Process-based soil gas leakage assessment at the Kerr Farm: comparison of results to leakage proxies at ZERT and Mt. Etna

by

Katherine Romanak, Brad Wolaver, Changbing Yang, George William Sherk, Janis Dale, Laura Dobeck,
Lee Spangler

Corresponding author Katherine Romanak, Research Associate, Gulf Coast Carbon Center, Bureau of Economic Geology, The University of Texas at Austin, Austin, Texas. katherine.romanak@beg.utexas.edu.

Key words; carbon storage, soil gas, monitoring, CO₂ sequestration, process-based, Kerr, ZERT, Weyburn

ABSTRACT

Claims of CO₂ leakage at the Kerr farm near the IEAGHG Weyburn-Midale CO₂ Monitoring and Storage project in Saskatchewan, Canada in 2011 presented an opportunity to test years of research in near-surface leakage detection in an operational setting. The claim was based on a study conducted by a private consultant that drew criticism from geologic CO₂ storage experts. To assess the origin of the claimed leakage, a soil gas assessment was conducted at the site using a relatively new process-based soil gas approach (Romanak et al., 2012). In order to assess leakage without years of background data or complex statistical analyses, this simple approach uses three fixed soil gas ratios (augmented by isotopic and hydrocarbon data when needed). Using this approach at the Kerr site, the relative contributions of various processes creating soil gas geochemical signatures were determined including: 1) biologic respiration, 2) CH₄ oxidation, 3) CO₂ dissolution/reaction with carbonate, 4) mixing with atmosphere, and 5) CO₂ leakage from the storage reservoir. For additional verification, the results of the Kerr assessment were compared to new data collected at the ZERT controlled release site in Bozeman, Montana and published data from a leakage proxy at the Mt. Etna volcano, Italy. The results from the Kerr site show no evidence for CO₂ leakage from the storage reservoir and also verify that a process-based approach can be used to quickly and economically assess leakage above geologic carbon storage sites. In addition, data from the ZERT release suggest quantification of a leakage signal apart from natural processes may be most easily accomplished using a process-based approach.

1. Introduction

Near-surface leakage assessment at geologic carbon storage sites is important for ensuring environmental safety, responding to public concerns, and accurately determining and/or quantifying potential release to atmosphere under carbon accounting regimes. Discriminating between natural variation and a leakage signal in the near-surface is a complex task and requires great care due to the many dynamic processes that can produce, consume, or otherwise alter soil gas in the vadose zone (e.g. Yang et al., 2013a,b). The complexity of near-surface leakage assessment increases significantly in CO₂-enhanced oil recovery settings where the presence of hydrocarbon gases and industrial activities add geochemical complexity (e.g. Wolaver et al., 2013). In the near surface, CO₂ and CH₄ may originate from biologic respiration, degradation of spills from historic industrial activity, or from gases migrating from depth. Gases migrating from depth may emanate from the CO₂ storage reservoir or other geologic zones by seepage over geologic time, historic well failures, or reservoir engineering activities. Hydrocarbons that migrate from depth to surface may readily oxidize to CO₂ in the vadose zone, mimicking a storage formation leak. Soil gas assessments in areas lacking background data are especially vulnerable to misinterpretation and, if not properly assessed, could lead to mistaking a natural CO₂ occurrence for a leakage signal.

The need for accurate leakage assessment was demonstrated in January 2011, when landowners living near the International Energy Agency Greenhouse Gas (IEAGHG) Weyburn-Midale CO₂ Monitoring and Storage Project (WMP) in Saskatchewan Canada (Fig. 1) announced to the press that leaking CO₂ from the storage reservoir was reaching ground surface and impacting their farmland. The WMP site is a CO₂-enhanced oil recovery operation where approximately 50% of injected CO₂ is naturally sequestered, thus making the site suitable for studying geologic carbon storage. Reported impacts were generally located in and around excavated gravel pit ponds in the NE portion of the Kerr family's quarter section. The Kerrs reported what they perceived as unusual bubbling, foaming, algal growths, and an "oily sheen" on the pond surface and dead animals in and around the ponds. In the summer of 2010, the Kerrs commissioned Petro-Find Geochem Ltd to conduct a soil gas study on the property (LaFleur, 2010), with another survey conducted in the winter of 2011 (LaFleur, 2011). Soil gas CO₂ concentrations measured on the property in the summer averaged approximately 2.3% with a soil gas anomaly of about 11% measured in the north portion of the property (Fig. 2). Petro-Find attributed the origin of the soil gas anomaly to injectate CO₂ based mostly on measured stable carbon isotope ratios ($\delta^{13}\text{C}$) of soil gas between -21.6 to -22.9 ‰, which was similar to the -20.4 +/- 0.4 ‰ value of the CO₂ injected into the Weyburn EOR reservoir, thus concluding: "the source of the high concentrations of CO₂ in soils of the Kerr property is clearly the anthropogenic CO₂ injected into the Weyburn reservoir" (LaFleur, 2010, 2011).

News of the supposed leaking carbon storage project flooded the media; however, experts in geologic CO₂ storage strongly questioned the scientific merit of the Petro-Find study (e.g. Petroleum Technology Research Centre, 2011). To address the mounting uncertainty over whether CO₂ leakage was actually occurring, three expert studies were independently undertaken by: 1) European scientists who had conducted 10 years of near-surface monitoring at the nearby WMP (Beaubien et al., 2013), 2) experts commissioned by Cenovus, the oilfield operator (Trium, 2011), and 3) academic researchers commissioned by the International Performance Assessment Centre for Geologic Storage of Carbon Dioxide (IPAC-CO₂), an agency whose mission was to advance best practices and performance verification for geologic carbon storage. This paper describes a subset of the IPAC-CO₂ study and how the use of a process-based soil gas approach quickly and economically determined that leakage was not occurring at the site.

2. Objectives and Approach

The primary objective of the IPAC-CO₂ field study was to reduce the uncertainty regarding the origin of CO₂ measured on the Kerr property. The study was a focused response to the soil gas surveys conducted by Petro-Find and was intended to be a targeted and timely response to landowner concerns with a conservative yet rigorous approach. The aim of the study was to assess the degree to which the gases present in the soil on the Kerr property were: 1) the result of natural (biological or geological) variability, 2) the result of leaks or spills associated with oil producing activities on the site, and/or 3) associated with CO₂ leakage from the CO₂-enhanced oil recovery in the underlying Weyburn-Midale reservoir. Study objectives concentrated on two broad focus areas which represent the foundations of a process-based approach to near-surface leakage assessment:

1. Determine whether gases originating in the deep subsurface have migrated to the near-surface: Evidence of deep gases in the near-surface indicates a potential avenue of gas transport from the reservoir but is not proof in itself that injectate CO₂ has migrated to the surface. Seepage from several intermediate hydrocarbon-bearing reservoirs and/or seepage of deep accumulations of CO₂ that exist in the subsurface beneath the study area were plausible.
2. Identify major in-situ processes active in the vadose-zone: Knowledge of carbon cycling processes is critical to correctly assessing the origin of soil gases and understanding the potential transformations that may have occurred since their formation.

The IPAC-CO₂ investigation comprised of three distinct activities undertaken on the Kerr property and surrounding area; (i) chemical analysis of soil gases, (ii) noble gas and C isotope analysis of the shallow groundwaters, (iii) hydrogeological analysis. The use of a process-based analysis of fixed soil gases (CO₂, N₂, O₂, CH₄) to meet the study objectives for (i) is discussed herein. To ensure the accuracy of observations and conclusions of the near-surface investigation, soil gas geochemical relationships observed at the Kerr Farm were compared to those observed at two leakage proxy sites; 1) the Zero Emission Research and Technology Center (ZERT) site where soil gas measurements were made under a controlled leakage scenario; and, 2) Mt. Etna volcano where volcanic gases migrate from depth to the surface. Comparing the geochemical ratios observed at the Kerr site with ratios from CO₂ leakage proxy sites is important for verifying the presence or absence of an actual leakage signal at the Kerr Farm.

3. Background

3.1 Leakage Proxy Comparison

The process-based method of soil gas analysis was first developed at a CO₂-rich perched wetland (a feature known as a “playa lake”) in West Texas, USA. Here, a high level of in-situ biologic gas production, dissolution of CO₂ into recharging groundwater and CH₄ oxidation could be systematically observed and coupled with characteristic geochemical ratios for each natural process (Romanak, 1987; Romanak et. al., 2012). No CO₂ leakage input from depth was present at the playa lake; therefore, soil gas ratios that would represent leakage could only be conceptualized. Additional verification of these concepts was achieved at a Gulf Coast oilfield where a process-based method successfully identified exogenous (i.e., originating from the reservoir) CH₄ in shallow sediments near a 1950s plugged and abandoned well (Romanak et. al., 2012). Pre-injection at the oilfield, isotopic analysis of gases indicated that CH₄ measured in the vadose zone originated within an oil and gas reservoir at depth, and that shallow CO₂ was produced from CH₄ oxidation. This proxy gives an idea of how process-based geochemical ratios can be used to identify exogenous CH₄ input from depth and the secondary CO₂ signal created by methane oxidation, but is not a straightforward example of a primary CO₂ leakage signal.

Therefore, to gain more experience with the simple case of CO₂ leakage input, the process-based analysis at the Kerr farm is compared with: 1) the ZERT field site (Spangler et al., 2010) where leakage of CO₂ into the near-surface is experimentally simulated; and, 2) a process-based analysis of data published in the literature and collected at Mt. Etna volcano where magmatic CO₂ migrates from depth to surface (Giammanco et al., 1998). Through an integration of these case studies, the process-based method not

only is used to assess leakage at the Kerr site but also is proven as a tool for quick and economical response to landowner claims of leakage near geologic carbon storage sites.

3.1.1 ZERT Site

The results from the Kerr Farm are compared to new research results from a controlled release experiment at the ZERT site where a leakage signal was artificially induced in the near-surface and monitored using a process-based approach (Romanak et al., 2013). The ZERT location provides a simple environment in which to observe the geochemical signature of CO₂ leakage input without the complexity of co-existing hydrocarbons. The experimental field site is located in the Gallatin Valley about 700 km SW of the Kerr Farm on agricultural land owned by Montana State University in Bozeman, Montana (Fig. 1) (Spangler et al., 2010). Locally at the test site, as much as 1.2 m of organic-rich silt and clay is underlain by silicic sandy gravel with a caliche layer at 0.5 to 0.8 m depth (Kharaka et al., 2010; Spangler, 2010). To simulate leakage, CO₂ at the site was released from a 100-m-long, 10-cm-diameter slotted pipe installed at ~1.8 m depth within a silicic sand-gravel aquifer with a trace of carbonates (Kharaka et al., 2010). The fixed gas relationships monitored at three locations during the CO₂ release provide a controlled proxy for CO₂ leakage into the near-surface (Fig. 3).

3.1.2 Mt. Etna Volcano

Despite differences in some conditions such as biologic activity, temperature and CO₂ flux rates, volcanic regions can serve as a general proxy for CO₂ leakage and can illustrate the general geochemical relationships expected if CO₂ were to invade the near surface from depth. The concept of using volcanic gas emissions as a proxy for a storage formation leak has been used by others (e.g. Jones et al., 2003; Beaubien et al., 2004; Riding and Rochelle, 2005). In our study, we present a process-based analysis of published soil gas data from Mt. Etna as a comparative example (Giammanco et al., 1998). Mt Etna, one of the most active stratovolcanoes in the world is located in eastern Sicily, Italy. Here, all gases of interest for a process-based analysis were measured from crater fumaroles that appear to be related to fractures and from soils on the volcano's flanks with more diffuse volcanic gas input compared to fumaroles (Giammanco et al., 1998).

3.2 Regional and Local Geologic Setting at the Kerr Site

The Weyburn-Midale field, located in southeastern Saskatchewan, Canada produces from within Ordovician, Devonian and Mississippian rocks (Saskatchewan Geological Survey, 2003). The carbonate

beds of the Madison Group including the Charles Formation at a depth of about 1500 m are particularly important in this area (Saskatchewan Ministry of Energy & Resources (SER), 2011). In addition to the numerous oil and gas bearing formations found beneath the Weyburn-Midale production zone, at least two Triassic-Jurassic oil-bearing units and two Upper Cretaceous-Tertiary lignite-bearing units also exist (SER, 2011). Natural accumulations of magmatic CO₂ are documented in Devonian and Cambrian formations in southwestern Saskatchewan (Whitaker et al., 2004) and may possibly be present beneath the Kerr property. Gases from any of these formations could potentially migrate to the surface over geologic time.

Regional Cenozoic stratigraphy of the Weyburn Valley, Saskatchewan, Canada is glacial-fluvial drift approximately 175 meters thick deposited unconformably upon the Cretaceous Pierre Shale (Simpson, 1993). Sequential cycles of glacial advance and retreat resulted in erosion and deposition of a highly heterogeneous, interbedded glacial-fluvial sedimentary section comprised of stratified and interbedded clays, silts, sands, and gravels. The complex stratigraphic heterogeneity causes disconnected sand and gravel-rich lenses. At the Kerr Farm (SW Section 30, Township 5, Range 13, W2M) near-surface sediments include approximately 60 m of interbedded glacial-fluvial clay, silt, sand, gravel, pebbles, and boulders (Simpson, 1993; Aqua Terre, 2006). Surface water is found in several gravel excavation pits at the site and in a 200-m-long, northeast-southwest trending slough located approximately 75 m to the northwest of the Kerr residence.

3.3 Process-based Leakage Detection Method

A process-based soil-gas approach is a direct, fast and economical way to assess near-surface leakage and to determine if environmental impacts arise from a storage formation leak or from natural variation. This method first aims to identify whether deep gas (either CH₄ or CO₂) has invaded the shallow subsurface (i.e. the vadose zone) or if gas has been produced and/or altered in the shallow subsurface. Examples of vadose zone processes influencing soil gas concentrations of CO₂ in the shallow subsurface include: 1) near-surface microbial and root respiration; 2) CO₂ dissolution and reaction with soil carbonate; 3) oxidation of CH₄ that is either biologically produced or originates from depth; 4) atmospheric mixing/dilution; and, 5) leakage of CO₂ from a storage reservoir into the near-surface.

The conceptual approach is based on the use of three geochemical relationships to characterize vadose zone processes that affect the composition and isotopic signature of soil gases and to indicate whether an active pathway of gas migration from depth to the surface exists (Fig. 4). Once these processes are

understood, the dominant sources of soil gases can be determined with reasonable certainty even in the absence of background data or when naturally occurring in-situ and exogenous gases are mixed.

3.3.1 Fixed gases

The various processes that produce and consume CO₂ have been shown to affect soil gas concentrations of N₂, O₂, and CH₄ in predictable ways (Romanak, 1997; Riding and Rochelle, 2005; Romanak et. al., 2011, 2012). The ratios of, or correlations among, these various gas component concentrations can help identify whether a signal is natural background noise or deep reservoir leakage. Analysis of detailed isotopic signatures and any existing hydrocarbon gases provides increased certainty in the interpretation of results.

Beginning with the composition of the natural atmosphere (78% N₂, 21% O₂, 0.0385% CO₂, 1.7-2.0 ppm CH₄), carbon cycling processes in the unsaturated zone will alter the geochemistry of soil gas in predictable ways that can be used to identify the processes involved. The level of certainty is increased by examination of several different relationships in sequence; O₂ versus CO₂, CO₂ versus N₂, and CO₂ versus N₂/O₂ (Fig. 4a). These relationships are described in more detail below.

Biologic respiration utilizes O₂ as the terminal electron acceptor for energy production and produces CO₂ as a by-product according to the reaction:

When the supply of organic matter outpaces that of O₂, anaerobic bacteria utilize alternate electron acceptors (SO₄²⁻, NO₃⁻, Fe³⁺ and oxyhydroxides) when available. In the absence of these electron acceptors, CH₄ is produced. When CH₄ migrates into oxic zones, or environmental change results in an influx of O₂ into a previously anoxic, CH₄-producing environment, CH₄ is oxidized to CO₂ according to the following equation:

These common biologic processes result in predictable deviations from atmospheric concentrations for CO₂ and O₂ along a trend with a slope of -1 for biologic respiration and -2 for methane oxidation (Fig. 4a). Addition of CO₂ such as might be released from a storage formation will create CO₂ concentrations larger than would be expected from corresponding O₂ concentrations based on these relationships.

Alternatively, CO₂ concentrations less than those predicted from O₂ concentrations may signal a loss of CO₂ due to dissolution and reaction with soil carbonate (Romanak, 1997; Romanak et. al, 2012).

Further knowledge of the carbon cycling processes that have occurred, and further certainty in the correct interpretation of measurement results can be gained by studying the relationship of N₂ with CO₂ (Fig. 4b). Because gas concentrations are measured in percent (by volume or molar), any non-reactive addition or subtraction of a gas component will, by definition, dilute or concentrate (respectively) all other gas components in a gas mixture. N₂, a relatively non-reactive but major component in air and soil gas can be used to indicate this process. Used in conjunction with the relationships between CO₂ and O₂ described above, CO₂ that shows a negative correlation with N₂ signals dilution by input of exogenous gas (Riding and Rochelle, 2005) and CO₂ that shows a positive correlation with N₂ indicates dissolution of CO₂ and reaction with soil carbonate (Romanak et. al, 2012). In the case of CO₂ dissolution and reaction with soil carbonate, the resulting loss of pore pressure from loss of a gas component into the aqueous phase may create advection of air (78% N₂) into the pore, enhancing enrichment of N₂ above atmospheric concentrations (Romanak, 1997).

Because N₂ essentially acts as a conservative tracer within the gas mixture, the ratio of N₂/O₂ can be used as a measure of the degree to which O₂ is consumed in the system (Fig. 4c). Ratios above atmospheric (3.7) illustrate that O₂ is being consumed. According to equations 1 and 2, O₂ consumption results from respiration and even more so during CH₄ oxidation; therefore in environments where CH₄ is present, a high N₂/O₂ value can signal the degree to which CH₄ oxidation is occurring. When CH₄ is constantly fluxing from depth into the near-surface, these ratios can become several orders of magnitude larger than atmospheric ratios.

3.3.2 Isotopic Data

Isotopic data provide important information about the origin of CO₂ and CH₄ in soil gas and the processes that gave rise to their formation (Schoell, 1983, 1988; Faber et. al., 1992; Rice, 1993; Whiticar, 1994, 1999). Coupled with analysis of fixed gas ratios and compared to data on higher hydrocarbons (C₂-C₆), analysis of isotopic signatures can provide a high level of certainty in the identification of the origin of CO₂ and CH₄ in soil gas. Carbon isotopes of CO₂ and CH₄ can be compared to distinguish between CO₂ that forms from biologic fermentation and that which forms from oxidation of CH₄. This information is especially important in organic-rich wet environments such as the prairie pothole wetlands of Saskatchewan where environmental factors support a wealth of biologic activity. If fixed gas and isotopic data indicate biologic origin of the CO₂, the likelihood that environmental anomalies are due to CO₂ injection practices is diminished. If methane oxidation is indicated as a major source of CO₂, the source of

methane must be determined as it may be from deep gas migrating from a storage formation or from a shallow biologic source. In either case, it is important to separate primary formation of CO₂ from secondary formation of CO₂ that results from CH₄ oxidation.

The stable isotopes of methane ($\delta^{13}\text{C}$ and δD) can provide information for determining whether methane is biogenic (shallow-sourced) or thermogenic (deep sourced) (Schoell, 1983, 1988; Faber et. al., 1992; Rice, 1993; Whiticar, 1994, 1999). The presence of methane may indicate one or more significant facts regarding the source of CO₂: 1) at least some, if not all CO₂ may be of a secondary origin in that it originates from CH₄ oxidation; and, 2) the presence of thermogenic methane in the near-surface indicates a pathway of migration from depth. Migration may be from the storage reservoir or from intermediate reservoirs and does not necessarily indicate that CO₂ has migrated out of the storage formation. This second outcome presents a scenario where more work would be needed to fingerprint the actual formation from which gas has migrated.

The relationship of $\delta^{13}\text{C}$ of CH₄ with C₁/(C₂+C₃) according to Whiticar (1999) provides additional information that improves the certainty that measured gases are either biologic or thermogenic and also provides information on the potential effects of transport and mixing. The information gained here may indicate from which type of reservoir deep gas migrates; kerogen type II (oil and gas) or kerogen type III (coal), and can, indicate whether gas is likely leaking from the storage reservoir or seeping naturally from an intermediate formation.

3.3.3 Hydrocarbons

Significant difficulty can be encountered when working in an area of petroleum production where a variety of sources of anthropogenic hydrocarbon gases can be confused with natural seeps and/or shallow biologic activity. Anthropogenic sources may include gasoline contamination or fresh or weathered crude oil spills and must be distinguished from natural seeps (Marrin, 1988, 1991; Ostendorff and Hampbell, 1991; Ririe and Sweeney, 1993). For example, soil gas resulting from gasoline spills is high in C₅ and C₆ components relative to lighter hydrocarbons. Crude oil spills tend to be relatively rich in C₃-C₅ components unless weathering has removed the light fractions, decreasing C₂, C₃, and C₄ relative to a fresh crude spill.

Seeps are best identified using C₂+ analyses because of the predictable effects that migration from the reservoir to the near-surface and ensuing oxidation has on hydrocarbon gas concentrations (Klusman, 2003a; 2003b; 2006; 2011). In nearly all oil fields, relative abundances of the alkanes (paraffins) are

generally $C_2H_6 > C_3H_8 > C_4H_{10}$. Differences in migration and oxidation rates among CH_4 and light alkanes during seepage result in a reversal of these relationships, with $C_4H_{10} > C_3H_8 > C_2H_6$ in unsaturated zone soil gas (Ronald W. Klusman, personal communication, 2012; Klusman, 2011).

Hydrocarbons also may result from in-situ microbial activity. Baseline soil gas data collected in the summer and fall of 2001 as a part of the WMP included detection of CH_4 , C_2H_6 and C_3H_8 (Riding and Rochelle, 2009). Distribution of C_2H_6 was similar to that of CH_4 . Temporal variations in C_2H_4 and C_3H_8 were similar to those of CO_2 , with concentrations decreasing significantly over successive seasons. These geochemical relationships led researchers to conclude a shallow biological origin for these hydrocarbon gases.

When combined, general hydrocarbon distributions within a gas sample, isotopes of CH_4 and CO_2 , and fixed soil gas analyses may indicate whether a signature most likely results from a seep, hydrocarbon spill, or in-situ microbial activity. If hydrocarbon data remain ambiguous, comparison of isotopic signatures of each individual hydrocarbon species (e.g. Szatkowski et al, 2002; Tilley and Muehlenbachs, 2006) with those in the reservoir may be necessary for definitive sourcing.

4. Methods

At the Kerr Farm, soil gas sampling locations were chosen to target areas of the 2010 and 2011 Petro-Find CO_2 anomalies (LaFleur, 2010, 2011) (Figs. 5, 6); however, locations available for well stations were constrained by setback requirements from oil field and utility infrastructure, agriculture activities at the site, and by the wetland habitat (slough and gravel pit ponds) of the protected Northern Spotted Leopard Frog. Boreholes for ten soil gas sampling stations were drilled at the Kerr site with sediment samples collected during auger drilling to characterize subsurface lithology. Sediment was collected from the flights of the drilling rig auger at 0.3-m intervals to maximum borehole depth and collected in clean 250 ml high-density polyethylene (HDPE) bottles labeled with the station name, date, and sample depth. A portion of the sediment sample was also used to classify color and sediment properties. Color was estimated by visual inspection using a Munsell Soil Chart (Munsell, 1975). Relative moisture content (i.e., dry, damp/moist, wet) was assigned to each depth interval to estimate groundwater level. Sediment type (i.e., sand, gravel, silt, clay) was characterized in the field using the Unified Soil Classification System (USCS) method (American Society of Testing and Materials, 2011). Sediment samples were stored on ice and subsequently placed in a freezer at the University of Regina for long-term storage.

Ten semi-permanent soil gas sampling stations, each consisting of sampling ports set at multiple depths were installed within the boreholes at the Kerr Farm (Fig. 5). Sampling port installation and design is described in the auxiliary material in Romanak et al. (2012). One main transect (transect 1-1' comprising eight stations) extended from an area of minimal CO₂ as measured by Petro-Find (representing site background conditions) northwest across areas of Petro-Find CO₂ anomalies in the northeast portion of the quarter section (Fig. 6). This transect also passed nearby a water injection well that disposes reservoir brine associated with oil field operations and across a slough in the north central portion of the property. A second lesser transect (transect 2-2' comprising three stations, one common to the main transect) includes the north and west portions of the gravel pit where various phenomena were reported by the Kerrs (EcoJustice, 2010).

At the ZERT site, gas was sampled from pre-existing 5-cm-diameter PVC water monitoring wells located 1–6 m down gradient from the controlled CO₂ release (Fig. 3). These wells were slotted both in the saturated and unsaturated zones. A custom-made double packer system was used to isolate and sample gases over a 0.15 m interval from the vadose zone portion of slotted PVC pipe at a depth of 1 m below ground surface. At the time of sampling, depth to groundwater was 1.4 meters and CO₂ was released at ~1.8 m depth in a sand and gravel aquifer. Gas was sampled from wells 5B, 3B, and 4B, each located at different distances from the release well, from 9 July, 2012 at 09:00 to 13 July at 16:00 and again from 15 July at 20:12 to 18 July at 20:48. On 10 July at 18:00, a release of 0.15 tonne/day of CO₂ began at the site. The release was interrupted between 11 July at 17:15 and 15 July at 18:15 when equipment failed due to a lightning strike.

For both studies, soil gas concentrations of CO₂, N₂, O₂ and CH₄ were determined by gas chromatography in the field with additional gas samples collected in Cali 5-bond® gas bags for laboratory analysis. Laboratory analyses included CO₂, N₂, O₂, Ar, CH₄, C₂-C₅ alkanes/alkenes and (δ¹³C) of CO₂ for the Kerr data set. All laboratory analyses were conducted by Isotech Laboratories (Champagne, IL) using gas chromatography coupled with an online isotope ratio mass spectrometer (GC-C-IRMS). Stated precision for δ¹³C is +/- 0.3 ‰. Stated precision for the gas concentrations is +/-2% of the reported value with a lower quantification limit of 3 ppm (0.0003 %). Thus, an uncertainty of +/- 3 ppm should be used in place of +/- 2% for values less than 150 ppm. The lower limit of detection is given as 1 ppm. Data were reduced for interpretation by adding 2.2 % water vapor (the saturated condition at ambient temperature and pressure) to each sample and normalizing total gas concentrations to 100 % for comparison purposes.

5. Results and Discussion

Two stratigraphic cross sections (Figs. 7, 8) were made using generalized sediment sample lithologic descriptions and moisture content from gas well boreholes. Land surface elevation is from Altus Geomatics (2011). Total well borehole depths ranged from 3.7 to 5.8 m below ground surface (Table 1). Generalized site geology is comprised of a thin, irregular soil veneer which overlies several meters of sand and gravel. Silt and clay underlie the site down to maximum borehole depth. Mature soil horizons are present in boreholes of six of the ten stations and range from a total depth of 0.3 to 1.2 m. Sand and gravel were found in all but one station (107) and typically was found at the surface or just below the soil horizon down to a depth of 2.1 to 4.6 m. Silt and clay were found in eight boreholes. The top of the silt/clay layer started at 0.6 to 3.4 m depth and continued to a depth of 0.9 to 5.5 m. Although boreholes were drilled to a depth of nearly 6 m, borehole sections with sands and gravels often collapsed below the water table.

CO₂ concentrations ranged from 0.1% at station 107 on the north side of the slough, to 7.3 % at station 104 on the south side of the slough (Table 2). The 7.3 % CO₂ value was measured near the eastern edge of the summer 2010 Petro-Find anomaly (maximum CO₂ of 11 %) and near a zone of high CO₂ concentration measured in the northeastern portion of the property by Petro-Find in the winter of 2010 (0.88 %) (Fig. 6). Differences in concentrations measured during the various studies are expected because soil CO₂ is known to vary over time in response to dynamic environmental conditions such as temperature, rainfall, plant growth and microbial respiration (e.g. Luo and Zhou, 2006).

Concentrations of methane ranged from below atmospheric values of 1.9 ppm to 10.8 ppm compared to a maximum of 27 and 30 ppm reported by Petro-Find from their summer and winter studies, respectively. Methane concentrations recorded by the WMP consistently ranged from 0.5 to 2 ppm (Jones and Beaubien, 2005).

Additional fixed soil gases such as O₂, N₂, and Ar (not measured by Petro-Find) were investigated. During the study, O₂ ranged from near-atmospheric values of 20.5 to 11.6 %. A general reverse association between O₂ and CO₂ was observed. Samples with higher CO₂ generally contained lower O₂. This type of trend in soils is widely known to result from biologic respiration (e.g. Hanson et al., 2000).

N₂ at the Kerr site was generally enriched relative to soil atmospheric values and ranged from 75.7 to 80.5 %. Normal atmosphere contains 78 % N₂; however atmosphere in soil contains 76.4 % N₂. This difference in N₂ concentrations is due to 2.2 % water vapor that is normally retained even in dry soils at ambient conditions (Fredlund and Rahardjo, 1993). The existence of water vapor in the soil gas mixture dilutes, or decreases the percentage of N₂ in that mixture relative to dry atmosphere. Extreme cases of denitrification may enrich N₂ above water-saturated atmospheric values (76.4%) but these cases are rare and can be identified by Ar/N₂ significantly less than 0.0119 (Martin et al, 1995). At the Kerr site, only one sample (station 202, 0.7 m) exhibits a CO₂ concentration that falls slightly beneath this value of 0.0119 indicating that widespread denitrification would not be responsible for any enriched N₂ values measured.

5.1 O₂ versus CO₂

A plot of O₂ versus CO₂ (Fig. 9a) shows that all gas samples from the Kerr study fall in geochemical fields indicating background processes, plotting along and below the line that represents bacterial respiration. If storage formation leakage were responsible for anomalous CO₂ gas concentrations at the Kerr farm, gas samples would be expected to lie to the right of the respiration line similar to what is observed at the ZERT site and Mt. Etna (Figs. 9b, c). Data collected at the ZERT site before CO₂ was released fall along the biological respiration trend and data collected after CO₂ release fall in the leakage signal field. The same leakage signature is seen at Mt. Etna, where all samples impacted by volcanic CO₂ emanating from depth lie to the right of biological respiration line in the area of exogenous CO₂. At Etna, compositions range from less-impacted soil gas samples (near 21% O₂ that plot near the biological respiration line), to nearly fully impacted fumarole samples (near 0% O₂ that plot to the far right of the biological respiration line). From these comparisons the CO₂ at the Kerr farm is not anomalous, but exhibits a natural background signature with CO₂ slightly below the biologic respiration trend.

5.2 CO₂ versus N₂

As previously discussed, N₂ is an inert gas and its concentration is most commonly affected only by addition or subtraction of a coexisting gas phase that will dilute or enrich the percentage of N₂, respectively, in the soil gas mixture. In the case of a leak from the storage formation entering the near-surface, N₂ values would become diluted relative to soil atmosphere; however, samples collected at the Kerr site are close or slightly enriched relative to the atmosphere (Fig. 10a). N₂ enrichment indicates subtraction of a gas component, namely by dissolution of CO₂ into recharging groundwater, which is a natural process. CO₂ dissolution is supported by the observation that samples with high N₂ also exhibit

CO₂ concentrations that lie to the left of the respiration line in Figure 9a due to CO₂ loss. In contrast, the N₂ signature from ZERT controlled release site and the volcanic proxy show the opposite effect (Fig. 10b, c). Upon addition of exogenous CO₂, N₂ becomes strongly depleted relative to atmosphere in the soil gas mixture. This depletion increases in magnitude as the concentration of CO₂ in the soil gas approaches 100%. The differing results at the Kerr site compared to those at the leakage proxy sites confirm that CO₂ on the Kerr property does not originate from deep CO₂ leakage into the near-surface, but results from natural in-situ processes. Leakage proxies confirm that addition of exogenous CO₂ from outside the near-surface system would plot to the right of the biological respiration line which is not the case at the Kerr site.

5.3 CO₂ versus N₂/O₂

Samples that lie below the respiration line in Figure 9a may indicate either methane oxidation or dissolution of CO₂ into recharging groundwater, or both. A plot of CO₂ versus N₂/O₂ (Fig. 11) can indirectly determine the degree to which methane oxidation contributes to CO₂ production by indicating O₂ consumption. O₂ is consumed both by biologic respiration and to a larger degree by CH₄ oxidation according to Eq. 1 and 2. CH₄ oxidation can continue as long as O₂ is supplied to the system from influx of atmosphere into the soils. In some instances, CH₄ oxidation and O₂ influx can be rather vigorous resulting in N₂/O₂ orders of magnitude higher than the atmospheric value of 3.7. For example, N₂/O₂ values > 250 were found at the West Texas playa lake where natural CH₄ concentrations were as high as 2 % and biologic CO₂ was as high as 17%. N₂/O₂ values > 750 were found at the Gulf Coast oilfield where CH₄ concentrations were as high as 33%, CO₂ was as high as 45%, and isotopic data indicated methane oxidation as the origin of CO₂ (Romanak et al., 2012). At the Kerr property, N₂/O₂ ranges from 3.7 to 6.9. Such small N₂/O₂ values together with CH₄ concentrations mostly below atmospheric values found at the site suggest a geochemistry influenced by biologic respiration with little or no CH₄ oxidation. Data from the Kerr Farm are therefore consistent with biologic respiration and dissolution of CO₂ into groundwater.

At the ZERT site, which is devoid of hydrocarbons, N₂/O₂ is relatively constant at near-atmospheric values, even when CO₂ is added to the system (Fig. 11b). The general trend of near-constant N₂/O₂ is an indicator that oxygen is not being significantly consumed and thus methane oxidation is not an important contributor to CO₂ concentrations. Magnification of a portion of the graph at the point where the CO₂ release began (inset in ZERT graph) shows pre-injection gas concentrations that lie along the biologic respiration line. As injected CO₂ reaches the monitoring wells, gas concentrations leave the biologic

respiration line and trend on a leakage input trajectory. This observation is important because it suggests that by using the relationship between CO₂ and N₂/O₂, the amount of CO₂ attributed to leakage may be easily separated and quantified apart from CO₂ produced by respiration. Ways to separate and quantify a CO₂ leakage signal over natural CO₂ are not as readily apparent with other methods of leakage assessment that depend on background measurements but have no way to define the processes affecting the CO₂.

At Mt. Etna, two geochemical populations are again apparent with lower-CO₂ (< 20%) soil gas samples and higher-CO₂ (> 70%) fumarole samples (Fig. 11c). Lower-CO₂ soil-gas samples exhibit a CO₂ leakage input trend while maintaining near-atmospheric N₂/O₂ ratios. These relationships suggest little to no oxidation or consumption of O₂. Higher-CO₂ samples also lie on a leakage input trend but exhibit a larger range in N₂/O₂ (3.7-18.2). The reason for the scatter in N₂/O₂ of higher-CO₂ samples is not known but and could be due to any number of conditions such as high gas flux (≤ 0.033 cm/second) at fumaroles, the potential for additional reduced gas species common to magmatic emissions but not reported in Giammanco et al. (1998) and/or fumarole temperatures as high as 730°C. In any case, Giammanco et al. (1998) do report CH₄ concentrations in Mt. Etna gas samples ranging from non-detectable to as high as 12.2%. Such variable concentrations of CH₄ would be expected to result in different degrees of methane oxidation. Areas with low methane concentrations might be expected to experience less CH₄ oxidation and O₂ consumption resulting in low N₂/O₂ and areas with high CH₄ concentrations might be expected to exhibit more CH₄ oxidation and O₂ consumption resulting in high N₂/O₂ and O₂.

5.4 Isotopes

Because reservoir-related isotopic ratios are not distinct from those of biologic respiration, isotopic signatures cannot be used to determine leakage at the Kerr Farm (e.g. Nickerson and Risk, 2013) (Fig. 12) as was claimed in the Petro-Find study. $\delta^{13}\text{C}$ of CO₂ measured in this study ranges from -27.1 to -11.4 ‰. When compared to various sources of CO₂ gas within the near-surface this range best fits that of soil CO₂ (Clark and Fritz, 1997). However this isotopic range is not distinct from the various sources of CO₂ that could signal a leak from the reservoir including baseline reservoir gas before injection (-22 to -12 ‰), reservoir gas produced after injection (-18 to -13 ‰), and injectate CO₂ (-21 to -20 ‰) (Emberley et al., 2005).

Linear data regression on a Keeling plot (Fig. 13) is traditionally used to determine the isotopic composition of ecosystem respiration (e.g. Pataki et al., 2003) and yields a $\delta^{13}\text{C}$ value of -24 ‰ at the Kerr site. This value is consistent with biologic respiration of C₃ plants ($\delta^{13}\text{C} = -24$ to -30 ‰), which

comprise the majority of plant species (Clark and Fritz, 1997). The linear regression is similar and consistent with mixing between substrate of -24 ‰ and atmosphere, supporting the conclusion that CO₂ on the Kerr property is the result of natural biologic respiration diluted to varying degrees with atmosphere, and not the result of leakage from the reservoir.

5.5 Hydrocarbons

In this study, trace amounts of higher hydrocarbons (C₂-C₅) were detected both at stations considered to be background sites (stations 101 and 102) and at stations near the Petro-Find CO₂ anomalies (stations 104, 107, and 108) (Table 2). Trace hydrocarbons also were found near the gravel pit at station 202, but not at gravel pit station 201. It is important to note that all trace detections of C₂-C₅ were at concentrations of either 1 or 2 ppm and according to Isotech, analytical uncertainty for trace analyses is conservatively +/- 3ppm: although it is believed that these low hydrocarbon detections are likely real, they may also be the result of chance.

Higher hydrocarbons (C₂-C₅) were also measured by Petro-Find and deemed as evidence supporting leakage of CO₂ from the storage reservoir (Lafleur, 2010, 2011). Higher hydrocarbons (C₂H₆ and C₃H₈) were also measured during the baseline survey of the WMP in the summer and fall of 2001 (Riding and Rochelle, 2005, 2009). In a summary report of the WMP, Whittaker et al. (2004) refer to the occurrence of hydrocarbons at the WMP stating; *“As heavier hydrocarbons do not normally originate via shallow biological reactions, it is difficult to reconcile these results with those of the other gases...A comparison of the grid data with that of the background site, located in similar surface geology but outside the Weyburn oilfield, shows a very similar statistical distribution for all monitoring parameters. This result supports the interpretations that the observed gas concentrations are not due to deep leakage.”*

We agree that hydrocarbon gases are most commonly thought to originate from deep hydrocarbon seepage; however, we have also found references within the scientific literature that indicate hydrocarbon gases may result from bacterial respiration in the near-surface (Smith and Restall, 1971). Ethane, propane, ethylene, propylene, *n*- and iso-butane and butane-1 have been documented in natural soils under laboratory conditions and in waterlogged soils similar to the prairie potholes of Saskatchewan (van Cleemput et al., 1983). Therefore, we agree that while the existence of hydrocarbons in soil at the Kerr property is puzzling, it is also not necessarily inconsistent with evidence that biologic respiration, not leakage from the storage reservoir, is the dominant process creating CO₂ at the site.

6. Conclusions

Fixed gas relationships and carbon isotope geochemistry of soil gas at the Kerr site strongly show that CO₂ on the Kerr property is biological in origin and not the result of leakage associated with the CO₂ storage reservoir. Traces of C₂-C₅ hydrocarbons, while not commonly a product of near-surface processes, have been documented to occur naturally in soils, and are therefore not necessarily problematic with the interpretation of a biological origin for gases: thus, no evidence was found to suggest that gases originating in the deep subsurface have migrated to the near-surface. This conclusion is verified by comparing results to leakage proxy sites at the ZERT controlled release facility and Mt. Etna volcano which illustrate how a leakage signal would manifest using a process-based analysis. Evidence at the Kerr site clearly shows that CO₂ is from natural biologic respiration modified by mixing with atmosphere and dissolution of CO₂ into recharging groundwater. This evidence includes: 1) relationships between CO₂ and O₂ that indicate biologic respiration and dissolution of CO₂ into groundwater; 2) N₂ enriched above atmospheric concentrations; 3) low N₂/O₂ consistent with biologic respiration; and, 4) $\delta^{13}\text{C}$ of CO₂ that represents mixing of atmosphere with microbial and C₃ plant respiration. The study confirms that a process-based approach can be used to quickly and economically assess leakage near geologic carbon storage sites. In addition, data from the ZERT release suggest that quantification of a leakage signal apart from natural processes may be most easily accomplished using a process-based approach.

Acknowledgements: This study was funded by IPAC-CO₂ under sponsored research agreement UTA11-000342 and by the Gulf Coast Carbon Center. Many thanks to collaborators on the Kerr study; Eric Ringler, Stuart Gilfillan, Hilary Olson, Thomas Ogilvie, Jennifer Stroh, Rhonda Shepek, Majid Nasehi, Amy Castner, Anita Arduini, Richard Adamson, Kevin Melle, Al Bjornson, Karen Collins, Peter Wyant, Carmen Dybwad, and Joe Ralko. Thanks to Tim Dixon for help with field work during the ZERT test. Also much appreciation goes to our colleagues who provided valuable support and input: David Jones, Malcolm Wilson, Steve Whittaker, Ron Klusman, Alan Greeves, Norm Sacuta, Sam Krevor, Dave Risk, Matt McCulloch, Matthew Bramley, Bernhard Mayer, Susan Hovorka, Bridget Scanlon, Michael Young and Scott Tinker. Thanks to Cam and Jane Kerr and Ian and Sheila Thackeray for providing land access. Also thanks for the support of Patti Sherk and Shannon Sherk. The Bureau of Economic Geology research collaborations with IPAC-CO₂ (Kerr study) and Montana State University (ZERT test) which made this study possible were the direct result of the authors' participation in IEAGHG Research Network meetings which provide exceptional environments for scientific exchange and building new collaborations. Publication authorized by the Director, Bureau of Economic Geology.

7. References

- Altus Geomatics, 2011, IPAC-CO₂ Topographic Survey of S.W. ¼ Section of 30 Township 5 – Range 13 – W.2 Meridian. R.M. of Lomond No. 37. Survey Date: August 2011 to October 2011. Job Number 146036. Weyburn, SK: Altus Geomatics.
- Aqua Terre Solutions Inc., 2006, Discussion of May 2, 2006 Water Quality Results at Domestic Water Well and Gravel Pit Water at Kerr Residence (SW 30-5-13 W2M). Calgary, AB: Aqua Terre Solutions Inc.
- ASTM (American Society for Testing and Materials), 2011, ASTM D2487-11, Standard Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System). West Conshohocken, PA: ASTM International.
- Beaubien, S., Strutt, M. H., Jones, D. G., Baubron, J.-C., Cardellini, C., Lombardi, S., Quattrochi, F. & I. Penner, 2004, D20 Report: Soil Gas surveys in the Weyburn oil field (2001-2003). Keyworth, Nottingham: British Geological Survey.
- Beaubien, S.E., Jones, D.G., Gal, F., Barkwith, A.K.A.P., Braibant, G., Baubron, J.-C., Ciotoli, G., Graziani, S., Lister, T.R., Lombardi, S., Michel, K., Quattrocchi, F., & M.H. Strutt, 2013, Monitoring of near-surface gas geochemistry at the Weyburn, Canada, CO₂-EOR site, 2001–2011; International Journal of Greenhouse Gas Control, Volume 16, Supplement 1, pp. S236–S262
- Clark, I. D. & P. Fritz, 1997, Environmental Isotopes in Hydrogeology. Boca Raton, FL: CRC Press/Lewis Publishers.
- EcoJustice, 2010, Site History, SW30-5-13-W2M Near Weyburn, Saskatchewan, Cameron and Jane Kerr. Calgary, AB: EcoJustice.
- Emberley, S., Hutcheon, I. Shevalier, M., Durocher, K., Mayer, B., Gunter, W. D. & E. H. Perkins, 2005, Monitoring of fluid–rock interaction and CO₂ storage through produced fluid sampling at the Weyburn CO₂-injection enhanced oil recovery site, Saskatchewan, Canada. Applied Geochemistry, 20, 1131–1157.
- Faber, E., Stahl, W.J. & M. J. Whiticar, 1992, Distinction of bacterial and thermogenic hydrocarbon gases, in R. Vially, ed., Bacterial Gas, Paris, Editions Technip, p. 63-74.
- Fredlund, D. G. & H. Rahardjo. 1993. Soil Mechanics for Unsaturated Soils. New York, NY: John Wiley & Sons, Inc.
- Giammanco, S., Inguaggiato, S. & M. Valenza, 1998, Soil and fumaroles gases of Mount Etna: Geochemistry and relations with volcanic activity. Journal of Volcanology and Geothermal Research, 81, 297–310.
- Hanson, P. J., Edwards, N. T., Garten, C. T. & J. A. Andrews, 2000, Separating root and soil microbial contributions to soil respiration: A review of methods and observations. Biogeochemistry, 48, 115-146.
- Kharaka, Y.K., Thordsen, J.J., Kakouros, E. & G. Ambats, 2010, Changes in the chemistry of shallow groundwater related to the 2008 injection of CO₂ at the ZERT field site, Bozeman, Montana, Environ Earth Sci (2010) 60:273–284.
- Jones, D. G. & S. E. Beaubien, 2005, Continued Soil Gas Monitoring at the Weyburn Unit in 2004, Report No. COAL R288, DTI/Pub URN 05/1261. Keyworth, Nottingham, UK: British Geological Survey.

- Jones, D. G., Strutt, M. H., Beaubien, S. E., Lombardi, S., Voltatoni, N., Baubron, J. C., Cardellini, C., Quattrocchi, F., Granieri, D. & L. Penner, 2003, Soil gas as a monitoring tool of deep geological storage of carbon dioxide: Results from the Encana EOR project in Weyburn, Saskatchewan (Canada). In The 226th American Chemical Society National Meeting, 7-11 September 2003. New York, NY: American Chemical Society.
- Klusman, R.W., 2003a, Rate measurements and detection of gas microseepage to the atmosphere from an Enhanced Oil Recovery/sequestration project, Rangely, Colorado, USA. *Applied Geochemistry*, v. 18, pp. 1825-1838.
- Klusman, R.W., 2003b, Computer modeling of methanotrophic oxidation of hydrocarbons in the unsaturated zone from an Enhanced Oil Recovery/sequestration project, Rangely, Colorado, USA. *Applied Geochemistry*, v. 18, pp. 1839-1852.
- Klusman, R.W., 2006, Detailed compositional analysis of gas seepage at the National Carbon Storage Test Site, Teapot Dome, Wyoming, USA. *Applied Geochemistry*, v. 21, pp. 1498-1521.
- Klusman, R.W., 2011, Comparison of surface and near-surface geochemical methods for detection of gas microseepage from carbon dioxide sequestration, *International Journal of Greenhouse Gas Control* 5, 1369–1392.
- Lafleur, P., 2010, Geochemical Soil Gas Survey: A Site Investigation of SW30-5-13-W2M Weyburn Field, Saskatchewan. Saskatoon, SK: Petro-Find Geochem Ltd.
- Lafleur, P., 2011, Geochemical Soil Gas Survey: A Site Investigation of SW30-5-13-W2M, Weyburn Field, Saskatchewan, Monitoring Project Number 2. Saskatoon, SK: Petro-Find Geochem Ltd.
- Luo, Y. & X. Zhou, 2006, *Soil Respiration and the Environment*. Amsterdam: Elsevier Academic Press.
- Marrin, D.L., 1988, Soil gas sampling and misinterpretation, *Ground Water Monitoring Rev.*, vol. 8, p.51-54.
- Marrin, D.L., 1991, Subsurface biogenic gas ratios associated with hydrocarbon contamination; in *In-situ Bioreclamation*, Stoneham, MA, Butterworth-Heinemann Publishers, p. 546-560.
- Martin, G. E., Snow, D. D., E. Kim & R. F. Spalding, 1995, Simultaneous determination of Argon and Nitrogen. *Ground Water*, 33, 781-785.
- Munsell Color Company, 1975, *Munsell Soil Color Charts*. Baltimore, MD: Munsell Color Company.
- Nickerson, N., and Risk, D., 2013, Using subsurface CO₂ concentrations and isotopologues to identify CO₂ seepage from CCS/ CO₂–EOR sites: A signal-to noise based analysis, *International Journal of Greenhouse Gas Control* 14 (2013) 239–246
- Ostendorf, D.W., & Hambell, D.H., 1991, Biodegradation of hydrocarbon vapors in the unsaturated zone: *Water Resources Research*, v.27, No. 4, p. 453-462.
- Pataki, D. E., Ehleringer, J. R., Flanagan, L. B., Yakir, D., Bowling, D. R., Still, C. , Buchmann, N., Kaplan, J. O. & J. A. Berry, 2003, The application and interpretation of Keeling plots in terrestrial carbon cycle research. *Global Biogeochemical Cycles*, 17, 22-1 - 22-14.
- Petroleum Technology Research Centre, 2011, IEAGHG Weyburn-Midale CO₂ Monitoring and Storage Project - Response to a Soil Gas Study Performed by Petro-Find Geochem Ltd. Regina, SK: Petroleum Technology Research Centre, <http://www.ptrc.ca/siteimages/WMP-Response-to-Petro-Find.pdf>.
- Rice, D. D., 1993, Biogenic gas: controls, habitats, and resource potential, in D. G. Howell, ed., *The Future of Energy Gases - U.S. Geological Survey Professional Paper 1570*, Washington, United States Government Printing Office, p. 583-606.

- Riding, J. B. & C. A. Rochelle, 2005, The IEA Weyburn CO₂ Monitoring and Storage Project: Final report of the European research team. Keyworth, Nottingham, UK: British Geological Survey.
- Riding, J. B. & C. A. Rochelle, 2009, Subsurface characterisation and geological monitoring of the CO₂ injection operation at Weyburn, Saskatchewan, Canada. In *Underground Gas Storage: Worldwide Experiences and Future Development in the UK and Europe*, Special Publication 313, eds. D. J. Evans & R. A. Chadwick, 227–256. London: Geological Society.
- Ririe, G.T., and R.E. Sweeney, 1993, Comparison of hydrocarbon gases in soils from natural seeps and anthropogenic sources. *Proc. 1993 Pet. Hydrocarbons Org. Chem. Ground Water: Prevent., Detect., Restor.*, Houston, Tex., 593 pp.
- Romanak, K.D., 1997, *Vadose-Zone Geochemistry of Playa Wetlands, High Plains, Texas*, PhD Dissertation, 273 pp.
- Romanak, K. D., Bennett, P. C., Yang, C. & S. D. Hovorka, 2012, Process-Based Approach to Soil Gas Monitoring at Geologic Carbon Storage Sites. *Geophysical Research Letters*. 60 (2), 227–239.
- Romanak, K., Dobeck, L., Dixon, T., & L. Spangler, 2013, Potential for a Process-based Monitoring Method above Geologic Carbon Storage Sites using Dissolved Gases in Freshwater Aquifers. *Procedia Earth and Planetary Science*, 7, 746-749.
- Saskatchewan Geological Survey, 2003, *Geology and mineral and petroleum resources of Saskatchewan; Saskatchewan Industry and resources*, Miscellaneous Report 2003-7, 173.
- SER (Saskatchewan Ministry of Energy and Resources), 2011, *New Saskatchewan Stratigraphic Correlation Chart*, internet resource, www.er.gov.sk.ca/stratchart.
- Schoell, M., 1983, Genetic characterization of natural gases, *AAPG Bulletin*, v. 67, p. 2225-2238.
- Schoell, M., 1988, Multiple origins of methane in the earth, *Chemical Geology*, v. 71, p. 1-10.
- Simpson, M. A., 1993, *Geology and Groundwater Resources of the Weyburn/Virden Area (62E/F)*, Saskatchewan. SRC Publication No. R-1210-3-E-93. Saskatoon, SK: Saskatchewan Research Council.
- Smith, K. A. & S. W. F. Restall, 1971, The occurrence of ethylene in anaerobic soil. *Journal of Soil Science*, 22, 430–443.
- Spangler LH, Dobeck, L.M., Repasky, K., Nehrir, A. et al., 2010, A controlled field pilot in Bozeman, Montana, USA, for testing near surface CO₂ detection techniques and transport models. *Environ Earth Sci* 6.
- Spangler, L.H., Dobeck, L.M., Repasky, K.S., Nehrir, A.R., Humphries, S.D., Barr, J.L., Keith, C.J., Shaw, J.A., Rouse, J.H., Cunningham, A.B., Benson, S.M., Oldenburg, C.M., Lewicki, J.L., Wells, A.W., Diehl, J.R., Strazisar, B.R., Fessenden, J.E., Rahn, T.A., Amonette, J.E., Barr, J.L., Pickles, W.L., Jacobson, J.D., Silver, E.A., Male, E.J., Rauch, H.W., Gullickson, K.S., Trautz, R., Kharaka, Y., Birkholzer, J., & L. Wielopolski., 2010. A shallow subsurface controlled release facility in Bozeman, Montana, USA, for testing near surface CO₂ detection techniques and transport models. *Environ. Earth Sci*. 6.
- Szatkowski, B., Whittaker, S., & B. Johnson, , 2002, Identifying the source of migrating gases in surface casing vents and soils using stable carbon isotopes, Golden Lake Pool, West-central Saskatchewan, in *Summary of Investigations 2002*, vol. 1, Saskatchewan Geological Survey, Sask Industry and Resources, Misc. Report 2002-4.1, p. 118-125.
- Tilley, B., and K. Muehlenbachs, 2006, Gas maturity and alteration systematics across the Western Canada Sedimentary Basin from four mud gas isotope depth profiles *Organic Geochemistry*, Volume 37, Issue 12, December 2006, Pages 1857-1868.

- Trium Environmental Inc., 2011, Site assessment Weyburn Unit SW30-5-13W2; www.cenovus.com
- van Cleemput, O., El-Sebaay, A. S. & L. Baert, 1983, Evolution of gaseous hydrocarbons from soil: Effect of moisture content and nitrate level. *Soil Biology and Biochemistry*, 15, 519-524.
- Whiticar, M. J., 1994, Correlation of natural gases with their sources, in L. B. Magoon, and W. G. Dow, eds., *The Petroleum System, From Source to Trap*, AAPG, p. 261-283.
- Whiticar, M. J., 1999, Carbon and hydrogen isotope systematics of bacterial formation and oxidation of methane, *Chemical Geology* 161, 291-314.
- Whittaker, S., White, D., Law, D., & R. Chalaturnyk, 2004, IEAGHG Weyburn CO₂ Monitoring & Storage Project, Summary Report 2000-2004. In M. Wilson & M. Monea (Eds.), *Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies*, September 5-9, 2004, Vancouver, Canada (Vol. III). Regina, SK: Petroleum Technology Research Centre.
- Wolaver, B. D., Hovorka, S. D., & R. C. Smyth, 2013, Greensites and brownsites: Implications for CO₂ sequestration characterization, risk assessment, and monitoring. *International Journal of Greenhouse Gas Control*, 19, 49-62.
- Yang, C., Romanak, K., Hovorka, S., Trevino, R., 2013a. Modeling CO₂ Release Experiment in the Shallow Subsurface and Sensitivity Analysis. *Environmental & Engineering Geoscience*, 19(3): 207-220.
- Yang, C., Romanak, K., Hovorka, S., Holt, R.M., Lindner, J., Trevino, R., 2013b. Near-Surface Monitoring of Large-Volume CO₂ Injection at Cranfield: Early Field Test of SECARB Phase III. *SPE Journal*, 18(3): 486-494.

Figure 1. Map showing the relative locations of the Weyburn-Midale oilfield, the Kerr Farm, and the soil gas study areas of the IEAGHG Weyburn-Midale CO₂ Monitoring and Storage Project (WMP). Hatched area denotes the approved CO₂-EOR area as of 2011. Figure is modified from Trium, 2011.

Figure 2. Georeferenced and digitized reproduction of the soil gas survey reported by Petro-Find Geochem Ltd. in the summer of 2010. The soil gas anomaly originally reported by Petro-Find to be the result of leakage from the Weyburn-Midale CO₂ Monitoring and Storage Project is shown in the northern portion of the Kerrs property and is contoured for CO₂ gas concentration.

Figure 3. ZERT site map showing wells used for vadose zone sampling (2B, 4B, 5B). Well 3B was used for groundwater monitoring (Romanak et al., 2013). Location of the horizontal well used for controlled CO₂ release is shown. Map modified from Kharaka et al. (2010).

Figure 4. Three simple ratios used in a process-based analysis to distinguish leakage signal from natural variation in the near-surface above geologic carbon storage sites.

Figure 5. Aerial view of property owned by Cameron and Jane Kerr near Goodwater, Saskatchewan (SW Section 30, Township 5, Range 13, W2M). Locations of soil-gas sampling stations, shallow groundwater wells and cross section locations are shown. Hydrogeologic cross sections are indicated by lines 1-1' and 2-2'. Historic aerial photo does not fully represent surface hydrologic conditions at the time of the IPAC-CO₂ study. (Aerial photo courtesy of SER).

Figure. 6. Soil gas stations and water well locations with respect to the summer 2010 Petro-Find CO₂ anomaly (left) and winter 2011 Petro-Find CO₂ anomaly (right). Historic aerial photo does not fully represent surface hydrologic conditions at the time of the IPAC-CO₂ study. (Aerial photo courtesy of SER).

Figure 7. Hydrogeologic Cross Section 1-1' includes land surface and slough water elevation from Altus Geomatics (2011), generalized sedimentary lithology described from sediment samples collected during gas well borehole drilling, and inferred groundwater elevation estimated from the depth of saturated sediments in gas well boreholes (indicated by “wet” in table 1). Sediments encountered during borehole drilling at station 107 were unsaturated; however, water was pumped from the gas well at a depth of 578.3 m. Sediments encountered during borehole drilling at stations 103 and 104 were saturated at 578.8 and 579.0 m (respectively); however, gas was collected from both stations 103 and 104 at 578.8 m.

Figure 8. Hydrogeologic Cross Section 2-2' includes land surface and gravel pit water elevation from Altus Geomatics (2011), generalized sedimentary lithology described from sediment samples collected during gas well borehole drilling, and inferred groundwater elevation estimated from the depth of saturated sediments in gas well boreholes. Sediments encountered during borehole drilling at station 103 were saturated at 578.8 m; however, gas was collected from station 103 at 578.8 m. Sediments encountered during borehole drilling at station 202 were saturated below 0.91 m; however, gas was collected from all three gas wells constructed in the borehole.

Figure 9. O_2 versus CO_2 at the Kerr Farm and leakage proxy sites (ZERT and Mt. Etna) along with a graph showing the general fields for various background and leakage processes. The data indicate that soil gas on the Kerr property results from biologic respiration modified by dissolution of soil carbonate into recharging groundwater. Leakage proxies confirm that addition of exogenous CO_2 from outside the near-surface system would plot to the right of the biological respiration line which is not the case at the Kerr site. Note also from the inset of the ZERT data that background CO_2 which clusters on the respiration trend line is relatively easily distinguished graphically from leakage signal CO_2 suggesting that background could be easily subtracted from leakage for quantification purposes.

Figure 10. CO₂ versus N₂ at the Kerr Farm and leakage proxy sites (ZERT and Mt. Etna) along with a graph showing the general fields for various background and leakage processes. At the Kerr site, most samples cluster around atmospheric N₂ compositions with variable CO₂ concentrations. Some samples show N₂ compositions enriched relative to atmosphere, a gas signature that is attributed to subtraction of CO₂ through dissolution into recharging groundwater. These geochemical signatures are in contrast to those at the leakage proxy sites which confirm that a leakage signal creates N₂ concentrations depleted relative to vapor-saturated atmosphere. Inset of ZERT data gives a more detailed view for comparing background samples (plotting near the respiration line) with samples in the early stages of leakage (plotting just off the respiration trend line).

Figure 11. CO₂ versus N₂/O₂ at the Kerr Farm and leakage proxy sites (ZERT and Mt. Etna) along with a graph showing the general fields for various background and leakage processes. Kerr Farm samples are consistent with the processes of respiration and CO₂ dissolution as compared to the leakage proxies which show CO₂ concentrations that are higher than would be produced by biologic trends. Inset of ZERT data gives a more detailed view suggesting graphical quantification of leakage CO₂ apart from background CO₂ could be accomplished using a process-based approach.

Figure 12. Carbon isotopic signatures of various potential natural CO_2 sources in the near-surface and of fluids from the Weyburn-Midale CO_2 storage reservoir. Shaded area indicates the range for natural soil CO_2 that fully overlaps all potential leakage signals. The overlap of signatures illustrates that injected CO_2 cannot be distinguished from natural sources using $\delta^{13}\text{C}$ of CO_2 alone. (Figure is modified from Clark and Fritz, 1997, with data for potential leakage signals from Emberley et al., 2005).

Figure 13. A Keeling plot indicates the average carbon isotope composition of CO₂ respired at the Kerr Farm (represented by the y intercept of the linear data regression) of -24‰. A mixing line between air and a substrate of -24‰ yields results similar to the data regression indicating that isotopic variation of CO₂ is consistent with the processes of biologic respiration and atmospheric mixing. Dissolution of CO₂ and reaction with soil carbonate may fractionate the δ¹³C of CO₂ by as much as 1.1‰ at 20°C (Clark and Fritz (1997)).

Table 1. Characteristics of soil gas wells. All values are elevations presented in meters relative to mean sea level (msl); however, borehole depths also are shown as meters below ground surface (bgs). Not applicable is indicated by a ‘-’ symbol.

Station	101	102	103	104	105	106	107	108	201	202
BOREHOLE										
DEPTH										
m msl	576.6	578.0	575.7	576.0	575.8	575.1	575.9	577.0	576.3	575.4
m bgs	4.6	3.0	4.6	3.7	3.7	4.6	5.5	5.8	4.0	4.6
GAS SAMPLE										
DEPTH										
Well 1	580.0	580.2	579.7	579.1	578.8	579.1	579.8	581.3	579.6	579.3
Well 2	579.5	579.6	579.2	578.8	578.2	578.6	578.3	579.8	579.2	578.7
Well 3	578.5	578.9	578.8	577.7	-	577.6	576.9	578.3	578.6	578.3
Well 4	-	-	-	-	-	-	575.6	577.2	-	-
GROUNDWATER										
LEVEL	579.0	579.2	578.8	579.0	578.8	578.8	-	-	579.0	579.0
SEDIMENT										
DEPTHS										
Soil Top	-	-	-	579.6	-	579.7	581.4	582.8	580.2	579.9
Soil Bottom	-	-	-	579.0	-	579.1	580.4	582.2	579.0	579.6
Sand/Gravel Top	581.1	581.1	580.3	579.0	579.5	578.8	-	579.5	579.0	579.6
Sand/Gravel Bottom	577.8	577.7	576.9	577.5	576.7	577.0	-	578.9	577.8	575.4
Silt/Clay Top 1	577.8	-	576.9	577.5	576.7	579.1	580.4	582.2	577.8	-
Silt/Clay Bottom 1	576.6	-	575.7	576.0	575.8	578.8	575.9	579.5	576.3	-
Silt/Clay Top 2	-	-	-	-	-	577.0	-	578.9	-	-
Silt/Clay Bottom 2	-	-	-	-	-	575.1	-	577.0	-	-

Table 2. Soil gas data from the Kerr study analyzed by Isotech Laboratories and corrected for water vapor content as described in the methods section. According to Isotech, analytical uncertainty for trace analyses is conservatively +/- 3ppm, and although it is believed that these low hydrocarbon detections are likely real, they may also be the result of chance.

Station Number	Sampling Depth (m)	Ar %	O ₂ %	CO ₂ %	N ₂ %	CO %	C ₁ ppm	C ₂ ppm	C ₂ H ₄ ppm	C ₃ ppm	iC ₄ ppm	nC ₄ ppm	iC ₅ ppm	nC ₅ ppm	C ₆₊ ppm	H ₂ O %	δ ¹³ CO ₂ ‰
101	1.1	0.9	20.1	0.6	76.2	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-22.17
101	1.1	0.9	20.5	0.6	75.8	nd	2.9	1.0	nd	nd	1.0	1.0	1.0	1.0	nd	2.2	-21.66
101	1.7	0.9	20.1	0.6	76.2	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-22.99
101	1.7	0.9	20.5	0.7	75.7	nd	2.0	1.0	nd	nd	1.0	1.0	1.0	1.0	nd	2.2	-20.58
102	0.9	0.9	20.1	0.7	76.1	nd	2.0	nd	nd	nd	nd	1.0	nd	nd	nd	2.2	-23.30
102	1.5	0.9	20.1	0.9	75.9	nd	1.0	nd	nd	nd	nd	1.0	nd	nd	nd	2.2	-23.40
103	0.6	0.9	19.6	0.5	76.8	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-25.10
103	1.1	0.9	19.7	1.1	76.1	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-23.55
103	1.5	0.9	19.6	0.9	76.4	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-26.00
103	1.5	0.9	19.7	0.9	76.3	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-25.61
104	0.5	0.9	13.2	5.6	78.2	nd	2.0	1.0	nd	nd	nd	1.0	nd	nd	nd	2.2	-24.50
104	0.5	0.9	13.9	5.3	77.7	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-24.33
104	0.8	0.9	13.0	6.6	77.3	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-23.37
104	0.8	0.9	13.3	7.3	76.3	nd	2.9	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-23.29
105	0.6	1.0	12.8	5.0	79.0	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-24.78
105	0.6	1.0	11.6	5.7	79.6	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-24.33
106	0.6	0.9	19.1	0.2	77.7	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-20.60
107	1.5	0.9	19.4	0.6	76.9	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-22.99
107	3.0	1.0	16.9	0.1	79.8	nd	5.9	1.0	1.0	nd	nd	nd	nd	nd	nd	2.2	-18.03
107	5.7	1.0	16.2	0.1	80.5	nd	10.8	1.0	1.0	1.0	nd	nd	nd	nd	nd	2.2	-11.44
108	1.5	0.9	19.4	1.6	75.9	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-22.80
108	3.0	0.9	18.7	0.6	77.6	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-27.12
108	4.6	0.9	18.2	1.5	77.2	nd	2.9	1.0	nd	1.0	1.0	2.0	1.0	2.0	nd	2.2	-24.38
108	5.6	1.0	16.6	0.1	80.1	nd	5.9	1.0	1.0	nd	nd	nd	nd	nd	nd	2.2	-18.70
201	0.6	0.9	19.3	0.6	77.0	nd	1.0	1.0	nd	1.0	1.0	2.0	1.0	2.0	nd	2.2	-20.21
201	1.1	0.9	19.4	0.3	77.2	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-17.62
202	0.7	0.9	19.2	1.0	76.8	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-24.11
202	0.7	0.9	19.5	1.0	76.4	nd	3.9	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-24.29
202	1.3	0.9	19.6	1.2	76.1	nd	2.9	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-24.04
202	1.6	0.9	19.5	1.3	76.1	nd	1.0	nd	nd	nd	nd	nd	nd	nd	nd	2.2	-25.08