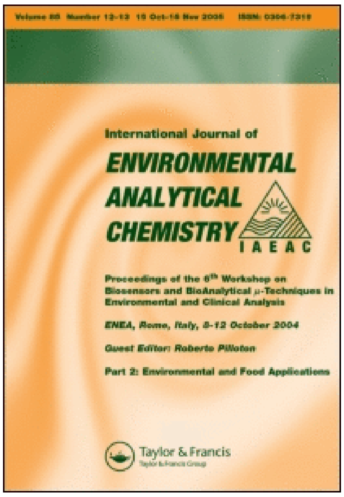

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G. A. Eiceman[a]; F. R. Sprester[a]; J. L. Gardea[a]; N. Y. Nan[a]
[a] Department of Chemistry, New Mexico State University, Las Cruces, NM, U.S.A.

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Distribution of Hydrocarbons in Soil Through Contamination from a Leaking Natural Gas Pipeline

G. A. EICEMAN, F. R. SPRESTER, J. L. GARDEA
and N. Y. NAN

Department of Chemistry, New Mexico State University, Las Cruces, NM 88003, U.S.A.

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A plume of hydrocarbon contamination in soil from a leaking natural gas pipeline located at a depth of 80 cm was defined on the basis of discoloration of soil at 3 to 7 cm depth. Eleven sites were selected randomly on a grid superimposed on a map of the 240 m^2 plume and 48 soil samples at depths from 7 cm to 150 cm were collected. Samples were individually extracted using cyclohexane in a Soxhlet extraction apparatus. Condensed extracts were analyzed using capillary GC and GC/MS techniques to determine quantitatively the dinstribution of C_{10} to C_{35} hydrocarbons in soil. In solvent extracts of the soils, over 150 organic compounds were resolved and detected at total concentrations from 0.1 to 2700 ppm. The vertical distribution of hydrocarbons was consistent throughout the plume with higher concentrations of all components with increased proximity to the surface. The hydrocarbons moved vertically from the leak and diffused horizontally along an interface created at 15 to 30 cm by the addition 20 years earlier of a dense clay soil to a naturally high-gypsum base. Ratios of soil concentrations in three size ranges for the hydrocarbons were used to evaluate the physical mechanism for gaseous migration and environmental fate of the hydrocarbons. These ratios were not uniform at every site and depth throughout the plume. Results were consistent with differences in mobility and fate of the hydrocarbons in the soil based on volatility and adsorption. Polycyclic aromatic hydrocarbons present in the natural gas and in the pipeline residue were also found in some but not all soil samples under the conditions of extraction and analyses which were not optimized in the soil-extraction of the aromatic compounds.

INTRODUCTION

Natural gas which was once flared during production of oil has become a major source of energy with annual demand of 17 trillion cubic feet (tcf) of gas nationally (U.S.) in 1983.[1] In 1984, monthly production was 4 to 5 tcf worldwide and 1.4 to 1.5 tcf in the U.S.[2] Although a slight decrease (1% per year) in gas demand has been predicted by year 2000, natural gas will remain a major source of energy through to the next century. The composition of natural gas has been well studied and major components include C_1 to C_7 aliphatic hydrocarbons, water, hydrogen sulfide, carbon dioxide, and nitrogen.[3] However, in addition to these components, a large molecular weight of organic compounds, including C_{10} to C_{40} alkanes, aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAH), have been detected as complex mixtures at concentrations of 0.36 mg/m^3 in natural gas.[4-6] These same compounds have also been found in wastes and wastewaters from production and processing of natural gas[7,8] and in the distribution systems including pipelines despite extensive treatment or refinement of the gas.

Pipelines were used with success early in the develop,ent of natural gas and over 1,000,000 km of main pipelines with a diameter of 12 to 100 cm presently exist nationally with an additional unknown length of branch lines with ID of <12 cm.[9] The presence of easily-condensable large molecular weight organic compounds in pipelines for transport of natural gas can result in disruption of flow efficiency should sufficient liquid condensate develop.[10] Engineering aspects of formation of such condensate in pipelines have been extensively explored[10-12] and methods were developed for reduction[5] and for prediction[12] of the extent of condensate formation. In addition to flow efficiency in pipelines, another area of intense concern for safe operation of pipelines is the physical integrity of buried pipelines. Detection of flaws in metal pipe or in pipeline welds is routinely accomplished using physical testing through hydrostatic testing[13] and X-ray techniques.[14] While explosions are considered an immediate consequence from severe leaks in natural gas pipelines, gaseous movement and fate in soils of hydrocarbons including PAH from natural gas released accidently through minor but continuous leaks in consumer distribution pipelines has not been documented. The mobility in soils of certain sulfur-based odorants for natural gas has been characterized in laboratory studies,[15] but such results may lead to unrealistic models and predictions due to the differences in molecular polarity of sulfides or mercaptans versus that for hydrocarbons. Similarly, a comparison of mobility for C_{10} to C_{30} hydrocarbons with that for methane or ethane will be inaccurate due to dissimilarities in vapor pressure. Therefore, prediction of movement and fate of larger hydrocarbons and PAH through gaseous mobility in soils is presently unreliable or unavailable.

In this study, an area was identified in southern New Mexico where a natural gas leak had been occurring for 2 to 10 years. Gaseous contamination of soil from this leak resulted in the formation of a plume which was discernable as a black color in normally lightly-colored soil. The objectives of this work were (a) determination of the composition of the plume-soil for large hydrocarbons *vis-à-vis* known composition of natural gas, (b) definition of the movement and distribution of these hydrocarbons in this soil-plume, and (c) assessment of the difference in gaseous mobilities of certain classes or sizes of compounds in the soil using an actual environmental field study.

EXPERIMENTAL

Location and collection of samples

Samples of soil were collected in southern New Mexico from a region with a natural gas pipeline which was suspected of leaking due to a localized odor of hydrogen sulfide. In this region, a naturally high-gypsum earth was covered 20 years ago with 15 to 30 cm of a clay soil suitable for lawns. When a section of the top soil was removed, a black hue was evident in the base soil which also had a strong sulfur odor. An approximation of the geometry of the plume in the earth at depth of 3 to 7 cm was first mapped by visual observation of soil collected from small test holes used to define the perimeter of the plume. A diagram of the location of homes, gas pipeline, and plume, 240 m^2 in area, is shown in Figure 1. A grid with 500 squares was laid over a map of the plume with each square equal to 0.75 meter per side. Squares were assigned identity and a random number table was used to select 11 squares as sites for collection of samples. Attempts to collect the soil samples with a core sampler were unsuccessful due to the hardness of moist packed high-gypsum soil. A posthole tool was then used to penetrate soil from a depth of 7 to 150 cm. Samples of soil at 4 to 5 depths were collected using a core sampler (Soiltest, Inc., Evanston, IL) at every site selected on the grid as shown in Figure 1. As a consequence of imprecision in the collection procedures, the samples were assigned a range of depths, for example 5 to 10 cm, rather than a single value for depth. Samples were stored in large-mouth glass jars with screw lids. An aluminium foil cap was used between the jars and lids. Samples were stored at 25°C until analyzed. A complication in the environmental sampling was construction activity during the last 2 years to remove and replace sections of leaking pipeline. Thus, no surface soil was collected and integrity of samples located near trenches prepared for the pipelines was immediately suspect. However, samples designated in the random number table were not rejected due to location near the areas of past construction or repair activities.

Extraction and analysis of samples

Each sample was treated and analyzed under the same conditions and procedures. Samples were air-dried at room temperature for 24 hours prior to the extraction steps. Forty to 60 grams of soil were placed in a glass fritted extraction thimble which was placed in a Soxhlet extraction apparatus. Sample was extracted for 24 hours using 200 ml of cyclohexane (distilled in glass grade, Burdick and Jackson, Muskegon, MI). The extract was condensed to near 30 ml using a rotary evaporator at 40°C and volume of the final condensate was reduced at 25°C to 1 ml using a stream of nitrogen gas. Extracts were stored in 1 ml Wheaton glass minivials (Southland Cryogenic, Carrolltown, TX). After the condensation step for certain samples, yellow and clear precipitates developed as the extract cooled. Clear crystals were re-solubilized by warming the condensate to 35°C in a water bath. However, the yellow solid was not resolubilized and was believed to be elemental sulfur on basis of odor and color. Final condensates of the samples and blanks were stored at −5°C until analyzed. Samples were analyzed without further treatment by gas chromatography (GC) and by selected ion monitoring (SIM) in gas chromatography/mass spectrometry

(GC/MS). A procedure blank was included in the analyses through complete replication of procedures without an actual soil sample included in extraction apparatus.

A Hewlett–Packard model 5880 (Level 3) GC was equipped with flame ionization detector (FID), 10 m DB-5 fused-silica capillary column, and automated splitless injector. Conditions for analysis were: initial temperature, 30°C; final temperature, 260°C; program rate, 6°C/min; FID temperature, 275°C; injector temperature, 250°C; attenuation, 4×10^{-12} amps; chart speed, 0.5 cm/min; and integration threshold, 2^4. All samples were analyzed within a period of 4 days to insure comparable chromatographic performance. A series of *n*-alkanes from C_{12} to C_{32} were used regularly to check retention characteristics of the column and for calculating Kovats retention indices. A response factor for the FID was also obtained using the same alkane standard which had been prepared at 100 ng/μL. A Hewlett–Packard model 5995A GC/MS was equipped with 10 m DB-5 fused silica capillary column, splitless inlet, jet separator, single disc drive, and X–Y plotter. Chromatographic conditions for the GC/MS analysis were same as in the GC analysis. Mass spectrometric conditions for SIM analysis were: dwell time, 100 msec; electron multiplier voltage, 1600 V; and SIM window, 0.2 amu. Ions which were chosen for monitoring included those for common PAH and alkylated derivatives. These ions were (in amu): naphthalenes (128, 142 and 156), biphenyls (154, 168), fluorenes (166, 180, 194), anthracenes (178, 192, 206) and pyrenes (202, 216) and benzanthrene (228). The ion 57 was monitored for the detection of alkanes.

RESULTS AND DISCUSSION

Background studies

The area defined by darkly-colored soil as part of the plume from the leaking natural gas pipeline is shown in Figure 1 with the location of each randomly selected site. The gas pipeline was located at 80 cm in depth while a nearby sewage line was at 200 cm and a drinking water pipeline was at 80 cm in depth. Positions of various pipelines are shown in Figure 1. The high gypsum-content native soil along with the moisture from leaking sewage lines were believed responsible for accelerated rate of corrosion of the buried steel

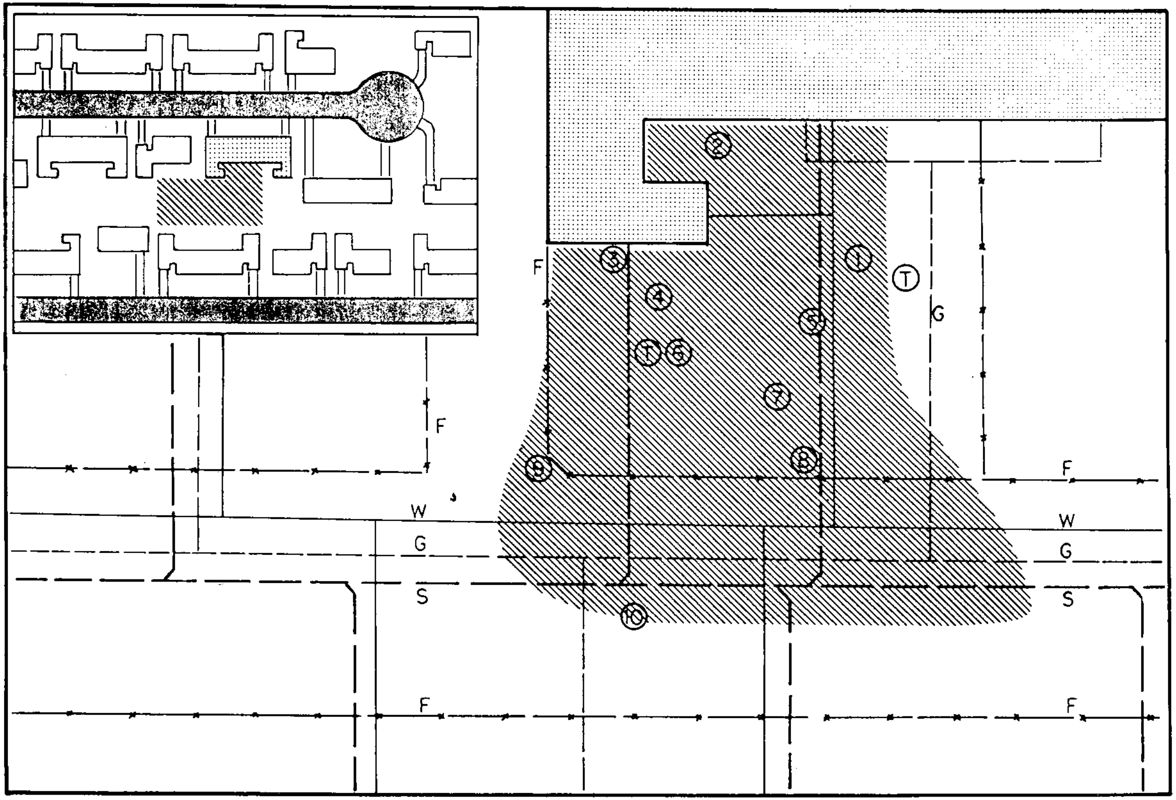

FIGURE 1 Map of plume from leaking natural gas pipeline. Neighborhood near plume is shown in upper-left corner. Enlarged area is highlighted. Locations of numbered sites where soil samples were collected are shown in enlargement of plume diagram. Legend: *G*, natural gas pipeline; *W*, drinking water pipeline; *S*, sewage pipeline; *T*, tree; *F*, fence.

natural gas pipeline. For example, within a 20-year period, sections of the pipeline were completely corroded and in some places only small pieces of the original metal pipe could be found. The hardness of moist gypsum soil, packed around the form of the original metal pipeline was responsible for a seemingly satisfactory flow. However, an estimated 40% of total gas consumption in the community was lost to the environment due to leaking pipelines. This percentage was based on comparison of summer versus winter use of natural gas. Based upon a flow figure of 10,000 m^3/year per home and total plume soil volume of 240 m^3, the contamination of soil may have been as large as 42 m^3 of gas per m^3 of plume soil. At concentrations of 0.3 to 3 mg/m^3 for C_{10} to C_{35} hydrocarbons in this gas, concentrations of these compounds should be expected at 0.1 to 1 mg/kg in the plume soil. The presence of low molecular weight sulfur-containing compounds such as hydrogen sulfide and methyl mercaptans was discernible (>1 ppm) in air above the suspected gas plume. The color in samples was remarkable inasmuch as the black color began to fade within 5 to 10 minutes after exposure of soil to air and become a medium intensity grey after several days. The composition and chemical reactivity of materials associated with this black color in the soil were unknown and not further explored here. This color may have been due to anaerobic conditions induced by high concentrations of methane.

Condensates from the soil extracts were varied in color and viscosity from a clear non-viscous fluid with slight yellow tint to a highly viscous opaque brown. While no attempt was made to quantitatively correlate optical spectroscopic properties of samples with the depth or location, large differences in the color and viscosity of different samples were preliminary suggestion of differences in composition (or extent of contamination) and capillary GC was used to measure the characteristics and quantitative nature of hydrocarbons contamination.

Chromatographic analysis of soil extracts

In total, extracts for 48 soil samples were analyzed using capillary GC-FID for compounds between C_{10} to C_{35}. A chromatogram which was typical of the samples with high concentrations of extractable organic compounds is shown in Figure 2*a*. Over 40 major (over 20% of full scale) components were resolved and detected while over 150 components were detected at all concentrations. The signal-to-noise ratio was good as seen in baseline noise between the peaks at retention indices greater than 2800 and in the limit of detection which was below 1 ng under these conditions. The range of molecular weights found in these analyses can be seen in values for retention indices instead of times. Carbon numbers were as large as C_{35} and as low as C_{10}. Organic compounds below C_{10} were likely present in these samples, but measurements for such compounds were made unreliable through use of Soxhlet extraction and of volume reduction with a rotary evaporator. Moreover, residual impurities in the fresh solvent used in the extractions were responsible for several artifact peaks between C_{10} to C_{12}.

Both the range of molecular weights and the complexity mixture in these analyses were consistent with the presence of organic compounds seen earlier in samples of natural gas taken from consumer distribution pipelines in southern New Mexico and Arizona.[6] However, a major difference between results from these soil analyses and those for analyses of natural gas or pipeline condensate was the relative concentrations of components as a function of molecular weight. For example in the condensate from natural gas, the major components were between C_{10} and C_{15} with minor contribution to total mass from compounds C_{15} to C_{30}. In contrast in these samples of soil, the major components were above C_{15} with low concentrations in the range C_{10} to C_{15}. The cause for such differences may be due to actual composition of samples or to partial changes in sample content during the extraction and condensation procedures. While concentrations of the higher molecular weight (lower volatility) compounds in soil and atmospheric loss of the lighter compounds are possible, the causes for the quantitative differences between gas composition and soil analyses are unknown. The major components in the soil extracts were identified as normal and branched aliphatic hydrocarbons using scanning GC/MS.

Environmental analyses

In most samples collected, a trend in the sample content versus depth was seen as shown in Figures 2 and 3. The concentration of

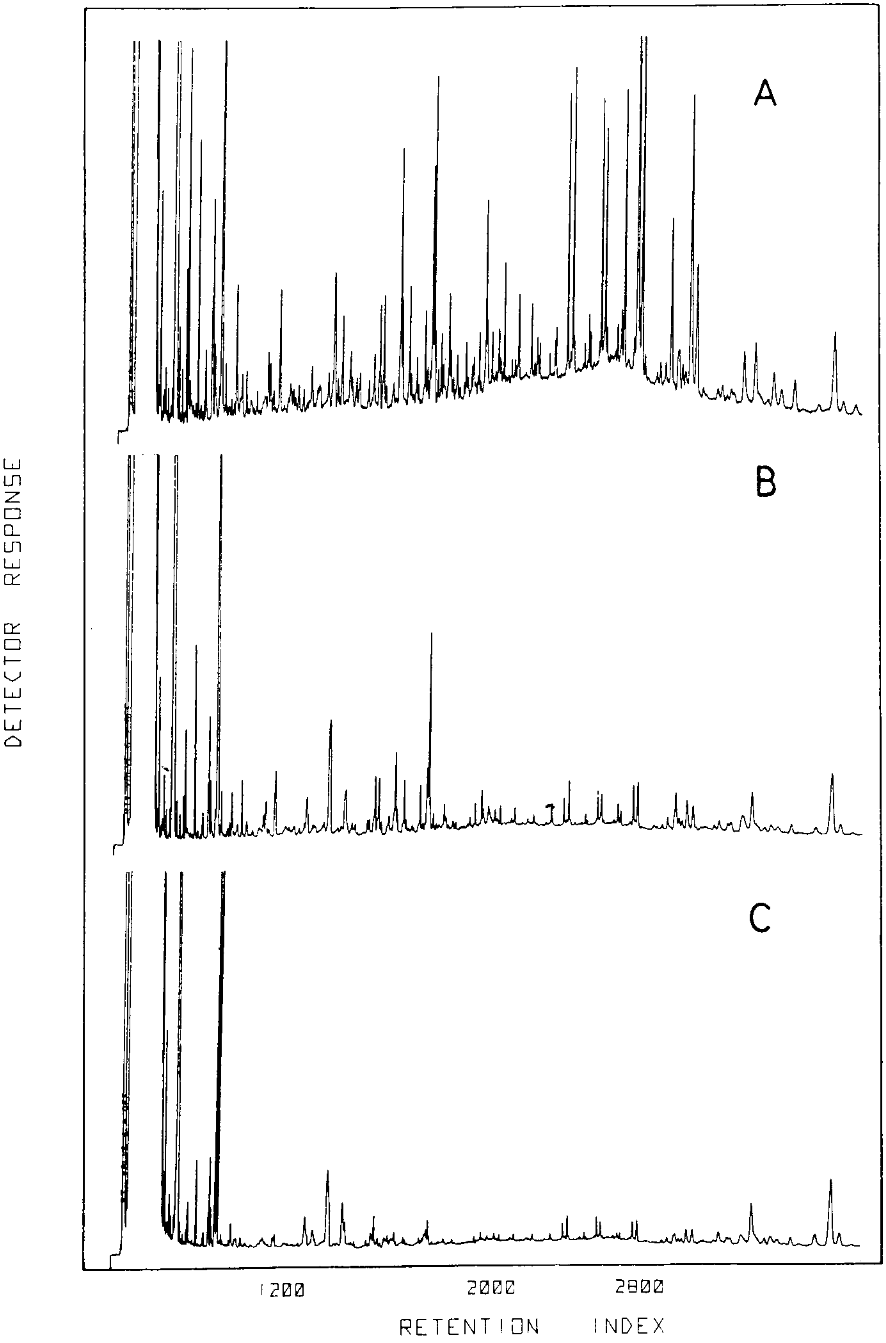

FIGURE 2 Chromatograms from GC–FID analysis of soil extracts from Site 5 at depths of (A) 15 to 30 cm; (B) 61 to 71 cm; and (C) 81 cm. Total concentrations of organic compounds detected were 15, 4 and 2 ppm respectively. Total time for analysis was 40 minutes.

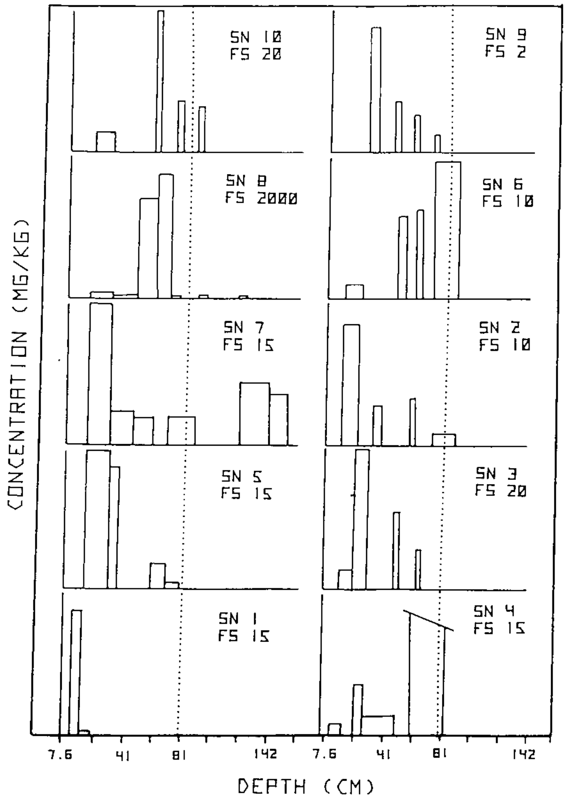

FIGURE 3 Bar plots of concentration of hydrocarbons in soil versus depth. Each plot was normalized to sample with greatest concentration in a site. Concentration is percent full-scale times the full-scale in each plot. Site number is in reference to Figure 1. Depth of natural gas pipeline is shown as dotted line. Width of zone collected is shown in width of bars.

all organic compounds detected increased dramatically with relatively slight increases in depth. At depths below 80 cm, the composition of samples was relatively clean as shown in the chromatogram in Figure 2*c*. Major peaks between 2 and 5 minutes were from impurities in the solvent. The total integrated area for each GC analysis was converted to soil concentrations with units of mg/kg and concentrations of extracted and detected hydrocarbons ranged from 0.1 to 2700 mg/kg in these soil samples. Bar plots for the concentrations versus depth are shown in Figure 3 for every sample at all 11 sites. A dashed line is placed in every plot to represent the depth of the pipeline. The widths of bars is representative of the spread in precision from sample collection in the hard-packed high gypsum soil. Most samples were collected within a stratum of earth between 5 to 15 cm thick and the results must be considered as integrated across that zone. Nevertheless, trends in results were evident particularly when evaluated in terms of environmental history. In only three locations (sites 7, 4 and 9) samples were collected where soil was undisturbed while all other sites were altered in prior years through pipeline repair or replacement. At each site (particularly undisturbed sites) profiles of concentration versus depth were similar with high concentrations of C_{10}–C_{35} hydrocarbons at depths of 5 to 15 cm and rapid decreases in concentrations of same compounds at lower depths. The decreases were relatively regular with no detectable components below 100 cm in sites 4 and 9. In site 7 a large concentration was also seen in a zone below 100 cm. The presence of this anomalous zone was consistent with field observations that fissures of seams of black soil existed through the plume. This was inconsistent with the classical models of a smooth spread or movement of plumes in soils. Such fissures are preliminary evidence that rates of gaseous movement of hydrocarbons in soils may not be described completely in the uniform diffusion and adsorption models developed from laboratory studies.

At site 6, the sample was collected from undisturbed soil but within 0.1 m of a tree which had an extensive root system near the earth surface and which had recently died from plume contamination. The depth profile in Figure 3 for site 6 was consistent with trapping of the hydrocarbons under the canopy from the root system. All other samples had a similar general trend of increased concentrations of the hydrocarbons at lower depths. However, in these same samples, soil at 5 to 60 cm from the surface was considered unreliable due to prior pipeline repairs. Nevertheless, a general pattern for movement of contaminants up toward the surface rather than in all directions was evident in the plots in Figure 3.

Physical mechanisms which affect the movement and fate of hydrocarbons in this system include adsorption of compounds on soils and vaporization of the components in air. Since these samples contained a wide range of molecular weights, several consequences to plume movement and composition of soils may exist and may be dependent on differences in contribution from particular mechanisms. For example, should vaporization dominate the processes in soil mobility, soils would be expected to be concentrated in larger hydrocarbons; or should adsorption be the major influence, lower concentrations of C_{25+} hydrocarbons would be expected particularly at greater distances from the pipeline. Alternately, should no preferential mechanism exist, all compounds should be found in relative concentrations which are the same for all samples regardless of location or depth. In Figure 4 ratios for concentrations of C_{10} to C_{15} versus C_{15} to C_{25} (Group I) and C_{15} to C_{25} versus C_{25} to C_{35} (Group II) are given for every site at all depths. Ratios were based on measurements of seven most abundant peaks in three sections of every chromatogram in carbon ranges C_{10} to C_{15}, C_{25} and C_{25} to C_{35}. Should no preferential mechanisms for movement and fate for hydrocarbons have occurred, lines for the ratios should be parallel. As seen in Figure 4, the plots were not parallel although some

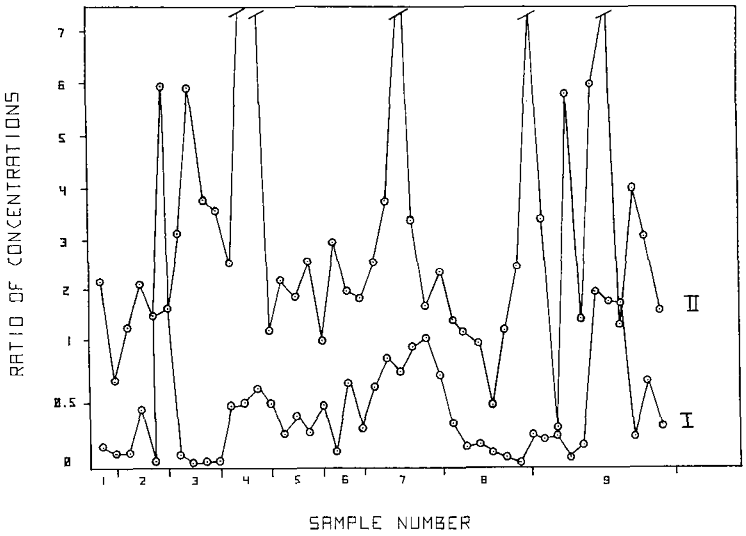

FIGURE 4 Plots of ratios of soil concentrations of selected peaks from three carbon number groups. Groups were (I) C_{10} to C_{15}/C_{15} to C_{20}; and (II) C_{15} to C_{20}/C_{20} to C_{40}.

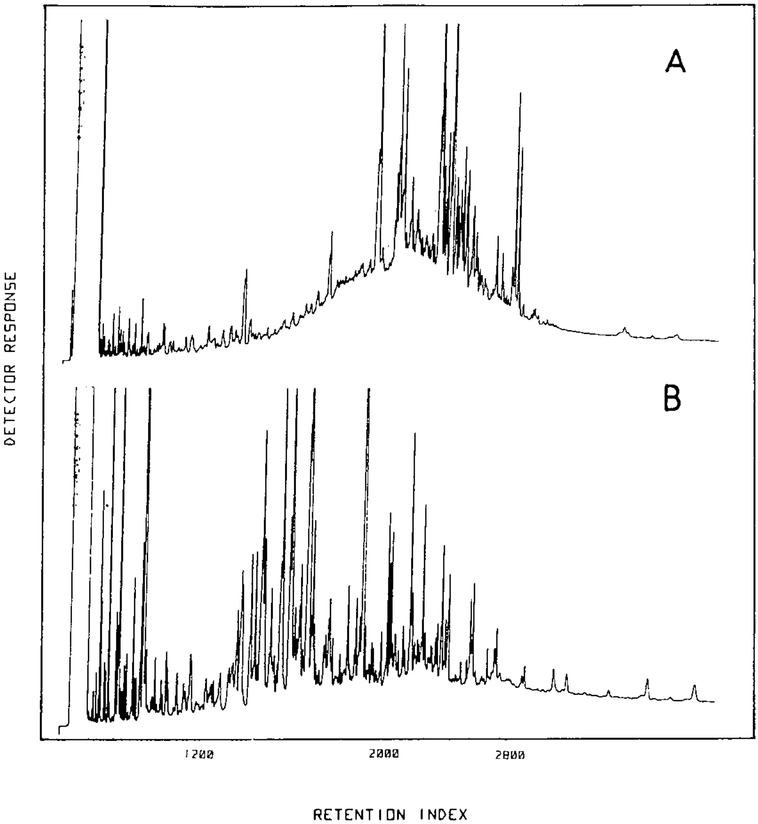

FIGURE 5 Chromatograms from extracts of (A) Deposits inside pipeline; (B) Soil near pipeline. Total time for analysis was 40 minutes.

regular trends were found in the top four samples for site 8. The exact cause for this behavior was not determined in this study which was not designed for measurement of such trends.

Pipeline analysis/analytical methods

Analysis of the deposits and residue inside pipeline taken from the same distribution system is shown in Figure 5. Large hydrocarbons ·C_{25} to C_{35} were detected in the extract of pipeline inner wall and were consistent in complexity as the origin of soil contamination.

Since this section of pipeline had been removed and stored in uncontrolled environment, extensive weathering of the inner wall residue may have occurred. While traces of C_{10} to C_{15} hydrocarbons were detected and a shifting baseline was evident, the absence of large concentrations of smaller C_{10} to C_{15} hydrocarbons was consistent with weathering of pipeline and loss of these hydrocarbons through volatilization. However, no fresher sections of pipeline were available for analysis as in earlier studies.[6] Nevertheless, large hydrocarbons were detected in deposits inside the pipelines and the results support the origin of hydrocarbons contamination from natural gas pipeline rather than from gasoline spills or storage tanks, neither of which were reported or found near the plume site.

In addition to alkanes, aromatic hydrocarbons including polycyclic aromatic hydrocarbons have been found in natural gas.[6,8] Although PAH are present in natural gas at total concentrations of less than 0.5% (wt/vol), presence of PAH in soil samples should be an additional indicator of soil contamination by natural gas. Selected ion monitoring in GC/MS was used to detect PAH in cyclohexane extracts of soil. Although PAH were detected in some samples, low concentrations in soil even near the pipeline was considered an artifact of sampling treatment inasmuch as cyclohexane may be a poor solvent for extraction of PAH from soil. Further studies on distribution of PAH in this plume will be reported later.

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References

1. *Oil and Gas Journal* **82,** 65 (1984).
2. *Oil and Gas Journal* **82,** 84 (1984).
3. G. J. Van Rossum and B. J. Wolkotte, *Gas/Erdgas* **121,** H.2, 47 (1980).
4. A. Herlan and J. Mayer, *Gas/Erdgas* **119,** H.8, 364 (1978).
5. D. L. Katz and D. F. Bergman. *Proceedings of the 55th Annual Convention of the Gas Processors' Association*, 1976, pp. 18–26.

6. B. Davani, M. Wilcox, J. Gardea-Torresdey, J. A. Dodson and G. A. Eiceman, *Environ. Sci. Tech.*, 1985, accepted.
7. B. Davani, J. L. Gardea, G. A. Dodson and G. A. Eiceman, *Int. Environ. Anal. Chem.*, 1985, in press.
8. G. A. Eiceman, B. Davani and J. A. Dodson, *Int. J. Environ. Anal. Chem.* **19,** 27 (1984).
9. P. J. Cory. In: *Nondestructive Testing for Pipe Systems* (Institute of Gas Technology, Chicago, IL, 1976), p. 142.
10. D. F. Bergman, M. R. Tek and D. L. Katz, *Final Report to American Gas Association, Project PR 26–29*, 1975, pp. 3–7, 75, 173.
11. J. A. Lescarboura, *Oil and Gas Journal* **82,** 68 (1984).
12. N. Oranje, *Oil and Gas Journal* **71,** 39 (1973).
13. R. L. Milton. In: *Nondestructive Testing for Pipe Systems* (Institute of Gas Technology, Chicago, IL, 1976), p. 185.
14. J. L. Ballard. In: *Nondestructive Testing of Pipe Systems* (Institute of Gas Technology, Chicago, IL, 1976), p. 103.
15. R. P. Williams, *Relative Resistance of Natural Gas Odorants to Soil Adsorption,* (*American Gas Association Conference,* 76-T-9.