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ORIGINAL ARTICLE

Influence of elevation, soil temperature and soil moisture content on reclaimed mine land soil CO_2 fluxes

Moagabo Mathiba · Kwame Awuah-Offei · Fred J. Baldassare

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Abstract Recently, incidents of hazardous accumulations of CO_2 in homes built on or near reclaimed mine land have been shown to be linked to neutralization reactions between acidic mine drainage and carbonate material. Surface CO_2 flux measurements have been proposed as a potentially cheap and effective strategy to monitor and delineate such hazards to avoid residential and commercial real-estate development on high risk zones. For this strategy to work, more work is needed to understand the strength of association between CO_2 fluxes on reclaimed mine land and relevant covariates (e.g. sample elevation, soil temperature and soil moisture) to ensure comprehensive monitoring. The objective of this study was to understand the extent to which CO_2 fluxes on reclaimed spoil are affected by sample elevation, soil temperature and soil moisture. Specifically, the work tested the hypothesis that CO_2 fluxes are correlated to elevation, soil temperature and soil moisture. Carbon dioxide fluxes from three study sites were measured and used in statistical analysis to test the research hypothesis. The results show statistically significant ($p < 0.05$) positive but monotonic correlation between CO_2 fluxes and soil temperature, while fluxes and elevation are negatively correlated, monotonically in a similar manner. Where significant, correlation between fluxes and soil moisture was observed to be negative. This result implies that flux surveys on reclaimed mine land need to measure elevation, soil temperature and soil moisture at survey points.

Keywords CO_2 fluxes · Soil moisture · Soil temperature · Sample elevation · Acid mine drainage · Mine reclamation

M. Mathiba (✉)
Department of Civil Engineering, University of Botswana, Private Mail Bag 0061, Gaborone, Botswana
e-mail: mathibam@mopipi.ub.bw

K. Awuah-Offei
Missouri University of Science and Technology, 226 McNutt Hall, Rolla, MO 65409, USA
e-mail: kwamea@mst.edu

F. J. Baldassare
ECHELON Applied Geoscience Consulting, 1229 Twelve Oaks Ct., Murrysville, PA 15668, USA
e-mail: fbaldassare@echelonagc.com

Introduction

Carbon dioxide (CO_2) efflux from soil is a natural phenomenon. Sources of soil CO_2 emissions include, but are not limited to, plant root and microbial respiration. Other sources on localized scales include volcanoes, geothermal springs and dissolution of limestone by weakly, acidic precipitation. Recent work shows that another source of soil CO_2 is neutralization reactions between acid mine drainage (AMD), a low pH and high metal content leachate from the oxidation of sulphide minerals, and carbonate materials associated with reclaimed surface coal mine lands. During mine reclamation, carbonate materials, usually crushed limestone, are added as an amendment to sulphide bearing overburden to neutralize AMD. Carbonate minerals may also exist naturally in the overburden material.

There have been reported incidents of elevated concentrations of CO_2 in homes constructed on or adjacent to reclaimed surface coal mine spoils (Ehler 2002; Laughrey and Baldassare 2003; Harrison et al. 2004; Robinson 2010). Stable carbon isotopic analysis has identified AMD neutralization reactions as the main source of the CO_2 that causes this hazard. While soil respiration has never caused

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any documented incident of high CO_2 concentrations in homes and structures, CO_2 derived from AMD neutralization reactions on reclaimed surface coal mines soils can result in high concentrations of the gas in basements and crawl spaces of homes constructed on or adjacent to such land. This stray CO_2 presents a new health and safety hazard to the occupants of such homes and their pets. Numerous incidents of potentially lethal concentrations of CO_2 in homes, some in excess of 25 % have been reported in the literature (Ehler 2002; Laughrey and Baldassare 2003; Robinson 2010). In some instances, these high CO_2 concentrations have resulted in fatalities (Dawson et al. 2009; Lahmira et al. 2009).

The natural concentration of CO_2 in the atmosphere is 0.035 %. The US Occupational Safety and Health Administration's (OSHA's) general permissible exposure limit is 0.5 %, which happens to be the American Conference of Industrial Hygienists' recommendation as well. OSHA's short-term exposure limit is 3 %. CO_2 concentrations above this threshold, which are usually accompanied by oxygen deficiency, can cause headaches, sweating, rapid breathing, increased heartbeat, shortness of breath, dizziness, mental depression, visual disturbances or shaking. Concentrations above 10 % can produce unconsciousness or death.

The efflux of gas from soils is influenced by, among others, barometric pressure changes, soil moisture content (or gas filled porosity) and temperature gradients (Tuli and Hopmans 2004; Davidson et al. 1998; Kätterer et al. 1998). If flux monitoring is to be useful in studying the hazards posed by CO_2 from AMD neutralization reactions, there is a need to understand these relationships for reclaimed mine land with known AMD-generated CO_2. This paper examines the correlation between CO_2 fluxes from reclaimed mine land with AMD-related CO_2 hazard and soil temperature, soil moisture content, elevation and barometric pressure. Fluxes were monitored at three reclaimed surface coal mines in the United States of America (USA) using the static chamber accumulation (CA) method. Elevation of the sample point, soil moisture and temperature was also measured at each of the sample locations. Barometric pressure was monitored during sampling. The data were used to test the hypothesis that CO_2 fluxes are correlated to elevation, soil temperature and moisture ($H_0 : \rho = 0$).

This work provides insight into the relationship between CO_2 fluxes on reclaimed mine land with AMD-generated CO_2 hazards, on one hand, and elevation, soil moisture and soil temperature, on the other. These relationships are critical in designing sampling protocols to monitor soil CO_2 on such reclaimed mine lands and understanding spatial variation in fluxes. Such understanding of spatial variation is crucial for using CA flux monitoring to delineate hazards prior to construction, post-mining.

Soil Co$_2$ transport mechanisms, emissions, and flux monitoring

CO_2, like other soil trace gases, has been monitored over the years from agricultural, forest, and pasture soils (Davidson et al. 1998, 2000; Pihlatie et al. 2007) and volcanic and hydrothermal activity areas (Lewicki et al. 2007; Bergfeld et al. 2001; Chiodini et al. 1998), in an effort to understand the mechanisms responsible for and conditions affecting efflux of these trace gases from soil. Some studies have focused on identifying sources of and factors affecting soil CO_2 fluxes (Tuli and Hopmans 2004).

Trace gas transport through most soils is understood to generally follow two main mechanisms: concentration-driven diffusive flow (Pihlatie et al. 2007; Scanlon et al. 2002) and pressure-driven advective flow (Scanlon et al. 2002). In reclaimed pyritic mine soils such as coal mine spoils, however, a temperature-driven diffusive transport may also be involved due the heat produced by the exothermic AMD formation reactions (Lefebvre et al. 2001; Hockley et al. 2009). Diffusion is driven by a concentration gradient between soil pores and the atmosphere. CO_2 diffuses from soil where its concentration is high into the atmosphere. Oxygen is consumed during soil (plant and microbial) respiration in natural soils and during AMD formation in sulphur-bearing reclaimed mine soils. CO_2 is produced in both soil respiration and AMD-carbonate neutralization reactions and, hence, its concentration in the soil is higher than in the atmosphere and it is emitted from the soil. Atmospheric pressure fluctuations are responsible for the advective transport of CO_2 and other soil trace gases from soil into the atmosphere, a phenomenon known as atmospheric pumping (Massman 2006). The response lag of subsurface pressure, to atmospheric pressure changes, results in pressure gradients, which drive advective flow.

CO_2 concentration and transport in soil are influenced by soil temperature, which affects respiration/metabolic rates, chemical reaction rates and molecular kinetic energy, all of which increase generally with increase in soil temperature. Higher soil temperature results in higher diffusion rates and, hence, higher CO_2 fluxes. However, it should be noted that temperature extremes together with non-optimal moisture conditions may be rate limiting for soil respiration processes. Gas transport in soil is known to be controlled by temperature, pressure and air-filled soil pore spaces (Davidson et al. 1998; Aachib et al. 2004; Pihlatie et al. 2007). The extent of this correlation varies in different types of soil and has not been fully investigated in reclaimed mine soils, which are highly heterogeneous (Jacinthe and Lal 2006; Lahmira and Lefebvre 2007). This heterogeneity (e.g. mineralogy and particle sizes) is affected by mining and reclamation practices, mining and reclamation equipment, environmental management practices (e.g. selective handling and burial of pyritic materials in pods in the spoil) and pre-mining soils.

Soil moisture content affects CO_2 emissions due to the effect on air-filled porosity and phase flow (single- or multi-phase flow) (Davidson et al. 1998; Harper et al. 2005). During rainfall events, water infiltrating into soil creates a wetting front from the surface that fills up the pore spaces displacing soil gases in the process and reducing soil air-filled porosity and gas diffusion. Thus, during a rain storm, soil CO_2 fluxes are expected to be generally low. Displacement of soil gases by the wetting front may also result in increased soil gas concentrations and partial pressures. However, the wetting front through the soil is usually not uniform horizontally, which results in front instability or finger-flow in areas of high water permeability due to varying initial soil moisture content, presence of fractures or micro-pores, varying soil texture and duration of precipitation event (Bauters et al. 2000; Glass et al. 1989, 1991; Kawamoto et al. 2006; Selker et al. 1992). The extent of the relationship between soil moisture content and fluxes on reclaimed mine spoils requires further attention for the same reasons as above.

AMD neutralization has been known to produce high soil CO_2 concentrations (Cravotta et al. 1994). However, in the past, this CO_2 has never been thought to be a hazard. In recent years, incidents of elevated CO_2 in homes constructed on or adjacent to reclaimed surface coal mines have highlighted the potential health and safety hazard posed by soil gas emissions from such lands. These incidents underscore the need for reliable monitoring and accurate predictions of CO_2 gas emissions from reclaimed coal mine spoils. This requires better understanding of the processes responsible for, and factors influencing, such emissions beyond what is already known about emissions from other soils. This understanding is critical for the development of appropriate monitoring and mitigation.

Methods

Study sites

The field study was conducted at three reclaimed surface coal mine sites in south-western Indiana, south-western Pennsylvania and west-central Missouri in the USA. Figures 1, 2 and 3 show the sites and the sampling locations.

The Hudson site, South-Western Indiana

This site is located in Pike County in south-western Indiana (Latitude: 38°19′42″ and Longitude: 87°08′27″)—Fig. 1. It has a single story building with a walk-in basement constructed on a reclaimed surface coal mine. The site covers

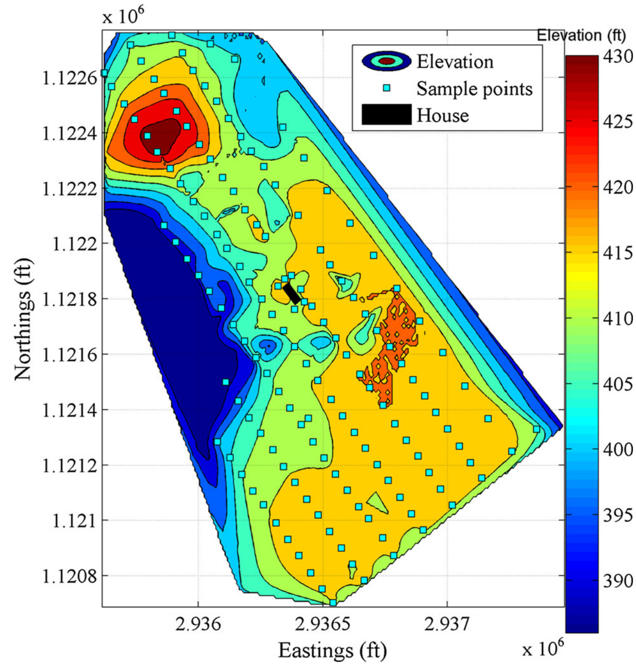

Fig. 1 Hudson study site with sample points and house (*black rectangle*)

an area of about 36 hectares with soils described as Fairpoint loam. The site was reclaimed at 1–15 slopes (NRCS 2011). Mining was carried out between 1986 and 1992 and the site was reclaimed with carbonate amendment and about 0.91 meters of top soil capping. The spoil material extends about 11.6 meters below the surface. The home has been experiencing intermittent episodes of elevated concentrations of stray CO_2 since 2006 (Robinson 2010). The area receives average total rainfall of 1,184.1 mm (46.6 inches) and 304.8 mm (12 inches) of snowfall. The average daily temperature is 12.7 °C (55 °F) with minimum and maximum temperatures of—6.1 °C (21 °F) and 31.1 °C (88 °F) for the winter (January) and summer (July) months, respectively (National Oceanic and Atmospheric Administration 1971–2000).

The sampling campaign at the Hudson site was on March 30 to April 1, 2010. Soil CO_2 fluxes were measured at 138 sample locations established on a 22.9 × 45.7 m (75 × 150 ft) sampling grid.

The Godin site, South-Western Pennsylvania

This site (Fig. 2) is situated near the town of Jenners in Somerset County in south-western Pennsylvania (Latitude: 40°08′2″ and Longitude: 79°02′52″). The home is built on spoil of the reclaimed Godin Mine, which is about 21.34 m (70 ft) thick. Stray CO_2 in the Godin residence was investigated by the Pennsylvania Department of Environmental Protection (PA-DEP) in 2003 (Laughrey and Baldassare

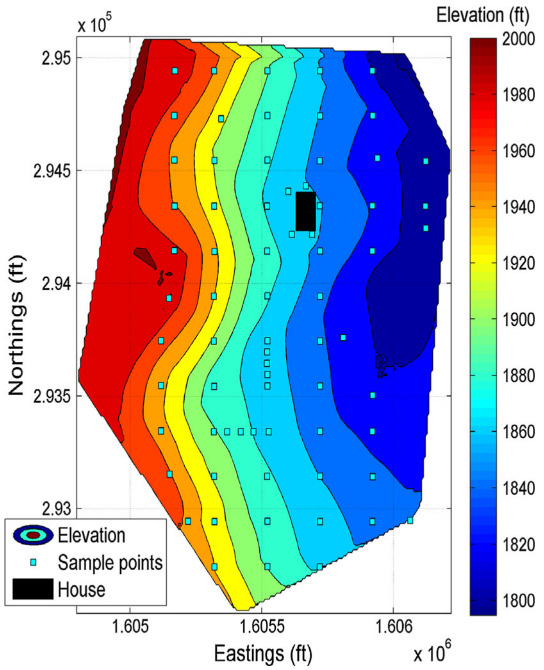

Fig. 2 Godin study site with sample points and house (*black rectangle*)

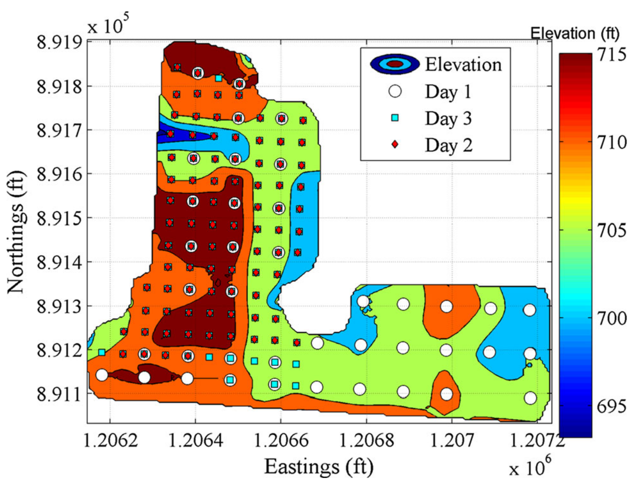

Fig. 3 Germantown study site with sample points

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 tonnes/hectare (20 tons/acre) prior to backfilling and grading. The total annual rainfall averages 1,053 mm (41.45 in.) and 881 mm (34.7 in.) of snowfall. The average daily temperature is 6.7 °C (44.1 °F) and ranges from an average minimum temperature of—4.9 °C (23.1 °F) to a maximum of 18.9 °C (66 °F) for the winter (January) and summer (July), respectively.

Flux sampling was carried out at the Godin site on July 13, 14 and 16, 2010. Soil CO_2 fluxes were measured from 71 sample locations established on a 61.0 m × 61.0 m (200 × 200 ft) sampling grid. Soil temperature and moisture content were not measured at this site due to equipment malfunction.

The Germantown site, West-Central Missouri

The Germantown site is located near Germantown in Henry County in west-central Missouri (Latitude: 38°16′17″ and Longitude: 94°01′04″). The site is a reclaimed surface coal mine that is being used as a pasture. Mining occurred in the area in the 1950s to early 1970s, when it was abandoned. The area, which covers about 14.2 ha (35 acres), 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. The sampled area covers about 2.3 hectares (5.6 acres). The soils are characterized as pits-dumps complex (NRCS 2011). The total annual rainfall averages 1,107 mm (43.6 in.) and 404 mm (15.9 in.) of snowfall. The average daily temperature is 12.2 °C (54 °F) and ranges from an average minimum temperature of 5.5 °C (41.9 °F) to a maximum of 18.9 °C (66 °F) for the winter (January) and summer (July), respectively.

Soil CO_2 flux sampling at Germantown was conducted in 2009. Sampling was on 15.24 × 15.24 m (50 × 50 ft) square grid pattern. The first sampling campaign at this site was on October 2, 2009 and measurements were made on double the grid spacing, (30.48 × 30.48 m), but on the same sample grid. It involved 40 samples. The subsequent flux measurements were made on October 24 and November 7, 2009 on the 15.24 by 15.24 m grid.

Sampling procedure

Soil CO_2 fluxes were measured at regular sampling grids at all sites using accumulation chamber (AC) method for trace gas measurements (Parkin et al. 2003). However, as discussed in the previous section, the grid spacing differed from site to site. A portable, automated soil-CO_2 flux system, (model: LI-8100-103) by Licor Biosciences, Inc. (Lincoln, Nebraska, USA) was used for flux measurements. The system comprises: (i) a 200 mm diameter, 100 mm high collar; (ii) an infrared gas analyser and (iii) a chamber. The collars were made by cutting 100 mm lengths off a 200-mm diameter SDR36 polyvinyl chloride (PVC) sewer pipe. One end of the cut pieces was bevelled for easy insertion into the soil. The collars were installed at least 24 h prior to flux measurements to allow the soil gas fluxes to equilibrate after initial disturbance during installation.

The LI-8100 is capable of simultaneous logging from up to four auxiliary sensors. For this project, auxiliary sensors were used to acquire soil moisture and temperature data at each sampling point.

An ECH2O EC-5 soil moisture probe (Decagon Devices, Inc., Pullman, WA), with at least 0.03 m^3/m^3 accuracy and 10 ms 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 soil moisture and temperature were measured to a depth of 50 mm at each CO_2 flux sampling point at all sites for consistent results.

Correlation analysis

The strengths of association between CO_2 flux and sample elevation, soil moisture and soil temperature were investigated using the parametric Pearson's and nonparametric Spearman's measures of correlation. A 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 between two variables. It is sensitive to non-normal data and presence of outliers.

The parametric Pearson's correlation coefficient, ρ, is given by Eq. (1). $\bar{x}$ 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. The Spearman's correlation coefficient is a rank-ordered, nonparametric measure of association and is more suited for nonlinear relationships. SAS correlation procedure, PROC CORR (SAS Institute Inc. 2004) was used to compute the Spearman's correlations (Eq. 2). p_i is the rank of x_i, Q_i is the rank of y_i, $\bar{R}$ is the mean of the p_i values, and $\bar{Q}$ is the mean of the Q_i, values.

$$\rho = \frac{\frac{1}{n}\sum_{i=1}^{n}(x_i - \overline{x})(y_i - \overline{y})}{s_x s_y} \quad (1)$$

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

If soil CO_2 flux, the dependent variable, generally increases or decreases (monotonic) as a covariate (elevation, soil temperature, or soil moisture) increases or decreases, a positive correlation exists and vice versa. If the relationship is perfect and positive, the correlation coefficient would be 1 and −1 if it is negative. When there is no linear predictability between the flux and any one of the other covariates, the correlation is 0 and they are said to be independent.

Both measures were used to evaluate the correlations between CO_2 flux as the dependent variable and the other variables as independent variables under the hypothesis that the correlation between CO_2 flux and these covariates is insignificant, using the hypothesis test in Eq. (3):

$$H_0 : \rho = 0 \text{ versus } H_1 : \rho \neq 0 \quad (3)$$

Results and discussions

Preliminary analysis

A summary of the data is shown in Table1. The soil-CO_2 fluxes, F_{CO_2}, were found to be positively skewed for all sampling days for all sites, although the data from the Hudson site seem to be the most skewed. This indicates

Table 1 Summary statistics of soil CO_2 fluxes

Study site	Hudson			Godin			Germantown		
Sampling day	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
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

Table 2 Tests for normality

		Hudson			Godin			Germantown		
		Day 1	Day 2	Day 3	Day 1	Day 2	Day 3	Day 1	Day 2	Day 3
F_{CO_2}	A^2	7.162	7.259	6.511	0.882	1.021	0.262	0.764	0.904	1.058
	p value	<0.005	<0.005	<0.005	0.023	0.010	0.696	0.043	0.020	0.008
$\ln(F_{CO_2})$	A^2	0.467	0.503	0.493	0.213	0.377	–	0.392	0.682	0.466
	p value	0.248	0.201	0.213	0.847	0.401	–	0.362	0.072	0.247

Table 3 Tests for sample day effects

Site	Sample day comparison		Difference between means μmol/m^2/s	Simultaneous 95 % confidence limits μmol/m^2/s		F value	p value
Hudson	Day 1	Day 2	0.3737	−0.7025	−0.0449	7.05	0.0010
	Day 1	Day 3	−0.7575	−1.0893	−0.4256		
	Day 2	Day 3	−0.3838	−0.7132	−0.0544		
Godin	Day 1	Day 2	−3.9949	−4.9510	−3.0389	51.36	<0.0001
	Day 1	Day 3	−2.9915	−3.9476	−2.0355		
	Day 2	Day 3	1.0034	0.0473	1.9594		
Germantown	Day 1	Day 2	0.8658	0.2492	1.4825	11.03	<0.0001
	Day 2	Day 3	−0.8562	−1.3311	−0.3813		
	Day 1	Day 3	0.0096	−0.5972	0.6163		

that the data were non-normal. Skewed data are not surprising given that generally environmental data have a lower bound of zero with possible outliers in the high values (Berthouex and Brown 1994). Since correlation tests assume normality, the authors tested for normality using the Anderson–Darling test (test statistic, A^2) and log-transformed those datasets that were not normal in an attempt to make them normally distributed (Table 2). The normality tests show that all the data, with the exception of Day 3 of the Godin site data, were non-normal. After log transforming the data, the non-normality was removed (Table 2).

Sampling day effects on CO_2 fluxes were analysed using multiple mean comparison t test using multivariate analysis of variance (MANOVA). The results (Table 3) show that the effects of sampling day are significant ($p \leq 0.001$) on CO_2 fluxes and this holds true for all the sites except for Day 1 and Day 3 of sampling at the Germantown site, which show a confidence interval that includes zero. The fact that sample day has significant effect on soil-CO_2 fluxes was to be expected as conditions, such as soil temperature and moisture conditions (Bergfeld et al. 2001; Raich and Tufekcioglu 2000; Rustad et al. 2000), atmospheric pressure (Chiodini et al. 1998; Lewicki et al. 2007), wind speed (Lewicki et al. 2007) and soil respiration rates (Davidson et al. 2000) would not be expected to be the same for all of the sampling days.

Finally, the effect of barometric pressure on the fluxes was evaluated, qualitatively. Figure 4 shows a typical plot of barometric pressure and fluxes for the sampling period in the day [similar plots for all data sets can be found in Mathiba (2013)]. There appears not to be a significant shift in fluxes as pressure changes gradually during the day. The correlation could not be tested quantitatively because the weather stations only logged barometric pressure periodically (1 h intervals) making it impossible to obtain barometric pressure readings for each flux reading.

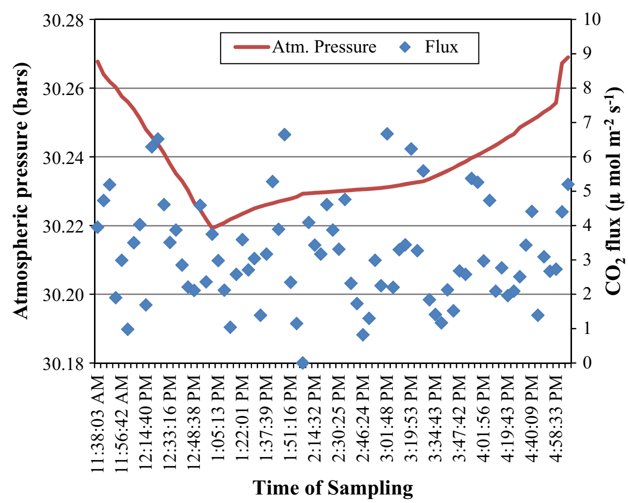

Fig. 4 Effect of barometric pressure on fluxes (sample plot using Germantown Day 3 data)

Correlation analysis

Hudson site

Table 4 shows the results of the Hudson site correlation analysis. CO_2 fluxes are significantly correlated with soil temperature. The Pearson's correlations are positive for all 3 days. The nonparametric Spearman's correlation coefficients show similar results except for sampling Day 2, which shows no significant correlation of flux with soil temperature. The data show a positive and monotonic relationship. That is, CO_2 flux increases (decreases) as soil temperature, but the relation may or may not be linear.

Figure 5 shows the scatter plots of CO_2 flux and soil temperatures for all 3 days of sampling. All 3 days show some patterns of positive correlation. The figure shows relatively strong positive correlation on Day 1 compared to the other two sampling days.

Figure 6 shows the scatter plots of CO_2 flux and soil moisture for the three sampling days. All three plots show some pattern of negative correlation even though the correlation is not very strong, which supports the observed correlation coefficients (−0.37 to −0.16).

Figure 7 shows scatter plots of CO_2 fluxes and sample elevation. This figure also shows weak (negative) correlations. The plots show the relative strength of the correlation on the different days.

Soil temperature and moisture show no significant correlation except for Day 1 ($\rho = -0.24$, $p = 0.007$; and $r = -0.21$, $p = 0.015$). There is significant, negative correlation between soil temperature and elevation on all of the three sampling days shown by both parametric and nonparametric coefficients. The data show no correlation between soil moisture and sample elevation.

Godin site

As mentioned above, due to equipment malfunction, no soil moisture and temperature measurements were taken from the Godin site. Table 5 shows the correlation analysis between $\ln(F_{CO_2})$ and elevation, except for Day 3, where the correlation is between F_{CO_2} and elevation (note that the rank correlations—Spearman correlations—are all between raw fluxes and covariates). The result shows no significant ($\alpha = 0.05$) correlation between CO_2 fluxes and sample elevation for the Godin site except for Day 3 of sampling, according to the Pearson's correlation coefficients. Spearman's correlation coefficients show significant negative correlations on all three days. This indicates the observed correlations are nonlinear (Pearson correlation coefficients measure linear correlations). Figure 8 shows the plots of CO_2 flux against sample elevation. Day 3 shows a general decrease in CO_2 fluxes as elevation increases.

Table 4 Correlation analysis results for Hudson site

Day	Correlated variables	Pearson's correlation coefficients			Spearman's correlation coefficients		
		Soil temperature	Soil moisture	Elevation	Soil temperature	Soil moisture	Elevation
1	$\ln(F_{CO_2})$	0.45	−0.37	−0.15	0.48	−0.39	−0.16
	p value	<0.0001	<0.0001	0.093	<0.0001	<0.0001	0.067
	Soil temperature		−0.24	−0.25		−0.21	−0.28
	p value		0.007	0.004		0.015	0.001
	Soil moisture			−0.13			−0.13
				0.146			0.150
2	$\ln(F_{CO_2})$	0.26	−0.16	−0.22	0.11	−0.14	−0.25
	p value	0.003	0.062	0.010	0.215	0.120	0.004
	Soil temperature		0.11	−0.17		−0.10	−0.20
	p value		0.186	0.051		0.244	0.022
	Soil moisture			−0.06			−0.10
	p value			0.525			0.23
3	$\ln(F_{CO_2})$	0.23	−0.30	−0.23	0.24	−0.34	−0.31
	p value	0.010	0.001	0.009	0.007	<0.0001	0.0003
	Soil temperature		−0.03	−0.21		−0.02	−0.30
	p value		0.740	0.016		0.865	0.0004
	Soil moisture			0.10			0.07
	p value			0.279			0.462

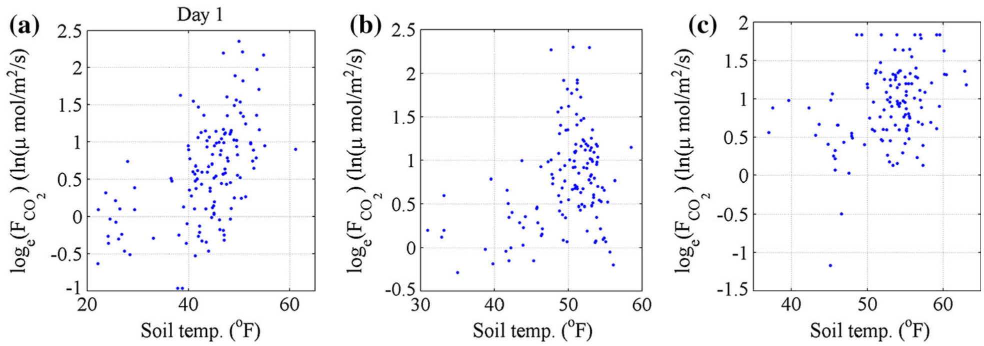

Fig. 5 CO_2 flux versus soil temperature at the Hudson site: **a** Day 1; **b** Day 2 and **c** Day 3

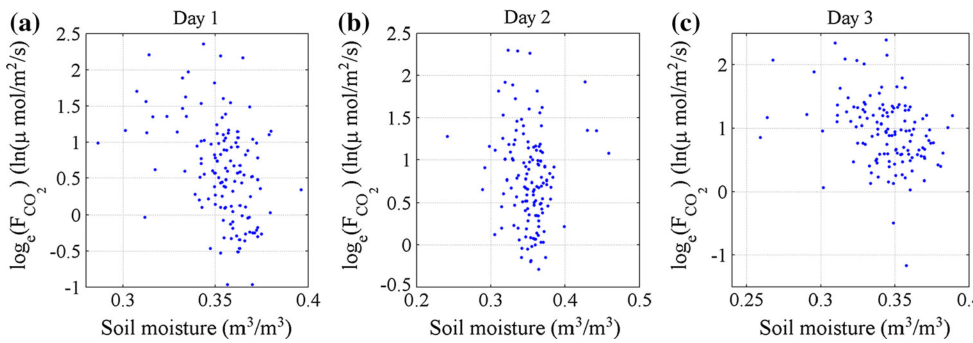

Fig. 6 CO_2 flux versus soil moisture at the Hudson site: **a** Day 1; **b** Day 2; and **c** Day 3

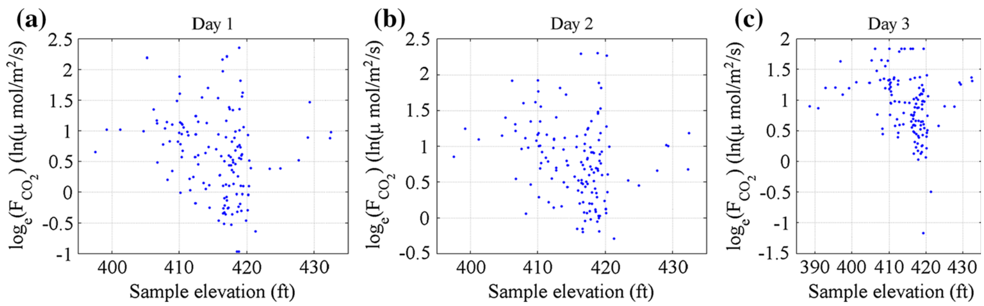

Fig. 7 CO_2 flux versus sample elevation at the Hudson site: **a** Day 1; **b** Day 2 and **c** Day 3

Table 5 Correlation analysis results for Godin site F_{CO_2} (Pearson)/ $\ln(F_{CO_2})$ (Spearman) versus elevation

	Pearson's correlation coefficients			Spearman's correlation coefficients		
Sample Day	1	2	3	1	2	3
Coefficient	−0.14	0.10	−0.28	−0.24	−0.24	−0.31
p value	0.261	0.417	0.018	0.042	0.041	0.009

Germantown site

Table 6 shows the results of correlation analysis for data from the Germantown site, which shows non-significant correlation between CO_2 flux and soil temperature. Both Pearson's and Spearman's correlation coefficients are negative for Days 1 and 2. CO_2 fluxes are shown to be significantly correlated with soil moisture for Days 1 and 3 but not for Day 2, which shows no significant correlation ($0.228 \leq p \leq 0.235$) between fluxes and soil moisture. Pearson's and Spearman's correlation coefficients are negative for all days.

Spearman's correlation coefficients indicate a negative (−0.35 and −0.15, respectively) and significant ($p \leq 0.033$) correlation between flux and elevation for Day 1 and Day 3. Pearson's correlation coefficients confirm the significant ($\alpha = 0.1$) correlation for Day 3 ($p = 0.091$) but not for Day 1. Both Pearson's and Spearman's correlation shows no significant correlation for Day 2.

Figure 9 shows the scatter plots of CO_2 flux and soil temperatures for all 3 days of sampling. The figure shows weak correlations, which confirm the low correlation coefficients (−0.19 to 0.04) observed in the correlation analysis. There is a relatively strong negative correlation on Day 1 compared to the other two sampling days with no discernible correlation on Day 3.

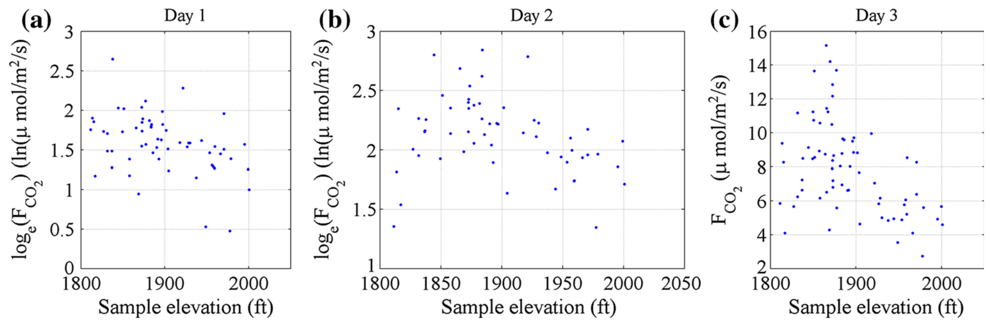

Fig. 8 CO_2 flux versus sample elevation at the Godin site: **a** Day 1; **b** Day 2; and **c** Day 3

Table 6 Correlation analysis results for Germantown site

Day	Correlated variables	Pearson's correlation coefficients			Spearman's correlation coefficients		
		Soil temperature	Soil moisture	Elevation	Soil temperature	Soil moisture	Elevation
1	$\ln(F_{CO_2})$	−0.19	−0.34	−0.37	−0.16	−0.37	−0.35
	p value	0.2502	0.038	0.233	0.327	0.023	0.033
	Soil temperature		0.08	−0.28		0.07	−0.31
	p value		0.615	0.080		0.666	0.056
	Soil moisture			−0.14			−0.18
	p value			0.381			0.275
2	$\ln(F_{CO_2})$	−0.14	−0.13	−0.03	−0.13	−0.15	−0.07
	p value	0.213	0.228	0.785	0.235	0.160	0.507
	Soil temperature		0.01	−0.17		0.03	−0.15
	p value		0.898	0.114		0.806	0.172
	Soil moisture			0.11			0.07
	p value			0.318			0.528
3	$\ln(F_{CO_2})$	0.04	−0.28	−0.11	0.01	−0.29	−0.15
	p value	0.600	<0.0001	0.091	0.844	<0.0001	0.027
	Soil temperature		−0.18	−0.12		−0.24	−0.13
	p value		0.005	0.080		0.0003	0.052
	Soil moisture			−0.06			−0.09
	p value			0.366			0.181

Figure 10 shows scatter plots of the fluxes against soil moisture. The figure shows fluxes, generally, decreases and soil moisture increases on Days 1 and 3. Although, it can be said that Day 2 also shows such a trend, it is much less apparent.

Figure 11 shows plots of CO_2 fluxes against sample point elevation. Day 1 shows a negative correlation between fluxes and elevation. Although Days 2 and 3 possibly show the same negative correlation, it is not that obvious. These are confirmed by the results in Table 6, with no significant correlation observed on Day 2, while significant correlation is only observed using the Spearman correlation coefficient. This will suggest the correlation in the Day 3 is not linear.

The data show no significant correlation between soil temperature and moisture for the Germantown data except for Day 3, which shows a negative correlation ($\rho = -0.18$, $p = 0.005$; $r = -0.24$, $p = 0.0003$). There are no significant correlations observed between soil temperature and sample elevation for the Germantown data at 95 % confidence. However, at 90 % confidence, Day 1 and Day 3 show weak ($-0.28 \le \rho \le -0.12$, $-0.31 \le r \le -0.13$), but significant correlation ($p < 0.080$). There is no significant relationship observed between the soil moisture and elevation for the Germantown data.

Discussion

CO_2 flux versus soil temperature

Statistically significant correlation between CO_2 fluxes and soil temperature was observed at the Hudson site but not at the Germantown site. The correlation was positive,

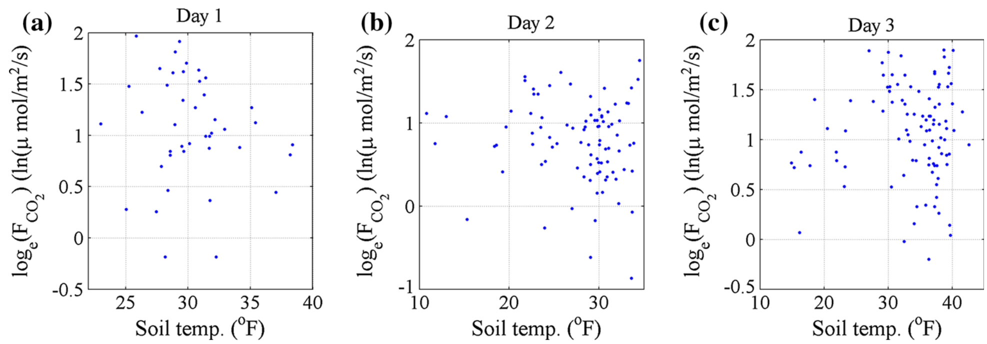

Fig. 9 CO_2 flux versus soil temperature at the Germantown site: **a** Day 1; **b** Day 2; and **c** Day 3

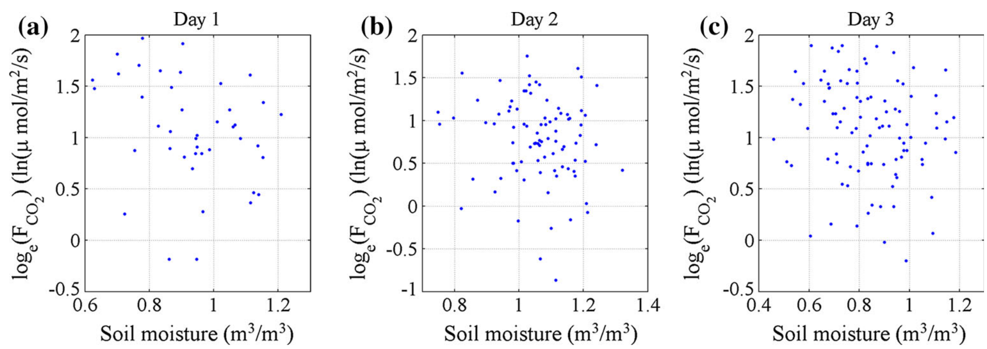

Fig. 10 CO_2 flux versus soil moisture at the Germantown site: **a** Day 1; **b** Day 2; and **c** Day 3

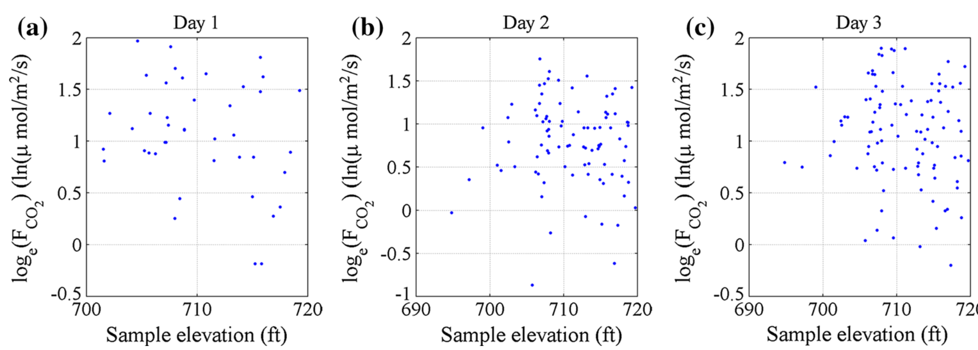

Fig. 11 CO_2 flux versus sample elevation at the Germantown site: **a** Day 1; **b** Day 2 and **c** Day 3

indicating that soil CO_2 flux increased as soil temperature increased. However, the correlation coefficients are relatively low (0.23–0.45) compared to what is reported in the literature for natural soils—0.36 to 0.68 (Davidson et al. 1998; Reth et al. 2005; Nkongolo 2010). The relationship between soil respiration, represented by soil CO_2 fluxes, and soil temperature is known to be inconsistent (Davidson et al. 1998). This may be due to confounding effects[1] of soil temperature and moisture (Risk et al. 2002; Borken et al. 2003). The weaker, compared to some natural soils, observed correlation between CO_2 fluxes and soil temperature is not what one would expect if there is significant contribution from AMD-generated CO_2, since sulphide oxidation is exothermic. It is also possible that on the day of sampling, the contribution of AMD-generated CO_2 may have been low. Systematic stable carbon and oxygen isotope analysis is required to examine the effect of the contribution of AMD-generated CO_2 on the correlation between temperature (indeed all the explanatory variables examined in this work) and CO_2 fluxes. The influx of CO_2 into these homes is episodic (Robinson 2010) suggesting that significant upward flow of CO_2 may also be episodic.

CO_2 flux from reclaimed mine land is likely to be a mixture from at least two sources: biogenic and AMD-derived CO_2. The latter source is characterized by heat generation from exothermic oxidation reactions, which lead to CO_2 production. The heat produced increases the internal temperature of the mine spoil and inducing a thermal gradient that may cause convective soil gas transport and heat transfer, both of which are not present in

[1] The masking of true effects of a variable by the effects of one or more other variable(s) that are so closely related that it is not easy to separate their individual effects.

natural soils. Hence, it was expected that there will be higher correlation between fluxes and temperature on reclaimed mine soils with AMD-caused CO_2. It appears the complexity of responsible factors mask any effect of the exothermic reactions on soil surface temperatures (temperatures were measured in the first 250 mm of soil). Soil gas efflux depends on the rate of gas production, degree of soil compaction (and hence macro-porosity) and presence of preferential flow paths. It may also be that the heat transfer to the surface is minimal and does not lead to any significant changes in soil temperature.

The lack of significant correlation between CO_2 efflux and soil temperature observed for the Germantown site is not uncommon (Reth et al. 2005). The seasonal and diurnal variations in CO_2 fluxes, and the conditions, can lead to variations in observed correlations. Due to the limited resources, it was not possible to collect the data simultaneously at all three sites. Further research is required to completely rule out the presence of any correlation between soil temperature and fluxes at this site. If that is shown to be true, then this further research will explore the differences between this site and the Hudson site.

CO_2 flux versus soil moisture

CO_2 fluxes were found to be negatively correlated with soil moisture for 67 % of the sampling days (2 out of 3 days) at each of the Hudson and Germantown sites. This is consistent with the literature. The correlation is reported to be negative due to effects of moisture on gas diffusivity through air-filled porosity (Bekele et al. 2007). Precipitation and, subsequent, infiltration result in a wetting front, which reduces soil air-filled porosity from the surface downwards (Risk et al. 2002; Guo et al. 2008). 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 %. Soil moisture relationship is reported to switch from being negative to positive at very low volumetric soil moisture content below 12 % (Davidson et al. 1998).

CO2 flux versus sample elevation

CO_2 flux is significantly correlated with sample elevation for 67 % of the data from the Hudson and Germantown sites and for 100 % of the data from the Godin site. The correlation was found to be significant at $\alpha = 0.05$ and was negative. The relationship appears to be nonlinear as the Spearman correlation coefficients appear to be more significant than the Pearson coefficients. Neto et al. (2011) reported a similar observation for CO_2 and nitrous oxide (N_2O) fluxes for much larger elevation differences (300–600 m). The results here show that this relationship (negative correlation between fluxes and elevation) exists, even for small elevation differences (15–76 m). The literature does not offer any particular explanation for this relationship. Neto et al. (2011) suggested that it may be due to a combination of air and soil temperature, soil properties, species composition and respiration rates and nutrient supply.

This research cannot offer any definitive explanation for this observation either. The authors can offer two possible hypotheses. Firstly, the authors hypothesize that correlation between fluxes and elevation could be caused by the fact that CO_2 is heavier than air and will migrate "downhill" if the flow pathways exist. For example, Laughrey and Baldassare (2003) show a house downhill of a mine which accumulated CO_2 in the basement because of dipping sedimentary seams in the direction of the house. However, this will only be true of the deeper AMD-generated CO_2 and not the CO_2 generated in the surface soil (root respiration and microbial activity). Secondly, if the majority of the CO_2 is from the surface soil, then the correlation between CO_2 fluxes and elevation is likely due to some soil property (e.g. labile C) that is varying with elevation. This is more likely to be the case at the Godin site, for instance, where this correlation was observed for all sampling days and less likely to be the explanation for the Hudson and Germantown sites where no significant correlation was observed on one of the three sampling days. This should be the focus of further research.

Correlation between explanatory variables

Soil temperature was found to be significantly correlated with soil moisture for only 33 % of the data sets at both the Hudson and Germantown sites. It was, however, correlated with sample elevation for all of the data sets at the Hudson site. There was significant ($\alpha = 0.1$) correlation observed between soil temperature and sample elevation for Germantown for 67 % of the data. There was no significant correlation between soil moisture and sample elevation.

The presence of significant correlation between some of the explanatory variables indicates possible confounding effects that may mask some of the correlation between CO_2 fluxes and the explanatory variables. Such confounding effects make it difficult to isolate the real correlation between fluxes and the explanatory variables in all the data sets.

Conclusions

This study's objective was to examine the relationship between soil CO_2 fluxes and elevation, soil moisture and soil temperature. Specifically, the study sought to examine this relationship on reclaimed mine land where there is CO_2 generated from AMD-carbonate reactions and evaluate whether the relationships are any different from those observed in natural soils. From the results, the following conclusions can be drawn:

- There is statistically significant correlation between soil CO_2 flux and soil temperature, just as has been observed in natural soils. The correlation coefficients on the reclaimed mine soils appear to be lower.
- Where present and significant, correlation between CO_2 flux and soil moisture is negative. This is consistent with observations on natural soils.
- CO_2 flux and sample elevation show significant and negative correlation even where the elevation differences are small. The authors are not aware of any other instances where this relationship has been examined for small (<100 m) differences in sample elevation.
- Statistically significant and negative correlation were observed between soil temperature and sample elevation. In a third of the cases, soil temperature was observed to be significantly correlated to soil moisture. These observed correlations between explanatory variables may be the source of confounding effects, which make it difficult to accurately characterize the relationships between the variables.

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