant removal for each compound between monitor wells after the enhanced aerobic bioremediation process. Results indicate that 85% and 99% of the total BTEX was removed from MW1 to MW2 and from MW1 to MW3, respectively.

Figure 5 shows the results of microbial enumeration analyses for five soil samples after the operation of enhanced aerobic bioremediation system. Results show that significant amount of total heterotrophs (>10<sup>5</sup> cells/g soil)

**Fig. 4** Variations in BTEX concentrations in monitor wells (MW1 to MW4) after the operation of the enhanced aerobic bioremediation system along the groundwater transport direction.

were detected in SB1 and SB2 soil sample collected from the contaminated areas. This indicates that the increased petroleum hydrocarbons concentrations caused an increase in bacterial population. Moreover, a decrease in total anaerobes was observed in SB2 and SB3 soil samples. Results show that only  $1.3 \times 10^2$  and  $1.6 \times 10^2$  cells of total anaerobes/g soil were observed in SB2 and SB3, respectively. This indicates that the anaerobic bacteria were not the dominant bacteria in contaminated areas due to the change of oxidation-reduction potential in these areas from anaerobic to aerobic conditions.

**Table 4** Concentrations of BTEX and indicating parameters in monitor wells after the operation of enhanced aerobic bioremediation system

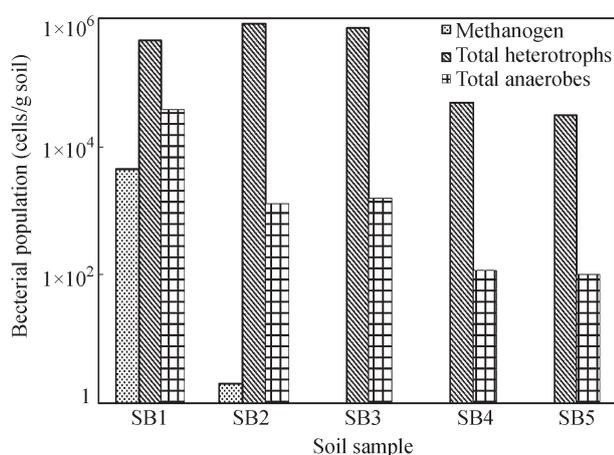
Monitor well	MW1	MW2	MW3	MW4	MW5
Location	High	Mid	Down	Edge	BK
Distance from MW1	0	200	300	415	–
Benzene (µg/L)	762	124	5	0.4	BDL
Toluene (µg/L)	731	78	1.3	BDL	BDL
Ethylbenzene (µg/L)	458	65	2	0.1	BDL
<i>m+p</i> -Xylene (µg/L)	441	76	2.6	0.1	BDL
<i>o</i> -Xylene (µg/L)	356	71	6.8	0.5	BDL
Total BTEX (µg/L)	2748	414	11.4	1.1	BDL
DO (mg/L)	0.1	1.6	2.0	2.4	2.8
Nitrate (mg/L)	0.16	1.7	2.8	4.1	6.2
Total iron (mg/L)	11.3	6.9	1.2	0.7	0.6
Ferrous iron (mg/L)	10.7	5.6	0.2	0.12	0.1
Sulfate (mg/L)	2	13	10.6	12	15
Sulfide (µg/L)	12	1.8	2.1	2.3	2.6
Carbon dioxide (mg/L)	145	176	86	67	54
Methane (mg/L)	12	6.1	0.08	0.05	0.07
pH	6.6	6.6	6.7	6.7	6.9
Redox potential (mV)	–185	45	122	158	196
Ammonia nitrogen (mg/L)	1.4	2.3	1.8	2.4	2.6
Phosphate (mg/L)	1.1	0.96	1.2	1.3	1.6
Temperature (°C)	24.7	24.2	24.1	24.3	24.2
Methanogen (cells/g)	$4.4 \times 10^3$ (SB1)	2 (SB2)	BDL (SB3)	BDL (SB4)	BDL (SB5)
Total heterotrophs (cells/g)	$4.5 \times 10^5$ (SB1)	$8.4 \times 10^5$ (SB2)	$7.1 \times 10^5$ (SB3)	$4.9 \times 10^4$ (SB4)	$3.1 \times 10^4$ (SB5)
Total anaerobes (cells/g)	$3.8 \times 10^4$ (SB1)	$1.3 \times 10^2$ (SB2)	$1.6 \times 10^2$ (SB3)	$1.2 \times 10^2$ (SB4)	$1.0 \times 10^2$ (SB5)

**Table 5** Percentage of contaminant removal for each compound between monitor wells after enhanced aerobic bioremediation process

	Benzene (%)	Toluene (%)	Ethylbenzene (%)	<i>m+p</i> -Xylene (%)	<i>o</i> -Xylene (%)	Total BTEX (%)
MW1–MW2	83.7	89.3	85.8	82.8	80	85
MW1–MW3	99.3	99.8	99.6	99.4	98.1	99

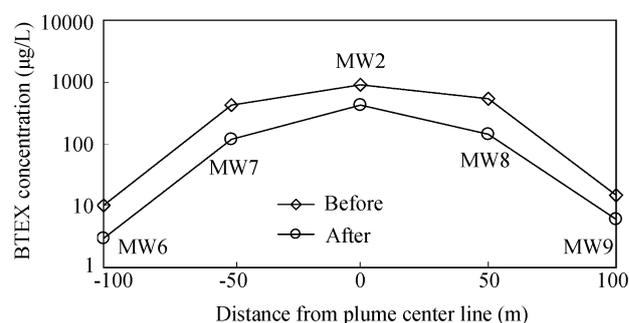
**Table 6** Calculated first-order natural attenuation rate for each compound between monitor wells after enhanced aerobic bioremediation process

	Benzene (day <sup>-1</sup> )	Toluene (day <sup>-1</sup> )	Ethylbenzene (day <sup>-1</sup> )	<i>m+p</i> -Xylene (day <sup>-1</sup> )	<i>o</i> -Xylene (day <sup>-1</sup> )	Total BTEX (day <sup>-1</sup> )
MW1–MW2	0.0101	0.0124	0.0109	0.0098	0.009	0.0105
MW1–MW3	0.0182	0.0229	0.0197	0.0186	0.0161	0.0188

**Fig. 5** Results of microbial enumeration analyses for five soil samples after the operation of the enhanced aerobic bioremediation system.

Results also show that the methanogen populations detected before and after the operation of enhanced aerobic bioremediation was in SB1 were similar. However, a low methanogen population was observed in SB2 after the operation of enhanced aerobic bioremediation process (Tables 1 and 4). This also reveals that the injection of air affected the redox conditions and caused the decrease in methanogen in SB2. Field results reveal that the aerobic biodegradation patterns were the dominant intrinsic biodegradation processes in mid plume and downgradient areas. The occurrence of aerobic biodegradation of BTEX due to the air injection can be confirmed by the increased population of total heterotrophs and decreased population of total anaerobes in sediments SB2 and SB3 (Table 4).

Figure 6 presents the variations in total BTEX concentrations in monitor wells located in cross section line as MW6–MW7–MW2–MW8–MW9 before and after the operation of the enhanced aerobic bioremediation system. Results show that significant drops of the total BTEX concentrations were observed along the cross section line from MW6 to MW9 after the operation of enhanced aerobic bioremediation system. This also confirms that the injected air caused the enhanced biodegradation of BTEX downgradient of the air injection wells. The limited spreading of the plume was attributed to the natural attenuation, and aerobic biodegradation was the major cause

**Fig. 6** Variations in total BTEX concentrations in monitor wells located in cross section line as MW6–MW7–MW2–MW8–MW9, before and after the operation of the enhanced aerobic bioremediation system.

of the BTEX reduction in those wells, especially 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, and thus enhanced biodegradation. This caused the semi-circular shapes of the mass flux results at the cross section (Fig. 6) and the elongated shape of the plume (Fig. 1).

Because bioremediation rates under aerobic conditions are generally higher than those under anaerobic conditions, air injection into the subsurface would enhance the BTEX biodegradation rates. Results from the field investigation also reveal that the enhanced aerobic bioremediation process caused significant changes in environmental conditions. Table 6 shows the calculated first-order decay rate for each compound between monitor wells after the enhanced aerobic bioremediation process. The total BTEX decay rates were 0.0105 day<sup>-1</sup> and 0.0188 day<sup>-1</sup> between MW1 to MW2 and MW1 to MW3, respectively. Results show that toluene was the most quickly degraded compound in BTEX (up to 0.0229 day<sup>-1</sup>), followed by ethylbenzene (0.0197 day<sup>-1</sup>), *m+p*-xylene (0.0186 day<sup>-1</sup>), benzene (0.0182 day<sup>-1</sup>), and *o*-xylene (0.0161 day<sup>-1</sup>) between MW1 to MW3 (Table 6). The observed decay rates for BTEX were much higher than the decay rates obtained before the enhanced aerobic bioremediation process (Table 3). This indicates that the enhanced aerobic bioremediation process caused the change of the treatment mechanisms from anaerobic biodegradation to aerobic biodegradation. Increased DO in the groundwater activated the aerobic

microorganisms and enhanced the BTEX removal rates.

Effects of enhanced aerobic bioremediation on the variations in indicating parameters and enhancement of aerobic biodegradation in mid-plume and downgradient areas include: (1) the increase in DO, CO<sub>2</sub>, redox potential, nitrate, and sulfate; (2) the decrease in pH, dissolved ferrous iron, sulfide, and methane; (3) the increased total heterotrophs; and (4) the decreased total anaerobes in studied areas.

## 4 Conclusions

Natural attenuation is an important process for contaminant mass reduction and plume containment. The investigation results showed that the intrinsic bioremediation mechanisms were occurring causing BTEX removal through mixed mass reduction processes. Evidences for the BTEX biodegradation include: (1) decreased BTEX concentrations along the transport path; (2) the depletion of dissolved oxygen, nitrate, and sulfate; (3) the production of dissolved ferrous iron, sulfide, methane, and CO<sub>2</sub>; (4) decreased pH in the spill source area and increased pH in iron reducing area; and (5) the preferential removal of certain BTEX components along the transport path.

Results also showed that the BTEX plume is not growing and has reached a pseudo-steady-state under mixed anaerobic and aerobic conditions. This suggested that natural attenuation can be used as the remedial option at the petroleum-hydrocarbon spill site to remediate the contaminated groundwater. In the second part of this study, enhanced aerobic bioremediation process was applied to enhance the BTEX biodegradation rates in the mid-plume area. Field results also revealed that the operation of enhanced aerobic bioremediation caused the change of anaerobic conditions inside the mid-plume area to aerobic conditions. This variation can be confirmed by the following field observations inside the BTEX plume due to the enhanced aerobic bioremediation process: (1) the increase in DO, Eh, nitrate, and sulfate, (2) the decrease in dissolved ferrous iron, sulfide, and methane, (3) increased total heterotrophs, and (4) decreased total anaerobes.

Results also showed that the aerobic biodegradation was the dominant degradation processes of BTEX after the operation of enhanced aerobic bioremediation. Field results showed that the percent of total BTEX removal increased to 99%, and the calculated total BTEX first-order natural attenuation rates increased to 0.0188% per day, after the application of enhanced aerobic bioremediation system from the spill location to the 300 m downgradient line. Field results from the enhanced aerobic bioremediation study indicated that enhanced aerobic bioremediation could significantly enhance the BTEX decay rate and accelerate the BTEX removal efficiency. Results from this study indicate that natural attenuation or intrinsic bioremediation is a very promising technology to effectively manage this petroleum-hydrocarbon spill site, and enhanced aerobic bioremediation is also a promising technology to enhance the BTEX biodegradation in contaminated groundwater. Knowledge and comprehension obtained in this study will be helpful in designing a

MNA or enhanced aerobic bioremediation systems for the remediation of BTEX-contaminated site.

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