GEOHORIZONS

Analysis of light hydrocarbons in soil gases, Lost River region, West Virginia: Relation to stratigraphy and geological structures

William Harbert, Victor T. Jones, John Izzo, and Thomas H. Anderson

ABSTRACT

Analyses of 471 near-surface soil-gas samples for light hydrocarbons, C_1–C_4, C_{2L}, C_{3L}, and H_2 from the Lost River gas field in Hardy County, West Virginia, reveal sites or clusters of sites containing anomalously high concentrations of light hydrocarbon gases, which occur directly over the faulted, eastern limb of the Whip Cove anticline. Compositional changes in the soil-gases data clearly define major changes in the maturity and locations of potential source beds. Grids placed on botanically defined anomalies confirm a possible correlation between these two independent indicators. Statistical analysis shows that samples from 45 sites contain anomalously large concentrations of light hydrocarbons in the soil-gas constituents. Large concentrations, coupled with high saturate-to-olefin ratios, further confirms that this active seepage is near macroseep levels. Variations in soil-gas compositional trends separate the soil-gas data into two domains, with oilier compositions to the west and gassier compositions to the east. Although the composition of the shallow soil gases above the Lost River gas field are oilier than the reservoir gases, they occur directly over the eastern, faulted limb of the producing anticlinal structure, suggesting that the dry gases from the Oriskany reservoir are probably mixed with oilier gases from organic-rich strata among Devonian shales. The eastern anomalies are much gassier and are very similar to the Oriskany gases produced by the Lost River gas field. The eastern anomalies directly overlie near-vertical beds of Devonian and older age formations that are likely conduits for deeper, mature thermal gases.

Manuscript received February 15, 2005; provisional acceptance May 23, 2005; revised manuscript received September 26, 2005; final acceptance October 17, 2005.
DOI:10.1306/10170505030

AUTHORS

W. Harbert ~ *Department of Geology and Planetary Science, University of Pittsburgh, Pittsburgh, Pennsylvania 15260; harbert@pitt.edu*

W. Harbert received an M.S. degree in exploration geophysics and a Ph.D. in geophysics from Stanford University, followed by a National Research Council postdoctoral study at the U.S. Geological Survey. His research includes environmental geophysics work to detect polluted subsurface water and mine voids in close collaboration with the National Energy Technology Laboratory at the U.S. Department of Energy. His research activities resulted in his being chosen by the governor of Pennsylvania to serve on the Governor's Commission Investigating Mine Voids and Mine Safety.

Victor T. Jones ~ *Exploration Technologies, Inc., 7755 Synott Road, Houston, Texas 77083*

Victor T. Jones obtained his Ph.D. in physics at Texas A&M University in 1969. Jones, an internationally recognized leader in surface geochemical methods, has more than 30 years of experience in research, management, execution, and interpretation of geochemical programs pertaining to petroleum and minerals exploration and environmental assessments. He has designed geochemical exploration programs for field operations onshore and offshore throughout the world and has generated more than 100 proprietary geochemical interpretation reports on the geochemistry of domestic United States and international basins. Jones has developed new instruments for the measurement of benzene and toluene by second-derivation spectroscopy for mud logging and has extensive experience in the use of mercury as a volatile pathfinder for mineral deposits, including silver and gold. Additionally, Jones has directed over 200 environmental impact evaluations using geochemical methods.

John Izzo ~ *Department of Geology and Planetary Science, University of Pittsburgh, Pittsburgh, Pennsylvania 15260*

John Izzo completed his B.S. degree at Duquesne University and an M.S. degree in geology at the University of Pittsburgh. He is presently employed as a geoscientist at the RJ Lee Group in Monroeville, Pennsylvania.

Thomas H. Anderson ~ *Department of Geology and Planetary Science, University of Pittsburgh, Pittsburgh, Pennsylvania 15260*

Thomas H. Anderson is a professor at the University of Pittsburgh with interests in structural geology and tectonics. He received his B.A. degree from Franklin and Marshall College and an M.A. degree and a Ph.D. in geology from the University of Texas at Austin. Subsequently, he worked as a research fellow at Caltech, where he applied U-Pb isotopic analyses of zircon to define regional magmatic domains in northwestern Mexico. Currently, his research focuses on the Appalachian and Cordilleran mountain belts of North America.

ACKNOWLEDGEMENTS

The authors acknowledge the excellent and helpful comments of AAPG editor Ernest A. Mancini, *AAPG Bulletin* editor Carol Christopher, Anne Pinkey, and Alexander A. Kitchka and two anonymous reviewers of this manuscript; their comments have improved this paper. Thanks to Olga Sandria-O'Neal for designing and drafting most of the the color figures and her assistance with our manuscript. The earlier support of Gulf Research and Exploration Technologies Incorporated (ETI) are gratefully acknowledged. Support by the National Energy Technology Laboratory of the Department of Energy to W. Harbert is also gratefully acknowledged.

INTRODUCTION

The primary goal of this soil-gas project was to assess the effectiveness of new shallow-probe soil-gas collection methods and geochemical analyses to characterize hydrocarbons trapped in deep subsurface reservoirs. Samples were collected in soil and weathered rocks 1.2 m (4 ft) below the surface. The magnitudes and compositions of the near-surface soil gases were used to identify locations of anomalous seepage and, in some cases, to constrain the source or sources of the light hydrocarbons. Another project goal was to assess the distribution of seepage with respect to areas underlain by highly fractured rock and faulted rock and to linear features recorded by vegetation or topography. A total of 471 near-surface soil-gas samples were collected (Figure 1) and analyzed to determine the quantity and composition of light hydrocarbons (methane to butane, C_1–C_4) and hydrogen (H_2). Equipment and personnel for this project were provided by the Gulf Research and Development Corporation (GR&DC) Geochemistry and Minerals group under the direction of V. T. Jones, M. D. Matthews, and J. Izzo and assisted by Harold Lang from the Jet Propulsion Laboratory. Sample sites, gas well locations, and other topographical and geological information were georeferenced and analyzed using geographic information system (GIS) technology on a UNIX and WinXP/Pro based system using ARC/INFO Version 7.X-9.0 and ArcView GIS Version 3.0-9.0 software.

The study area was located in Hardy County, West Virginia, (between 78°45′ and 79° W and 38°52′30″ and 39°7′30″ N), on the easternmost edge of the Valley and Ridge physiographic province in the central Appalachian region. All sample sites, including 13 gas wells, lie within the boundaries of three 7.5′ quadrangles (the Lost City, Lost River State Park, and Needmore quadrangles) in Hardy County, West Virginia. The study area is sparsely populated and has extensive oak-hickory–dominated forests on moderate- to high-relief terrain. Stream drainage throughout the area is predominantly a trellis drainage pattern, typical of the Valley and Ridge Province.

This region had been investigated previously and was appropriate for soil-gas–based investigation of subsurface structure. A joint National Aeronautics and Space Administration (NASA) and Geosat project was undertaken in the early 1980s (Lang et al., 1985; Matthews, 1986). The purpose of the project was for the NASA-sponsored groups to use remote-sensing techniques to assist in geochemical and/or mineral exploration. Three oil and gas fields were studied: Patrick Draw, Wyoming; Coyanosa, Texas; and Lost River, West Virginia. The first two sites are located in areas of sparse foliage, where it is possible to detect pronounced changes in soil coloration through remote sensing. The Lost River site, in contrast, is densely vegetated. A series of edge-enhanced radar images were analyzed by several interpreters, resulting in a lineament density map (figures 12–60 in Lang et al., 1985) of the study region. The highest density of lineaments occurred at the crest of the Whipcove

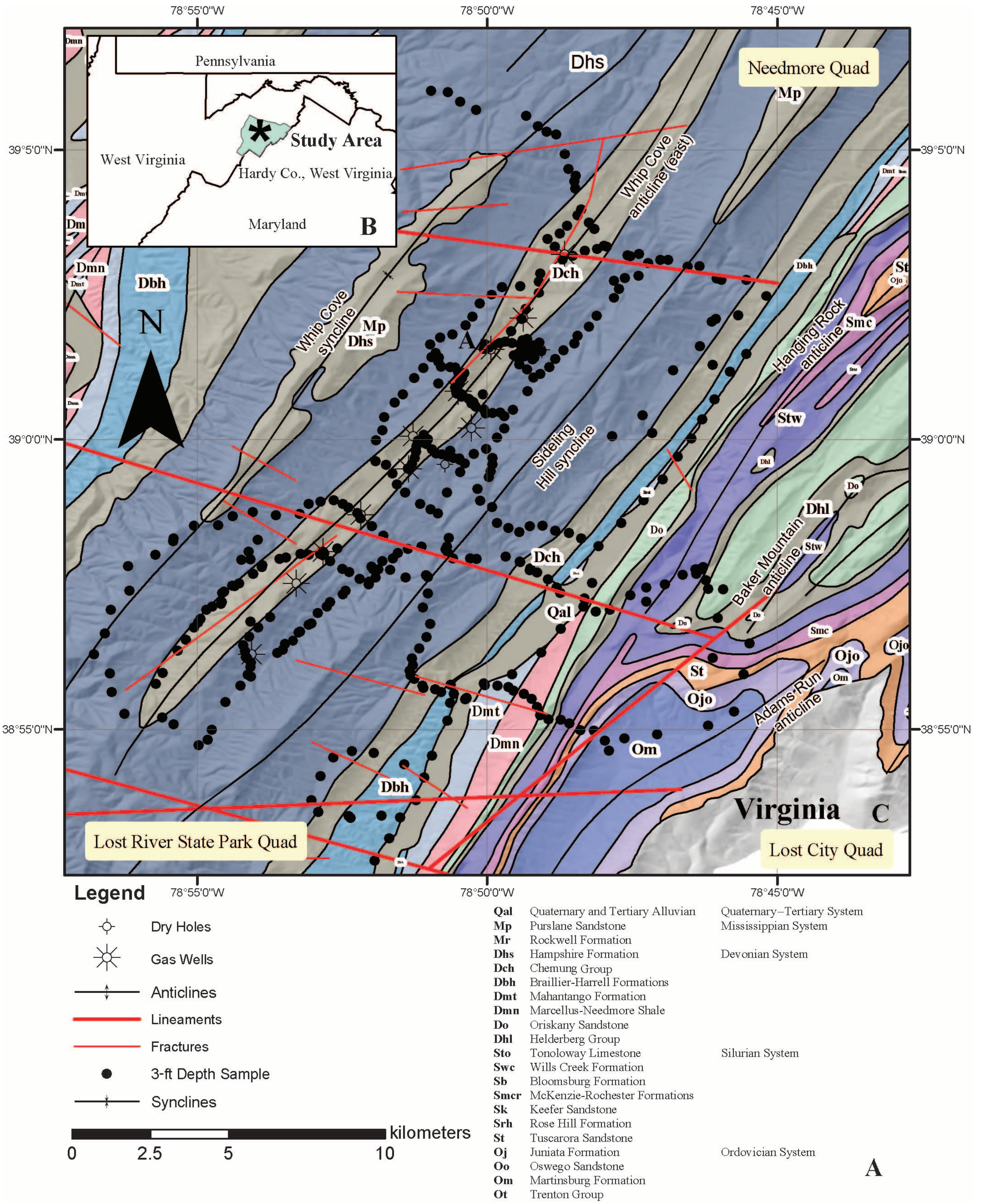


Figure 1. (A) Reference for simplified stratigraphic section (Izzo, 1999). (B) Reference map of study area in Hardy County, West Virginia. (C) Map showing sampling localities.

anticline in the vicinity of the best production wells in the Lost River gas field (Lang et al., 1985). We postulated that intersections of fracture planes may extend to depth and act as conduits for vertical migration of hydrocarbons or other pore-filling phases (Matthews, 1986). In addition, a tricounty water resources survey was performed by the U.S. Geological Survey in cooperation with the West Virginia Geologic and Economic Survey (Hobba, 1985). This report identified several lineaments and fracture traces that were recognized by the alignment of high-volume water wells in the study area. The traces of lineaments and surface fractures from this report were digitized in this study and compared with anomalous soil-gas sites and/or regional trend analyses. Other work performed in the study area includes geologic mapping interpretations of stratigraphy and sedimentology and regional structure (Tilton et al., 1927; Ludlum, 1952; Dean et al., 1991, 1992).

Dense vegetation in the Lost River area precluded the direct observation of rocks and soil by satellite imagery. However, a reinterpretation of these Landsat Thematic Mapper images revealed stands of red maples on east-facing slopes and in the bottom of valleys and ravines. Red maples are not expected to be abundant in a climax forest because they are commonly dominated (~88% in the study area) by various oak and hickory species (Lang et al., 1985). The maple trees in this area are too old and well established to be related to either burn areas or clear cuts.

In the study area, lower Mississippian strata comprising Purslane and Rockwell formations (Mp) and underlying units as low as the Upper Ordovician Martinsburg Formation (Om) and the Trenton Group (Ot) crop out (Figure 1). The lower Mississippian formations extend along the hinges of the Whipcove and Sideling Hill synclines and form the highest topographic points in the region. The oldest strata, Upper Ordovician Martinsburg and Trenton, crop out in the southeast within the core of the Adams Run anticlinorium. The sample sites near producing gas wells are located in the Devonian Chemung Formation (Dch). The unit nomenclature, thicknesses, and descriptions are a compilation of information based on previous studies (Tilton et al., 1927; Patchen, 1968; Cardwell, 1977; Chen, 1980; Hobba, 1985; Dean et al., 1991, 1992; Price and Schoell, 1995).

Major fold structures from the northwest to the southeast are the Elk Horn Mountain anticline, Town Hill syncline, Whipcove anticline west, Whipcove syncline, Whipcove anticline east, Sideling Hill syncline, and the Adams Run anticlinorium, some of which are shown in Figure 1. The Adams Run anticlinorium includes the Hanging Rock anticline, Brushy Hollow syncline, Snyder Knob syncline, and Trout Pond anticline. The Pennsylvanian and Permian Alleghenian orogeny resulted in the observed structural deformation in the study area. The surface structures reflect the imbrications of hanging walls of Cambrian–Ordovician carbonate units at depth (Gwinn, 1964; Jacobeen and Kanes, 1974, 1975; Mitra, 1986, 1987; Evans, 1989). Major thrust sheets are detached along two incompetent units. The lowest detachment occurs in the Lower Cambrian Waynesboro Formation. A stratigraphically higher major detachment may coincide with the Upper Ordovician Martinsburg Formation. Fold structures recorded by younger rock units in the study area mimic the structural relief among the fault blocks below, typifying a thin-skinned tectonic style (Gwinn, 1964; Ferrill and Dunne, 1989).

OIL AND GAS

Hydrocarbon exploration in eastern West Virginia was concentrated along the surface hinges of major anticlines (Figure 1). Gas was discovered in the Devonian Oriskany Sandstone in 1962. The Lost River gas field in the South Fork district of Hardy County, West Virginia, parallels the regional structural trend (N32°E). The field is about 10 mi (16 km) long and lies within the confines of the Whipcove anticline east. The discovery well, which bottomed in the Martinsburg Shale, was later sealed below the Oriskany Sandstone. It produced 4.6 bcf of gas from fractured Oriskany Sandstone, which was acidized to enhance production (Cardwell, 1982). In 1965, the field consisted of 13 deep wells aligned in a nearly straight line along the hinge of the thrust-faulted Whipcove anticline east. The 11 producing wells, all belonging to Columbia Gas Transmission Corporation, produced an estimated total of 13.8 bcf. Two nonproducing wells along the southeast flank of the field are thought to be isolated from the active field by a fault (Cardwell, 1977).

In the Lost River field, Oriskany Sandstone occurs at an average depth of approximately 2073 m (6800 ft) below the well head. Gas-well drillers commonly followed the lead of water-well drillers who purposely moved well-drilling locations an average of 152 m (500 ft) downdip of the anticipated total depth location to compensate for the drift of the borehole (Wagner, 1966a, b). All gas wells drilled in the Lost River field are considered to be deep wells (Patchen, 1968; Cardwell, 1982) because they were drilled to a depth of 1829 m (6000 ft) or more, to the depth of the Devonian Onesquethaw Stage unit (Onondaga Limestone, Huntersville Chert, or Needmore Shale). Two additional deep Devonian Oriskany exploratory wells were drilled in the early 1980s. One well was drilled to a total depth of 4900 m (16,075 ft), reaching the Early Cambrian Shady Dolomite; the second well reached the Ordovician Knox Formation. Neither of the two wells had gas shows and were dry holes. The Needmore Shale is the only Onesquethaw Stage unit present in the Lost River gas wells. It occurs in every well where it is overlain by the Tioga metabentonite, which marks the boundary between the Needmore and Marcellus shales.

Eastern West Virginia gas fields produced predominantly dry gas from the Lower Devonian Oriskany Sandstone. The Oriskany Sandstone is typically a very clean, coarse-grained, calcareous marine sandstone. Most beds are composed of tightly packed, calcite-cemented quartz grains; however, some beds may be slightly friable with a trace of porosity. Production from the Oriskany relies primarily on fracture permeability developed in thick sections of folded and faulted beds.

Currently, some of the eastern West Virginia gas fields are used for storage. The original gas reservoirs are replenished with gas from Texas and/or Louisiana during the summer months for use later during peak winter demand (Cardwell, 1982; Patchen et al., 1985). However, the Lost River gas field, which has been shut in since production ceased in 1971, has not been used for storage. Presently, the owners (Columbia Gas Transmission Corporation) are considering further development of the field based on seismic data (proprietary) collected in the early 1990s.

COLLECTION METHODS

A total of 471 shallow soil-gas probe samples were collected from depths of 4 ft (1.2 m). The portable shallow-probe system was developed and tested at Gulf Research and Development Corporation (GR&DC) prior to its merger with Chevron Oil (Burtell, 1989; Jones et al., 2000). This method provides a means to acquire gas samples rapidly throughout a broad area (excellent for regional grid or matrix surveys). This portable system, requiring a minimal amount of logistics (both personnel and equipment), is employed to sample at locations inaccessible to a drilling rig. It results in very little impact on the environment and is looked upon favorably by permit-issuing agencies. Since this work was completed in 1983, several thousand additional soil-gas samples for oil and gas exploration surveys have been successfully collected worldwide using the 4-ft (1.2-m) shallow-probe system (Burtell, 1989; Jones and Burtell, 1996; Jones et al., 2000).

The shallow-probe (4-ft; 1.2-m) system uses a slide-hammer device to pound a rod into and out of the ground, providing a shallow hole into which a probe assembly is immediately inserted. Nearly 500 samples were collected into 125-mL evacuated glass bottles for hydrocarbon analysis set up in an onsite laboratory.

Because a soil-gas survey identifies gases, which have migrated to the surface and reside in the soil pore space, it is important that sample locations are chosen in areas with at least 91 cm (35 in.) of residual soil. In the Lost River study area, along steep sloping ridges, bedrock was contacted within less than 61 cm (2 ft) of surface penetration. If this condition occurred, multiple attempts were made to achieve the required sampling depth at another nearby location. In almost all cases, it was possible to find a nearby location where an adequate volume of soil gas could be collected.

A specialized gas chromatograph designed and constructed by GR&DC was used for the analyses of the light hydrocarbons: methane, C_1; ethane, C_2; propane, C_3; isobutane, IC_4; normal butane, NC_4; ethylene, C_{2L}; and propylene, C_{3L} (the first five are alkanes and the last two are alkenes). Each sample was analyzed on a flame ionization detector gas chromatograph coupled to a 1-m (3.3-ft) aluminum column used to retard the arrival of the different light hydrocarbons in order of size and mass (first C_1, then C_2, etc.) (Jones and Drozd, 1979, 1983). Sensitivity for detecting hydrocarbons is approximately 10 ppb, but all results were calculated and reported in parts per million. The GR&DC gas chromatographs were set up to analyze only the C_1-C_4 light hydrocarbons using a precolumn located in front of the analytical column to reject the pentane and heavier hydrocarbons. This column configuration allows the heavier C_{5+} components to be trapped and backflushed, preventing them from loading up the analytical column. This approach allows a very low detection limit of 10 ppb for the C_1-C_4 light gases to be achieved. This analytical protocol excludes the analysis of the heavier C_{5+} (pentane, hexane, etc.) hydrocarbons.

MIGRATION OF LIGHT HYDROCARBONS TO THE SURFACE

Light hydrocarbons generated in source rocks and trapped in a deep reservoir leak in varying quantities toward the surface of the Earth. Such leakage is driven principally by pressure and permeability; thus, the amount of leakage is dependent on the number and magnitude of openings, such as faults, fractures, and bedding planes that reach the surface (Sokolov, 1935; Link, 1952; Matthews, 1986; Dickinson and Matthews, 1993; Jenden et al., 1993; Jones and Burtell, 1996; Saunders et al., 1999; Brown, 2000; Jones et al., 2000). Mechanisms that transport hydrocarbons from the source rock to the reservoir may also transport hydrocarbons from the reservoirs to the near-surface environment (Price and Schoell, 1995; Saunders et al., 1999).

Hydrocarbon macroseeps or microseeps are commonly the result of seeps emerging from the end of homoclinal beds exposed at the surface, source beds located at the surface, seeps coming from large hydrocarbon accumulations that were bared by erosion or ruptured by faulting or folding, seeps along unconformities, or seepage associated with intrusions, such as mud volcanoes, igneous intrusions, or piercement salt domes (Link, 1952; Horvitz, 1969, 1972, 1980; Jones and Drozd, 1979, 1983; Stahl et al., 1981; Jones and Thune, 1982; Jones and Burtell, 1996; Saunders et al., 1999).

Effusion (rapid outflow) is believed to be the dominant mode of hydrocarbon transport (Link, 1952; Hunt, 1979; Tissot and Welte, 1984; Jones et al., 2000). The localized nature of many anomalies (high-concentration sites) associated with microseeps and/or macroseeps at the surface suggests a migration of gases along surface fractures, joints, fault planes, unconformities, and bedding planes (Link, 1952; Jones and Burtell, 1996; Jones et al., 2000). This focused and rapid-upward, near-vertical migration is described as effusion and is driven by pressure and permeability. Hydrocarbons migrate from their sources to the reservoir along similar pathways. As a basin dewaters and compacts, large quantities of fluids (water, oil, and their associated gases) are expulsed, not all of which are trapped within commercial fields. Macro- and microseeps occur from both reservoirs and source rocks. Studies of leakage from gas storage reservoirs, as well as controlled experiments in gas-flux measurement, suggest vertical transport at a rate of hundreds of centimeters per day. This is orders of magnitude greater than migration distances detected by the diffusion mechanism alone (Jones and Thune, 1982; Jones and Burtell, 1996; Jones et al., 2000). For example, in an underground coal gasification experiment conducted in Rawlings, Wyoming, it was demonstrated that reactor gases reached the surface in 2–15 days, whereas a diffusion calculation indicated that this migration should have required approximately 70 yr.

Diffusion is a slow process in which gas or liquid broadly dissipates outward along any navigable route (Leythaeuser et al., 1980; Saunders et al., 1999). It is unlikely to be a major contributor to near-surface soil-gas anomalies. The surface distribution of such a pattern would most probably exhibit a broad, anomalous zone (Leythaeuser et al., 1980) and not the typical irregular point-type anomalies that are observed in most field data. If the diffusion-transported gases do reach the near surface, they may or may not become part of the background hydrocarbon composition observed in near-surface soil-gas samples (MacElvain, 1969; Hunt, 1979; Tissot and Welte, 1984; Jones and Burtell, 1996; Jones et al., 2000).

The Lost River gas field reservoir is an anticlinal trap in the Oriskany Sandstone. The field is contained within the Whipcove anticline east. Interpretation of multichannel seismic reflection profiles suggests that the reservoir is fractured (Lang et al., 1985; Matthews, 1986) and appears to allow some leakage of hydrocarbons toward the surface. Leakage flux would be dependent on the continuity, size, and number of the faults and/or fractures in the migration to the surface (Matthews, 1986). Although few visible linear surface expressions of faulting in the study area exist, the very large-magnitude soil-gas anomalies suggest that there are subareas of increased fracture permeability. Only one exposed fault trace could be visibly located within the region, and this one crops out in a road cut outside the study area near the city of Moorefield, West Virginia (Hobba, 1985). Of the linear features interpreted from remotely sensed images or aerial photos, most of the prominent lineaments and linear traces follow, instead of cross, natural geomorphic and regional structural trends. Traces that cross geological structures may contain fracture zones of increased permeability (Gwinn, 1964; Rodgers and Anderson, 1984). The geochemical hypothesis for choosing Lost River for a test case was that higher concentrations of light hydrocarbons should be present where either lineaments and/or biological anomalies (such as maple trees) were present (Hobba, 1985; Lang et al., 1985).

HYDROCARBONS IN THE NEAR SURFACE

Hydrocarbons reside in the near surface as free and bound gases; however, only the free gases migrate from depth (Jones et al., 2000). Free gases occur as either vapor in pore spaces or as a gas dissolved in an aqueous solution. If the gas is attached to the sediment matrix or contained within the interstices of rocks or certain minerals, such as calcite or oxide coatings, (Hunt, 1979; Jones et al., 2000) it is considered to be bound. Bound gases include adsorbed and chemiadsorbed gases. Actual measurements of both free and bound gases over several macroseeps have demonstrated an absence of bound gases in three of the four cases studied. It appears that the bound gases are detritially distributed with the soil and rocks and are not migrated gases. The only positive case where bound gases were found associated with a macroseep occurred in the Green Canyon area of the Gulf of Mexico, where the bound gases were trapped within authogenic carbonates formed from the biological oxidation of free gases and oils that had migrated from depth (Jones et al., 2000). In our experience, sediments may contain epigenetic (gases that migrated through the rock-soil matrix after sediment deposition) and/or indigenous gases (syngenetic gases formed at the same time as the enclosing rocks). Gases that have reached the soil horizon may also contain biogenic, thermogenic, and/or abiogenic gases that migrated to the surface from deep sources (Horvitz, 1969, 1972, 1980; Stahl et al., 1981; Matthews, 1986; Saunders et al., 1991, 1993, 1999). Near-surface free gases are dominated by gases from deep sources but may also contain gases formed during diagenesis, such as biogenic methane (Waples, 1985; Dickinson and Matthews, 1993; Jenden et al., 1993).

Thus, volatile gas composed of hydrocarbons generally occurs as vapor in free pore space of most rock or soil zones above the water table. These gases may also be dissolved in an aqueous solution, which results from seepage of hydrocarbons through water-filled porous systems. Free gas in the vapor phase is the easiest to collect by the shallow probe. Samples may be collected quickly, minimizing probe contamination, and little to no special sample preparation is needed before analysis.

Hydrocarbon concentrations in the very near-surface environment may also vary with time because of displacement by wind, rain, and barometric pumping. For example, rain may drain into the ground displacing gases in the near surface, or wind may draw out and dissipate free soil gases in the very near surface. It has also been observed that during times of low barometric pressure, the gas flux increases and, conversely, decreases when barometric pressure rises (Burtell, 1989; Jones and Burtell, 1996; Laughrey and Baldassare, 1998; Jones et al., 2000). Although such effects do occur, their influence is small in comparison with the differences typically observed between anomalous and background concentrations.

Bacteria in the near surface may contribute to the noisy appearance of some soil-gas seepage data. Certain bacteria have the ability to produce anaerobic methane (C_1) in the near-surface environment when anaerobic conditions prevail; however, other strains consume hydrocarbons in the near surface under oxidizing conditions (Schoell et al., 1993; Laughrey and Baldassare, 1998). Price and Schoell (1995) suggest that surface bacterial activity can totally obliterate the gases in a microseep; however, extensive field measurements in highly contaminated environments (Jones and Agostino, 1998; Agostino et al., 2002) and extensive research over both micro- and macroseeps have not corroborated this suggestion. To minimize the influence of biogenic or another source of C_1, some other hydrocarbon constituent (for example, ethane, propane, and butanes) should be measured (Matthews, 1986; Jones et al., 2000).

Composition and concentration of soil-gas constituents are the principal parameters used to recognize anomalous occurrences. Light hydrocarbons, irrespective of their origins, are mobile and tend to migrate toward the surface of the Earth because of pressure and buoyancy effects (Hunt, 1979). Leaks (microseeps) detected in the near surface signal the presence of a hydrocarbon reservoir or other source in the subsurface (Richers et al., 1982, 1986; Jones and Drozd, 1983). The composition of microseep gases commonly mimics that of the associated subsurface source and generally provides a geochemical signature of the gas, gas condensate, or oil at depth (Jones and Drozd, 1983; Richers et al., 1986; Klusman, 1993, 2002; Klusman and Saeed, 1996; Rice et al., 2002). An exception may occur if the near-surface soil gases are formed from multiple sources (Jones and Drozd, 1983; Jones et al., 2000). Compositional analysis reveals the type or types of subsurface hydrocarbon accumulations present. Gas reservoirs are commonly dominated by methane, whereas oil reservoirs commonly contain a higher percentage of heavier hydrocarbons (C_{2+}) (Jones et al., 2000).

The geochemical signature (gas, gas condensate [liquid hydrocarbons dissolved in the gas; Tissot and Welte, 1984] or oil) is determined using ratios of hydrocarbon constituents detected in the soil-gas sample. The percent methane ($\%C_1$) and the percent gas wetness (Horvitz, 1980; Jones and Drozd, 1983; Richers et al., 1986; Dickinson and Matthews, 1993; Jenden et al., 1993; Laughrey and Baldassare, 1998; Jones et al., 2000) may further quantify the compositional signature of a soil gas.

Faults and fracture systems may have an effect on the magnitude and composition of the near-surface soil gases (Horvitz, 1969, 1972, 1980; Stahl et al., 1981; Richers et al., 1982; Jones and Drozd, 1983; Matthews, 1986; Saunders et al., 1991, 1993, 1999; Jones et al., 2000). Fractures provide pathways so that permeability is enhanced, and therefore, more gas reaches the surface above a reservoir or strata bearing hydrocarbons (Link, 1952; Horvitz, 1972; Jones and Thune, 1982; Jones and Drozd, 1983). Active migration may be identified by ratios of alkanes to alkenes (C_2/C_{2L} and C_3/C_{3L}) (Saunders et al., 1999; Jones et al., 2000). Typically, an alkane/alkene value greater than 1 implies an active seep. In the Lost River study area, some of these values exceed 70.

Two fundamentally different approaches exist in defining the occurrence of anomalies. The traditional concept that is commonly held (Jones et al., 2000) generally focuses on calculating the mean plus two or three standard deviations as an anomaly; however, this approach is generally not applicable to most geochemical soil-gas data sets. Soil-gas data are generally highly skewed toward larger magnitude values, and this is certainly true in the Lost River data. Such highly skewed data are formed by combining samples from different regimes into a single data set, thereby forming a non-normal population, which consists of two or more subpopulations. In such cases, the only correct approach would be to use probability plots to separate the data set into separate populations (Sinclair, 1976) to determine the relationships of the various subpopulation to the underlying geological system. Fortunately, this can commonly be accomplished by inspection, with anomalies defined solely on the distribution and relative locations of hydrocarbon magnitudes and compositions. For example, in this data set, the compositions, coupled with the locations of the samples, separate the data into western (oilier) and eastern (gassier) domains. These two different compositional groups of data are clearly (in this case) related to separate geological regimes and should not be mixed for the calculation of meaningless statistical parameters.

In addition to this obvious compositional difference, a simple plot (Figure 2) of the methane and ethane magnitudes of the western data set clearly defines a series of much larger magnitude, clustered anomalies that occur along the strike of the Whip Cove anticline that forms the trap for the Lost River gas field. Very conservative background concentrations suggested by these dot maps and histograms are in the range of 5 ppm for methane, 0.3 ppm for ethane, 0.150 ppm for propane, 0.050 for isobutane, and 0.100 for normal-butane. Median values for all components are also very close to these estimates. Another approach, the regional assay technique, uses the spatial clustering of observations (Dickinson and Matthews, 1993). This technique was considered, but not used for this study because individual anomalies lose their identity within the larger search cell, whereas the smaller (less than regional) anomalies may be overlooked.

In addition to these empirical estimates made from inspection of the data, we have also applied some of the traditional methods for choosing a magnitude threshold value or series of threshold values above which a site may be considered to have anomalously high concentrations of hydrocarbons. Anomalous values may be (1) greater than the mean plus two times the standard deviation (value > mean + 2 × standard deviation); (2) within the top 5 or 10%; (3) greater than the median (those less than the median are considered as background); or (4) using the summation of C_2 to C_4 (ΣC_2–C_4) to minimize the influence of other non-thermogenic sources that may affect C_1 concentrations. Results demonstrate that either approach yields similar conclusions, and that a series of large-magnitude anomalies occur along the eastern, faulted strike of the Whip Cove anticline.

RESULTS FROM SHALLOW-PROBE SAMPLES

Soil-gas samples were collected and analyzed by gas chromatography. The magnitude of each of the seven organic constituents (alkane series [paraffins] C_1, C_2, C_3, IC_4, and NC_4; and alkene series (olefins) C_{2L} and C_{3L}) were measured and are expressed in parts per million of gas per unit volume of the soil-gas mixture. Hydrogen was analyzed contemporaneously with the light hydrocarbons. The number of sample sites, ranges of values, and useful statistical values for each analyzed soil-gas constituent, are summarized in Table 1. Histograms and scatter plots are also included with this statistical table.

A review and comparison of this soil-gas data with many other soil-gas shallow-probe surveys shows that these Lost River soil-gas data are one of the largest sets ever collected with this method. In many cases, soil-gas probe anomalies range as low as 0.030–0.100 ppb of ethane, with background values approaching zero. A recent 1000-site survey conducted in the Oriente Basin in Ecuador produced an ethane median of only 0.011 ppb, with focused anomalies ranging to values as large as these Lost River data. No source exists for the

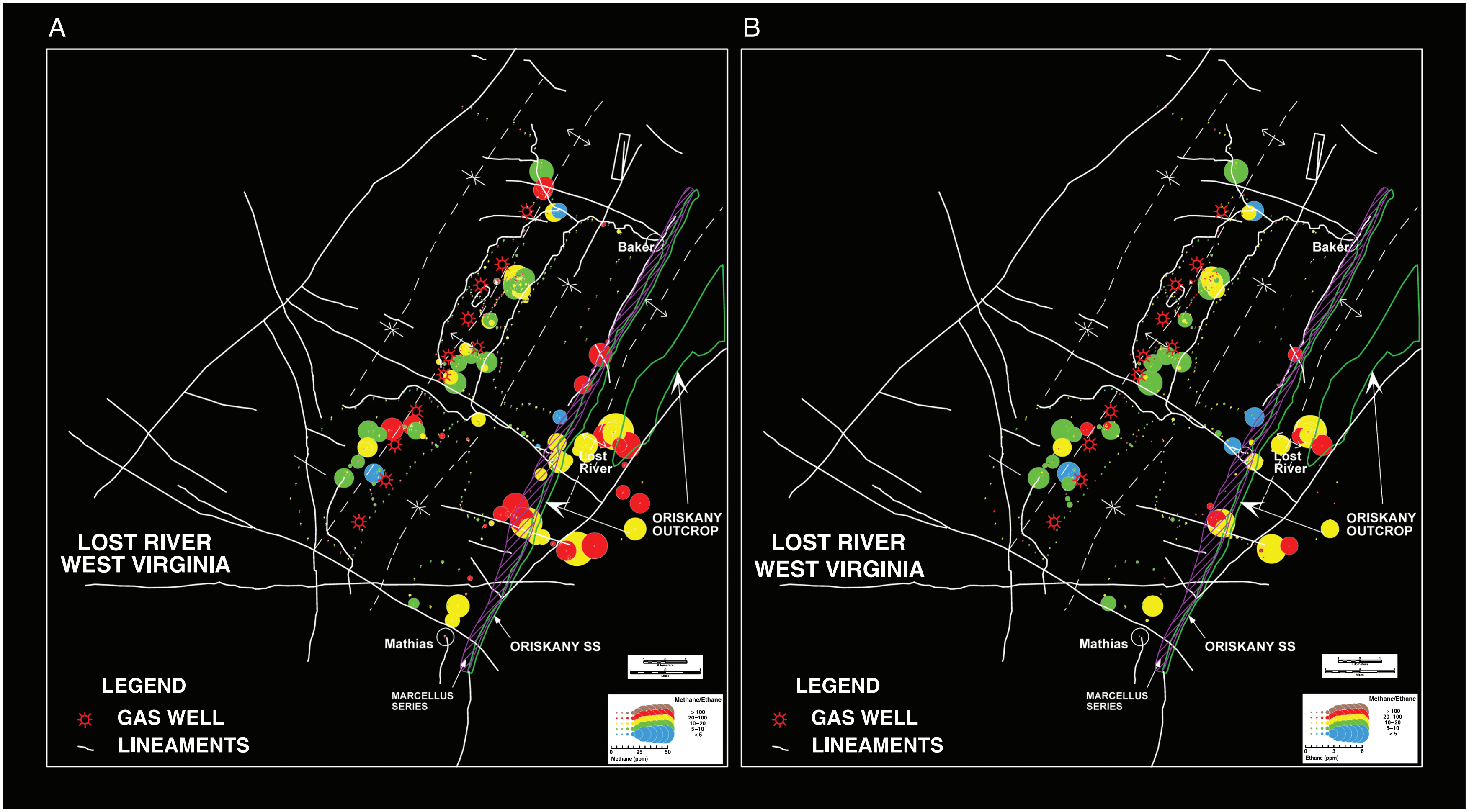


Figure 2. Spatial distribution of larger magnitude methane (A) and ethane (B) anomalies in the study region. Dot size is related to concentration in ppm, and dot color is related to compositions as defined by C_1/C_2, C_1/C_3 and C_1/C_4 ratios. The color distributions selected to display the compositional of these anomalous samples are displayed in Figure 3, plotted on log-linear plots originally defined by mud logging applications, Pixler (1969).

Table 1. Statistics for Individual Soil-Gas Constituents*

Type of Gas	Number of Samples	Maximum Value (ppm)	Minimum Value (ppm)	Mean	Median	Standard Deviation
Methane (C_1)	471	700.000	0.367	20.658	5.627	57.010
Ethane (C_2)	471	55.570	0.000	1.622	0.359	4.408
Propane (C_3)	471	16.410	0.007	0.907	0.165	2.241
Isobutane (C_4)	471	5.875	0.000	0.338	0.061	0.855
n-Butane (NC_4)	471	12.260	0.000	0.544	0.105	1.361
Ethylene (C_{2L})	471	4.541	0.000	0.413	0.200	0.586
Propylene (C_{3L})	471	2.316	0.000	0.265	0.164	0.300
Hydrogen	333	860.000	4.000	78.300	36.000	113.000

*Collected as shallow-probe 125-mL samples.

ethane through butane hydrocarbons, except for deep petrogenic sources. These very large soil-gas concentrations were also supported by the presence of methane gas in shallow-water wells in the town of Lost River.

The identification of high-concentration sample sites and the areal distribution of these sites suggest clear trends involving individual sites or groups of sites that are indicative of gas-charged subsurface structures. Two different techniques of mapping the distribution of the magnitudes of the hydrocarbon constituents have been applied in this study. One technique displays the individual sites proportionally sized to their magnitudes and compositions, and the other provides an areal relationship of the magnitudes in the form of contours and background shading variations.

A Dot Map program provides a display of the geographic distribution of the more anomalous sample sites, where the magnitudes of the soil-gas light hydrocarbon constituents, methane (Figure 2A), and ethane (Figure 2B) are shown by the size of the dots and the color is used to represent the compositions, as defined by methane/ethane, methane/propane, and methane/total butanes ratios. Figure 3 shows the compositional signatures associated with these high-concentration sites (hot spots) in the eastern and western domains. Plots of this type were first used by Pixler to quantify compositional signatures in mud logging applications (Pixler, 1969) and have proven to be very useful for interpretation of soil-gas sources.

As shown by these dot maps, similar representations of background versus anomaly are shown by each component. The main difference between the anomalies defined by the eastern and western domains lies in their compositional differences, which can be defined by using the methane/ethane ratio. GIS has been used to display the magnitude variations of the higher concentration samples by means of a shaded map (Figure 4), which shows areas of higher (darker) and lower (lighter) magnitudes.

The values of hydrocarbon constituent ratios provide an identifying compositional signature for each sample (Table 2). Values of ratios of hydrocarbons may also indicate the most probable source of light hydrocarbons (Richers et al., 1982, 1986; Jones and Drozd, 1983; Matthews, 1985; Jones et al., 2000). Other ratios and values (ΣC_2–C_4, $\%C_1 = 100 \times C_1/\Sigma C_1$–$C_4$) may be used to constrain further the type of hydrocarbon source contributing to the compositional signature of the soil-gas sample. Geographic trends of changes in composition were detected and shown in a map, where tonal differences represent the high (lighter) and low (darker) hydrocarbon ratio values. Based on observed regional differences in hydrocarbon compositions in the study area, the Lost River soil-gas sites were divided into eastern and western domains (Figure 5).

Anomalous soil-gas samples, those with high concentrations of hydrocarbons (high-concentration sites), were identified using GIS. Through attribute-based selection, samples with any number of hydrocarbon constituents whose magnitude is greater than the median value plus two times the value of the standard deviation (median + 2 × standard deviation) were identified. Fifty-six soil-gas samples had anomalous hydrocarbon concentrations of one to seven constituents.

Saunders et al. (1993) identify sites with anomalous concentrations of hydrocarbons by subtracting methane from the sum of the light (C_2 to C_4s) hydrocarbons. Anomalies are separated into three subcategories; strong, medium, or weak, based on the following: strong anomalies (mean + 3 or more × standard deviation, 95 sites), medium anomalies (mean + 2 to 3 × standard deviation, 16 sites), and weak anomalies (mean + 1 to 2 × standard deviation, 35 sites). Jones et al. (2000) have suggested that the median value may

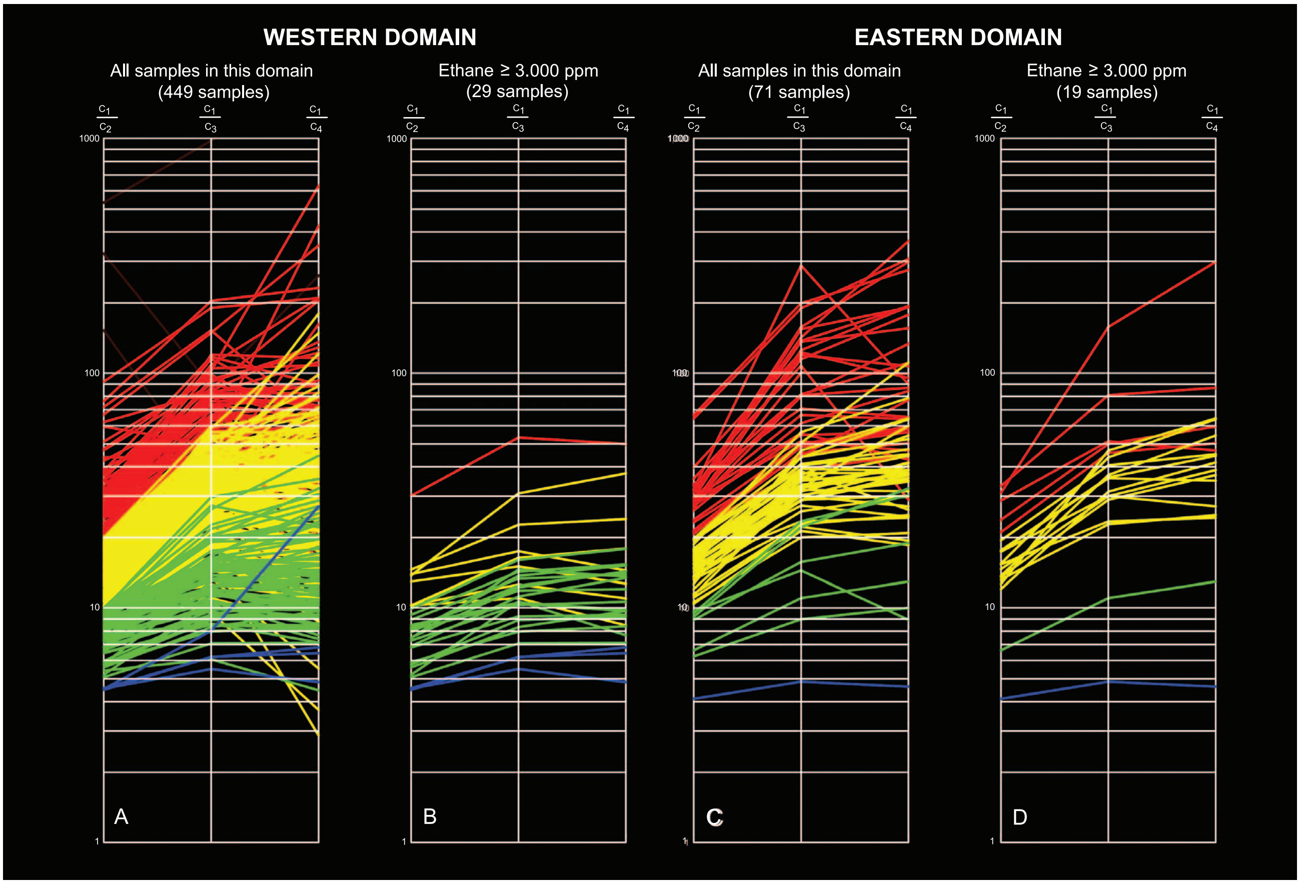


Figure 3. Pixler plots for representative samples collected within the eastern and western soil-gas defined domains. Here, for each domain, all samples are plotted on the leftmost diagram A, C, and all anomalous samples having ethane > 3.000 ppm are plotted on the rightmost diagram B, D. Colors are defined by the C_1/C_2 ratio and vary between blue (lowest C_1/C_2 ratio < 5) to red (highest C_1/C_2 ratio > 20). These data indicate that a significant compositional difference exists (see the anomalies Figure 2) between the eastern and western domains.

be used as an estimate of background versus anomaly, with samples above the median considered as anomalous, whereas the sites less than the median may be considered to be background.

A mean-score calculation, where the score equals 100% × (sample − mean)/standard deviation) (Richers et al., 1986), was performed on the 125-mL data set. This calculation normalizes the mean to be equal to zero and the standard deviation to become 100%. In our study, sites with mean scores greater than 100 are considered as anomalous. In groupings of mean score C_1C_4 (C_{1+}) and mean score C_2C_4 (C_{2+}), 42 and 34 sites were respectively identified.

Anomalies determined from all of the previously described techniques (median + 2 × standard deviation, ΣC_2–C_4, median + and mean-score calculations), were compared to identify sites common to all methods. Forty-five anomalous sites were identified on the basis of these multiple correlation criteria.

DISCUSSIONS AND INTERPRETATIONS

The compositional coherence demonstrated by this entire data set argues for thermogenic sources. The gas produced from the Lost River gas field (Table 3) is a very dry (%C_1 > 95 with little to no heavier hydrocarbons), methane-rich composition (Cardwell, 1977, 1982). If this reservoir acts as the sole source of hydrocarbons in the area, then the soil gas would reflect a similar compositional signature of a very dry gas. However, of the 471 sample sites in the study area, only seven sites have a %C_1 greater than or equal to 98%. Three of these seven sample sites are located over the gas field and are in close proximity with two of the maple anomalies. Of the remaining sites, one is located on the hinge of the Whipcove anticline east, north of the gas field; another is positioned midway along the gas field but east of the hinge. The latter anomalies lie within the eastern domain. Although

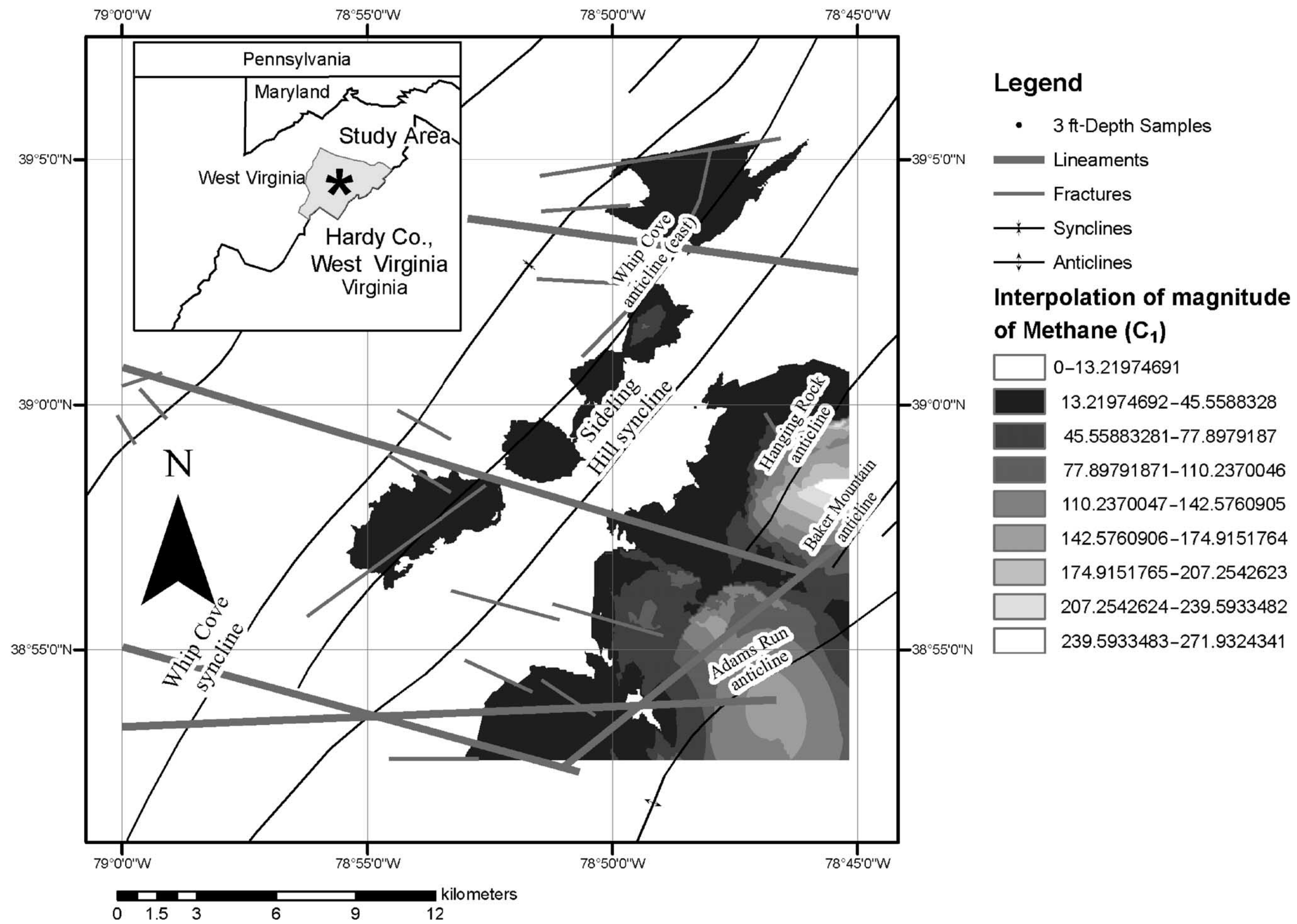


Figure 4. Interpolation of the magnitude of methane (C_1) shown in Figure 2.

some sites with high $\%C_1$ values could result from the addition of biogenic C_1, we do not believe that this interpretation is supported by the data presented in our study. Essentially, all of the methane anomalies are coordinated with appropriate amounts of C_{2+} components, and these heavier hydrocarbons do not occur within biogenic gas. The dry signature exhibited by the Lost River production gases does prove that the surface gases are, at best, a mixture of these reservoir gases with another thermal source.

Table 2. Approximate Empirical Range of Microseep Compositional Ratios for Gas, Gas Condensate, and Oil*

Hydrocarbon Composition	$C_1/\Sigma C_1-C_4$ or % C_1	C_1/C_2	$(C_2/C_3) \times 10$
Gas	100–90	100–20	25–50
Gas condensate	90–75	20–10	16.5–25
Oil	50–5	10–4	10–16.7

*Adapted from Jones and Drozd (1983). Values may predict hydrocarbon composition at depth.

Other possible subsurface sources of interest could be the organic-rich Devonian shale units (Marcellus-Needmore [Dmn], Mahantango [Dmt], and the Braillier-Harrell [Dbh]). These units lie above the Oriskany reservoir and would likely influence the composition of migrating gases that pass through them by adding some ethane through butanes. In addition, the presence of anomalous amounts of ethane through butanes could also originate from strata located below the Oriskany, implying the presence of a somewhat deeper and slightly oilier gas source. Associated gas is commonly found in shallower traps located above their oilier sources. The assumption that the Oriskany is the source of the gas in the Lost River field may or may not be correct. The soil-gas data definitely indicate the possibility of somewhat oilier sources. Perhaps the Lost River gas is not all that is present in this study area.

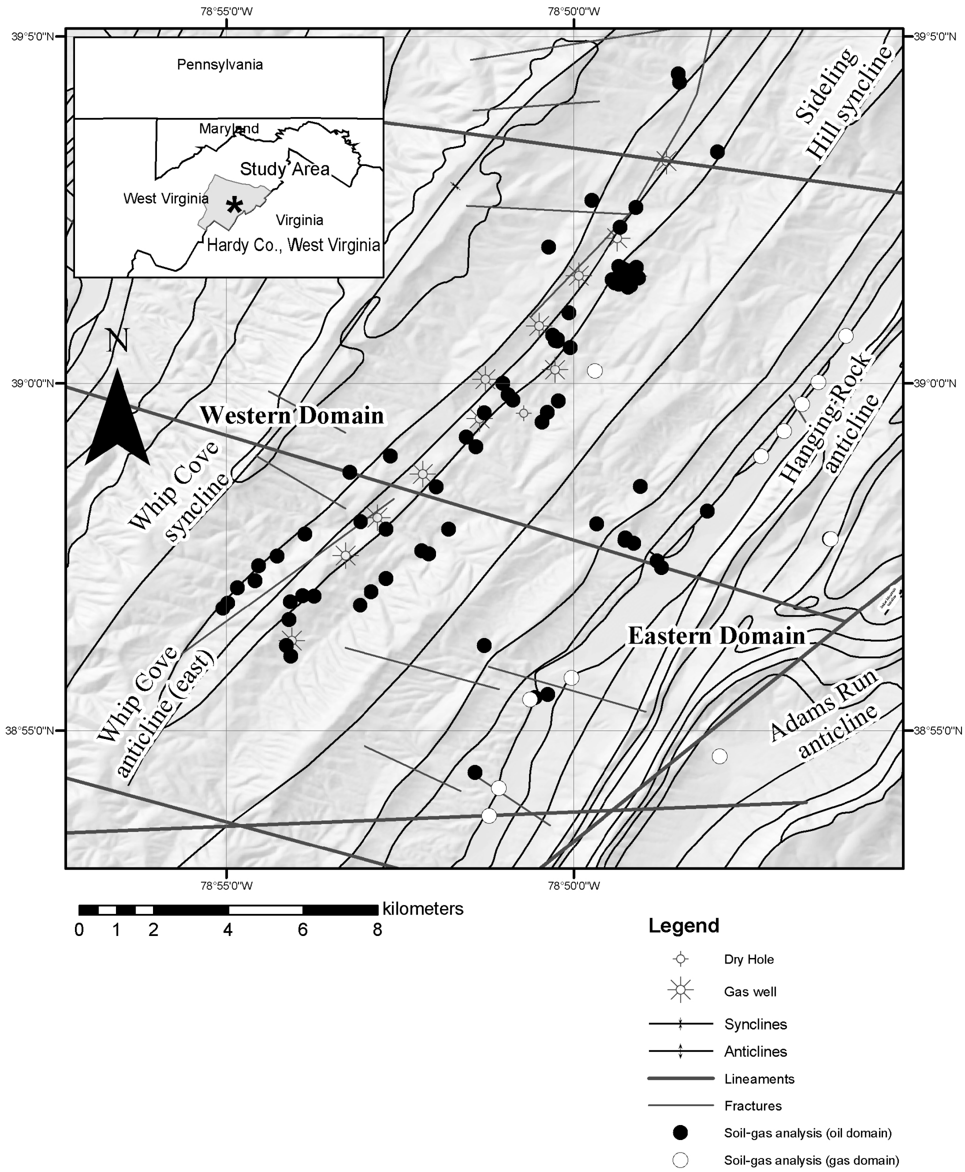


Figure 5. Soil gas defined oil- and gas-dominated domains. The criteria used are $C_1 > 6.63$ ppm and in the oil domain $(C_2C_3 \times 10) < 16.5$. In the gas domain, we used $C_1 > 6.63$ ppm and the quantity $(C_2C_3 \times 10) > 33$.

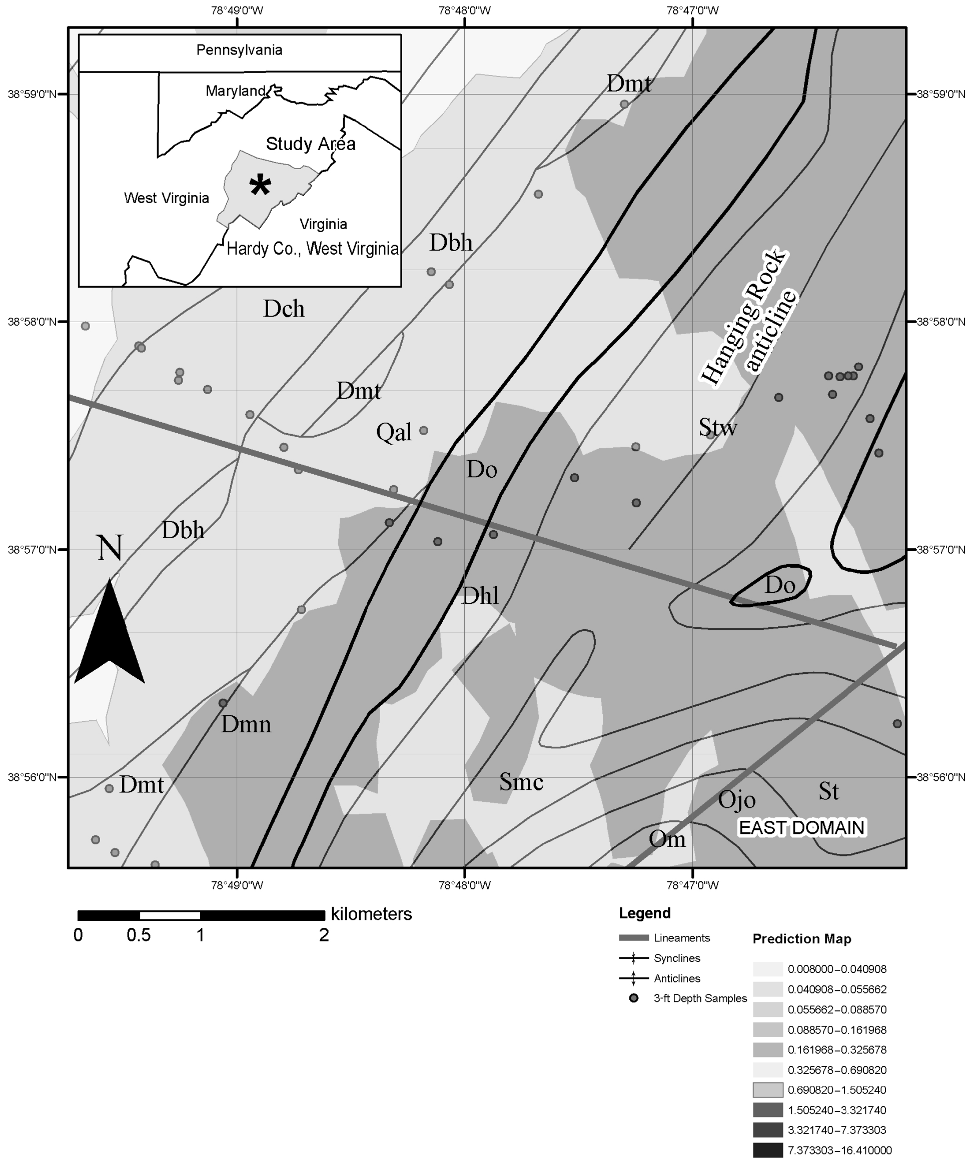
Table 3. Hydrocarbon Composition of Two Wells from the Lost River Gas Field and Another from a Gas Field in Grant County, West Virginia*

Gas Type	Lost River Gas Field Well 3	Lost River Gas Field Well 9	Jordan Run Field CNR 1
C_1	99.27	98.88	98.17
C_2	0.51	1.02	1.42
C_3	0.20	0.10	0.21
IC_4	0.01	0.00	0.20
NC_4	0.01	0.00	0.00

*Harper and Patchen (1996). Isobutane (IC_4) and normal butane (NC_4) measurements are included; detailed well identification information can be found in Harper and Patchen (1996). A complete data table showing all measurements is given in appendix A of Izzo (1999).

One prominent feature in the study area that could potentially act as a deep conduit from depth to the surface is the east limb of the Sideling Hill syncline. Within it, the Oriskany Sandstone passes from a depth of nearly 2134 m (7000 ft) below ground level upward toward the surface, where it crops out just east of the Lost River Valley. A map view overlay of this outcrop contains high-concentration sites and contour lines of C_3 concentration (Figure 6). No appreciable correlation of the anomalous gas sample sites on or near the outcrop trace exists. Zones of high fracturing may create a pathway traversable by light hydrocarbons, although these are shale-dominated strata (McDermott, 1940; Rosaire, 1940).

Figure 6. Interpolated C_3 concentration in parts per million compared with the surface outcrop geological units including the Oriskany Sandstone (Do; note bold outline around this unit) in the study region.



Several locations exist throughout the study area where either a particular sample site or cluster of sites contain anomalous concentrations of light hydrocarbons. These anomalous sample sites may represent the terminus locations of a well-developed fracture system or fault that allow migration from the hydrocarbon source at depth to the surface (Jones and Drozd, 1983; Matthews, 1986). These high-concentration sites are potential candidates for active hydrocarbon seepage. An indicator of active seepage is a high alkane/alkene ratio (Saunders et al., 1999; Jones et al., 2000). Typically, saturate to olefin values between 1 and 3 are considered as anomalous for shallow-probe samples, and many sites in the Lost River study area greatly exceed these values (C_2/C_{2L} range of values 76.386–0.157). More than 120 sites have C_2/C_{2L} values greater than 3 and must be considered as anomalous (very active seepage) for this study (Figure 7). Sites over the gas field appear as separate, well-defined anomalies that occur along strike of the anticline, along the faulted east flank, just to the east of its highest point of curvature.

The eastern domain includes sample sites (~71 sites) that occur mainly within the Lost River Valley and over the outcrop that lies to the east of this valley. These sites follow the existing roads, providing a near-circular pattern of sample sites that lie east of the river, referred to as the east loop. The western domain sample population (~400 sites) incorporates all sites that occur to the west or over the Whipcove anticline, and those sites that are on the east flank of the anticline, but west of the Lost River Valley. As previously

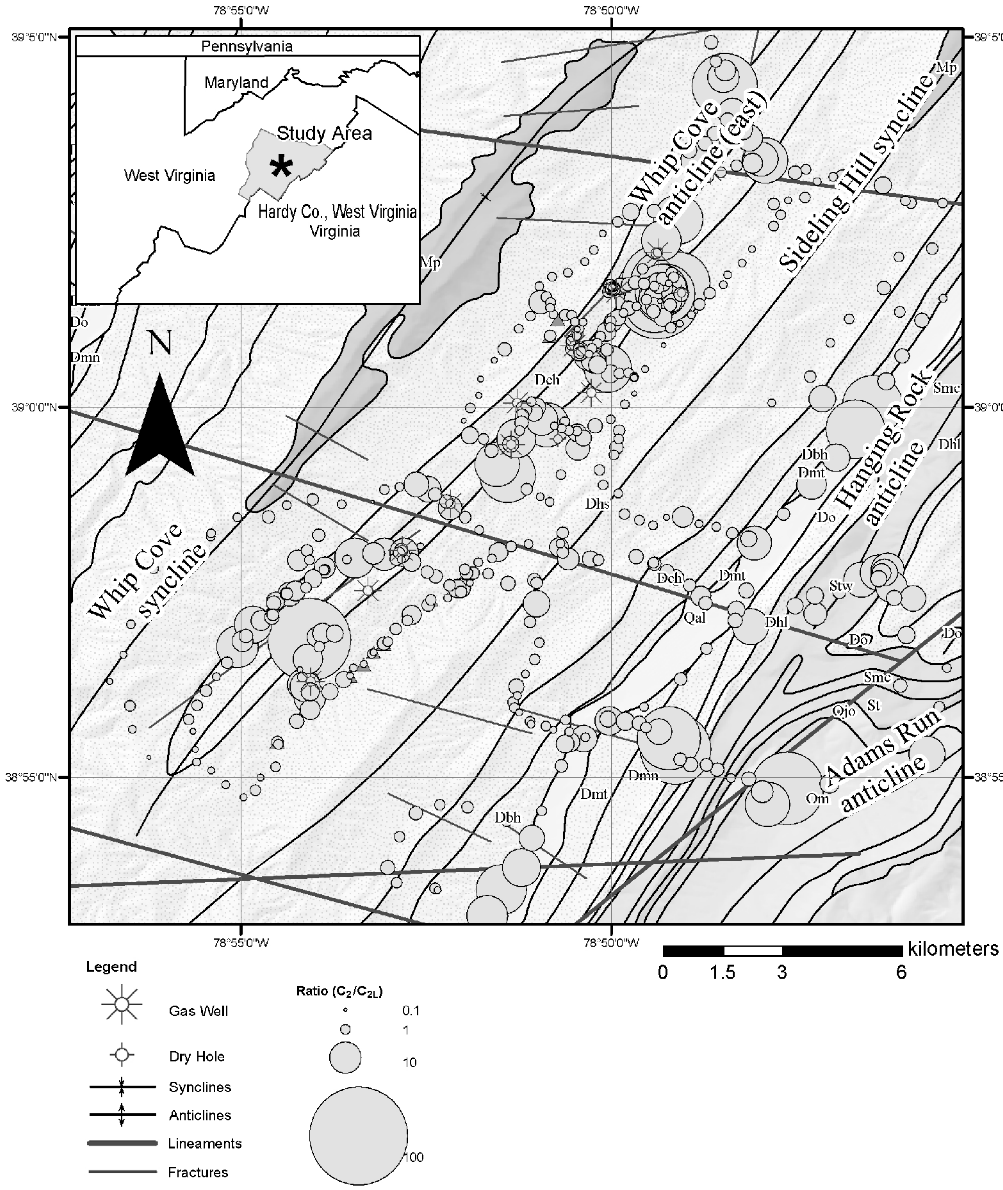


Figure 7. C_2/C_{2L} ratios for the study region. See Figure1 for a description of the abbreviations.

noted, the composition of the near-surface samples in the eastern domain exhibit a gassier signature, whereas those in the western domain have an oilier signature (Figure 5). Typically, surface soil gases actively expelled at the surface are representative of their subsurface sources (Jones and Drozd, 1983; Jones et al., 2000). The Oriskany reservoir beneath the Lost River gas field produces a very dry gas, with little to no heavier hydrocarbons $-C_{2+}$, and this suggests that the signature includes a mixture of gases, of which at least one is oilier than those of the Lost River gas field. Although gas/oil ratios have been observed to change and become oilier as fields are depleted (Hunt, 1979), this appears unlikely. Most likely, dry gases from the reservoir may have mixed with other gases in organic-rich shale units above the Oriskany Sandstone, creating an oilier composition. Thus, methane migrating to the surface may have acted as a carrier of C_{2+} hydrocarbons (Schoell, 1983) when passing through strata containing mature heavier hydrocarbons.

Additional observations are a mottled-looking pattern along the hinge of the Whipcove anticline east, consisting of irregularly spaced smaller pockets of high and low $\%C_1$. Areas of lower C_1 appear to be more prominent where underlain by organic-rich Devonian shale units. The above patterns may be influenced by deep-seated fractures or faults along the anticline. Relating the above possibilities to the observed results along the hinge of the anticline, it is possible that the oilier sites may be above or near zones of increased permeability. This would allow larger hydrocarbon molecules to migrate with C_1 more easily to the surface, whereas sites that are C_1 rich at the surface may be located above selected zones of decreased permeability that permits only the smallest hydrocarbon member to pass. Lineaments and fracture traces interpreted by the test case survey and the groundwater resources survey (Hobba, 1985; Lang et al., 1985; Matthews, 1986) show little to no correlation to sites with high concentrations.

Three stands of maple trees were identified as recording anomalous growth conditions. Two of these stands were selected to be surveyed to assess the level of hydrocarbon gases in the soil. These stands were detected visibly by their yellow foliage in contrast to the surrounding green oak trees. Although the yellow leaf coloration was caused by early fall color changes, it could have been enhanced as the result of a chloratic characteristic of maples that occurs if they are stressed because of a change in or absence of required mineral nutrients in the soil. It was postulated that methane leaking upward through fractures concentrated in the soil at the surface, creating a reducing environment, providing the maples with a competitive advantage, because the presence of gassy soils is not conducive to an oak or hickory habitat, whereas red maples are tolerant of methane-rich soil and anaerobic soil conditions (Leone et al., 1977; Flower et al., 1981).

A team from Mobil Oil Corp. conducted a reconnaissance study of soil microbes (Lang et al., 1985), which sought to identify soil rich in ethane-oxidizing bacteria that thrive where natural-gas seepage occurs (Davis, 1967). No significant bacterial growth was observed in the samples, and they concluded that natural gas may not be seeping from the Lost River gas field. Therefore, no further sampling using this method was recommended by the Mobil team. However, our study indicates that methane is the dominant component in the Lost River reservoir, with ethane through butane observed in lower but significant concentrations. Thus, there may be insufficient ethane present (particularly directly over the gas field) to support extensive colonies of ethane-oxidizing bacteria in soils overlying the gas field.

The ravine maple anomaly is the most positive example of light hydrocarbon seepage in the entire study area. Eleven of forty-five high-concentration sites lie along the ravine or in near proximity to it. Very high concentrations of C_1 are present in the ravine maple anomaly site, which supports the original hypothesis of stressed maples caused by increased concentrations of C_1 and associated light methane homologs in the soil. All of the alkanes (C_1 to C_4), the alkenes (C_{2L} and C_{3L}), H_2, and both alkane/alkene ratios (C_2/C_{2L} and C_3/C_{3L}) show high concentration values along the ravine anomaly, with nearly concentric contour patterns for C_1, C_2, and C_3. These large-magnitude overlapping contours with large alkane/alkene ratios imply that active migration is occurring. This location appears to be a vent for active hydrocarbon migration from below, possibly the result of a very steep blind listric fault (Boyer and Elliot, 1982).

Another stand of maple trees, identified as a hook-shaped maple anomaly, is located on an east-facing ridge northeast of well 10. A picture of this anomaly taken in the fall when the leaves change color explains the name attributed to this anomaly (Figure 8). A supplemental, closer detailed (150-ft [45-m] increment) minisurvey of 19 soil-gas samples was collected in a U-shaped pattern in this stand of maple trees. Soil-gas sites 608 and 609 contain slightly larger C_1 concentration values relative to the other sites in the anomaly; although values are lower in magnitude than observed in the ravine maple, they are still quite anomalous. Compositional signatures in the hook-shaped maple anomaly are indicative of a gassier (methane rich, $\%C_1 \geq 90$) nature than those observed in the ravine anomaly. Sites 608 and 609 have $\%C_1$ values of 97.6 and 99.7, respectively, and are very similar to the Lost River produced gases. These higher $\%C_1$ values certainly support the hypotheses of the Geosat study that the maple anomalies were a result of increased C_1 in the soil caused by enhanced fracturing in lineament zones. Although no obvious major lineament crosses this anomaly, a fracture trace from the regional water survey does traverse the area (Figure 8). The hook-shaped maple anomaly is near the hinge of the Whipcove anticline east, where the lightest hydrocarbons may concentrate because of the geometry of the anticlinal structure and not necessarily because of an enhanced fracture pathway. This anomaly may be the result of the selective processes of buoyancy involving colloidal-size molecules of C_1 migrating upward via routes of lower concentration and Brownian movement (MacElvain, 1969; Saunders et al., 1999).

SOURCES OF GASES

These data contain interesting and very large-magnitude anomalies and compositional changes that are localized and clearly domain (source) dependent. The exact location of the source or sources is not known; however, it

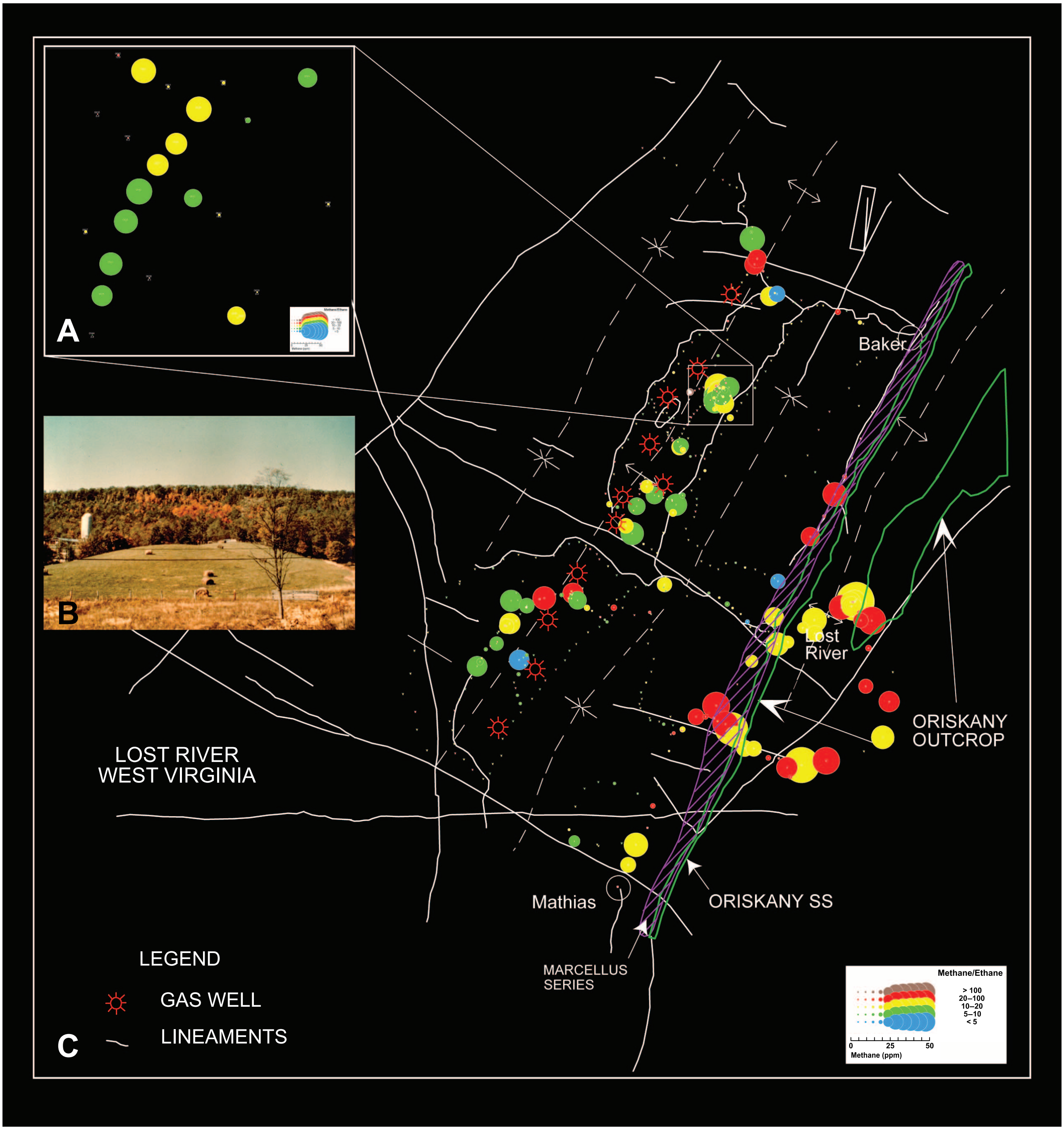


Figure 8. (A) The maple anomaly is shown with soil-gas symbols proportionally scaled by the measured amount of C_1 and where the symbol color is defined by the methane/ethane ratio. (B) Photograph of the red maples in the forest. (C) Study region in which gas sampling point symbolization described in (A) is applied to the gas survey data.

appears likely that at least two different sources or processes might have contributed to the observed soil gases. The soil gas at the surface is likely a combination of thermogenic hydrocarbons from the Lost Hill reservoir and source rocks mixed with migrated hydrocarbons from another organic-rich rock source. These considerations suggest that the soil gas in the near surface of the western domain of the Lost River study area is a mixture of migrated gases from mixed subsurface sources. The gas composition of the Oriskany reservoir produced thus far is a very dry, methane-rich gas. The source of this gas was suggested by Cardwell (1977), who observed that several gas shows were encountered in Cambrian–Ordovician rock units, in addition to the Lower Devonian Helderberg Limestone. Jenden et al. (1993) also mention the Ordovician Trenton Group as a potential source rock. Although the Trenton may be a potential source for the deeper Oriskany, to date, two additional deep wells that reached the Cambrian Rome and Elbrook formations in the early 1980s in Hardy County were dry holes.

Another potential gas source for the Oriskany reservoir may be the organically rich black shale strata above the Oriskany. The Oriskany may have been charged by lateral migration of gas from black shale source beds (Patchen and Hohn, 1992). Finally, gas is escaping from the near surface in the east domain. If the Trenton Group was an ancient methane-rich source, it may, when near the surface, continue to outgas, although no accumulation is obvious. However, previous experience of sampling in exposed source beds has always produced a lower magnitude, oilier signature caused by preferential evaporation of the gases contained within the shallow source bed. Although the soil-gas data do not determine the source of the gas, they do define some interesting compositional differences that require interpretation.

CONCLUSIONS

Soil-gas samples were collected using a shallow-probe (1.2-m; 4-ft) technique. The samples were analyzed for light hydrocarbon constituents C_1–C_4, C_{2L}, C_{3L}, and H_2. Sites or clusters of sites that contain anomalously high concentrations of light hydrocarbon constituents were identified by inspection and verified by statistical analyses. The locations of the soil-gas sites were compared to surface structures such as lineaments and fracture traces; overall, the spatial correlation was poor. Samples from 45 sites out of 471 sites contain anomalously high concentrations of soil-gas constituents. High ratios of C_2/C_{2L} and C_3/C_{3L} indicated that active seepage persists at numerous sites. Variations in soil-gas compositional trends reveal two (east and west) domains with distinct compositions. The composition of shallow soil gas above the Lost River gas field does not correlate with the composition of reservoir gas, and the results would lead to misinterpretation of the hydrocarbons trapped in the deep reservoir. In the western domain, dry gases from the Oriskany reservoir appear to be supplemented by oilier gases from organic-rich strata among Devonian shale to form an overall oilier composition above the dry-gas field. Although biogenic methane may be present in some samples, it is not present in significant enough quantities to bias these results. Large-magnitude gas seeps occurring in close correspondence to maple anomalies occur within a ravine, suggesting a zone of increased fracture permeability. Although the soil-gas signatures would not have predicted the correct composition for the Lost River dry-gas reservoir, the high-concentration samples do fall within the boundaries of the structural high that forms the trap for deep gas and would have highlighted the productive area of the field.

REFERENCES CITED

Agostino, P. N., R. J. LeBlanc Jr., and V. T. Jones III, 2002, Assessment of subsurface hydrocarbon contamination resulting from multiple releases at six former bulk fuel storage and distribution terminals, Austin, Texas: A case study, *in* D. Schumacher and L. LeShack, eds., Application of geochemistry, magnetics and remote sensing: AAPG Studies in Geology 48 and SEG Geophysical References Series 11, p. 229–325.

Boyer, S. B., and D. Elliot, 1982, Thrust systems: AAPG Bulletin, v. 66, p. 1196–1230.

Brown, A., 2000, Evaluation of possible gas microseepage mechanisms: AAPG Bulletin, v. 84, p. 1775–1789.

Burtell, S. G., 1989, Geochemical investigations at Arrowhead Springs San Bernardino and along the San Andreas fault in southern California: M.S. thesis, University of Pittsburgh, Pittsburgh, 169 p.

Cardwell, D. H., 1977, Oil and gas fields of West Virginia: West Virginia Geological and Economic Survey, Mineral Resources Series no. 7, 171 p.

Cardwell, D. H., 1982, Oriskany and Huntersville gas fields of West Virginia: West Virginia Geological and Economic Survey, MRS-5A, 180 p.

Chen, P. F., 1980, Oil and gas exploration and potential in the northwestern part of Ridge and Valley Province in West Virginia (Berkeley, Morgan, Hampshire, Hardy, Mineral, Grant and Pendleton counties): West Virginia Geological and Economic Survey, OF8101, 140 p.

Davis, J. B., 1967, Petroleum microbiology: New York, American Elsevier Scientific Publishing Co., 604 p.

Dean, S. L., B. R. Kulander, and P. Lessing, 1991, Geology of the Bergton, Lost City, Lost River State Park, and Orkney Springs quadrangles, Hardy County, West Virginia: West Virginia Geological and Economic Survey, Map-WV37, scale 1:24,000, 47 × 63 in., full color.

Dean, S. L., P. Lessing, B. R. Kulander, R. R. Fisher, M. P. Kurtz, M. L. McKoy, and M. L. Orzechowski, 1992, Geology of the Baker, Needmore, and Wolf Gap quadrangles, Hardy County, West Virginia: West Virginia Geological and Economic Survey, Open File OF-9201, 11 p.

Dickinson, R. G., and M. D. Matthews, 1993, Regional microseep survey of part of the productive Wyoming–Utah thrust belt: AAPG Bulletin, v. 77, p. 1710–1722.

Evans, M. A., 1989, The structural geometry and evolution of foreland thrust systems, northern Virginia: Geological Society of America Bulletin, v. 101, p. 339–354.

Ferrill, D. A., and W. M. Dunne, 1989, Cover deformation above a

blind duplex: An example from West Virginia, U.S.A.: Journal of Structural Geology, v. 11, no. 4, p. 421–431.
Flower, F. B., E. F. Gilman, and I. A. Leone, 1981, Landfill gas, what it does to trees and how its injurious effects may be prevented: Journal of Arboriculture, v. 7, p. 43–51.
Gwinn, V. E., 1964, Thin-skinned tectonics in the Plateau and northwestern Valley and Ridge Provinces of the central Appalachians: Geological Society of America Bulletin, v. 75, p. 863–900.
Harper, J. A., and D. G. Patchen, 1996, Play dos: The Lower Devonian Oriskany Sanstone stuctural play, *in* J. B. Roen and B. J. Walker, eds., The atlas of major Appalachian gas plays: West Virginia Geological and Economic Survey Publication, v. 25, p. 109–117.
Hobba, W. A., 1985, Water in Hardy, Hampshire, and western Morgan counties, West Virginia: West Virginia Geological and Economic Survey, Environmental Geology Bulletin EGB-19, 91 p.
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.
Horvitz, L., 1972, Vegetation and geochemical prospecting for petroleum: AAPG Bulletin, v. 56, p. 925–940.
Horvitz, L., 1980, Near-surface evidence of hydrocarbon movement from depth, *in* W. H. Roberts and R. J. Cordell, eds., Problems of petroleum migration: AAPG Studies in Geology 10, p. 241–263.
Hunt, J. M., 1979, Petroleum geochemistry and geology: San Francisco, W.H. Freeman and Co., 617 p.
Izzo, J. O., 1999, Light hydrocarbons in soil-gases, Lost River region West Virginia: Relation to stratigraphy and geological structures: M.S. thesis, University of Pittsburgh, Pittsburgh, 105 p.
Jacobeen Jr., F. , and W. H. Kanes, 1974, Structure of Broadtop synclinorium and its implications for Appalachian structural style: AAPG Bulletin, v. 58, p. 362–365.
Jacobeen Jr., F. , and W. H. Kanes, 1975, Structure of Broadtop synclinorium and Allegheny frontal zone: AAPG Bulletin, v. 59, p. 1136–1150.
Jenden, P. D., D. J. Drazan, and I. R. Kaplan, 1993, Mixing of thermogenic natural gases in northern Appalachian basin: AAPG Bulletin, v. 77, p. 980–998.
Jones, V. T., and P. N. Agostino, 1998, Case studies of anaerobic methane generation at a variety of hydrocarbon fuel contaminated sites: http://www.eti-geochemistry.com/anaerobic/ (accessed February 20, 2006).
Jones, V. T., and S. G. Burtell, 1996, Hydrocarbon flux variations in natural and anthropogenic seeps, *in* D. Schumacher and M. A. Abrams, eds., Hydrocarbon migration and its near-surface expression: AAPG Memoir 66, p. 203–221.
Jones, V. T., and R. J. Drozd, 1979, Predictions of oil and gas potential by new surface geochemistry (abs.): AAPG Bulletin, v. 63, p. 699.
Jones, V. T., and R. J. Drozd, 1983, Predictions of oil and gas potential by near-surface geochemistry: AAPG Bulletin, v. 67, p. 932–952.
Jones, V. T., and H. W. Thune, 1982, Surface detection of retort gases from an underground coal gasification reactor in steeply dipping beds near Rawlins, Wyoming: Society of Petroleum Engineers, SPE Paper 11050, 24 p.
Jones, V. T., M. D. Matthews, and D. M. Richers, 2000, Light hydrocarbons in petroleum and natural gas exploration, *in* Handbook of exploration geochemistry: Gas geochemistry: Elsevier Science Publishers, v. 7, chapter 5, p. 133–212.
Klusman, R. W., 1993, Soil gas and related methods for natural resource exploration: Chichester, Wiley and Sons, 483 p.
Klusman, R. W., 2002, Interpretation and display of surface geochemical data, *in* D. Schumacher and L. A. LeSchack, eds., Surface exploration case histories: AAPG Studies in Geology 48, p. 1–24.
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.
Lang, H. R., J. B. Curtis, and J. S. Kovacs, 1985, Lost River, West Virginia, petroleum test site report, Section 12: The Joint NASA/Geosat Test Case Project, final report, 104 p.
Laughrey, C. D., and F. J. Baldassare, 1998, Geochemistry and origin of some natural gases in the Plateau Province, central Appalachian basin, Pennsylvania and Ohio: AAPG Bulletin, v. 82, p. 317–335.
Leone, I. A., F. B. Flower, J. J. Arthur, and E. F. Gilman, 1977, Damage to woody species by anaerobic landfill gases: Journal of Arboriculture, v. 3, p. 221–225.
Leythaeuser, D., R. G. Schaefer, and A. Yukler, 1980, Diffusion of light hydrocarbons through near-surface rocks: Nature, v. 284, p. 522–525.
Link, W. K., 1952, Significance of oil and gas seeps in world oil exploration: AAPG Bulletin, v. 36, p. 1505–1541.
Ludlum, J. C., 1952, The geology of Lost River State Park, West Virginia: West Virginia Geological and Economic Survey, State Park Bulletin 3, 33 p.
MacElvain, R. C., 1969, Mechanics of gaseous ascension through a sediment column, *in* W. B. Heroy, ed., Unconventional methods in exploration for petroleum and natural gas: Dallas, Texas, Southern Methodist University Press, p. 15–28.
Matthews, M. D., 1985, Effects of hydrocarbon leakage on Earth surface materials, *in* M. J. Davidson, ed., Unconventional methods in exploration for petroleum and natural gas IV: Dallas, Texas, Southern Methodist University, p. 27–44.
Matthews, M. D., 1986, The effects of hydrocarbon leakage on Earth surface materials, *in* M. J. Davidson, ed., Unconventional methods in exploration for petroleum and natural gas, Symposium IV: Dallas, Texas, Southern Methodist University Press, p. 27–44.
McDermott, E., 1940, Geochemical exploration (soil analysis) with speculation about the genesis of oil, gas, and other mineral accumulations: AAPG Bulletin, v. 24, p. 859–881.
Mitra, S., 1986, Duplex structures and imbricate thrust systems: Geometry, structural position, and hydrocarbon potential: AAPG Bulletin, v. 70, p. 1087–1112.
Mitra, S., 1987, Regional variation in deformation mechanisms and structural styles in the central Appalachian orogenic belt: Geological Society of America Bulletin, v. 98, p. 569–590.
Patchen, D. G., 1968, Oriskany Sandstone–Huntersville Chert gas production in the eastern half of West Virginia: West Virginia Geological and Economic Survey, Circular Series 9, 38 p.
Patchen, D. G., and M. E. Hohn, 1992, Production and production controls in Devonian shales, West Virginia, *in* J. B. Roen and R. C. Kepferle, eds., Petroleum geology of the Devonian and Mississippian black shales of eastern North America: U.S. Geological Survey Bulletin, v. 1909, p. L1–L28.
Patchen, D. G., K. A. Schwarz, T. A. Debrosse, M. P. McCormac, J. A. Harper, W. W. Kelly Jr., and K. L. Avery, 1985, Oil and gas development in mid-eastern states in 1985: AAPG Bulletin, v. 70, p. 1259–1272.
Pixler, B. O., 1969, Formation evaluation by analysis of hydrocarbon ratios: Journal of Petroleum Technology, v. 21, p. 665–670.
Price, L. C., and M. Schoell, 1995, Constraints on the origins of hydrocarbon gas from compositions of gases at their site of origin: Nature, v. 378, p. 368–371.
Rice, G. K., J. Q. Belt Jr., and G. E. Berg, 2002, Hydrocarbon soil gas pattern changes during a west Texas waterflood, *in* Surface

exploration case histories: Applications of geochemistry, magnetics and remote sensing: AAPG Studies in Geology 48, p. 157–174.

Richers, D. M., R. J. Reed, K. C. Horstman, G. D. Michels, R. N. Baker, L. Lundell, and R. W. Marr, 1982, Landsat soil-gas geochemical survey of Patrick Draw oil field, Sweetwater County, Wyoming: AAPG Bulletin, v. 66, p. 903–922.

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, p. 869–887.

Rodgers, M. R., and T. H. Anderson, 1984, The Tyrone–Mt Union cross-strike lineament of Pennsylvania: A major Paleozoic basement fracture and uplift boundary: AAPG Bulletin, v. 68, p. 92–105.

Rosaire, E. E., 1940, Symposium on geochemical exploration: Geochemical prospecting for petroleum: AAPG Bulletin, v. 24, p. 1400–1433.

Saunders, D. F., K. R. Burson, and C. K. Thompson, 1991, Observed relation of soil magnetic susceptibility and soil-gas hydrocarbon analyses to subsurface hydrocarbon accumulations: AAPG Bulletin, v. 75, p. 389–408.

Saunders, D. F., K. R. Burson, J. J. Brown, and C. K. Thompson, 1993, Combined geological and surface geochemical methods discovered Agaritta and Brady Creek fields, Concho County, Texas: AAPG Bulletin, v. 77, p. 1219–1240.

Saunders, D. F., K. R. Burson, and C. K. Thompson, 1999, Model for hydrocarbon microseepage and related near-surface alterations: AAPG Bulletin, v. 83, p. 170–185.

Schoell, M., 1983, Genetic characterization of natural gases: AAPG Bulletin, v. 67, p. 2225–2238.

Schoell, M., P. D. Jenden, M. A. Beeunas, and D. D. Coleman, 1993, Isotope analysis of gases in gas field and gas storage operations: Society of Petroleum Engineers, SPE Paper 26171, p. 337–344.

Sinclair, A. J., 1976, Probability graphs: Association of Exploration Geochemists, Special Publication 4, 95 p.

Sokolov, V. A., 1935, Summary of the experimental work of the gas survey: Neftjanoe Khozjostwo, v. 27, p. 28–34.

Stahl, W., E. Faber, B. D. Carey, and D. L. Kirksey, 1981, Near-surface evidence of migration of natural gas from deep reservoirs and source rocks: AAPG Bulletin, v. 65, p. 1543–1550.

Tilton, J. L., W. F. Prouty, R. C. Tucker, and P. H. Price, 1927, Hampshire and Hardy counties: West Virginia Geological and Economic Survey, County Report CGR-8, 624 p.

Tissot, B. P., and D. H. Welte, 1984, Petroleum formation and occurrence: Berlin, Springer-Verlag, 699 p.

Wagner, W. R., 1966a, Exploration for hydrocarbons in Cambrian rocks of northwestern Pennsylvania, *in* Petroleum geology of the Appalachian basin: Proceedings of the 25th Symposium on Petroleum Geology of the Appalachian Basin, University Park, Pennsylvania, p. 75–95.

Wagner, W. R., 1966b, Pennsylvanians must delve into rocks of ancient age: Oil & Gas Journal, v. 64, no. 50, p. 152–158.

Waples, D. W., 1985, Geochemistry in petroleum exploration: Boston, International Human Resources Development Corp., 232 p.