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Controls on boreal peat combustion and resulting emissions of carbon and mercury

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Abstract

Warming in the boreal forest region has already led to changes in the fire regime. This may result in increasing fire frequency or severity in peatlands, which could cause these ecosystems to shift from a net sink of carbon (C) to a net source of C to the atmosphere. Similar to C cycling, peatlands serve as a net sink for mercury (Hg), which binds strongly to organic matter and accumulates in peat over time. This stored Hg is also susceptible to re-release to the atmosphere during peat fires. Here we investigate the physical properties that influence depth of burn in experimental peat columns and the resulting emissions of CO, CO_2, CH_4, and gaseous and particulate Hg. As expected, bulk density and soil moisture content were important controls on depth of burn, CO_2 emissions, and CO emissions. However, our results show that CH_4 and Hg emissions are insensitive to combustion temperature or fuel moisture content. Emissions during the burning of peat, across a wide range of moisture conditions, were associated with low particulate Hg and high gaseous Hg release. Due to strong correlations between total Hg and CO emissions and because high Hg emissions occurred despite incomplete combustion of total C, our results suggest that Hg release during peat burning is governed by the thermodynamics of Hg reduction more so than by the release of Hg associated with peat combustion. Our measured emissions ratios, particularly for CH_4:CO_2, are higher than values typically used in the upscaling of boreal forest or peatland fire emissions. These emission ratios have important implications not only for our understanding of smouldering chemistry, but also for potential influences of peat fires on the Earth's climate system.

1. Introduction

Boreal peatlands play an important role in ecosystem-climate feedbacks due to their role as long-term sinks of atmospheric carbon (C). Globally, peatlands today store over 600 Pg of C, with more than 80% of this C stored in northern high latitude peatlands (Yu *et al* 2010 2011). Despite serving as net sources of atmospheric methane (CH_4), peatlands have had a net cooling effect on the climate system because of peat C storage over time. The future of peatlands as a net C sink is uncertain, given that warming influences carbon dioxide (CO_2) and CH_4 production and fluxes in different ways

(Blodau 2002). The accumulation of organic matter as peat also makes peatlands effective biogeochemical sinks of other elements, including Hg (Outridge *et al* 2011). Over time, large quantities of Hg have accumulated in northern peatlands, though in general the peatland Hg stock is not well quantified. However, boreal peatland Hg stocks can be as much as ten times greater than stocks in boreal upland forests, due mostly to the thickness of the organic soil layer in peatlands (Turetsky *et al* 2006).

While fire is considered to be one of the most important factors driving succession and C cycling in boreal upland stands (Harden *et al* 2000,

Bond-Lamberty *et al* 2007), its role is not as well understood in peatlands. While several studies have examined the role of fire in driving peatland vegetation succession and patterns of microtopography (Benscoter and Vitt 2008), northern undisturbed peatlands in general are viewed to be resistant to burning due to their high moisture levels (Turetsky *et al* 2015). During drought or in areas of hydrologic disturbance, fire activity in peatlands can release significant amounts of stored C (Turetsky *et al* 2011a, 2011b) as well as Hg (Turetsky *et al* 2006). Burn severity in peatlands ultimately will be regulated by the position of the water table and how it influences the moisture content of peat layers with depth (Waddington *et al* 2012). At regional scales, multiple changes to the fire regime (greater probability of ignition, lengthening of the fire season, and increases in overall fire occurrence; Flannigan *et al* 2009, 2005), all have the potential to increase burning across the landscape. Even small increases (<20%) in both annual burned area and fire intensity is expected to shift boreal bogs from net C sinks to net sources (Wieder *et al* 2009).

Peatland fires are dominated by smouldering combustion because the smouldering reaction is less constrained by fuel moisture than flaming combustion and can occur in wetter fuels, such as peat (Zoltai *et al* 1998, Turetsky *et al* 2004, Rein *et al* 2008). Smouldering combustion is a non-flaming, self-sustaining form of combustion that derives its principal heat from heterogeneous fuel consumption (Aldushin *et al* 2006). Fuels with low moisture content require less energy to propagate, resulting in faster spread of the smouldering front and greater fuel consumption (Benscoter *et al* 2011, Huang and Rein 2014). Smouldering produces a different emission profile than flaming combustion. In general for boreal fuels, smouldering is responsible for a larger fraction of fuel consumption and emissions than flaming combustion, and produces more CO, CH_4, and particulate emissions (Yokelson *et al* 1997, Rein *et al* 2008, Hamada *et al* 2013). Despite its importance to organic C release, little is known about the emission dynamics of smouldering combustion.

Wildfire is likely to be a significant source of Hg to the atmosphere under future climate change scenarios (Turetsky *et al* 2006, Krabbenhoft and Sunderland 2013). Recognizing that terrestrial soils are the largest stock of Hg globally, the forecasted increase in Hg emissions from wildfires casts significant uncertainty on future Hg mass balance estimates and atmospheric concentrations, despite stringent efforts to regulate anthropogenic Hg emissions (Amos *et al* 2013). While studies have shown that flaming combustion is efficient at releasing Hg (Obrist 2007, Friedli *et al* 2001), release of Hg during smouldering and ground fire conditions appear to be much more variable and are dependent on fuel conditions as well as heat release rates during burning. Although there has been some consideration of the impacts of combustion on Hg concentrations and methylation in boreal

vegetation and upland soils (Mailman and Bodaly 2005, 2006, Mitchell *et al* 2012) there is limited information about the effects of wildfire on peatland Hg stocks, and no direct quantification of the losses of soil-bound Hg as gaseous Hg(0) due to thermal decomposition and emission due to wildfire.

The main objective of this study was to gain insight into the controls on peat combustion and the resulting C and Hg emissions. To achieve this objective, we conducted laboratory peat combustion experiments under a range of controlled moisture contents to examine the physical characteristics of peat that influence depth of burn, CO, CO_2, CH_4, as well as gaseous and particulate Hg emissions.

2. Materials and methods

2.1. Site selection and sample collection

Samples were collected at two bogs and two fens located in the Slave Lake—Athabasca region of northern Alberta, Canada. Sites were selected as being representative of western Canadian bogs and treed fens (Vitt *et al* 1995). Canopy vegetation of the bogs was dominated by *Picea mariana* and had an equal distribution of hummocks and hollows. Both fen sites were treed fens with a canopy of *P. mariana* and *Larix laricina* and were comprised of 65% hummocks and 35% hollows. Within each site, we selected three hollows and two hummocks. Because hollows represent a larger proportion of the more deeply burned area in peatlands than hummocks (Shetler *et al* 2008), we oversampled hollows to account for this pattern of variation seen in burned peatlands. Sampling locations within each site were selected to maximize the heterogeneity of vegetation and microtopographic relief present at that site. In each sampling location, one $40 \times 60 \times 30$ cm block of peat was collected. All peat blocks represented aerobic peat layers above the water table. We kept each block at field moisture content and immediately transported each block to Edmonton where they were frozen prior to the experiments described below.

2.2. Laboratory burn experiments

Each peat block was assigned to one of three drying treatments upon thawing: field moisture (no drying), air dried at approximately 23 °C for 1 week, or dried at 40 °C in a drying room for 1 week plus 1 week at room temperature. Peat was dried in elevated open top plastic containers with 15 holes 4 cm in diameter to allow free water drainage from below. Air movement above the samples was provided by an oscillating fan operating at 1 m s^{-1}. The relative humidity of the drying room at 40 °C was approximately 12%, and 30%–35% for the ambient room at 23 °C. The moisture contents achieved during the drying treatments are meant to simulate the range in moisture conditions at the time of wildfire in boreal peatlands, which do not necessarily occur during periods of drought and water table decline, though

large peatland fires in general are more likely during drought periods (Turetsky *et al* 2004). The lower range of moisture content in surface feather moss is consistent both with prior laboratory studies (Benscoter *et al* 2011), as well as prescribed burns in peatlands with a feather moss and *Sphagnum* mix (Hvenegaard *et al* 2016).

Following the application of the drying treatment, a $25 \times 24 \times 20$ cm sample was cut from the centre of each peat block to minimize any edge effects. These samples were placed in a fire-proof box of the same dimensions; fire boxes were constructed of 1.3 cm thick ceramic fibreboard (Cotronics Corp, Brooklyn, NY). Prior to the onset of our burn experiments, a vertical cross section was cut by hand from each sample and a small volume of soil was taken every 5 cm along the depth of each sample. These volumetric samples were used to measure pre-burn bulk density and water content with depth (see below for methods). These same samples also were used for analysis of solid-phase C and Hg concentrations.

A fibreboard spacer ensured all samples were flush with the top of the burn box to eliminate any influence of edges on the air flow into the box during burning. Once the samples were placed in the burn box, 2 K-type thermocouple probes were inserted 10 cm (horizontally) into the sample at 5, 10, 15, and 20 cm depths. An additional 4 E-type surface thermocouples were placed five cm from each side of the box (four per sample). Temperature data were recorded on a Campbell Scientific CR5000 data logger (Campbell Scientific, Logan, USA) at 1 second intervals. Mass loss was recorded every second for the duration of each experiment.

Each burn was initiated by placing a high output heater over each sample to simulate the heat pulse from a crown fire, $\sim$3 MJ m^{-2}. Heat was applied for a total of 10 min to reach the desired heat output. Thompson *et al* (2015) estimated between $2.7-7.8$ MJ m^{-2} of radiant heat is transferred to the peat surface during the passage of a crown fire. We used a quartz electric heater with 5 kW m^{-2} output; since the apparatus is not able to achieve the $>$1000 °C maximum surface temperatures observed during crown fires in boreal forests (Taylor *et al* 2004), we used a longer duration of heating of 10 min to achieve cumulative heat inputs of 3 MJ m^{-2} that are otherwise transferred during $\sim$75 seconds of active fire activity at the surface followed by up to 90 seconds of residual flaming (Taylor *et al* 2004).

Combustion was judged to have ceased when mass loss had plateaued and fuel thermocouple readings fell below 50 °C. The duration of smouldering combustion observed in our burn tests is comparable to the experimental trials of Benscoter *et al* (2011) that involved significant smouldering. Comparison of results from experimental burn tests to field conditions is difficult due to a general lack of robust field observations of peat smouldering. Smouldering in black spruce peatlands occurred on the order of $2-6$ h during a prescribed

burn documented by Hvenegaard *et al* (2016) in a black spruce peatland in Alberta, Canada.

Throughout the burn experiments, an exhaust fan in the flue was used to draw a constant volume of emissions up at a rate of 0.135 m^3 s^{-1}. Gases were drawn through a copper pipe fixed inside the flue two metres above the peat surface. Emission gases then passed through 0.675 cm diameter vinyl tubing connected to a Siemens Ultramat 23 and Ultramat 6 (Siemens AG, Berlin, Germany), calibrated with a nitrogen standard, running in series. CO and CO_2 concentrations were measured with the Ultramat 23 while CH_4 concentration was measured with the Ultramat 6. Concentrations from both instruments were recorded via a Campbell Scientific CR1000 every second along with 1 minute totals of emissions. All C gas concentrations were recorded in ppmv.

In a similar fashion, emissions were drawn through vinyl tubing connected to a Teflon particulate filter pack to capture particulate Hg (PHg), then to a glass trap filled with gold-coated quartz beads (Tekran Instruments Corp., Toronto, Canada) to capture total gaseous Hg. The Hg sampling apparatus was connected to a vacuum drawing emissions in at $\sim$3.5 L min^{-1}. Gold traps were sealed with Teflon plugs and analyzed by thermal desorption, atomic fluorescence spectrometry, using USEPA method IO-5 (US Environmental Protection Agency 1999) on a Tekran 2600 system.

Upon completion of each burn experiment (end of smouldering combustion), surface ash was collected with a hand-held vacuum. Ash samples were used for post-burn Hg and C content analyses.

Masses of CO_2, CO, CH_4, and Hg emissions were calculated from the recorded concentrations using:

$$m_{\text{gas}} = V \left(10^6 \right) \cdot v_{\text{fan}} \cdot p_{\text{gas}} - \text{baseline} \qquad (1)$$

where V is the observed concentration of the C or Hg species, v_{fan} is the observed velocity of gases in the flue, p_{gas} is the density of the gas, and baseline is the observed ambient concentration of the gas present. The cumulative mass of each C gas as well as gaseous and particulate Hg emissions emitted over the course of each experiment were calculated from these masses along with key emission ratios.

2.3. Chemical analysis of peat samples

Peat samples were assessed for total C and Hg stocks before and after the burn experiments so that we could use change in soil stocks as an alternative assessment of emissions. As mentioned above, prior to burning, a cross section was cut from each peat sample and volumetric sub-samples were taken at five cm depth increments and analysed for pre-burn bulk density and water content. These same samples were used for analysis of heat of combustion, total Hg and C content. Volumetric sub-samples were weighed immediately following collection and dried at 45 °C to avoid any Hg loss until a constant mass was reached. These

data were used to calculate bulk density (dry fuel mass per sample volume, g cm^{-3}), volumetric water content (water volume per sample volume), and percent gravimetric water content (water mass per unit of dry peat). Average bulk density and volumetric water content values were calculated only for those layers that had been consumed during the experiments; data from unburned peat at depth were excluded. For both pre-burn peat and post-burn ash, we homogenized samples followed by analysis on an Elementar Vario Max elemental analyzer (Elementar Analysensysteme, Hanau, Germany) to measure %C. Carbon stocks were calculated by multiplying %C, peat or ash density, and depth. Total Hg analyses on the pre-burn peat and post-burn ash samples were conducted by direct mercury analysis on a Milestone DMA-80 (USEPA Method 7473 (USEPA 2007)). Total Hg on Teflon filters (PHg) was first extracted by acid digestion, then digestates were brought to volume using 0.5% BrCl and left to oxidize overnight. Aliquots of this solution were then further diluted into deionized water (18.0 M.cm) to achieve the target concentration range of 0.5−100 ppt. Detection was by cold vapour atomic fluorescence spectroscopy (Tekran 2600; USEPA Method 1631 (USEPA 2001)). All THg analyses on solid materials were conducted by the Biotron Analytical Services Laboratory at the University of Western Ontario, which is an accredited, ISO 17025 compliant facility.

2.4. Statistical analysis

Factors controlling depth of burn were analysed using a series of general linear models (GLMs) to examine the effects of bulk density and water content, and to determine whether these relationships were dependent on moss species (*Sphagnum* versus feather moss), microtopography (hummock versus hollow), or peatland type (bog versus fen). A 'base model' GLM was constructed using bulk density, moisture content, and the bulk density × moisture content interaction as fixed effects. The base model was compared to three, more complex models created through iterative additions of landscape variables (e.g. peatland type, vegetation type, and microtopography).

The most parsimonious model was selected by comparing the corrected Akaike Information Criterion (AICc) across all base and candidate models. AICc was used to account for over-fitting by the addition of extra parameters and the small sample size (Hurvich and Tsai 1989). Once the most parsimonious model was selected, we explored relationships between each significant predictor and depth of burn using linear regressions.

We identified one observation as an outlier. This point had an unusually high average bulk density. The bulk density of the middle peat layer of this sample was much greater than the layer below, which is not typical for boreal peat deposits, and likely reflected a historical fire layer or layer of buried wood. The influence of this observation over analysis was evaluated statistically

and was found to have an undue influence over relationships, as judged by a Cook's distance greater than 1. This single outlying observation was removed from all models, though we note that the inclusion of this observation in our models did not alter the qualitative conclusions of any of our findings.

Similar to the depth of burn model described above, controls on total gaseous C, cumulative CO_2, CO, and CH_4 emissions, total Hg (total gaseous Hg + PHg), gaseous Hg, and PHg emissions were analysed using a GLM and AICc framework. In these analyses, a model consisting of only depth of burn was used as a base model. We used Pearson correlation tests to investigate the relationships between CO_2, CO, CH_4, total gaseous Hg, and PHg emissions. One tailed t-tests were used to determine if average emission ratios ($CO:CO_2$ and $CH_4:CO_2$) for each experiment were greater than those previously reported in the literature. The effect of water content on emission ratios was analysed using GLMs. We also used a one tailed *t*-test to investigate whether cumulative total gaseous Hg collected during burn experiment was greater than cumulative PHg collected.
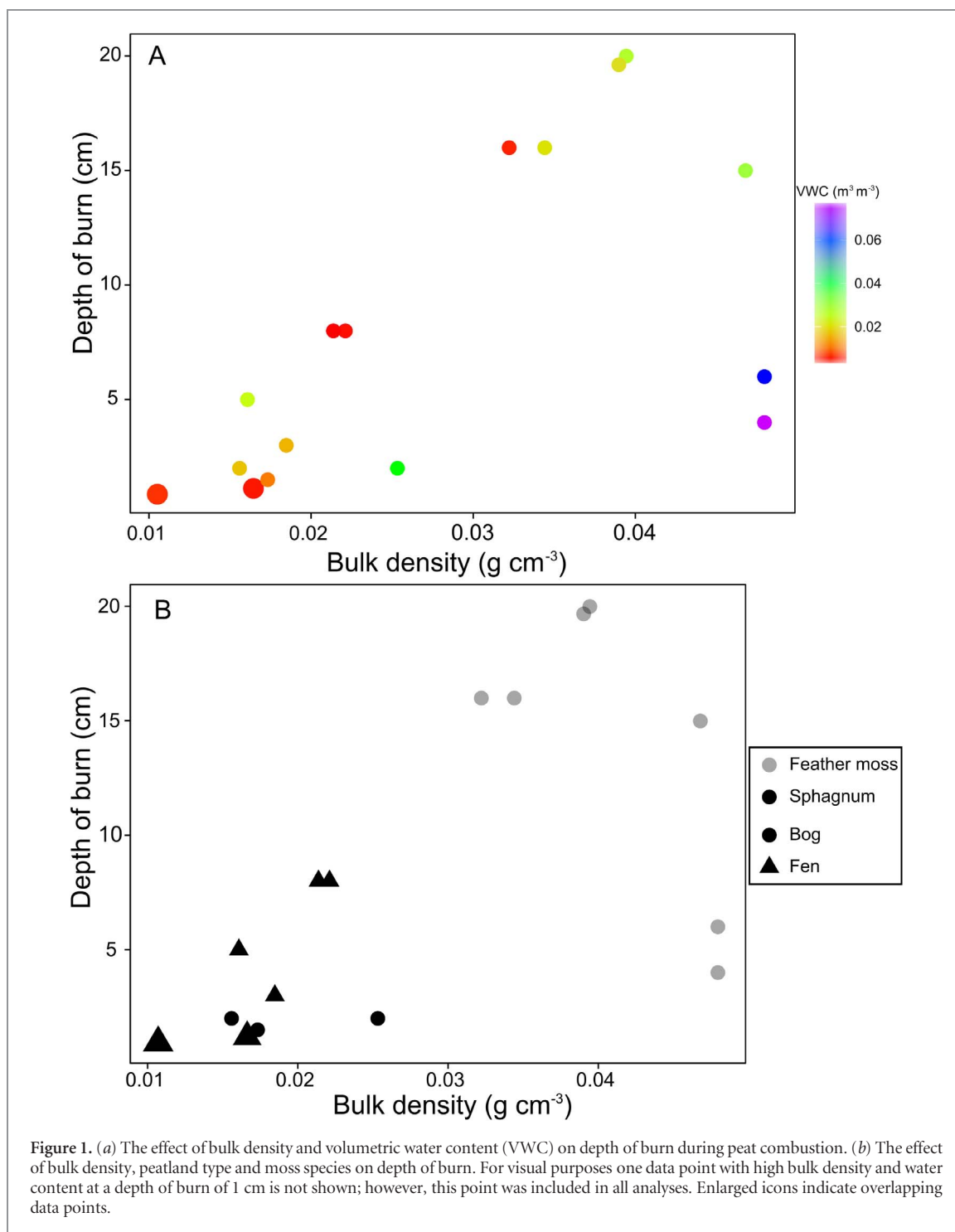
All data are reported as means ± one standard error.

3. Results

3.1. Controls on fuel consumption and C emissions

Across all of our samples, bulk density in the upper 0–30 cm of each peat column ranged from 0.01–0.1 g cm^{-3}, which is similar to field datasets of surface peat (Thompson and Waddington 2014). Our three experimental treatments varied in volumetric soil moisture content (field moisture: 0.083 ± 0.02, air dry: 0.020 ± 0.004, oven dry: 0.007 ± 0.001 m^3/m^3). The experimental treatments also varied in the mean duration of combustion (83 ± 20, 216 ± 66, and 227 ± 60 min for the field moisture, air dry, and oven dry treatments, respectively). Depth of burn averaged 3 ± 1 cm, 9 ± 3 cm, and 11 ± 3 cm while total fuel consumption averaged 312.33 ± 171.1, 503.3 ± 195.2, and 574.7 ± 141.1 g respectively for the field moisture, air dry and oven dry treatments. These depth of burn and fuel consumption values are consistent with previous laboratory experiments (Benscoter *et al* 2011). Our results tend to be on the smaller end of variation observed in field settings (Turetsky and Wieder 2001, Turetsky *et al* 2002). This is not surprising given that total fuel consumption was limited to the depth of our experimental samples (20 cm total depth of fuel available for burning), whereas in natural peatlands the depth of peat above the water table can often exceed 20 cm.

The most parsimonious model predicting variation in depth of burn included volumetric moisture content, bulk density, and the interaction between these two variables (AICc = 106.9, $F_{3,14} = 17.2$, $R^2 = 0.79$, $p < 0.0001$). Models containing additional variables (vegetation type or microtopography effects), or interactions

Figure 1. (*a*) The effect of bulk density and volumetric water content (VWC) on depth of burn during peat combustion. (*b*) The effect of bulk density, peatland type and moss species on depth of burn. For visual purposes one data point with high bulk density and water content at a depth of burn of 1 cm is not shown; however, this point was included in all analyses. Enlarged icons indicate overlapping data points.
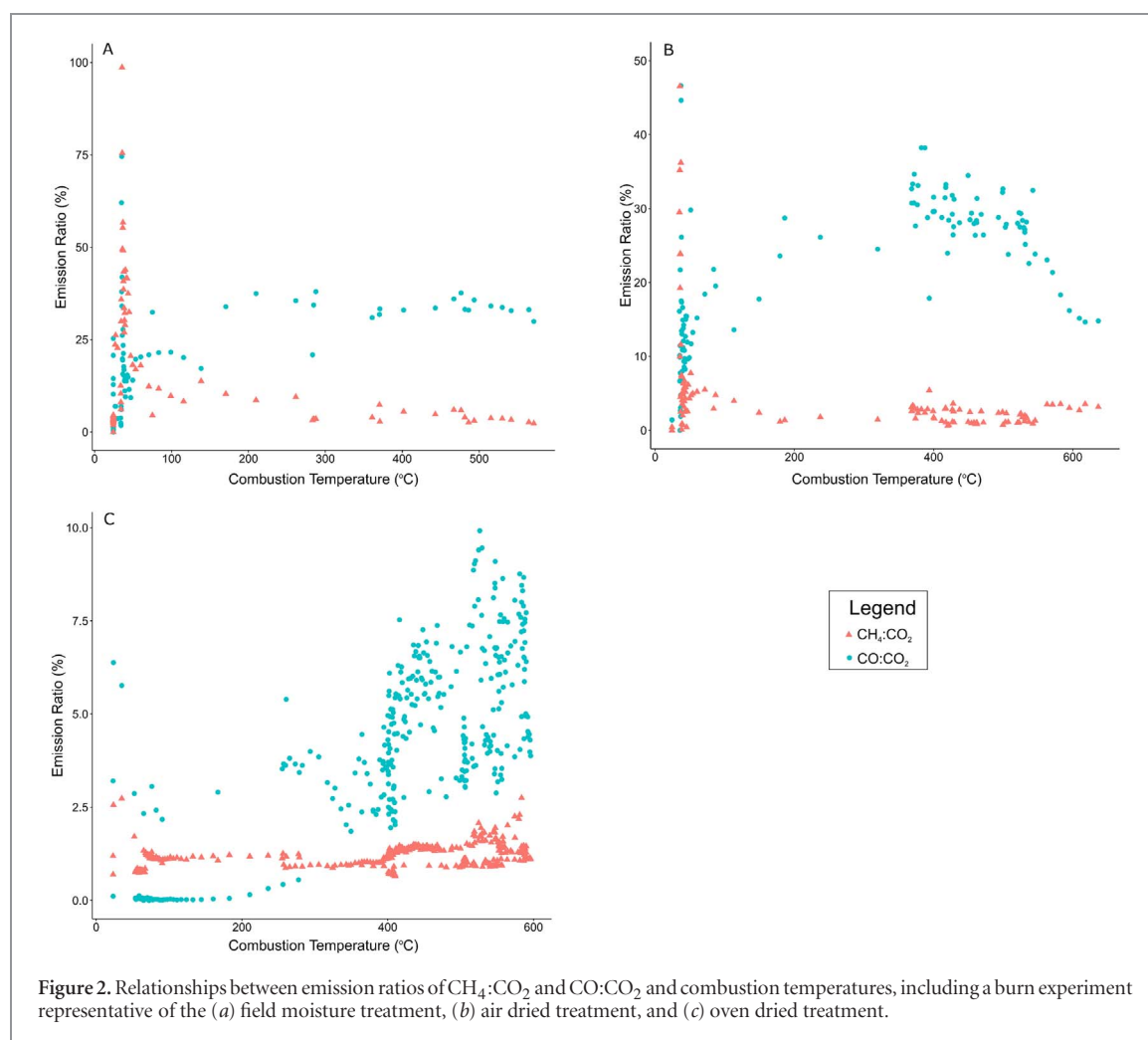
among these variables and either moisture content or bulk density, did not improve model fit. Our results showed that denser peat tended to support greater depths of burning. The exception to this trend was samples with high moisture content, which did not burn deeply despite having high bulk density (figure 1).

In general, C gas emissions peaked within the first 10 min following ignition and diminished until combustion ceased (supplemental figure 1 available at stacks.iop.org/ERL/13/035005/mmedia). Across all experiments and moisture treatments, combustion occurred at relatively low temperatures (< 600 °C),

which suggests that smouldering was a dominant combustion process. Emission ratios of $CO:CO_2$ tended to peak at lower temperatures in the burn experiments conducted under field moisture conditions, at moderate temperatures in the air dried fuel treatments, and at higher temperatures in the oven dried fuel treatments (figure 2). Ratios of $CH_4:CO_2$ often peaked at very low combustion temperatures but appeared to be insensitive to either combustion temperature or peat fuel properties such as moisture content.

As expected, total gaseous C release (sum of CO_2, CO, and CH_4) during combustion increased with depth

Figure 2. Relationships between emission ratios of $CH_4:CO_2$ and $CO:CO_2$ and combustion temperatures, including a burn experiment representative of the (*a*) field moisture treatment, (*b*) air dried treatment, and (*c*) oven dried treatment.

of burn ($F_{1,17} = 17.3$, $R^2 = 0.51$, $p = 0.0007$). Across all of our burn experiments, emission rates averaged 330 ± 80 mg CO_2 m^{-2} min^{-1}, $120 \pm 2\,0$ mg CO m^{-2} min^{-1}, and 7.1 ± 2.0 g CH_4 m^{-2} min^{-1} while cumulative emissions averaged 68.63 ± 15.3 g CO_2, 17.59 ± 4.5 g CO, and 1.55 ± 0.36 g CH_4 m^{-2}. The air and oven dry treatments had greater levels of fuel consumption as well as cumulative CO, CO_2, and CH_4 emissions that tended to be higher than the field moisture treatment (table 2). However, total gaseous C, cumulative CO_2, and cumulative CO emissions were best predicted by the interaction between volumetric moisture content and bulk density (figure 3). The only predictor of cumulative CH_4 emissions was volumetric moisture content, but this relationship was not significant and had little predictive power.

Ratios of cumulative $CO:CO_2$ and $CH_4:CO_2$ emissions averaged $16\%\pm3\%$ and $4\%\pm1\%$ across all burn experiments, respectively (figure 3). Even when corrected for total fuel consumption, the air and oven dry treatments had higher $CO:CO_2$ and $CH_4:CO_2$ ratios than in the field moisture treatment (table 2). This shows that the smouldering combustion of peat can lead to high trace gas emissions across a range of soil moisture contents.

Table 1. Results of correlation analyses between of C gases and total Hg emissions (gaseous + particulate Hg). Values are Pearson correlation coefficients, with p values in parentheses.

	CH_4	CO	CO_2	THg
CH_4	–			
CO	0.655 (0.002)	–		
CO_2	0.628 (0.004)	0.695 (0.001)	–	
THg	0.706 (0.02)	0.895 (0.0002)	0.850 (0.0009)	–

3.2. Controls on gaseous and particulate Hg emissions during peat burning

Across the burn experiments, more Hg was released as total gaseous Hg (97% of total Hg loss) than PHg (3% of Hg loss) ($t_{10} = 4.4$, $p = 0.0006$). Moisture treatment had no effect on gaseous Hg or PHg release, though the oven dry treatment with low moisture content tended to have the highest emissions of gaseous + particulate Hg (table 2). While total gaseous Hg emission increased with greater bulk density ($F_{1,17} = 19.5$, $R^2 = 0.68$, $p = 0.002$), there were no significant predictors of PHg release. Total gaseous + particulate Hg release was most strongly correlated with cumulative CO emissions (table 1; $r = 0.895$).

In addition to quantifying the chemistry of emissions during burning, changes in soil stocks before
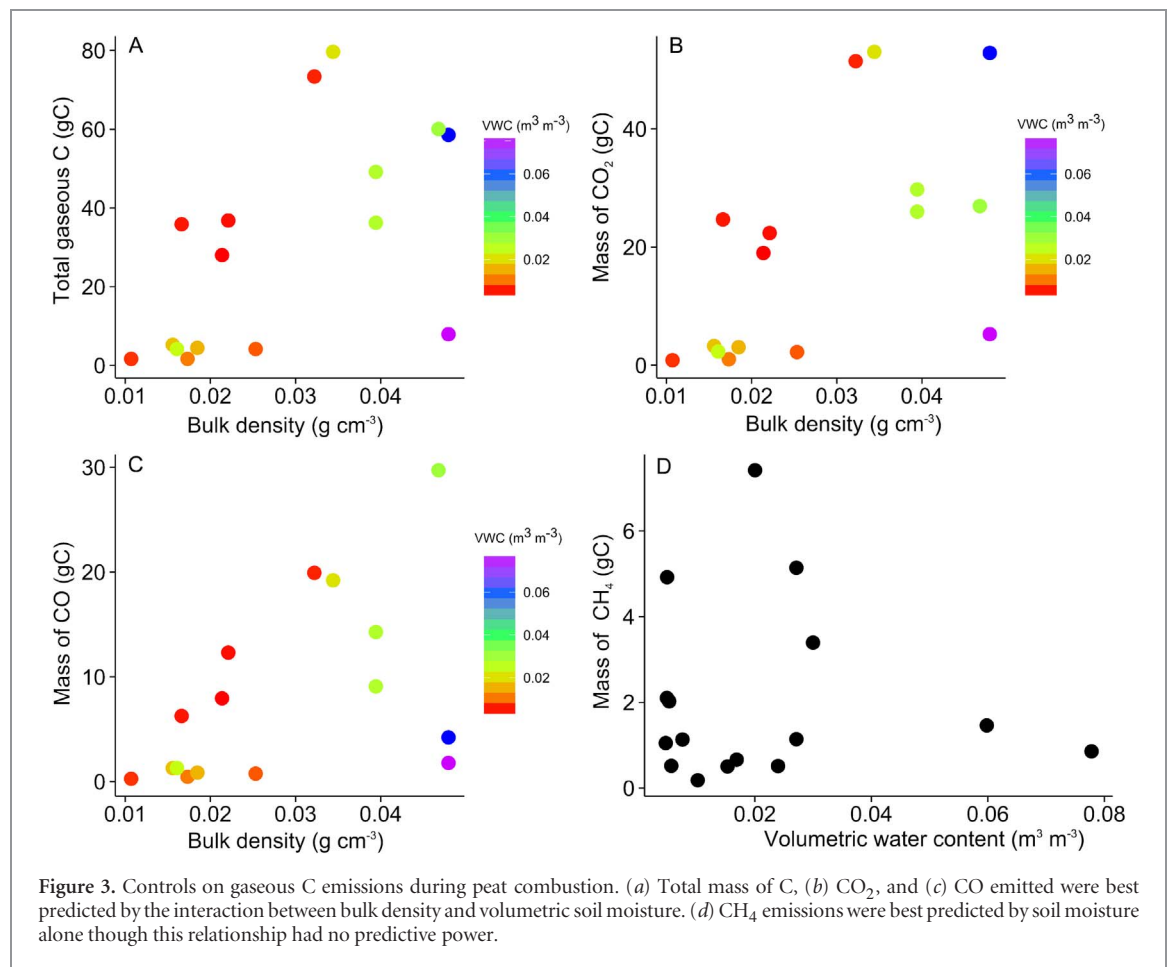
Figure 3. Controls on gaseous C emissions during peat combustion. (*a*) Total mass of C, (*b*) CO_2, and (*c*) CO emitted were best predicted by the interaction between bulk density and volumetric soil moisture. (*d*) CH_4 emissions were best predicted by soil moisture alone though this relationship had no predictive power.

Table 2. Cumulative emissions of CO, CH_4, CO_2, and gaseous + particulate Hg averaged by experimental treatment.

		Field moisture treatment	Air dry treatment	Oven dry treatment
CO	g	4.03 ± 1.30	23.89 ± 6.56	25.27 ± 10.40
	g/g fuel combusted	0.01 ± 0.01	0.05 ± 0.01	0.04 ± 0.01
CH_4	g	0.63 ± 0.14	5.95 ± 2.83	5.10 ± 2.32
	g/g fuel combusted	0.01 ± 0.01	0.01 ± 0.00	0.01 ± 0.00
CO_2	g	45.21 ± 30.07	128.18 ± 62.51	173.31 ± 120.74
	g/g fuel	0.15 ± 0.07	0.26 ± 0.29	0.30 ± 0.32
Hg	μg	2.72 ± 0.34	6.68 ± 0.64	8.74 ± 3.72
	μg/g fuel combusted	0.03 ± 0.00	0.01 ± 0.00	0.03 ± 0.01

and after burning can used to estimate loss from soils via emissions (Harden *et al* 2004). Like the emissions chemistry, the change in soil Hg and C stocks pre- versus post-burning were correlated with one another (figure 4, $r = 0.30$). Carbon and Hg losses estimated by change in soil stocks exceeded the measured gaseous or particulate emissions (C: $r = 0.52$; Hg: $r = 0.85$).
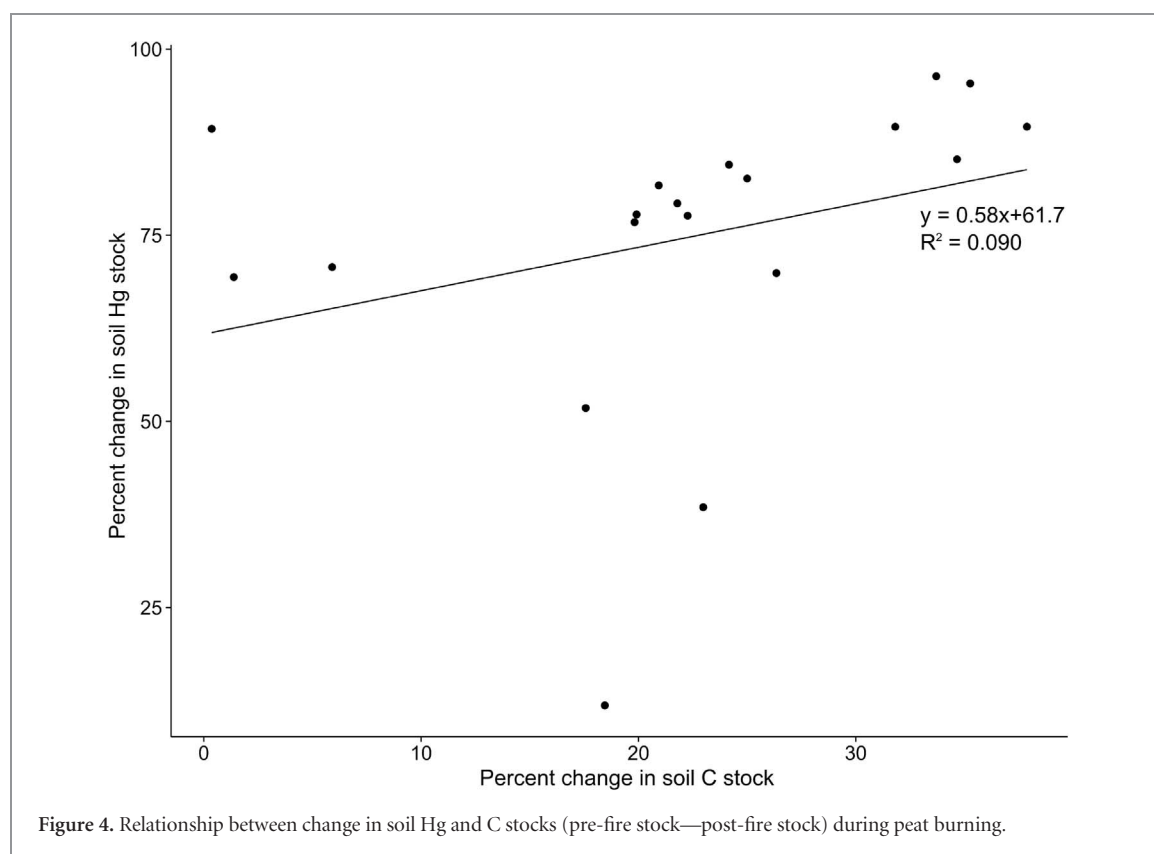
4. Discussion

4.1. Loss and speciation of C during peat burning
In general, our results are consistent with previous studies in showing that low bulk density limits combustion of peat (Van Wagner 1972, Frandsen 1997, 1987, 1991, Benscoter *et al* 2011, Prat-Guitart *et al* 2016). The propagation of combustion into deeper peat layers requires sufficient heat transfer to ignite lower soil layers, and combustion of low density fuels like *Sphagnum* often cannot generate enough energy to ignite wetter, higher density peat below (Frandsen 1987, Miyanishi and Johnson 2002, Thompson and Waddington 2014). In our experiments, increases in bulk density promoted combustion until the peat was too wet to ignite, usually corresponding to a volumetric moisture content of approximately 0.04 m^3 m^{-3}. Relationships between bulk density and soil moisture content can be complex in organic soils, as changes in bulk density affect the water storage capacity of peat (Benscoter *et al* 2011). However, organic soils with sufficient density are able to produce enough energy to make up for heat lost to water, enabling combustion to propagate both horizontally and vertically through the peat (Prat-Guitart *et al* 2016, Huang and Rein 2015).

Our emission findings suggest that the same general controls on depth of burn can be used to predict total

Figure 4. Relationship between change in soil Hg and C stocks (pre-fire stock—post-fire stock) during peat burning.

gaseous C, CO_2 and CO emissions. The peat properties, including bulk density and soil moisture content, that lead to high depth of burn cause greater emissions of total C release as both CO_2 and CO, but do not necessarily relate to CH_4 emissions. Overall our results show that factors contributing to drying of peat—either during the growing season with water table drawdown or seasonal thaw or as a result of human disturbance or drought—will stimulate total peat consumption as well as CO_2 and CO emissions.

Emission ratios are used frequently to estimate total CO and CH_4 emissions from wildfires (cf. Kasischke and Bruhwiler 2002, Andreae and Merlet 2001, French *et al* 2003) and to estimate the climatic impacts of fire emissions (Randerson *et al* 2006). These values are often assumed, and tend to be based on a limited number of measurements often stratified by biome. The emission ratios measured in this study are greater than those typically used to predict the ratio of emissions stemming from northern wildfires, particularly for CH_4:CO_2, but are in the range of studies that have measured or utilized emission ratios from Indonesian fires (table 3). This suggests that previous studies utilizing boreal emission ratios may be underestimating CH_4 trace gas emissions, at least over northern regions where the combustion of peat in forests or peatlands dominates total fuel consumption. While we expected CO and CH_4 emissions to be highest in our field moisture trial due to incomplete smouldering combustion, our drying treatments tended to have higher emissions of all C species (g emitted per g fuel consumption) as well as higher mean

CO:CO_2 and CH_4:CO_2 ratios than the field moisture treatment (see table 2).

Burn experiments like those utilized in this study are useful for obtaining accurate emissions during fuel combustion. However, they provide point information and often are difficult to generalize to field settings. Given that northern peatlands are likely to become more vulnerable to burning with ongoing climate change or human land use, the ratios quantified in our study are likely to become more reasonable for characterizing future fire emissions in peatland-rich areas. Our results also provide some insight on how trace gas emissions are likely to vary as a function of soil moisture. We show that even when corrected for variation in total fuel combustion, CO and CO_2 emissions during peat burning tend to increase with peat moisture content. Our results related to CH_4 emissions are particularly surprising, showing that more than 5% of total C emissions can be emitted as CH_4 and that this fraction of C released during peat burning is insensitive to soil moisture.

4.2. Loss and speciation of Hg during peat burning
Our results differ from some previous studies in that we found that components of Hg emissions were driven more by bulk density than soil moisture characteristics. During experimental burning of surface forest fuels, Obrist *et al* 2008 found that burning of wetter fuels (albeit surface fuels) led to increasing PHg emissions. In our burn trials of vertical peat samples, gaseous and particulate Hg emissions were both insensitive to soil moisture content or fuel moisture treatment. We also

Table 3. Synthesis of emission ratios of $CO:CO_2$ and $CH_4:CO_2$. Mean emissions ratios from our peat burn experiments were greater than the average of previously published values, particularly for $CH_4:CO_2$ ($t_{18} = 2.6$, $P = 0.009$), but tend to agree with emission ratios from burning of Indonesian fuels.

	$CO:CO_2$ (%)	$CH_4:CO_2$ (%)	Data collection method
This study	16.3	3.8	Laboratory experiments
Crutzen *et al* 1979	14.0	1.6	Synthesis
Nance *et al* 1993	7.8	0.4	Airborne sampling
Cahoon *et al* 1994	12.3	1.3	Satellite imagery analysis
Cofer *et al* 1998	21.4	1.3	Airborne sampling
van der Werf *et al* 2010	12.3	1.2	Satellite imagery analysis
Muraleedharan *et al* 2000[a]	15.1	5.4	Laboratory experiments
Chand 2005[a]	40.6	N/A	Laboratory experiments
Hamada *et al* 2013[a]	38.2	2.6	Field/ground sampling
Parker *et al* 2016[a]	–	0.6–1.4	
Stockwell *et al* 2016[a]	18.6	0.6	Field/ground sampling

[a] Studies measuring emissions from Indonesian wildfires or emissions from Indonesian peat.

found that PHg comprised a small fraction of total Hg release. This is consistent with measurements from airborne smoke plume studies that found a greater fraction of Hg emitted as gaseous Hg (Friedli *et al* 2003, Finley *et al* 2009).

Several lines of evidence from our experiments suggest that Hg release during peat burning is dominated more by the thermodynamics of Hg reduction than by the combustion of Hg bound to organic molecules in the peat. Total Hg emissions were correlated strongly with CO emissions (table 1), which represent a relatively small fraction of total C emissions. There were weaker correlations between C and Hg emissions or change in soil Hg and C pools, and these relationships show that proportionally more Hg is lost relative to C (figure 4). This makes sense given that Hg is a volatile element, but our results show that modest heating of organic soils can induce large emissions even when C is incompletely combusted.

Research understanding the ultimate fate of fire-released Hg is important, since the speciation of these emissions is critical to understanding whether Hg losses are likely to have global or regional impacts. While our results show that most of the Hg released from peat smouldering is gaseous, we are not able to delineate measurements between Hg(0) and Hg(II). Hg(0) can oxidize to Hg(II) during combustion; however, given the low particulate-bound emissions and the importance of thermodynamics over combustive Hg releases, we believe that Hg(0) emissions predominate during peat burning. This general conclusion is supported by Wang *et al* (2010), who despite measuring significant increases in gaseous Hg(II) during forest fire emissions in Quebec Canada, found that these emissions represented an extremely small component of total gaseous Hg emissions.

Given that we observed little particulate Hg emissions and that significant amounts of Hg(II) emissions are unlikely, we conclude that the Hg release impacts from peat burning are more likely to be global rather than local or regional. Hg(0) emissions will enter into the global and long-range transport pools for months. Therefore, these emissions will have much broader implications than gaseous Hg(II) emissions

and particulate bound emissions, which will have more local/regional scale re-deposition into the landscape (on the order of a few hundred km radius) (Fitzgerald and Mason 1998), though the speciation of the total gaseous mercury is unknown. Overall, we argue that peat fires are likely to serve as important disturbances that could remobilize a significant store of largely sequestered Hg in peatlands back to the atmosphere, reactivating it back into the more biologically-relevant surface biogeochemical cycle. This fire-mediated remobilization is likely to become more significant as boreal wildfire regimes intensify, affecting northern peatlands that were perhaps previously too wet to burn.

For both C and Hg, our comparison of emission chemistry to pre- versus post-burn soil and ash samples showed much smaller losses quantified directly through emissions than indirectly via changes in elemental soil stocks. Losses estimated through changes in soil and char pools averaged 60.3 g C and 26.6 μg Hg per burn experiment, while our directly measured emissions to the atmosphere averaged 28.3 g C and 6.7 μg Hg. While our measurement of Hg emissions was based on a sub-sample of the whole burn, we calculated the mass of C gas emissions as the cumulative record of gas concentrations measured every second. This may have led to an underestimate of the mass of C emissions, especially during periods of high gas production. However, it seems more likely that our indirect assessment of soil pool changes led to overestimation of C and Hg losses. It is possible that the 5 cm depth increments used to calculate soil pools were too large to accurately portray changes in bulk density across the peat profile, resulting in an over-estimation of soil C and Hg losses. The bulk density of boreal soils can exhibit tremendous variation at a local scale, which means that subsampling could have affected our emissions calculations based on change in soil pools. Given that this indirect approach is logistically easier and much more common than direct measurement of fire emissions, future studies need to pay close attention to proper and robust measurement of variation in soil bulk density, along with other fuel properties that could influence emissions estimates.

These methodological issues, combined with constraints on depth of burn posed by our experimental

peat samples (20 cm depth), led to observed emissions of both C and Hg in this study that are on the low end of published values. Our focus, however, was on exploring the stoichiometry of emissions and understanding the sensitivity of emission ratios to combustion temperature and fuel properties such as moisture content. We found strong correlations between Hg and CO release during peat burning, and this correlation was robust across a range of fuel moisture contents. Given that CO often is used in atmospheric inversion studies as a tracer for biomass burning, this observation may be helpful in furthering our understanding of the contribution of smouldering ground fires to Hg emissions.

5. Conclusion

Bulk density and soil moisture content have long been used as predictors of depth of burning in boreal ecosystems, and our results demonstrate that these also are important for predicting total gaseous C, CO_2, and CO emissions from burning peat. We report greater CH_4:CO_2 ratios than what has been used in previous modeling studies, suggesting that cumulative CH_4 from burning boreal peat could be greater than expected. Our results suggest that Hg release during peat burning is dominated by gaseous Hg emissions and that Hg emissions are governed more by the thermodynamics of Hg reduction than by the combustion of Hg bound to organic molecules in the peat. Overall, more research is needed to understand controls on Hg release during smouldering combustion as well as the ultimate fate of fire-released Hg (Fitzgerald and Mason 1998). Some fire-emitted Hg is likely vulnerable to long-range transport, though some may fall out locally, where it could be rebound by soil organic matter or deposited to methylating environments such as wetlands (including peatlands) and lakes where it could be transformed to methylmercury (Zillioux *et al* 1993, Grigal 2003). Thus, peat fires are likely to serve as important disturbances that could diminish the strength of biogeochemical sinks in peatlands, but also could serve as a mechanism for distributing Hg across the landscape, potentially moving Hg from ecosystems with high preservational environments like peatlands to systems more vulnerable to biomagnification.

Acknowledgments

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