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Intrinsic Bioremediation of Gas Condensate Hydrocarbons

Results of Over Two Years of Ground Water and Soil Core Analysis and Monitoring

KERRY L. SUBLETTE,*,[1] RAVINDRA V. KOLHATKAR,[1]
ABHIJEET BOROLE,[1] KEVIN T. RATERMAN,[2] GARY L. TRENT,[2]
MINOO JAVANMARDIAN,[3] AND J. BERTON FISHER[4]

[1]Center for Environmental Research and Technology, University of Tulsa, 600 S. College Avenue, Tulsa, OK 74104; [2]Amoco Tulsa Technology Center, PO Box 3385, Tulsa, OK 74102; [3]Amoco Corporation, Amoco Research Center, 150 West Warrenville Road, Naperville, IL 60563; and [4]Gardere and Wynne, 2000 Mid Continent Tower, 01 S. Boston, Tulsa, OK 74103

ABSTRACT

Condensate liquids have been found to contaminate soil and ground water 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. Ground water monitoring, soil gas analysis, and analysis of soil cores suggest that bioremediation is occurring at these sites by multiple pathways, including aerobic oxidation, sulfate reduction, and methanogenesis. Results of over two years of monitoring of ground water and soil chemistry at these sites are presented to support this conclusion.

Index Entries: Intrinsic bioremediation; gas condensate; hydrocarbons; ground water; sulfate reduction; hydraulic gradient.

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*Author to whom all correspondence and reprint requests should be addressed.

INTRODUCTION

Amoco operates more than 800 natural gas wells within the Denver Basin, Colorado, which each average about 10^5 std ft^3/d (2830 std m^3/d) of gas and less than about 3 barrels/d of associated water and condensate liquids. Condensate has been found to contaminate soil and ground water at certain sites, and Amoco has sought a low-cost alternative to active remediation of these sites wherein acceptable environmental conditions would be restored. Natural or intrinsic bioremediation is one such option. This option recognizes that indigenous microorganisms in the subsurface are capable of hydrocarbon degradation when critical environmental factors are not limiting (e.g., nutrients, temperature, moisture, pH, salinity, and electron acceptor). Recently, researchers have convincingly demonstrated the natural attenuation of hydrocarbon plumes in ground water under both aerobic and anaerobic conditions *(1,2)*. Oxygen, nitrate, Fe(III) oxides, sulfate, and carbon dioxide have all been identified as terminal electron acceptors for the biochemical oxidation of hydrocarbons *(3–7)*.

Amoco has initiated a study 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 intrinsic remediation option. Tasks specific to this objective are:

1. Long-term ground water and soils monitoring (initiated July 1993) to document field hydrocarbon losses and bioactivity over time (quarterly sampling events for 5–6 yr for ground water; annual sampling events for soils);
2. Laboratory verification of hydrocarbon degradation by field microorganisms and identification of primary biodegradation mechanisms (initiated September 1993); and
3. Microbiological characterization of the sites to understand the spatial utilization of electron acceptors in and around the hydrocarbon plume (initiated November 1995).

We report in this article preliminary results (July 1993 to November 1995) from the ground water and soils monitoring program. The implications of these data to natural attenuation of hydrocarbons are discussed. An additional three years of sampling are planned. Further laboratory investigations and the microbial characterization of the sites will be reported at a later date.

SITE CHARACTERIZATION AND MONITORING

In July 1993, two sites situated near the Platte River in agricultural areas near Ft. Lupton, Co, were chosen for in-depth site assessments. Preliminary evaluations had shown that both soil and shallow ground water beyond the storage tank containment area were contaminated with gas condensate. The

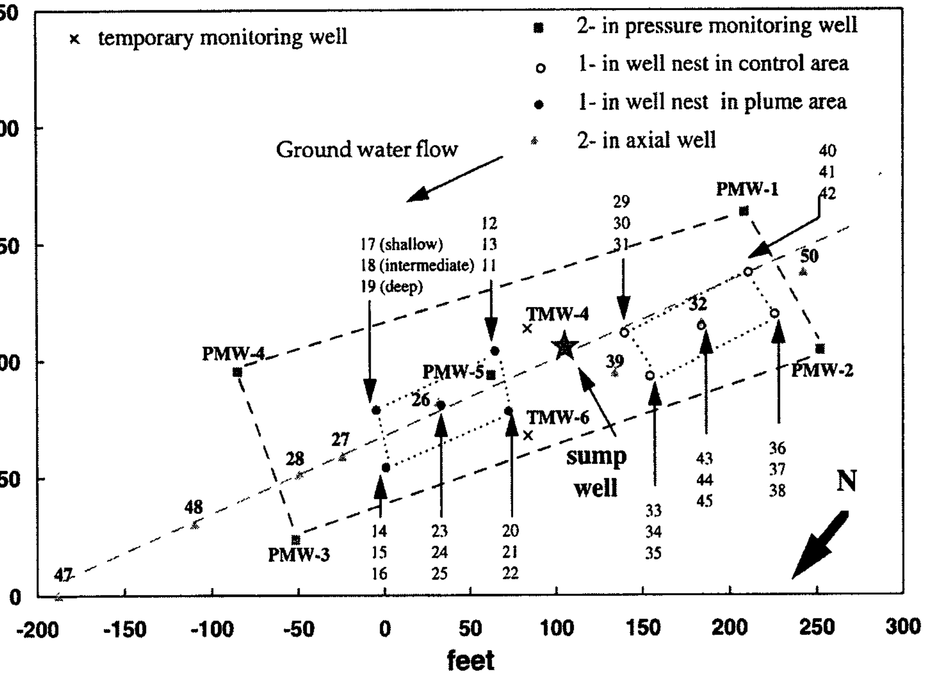

Fig. 1. Site map of KPU-2 showing types of wells and their locations. (Numbers shown are well identification numbers.)

aquifer material (gravely sands, sands, and silty sands) is highly permeable, and the water table elevations fluctuate greatly with seasonal irrigation. Further, potential surface water receptors are near both sites. Therefore, the potential for contaminant transport was deemed high, and both sites were placed in a high-priority category for further investigation.

Ground Water Monitoring

Based on an initial soil gas survey *(8)*, permanent ground water monitoring wells were installed to determine the extent of hydrocarbon loss and the degree of bioactivity over time. Figure 1 shows the locations of 1-in. (2.54-cm) OD vertically nested monitoring wells that were installed in five-spot patterns within both the plume and control areas of the KPU-2 site. This monitoring arrangement was adopted to define areal and vertical variations of hydrocarbon and electron acceptor concentrations in ground water. Each vertical well nest consisted of three wells screened over 18-in. (45.7-cm) intervals and placed 0, 5, and 10 ft (0, 1.52, and 3.05 m) below the water table at the time of installation. At the time of installation, the water table was high. However, the water table has never been lower than just below the bottom of the topmost screened interval. Additional 2-in (5.1-cm) OD monitoring wells were placed along the longitudinal axis of predominant ground water flow to monitor plume migration and electron acceptor transport. These axial wells were arranged along a path extending from upgradient of the control area, through the original source area and downgradient of the plume. The 2-in. (5.1-cm) wells were screened over a 10-ft (3.05-m) interval to allow for seasonal ground water fluctuations.

To address hydraulic modeling requirements adequately and thereby ultimately to assess the role of abiotic mechanisms (e.g., dispersion, advection) in hydrocarbon loss, both the downgradient area with hydrocarbons and the upgradient area without hydrocarbons were contained within a larger hydraulic five-spot monitoring pattern. Hydraulic monitoring wells were completed as the 2-in. (5.1-cm) monitoring wells. Pressure transducers were permanently installed at a fixed depth in each well. Average, maximum, and minimum water table fluctuations were recorded daily. These measurements have a resolution of 0.5 in (1.3 cm). In addition to these pressure monitoring wells, the axial 2-in. wells were also used to measure water level during ground water sampling.

Soil Core Sampling

Soil cores were obtained from each site in November 1993 to document the initial soil hydrocarbon and electron acceptor distributions. Four cores were taken from within each control and plume area. 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 at 1.5-ft (45.7-cm) intervals and stored in a reduced oxygen environment at 4°C until requisite analyses could be performed. A second set of cores was collected in November 1994 to document changes in the hydrocarbon concentrations. These cores were taken within 1 m of the 1993 coring locations. To minimize disturbance, the cores taken in November 1994 were obtained by vibracoring. In the vibracoring operation, continuous cores were obtained in a 3-in (7.6-cm) acrylic sleeve from surface to a total planned depth of 10 ft (3.0 m). The coring done in November 1995 was again done with a split-spoon sampler to a total depth of 15 ft (4.5 m). Material from these cores was composited and analyzed in the same manner each year.

Analytical

Baseline ground water samples were collected during the first week of November 1993. Fresh water samples were obtained by producing approximately three well volumes from each monitoring well prior to sampling. Individual samples were collected and analyzed within 24 h for inorganic constituents, such as nitrate, sulfate, total alkalinity (as mg/L $CaCO_3$), and Fe(II) *(8)*. Samples for BTEX and TPH were collected in clean VOA vials, immediately extracted with Freon and shipped to Amoco's

Groundwater Management Section Laboratory, Tulsa, OK for analysis by Amoco-modified EPA method 8015.

Soil solids were analyzed for moisture content, acid extractable Fe(II) and Fe(III), porosity, bulk density and saturated paste pH, nitrate, and sulfate. Details of the preparation of saturated soil paste and the individual analyses are described in ref. *(9)*. Soil solids were also analyzed for BTEX and TPH after extracting the soil with methylene chloride by EPA method 8020 *(8)*.

RESULTS

Ground Water

Based on the baseline ground water data collected in the first week of November 1993, it was inferred that the contamination was largely confined to shallow depths and that sulfate reduction was an important mechanism in hydrocarbon attenuation at this site *(8,9)*. The importance of sulfate as an electron acceptor was also corroborated by microcosm studies undertaken in the laboratory *(10,11)*. Additional sampling since that time continues to support sulfate reduction as an important pathway for the attenuation of hydrocarbons at the site.

Initial ground water data indicated that BTEX and TPH were confined primarily to the shallow well depth (3.5 to 5 ft below grade) *(12)*. At this depth, various electron acceptors including sulfate, nitrate and dissolved oxygen (DO) exhibited diminished concentrations in the plume the control zone. Similarly, concentrations of Fe(II), a product of Fe(III) reduction, and total alkalinity (mainly bicarbonate) were higher. Lower hydrocarbon concentrations were detected at the intermediate depth (6.5–8 ft below grade) in the plume. Trends in electron acceptor utilization at the intermediate depth within the plume were similar to those at the shallow depth, but less pronounced. Deep well data indicated nondetectable levels of hydrocarbons in both plume and control. Likewise, electron acceptor data showed no appreciable differences. Since most of the activity is occurring at shallow depths, further discussion will be restricted to only the shallow-screened wells.

BTEX data are plotted in Fig. 2 for shallow-screened, 1-in. wells using complete data collected from November 1993 through November 1995. BTEX was completely absent from wells upgradient of sump (i.e., control zone), whereas considerable concentrations of BTEX (20–40 mg/L) were detected in the downgradient wells (i.e., plume zone). Extremely high BTEX concentrations seen in wells 14 and 17 in February 1994 were owing to sample collected from a vapor point, since the water table was below the screen. These were point samples as opposed to volume averaged samples over the 18-in. screened interval for the other samples. Lower values of BTEX were observed in the sump compared to plume, indicating that

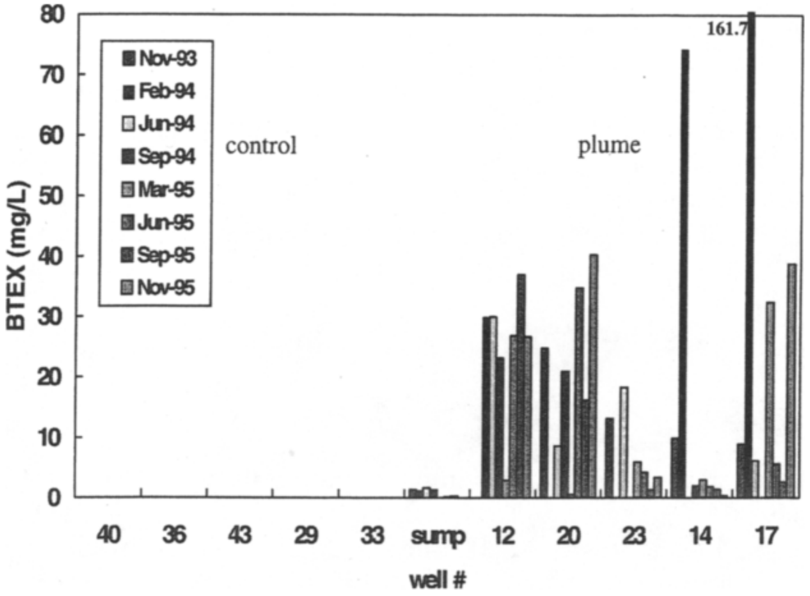

Fig. 2. BTEX in 1-in. shallow wells.

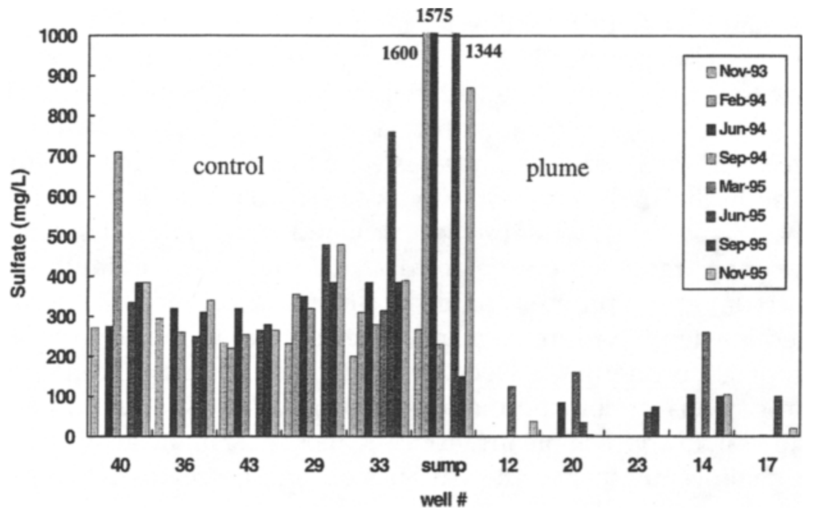

Fig. 3. Sulfate in 1-in. shallow wells.

this region did not have any further source of contamination, such as a non aqueous-phase liquid (NAPL).

A similar plot for sulfate concentrations (Fig. 3) indicates considerably diminished sulfate in the plume zone associated with the presence of hydrocarbons, whereas wells in the control zone had sulfate on the order of 230 mg/L. In addition, all the ground water samples from the wells in plume zone had a strong hydrogen sulfide smell.

Similarly, increased Fe(II) and total alkalinity as well as reduced DO were observed in the plume zone compared to in the control zone (data not shown). Increased levels of Fe(II) in the plume (4–6 mg/L compared to near zero concentrations in control) indicate Fe(III) reduction occurring in this zone, although the utilization of Fe(III) as electron acceptor cannot be quantified because of its low solubility. Fe(III) reduction may be biotic or abiotic. Hydrogen sulfide produced by biological sulfate reduction can reduce Fe(III) to Fe(II) and precipitate it as iron sulfide *(6)*.

DO in the plume ranged from 0.25–1.4 mg/L in the absence of sulfate. Bicarbonate, the major component of total alkalinity, is a product of biodegradation of hydrocarbons. Considerably higher values of alkalinity in the plume (average 600 mg/L $CaCO_3$ compared to 300 mg/L in control) strongly suggest that biodegradation of hydrocarbons is occurring in the plume. The diminished sulfate concentrations in the plume suggest that sulfate reduction is a major contributor to biodegradation of the hydrocarbons.

As seen in Fig. 2, no clear decrease in BTEX concentrations in ground water has been observed to date (November 1995) owing presumably to replenishment of dissolved hydrocarbons from a sink of sorbed hydrocarbons and water table fluctuations. Individual water level measurements from the 2-in. axial wells showed water table fluctuations of 2.5–3 ft (0.76–0.91 m) with the water table being higher during the summer (June to September) and lower during winter (November to March). Based on the water level data obtained from these wells, it was evident that the local gradient exhibited fourfold seasonal variations (Fig. 4). Higher gradient was seen during winter and lower gradient during summer. This could be the result of flooding in a downgradient stream (that discharges into the Platte River) during summer when meltdown of snow increases recharge in this area. During the winter months, when the stream level is low and less recharge occurs owing to freezing temperatures, higher gradient is established. This has important bearing on relative magnitudes of hydrocarbon mobility and attenuation rate. During winter, when biological activity would be slower, mobility of dissolved hydrocarbons would be higher because of higher ground water velocity, causing the dissolved plume to migrate at a higher rate. The reverse phenomena would take place during summer, resulting in increased attenuation.

Finally, axial monitoring well data indicated that highly soluble BTEX components had migrated to well 28, i.e., a distance of only 165 ft (50.3 m) from the source over an estimated 20-year time period (Fig. 5). Sulfate and Fe(II) concentrations were at background levels at this distance (data not shown).

In summary, the following observations are made on the basis of ground water data acquired to date. The aerobic biodegradation potential of hydrocarbon appears limited owing to uniformly low DO concentrations (1.4 mg/L or less) throughout the investigated area; however, the role of oxygen at the edge of the plume is potentially important. Nitrate is

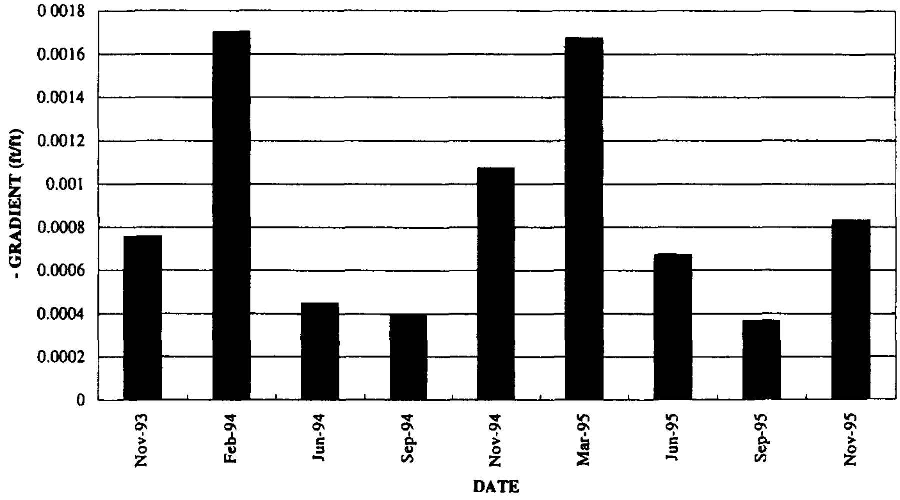

Fig. 4. Hydraulic gradients in 2-in. axial wells.

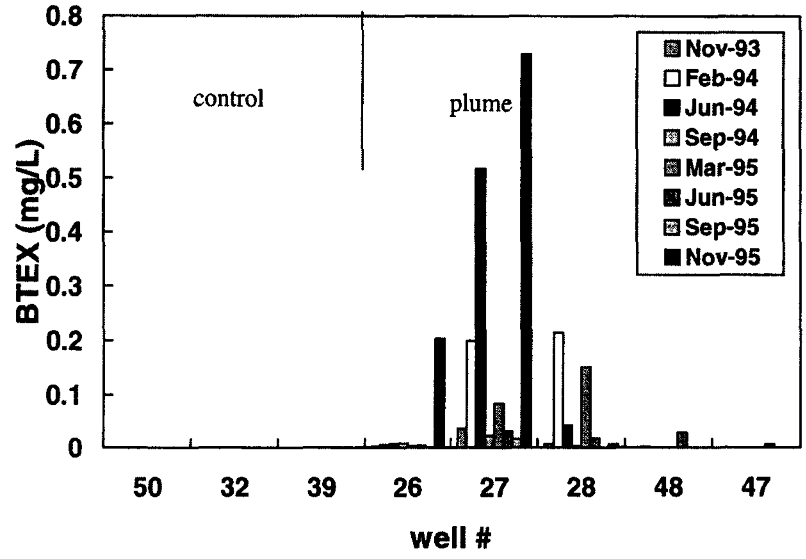

Fig. 5. BTEX in 2-in. axial wells.

present as a result of agricultural applications of fertilizer, but because of its low concentration, has limited potential for hydrocarbon degradation (*9*). In contrast, the utilization of sulfate appears significant. Background concentrations are on the order of 230 mg/L, whereas sulfate is practically absent in the shallow area containing hydrocarbons. Given the large initial concentrations of sulfate and its favorable stoichiometric utilization for hydrocarbon degradation, it appears that sulfate reduction is a major means of hydrocarbon remediation at these sites. Moreover, concentrations of sulfate observed in June 1995 sampling show that a substantial amount of sulfate is transported by infiltration of rainwater and that the rate of sulfate consumption in the hydrocarbon-contaminated ground water exceeded the rate of supply by infiltration. This sampling was conducted immediately after a period of persistent heavy rainfall. In the control area at KPU-2, background sulfate levels in the shallow wells had nearly doubled (average of 5 wells = 418 mg/L sulfate), whereas sulfate concentrations for intermediate and deep wells were comparable to those observed previously. In contrast, sulfate concentrations in shallow wells from plume area showed an absence of sulfate.

Soil Cores

Soil core analyses for total iron, Fe(II), BTEX, and TPH were performed on composited samples from each 1.5-ft (45.7-cm) interval. Within the plume area (Figs. 6 and 7), BTEX and TPH were consistently present in soil cores, but were confined to an approx 3-ft (0.91-m) interval at the water table/air interface. Soil samples acquired from upgradient cores within the plume showed less BTEX and TPH than their downgradient counterparts. Because upgradient cores were situated nearest the original hydrocarbon source, this evidence supports the contention that the original source of the existing hydrocarbons in soil and ground water has been effectively eliminated at these sites. Total petroleum hydrocarbon concentrations decreased in the first year, and then were more or less constant; however, BTEX concentrations observed in soil cores collected in November 1994 and 1995 are greatly reduced compared to total BTEX concentrations observed in November 1993. Since BTEX concentrations observed in ground water monitoring wells have remained essentially unchanged, this is interpreted to indicate that the total hydrocarbon inventory at this site is being decidedly reduced by natural attenuation. As discussed earlier, BTEX concentrations in the ground water did not show a temporal trend because of the presence of a residual hydrocarbon phase (Fig. 2). Also, no specific movement of the dissolved hydrocarbon plume was observed (Fig. 5). The plume appears to be stable based on the available data; however, once the BTEX inventory diminishes, ground water BTEX concentrations may start decreasing and the plume also may start shrinking.

Soil sulfate concentrations and Fe(II)/Fe(III) ratios obtained by saturated paste extract method *(3)* showed distinct differences between plume and control zone samples (data not shown). Sulfate concentrations were lower in the plume region (4–100 mg/kg compared to 100 mg/kg and above for control). Although sulfate was absent in many of the 1-in. shallow-screened wells in the plume, soil still contained sulfate in mineral form. Dissolution of sulfate minerals might have controlled the supply of sulfate to the ground water. No specific change was observed in sulfate concentrations in the soil cores from November 1993 to November 1994 (data not shown).

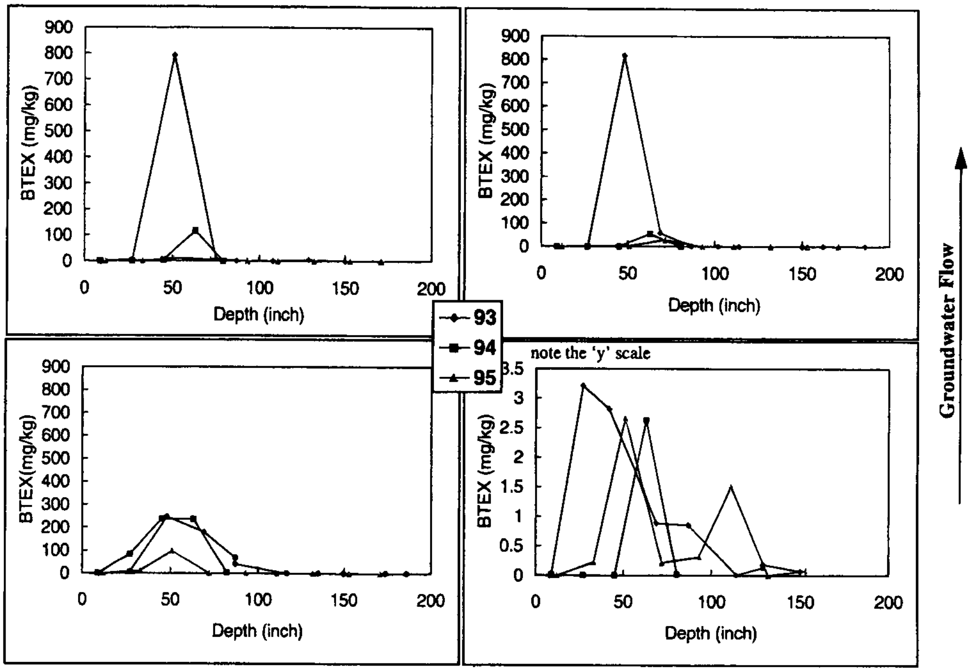

Fig. 6. Soil core BTEX in plume region.

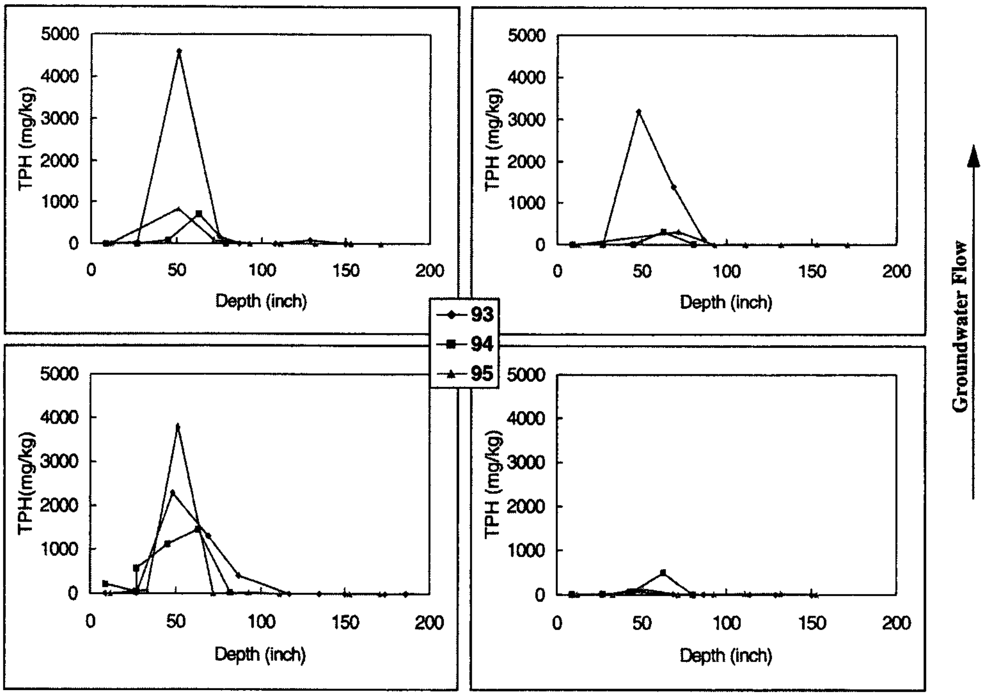

Fig. 7. Soil core TPH in plume region.

When hydrocarbons were present, the ratio of Fe(II) to Fe(III) in soils was increased. 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 presence. The reduction of iron in the presence of hydrocarbons 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 sulfide) associated solely with the presence of hydrocarbons. The accumulation of iron sulfide (FeS) in the presence of hydrocarbon is consistent with the anaerobic biodegradation of hydrocarbons by sulfate reduction *(6)*.

CONCLUSIONS

At the sites investigated, intrinsic aerobic and anaerobic bioremediation play a strong role in attenuating hydrocarbons. Even though the sites are old (>20 yr), hydrocarbons are laterally and vertically confined to a small portion of the total aquifer. Further, there is strong geochemical evidence of both aerobic and anaerobic bioactivity. Oxygen is much depleted and carbon dioxide is much elevated in the soil gas immediately overlying the ground water associated with the hydrocarbon plume. Ground water that is immediately associated with the hydrocarbon plume shows depleted levels of both nitrate and sulfate compared to ground water from the upgradient uncontaminated zone. Moreover, based on anecdotal observations of the response of the uppermost level of ground water to the infiltration of sulfate-laden rainwater, the rate of sulfate consumption in ground water immediately associated with hydrocarbons is very high compared to that of ground water not associated with hydrocarbons. Soils associated with hydrocarbons show abundant iron sulfide production. Although sulfate is depleted in ground water associated with hydrocarbons, sulfate remains available as an electron acceptor by means of diffusion from the surrounding aquifer, by dissolution of sulfate from the solid phase, and by importation of sulfate by infiltration of rainwater. Potentially, sulfate reduction could be accelerated in the hydrocarbon-impacted areas through the addition of sulfate.

REFERENCES

1. Norris, R. D., Hinchee, R. W., Brown, R., McCarty, P. L., Semprini, L., Wilson, J. T., Kampbell, D. H., Reinhard, M., Bouwer, E. J., Borden, R. C., Vogel, T. M., Thomas, J. M., and Ward, C. H. (1993), In-Situ *Bioremediation of Groundwater and Geological Material: A Review of Technologies*, 68-C8-0058, Robert S. Kerr Environmental Research Laboratory, Ada, OK.
2. Bennett, P. C., Siegel, D. E., Baedecker, M. J., and Hult, M. F. (1993), *Appl. Geochem.* **8**, 529–549.

3. Barker, J. F., Patrick, G. C., and Major, D. (1987), *Groundwater Monitoring Rev.*, 64–71.
4. Hutchins, S. R., Sewell, G. W., Kovacs, D. A., and Smith, G. A. (1991), *Environ. Sci. Technol.* **25(1),** 68–76.
5. Lovley, D. R. and Lonergan, D. J. (1990), *Appl. Environ. Microbiol.* **56(6),** 1858–1864.
6. Edwards, E. A., Wills, L. E., Reinhard, M., and Grbic-Galic, D. (1992), *Appl. Environ. Microbiol.* **58(3),** 794–800.
7. Grbic-Galic, D. and Vigel, T. M. (1987), *Appl. Environ. Microbiol.* **53(2),** 254–260.
8. Raterman, K. T., Barker, G. W., Corgan, J. M., Fisher, J. B., and Trent, G. L. (1994), in *Proceedings of 1994 Rocky Mountain Symposium on Environmental Issues in Oil and Gas Operations*, pp. 229–238.
9. Barker, G. W., Raterman, K. T., Fisher, J. B., Corgan, J. M. Trent, G. L., Brown, D. R., Kemp, N. P., and Sublette, K. L. (1996), *Appl. Biochem. Biotechnol.*, **57/58,** 791–802.
10. Borole, A. P. (1996), Intrinsic bioremediation of gas condensate hydrocarbons, Ph.D. thesis, The University of Tulsa, Tulsa, OK.
11. Borole, A. P., Fisher, J. B., Raterman, K. T., Kemp, N., Sublette, K. L., and McInerney, M. J. (1995), *Appl. Biochem. Biotechnol.*, **57/58,** 817–826.
12. Fisher, J. B., Sublette, K. L., Kolhatkar, R. V., Brown, D. R., Barker, G. W., Raterman, K. T., Trent, G. L., and Corgan, J. M. (1995), in *Proceedings of 1995 Rocky Mountain Symposium on Environmental Issues in Oil and Gas Operations*, pp. 235–249.