



Groundwater contamination and natural attenuation capacity at a petroleum spilled facility in Korea

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Abstract

As a remedial option, the natural attenuation capacity of a petroleum contaminated groundwater at a military facility was examined. Hydrogeological conditions, such as high water level, permeable uppermost layer and frequent heavy rainfall, were favorable to natural attenuation at this site. The changes in the concentrations of electron acceptors and donors, as well as the relevant hydrochemical conditions, indicated the occurrence of aerobic respiration, denitrification, iron reduction, manganese reduction and sulfate reduction. The calculated BTEX expressed biodegradation capacity ranged between 20.52 and 33.67 mg/L, which appeared effective for the reduction of the contaminants levels. The contribution of each electron accepting process to the total biodegradation was in the order: denitrification > iron reduction > sulfate reduction > aerobic respiration > manganese reduction. The BTEX and benzene point attenuation rates were 0.0058–0.0064 and 0.0005–0.0032 day⁻¹, respectively, and the remediation time was 0.7–1.2 and 2.5–30 years, respectively. The BTEX and benzene bulk attenuation rates were 8.69 × 10⁻⁴ and 1.05 × 10⁻³ day⁻¹, respectively, and the remediation times for BTEX and benzene were 7.2 and 17.5 years, respectively. However, most of the natural attenuation occurring in this site can be attributed to dilution and dispersion. Consequently, the biodegradation and natural attenuation capacities were good enough to lower the contaminants levels, but their rates appeared to be insufficient to reach the remediation goal within a reasonable time frame. Therefore, some active remedial measures would be required.

Key words: petroleum contaminated site; BTEX; electron acceptor; expressed biodegradation capacity; natural attenuation

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Introduction

Groundwater contamination by petroleum hydrocarbons including BTEX, is widespread in Korean military bases and; thus, remediation works are ongoing at numerous sites across the country (Lee, 2011). In the past, the environmental control and management of many wastes were not sufficient at military bases. With most of the remediation works of contaminated site, active and pervasive technologies, such as pump and treat and air sparging, have been adopted which have also aggravated the economic burden. After the first official (government conducted) remediation project (cost 10.7 million dollars) of a petroleum contaminated military site (formerly military maintenance facility) in 2001, the remediation budgets or costs have greatly increased (Ministry of Environment, 2010).

Remediation by natural attenuation (named RNA) is well known as one of the remedial options for contaminated sites, especially petroleum contaminated groundwater, and has been applied worldwide (Wiedemeier et al., 1999; Kao and Prosser, 2001; Scow and Hicks, 2005; Cozzarelli

et al., 2010). Even though RNA is well established and frequently applied it has not been adopted at any site requiring remediation in Korea. In addition, detailed investigations and evaluations of the feasibility of RNA have not been conducted. In the mean time, biodegradation is a destructive and effective natural attenuation process, which can reduce the net contaminant mass. Thus, evaluation of the indigenous biodegradation capacity is essential for RNA. The indigenous biodegradation is generally controlled by site hydrogeological and hydrochemical conditions, including stratification of hydrogeological layers and the distribution and levels of electron acceptors, such as dissolved oxygen and nitrate.

Many of the Korean military bases are located in somewhat distant areas from main residential areas and; thus, RNA can be considered as a serious remedial option if natural attenuation is sufficient. In this respect, the objectives of this study were to examine the levels and extent of groundwater contamination and evaluate the rates of natural attenuation and biodegradation capacity for a petroleum contaminated military base in Chuncheon, Korea.

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1 Materials and methods

1.1 Study site

The studied military facility is located in Chuncheon, about 60 km northeast of Seoul, the capital of Korea (Fig. 1), and is situated on low relief hills (105–130 m above mean sea level) on the outskirts of Chuncheon city. The military facility has stored unleaded gasoline (tanks #1, 2, 5) and diesel (tanks #3, 4, 6, 7, 8) since 1981, and each semi-buried tank can store up to 1600 tons of petroleum hydrocarbons. Many oil spill events from these storage tanks and connection pipes were reported between 1993 and 2006 and, hence, some of the tanks (#1–4) were replaced with several maintenance activities

of the other tanks also conducted (KRC, 2007). However, after all these efforts at the site, extensive contaminations of soil and groundwater were inevitable. In a 2004–2005 investigation, a relevant environmental authority found that the soil and groundwater around the tanks were highly contaminated with petroleum hydrocarbons (soil: up to 1691 mg/kg BTEX, groundwater: up to 63.289 mg/L BTEX). The authority was concerned about the migration of these contaminant plumes to a down-gradient area along with the groundwater flow.

The topographic elevations were distinctively divided in one third of the upper area (mid-point between WE1 and WE4 wells), where an approximate 2 m elevation difference occurred (Fig. 1), which was due to artificial

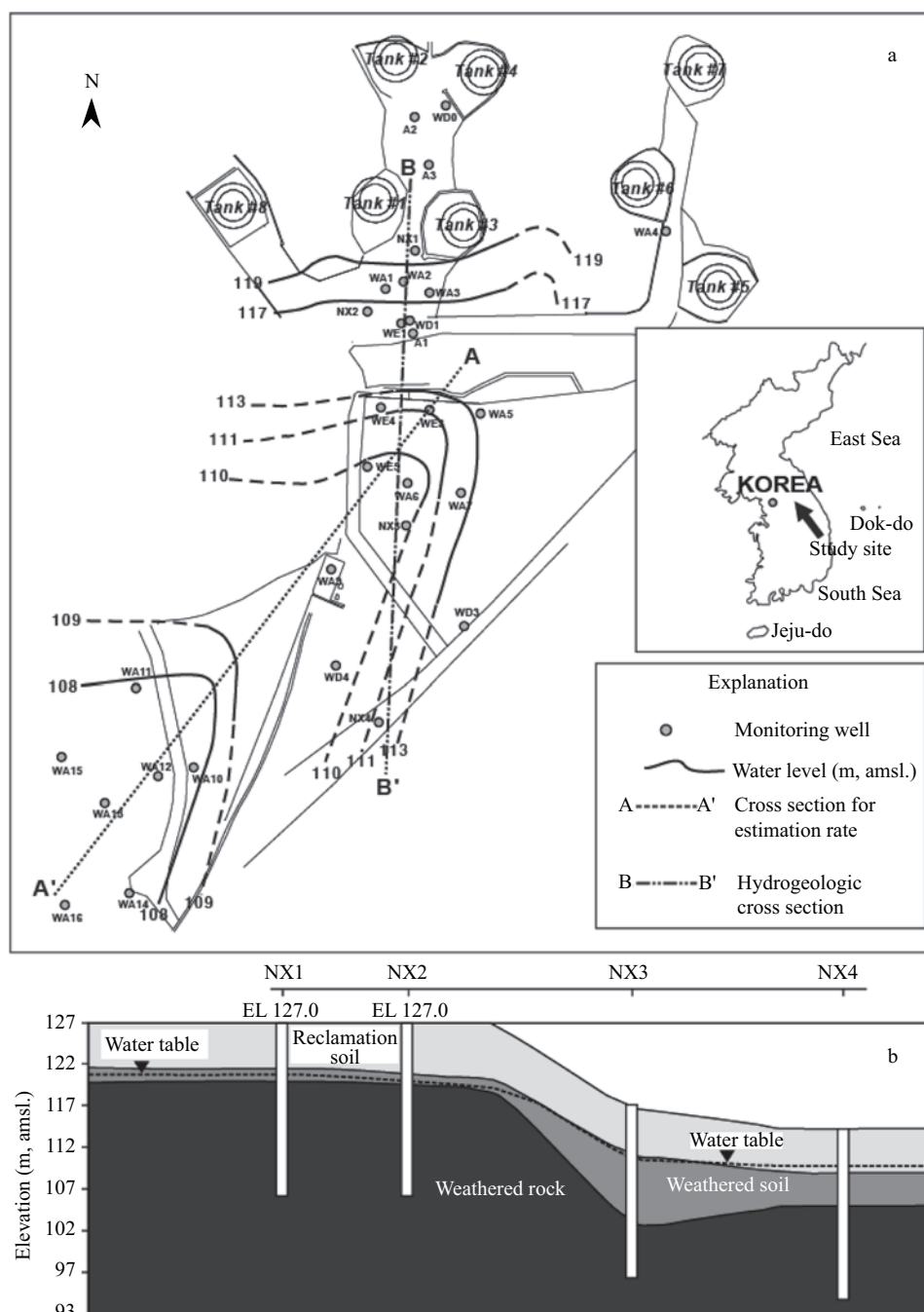


Fig. 1 Location of the study site showing monitoring well and groundwater level (May 2008) (a) and hydrogeologic cross-section (b).

excavation of the lower area. The hydrogeology of the site is comprised of three layers. The uppermost layer is reclamation soil (2.4–5.7 m thickness), mostly composed of fine to coarse sands, with gravels. Weathered soil (1.5–8.8 m thickness) underlies the uppermost layer, and was formed by complete weathering of indigenous Jurassic granites. The soil grains in this layer are fine to coarse sands, with sporadic rock fragments. The groundwater levels are generally formed in this layer. The hydraulic conductivity of this layer, estimated from slug tests, ranged between 2.29×10^{-4} and 5.97×10^{-4} cm/sec (mean 3.81×10^{-4} cm/sec) (KRC, 2007). The lowermost layer of the shallow aquifer is highly weathered rocks (granites), which are encountered at depths of 7–14.5 m. The hydraulic conductivity of this layer ranged from 2.93×10^{-4} to 1.34×10^{-3} cm/sec (mean 7.07×10^{-4} cm/sec), which is not much different from that of the weathered soil. Shallow groundwater mostly flows in the two lower layers.

Groundwater levels are generally formed at depths of 1.5–6.7 m, with annual fluctuations of 1.5–5 m and a very quick response (a few hours) to rainfall events. Groundwater flow occurs from northeast to southwest (Fig. 1), with a hydraulic gradient ranging from 0.002 in the dry season to 0.0915 in the wet season. The average porosity and longitudinal dispersivity of the weathered layers, estimated from physical experiments and tracer tests, were 0.175 and 0.1 m, respectively (Kim et al., 2009). The average annual precipitation at the site over the last 30 years (1971–2000) is 1267 mm, with over 70% of this occurring during June–September, which is the monsoon characteristic of eastern Asia (Lee and Lee, 2000). The mean air temperature is 10.8°C.

1.2 Sampling and analysis

A total of 24 monitoring wells were installed at the study site, which were screened in the weathered soil and/or weathered rock. To examine the levels and extent of groundwater contamination and evaluate the biodegradation capacity, six rounds of field parameters measurements, and four rounds of groundwater sampling for all available wells, including a few background wells (in an up-gradient area about 800 m), and subsequent laboratory chemical analyses were conducted between May 2008 and July 2009. In each sampling round, the water level, pH, electrical conductivity (EC), oxidation-reduction potential (ORP), water temperature and dissolved oxygen (DO) were measured using standard probes (Solinst waterlevel meter and Horiba D-53, 54, 55). In addition, the levels of dissolved iron (Fe^{2+}) and manganese (Mn^{2+}) were determined in the field using a field spectrophotometer (Hach DR2800, USA).

In each sampling round, four kinds of water sample were collected, for the analyses of volatile organic carbons (BTEX), anions, cations, including heavy metals, and alkalinity. Groundwater was collected in 40 mL clear vials without a headspace for the analysis of BTEX. For cations and heavy metals, 30 mL HDPE bottles were used, and after 0.45 μm filtration, the groundwater was acidified to below pH 2 using HNO_3 . Groundwater for anions and

alkalinity tests were collected, after filtration, in 100 mL and 40 mL bottles, respectively. All samples were stored at 4°C until used for the laboratory analyses. The alkalinity was determined by potentiometric titration on the day of sampling. Ionic constituents and cationic elements were analyzed by ion chromatography (DX-120, Dionex, USA), and atomic absorption spectrometry (5100PC, PerkinElmer, USA) or inductively coupled plasma-mass spectrometry (Ultramass700, Varian, USA), respectively. Volatile organic compounds (BTEX) were analyzed by gas chromatograph/mass spectrometry (GC/MS), with a purge-and-trap system (Saturn2100T Velocity XPT, Varian, USA). The concentration of NH_4^+ was determined using a spectrophotometer (Cary50, Varian, USA).

1.3 Expressed biodegradation capacity and attenuation rate

The expressed biodegradation capacity (EBC) is an indication of the potential of biodegradation for contaminants as a main destructive natural attenuation process at a given site, and the mass of contaminants removed by the biodegradation when electron acceptors, including dissolved oxygen, are additionally provided (Wiedemeier et al., 1999). Aerobic and anaerobic biodegradation may be simply evaluated from changes in the concentrations of electron acceptors (Lee and Lee, 2003). In this study, a simple calculation of the EBC was used for a specific terminal electron accepting process (Wiedemeier et al., 1999).

$$\text{EBC} = |C_p - C_B| / F \quad (1)$$

where, EBC (mg/L) is the expressed biodegradation capacity, C_p (mg/L) is the concentration of the electron acceptor or metabolic byproduct within the plume, C_B is the average background concentration of electron acceptor or metabolic byproduct and F is the utilization factor.

In addition, to examine the contaminant attenuation rate at each monitoring well (point attenuation rate), first order reaction kinetics was applied, as follows (McAllister and Chiang, 1994; Lu et al., 1999; Bockelmann et al., 2003),

$$C_t = C_0 e^{-kt} \quad (2)$$

where, C_t is the attenuated concentration of the contaminant at time t , C_0 the initial concentration, k the first order attenuation (decay) rate constant and t the elapsed (monitoring) time. Using the first order kinetics and measured concentration data, the decay constant (k) and corresponding half life ($t_{1/2}$) were computed. Furthermore, the bulk attenuation rate, representing contaminant attenuation along the groundwater flow path, and the corresponding first order biodegradation rate were also computed using the one dimensional steady-state analytical solution of Buscheck and Alcantar (1995),

$$\lambda = \frac{v_c}{4\alpha_x} ([1 + 2\alpha_x |k/v_x|]^2 - 1) \quad (3)$$

where, λ is the first order biodegradation rate, v_c the retarded contaminant velocity in direction x , α_x the dispersivity,

v_x the average groundwater seepage velocity and k/v_x the slope of line formed by plotting the natural logarithm of the contaminant concentrations versus the arithmetic distance down-gradient along the groundwater flow path.

Based on these estimated attenuation rates, the remediation times required reducing the contaminants concentrations to the Korean groundwater guidelines by natural attenuation or biodegradation were calculated.

2 Results and discussion

2.1 Groundwater quality and contamination levels

Table 1 shows the field measured parameters of the groundwater at the study site. Groundwater temperatures ranged between 7.9 and 24.2°C, indicating the effects of the outdoor air temperature on the shallow groundwater which were higher during summer (May–October), but much lower during winter (December–February). The pH of the groundwater was close to neutral or slightly acidic, with little seasonal variations. The DO concentration showed a wide variation (0.8–8.2 mg/L), with high levels of DO attributed to frequent replenishment of infiltrated rainwater. The DO was highest in the background and most of the down-gradient areas (WA13–16 wells), and lowest (< 1 mg/L) in the central area of the study site, where substantial BTEX contamination was found. Depletion of DO, low levels of ORP and high levels of contaminants are indicative of the occurrence of aerobic biodegradation (Wiedemeier et al., 1999).

The EC values ranged between 26 and 820 $\mu\text{S}/\text{cm}$. The

high EC values, mainly in the central area, were indicative of petroleum hydrocarbon contamination, while very low values represent the effects of direct and rapid rain infiltration into the shallow groundwater. Substantially elevated amounts of dissolved iron (Fe^{2+}) and manganese (Mn^{2+}), compared with background values, were indicative of the occurrence of iron and manganese reduction processes, especially in the most contaminated areas, where very low levels of DO and ORP were also observed (Cozzarelli et al., 2001). Iron and manganese oxides, as sources of dissolved species, are frequently found in reclamation soil and weathered soil (Kim et al., 2009). Under reduced redox conditions, these oxides will readily provide dissolved species into groundwater (Lovely and Phillips, 1986).

Table 2 shows the Pearson correlation matrix for the biodegradation relevant parameters. Different to what was expected; the correlation coefficients among the parameters were generally low to moderate. Statistically meaningful correlations ($p < 0.05$) were only found for a few sets of parameters. The highest correlation was 0.72, between Fe^{2+} and Mn^{2+} , which is common in petroleum contaminated groundwater (Wiedemeier et al., 1999; Lee and Lee, 2003). The BTEX levels showed a moderately negative correlation with the concentrations of nitrate and sulfate, which indicates the occurrence of nitrate and sulfate reduction. The sulfate concentration showed a somewhat high negative correlation ($r = -0.64$) with alkalinity, which is another indication of biodegradation, because the alkalinity would increase in an area affected by petroleum hydrocarbons (Cozzarelli et al., 1995; Lee et al., 2001). The elevated or excess alkalinity can be derived

Table 1 Field measured parameters

Parameter		May 2008 (<i>n</i> = 17)	Jun 2008 (<i>n</i> = 17)	Oct 2008 (<i>n</i> = 13)	Dec 2008 (<i>n</i> = 16)	Feb 2009 (<i>n</i> = 15)	Jul 2009 (<i>n</i> = 15)
Temp. (°C)	Maximum	17.1	23.4	20.7	14.1	16.5	24.2
	Minimum	12.8	16.4	15.9	7.9	8.5	18.5
	Median	15.8	19.6	18.0	10.2	11.8	20.3
	Variation coefficient	0.08	0.09	0.07	0.17	0.21	0.01
pH	Maximum	7.1	7.2	6.5	6.8	6.9	6.7
	Minimum	5.0	5.4	5.8	5.3	6.2	6.0
	Median	6.1	6.1	6.0	5.6	6.6	6.2
	Variation coefficient	0.10	0.07	0.04	0.09	0.04	0.03
DO (mg/L)	Maximum	8.2	3.8	2.1	5.7	2.8	4.8
	Minimum	1.7	1.5	0.9	1.4	0.8	1.5
	Median	3.0	2.1	1.2	3.0	1.2	1.8
	Variation coefficient	0.48	0.33	0.29	0.42	0.44	0.45
EC ($\mu\text{S}/\text{cm}$)	Maximum	820	711	710	708	668	429
	Minimum	120	96	129	82	91	26
	Median	218	196	247	230	220	264
	Variation coefficient	0.62	0.57	0.55	0.56	0.54	0.46
ORP (mV)	Maximum	340	241	222	376	200	250
	Minimum	-78	-82	-56	-4	-100	-39
	Median	109	118	49	186	93	64
	Variation coefficient	1.12	1.16	1.70	0.72	1.05	1.23
Fe^{2+} (mg/L)	Maximum	299.0	102.0	na	91.9	38.4	na
	Minimum	0.1	0.2	na	0.1	0.1	na
	Median	27.3	35.9	na	5.1	11.1	na
	Variation coefficient	1.41	0.98	na	1.43	0.87	na
Mn^{2+} (mg/L)	Maximum	25.3	29.4	na	16.4	22.0	na
	Minimum	0.2	0.0	na	0.1	0.0	na
	Median	7.8	6.7	na	8.4	6.3	na
	Variation coefficient	0.68	1.06	na	0.65	0.87	na

DO: dissolved oxygen; EC: electrical conductivity; ORP: oxidation-reduction potential; *n*: number of samples; na: not available (not measured).

Table 2 Pearson correlation coefficients among biodegradation relevant parameters

Parameter	BTEX	Temp	pH	EC	DO	ORP	Fe ²⁺	Mn ²⁺	Alkalinity	NO ₃ ⁻	SO ₄ ²⁻
BTEX	–	0.043	0.805	0.714	0.950	0.395	0.453	0.524	0.269	0.035	< 0.001
Temp	-0.40	–	0.937	0.243	0.102	0.207	0.035	0.005	0.197	0.347	0.559
pH	-0.14	0.11	–	0.403	0.038	0.162	0.105	0.568	0.067	0.206	0.178
EC	-0.16	0.28	0.23	–	0.516	0.095	0.796	0.085	0.658	0.665	0.169
DO	0.11	0.34	-0.41	-0.20	–	0.010	0.906	0.612	0.975	0.728	0.484
ORP	-0.23	-0.29	-0.31	-0.35	0.47	–	0.012	0.066	0.941	0.106	0.134
Fe ²⁺	0.21	0.41	-0.34	0.14	0.12	-0.46	–	< 0.001	0.616	0.808	0.262
Mn ²⁺	0.20	0.51	-0.19	0.36	0.18	-0.37	0.72	–	0.958	0.192	0.347
Alkalinity	0.27	0.29	0.37	0.17	-0.10	0.11	-0.18	0.11	–	0.190	< 0.001
NO ₃ ⁻	-0.41	0.24	0.29	0.17	-0.15	-0.34	0.14	0.30	-0.30	–	0.583
SO ₄ ²⁻	-0.64	-0.19	-0.30	0.31	0.21	0.33	-0.27	-0.24	-0.66	0.18	–

Levels of BTEX, EC, DO, Fe²⁺, alkalinity, NO₃⁻ and SO₄²⁻ were log-transformed for normal distribution. Correlation values are given in the lower triangle and probabilities that the parameters uncorrelated are given in the upper triangle. The correlation values greater than 0.4 are in bold.

from biodegradation (Borden et al., 1995; Basberg et al., 1998). In the mean time, the overall low correlations may be attributed to the frequently fluctuating or very variable chemical and redox conditions as a result of heavy rainfall, mainly during summer.

Most of the major ion compositions showed a Ca-HCO₃ type, which is typical of shallow groundwater (Appelo and Postma, 2005); while some of the groundwaters within the studied military facility (the lowermost boundary), and most of groundwaters in the background wells, exhibited a different Ca-SO₄ type (Fig. 2). Elevated or non depressed SO₄ concentrations indicated less active or no sulfate reduction in these areas, as there was no organic contamination in the background wells or only slight contamination in the boundary wells. However, no substantial seasonal changes in the water types were observed.

Figure 3 shows the seasonal variation in the BTEX concentrations in the groundwater between May 2008 and July 2009. The most concerning benzene concentrations ranged between 0.001 and 14.403 mg/L and; hence, the highest concentration exceeded the Korean groundwater guideline (0.015 mg/L benzene) 960 times. The peak benzene concentrations were still very high in July 2009, although the mean concentration was substantially decreased (Fig. 3a). The highest toluene concentration was 88.635 mg/L in December 2008, which was 88 times greater than the groundwater guideline (1 mg/L toluene). However, the

toluene concentrations greatly and rapidly decreased with time, and were close to or below the groundwater guideline in 2009 (Fig. 3b). The ethylbenzene concentrations showed a drastically decreasing trend over the analysis period (Fig. 3c). In 2009, all the concentrations were below the groundwater guideline (0.45 mg/L ethylbenzene). The peak xylene concentration was 119.535 mg/L in December 2008, which was 159 times greater than the groundwater guideline (0.75 mg/L xylene) but were greatly reduced to below or close to the guideline in 2009 (Fig. 3d).

In the meantime, with these decreasing trends, the contaminant concentrations generally showed seasonal fluctuations, that is, they were high during the dry winter (December and February), but low during the summer monsoon season (May and July). Based on these results, it was inferred that dilution due to heavy rainfall during the wet season greatly affected the decrease in the contaminant concentrations in this petroleum contaminated site, which is an example of natural attenuation (Lee and Lee, 2003). The BTEX concentrations were actually somewhat increased during the winter of 2010 (data not shown).

2.2 Biodegradation capacity and attenuation rates

Table 3 shows the results of EBC calculations, which were conducted for the four sampling events. The calculations were based on the lowest and highest concentrations of the electron acceptors or donors measured in the back-

Table 3 Results of EBC calculation in the study site for the study period

Parameter	May 2008		Dec 2008		Feb 2009		Jul 2009		F (mg/mg)
	C _B (mg/L)	C _P (mg/L)	C _B (mg/L)	C _P (mg/L)	C _B (mg/L)	C _P (mg/L)	C _B (mg/L)	C _P (mg/L)	
DO	6.03	1.70	6.90	1.40	3.00	0.80	5.60	1.50	3.14
NO ₃ ⁻	69.97	0.32	73.38	0.28	81.57	0.53	75.31	0.18	4.90
Mn ²⁺	0.02	25.25	0.00	16.40	0.00	22.10	0.00	8.97	10.78
Fe ²⁺	0.00	298.96	0.00	91.90	0.00	38.40	0.01	35.98	21.80
SO ₄ ²⁻	9.83	0.31	7.23	0.40	9.39	0.27	9.15	0.58	4.70
	May 2008		Dec 2008		Feb 2009		Jul 2009		Mean
EBC _{DO} (mg/L)	1.38		1.75		0.70		1.31		1.28
EBC _{NO₃⁻} (mg/L)	14.21		14.92		16.54		15.33		15.25
EBC _{Mn(IV)} (mg/L)	2.34		0.65		1.35		0.41		1.19
EBC _{Fe(III)} (mg/L)	13.71		4.22		1.76		1.65		5.34
EBC _{SO₄²⁻} (mg/L)	2.03		1.45		1.94		1.82		1.81
Total (mg/L)	33.67		22.99		22.99		20.52		24.87

EBC: expressed biodegradation capacity; F: BTEX utilization factor.

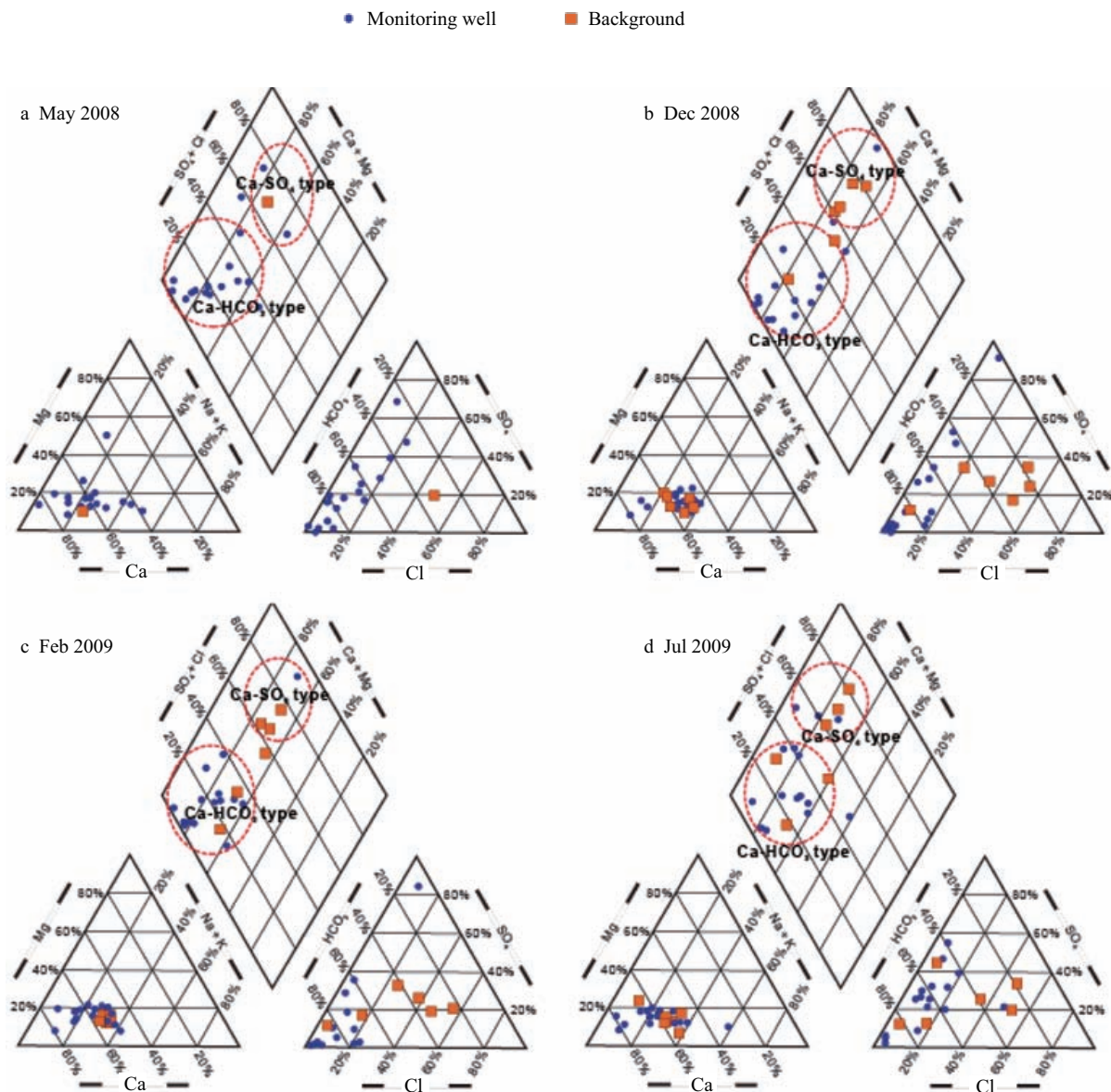


Fig. 2 Piper diagrams of the groundwater samples.

ground or contaminated monitoring wells. The calculated total EBC for BTEX ranged between 20.52 and 33.67 mg/L (mean 24.87 mg/L). Considering the BTEX levels of 0.002–239.906 mg/L (mean 7.931 mg/L; excluded not detected) in the groundwater at the site (2008–2009), the biodegradation capacity appeared to be good enough for the removal of BTEX if the electron acceptors are adequately replenished. The contribution of each electron accepting process to the total biodegradation was larger in the order: denitrification > iron reduction > sulfate reduction > aerobic respiration > manganese reduction. The denitrification accounted for 61.32% of the total expressed biodegradation (Fig. 4).

To evaluate the attenuation rate for the contaminated groundwater, a first order decay was applied to the monitored concentration data, which also included concentration data of a previous study (KRC, 2007). Many monitoring wells showed some erratic concentration be-

haviors, and were not suitable for first order or zero order decays (that is those that fluctuated most). Thus, only a few of the appropriate data sets for the first order decay were selected for the calculation (Fig. 5). Table 4 shows the calculated point attenuation rates for BTEX and benzene. The BTEX point attenuation rates were calculated to be 0.0058 and 0.0064 day⁻¹, which are equivalent to half lives of 120 and 108 days, respectively. These attenuation rates of BTEX were relatively larger than those (mean 0.0048 day⁻¹) of a shallow sandy alluvial aquifer in Uiwang, Korea (Lee and Lee, 2003). The remediation times required to reach the Korean groundwater guideline (total BTEX 2.215 mg/L) were only 0.7–1.2 years. These very short remediation times are due to the low levels of BTEX in these wells; the uppermost perimeter of the contaminant plume. Even though those wells were very close to the contamination source tanks, it is expected that the main plume had already been swept away from around the wells.

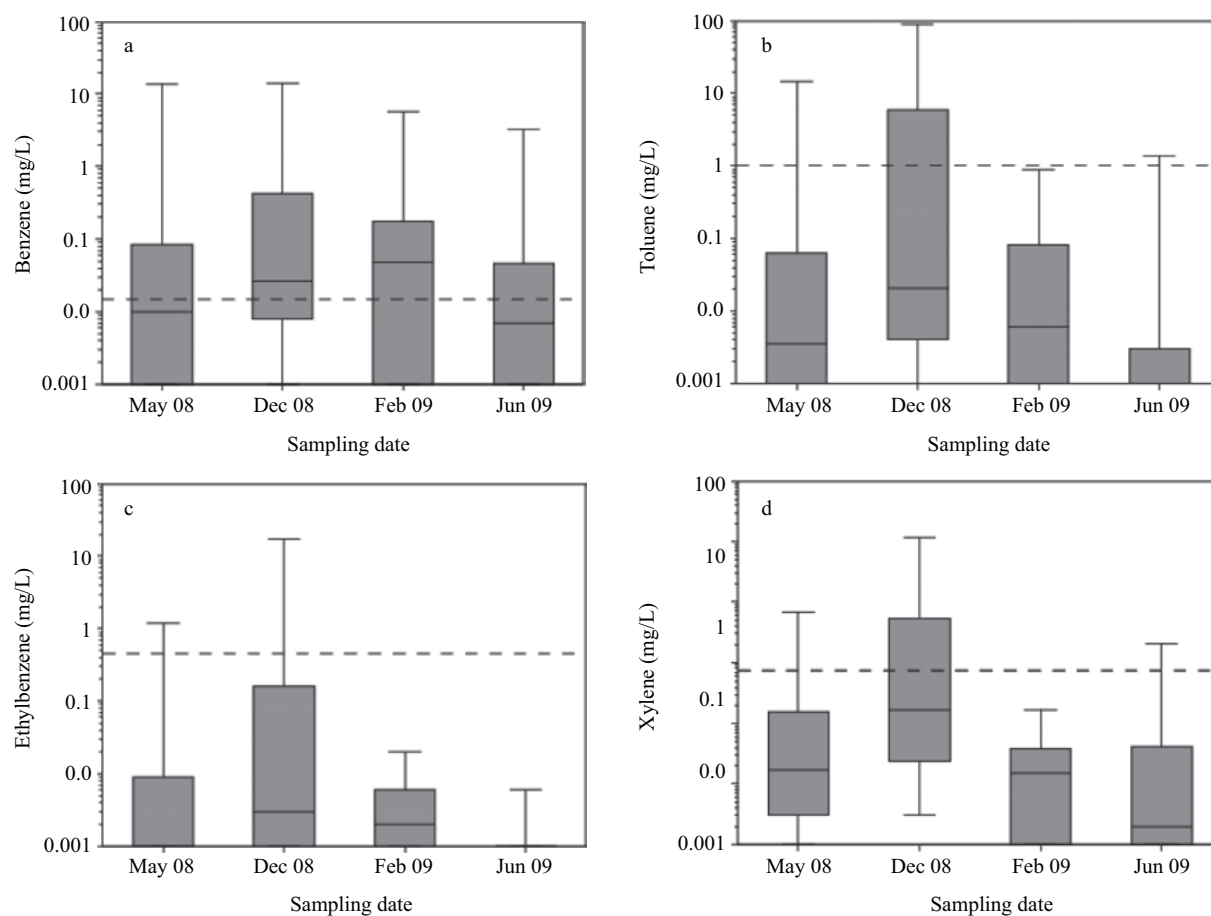


Fig. 3 BTEX concentrations of groundwater in the study area for 2008–2009. The dotted lines indicate the Korean groundwater guidelines.

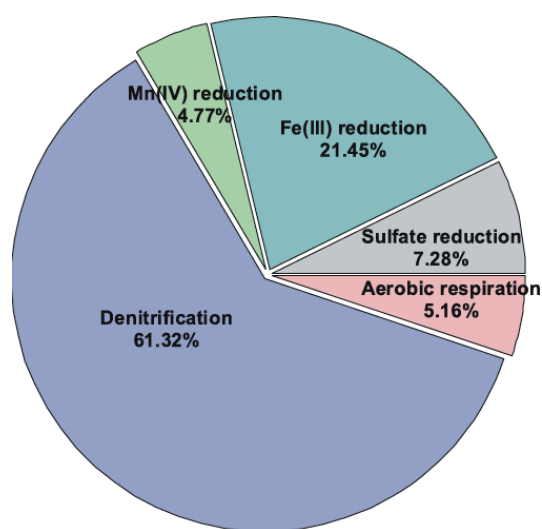


Fig. 4 Contribution of each electron accepting process to total biodegradation in the study site.

Because the spilled tanks were repaired and replaced, no further petroleum leakage was expected.

The point attenuation rates of benzene, the most dominant and worrying contaminant at this site, were much smaller, ranging from 0.0005 to 0.0032 day⁻¹ with half lives of 217–1386 days. The corresponding remediation

times (target 0.015 mg/L benzene) were calculated to be between 2.5 and 35.0 years. The longest remediation time was for the highest benzene concentration at well WE3. The moderate remediation times (2.5–5.1 years) were for the upper and lower boundary of the plume (NX1, WA7 and WA13). Thus, in the most conservative respect, at least 35 years should elapse to allow the cleaning up of benzene at each monitoring well due to natural attenuation.

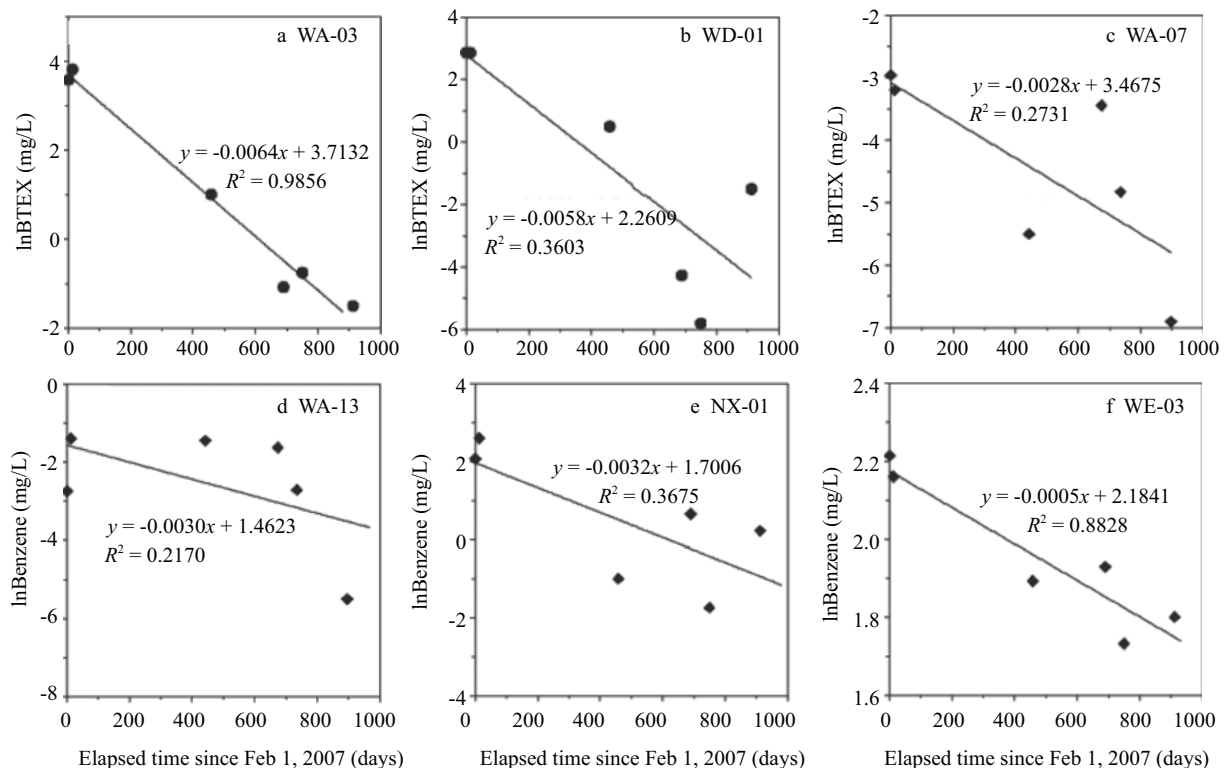
As shown above; however, the point attenuation rates and corresponding remediation times varied greatly, depending on the monitoring location (wells), with it being difficult to represent an attenuation rate or remediation time for the entire contaminated area. Thus, a bulk attenuation rate was calculated, which was considered to account for the concentration variation along the groundwater flow path. Figure 6 shows the variations in the BTEX and benzene concentrations with distance from the highest concentration point (WE3) along the A-A' cross section. Using the regression slope and groundwater linear velocity, the bulk attenuation rates were calculated to be 8.69×10^{-4} and 1.05×10^{-3} day⁻¹ for BTEX and benzene, respectively (Table 5). These attenuation rates corresponded to remediation times of 2620 days (7.2 years for BTEX) and 6387 days (17.5 years for benzene), respectively. The calculated rates of BTEX and benzene biodegradation were 7.92×10^{-5} and 1.32×10^{-4} day⁻¹, respectively (Eq. (3)). The remediation times, solely by biodegradation,

Table 4 Estimated point attenuation rates for total BTEX and benzene

Monitoring wells	Remediation target (mg/L) ^a	Point attenuation rate (day ⁻¹)	Half life (day)	Remediation time (yr) ^b
Total BTEX	WA3	2.215	0.0064	108
	WD1		0.0058	120
Benzene	WA7	0.015	0.0028	248
	WA13		0.0030	231
	NX1		0.0032	217
	WE3		0.0005	1386

^a Groundwater guideline of Korea.**Table 5** Estimated bulk attenuation rates for total BTEX and benzene

Parameters	Total BTEX	Benzene
Remediation target concentration (mg/L) ^a	2.215	0.015
Regression slope (k/v_x)	0.01670	0.02020
Bulk attenuation rate (day ⁻¹)	8.69×10^{-4}	1.05×10^{-3}
Half life (day)	797	659
Remediation time for bulk attenuation rate (day) ^b	2620	6387
Remediation time for bulk attenuation rate (yr) ^b	7.2	17.5
Biodegradation rate (day ⁻¹)	7.92×10^{-5}	1.32×10^{-4}
Remediation time for biodegradation rate (day) ^b	28752	63949
Remediation time for biodegradation rate (yr) ^b	79	139

^a Groundwater guideline of Korea; ^b time required to reach the remediation goal.**Fig. 5** Estimation of point attenuation rates for total BTEX and benzene.

were estimated to be 79 years for BTEX and 139 years for benzene.

From the view point of the attenuation rates, biodegradation would account for 9.1% (BTEX) and 12.6% (benzene) of the total bulk attenuation. Thus, this inferred that most of the natural attenuation occurring at this site

may be attributable to dilution due to heavy rainfall during summer and dispersion by the facilitated groundwater flow. Even though the capacity of natural attenuation at this site was not small, it would take between 17.5 and 35 years to reach the Korean groundwater guideline (in respect of benzene). Consequently, further active remediation works

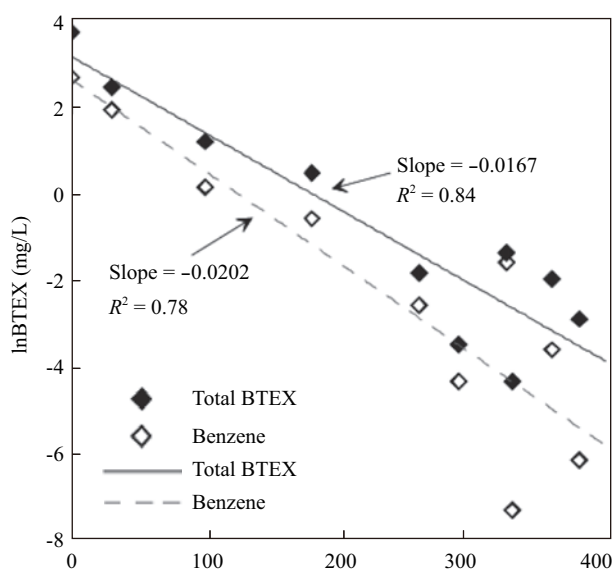


Fig. 6 Estimation of bulk attenuation rates for total BTEX and benzene using the concentration data obtained in May 2008.

will be required to reduce the remediation times.

3 Conclusions

The natural attenuation capacity, including biodegradation, point attenuation and bulk attenuation, was examined for petroleum (BTEX) contaminated groundwater at a military facility in Korea. The hydrogeological conditions, including high water level, permeable uppermost layer and frequent heavy rainfall during summer, were favorable for natural attenuation at this site. Changes in the concentrations of electron acceptors and donors, and relevant hydrochemical conditions, such as oxidation-reduction potential, are indicative of the occurrence of biodegradation processes, including aerobic respiration, denitrification, iron reduction, manganese reduction and sulfate reduction. Detectable methane gas concentrations at a few of the monitoring wells also indicated the occurrence of methanogenesis (not quantified).

The calculated BTEX expressed biodegradation capacity ranged between 20.52 and 33.67 mg/L, and appeared to be substantially effective at reducing the levels of contaminants which ranged from 0.002 to 239.906 mg/L in 2008–2009. The contribution of each electron accepting process to the total biodegradation was larger in the order denitrification > iron reduction > sulfate reduction > aerobic respiration > manganese reduction. The BTEX and benzene point attenuation rates were 0.0058–0.0064 day⁻¹ and 0.0005–0.0032 day⁻¹, corresponding to remediation times of 0.7–1.2 and 2.5–30 years, respectively. The BTEX and benzene bulk attenuation rates evaluated along the groundwater flow path were 8.69×10^{-4} and 1.05×10^{-3} day⁻¹, respectively. These attenuation rates corresponded to remediation times of 7.2 years for BTEX and 17.5 years for benzene. Most of the natural attenuation occurring during this site can be attributed to dilution and dispersion.

In summary, the biodegradation and natural attenuation capacities are sufficient to lower the contaminant levels,

but their rates appeared to slow for the remediation goal to be attained within a reasonable time frame at this site, where military operations will be commenced immediately. Thus, further active remedial measures are essential.

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