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ORIGINAL ARTICLE

Spatial autocorrelation of soil CO_2 fluxes on reclaimed mine land

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Abstract Recent evidence has shown that CO_2 emissions from reclaimed mine soil with acid mine drainage and carbonate material is an emerging geohazard. Surface CO_2 flux measurements can be a cheap and effective way to delineate such hazards and avoid residential and commercial real-estate development on high-risk zones. Very little work has been done to ascertain whether or not such fluxes are spatially correlated, which has significant implications on the choice of statistical methods for analysis. The objective of this study was to understand the extent to which CO_2 fluxes on a reclaimed mine spoil, with CO_2 from carbonate neutralization of acidic drainage, are spatially autocorrelated. CO_2 fluxes from three reclaimed surface coal mine sites were measured and used in statistical analysis to test the research hypothesis. The results show that the spatial variability of fluxes is not always random but can show significant ($p < 0.0001$) spatial autocorrelation. This result implies that classical statistical analysis of CO_2 fluxes from reclaimed mine land may lead to wrong inferences, since such analysis ignores the spatial correlation. It appears spatial autocorrelation in CO_2 fluxes may be related to spatial autocorrelation in soil temperatures, suggesting a common underlying phenomenon. Significant contribution of CO_2 from exothermic acid mine drainage to soil CO_2 flux is suggested as a possible explanation.

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Introduction

Acid mine drainage (AMD), also referred to as acid rock drainage, is an acid leachate produced when sulfidic mine overburden and coal mine spoils are exposed to water and oxygen, resulting in a low pH discharge with elevated dissolved metals and equally high sulfate content. Blending of these materials with crushed agricultural limestone during mine reclamation is presently the most efficient method, in terms of effectiveness, cost, and practicality, to control the adverse environmental impacts of AMD. The added limestone, or other carbonaceous materials occurring naturally in the overburden, neutralizes the acidic leachate, raising its pH and causing the dissolved metals to precipitate out. The oxidation and neutralization reactions are illustrated by Eqs. 1 and 2, respectively.

$$2FeS_{2(s)} + 7O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+}_{(aq)} + 4SO^{2-}_{4(aq)} + 4H^{+}_{(aq)} \quad (1)$$

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

CO_2 is a product of the neutralization reactions (e.g., Eq. 2), which results in higher, than normal, concentrations of the gas in coal mine spoil (Cravotta III et al. 1994a, b). This has resulted in elevated concentrations of CO_2, to lethal levels, in homes and structures constructed on or adjacent to reclaimed mine lands with sulfidic overburden such as coal mine spoils. There are documented incidents where elevated CO_2 concentrations (>25 %), with attendant oxygen deficient atmospheres (<10 %), have rendered such homes uninhabitable at times (Ehler 2002; Harrison et al. 2004; Laughrey and Baldassare 2003; Robinson 2010) or even have proven fatal (Dawson et al. 2009; Lahmira et al. 2009). This stray CO_2 presents a new environmental, health and safety hazard to the occupants of such homes. These occurrences of stray CO_2 intrusions into homes threaten advances so far made by the mining industry in mitigating the adverse environmental effects of AMD. Consequently, it puts in doubt the development of reclaimed mine lands for residential, commercial or industrial purposes as a post-mining land use alternative.

There is a need for reliable monitoring of CO_2 gas emissions from reclaimed coal mine spoils and statistically valid methods for delineating high-risk zones. Static chamber accumulation trace gas monitoring is a potential method for such monitoring. Effective flux monitoring plans will require better understanding of the processes responsible for these CO_2 emissions and the factors influencing the resultant fluxes, beyond what is already known about fluxes from other soils. To determine valid statistical methods for hazard delineation, further investigation is required to determine whether the spatial variability of fluxes on such lands is random or not.

Spatial variation of CO_2 fluxes have been widely studied in other contexts (Chiodini et al. 2008; Fang et al. 1998; Kämpf et al. 2013; Wright et al. 2013). Research has shown that this is due to variables such as elevation (microtopography) (Wright et al. 2013), biomass on forest floor and soil organic content (Fang et al. 1998), and degassing structures and diffusion mechanisms (Chiodini et al. 2008; Kämpf et al. 2013). It is not always clear, from the literature, whether or not the spatial variability is random, because many authors do not test this hypothesis explicitly. The only exceptions are researchers who apply spatial statistical techniques (geostatistics) to describe the nature of the spatial variability through semi-variogram or covariance models (Chiodini et al. 2008). If strong spatial association (i.e., the spatial variation is not random) is observed then spatial statistics will be more valid and classical statistical techniques will be limited (Schabenberger and Gotway 2005). Certainly, the nature of spatial variation of CO_2 fluxes on reclaimed mine land has not been explored in prior work.

Reclaimed mine spoils are a heterogeneous mixture of materials with varying mineralogy and particle sizes (Jacinthe and Lal 2006; Lahmira and Lefebvre 2007). The spoils or piles are constructed by grading mine waste rock piles that have been placed using different methods (such as end dumping; benches or dragline casting) and equipment, which induce heterogeneity through compaction, gullying (material intersections formed when material was dumped and then dozed from different directions), segregation and creation of preferential flow paths for both water infiltration and gaseous transport. Environmental management practices such as selective handling and burial of pyritic materials in pods in the spoil during reclamation also add to the heterogeneity of reclaimed mine spoils. This heterogeneity, especially the creation of preferential flow paths and isolated patches of oxidizing materials, is likely to affect the spatial distribution of carbon dioxide (CO_2) gas fluxes from reclaimed mine soils. The authors could find any previous study that evaluated spatial autocorrelation of CO_2 fluxes on reclaimed mine land. A random spatial distribution has been assumed in the past (Jacinthe and Lal 2006) but no work has been done to evaluate the validity of this assumption.

CO_2 efflux from conventional sources (such as plant root and microbial respiration, volcanic activity, geothermal springs, and dissolution of limestone by weakly acidic precipitation) in natural soils is well documented in the literature (Bergfeld et al. 2001; Chiodini et al. 1998; Davidson et al. 1998, 2000; Lewicki et al. 2008; Pihlatie et al. 2007; Ramsey et al. 2005). However, there is very limited documentation on AMD-derived CO_2 from reclaimed mine soils (Awuah-Offei and Baldassare 2011; Awuah-Offei et al. 2009; Mathiba and Awuah-Offei 2010; Robinson 2010). There are unique characteristics of reclaimed mine soils and the CO_2 source that warrant further study.

Cravotta III et al. (1994a) report locally more acidic pore water near isolated pyritic pods in reclaimed coal mine spoil. Preferential flow paths are likely to act like mineralization trends, similar to gold veins, with areas of high pyritic content behaving like pollution point sources. Lahmira and Lefebvre (2007) showed that spoil material constructed using benches had higher horizontal fluid permeability than vertical permeability and that the reverse was true for material constructed using end dumping. Concentration gradient-driven gas diffusion is believed to be the dominant transport mechanism in natural soils (Pihlatie et al. 2007). However, in the documented incidents of CO_2 intrusions, the episodes are reported to be generally associated with pressure-driven advective transport following low atmospheric pressure fronts (Fang and Moncrieff 2001; Tackle et al. 2004). The oxidation and neutralization reactions in the reclaimed spoils are exothermic and temperatures in the spoil may reach 70 °C (Lefebvre et al. 2001) and the heat produced may lead to convective transport likely to be very significant in these soils. Higher fluxes may be expected when spoil interior temperature is higher than ambient temperature and vice versa. These processes, pockets of high pyritic content, presence of macropores (Ehler 2002), preferential flow paths, variation in elevation, and effects of fine-grain soil covers add to the variability of soil gas emissions and, hence, the complexity of soil gas flux studies in reclaimed mine soils.

If meaningful information is to be extracted from studying AMD-derived CO_2 fluxes from reclaimed mine land (and, therefore, the risks it poses), there is the need to evaluate the spatial autocorrelation[1] of such fluxes. This is important in characterizing the structure of the spatial variation and in delineating "hot spots". The objective of this study was to test the hypothesis that CO_2 fluxes on reclaimed mine lands are spatially autocorrelated. The research team took measurements of soil CO_2 flux, moisture and temperature at three reclaimed surface coal mine sites in (1) Pike County, south-western Indiana, (2) Somerset County, south-western Pennsylvania, and (3) Henry County, west-central Missouri, in the United States of America (USA), using the accumulation chamber method with auxiliary probes. The Indiana and Pennsylvania sites have, at some point, been the subjects of investigations due to incidents of CO_2 intrusions into homes constructed on these spoils (Laughrey and Baldassare 2003; Robinson 2010). The Missouri site, which has no structure built on it and is used as pasture, was chosen as a control site. The Moran *I* statistic was used to test the spatial autocorrelation of the CO_2 fluxes from the soil surface samples (Anselin 1995).

Methods

Study sites

The field study was conducted at three reclaimed surface coal mine sites in Indiana, Pennsylvania and Missouri in the USA. Table 1 shows summary information about the three sites.

The Hudson site has a single storey building with a walk-in basement constructed on a reclaimed surface coal mine. The home has been experiencing intermittent episodes of elevated concentrations of stray CO_2 since 2006 (Robinson 2010). The Godin site also has a single storey home built on it. Stray CO_2 in the Godin residence was investigated by the Pennsylvania Department of Environmental Protection (PA-DEP) in 2003 (Laughrey and Baldassare 2003). The mining permit required an operational plan that included spoiling pit cleanings in pods at least 3.05 m (10 ft) above the pit floor. Crushed limestone was added to the pit floor at a rate of 7.34 t/ha (20 tons/acre) prior to backfilling and grading. The Germantown site is a reclaimed abandoned surface coal mine that is being used as a pasture. The area was reclaimed by the Missouri Department of Natural Resources (MODNR) under the Office of Surface Mining, Reclamation and Enforcement's (OSMRE's) Abandoned Mine Land program. Reclamation included the addition of 73 t/ha (200 tons/acre) of crushed limestone. The reclamation was completed in 2002 (MODNR n.d.). The sampled area covers about 2.3 ha (5.6 acres).

[1] Autocorrelation (or spatial dependence) refers to correlation between the same variable measured at different locations (Schabenberger and Gotway 2005).

Soil CO_2 flux sampling procedure

Soil CO_2 fluxes were measured at sample locations established on a regular grid using a portable LI-8100-103 automated soil CO_2 flux system (Licor Biosciences, Inc., Lincoln, Nebraska, USA). The grid nodes were first established by staking and then surveying using a TOPCON Hyperlite global positioning system (GPS), (Topcon Positioning Systems, Livermore, CA). 200 mm diameter, 100 mm high, PVC collars were inserted into the soil leaving 20 mm of collar above the soil (Parkin and Venterea 2003). All collars were installed at least 24 h prior to flux measurements to allow the soil gas fluxes to stabilize after initial disturbance during installation. The chamber was deployed for a short period, 2 min, during measurements to minimize pressure buildup inside, which may impact the CO_2 flux and lead to underestimating the flux.

Preliminary data collected at the Godin site were used to inform the regular sampling design adopted in this research. The preliminary data and analysis indicated that spatial correlation may exist up to 116.4 m (382 ft) (the variogram range) with recommended optimal grid spacing between 30 and 61 m (100–200 ft)-based resource (flux equipment and labor) availability (Awuah-Offei et al. 2010). Sampling was carried out on October 2 and 24, and November 7, 2009 at the Germantown site. The October 2 sampling campaign was conducted on a 30.48 m (100 ft) square grid and involving 40 samples. For the two remaining campaigns, sampling was carried out on a 15.24 m (50 ft) square grid and involved 88 and 98 samples for October 24 and November 7, respectively. At the Hudson site, sampling was conducted on March 30 and 31, and April 2, 2010. It involved 138 sampling points on the 22.9 m × 45.7 m (75 ft × 150 ft) grid except for the north-eastern boundary, where samples were 45.7 m (150 ft) apart. There were also extra points around the home. Seventy-one (71) sample points were established at the Godin site on a 61 m (200 ft) square grid. Figure 1 shows sampling points at all three study sites.

Analysis

Classical statistical analysis

Data descriptive statistics, including the mean, standard deviation, coefficient of variation, and skewness, were

Table 1 Study sites

Site	The Hudson site, South-Western Indiana	The Godin site, South-Western Pennsylvania	The Germantown site, West-Central Missouri
Location	Lat.: 38°19′42″	Lat.: 40°08′2″	Lat.: 38°16′17″
	Long.: 87°08′27″	Long.: 79°02′52″	Long.: 94°01′04″
Area (ha)	36	20	14.2
Soil[a]	Fairpoint loam	Pits-dump complex	Pits-dumps complex
Depth of spoil (m)	11.6	21.34	17.5
Mining period	1986–1992	Mid 1990s	Early 1950s to 1970s
Precipitation[b]			
Average rainfall (mm)	1184.1	1,053	1,107
Snowfall (mm)	304.8	881	404
Temperatures[b]			
Avg. daily (°C)	12.7	6.7	12.2
Avg. minimum (°C)	−6.1	−4.9	5.5 °C
Avg. maximum (°C)	31.1	18.9	18.9

[a] Source: Soil Survey Staff (2013)

[b] National Oceanic and Atmospheric Administration–National Climatic Data Center 1971–2000

calculated. Exploratory data analysis (EDA) using the Anderson–Darling test, histograms, box plots and probability plots was also carried out on the data to check for normality, outliers, and sample day effects. The data sets were corrected for outliers using the interquartile method: $Q_i \pm (1.5(Q_3 - Q_1))$ where Q_i is the upper or lower quartile for the upper or lower limit, respectively; and Q_1 and Q_3 refer to the lower and upper quartiles, respectively. Any values lying outside of $Q_i \pm (1.5(Q_3 - Q_1))$ were considered outliers. The normality tests test the hypothesis that the data follows a normal distribution at a significance level of $\alpha = 0.05$. Non-normal data sets were log transformed.

Autocorrelation analysis

The spatial autocorrelation of CO_2 fluxes was investigated using Moran's I statistic as implemented in the SAS software (SAS Institute, Cary, NC, USA). Moran's I statistic is a measure of how values of the same variable, taken at different locations, are correlated spatially. Moran's I statistic was used to test the hypothesis and it is described by Eq. (3).

$$I = \frac{n}{(n-1)S^2 w_{..}} \sum_{i=1}^{n} \sum_{j=1}^{n} w_{ij}(Z(\mathbf{x}_i) - \bar{Z})(Z(\mathbf{x}_j) - \bar{Z}) \quad (3)$$

where $S^2 = \frac{\sum_{i=1}^{n} (Z(\mathbf{x}_i) - \bar{Z})^2}{n-1}$ is the variance; $Z(\mathbf{x}_i)$ is variable (CO_2 flux in this case) observed at sampling locations $\mathbf{x}_i$, $\bar{Z}$ is the mean of the flux observations; $w_{ij} = \frac{1}{1+|\mathbf{h}|^2}$, where h is the lag (separation) vector between locations $\mathbf{x}_i$ and $\mathbf{x}_j$, is the weight assigned a pair i and j; $w_{..} = \sum_{i=1}^{n} \sum_{j=1, j\neq i}^{n} w_{ij}$ is the sum of weights; and n is the number of observations.

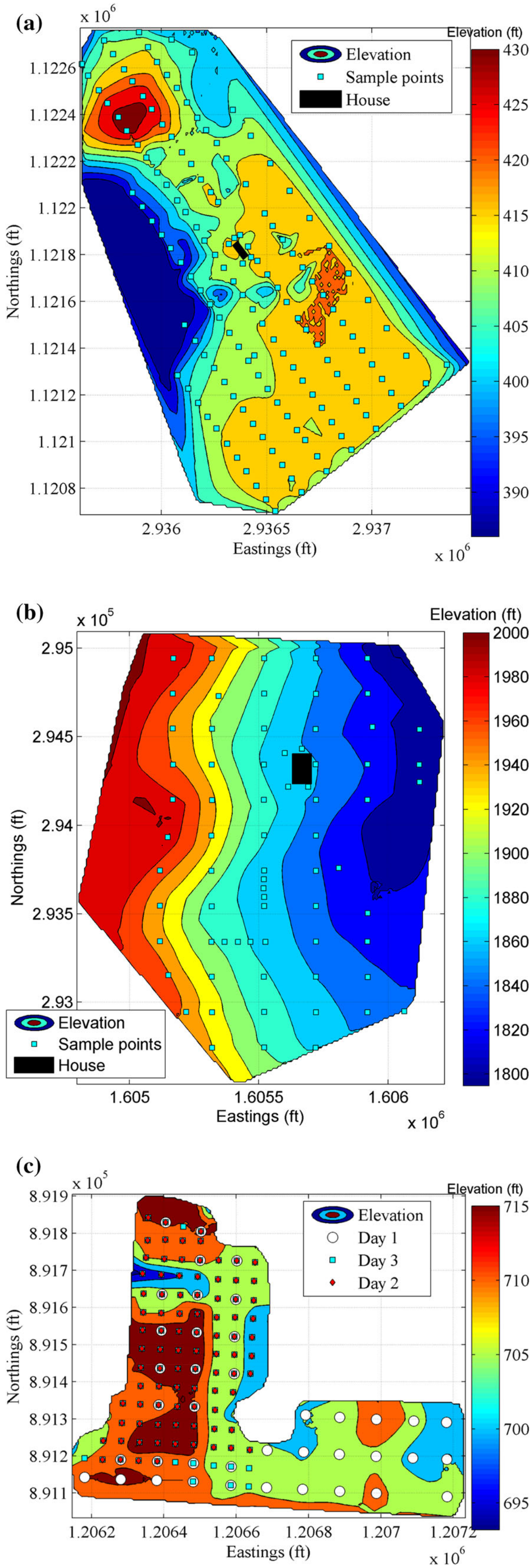
The expected value and variance of the Moran's I statistic is described by Eqs. 4 and 5:

$$\mathrm{E}[I] = -\frac{1}{n-1} \quad (4)$$

$$\mathrm{VAR}[I] = \frac{n[n^2 - 3n + 3]S_1 - nS_2 + 3w_{..}^2 - b\left[(n^2 - n)S_1 - 2nS_2 + 6w_{..}^2\right]}{(n-3)(n-2)(n-1)w_{..}^2} \quad (5)$$

where $S_1 = \frac{1}{2}\sum_{i=1}^{n}\sum_{j=1}^{n}(w_{ij} + w_{ji})^2$, $S_2 = \sum_{i=1}^{n}\left\{\sum_{j=1}^{n} w_{ij} + \sum_{j=1}^{n} w_{ji}\right\}^2$, and $b = n\frac{\sum_{i=1}^{n}(Z(\mathbf{s}_i) - \bar{Z})^4}{\left\{\sum_{i=1}^{n}(Z(\mathbf{s}_i) - \bar{Z})^2\right\}^2}$.

To draw inferences, the observed statistic for each data set (observation) is compared to this expected value. If the



◀**Fig. 1** Sampling schemes: **a** Hudson site showing topography and sample locations; **b** Godin site showing topography and sample locations; **c** Germantown site showing topography, sample locations and dates sampled

observed Moran's I, $I_{\text{obs}} > E[I]$ then the samples are positively autocorrelated, and negatively autocorrelated if $I_{\text{obs}} < E[I]$. Equation 6 describes the standardized scores for the Moran's I statistic.

$$Z_I = \frac{I - E[I]}{\sqrt{\text{VAR}[I]}} \tag{6}$$

$Z_I > 0$ indicates a positive autocorrelation and otherwise if $Z_I < 0$. Positive autocorrelation indicates clustering of similar values—for example, high values associated with similarly high values as would be expected in the center of a pollution plume. Negative autocorrelation on the other hand shows dissimilar values or "outliers", that is, a high (low) value surrounded by low (high) values. The values are significantly dissimilar than would be likely by random chance. The Moran's I near E[I] or standard scores near zero indicate samples with no discernible pattern in the arrangement of values over space or random spatial variation.

The weights used in estimating the Moran's I statistic can be binary or non-binary. Binary weights are suitable in cases where either two sampling locations are related or not. This can be done by choosing a lag distance and assuming that all samples within that lag distance are related and samples farther than that are not related. In the case of this research, a non-binary weighting scheme is suitable since a binary scheme will require the researchers to make choices about a suitable lag distance. The authors opted for an inverse distance weighting scheme. Such weighting schemes can have any power, although higher powers lead to greater discrimination between samples that are farther apart (i.e., samples that are farther receive much lower weights than when a lower power is used). The researchers chose to use the popular squared distance scheme, although there is no theoretical justification as to why any other power is not more suitable.

Knowing the spatial distribution of the data is important in deciding the most appropriate statistical tools to use in the analysis to yield valid inferences about the population parameters. Spatially correlated data are best described using spatial statistics rather than classical statistics as the former takes into account the locational aspect of the data as well as the attribute values.

Results and discussions

Exploratory data analysis and descriptive statistics

Table 2 shows the summary statistics of CO_2 fluxes and results of the Anderson–Darling normality test. The soil CO_2 fluxes for the Hudson and Germantown sites were found to be positively skewed (skewness: 0.55–1.04) and were significantly non-normal according to the Anderson–Darling normality test ($p < 0.05$). The normality test for the Godin site data on the other hand (skewness: 0.21–0.58, $0.099 \leq p \leq 0.847$) failed to reject the null hypothesis that CO_2 fluxes are normally distributed. The Godin site fluxes were also found to be less variable (CV: 30.3–36.1 %) than at the Hudson (CV: 48.7–61.8 %) and the Germantown (CV: 43.9–48.3 %) sites. The Godin site also had relatively higher fluxes (mean 4.915–8.898 μmol m^{-2} s^{-1}). The Godin average flux was two-and-a-half times and three times that at Germantown (mean 2.414–3.265 μmol m^{-2} s^{-1}) and Hudson (mean: 2.202–2.821 μmol m^{-2} s^{-1}) sites, respectively. Although, the Hudson and Germantown data are non-normal ($p < 0.0005$), normality is achieved after log-transforming the data.

The data show significant variation (coefficient of variation ranging from 30 to 77 %) indicating there is some spatial variation in fluxes. This is consistent with the literature, in which various covariates have been found to be responsible for the variation (Fang et al. 1998; Kämpf et al. 2013; Wright et al. 2013). What needs to be evaluated is whether there is spatial autocorrelation (the variation is random or not).

The data were analyzed for sample day effects on CO_2 fluxes, which may be caused by shifting meteorological conditions, using the analysis of variance (ANOVA) method. The analysis was done on the log-transformed data for those data sets found to be non-normal (Table 2). The results are shown in Table 3. Sample day effect was found to be significant at all the study sites where each day's data set is different, with the exception for the Germantown site where Day 1's (10/02/2009) is not different from Day 3's (11/07/2009). The significance of the sample day effect is indicated by the Bonferroni's simultaneous confidence intervals for the difference between means that do not include zero and the results of the F test (Hudson: F value = 6.72, $p = 0.0013$; Godin: F value = 55. 05, $p < 0.0001$; Germantown: F value = 11.03, $p < 0.0001$). The simultaneous confidence intervals which do not include zero suggest that the difference between means is significant and cannot be zero at 95 % confidence. This suggests that soil gas flux data sets taken from the same sampling points but on different days may represent different populations when meteorological and soil conditions change. This is consistent with what has been reported in the literature regarding the influence of soil temperature and moisture conditions (Bergfeld et al. 2001; Rustad et al. 2000), atmospheric pressure (Chiodini et al. 1998; Lewicki et al. 2008), wind speed (Lewicki et al. 2008), soil respiration (Davidson et al. 2000) and exothermic reactions

Table 2 Summary statistics of raw CO_2 fluxes (μmol m^{-2} s^{-1})

Study site		Hudson			Godin			Germantown		
Sampling day		Day 1 (3/30/10)	Day 2 (3/31/10)	Day 3 (4/2/10)	Day 1 (7/13/10)	Day 2 (7/14/10)	Day 3 (7/16/10)	Day 1 (10/2/09)	Day 2 (10/24/09)	Day 3 (11/7/09)
Mean		2.35	2.58	2.96	4.90	8.93	7.88	3.26	2.42	3.27
Std. deviation		1.81	1.71	1.80	1.74	2.76	2.71	1.58	1.08	1.46
Variance		3.29	2.93	3.24	3.03	7.61	7.36	2.48	1.17	2.13
Coeff. of variation (%)		77.0	66.3	60.8	35.5	30.9	34.4	48.5	43.5	44.6
Skewness		2.17	2.17	2.11	0.24	0.34	0.58	0.69	0.68	0.56
Kurtosis		5.76	5.90	5.61	−0.09	0.63	−0.02	−0.09	0.30	−0.35
No. of samples		132	136	131	71	71	71	41	89	90
Minimum		0.38	0.75	0.31	1.25	1.88	2.73	0.83	0.42	0.82
1st quartile		1.11	1.47	1.79	3.63	7.08	5.76	2.29	1.62	2.13
Median		1.82	2.12	2.59	4.80	8.91	7.89	2.88	2.20	3.02
3rd quartile		2.87	3.11	3.59	6.04	10.55	9.50	4.52	2.98	4.17
Maximum		10.57	9.94	10.96	9.19	15.76	15.11	7.16	5.77	6.67
F_{CO_2}	A^2	7.162	7.259	6.511	0.213	0.377	0.262	0.764	0.904	1.058
	p value	<0.005	<0.005	<0.005	0.847	0.401	0.696	0.043	0.020	0.008
$\ln(F_{CO_2})$	A^2	0.467	0.503	0.493	–	–	–	0.392	0.682	0.466
	p value	0.248	0.201	0.213	–	–	–	0.362	0.072	0.247

Table 3 Test for sample day effects on fluxes for all the sites data sets

Site	Sample day comparison		Difference between means	Simultaneous 95 % confidence limits			F value	p value
Hudson	Day 1 (3/30/10)	Day 2 (3/31/10)	0.3737	−0.7025	−0.0449	***	6.72	0.0013
	Day 1 (3/3/10)	Day 3 (4/02/10)	−0.7575	−1.0893	−0.4256	***		
	Day 2 (3/31/10)	Day 3 (4/02/10)	−0.3838	−0.7132	−0.0544	***		
Godin	Day 1 (7/13/10)	Day 2 (7/14/10)	−3.9949	−4.9510	−3.0389	***	55.05	<0.0001
	Day 1 (7/13/10)	Day 3 (7/16/10)	−2.9915	−3.9476	−2.0355	***		
	Day 2 (7/14/10)	Day 3 (7/16/10)	1.0034	0.0473	1.9594	***		
German town	Day 1 (10/2/09)	Day 2 (10/24/09)	0.8658	0.2492	1.4825	***	11.03	<0.0001
	Day 2 (10/24/09)	Day 3 (11/7/09)	−0.8562	−1.3311	−0.3813	***		
	Day 1 (10/2/09)	Day 3 (11/7/09)	0.0096	−0.5972	0.6163			

*** Indicates significance at $\alpha = 0.05$

Table 4 Results of spatial autocorrelation hypothesis testing for CO_2 fluxes

Study site	Data set	No. of samples	Global Moran's I	Expected value	Std. deviation	Z value	p value
Hudson	Day 1 (3/30/10)	131	0.481	−0.00763	0.0376	13.00	<0.0001
	Day 2 (3/31/10)	136	0.310	−0.00741	0.0364	8.73	<0.0001
	Day 3 (4/02/10)	131	0.292	−0.00763	0.0342	8.77	<0.0001
Godin	Day 1 (7/13/10)	71	−0.198	−0.0143	0.201	−0.912	0.3618
	Day 2 (7/14/10)	71	0.098	−0.0143	0.202	0.555	0.5772
	Day 3 (7/16/10)	71	0.241	−0.0143	0.208	1.228	0.2193
German town	Day 1 (10/2/09)	40	−0.106	−0.0256	0.489	−0.1652	0.8688
	Day 2 (10/24/09)	88	−0.093	−0.0115	0.984	−0.0829	0.9339
	Day 3 (11/7/09)	98	0.154	−0.0103	0.0536	3.070	0.0021

within mine spoils (Hockley et al. 2009; Lefebvre et al. 2001;) on soil trace gas fluxes. Consequently, data from each day was treated as a separate data set in this work.

Spatial autocorrelation

Table 4 shows the results of Moran's I hypothesis testing for spatial autocorrelation. The CO_2 fluxes at the Hudson site show significant spatial autocorrelation for all 3 days sampled ($p < 0.0001$). This spatial autocorrelation is again reflected on Day 3 of Germantown site ($p = 0.0021$). Day 2 and Day 3 of the Godin site show positive Moran's I ($I > \mathrm{E}[I]$) and standard scores ($Z_I > 0$) even though these are not statistically significant. Only three of the nine data sets are distinctly non-spatially autocorrelated. This finding is significant and shows that the variability of CO_2 fluxes from reclaimed mine land may not always be random. The authors are unaware of any other study that has shown the existence of spatial autocorrelation in CO_2 fluxes on reclaimed mine land. This finding means that where the data are spatially correlated, any statistical analysis that does not combine the geographical characteristics (sample coordinates) of the data to the observed values would lead to invalid inferences. Spatial autocorrelation implies: (1) the sample mean would not be a consistent estimator of the population mean, (2) larger samples are required to obtain the same information than would be the case for non-spatially correlated data, (3) the sample variance is inflated resulting in the sample mean being an inefficient estimator of the mean, and (4) classical statistical test for equality of means is too large and the p value too small resulting in increased risk of Type I error (the probability of rejecting the null hypothesis when it is true) (Schabenberger and Gotway 2005).

The differences in spatial autocorrelation from one site to the other suggests that local conditions may play a role and spatial correlation, or its absence, cannot be assumed at all sites. The dynamic results at the Germantown site may also indicate that such an assumption cannot be made even for the same site on different sampling days. Instances of strong spatial association in CO_2 fluxes have been observed in volcanic areas (Chiodini et al. 2008) rather than biogenic CO_2 flux fields. As explained earlier, CO_2 migration into the homes at the Godin and Hudson sites are episodic and seem to be controlled by barometric pressure changes (Laughrey and Baldassare 2003; Robinson 2010). The authors hypothesize that when there is significant contribution from AMD-generated CO_2 to the flux, the field approaches (in a small way) the magmatic or hydrothermal CO_2 fields and is similar to biogenic fields when there is negligible contribution from the AMD-CO_2. Since the contribution of AMD-CO_2 to the overall efflux varies from day to day, the observed spatial association will also vary from day to day.

The strength of spatial association usually decreases with increasing lag distances. When sampling is done with a regular grid, the grid spacing can then affect whether spatial autocorrelation is observed or not (Fortin et al. 1989). Given the variable grid spacing in this research, it is important to explore this question. However, it is important to note first that the sampling design was done with preliminary data that suggest that any sampling scheme with grid spacing below ~ 115 m will be adequate to observe spatial correlation (Awuah-Offei et al. 2010). The Germantown data are important data sets in this regard. Day 2 and 3 were collected on the same grid spacing (Fig. 1). However, there is no apparent spatial autocorrelation on Day 2 while test on the Day 3 shows significant ($p = 0.0021$) spatial autocorrelation (Table 4).

To further explore the effect of grid spacing on spatial autocorrelation, the authors used the Day 2 data from the Hudson site to evaluate the sensitivity of the spatial autocorrelation tests to grid spacing. The spatial autocorrelation tests were repeated for sparser data sets (Fig. 2). Table 5 shows that the spatial autocorrelation tests showed significant ($p \leq 0.0052$) autocorrelation for all three grid spacings. The results confirm the sampling design as adequate for tracking spatial autocorrelation. Also, taken together with the Germantown data, it appears that the observed dynamic changes in spatial autocorrelation are not due differences in sampling practices.

It is also possible that spatial correlation in CO_2 fluxes is the result of spatial correlation in some covariate that may have nothing to do with AMD-generated CO_2. This research cannot test all possible covariates and further research is necessary to examine important covariates like labile C and macro-porosity (Jacinthe and Lal 2006). However, the data in this research can be used to examine whether soil temperature, soil moisture content or sample elevation is responsible for the observed spatial autocorrelation in CO_2 fluxes.

Table 6 shows that soil temperature is significantly ($\alpha = 0.05$) spatially autocorrelated for all the three sampling at the Hudson site (note that equipment malfunction prevented the authors from retrieving the data from the Godin site). At the Germantown site, the observed spatial autocorrelation (Moran's I values) for soil temperature is not significant, suggesting that soil temperature at this site is not spatially autocorrelated. It is interesting to note that at this site, although significant spatial autocorrelation is observed for the fluxes only on Day 3 of sampling, Moran's I statistic for soil temperature is the most insignificant ($p = 0.9$).

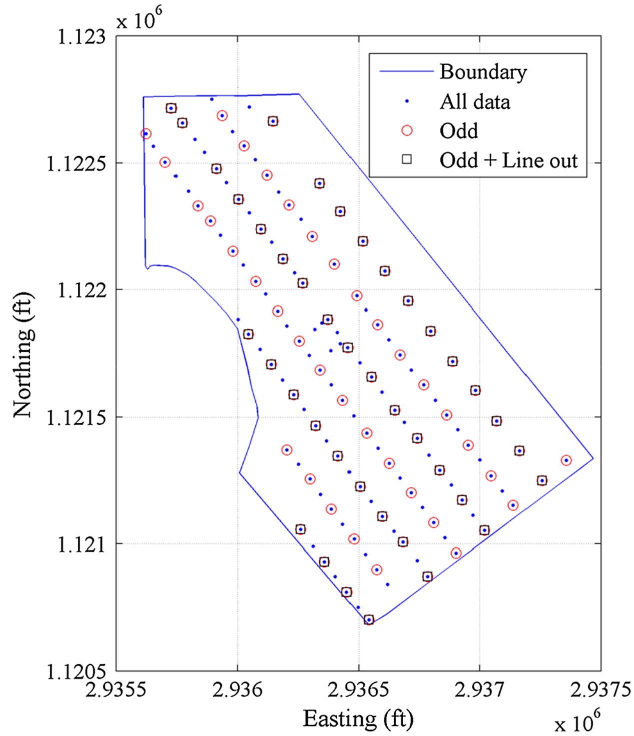


Fig. 2 Hudson day 2 data set prepared for sensitivity analysis

It is worth noting that in the analysis of correlation, it is shown that: (1) CO_2 fluxes were significantly correlated to soil temperature on all of the sampling days for the Hudson site, and (2) there was no corresponding significant correlation for the Germantown site (Mathiba 2013). We observe then that: (1) at the Hudson site, CO_2 fluxes are significantly correlated to soil temperature and there is significant spatial autocorrelation of fluxes and soil temperature, and (2) at the Germantown site, CO_2 fluxes are not correlated to soil temperature and there is no spatial autocorrelation of fluxes or soil temperature. Therefore, it appears autocorrelation in soil temperature is related to or caused by the same process as autocorrelation in fluxes.

The one possible explanation for such a scenario is the exothermic sulfide oxidation and AMD neutralization reactions in the reclaimed spoil. These reactions produce heat, which in turn raises the temperature within the mine spoil (Lefebvre et al. 2001). The generation of heat induces convective and diffusive transport of soil gases and water vapor as well as heat transfer, to the spoil surface and soil. Many factors may affect reaction rates in the spoil, among them are amount of reactive sulfides, availability of oxygen, macropores, moisture content and degree of compaction. Figure 3 shows average soil temperature for the Germantown and Hudson sites. The Hudson site exhibited higher temperatures than the Germantown site. While this may not

Table 5 Evaluating the effect of grid spacing on spatial autocorrelation using Hudson day 2 data

Data set	No. of samples	Global Moran's I	Expected value	Std. deviation	Z value	p value
All (75 ft × 150 ft)	136	0.310	−0.00741	0.0364	8.73	<0.0001
Odd rows (150 ft × 150 ft)	75	0.234	−0.0135	0.0365	6.79	<0.0001
Odd rows + removing one line out (150 ft × 300 ft)	40	0.196	−0.0256	0.0794	2.79	0.0052

Table 6 Spatial autocorrelation test for soil temperature—Hudson and Germantown sites

Study site	Data set	No. of samples	Global Moran's I	Expected value	Std. deviation	Z value	p value
Hudson	Day 1 (3/30/10)	132	0.730	−0.00763	0.0835	8.84	<0.0001
	Day 2 (3/31/10)	136	0.222	−0.00741	0.0782	2.93	0.0034
	Day 3 (4/02/10)	131	0.504	−0.00769	0.0906	5.65	<0.0001
Germantown	Day 1 (10/2/09)	40	0.554	−0.0256	0.485	1.20	0.2318
	Day 2 (10/24/09)	88	0.0131	−0.0115	0.0425	0.579	0.5628
	Day 3 (11/7/09)	98	0.065	−0.0103	0.696	0.108	0.9143

be used conclusive evidence of higher sulfide oxidation at Hudson than at the Germantown, it is suggestive that there may be heat generating process at former site. Also, the temperature on Day 3 of sampling at the Germantown site was higher than that on the other 2 days, when no significant autocorrelation was observed. This phenomenon was beyond the scope of this research and further work should be conducted to ascertain whether exothermic AMD reactions explain the observed spatial autocorrelations.

Table 7 shows significantly positive autocorrelation of soil moisture at the Hudson site (Days 1 and 3). All of the sampling days at the Germantown site show no significant spatial autocorrelation in soil moisture. CO_2 fluxes are spatially autocorrelated on all three sampling days at the Hudson site, while moisture is autocorrelated only on 2 of the 3 days. At the Germantown site, fluxes are only autocorrelated on Day 3 while soil moisture is not spatially autocorrelated at any of the sampling days. It seems to suggest that the spatial autocorrelation of CO_2 fluxes and soil moisture are not related. This leads one to conclude that the spatial autocorrelation CO_2 fluxes is independent of soil moisture variation.

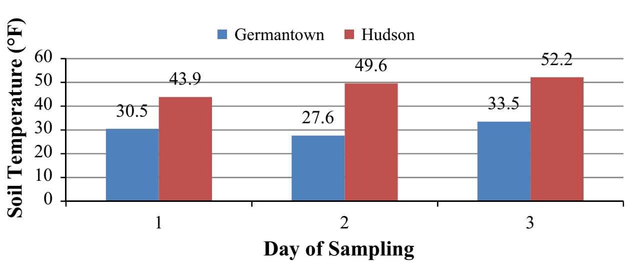


Fig. 3 Average soil temperatures at the Germantown and Hudson sites

Elevations are known to be spatially correlated (Isaaks and Srivastava 1989) because geomorphological features do not result in spatially random elevations. The spatial autocorrelation tests were done for completeness of the analysis. Sample elevation shows highly significant (p value < 0.0001) spatial autocorrelation (positive Moran's I) for all three sites (Table 8), as would be expected.

Since CO_2 fluxes are significantly spatially autocorrelated on all three sampling days at only the Hudson site and for only one sampling day at the Germantown site, and not at all at the Godin site, this suggests that sample elevation cannot possibly have an effect on the spatial autocorrelation of fluxes.

Based on the available data and analysis, only soil temperature appears to show the same patterns of spatial autocorrelation as CO_2 fluxes. Elevations are always going to be spatially autocorrelated and, if responsible for spatial autocorrelation in flux, should lead to consistent spatial autocorrelation in fluxes. This is not supported by the available data (Table 4). There is observed spatial autocorrelation in moisture content on some of the sampling days, although, the observed spatial autocorrelations do not coincide well with the observed spatial autocorrelation in fluxes. Given that soil temperature is expected to rise with significant contribution from AMD-generated CO_2, it is possible that fluxes are autocorrelated when there is significant contribution of CO_2 from the AMD. However, other covariates such as porosity and permeability, and distribution of sulphidic material, may play an even greater role in the spatial correlation of CO_2 fluxes on reclaimed mine land. These effects were not examined in this research and should be studied in future work.

Table 7 Spatial autocorrelation test for soil moisture content—Hudson and Germantown sites

Study site	Data set	No. of samples	Global Moran's *I*	Expected value	Std. deviation	*Z* value	*p* value
Hudson	Day 1 3/30/10	132	0.656	−0.00763	0.0831	7.99	<0.0001
	Day 2 3/31/10	136	0.0837	−0.00741	0.0822	1.11	0.2673
	Day 3 4/02/10	131	0.237	−0.00769	0.0916	2.67	0.0075
Germantown	Day 1 10/2/09	40	−0.174	−0.0256	0.4920	−0.301	0.7635
	Day 2 10/24/09	88	0.066	−0.0115	0.0426	1.820	0.0689
	Day 3 11/7/09	98	−0.253	−0.0103	0.701	−0.346	0.7293

Table 8 Spatial autocorrelation test for sample elevation

Study site	No. of samples	Global Moran's *I*	Expected value	Std. deviation	*Z* value	*p* value
Hudson	399	0.763	−0.00251	0.0256	29.9	<0.0001
Godin	213	0.654	−0.00472	0.0478	13.8	<0.0001
Germantown	226	0.642	−0.00444	0.0238	27.1	<0.0001

Conclusions

Soil CO_2 fluxes from reclaimed mine land soils may not always be spatially independent. The study showed statistically significant spatial autocorrelation of soil CO_2 fluxes (i.e., local clustering of similar values) in some instances. This means analyses using classical statistical techniques are likely to result in wrong inferences in such cases. The study also showed that sample day effects are significant implying that data sets from different sampling days have to be treated as separate and independent data sets. The reasons why spatial autocorrelations are observed in some instances, and not in others, should be the subject of further research. However, the observed spatial autocorrelation bodes well for hazard delineation using geostatistics.

Analysis of spatial autocorrelation in soil temperature, soil moisture content and sample elevation conducted in an attempt to explain the observed spatial correlation in fluxes observed that soil temperature and CO_2 fluxes are either both spatially autocorrelated or they both are not, suggesting a common source for their spatial correlation. This may support the hypothesis that significant contribution to CO_2 fluxes from AMD-generated CO_2 from exothermic reactions explains the spatial autocorrelation. Further work is required to confirm this hypothesis and explore the effect of other important covariates.

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