

Application of monitored natural attenuation to remediate a petroleum-hydrocarbon spill site

C.M. Kao*, W.Y. Huang*, L.J. Chang*, T.Y. Chen*, H.Y. Chien* and F. Hou**

*Institute of Environmental Engineering, National Sun Yat-Sen University, Kaohsiung, Taiwan

**Department of Occupational Safety and Health, China Medical University, Tai-Chung, Taiwan

Abstract Contamination of groundwater by petroleum-hydrocarbons is a serious environmental problem. The Monitored Natural Attenuation (MNA) approach is a passive remediation to degrade and dissipate groundwater contaminants *in situ*. In this study, a full-scale natural bioremediation investigation was conducted at a gasoline spill site. Results show that concentrations of major contaminants (benzene, toluene, ethylbenzene, and xylenes) dropped to below detection limit before they reached the downgradient monitor well located 280 m from the spill location. The results also reveal that natural biodegradation was the major cause of the observed contaminant reduction. The calculated natural first-order attenuation rates for BTEX and 1,2,4-trimethylbenzene (1,2,4-TMB) ranged from 0.051 (benzene) to 0.189 1/day (1,2,4-TMB). Evidence for the occurrence of natural attenuation includes the following: (1) depletion of dissolved oxygen, nitrate, and sulfate; (2) production of dissolved ferrous iron, sulfide, and CO₂; (3) decreased BTEX concentrations and BTEX as carbon to TOC ratio along the transport path; (4) increased alkalinity and microbial populations; (5) limited spreading of the BTEX plume; and (6) preferential removal of certain BTEX components along the transport path. Additionally, the biodegradation capacity (44.73 mg/L) for BTEX and 1,2,4-TMB was much higher than other detected contaminants within the plume. Hence, natural attenuation can effectively contain the plume, and biodegradation processes played an important role in contaminant removal.

Keywords BTEX; groundwater; methanogenesis; MNA; natural attenuation; petroleum-hydrocarbon

Introduction

Accidental release of petroleum products from underground storage tanks (USTs) is one of the most common causes of groundwater contamination. There are more than three million USTs storing petroleum products in the US, and as many as 500,000 may be leaking petroleum into the ground (AFCEE, 1994; US EPA, 2004). 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 isomers (BTEX), the major components of fuel oils (especially gasoline); they 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. Results of field investigation suggest that many of these spills have been naturally biodegraded before the contaminants reach a drinking water receptor (Borden *et al.*, 1995; Kao and Wang, 2000; Kao and Prosser, 2001). Because the petroleum-hydrocarbon caused plumes that could be quite diffuse and widespread, some more economic approaches are desirable for *in situ* remediation to provide for a long-term control of the contaminated groundwater. The Monitored Natural Attenuation (MNA) approach is a passive remedial method that depends upon natural processes to degrade and dissipate contaminants in soil and groundwater. This natural process includes physical, chemical, and biological transformations, e.g. aerobic/anaerobic biodegradation, cometabolism, dispersion, volatilization,

oxidation, reduction, and adsorption (Rifai *et al.*, 1995; Bedient *et al.*, 1999; Surampalli and Banerji, 2002). Aerobic and anaerobic biodegradations are believed to be the major mechanisms that account for both containment of the petroleum-hydrocarbon plume and reduction of the contaminant concentrations. The aerobic biodegradation relies on dissolved oxygen (DO) as the electron acceptor used by the subsurface microorganisms while the anaerobic processes depend on a variety of biodegradation mechanisms to use nitrate, ferric iron [Fe(III)], sulfate, and carbon dioxide (CO₂) as terminal electron acceptors (Hunt *et al.*, 1997; Kota, 1998; Kao and Wang, 2000).

Environmental conditions and microbial competition will ultimately determine which anaerobic biodegradation processes would dominate. When oxygen is depleted and nitrate is present, the latter can be used as an electron acceptor by facultative denitrifiers to mineralize the fuel hydrocarbons in denitrification (Kao and Wang, 2000; Johnson *et al.*, 2003). Once the available DO and nitrate in the aquifer are depleted, ferric iron can be used as an electron acceptor. A large quantity of ferric iron is present in the sediments of most aquifers, which could potentially provide a large reservoir of electron acceptor for hydrocarbon biodegradation (Kota, 1998; Kao and Wang, 2000). The available evidence suggests that the iron-reducing process can significantly influence the fate and transport of hydrocarbons in the subsurface (Kota, 1998; Kao *et al.*, 2001). After the depletion of DO, nitrate, and ferric iron, sulfate-reducing bacteria could then degrade petroleum hydrocarbons using sulfate as the electron acceptor in the sulfate reduction process. After sulfur is depleted, methanogenic consortia could potentially biodegrade fuel hydrocarbons, and CO₂ could be used as the electron acceptor. The presence of elevated methane levels in the groundwater relative to background methane concentrations is a good indicator of methane formation (Brown *et al.*, 1997; Bedient *et al.*, 1999; Seagren and Becker, 2002).

At present, many research efforts have been directed toward applying the natural attenuation to control the dissolved contaminant migration. However, results of full-scale demonstrations of the natural attenuation process and its mechanisms, especially at the demonstration site where mixed biodegradation patterns (e.g. aerobic degradation, denitrification, iron reduction, methanogenesis) are occurring within the plume have not been well documented in the literature. The objectives of this study were to: (1) characterize a hydrocarbon contaminated aquifer at a petroleum-hydrocarbon spill site, (2) characterize the variations in aqueous phase geochemistry, (3) assess the occurrence and mechanisms of natural attenuation, (4) calculate the field-scale natural attenuation rates of the contaminants, and (5) evaluate the effects of using MNA as a remedial option.

Study site description

A government owned tank farm facility site located in southern Taiwan (Kaohsiung County) was selected for this MNA study. In 1998, leakage from a fuel-oil pipeline resulted in groundwater contamination by petroleum hydrocarbons (mainly BTEX). During the following six-year investigation period (from 1998 to 2004), more than 100 soil gas and soil samples were collected; meanwhile 15 monitor wells and two recovery wells were installed for site characterization and contaminated-groundwater extraction. On-site borings encountered up to 25 m of mostly brownish to grayish, fine to medium sand to silty sands. The average groundwater elevation within the shallow aquifer is approximately 1.5 to 3 m below the ground. Groundwater in the unconfined aquifer, according to the groundwater elevation in on-site monitor wells, flows to the southwest. The measured effective porosity is 0.3, and the average hydraulic conductivity for the surficial, unconfined aquifer is 2.9×10^{-5} m/sec (2.5 m/day). The calculated site groundwater flow velocity is 3.7×10^{-5} m/sec (3.2 m/day). The measured groundwater temperature in the surficial

aquifer varies from 17 to 29 °C. Since the year 2001, MNA has been applied to remediate the contaminated groundwater. Figure 1 presents the site map showing the estimated plume boundary, locations of monitor wells and soil sampling locations, and groundwater flow direction.

Natural attenuation investigation

In the spring of 2001, a MNA study at the Kaohsiung site was conducted with the funding provided by the Chinese Petroleum Corp. and Taiwan's National Science Council. During the two-year investigation period, a monitoring network system was installed to delineate the dissolved contamination (Figure 1). The most probable number (MPN) enumeration studies were performed to define the distribution of microorganisms; natural attenuation rates were calculated to evaluate the effectiveness of MNA on plume containment.

Monitoring network installation

A total of 15 monitor wells (5.1-cm I.D.; 0.025-cm slot screen) were installed to delineate the longitudinal distribution of the dissolved BTEX plume (Figure 1). For simplicity and ease of identification, the plume was divided into four different areas, i.e. Area 1 to Area 4, to represent the source area, mid-plume area, downgradient area, and background area, respectively. The representative monitor wells in these four areas were designated as

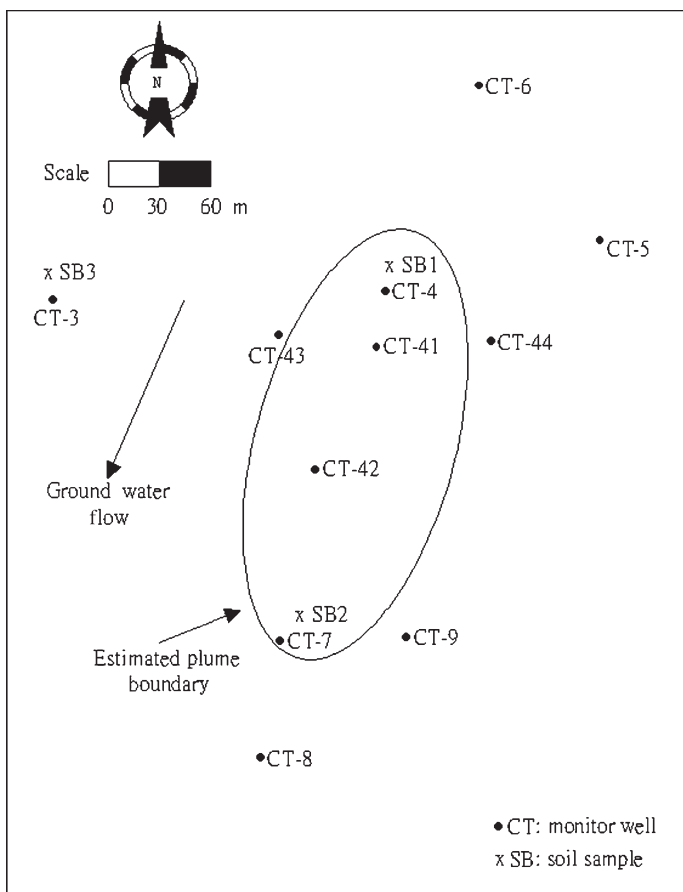


Figure 1 Site map showing the groundwater flow direction, estimated plume boundary, and soil and groundwater sampling locations

CT4, CT42, CT7, and CT3 respectively. Groundwater samples collected from these four representative wells were analyzed and compared in this study. All four wells were screened from 2 to 5.1 m below land surface (bls).

Groundwater monitoring and microbial enumeration

Groundwater samples from the monitor wells were collected and analyzed for organic compounds and geochemical indicators including BTEX, 1,3,5-TMB, 1,2,4-TMB, CH₄, CO₂, inorganic nutrients, anions, pH, redox potential (Eh), and DO. Organic compound analyses were performed in accordance with US EPA Method 502.2, using a Varian 3800 Gas Chromatograph (GC). Methane was analyzed using a Shimadzu GC-9A GC using headspace techniques. Ion chromatography (Dionex) was used for analyzing inorganic nutrients and anions (NO₃⁻, NO₂⁻, SO₄⁻², PO₄⁻³). On-site measurements of Eh and pH were done with two MP120 pH/Eh meters (Mettler-Toledo). A WTW DO meter (Oxi 330) was used for on-site DO and temperature measurements, and a Hach digital titrator cartridge was used for on-site CO₂ measurements. Aquifer sediments were collected from the soil borings SB1, SB2, and SB3, which were adjacent to CT4, CT7, and CT3, respectively. The collected aquifer sediments were used for microbial enumeration to determine the number of total heterotrophs, total heterotrophic anaerobes (total anaerobes), and methanogens. Total plate counts were conducted using plate count agar (Difco) to assess the approximate number of the total heterotrophic bacterial growth using the spread plate method (APHA, 1995). Prepared plates were incubated at 30 °C for 48 hours, then counted for colony forming units (CFU). Total anaerobes were enumerated using the five-tube MPN assay (Kota, 1998; Kao and Wang, 2000). The total anaerobe tubes containing media described by Kota (1998) and Kao and Wang (2000) were score positive based on optical density.

Calculation of natural attenuation rates and biodegradation capacity

The first-order decay model (Equation 1) was applied to estimate the natural attenuation rate between CT4 and CT42 using the measured contaminant concentrations in CT4 and CT42 in the following equation:

$$C_{42} = C_4 \exp(-Kt) \quad (1)$$

where

C_{42} = measured contaminant concentration (µg/L) at CT42

C_4 = measured contaminant concentration (µg/L) at CT4

K = first-order decay rate (natural attenuation rate) (day⁻¹)

t = distance between two cross-sections/groundwater flow velocity

Based on the calculated natural attenuation rates, the order of preferential removal of certain BTEX components can be determined.

The biodegradation capacity was calculated using the total amount of electron acceptor available for biological reactions. The procedure includes: (1) calculating the difference between the upgradient wells and source zone wells for oxygen, nitrate, and sulfate; and (2) measuring the production of by-products ferrous iron and methane in the source zone (US EPA, 1998). Using stoichiometry, a utilization factor can be developed to convert the mass of oxygen, nitrate, and sulfate consumed to the mass of dissolved hydrocarbons that are used in the biodegradation reactions. Similarly, the utilization factor can be developed to convert the mass of metabolic by-products that are produced to the mass of dissolved hydrocarbon to be used in the subsequent biodegradation reactions. Thus, the biodegradation

capacity can be calculated using the following equation:

$$\begin{aligned} \text{biodegradation capacity (mg/L)} = & (\text{upgradient DO concentration} \\ & - \text{DO concentration in the source zone})/3.15 \\ & + (\text{upgradient nitrate concentration} \\ & - \text{nitrate concentration in the source zone})/4.86 \\ & + (\text{upgradient sulfate concentration} \\ & - \text{sulfate concentration in the source zone})/4.71 \\ & + (\text{ferrous iron concentration in the source zone})/21.89 \\ & + (\text{methane concentration in the source zone})/0.78 \end{aligned}$$

Results and discussion

Groundwater samples were collected from monitor wells CT4, CT42, CT7, and CT3, which were located near the spill location, mid-plume area, downgradient area, and background area of the plume, respectively. Table 1 shows the averaged results of seven groundwater sampling events during the two-year investigation period. The aquifer sediment samples collected from soil borings SB1, SB2, and SB3 were used for microbial enumeration. Results of the bacterial population assessment are also shown in Table 1. Figure 2 presents variations in BTEX and 1,2,4-TMB concentrations along the transport path from source (monitor well CT4) to the most downgradient monitor well (CT8).

The decline in Eh and DO near the source area reflects the change from oxidizing to reducing conditions. High CO₂ concentrations and alkalinity were observed in CT4. This indicates that significant microbial activity and natural bioremediation occurred in this area. The lower nitrate and sulfate concentrations within the plume reveal that both nitrate and sulfate were used as the electron acceptors after the depletion of oxygen. The production of sulfide in CT4 also confirmed the occurrence of the sulfate reduction process. High ferrous concentrations were detected in CT4 indicating that ferric irons might have also been used as the electron acceptor around the source area. Moreover, a relatively higher concentration of methane was also detected in CT4. This indicates that mixed anaerobic biodegradation processes occurred within the most contaminated zone. The decrease in BTEX concentrations from CT4 to CT7 suggests the occurrence of natural attenuation of BTEX. The declined BTEX expressed as carbon to TOC ratio (BTEX as C/TOC) along the transport path reveals that total BTEX caused the high TOC measurements near the source area and increasing BTEX degradation by-products along the transport path. The results show that a significant amount of total heterotrophs and total anaerobes (> 10⁶ cells per g of soil) were detected in the SB1 soil sample collected from the most contaminated area. This points out that higher petroleum-hydrocarbon concentrations caused a more measured bacterial population.

The calculated first-order decay rates for contaminants between CT4 and CT42 are presented in Table 1. Results show that 1,2,4-TMB had the highest first-order decay rate (0.189 day⁻¹), followed by toluene (0.166 day⁻¹), *m* + *p*-xylene (0.149 day⁻¹), *o*-xylene (0.124 day⁻¹), ethylbenzene (0.098 day⁻¹), and benzene (0.051 day⁻¹). Benzene was the least biodegradable compound under anaerobic conditions and toluene was the most biodegradable compound among BTEX. The observed biodegradation trend for BTEX

Table 1 Average concentrations of petroleum-hydrocarbons and indicator parameters in a profile along the plume centerline

Monitor well	CT-3	CT-4	CT-42	CT-7	Decay rate ⁴
Distance to CT-4 (m)	– ¹	0	100	210	–
Location	Background	Source	Mid-plume	Downgradient	–
Benzene (μg/L)	BDL ²	170.1	34.4	0.8	0.051
Toluene (μg/L)	BDL	88.8	0.5	BDL	0.166
Ethylbenzene (μg/L)	BDL	182.6	8.5	BDL	0.098
<i>m,p</i> -xylene (μg/L)	BDL	202.4	1.9	BDL	0.149
<i>o</i> -xylene (μg/L)	BDL	9.5	0.2	BDL	0.124
Total BTEX (μg/L)	BDL	653.4	45.5	0.8	0.085
1,2,4-TMB (μg/L)	BDL	35.2	0.1	BDL	0.189
1,3,5-TMB (μg/L)	BDL	BDL	BDL	BDL	–
DO (mg/L)	2.4	0.5	1.4	1.5	–
Nitrate (mg/L)	83.4	0.2	37.6	41.3	–
Total iron (mg/L)	1.7	19.0	1.5	2.0	–
Ferrous iron (mg/L)	0.2	11.7	0.1	0.04	–
Sulfate (mg/L)	102.2	10.1	69.4	37.8	–
Sulfide (μg/L)	10	17	11	6	–
Carbon dioxide (mg/L)	167	250	177	179	–
Methane (mg/L)	0.002	2.1	0.056	0.010	–
pH	6.8	6.7	7.1	6.5	–
Redox potential (mV)	168.2	–44.0	158.8	178.4	–
Alkalinity (mg/L as CaCO ₃)	164.9	374.2	232.4	154.9	–
Ammonia nitrogen (mg/L)	0.13	0.95	0.13	0.12	–
TOC (mg/L)	7.0	18.9	5.7	17.7	–
BTEX as C/TOC	–	0.033	0.008	4 × 10 ^{–5}	–
Total heterotrophs (cell/g)	5 × 10 ⁵ (SB3) ³	4.6 × 10 ⁷ (SB1)	–	3.0 × 10 ⁶ (SB2)	–
Total anaerobes (cell/g)	2 × 10 ⁴ (SB3)	1.3 × 10 ⁶ (SB1)	–	7.4 × 10 ⁴ (SB2)	–

¹ –: not available²BDL: below detection limit³SB: soil sample⁴First order decay rate (1/day)

matched with the results presented by other investigations (Hunt *et al.*, 1997; Kota, 1998; Kao and Wang, 2000).

The observed decay rate for 1,2,4-TMB has drawn more attention. Most researchers indicate that 1,2,4-TMB might not be biodegradable, and thus, it has been suggested as a tracer to evaluate the natural biodegradation rate of BTEX (Wiedemeier *et al.*, 1996; Kao and Prosser, 2001). However, results from this study indicate that the 1,2,4-TMB has a much higher decay rate than BTEX. This reveals that 1,2,4-TMB might be biodegradable under certain conditions, especially under anaerobic conditions. Thus, preliminary studies must be done prior to using 1,2,4-TMB as a tracer during the MNA study. Moreover, the observed decay rates for BTEX are higher than those reported by other researchers (Borden *et al.*, 1995; Hunt *et al.*, 1997; Kota, 1998; Kao and Wang, 2000; Kao and Prosser, 2001) demonstrating that significant natural attenuation processes occurred at this site to cause the removal of contaminants in groundwater.

If dilution was the only cause for the observed BTEX reduction, the plume width should increase inversely proportional to the decreasing BTEX concentrations along the transport path. However, the plume width was not observed to increase over the distance

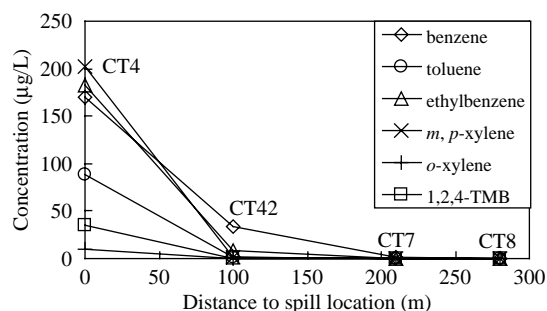


Figure 2 Variations in BTEX and 1,2,4-TMB concentrations along the transport path

while significant drops of the BTEX concentrations were detected. As the plume spread slightly in width due to dispersion, oxygen in the uncontaminated groundwater mixed with BTEX at the plume sides causing enhanced biodegradation. Thus, the limited spreading of the plume was attributed to some mixed natural attenuation processes including natural biodegradation, dilution, and dispersion, with the natural biodegradation playing an important role in plume containment. Based on the measured concentrations of DO, nitrate, ferrous iron, sulfate, and methane, the calculated biodegradation capacities for BTEX and 1,2,4-TMB aerobic biodegradation were 0.55 mg/L for denitrification, 20.96 mg/L for iron reduction, 0.48 mg/L for sulfate reduction, and 3.6 mg/L for methanogenesis. These values are much higher than the measured contaminant concentrations in groundwater thus indicating that the total amount of electron acceptors available for natural biodegradation would be sufficient for removing the total contaminant mass (BTEX and 1,2,4-TMB) found in the contaminated groundwater.

Conclusions

A detailed full-scale investigation on natural attenuation has been completed at a petroleum-hydrocarbon contaminated site located in Kaohsiung County, Taiwan. This study was conducted to assess if the MNA processes can be applied as a remedial option to reduce the contaminant concentrations to below regulatory standards before the contaminants are transported to downgradient potential receptors. The two-year investigation results show that natural attenuation mechanisms occurred at this site to cause the removal of the groundwater contaminants through mixed physical, chemical, and biological processes. Evidence for natural attenuation includes:

- (1) depletion of DO, nitrate, and sulfate within the plume;
- (2) production of dissolved ferrous iron, sulfide, and CO₂ within the plume;
- (3) decreased BTEX concentrations and BTEX measured as the carbon to TOC ratio along the transport path;
- (4) increased alkalinity and microbial populations within the plume;
- (5) limited spreading of the BTEX plume; and
- (6) preferential removal of certain BTEX components along the transport path.

The monitoring results, which show high contaminant decay rates and high biodegradation capacity, demonstrate that the contaminants could be attenuated naturally before they reach any farther downgradient receptors. The results also point out that the BTEX plume is not growing but reaching a steady-state condition when it is subject to natural bioremediation under mixed aerobic and anaerobic conditions. Results from this study indicate that the MNA approach is an acceptable remedial option; it is effective in remediating and managing this petroleum hydrocarbon spill site. With increasing knowledge on the

mechanism of natural attenuation less conservative regulatory decisions may be possible such that the costs associated with site remediation can be minimized.

Acknowledgements

This study was funded by National Science Council in Taiwan and Chinese Petroleum Corp., Taiwan. Additional thanks to Mr. C.Y. Yu of Chinese Petroleum Corp., Taiwan, and Mr. J.K. Fu and C.M. Tang of National Sun Yat-Sen University for their assistance throughout this project.

References

- AFCEE (Air Force Center for Environmental Excellence), Armstrong Laboratory, and Air Force Institute of Technology (1994). Use of risk-based standards for cleanup of petroleum contaminated soil. Brooks Air Force Base, TX.
- APHA/AWWA/WEF (1995). *Standard Methods for the Examination of Water and Wastewater*, 11th edn., Washington, DC, USA.
- Bedient, P.B., Rifai, H.S. and Newell, C.J. (1999). *Ground Water Contamination – Transport and Remediation*, PTR Prentice-Hall, Inc., New Jersey.
- Borden, R.C., Gomez, C.A. and Becker, M.T. (1995). Geochemical indicators of natural bioremediation. *Ground Water*, **33**, 180–189.
- Brown, K., Sekerka, P., Thomas, M., Perina, T., Tyner, L. and Sommer, B. (1997). Natural attenuation of jet fuel-impacted groundwater. In *Situ and On-site Bioremediation*, Alleman, B.C. and Leeson, A. (eds), Battelle Press, Columbus, Ohio, Vol. 1, pp. 83–88.
- Hunt, M.J., Shafer, M.B., Barlaz, M.A. and Borden, R.C. (1997). Anaerobic biodegradation of alkylbenzenes in aquifer material under methanogenic and iron-reducing conditions. *Bioremediation J.*, **1**, 53–64.
- Johnson, S.J., Woolhouse, K.J., Prommer, H., Barry, D.A. and Christofi, N. (2003). Contribution of anaerobic microbial activity to natural attenuation in groundwater. *Engineering Geology*, **70**, 343–349.
- Kao, C.M., Kota, S., Ress, B., Barlaz, M.A. and Borden, R.C. (2001). Effects of subsurface heterogeneity on natural bioremediation at a gasoline spill site. *Wat. Sci. Tech.*, **43**(5), 341–348.
- Kao, C.M. and Prosser, J. (2001). Evaluation of natural attenuation rate at a gasoline spill site. *J. of Hazardous Materials*, **B82**, 275–289.
- Kao, C.M. and Wang, C.C. (2000). Control of BTEX migration by intrinsic bioremediation at a gasoline spill site. *Wat. Res.*, **34**, 3413–3423.
- Kota, S. (1998). Biodegradation in contaminated aquifers: influence of microbial ecology and iron bioavailability. Ph.D. Dissertation, North Carolina State University, Raleigh, NC.
- Rifai, H.S., Borden, R.C., Wilson, J.T. and Ward, C.H. (1995). Intrinsic bioattenuation for subsurface restoration. In *Intrinsic Bioremediation*, Hinchee, R.E., Wilson, J.T. and Downey, D.C. (eds), CRC Press, Boca Raton, FL, pp. 1–30.
- Seagren, E. and Becker, J. (2002). Review of natural attenuation of BTEX and MTBE in groundwater. *Practice periodical of hazardous, toxic, and radioactive waste management*, **6**, 156–172.
- Surampalli, R. and Banerji, S. (2002). Long-term performance monitoring at natural attenuation site. *Practice periodical of hazardous, toxic, and radioactive waste management*, **6**, 173–176.
- Wiedemeier, T.H., Wilson, J.T., Kampbell, D., Jansen, J.E. and Haas, P. (1996). Technical protocol for evaluating the natural attenuation of chlorinated ethenes in groundwater. In *Proceedings of the 1996 Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation Conference*, Nat. Water Well Asso., Houston, TX, pp. 425–444.
- US EPA (1998). *BIOPLUME III: Natural Attenuation Decision Support System, User's Manual*, Ver. 1.0. EPA/600/R-98/010.
- US EPA (2004). How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites: a Guide for Corrective Action Plan Reviewers. EPA/510/R-04-002.