

Soil-gas Hydrocarbon Pattern Changes During a West Texas Waterflood

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ABSTRACT

Soil-gas light-hydrocarbon (methane through *n*-butane) pattern changes were measured annually for five years over part of an oil field in Brown County, Texas, U.S.A. During the monitored period, additional wells were drilled, depleted, and subjected to a waterflood. Annual soil-gas measurements detected changes in light-hydrocarbon concentrations attributable to these field operations.

Soil-gas sample reproducibility was important for comparing annual data. Background concentration, which was the reference for all measurements, reproduced within 20% during the 5-year monitoring period.

An oil well drilled on the west side of the study area depleted within two years. During that time, near-surface soil-gas hydrocarbon concentrations also decreased. After depletion, this well became the waterflood injection well. Soil-gas hydrocarbon concentrations increased near the injection well within one year after the waterflood began. While the waterflood continued, soil-gas hydrocarbon concentrations increased again the following year.

Calculated hydrocarbon vertical migration rates were 0.6–2 m/day. This result can be explained by an effusion mechanism whereby gases escaped the petroleum reservoir and migrated vertically through the water table in a gaseous phase.

INTRODUCTION

Low-molecular-weight hydrocarbons in soil gas were monitored annually over part of an oil field in Brown County, Texas, U.S.A., from 1989 through January 1994. Soil-gas samples, taken from 1.5–3.0-m depths, were analyzed for methane through *n*-butane. During the monitored period, soil-gas concentration patterns were integrated with subsurface geology to determine infill drilling locations.

Produced water was injected back into the production zone for disposal. Water injection rates were typically less

than 20 barrels per day (bbl/day) until 1991. During 1991, additional water was produced and injected into a depleted well for enhanced recovery. Soil-gas concentration changes were observed during production, depletion, and water injection. These events provided an opportunity to study reservoir communication through the vertical migration of hydrocarbon gas. Reservoir communication is information transferred from the reservoir to the observer. This study examined the quality, content, and application of reservoir information from near-surface hydrocarbon gases.

Three factors contributed to this study. First, a soil-

gas sampling tool was engineered to provide reproducible data. Second, the landowner and operator provided unlimited surface access and production information, and granted us permission to publish the data. Third, the field produced from shallow (about 365 m, or 1200 ft), low-volume Crosscut sandstone¹ reservoirs (Pennsylvanian).

These low-volume Crosscut sandstone reservoirs depleted within months. Injected water produced rapid reservoir changes that were observed in producing wells. Changes also were observed in soil-gas hydrocarbon measurements. Reservoir dynamics, expressed by hydrocarbon concentrations in near-surface soils, were accelerated compared with those expected from deeper, higher-volume reservoirs.

STUDY OBJECTIVES

Two objectives of the monitoring study were (1) to determine if annual soil-gas concentration measurements were reproducible; and (2) to determine whether the dynamics of reservoir depletion and waterflooding could be observed in soil-gas patterns.

DEFINITIONS

Technical terms in this paper are used in their normal geochemistry context. Because some readers may not be familiar with the terminology of geochemistry, operational definitions of key technical terms follow.

background data	data from hydrocarbons other than those migrating from petroleum reservoirs
diffusion	mass transport by molecular motion—see additional information in the “Literature Review, Diffusion” section of this paper
effusion	pressure- or buoyancy-driven mass transport of a fluid
mass transport	movement (transport) of materials (mass) over a distance

¹The Crosscut sandstone discussed in this chapter has also been referred to in the literature as the Cross Cut sandstone and the Cross Cut sand (presumably the unit is named after the town of Cross Cut, Texas). This stratigraphic unit has not been formally recognized by the U.S.G.S.; thus, no standard has been designated for its spelling. All three names refer to the same unit.

microseepage invisible leaking of minute quantities of fluids, e.g., hydrocarbons, near a soil-air or sediment-water interface—contrast with macroseepage, which involves larger quantities that are usually visible

petroleum reservoir that part of the reservoir rock containing the oil or gas pool (Hunt, 1979)

primary migration mass transport out of source rock and into reservoir rock (Hunt, 1979)

vertical migration the process of mass transport of fluids (gases or liquids) in an upward direction, from depths (e.g., reservoir depth) to near the surface

vertical migration rate the speed of vertical mass transport, usually to near the surface—in units that are distance per time, e.g., meters per day

LITERATURE REVIEW

Expert readers may scan or skip this section, which summarizes portions of the literature important to this study. This brief review illustrates the relevance of and the need for studies such as the one reported here.

Vertical Migration Defined

Vertical migration is the process that moves hydrocarbons from petroleum reservoirs or hydrocarbon sources to near the surface. Good overviews of vertical migration detection, interpretation, and results are available. Interested readers are referred to AAPG Memoir 66 (Schumacher and Abrams, 1996), Klusman (1993), Fullagar (1989), and APGE Special Publication No. 1 (Klusman, 1985). Davidson (1994) provided an excellent historical perspective. Note that the words *vertical migration* literally mean migration in a vertical direction, without reference to distance. However, *near-surface* geochemistry is always conducted *near the surface*. *Vertical migration*, in this context and by common usage, implies vertical migration that reaches *near the surface*.

Vertical Migration Mechanisms

Vertical migration mechanisms describe how vertical mass-transport processes occur. However, vertical migration mechanisms receive less attention in the literature than do methods applications. Because vertical migration mechanisms are important to this study, we briefly review them here.

Three frequently cited vertical mass-transport mechanisms are diffusion, water solution, and effusion (Donovan, 1981; Meyer et al., 1983; Arp, 1992b; Klusman and Saeed, 1996). Another water-related hydrocarbon transport mechanism is the migration of a separate hydrocarbon phase that is carried by water (i.e., by hydrodynamic flow) (Tóth, 1980).

Diffusion

Diffusion is molecular transport controlled by kinetics (molecular motion). Diffusion transport is driven by concentration and always transports materials from higher concentrations to lower concentrations. Individual molecules travel through semiporous media according to Fick's laws, which describe rates and quantities of material transported by diffusion.

Early attempts to explain vertical hydrocarbon migration involved diffusion as the principal mechanism. Stegena (1961) calculated diffusion-controlled vertical mass transport from Fick's laws. Diffusion-controlled migration from an oil reservoir 1000 m deep, with an average overburden diffusion coefficient of $10^{-6} \text{ cm}^2\text{s}^{-1}$, would require about 100 million years to reach a steady-state concentration at the surface. This is greater than the age of some reservoir rocks at 1000 m. Diffusion data and calculations did partially explain concentrations increasing with depth, as observed in shallow samples. Stegena recognized that effusion would alter vertical migration significantly compared with the pure diffusion model, but data were not available for effusion calculations.

Leythaeuser et al. (1980) used diffusion to explain vertical concentration gradients of C_2 – C_7 hydrocarbons that had been depleted from upper layers of shallow, organic-bearing shales. Calculated diffusion coefficients between 10^{-6} and $10^{-8} \text{ cm}^2\text{s}^{-1}$ were determined by fitting the data to calculated depth-versus-concentration curves. Leythaeuser et al. (1982) studied the role of diffusion as a primary migration mechanism for petroleum hydrocarbons. They found that geologic time was sufficient for hydrocarbon gases to migrate from some sources to reservoirs by diffusion. Flux rates for liquid hydrocarbons were too low to allow significant mass transport by diffusion in the primary migration of oil. Krooss et al. (1992) showed that there was much less diffusion through water-saturated cap rock than Leythaeuser et al. (1982) had calculated. Therefore, diffusion through water-saturated rock could not migrate significant hydrocarbons to the surface.

Water Solution and Hydraulic Transport

Hydrocarbon transport by a water carrier is a migration mechanism that some investigators favor. Water solution requires hydrocarbons to be dissolved in water, transported by water flow, and then exsolved back to a

hydrocarbon phase. Roof and Rutherford (1958) investigated possible migration mechanisms, including water transport. Only hydraulic flow, whereby water carries oil droplets as a separate phase, could explain large lateral migration distances or migration downdip from sources.

A single-phase hydraulic transport mechanism whereby hydrocarbons are dissolved in water, transported, and then exsolved elsewhere can work only where a large vertical component is present. Price (1976, 1981b) determined that hydrocarbon solubilities in water increase with temperature and decrease with pressure. However, the decrease caused by pressure lessens at higher temperatures (Price, 1981b). Net results are that hydrocarbon solubility increases with depth. As deeper waters containing dissolved hydrocarbons migrate upward to where pressures and temperatures decrease, a saturation point can be reached at which hydrocarbons separate out. This process requires vertical flow to shallow depths where hydrocarbons can undergo exsolution. However, exsolution processes require petroleum hydrocarbon compositions to be strong functions of aqueous solubility and to have compositions similar to those of condensates (Price, 1981a, b). Only at temperatures of 275° to 375°C would an aqueous solubility transport result in oil-like compositions (Price, 1981a). However, Jones and Drozd (1983) observed oil-like compositions (C_1 – C_4 gases only) in near-surface samples. Kennicutt et al. (1988) found liquid hydrocarbons in Gulf of Mexico sediments with compositions similar to those of reservoir oil. Did they get there by aqueous transport?

High-temperature aqueous transport to the surface seldom occurs. Oil-like compositions are routinely measured in near-surface samples, with no indications of recent or historical high-temperature discharge. Other transport mechanisms must occur in these cases. Therefore, although aqueous solubility could be a feasible mechanism for deep petroleum transport, it is not an important vertical transport mechanism, especially in shallow sediments.

Rostron and Tóth (1996) numerically simulated hydrologic models of oil above pinnacle reefs. Their conceptual model suggested that a liquid hydrocarbon phase would migrate vertically in nonfractured rock on the order of 100 m in about 10,000 years. Clearly, this mechanism could not apply to more rapid migration rates (hundreds of meters in months or years).

Holysh and Tóth (1996) suggested a groundwater-flow mechanism that could displace hydrocarbons at the surface or, in groundwater recharge areas with downward flows, suppress surface hydrocarbon expression completely. These hydrologically controlled mechanisms would apply to liquid or dissolved hydrocarbons that move with groundwater flow. In such cases, vertical migration rates would be similar to groundwater flow rates. However, immiscible gases rapidly rising by buoyancy would be less affected by groundwater flow.

Effusion

Effusion is bulk mass transport of hydrocarbons in either gas or liquid phase, without a separate phase carrier. Driving forces are: higher pressure to lower pressure and, with two or more phases, buoyancy. Effusion only recently evolved as an accepted vertical migration mechanism. Although the foundations for effusion in vertical migration were laid out early by Tripp (1944, 1945), effusion received little attention in early literature on vertical migration. Stegena (1961) identified effusion as a possible mechanism during his diffusion study described above. MacElvain (1969) offered a theory of separate gas-phase vertical migration by a bubble transport mechanism. His idea of bubble migration was an early version of vertical migration by effusion. However, the microbubble concept is not favored because:

- 1) Microbubbles sufficiently small to be influenced by Brownian motion would have little buoyancy.
- 2) Large surface-area-to-volume ratios assure rapid dissolution on first encountering undersaturated water; therefore, microbubbles can exist only in hydrocarbon-saturated water.
- 3) MacElvain's arguments show that large bubbles are more stable (i.e., have lower energy) than small bubbles; microbubbles would have short lives, because they would quickly coalesce into larger bubbles.
- 4) Vertical migration by effusion is readily explained within the context of normal bubbles. A theoretical, heretofore unknown, type of bubble is not required to explain this physical process.

Richers et al. (1982) and Arp (1992a) described effusion as the predominant vertical migration mechanism in the Patrick Draw oil field, Wyoming, U.S.A. Arp (1992b) provided a detailed description of "effusive microseepage" as a predominant vertical migration mechanism. Extending the pioneering work of Tripp (1944, 1945), Arp applied Darcy's law to vertical mass transport. Darcy's law describes pressure-driven flow through porous media. Calculations using reasonable values for rock properties and subsurface fluids showed that effusion could account for empirically observed, near-surface concentrations and vertical migration rates of hydrocarbon gases. Because effusion is bulk mass transport of hydrocarbons, this mechanism could account for the reservoirlike compositions reported in near-surface soil-gas samples by Jones and Drozd (1983).

Saeed (1991) and Klusman and Saeed (1996) reported computer-simulation models of effusion based on Darcy's law calculations. Comparing models of diffusion, hydraulic transport, and effusion, Klusman and Saeed (1996) conclude that only the effusion mechanism could account for cases in which (1) migration is nearly vertical; (2) anomalies are sharply defined, e.g., have a high concentration gradient, as described by Rice (1986); and (3)

rapid vertical migration is observed as shallow gas-hydrocarbon concentrations change during production.

Mass-transport Dilemma

All these mechanisms are plausible and, no doubt, all these mechanisms occur. Our mass-transport problem is to decide which mechanism or mechanisms predominates in transporting low-molecular-weight hydrocarbons to the surface, and under what conditions. This problem applies to all mass transport through subsurface rocks, including primary migration from source to reservoir. Primary migration studies deal with migration through hundreds of kilometers. Many possible migration mechanisms exist. Looking at the end products of migration may not allow unequivocal explanations of the mechanisms (Roberts and Cordell, 1980). All mechanisms proposed for vertical migration also occur in primary migration. All are subsurface mass-transport problems. The same forces, rules, and problems apply in all cases.

Fortunately, vertical migration is simpler than primary migration—which may also contain a vertical component—because:

- 1) Vertical migration occurs through only a few kilometers.
- 2) Buoyancy of petroleum in water causes a natural tendency toward vertical migration.
- 3) Near-surface soil-gas-concentration patterns associated with vertical migration are measurable and can be studied in detail. Therefore, we can observe one end of the process.
- 4) A growing body of hydrologic and environmental literature includes substantial information about mass transport in the shallow subsurface (for example, see Devitt et al., 1987).

Reservoir Communication through Vertical Migration

Exploration is determining information about a possible petroleum reservoir before drilling. Because exploration risk derives from a combination of (1) missing and (2) unreliable information, increasing the quantity and quality of reservoir information decreases risk (Belt and Rice, 1995). Information is transferred by communication links. Although much exploration research centers on improving the existing communication links, a pragmatic appraisal raises the expectation that establishing new communication links will result in greater increases in information content. Vertical migration could be another communication link with petroleum reservoirs (Belt and Rice, 1996a, b). However, questions remain. What information does the link convey about a petroleum reservoir? Does it relay size, location, depth, or content? How vertical is "vertical"? How current is the information? Does vertical migration require thousands of years, as pre-

dicted by diffusion theory? The data presented here address some of these questions.

Rapid Changes in the Surface Hydrocarbon Pattern

Horvitz (1969), on reviewing 30 years of information on geochemical hydrocarbon prospecting, introduced evidence for a rapid, dynamic communication link between the reservoir and the surface through vertical migration. In his well-known Hastings field case history in Brazoria County, Texas, Horvitz compared a 1946 soil-gas survey, done early in the life of the field, with another survey conducted 22 years later. At the time of the 1968 survey, anomalies observed in the 1946 data had virtually disappeared. Because some wells were producing large volumes of water by 1968, Horvitz concluded that near-surface hydrocarbon concentrations had decreased because the reservoir was partially depleted.

Rapid Vertical Migration

In an important paper first cited in the vertical-migration literature by Arp (1992a), Araktingi et al. (1982) used chemical tracers to study surface leaks above a gas storage reservoir about 900 m (3000 ft) deep. Visible seepage at the surface, about five years after pressurization, prompted an engineering study to determine how to stop the gas loss. Detailed reservoir information and computer modeling showed that leakage through the reservoir seal was related to reservoir pressure. At pressures above 12,400 kPa (1800 psi), continuous gas migration to the surface was observed. Surface migration decreased when reservoir pressures fell below 11,000 kPa (1600 psi). Araktingi described breaching the hydraulic seal as a “check-valve” effect. Klusman and Saeed (1996) suggested that a “pressure relief valve” was a better analogy. Based on data reported by Araktingi et al. (1982), vertical migration rates can be estimated. Vertical migration rates, from the reservoir to the surface, were approximately 300 m/yr (1000 ft/yr). Tracer data showed much faster rates, but they may have been related to well-casing leaks.

Hydrocarbon Surface Expressions as Communicators of Reservoir Information

A thorough vertical migration study was conducted with the NASA GeoSat Committee’s study of Patrick Draw oil field. A series of papers, beginning with Richers et al. (1982), described the characterization of surface hydrocarbon expressions of vertical migration as communicators of reservoir information. The Patrick Draw reservoir was moderately deep (1500–2000 m, or 4900–6500 ft). Soil-gas data showed communication with the reservoir through surface-mapped lineaments. These hydrocarbon surface features were probably mapping the surface expression of

faults and macrofractures. Sparse sampling away from these major lineaments showed lower concentrations. Stunted sagebrush and native grasses appeared to be stressed by vertically migrating hydrocarbons. This observation suggested that reservoir communication was occurring with the surface distally from these major lineaments.

In a follow-up study, Richers et al. (1986) found a correlation between soil-gas hydrocarbon concentrations and a blighted-sage area. These authors concluded that gas, reinjected into the reservoir, could have been leaking to the surface. However, there was evidence that some surface effects preceded reservoir production. Scott et al. (1989) questioned the conclusions of Richers et al. (1986), because no temporal correlation existed between the satellite-imaged blighted-sage anomaly and any gas or water reinjected into the reservoir. Arp (1992a) explained that this timing discrepancy resulted from vertical migration rates of 76–305 m/yr (250–1000 ft/yr). This hysteresis in vertical migration data must be taken into account when studying changes in surface expressions that are caused by production.

GEOLOGIC SETTING

The study area, identified in Figure 1, was in Brown County, Texas, U.S.A., approximately 3 km (2 mi) south of the Eastland County and Brown County boundary in the northern portion of the Crosscut oil field. The study area covered approximately 2.3 km² (0.9 mi²). Most production in the area is from the Crosscut sandstone formation, which is of Pennsylvanian age.

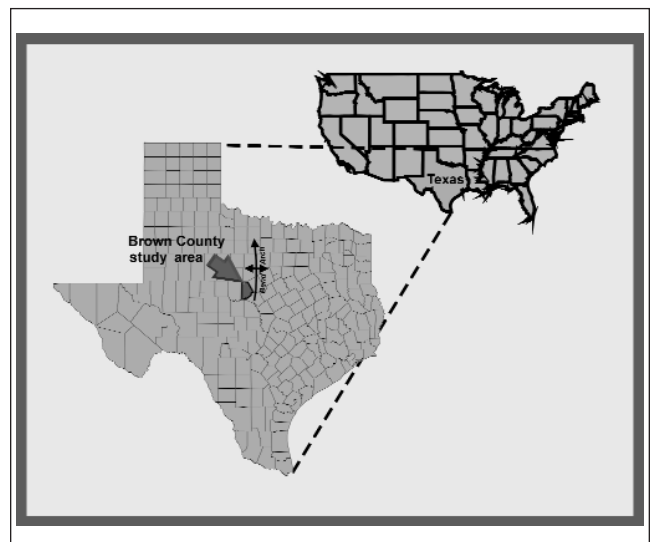


FIGURE 1. Study area in Brown County, Texas, U.S.A., west of Bend Arch.

Regional Geology

Klinger (1941) described the geology of the Crosscut sandstone in the Brown County study area. The Crosscut sandstone lies near the division of the Strawn Series and the Canyon Group. Absence of the Palo Pinto Formation

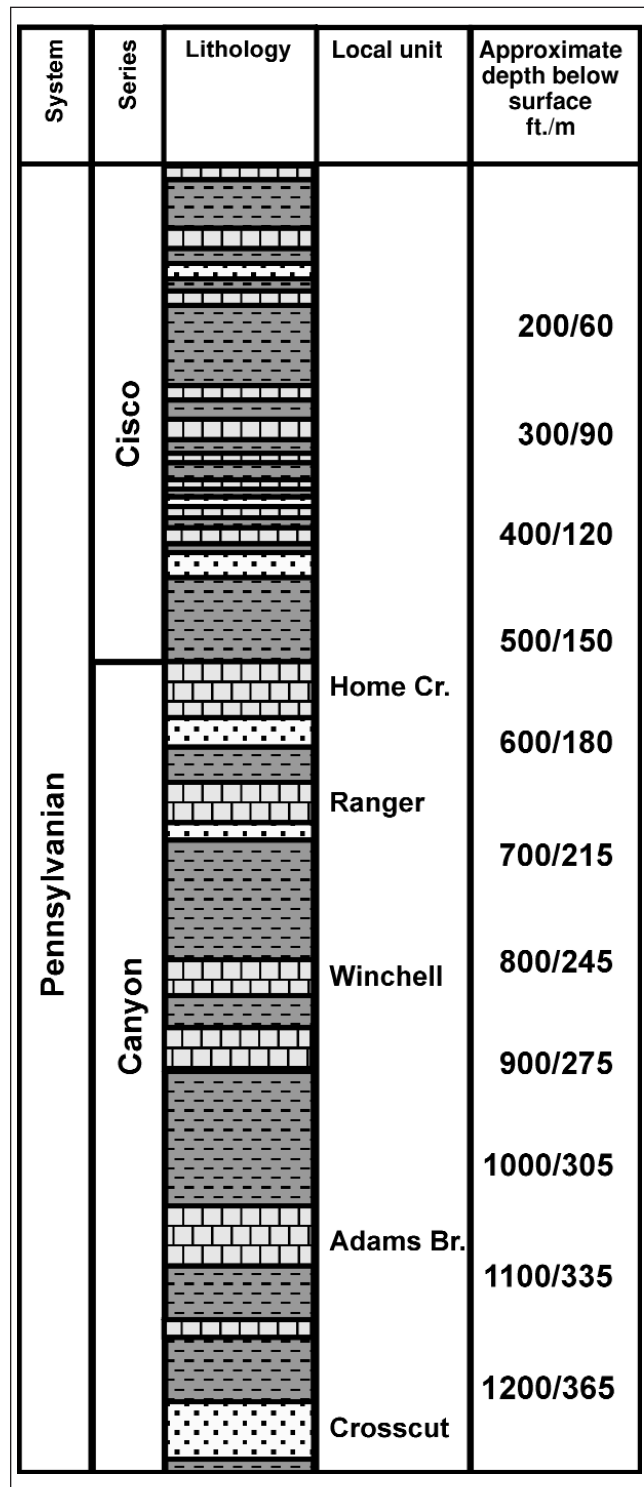


FIGURE 2. Stratigraphic section of the study area. Local units from Klinger (1941).

in the Brown County area made determining the exact age of the Crosscut sandstone difficult. However, based on its being above the earliest appearance of *Triticites*, Klinger placed the Crosscut sandstone in the Canyon Group. The sandstone appeared to have developed in a marginal-marine or nearshore depositional environment. The vertical section in Figure 2 shows the stratigraphic interval to the Crosscut sandstone.

The Crosscut-Blake district lies near the axis of the Bend Arch (approximate location is shown in Figure 1). The arch extends northeast of the Llano uplift into Young County, Texas. East of the axis, a rapid thickening occurs in the Strawn beds. Minor structural features include a series of west- and northwest-trending noses extending through the district. The Beck anticline is one of the most notable structural features. Although oil and gas accumulation is more likely in structurally high areas, it has also developed in adjacent synclinal regions. This development appears to be associated more with regional bands than with underlying structural highs. Within these regional bands, oil and gas accumulations occur in the structurally high portions of individual sandstone bodies, regardless of their position on structure.

In the Crosscut-Blake district, the Crosscut sandstone is found approximately 204 m (670 ft) to 240 m (790 ft) below the Ranger Limestone Member marker bed. The thickness of the sandstone varies, reaching a maximum of approximately 15 m (50 ft). In different areas of the dis-

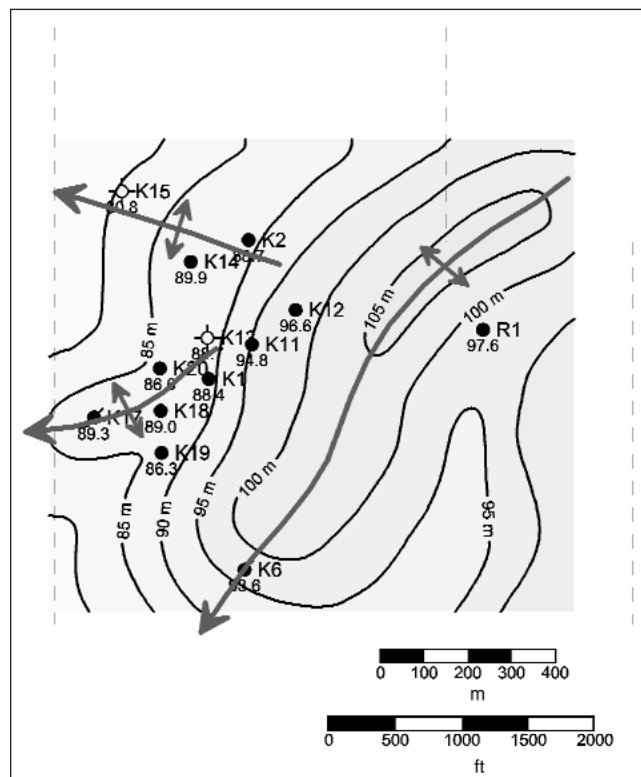


FIGURE 3. Structure at the top of the Crosscut sandstone.

trict, the Crosscut sandstone can (1) grade upward into a sand-shale sequence, (2) split into two distinct members, or (3) be overlain by a separate sandstone body.

Another noteworthy feature of the Crosscut sandstone is its thickness relative to structural position. Generally, thicker sandstone bodies occur on the higher positions of the structural features, whereas in the synclinal areas, the sandstone is usually absent, thin, or shaled out.

Geology of the Study Area

Figure 3 is a structure map at the top of the Crosscut sandstone. A major anticlinal structure, plunging southwest, trends northeast to southwest across the central portion of the study area. Two minor structural noses extend west of the major structural axis.

Figure 4 is an isopach map of the producing Crosscut sandstone. The producing sandstone thickness in well logs ranged from 0.9 m to 7.3 m (3 ft to 24 ft). Two large sandstone bodies are present in the study area. One sandstone body trends southwest to northeast near the axis of the major anticlinal structure. The second sandstone body is northwest of, and trends parallel to, the first sandstone body. This sandstone body traverses the two minor structural noses. Well control indicates a possible trough between the two sandstone bodies, where the sands have either shaled out or become very thin.

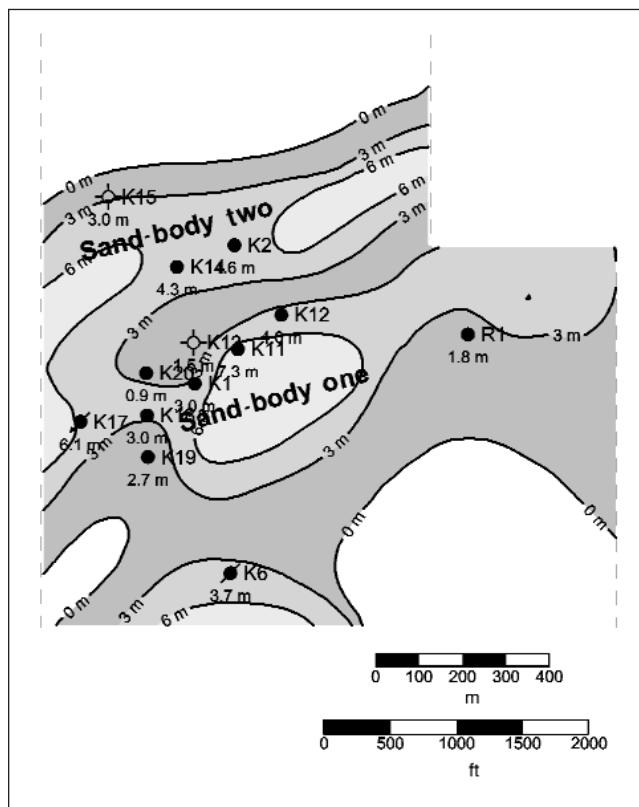


FIGURE 4. Isopach map of the Crosscut sandstone.

Production in the Study Area

Crosscut sandstone production at the time of this study was about 40° API gravity oil, with a gas-oil ratio (GOR) of <1000. According to records, earlier production exhibited a much higher GOR, but production in parts of the field had been ongoing since about 1930, which depleted most of the gas. Current production was water driven, with no discernible gas cap over produced oil.

Production for wells K1, K11, K12, K17, K18, K19, and K20 developed in sand-body one. Production for wells K2 and K14 developed in sand-body two. Wells in either sand body on the higher positions of each structural feature, e.g., on the west flank of the major structural axis or the two minor structural noses, generally resulted in producing wells.

STATISTICAL GEOCHEMICAL PARAMETERS

Controlled Variables

A primary objective of this study was to determine temporal sample reproducibility. Ideally, for such a scientific study we would like to deal only with the single variable—time—while holding all other variables constant. However, we were not working in a laboratory where conditions can be controlled. In earth sciences, we control the variables we can control, and we account for uncontrolled variables that may affect results.

The study area was moderately difficult to sample because soils were thin and sandstone covered the surface. Most samples were collected in sandstone. Many samples were taken at less than the maximum 3-m (10-ft) depth. Spatial variation between sampling periods was controlled by permanently marked sample stations. During each survey, samples were collected near, but not on, previous data locations. Limited spatial variation helped to maintain constant lithology and sample depths at each station.

Soil-gas sampling was carried out using a truck-mounted auger drill. Soil-gas samples were collected through the hollow-stem drill. Samples were taken from as deep as possible, as much as 3 m (10 ft) deep, to reduce atmospheric effects. Weather conditions affecting soil-gas data were controlled, to the extent possible, by sampling in similar seasons, e.g., late summer or fall. All data were collected when the soil was dry.

Uncontrolled Variables

Although some variables were subject to limited control, other variables affecting soil-gas hydrocarbon measurements were not controlled. The field produced oil before and during this study. Depletion effects on near-surface hydrocarbon concentrations were discussed earlier

in this paper. It was not known if, or to what extent, depletion would affect these annual soil-gas measurements.

Additional wells were drilled during the ongoing study. Although depletion over time affects soil-gas concentrations (Horvitz, 1969), how fast the newly drilled, producing wells would change the concentrations at the surface was unknown. Also unknown were what effects, if any, might be measured in near-surface hydrocarbon concentrations that might be caused by reservoir depletion and by shutting in wells during the monitoring period.

Water was injected into the field at variable rates throughout the study. During the monitoring program, a waterflood was initiated. At the time of this study, nothing was known about soil-gas hydrocarbon concentration changes associated with water injection into petroleum reservoirs. Schumacher et al. (1997) reported recent application of microbial techniques to a waterflood project. However, prior to this study, no reports existed concerning soil-gas monitoring before and during an oil-field waterflood.

Moderately difficult sampling conditions and major changes in production and field development made sample reproducibility challenging. However, the study was designed to test real conditions. The necessity of determining the impact of uncontrolled variables on soil-gas concentrations for the reproducibility program led to the results reported here.

Measuring Sample Reproducibility

Sampling variation defines the “noise” above which the soil-gas concentration “signal” must be observed. Soil-gas data are often regarded as difficult to reproduce. Changes in vertical migration, microbial activity, and soil moisture have been cited as causing the differences in data from one sampling time to the next. However, recent experience shows that soil-gas data can be reproduced. Resampled areas with high amounts of soil-gas hydrocarbons may exhibit different concentrations between sampling periods, but they usually remain high. Resampled locations on the edge of high soil-gas concentration features (high-concentration gradients) may yield high, low,

or intermediate concentrations. Similarly varying results on the edges of areas with high seepage rates have been noted in microbial studies (Price, 1993).

Background areas, in theory, represent hydrocarbons that are *not* migrating from reservoir sources. If this is true, background data should be immune to reservoir changes. Therefore, background data were used to measure sample reproducibility independently of the changes occurring in the reservoir.

Selecting What to Map

Seven hydrocarbon gases, listed in Table 1, were measured in each sample collected during this study. Although each gas could be mapped for each sampling period, the question remains: What gas or combination of gases best reflects the existence of a petroleum reservoir? A pragmatic appraisal of data characteristics answers this question.

Simple graphical procedures help determine the relationship, or association, between two variables. One variable is plotted along the *x*-axis, and the other variable is plotted along the *y*-axis. Therefore, each sample is represented by a single point on the graph, where its location is determined by *x* (first variable) and *y* (second variable). When data sets are crossplotted in this manner, the resulting graphical patterns describe the relationship between the two plotted variables. The more linear the relationship among the plotted points, the more strongly the data are related (correlated) and not random (noncorrelated). Figure 5 shows a graph of propane versus ethane. The linear relationship between these variables shows that these data were not random. Therefore, the data contained little biologically induced noise. Random data would plot as scattered points.

The measured gases that we assume are associated with biological activity include the olefins, or unsaturated hydrocarbons, ethylene and propylene (Ullom, 1988), and sometimes methane. The plot of ethylene versus ethane (Figure 6) shows increased random noise. Ethylene and ethane gases are not highly correlated. However, the ethylene-versus-propylene graph (Figure 7) shows better

TABLE 1. Univariate statistical values for August 1991 base-year data; *n* = 107 samples. Other data sets had similar values.

	<i>Mean</i>	<i>Std. dev.</i>	<i>Minimum</i>	<i>Maximum</i>	<i>Median</i>
Methane	199.41	296.27	9.58	1561.12	83.08
Ethane	11.23	15.5	0.58	101.11	6.28
Ethylene	5.23	7.68	0.28	43.28	2.47
Propane	3.86	5.28	0.23	36.84	2.09
Propylene	3.48	4.69	0.18	28.94	1.81
<i>i</i>-Butane	0.54	0.64	0.02	3.44	0.32
<i>n</i>-Butane	1.48	2.02	0.08	12.2	0.79

TABLE 2. Pearson product-moment correlation coefficients for August 1991 base-year data. Other data sets had similar correlation coefficients. Note that the data in the table are symmetrical about the diagonal of 1.0000 values. On each side of this diagonal are the 21 possible combinations of the seven gases, compared two at a time.

	<i>Methane</i>	<i>Ethane</i>	<i>Ethylene</i>	<i>Propane</i>	<i>Propylene</i>	<i>i-Butane</i>	<i>n-Butane</i>
Methane	1.0000	0.9187	0.6371	0.8863	0.6537	0.9368	0.8727
Ethane	0.9187	1.0000	0.7854	0.9948	0.8359	0.9311	0.9094
Ethylene	0.6371	0.7854	1.0000	0.8157	0.9838	0.6871	0.8253
Propane	0.8863	0.9948	0.8157	1.0000	0.8691	0.9156	0.8983
Propylene	0.6537	0.8359	0.9838	0.8691	1.0000	0.7265	0.8300
i-Butane	0.9368	0.9311	0.6871	0.9156	0.7265	1.0000	0.8527
n-Butane	0.8727	0.9094	0.8253	0.8983	0.8300	0.8527	1.0000

correlation. These graphs indicate a high probability that ethylene and propylene are from the same source, but a source different from that for the ethane and propane.

Graphing all the possible combinations of our seven gases, two at a time, would result in 21 graphs. Instead of making all these graphs, Pearson product-moment correlation coefficients are used for comparing the linear relationships between our geochemical variables, two at a time (Table 2). Correlation coefficients of 1 or -1 indicate perfect linear and inverse linear relationships, respectively. A correlation coefficient of 0 means the variables are independent of each other.

Data in Table 2 for August 1991 show that methane, ethane, propane, *i*-butane, and *n*-butane were highly correlated. Ethane, propane, *i*-butane, and *n*-butane were highly correlated with each other in every data set. Therefore, mapping each of these gases or a sum of these gases would show similar surface expressions. Correlation coefficients for ethane and propane were greater than 0.98 in each data set. Therefore, either ethane or propane data would give similar relative concentration patterns.

According to the data in Table 1, ethane was the most abundant gas measured, other than methane. Because methane could have significant biogenic sources, it may not represent petroleum-reservoir-generated gases. Ethane is the most abundant measured hydrocarbon that could safely be considered to derive from petroleum.² Therefore, ethane was used to map near-surface petroleum gas distributions.

² Avoiding methane for determining surface expressions of petroleum is a common practice in surface geochemistry and was continued in this study. However, correlation coefficients in Table 2 show high (> 0.9) correlation coefficients between methane and the petroleum gases ethane, propane, and the butanes. High correlations of methane with petroleum gases are evidence that these methane data had little biogenic contribution. After using a crossplot of methane versus ethane to confirm this relationship and to remove individual outliers, methane could have been mapped as a surface expression of petroleum. Such data analysis uses relationships within the existing data and reduces the need for isotope ratios on every sample.

Determining Background

Accurate determination of background hydrocarbon concentrations is paramount. Background hydrocarbon concentrations are considered to be normal data from

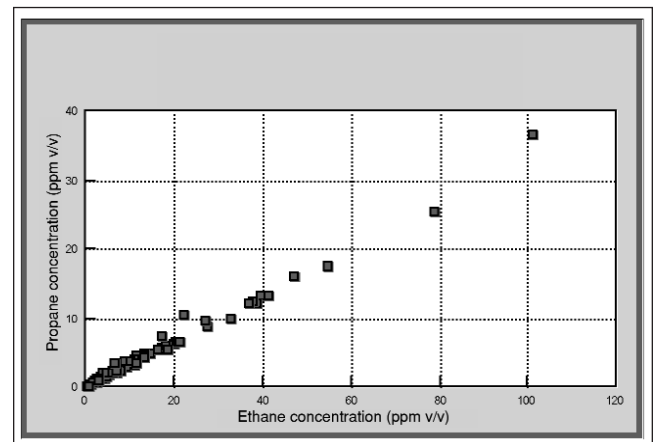


FIGURE 5. Crossplot of propane versus ethane for August 1991 baseline data.

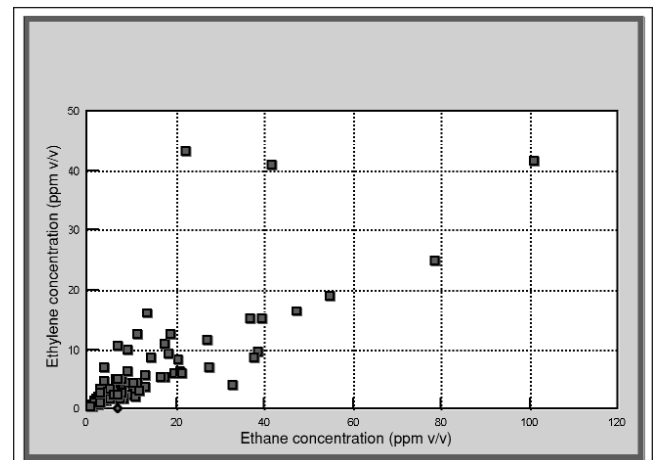


FIGURE 6. Crossplot of ethylene versus ethane for August 1991 data, with low correlation.

sources other than vertical migration. Therefore, hydrocarbon data above the background level can include *some* vertical migration data. Three background determination methods were used: ordered data inflection, maximum background, and probability plots. Ordered-data inflection is illustrated in Figure 8 for the 1991 data. Using the ordered-data-inflection method, we visually determined the first significant slope change on an ordered plot (data plotted in order of ascending concentration). Significant slope changes do not include minor changes, which probably are caused by noise in small data sets. Most ordered plots of background data increase gradually and nearly monotonically. An inflection (change in slope) occurs where concentrations above the background level influence the data. The inflection at 11 ppm is marked in Figure 8. The method shown in Figure 8 is the same as the “declining-value-distribution-curve” technique described

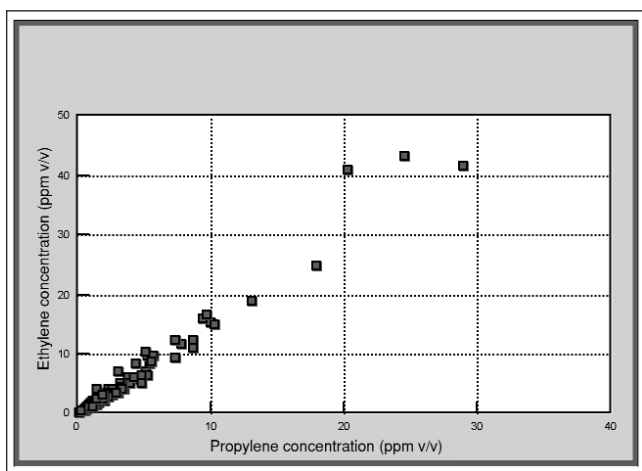


FIGURE 7. Crossplot of ethylene versus propylene for August 1991 data, with high correlation.

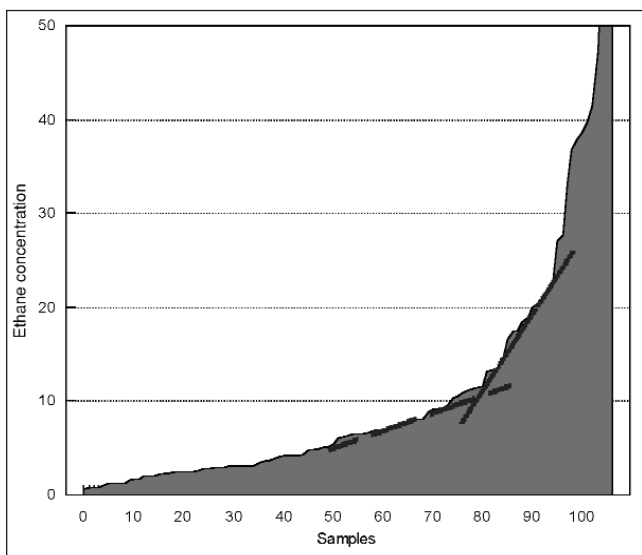


FIGURE 8. August 1991 ordered-data-inflection background determination.

by Saunders (1989), but the sample order is reversed. This type of method is commonly used for determining the background in soil-gas hydrocarbon data.

The maximum-background method, shown in Figure 9, determines a maximum value for background (low-concentration) values. This method simply selects the appropriate background from a profile plot of the data. Background is based on arbitrary selection in what appears to be just below maximum-background data values. This method indicated that approximately 11 ppm was the background’s upper boundary.

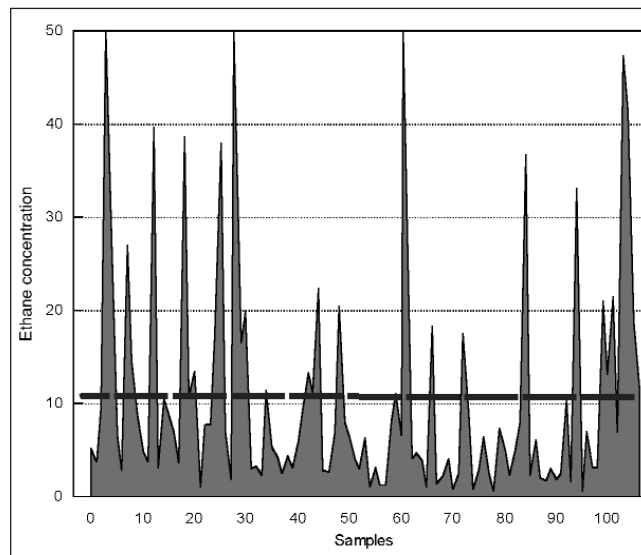


FIGURE 9. August 1991 background determination, using the maximum-background method.

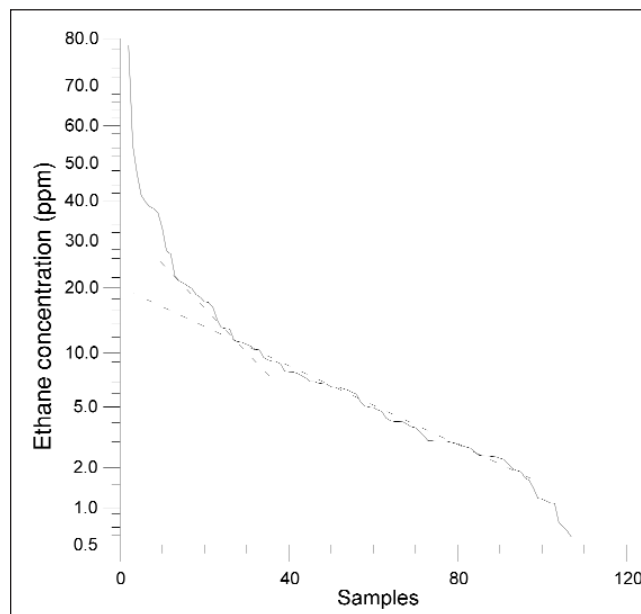


FIGURE 10. Probability plot of August 1991 ethane concentration data. Y-axis is ethane concentration on a probability scale.

A probability plot, in Figure 10, records the August 1991 data. Sinclair (1976) provided an excellent introduction and description of probability plots. A probability plot is an ordered plot similar to the ordered-data-inflection curve. However, instead of plotting ethane concentration on a linear axis, as in Figure 8, we now plot ethane concentration on a probability scale. A probability scale is a linear transformation of a normal distribution. A normally distributed population would plot as a straight line, using the probability scale. Deviations from the straight line reflect a data set's deviation from statistical normality. A mixture of two normally distributed (bimodal) populations plots as a line with an inflection point where the populations intersect. In theory, background and significant (not anomalous, just larger than background) geochemical data approximate a bimodal distribution. Therefore, determining the inflection point can determine where background and significant data intersect. An inflection at 12 ppm is shown in Figure 10.

Normally, two data-inflection techniques would not both be used. Note that Figures 8 and 10 are similar. The *x*-axes in both graphs show samples in concentration order. Figure 8 samples are in increasing-concentration order. Figure 10 samples are in decreasing-concentration order. The *y*-axis on both graphs represents ethane concentration. Figure 8 shows ethane on a linear scale, and Figure 10 uses a probability scale.³ Therefore, these methods are related. The only significant difference is how the ethane concentration is scaled. If monotonic functions are used to rescale the *y*-axis, an inflection will occur in ordered data plots where different populations overlap. All these techniques are looking for inflections in the original data, not inflections caused by technique. Therefore, users should choose a data-inflection method based on their experience and the method's effectiveness with their particular data. Methods may include ordered plots with concentrations expressed as linear, logarithmic, probability, probability-log, or derivative scales. Two methods, linear and probability, were used for our comparison.

All these background determination methods are subjective. However, after substantial experience in a particular area, we have found that the results are consistently reproducible, even among different personnel. Because the methods are subjective, all are shown in Table 3, and the results are averaged.

Reproducibility Results

Background ethane concentrations, determined at each measurement period during this study, are summa-

rized in Table 3. Compared with the 1991 data, the maximum deviation was within $\pm 20\%$ during the 5 years of sampling. Because this background variation was small compared with the data of interest, results were compared among years without correction.

Temporal Data

When interpreting soil-gas data, absolute-magnitude changes at individual sample locations are not as important as the overall size and shape, or geometry, of the soil-gas concentration patterns. We can determine significant hydrocarbon microseepage using an approach that is similar to the way we determine a "forest."⁴ We do not define a forest solely by a few of its tallest trees, because the height of trees may change, but the location of the forest remains the same. Likewise, we do not define significant hydrocarbon microseepage by only a few "anomalous samples."

Most important to defining a forest are its location, size, and shape. Most important to hydrocarbon microseepage are location, size, and shape of the soil-gas patterns. In monitoring applications, we are interested in observing changes in location, size, and shape of the soil-gas patterns during the production or recovery processes. Differences in the geochemical data from one monitored interval to the next represent the temporal changes we wish to observe.

We can use mathematical methods, such as difference maps, to represent temporal changes. However, large changes can be observed by simple visual comparison. Therefore, in this study, temporal changes in soil-gas patterns were determined by using visually identified changes in size and shape of near-surface soil-gas hydrocarbon concentration patterns.

⁴ If our task is to map a forest, we must determine a large area containing high densities of tall trees. Before proceeding, we have to define "large areas," "high densities," and "tall." For illustrative purposes, we define large areas as $\approx 10 \text{ km}^2$. Because only one tall tree does not make a forest, we also need a tall-tree density requirement, e.g., a minimum of 100 tall trees per km^2 . Also, let us arbitrarily define tall trees as more than 6 m (20 ft) high. Some trees may be much taller than 6 m, but anything taller than 6 m meets our definition of a tall tree. Although we could use statistics to more rigorously define "tall" for a particular sample of trees, we use 6 m, which is arbitrarily defined based on our logic-based perception of minimum tree heights for a forest. According to our definition, a forest is a wooded area covering at least 10 km^2 , which contains at least 100 6-m or taller trees per km^2 . Therefore, we have quantified a minimal forest. Now we can measure any group of trees and determine whether they meet our minimum forest requirement. Over a long period of time, e.g., hundreds of years, a forest is dynamic. Trees grow at various rates, die, and new trees sprout. Fire, floods, and disease may alter parts of a forest or even destroy it. Therefore, changes in the trees cause portions of the forest to change continuously. Hydrocarbon concentrations are analogous to tree heights. Both indicate how much (hydrocarbon or tree) is present at a given location. Tall-tree density is analogous to density of high-concentration samples. Area is measured the same way in both cases. Some forests may die and reappear. Over a long period, the data will change. Such also is the nature of soil-gas hydrocarbon data.

³ Some investigators argue that probability scales should be based on $\log(\text{concentration})$, which tends to make plots be more linear. However, a large part of the data above background in Figure 10 is reasonably linear. Logarithms of concentration sometimes obscure data inflections. Our requirement was to find inflection points. Therefore, we chose not to use logarithms of concentration data in probability plots.

TABLE 3. Background ethane concentrations, as determined by ordered-data-inflection, maximum-background, and probability-plot methods for each study year, and comparison of each with 1991 data.

<i>Date</i>	<i>Data-inflection method (ppm v/v)</i>	<i>Maximum-background method (ppm v/v)</i>	<i>Probability-plot method (ppm v/v)</i>	<i>Average background correlation (ppm v/v)</i>	<i>% Deviation from comparison year</i>
November '89	11	10	12	11.0	-3
October '90	13	12	14	13.0	+15
August '91 (comparison year)	11	11	12	11.3	0
October '92	14	12	14	13.3	+18
October '93	12	13	12	12.3	+9
January '94	9	11	9	9.7	-14

Mapped Ethane Concentration Data from 1989 to 1994

The mapped displays in Figure 11 show ethane concentration data for each reported measurement period. The area sampled measured about 1.6 km (1 mi) both north-south and east-west. Sample locations, represented on the data maps by "+," were collected on a spacing of approximately 150 m (500 ft) in a regular grid pattern. Side-by-side mapping of the six data sets in Figure 11 illustrates background-data reproducibility. The maximum background ethane concentration ranged from 10 to 13 parts per million by volume (ppm v/v) (Table 3). Ten ppm (v/v) was selected as a round number representing the ethane concentration background for all data displays. The same contouring intervals were used for all maps. Visual comparison of the six monitoring periods showed that:

- 1) More background-level data occurred in the central and southeastern parts of the study area, compared with the distribution of background-level data in the other parts.
- 2) Concentrations above the background level were usually present in the southwest corner, northwest corner, and east of well R1.

GEOLOGIC AND PRODUCTION EFFECTS ON VERTICAL MIGRATION PATTERNS

Drilling and Depletion Effects on Soil-gas Hydrocarbon Concentrations

Some soil-gas pattern changes, shown in Figure 11, could be related to production. For example, well R1 was drilled in a high-concentration area from an April 1989 soil-gas survey (data not shown). R1, completed in June 1989, initially flowed 60 bbl of oil/day from an Ellenburger reservoir (Ordovician age) about 1000 m (3300 ft) deep.

Production declined to 0.5 bbl of oil/day by December 1989. When monitoring was begun in November 1989, four permanent stations were placed immediately surrounding R1. The November 1989 data showed background soil-gas hydrocarbon concentrations in these four sample sites nearest R1, while ethane concentrations were much higher to the east. Later sampling exhibited similar soil-gas hydrocarbon concentration patterns relative to R1.

Following the reasoning of Horvitz (1969), decreased hydrocarbon concentrations near producing wells are often attributed to reservoir changes during production.⁵ Therefore, this surface expression with decreased concentrations near R1 could have been caused by reservoir changes during 7 months of production. If surface soil-gas hydrocarbon concentrations decreased this rapidly because of production, then vertical migration from the Ellenburger reservoir approximately 1000 m (3300 ft) deep must have been very rapid. Vertical migration from 1000 m (3300 ft) in 7 months would have required a minimum vertical migration rate of 4.7 m/day (15 ft/day).

Alternative Explanation for Decreased Soil-gas Hydrocarbon Concentrations

Decreased hydrocarbon concentrations near R1 after production could have another explanation. The wellbore drilled for R1 provided an escape route for vertically migrating hydrocarbons. Any hydrocarbons migrating vertically along serpentine pathways and encountering the borehole would use the borehole as a preferential migration pathway. The effect is similar to hydrocarbon gas mi-

⁵ Authors Rice and Belt of this paper, as well as others in the industry, frequently observe relatively low hydrocarbon concentrations near producing wells. Surface hydrocarbon concentrations decreasing near wellbores and increasing away from wellbores is common and expected. This phenomenon could be responsible for "halo patterns" reported in the literature when soil-gas hydrocarbon measurements are made over existing production.

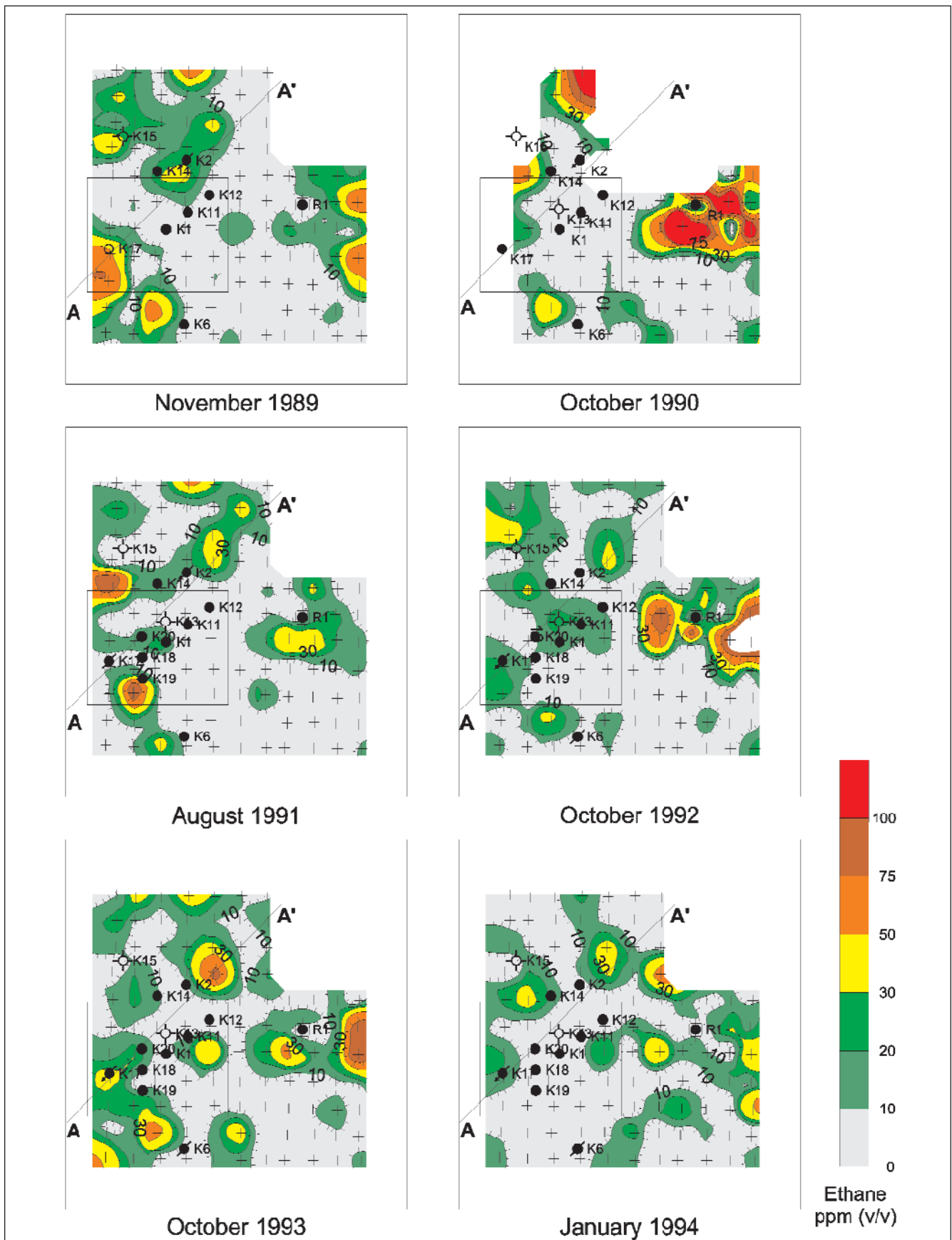


FIGURE 11. Ethane concentration patterns during six monitoring periods.

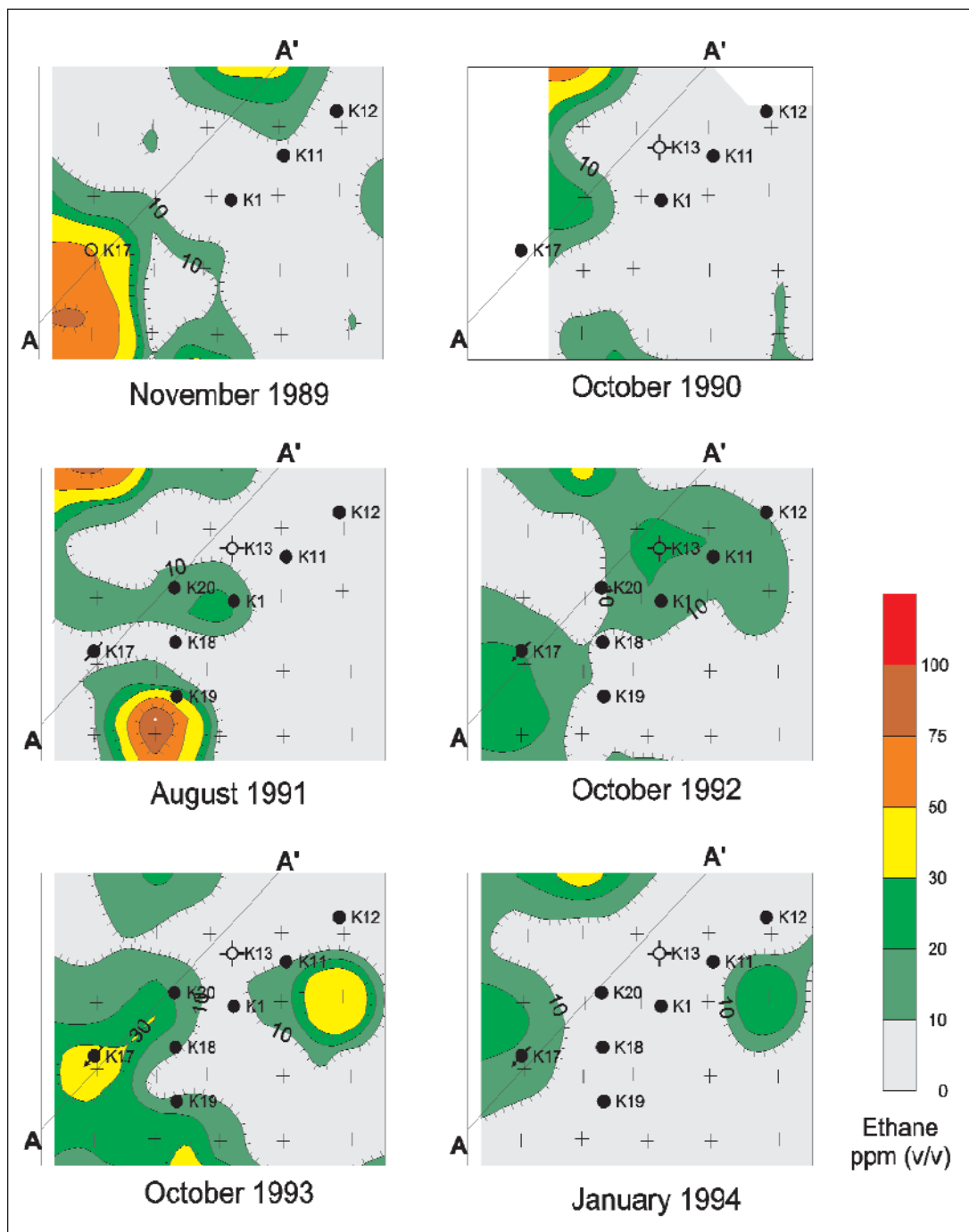


FIGURE 12.
Ethane concentration details in rectangular areas of Figure 11.

gration observed along faults and macrofractures. These preferential pathways exhibit increased gas concentrations relative to nearby decreased-concentration areas (Rice and Jackson, 1984). Gases migrating up preferential pathways (those having higher permeability) will cause surrounding areas over any paths not selected (those having lower permeability) to exhibit decreased concentrations. These data are not sufficient to determine which mechanism, or whether a combination of both, is causing the decreased hydrocarbon concentrations near R1.

Production and Soil-gas Hydrocarbon History of Well K17

In November 1989, an ethane concentration trend at the western edge of the study area was thought to indicate the presence of reservoir oil drained by a lease to the west. In April 1990, K17 was drilled and produced from the Crosscut sandstone at a depth of approximately 365 m (1200 ft)⁶. The inset boxes in Figure 11 are expanded in Figure 12, showing details near K17.

⁶ All wells in the surveyed area, with the exception of R1, produced from Crosscut sandstone.

By October 1990, samples near K17 exhibited lower concentrations. The well had been producing for only 7 months. Sampling in October 1990 was part of a training exercise for an international oil-company delegation. Because of the training schedule, the sampling program did not reach K17. Therefore, these data were not sufficient for a decision about whether concentration differences resulted from drilling or depletion.

Production declined as K17 depleted its low-capacity reservoir within months. Production practically ceased by year-end. A comparison of the October 1990 data and August 1991 data with the preproduction November 1989 data shows a definite decrease in high-concentration features. Changes in soil-gas concentrations could have resulted from K17 production. However, more information was needed to support this conclusion.

K17 Water Injection Effects on Soil-gas Hydrocarbon Concentrations

Well K17 was converted to water injection in March 1991. The waterflood was designed to move remaining reservoir oil east toward wells on the lease. K18 was drilled and started production in December 1990. K19 and K20 were drilled and brought on-line in June 1991.

During August 1991, soil-gas concentrations remained low around K17, but they had increased around that well by October 1992. A significant soil-gas hydrocar-

bon increase by October 1993 showed concentrations greater than the predrilled November 1989 data.

Profiled Soil-gas Concentrations and Water-injection Rates

Profile line A-A', in Figures 11 and 12, runs approximately through wells K17 and K20. In Figure 13, an ethane cross section of profile line A-A' is displayed for each monitoring period in Figure 11. Water-injection rates are displayed as a function of time. The positions of the five soil-gas surveys correspond to the timed water-injection rates below the respective profile line. The well symbol on Profile Line A-A' on the graphs represents the location and status of well K17.

K17's life cycle is shown in the chronology of Cross-cut water injection displayed in Figure 13. Soon after completion of K17, soil-gas concentrations decreased. After initiation of water injection, soil-gas concentrations near K17 quickly increased but remained below pre-drilling levels. Both depletion and water injection of K17 affected soil-gas concentrations as far away as K20.

Considering both the production and the waterflood data, we conclude that hydrocarbon concentrations near K17 were reflecting changes in the Crosscut sandstone reservoir. Soil-gas hydrocarbon concentrations decreased after production, but increased after K17 became an injection well. The increased soil-gas hydrocarbon concentra-

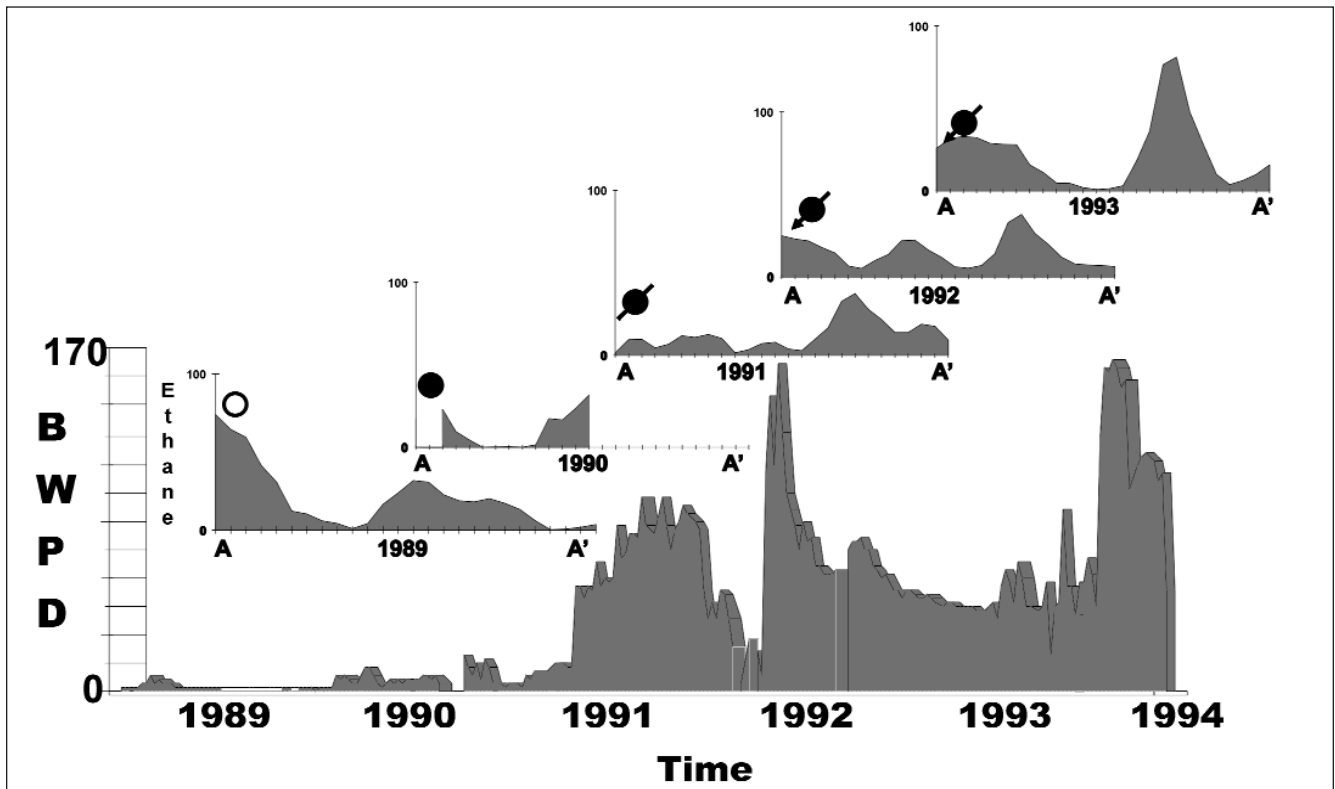


FIGURE 13. Time line of ethane profiles A-A' from Figures 11 and 12, with water-injection rates. BWP D = bbl of water (injected) per day.

tions were caused by water-injection-induced reservoir changes. Water-injection effects were observed in near-surface soil-gas data within two years.

A probable mechanism for water-injection-stimulated changes in overlying soil-gas hydrocarbon concentrations can be deduced from current vertical migration theory. Additional water is added to a petroleum reservoir to move oil toward producing wells. Fluid flow gradients in the oil reservoir are from the injection wells to the production wells. Oil, above the water, is moved in the direction of this reservoir fluid flow gradient. Increased fluid pressure in the reservoir is required to move water and oil through porous reservoir rock. This movement of oil and the increased reservoir pressure place more oil under greater pressure against the reservoir seal. More oil, oil replacing water, and higher reservoir pressures open more capillary spaces in the reservoir seal to hydrocarbons, which allows hydrocarbons to flow through the seal (Klusman and Saeed, 1996). Increased hydrocarbon migration out of the reservoir results in increased hydrocarbon gas concentrations at the surface (Araktingi et al., 1982; Arp, 1992b; Klusman and Saeed, 1996). Reservoir parameters needed to confirm this mechanism were not available for this study.

Vertical Migration Rates

Upper and lower limits of vertical migration rates can be calculated from the K17 observations. Water injection increased in K17 during February 1991. Soil-gas concentrations showed no significant increase by August 1991. Therefore, vertical migration from a depth of 365 m (1200 ft) was not observed at the surface after 6 months. This places an upper boundary on vertical migration of <2 m/day (7 ft/day).

Migration-rate accuracy is limited by hysteresis between increased water injection and gas leakage from the reservoir. However, a concentration change was observed in October 1992. About 365 m (1200 ft) of vertical migration was detected at the surface after 20 months. This established a lower boundary for vertical migration of at least 0.6 m/day (2 ft/day). These vertical migration rates, 0.6–2 m/day, are consistent with the higher range of 0.2–0.8 m/day (0.7–2.7 ft/day) reported for other geographic areas (Arp, 1992a).

Additional Observations

Well R1 was completed in Fry sandstone (Pennsylvanian) strata in October 1993 as an additional water source. As water injection increased, a vacuum was applied to wells K18, K19, and K20 to increase oil flow to these wells. After applying the vacuum, production increased only in K20. Soil-gas concentrations near K20 increased during the October 1993 monitoring period, while concentrations near K18 and K19 remained low.

After several weeks, the reservoir again was depleted, and production in K20 quickly decreased to prevacuum levels. Soil-gas concentrations near K20 also decreased by January 1994.

A vacuum was applied in an attempt to spread the waterflood uniformly among K18, K19, and K20. Soil-gas hydrocarbon concentration gradients became more uniformly distributed around the injection well by January 1994. Soil-gas hydrocarbon concentration patterns in January 1994 were consistent with the achievement of a uniform waterflood distribution in the reservoir.

By January 1994, production in K14 increased because of water injection. The isopach of the Crosscut sandstone, shown in Figure 4, depicts decreased sandstone thickness and the K13 drilling log reported “no shows.” This geologic information indicates a low-permeability barrier between K14 and K17. Therefore, water should not have flowed north from the injection well to K14. This geologic information suggests instead that water flowed northwest from K17, bypassing this low-permeability barrier and migrating to K14 from the west.

The January 1994 soil-gas hydrocarbon data showed increased surface concentrations near and west of K14, but not south toward K17. Therefore, the soil-gas hydrocarbon data supported the independent geologic hypothesis that water flowed from the west toward K14.

End of Monitoring

After January 1994, oil prices dropped below break-even for this field. Water injection, other than for disposal, ended. Only wells K11, K14, and K20 produced during August 1994. Therefore, monitoring was halted.

CONCLUSIONS

Soil-gas sampling reproducibility was confirmed in a five-year study of an oil field in Brown County, Texas, U.S.A. Variations in background hydrocarbon concentrations were within 20% during the five years of the study. Soil-gas hydrocarbon concentrations in background areas remained constant. Aside from depletion effects, high-hydrocarbon-concentration areas remained high and variable.

Decreasing soil-gas hydrocarbon concentrations during oil-reservoir depletion were demonstrated near production wells. Production from two separate reservoirs resulted in decreased near-surface soil-gas hydrocarbon concentrations. Conversely, increased soil-gas hydrocarbon concentrations occurred surrounding injection wells. These results illustrate the dynamics of soil-gas measurements and establish vertical migration rates of at least tenths of meters (a few feet) per day. Such rapid response supports effusion as the predominant vertical migration mechanism in this oil field.

Rapid vertical migration rates create potential appli-

cations for soil-gas measurements in oil-field development. Produced versus nonproduced reservoir compartments can be detected by the relative differences in soil-gas concentrations. Soil-gas concentration patterns, or their geometry, for produced portions of reservoirs can be determined by mapping soil-gas concentrations and comparing them with preproduction data.

This study suggests that measuring soil gas is a valid geochemical technique for managing enhanced-recovery programs. As water or CO₂ is injected, near-surface geochemical data could help in mapping hydrocarbon movement between wells and within the petroleum reservoir.

Although they suggest applications of soil-gas hydrocarbon data for reservoir monitoring, these results are even more important for supplying information about the vertical migration process. Only an effusion mechanism can explain the vertical migration rates observed in this study. Vertical migration rates are sufficiently rapid that near-surface soil-gas hydrocarbon data can be used as an additional communication link between the surface and a petroleum reservoir. Therefore, vertical migration of hydrocarbons from petroleum reservoirs to the surface offers a source of information about fluid content and movement within petroleum reservoirs.

This study suggests the use of vertical migration monitoring techniques for both exploration and field development. In a producing field, soil-gas hydrocarbon data can define recent reservoir changes related to production. Additional research is needed to prove the value of soil-gas data as a routine reservoir-monitoring tool. However, current technology is sufficient for evaluating these concepts in deeper fields and in other geologic areas.

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REFERENCES CITED

- Araktingi, R. E., M. E. Benefield, Zoltan Bessenyei, K. H. Coats, and M. R. Tek, 1982, Leroy Storage, Unita County, Wyoming: A case history in attempted control of gas migration, 57th Annual Society of Petroleum Engineers of AIME, Fall Technical Conference: Preprint No. SPE-11180, p. 59–64.
- Arp, G. K., 1992a, An integrated interpretation for the origin of the Patrick Draw oil field sage anomaly: AAPG Bulletin, v. 76, no. 3, p. 301–306.
- Arp, G. K., 1992b, Effusive microseepage: A first approximation model for light hydrocarbon movement in the subsurface, Association of Petroleum Geochemical Explorationists Bulletin, v. 8, p. 1–17.
- Belt, J. Q. Jr., and G. K. Rice, 1995, Macro exploration modeling: A pragmatic multidisciplinary team process: Oil & Gas Journal, June 5, 1995, p. 43–45.
- Belt, J. Q. Jr., and G. K. Rice, 1996a, Offshore 3D seismic, geochemical data integration, Main Pass Project, Gulf of Mexico: Oil & Gas Journal, April 1, 1996, p. 76–81.
- Belt, J. Q. Jr., and G. K. Rice, 1996b, Advantages seen in integrated offshore 3D seismic, geochemical data: Oil & Gas Journal, April 8, 1996, p. 100–102.
- Davidson, M. J., 1994, On the acceptance and rejection of surface geochemical exploration: Oil & Gas Journal, June 6, 1994, p. 70–76.
- Devitt, D. A., R. B. Evans, W. A. Jury, T. H. Starks, B. Ek-lund, and A. Gholson, 1987, Soil gas sensing for detection and mapping of volatile organics: Dublin, Ohio, National Water Well Association, 270 p.
- Donovan, T. J., 1981, Geochemical prospecting for oil and gas from orbital and suborbital altitudes, in B. M. Gottlieb, ed., Unconventional methods in exploration for petroleum and natural gas II: Dallas, Texas, Southern Methodist University Press, p. 96–115.
- Fullagar, P. K., 1989, Petroleum exploration by geochemical & geophysical detection of vertical migration: Glenside, South Australia, Petroleum Exploration Society of Australia Course Notes, Australia Mineral Foundation, 118 p.
- Holysh, S., and J. Tóth, 1996, Flow of formation waters: Likely cause for poor definition of soil gas anomalies over oil fields in east-central Alberta, Canada, in D. Schumacher and M. A. Abrams, eds., Hydrocarbon migration and its near-surface expression: AAPG Memoir 66, p. 255–277.
- Horvitz, L., 1969, Hydrocarbon geochemical prospecting after thirty years, in W.B. Heroy, ed., Unconventional methods in exploration for petroleum and natural gas: Dallas, Texas, Southern Methodist University Press, p. 205–218.
- Hunt, John M., 1979, Petroleum geochemistry and geology: San Francisco, W.H. Freeman and Company, 186 p.
- Jones, V. T., and R. J. Drozd, 1983, Predictions of oil or gas potential by near-surface geochemistry: AAPG Bulletin, v. 67, no. 6, p. 932–952.
- Kennicutt, M.C. II, J.M. Brooks, and G.J. Denoux, 1988, Leakage of deep, reservoired petroleum to the near surface on the Gulf of Mexico Continental Slope: Marine Chemistry, v. 24, p. 39–59.
- Klinger, E. D., 1941, Cross-Cut Blake district, Brown County, Texas, in A. I. Levorsen, ed., Stratigraphic type oil fields: Tulsa, Oklahoma, The American Association of Petroleum Geologists, p. 548–563.
- Klusman, R., 1985, Surface and near-surface geochemical methods in petroleum exploration: APGE Special Publication No. 1, Denver, Colorado, Association of Petroleum Geochemical Explorationists, 284 p.
- Klusman, Ronald W., 1993, Soil gas and related methods for natural resource exploration: New York, John Wiley & Sons, 483 p.
- Klusman, R. W., and M. A. Saeed, 1996, Comparison of light hydrocarbon microseepage mechanisms, in D. Schumacher and M. A. Abrams, eds., Hydrocarbon migration and its near-surface expression: AAPG Memoir 66, p. 157–168.

- Krooss, B. M., D. Leythaeuser, and R. G. Schaefer, 1992, The quantification of diffusive hydrocarbon losses through cap rocks of natural gas reservoirs—A reevaluation: *AAPG Bulletin*, v. 76, no. 3, p. 403–406.
- Leythaeuser, D., R. G. Schaefer, and A. Yukler, 1980, Diffusion of light hydrocarbons through near-surface rocks: *Nature*, v. 284, no. 5756, p. 522–525.
- Leythaeuser, D., R. G. Schaefer, and A. Yukler, 1982, Role of diffusion in primary migration of hydrocarbons: *AAPG Bulletin*, v. 66, no. 4, p. 408–429.
- MacElvain, R. C., 1969, Mechanics of gaseous ascension through a sedimentary column, *in* W. B. Heroy, ed., *Unconventional methods in exploration for petroleum and natural gas*: Dallas, Texas, Southern Methodist University Press, p. 15–28.
- Meyer, W. T., J. S. Lovell, and M. Hale, 1983, Detection of concealed mineral and energy resources by vapour geochemistry, *in* I. Thornton and R. J. Howarth, eds., *Applied geochemistry in the 1980s*: London, Graham & Trotman, p. 86–102.
- Price, L. C., 1976, Aqueous solubility of petroleum as applied to its origin and primary migration: *AAPG Bulletin*, v. 60, no. 2, 1976, p. 213–244.
- Price, L. C., 1981a, Primary petroleum migration by molecular solution: Consideration of new data: *Journal of Petroleum Geology*, v. 4, no. 1, p. 89–101.
- Price, L. C., 1981b, Aqueous solubility of crude oil to 400 degrees C and 2,000 bars pressure in the presence of gas: *Journal of Petroleum Geology*, v. 4, no. 2, p. 195–223.
- Price, L., 1993, Microbial-soil surveying: Preliminary results and implications for surface geochemical oil exploration: *Association of Petroleum Geochemical Explorationists Bulletin*, v. 9, p. 81–129.
- Rice, G. K., 1986, Near-surface hydrocarbon gas measurement of vertical migration, *in* M. J. Davidson, ed., *Unconventional methods in exploration for petroleum and natural gas IV*: Dallas, Texas, Southern Methodist University Press, p. 183–200.
- Rice, G. K., and V. N. Jackson, 1984, Geochemical techniques in exploration: 1984 ASP-ASCM Fall Convention Technical Papers, p. 606–619.
- Richers, D. M., V. T. Jones, M. D. Matthews, J. Maciolek, R. J. Pirkle, and W. C. Sidle, 1986, The 1983 Landsat soil-gas geochemical survey of Patrick Draw area, Sweetwater County, Wyoming: *AAPG Bulletin*, v. 70, no. 7, p. 869–887.
- Richers, D. M., F. J. Reed, K. C. Horstmand, G. D. Michels, R. N. Baker, L. Lundell, R. W. Marrs, 1982, Landsat and soil-gas geochemical study of Patrick Draw oil field, Sweetwater County, Wyoming: *AAPG Bulletin*, v. 66, no. 7, p. 903–922.
- Roberts, W. H. III, and R. J. Cordell, eds., 1980, Problems of petroleum migration: *AAPG Studies in Geology* No. 10, 273 p.
- Roof, J. G., and W. M. Rutherford, 1958, Rate of migration of petroleum by proposed mechanisms: *AAPG Bulletin*, v. 42, no. 5, p. 963–980.
- Rostron, B. J., and J. Tóth, 1996, Ascending fluid plumes above Devonian pinnacle reefs: Numerical modeling and field example from west-central Alberta, Canada, *in* D. Schumacher and M. A. Abrams, eds., *Hydrocarbon migration and its near-surface expression*: AAPG Memoir 66, p. 185–201.
- Saeed, M., 1991, Light hydrocarbon microseepage mechanism(s): Theoretical considerations: Ph.D. thesis No. T-4081, Colorado School of Mines, Golden, Colorado.
- Saunders, D.F., 1989, Simplified evaluation of soil magnetic susceptibility and soil gas hydrocarbon anomalies, Alabama Ferry field, Leon County, Texas: *Association of Petroleum Geochemical Explorationists Bulletin*, v. 5, no. 1, p. 30–48.
- Schumacher, D., and M. A. Abrams, eds., 1996, *Hydrocarbon migration and its near-surface expression*: AAPG Memoir 66, Tulsa, Oklahoma, American Association of Petroleum Geologists, 446 p.
- Schumacher, D., D. C. Hitzman, J. Tucker, and B. Rountree, 1997, Applying high-resolution surface geochemistry to assess reservoir compartmentalization and monitor hydrocarbon drainage, *in* R. J. Kruijenga and M. W. Downey, eds., *Applications of emerging technologies: Unconventional methods in exploration for petroleum and natural gas V*: Dallas, Texas, Southern Methodist University Press, p. 309–322.
- Scott, L. F., R. M. McCoy, and L. H. Wullstein, 1989, Anomaly may not reflect hydrocarbon seepage: Patrick Draw field, Wyoming, revisited: *AAPG Bulletin*, v. 73, no. 7, p. 925–934.
- Sinclair, A. J., 1976, Application of probability graphs in mineral exploration: *The Association of Exploration Geochemists, Special Volume* no. 4, p. 1–95.
- Stegena, L., 1961, On the principles of geochemical oil prospecting: *Geophysics*, v. 26, no. 4, p. 447–451.
- Tóth, J., 1980, Cross-formational gravity-flow of groundwater: A mechanism of the transport and accumulation of petroleum (the generalized hydraulic theory of petroleum migration), *in* W. H. Roberts III and R. J. Cordell, eds., *Problems of petroleum migration*: AAPG Studies in Geology No. 10, p. 121–168.
- Tripp, R. M., 1944, Analytical and experimental data concerning a solid hydrocarbon survey of the Fort Collins anticline: *Geophysics*, v. 9, no. 3, p. 367–387.
- Tripp, R. M., 1945, Thermodynamics of a gas migrating vertically through the sedimentary column: *Geophysics*, v. 10, no. 2, p. 229–237.
- Ullom, W. L., 1988, Ethylene and propylene in soil gas: Occurrence, sources and impact on interpretation of exploration geochemical data: *Association of Petroleum Geochemical Explorationists Bulletin*, v. 4, p. 62–81.