Intrinsic bioremediation of fuel contamination in ground water at a field site

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Abstract

A spill of gasoline occurred at an automobile service station in 1986. Oily phase residue in the subsurface has continued for the past 8 yr to release water soluble fuel hydrocarbons into the aquifer. The site was characterized for implementation of intrinsic remediation. The subsurface was a beach sand with sea shell fragments. The water table was near 1.3 m below ground surface. Surface dimensions over the plume were about 200 m downgradient and 60 m in width. Three points to coincide with direction of ground-water flow were selected in the plume for water quality assessments. Both methane and trimethylbenzene were used as surrogate tracers to normalize loss of contaminants. Aerobic respiration and methanogenesis accounted for most biodegradation obtained. Assimilation capacities of dissolved oxygen, ferrous iron, and methane distributions when compared to BTEX concentrations showed that the ground water has sufficient capacity to degrade all dissolved BTEX before the plume moves beyond 250 m downgradient. Evidence obtained from loss of contaminants, geochemistry, and microbial breakdown chemicals showed that intrinsic bioremediation technology would be a viable option to restore the site.

Keywords: Bioremediation; Fuel contamination; Ground water

1. Introduction

A detailed characterization study was conducted during March 1994 at a fuel spill location on Patrick Air Force Base in Cocoa Beach, Florida. Core material and ground-water samples were collected and analyzed to predict the influence of natural

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Table 1
Benzene biodegradation reactions

Aerobic respiration	$7.5O_2 + C_6H_6 = 6CO_2 + 3H_2O$
Denitrification	$6NO_3^- + 6H^+ + C_6H_6 = 6CO_2 + 6H_2O + 3N_2$
Iron reduction	$6OH^+ + 3OFe(OH)_3 + C_6H_6 = 6CO_2 + 3OFe^{2+} + 78H_2O$
Sulfate reduction	$7.5H^+ + 3.75SO_4^{2-} + C_6H_6 = 6CO_2 + 3.75H_2S + 3H_2O$
Methanogenesis	$4.5H_2O + C_6H_6 = 2.25CO_2 + 3.75CH_4$

attenuation on dissolved contaminant migration and attenuation. The technical protocol followed was reported by Wiedemeier et al. [1]. The remediation of contaminants in ground water is called intrinsic remediation which incorporates mechanisms of biodegradation, sorption, dilution, volatilization, dispersion, and advection. All of these processes can operate concurrently during field scale implementation of bioremediation technology. The respiration processes microorganisms used to bring about a reduction in total contaminant mass in ground water are aerobic respiration, denitrification, iron or manganese reduction, sulfate reduction, and methanogenesis (Table 1). These processes, called intrinsic bioremediation, are important contributors to benzene, toluene, ethylbenzene, xylenes (BTEX) removal from ground water.

If oily phase residue is present in the subsurface, it can act as a continuing source of contamination. To demonstrate intrinsic bioremediation at field spill sites, the quantification of biodegradation of BTEX which are major fuel constituents is very important. Patterns and rates can vary from site to site. The loss of contaminants downgradient to our site characterized was used as evidence for the occurrence of intrinsic bioremediation.

2. Spill site

About 700 gallons of unleaded gasoline was released into the subsurface in 1986 at an on-base service station location. The subsurface matrix consisted of beach sand containing sea shell fragments to a depth of about 7.5 m below ground surface (bgs) where a confining marl formation was located. The water table was near 1.3 m bgs and the gradient measured in monitoring point wells was 0.002 m/m. Slug testing indicated that average hydraulic conductivity was near 0.026 cm s^{-1}. The average advective ground-water velocity was about 48 m yr^{-1} assuming a sand porosity of 0.35. Using total organic carbon concentrations in uncontaminated portions of the aquifer and published soil sorption coefficients [2] an average coefficient of retardation for benzene was calculated to be 2.6. The effective solute transport velocity was (48 m yr^{-1})/2.6 = 18.3 m yr^{-1}.

3. Results

The extent of the plume was measured by the BTEX (Fig. 1) dissolved in the ground water. The surface area over the plume was about 200 m long and 60 m wide. Free-floating gasoline was not detected in any well sampled.

4. Loss of contaminants

4.1. Dissolved BTEX

Point A (Fig. 1) was selected for the highest dissolved BTEX with points B and C at 38 and 98 m, respectively, downgradient in the plume. Ground water isopleth maps for BTEX, dissolved oxygen, ferrous iron, and methane are shown in Fig. 1, Fig. 2, Fig. 3, Fig. and Fig. , and Fig. 4 respectively. Both methane and trimethylbenzene (TMB) were selected as surrogate tracers.

4.2. Methane

Potential methane produced from BTEX and TMB was calculated from measured BTEX + TMB multiplied by the conversion factor of 0.78. Our approach was to assume that all methane produced was from BTEX and TMB biodegradation particularly beyond point A. We also assumed that aliphatic hydrocarbons were rapidly mineralized and did not contribute methane beyond Point A. Once formed, methane was assumed stable and was used as a tracer. For example, methane at Point A as a tracer was $14000 + 6282 = 20282$ μg l^{-1}, at Point B was $8800 + 887$, and at Point C was $2140 + 18$ (Table 2). The relatively large losses of toluene, ethylbenzene, and xylenes confirmed that biodegradation occurred. The % losses using methane-corrected levels are shown in Table 3.

4.3. Trimethylbenzene

Our usual approach has been to use TMB as a recalcitrant compound to correct BTEX concentrations for dispersion, dilution, sorption, and volatilization. For some
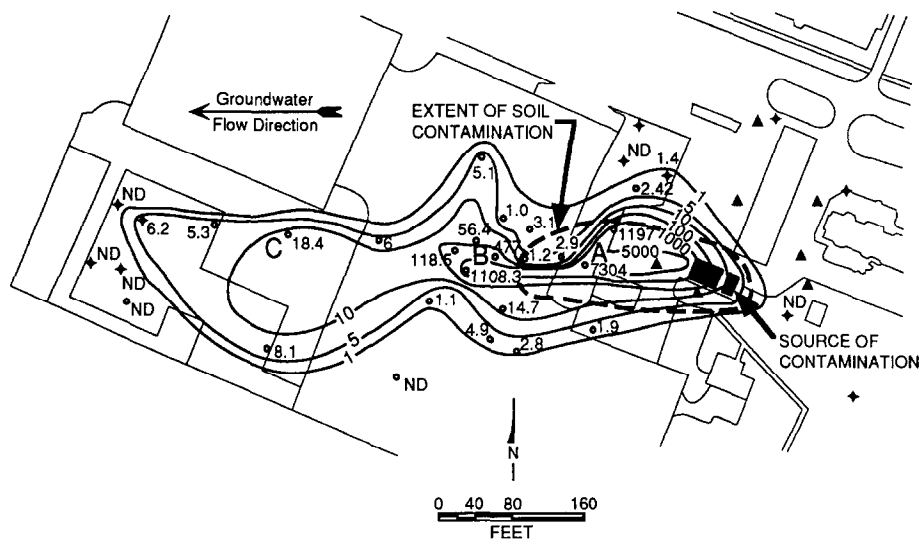

Fig. 1. Total BTEX (μg l^{-1}) in Groundwater, Patrick AFB, Florida.
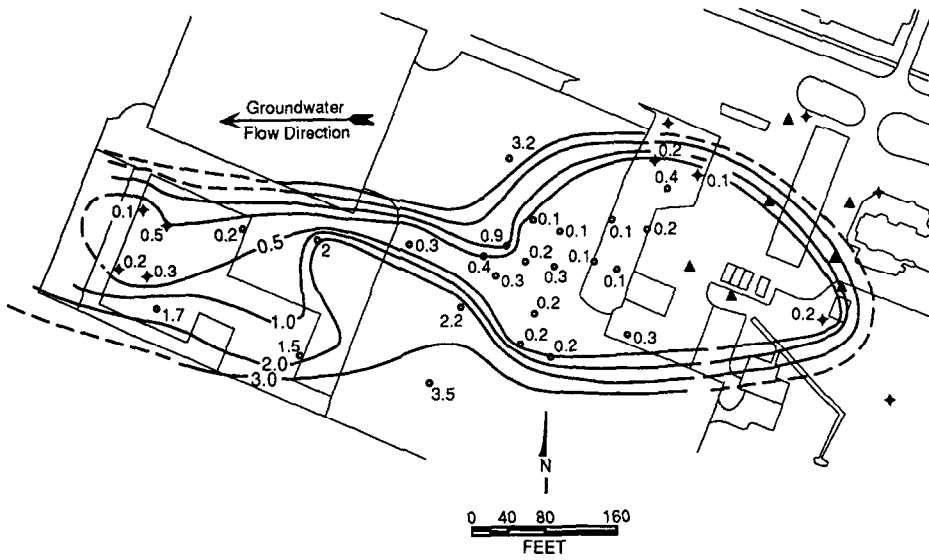
Fig. 2. Dissolved Oxygen (mg l^{-1}) in Groundwater, Patrick AFB, Florida.

reason benzene was higher at Point B than at Point A. However, the TMB corrected toluene, ethylbenzene, and xylenes decreased 30 to 60% between Point A and Point B which confirmed that biodegradation occurred (Table 4). If some biodegradation of TMB occurred the corrected values would underestimate the percent BTEX biode-
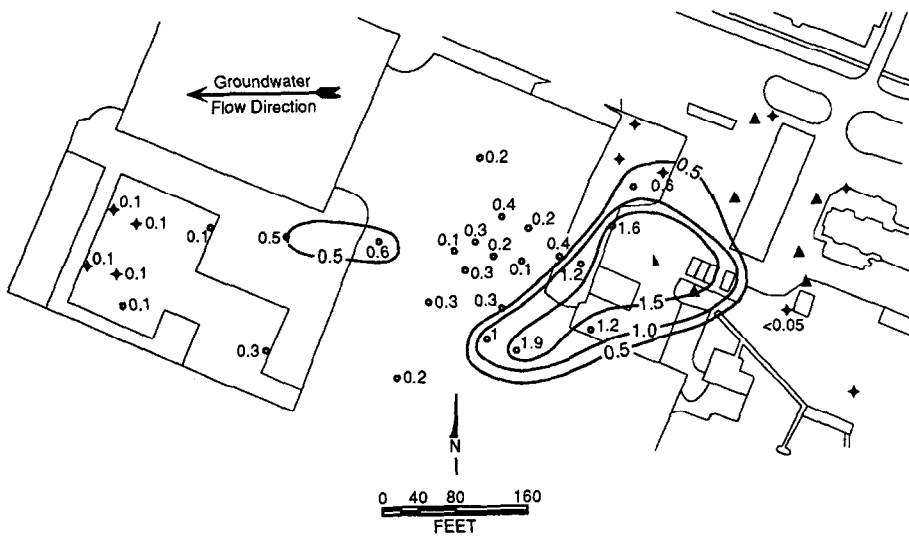

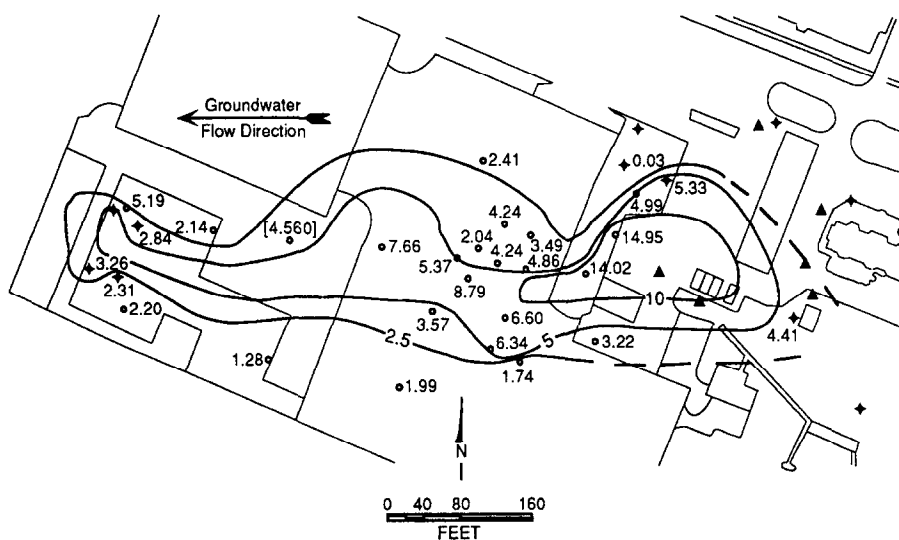Fig. 3. Ferrous Iron (mg l^{-1}) in Groundwater, Patrick AFB, Florida.

Fig. 4. Methane (mg l^{-1}) in Groundwater, Patrick AFB, Florida.

Table 2
BTEX Concentrations (μg l^{-1})

Compound	Point A	Point B	Point C
Benzene	724	960	1
Toluene	737	17	2
Ethylbenzene	823	12	1
Xylenes	5020	120	15
Trimethylbenzene	750	28	3
Total BTEX + TMB	8054	1137	23
Measured methane	14000	8800	2140
Methane produced from BTEX & TMB	6282	887	18

Table 3
Percent loss using methane-corrected levels

Compound	Point B Corrected (μg l^{-1})	Biodegradation A to B (%)	Point C Corrected (μg l^{-1})	Biodegradation B to C (%)
Benzene	2008	0	4	100
Toluene	35	95	9	46
Ethylbenzene	24	97	9	22
Xylenes	251	95	67	43
Total BTEX & TMB	2400	70	103	91

Table 4
Percent loss using TMB - corrected concentrations

Compound	Point B Corrected	Biodegradation A to B	Point C Corrected	Biodegradation B to C
	$(\mu g\ l^{-1})$	(%)	$(\mu g\ l^{-1})$	(%)
Benzene	25710	0	9	99
Toluene	455	38	19	0
Ethylbenzene	321	61	19	0
Xylenes	3214	36	139	0
Trimethylbenzene	750	0	28	0

graded. Between Points B and C the relative decrease in TMB had a reduction rate similar to BTEX.

5. Ground water geochemistry

The redox potential at the site ranged from 54 to -293 mV. Low redox potential coincided with sampling points of high BTEX contamination, low dissolved oxygen, some ferrous iron, and elevated methane concentrations. Water temperature was a warm 26 °C which suggested that bacterial growth rates could be high. Total alkalinity ranged from 148 to 520 mg l^{-1} which would suffice to buffer pH changes caused by BTEX bio-oxidation reactions. pHs near 7 were in the optimal range of BTEX-degrading microbes. Nitrate was very low so denitrification for BTEX removal was not viable. Sulfate at levels up to 86 mg l^{-1} was fairly high, but a relationship between sulfate and BTEX changes was not apparent. Many of the water samples with depleted dissolved oxygen did contain small amounts of dissolved hydrogen sulfide. The water chemistry suggested that dissolved BTEX would be subjected primarily due to aerobic respiration, iron reduction and methanogenesis.

The distribution of dissolved oxygen is shown (Fig. 2) for the site. Site areas with depleted dissolved oxygen coincided with areas of elevated BTEX which indicated that aerobic biodegradation was occurring. Background dissolved oxygen was 3.7 mg l^{-1}, so, based on the Table 1 stoichiometry, the shallow ground water had an assimilation capacity of 1200 $\mu g\ l^{-1}$ total BTEX (Table 5).

Ferrous iron distribution (Fig. 3) in the site ground water showed a direct relationship with elevated total BTEX. Background of ferrous iron was near 0.1 mg l^{-1} while levels

Table 5
Assimilative capacity of site ground water

Aerobic Respiration	1200 $\mu g\ l^{-1}$
Ferric Hydioxide Reduction	90
Methanogenesis	17400
Total	18690
Highest total BTEX	7300

up to 1.9 mg l^{-1} were present in the plume. Based on the Table 1 stoichiometry, the iron reduction would have the capacity to assimilate at least 90 μg l^{-1} of the total BTEX. Replenishment of the ferrous iron from soil iron oxides could occur to increase iron reduction capacity.

Methane distribution (Fig. 4) is also shown. A direct relationship occurred between elevated methane and total BTEX concentrations which indicated that methanogenesis was occurring. Background methane was near 1 mg l^{-1} while the highest plume methane concentration was 14.6 mg l^{-1}.

6. Assimilative capacity

The expressed BTEX assimilative capacity of the site ground water was 18 690 μg l^{-1} (Table 5) based on stoichiometry and site geochemical data. Since the highest dissolved BTEX concentration at the site was 7300 μg l^{-1} the ground water has sufficient capacity to degrade dissolved BTEX that partitions from the soil oily residual into ground water before the plume moves beyond 250 m downgradient from the source. The remainder assimilative capacity could be consumed by other gasoline components such as aliphatic hydrocarbons. Assimilative capacity during methanogenesis based on stoichiometry would be at least 17 400 μg l^{-1} of total BTEX (Table 5). Actual assimilative capacity could be much higher because the amount of carbon dioxide produced was not measured.

7. Microbial breakdown components

A ground-water sample was collected at Point A (Fig. 1) for analysis of phenols and aliphatic/aromatic acids. The technique involved liquid-liquid extraction, derivatization, and gas chromatography/mass spectrometry analysis. Major components detected were branched heptanoic and octanoic acids, trimethylbenzoic acids, dimethylbenzoic acids, and some lower molecular weight acids such as propanoic and butyric. The presence of these fatty acid components in the BTEX plume is further evidence that viable microbial biodegradation processes are functional at the site.

8. Biodegradation rate constant

Rate constants are needed to simulate the fate and transport of fuel hydrocarbons dissolved in aquifer water. Normalization of the downstream concentrations needs to be done for dilution, volatilization, and sorption. A first-order biological decay rate was calculated using methane as a surrogate tracer [2]. We assumed that once methane was produced from the fuel biodegradation it was stable and, therefore, could be used as a tracer. Methane-corrected BTEX concentrations and travel time from Point A to Points B and C are shown in Table 2. Assuming a first-order reaction rate, the transport velocity for total BTEX, from Points B to C was 0.014 wk^{-1}. This rate constant was within the range reported by others [3].

9. Conclusion

Three lines of evidence to identify intrinsic bioremediation at the site were loss of contaminants at field scale, geochemical data, and the presence of intermediate microbial BTEX breakdown products. Contaminant loss showed that natural attenuation was occurring. Ground water chemistry determined the relative importance of each operating natural attenuation mechanism. The presence of volatile organic acids showed that microbial biodegradation processes were viable. Aerobic respiration and methanogenesis accounted for the greatest mass of BTEX mineralized.

10. Disclaimer

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