Geochemical Analyses of Surface and Shallow Gas Flux and Composition Over a Proposed Carbon Sequestration Site in Eastern Kentucky

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ABSTRACT

Using soil gas chemistry to detect leakage from underground reservoirs (i.e. microseepage) requires that the natural range of soil gas flux and chemistry be fully characterized. To meet this need, soil gas flux (CO_2, CH_4) and the bulk (CO_2, CH_4) and isotopic chemistry ($\delta^{13}C$-CO_2) of shallow soil gases (<1 m, 3.3 ft) were measured at 25 locations distributed among two active oil and gas fields, an active strip mine, and a relatively undisturbed research forest in eastern Kentucky. The measurements apportion the biologic, atmospheric, and geologic influences on soil gas composition under varying degrees of human surface disturbance.

The measurements also highlight potential challenges in using soil gas chemistry as a monitoring tool where the surface cover consists of reclaimed mine land or is underlain by shallow coals. For example, enrichment of $\delta^{13}C$-CO_2 and high CH_4 concentrations in soils have been historically used as indicators of microseepage, but in the reclaimed mine lands similar soil chemistry characteristics likely result from dissolution of carbonate cement in siliciclastic clasts having $\delta^{13}C$ values close to 0‰ and degassing of coal fragments. The gases accumulate in the reclaimed mine land soils because intense compaction reduces soil permeability, thereby impeding equilibration with the atmosphere. Consequently, the reclaimed mine lands provide a false microseepage anomaly.

Further potential challenges arise from low permeability zones associated with compacted soils in reclaimed mine lands and shallow coals in undisturbed areas that might impede upward gas migration. To investigate the effect of these materials on gas migration and composition, four 10 m (33 ft) deep monitoring wells were drilled in reclaimed mine material and in undisturbed soils with and without coals. The wells, configured with sampling zones at discrete intervals, show the persistence of some of the aforementioned anomalies at depth. Moreover, high CO_2 concentrations associated with coals in the vadose zone suggest a strong affinity for adsorbing CO_2. Overall, the low permeability of reclaimed mine lands and coals and CO_2 adsorption by the latter is likely to reduce the ability of surface geochemistry tools to detect a microseepage signal.

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EXECUTIVE SUMMARY

Using soil gas chemistry to detect leakage from underground reservoirs (i.e. microseepage) requires that the natural range of soil gas flux and chemistry be fully characterized. To meet this need soil gas flux (CO_2, CH_4), and the bulk (CO_2, CH_4) and isotopic chemistry ($\delta^{13}C$-CO_2) of shallow soil gases down to 1 m (3.3. ft) were measured under summer and winter conditions at 25 locations in eastern Kentucky. The locations are distributed among a research forest in which the surface and soils are relatively undisturbed by human activity, two active oil and gas fields having moderate levels of human disturbance, and active and historic strip mine areas having significant levels of human disturbance. The shallow measurements were followed by deeper investigations using four 10 m (33 ft) wells that allowed sampling of gases and measurement of temperatures at discrete intervals without contamination from over- and underlying soil and strata.

Measurements in the undisturbed to moderately disturbed settings showed soil gas CO_2 concentrations 1 to 2 orders of magnitude greater than atmospheric, and pronounced seasonal differences in which winter soil gas CO_2 concentrations (~10^3 ppmv) were consistently less than in summer (~10^4-10^5 ppmv). Most soil gas $\delta^{13}C$-CO_2 values were similar to bulk organic carbon (-23.8±1.5‰), suggesting CO_2 was derived primarily from microbial and/or inorganic oxidation of soil organic matter and root respiration. Slight shifts to lower concentration and enriched $\delta^{13}C$ values likely reflect a small amount of mixing of atmospheric CO_2 with biologically-derived CO_2. Soil gas CH_4 concentrations, in contrast, were on the order of 10^{-1} to 10^0 ppmv and slightly less than atmospheric values. Fluxes of CO_2, measured in triplicate at each location, were all positive and displayed a wide range of values. Summer fluxes were 3 to 4X greater than those in winter, but winter fluxes were less variable and 56% ranged from 1 to 2 μmoles/m^2/sec. By contrast, 85% of CH_4 fluxes were negative and low magnitude with summer values being slightly higher than winter.

The soil gas chemistry of the reclaimed mine lands represented an anomalous contrast to the relatively undisturbed settings. Concentrations of soil gas CO_2 (up to 297,456 ppmv) and CH_4 (up to 1,007 ppmv) were higher and more variable for all seasons in the reclaimed mine lands, and $\delta^{13}C$-CO_2 values were significantly more enriched. The isotopically enriched CO_2 was likely derived from reactions with carbonate carbon ($\delta^{13}C$~ 1.0‰). Fluxes of CO_2 and CH_4 were not commensurate with the high soil gas concentrations. For example, CO_2 fluxes in the reclaimed mine lands were actually less than those in the relatively undisturbed settings and it was only during the summer that positive fluxes of CH_4 were measured. The contradiction between high soil gas concentrations and low fluxes likely results from the mine reclamation process in which coal and other rock fragments are incorporated into a poorly-sorted heterogeneous mixture that is heavily compacted to minimize erosion. Consequently, soil permeability is reduced and gas concentrations build to high concentrations. Low permeability also reduces the ability of gas to diffuse to the atmosphere, hence the low fluxes.

The 10 m (33 ft) soil gas wells were deployed so that soil gas chemistry could be investigated below the level of strong biologic influence and to further characterize the

soil gas anomalies associated with the reclaimed mine lands. Measurements on the well samples included $\delta^{13}C$ composition of CH_4, ethane and propane concentrations, and the suite of measurements done on the shallow soil gases. Two wells were located in relatively undisturbed soil zone settings, one of which intersected two shallow coals. Analysis of gases showed that the shallowest coal at 5 m (16.5 ft) contained the highest CO_2 and lowest CH_4 concentrations in the well. A lower coal at 9 m (29.5 ft) also contained high CO_2 and low CH_4, but not of the same magnitude. This distribution suggests that the coals have desorbed CH_4 and adsorbed CO_2. If desorbed coals in the vadose zone adsorb CO_2, then CO_2 microseepage to the surface from a deeper reservoir would be diminished. From a monitoring perspective, this would increase the difficulty in resolving a potentially subtle microseepage signal. If coals are sinks for CO_2 in the near-surface environment, then gas monitoring might need to be conducted below the depth of the coals.

Two wells located in the reclaimed mine lands confirmed that anomalies documented in the shallow soil gas measurements extended to depth. One well showed a remarkable variation in the $\delta^{13}C$-CH_4 values with enriched values of -20 to -35‰ in the upper 3 m (9.9 ft) overlying a depleted value of -62‰ at 5 m (16.5 ft). The variable $\delta^{13}C$ values suggest that CH_4 has different origins even though the samples are separated by only 2 to 4 m (6.6 to 13.1 ft). This well also contained anomalous amounts of ethane (8.9 ppmv) and propane (10.1 ppmv).

Measurements in the relatively undisturbed and reclaimed mine settings provide insight into the utility and challenges of soil gas measurements as a monitoring tool. With the exception of winter measurements when biologic output is diminished, the wide range and large magnitude of CO_2 soil gas concentrations and fluxes suggest insufficient resolution to detect microseepage. Measurement of $\delta^{13}C$-CO_2 would appear to be more prospective for monitoring because most soil gas CO_2 has depleted $\delta^{13}C$ values similar to organic carbon and a shift away from the mixing line with atmospheric CO_2 would signify possible microseepage. Consistently low concentrations of soil gas CH_4 and low magnitude CH_4 fluxes would also appear to have significant utility as detectors of microseepage. For example, soil gas CH_4 concentrations greater than atmospheric and/or positive fluxes would constitute an anomaly with regard to “normal” conditions in an oxidized soil.

Soil gas anomalies associated with the reclaimed mine locations are significant for two reasons. First, similar anomalies have been used as evidence for microseepage in oil and gas fields. Here, however, the anomalies originate from the mine reclamation process as described above. The reclaimed mine anomalies thus provide a false microseepage signal. Second, the presence of un-oxidized ethane and propane, high CO_2 and CH_4 concentrations, and variable $\delta^{13}C$-CH_4 values suggest restricted gas migration in the reclaimed mine land material. The reclaimed mine lands thus represent a low permeability surface layer that will act as a barrier to CO_2 migrating upward, which will hinder shallow soil gas monitoring. Circumventing the potential challenge presented by the reclaimed mine lands may require deployment of monitoring tools around and below the level of their influence. Doing so will require the investigator to be cognizant of their spatial distribution and depth.

INTRODUCTION

Soil gas chemistry is one of many technologies being used and evaluated for monitoring the fate of injected CO_2 in geologic sequestration projects. The use of soil gas chemistry for monitoring, however, requires a well documented baseline data set that captures the full range of natural variation in fluxes and soil gas chemistry. As originally stated in the "Statement of Project Objectives," the goals of this project were to document rates of surface gas flux and shallow gas composition in areas overlying possible carbon sequestration sites in eastern Kentucky. These goals have been largely met as soil gas flux and composition data were collected and analyzed based on an early phase of shallow measurements down to 1 m (3.3 ft) followed by a later phase of deeper measurements down to 10 m (33 ft). The measurements were conducted in an oil field that remains a candidate for CO_2 enhanced oil recovery-sequestration and a Devonian shale gas field that is representative of other shale gas fields in Kentucky and the Appalachian basin. Shale gas reservoirs remain under investigation as candidates for enhanced gas recovery-sequestration targets.

In a broader context, and perhaps just as importantly, this study addresses the influence of basin specific factors associated with coals and coal mining on the utility of soil gas chemistry as a Monitoring, Verification, and Accounting (MVA) tool. More specifically, this study assesses: (1) the soil gas chemistry of reclaimed mine lands and the implications for recognizing microseepage, and (2) the potential influence of shallow coals on CO_2 transport in the vadose zone. Both of these factors have the potential to influence strategies for using soil gas chemistry as a MVA tool in basins where coal exploitation occurs in close proximity to geologic sequestration projects in saline aquifers or coupled to enhanced oil or gas recovery.

METHODS

Study Sites

As noted, the study was broadly divided into an early phase of measuring gas flux and shallow gas composition down to 1 m, and a later phase analyzing deeper soil gases down to 10 m. The measurements were conducted among three study sites in eastern Kentucky representing a variety of physiographic, surface, and geologic conditions, and having variable levels of human disturbance (Figure 1). Much of eastern Kentucky is characterized by steep-sided valleys culminating in ridges, so measurements were made at locations representing the varied dissected terrain.

Robinson Forest in Breathitt and Knott Counties is a 10,122 acre (15.8 mi^2) forest owned and administered by the University of Kentucky for research purposes (Figures 1 and 2). The forest contains a mixed hardwood assemblage of trees (e.g. hemlock, red maple, ash, and oak), which were last logged in the mid-1920's. As a relatively undisturbed forest, the three measurement locations in Robinson served as control points for quasi-pristine soil and shallow subsurface conditions. Robinson is also notable because it is one of the few areas in eastern Kentucky where significant coals within a few meters of the surface remain unmined. This attribute was used in the deep soil gas analysis to examine the influence of coals on soil gas composition and distribution.

The Ario site in Knott County is located in an active gas field in which wells are interspersed with present-day strip mining activity (Figure 3). Located on the southern boundary of Robinson Forest, the Ario site covers an area of approximately 4,257 acres (6.7 mi^2) and contains approximately 25 gas wells that produce natural gas primarily from the Devonian Ohio Shale at depths of 730 to 825 m (2400 to 2700 ft). Shallow soil gas measurements were conducted at eight to nine locations most of which were in forested areas having low to moderate levels of human disturbance. All soil gas locations were at least 61 m (200 ft) from gas wells and 15 m (50 ft) from roads. In order to investigate the soil gas characteristics of reclaimed mine lands, one of the Ario locations was sited on a bench made up of reclaimed mine material and, as such,

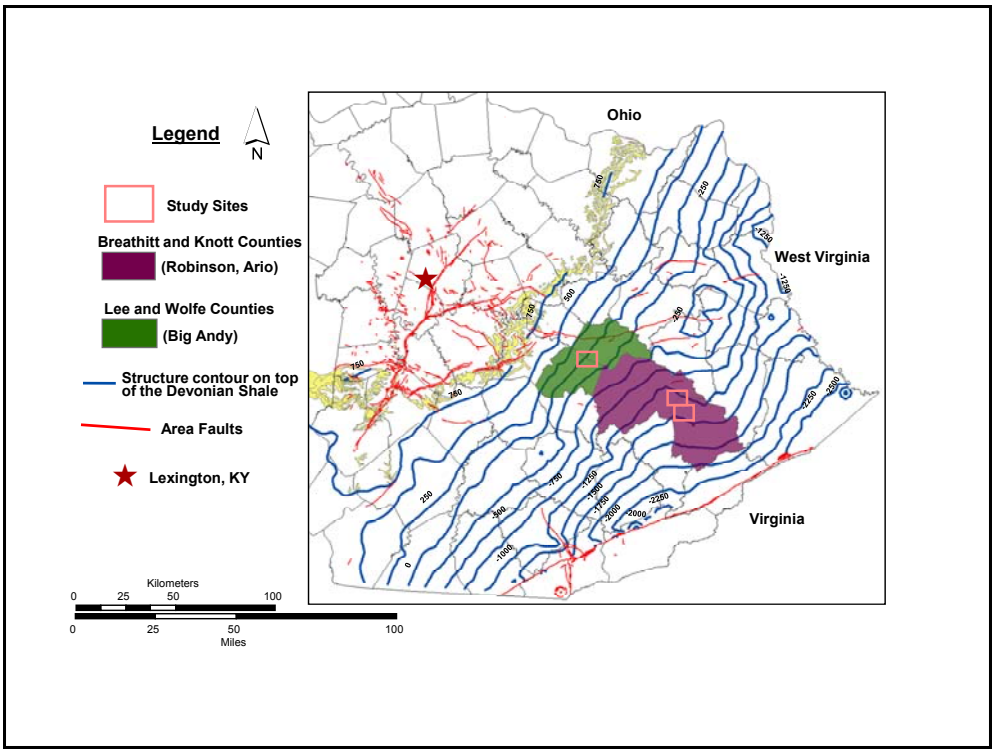

Figure 1—administrative map of eastern Kentucky showing location of study sites.

Figure 2—Robinson Forest that served as the control site for relatively undisturbed soil and surface conditions.

represented a heavily disturbed setting. The bench is covered only with grasses, which typifies reclaimed mine lands in the area (Figure 4).

The Big Andy site in Lee and Wolfe Counties mostly coincides with the Big Andy oil field, which covers an area of approximately 13.061 acres (20.4 mi^2) and contains over 1,000 wells (Figure 5). The Big Andy field produces oil from the Silurian Lockport Dolomite and Keefer Sandstone at depths of 300 to 427 m (1,000-1,400 ft), and has reservoir properties similar to the Big Sinking oil field to the east, which is Kentucky's largest oil field with more than 100,000,000 barrels of oil produced. Big Andy has undergone a limited amount of enhanced oil recovery (EOR) using N_2 and CO_2, and it remains prospective for future EOR-sequestration projects, although the shallow depth would likely cause CO_2 to reside as a gas in the reservoir. Within the field area, small-scale coal mining occurred in the 1970's and 1980's, and the reclaimed mine lands, unlike those in the Ario area, are covered with pine trees 5 to 15 feet tall or pasture grass used for grazing (Figure 6). Soil gases were measured at 13 to 15 locations with 2 locations on reclaimed mine lands and the remaining in variably forested areas. Because of the close well-spacing (122 m, 400 ft) in the field, some of the soil gas locations were within 30 m (100 ft) of producing wells and 15 m (50 ft) of service roads.

In this report the term "undisturbed soils" refers to the majority of locations (n= 24) distributed among the three study sites that have had little (Robinson Forest) to moderate (Ario and Big Sinking) amounts of human disturbance. These locations contrast to the smaller number of locations (n= 3) in Ario and Big Andy that are sited on reclaimed mine lands and represent highly disturbed soil and shallow subsurface conditions.

Shallow Soil Gas Measurements

Surface fluxes of CO_2 and CH_4, and the bulk (CO_2, CH_4) and carbon isotopic composition of CO_2 ($\delta^{13}C$-CO_2) in soil gases down to 1 m (3.3 ft) were measured at all locations (n= 26) distributed among the three study sites. Measurements were conducted in two periods in 2006 from mid-February to early March and again in August. The purpose for two sampling periods was to characterize the seasonal

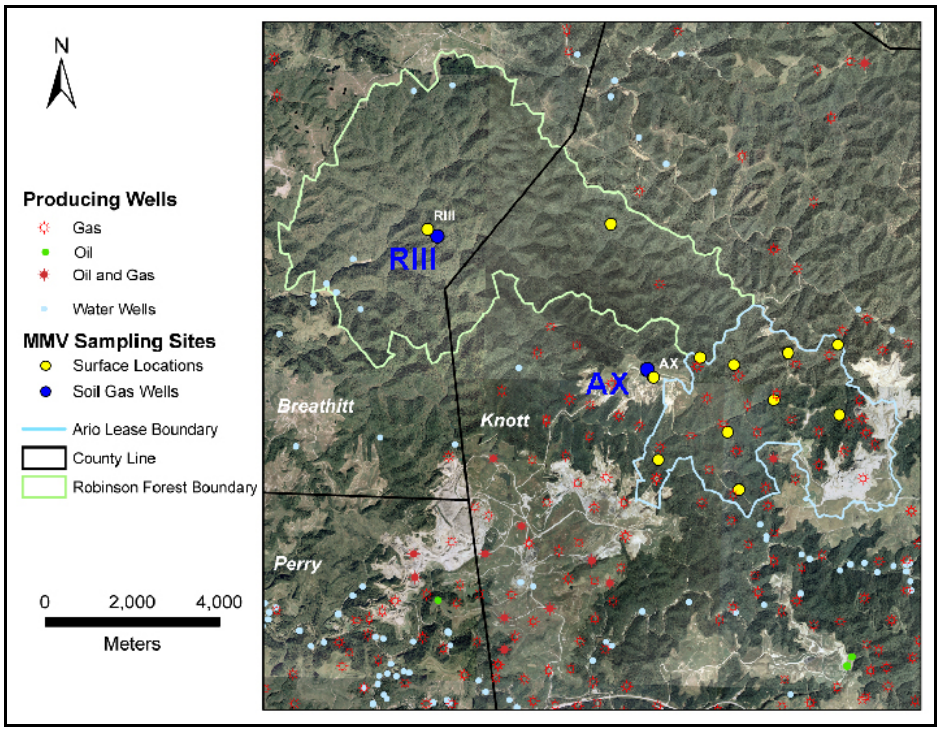

Figure 3—aerial photograph of the Ario and Robinson study sites.

Figure 4—truck mounted rig air-drilling the 10 m (33 ft) soil gas well at Ario location AX sited on reclaimed mine material. The tree line in the background is the southern boundary of Robinson Forest.

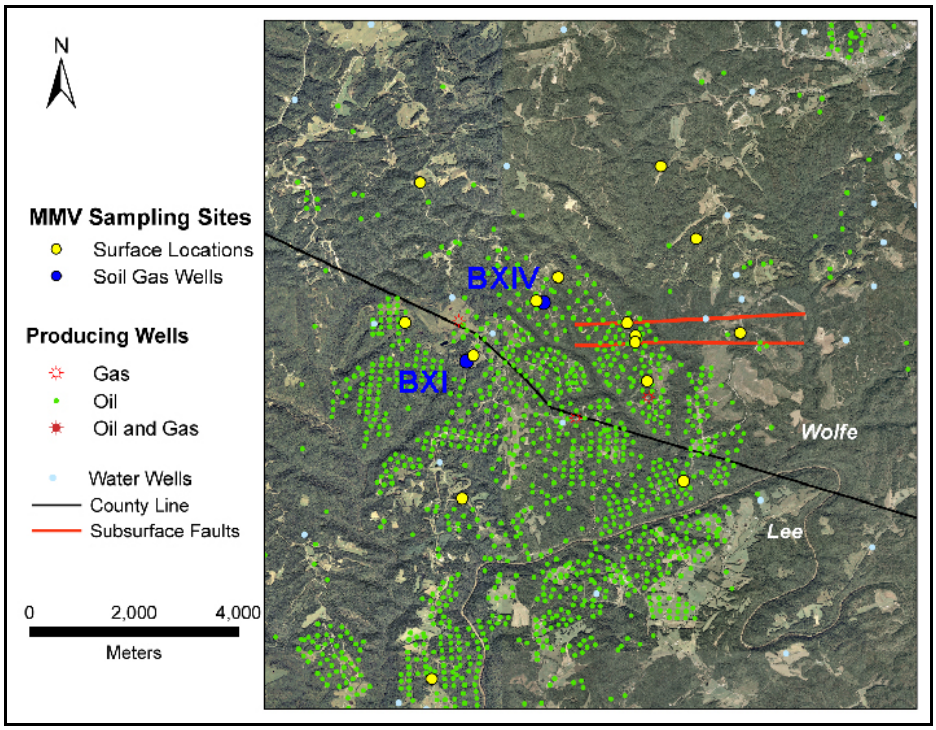

Figure 5—aerial photograph of the Big Andy study site.

Figure 6—shallow soil gas location at Big Andy that occurs on reclaimed mine land. The location is near soil gas well BXIV. Note the vegetation difference as compared to location AX (see Figure 4).

influence of temperature and moisture on soil gas flux and chemistry under winter and summer conditions. A more limited program of shallow measurements (n= 7) was conducted in the summer of 2007 at locations having anomalies identified in the 2006 measurements and/or near future 10 m (33 ft) soil gas wells.

Fluxes of CO_2 were measured using chamber methods described by Livingston and Hutchinson (1995). More specifically, CO_2 fluxes were measured directly with a Licor LI-8100 infrared gas analyzer (IRGA) equipped with a 20 cm (8 in) survey chamber (Figure 7). The IRGA was calibrated for CO_2 and moisture content using 1000 ppm CO_2 and "zero air" standards per Licor's specifications. Daily calibration while sampling showed no significant drift for the IRGA. The sample chamber was coupled to the ground surface with a collar constructed from 20 cm (8 in) diameter X 8 cm (~3 in) deep drain pipe. The edges of the collar were beveled on the side facing the ground to allow for easier insertion. The collars were typically put into position the day before measurements to allow ground disturbance effects on flux to subside. The LI-8100 was also equipped with a probe to measure soil temperature down to 5 to 8 cm (2 to 3 in), and internal sensors to measure air temperature and moisture content. Chamber CO_2 concentration, air and soil temperature, and air humidity were saved to a flash card, and the data later processed and analyzed with LicorViewer, a software designed to calculate and analyze fluxes. Analysis shows that, once the chamber was closed, CO_2 concentrations would show a steady state linear increase after about 40 seconds and the linear trajectory would persist for at least 5 to 7 minutes. Therefore, CO_2 fluxes were measured with the chamber in the closed position over a 3 minute period, which assured accurate flux measurements and optimal use of field time.

After CO_2 fluxes were measured, fluxes of CH_4 were measured indirectly by calculating the change in CH_4 concentration with time for samples collected from a sampling port in the soil collar (Figure 7). The concentration difference between atmospheric and soil gas CH_4 is typically small, consequently, fluxes are small and longer measurement times with the chamber closed are needed to resolve the flux. Thus, with the chamber in the closed position, samples were collected with a 25 mL gas tight syringe at 8, 16, and 24 minutes and injected into 10 mL serum vials with crimp tops. The concentration of CH_4 and CO_2 in the vials was subsequently measured in the

lab using gas chromatograph (GC) methods (see below). Flux magnitudes were calculated using a Fortran program developed by Klusman (unpublished data) and based on the model of Hutchinson and Mosier (1981). In order to assess variation at each location, fluxes of CO_2 and CH_4 were measured in triplicate at collars separated by approximately 10 m (Figure 8).

Soil gas samples were collected at the midway points between the soil collars at depths of 30, 60, and 100 cm (Figure 8). At each depth, one 10 mL sample was collected for bulk composition (CO_2, CH_4) and one for isotopic composition (del13C-CO_2). The summer 2006 and 2007 samples were also analyzed for ethane (C_2H_6) and propane (C_3H_8). The soil gas samples were collected with a 6 ft. soil probe (3/8" X 1/8" CDS tubing) having a Swagelok fitting and septum at the top through which samples could be collected with a gas tight syringe (Figure 9). The probe was evacuated at each sample depth to remove any atmospheric gas and to ensure that the gas sample originated at the target depth. In addition, two atmospheric gas samples were collected at each location for bulk and isotopic composition. Thus, on average each location generated 17 samples for bulk chemistry and 7 for isotopic chemistry and the number would increase slightly when duplicates were collected.

The bulk gas composition for shallow soil gas and the 10 m soil gas samples was measured at the Environmental Research and Teaching Laboratory at the University of Kentucky (http://ertl.uky.edu/). Specifically, a dual channel Varian CP-3800 gas chromatograph equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID) was used to measure CO_2 and CH_4 concentrations, respectively. The gas chromatograph was equipped with an injection port and sampling loop for gas analysis, and a Poraplot capillary column that facilitated the measurement of CH_4 concentrations less than 2 ppmv. The gas chromatograph was calibrated with 1, 5, and 10 ppmv CH_4 standards; and 300, 1,000, 2,000, and 10,000 ppmv standards for CO_2. In addition, single point 10 ppmv standards were run on C_2H_6 and C_3H_8. Duplicate GC samples were collected at each location for the 24 minute sample taken from the last flux measurement (i.e. collar c, Figure 8). Nevertheless, the GC measurements do

Figure 7—Licor LI-8100 infrared analyzer used to measure CO_2 fluxes.

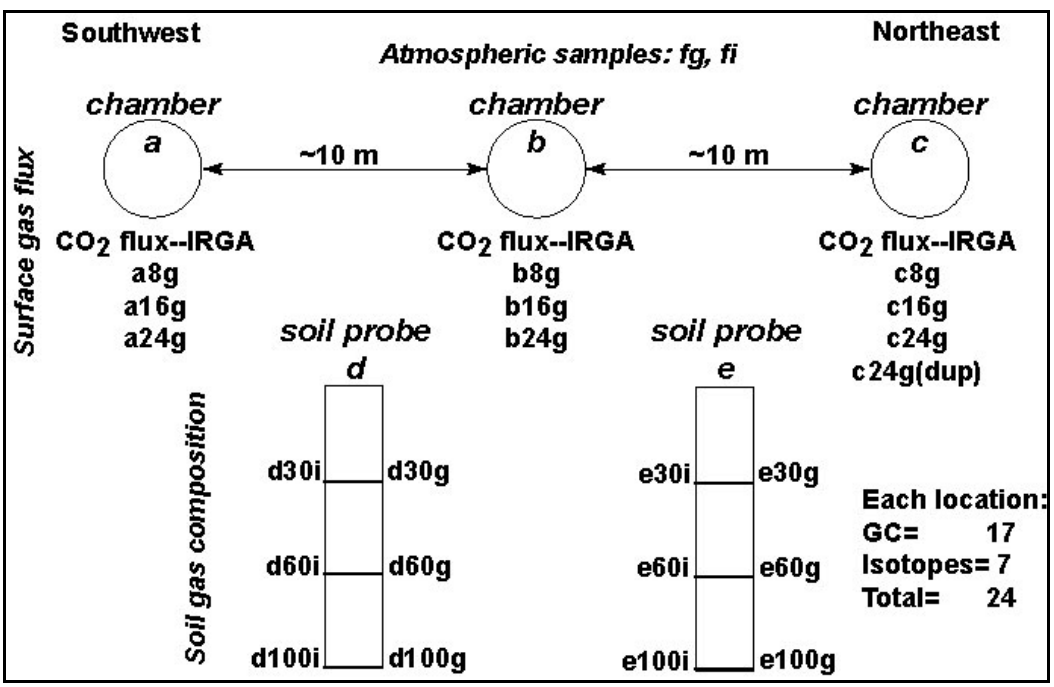

Figure 8—schematic showing the types and relative positions of measurements conducted at each location in the shallow soil gas measurements.

accurately record the anomalous order of magnitude difference in CH_4 and CO_2 concentrations between the reclaimed mine lands and soils having little to moderate disturbance.

The carbon isotopic composition of CO_2 from the winter 2006 samples was also measured at the Environmental Research and Teaching Laboratory using a ThermoFinnigan Delta Plus XP Mass Spectrometer equipped with a Gas Bench. Changes in lab personnel, however, resulted in subsequent samples being measured at Isotech Laboratories (http://www.isotechlabs.com/), where measurements were done with an Agilent 6890 GC combustion unit and Finnegan GCCIII interfaced with a mass spectrometer (Finnegan Delta+ or Finnegan Delta V Plus). For the gas mixtures, CO_2 was separated from the other gas components by GC and introduced directly into the mass spectrometer. Finnegan's Isodat software was utilized for peak detection and quantification. The precision of the carbon isotope data was ± 0.3‰.

Deep Soil Gas Measurements

Analysis of the 2006 shallow soil gas measurements provided the background data that were used, in part, to locate and drill four soil gas wells to a depth of 10 m (33 ft). The wells were distributed among the Ario (well AX), Robinson Forest (well RIII), and Big Andy (wells BXI and BXIV) study sites (Figures 3 and 5). A fifth well was planned for Big Andy near a shallow soil gas location on one of the east-west graben faults, but the property owner would not provide permission for the well. The wells were sampled under winter (March and April 2008) and summer (September 2008) conditions.

The soil gas wells were drilled with a truck mounted air rotary rig over a four day period in August 2007 (Figure 4). The wells were completed open-hole—that is, no casing—with a diameter of 10 cm (4 in) and each drilled to a total depth of 10 m (33 ft). The wells were configured using a "nested" format developed by Klusman (e.g. 2003a) in which gas samples can be collected from discrete intervals at depth. The designated gas sample intervals were positioned at 1, 2, 3, 5, and 10 m for wells AX, BXI, and BXIV. Well RIII differed slightly in order to investigate the influence of shallow coals, and sample intervals were placed at 1, 2, 3.8, 5, 6.5, and 10 m. Each of the sample intervals

Figure 9—sampling soil gases in Robinson Forest.

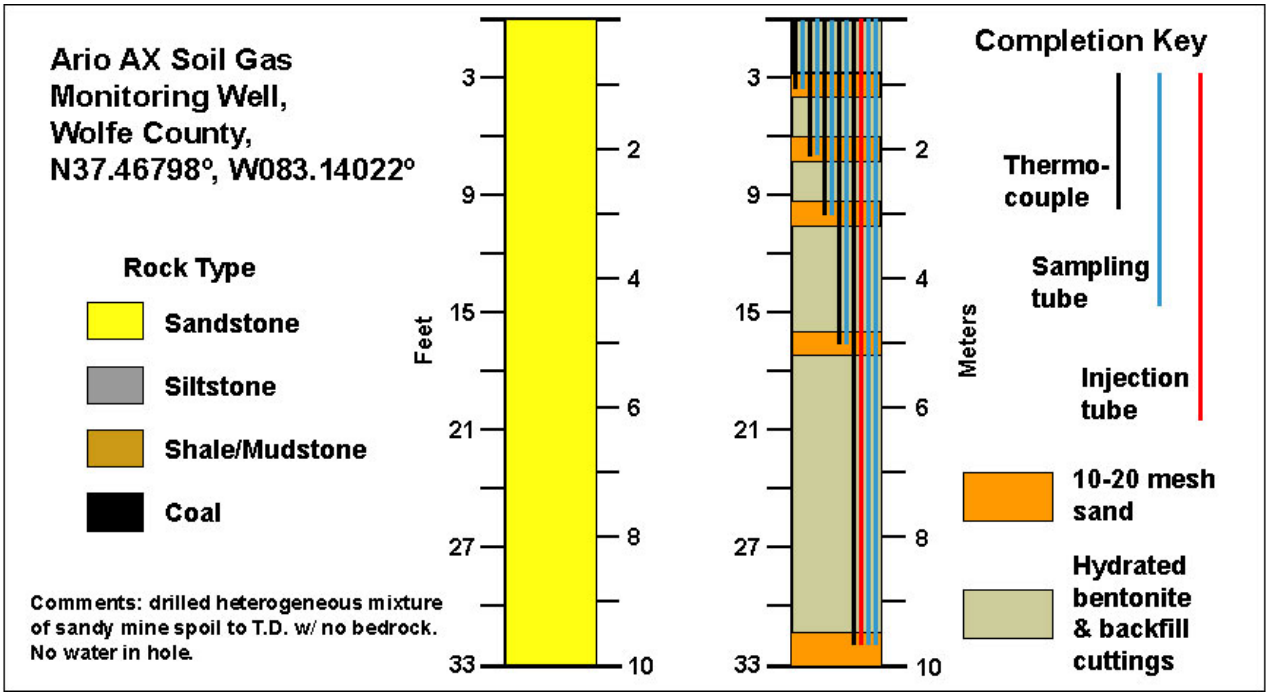

Figure 10—schematic of 10 m (33 ft) soil gas well showing configuration of sample zones equipped with thermocouples and sample and injection tubes. The samples zones are separated and isolated by intervening bentonite and backfill cuttings.

was covered with a 30 cm (12 in) thick porous sand pack (10-20 mesh sand), and the intervening wellbore was filled with hydrated bentonite and back-fill cuttings (Figure 10). The configuration isolated the sand packs and ensured that gas into them would come primarily from the laterally adjacent soil and rock horizon.

Each sand pack contained one sample tube (0.25” OD X 0.17” ID poly-tube) and thermocouple (insulated Type T) that extended to the surface. The sand pack at 10 m, however, contained a thermocouple and three tubes, one each for sampling, injecting a tracer gas, and pressure relief. The down-hole ends of the tubes were fitted with fine mesh paint filters to prevent sand from clogging the tubes. At the surface, brass Swagelok unions were attached to the tubes, and the ferrule on the free side of the union was replaced with a rubber septum. This allowed gas samples from the sand packs to be acquired with a gas tight syringe with no atmospheric contamination. Thermocouples provided temperatures at the depths of the sand packs, and the temperatures can be used in modeling gas transport and other processes such as oxidation (e.g. Klusman, 2003b).

At approximately 45 cm (18 in) below ground level, the thermocouples and sample tubes were directed away from the wellbore through a 1 to 1½ m (3-5 ft) long trench that intersected the wellbore (Figure 11). At the end of the trench, thermocouples and tubes were brought to the surface through 10 cm (4 in) and 15 cm (6 in) diameter PVC pipes, respectively. Tubes and thermocouples at the bottom of the trench were covered with dirt and the PVC pipes set in concrete. Offsetting the thermocouples and sample tubes was done to minimize soil compaction from foot traffic around the wellbore and decrease potential damage to the thermocouple and tubes. Locking caps were put on the PVC pipes to reduce the risk of vandalism or inadvertent damage.

Soil and rock cuttings generated during the drilling of the wells were collected from intervals that coincided with the sand packs and significant changes in rock type. A portion of the cuttings was sent to Huffman Laboratories (Denver, CO) to measure total inorganic carbon, total organic carbon, and total carbon. The cuttings were combusted to ~1350°C with an oxygen carrier gas, and carbon was oxidized to CO_2, which was measured with infrared detection. Total carbon was measured using a Leco CR 12 Carbon Analyzer (detection limit= 0.05%). Carbonate (i.e. inorganic) carbon was

determined by acidifying the samples with 0.1N perchloric acid that converts the carbonate to CO_2. The CO_2 was then analyzed using a UIC/Coulometrics System 140 Carbonate Carbon Analyzer (detection limit= 0.02%). Organic carbon equals the difference between the total and inorganic carbon.

The $\delta^{13}C$ composition of CO_2 (described above) and CH_4 were measured and the latter measurements were conducted by Todd Sowers at Pennsylvania State University. The following general discussion describing the measurement of $\delta^{13}C$-CH_4 comes from Sowers et al. (2005), to which the reader is referred for more details. The $\delta^{13}C$-CH_4 measurements were made with a Finnigan MAT 252 mass spectrometer coupled to a Finnigan GC/combustion interface in continuous flow mode. CH_4 was isolated from gas species in air using a cryogenic and GC pre-concentration device. The values were referenced to the VPDG scale using a pure CO_2 working standard having a value of -45.98±0.02‰. Over three years of measurements, the average value on the reference tank was -47.07±0.18‰ (n= 201).

Figure 11—sample and injection tubes (right) and thermocouples (left) extending from sample zones and being offset from bore hole (bottom) through a trench.

RESULTS AND DISCUSSION

Shallow Soil Gas Measurements

The flux of gas species between the soil and atmosphere is strongly influenced by the concentration differences of the gases between these reservoirs (Matson and Harriss, 1995). Thus, we start with an analysis of soil gas CO_2 and CH_4 concentrations. When plotted versus depth, one of the most prominent demarcations in the data occur between lower CO_2 concentrations in relatively undisturbed soils versus higher concentrations in reclaimed mine lands (Figure 12). As will be demonstrated, the distinction between undisturbed soils and reclaimed mine lands also applies to CH_4 concentrations and $\delta^{13}C$-CO_2 values. The geochemical differences provide the basis for inferring soil processes and properties that influence soil gas composition.

For undisturbed soils at Ario, Robinson, and Big Andy, CO_2 concentrations vary widely for a given depth resulting in large standard deviations (Table 1). Nevertheless, average values show a regular increase in soil gas CO_2 concentration down to 1 m (3.3 ft), and concentrations are typically 1 to 2 orders of magnitude greater than atmospheric (Figure 12). A seasonal difference in soil gas CO_2 concentrations is clear as winter values on the order of 10^3 ppmv are consistently less than those for summer, which range up to 10^4 to 10^5 ppmv. Compared by depth, average CO_2 concentrations for summer 2006 values exceed winter 2006 values by 33 to 173%. Maintenance of soil CO_2 concentrations in excess of atmospheric values likely reflects the influence of soil microbe and root respiration and, under warmer conditions, these processes accelerate producing more CO_2. Atmospheric CO_2 concentration by site also increased 11 to 15% for summer versus winter measurements, which likely reflects the canopy effect that results from increased leaf respiration in summer.

Average soil gas CO_2 concentrations in the reclaimed mine lands are higher and even more heterogeneous than those for undisturbed soils (Figure 12, Table 1). Remarkably, individual CO_2 measurements in the reclaimed mine lands ranged up to 48,593 and 297,456 ppmv in the winter and summer, respectively. Because soil gas measurements were conducted under colder conditions at a single reclaimed mine location (AX) during the winter 2006, it is difficult to determine if a seasonal change in

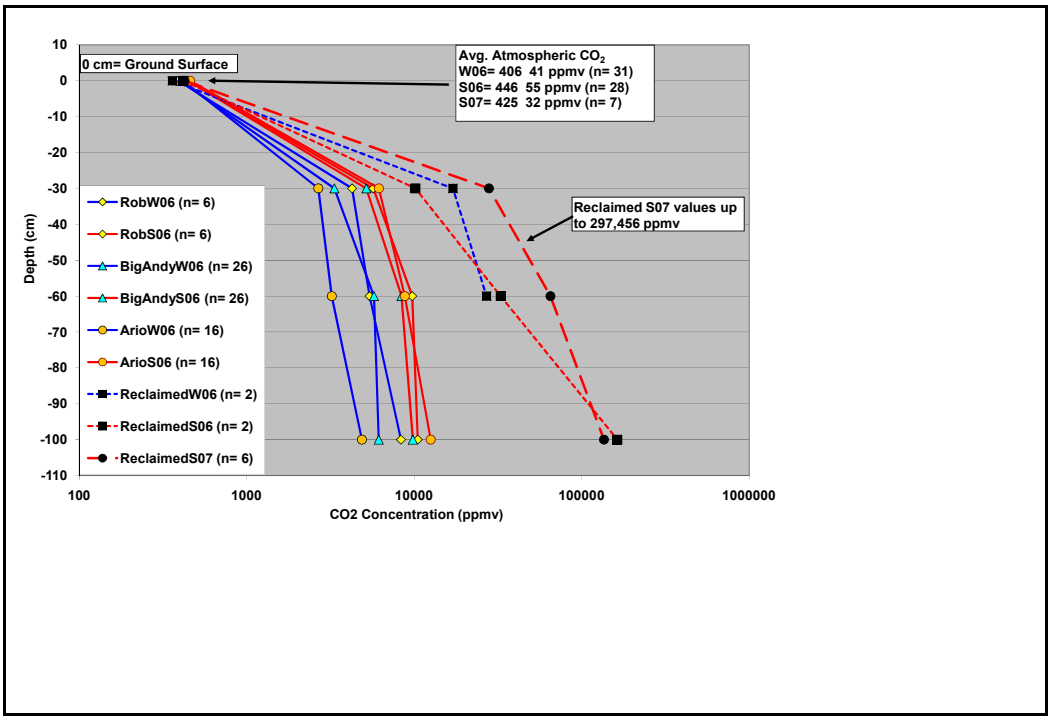

Figure 12—average CO_2 concentration (log,) versus depth (cm) for the shallow soil gas measurements. Blue and red curves represent winter and summer measurements, respectively. Solid curves are measurements from relatively undisturbed soils, whereas dashed curves are for reclaimed mine land measurements. Fine dashes represent winter and summer 2006 measurements and the coarse dashed curve represents summer 2007 measurements.

soil gas CO_2 concentration exists for the reclaimed mine lands, such as with the undisturbed soils. Results from the summer 2006 (location AX) and summer 2007 (locations AX, BXIV, BXV) measurements as compared to the winter 2006 measurements (location AX) suggest that a seasonal difference, if it exists, might not be pronounced as with the undisturbed soils.

The redox counterpart to CO_2, CH_4, shows very different concentrations and distribution in the soil zone. Concentrations of CH_4 for samples from undisturbed soils are typically on the order of 10^{-1} to 10^{0} ppmv and slightly less than atmospheric

Table 1—average CO_2 and CH_4 concentration (ppmv) of shallow soil gases down to 1 m. Two sets of soil gases were collected for each location (Figure 8). In the first row the number of locations in the summer 2007 sampling program is shown in parentheses and the adjacent non-parenthetic numbers are the number of locations in the winter and summer 2006 sampling programs. Reclaimed mine land measurements include Ario location AX for summer and winter 2006, and Big Andy locations BXIV and BXV were added for summer 2007 measurements. ***Because the reclaimed mine locations come from the Big Andy and Ario sites, the values for average atmospheric CO_2 correspond to those sites as shown under the summer 2007 measurements.

	Robinson Forest	**Big Andy**	**Ario**	**Reclaimed Mine Land**
Number of Locations	3(1)	13(2)	8(1)	1(3)
CO2				
Winter 2006				
30 cm	4,254±2,195 (n= 6)	3,335±1,526 (n= 26)	2,677±1,505 (n= 16)	17,056±17,351 (n= 2)
60 cm	5,405±3,750 (n= 6)	5,750±3,656 (n= 26)	3,221±1,822 (n= 16)	27,037±30,485 (n= 2)
100 cm	8,329±5,037 (n= 6)	6,137±3,607 (n= 26)	4,933±1,943 (n= 15)	5,120 (n= 1)
Atmosphere	389±28 (n= 3)	400±49 (n= 13)	415±40 (n= 9)	360 (n= 1)
Summer 2006				
30 cm	5,681±2,632 (n= 6)	5,178±2,776 (n= 26)	6,158±2317 (n= 16)	10,412±1915 (n= 2)
60 cm	9,711±5777 (n= 6)	8,394±3,761 (n= 26)	8,779±2,678 (n= 16)	32,818±15,225 (n= 2)
100cm	10,482±6,410 (n= 6)	9,811±3,633 (n= 26)	12,550±4,566 (n= 16)	163,424±45,733 (n= 2)
Atmosphere	448±28 (n= 3)	444±28 (n= 11)	459±74 (n= 7)	417 (n= 1)
(Summer 2007)				
30 cm	16,482±9,687 (n= 2)	3,975±2,036 (n= 4)	7,096±416 (n= 2)	27,921±9,038 (n=6)
60 cm	32,974±11,727 (n= 2)	9,933±6,489 (n= 4)	10,331±1,305 (n= 2)	64,960±27,229 (n= 6)
100 cm	18,748±3,480 (n= 2)	13,014±7,183 (n= 4)	16,480±8 (n= 2)	135,654±118,154 (n= 6)
Atmosphere	418 (n= 1)	436±40 (n= 4)	406±113 (n= 2)	***
CH4				
Winter 2006				
30 cm	0.54±0.23 (n= 6)	0.76±0.43 (n= 26)	0.82±0.53 (n= 16)	4.08±2.09 (n= 2)
60 cm	0.83±0.46 (n= 6)	0.73±0.42 (n= 26)	1.0±0.56 (n= 16)	5.08±3.61 (n= 2)
100 cm	1.06±0.82 (n= 5)	1.42±1.71 (n= 26)	1.47±1.22 (n= 15)	2.32 (n= 1)
Atmosphere	1.95±0.16 (n= 3)	1.91±0.14 (n= 13)	1.98±0.19 (n= 9)	2.03 (n= 1)
Summer 2006				
30 cm	0.73±0.1 (n= 6)	1.08±0.34 (n= 26)	0.67±0.37 (n= 16)	4.22±0.64 (n= 2)
60 cm	0.94±0.53 (n= 6)	0.96±0.4 (n= 26)	1.12±0.95 (n= 16)	6.64±2.19 (n= 2)
100 cm	0.95±0.3 (n= 6)	1.12±0.8 (n= 26)	0.96±0.47 (n= 16)	25.81±4.34 (n= 2)
Atmosphere	1.91±0.06 (n= 3)	1.9±0.06 (n= 13)	1.96±0.08 (n= 7)	2.12 (n= 1)
(Summer 2007)				
30 cm	0.75±0.14 (n= 2)	1.16±0.69 (n= 4)	0.53±0.2 (n= 2)	4.87±3.69 (n= 6)
60 cm	0.62±0.21 (n= 2)	0.88±0.62 (n= 4)	0.89±0.26 (n= 2)	11.3±6.2 (n= 4)
100 cm	0.96±0.1 (n= 2)	0.89±0.43 (n= 4)	2.71±2.72 (n= 2)	177±407 (n= 6)
Atmosphere	2.19 (n= 1)	1.97±0.1 (n= 4)	1.88±0.14 (n= 2)	***

(Figure 13a, Table 1). The lowest CH_4 concentrations in the undisturbed soils usually occur at 30 cm and then increase slightly with depth. Soil gas CH_4 concentrations in the soil that are less than atmospheric levels likely reflect oxidation at a rate that outpaces the rate at which atmospheric CH_4 is able to diffuse into the soil (Klusman, 2003b). When compared for a given study site and depth, average summer soil gas CH_4 concentrations tend to be slightly higher in summer versus winter, although overlap exists within one standard deviation. This suggests that CH_4 oxidation in the soil is somewhat temperature dependent. Reclaimed mine lands are again anomalous with average concentrations of CH_4 and individual measurements (up to 7.6 and 1,007 ppmv in winter and summer, respectively) being well above values measured in undisturbed soils (Figures 13a and 13b).

An important consideration in this study was how measurements in a relatively undisturbed setting, such as Robinson Forest, compared to those having moderate levels of human disturbance, such as Ario and Big Andy, and the significantly disturbed reclaimed mine lands. Examination of 2006 average winter and summer soil gas CO_2 and CH_4 concentrations for Robinson, Ario, and Big Andy are comparable and overlap within one standard deviation (Table 1). The similarity probably reflects two influences. First, the range of measured CO_2 and CH_4 concentrations for a given depth among locations at a study site results in a standard deviation sufficiently large to produce statistical overlap. Second, despite being in an area of active oil and gas activity, most locations in Ario and Big Andy were at least 15 m (50 ft) removed from areas of significant disturbance, such as roads and well heads. Therefore, soil conditions were likely similar among locations for the three study sites. It is likely that in close proximity to well bores that anomalies associated with contamination would be encountered, and a possible example of this will be provided with the deep soil gas well at location BXIV in Big Andy.

The carbon isotopic composition of CO_2 ($\delta^{13}C$-CO_2) provides important insights into the sources and factors influencing the distribution of CO_2 in the soil zone. These factors include the composition of the substrate compounds from which CO_2 is derived, biologic fractionation, equilibrium chemical reactions that involve CO_2, and kinetic effects such as diffusion and degassing (Trumbore, 1995). The main substrates and

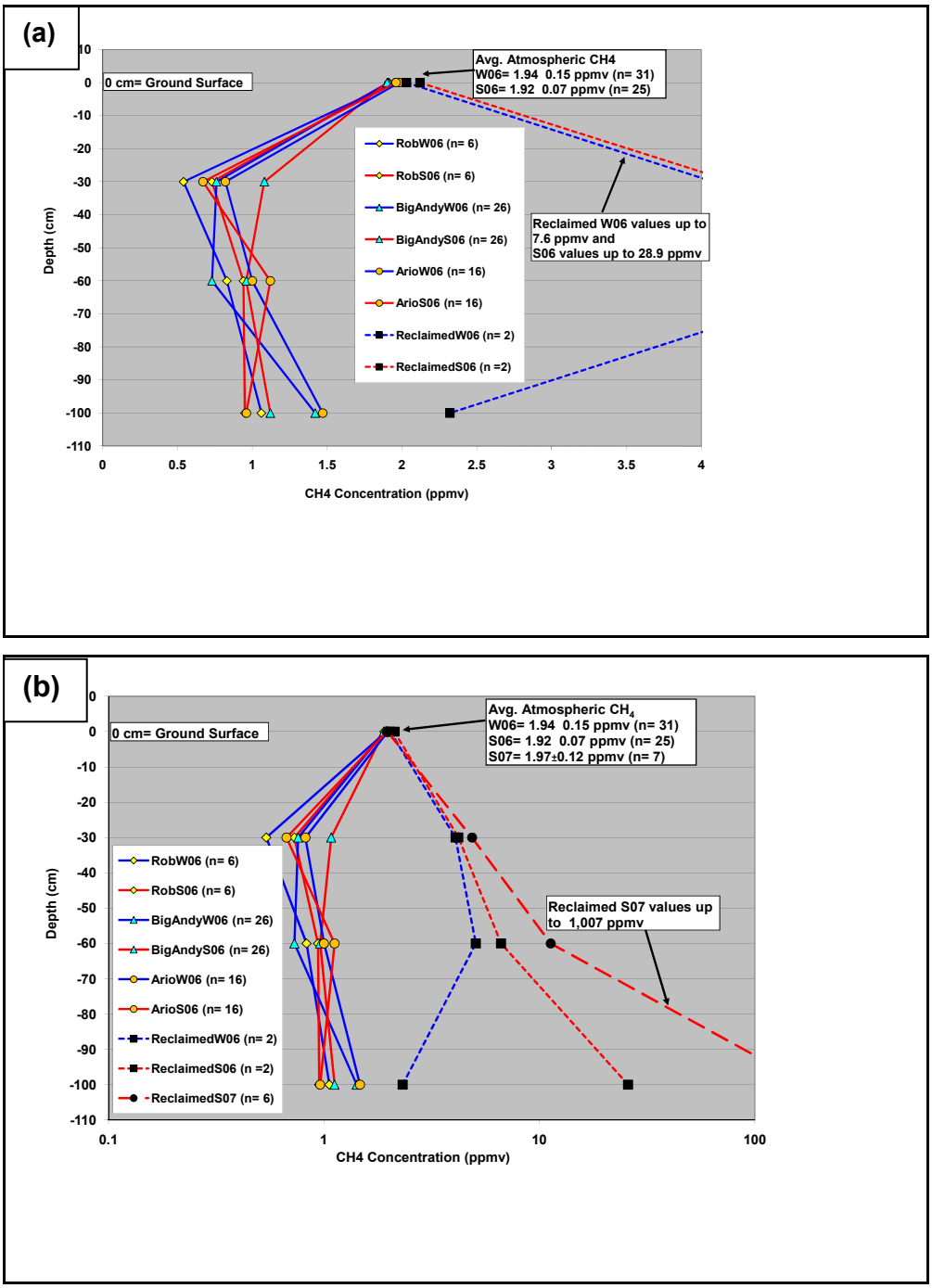

Figure 13—(a) average CH_4 concentration versus depth for the shallow soil measurements. Blue and red curves represent winter and summer measurements, respectively. Solid curves are measurements from relatively undisturbed soils, whereas dashed curves are for reclaimed mine land measurements. (b) Similar to 13a, but summer 2007 measurements from reclaimed mine lands (coarse dash) have been added. Fine dashes represent winter and summer 2006 measurements from reclaimed mine lands. Because of high values in the reclaimed mine lands, the concentration of CH_4 is plotted on a log scale.

sources contributing to soil gas CO_2 include organic and inorganic carbon matter in the soil and CO_2 from the atmosphere. In this study we analyzed bulk organic carbon matter only, but other studies show that this fraction is a heterogeneous mixture of cellular (plant litter, microbes) and non-cellular (humus) components (Schlesinger, 1997). Inorganic carbon matter is primarily carbonate, which we identified through X-ray diffraction as calcite ($CaCO_3$) and siderite ($FeCO_3$).

The $\delta^{13}C$-CO_2 measurements from the relatively undisturbed soils at Robinson, Big Andy, and Ario are similar to, but slightly enriched with respect to bulk soil organic carbon at about -24‰ (Figure 14a, Table 2). The similarity accords with other studies in oxidized upland soils that show the main influence on soil gas CO_2 is microbial consumption and oxidation of soil organic matter, and root respiration (Schlesinger, 1997). Winter and summer measurements are about 1 to 3‰ enriched with respect to bulk organic carbon. The slight enrichment may reflect mixing with more isotopically enriched atmospheric CO_2 (-9.4 to -13.8‰) and/or an isotopic kinetic effect in which CO_2 rich in ^{12}C diffuses more quickly to the atmosphere leaving the remaining soil CO_2 enriched in ^{13}C. Regardless of season, close proximity to the bulk organic carbon value suggests that oxidation of this substrate is the main contributor to soil gas CO_2.

When CO_2 concentrations versus $\delta^{13}C$-CO_2 values are examined more closely, inferences can be made about processes affecting soil gas CO_2 composition (Figure 14b). Winter CO_2 measurements are scattered along a somewhat linear trend toward lower concentrations and slightly enriched $\delta^{13}C$ values. This trend is similar to, but does not coincide with, a hypothetical mixing line between winter atmospheric CO_2 and bulk organic carbon. The coincidence suggests some atmospheric influence, but the winter CO_2 measurements are mostly isotopically depleted compared to the mixing line; that is, they fall below the mixing line. Their position below the mixing line suggests that even in winter, soil microbial activity and root respiration are the main influences on soil gas CO_2, and reduced permeability, because of wetter conditions, may reduce mixing with the atmosphere.

The summer data, in contrast, define a somewhat linear scatter to higher CO_2 concentrations and more enriched $\delta^{13}C$ values—up to about -16‰ (Figure 14b). This

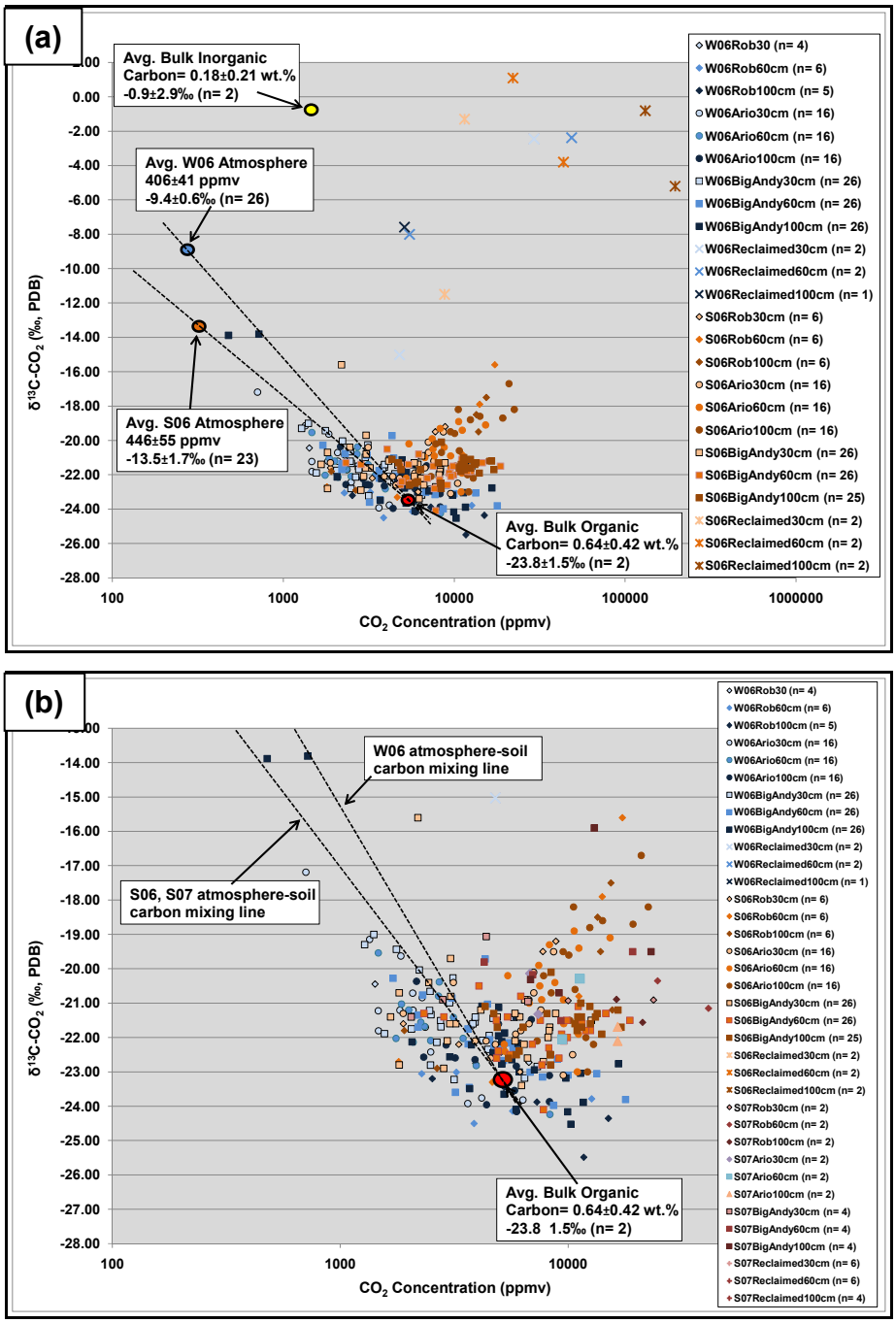

Figure 14—(a) log CO_2 concentration versus $\delta^{13}C$-CO_2 for the shallow soil gas measurements. Winter and summer data are shown with blue and orange-brown symbols, respectively. Data from relatively undisturbed soils are shown with filled polygons, whereas measurements from reclaimed mine lands are shown with "X" type symbols. Dashed lines extending from average atmospheric anchor points to the average bulk organic carbon point represent hypothetical mixing lines between these potential CO_2 sources. (b) Enlarged view of 14a showing difference in winter and summer CO_2 concentrations and $\delta^{13}C$-CO_2 values for relatively undisturbed soils.

Table 2—$\delta^{13}C$ composition of shallow soil gas CO_2 down to 1 m and organic and inorganic soil matter at 1 m. Values are reported on a ‰ basis and referenced to PDB. For the summer 2007 sampling program, the number of locations measured is shown in parentheses and the adjacent non-parenthetic numbers are the number of locations measured during the winter and summer 2006 sampling programs each. Two sets of soil gases were collected for each location as shown in Figure 15. Reclaimed mine land measurements include Ario location AX for summer and winter 2006, and Big Andy locations BXIV and BXV were added for summer 2007 measurements. ***Because the reclaimed mine locations come from the Big Andy and Ario sites, the values for atmospheric CO_2 correspond to those sites as shown under the summer 2007 measurements. The absence of inorganic carbon data at Robinson and Big Andy reflects the absence of inorganic carbon at 1 m

	Robinson Forest	**Big Andy**	**Ario**	**Reclaimed Mine Land**
Number of Locations	3(1)	13(2)	9(1)	1(3)
Soil Gases				
Winter 2006				
30 cm	-22.4±1.3 (n= 4)	-20.9±3.0 (n= 26)	-21.4±1.8 (n= 16)	-8.7±8.9 (n= 2)
60 cm	-23.5±0.8 (n= 6)	-21.6±3.2 (n= 26)	-21.8±1.2 (n= 16)	-5.2±3.9 (n= 2)
100 cm	-23.9±1.2 (n= 5)	-21.9±3.1 (n=26)	-22.7±1.0 (n= 16)	-7.6 (n= 1)
Atmosphere	-9.8±1.0 (n= 3)	-9.6±0.5 (n= 13)	-9.1±0.4 (n= 9)	-8.4 (n= 1)
Summer 2006				
30 cm	-21.1±1.5 (n= 6)	-21.4±1.4 (n= 26)	-21.5±1.0 (n= 16)	-6.4±7.2 (n= 2)
60 cm	-20.4±3.0 (n= 6)	-21.9±0.7 (n= 26)	-20.7±1.2 (n= 16)	-2.5±1.9 (n= 2)
100cm	-20.2±2.1 (n= 6)	-21.7±0.7 (n= 26)	-20.0±1.8 (n= 16)	-3.0±3.1 (n= 2)
Atmosphere	-14.4±1.8 (n= 3)	-13.7±1.3 (n= 13)	-12.8±2.3 (n= 7)	-8.5 (n= 1)
Summer 2007				
30 cm	-20.9±0.0 (n= 2)	-20.6±1.0 (n= 4)	-20.7±0.8 (n= 2)	-7.7±3.6 (n= 6)
60 cm	-20.8±0.6 (n= 2)	-20.3±0.9 (n= 4)	-21.2±1.3 (n= 2)	-3.8±2.6 (n= 6)
100 cm	-21.3±0.5 (n= 2)	-19.1±2.2 (n= 4)	-21.9±0.3 (n= 2)	-3.2±2.3 (= 4)
Atmosphere	-14.5 (n= 1)	-15.0±0.7 (n= 4)	-11.0±4.1 (n= 1)	***
Soil Carbon (1 m)				
Organic	-24.4 (n= 1)	-25.0 (n= 1)	nd	-22.9±1.7 (n= 2)
Inorganic	nd	nd	nd	-0.9±2.9 (n= 2)

Figure 15—tan to buff colored sandstone and dark colored coal clasts in sandy reclaimed mine material.

trend is orthogonal to the hypothetical summer-bulk organic carbon mixing line with summer atmospheric CO_2 and the divergence suggests that simple mixing between these two sources cannot explain the origin of summer soil gas CO_2. The excursion to higher concentrations shows the strong influence of higher temperatures on soil microbial activity and the attendant increase in soil gas CO_2. The increase in soil temperature in summer might also account for the shift to more enriched $\delta^{13}C$ values because CO_2 solubility is inversely related to temperature (Faure, 1991). Consequently, with higher temperatures CO_2 would tend to degas more from pore water in the soils

leaving residual CO_2 enriched in ^{13}C. Potential contributions from carbonate carbon that has a $\delta^{13}C$ value of about -1‰ cannot also not be discounted (Figure 14a).

As with the soil gas concentration measurements, the $\delta^{13}C$-CO_2 measurements are markedly different between samples from relatively undisturbed soils and the reclaimed mine lands. The reclaimed mine lands have $\delta^{13}C$ values that are significantly enriched, even more so than atmospheric CO_2 (Figure 14a). The enrichment strongly suggests that CO_2 in the reclaimed mine lands was derived in large part from reactions with isotopically enriched carbonate carbon (avg.= -0.9±2.9‰). The source of the carbonate in the reclaimed mine lands was most likely sandstone clasts in which the predominant intergranular cement was calcite and siderite (Figure 15). The clasts would have come from Pennsylvanian Breathitt Group sandstones deposited in nearshore marine environments, and the marine environment would have been the source of the isotopically enriched carbonate.

The documentation of atmospheric and soil gas CO_2 and CH_4 concentrations provides a framework for a more complete understanding of surface fluxes. Measurements of CO_2 flux show that all locations recorded positive fluxes—that is, gas transport from the soil into the atmosphere—in all seasons (Figure 16a, Table 3). Average fluxes of CO_2 during the summer were 3 to 4X greater than in winter and the seasonal difference accords with concentration differences measured in the soil gases. Fluxes of CO_2 were also more variable in summer than in winter, with 56% of all measurements in the latter ranging from 1 to 2 μmoles/m^2/sec (Table 3).

Despite having significantly higher soil gas CO_2 concentrations, fluxes of CO_2 in the reclaimed mine lands were lower than those for undisturbed soils in each of the sample periods (Figure 16b, Table 3). Moreover, the pronounced seasonal difference observed in the measurements for undisturbed soils is not well developed in the reclaimed mine lands.

By contrast, CH_4 fluxes in the undisturbed soils are mostly low magnitude and 85% are negative—that is, gas transport from the atmosphere into the soil (Figure 17a, Table 3). This flux behavior reflects the slightly higher concentration of CH_4 in the atmosphere versus the soil zone (Table 1). Average fluxes for CH_4 are slightly higher in the summer versus winter, but overlap within one standard deviation.

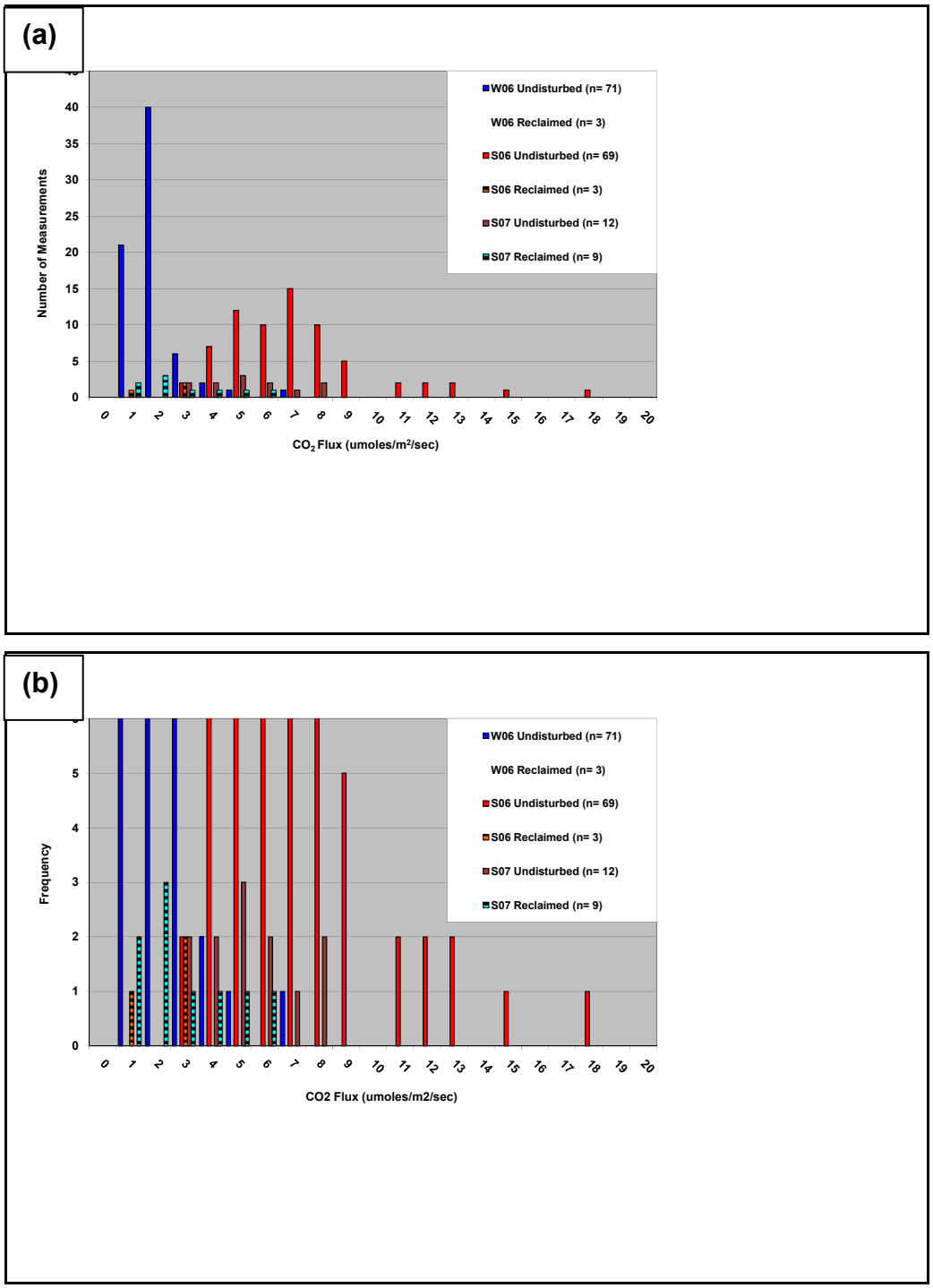

Figure 16—(a) histogram of CO_2 fluxes (µmoles/m^2/sec) for winter and summer 2006, and summer 2007. Winter and summer measurements are shown with bluish and reddish bars, respectively, and undisturbed measurements are shown with solid bars and reclaimed mine lands with striped bars. (b) Enlarged view of 16a highlighting the relatively flow flux magnitudes of fluxes on reclaimed mine lands versus relatively undisturbed soils.

Table 3—summary statistics for CO_2 and CH_4 fluxes in µmoles/m^2/sec. Typically each location has flux measurements at three different collar locations (see Figure 8). The number of measurement locations decreased for all study sites in 2007 excepting those for reclaimed mine lands. Reclaimed mine land measurements include Ario location AX for summer and winter 2006, and Big Andy locations BXIV and BXV were added for summer 2007 measurements.

	Robinson Forest	**Big Andy**	**Ario**	**Reclaimed Mine Land**
Number of Locations:				
W06, S06	3	13	8	1
S07	1	2	1	3
CO_2 Flux				
Winter 2006				
Average	1.72 (n= 9)	1.56 (n= 39)	1.35 (n= 24)	0.84 (n= 3)
Std. Deviation	0.83	1.07	0.97	1.00
Median	1.53	1.17	1.06	0.31
Maximum	3.7	6.25	4.91	2.00
Minimum	0.99	0.70	0.39	0.22
Summer 2006				
Average	5.28 (n= 9)	7.44 (n= 39)	5.71 (n= 24)	1.93 (n= 3)
Std. Deviation	2.31	2.92	1.99	0.96
Median	5.50	6.80	5.50	2.10
Maximum	8.80	17.20	12.60	2.80
Minimum	2.50	3.40	2.80	0.90
Summer 2007				
Average	3.33 (n= 3)	5.10 (n= 6)	5.67 (n= 3)	2.64 (n= 9)
Std. Deviation	1.10	2.00	1.46	1.00
Median	3.40	5.30	5.50	1.90
Maximum	4.40	7.60	7.20	5.70
Minimum	2.20	2.50	4.30	0.90
CH_4 Flux				
Winter 2006				
Average	-0.34 (n= 9)	-0.14 (n= 37)	-0.44 (n= 24)	-0.36 (n= 3)
Std. Deviation	0.57	0.44	0.43	0.14
Median	-0.16	-0.22	-0.41	-0.31
Maximum	0.29	1.01	0.51	-0.25
Minimum	-1.16	-0.96	-1.28	-0.52
Summer 2006				
Average	-0.55 (n= 8)	-0.34 (n= 36)	-0.70 (n= 24)	0.35 (n= 3)
Std. Deviation	0.25	0.29	0.33	0.15
Median	-0.46	-0.39	-0.63	0.30
Maximum	-0.25	0.25	-0.05	0.52
Minimum	-0.94	-0.89	-1.48	0.20
Summer 2007				
Average	-0.73 (n= 3)	-0.62 (n= 9)	-0.87 (n= 3)	0.28 (n= 6)
Std. Deviation	0.28	0.28	0.11	0.31
Median	-0.60	-0.66	-0.93	0.38
Maximum	-0.52	-0.22	-0.74	0.57
Minimum	-1.05	-1.02	-0.93	-0.13

Winter fluxes for CH_4 in the reclaimed mine lands are low magnitude and negative and comparable to winter measurements in the undisturbed soils (Figure 17b, Table 3). In contrast, 58% of all summer measurements on the reclaimed mine lands resulted in slightly positive CH_4 fluxes. Positive fluxes are expected given that soil gas CH_4 concentrations were significantly greater than atmospheric concentrations. What is surprising, however, is that flux magnitudes are not higher.

The reclaimed mine lands thus contain several anomalous characteristics. First, the concentrations of soil gas CO_2 and CH_4 are significantly higher as compared to the relatively undisturbed soils. The high concentrations relative to atmospheric values do not translate, however, into commensurately high fluxes. Indeed winter fluxes for CH_4 are negative despite having soil gas concentrations that are sometimes several orders of magnitude greater than atmosphere (Figure 13b, Table 1). The antithetic juxtaposition between high soil gas concentrations and low fluxes likely results from the mine reclamation process in which coal fragments are incorporated into a heterogeneous mixture of poorly-sorted materials that is heavily compacted (Figure 15). The material is compacted to minimize erosion, but in doing so, soil permeability is reduced and gas concentrations consequently build to levels much higher than in the relatively undisturbed soils. The low permeability also reduces the ability of gas to diffuse to the atmosphere, hence the low fluxes. Sandstone clasts cemented with carbonate are also included in the compacted reclaimed mine material and these are the likely source of the CO_2 that has enriched in $\delta^{13}C$ values (Figure 14a).

From a MVA standpoint, the soil gas anomalies at the reclaimed mine locations are significant because enriched $\delta^{13}C$-CO_2 values, positive fluxes of CH_4, and soil gas CH_4 concentrations consistently greater than atmospheric have been used along with other criteria (e.g. presence of ethane and propane) as evidence for microseepage in oil and gas fields, some of which have undergone CO_2 enhanced oil recovery (Klusman 2003a, 2006). In this study, however, the preponderance of these anomalies associated with reclaimed mine lands strongly suggests that they originate not from microseepage from a deeper oil or gas reservoir, but rather from the reclamation process as described in the previous paragraph. The anomalies at the reclaimed mine site are thus false

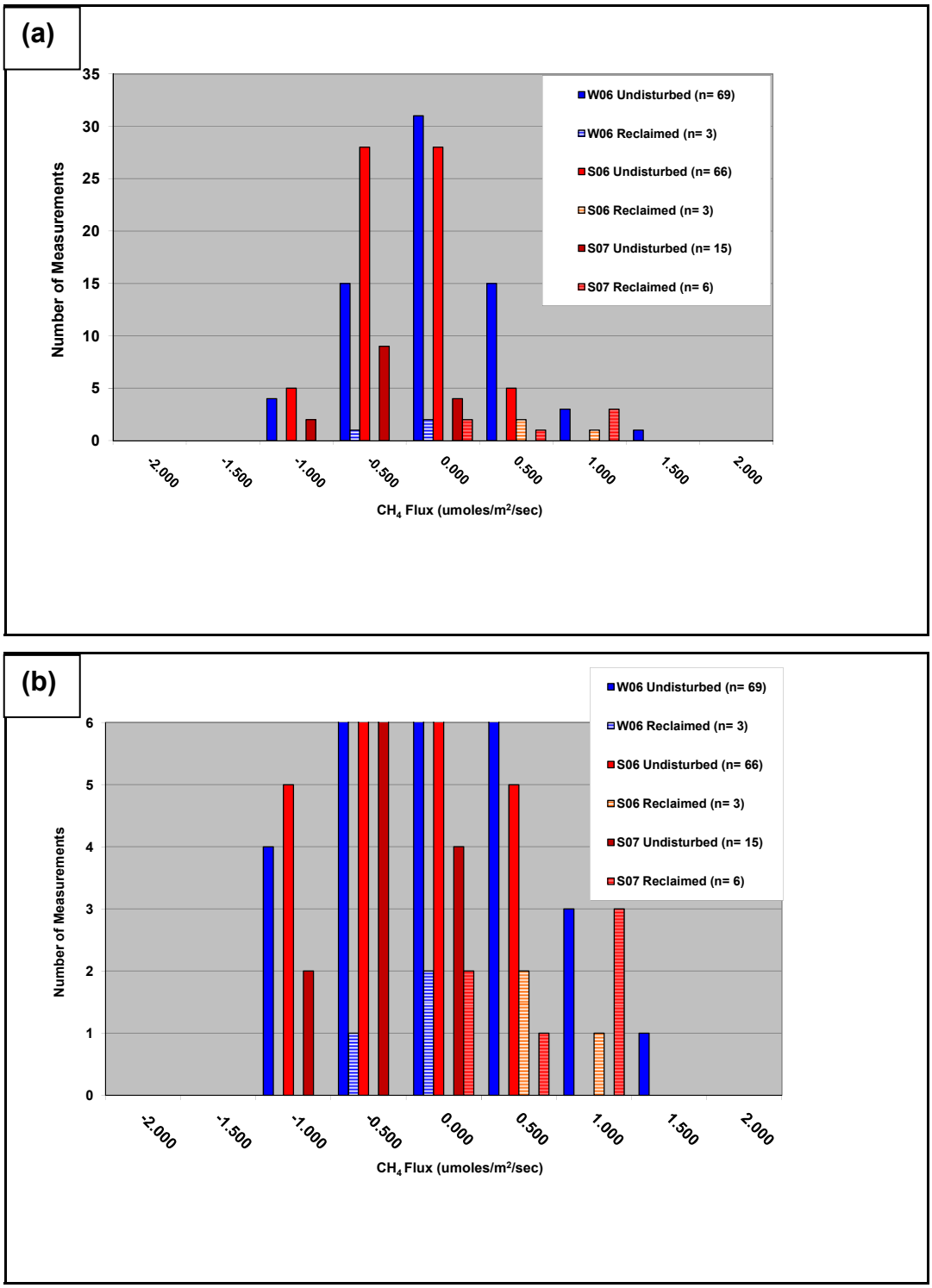

Figure 17—(a) histogram of CH_4 fluxes (µmoles/m^2/sec) for winter and summer 2006, and summer 2007. Winter and summer measurements are shown with bluish and reddish bars, respectively, and undisturbed measurements are shown with solid bars and reclaimed mine lands with striped bars. (b) Enlarged view of 17a highlighting the relatively large proportion of low magnitude positive fluxes on reclaimed mine lands versus relatively undisturbed soils.

indicators of microseepage, and, as such, potentially hinder the ability to resolve a true microseepage signature from a leaking reservoir at depth.

The potential for hindrance is highlighted in Figure 14a, which shows that the $\delta^{13}C$ composition of CO_2 from two lower Paleozoic reservoirs in eastern Kentucky (Harris et al., 2004) is similar to the isotopically enriched soil gas CO_2 at the reclaimed mine sites. The similarity is significant especially for using soil gas chemistry as a tool to detect microseepage say, for example, along a fault that cuts through reclaimed mine material. If soil gas measurements are being conducted as part of a pre-injection screening program, then it is highly unlikely the investigator will be able to accurately attribute the anomalies to either the reclaimed mine material or actual microseepage.

Deep Soil Gas Measurements

The analysis of the $\delta^{13}C$ values in the previous section underscores the major influence that biologic activity has on the concentration of CO_2 in the shallow soil zone (Schlesinger, 1997; Parris et al., 2007). From a MVA perspective, the high concentration of biologically-derived CO_2 and associated high fluxes represents an impediment to resolving a microseepage signal, which is likely to be more subtle (Klusman, 2003a). Hence, one of the main motivations for drilling four 10 m (33 ft) deep soil gas wells was to examine soil gas chemistry below the zone of intense biologic activity. Additional criteria used to select specific well locations included the need to further characterize locations having anomalous and non-anomalous soil gas chemistry as determined in the shallow soil gas measurements. Locations were also selected so that deeper soil gas chemistry in a variety of soil settings could be analyzed. These include relatively undisturbed soil zones with and without shallow coal beds and the reclaimed mine lands. Given the potential for reclaimed mine lands to provide false indications of microseepage, it was important to determine if such anomalies extended to depth and how deep a monitoring program would have to probe to avoid them.

In order to meet these criteria two wells were drilled and completed in relatively undisturbed soil zone settings with (RIII, Robinson Forest) and without (BXI, Big Andy) shallow coals, and two wells were located in reclaimed mine lands at Ario (AX) and Big Andy (BXIV) (Figures 3,5, and 18). Well BXI provided the opportunity to characterize a

location having shallow soil gas chemistry characteristics that typified more than 90% of measurements in this study; that is, soil gas CH_4 concentrations less than atmospheric, negative CH_4 fluxes, soil gas CO_2 concentrations greater than atmospheric, positive CO_2 fluxes, and depleted $\delta^{13}C$-CO_2 values reflecting the dominant influence of biologic activity in the shallow soil zone (Parris et al., 2007). Well AX, also located in an undisturbed setting, differs in that it penetrated two shallow coal beds and this provided the opportunity to assess how shallow coals affect soil gas chemistry and gas transport in the vadose zone. Wells AX and BXIV coincided with the soil chemistry anomalies associated with the reclaimed mine lands described in the previous section.

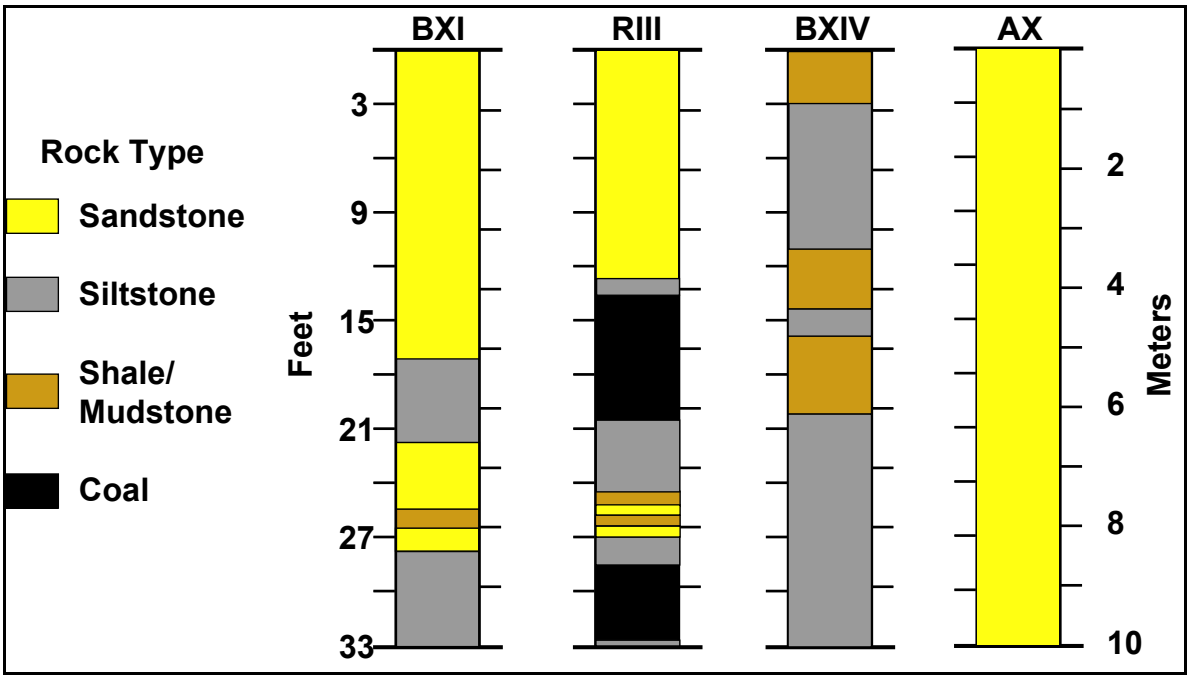

Figure 18—stratigraphy and rock and soil types in the four 10 m (33 ft) soil gas wells at the Big Andy (BXI, BXIV), Robinson Forest (RIII), and Ario study sites. The logs are based on cuttings generated during the drilling of the wells.

Numerous soil biogeochemical and chemical reactions, such as respiration of CO_2 from microbial activity and the solubility of CO_2, are influenced by temperature (Schlesinger, 1997). Thermocouples installed in each of the sample intervals thus provided the opportunity to document the variation of temperature with depth and under different seasonal conditions. In both the undisturbed and reclaimed mine land wells,

winter temperatures, measured in late March-early April 2008, are distinctly cooler than summer temperatures, measured in September 2008 (Figures 19 and 20). The maximum seasonal temperature difference occurs from the surface down to 1 m (3.3 ft), and the largest recorded difference was in BXIV and equaled 16.7ºC (~30 ºF). Below 1 m (3.3 ft), however, summer and winter temperatures converge for a given well and the depth of convergence differs between the undisturbed and reclaimed mine land wells. For the former, temperatures converge at approximately 5 m (16.4 ft), whereas temperatures converge at 7 to 8 m (23-26 ft) for the latter. This difference may reflect different heat conductance characteristics related to soil compaction and sun exposure. The high concentrations of CO_2 and CH_4 documented in the shallow measurements suggest that the reclaimed mine lands are highly compacted and, as such, may conduct heat more readily than the undisturbed soils. Moreover, the paucity of tree cover, especially in the case of well AX, would result in more sun exposure on the soil surface (Figure 4). The effect of increased sun exposure is supported by summer temperature measurements in the reclaimed mine land wells that tend to be about 1 to 2°C hotter for a given depth as compared to the undisturbed wells (Figures 19 and 20). Well AX is particularly anomalous showing the hottest temperatures in summer and winter among all the wells.

The concentration and distribution of carbon matter substrates in the soil and rock zones is a major influence on soil gas concentration. Our analysis of carbon matter from the cuttings generated during the drilling of the wells shows a fairly consistent range of 0.1 to 4.4 wt.% total carbon (Figures 19 and 20). The notable exception occurs in well RIII where total carbon reaches 67 wt.% over the intervals coincident with the coal beds. With the exception of samples in BXI (5 m, 16.5 ft) and AX (2 m, 6.6 ft), organic carbon makes up more the largest proportion of total carbon. The remaining carbon is inorganic carbon mainly in the form of carbonate including siderite and calcite. The dominance of organic carbon suggests that it should be the main influence on soil gas CO_2 composition, and this relationship is supported by the shallow soil gas measurements in which the $\delta^{13}C$-CO_2 values are similar to the $\delta^{13}C$ values for organic carbon (Table 2).

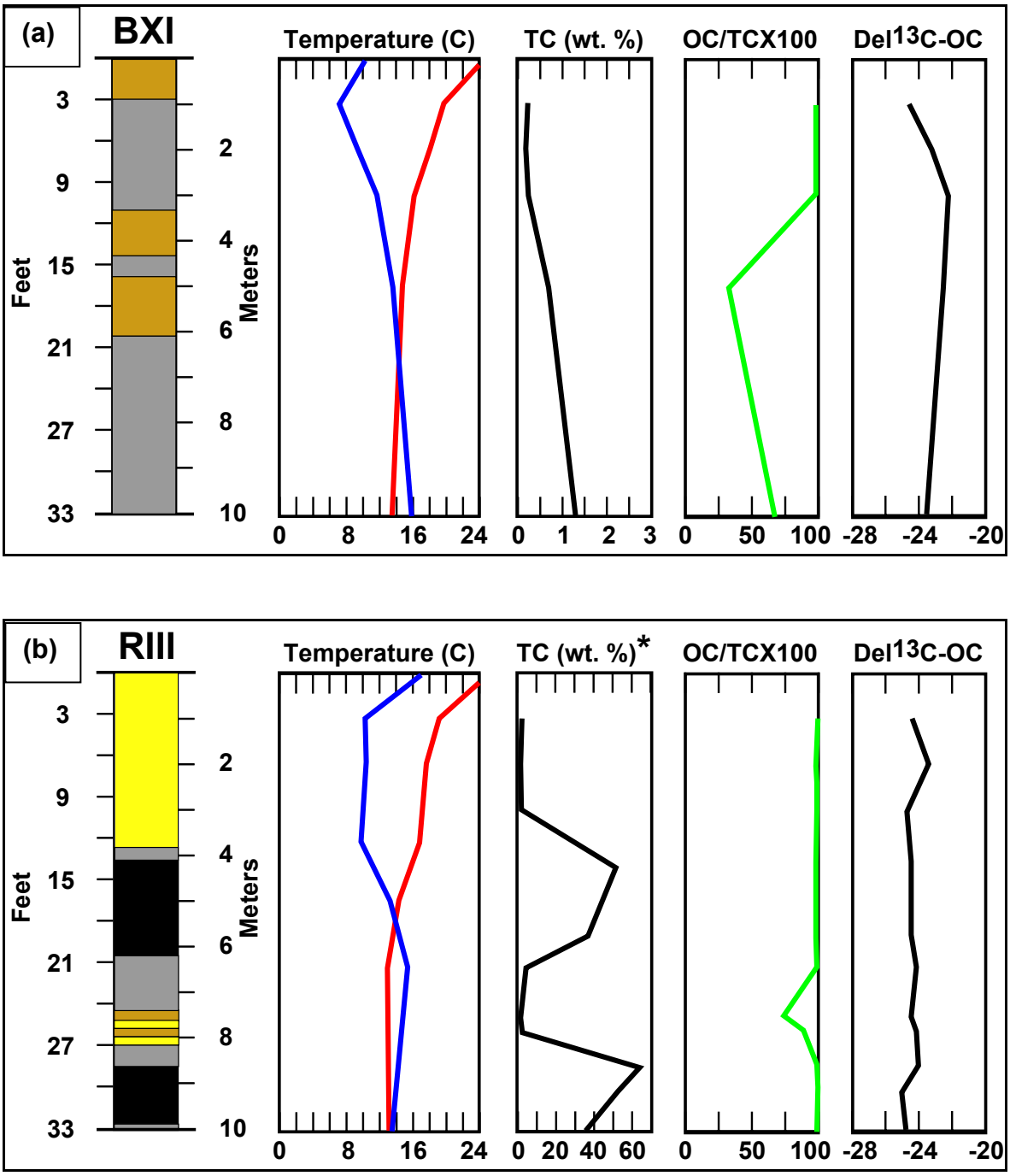

Figure 19—profiles showing temperature, amount of total carbon (TC), and the proportion of organic carbon (OC) as part of TC, and the $\delta^{13}C$ composition of OC in the undisturbed wells (a) BXI and (b) RIII.

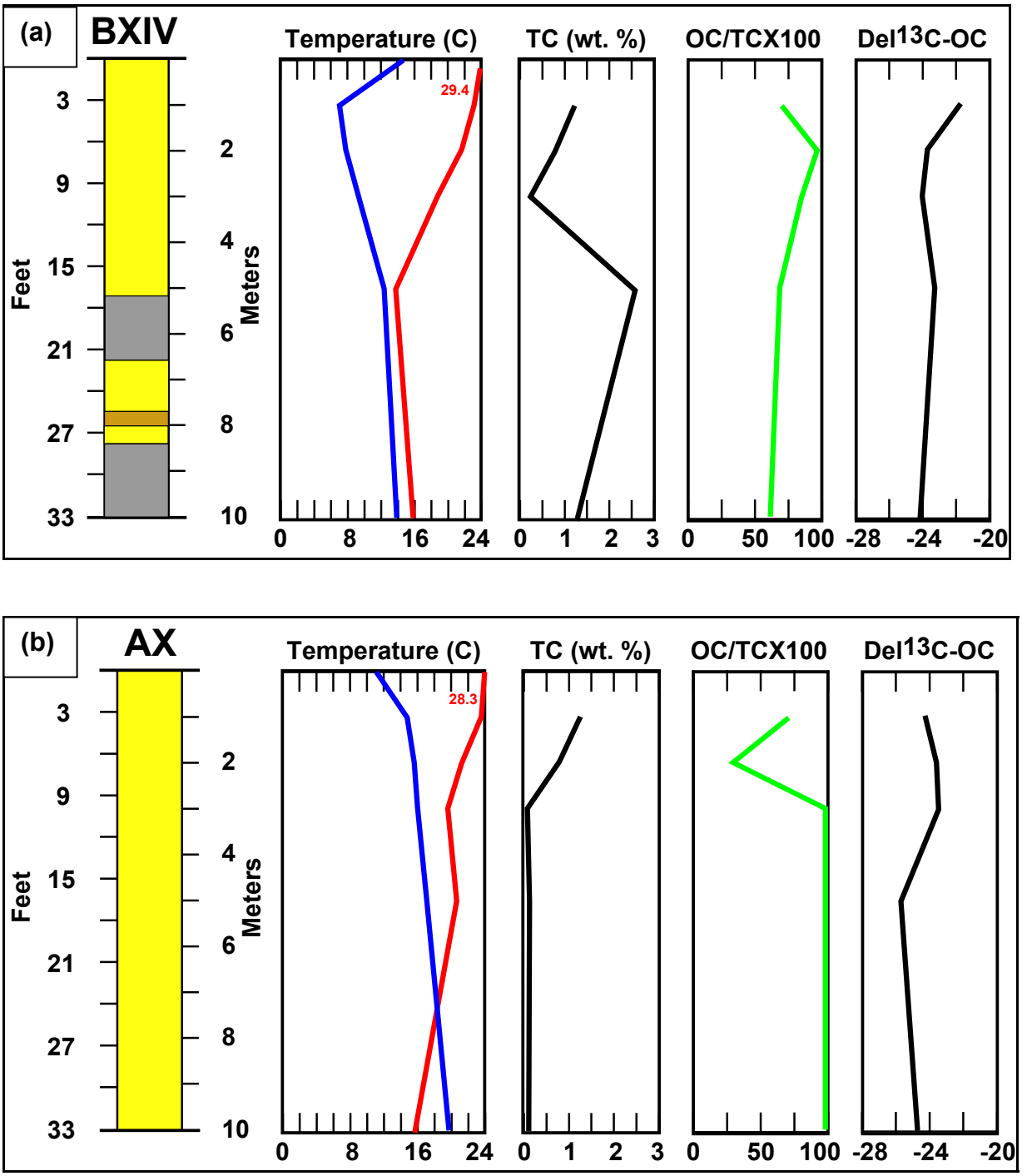

Figure 20—profiles showing temperature, amount of total carbon (TC), and the proportion of organic carbon (OC) as part of TC, and the $\delta^{13}C$ composition of OC in the reclaimed mine land wells (a) BXIV and (b) AX.

Expanding on the suite of measurements made in the shallow investigations, measurements in the 10 m (33 ft) wells also included the $\delta^{13}C$ composition of CH_4 along with concentrations of ethane and propane. By analyzing the $\delta^{13}C$ composition of CO_2 and CH_4, a more complete assessment can be done on the origin and processes affecting the gas composition of these redox end-members (e.g. Schoell, 1983). Ethane and propane are mostly associated with oil accumulations in natural environments or refined petroleum products. They are not products of biologic activity, and therefore can be used as indicators of potential microseepage or contamination by human activities (e.g. Klusman, 2003a).

Beginning first with data from the undisturbed wells, summer and winter CO_2 concentrations show a relatively uniform increase down to 2 to 3 m (6.6 to 9.9 ft) and summer concentrations are higher than winter (Figure 21). The $\delta^{13}C$ values for CO_2 also become more depleted coincident with the increase in CO_2 concentration. Similar to the shallow measurements in the relatively undisturbed soils, these trends likely represent the mixing of atmospheric CO_2 enriched in ^{13}C with more depleted soil CO_2 derived from microbial and root respiration. The corollary to this observation is that mixing of atmospheric CO_2 with that derived from soil biologic activity extends to a depth of approximately 2 to 3 m (6.6 to 9.9 ft).

Below 2 m (6.6 ft), a variety of factors are inferred to have caused a more complex distribution of CO_2 and CH_4. The winter and summer 2008 sampling periods not only represented different soil and atmospheric temperature conditions, but different soil moisture conditions. Winter samples were collected under wetter conditions as compared to those in summer. The possible influence of wetter soil conditions can be seen, for example, in well BXI where summer CO_2 concentrations at 5 and 10 m (16.5 and 33 ft) are significantly greater than winter CO_2 concentrations. There is little difference between winter and summer temperatures at 5 and 10 m (16.4 and 33 ft), and accordingly the higher summer values might not be attributable to more intense biologic activity. When the 5 and 10 m (16.5 and 33 ft) samples were collected in the winter, the sample tubes went on a slight vacuum indicating obstructed gas flow into the sample zones. It is likely that the zones had low permeability even under dry conditions since siltstone and mudstone were the main rock materials logged in the well.

Permeability may have been further reduced as water saturation increased. Note that CH_4 shows a similar pattern at 10 m (33 ft) in BXI with summer values being significantly greater than those for winter. A similar example may be represented by the 3.8 m (12.5 ft) sample in well AX (Figure 21b). Thus it appears that high water saturation in low permeability soils or rocks might hinder the ability to physically sample gases and obtain data that accurately represent gas composition.

For the most part, concentrations of CH_4 at all sample depths in wells BXI and RIII are close to atmospheric values suggesting that CH_4 in the pore space of the surrounding soil and rock may be residual atmospheric CH_4. This inference is supported by $\delta^{13}C$-CH_4 values that are near average atmospheric values (-47.6 to -48.4‰). Exceptions exist in both wells, but the most significant departure occurs at 10 m (33 ft) in BXI, where the summer CH_4 concentration spiked to 12,636 ppmv. The increase was accompanied by a significant enrichment in $\delta^{13}C$-CH_4 to 27‰ and ethane and propane concentrations of 0.16 and 0.36 ppmv, respectively. Collectively, these characteristics suggest that the CH_4 was derived from petroleum (Schoell, 1983). Had a similar anomaly been documented in the winter measurements, then microseepage would have been a possible cause. Since the anomaly occurred only with the summer measurement, it is more likely that it resulted from contamination in the sampling process. Nevertheless, had the area of BXI been under serious consideration for sequestration, it would have been prudent to measure the 10 m (33 ft) interval again.

The preceding example provides some important points regarding the utility of CH_4 as an indicator of microseepage especially when screening an area for sequestration. First, oxidation of CH_4 in the soil zone will typically keep values uniformly low and therefore departures to higher values can be important indicators of microseepage or contamination. Discriminating between these mechanisms is important and can be accomplished by taking repeated samples and viewing the data within a broader context to see if a fault might be responsible for the anomaly or a leaking well bore. In turn, identifying the underlying reason could impact the viability of a sequestration project; that is, leaking well bores can often be fixed whereas fluid migration up a fault cannot.

The two coal beds penetrated by well RIII occur at about 5 and 9 m (16.5 and 29.7 ft), and are approximately 2 and 1 m (6.6 and 3.3 ft) thick, respectively (Figure 18). Profiles of CO_2 and CH_4 in the well show that the coals have likely influenced the distribution of these gases (Figure 21b). This influence is especially evident with the winter measurements in which the highest CO_2 concentrations (winter= 59,882 ppmv; summer= 72,540 ppmv) coincide with the coal at 5 m (16.5 ft) and CH_4 concentrations (winter= 0.56 ppmv; summer= 0.42 ppmv) are below atmospheric values (Table 1). This contrast in concentrations is somewhat surprising since the coals would be expected to be a principal source of CH_4. The coal at 9 m (29.7 ft) shows similar relative concentrations of CO_2 and CH_4, although not of the same magnitude.

The high concentration of CO_2 in the coals along with CH_4 concentrations at or below atmospheric values suggests that CH_4 generated in the coals has been lost possibly through desorption potentially coupled to adsorption of CO_2. Such adsorption-desorption processes have been documented in coals and the process is the basis for trying to recover additional CH_4 from coal beds as part of a CO_2 enhanced gas recovery process. Evidence for desorption might be provided in the isotopic measurements. Specifically, the $\delta^{13}C$ values for CH_4 in the 5 m (16.5 ft) coal are enriched by approximately 2‰ (winter= -45.8‰, summer= -45.2‰) relative to atmospheric values (-47.1‰). Enrichment might reflect diffusion of CH_4 rich in ^{12}C out of the coal leaving the residual CH_4 enriched in ^{13}C. Alternatively, oxidation of CH_4 could also leave the residual CH_4 enriched in ^{13}C (Whiticar, 1999; Hoefs, 2004). The opposite trend showing depletion in ^{13}C in CO_2 would be expected if it were being adsorbed from the surrounding soil and rock zone. Depletion is not observed, however, and indeed the $\delta^{13}C$-CO_2 values are slightly enriched (-22 to -23.3‰) with respect to organic carbon (-24.4‰). The absence of depletion might indicate that most CO_2 in the coal is being generated by local methanotrophic activity in the coal where it is adsorbed onto the surfaces of organic matter. Consequently, there is little diffusion transport from the site of generation to the site of adsorption and therefore little kinetic isotope effect (Hoefs, 2004).

At 3.8 m (12.5 ft) and 6.5 m (21.3 ft) in well RIII the CO_2 concentrations decrease to near atmospheric values and the $\delta^{13}C$-CO_2 values are enriched to values of about -

15‰ (Figure 21b). The exception to this pattern is the summer measurement at 3.8 m (12.5 ft) in which CO_2 concentration is high (53,442 ppmv) and the $\delta^{13}C$-CO_2 values are depleted (-22.9‰). It is possible that the difference between the summer and winter measurements at 3.8 m (12.5 ft) is related to the seasonal water saturation and permeability effect discussed above. For the other three measurements, however, the shift to more enriched $\delta^{13}C$ values suggests that some CO_2 was derived from carbonate carbon.

The CO_2 concentrations in the reclaimed mine land wells show a wide range of values that are higher than those for the undisturbed wells (Figure 22). For example, the highest and lowest CO_2 concentrations measured in the reclaimed mine land wells are 160,695 and 1,107 ppmv, respectively, whereas for the undisturbed wells those values are 72,540 and 448 ppmv, respectively. On the contrary, winter measurements at 1 to 3 m (3.3 to 9.9 ft) in well AX and the summer 10 m (33 ft) measurement in the same well were closer to atmospheric CO_2 values (Figure 22b). Other measurements from these same intervals, such as CH_4 concentration and the $\delta^{13}C$ values for CO_2 and CH_4, were also near atmospheric values suggesting the samples were contaminated with atmosphere. The reasons for contamination are discussed below.

What really distinguishes CO_2 in the reclaimed mine land wells from that in the undisturbed wells are $\delta^{13}C$-CO_2 values that are significantly more enriched in the former versus the latter (Figures 21 and 22). For example, samples in the upper 3 m of BXIV and RIII have $\delta^{13}C$-CO_2 values on the order of -14.5 to -2.6‰, whereas in BXI and RIII the values range from -23.3 to -14.8‰. As with the shallow soil gas measurements, the enriched $\delta^{13}C$-CO_2 values in the reclaimed mine land wells is interpreted to reflect CO_2 that is derived, at least in part, from carbonate carbon. With depth, the $\delta^{13}C$-CO_2 values generally become more depleted in the reclaimed mine land wells. The cause for the depletion trend with depth is not clear, but it could signal input of biologically derived CO_2 from undisturbed rock below the depth of the reclaimed mine material.

Like CO_2, the concentration of CH_4 is variable in the reclaimed mine land wells and concentrations are much higher—up to 7,454 ppmv!—than wells in the undisturbed settings (Figures 21 and 22). The $\delta^{13}C$-CH_4 values in the reclaimed mine land wells are also variable and this is especially true of well BXIV. Samples from the upper 3 m (9.9

ft) in BXIV have $\delta^{13}C$-CH_4 values on the order of -20 to -34‰ and represent the most isotopically enriched CH_4 samples measured in this study. The magnitude of enrichment suggests that the CH_4 was derived from a petroleum source (Schoell, 1983). In contrast, the 5 m (16.5 ft) sample is isotopically depleted and has a $\delta^{13}C$-CH_4 value equal to -62‰. Depleted values similar to this are interpreted to represent CH_4 derived from a biogenic source (Whiticar, 1996).

In addition to having anomalous $\delta^{13}C$-CH_4 values, well BXIV also has ethane and propane concentrations that exceed 1 ppmv in all sample intervals. The highest measured concentrations were 8.9 ppmv for ethane and 10.0 ppmv for propane at 2 m (6.6 ft). Collectively, these geochemical characteristics strongly point to a petroleum source for CH_4 in BXIV. What is not known, however, is whether the anomalies result from microseepage from the underlying Lockport Dolomite oil reservoir or contamination from human activities related to development of the oil field. Microseepage could occur along faults, of which none are documented in the immediate area, or along a leaky wellbore. Although well BXIV is located approximately 122 m (400 ft) from the nearest producing oil wells, the large number of nearby wells suggests that leakage along a wellbore(s) should be given careful consideration. Alternatively, given the traffic in the area due to oil exploitation activity, the anomalies could have been caused by surface contamination that seeped downward.

By comparison, well AX does not show the magnitude or the diversity of geochemical anomalies as shown in BXIV. This is somewhat surprising since the area near AX showed anomalies as part of the shallow soil gas investigations (see winter and summer 2006 reclaimed mine land results in Figures 12-14). We previously discussed the likely atmospheric contamination of winter samples collected at 1 to 3 m (3.3 to 9.9 ft), and it is possible that operator error is responsible for contamination. An alternative mechanism, however, may be responsible for contamination and the lack of anomalies; namely the manner in which the well was drilled. All of the wells were drilled with air, but well AX was drilled with an air hammer bit, whereas the other wells were drilled with an air rotary bit. The air hammer bit produces more percussion during drilling as compared to the air rotary bit. Thus, it is possible that drilling with an air hammer disrupted the otherwise low permeability reclaimed mine material in the near wellbore

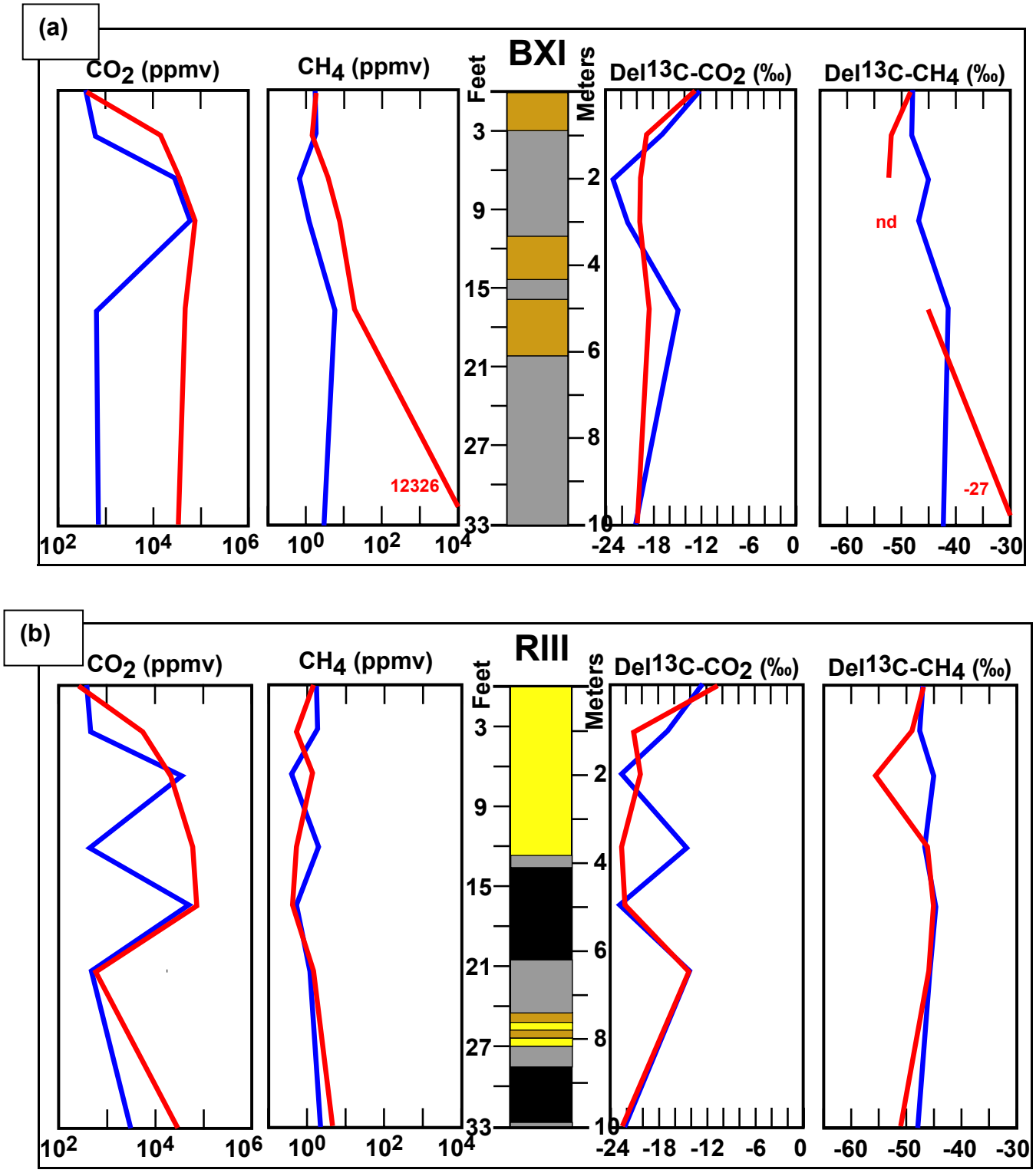

Figure 21—profiles showing the CO2 and CH4 concentrations and the $\delta^{13}C$ composition of these gases in the undisturbed wells (a) BXI and (b) RIII.

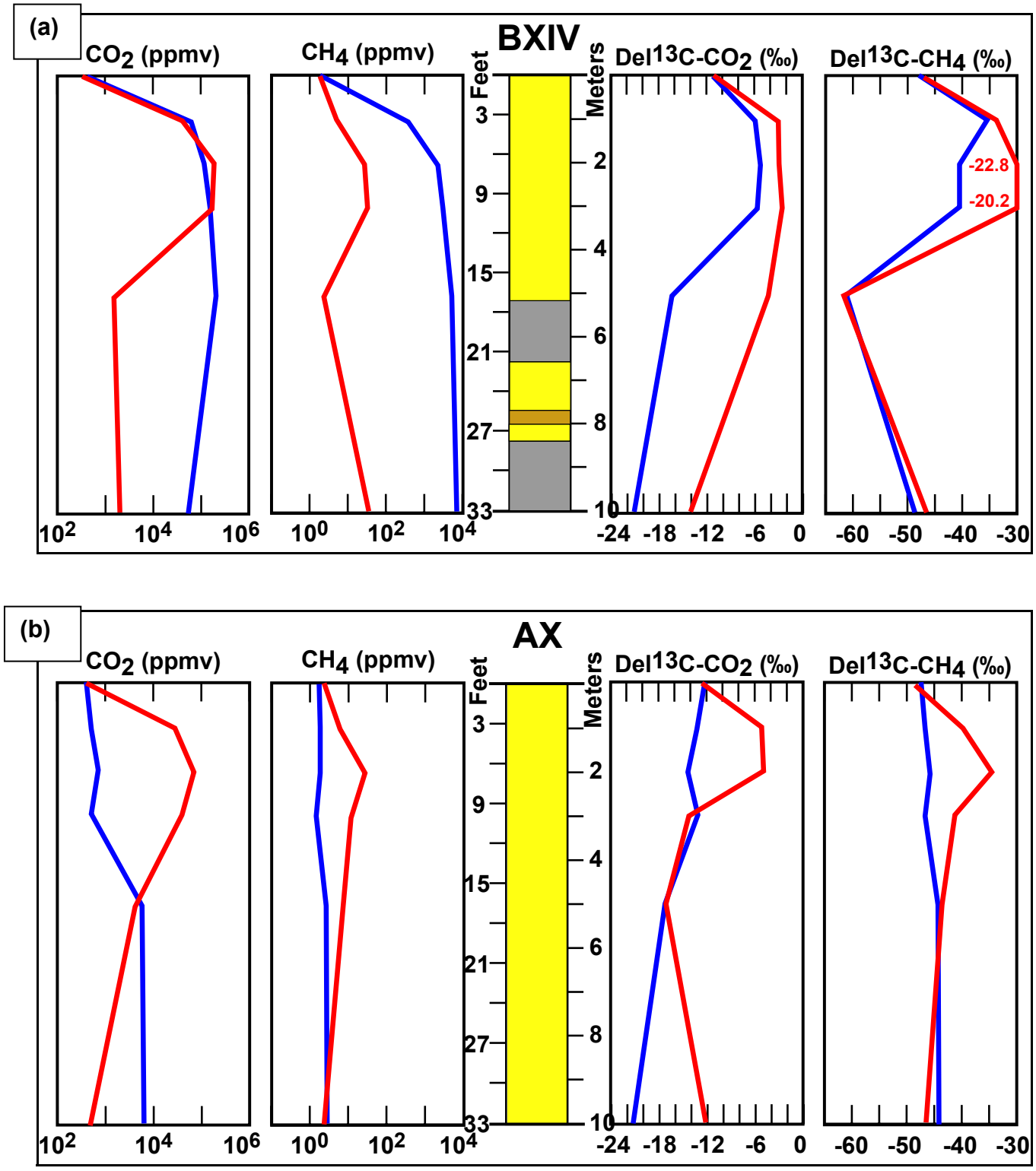

Figure 22—profiles showing the CO2 and CH4 concentrations and the $\delta^{13}C$ composition of these gases in the reclaimed mine land wells (a) BXIV and (b) AX.

area allowing atmospheric gas to infiltrate it. This infiltration would explain why so many of the winter measurements, especially at 3 m (9.9 ft) and shallower, had values indicating a dominantly atmospheric component. It is notable that the later summer measurements showed some anomalous characteristics, such as elevated CH_4 concentrations and enriched $\delta^{13}C$ values for CO_2 and CH_4. The shift to more anomalous characteristics might represent the purging of atmospheric gas in the near wellbore area that was subsequently replaced with indigenous gas.

Notwithstanding the issues associated with well AX, results from it and well BXIV underscore important points about the properties of reclaimed mine lands within the context of monitoring geologic sequestration projects. First, anomalies described in the shallow soil gas measurements that are false indicators of microseepage do persist at depth in the reclaimed mine lands. These anomalies include enriched $\delta^{13}C$-CO_2 values, elevated soil gas CH_4 concentrations, and the presence of ethane and propane. Geochemically, these anomalies will complicate efforts to resolve true microseepage on a pre-injection basis for a sequestration project.

The second important point regards the apparent low permeability of reclaimed mine lands. The presence of ethane and propane suggests that little atmospheric oxygen is able to infiltrate the reclaimed mine land material and oxidize these gases. Along with the previously documented high CO_2 and CH_4 concentrations, the persistence of ethane and propane reinforces the observation that low permeability in the reclaimed mine lands restricts impedes gas migration. The lack of vertical migration and attendant mixing of gases is further supported by measurements in well BXIV where CH_4, having different origins based on $\delta^{13}C$ values, is juxtaposed over short intervals on the order of meters. This lack of permeability is critical for shallow soil gas monitoring because surface detection of microseepage from a deeper reservoir depends on a relatively unimpeded path from the reservoir to the surface. The compacted and relatively impermeably reclaimed mine lands would thus act as a surface barrier to CO_2 migrating upward.

Spatial Considerations

As documented in the previous sections, the anomalous soil gas chemistry associated with the reclaimed mine lands has the potential to obscure detection of microseepage, which, in turn, would diminish the efficacy of soil gas chemistry as a MVA tool in basins where past and present coal mining might occur in close proximity to CO_2-EOR sequestration and aquifer sequestration. Given this potential difficulty it is clear that understanding the spatial distribution of reclaimed mine lands in areas of possible sequestration projects is important. In settings such as the Ario study site that is adjacent to a large and aerially extensive strip mine, the distribution of of reclaimed mine areas is obvious (e.g. Figure 4). In other areas, however, the presence of reclaimed mine lands might not be obvious. The Big Andy study site, where well BXIV is located, provides such as example. A high resolution aerial photograph provides a view of forested areas, open pasture, and a high density of oil wells (Figure 5). However, it is not until an Arc-GIS map containing polygons representing old mine and reclaimed mine areas that the close proximity of past mining activity within the oil field becomes obvious (Figure 23).

Similar GIS analysis by author Takacs was used to analyze how frequently and over what area polygons representing oil and gas pools intersect mine area polygons. The analysis showed that up to 20% of Kentucky's most prospective oil and gas fields for CO_2-EOR sequestration have or had mining activity within the field boundaries. These include presently active projects at Sugar Creek field (Hopkins County) and Euterpe (Henderson County). Notably, 18% of the area submitted by Kentucky for the FutureGen project contained reclaimed mine lands or other impacts from strip mining. To date, our GIS analysis has only looked at oil and gas fields, but the area for saline aquifer sequestration would be larger and presumably contain more reclaimed mine lands.

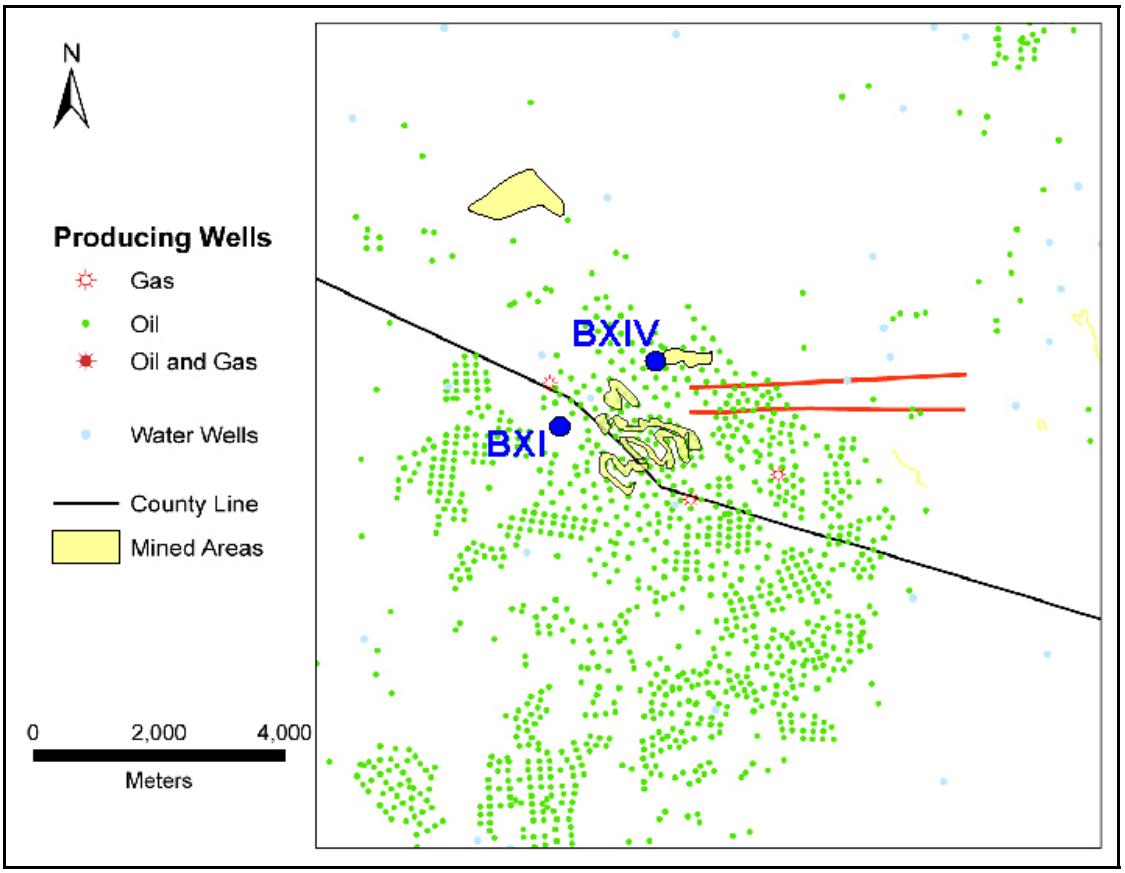

Figure 23—Big Andy site with an ArcGIS overlay showing reclaimed mine areas (yellow shaded polygons) in close proximity to oil wells.

CONCLUSIONS

This analysis of the bulk and isotopic chemistry of soil gases in the Appalachian basin of eastern Kentucky provides a heretofore absent database that can be used as a reference baseline in geologic sequestration projects. More specifically, the analysis provides data regarding the concentration of CO_2 and CH_4 and the $\delta^{13}C$ composition of CO_2 down to a depth of 1 m (3.3 ft) under summer and winter conditions. In an effort to investigate the variation in soil gas chemistry among different physiographic and geologic settings with different levels of human disturbance, measurements were conducted at 25 locations in a relatively undisturbed research forest, moderately disturbed active oil and gas fields, and heavily disturbed coal strip mine areas.

Little, if any, difference was observed in the soil gas chemistry between the relatively undisturbed and moderately disturbed settings. In these settings soil gas CO_2 concentrations were 1 to 2 orders of magnitude greater than atmospheric values, and winter values on the order of 10^3 ppmv were consistently less than those for summer that ranged up to 10^4 to 10^5 ppmv. The $\delta^{13}C$ values for CO_2 in most of the soil gas samples were slightly enriched by 1 to 2‰ with respect to bulk organic carbon (-23.8±1.5‰). The similarity suggests that most soil gas CO_2 was derived from microbial and/or inorganic oxidation of the soil organic matter and root respiration. Atmospheric CO_2, which is more enriched in ^{13}C, also influenced soil gas CO_2 although to a lesser degree. Soil gas CH_4 concentrations, in contrast, were on the order of 10^{-1} to 10^0 ppmv and slightly less than atmospheric. The low concentration of soil gas CH_4 likely reflects an oxidation rate that outpaces the rate at which CH_4 is able to diffuse into the soil.

Relative differences in gas concentration between the atmosphere and soil zone provide one of the main influences driving flux direction and magnitude. Fluxes for CO_2 were positive at all locations and displayed a wide range of values. In accordance with the seasonal variation documented in the soil gas concentrations, summer fluxes were 3 to 4X greater than those in winter, but the latter showed less variation in magnitude with 56% of measurements ranging from 1 to 2 μmoles/m^2/sec. By contrast, 85% of CH_4 fluxes were negative and low magnitude with summer values being slightly higher than winter.

The measurements in the relatively undisturbed soil settings provide insight into the utility of soil gas measurements as a MVA tool in a sequestration project. First, the wide range and large magnitude of CO_2 soil gas concentrations and fluxes suggest that they will likely not have sufficient resolution to detect microseepage. The exception to this might be with winter measurements when cooler weather and soil conditions diminish the biologic output of CO_2. Measurement of $\delta^{13}C$-CO_2 values would appear to be more prospective as a detector of microseepage. This is because much of the soil gas CO_2 has depleted $\delta^{13}C$ values near the values for organic carbon with a possible small contribution from isotopically enriched atmospheric CO_2. Consequently, CO_2 microseepage having a different $\delta^{13}C$ value should be readily detected as a shift away from a mixing line between organic carbon and atmospheric CO_2. Measurements of soil

gas CH_4 concentrations and fluxes would also appear to have significant utility as detectors of microseepage. For example, soil gas CH_4 concentrations greater than atmospheric and/or positive fluxes would constitute an anomaly with regard to “normal” conditions in an oxidized soil setting. Having recognized the CH_4 anomaly, however, the challenge would be to discriminate between microseepage and contamination from human activities. Context and repeated measurements would be the best opportunity to resolve the underlying mechanism.

The soil gas chemistry of reclaimed mine land material represented a significant contrast to the measurements in the relatively undisturbed settings. In the former, concentrations of soil gas CO_2 (up to 297,456 ppmv) and CH_4 (up to 1,007 ppmv) were higher for all seasons and more variable, and $\delta^{13}C$-CO_2 values were significantly more enriched. Unlike the inferred strong biologic influence on CO_2 in the relatively undisturbed soils, CO_2 in the reclaimed mine lands appears to have been derived primarily from reactions with isotopically enriched carbonate carbon (avg.= -0.9±2.9‰). The carbonate likely resided as intergranular cement in sandstone clasts that were part of the reclaimed mine material.

Despite having higher soil gas CO_2 concentrations than in the undisturbed soils, CO_2 fluxes in the reclaimed mine lands were actually lower. Moreover, even with soil gas CH_4 concentrations that were consistently higher than atmospheric values, it was only during the summer that positive CH_4 fluxes were measured in the reclaimed mine lands. The apparent contradiction between high soil gas concentrations and low fluxes likely results from the mine reclamation process in which coal fragments and other materials, including carbonate cemented sandstone, are incorporated into a heterogeneous mixture of poorly-sorted materials that is heavily compacted. The material is compacted to minimize erosion, but soil permeability is also reduced and gas concentrations consequently build to high concentrations. Low permeability also reduces the ability of gas to diffuse to the atmosphere, hence the low fluxes.

In order to sample below the shallow zone of dominant biologic influence, four 10 m (33 ft) soil gas wells were drilled and configured so that soil gases could be sampled and temperatures measured at discrete intervals without contamination from over- and underlying soil and strata. Gas measurements in the wells included those done in the

shallow investigations and the $\delta^{13}C$ composition of CH_4, and concentrations of ethane and propane. Two wells were located in relatively undisturbed soil zone settings, one of which intersected two coal beds whereas the other did not. Analysis of gases in the well containing the coals shows that the shallowest coal at approximately 5 m (16.5 ft) contained the highest CO_2 and lowest CH_4 concentrations in the well. The lowermost coal also contained high CO_2 and low CH_4, but not of the same magnitude. The distribution of gases suggests that the coals have desorbed CH_4 and adsorbed CO_2. If desorbed coals in the vadose zone adsorb CO_2, then CO_2 microseepage to the surface from a deeper reservoir would be diminished. From a MVA perspective, this would increase the difficulty in resolving a potentially subtle microseepage signal. Thus, if coals are interpreted to be possible sinks for CO_2 in the near-surface environment, then gas monitoring might need to be conducted below the depth of the coals.

Two of the 10 m (33 ft) wells located in the reclaimed mine lands confirmed that the anomalies documented in the shallow soil gas measurements extended to depth. One of the wells showed a remarkable variation in the $\delta^{13}C$-CH_4 values of with enriched values of -20 to -35‰ in the upper 3 m (9.9 ft) overlying a depleted value of -62‰ at 5 m (16.5 ft). This well also contained anomalous amounts of ethane (8.9 ppmv) and propane (10.1 ppmv).

From a MVA standpoint, the soil gas anomalies associated with the reclaimed mine locations are significant for two reasons. First, similar anomalies have been used elsewhere as evidence for microseepage in oil and gas fields, some of which have undergone CO_2 enhanced oil recovery. Here, however, the anomalies originate not from microseepage from a deeper oil or gas reservoir, but rather from the mine reclamation process described above. Therefore, the reclaimed mine site anomalies are false indicators of microseepage, and, as such, potentially hinder the ability to resolve a true microseepage.

The second important point regards the apparent low permeability of reclaimed mine lands. The presence of unoxidized ethane and propane, and high CO_2 and CH_4 concentrations all suggest that gas migration into or out of the reclaimed mine land material is highly restricted. Lack of vertical migration and attendant mixing of gases is further supported by $\delta^{13}C$ measurements where CH_4 having apparent different origins

are juxtaposed over short intervals on the order of meters. The reclaimed mine lands thus represent a low permeability surface layer that will act as a barrier to CO_2 migrating upward. This barrier will hinder shallow soil gas monitoring because surface detection of microseepage from a deeper reservoir depends on a relatively unimpeded path from the reservoir to the surface. Circumventing the potential challenge presented by the reclaimed mine lands will require that the investigator be cognizant of their spatial distribution and depth. In many cases the dramatic change in vegetation between relatively undisturbed lands and reclaimed mine lands will be apparent, however, this will not always be the case and it will be necessary to check with the state organization overseeing mine operations to see if ArcGIS or other information is available. Successful deployment of soil gas measurements in the area of reclaimed mine lands will also require that the depth of investigation be sufficiently deep to obtain measurements below the influence of the reclaimed mine material. In areas where the reclaimed mine material is located just above the water table, then soil gas measurements might not be possible.

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