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The stoichiometry of carbon, hydrogen and oxygen in peat

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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

23 **Abstract**

24 Carbon (C), hydrogen (H) and oxygen (O) form ~90% by mass of peat, a product of the input of
25 plant tissues and litter and the output of decomposition under aerobic and anaerobic conditions.
26 We examined patterns of these elements, as the O:C and H:C atomic ratios, in over 1300 peat
27 samples collected from over 400 profiles in Ontario, Canada, representing bogs, fens and
28 swamps. The overall O:C ratio decreased from the surface (0.6 to 0.7) to ~0.5 at a depth of 50
29 cm and showed little further change to a depth of 5 m. In contrast, the H:C ratio decreased only
30 slightly (1.30 to 1.25) over the top 1 m and showed no further significant decline with depth. The
31 carbon oxidative state (C_{ox}) and oxidation ratio (OR) showed strong decreases and increases,
32 respectively, with depth with most changes occurring in the top 1 m. The O:C ratio, and C_{ox} and
33 OR values were significantly correlated with the von Post Humification Index, with most
34 changes occurring in Index values 1 through 4, the latter representing a slight degree of
35 decomposition. Collation of the Ontario peats with other data sets revealed the very large range
36 in O:C and H:C values, with a general decrease from temperate to tropical and sub-tropical
37 peatlands. Estimation of the O:C and H:C ratios of input (litter) and output (mineralization to
38 CO_2 , methanogenesis to CH_4 and CO_2 and loss as dissolved organic carbon) allowed an
39 estimation of the degree of decomposition or C loss.

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41 **Plain Language Summary**

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

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51 **1 Introduction**

52 Peat soils contain very large amounts of organic carbon (C), generally between 30 and
53 200 kg C m⁻², and it is estimated that northern peatland soils contain over 400 Gt globally (Loisel
54 et al., 2014). This accumulation arises from the rates of plant production being faster than the
55 rates of litter and soil organic matter decomposition, associated with a high water table and the
56 development of anoxic conditions, as well as peat plants, such as *Sphagnum* moss, having a slow
57 intrinsic rate of decomposition (Rydin and Jeglum, 2013). Organic C generally forms 45-50% of
58 the mass of peat and another ~35% is comprised of oxygen (O) and ~5% hydrogen (H). Thus,
59 85-90% of the peat mass comprises C, H and O, with smaller amounts of nutrients and metals.

60 During decomposition, organic molecules are broken down by microbes, resulting in the
61 loss of decomposition products such as carbon dioxide (CO₂), methane (CH₄) and dissolved
62 organic carbon (DOC). Patterns of organic matter decomposition in peat have been approached
63 in many ways, ranging from the simple von Post Humification Index, ash content and C:N ratio,
64 to nuclear magnetic resonance, Fourier transform infrared spectroscopy and isotopes of C and N
65 (e.g. Biester et al., 2014; Tfaily et al., 2014). Given the differences in C, H and O stoichiometry
66 between the input of organic matter to peatlands in plant tissues and litter and that of the
67 decomposition products, one could expect changes in the C, H and O stoichiometry of peat as it
68 undergoes decomposition. Peat is the precursor to coal deposits which are often characterized by
69 the atomic ratios of O to C, and H to C, commonly illustrated as a van Krevelen diagram (van
70 Krevelen, 1961). These diagrams show decreases in both O:C and H:C ratios as material passes
71 from vegetation through soil organic matter and peat into coal. These ratios have also been used
72 to characterize the chemistry of DOC (e.g. D'Andrelli et al., 2010; Kim et al., 2003).

73 Worrall and colleagues (e.g. Clay and Worrall, 2015; Worrall et al., 2016) have used the
74 concentration of C, H, O and N to assess the oxidation state of a variety of soils, including peats,
75 as part of a global stoichiometric approach to C cycling and sinks (e.g. Masiello et al., 2008;
76 Worrall et al., 2013). Two metrics have been applied to soil organic matter, the carbon oxidation
77 state (C_{ox}) which is based on the relative atomic concentrations of C, H, O and N, and the
78 oxidative ratio (OR), which is a derivative of C_{ox} and C and N concentrations (Masiello et al.,
79 2008). Clay and Worrall (2015) concluded that, for a range of samples collected from the upper 1
80 m of peat soils in the UK, the average C_{ox} and OR values were -0.33 and 1.10, respectively,
81 compared to -0.05 and 1.03 for vegetation. They then applied these metrics to assess the

82 oxidation state of a blanket peatland within the Moor House National Nature Reserve in the UK
83 (Worrall et al., 2016).

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

- 89 1. We examine how O:C and H:C ratios and C_{ox} and OR vary with peatland type, depth and von
90 Post Humification Index.
- 91 2. Combining these data with C, H and O analyses of peat from temperate (UK, Latvia,
92 northeastern USA) and sub-tropical and tropical (southeastern USA and Indonesia) regions, we
93 compare how O:C and H:C ratios change, in relation to the input from vegetation/litter and the
94 output from decomposition processes.
- 95 3. Assuming decomposition processes introduce changes in the O:C and H:C ratios of peat, we
96 examine whether these stoichiometries can be used to estimate degree of decomposition of the
97 peat, based on what would be the input from vegetation and litter and the stoichiometry of
98 decomposition.

99 **2 Materials and Methods**

100 The sampling sites in Ontario were part of a large scale survey of peat resources
101 extending from 74°W to 94°W and 43°N to 51°N in northwestern, northeastern and southeastern
102 regions (Riley, 1994a, b; Riley and Michaud, 1989). The sites were selected to represent a range
103 of typical peat accumulation conditions, had a uniform vegetation cover, were > 100 ha in size
104 and had at least 40 cm of peat accumulation. They were classified into bogs, fens and swamps,
105 depending on their pH, surface peat botanical composition and tree cover (Riley and Michaud,
106 1994). Bogs had a pH lower than 5.2 and surface peat was dominated by *Sphagnum* remains,
107 whereas fens and swamps have a higher pH and a graminoid, woody or brown-moss dominated
108 surface peat. Swamps have a tree or tall shrub cover higher than 25%. Peat cores were sampled
109 using a mini-Macaulay or Hiller sampler and divided into four intervals or more for deeper
110 profiles, based on their botanical composition and apparent degree of humification. The highest
111 and lowest depth of each section was recorded, as well as the degree of humification based on
112 the von Post Humification Index (Table S1), ash content, botanical content of the peat (as % of

113 moss, sedge and other graminoids, wood, and ‘other material’), and the chemical composition of
114 the samples (Riley and Michaud, 1994).

115 For details on the C, H, O, ash, nitrogen (N) and sulphur (S) analyses, see Riley
116 (1989). Briefly, organic C concentration was determined by treatment with HCl and then
117 ignition in a Leco Induction Furnace at 500°C and trapping in KOH. The H concentration
118 was determined by ignition in a Leco Induction Furnace under a stream of oxygen and
119 absorption of water by a magnesium perchlorate absorption tube. The O concentration
120 was determined by difference:

$$121 \quad \%O = 100 - \% (\text{Ash} + \text{Total C} + \text{N} + \text{H} + \text{S}) \quad \text{eq 1}$$

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

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

130 We calculated the C_{ox} and OR values of each peat sample, as defined in Worrall et al.
131 (2016) from atomic concentrations:

$$132 \quad C_{ox} = \frac{2[O] - [H] + 3[N]}{[C]} \quad \text{eq 2 (from Masiello et al., 2008)}$$

$$133 \quad OR = 1 - \frac{C_{ox}}{4} + \frac{2[N]}{[C]} \quad \text{eq 3 (from eq 6 in Worrall et al., 2015)}$$

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

143 We applied decomposition stoichiometries involving respiration to CO_2 and H_2O and
144 methanogenesis to CH_4 and CO_2 (both resulting in CH_2O), as well as loss of DOC, such as fulvic
145 and humic acids. We did not apply stoichiometric changes associated with fire.

146 **3 Results**

147 **3.1 CHO composition, Von Post Humification Index, H:C and O:C ratios and C_{ox}**
148 **and OR in Ontario peat**

149 The average composition of the large number of Ontario peat samples by mass (%±sd)
150 was C 49.4 (5.0); H 5.2 (0.6); O 34.9 (5.6); thus, these three elements represent an average of
151 89.5%. Other elements included N (1.9%), calcium (1.7%), iron (0.4%), aluminum (0.3%), S
152 (0.2%), magnesium (0.2%), potassium (0.1%) and phosphorus (0.1%).

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

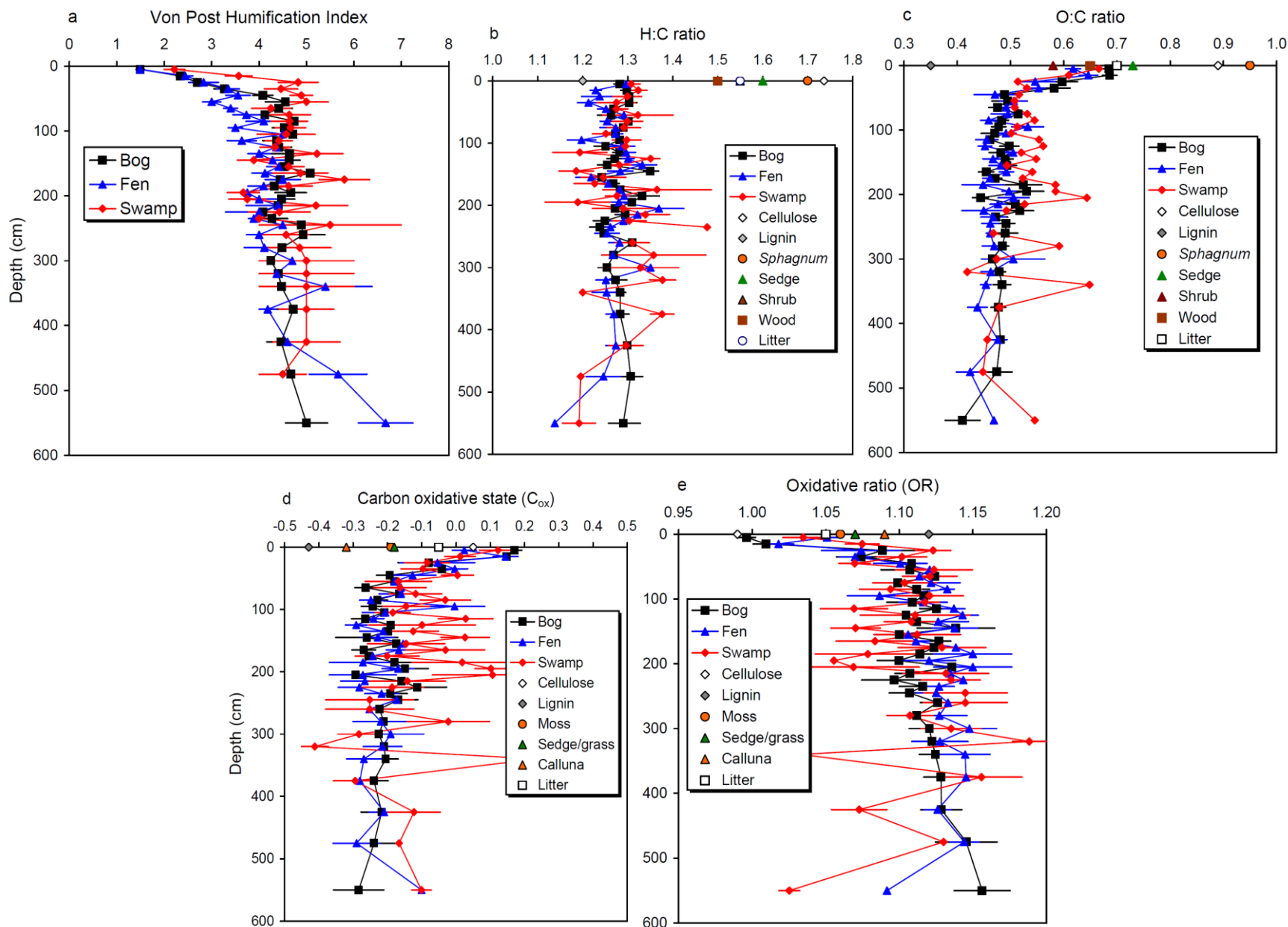
158 There was also a pronounced decrease in the H:C ratios from typical peatland
159 vegetation and litter to the uppermost layers of the peat profiles (Fig. 1b), but there was
160 no significant relationship between H:C ratio and depth in the peat types, nor a significant
161 difference between bog,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

166 There was a decrease in the C_{ox} value from the surface layers of the peat (average
167 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
168 (Fig. 1d), with a significant logarithmic relationship with depth in the bog and fen
169 profiles, but not the swamp (Table S2). The OR value showed an increase from 1.05 to
170 1.10 at the peat surface to averages of 1.10 to 1.13 at a depth of about 50 cm, with no
171 further increase deeper in the profile (Fig. 1e). There was a significant logarithmic
172 relationship with depth in the bog and fen profiles, but not the swamp (Table S2).

173 Comparison of the ratios with the von Post Humification Index showed no
174 significant change in H:C ratio with increasing degree of decomposition, whereas there
175 was a significant decrease in O:C ratio, though most of this change occurred between
176 Index values 1 and 4 (Fig. 2a). Combination of the two ratios resulted in an increase in

177 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
178 OR showed a significant relationship with the Index, C_{ox} showing a decline from 0.10 to -
179 0.29 and OR an increase from 1.03 to 1.12, with the change being most pronounced from
180 Index values 1 to 4 (Fig. 2c). A breakpoint analysis suggested that an Index of 3 was
181 critical for all properties, except for H:C (data not shown).

182 There was no significant relationship between the H:C and O:C ratios and the
183 origin of the peat, when peat was binned into the von Post Humification Index (Fig. 3).
184 Samples that were considered uniform in terms of botanical composition (>80% of their
185 content dominated by one peat type) were grouped into moss, sedge and wood types. It
186 should be noted that the least decomposed samples (von Post Humidification Index of 1)
187 did not have enough uniform samples of all three types to allow a comparison.

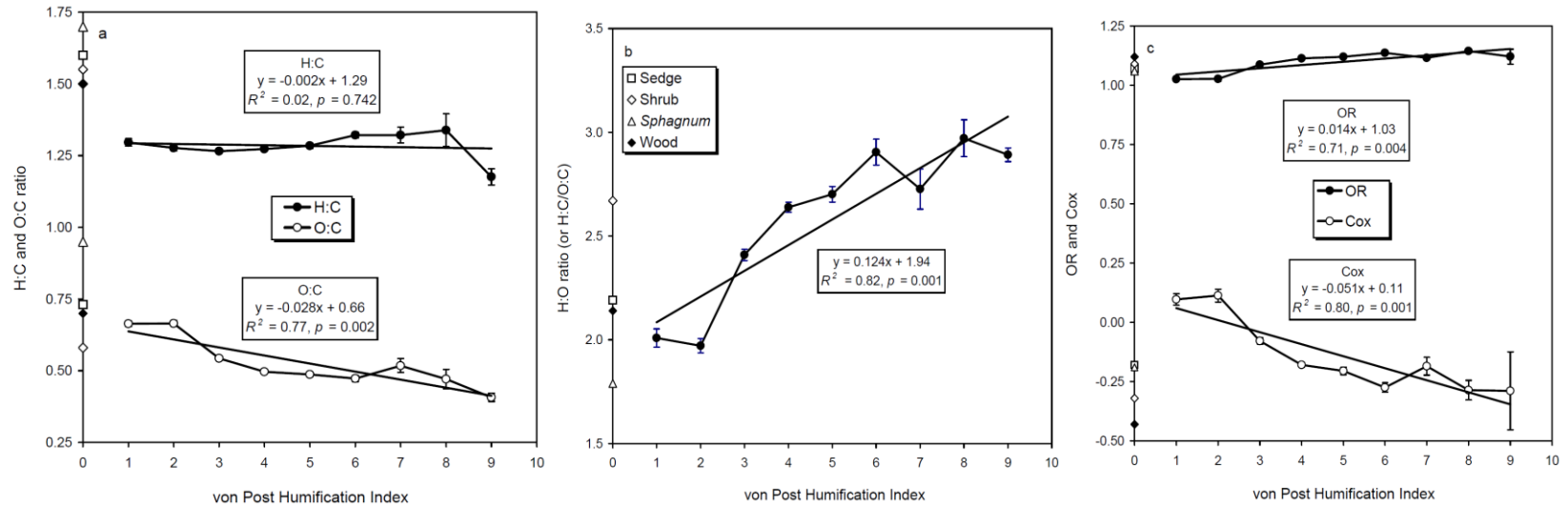


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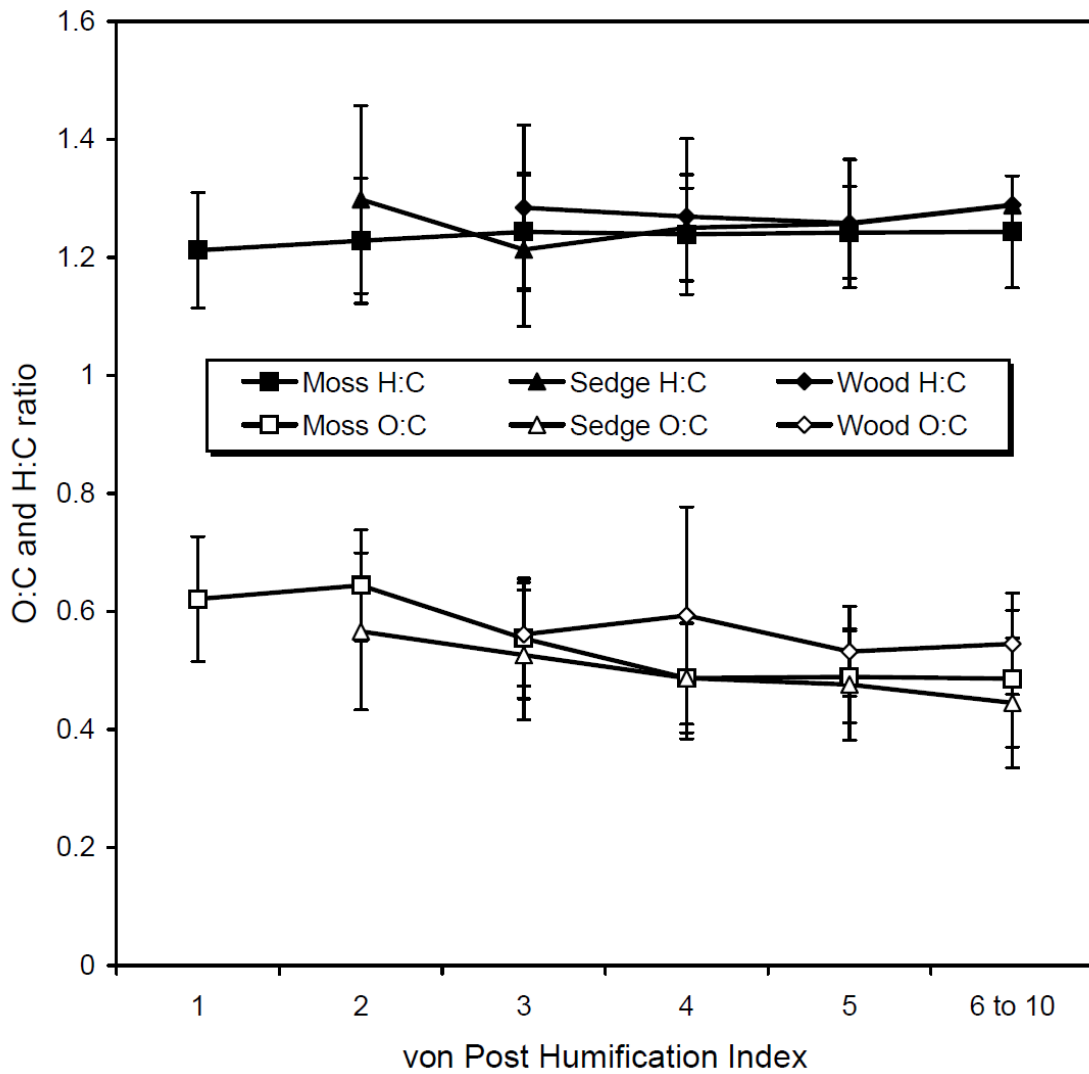
191 **Figure 1.** Patterns of von Post Humification Index (a), H:C and O:C ratios (b and c), and C_{ox} and OR (d and e) with depth in Ontario
192 peat profiles, grouped by peatland type, along with values commonly found in organic compounds, plants and litter. Values represent
193 the mean and standard error of samples binned by depth.
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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.



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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.

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220 **3.2 Relationship between H:C and O:C ratio of Ontario and other peats**

221 The relationship between the H:C and O:C ratio among the 1313 peat samples from
222 Ontario is depicted in Fig 4a, showing the very wide range of ratios recorded, with a mean of
223 1.28 H:C and 0.62 O:C and standard deviation of 0.13 and 0.12, respectively (Fig. 4b). Overall,
224 there was a weak ($R^2_{adj} = 0.040$), but statistically significant ($p = 0.001$) relationship between
225 H:C and O:C ratios with a shallow slope (0.22) of H:C on O:C (Table S3).

226 Peat samples from other temperate regions showed similar patterns with H:C and O:C
227 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
228 the northeastern USA (Maine and New Hampshire). The two tropical/sub-tropical regions
229 showed generally smaller mean H:C and O:C ratios (1.12 and 0.45 for Indonesia and 1.06 and
230 0.37 for southeastern USA, respectively). In all cases, however, there is a great variation among
231 peat samples from each location. There was also a statistically significant ($p < 0.05$) relationship
232 between H:C and O:C in all regions, except for northeastern USA ($p = 0.063$), with variable
233 regression slopes (Table S3). The slopes were shallow (0.22 to 0.47) for the temperate Ontario,
234 Latvia and northeastern USA peats, but steeper for the UK peat (1.21), and the samples from
235 southeastern USA and Indonesia (0.74 and 1.62), suggesting a greater loss in H accompanying
236 the O loss in decomposition in the latter.

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238 **3.3 Estimating the degree of decomposition of peat from the H:C and O:C stoichiometry of** 239 **peat and decomposition processes**

240 The H:C and O:C characteristics of the peat result from the effect of decomposition
241 processes acting upon the plant tissues and litter from which the peat formed and released C, H
242 and O. The H:C and O:C ratios of sedge, shrub, *Sphagnum* and wood, common contributors to
243 peatlands, are illustrated in Fig. 5a, along with the range of ratios input for bog, fen and swamp
244 peatlands, based on a variable contribution of the 4 plant categories. This suggests that most
245 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
246 represents losses as respiration and methanogenesis with ratios of H:C of 2 and O:C of 1,
247 respectively, DOC (as fulvic and humic acids) of H:C ~1.25 and O:C of ~0.7, and combustion
248 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
249 values encountered in coal.

250 Based on the range of original O:C and H:C ratios for bog, fen and swamp peatlands, the
251 trajectories of ratios associated with increasing decomposition and mode of decomposition can
252 be plotted. As an example, the trajectories of the bog and swamp peat associated entirely with
253 respiration and methanogenesis are plotted in Fig. 5b, as well as the trajectories if decomposition

254 was 75% respiration and methanogenesis and 25% DOC (combining fulvic and humic acids).
255 The latter, with decomposition output lower in H:C and O:C ratio than gas losses, results in peat
256 with larger H:C and O:C ratios. These trajectories encompass much of the variation in H:C and
257 O:C ratios found in peats and suggest that about 50-75% of the original C has been lost. Fire,
258 important in some peatlands, would result in smaller H:C and O:C ratios; Conodera et al. (2009)
259 cite average O:C ratios of 0.5 and 0.3 for slightly charred biomass and charcoal, respectively,
260 and the equivalent values for H:C are 1.0 and 0.6. However, differences in original composition
261 of litter input and the type and degree of decomposition may explain the very large variability in
262 H:C and O:C ratios observed in peat.

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264 **4. Discussion**

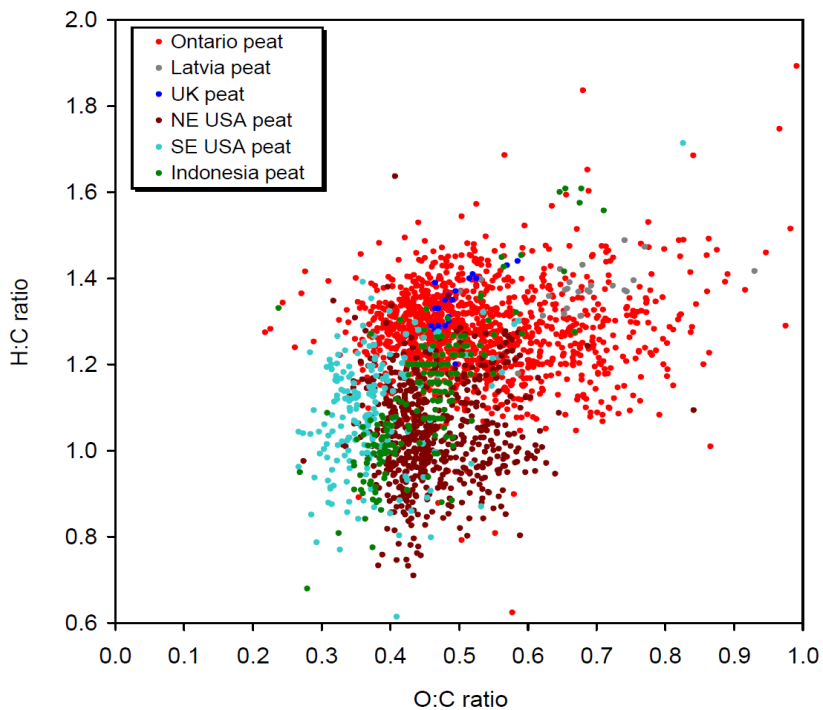
265 There are major changes in the H:C and O:C ratios as plant tissues senesce into litter and
266 then as that litter decomposes in the surface layers of the peat. Plant compounds vary
267 considerably in their H:C and O:C ratios, such as 2 and 1 for glucose, 1.7 and 0.8 for cellulose,
268 1.2 and 0.3 for protein and 1.2 and 0.35 for lignin, as do the inputs from plants varying from
269 *Sphagnum* moss (1.7 and 1.0), shrubs (1.6 and 0.6), sedges (1.6 and 0.7) and woody plants (1.5
270 and 0.7) (e.g. Clay and Worrall, 2013; Klavina et al., 2012). In peatlands, the below- to above-
271 ground biomass ratio is relatively large, for example Murphy et al. (2009), fine root production is
272 often tied to above ground biomass and water table position (Murphy and Moore, 2010), and less
273 is known about the composition and amounts of below-ground inputs to soil organic matter
274 (Kögel-Knabner, 2002, 2017). There is a rapid change in H:C ratio from some plant tissues to
275 uppermost layer of peat, but little change with depth in the peat column: H is lost at the same rate
276 as C. In contrast, the O:C ratio shows a decline from most plant tissues and continues to decline
277 in the uppermost layers (0 – 50 cm) of the bog, fen and swamp profiles, with few changes lower
278 in the profile. This depth coincides with the position of the water table in many peatlands and the
279 conversion from aerobic to anaerobic decomposition.

280 The Ontario peatlands, with a large number of samples analyzed from varying
281 peat types and depths, showed that there was a strong variation in C_{ox} and OR with depth
282 in the upper part of the three peatland types, C_{ox} decreasing and OR increasing, but that
283 there was little change beneath 50 cm (Fig. 1d, e). Given average growth rates of peat in
284 bog profiles in Canada (see Talbot et al., 2017), the upper 50 cm represents material
285 mainly accumulated in the last 200 yr and under mainly aerobic conditions.

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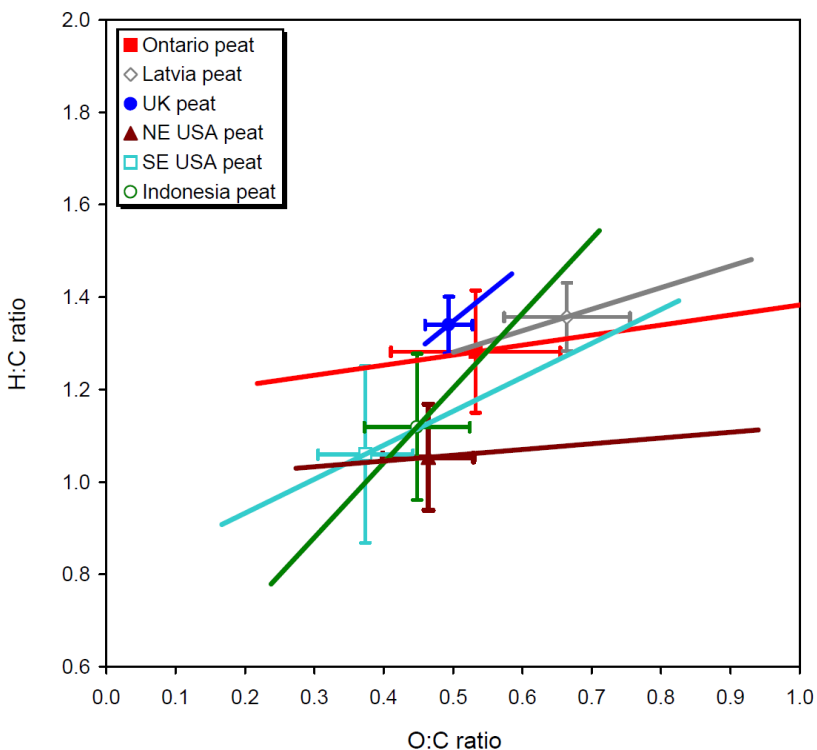
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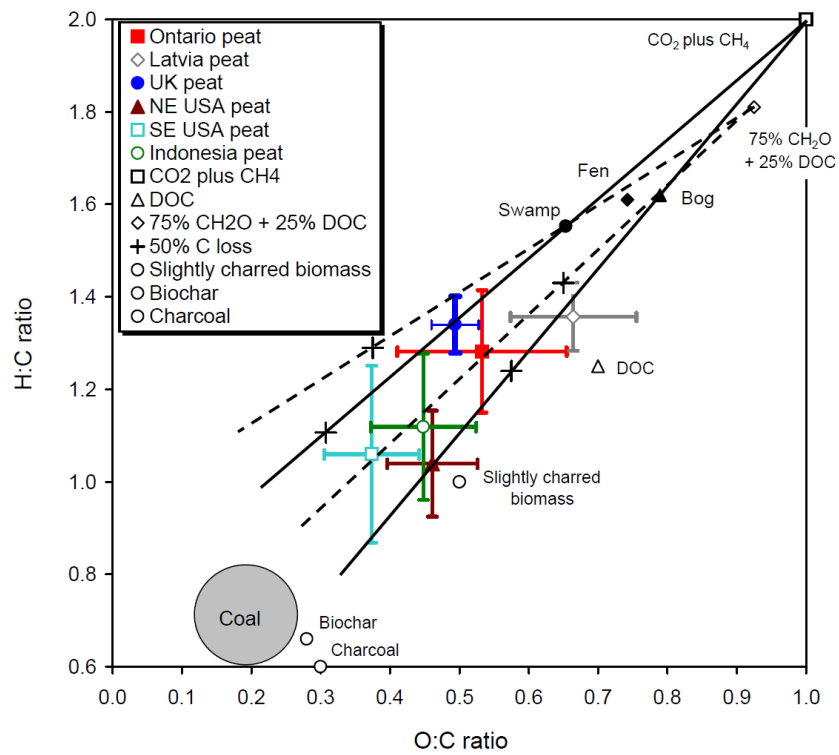
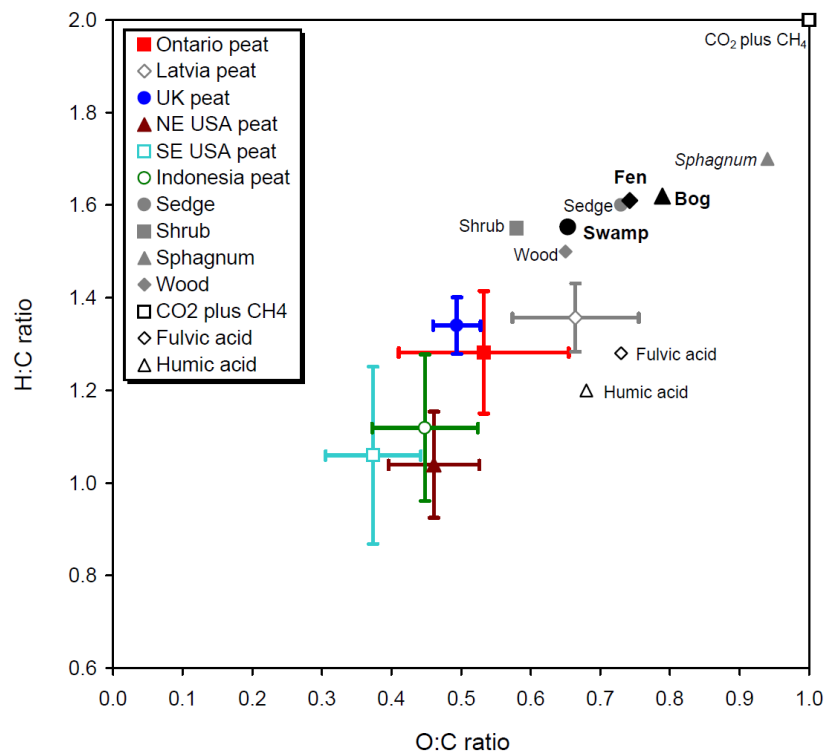
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292 **Figure 4.** (a) Scatter diagram of atomic O:C and H:C ratios for peat samples from
293 Ontario (this study, $n = 1313$), United Kingdom (UK, means from Figure 2, Clay and
294 Worrall (2015), $n = 20$), Latvia (from Table 1, Klavins et al. (2008), $n = 27$), northeastern
295 USA (USGS Peat data base, $n = 630$), southeastern USA (USGS Peat data base, $n = 200$)
296 and Indonesia (USGS Peat data base, $n = 175$); (b) Mean and standard deviation for each
297 location of peat samples, with regression line of H:C on O:C indicated (see Table S2).
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307 **Figure 5.** (a) Estimated input of H:C and O:C ratio from plant tissues and resulting input
308 into bog, fen and swamp peatlands, along with ratios of decomposition to CO₂,
309 methanogenesis and creation of DOC (fulvic and humic) and burning to biochar.

310 Estimated ratios in plant tissues are derived from Clay and Worrall (2015), Klavina et al.
311 (2012) and assuming wood is 60% cellulose and 40% lignin. The estimated input into
312 peatlands is based on: bog 10% sedge, 20% shrub, 50% *Sphagnum* and 20% wood; fen
313 60% sedge, 20% shrub, 20% *Sphagnum* and 0% wood; swamp 35% sedge, 35% sedge,
314 0% *Sphagnum* and 30% wood. The outputs are based on respiration (to CO₂),
315 methanogenesis (to CH₄ and CO₂), creation of fulvic and humic acids from Rice and
316 MacCarthy (1991) and Clay and Worrall (2015), and biochar from Domingues et al.
317 (2017).

318 (b) Trajectory of changes in H:C and O:C ratios passing through the initial bog and
319 swamp ratios as a function of loss of C, H and O through respiration and methanogenesis
320 (solid lines) and through a mixture of respiration and methanogenesis (75%) and DOC
321 (25%, using the average fulvic and humic acid ratios, dashed lines). The estimated ratios
322 representing a C loss of 50% in swamp and bog peatlands is indicated. The central
323 distribution of ratios in coal is indicated (from Large and Marshall, 2014).

324 While there is a great variation among samples, the data from the Ontario peatlands
325 suggest that an overall C_{ox} value of -0.002 would be applicable to the top 50 cm (and -0.09 to the
326 top 100 cm), the large amount of peat stored beneath 50 cm would have a C_{ox} value of -0.21.
327 Similarly, the values for OR would be 1.06 for 0 – 50 cm (and 1.09 for 0 – 100 cm) and 1.12
328 below 50 cm. These values contrast with a median C_{ox} value of -0.33 for UK peat and median
329 OR values of 1.03 for Histosols globally and 1.10 for UK peat (Clay and Worrall, 2015; Worrall
330 et al., 2013). As the OR value has been used to estimate the C flux to the terrestrial biosphere
331 (Worrall et al., 2013) the variation in OR with peat depth and age and the large proportion of soil
332 C stored in peatlands need to be taken into consideration. Assuming that northern peatlands store
333 436 Pg of C (Loisel et al., 2014) and that the average atomic H:C and O:C ratios of 1.3 and 0.5,
334 respectively, from the Ontario data (Fig. 1) are applicable, then northern peatlands, which have
335 stored C primarily in the last 8000 yr (Yu et al., 2010) contain ~ 45 Pg H and 290 Pg O,
336 compared to ~ 19 Pg N (Wang et al., 2015).

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

352 Although there was a great variability among samples, the H:C and O:C ratios for the
353 peat samples from northeastern and southeastern USA and Indonesia were substantially smaller
354 than those from Ontario, UK and Latvia. In part, this may reflect differences in the analytical

355 methods employed by the USGS for coal (the ‘ultimate analysis’ ASTM D3176, expressed as the
356 elemental composition of the organic material) and the other groups. This would imply a larger C
357 content than the other methods or a smaller H and O content, or a combination. Differences in
358 moisture content of the sample when analyzed may account for this, with the USGS method
359 using ‘proximate analysis’ to provide an independent correction for the equilibrium moisture
360 content, thereby reducing the H:C and O:C ratios to a truly dry basis. Alternatively, this may
361 reflect a greater degree of decomposition, which could be expected in the tropical and
362 subtropical samples, though unlikely in most of the samples collected from northeastern US.
363 Moreover, the Ontario samples suggest that there are few changes in H:C and O:C ratio from
364 slightly to well decomposed peat.

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

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

385 based on cohort inputs and estimated decomposition rates, estimates that about half the
386 annual cohort mass of a bog would be lost at a depth of about 15 cm.

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