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A Case Study of the Natural Attenuation of Gas Condensate Hydrocarbons in Soil and Groundwater

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ABSTRACT

Condensate liquids have been found to contaminate soil and groundwater at two gas production sites in the Denver Basin operated by Amoco Production Co. These sites have been closely monitored since July 1993 to determine whether intrinsic aerobic or anaerobic bioremediation of hydrocarbons occurs at a sufficient rate and to an adequate end point to support a no-intervention decision. Groundwater monitoring and analysis of soil cores suggest that intrinsic bioremediation is occurring at these sites by multiple pathways, including aerobic oxidation, Fe(III) reduction, and sulfate reduction.

Index Entries: Gas condensate; intrinsic bioremediation; soil gas; alternate electron acceptors; hydrocarbons.

INTRODUCTION

Amoco Production Company presently operates over 800 natural gas wells within the Denver Basin, CO, which produce about 100 Mscf/d (10^5 standard ft^3/d) of gas each with associated water and condensate liquids (<3 barrels/d). Structural failures of concrete sumps, used to contain produced water, have resulted in hydrocarbon leaks into the environment at 86 sites, which have adversely impacted groundwater and soil.

Within the context of Amoco's E&P operations in the Denver Basin, potential costs for active remediation of these sites are conservatively estimated at $10 million. Real costs are likely to exceed these estimates given the remote and inaccessible nature of many of these sites. Because of the large potential economic impact of these future environmental costs on E&P operations in this area, Amoco has sought an alternative to active remediation wherein costs might be reduced at an acceptable environmental risk. Natural or intrinsic bioremediation is one such option, which,

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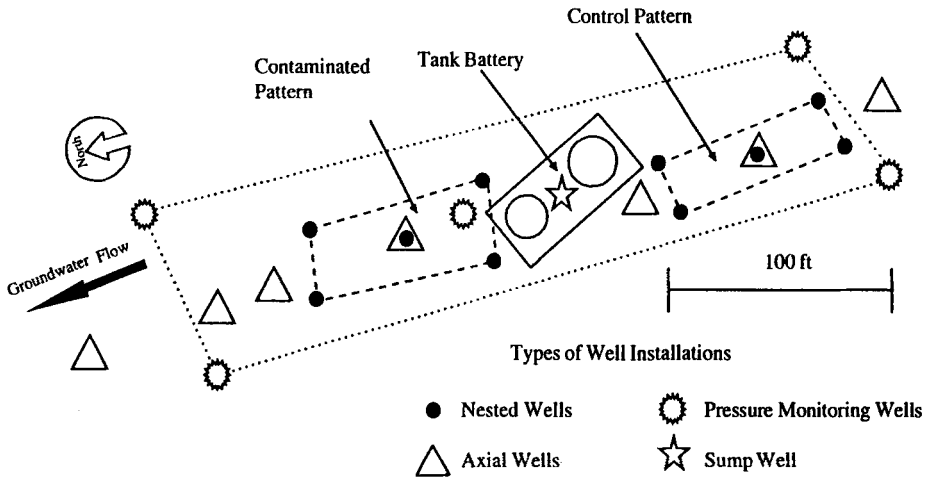

Fig. 1. KPU-2 site map.

in principle, does not require costly active intervention. In this option, it is recognized that indigenous microorganisms in the subsurface are capable of hydrocarbon degradation when critical environmental factors are not limiting (especially nutrients—nitrogen and phosphorous, temperature, moisture, pH, salinity, and electron acceptor). Recently, researchers have convincingly demonstrated the natural attenuation of hydrocarbon plumes in groundwater through bioremediation under both aerobic and anaerobic conditions. Oxygen, nitrate, iron(III) oxides, and sulfate have all been identified as potential terminal electron acceptors in the biochemical pathway for hydrocarbon degradation *(1,2)*.

Amoco Production Co. has initiated a study that seeks to determine whether intrinsic aerobic or anaerobic bioremediation of hydrocarbons occurs at the Denver Basin sites at a sufficient rate and to an adequate end point to support a no-intervention or passive remediation scheme. Tasks specific to this objective are:

1. Long-term groundwater and soil monitoring (initiated 7/93) to document field hydrocarbon losses and bioactivity over time (quarterly sampling events for 2–3 yr);
2. Laboratory verification of hydrocarbon biodegradation by field microorganisms and identification of primary biodegradation mechanisms (initiated 9/93);
3. Mathematical modeling to estimate biotic and abiotic losses for comparison with field observations; and
4. Risk evaluation to determine potential environmental exposure pathways and anticipated doses.

In this article we report the results of the initial site assessments and groundwater and soil monitoring results to date. The implications of these data to the natural attenuation of hydrocarbons at the sites are discussed.

SITE CHARACTERIZATION AND MONITORING

In July 1993, two gas condensate contaminated sites near Ft. Lupton, CO, were chosen for in-depth site assessments. (One of these sites [KPU2] is described in Fig. 1.) These sites are situated near the Platte River in agricultural areas. Prelimi-

nary evaluations had shown that both soils and shallow groundwater had been contaminated beyond the storage tank containment area. Given the highly permeable nature of the aquifer material (gravelly sands, sands, and silty sands) and the dynamic fluctuations in water table elevations with seasonal irrigation, the potential for contaminant transport was deemed high. The groundwater velocity was estimated at 1.3 m/yr based on a gradient of 0.4 cm/m. Coupled with the proximity of surface water receptors, both sites were placed in a high-priority category.

Initial site assessment focused on the delineation of the contaminant plume. Because of shallow groundwater (3–5 ft or 0.91–1.52 m), a soil gas survey of the vadose zone could be rapidly conducted. A minimum of 30 vapor probes were deployed/site initially along the anticipated direction of groundwater flow and real time measurements of soil gas O_2, CO_2, and volatile organic carbons (VOCs) were made.

Soil vapors were sampled with an AMS Soil Gas Vapor Probe (SGVP; Forestry Suppliers, Jackson, MS). SGVP dedicated sampling tips, perforated with vapor inlet holes, were driven 1.5–3 ft (0.46–0.92 m) into the subsurface with an electric roto hammer. The SGVP drive tubes were removed with a portable jack, leaving the vapor tip probe imbedded at the desired sampling depth. A Teflon® vapor tube, connected to the tip and extending to the surface, was used to sample soil gases near the tip.

The VOCs in soil gases were measured using a Gastech Trace-Techtor™ hydrocarbon analyzer with range settings of 100, 1000, and 10,000 ppm. A dilution fitting permitted quantification of VOCs in soil gases to 20,000 ppm. The analyzer was calibrated against hexane calibration gas (4350 ppm).

Soil gas concentrations of CO_2 and O_2 were measured using a Gastech model 32520 X CO_2/O_2 analyzer. The CO_2 calibration was performed against atmospheric CO_2 concentration (0.05%) and a 2.5% standard. The O_2 was calibrated using an atmospheric standard (20.9%). Both analyzers had an internal vacuum pump for sampling soil gases.

The KPU2 site topsoil is a sandy loam, although a sandy/gravel road fill has been spread over a significant area of the site. Beneath the topsoil/road fill, the sediment type varies from a gravelly sand to silt-rich sand horizons. Soil gas contours for the KPU2 site are shown in Figs. 2, 3, and 4. Background soil gas VOC measurements were 0–30 ppm (VP3 and VP36, respectively). Soil gas VOC measurements suggested the presence of hydrocarbon-contaminated soil and/or a groundwater plume northeast of the contaminant source and a groundwater plume that had migrated to the north. Soil gas VOC levels exceeding 20,000 ppm were measured immediately east of the contaminant source (VP2) and at VP22 and VP28. Elevated VOC levels were measured approx 110 ft (30.5 m) north of the contaminant source (VP26), suggesting the presence of a groundwater BTEX plume extending at least this distance from the source.

Soil gas O_2 and CO_2 data (Figs. 3 and 4) were consistent with the VOC data. Background soil gas O_2 levels were 20.9 and 20.8% (VP3 and VP36, respectively). Background CO_2 levels were 0.5 and 0.6% (VP3 and VP36, respectively). In general, elevated VOC levels were associated with elevated CO_2 and depressed O_2 levels. For example, the soil gas VOC level measured at VP2 was >20,000 ppm whereas O_2 and CO_2 were 1 and 12.5%, respectively. Contours of soil gas O_2 and CO_2 data also suggested the presence of hydrocarbon-contaminated soils and/or a groundwater plume, which had migrated in a northerly direction from the source.

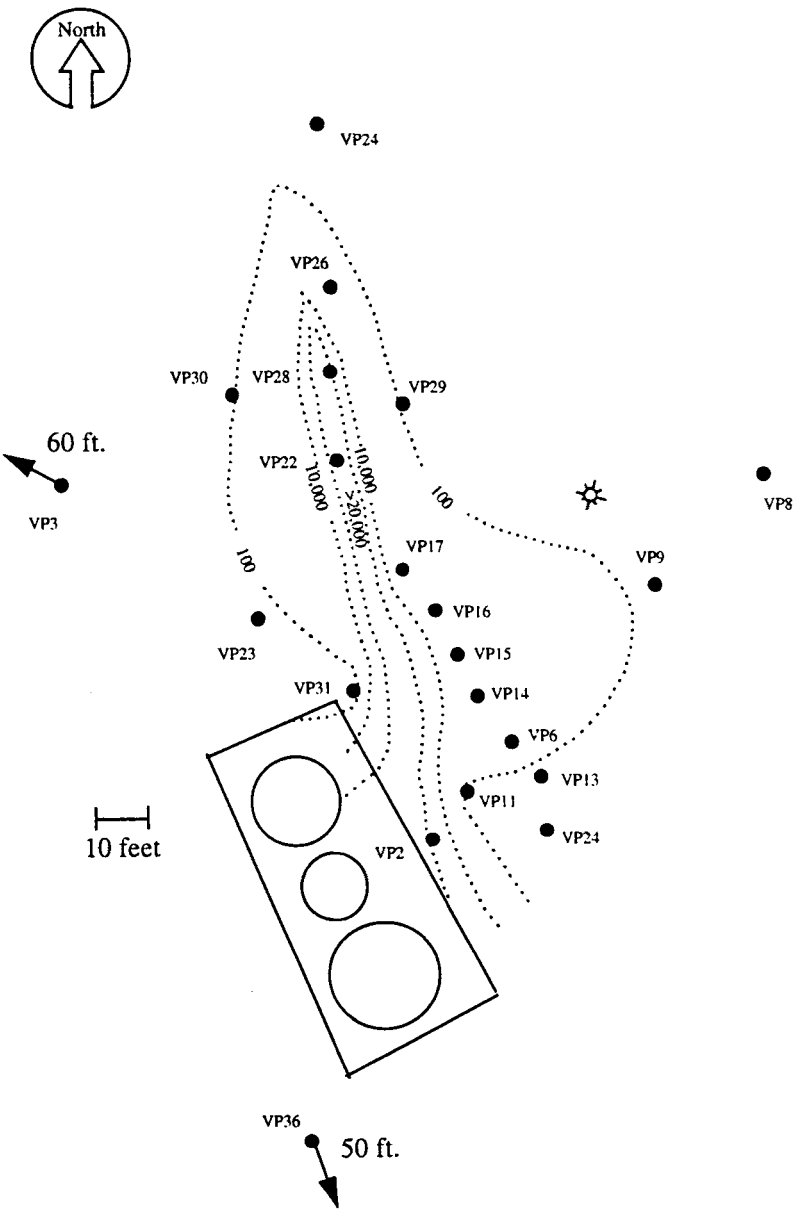

Fig. 2. Results of the soil gas survey for VOCs at the KPU-2 site. VOC levels are given as ppm.

Based on the soil gas survey data, permanent groundwater monitoring wells were installed to determine the extent of hydrocarbon losses and the degree of bioactivity over time. One inch (2.54 cm) OD vertically nested monitoring wells were installed in five-spot patterns (Fig. 1) within a downgradient contaminated and upgradient uncontaminated area. This monitoring arrangement was adopted in an effort to define both areal and vertical variations of hydrocarbon and electron acceptor concentrations in groundwater. Vertical nesting consisted of a series of three wells screened over 18-in (45.7-cm) intervals and placed 0, 5, and 10 ft (0, 1.52,

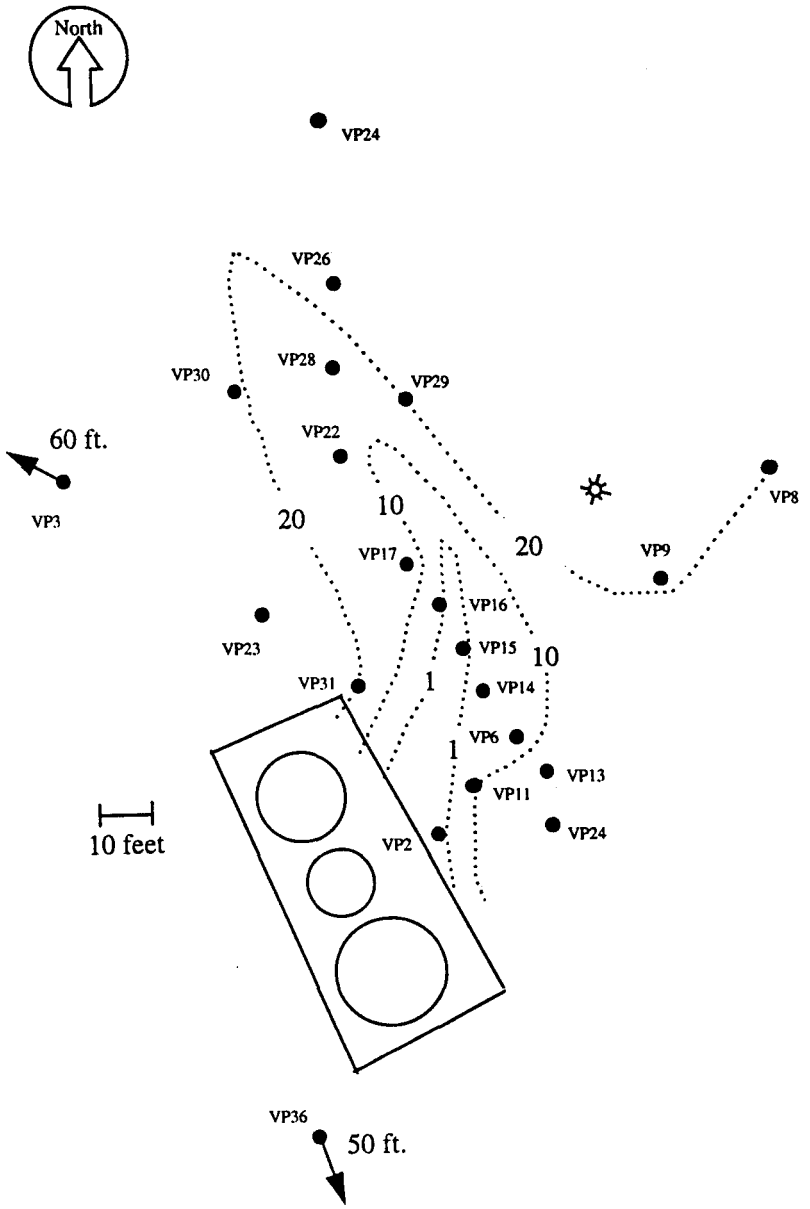

Fig. 3. Results of the soil gas survey for oxygen at the KPU-2 site. Oxygen levels are given as volume percent.

and 3.05 m) below the water table at the time of installation. Additional 2-in (5.1-cm) monitoring wells were placed along the longitudinal axis of predominant groundwater flow in an effort to monitor plume migration and electron acceptor transport. These wells were arranged along a path extending from upgradient of the control area, through the source, and downgradient of the contaminated zone. The 2-in (5.1-cm) wells were screened over a 10-ft (3.05-m) interval to allow for seasonal groundwater fluctuations. Well completions were by standard practices for groundwater monitoring applications.

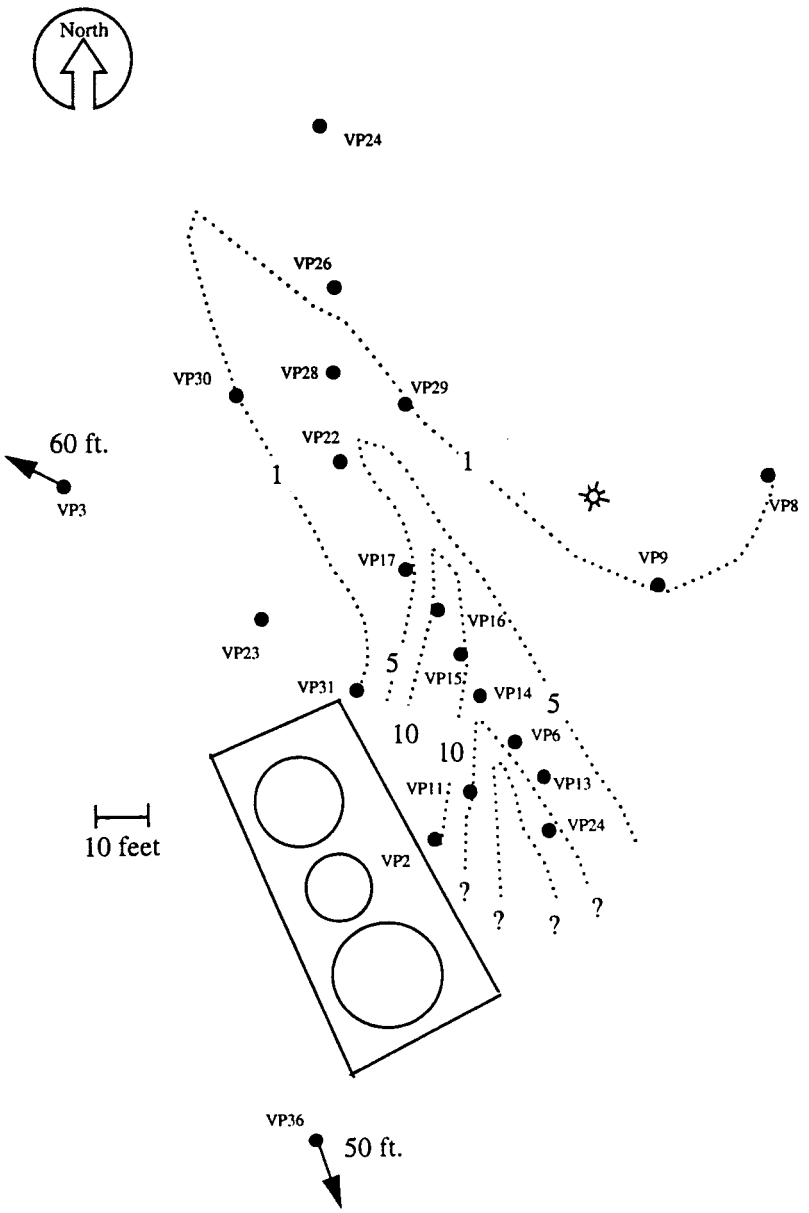

Fig. 4. Results of the soil gas survey for carbon dioxide at the KPU-2 site. Carbon dioxide levels are given as volume percent.

To address hydraulic modeling requirements adequately and thereby ultimately assess the role of abiotic mechanisms (e.g., dispersion, advection) in contaminant loss, both the contaminant and control study areas were contained within a larger hydraulic five-spot monitoring pattern. Hydraulic monitoring wells were completed identically to the 2-in (5.1-cm) monitor wells. Pressure transducers were permanently installed at a fixed depth below the water table in each well. Average, maximum, and minimum water table fluctuations are recorded daily within a 0.5-in (1.3-cm) resolution.

Soil cores were obtained from each site in November 1993 to document initial soil hydrocarbon and electron acceptor distributions. Four cores were taken from within each control and contaminated pattern. Coring locations were situated approximately halfway between the center and corner well clusters in each pattern quadrant. Continuous cores were obtained with a 2-in (5.1-cm) split-spoon sampler from the surface to a total depth of 15 ft (4.6 m). Core samples were composited in 1.5-ft (45.7-cm) intervals and stored in a reduced oxygen atmosphere at 4°C until requisite analyses could be performed.

Analytical

Baseline groundwater samples were collected during the first week of November 1993. Fresh water samples were obtained by producing approx 3-well volumes from each monitoring well prior to sampling. Dissolved oxygen (DO), pH, and temperature were determined immediately. Individual samples were collected and analyzed within 24 h for inorganic constituents, such as nitrate, sulfate, and Fe(II). Samples for BTEX and TPH were collected in clean 40-cm^3 VOA vials, immediately extracted with Freon, and shipped to Amoco's Groundwater Management Section Laboratory, Tulsa, OK, for analysis. Nitrate, sulfate and Fe(II) were determined as described below.

Soil solids were analyzed for moisture content, acid-extractable Fe(II) and Fe(III), porosity, bulk density, and saturated paste pH, nitrate, and sulfate. Moisture content was determined by drying a nominal 10 g sample of core material at field moisture content to constant mass in a Denver Instruments moisture balance (P/N 900207.1). To determine acid-extractable Fe(II) and Fe(III), a nominal 5 g of core material at field moisture content were weighed into a 60-mL capacity amber serum bottle. The bottle was then filled with a known volume of 0.77*N* hydrochloric acid (57.0–58.5 mL), and capped and sealed without headspace. The bottle was then shaken by hand for 30 s prior to sonication for 60 min. After sonication, the bottle was allowed to stand for 72 h prior to analysis. The extract was analyzed for Fe(II) and Fe(III) by ion chromatography using a Dionex AGP-1 ion chromatograph fitted with a Dionex CS5 IonPak separator. The eluant used was a 10% (v:v) methanol in water solution containing 50 m*M* acetic acid–50 m*M* sodium acetate and 6 m*M* 2,6-dicarboxylic acid (PDCA) at a flow rate of 1 mL/min. After passing through the separator column, the eluant was mixed with a solution containing 0.3 m*M* 4-(2-pyridylazo) resorcinol, monosodium salt hydrate (PAR), 1*M* acetic acid, and 3*M* ammonium hydroxide in a postcolumn reactor (PAR flow rate was 0.6 mL/min). The concentrations of Fe(II) and Fe(III) were then detected by measuring absorbance of their PAR complexes at 520 nm.

The saturated paste extract was prepared by placing a known volume and mass of core material at field moisture content in a 1-pt wide mouth jar and weighing in enough deionized water to achieve a fully saturated condition. The jar was then sealed and allowed to stand for 60 min. The water was then removed by vacuum filtration through a Whatman No. 4 filter paper. The pH of the filtered water was then determined. A 2-mL aliquot of this water was then filtered through a 0.45-μm syringe and stored at 4°C prior to analysis for sulfate and nitrate. The bulk density and porosity of the material were then determined by drying and weighing the remaining solids. The sulfate and nitrate content of the saturated paste extract was determined using a Dionex AGP-1 ion chromatograph fitted with a 4-mm Dionex

AS5 IonPak separator. A gradient elution was performed using an NaOH gradient of 1–64 m*M* (changing linearly over a 25-min period), which then switched to an isocratic 1 m*M* NaOH eluant for the remaining 20 min of the analytical program. Eluant flow was constant at 1 mL/min, and the eluant contained a constant concentration of methanol (10% v:v). Detection was by conductivity following chemical conductivity suppression in a Dionex membrane suppresser (suppresser reagent = 25 m*M* sulfuric acid at a flow rate of 10 mL/min).

PRELIMINARY RESULTS

Groundwater Analysis

Table 1 summarizes baseline groundwater data for the KPU2 site. (Data from the second site shows similar trends and are not reported here.) The data are organized by well depth for both control and plume volumes. As the data indicate, BTEX and TPH were confined primarily to the shallow well depth within the contaminated area. At this depth, median electron acceptor concentrations were uniformly lower in the contaminated vs the control zone. Iron(II), a product of the utilization of Fe(III) as an electron acceptor, is higher. At the intermediate well depth, hydrocarbon concentrations were considerably lower than similarly located shallow concentrations within the contaminated area. No BTEX or TPH was noted in the control samples. Trends in electron acceptor utilization at the intermediate depth within the plume were identical to those at shallow depths although less pronounced, presumably because of lower hydrocarbon concentrations. Deep well data indicated no appreciable hydrocarbon presence in either study area. Likewise, electron acceptor data showed no appreciable differences. Finally, axial monitoring well data (not shown) indicated that highly soluble BTEX components had migrated a distance of only 165 ft (50.3 m) from the source over an estimated 20-yr time period. Subsequent quarterly groundwater sampling events have produced similar results in terms of electron acceptor, Fe(II), BTEX, and TPH concentrations. No clear decrease in BTEX or TPH concentrations has been observed to date presumably owing to replenishment of dissolved hydrocarbons from a sink of adsorbed hydrocarbons and fluctuations in the water table.

The following observations are made on the basis of groundwater data acquired to date. The aerobic biodegradation potential of hydrocarbon appears limited because of uniformly low DO concentrations (1.4 mg/L or less) throughout the contaminant and control volumes. Nitrate, although present as a consequence of agricultural applications of fertilizer, also seems to have limited potential for hydrocarbon degradation. This again is attributed to low background concentrations (<20 mg/L) within the subsurface. In contrast, the utilization of sulfate appears significant. Background (control) concentrations are on the order of 230 mg/L, whereas concentrations within the shallow contaminated area are 0. Given the large initial concentration of sulfate and its favorable stoichiometric utilization for hydrocarbon degradation, it appears that sulfate reduction may be a major means of hydrocarbon remediation at these sites. Although evidence for iron reduction exists within the contaminated area, the utilization of Fe(III) cannot be quantified from groundwater samples owing to its sparing solubility. In addition, the solubility of Fe(II) is very low in the presence of sulfide, which is the product of sulfate reduction.

Table 1
Baseline KPU2 Groundwater Analysis

	Average		Median		Minimum		Maximum	
	Control	Plume	Control	Plume	Control	Plume	Control	Plume
Shallow								
pH	6.92	6.95	7.27	6.81	6.00	6.74	7.38	7.43
Temperature, C	10.1	9.4	10.5	9.5	8.9	8.8	10.9	9.8
Sulfate, mg/L	246.3	0	233.3	0	200.0	0	294.4	0
Nitrate, mg/L	7.7	0.2	3.1	<0.4	1.3	<0.4	19.0	0.6
Fe(II), mg/L	1.8	3.3	0.4	2.5	0.1	1.5	6.5	6.5
DO, mg/L	1.25	0.70	1.40	0.50	0.50	0.35	1.70	1.25
BTEX, mg/L	.003	14.2	ND	11.6	ND	8.9	.017	24.9
TPH, mg/L	ND	23.0	ND	20.5	ND	16.0	ND	35.0
Intermediate								
pH	5.88	6.46	5.61	6.40	5.36	6.16	7.23	6.72
Temperature, C	10.4	11.2	10.9	11.0	9.2	10.5	11.2	12.0
Sulfate, mg/L	213.0	116.0	211.1	127.8	211.1	0.0	216.7	175.0
Nitrate, mg/L	20.2	1.9	21.7	0.8	16.8	<0.4	22.6	4.9
Fe(II), mg/L	0.1	3.2	0.05	3.0	0.05	0.3	0.1	6.0
DO, mg/L	0.49	0.45	0.40	0.38	0.40	0.30	0.75	0.60
BTEX, mg/L	ND	1.673	ND	0.51	ND	0.11	ND	4.7
TPH, mg/L	ND	2.8	ND	2.0	ND	ND	ND	8.0
Deep								
pH	6.25	6.71	5.83	6.62	5.15	6.54	7.47	7.00
Temperature, C	10.6	11.7	10.6	11.8	9.9	10.9	11.5	12.2
Sulfate, mg/L	206.0	215.0	206.3	218.8	188.9	187.5	216.7	240.5
Nitrate, mg/L	23.2	19.0	22.6	17.7	18.2	14.2	27.5	24.4
Fe(II), mg/L	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
DO, mg/L	0.87	0.53	0.75	0.50	0.45	0.30	1.35	0.95
BTEX, mg/L	ND	0.010	ND	ND	ND	ND	ND	0.052
TPH, mg/L	ND	ND	ND	ND	ND	ND	ND	ND

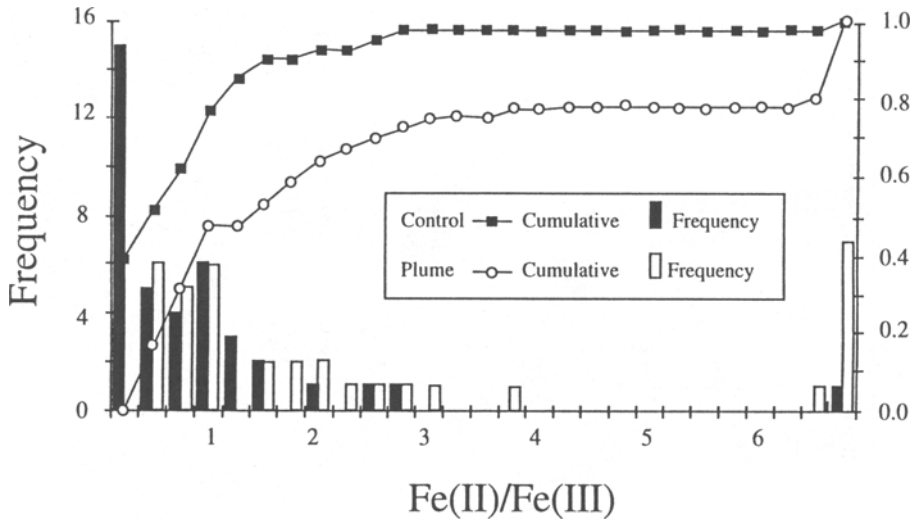

Fig. 5. Distributions of Fe(II) and Fe(III) in soil samples from the plume and control areas of the KPU-2 site. The right axis is the cumulative fraction of all observations with indicated Fe(II)/Fe(III) ratios.

In summary, the groundwater data suggest that significant hydrocarbon contamination is laterally and vertically confined to a small portion of the total aquifer. Given the age of the site (>20 yr), the limited extent of contamination, and supporting evidence for aerobic and anaerobic bioactivity, the data further suggest that intrinsic bioremediation may play a large role in attenuating hydrocarbon contaminants at these sites.

Soil Core Analysis

Soil core analyses for total iron, Fe(II), BTEX, and TPH were performed on representative samples from each 1.5-ft (45.7-cm) interval. The average and median background BTEX concentrations within the KPU2 control volume were 0.036 and 0.02 mg/kg, respectively. Surface soil samples showed typically higher concentrations at about 0.1 mg/kg, possibly indicating exposure to airborne BTEX. TPH values from control core samples were uniformly nondetectable (<1 mg/kg). Comparable values within the contaminated volume for average, median, and maximum BTEX concentration were 60.8, 0.27, and 817 mg/kg. The large difference between the average and median value reflects the vertical distribution of BTEX, which is narrowly confined to an approx 3-ft (0.91-m) interval at the water table/air interface. The majority of samples outside of this interval had BTEX concentrations well below 1 mg/kg. TPH values were similarly distributed with the average, median, and maximum of 379.6, nondetectable, and 4590 mg/kg. Finally, soil samples acquired from upgradient cores within the contaminated zone showed less BTEX and TPH than their downgradient counterparts. Since upgradient cores were situated nearest the original contaminant source, this evidence supports the contention that the cause of the existing hydrocarbon contamination had been effectively eliminated at these sites.

When control and contaminant distributions of Fe(II) and Fe(III) in soil samples were compared, it was noted that the ratio of iron(II) to iron(III) was shifted toward proportionately higher Fe(II) concentrations within the contaminated zone (Fig. 5).

Assuming both iron species were initially distributed uniformly across the site, it appears that Fe(III) was subsequently reduced to Fe(II) within the zone of significant hydrocarbon contamination. The reduction of iron in the presence of hydrocarbon is indicative of anaerobic biodegradation and further supports the hypothesis that intrinsic bioremediation of hydrocarbons is occurring at these sites by multiple pathways.

Finally, visual inspection of soil cores showed a significant accumulation of a black precipitate (acid-volatile iron sulfide) associated solely with hydrocarbon contamination. The accumulation of iron sulfide (FeS) in the presence of hydrocarbon is consistent with anaerobic biodegradation of hydrocarbons by sulfate reduction.

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