CO_2 Flux Field Delineation for Construction on Reclaimed Mine Land

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ABSTRACT

The objectives of this work were to develop a soil CO_2 flux survey protocol for assessing reclaimed mine land for construction purposes and an approach to delineate high CO_2 flux fields for making decisions on post-mining land uses. The research involved CO_2 chamber accumulation flux surveys; stable carbon isotope ratio analysis; statistical techniques hypothesis testing to examine correlation between CO2 flux and soil temperature and moisture as well as spatial dependence; and geostatistics to map CO_2 and delineate high flux zones.

Soil temperature was observed to have a positive, monotonic correlation with fluxes while soil moisture was observed to have a negative, monotonic correlation. Spatial dependence of CO_2 fluxes on reclaimed mine land was observed on one of the two study sites. The research suggests that macro-porosity and gas permeability may be important factors that explain CO_2 migration in mine spoil. A flux survey protocol has been developed, based on these results, for reclaimed mine lands. The work demonstrates the capability of geostatistical methods to delineate high flux fields. Further research will be required to determine suitable thresholds for such analysis.

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EXECUTIVE SUMMARY

Elevated concentrations of carbon dioxide (CO_2) have been found in homes built on reclaimed mine land and land adjacent to active mines. Forensic geochemistry has identified acid mine drainage (AMD) neutralization reactions between the acidic waters and alkaline addition in mine spoil as the source of this CO_2. Fast and reliable survey methods are needed to assess reclaimed mine land to determine the extent and intensity of the CO_2 flux field. Current forensic approaches are retrospective and cannot be easily implemented as a survey technique over large parcels of land, prior to construction.

The objectives of this project were to develop:

(i) A soil CO_2 flux survey protocol for assessing reclaimed mine land for construction purposes; and
(ii) An approach to delineate high CO_2 flux fields for making decisions on post-mining land uses.

Two reclaimed mine sites with homes, which have a history of elevated CO_2 concentrations attributed to AMD-carbonate reactions, were used as study sites. The research involved conducting chamber accumulation flux surveys; stable carbon isotope ratio analysis; statistical techniques hypothesis testing to examine correlation between CO_2 flux and soil temperature and moisture as well as spatial dependence*; and geostatistics to map CO_2 and delineate high flux zones.

Based on the research results, a flux survey protocol has been developed for reclaimed mine lands. The main components of this protocol are:

- Flux samples should be taken at less than 61 m (200 ft) spacing, respecting best practice for chamber accumulation flux measurement (Parkin, et al., 2003).
- Soil temperature and moisture need to be measured at each sample point during flux measurement. Soil temperature was observed to have a positive, monotonic correlation with fluxes while soil moisture was observed to have a negative, monotonic correlation. Spearman's rank correlation coefficient of 0.32-0.55 ($p < 0.0001$) and 0.34-0.42 ($p < 0.0001$) were observed for correlation between CO_2 flux and soil temperature and moisture, respectively.
- All data should be collected in one day, preferably, during the period from mid-morning to mid-afternoon. Data from different days should be treated as separate, since sample day effects are significant ($p < 0.0001$).

The results show that spatial variation of CO_2 fluxes on reclaimed mine land is not always random. Tests of spatial dependence yielded Moran's I values ranging from 0.15-0.43, which were found to be significant ($p < 0.025$). Given the observed spatial dependence, geostatistical

* Spatial dependence refers to correlation between the same variable measured at different locations (Schabenberger & Gotway, 2005).

methods have been demonstrated to be capable of delineating high flux fields, although, further research is needed to establish thresholds for such analysis.

The research suggests that macro-porosity and gas permeability may be important factors that explain CO_2 migration in mine spoil. Low soil-atmosphere CO_2 exchange, under normal circumstances, was observed even though CO_2 concentrations at depth in the spoil were high (up to 17.6%). In addition, surface CO_2 carbon isotopic composition indicates very little upward migration, under normal diffusive fluxes. Parts of the property disturbed by construction activities appear to have the higher fluxes. This can lead to misleading conclusions from isotope ratio results if soil gas samples are not acquired from depth.

1 INTRODUCTION

Elevated levels of carbon dioxide (CO_2) have been found in homes built on reclaimed and abandoned mine land in recent years CO_2 (Ehler, 2002; Laughrey C. D., Baldassare, Ehler, & Rathburn, 2002; Laughrey & Baldassare, 2003; PGS, 2008). In some instances, CO_2 concentrations in excess of 25% and oxygen (O_2) concentrations of less than 10% have been reported in the literature (Laughrey & Baldassare, 2003; Robinson, 2010). OSHA has a CO_2 general permissible exposure limit of 0.5% (5,000 ppm) and a short term exposure limit of 3%. CO_2 concentrations above 10% can produce unconsciousness or death while lower concentrations may cause headaches, sweating, rapid breathing, increased heartbeat, shortness of breath, dizziness, mental depression, visual disturbances, or shaking.

Geologic forensic studies have attributed the elevated CO_2 concentrations in some homes built on or adjacent to reclaimed mine spoil, in large part, to neutralization reactions between acid mine drainage (AMD) and mineral carbonates (Eq. 1). Figure 1 shows driving mechanisms that cause CO_2 migration to homes built on reclaimed mine land.

$$2H^{+}_{(aq)} + CaCO_{3(s)} \rightarrow Ca^{2+}_{(s)} + H_2O_{(l)} + CO_{2(g)} \quad (1)$$

The presence of elevated CO_2 concentrations, however, does not completely eliminate commercial and residential development as a viable post-mining land use for coal mine land with AMD potential and alkaline addition. There is a need for techniques to delineate the spatial limits of the CO_2 flux (F_{CO_2}) field and map the intensity of the CO_2 flux at different points on such reclaimed mine land. Such a technique can be the basis for including pre-construction building mitigation techniques (e.g. sub-slab pressurization systems) or deciding whether or not these parcels of land are suitable for development. The goal of this project was to investigate the use chamber accumulation (CA) trace gas flux surveys and geostatistical analysis to delineate high risk zones prior to construction. The specific objectives were to develop: (i) a carbon dioxide (CO_2) trace gas flux survey protocol for assessment of reclaimed mine land for construction purposes; and (ii) an approach to delineate high

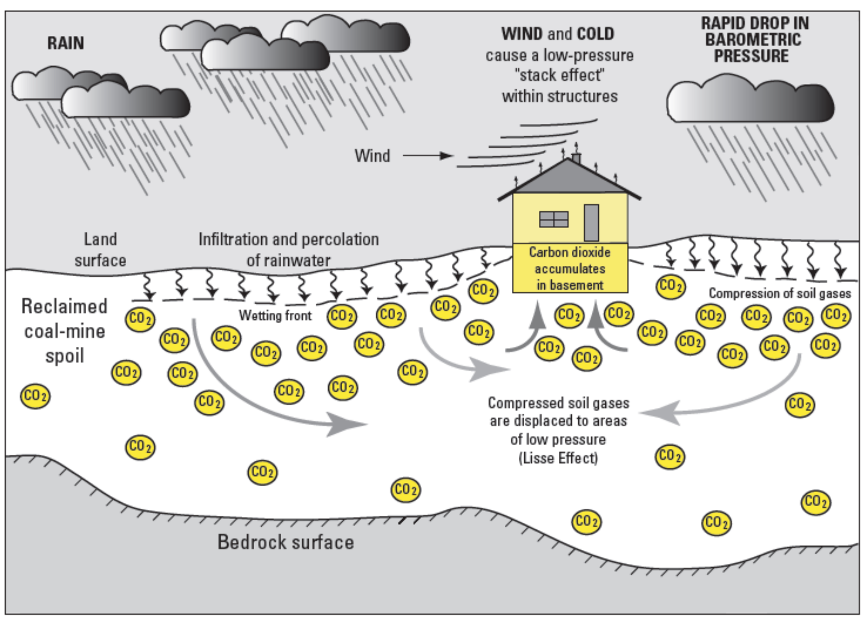


Figure 1 Common pathways and driving mechanisms of CO_2 in residential construction on reclaimed and abandoned mine land (Robinson, 2010)

(above established threshold) CO_2 flux field for decision making.

The work involved CA flux surveys on two reclaimed mine sites with homes, which have experienced episodes of elevated CO_2 concentrations attributed to AMD-carbonate reactions. Stable carbon isotope analysis, using isotope ratio mass spectrometry (IRMS), was used to investigate the presence of AMD generated CO_2. Statistical techniques were used to test for correlation between CO_2 flux (F_{CO_2}) and soil temperature and moisture as well as spatial dependence. Spatial dependence (also referred to as autocorrelation) refers to correlation between the same variable measured at different locations (Schabenberger & Gotway, 2005). Sequential Gaussian simulation (sGs) was used to delineate the spatial boundaries of CO_2 fluxes above certain limits.

2 RECLAIMED MINE SOIL CO_2 & TRANSPORT MECHANISMS

Soil CO_2, like other trace gases, has been monitored on agricultural, forest and pasture soils (Davidson, Belk, & Boone, 1998) and volcanic and hydrothermal activity areas (Lewicki, Hilley, Tosha, Aoyagi, Yamamoto, & Benson, 2007; Chiodini, Caliro, Cardellini, Avino, Granieri, & Schmidt, 2008), in an effort to understand the mechanisms responsible for and conditions affecting efflux of these gases from the soil. Sources of soil CO_2 such as root respiration, soil organic carbon and microbial activity have been well documented (Davidson, Belk, & Boone, 1998; Jacinthe & Lal, 2006). Even though AMD-mineral carbonate reactions have been known to produce significant quantities of CO_2 (Cravotta III, Dugas, Brady, & Kovalchuk, 1994), its contribution to soil-atmosphere exchange has not been as well studied.

Trace gas transport through soils is primarily by diffusive and advective fluxes.. The major diffusive fluxes are molecular diffusion and pressure driven advective flux. Thermal gradients in soil are generally too low to drive gas migration (Scanlon, Nicot, & Massmann, 2002). In reclaimed pyritic mine soils such as coal mine spoils, however, a significant temperature gradient may exist (Lefebvre, Lamontagne, Wels, & Robertson, 2002). Molecular diffusion is mainly driven by concentration gradient between the soil pores and the atmosphere. CO_2 diffuses from the soil where its concentration is high into the atmosphere. Oxygen is consumed during soil respiration in natural soils and during AMD formation in sulfidic mine spoils. AMD neutralization by mineral carbonates produces significant amounts of CO_2. Hence, soil CO_2 concentration at depth is much higher than atmospheric concentrations (Cravotta III et al., (1994), for instance, recorded concentrations in excess of 16% at 11 m below surface).

Atmospheric pressure fluctuations are responsible for the advective transport of CO_2 and other soil trace gases from the soil into the atmosphere, a phenomenon known as barometric pumping (Scanlon, Nicot, & Massmann, 2002; Massman, 2006). Pressure gradients between the atmosphere and the soil results from the response lag of soil pressure to changes in atmospheric pressure. Barometric pumping significantly affects gas transport since advective fluxes, resulting from relatively small pressure gradients, are much larger than diffusive fluxes. It has been well documented that episodes of CO_2 influx into homes with AMD-generated CO_2 hazards occur immediately after a sharp drop in atmospheric pressure (Robinson, 2010).

CO_2 concentration in the soil is influenced by soil temperature which affects respiration/metabolic rates, chemical reaction rates, and molecular kinetic energy. All of these factors generally increase with increase in soil temperature. Higher soil temperature results in higher diffusion rates and hence higher CO_2 fluxes. Soil gas concentrations are controlled by temperature, pressure and air-filled soil pore spaces, which is a function of soil moisture (Davidson, Belk, & Boone, 1998; Aachib, Mbonimpa, & Aubertin, 2004; Pihlatie, et al., 2007).

Stable isotope geochemistry is a proven way of distinguishing between different sources of CO_2 (Laughrey & Baldassare, 2003; Chiodini, Caliro, Cardellini, Avino, Granieri, & Schmidt, 2008). The $\delta^{13}C$, in parts per thousand or per mill (‰), which is defined by Eq. (2), is used to express the stable carbon isotope composition in a sample. The $\delta^{13}C$-CO_2, based on the Pee Dee Belemnite (PDB) reference standard, was used in this project. The PDB standard is assigned 0 ‰; negative $\delta^{13}C$ values indicate ^{12}C enriched samples; and positive $\delta^{13}C$ values indicate ^{13}C enriched samples (Hoefs, 1997). Laughrey and Baldassare (2003) show that $\delta^{13}C$ of CO_2 from AMD neutralization reactions in the studied reclaimed mine lands in Pennsylvania range from -7.01 to +2.86‰. Chiodini, et al. (2008) show the mean $\delta^{13}C$ of CO_2 from biogenic sources to be between -27 and -15‰.

$$\delta^{13}C_{\text{sample}} = \left(\frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \right) 1000 \qquad (2)$$

Measurement of gas isotopic composition during chamber accumulation soil flux measurement is affected by gas mixing (between atmospheric and soil gases in the chamber) and diffusion (Bertolini, et al., 2006). Keeling (1958 & 1961) proposed the linear mixing model shown in Eq. (3). $\delta^{13}C_M$, $\delta^{13}C_B$, and $\delta^{13}C_S$ are the delta-13 of the CO_2 mixture (in the chamber), background CO_2, and the source (soil) CO_2, respectively; and c_B and c_M are the background and mixture CO_2 concentrations, respectively. Eq. (3) allows one to obtain the $\delta^{13}C$ of the source graphically as the vertical axis intercept by plotting $\delta^{13}C$ of the chamber CO_2 against the inverse of the mixture CO_2 concentration. This is the so called Keeling plot.

$$\delta^{13}C_M = c_B \left(\delta^{13}C_B - \delta^{13}C_S \right) \frac{1}{c_M} + \delta^{13}C_S \qquad (3)$$

Diffusion effects make isotope ratios determined from CO_2 flux different from a grab sample of soil pore gas (i.e. a sample that does not diffuse through soil). It has been shown theoretically, and validated experimentally, that the diffusion coefficients of $^{13}CO_2$ and $^{12}CO_2$ differ by 4.4 parts per thousand (‰) (Davidson, 1995). Hence, the $\delta^{13}C$ of the soil CO_2 in this work determined from the Keeling plot was reduced by 4.4 ‰ to account for the diffusion effects.

3 EXPERIMENTAL METHODS & PROCEDURES

3.1 Study sites

Field sampling was conducted at two reclaimed mine sites: one in Pike County, IN and the other in Sommerset County, PA. Both sites have been the subject of CO_2 studies to mitigate hazards in homes built on reclaimed mine spoil (Laughrey & Baldassare, 2003; Robinson, 2010).

The first study site is located in Pike County, (Latitude: 38° 19′ 42″ N and Longitude: 87° 08′ 27″ W) in southwestern Indiana. Robinson (2010) describes the site history. The soils are described as Fairpoint loam, reclaimed (unit FaB) at 1 to 15° slopes (Natural Resources Conservation Service (NRCS), 2009). The site is a reclaimed surface coal mine covering an area of about 90 acres. Mining was carried out from 1986 to 1992 and the site was reclaimed with lime amendment and about 3 ft of top soil capping. The spoil material extends about 40 ft below the single story home, with a basement, build on it. The home has been experiencing intermittent episodes of elevated concentrations of stray CO_2 in its basement since 2006 (Robinson, 2010).

The second site is the reclaimed Godin Mine - Permit No. 56010105 - (the current Godin family residence) in Jeners, Sommerset County, PA (Latitude: 40° 08′ 2″ N and Longitude: 79° 02′ 52″). The soils in the area are the Wharton and Rayne-Gilpin channery silt loams (units WhC and RgF) (NRCS, 2009). Stray CO_2 in the Godin residence was investigated by the Pennsylvania Department of Environmental Protection (PA-DEP) in 2003 (Laughrey & Baldassare, 2003). The home is built on the spoil of the reclaimed Godin Mine, which is about 70 ft thick. The permit required an operational plan that included spoiling pit cleanings in pods at least 10 ft above the pit floor. Additionally, 20 tons/acre of lime addition to the pit floor was required prior to backfilling. Isotopic analyses of the CO_2 yielded a $\delta^{13}C$ of -4.07‰ for the gas accumulating in the basement compared to -4.18‰ for the gas in a monitoring well drilled to the pit floor. These results led PA-DEP investigators to conclude that the source of the CO_2 in the home was the AMD-carbonate reactions in the spoil.

3.2 Field sampling procedures

3.2.1 Flux Sampling

Soil CO_2 fluxes were measured using an LI-8100-103 automated soil CO_2 flux monitoring system (Licor Biosciences, Inc., Lincoln, Nebraska). Collars (100 mm high) were made from 200 mm diameter PVC pipes. Collars were inserted into the soil to leave 20 mm of collar above the soil (Parkin, et al., 2003). All collars were installed at least 24 hours prior to flux measurements to allow the soil gas fluxes to stabilize after initial disturbance from installation. The chamber was deployed for a short period, 2 minutes, to minimize pressure buildup, which may impact the CO_2 flux and lead to flux underestimation. The LI-8100 is capable of simultaneous logging from auxiliary sensors. For this project, auxiliary sensors were used to acquire soil moisture and temperature data.

An ECH_2O EC-5 soil moisture probe (Decagon Devices, Inc., Pullman, WA), with at least 0.03 m^3/m^3 accuracy and 10 milliseconds measurement time, was used for measuring volumetric soil moisture content. An Omega (Omega Engineering Inc., Stamford, Connecticut) soil temperature probe (a T-handled Type E thermocouple with 6.4 mm (0.25") diameter and 250 mm (10") immersion length) was used to measure soil temperature. The thermocouples measurement range is from -40 to >100°C. The thermocouple was inserted 7.5 cm (3 in) into the soil for measurement.

The objective of the flux sampling was to characterize the CO_2 emission rate and the spatial dependence of the fluxes. Geostatistics is useful for describing the spatial correlation of variables (e.g. metal concentrations in ores and environmental pollutants). The problem of spatial sampling design is well known in geostatistics. The objective of spatial sampling design is to come up with a sampling design that minimizes the prediction error subject to constraints. If kriging is the prediction method, then the kriging variance can be shown to be the mean squared prediction error criterion (Cressie, 1993). The kriging variance depends on the number of sample points used for the estimation, the relative location of these sample points, and the chosen variogram model. It does not depend on the measured values at these points (which are not available during sampling design). This makes kriging the method of choice for spatial sampling design (Cressie, 1993). The problem is that a variogram model is required for spatial sampling design. At the sampling design stage, there is no data with which to predict the variogram model.

In this work, the spherical variogram model was assumed based on preliminary data collected at the Godin site prior to this project. Model parameters for the spherical model were determined based on least square fitting of experimental variogram using this data. Using this assumed variogram model, it was determined that a grid with points spaced less than 61 m (200 ft) apart is desirable to describe the spatial dependence of the fluxes (Awuah-Offei, Mathiba, & Baldassare, 2010). Lower grid spacing provides more confidence in the data but requires more resources (man-hours and/or equipment) to complete a survey in a single day.

One 1-week field survey was executed for each site. Each visit included establishing sample collars, flux surveys, and isotope sampling. This work schedule allowed for three days of flux monitoring. In all, 138 sampling locations were established at the Pike County site (Figure 2) and 71 locations were established at the Godin site (Figure 3). The grid nodes were first established by staking and then surveying using a global positioning system (GPS), (Topcon Positioning Systems, Livermore, CA), to establish the true coordinates of each sample point.

The survey at Pike County was conducted in early spring (March 29-April 2, 2010) while the Godin survey was conducted in summer (July 12-16, 2010). Total precipitation for March 2010 and the week before the survey (March 22-28, 2010) at the Evansville Airport (approx. 33 miles SE of Pike County site) was 100.8 mm (3.97 in) and 47.8 mm (1.88 in), respectively. The USGS weather station on the property recorded 12.7 mm (0.5 in) of rainfall on March 28, 2010. Total rainfall recorded at the Johnstown Airport (approx. 17 miles NE of Godin site) was 31 mm (1.22

in) from July 4-10, 2010 (week before survey) and 109 mm (4.29 in) for June 2010. Due to equipment issues, soil temperature and moisture data for the Godin site were not obtained.

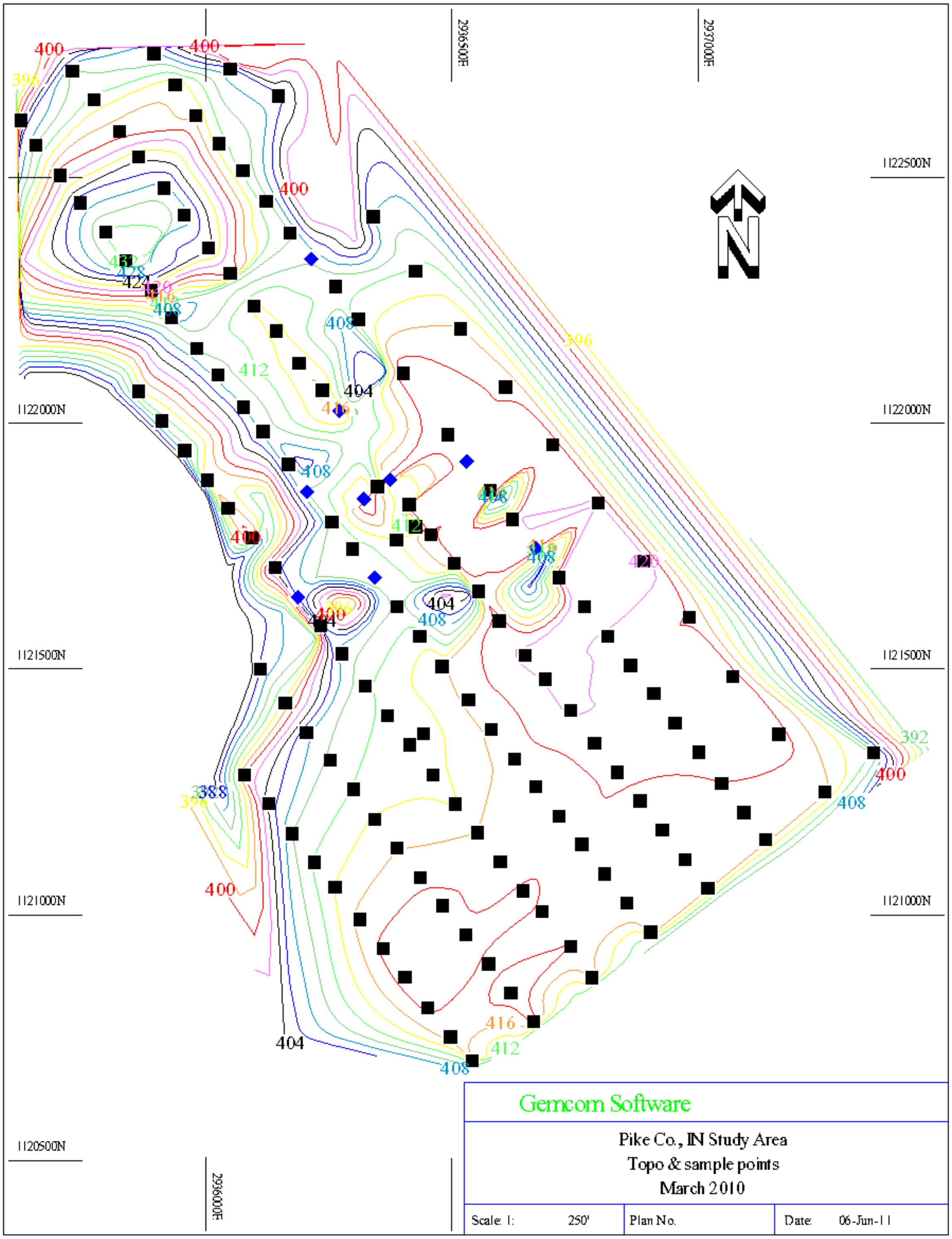


Figure 2 Pike County study site with sample points. Blue points indicate points where soil gas samples were taken for isotope testing.

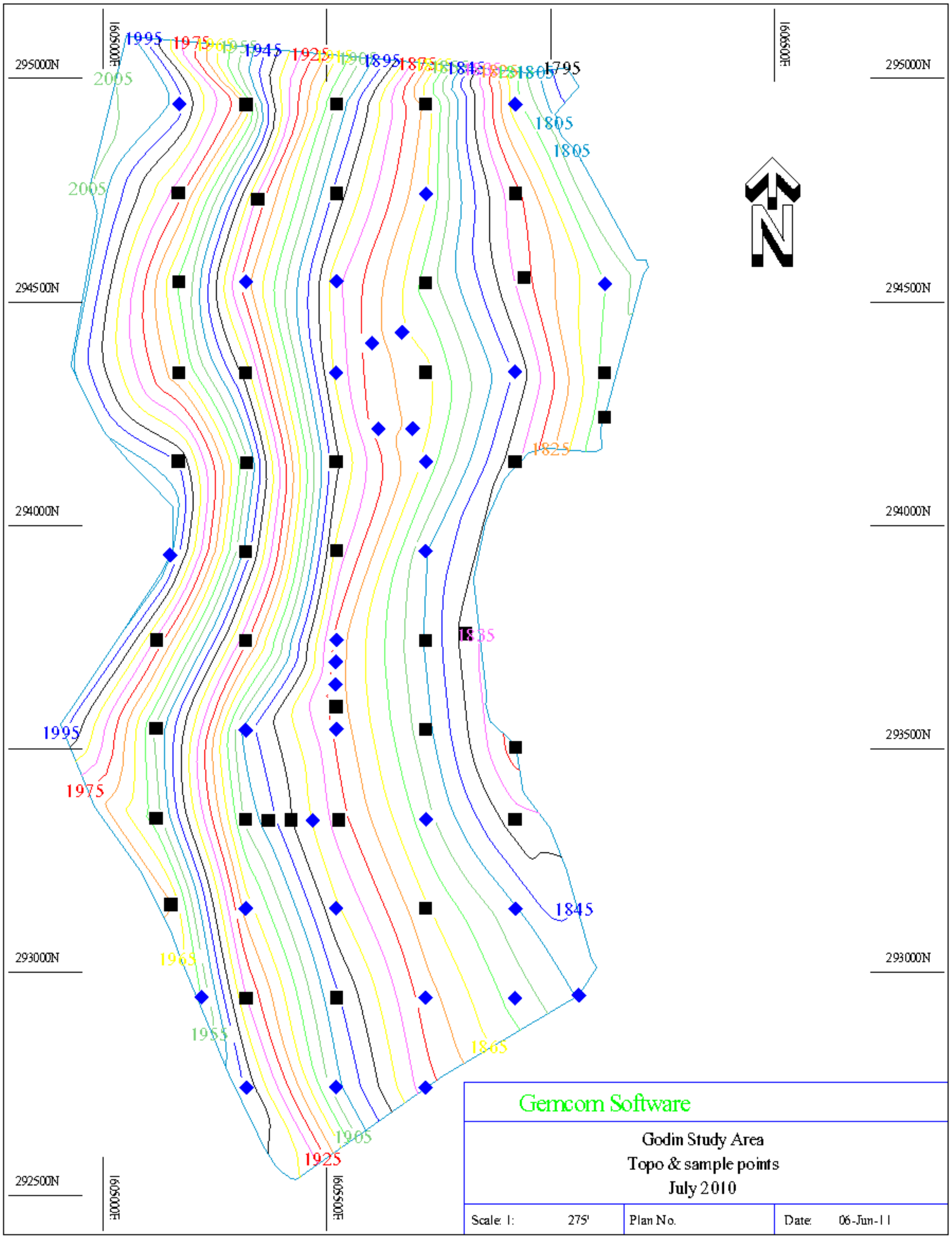


Figure 3 Godin study site with sampling points. Blue points indicate points where soil gas samples were taken for isotope testing.

3.2.2 Isotope Sampling

Two approaches were used in this study – isotope sampling during CA flux measurement and grab soil gas sampling. The grab soil gas sample was obtained by using a slam bar to drive a 0.6 m (2 ft) deep hole into the soil and hand aspirating a sample into the sample bag. Isotope sampling during CA flux measurement involved drawing chamber gas samples during flux measurement for isotope ratio mass spectroscopy (IRMS). Grab sampling relies on only one sample (cheap to analyze) and is simple but interferes with flux sampling (since driving the hole in the collar prevents reusing the sample location for flux) and the isotope signature may not necessarily correspond to flux reading at the location. Sampling during flux measurement requires at least three samples (expensive to analyze), provides isotope signatures that can be directly correlated to the flux reading at the location, and does not interfere with flux measurement (collars can be reused). The disadvantage is that, determining the CO_2 isotope signature is not straightforward as gas mixing and differential diffusion has to be accounted for. Grab sampling was used at the Godin site while sampling during flux measurement was used at the Pike County site. All soil gas samples were analyzed using IRMS at Isotech Laboratories (www.isotechlabs.com).

The approach used in the Pike County survey was to draw three 60 ml chamber gas samples during a 20-minute CA flux measurement run for isotope ratio analysis. Three samples were deemed the minimum to account for gas mixing as discussed in Section 2. The first sample was drawn after 10 minutes or when the chamber CO_2 concentration was greater than 500 ppm, which ever came later. 500 ppm was the laboratories minimum concentration for the IRMS analysis. Two more samples were drawn spread over the remaining time. In all, 27 samples at nine sample locations over the property were analyzed for isotope ratios. Eight of the 27 samples were also analyzed using gas chromatography (GC) to determine the CO_2 concentration. This was for quality control – to ensure that the estimates of the CO_2 concentrations from the LI-8100 system were accurate.

At the Godin site, 32 samples from 32 sample locations were analyzed. The sampling protocol involved driving a ~1.25 cm diameter drive point to a depth of 0.3-0.6 m in the soils within the sampling collar. A soil gas sample is then hand aspirated into a sample bag for IRMS analysis (Laughrey & Baldassare, 2003).

3.3 Data Analysis

3.3.1 Correlation Analysis

The strengths of association between CO_2 flux and soil moisture and temperature were investigated using the parametric Pearson's and the nonparametric Spearman's measure of correlation. Correlation coefficient is a measure of how two variables vary with respect to each other. The Pearson's product-moment correlation measures both the strength and direction of a linear relationship. A Pearson's correlation coefficient of 1 indicates an exact positive gradient (increase in independent variable causes an increase in the dependent variable) linear relationship while an exact negative gradient linear relationship exists if the correlation is -1. If there is no linear predictability between the variables, the correlation coefficient is 0 and they are said to be independent. The Spearman's correlation coefficient is a rank-ordered, nonparametric measure of association and is more suited for non-linear relationships. A positive Spearman correlation coefficient indicates an increasing monotonic trend between the two variables while a negative coefficient indicates a decreasing monotonic trend. Eqs. (4) and (5) describe the Pearson's and Spearman's correlation coefficients, respectively. $\bar{x}$ is the mean of x, $\bar{y}$ is the average of y and s_x and s_y are standard deviations of x and y, respectively. P_i is the rank of x_i, Q_i is the rank of y_i, $\bar{P}$ is the mean of the P_i values, and $\bar{Q}$ is the mean of the Q_i, values.

$$\rho = \frac{\frac{1}{n}\sum_{i=1}^{n}\left(x_i - \bar{x}\right)\left(y_i - \bar{y}\right)}{s_x s_y} \tag{4}$$

$$r = \frac{\sum_{i=1}^{n}\left(P_i - \bar{P}\right)\left(Q_i - \bar{Q}\right)}{\sqrt{\sum_{i=1}^{n}\left(P_i - \bar{P}\right)^2\left(Q_i - \bar{Q}\right)^2}} \tag{5}$$

Both correlation measures were used to evaluate the correlations between CO_2 flux, the dependent variable, and soil temperature and moisture, the dependent variables, under the hypothesis that the correlation between CO_2 flux and these factors is insignificant ($H_0 : \rho = 0$ versus $H_1 : \rho \neq 0$).

3.3.2 Tests for Spatial Dependence

In order to use geostatistics to describe CO_2 flux on reclaimed mine spoil, it is important to show that CO_2 flux is spatially dependent. The global and local indicator of spatial association (LISA) was estimated using the Moran's I statistic (Anselin, 1995). The estimated Moran's I (Eq. 6 shows the global Moran's I) was compared to the expected value (Eq. 7). $Z\left(\mathbf{s}_i\right)$ is the natural log of the flux at location $\mathbf{s}_i$; $\bar{Z}$ is the sample mean of the natural log of the flux; w_{ij} is the weight given to the spatial relationship between samples i and j; and n is the number of samples. We chose to use the inverse square distance as the weight (Eq. 8). If the estimated Moran's I is significantly greater than the expected value, then the data shows spatial dependence (for the local statistic, then the flux at that location shows spatial dependence). Spatial dependence was tested at 95% confidence level by using the variance of the Moran's I under the randomization assumption (Anselin, 1995; Schabenberger & Gotway, 2005).

$$I = \frac{n}{(n-1)S^2 w_{..}}\sum_{i=1}^{n}\sum_{j=1}^{n} w_{ij}\left(Z\left(\mathbf{s}_i\right) - \bar{Z}\right)\left(Z\left(\mathbf{s}_j\right) - \bar{Z}\right) \tag{6a}$$

$$S^2 = \frac{\sum_{i=1}^{n}\left(Z(\mathbf{s}_i) - \overline{Z}\right)^2}{n-1} \tag{6b}$$

$$\mathrm{E}[I] = -\frac{1}{n-1} \tag{7}$$

$$w_{ij} = d_{ij}^{-2} \tag{8}$$

3.3.3 Geostatistical Modeling

Geostatistical analysis in this work includes variogram modeling, and estimation and probability maps using sequential Gaussian simulation (sGs). GS+ version 9 (Gamma Design Software, Plainwell, Michigan) was used for geostatistical work. Spherical, exponential and gaussian variogram models have been implemented in GS+. Variogram fitting is by least squares. 1,000 simulations were carried out for each scenario.

4 RESULTS & DISCUSSIONS

4.1 Preliminary Data Analysis

Table 1 shows summary statistics of soil CO_2 flux data from both sites. The Pike County fluxes were found to be positively skewed according to the Anderson-Darling normality test (p < 0.005) for all sampling days (Table 1a). This is not surprising given that fluxes are bounded at zero with the possibility of high values. However, after log transforming the data, the non-normality was removed as indicated by the lower A^2 values with higher p-values (p > 0.05) (Table 1a). Probability plots of the data visually confirm this (e.g. Figure 4). The raw data probability graphs show distinct curvature while the log transformed flux graphs plot on a fairly straight line as expected for normally distributed data. The Godin data, on the other hand, does not show as much skewness, even though log transforming the data seems to help (with the exception of July 14).

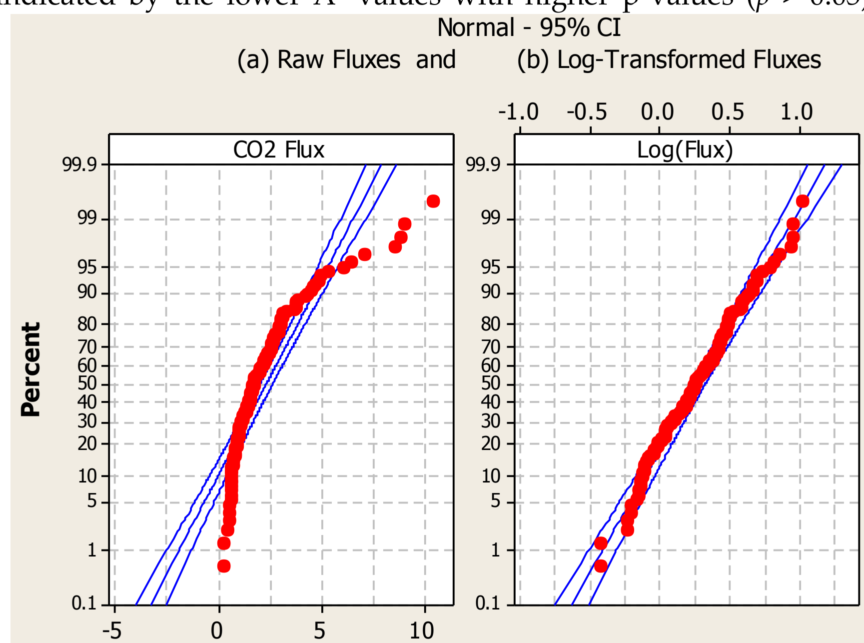


Figure 4 Sample probability plot of fluxes (Pike County – March 30)

Table 1a Summary statistics of Pike County, IN flux data

Parameter		March 30, 2010 F_{CO_2} [μmol/m²/sec]	March 30, 2010 $\log(F_{CO_2})$	March 31, 2010 F_{CO_2} [μmol/m²/sec]	March 31, 2010 $\log(F_{CO_2})$	April 1, 2010 F_{CO_2} [μmol/m²/sec]	April 1, 2010 $\log(F_{CO_2})$
Anderson-Darling normality test	A^2	7.15	0.29	7.27	0.49	6.44	0.70
	p-value	< 0.005	0.600	< 0.005	0.216	< 0.005	0.064
Mean		2.345	0.269	2.512	0.330	2.960	0.401
Standard deviation		1.820	0.294	1.676	0.238	1.806	0.236
Variance		3.313	0.086	2.809	0.056	3.262	0.056
Skewness		2.167	0.187	2.355	0.493	2.095	-0.078
Kurtosis		5.695	-0.175	7.077	0.147	5.539	1.540
Number of samples, N		131	131	131	131	130	130
Minimum		0.380	-0.420	0.750	-0.125	0.310	-0.509
1st Quartile		1.110	0.045	1.430	0.155	1.790	0.253
Median		1.820	0.260	2.040	0.310	2.600	0.415
3rd Quartile		2.880	0.459	2.99	0.476	3.595	0.556
Maximum		10.520	1.022	9.94	0.997	10.960	1.040

Table 1b Summary statistics of Godin flux data

Parameter		July 13, 2010 F_{CO_2} [μmol/m²/sec]	July 13, 2010 $\log(F_{CO_2})$	July 14, 2010 F_{CO_2} [μmol/m²/sec]	July 14, 2010 $\log(F_{CO_2})$	July 16, 2010 F_{CO_2} [μmol/m²/sec]	July 16, 2010 $\log(F_{CO_2})$
		SAMPLE DAY					
Anderson-Darling normality test	A^2	1.57	0.88	0.68	1.89	0.63	0.26
	p-value	< 0.0005	0.023	0.071	< 0.005	0.099	0.700
Mean		5.029	0.664	8.859	2.132	7.878	2.00
Standard deviation		2.264	0.186	3.049	0.400	2.716	0.3539
Variance		5.123	0.0345	9.295	0.160	7.374	0.1252
Skewness		2.472	-0.4098	0.0934	-2.330	0.584	-0.2614
Kurtosis		12.627	1.6950	1.428	11.439	-0.008	-0.1342
Number of samples, N		71	71	73	72	71	71
Minimum		1.250	0.097	0.000	-0.041	2.730	1.00
1st Quartile		3.630	0.560	7.055	1.959	5.760	1.751
Median		4.800	0.681	8.910	2.191	7.890	2.066
3rd Quartile		6.040	0.781	10.620	2.366	9.500	2.251
Maximum		17.59	1.245	17.160	2.843	15.160	2.719

The effect of sample day on the data was evaluated by multiple mean comparison t-test using (multivariate) analysis of variance (ANOVA). Table 2a shows April 1 (Day 3) fluxes at the Pike County site to be significantly different from those for March 30 and 31 (Day 1 and 2). Soil temperatures are significantly different for all the three days while soil moisture for March 30 (Day 1) is significantly different from March 31 and April 1 (Days 2 and 3). For Godin, Table 2b shows that July 13 (Day 1) soil fluxes are significantly different from July 14 and 16 (Days 2 and 3).

Table 2a Bonferroni's mean comparison t-test for Pike County

Sample Day Comparison	**CO_2 Flux [μmol/m²/sec]**			**Soil Temperature (°C)**			**Soil Moisture (% by volume)**		
	Diff. between means	*Simultaneous 95% confidence limits*		*Diff. between means*	*Simultaneous 95% confidence limits*		*Diff. between Means*	*Simultaneous 95% confidence limits*	
3 - 2	0.615	0.093	1.137*	3.0072	1.202	4.812 *	-0.8988	-1.801	0.004
3 - 1	0.801	0.276	1.327*	8.1713	6.3532	9.990 *	1.6988	0.790	2.608*
2 - 1	0.187	-0.337	0.711	5.1641	3.3525	6.976 *	2.5976	1.692	3.503*

* Significant at 95% confidence level

Table 2b Tukey's mean comparison t-test for Godin

Sample Day Comparison	**CO_2 Flux [μmol/m²/sec]**		
	Diff. between means	*Simultaneous 95% confidence limits*	
3 - 2	-0.981	-2.042	0.081
3 - 1	2.850	1.781	3.919*
2 - 1	3.830	2.768	4.892*

* Significant at 95% confidence level

The Wilk's Lambda for test of sample data effect for the Pike County site is 0.71500 ($p < 0.0001$) while the ANOVA test, for the hypothesis of no overall sample day effect, F-test statistic is 38.94 ($p < 0.0001$) for the Godin site. These confirm that sample data significantly affects the data and hence each day should be treated differently. This was to be expected given the different atmospheric conditions on the different days.

Finally, the effect of barometric pressure on the fluxes was evaluated, qualitatively. Figure 5 shows a typical plot of barometric pressure and fluxes for the sampling period in a day. There appears not to be a significant shift in fluxes as pressure drops gradually during the day. The correlation could not be tested quantitatively because the weather stations only logged barometric pressure periodically (30 mins to 1 hour) making it impossible to obtain barometric pressure readings for each flux reading.

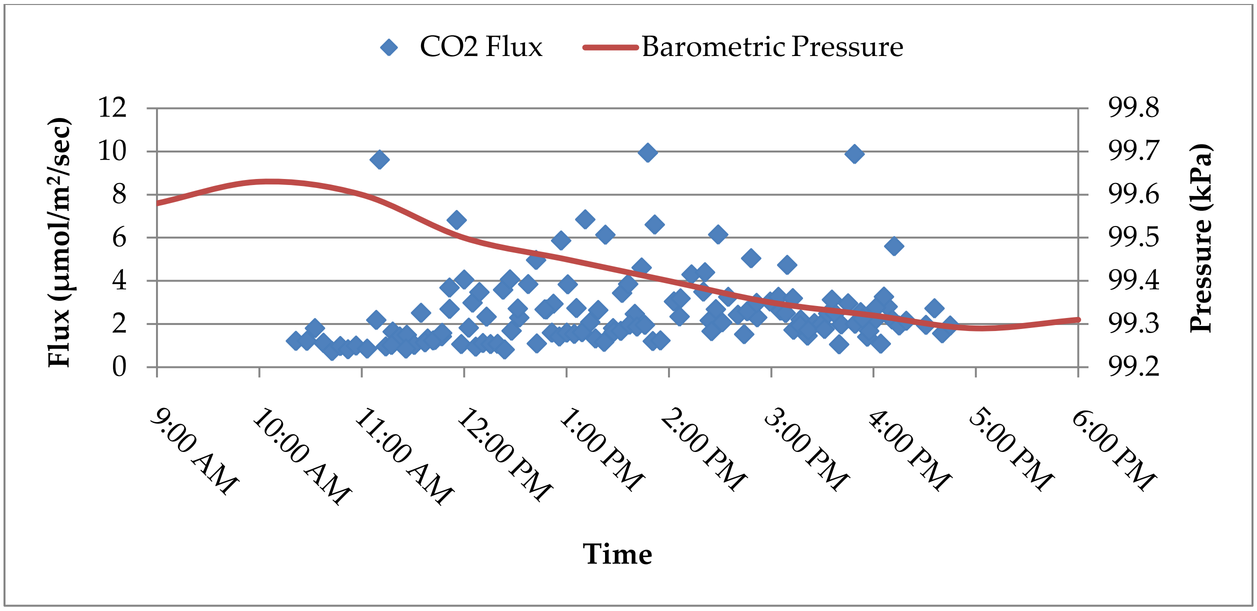


Figure 5 Effect of barometric pressure on fluxes: March 31, 2010 at Pike County site.

4.2 Isotope Results

Two sampling procedures were used to determine carbon isotope ratios at sampled locations. All gas samples were analyzed using isotope ratio mass spectroscopy (IRMS). CO_2 concentrations of the gas samples, acquired during flux monitoring, were estimated using the average CO_2 reading from the flux monitor during gas sampling.

Eight of the 28 samples (acquired from nine locations) during the Pike County survey were analyzed using gas chromatography (GC) to verify this approach (Figure 6). The mean error was 1.8% and ranged from 0.3% to 4.8%. The research team then proceeded to use the flux monitor estimates to plot Keeling plots for the nine sample points with three isotope samples. Figure 7 shows a sample Keeling plot. The y-intercept (-25.96 – 4.4 ‰) is the $\delta^{13}C$ of the soil CO_2 (Eq. 3). Table 3 shows the inferred stable isotope ratios for the soil CO_2 from all nine sampled locations from Pike County.

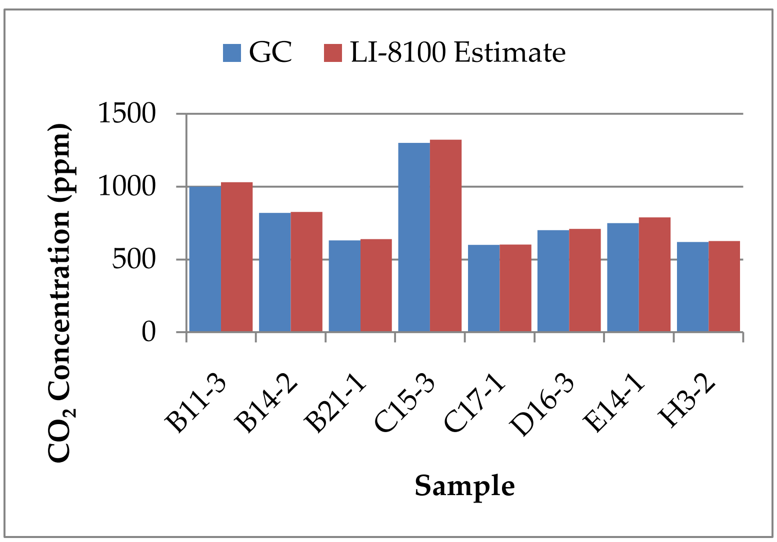


Figure 6 Comparison of GC results and flux monitor CO_2 concentrations

These isotope results were inconclusive. The highly negative $\delta^{13}C$ values indicate that majority of the CO_2 emitted at these locations were from microbial activity. However, this does not rule out some contribution from a limestone source. Additionally, isotope fractionation and dynamic effects from sampling through the chamber may be contributing to the inconclusive results (Risk & Kellman, 2008). The only way to rule out fractionation and the transient effects is to take more samples over a longer period. This option would have been too expensive, given the budgetary constraints of this project. An efficient alternative is to collect samples for isotope analysis through grab soil pore gas samples. This approach was employed during sampling at the Godin site.

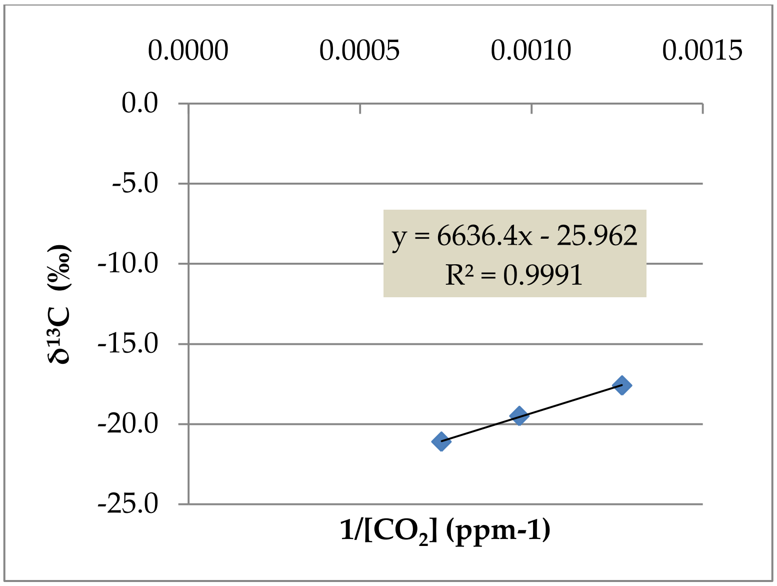


Figure 7 Sample Keeling plot (sample point D-13)

Table 3 Pike County isotope results

Sample	$\delta^{13}C$ (‰)	R^2
B11	-29.25	0.9924
B14	-32.12	0.9931
B21	-30.60	0.8978
C15	-30.99	0.9998
C17	-24.89	0.9975
D13	-30.36	0.9991
D16	-32.53	0.8616
E14	-31.82	0.9990
H3	-27.75	0.9945

Godin isotope results are shown in Table 4. The mean $\delta^{13}C$ is -20.2 ‰ and ranges from -24.5 to -11.0 ‰. The $\delta^{13}C$ for the gas samples are slightly more positive than the samples from the Pike County, IN site (mean of -30.3 ‰). These values are more negative than expected for a site that still shows signs of anthropogenic CO_2 migration (with the exception of a few samples – four samples had $\delta^{13}C > -16$ ‰). This leads the team to conclude that the protocols used at both sites are both valid. However, the issue is the proper characterization of the vertical profile of carbon isotope ratios and its temporal variation.

Table 4 Isotope results.

Sample	A-1	A-11	A-6	B-3	B-8	BC9-150	B-10	B-12
$\delta^{13}C$ (‰)	-23.4	-20.2	-16.4	-22.7	-20.5	-16.2	-21.6	-23.1
Sample	C-3	C-4	C-7	C7-50	C7-100	C-8	C-10	C-12
$\delta^{13}C$ (‰)	-22.7	-23.1	-22.3	-24.1	-11.0	-18.9	-15.5	-19.2
Sample	D-2	D-5	D-6	D-9	D-11	D-12	E-1	E-4
$\delta^{13}C$ (‰)	-24.0	-16.6	-20.4	-20.4	-15.8	-19.5	-19.4	-22.9
Sample	E-10	E-11	F-3	F-11	H-1	H-2	H-3	H-4
$\delta^{13}C$ (‰)	-24.5	-21.3	-21.2	-24.3	-18.8	-14.3	-18.9	-22.0

In order to show that deep anthropogenic CO_2 still exists at these sites, an additional experiment was conducted to examine the vertical isotope ratio profile. The goal was to show that deep anthropogenic CO_2 still exists at this site and that under normal conditions this CO_2 migrates upward only slowly. The LI-8100 flux monitor was modified for sampling soil gases at depth for laboratory analysis. Six wells were sampled around the house (Figure 8). The six 51 mm (2 in) wells were previously drilled by USGS (Robinson, 2010).

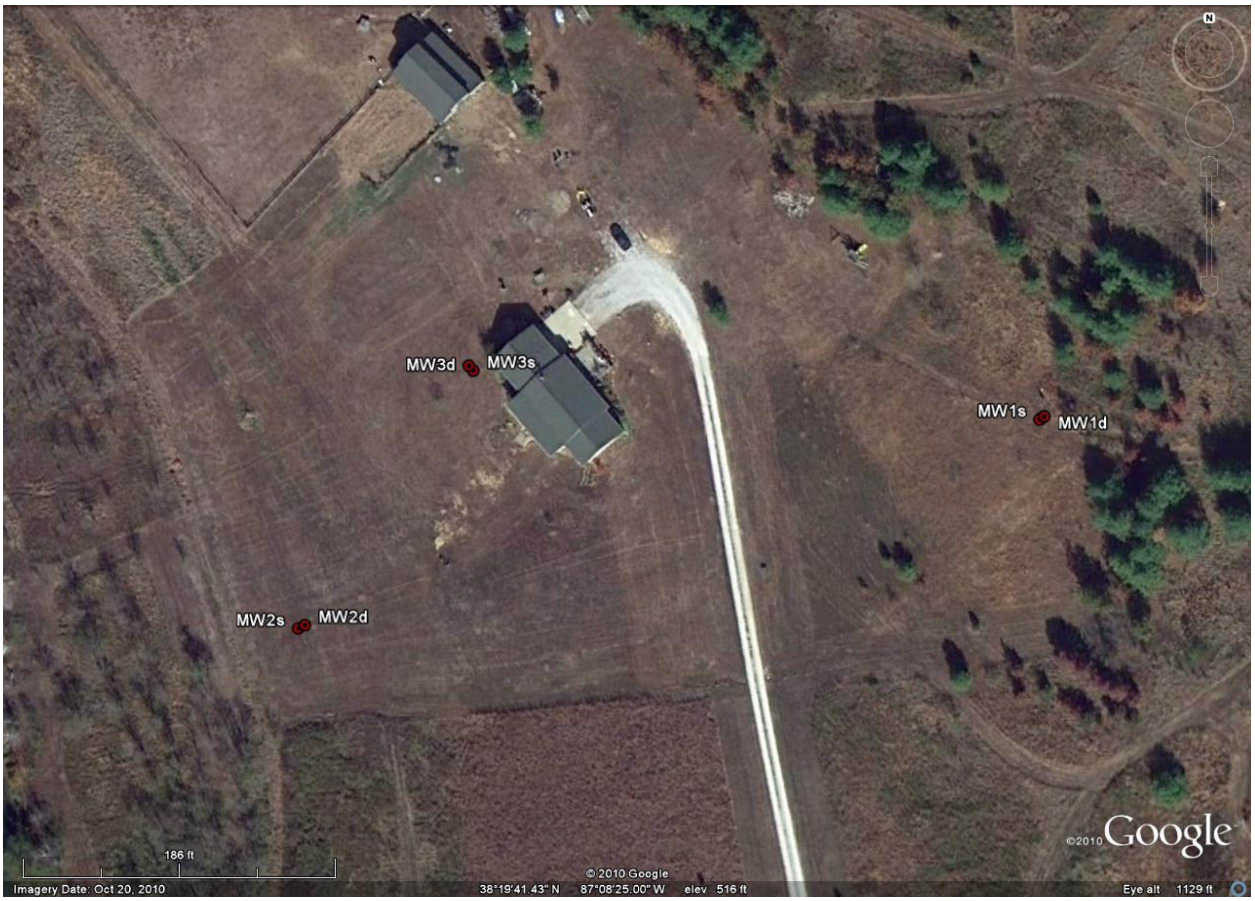


Figure 8 Well locations (Image copyright: Google Earth)

The flux monitor was modified with long (two 12 m/40 ft sections) "air-in" and "air-out" tubes capable of drawing air from the full depth of the holes. These tubes were then lowered into the holes to draw samples through the LI-8100 infra-red gas analyzer (IRGA) bench. This allowed the research team to continuously monitor CO_2 concentration during tests. The monitor is rated up to 3,000 ppm of CO_2. This was, however, enough to record the spike in CO_2 concentration once the deep CO_2 reaches the IRGA. The team collected gas samples from the tubes, once this spike in concentration was recorded. The samples were then sent to the lab for IRMS and GC analysis.

Table 5 shows CO_2 concentration and $\delta^{13}C$ recorded in each of the wells. The results show that:

- Soil gas CO_2 concentrations at depth are much higher than any recorded in this research.

- Soil gas CO_2 $\delta^{13}C$ at depth is between -11.4 and -5.0 ‰. This gas is ^{12}C deficient and derived from an inorganic carbonate source.
- With the exception of MW2, the deeper wells have higher soil gas CO_2 concentration than the shallower wells.
- Soil gas CO_2 in the deeper wells was less ^{12}C deficient than those from the shallower wells.

Table 5 Isotope and CO_2 concentration results

Well name	Northing (ft)	Easting (ft)	Screened interval (ft below land surface)	Land-surface elevation (ft)	CO_2 Concentration (ppm)	$\delta^{13}C$ (‰)
MW1D	1121807.74	2936650.67	33–38	420.729	175,800	-11.4
MW1S	1121806.129	2936648.111	13–18	420.67	86,600	-5.0
MW2D	1121688.754	2936228.984	34–39	410.17	5,200	-9.5
MW2S	1121686.855	2936224.983	13–18	410.12	133,000	-5.3
MW3D	1121836.885	2936324.526	33–38	419.982	112,400	-10.2
MW3S	1121834.097	2936327.069	13–18	419.88	94,000	-5.3

Based on the results in Table 5, it can be concluded that there is limestone derived CO_2 in the soil gases at the site. This is not evident in the surface soil isotope signatures because under normal diffusive conditions, the $\delta^{13}C$ values may be misleading since the $\delta^{13}C$ values of the native soil gases are unknown. This is consistent with Robinson's (2010) observations of CO_2 concentrations in the home atmosphere. He observed that CO_2 concentrations increase when there are meteorological events, which, we postulate, initiate advective flow conditions due to the resulting pressure gradient. Hence, highly negative $\delta^{13}C$ values (Tables 3 and 4) may be recorded at the surface even when anthropogenic CO_2 is present because of the low upward migration rates under normal diffusive flux conditions. This is an important finding since carbon isotope ratios are the primary source of establishing cause and liability of elevated CO_2 concentrations in homes.

Also, the results show that there is reduced upward migration under normal conditions. Given, the significantly higher concentrations at depth, the CO_2 fluxes should be higher than the observed fluxes. This may suggest low macro-porosity, and consequently gas permeability, in the spoil due to compaction (Jacinthe & Lal, 2006). Quite possibly, the measured surface fluxes include limestone derived CO_2, since the high concentrations of CO_2 at depth is bound to create diffusion driven transport. But this diffusive flux is not high enough to contribute significant amounts to the surface fluxes.

4.3 Correlation Analysis

Correlation between fluxes and soil temperature and moisture were analyzed using statistical techniques for the Pike County data (Table 6). All correlations were tested at 95% confidence (α

= 0.05). The Pearson's correlation coefficients were for log-transformed CO_2 flux data while the Spearman coefficients were based on raw data.

March 30 data showed significant correlations between soil-CO_2 fluxes and soil temperature and moisture (p <0.0001). The Pearson's and Spearman's correlation coefficients were found to be in agreement: 0.521 and 0.554, respectively, for CO_2 flux versus soil temperature and -0.402 and -0.416 for flux versus soil moisture. The soil temperature and soil moisture were also found to be significantly but negatively correlated, -0.220 (p = 0.012) and -0.197 (p = 0.024) for Pearson's and Spearman's, respectively. For March 31, however, only Pearson's coefficient indicates significant correlation between CO_2 flux and soil temperature (ρ = 0.280; p = 0.001). Spearman's coefficients indicates insignificant correlations between fluxes and soil temperature and moisture (r = 0.122, p = 0.165 for soil temperature and r = -0.113, p = 0.202 for soil moisture). For April 1, the tests show significant correlation between CO_2 fluxes and soil moisture. The Pearson's and Spearman's coefficients were in agreement (-0.325 and -0.338, respectively) even though the Spearman's is an order factor of magnitude more significant. Similarly, flux and soil temperature were found to be correlated both with Pearson's (ρ = 0.263, p = 0.002) and Spearman's (r = 0.337, p = 0.0002) coefficients.

Table 6 Correlation coefficients between CO_2 flux and soil temperature and moisture

DAY		Pearson's correlation coefficients of $\log\left(F_{CO_2}\right)$		Spearman's correlation coefficients of F_{CO_2}	
	Correlated Variable	Soil Temperature	Soil Moisture	Soil Temperature	Soil Moisture
March 30	CO_2 Flux	0.521	-0.402	0.554	-0.416
	p-value	< 0.001	< 0.001	< 0.0001	< 0.0001
	Soil Temperature		-0.220		-0.197
	p-value		0.012		0.024
March 31	CO_2 Flux	0.280	-0.106	0.122	-0.113
	p-value	0.001	0.230	0.165	0.202
	Soil Temperature		-0.041		-0.069
	p-value		0.639		0.436
April 1	CO_2 Flux	0.263	-0.325	0.318	-0.338
	p-value	0.002	<0.001	0.0002	< 0.0001
	Soil Temperature		-0.051		-0.037
	p-value		0.564		0.673

Generally, the correlations were weak except for March 30. Also, Spearman's coefficients were an order of magnitude more significant than Pearson's. This is consistent with literature that nonlinear, monotonic relationships tend to lower the strength and significance of the correlations especially for the Pearson's coefficient, which is also sensitive to outliers. This seems to be supported by the scatterplots of the variables (Figures 9-11). CO_2 fluxes versus soil temperature graphs seem to exhibit this monotonic relationship.

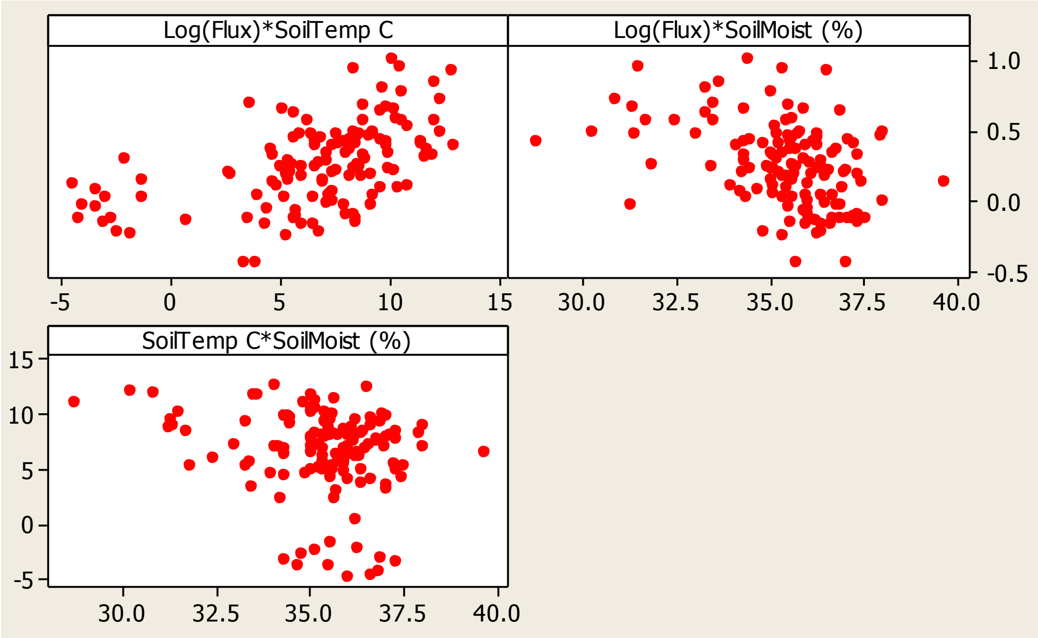


Figure 9 Scatterplots for March 30 CO_2 flux data

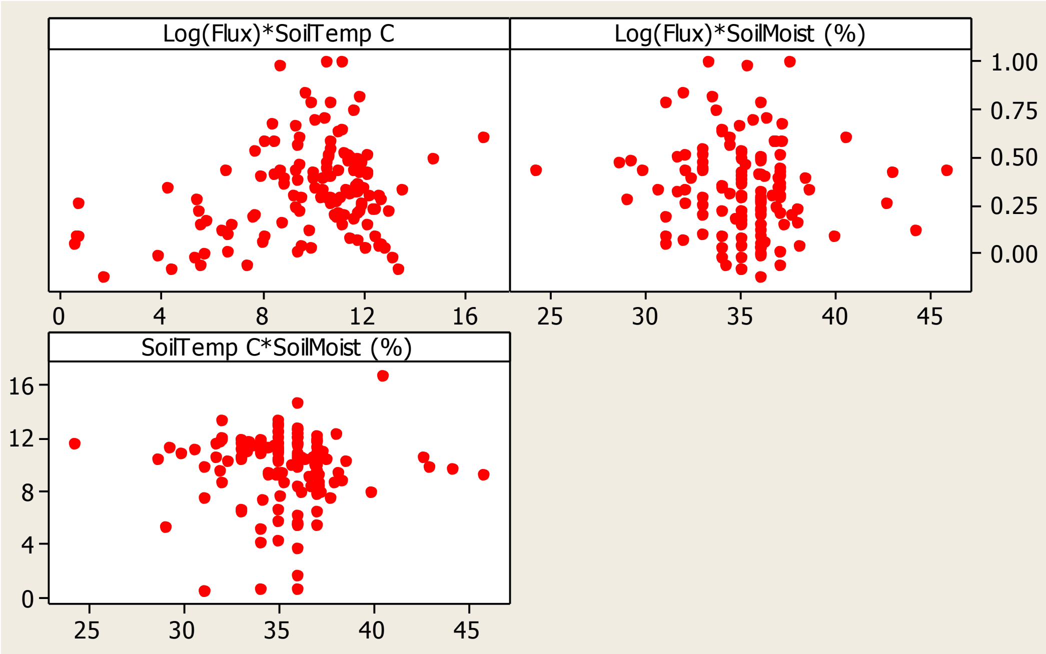


Figure 10 Scatterplots for March 31 CO_2 flux data

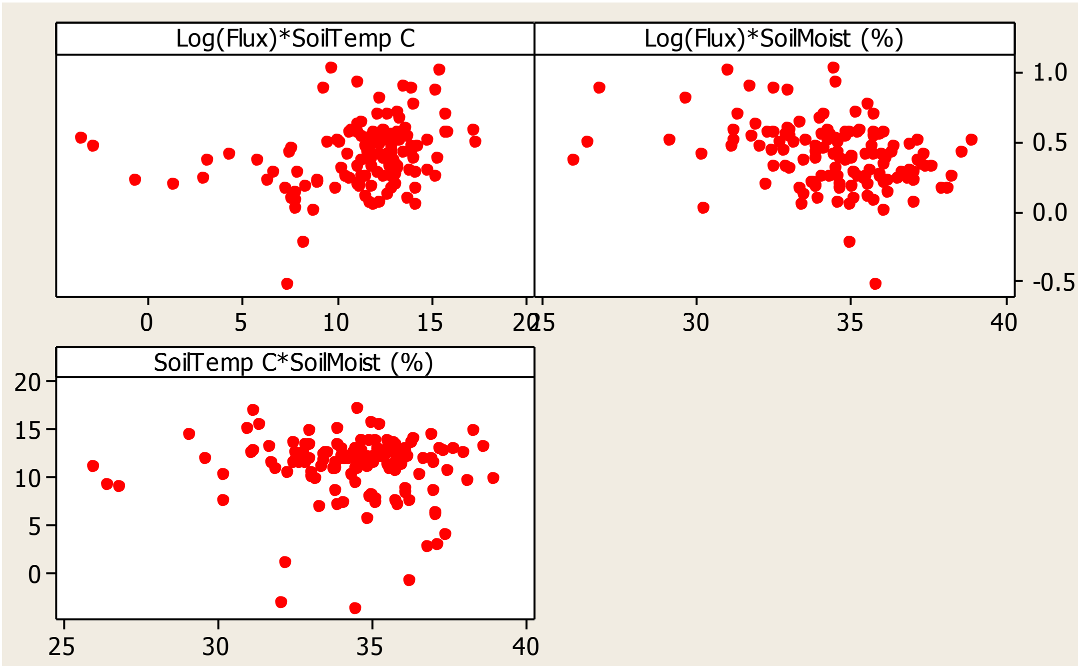


Figure 11 Scatterplots for April 1 CO_2 flux data

The correlation between CO_2 fluxes and soil temperature was positive indicating that soil CO_2 flux increased as soil temperature increased. This was to be expected as soil CO_2 producing processes, such as soil respiration comprising plant root respiration and microbial decomposition of soil organic matter, increase with soil temperature and vice versa (Davidson, Verchot, Cattânio, Ackerman, & Carvalho, 2000; Kirshbaum, 2000; Wennman, 2004). Soil temperature directly influences soil gas molecular kinetic energy and diffusion. However, the correlation coefficients were generally low, the only exception being March 30 when coefficients were greater than 0.5.

CO_2 fluxes were found to be negatively correlated with soil moisture. This was not surprising as precipitation and subsequent infiltration into the soil results in a wetting front reduces air-filled porosity of the soil from surface down. The soil-CO_2 efflux at the surface is suppressed as the soil gases are forced and compressed into the deeper soil pores where the degree of saturation is less than 100%. Day 1 sampling was carried out just two days after a 12.7 mm precipitation event and, therefore, the soil moisture content was still quite high compared to the subsequent sampling days (Table 6).

The results show no significant correlation between soil temperature and moisture. Days 2 and 3 show p-values greater than 0.4 for both Pearson and Spearman coefficients (Table 6). Day 1 is the exception with significant negative Pearson's and Spearman's correlation coefficients of -0.220 (p = 0.012) and -0.197 (p = 0.024), respectively. This indicates moderation of soil temperature by high moisture contents on Day 1 when there was significant moisture in the soil.

Figures 9-10 seem to confirm the results in Table 6, that is, a non-linear, monotonic relationship between CO_2 fluxes and soil temperature, and a negative, somewhat, linear relationship between fluxes and soil moisture.

4.4 Spatial Dependence

Table 7 shows the results of tests for spatial dependence. The results show that the Pike County data sets are all significantly spatially dependent at 95% confidence ($p < 0.05$) whereas the Godin data shows no spatial dependence, except for the July 16 data. This is a significant result, since the only published work the research team is aware of on this issue concludes that CO_2 fluxes on reclaimed mine land shows no spatial dependence (Jacinthe & Lal, 2006). Spatial dependence is important for geostatistical modeling, which is a key goal of this work. Prior to this work, spatial variation in CO_2 fluxes on reclaimed mine land has been attributed to high variability in soil properties in reclaimed mine soil.

Our working hypothesis is that, when the conditions (including pressure gradient) are such that there is *significant* contribution of AMD-generated CO_2 to the fluxes, then spatial dependence will exist since the phenomenon is not only controlled by the soil biological activity. This also shows that the original premise of the research (i.e. geostatistical delineation of hazards) is viable under the hazardous conditions. Based on Godin results, there is no basis for geostatistical modeling of fluxes at the Godin site, since there is no significant spatial dependence.

Table 7 Results of spatial dependence hypothesis tests

Data Set	No of Samples	Global Moran's I	Expected Value	p-value
Pike Co. Day 1	136	0.4284	-0.0074	0.0000
Pike Co. Day 2	136	0.3190	-0.0074	0.0000
Pike Co. Day 3	132	0.2666	-0.0076	0.0000
Godin Day 1	71	-0.0404	-0.0143	0.6219
Godin Day 2	71	0.1074	-0.0143	0.0755
Godin Day 3	71	0.1535	-0.0143	0.0242

Figures 12 and 13 show hypothesis testing results for local spatial dependence. Local indicators of spatial association provide insight into possible hot spots during exploratory data analysis (Anselin, 1995). Figure 12 shows strong local spatial dependence in two regions at the Pike County site: the southeastern corner of the property and the area around the house and towards the lake. The flux data shows, these areas are clusters of low and high fluxes, respectively. It must be noted that the Bonferroni bounds (α/n) used in determining the significant level is conservative and may result in acceptance of the null hypothesis (no spatial dependence) when in fact the opposite is true.

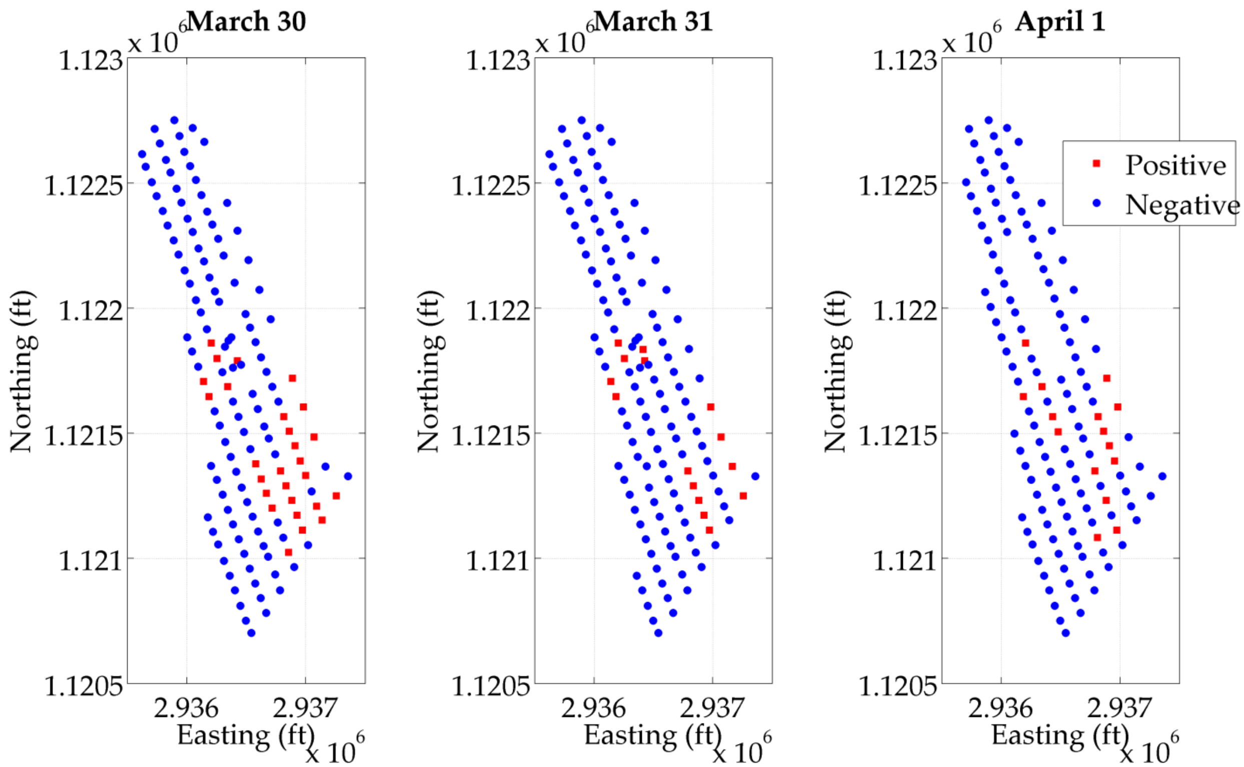


Figure 12 Tests of local spatial dependence: Pike County

Figure 13 shows results of test of local spatial dependence for Godin on July 16. The July 13 & 14 data show no spatial association at the global (Table 7) or local level. Very few points at the Godin site show any significant global association, which is consistent with the low global Moran's I (0.15).

Table 8 Variogram models for Pike County site

Day	Nugget variance (log[μ mol/m²/sec]²)	Sill variance (log[μ mol/m²/sec]²)	Range (ft)
March 30	0.123	0.483	667
March 31	0.094	0.250	507
April 1			

4.5 Geostatistics

Geostatistical modeling was only carried out for the Pike County data, where spatial dependence was observed. Table 8 shows the results of variogram modeling in GS+. Spherical variogram models were fitted to experimental variograms through least squares fitting. Figure 14 shows a sample variogram model fitted to the experimental variogram for the March 30 data. The resulting variogram models were then used in sequential Gaussian simulation (sGs). All simulations were conducted by limiting the search radius to 507 ft, which was more than adequate to assure more than 15 samples in the search radius.

Figures 15-17 show flux simulation results. The figures show the outline of the house surrounded by the lawn area and the barn adjacent to the lawn. High fluxes appear to coincide with the lawn with the very high fluxes around the house and to the southwest, towards the pond. Similar trends can be observed for all three days. One would assume that the periodic mowing returns more organic content into the soil resulting in higher soil CO_2 production. However, even in the lawn, there are higher fluxes around the house and toward the pond. These could be the result of greater soil permeability for the post-construction soils (Jacinthe & Lal, 2006), abrupt changes in topography, and/or relative proximity to the water table (USGS wells in the area towards the pond are the only ones, of the wells, that show some water). Particularly, Jacinthe and Lal (2006) show that reduced soil macro-porosity from over compaction during reclamation can hamper soil-atmosphere CO_2 exchange. If this is, in fact, a key factor then it may explain the reduced fluxes everywhere else but around the house where the soil has been disturbed by construction.

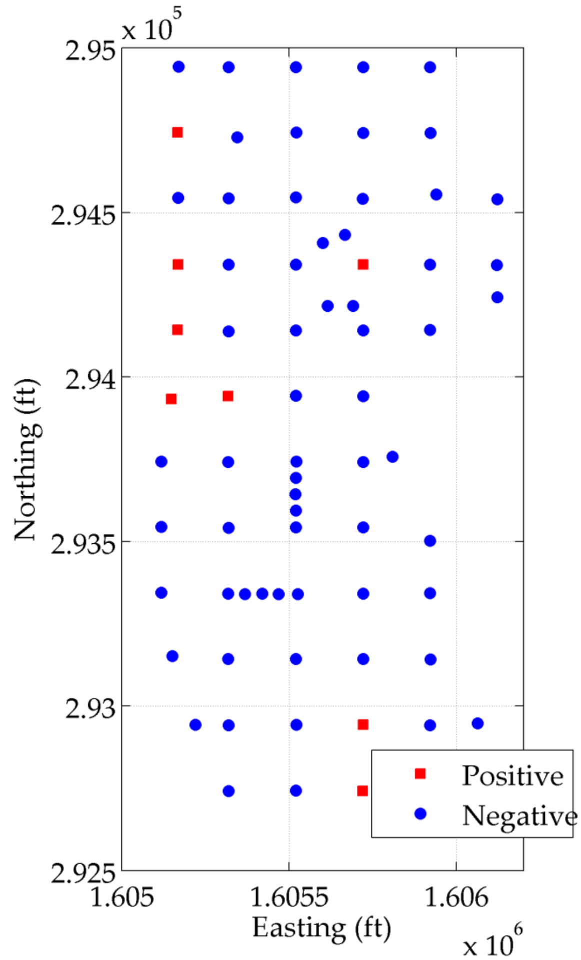
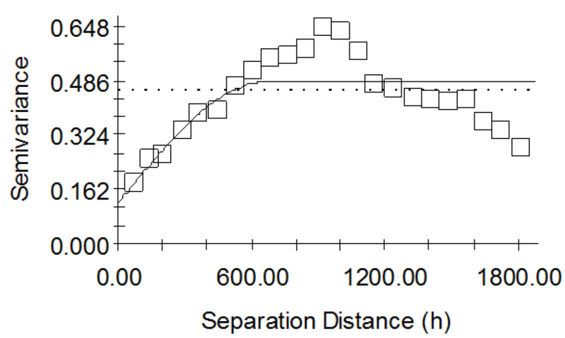


Figure 13 Tests of local spatial dependence: Godin-July 16



Spherical model (Co = 0.1230; Co + C = 0.4830; Ao = 667.00; r2 = **0.509**; RSS = 0.167)

Figure 14 Variogram model for Pike County March 30 data

From the simulation results, total CO_2 emissions for the 185,000 m^2 (45.7 acres) are estimated at 1,508, 1,514, and 1,844 kg/day of CO_2 for March 30 and 31, and April 1, respectively. April 1 emissions were highest, which is consistent with the observed differences in fluxes (Table 2a).

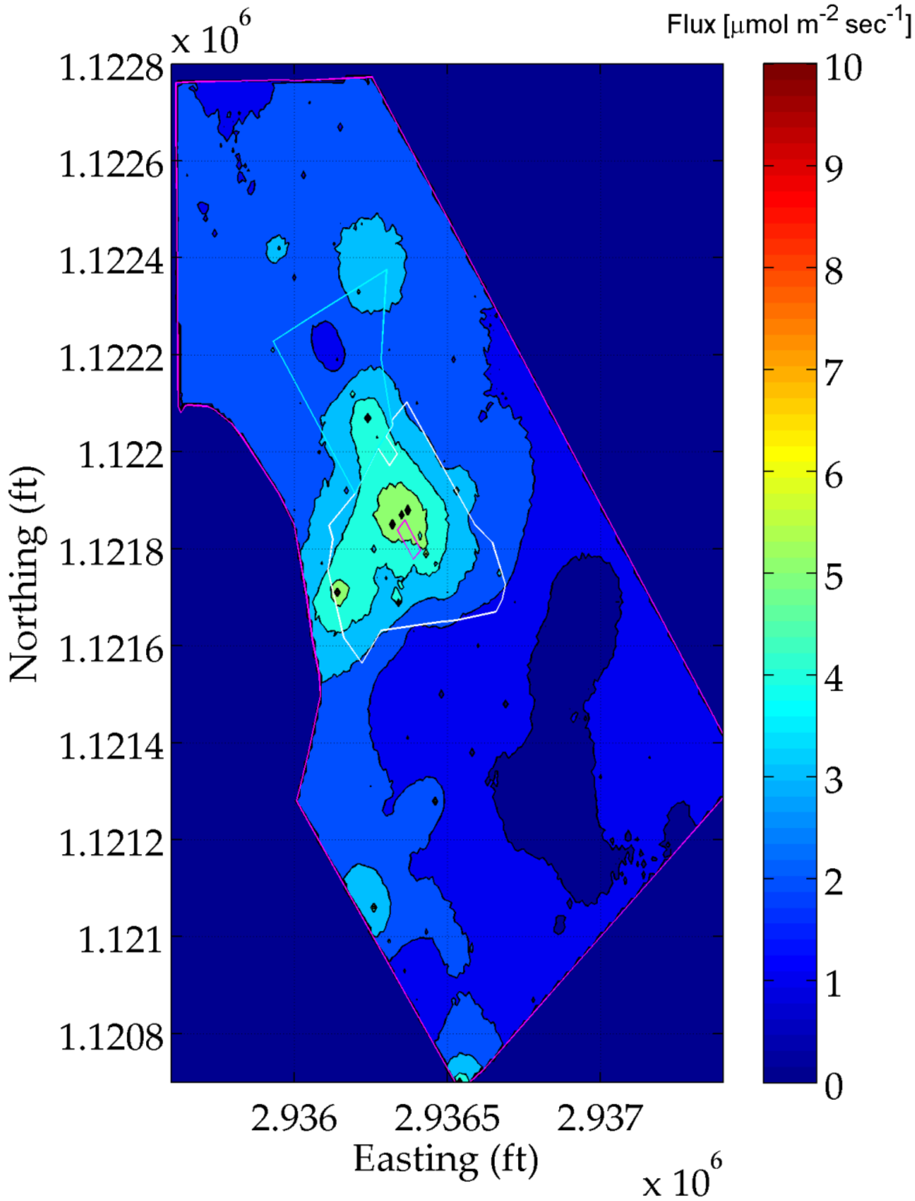


Figure 15 March 30 CO_2 fluxes for Pike County site

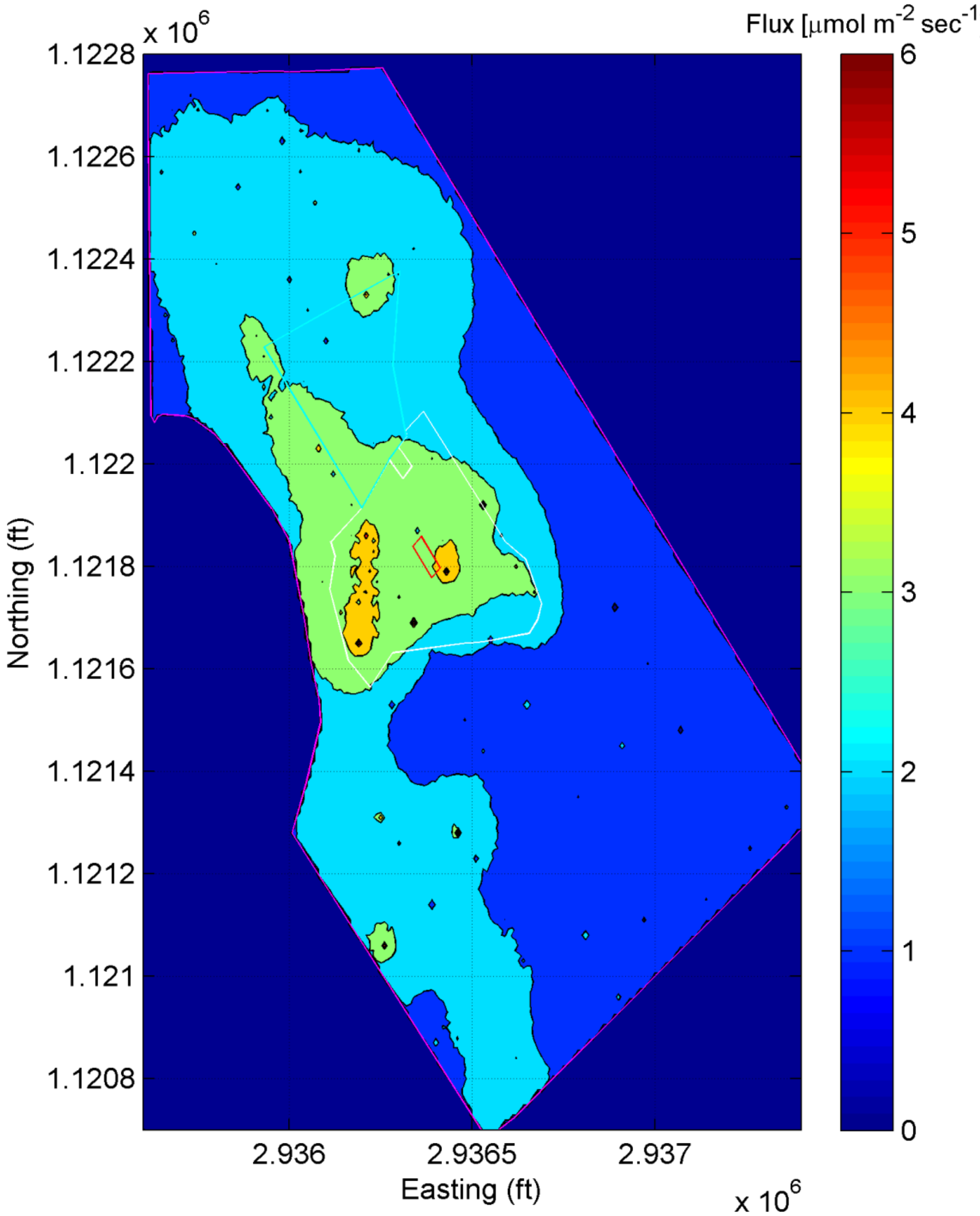


Figure 16 March 31 CO_2 fluxes for Pike County site

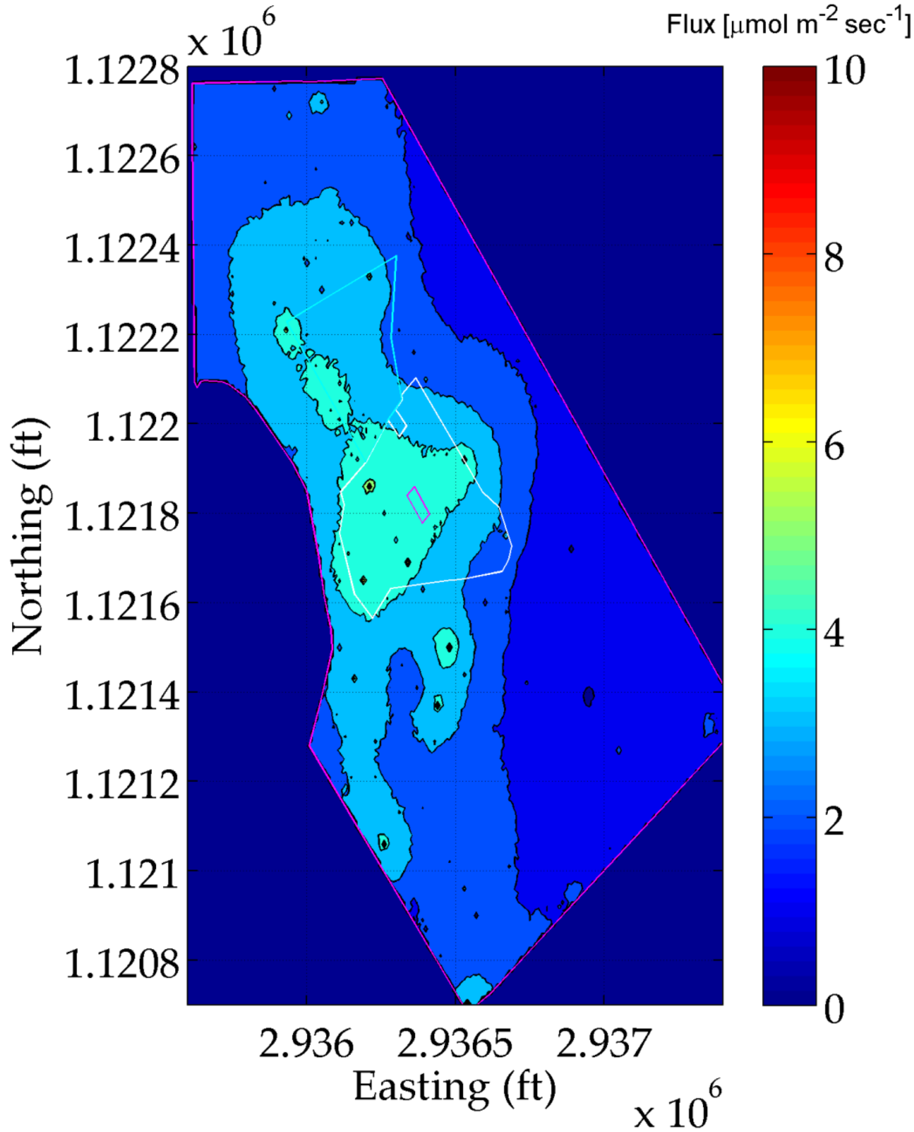


Figure 17 April 1 CO_2 fluxes for Pike County site

Figure 18 shows sample probability maps, which can be used for delineating high risk areas. The thresholds used for the probability plots are the 50^{th}, 75^{th}, 90^{th}, and 95^{th} percentiles of the log transformed data. As the threshold is raised, the high risk region (defined here as >50% probability of exceeding the threshold value) reduces and vanishes (except for isolated points where the observed value exceeded the threshold). The elevated risk region coincides with the high flux regions in Figure 15, as would be expected.

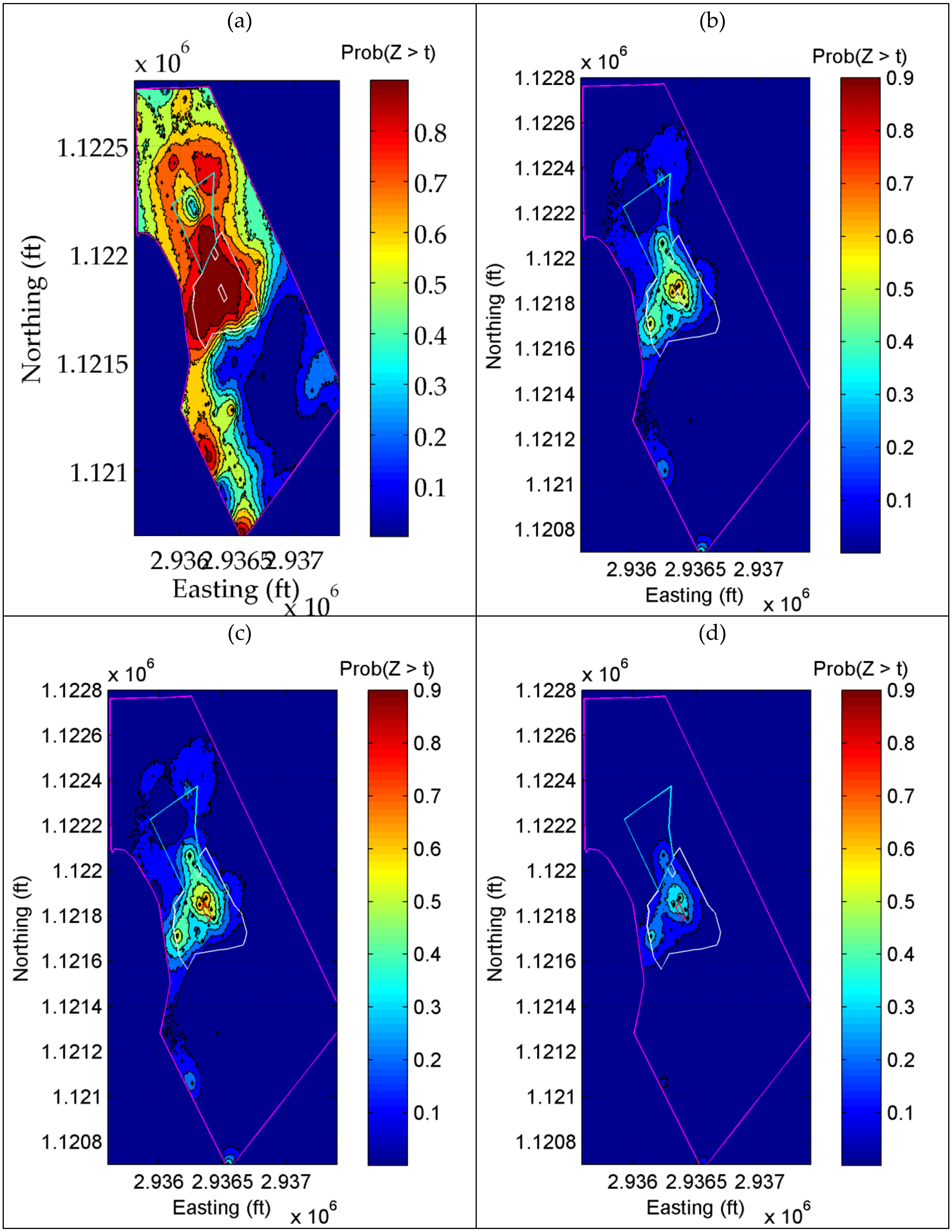


Figure 18 Probability maps of March 30 Pike County data. Probability of exceeding: (a) 50th percentile; (b) 75th percentile; (c) 90th percentile; (d) 95th percentile of the log transformed distribution

One of the goals of this project was to develop an approach to delineate high (above established threshold) CO_2 flux fields for post-mining land use decision making. Figure 18 shows this is possible with CA flux monitoring. The challenge is establishing thresholds above which there is a high likelihood of CO_2 accumulation in structures built on the land. These thresholds could not be established because there were no observed multi-modal distributions of fluxes characterized by differing isotopic compositions (Chiodini, Caliro, Cardellini, Avino, Granieri, & Schmidt, 2008). It appears the spoil gas permeability is low under diffusive flux and therefore does not allow significant contribution of the deep AMD-related CO_2 to the soil-atmospheric exchange under normal conditions. This low contribution does not change the isotopic signature significantly or contribute to unusually high soil fluxes under normal conditions (there was no reported episode during the monitoring periods). The authors hypothesize that the situation changes when sudden drops in barometric pressure induce advective fluxes, which result in significant flow of the deep AMD-related CO_2. Testing this hypothesis is beyond the scope of this project and is only possible with a continuous long term flux monitor. Such a monitor can sample eight to sixteen strategically located sample points at 30-minute intervals over a year, correlate flux values with barometric pressure, subsurface pressure, and episodes in a house.

5 CONCLUSIONS

The objectives of this project were to develop: (i) a carbon dioxide (CO_2) trace gas flux survey protocol for assessing reclaimed mine land for construction purposes; and (ii) an approach to delineate high CO_2 flux fields for decision making on post-mining land uses.

The project has successfully developed a flux survey protocol to adequately capture spatial variation over reclaimed mine land. The key elements of this protocol are:

- Flux samples should be taken at less than 61 m (200 ft) spacing, in accordance with flux measurement best practice (Parkin, et al., 2003). Flux measurements should be taken at least 24 hours after collar installation.
- Soil temperature and moisture are important parameters that need to be monitored with fluxes. Soil temperature was observed to have a positive, monotonic correlation with fluxes (Spearman's correlation coefficient from 0.32-0.55 with $p < 0.0001$) while soil moisture was observed to have a negative, monotonic correlation (Spearman's correlation coefficient from 0.34-0.42 with $p < 0.0001$).
- Barometric pressure should be monitored during flux sampling for the absence of sharp drops, which may signify the onset of advective fluxes.
- All data should be collected in one day (preferably mid-morning to mid-afternoon). Data from different days should be treated as separate. Multiple mean comparison t-test using (multivariate) analysis of variance (ANOVA) tests show that sample day effect is statistically significant ($p < 0.0001$).

The project has shown that spatial variation of CO_2 fluxes on reclaimed mine land is not always random. Tests of spatial dependence yielded statistically significant Moran's I values ranging from 0.15-0.43 ($p < 0.025$). This is contrary to the view that variability in soil properties on reclaimed mine land results in random spatial variability in fluxes (Jacinthe & Lal, 2006). Based on the observed spatial dependence, this project has, thus, shown that geostatistical methods (spherical variograms with sequential Gaussian simulation) are capable of delineating high flux fields. However, further research is necessary to establish thresholds that can be used in such flux field delineation.

Macro-porosity and gas permeability seem to be a controlling factor in CO_2 migration in mine spoil. High CO_2 concentrations (up to 17.6%) were observed at depth in the spoil. However, soil-atmosphere CO_2 exchange, under normal circumstances, was low (1,500-1,800 kg/day over 185,000 m^2 or 45.7 acres). Also, surface CO_2 carbon isotopic composition indicates very little upward migration, under normal diffusive fluxes. Areas of the property that have been disturbed by construction appear to have the higher fluxes.

It is also important to note that, the limited migration of deep AMD-related CO_2 results in a situation where surface carbon isotope ratios may be misleading. None of the nine locations at the Pike County site and four out of the 32 locations at the Godin site indicated possible presence of anthropogenic CO_2. Any soil gas sampling for isotope analysis needs to sample much deeper than the 0.6 m in this work to ensure capturing the anthropogenic CO_2.

6 ACKNOWLEDGEMENTS

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