The stoichiometry of carbon, hydrogen and oxygen in peat

Tim R. Moore¹, David Large², Julie Talbot³, Meng Wang⁴ and John L. Riley⁵

¹Department of Geography, McGill University, Montreal, QC, Canada H3A 0B9
²Department of Chemical and Environmental Engineering, University of Nottingham, Nottingham, UK NG7 2RD
³Département de Géographie, Université de Montréal, Montréal, QC, Canada H2V 2B8
⁴Center for Ecological Forecasting and Global Change, College of Forestry, Northwest A&F University, Yangling, Shaanxi, China 712100
⁵Nature Conservancy of Canada, Toronto, ON, Canada M4R 1A1

Corresponding author: Tim Moore (tim.moore@mcgill.ca)

Key Points:

- C, H and O form 90% of the mass of peat and we examine variations in the atomic O:C and H:C ratios for peatlands in Ontario
- The O:C and H:C ratios are a function of their input in litter and decomposition pathways and intensity in peat formation
- The ratios, especially O:C, can be used to predict the proportion of C that has been lost through decomposition in peat formation
Abstract

Carbon (C), hydrogen (H) and oxygen (O) form ~90% by mass of peat, a product of the input of plant tissues and litter and the output of decomposition under aerobic and anaerobic conditions. We examined patterns of these elements, as the O:C and H:C atomic ratios, in over 1300 peat samples collected from over 400 profiles in Ontario, Canada, representing bogs, fens and swamps. The overall O:C ratio decreased from the surface (0.6 to 0.7) to ~0.5 at a depth of 50 cm and showed little further change to a depth of 5 m. In contrast, the H:C ratio decreased only slightly (1.30 to 1.25) over the top 1 m and showed no further significant decline with depth. The carbon oxidative state (C_{ox}) and oxidation ratio (OR) showed strong decreases and increases, respectively, with depth with most changes occurring in the top 1 m. The O:C ratio, and C_{ox} and OR values were significantly correlated with the von Post Humification Index, with most changes occurring in Index values 1 through 4, the latter representing a slight degree of decomposition. Collation of the Ontario peats with other data sets revealed the very large range in O:C and H:C values, with a general decrease from temperate to tropical and sub-tropical peatlands. Estimation of the O:C and H:C ratios of input (litter) and output (mineralization to CO_{2}, methanogenesis to CH_{4} and CO_{2} and loss as dissolved organic carbon) allowed an estimation of the degree of decomposition or C loss.

Plain Language Summary

Carbon, hydrogen and oxygen form about 90% of the mass of peat, derived from the decomposition of dead plant and animal material. Using a large data base from bog, fen and swamps peatlands in Ontario, and in Europe, North America and Indonesia, we show that the ratios, or stoichiometry, between these three elements is a function of their input in litter and decomposition pathways and intensity. We suggest that the ratios, particularly the atomic oxygen:carbon ratio, can be used to predict the proportion of carbon that has been lost through decomposition and peat formation.
1 Introduction

Peat soils contain very large amounts of organic carbon (C), generally between 30 and 200 kg C m$^{-2}$, and it is estimated that northern peatland soils contain over 400 Gt globally (Loisel et al., 2014). This accumulation arises from the rates of plant production being faster than the rates of litter and soil organic matter decomposition, associated with a high water table and the development of anoxic conditions, as well as peat plants, such as *Sphagnum* moss, having a slow intrinsic rate of decomposition (Rydin and Jeglum, 2013). Organic C generally forms 45-50% of the mass of peat and another ~35% is comprised of oxygen (O) and ~5% hydrogen (H). Thus, 85-90% of the peat mass comprises C, H and O, with smaller amounts of nutrients and metals.

During decomposition, organic molecules are broken down by microbes, resulting in the loss of decomposition products such as carbon dioxide (CO$_2$), methane (CH$_4$) and dissolved organic carbon (DOC). Patterns of organic matter decomposition in peat have been approached in many ways, ranging from the simple von Post Humification Index, ash content and C:N ratio, to nuclear magnetic residence, Fourier transform infrared spectroscopy and isotopes of C and N (e.g. Biester et al., 2014; Tfaily et al., 2014). Given the differences in C, H and O stoichiometry between the input of organic matter to peatlands in plant tissues and litter and that of the decomposition products, one could expect changes in the C, H and O stoichiometry of peat as it undergoes decomposition. Peat is the precursor to coal deposits which are often characterized by the atomic ratios of O to C, and H to C, commonly illustrated as a van Krevelen diagram (van Krevelen, 1961). These diagrams show decreases in both O:C and H:C ratios as material passes from vegetation through soil organic matter and peat into coal. These ratios have also been used to characterize the chemistry of DOC (e.g. D’Andrelli et al., 2010; Kim et al., 2003).

Worrall and colleagues (e.g. Clay and Worrall, 2015; Worrall et al., 2016) have used the concentration of C, H, O and N to assess the oxidation state of a variety of soils, including peats, as part of a global stoichiometric approach to C cycling and sinks (e.g. Masiello et al., 2008; Worrall et al., 2013). Two metrics have been applied to soil organic matter, the carbon oxidation state ($C_{ox}$) which is based on the relative atomic concentrations of C, H, O and N, and the oxidative ratio (OR), which is a derivative of $C_{ox}$ and C and N concentrations (Masiello et al., 2008). Clay and Worrall (2015) concluded that, for a range of samples collected from the upper 1 m of peat soils in the UK, the average $C_{ox}$ and OR values were -0.33 and 1.10, respectively, compared to -0.05 and 1.03 for vegetation. They then applied these metrics to assess the
oxidation state of a blanket peatland within the Moor House National Nature Reserve in the UK (Worrall et al., 2016).

Data on C, H and O concentrations in peat soils are sparse, but a detailed survey of peatlands in Ontario, Canada, by the Ontario Geological Survey (Riley, 1994a, b; Riley and Michaud, 1989) resulted in the collection of cores from over 400 sites, representing bogs, fens and swamps, and the analysis of over 1300 samples for a variety of elements and properties. In this study, we start with these data to address three objectives:

1. We examine how O:C and H:C ratios and C_{ox} and OR vary with peatland type, depth and von Post Humification Index.

2. Combining these data with C, H and O analyses of peat from temperate (UK, Latvia, northeastern USA) and sub-tropical and tropical (southeastern USA and Indonesia) regions, we compare how O:C and H:C ratios change, in relation to the input from vegetation/litter and the output from decomposition processes.

3. Assuming decomposition processes introduce changes in the O:C and H:C ratios of peat, we examine whether these stoichiometries can be used to estimate degree of decomposition of the peat, based on what would be the input from vegetation and litter and the stoichiometry of decomposition.

2 Materials and Methods

The sampling sites in Ontario were part of a large scale survey of peat resources extending from 74°W to 94°W and 43°N to 51°N in northwestern, northeastern and southeastern regions (Riley, 1994a, b; Riley and Michaud, 1989). The sites were selected to represent a range of typical peat accumulation conditions, had a uniform vegetation cover, were > 100 ha in size and had at least 40 cm of peat accumulation. They were classified into bogs, fens and swamps, depending on their pH, surface peat botanical composition and tree cover (Riley and Michaud, 1994). Bogs had a pH lower than 5.2 and surface peat was dominated by Sphagnum remains, whereas fens and swamps have a higher pH and a graminoid, woody or brown-moss dominated surface peat. Swamps have a tree or tall shrub cover higher than 25%. Peat cores were sampled using a mini-Macaulay or Hiller sampler and divided into four intervals or more for deeper profiles, based on their botanical composition and apparent degree of humification. The highest and lowest depth of each section was recorded, as well as the degree of humification based on the von Post Humification Index (Table S1), ash content, botanical content of the peat (as % of...
moss, sedge and other graminoids, wood, and ‘other material’), and the chemical composition of the samples (Riley and Michaud, 1994).

For details on the C, H, O, ash, nitrogen (N) and sulphur (S) analyses, see Riley (1989). Briefly, organic C concentration was determined by treatment with HCl and then ignition in a Leco Induction Furnace at 500ºC and trapping in KOH. The H concentration was determined by ignition in a Leco Induction Furnace under a stream of oxygen and absorption of water by a magnesium perchlorate absorption tube. The O concentration was determined by difference:

\[ \%O = 100 - \% (\text{Ash} + \text{Total C} + \text{N} + \text{H} + \text{S}) \]  

(eq 1)

The ash content was determined by ignition at 750ºC for 30 minutes, N concentration by a Kjeldahl method and S by ignition with tin and copper, absorption in HCl and titration with potassium iodate. Atomic ratios of H:C and O:C were calculated from the individual sample mass values.

To generate the average von Post Humification Index and H:C and O:C ratios with depth in profiles representing bog, fen and swamp peatlands, we used the average depth of each sample, and binned them by 10 cm depth intervals for the top 250 cm of the profile, and by 20 cm depth intervals for the rest of the profile.

We calculated the \( C_{\text{ox}} \) and OR values of each peat sample, as defined in Worrall et al. (2016) from atomic concentrations:

\[ C_{\text{ox}} = \frac{2[O] - [H] + 3[N]}{[C]} \]  

(eq 2 (from Masiello et al., 2008))

\[ \text{OR} = 1 - \frac{C_{\text{ox}} + 2[N]}{4[C]} \]  

(eq 3 (from eq 6 in Worrall et al., 2015))

We accessed other peat data from the UK (Clay and Worrall, 2015, Figure 2), Latvia (Klavins et al., 2008, Table 1), and the northeastern USA (Maine and New Hampshire), southeastern USA (Florida and Louisiana) and Indonesia (Borneo and Sumatra) from the United States Geological Survey peat database (https://energy.usgs.gov/Coal/Peat.aspx#378847-data).

We applied decomposition stoichiometries involving respiration to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) and methanogenesis to \( \text{CH}_4 \) and \( \text{CO}_2 \) (both resulting in \( \text{CH}_2\text{O} \)), as well as loss of DOC, such as fulvic and humic acids. We did not apply stoichiometric changes associated with fire.
3 Results

3.1 CHO composition, Von Post Humification Index, H:C and O:C ratios and $C_{\text{ox}}$ and OR in Ontario peat

The average composition of the large number of Ontario peat samples by mass (%±sd) was C 49.4 (5.0); H 5.2 (0.6); O 34.9 (5.6); thus, these three elements represent an average of 89.5%. Other elements included N (1.9%), calcium (1.7%), iron (0.4%), aluminum (0.3%), S (0.2%), magnesium (0.2%), potassium (0.1%) and phosphorus (0.1%).

There was a pronounced decrease in the von Post Humification Index in the upper layers of the peat, from average values of 1 to 2 at 5 cm depth, to 3 to 5 at 100 cm, with the decline fastest in the swamp peatlands (Fig. 1a). Below 100 cm, average values ranged from 4 to 5, with little variation with depth or difference among bog, fen and swamp peatlands. There was a significant logarithmic relationship with depth in all three peatland types (Table S2).

There was also a pronounced decrease in the H:C ratios from typical peatland vegetation and litter to the uppermost layers of the peat profiles (Fig. 1b), but there was no significant relationship between H:C ratio and depth in the peat types, nor a significant difference between bog, fen and swamp (Table S2). There was also a decrease in the O:C ratio from typical peatland vegetation and litter to the uppermost layers of the peat profiles and then a further decline to a depth of 50 cm (Fig. 1c). Below 50 cm, the change was small, and there was a significant logarithmic relationship between O:C ratio and depth in the bog, fen and swamp (Table S2).

There was a decrease in the $C_{\text{ox}}$ value from the surface layers of the peat (average 0 to 0.2) to a value of -0.2 to -0.3 at a depth of 50 cm and little further decline with depth (Fig. 1d), with a significant logarithmic relationship with depth in the bog and fen profiles, but not the swamp (Table S2). The OR value showed an increase from 1.05 to 1.10 at the peat surface to averages of 1.10 to 1.13 at a depth of about 50 cm, with no further increase deeper in the profile (Fig. 1e). There was a significant logarithmic relationship with depth in the bog and fen profiles, but not the swamp (Table S2).

Comparison of the ratios with the von Post Humification Index showed no significant change in H:C ratio with increasing degree of decomposition, whereas there was a significant decrease in O:C ratio, though most of this change occurred between Index values 1 and 4 (Fig. 2a). Combination of the two ratios resulted in an increase in
the H:O ratio from 2-2.5 to 3.0 as the Index rises from 1-2 to > 4 (Fig. 2b). Both C_{ox} and
OR showed a significant relationship with the Index, C_{ox} showing a decline from 0.10 to -
0.29 and OR an increase from 1.03 to 1.12, with the change being most pronounced from
Index values 1 to 4 (Fig. 2c). A breakpoint analysis suggested that an Index of 3 was
critical for all properties, except for H:C (data not shown).

There was no significant relationship between the H:C and O:C ratios and the
origin of the peat, when peat was binned into the von Post Humification Index (Fig. 3). Samples that were considered uniform in terms of botanical composition (>80% of their
content dominated by one peat type) were grouped into moss, sedge and wood types. It
should be noted that the least decomposed samples (von Post Humidification Index of 1)
did not have enough uniform samples of all three types to allow a comparison.
Figure 1. Patterns of von Post Humification Index (a), H:C and O:C ratios (b and c), and C$_{ox}$ and OR (d and e) with depth in Ontario peat profiles, grouped by peatland type, along with values commonly found in organic compounds, plants and litter. Values represent the mean and standard error of samples binned by depth.
**Figure 2.** Relationship between von Post Humification Index and H:C, O:C and H:O ratios, and $C_{ox}$ and OR, based on the mean and standard error of each Index unit. Values at Index 0 represent sedge, shrub, *Sphagnum* and wood inputs.
Figure 3. Relationship between H:C and O:C ratios and von Post Humification Index for samples with 80% or more proportion of peat derived from moss, sedge and wood. Values represent mean and standard deviation.
3.2 Relationship between H:C and O:C ratio of Ontario and other peats

The relationship between the H:C and O:C ratio among the 1313 peat samples from Ontario is depicted in Fig 4a, showing the very wide range of ratios recorded, with a mean of 1.28 H:C and 0.62 O:C and standard deviation of 0.13 and 0.12, respectively (Fig. 4b). Overall, there was a weak ($R^2_{adj} = 0.040$), but statistically significant ($p = 0.001$) relationship between H:C and O:C ratios with a shallow slope (0.22) of H:C on O:C (Table S3).

Peat samples from other temperate regions showed similar patterns with H:C and O:C means of 1.36 and 0.66 (Latvia) and 1.34 and 0.49 (UK), but smaller values of 1.05 and 0.46 for the northeastern USA (Maine and New Hampshire). The two tropical/sub-tropical regions showed generally smaller mean H:C and O:C ratios (1.12 and 0.45 for Indonesia and 1.06 and 0.37 for southeastern USA, respectively). In all cases, however, there is a great variation among peat samples from each location. There was also a statistically significant ($p < 0.05$) relationship between H:C and O:C in all regions, except for northeastern USA ($p = 0.063$), with variable regression slopes (Table S3). The slopes were shallow (0.22 to 0.47) for the temperate Ontario, Latvia and northeastern USA peats, but steeper for the UK peat (1.21), and the samples from southeastern USA and Indonesia (0.74 and 1.62), suggesting a greater loss in H accompanying the O loss in decomposition in the latter.

3.3 Estimating the degree of decomposition of peat from the H:C and O:C stoichiometry of peat and decomposition processes

The H:C and O:C characteristics of the peat result from the effect of decomposition processes acting upon the plant tissues and litter from which the peat formed and released C, H and O. The H:C and O:C ratios of sedge, shrub, *Sphagnum* and wood, common contributors to peatlands, are illustrated in Fig. 5a, along with the range of ratios input for bog, fen and swamp peatlands, based on a variable contribution of the 4 plant categories. This suggests that most input to peatlands may fall within a H:C ratio of 1.5 to 1.6 and a O:C ratio of 0.6 to 0.8. Output represents losses as respiration and methanogenesis with ratios of H:C of 2 and O:C of 1, respectively, DOC (as fulvic and humic acids) of H:C ~1.25 and O:C of ~0.7, and combustion which can result in biochar with a H:C ratio of 0.7 and a O:C ratio of 0.3, close the range of values encountered in coal.

Based on the range of original O:C and H:C ratios for bog, fen and swamp peatlands, the trajectories of ratios associated with increasing decomposition and mode of decomposition can be plotted. As an example, the trajectories of the bog and swamp peat associated entirely with respiration and methanogenesis are plotted in Fig. 5b, as well as the trajectories if decomposition
was 75% respiration and methanogenesis and 25% DOC (combining fulvic and humic acids). The latter, with decomposition output lower in H:C and O:C ratio than gas losses, results in peat with larger H:C and O:C ratios. These trajectories encompass much of the variation in H:C and O:C ratios found in peats and suggest that about 50-75% of the original C has been lost. Fire, important in some peatlands, would result in smaller H:C and O:C ratios; Conodera et al. (2009) cite average O:C ratios of 0.5 and 0.3 for slightly charred biomass and charcoal, respectively, and the equivalent values for H:C are 1.0 and 0.6. However, differences in original composition of litter input and the type and degree of decomposition may explain the very large variability in H:C and O:C ratios observed in peat.

4. Discussion

There are major changes in the H:C and O:C ratios as plant tissues senesce into litter and then as that litter decomposes in the surface layers of the peat. Plant compounds vary considerably in their H:C and O:C ratios, such as 2 and 1 for glucose, 1.7 and 0.8 for cellulose, 1.2 and 0.3 for protein and 1.2 and 0.35 for lignin, as do the inputs from plants varying from Sphagnum moss (1.7 and 1.0), shrubs (1.6 and 0.6), sedges (1.6 and 0.7) and woody plants (1.5 and 0.7) (e.g. Clay and Worrall, 2013; Klavina et al., 2012). In peatlands, the below- to above-ground biomass ratio is relatively large, for example Murphy et al. (2009), fine root production is often tied to above ground biomass and water table position (Murphy and Moore, 2010), and less is known about the composition and amounts of below-ground inputs to soil organic matter (Kögel-Knabner, 2002, 2017). There is a rapid change in H:C ratio from some plant tissues to uppermost layer of peat, but little change with depth in the peat column: H is lost at the same rate as C. In contrast, the O:C ratio shows a decline from most plant tissues and continues to decline in the uppermost layers (0 – 50 cm) of the bog, fen and swamp profiles, with few changes lower in the profile. This depth coincides with the position of the water table in many peatlands and the conversion from aerobic to anaerobic decomposition.

The Ontario peatlands, with a large number of samples analyzed from varying peat types and depths, showed that there was a strong variation in $C_{ox}$ and OR with depth in the upper part of the three peatland types, $C_{ox}$ decreasing and OR increasing, but that there was little change beneath 50 cm (Fig. 1d, e). Given average growth rates of peat in bog profiles in Canada (see Talbot et al., 2017), the upper 50 cm represents material mainly accumulated in the last 200 yr and under mainly aerobic conditions.
Figure 4. (a) Scatter diagram of atomic O:C and H:C ratios for peat samples from Ontario (this study, $n = 1313$), United Kingdom (UK, means from Figure 2, Clay and Worrall (2015), $n = 20$), Latvia (from Table 1, Klavins et al. (2008), $n = 27$), northeastern USA (USGS Peat data base, $n = 630$), southeastern USA (USGS Peat data base, $n = 200$) and Indonesia (USGS Peat data base, $n = 175$); (b) Mean and standard deviation for each location of peat samples, with regression line of H:C on O:C indicated (see Table S2).
Figure 5. (a) Estimated input of H:C and O:C ratio from plant tissues and resulting input into bog, fen and swamp peatlands, along with ratios of decomposition to CO$_2$, methanogenesis and creation of DOC (fulvic and humic) and burning to biochar. Estimated ratios in plant tissues are derived from Clay and Worrall (2015), Klavina et al. (2012) and assuming wood is 60% cellulose and 40% lignin. The estimated input into peatlands is based on: bog 10% sedge, 20% shrub, 50% Sphagnum and 20% wood; fen 60% sedge, 20% shrub, 20% Sphagnum and 0% wood; swamp 35% sedge, 35% sedge, 0% Sphagnum and 30% wood. The outputs are based on respiration (to CO$_2$), methanogenesis (to CH$_4$ and CO$_2$), creation of fulvic and humic acids from Rice and MacCarthy (1991) and Clay and Worrall (2015), and biochar from Domingues et al. (2017).

(b) Trajectory of changes in H:C and O:C ratios passing through the initial bog and swamp ratios as a function of loss of C, H and O through respiration and methanogenesis (solid lines) and through a mixture of respiration and methanogenesis (75%) and DOC (25%, using the average fulvic and humic acid ratios, dashed lines). The estimated ratios representing a C loss of 50% in swamp and bog peatlands is indicated. The central distribution of ratios in coal is indicated (from Large and Marshall, 2014).
While there is a great variation among samples, the data from the Ontario peatlands suggest that an overall $C_{ox}$ value of -0.002 would be applicable to the top 50 cm (and -0.09 to the top 100 cm), the large amount of peat stored beneath 50 cm would have a $C_{ox}$ value of -0.21. Similarly, the values for OR would be 1.06 for 0 – 50 cm (and 1.09 for 0 – 100 cm) and 1.12 below 50 cm. These values contrast with a median $C_{ox}$ value of -0.33 for UK peat and median OR values of 1.03 for Histosols globally and 1.10 for UK peat (Clay and Worrall, 2015; Worrall et al., 2013). As the OR value has been used to estimate the C flux to the terrestrial biosphere (Worrall et al., 2013) the variation in OR with peat depth and age and the large proportion of soil C stored in peatlands need to be taken into consideration. Assuming that northern peatlands store 436 Pg of C (Loisel et al., 2014) and that the average atomic H:C and O:C ratios of 1.3 and 0.5, respectively, from the Ontario data (Fig. 1) are applicable, then northern peatlands, which have stored C primarily in the last 8000 yr (Yu et al., 2010) contain ~ 45 Pg H and 290 Pg O, compared to ~ 19 Pg N (Wang et al., 2015).

The von Post Humification Index, created almost a century ago (von Post, 1924), is based on the distinctness of the original plant structure, the colour of water squeezed from the peat and on the tactile properties of the peat (Table S1). Although it is a qualitative measure of the peat and subject to operator variability, it does appear to capture variations in the chemistry of the peat. Here, we show that the Index is strongly correlated, over a wide range of peat samples, with the O:C and H:O ratios and the $C_{ox}$ and OR values, but not H:C ratio (Fig. 2). Most of the changes occur from 1 to 4 in the Index, with little further change with increasing degree of humification. However, based on a broad classification of samples, botanical origin of the peat did not appear to be influential on the ratios. Analysis of the same set of Ontario peat samples showed that the nutrient content, expressed as the C:nutrient ratio, was also related to the Index for nitrogen, phosphorus, calcium, magnesium and potassium, with most of the change observed from 1 to 4 (Wang et al., 2015, Fig. 4). The incubation of peat samples collected from natural, harvested and restored bogs in eastern Quebec, also showed a correlation between aerobic $CO_2$ and anaerobic $CH_4$ production with von Post Humification Index, with much of the change occurring between 1 and 4 (Glatzel et al., 2004, Fig. 5).

Although there was a great variability among samples, the H:C and O:C ratios for the peat samples from northeastern and southeastern USA and Indonesia were substantially smaller than those from Ontario, UK and Latvia. In part, this may reflect differences in the analytical
methods employed by the USGS for coal (the ‘ultimate analysis’ ASTM D3176, expressed as the elemental composition of the organic material) and the other groups. This would imply a larger C content than the other methods or a smaller H and O content, or a combination. Differences in moisture content of the sample when analyzed may account for this, with the USGS method using ‘proximate analysis’ to provide an independent correction for the equilibrium moisture content, thereby reducing the H:C and O:C ratios to a truly dry basis. Alternatively, this may reflect a greater degree of decomposition, which could be expected in the tropical and subtropical samples, though unlikely in most of the samples collected from northeastern US. Moreover, the Ontario samples suggest that there are few changes in H:C and O:C ratio from slightly to well decomposed peat.

There do, however, appear to be differences in the overall relationship between the H:C and O:C ratio in 3 of the 4 temperate peat sets (Ontario, Latvia and northeastern US) compared to the two tropical/subtropical sets (southeastern US, Indonesia). The steeper regression in the latter pair suggests that H is being lost at a faster rate relative to O, compared to the temperate peatland, which may result from differences in decomposition pathways or may indicate that decomposition has progressed further in regions with warmer soil temperatures. Fire will accelerate the reduction in H:C and O:C ratios, particularly the former.

The stoichiometric relationship between the peat and the major decomposition pathways can be used to estimate how much of the original plant material has been decomposed, although there is a great variability in individual peat stoichiometry as well as potential decomposition pathways. The H:C and O:C ratios varies among vegetation, which is the input to the peatlands. The ratios in decomposition pathways also vary, such as through aerobic respiration, anaerobic methanogenesis by acetoclastic or hydrogenotrophic pathways, DOC with a range of compounds and finally the effect of combustion. Nevertheless, there appears to be evidence that a simple combination of inputs for bog, fen and swamp peatlands, combined with outputs through respiration and methanogenesis with or without DOC can be used to estimate how much of the original C has been lost. For example, our estimate of 50% C loss for a bog peatland (Fig. 5b) occurs at an average O:C ratio of 0.62, which is at a depth of about 20 cm based on the Ontario bog profiles (Fig. 1c). The Peat Decomposition Model (Frolking et al., 2001)
based on cohort inputs and estimated decomposition rates, estimates that about half the annual cohort mass of a bog would be lost at a depth of about 15 cm.

Acknowledgments

There are no real or perceived financial conflicts of interests for any author. The Ontario Peatland Data are available at http://peatland.geog.mcgill.ca/. Funding to TRM and JT came from the Natural Sciences and Engineering Research Council of Canada.

References

ASTM, 2011a, Annual Book of ASTM standards, Soil and rock, I, v. 4.08, 1848 p.

Biester, H., K. H. Knorr, J. Schellekens, A. Basler, and Y.-M. Hermanns (2014), comparison of different methods to determine the degree of peat decomposition in peat bogs, *Biogeoosciences*, 11, 2691–2707.

Clay, G.D., and F. Worrall (2015), Estimating the oxidative ratio of UK peats and agricultural soils, *Soil Use and Management*, 31, 77–88.

Conedera, M., W. Tinner, C. Neff, M. Meurer, A.F. Dickens, P. Krebs (2009), Reconstructing past fire regimes: methods, applications, and relevance to fire management and conservation. *Quaternary Science Reviews* 28: 555–576.

D’Andrilli, J., J. P. Chanton, P. H. Glaser, and W. T. Cooper (2010), Characterization of dissolved organic matter in northern peatland soil porewaters by ultra high resolution mass spectrometry, *Organic Geochemistry*, 41, 791–799.

Domingues, R. R., P. F. Trugilho, C. A. Silva, I. Cristina, N. A. de Melo, L. C. A. Melo, Z. M. Magriotis, and M. A. Sánchez-Monedero (2017), Properties of biochar derived from wood and high-nutrient biomasses with the aim of agronomic and environmental benefits. *PLoS ONE* 12(5): e0176884. [https://doi.org/10.1371/journal.pone.0176884](https://doi.org/10.1371/journal.pone.0176884)

Frolking, S., N. T. Roulet, T. R. Moore, P. J. H. Richard, M. Lavoie, and S. D. Muller (2001), Modelling northern peatland decomposition and peat accumulation, *Ecosystems*, 4, 479-498.

Glatzel, S., N. Basiliko, and T. R. Moore (2004), Carbon dioxide and methane production potentials of peats from natural, harvested and restored sites, eastern Québec, Canada, *Wetlands*, 24, 261-267.
Kim, S., R.W. Kramer, and P.G. Hatcher (2003) Graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter, the Van Krevelen diagram. *Anal. Chem.*, 75, 5336-5344.

Kļaviņa, L., O. Bikovens, I. Šteinberga, V. Maksimova, and L. Eglīte (2012), Characterization of chemical composition of some bryophytes common in Latvia, *Envir. Exper. Biol.*, 10, 27–34.

Klavins, M., J. Sire, O. Purmalis, and V. Melecis (2008), Approaches to estimating humification indicators for peat, *Mires and Peat*, 3, 07.

Kögel-Knabner, I. (2002), The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. *Soil Biol. Biochem.*, 34, 139-162.

Kögel-Knabner, I. (2014), The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter: Fourteen years on, *Soil Biol. Biochem.*, 105, A3-A6.

Large, D.J., and C. Marshall (2015), Use of carbon accumulation rates to estimate the duration of coal seams and the influence of atmospheric dust deposition on coal composition. In: Smith, D. G., Bailey, R. J., Burgess, P. M. & Fraser, A. J. (eds) Strata and Time: Probing the Gaps in Our Understanding. Geological Society, London, Special Publications, 404, http://dx.doi.org/10.1144/SP404.15.

Loisel, J., Z. Yu, D.W. Beilman, P. Camill, J. Alm, M.J. Amesbury, D. Anderson, S. Andersson, C. Bochicchio, K. Barber, L.R. Belyea, J. Bunbury, F. M. Chambers, D.J. Charman, F. De Vleeschouwer, B. Fialkiewicz-Koziel, S.A. Finkelstein, M. Galka, M. Garneau, D. Hammarlund, W. Hinchcliffe, J. Holmquist, P. Hughes, M.C. Jones, E.S. Klein, U. Kokfelt, A. Korhola, P. Kuhry, A. Lamarre, M. Lamentowicz, D. Large, M. Lavoie, G. MacDonald, G. Magnan, M. Makila, G. Mallon, P. Mathijssen, D. Mauquoy, J. McCarroll, T.R. Moore, J. Nichols, B. O’Reilly, P. Oksanen, M. Packalen, D. Peteet, P.J.H. Richard, S. Robinson, T. Ronkainen, M. Rundgren, A. Britta, K. Sannel, C. Tarnocai, T. Thom, E.-S. Tuittila, M. Turetsky, M. Valiranta, M. van der Linden, B. van Geel, S. van Bellen, D. Vitt, Y. Zhao, and W. Zhou (2014), A database and synthesis of northern peatland soil properties and Holocene carbon and nitrogen accumulation, *The Holocene*, 24, 1028-1042.

Masiello, C. A., M. E. Gallagher, J. T. Randerson, R. M. Deco, and O. A. Chadwick (2008), Evaluating two experimental approaches for measuring ecosystem carbon oxidation state and oxidative ratio, *J. Geophys. Res.*, 113, G03010, doi:10.1029/2007JG000534.
Rice, J. A., and P. McCarthy (1991), Statistical evaluation of the elemental composition of humic substances, *Org. Geochem.*, 17, 635-648.

Riley, J. L. (1989), Laboratory Methods for Testing Peat Ontario Peatland Inventory Project, vol. 145, 51 pp., Ontario Geological Survey, Miscellaneous Paper, Toronto, Canada.

Riley, J. L. (1994a), Peat and Peatland Resources of Northeastern Ontario, vol. 153, 155 pp., Ontario Geological Survey, Miscellaneous Paper, Toronto, Canada.

Riley, J. L. (1994b), Peat and Peatland Resources of Southeastern Ontario, vol. 154, 167 pp., Ontario Geological Survey, Miscellaneous Paper, Toronto, Canada.

Riley, J. L., and L. Michaud (1989), Peat and Peatland Resources of Northwestern Ontario, vol. 144, 175 pp., Ontario Geological Survey, Miscellaneous Paper, Toronto, Canada.

Riley, J. L., and L. Michaud (1994), Ontario Peatland Inventory: Field-Work Methods, vol. 155, 62 pp., Ontario Geological Survey, Miscellaneous Paper, Toronto, Canada.

Rydin, H., and J. K. Jeglum (2013), *The Biology of Peatlands*, 2nd ed., Oxford Univ. Press, Oxford, UK.

Talbot, J., T. R. Moore, M. Wang, C. Ouellet Dallaire, and J. L. Riley (2017), Distribution of lead and mercury in Ontario peatlands. *Envir. Poll.*, 231, 890-898. doi: org/10.1016/j.envpol.2017.08.095.

 Tfaily, M. M., W. T. Cooper, J. E. Kostka, P. R. Chanton, C.W. Schadt, P. J. Hanson, C. M. Iversen, and J. P. Chanton (2014), Organic matter transformation in the peat column at Marcell Experimental Forest: Humification and vertical stratification, *J. Geophys. Res. Biogeosci.*, 119, 661–675.

USGS (2012) Peat database. https://energy.usgs.gov/coal/peat.aspx

van Krevelen D.W. (1961), Graphical-statistical method for the study of structure and reaction processes of coal, *Fuel*, 29, 269-284.

von Post, L. (1924), Das genetische System der organogenen Bildungen Schwedens. *Comité International de Pédologie IV*, Communication 22 : 287–304.

Wang, M., T. R. Moore, J. Talbot, and J. L. Riley (2015), The stoichiometry of carbon and nutrients in peat formation, *Global Biogeochem. Cycles*, 29, 113–121.
Worrall, F., G. D. Clay, C. S. Moody, T. P. Burt, and R. Rose (2016), The effective oxidative state of a peatland, *J. Geophys. Res. Biogeosci.*, 121, 145-158.

Worrall, F., G. D. Clay, C. A. Masiello, and G. Mynheer (2013), Estimating the oxidative ratio of the global terrestrial biosphere, *Biogeochem.*, 115, 23-32.

Yu, Z., J. Loisel, D. P. Brosseau, D. W. Beilman, and S.J. Hunt (2010), Global peatland dynamics since the Last Glacial Maximum, *Geophys. Res. Lett.*, 37, L13402, doi:10.1029/2010GL043584.