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01 May 2015

Version of attached file:

Accepted Version

Peer-review status of attached file:

Peer-reviewed

Citation for published item:

Clay, G.D. and Worrall, F. (2015) 'Estimating the oxidative ratio of UK peats and agricultural soils.', *Soil use and management.*, 31 (1). pp. 77-88.

Further information on publisher's website:

<http://dx.doi.org/10.1111/sum.12155>

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1 Estimating the oxidative ratio of UK peats and agricultural soils

2

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4

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9

10 **Abstract**

11 Organic matter in the terrestrial biosphere has a fundamental role in moderating the exchange
12 of CO₂ between the atmosphere and the biosphere. One important property of organic matter
13 is its oxidative ratio (OR); that is the ratio of moles O₂ released per mole CO₂ sequestered
14 through photosynthesis i.e. the lower the OR, less O₂ is released per mole of CO₂ fixed. In
15 global assessments of CO₂ partitioning, the failure to account for changes in OR could lead to
16 an underestimate of terrestrial carbon sequestration. It is known that OR can vary between
17 environments and management, but what other factors could be playing a role in controlling
18 OR?

19 This study measured the OR of a range of peat (Histosols) and mineral soils
20 (Inceptisols) under similar management from ~~the~~ across the United Kingdom to investigate
21 how OR varies within and between material types. The study shows that OR values varied
22 significantly between material types (median peat OR = 1.10, median vegetation OR = 1.03

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23 and median mineral soil OR = 1.14) and they also varied between study sites. Furthermore
24 there were no significant differences in OR with peat depth.

25 Given the results from this study we can suggest that future sampling strategies
26 should include sampling of the major carbon pools (i.e. vegetation, litter and soil) and that, as
27 a first approximation, OR can be examined on the basis of these carbon pools alone. The
28 values measured in the study give a new residence time weighted global OR estimate for the
29 terrestrial biosphere (OR_{terra}^{global}) of 1.056 ± 0.02 .

30

31 **Keywords**

32 Terrestrial carbon cycle; elemental composition; organic matter; peatlands;

33

34 **1. Introduction**

35 In 2011 anthropogenic emissions of CO₂ reached 9.5 ± 0.5 PgC yr⁻¹ (Le Quéré et al., 2013)
36 and in May 2013 atmospheric concentrations of CO₂ surpassed 400 ppm for the first time in
37 human history (Jones, 2013). By using a carbon budget approach (e.g. Le Quéré et al.,
38 2013), [and assessing changes in atmospheric O₂ and CO₂ concentrations](#) (Keeling et al.,
39 1996), atmospheric carbon ~~is~~ can be partitioned between the carbon pools in the atmosphere,
40 oceans and terrestrial biosphere (residual sink). Battle et al. (2000) used changes in
41 atmospheric levels of O₂ and N₂ in order to calculate the sizes of annual sinks between
42 reservoirs and for the CO₂ flux to the land proposed the following equation:

43

$$44 \quad f_{land} = -\frac{OR_{ff}}{OR_{terra}} f_{fuel} + \frac{1}{(4.8 \times 0.471 \times OR_{terra})} \frac{d\left(\frac{O_2}{N_2}\right)}{dt} \quad \text{Equation 1}$$

45

46 where: f_{fuel} = flux of CO₂ due to fossil fuel combustion; $\frac{d(\frac{O_2}{N_2})}{dt}$ is rate of change of molar ratio
47 of atmospheric O₂ and N₂; OR_{ff} ~~is~~ the combustion stoichiometry; OR_{terra} ~~is~~ the oxidative
48 ratio of the terrestrial biosphere.

49 Within equation 1 there are two terms that play an important role in understanding the
50 partitioning of atmospheric carbon, the oxidative ratio (OR) which is the molar ratio of O₂
51 and CO₂ fluxes associated with either fossil fuel combustion (OR_{ff}) or photosynthesis
52 (OR_{terra}). ~~This ratio is an important component in equation 1 and so research has considered~~
53 ~~the relative changes in O₂ and CO₂ in the atmosphere as a means of understanding the relative~~
54 ~~magnitude of global sinks and sources of CO₂ (Keeling and Shertz, 1992; Keeling et al.,~~
55 ~~1996).~~ Until recently there has only been one estimate of OR for the terrestrial biosphere
56 (OR_{terra}) that has been used with equation 1. ~~This and that~~ came from Severinghaus (1995)
57 who estimated the value to be 1.1. This value of 1.1 has been commonly adopted ~~through in~~
58 several global studies (e.g. IPCC, 2007). However, more recent work has shown that this
59 value may not be appropriate ~~for equation 1~~. In a recent meta-analysis of global OR values,
60 Worrall et al. (2013) showed that, whilst within the range of natural occurrence, the
61 commonly used value of 1.1 is probably not the most accurate value. Worrall et al. (2013)
62 ~~showed suggested~~ that 1.04 ± 0.03 was a more appropriate choice and that adopting this value
63 meant that the sink of carbon to the land has been underestimated by up to 14%.

64 Direct ~~atmospheric~~ measurement ~~of OR is possible through simultaneous~~
65 ~~measurements of~~ atmospheric O₂ and CO₂ (e.g. Seibt et al., 2004), however several technical
66 challenges have been noted with this method (see discussion in Masiello et al., 2008). An
67 alternative and complementary approach is to directly measure the OR of biomass pools in
68 the terrestrial biosphere. Masiello et al. (2008) detail the mathematical linkage between the
69 oxidation state of organic carbon (C_{ox}) and OR ~~and another fundamental properties of the~~
70 ~~carbon cycle that of the oxidation state of organic carbon (C_{ox})~~. It is possible to calculate C_{ox},

71 and therefore OR, for the carbon pools (e.g. aboveground biomass) of an ecosystem using
72 elemental analysis of %C, %H, %N and %O.

73 Worrall et al. (2013) based their global estimate of OR on a weighted average of OR
74 values for different soil orders and global-scale biomes. ~~The assumption was, but in so doing~~
75 ~~assumed~~ that the major control on differences in OR was ~~indeed~~ the differences between
76 carbon pools (e.g. soil vs. vegetation) and between soil orders and ~~between~~ vegetation
77 biomes, i.e. that the greatest control on OR variation was a difference between, for example,
78 Inceptisols and Mollisols, or between savannah and boreal forest. This assumption was a
79 necessity arising from the limited amount of data available for individual environments
80 across the globe. Additionally no studies ~~were included~~ where both soil and vegetation were
81 analysed for the same site ~~were included~~ and given the limited number of studies targeted at
82 OR this assumption could not be tested.

83 ~~Therefore, t~~his study aims to assess ~~and understand~~ the variation in OR between two
84 biomes and two soil orders across one country. ~~Thus in this study w~~We aim to test whether
85 the assumption that OR is controlled by differences between soil orders and biomes is true by
86 assessing the magnitude of variation between soil orders and vegetation ~~biomes types in~~
87 comparison to other possible sources of variation. ~~In this study we will consider the variation~~
88 ~~between organic matter types in comparison to the variation within a soil order and the site at~~
89 ~~which we find a soil and its associated vegetation.~~

90

91 **2. Materials and Methods**

92 The approach of this study was to consider the variation in two soil types – peat soils
93 (Histosols) and mineral soils (Inceptisols) across a north-south transect through the United
94 Kingdom. For each site all the possible organic matter types were sampled with the view of

95 comparing the between site, between organic matter types and within site variation in the
96 values of OR.

97

98 2.1. Sampling sites and methodology

99 ~~In~~During the summer of 2011 peat cores were taken from ~~8-eight~~ sites across ~~a climatic~~
100 ~~gradient through~~ the UK (Figure 1; Table 1). Within each peat site the actual location of
101 sampling was chosen as being the least disturbed location available i.e. little or no ~~visible~~
102 land management in recent years. At each ~~sampling~~ location two peat cores of up to 1_m
103 depth were taken using a 70 mm diameter gouge auger. Each core was subdivided into 50
104 mm sections ~~in~~ the field and placed into sealed plastic ~~sample~~ bags. ~~In addition to collecting~~
105 ~~two peat cores at each site,~~ ~~R~~representative samples of dominant vegetation types and surface
106 litter were also collected ~~at each site~~. The exact vegetation composition varied amongst sites
107 (Table 1) but typically at each site the following were sampled: mosses (e.g. *Sphagnum* spp.);
108 sedges (e.g. *Eriophorum* spp.) and shrubs (e.g. *Calluna vulgaris*). ~~The vegetation data were~~
109 ~~split into seven functional groups – shrubs, grasses, sedges, Sphagnum mosses, non-~~
110 ~~Sphagnum mosses, cropland vegetation, and litter.~~

111 ~~To act as a comparative sample f~~For each peat site, two nearby locations ~~not on peat~~
112 ~~soils~~ were ~~also~~ selected for sampling – both ~~locations were~~ on mineral soils, ~~but one was~~
113 ~~chosen~~ under arable and the other under pasture land use. For these comparator sites, soils,
114 litter, and vegetation were sampled. In mineral soils no profile samples were taken because
115 of the paucity of organic carbon at depth ~~in most mineral soils~~ but soil samples were taken
116 from the upper 100 mm ~~using a trowel~~, whilst litter and vegetation were sampled in the same
117 way as for the peatland sites. ~~For the purposes of analysis and reporting,~~ ~~The vegetation data~~
118 ~~were split into seven functional groups – shrubs, grasses, sedges, Sphagnum mosses, non-~~
119 ~~Sphagnum mosses, cropland vegetation, and litter.~~

120 All samples were dried at 105°C for 48 hours prior to further analysis. Peat Bulk
121 density was then calculated on a dry weight basis using the volume of the core section and
122 mass of dry soil solids. The mineral soils were pre-treated using a 2% HF acid solution based
123 on the methods of Mathers et al. (2002) and Skjemstad et al. (1994). ~~Approximately 5g of~~
124 ~~mineral soils were treated with five 50mL aliquots of 2% HF acid and shaken. Supernatants~~
125 ~~were centrifuged and decanted between treatments. Soils were then rinsed with deionised~~
126 ~~water at least 3 times and then dried at 75°C.~~ HF-treated soils, peat, litter and vegetation
127 samples were all ground using a Spex 6770 Cyromill.

128 For comparative purposes, three standard, naturally-occurring organic materials were
129 considered: lignin, humic acid, and cellulose. The lignin and humic acid were from supplied
130 by Aldrich and the cellulose was taken from ash-free paper. ~~The standards were analysed for~~
131 ~~their elemental composition (C, H, N and O) and their energy content (gross heat value, ΔH_c).~~

132

133 2.1.1. CHNO Analysis

134 ~~All samples were analysed for CHNO elemental content.~~ Samples were analysed for their
135 carbon, hydrogen and nitrogen (CHN) and oxygen (O) concentration on a Costech ECS 4010
136 Elemental combustion system with pneumatic autosampler. Oxygen concentrations were
137 analysed on a separate set up to the CHN set up. ~~It was set up for CHN analysis where~~
138 ~~Reactor 1 consisted of chromium (III) oxide/Silvered cobaltous cobaltic oxide catalysts @~~
139 ~~950°C and Reactor 2 consisted of reduced high purity copper wires @ 650°C. Helium was~~
140 ~~used as the carrier gas at a flow rate of 95 ml min⁻¹. This was filtered for hydrocarbons~~
141 ~~upstream of the instrument. A packed 3m GC column was used for separation of the gases.~~
142 ~~A thermal conductivity detector (TCD) was used to calculate the signal of each sample. For~~
143 ~~oxygen (O) concentration, the Costech ECS was also used but was set up for O analysis.~~
144 ~~Reactor 1 consisted of a nickelised carbon/silica chips/nickel wool pyrolysis tube @ 1060°C~~

145 ~~whilst Reactor 2 was left empty. Helium was used as the carrier gas at a flow rate of 130 ml~~
146 ~~min⁻¹ but no oxygen was used. A 2m packed oxygen GC column was used for separation of~~
147 ~~the gases. Chloropentane vapour was added to the carrier gas to enhance decomposition of~~
148 ~~the oxygen compounds and to reduce possible memory effects from previous samples~~
149 ~~(Kirsten, 1977).~~

150 ~~Computer software used was EAS Clarity (DataApex Ltd, Prague, Czech Republic). For~~
151 both CHN and O setups a calibration curve of $r^2 > 0.999$ were created using acetanilide as the
152 standard. Samples of acetanilide were included within each run as unknown samples to act as
153 internal quality control checks. Each sample (peat, soil or vegetation) was analysed in
154 ~~triplicate, i.e. three times on the CHN setup and a further three times on O set up, and a mean~~
155 ~~calculated for C, H, N and O.~~

156

157 2.1.2. Calorimetry

158 Energy content, as gross heat value (ΔH_c), was measured for all peat, vegetation and litter
159 samples. Masiello et al. (2008) has shown that it is possible to derived C_{ox} values (and
160 therefore OR values) from calorimetry data. Analysis was performed on a 6200 Isoperibol
161 Calorimeter (0.1% Precision Classification, Parr Instrument Company, Illinois, USA) with
162 1108(P) Oxygen Bomb. Calibration was performed as a rolling average of 10 measurements
163 using benzoic acid standards. ~~Samples were placed in crucibles and compressed to stabilise~~
164 ~~the peat surface and weighed following compression, with a weight of approximately 0.8 g~~
165 ~~used. Where sample amount was deficient, a benzoic acid spike was used. Following~~
166 ~~analysis, fuse corrections were performed by measuring the length of fuse wire remaining,~~
167 ~~measured in calories and converting to MJ/Kg. The difference was taken away from the~~
168 ~~energy content recorded during analysis.~~ Limited organic matter contents ~~sample~~ meant that
169 gross heat values could not be calculated for mineral soils.

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170

171 2.1.3. C_{ox} and oxidative ratio (OR) calculation

172 A value of OR can be calculated from the carbon oxidation state (C_{ox}) which in turn can be
173 calculated from elemental compositions of organic matter as follows (Masiello et al., 2008):

174

175
$$C_{ox} = \frac{2[O] - [H] + 3[N]}{[C]}$$
 Equation 2

176

177 Where: [X] = molar concentration of C, H, N or O, and assuming the majority of organic
178 nitrogen exists as amine groups in amino acids. Furthermore, sulphur is not included in this
179 equation as it is assumed to form < 0.25% of biomass (Charlson et al., 2000).

180

181 As C_{ox} and OR are related through the balancing of organic matter synthesis, the OR value is
182 calculated as the ratio of O_2 and CO_2 coefficients (for further details see Masiello et al.,
183 2008). ~~(for further details see Masiello et al. (2008)).~~ Simplified, it is ~~then~~ calculated as:

184

185
$$OR = 1 - \frac{C_{ox}}{4} + \frac{3[N]}{4[C]}$$
 Equation 3

186

187 Equation 3 assumes that there is no contribution to the C_{ox} from S or P, and it has been shown
188 that the error in the OR of making such an assumption would be only ± 0.002 (Hockaday et
189 al., 2009). This equation also assumes that the nitrogen source in carbon fixation is N_2 . ~~There~~
190 ~~are two further possible nitrogen (N) conversions (Masiello et al., 2008):~~

191

192 ~~Ammonia (NH_3): $OR = 1 - \frac{C_{ox}}{4}$ Equation 4~~

193 ~~Nitrate (HNO_3): $OR = 1 - \frac{C_{ox}}{4} + \frac{2[N]}{[C]}$ Equation 5~~

194
195 ~~For the purposes of this paper, Equation 3 was used as N₂ is the dominant form in the~~
196 ~~peatland ecosystem.~~ The agricultural soils will likely received N in other forms in addition to
197 N₂, but no data were available for these sites and other studies have shown minimal changes
198 in OR when using alternative assumptions ~~for the reason that [N]/[C] is always likely to be <~~
199 ~~0.1~~ (Gallagher et al., in review).

200 As a quality control check, OR values were only calculated for those samples that had
201 measured data for C, H, N and O; if one of these data were missing (e.g. lost sample), no OR
202 value was calculated.

203

204 2.2. Statistical analysis

205 2.3. Analysis of Variance (ANOVA)

206 The design of the study allows for a several statistical comparisons to be made using an
207 ANOVA approach. Firstly, one-way ANOVA was used to test whether there were
208 significant differences within the organic matter types being considered. This set of ANOVA
209 could be sub-divided into ~~several~~ separate ANOVA: the difference in OR for mineral soils
210 under arable and under pasture; the difference in OR between vegetation functional groups
211 ~~where the factor levels were: shrubs, grasses, sedges, Sphagnum mosses, non-Sphagnum~~
212 ~~mosses, cropland vegetation, and litter~~. The second set of ANOVA that could be performed
213 was for the peat soils only. A two-way ANOVA was used to determine the statistical
214 significance of the factors – site and peat depth. Finally, the variation in organic matter types
215 between sites was examined. All types of ~~the~~ organic matter ~~types~~ were considered and all
216 sites but for comparison with the mineral soil samples, only the surface samples of peat soils
217 from each site were included (depth < 20 cm). Further, for reasons of cross-classification

218 between the factor levels the depth in the peat profile, the vegetation functional group, and
219 the land use of the mineral soil were not considered as a separate factor.

220 ~~Response variables used were energy content, C_{ox}, and OR. If necessary t~~The
221 response variables were ~~log-transformed to ensure data normality prior to ANOVA. tested for~~
222 ~~normality prior to ANOVA using the Anderson Darling test; if the response variable failed~~
223 ~~the test it was log-transformed and re-tested. Further transformation to ensure normality of~~
224 ~~the response variable did not prove necessary. The Post-hoc testing of the results was~~
225 ~~performed using the~~ Tukey test at 95% level was used to determine significant differences
226 between levels of any factor. The magnitude of the effects of each significant factor and
227 interaction were calculated using the generalized ω^2 (Olejnik and Algina, 2003). ~~Response~~
228 ~~variables used were: C/N ratio, H/C ratio, O/C ratio, energy content, C_{ox}, and OR.~~

229 ~~A power analysis was used to assess the minimum effect size that could be detected~~
230 ~~within this latter comparison of organic matter type and site. The study was fully factorial~~
231 ~~with respect to each of 2 factors, 3 centre points were assumed; the standard deviation was~~
232 ~~estimated as the square root of the mean square difference; and the required experimental~~
233 ~~power was set at 80%.~~

235 2.4. OR and ΔH_c

236 Masiello et al. (2008) used ΔH_c from calorimetry to calculate C_{ox} values for a range of
237 standard materials. If ~~then~~ there is a relationship between C_{ox} and ΔH_c it might be reasonable
238 to expect there to be a relationship between ΔH_c and OR values from this study. If so it may
239 be able to shed some light on underlying mechanisms leading to OR variation ~~and also~~
240 ~~provide a simpler method of calculating OR for many materials.~~ Therefore, ΔH_c values were
241 plotted against OR values for the peat soils and vegetation along-together with the standard

Comment [F1]: 80% is like 95% in stats test – I SHALL TRY AND FIND A REFERENCE OTHERWISE I WILL USE A FOOTNOTE

Comment [GC2]: R2: can you justify this percentage

Comment [F3]: You might want to cut this.

Comment [GC4]: Think we just cut this to save on space

242 materials – cellulose, lignin and humic acid. Mineral soils were excluded from this analysis
243 as no ΔH_c values could be calculated.

244

245 2.5. Global OR values

246 The data from this survey can be used to update the estimation of global OR made by Worrall
247 et al. (2013). Worrall et al. (2013) have proposed a weighted average ~~approach based upon~~
248 ~~the residence time of carbon in vegetation and in soil as this gives a greater importance to the~~
249 ~~faster turnover of carbon in the vegetation pool. Therefore:~~

250

$$251 \quad OR_{terra}^{global} = f_{soil}^{terra} OR_{soil}^{global} + f_{veg}^{terra} OR_{veg}^{global} \quad \text{Equation 64}$$

252

253 Where: OR_{terra}^{global} = the oxidative ratio of the global terrestrial biosphere; OR_{soil}^{global} = the
254 oxidative ratio of the global soils; OR_{veg}^{global} = the oxidative ratio of the global vegetation;
255 f_{soil}^{terra} = the proportion of the terrestrial biosphere C annual flux that is due to soils; and
256 f_{veg}^{terra} = the proportion of the terrestrial biosphere C annual flux that is due to vegetation.

257

258 The annual flux from the soils or vegetation was based upon the size of reservoir divided by
259 the average residence time. The comparative sizes of the soil and vegetation reservoirs ~~was~~
260 ~~were~~ estimated from Eswaran et al. (1993) and Olson et al. (2001), ~~where~~ the proportion of
261 carbon in the vegetation reservoir was 0.28 and in the soil reservoir ~~as~~ 0.72. The average
262 carbon residence time for soils was taken as between 20 and 40 years based upon a study by
263 Jenkinson and Rayner (1977). ~~Mills et al. (2014)~~ (2014) ~~examined radiocarbon results for~~
264 ~~133 UK soils and found that the carbon turnover was best modelled as two pools – a fast~~
265 ~~pool with 20 year residence time and a slow, 1000 year turnover pool.~~ –The average carbon
266 residence time for vegetation was taken as between 2 and 5 years (e.g. Gaudinski et al.,

267 | 2000). We recognize that the OR of soil fluxes and soil pools may not be identical (just as the
268 | carbon isotopic values of the bulk soil carbon pool rarely match the carbon isotopic values of
269 | the soil CO₂ flux). However, we must start with the assumption of equivalence between soil
270 | OR flux values and OR pool values because no data yet exist comparing soil pool and flux
271 | OR values. Given the above approach the values of $f_{soil}^{terra} = 0.27$ and $f_{veg}^{terra} = 0.73$. The
272 | value of OR_{veg}^{global} is the weighted average of the expected values of the 16 global biomes
273 | where the weighting is the area of each biome (Loveland and Belward, 1997). ~~and~~ OR_{soil}^{global}
274 | is the weighted average of the expected values of each of the soil orders of USDA soil
275 | taxonomy where the weighting is the organic carbon content of each order (Eswaran et al.,
276 | 1993). Since in both cases the data for any one biome or soil order ~~is-are~~ scarce, then the
277 | expected value is taken as the median of each biome or soil order.

278 | Worrall et al. (2013) applied Equation ~~6-4~~ based upon the classifying organic material
279 | samples into one of either the 12 USDA soil orders (~~although~~ Gelisols and Histosols were
280 | combined into ~~one because of lack of data~~) or 16 global biomes (Loveland and Belward,
281 | 1997). The soil samples collected as part of this study were classified as either Inceptisols or
282 | Histosols. The vegetation samples can be classified ~~as in one of the following~~: Grassland,
283 | Cropland, Shrubland or Permanent wetland.

285 | 3. Results

286 | Overall OR could be calculated for 251 peat samples, 49 vegetation samples and 14 mineral
287 | soil samples. Table 2 shows the data ~~for the individual elemental concentrations~~ for each of
288 | the material types whilst Tables 3 and 4 show the parameters for vegetation and peat soils
289 | respectively. ~~and~~ ~~†~~ The composition of the standard ~~materials~~, ~~naturally occurring organic~~
290 | ~~types~~ are listed in Table 5. None of the datasets needed to be transformed prior to ANOVA.

291 Of the three material types, vegetation samples had the lowest OR values followed by
292 peat soils; mineral soils showed the highest OR values (Table 2). The values for mineral soils
293 are within the range of previously reported values (Hockaday et al., 2009) though the peat
294 and vegetation means were lower than 1.1 ~~though-but~~ still within the range of results reported
295 by Worrall et al. (2013).

296

297 3.1. Variation within organic matter type

298 Mineral soils

299 Within the mineral soil dataset it was possible to determine whether there was a significant
300 difference between land uses, i.e. between soils under arable and soils under pasture. Results
301 from the one-way ANOVA shows that there were no significant differences in ~~elemental ratio~~
302 ~~data (C/N, O/C, and H/C), C_{ox} or OR~~ between mineral soils (n = 14) under different land
303 uses.

304

305 Vegetation types

306 Within the vegetation data, there were significant ~~(p < 0.05)~~ differences in ~~all elemental~~
307 ~~ratios,~~ energy content (p < 0.001), C_{ox} (p < 0.018) and OR (p < 0.001) values between
308 vegetation functional groups ~~(Table 6)~~ from the one-way ANOVA. The *post hoc* testing
309 showed ~~a great deal of variation in where the significant differences lay. For example, for~~
310 ~~C/N ratio the only difference lay between non-Sphagnum mosses and arable crops and~~
311 ~~grasses (Table 6) with grasses and crops having the lower C/N ratio (Table 3). However, for~~
312 ~~other elemental ratios and energy content there were a number of significant differences~~
313 ~~between functional groups (Table 6).~~ The highest OR values were found in shrubs (e.g.
314 *Calluna vulgaris*, *Erica tetralix*) whilst the lowest values were found in mosses, both
315 *Sphagnum* and non-*Sphagnum* (Table 3). The reverse of this ~~is-was~~ true for C_{ox} values where

316 the lowest values were found on shrubs and the highest on *Sphagnum*. ~~However, the variation~~
317 ~~within these functional groups meant that only certain combinations of groups were~~
318 ~~statistically different from one another (Table 6).~~

319

320 *Peat Soils*

321 In the ANOVA model, site and peat depth were included but due to a collinearity between
322 site and depth, the interaction term could not be plotted.

323 For all the measured parameters, the site factor was found to be significant (Table 76).
324 ~~Post hoc testing of site factor for each parameter showed considerable variation between sites~~
325 ~~(Table 8). For example, with C/N ratios, Auchencorth and Forsinard showed the lowest~~
326 ~~values whilst the highest values were found on Westhay Moor (Table 4). The extremes for~~
327 ~~O/C ratios were found between Whixhall and Dartmoor, whilst for H/C ratios the largest~~
328 ~~ratios were found on Forsinard and the lowest on Thorne (Table 4). showed T the lowest~~
329 energy contents were found at Auchencorth with the highest at Dartmoor (Table 4). There
330 were significant differences between peatland sites in terms of C_{ox} and OR values explaining
331 21% and 39% of the variation in the data respectively (Table 76). ~~Post hoc testing (Table 8)~~
332 ~~showed that The lowest OR values gave some similar patterns to the elemental data~~
333 ~~were found at Thorne resulting in the lowest OR values whilst and Forsinard and Bodmin~~
334 ~~having had the highest OR values.~~

335 Depth was a significant factor for ~~all parameters~~ bulk density and energy content
336 although not significant for -with the exception of C_{ox} and OR (Table 76). ~~In terms of down~~
337 ~~core profiles generally t~~ There were increases in ~~C/N ratio and~~ energy content down the core
338 ~~and decreases in O/C and H/C ratios with depth (Figure 2). These profiles were as would be~~
339 ~~expected as the peat becomes more carbon rich with depth. whilst t~~ The observed data for bulk

340 density ~~was were~~ more complex ~~and; across all cores the~~ bulk density ~~generally~~ increased in
341 the upper 30 centimetres before decreasing with depth (Figure 2).

342

343 3.2. Organic matter type vs. site

344 It was possible to analyse the differences between surficial peat (0 – 20 cm), vegetation and
345 surface mineral soils across all the sites considered in study for ~~the element ratios and OR.~~
346 Bulk density and energy content were not considered because neither could be measured for
347 all sample types. ~~but because the analysis covered all the organic matter types being~~
348 considered then it was not possible to include the bulk density and the energy content. The
349 analysis was performed with the caveats that the above analysis found the following
350 significant differences: there were significant differences in the OR between vegetation
351 functional group; there were no significant differences between OR for different land uses on
352 the mineral soils; and there were no significant differences with depth for the OR of peat
353 soils. ~~The power analysis shows that this design was capable of detecting a difference of 0.02~~
354 ~~in the OR at the 80% probability.~~

355 When comparing all organic matter types and all sites for elemental ratios and OR
356 there were significant differences between the site and organic matter type factors (Table 97).
357 For the OR values the most important of the factors was the difference between organic
358 matter types (explaining 70% of the original variance) and *post hoc* testing showed that there
359 were significant differences between all the organic matter types considered. The highest OR
360 values given by the mineral soils (1.15 ± 0.01) followed by peat soils (1.079 ± 0.006) with
361 the lowest OR represented by vegetation (1.037 ± 0.007) where the values are given as the
362 estimated marginal means (averages accounting for all other factors and covariates) and the
363 uncertainty in each is given as the standard error. The variation between organic matter types
364 was greater than the variation between sites with the site factor explaining only 21% of the

365 original variance. The *post hoc* testing between the individual sites shows that only one site,
366 Thorne, was significantly different from all the others ~~—Thorne was significantly lower than~~
367 ~~all other sites~~ (Figure 3; ~~Table 10~~). When the data for Thorne were removed then
368 Auchencorth was found to have OR values significantly higher than all other sites: there were
369 no other significant differences between any other sites considered in this study.

370 ~~When the elemental ratios were considered then the first observation was that there~~
371 ~~were no significant differences between the sampled sites for the O/C ratio (Table 9); this~~
372 ~~study could find no evidence that O/C varied across the UK. For both the C/N and H/C ratios,~~
373 ~~and as for the OR values, the organic matter type factor was more important than the site~~
374 ~~factor (Table 9). Post hoc testing of the elemental ratios shows two distinct patterns. For the~~
375 ~~C/N ratio the post hoc testing shows that the significant difference between sites was been~~
376 ~~Westhay (C/N = 43 ± 3) and the samples from both Dartmoor (C/N = 26 ± 3) and Bodmin~~
377 ~~(C/N = 24 ± 4). For the H/C ratio the significant difference between sites lay between Thorne~~
378 ~~and Auchencorth, Bodmin, Dartmoor, Forsinard and Whixall with Thorne having~~
379 ~~significantly lower values. The pattern of the differences in the H/C ratios is distinctly closer~~
380 ~~to that observed for the OR values than the pattern observed for C/N ratios and thus implying~~
381 ~~that the difference at the Thorne site was due to the H/C ratios and not due to differences in O~~
382 ~~or N.~~

383 There was no significant interaction between the site and organic matter type factors
384 for any of the parameters considered in this study. The lack of significant interaction between
385 the two factors means that the difference between organic matter types does not vary with site
386 suggesting that Inceptisol is different from a Histosol regardless of the position within the UK
387 and as such there is a fixed relationship between the organic matter types. Regressing the
388 mean vegetation OR and mean bulk peat OR for each of the eight sites shows no significant
389 relationship between them.

390

391 3.3. Variation in Organic Matter Composition

392 A comparison of OR and ΔH_c ~~with respect to~~ peat soil samples and ~~the~~ vegetation samples
393 show several possible patterns (Figure 4a and b). Given the result of Masiello et al. (2008) it
394 would be expected that OR would increase with ΔH_c and ~~this is true for such a relationship is~~
395 ~~discernible in these plots as the line between~~ the organic material standards (humic acid,
396 cellulose and lignin). With respect to the sampled peat sites some of the soils sampled from
397 Thorne, Westhay and the Peak District plot below this line with lower ΔH_c values than would
398 be expected for their OR values (Figure 4a). Conversely, all the samples from all the other
399 sites (Auchencorth, Bodmin, Dartmoor, Forsinard and Whixall) plot above this line with OR
400 greater than the equivalent mix of the organic matter standards. Furthermore, it could be
401 proposed that majority of samples form a 3 end- member triangle the end-members of which
402 are marked by humic acid, lignin and a high OR end-member represented by peat soil
403 samples from Forsinard (Figure 4a). The latter end-member with high OR represents organic
404 matter that is as reduced as the lignin standard but does not have the calorific value. Some
405 soil samples plotted at even lower values of ΔH_c than those from Forsinard and these come
406 from Auchencorth. ~~One possible explanation of this is that the peat soil at Auchencorth has~~
407 ~~received inputs of mineral matter. It had visible evidence of trace mineral matter in the field.~~
408 Inputs of fine silt or clay into the peat would not alter the measurement of OR as it is based
409 on a ratio of elements in the organic matter but it would ~~in effect dilute out~~ the energy value
410 of any sample. ~~It it~~ may also explain large values of bulk density observed for this site
411 which contribute to inflexion in the bulk density profile (Figure 2).

412 ~~With respect to vegetation type m~~Most vegetation types were better constrained
413 within the line defined by the organic matter standards (Figure 4b) and the peat samples from
414 Forsinard than was observed for the peat soils (Figure 4a). The end-member represented by

Comment [GC5]: R2: Surely you could test this through lab analyses

Comment [F6]: We can confirm by ash content if you want?

Comment [GC7]: Sentence updated to say mineral matter was observed

415 the peat soils of Forsinard plots close to the samples of *Erica tetralix*. Some samples of both
416 grass and *Sphagnum* plot at lower values of OR than would be expected from a combination
417 of the organic matter standards ~~and this type of plant material which is more oxidised than~~
418 ~~any combination of the standards but at similar calorific value.~~

419

420 4. Discussion

421 This study has ~~been able to comment on~~ evaluated the oxidation status of peat (Median OR =
422 1.10) and agricultural soils (Median OR = 1.14) across a latitudinal transect across the United
423 Kingdom. Significant differences were found in the oxidative ratio of major terrestrial
424 carbon pools (soil and vegetation). This is perhaps not unsurprising given the different
425 processes operating in each carbon pool but this study has been able to quantify the
426 difference with respect to OR.

427 Within-group variation of OR generated a number of interesting results. Firstly, soils
428 under agricultural management did not vary significantly in their OR value. One might expect
429 that different management practices, and different vegetation types, would influence soil
430 processes ~~that which~~ would, in turn, affect OR. ~~Even from this study it~~ It is possible to see the
431 large contrast between cellulose and lignin, and so woody vegetation ~~that is woodier~~ would
432 be expected to have a higher OR than non-woody types. Furthermore, N is a component of
433 the oxidation state of an ecosystem (Equation 2) and so diversity of N inputs and N sources
434 (e.g. organic wastes vs. inorganic fertiliser) might be expected to shift the OR of an
435 environment. ~~However, this result is for the ecosystem and not the components of that~~
436 ~~ecosystem (e.g. soil or vegetation) and the lack of observed difference between grasslands~~
437 ~~and croplands in this study may reflect totality and not just processes that affect vegetation~~
438 ~~alone.~~

439 Secondly, OR did not vary significantly with depth and there was ~~not no~~ consistent
440 ~~OR depth profile variation between~~ across all the sites. ~~Peat depth was an important factor in~~
441 ~~the elemental ratio datasets and many of these trends can be used to identify structural~~
442 ~~changes in the peat and to infer changes in the peat decomposition process. The C/N ratio~~
443 ~~can be used to infer decomposition rates, specifically the loss of mass, whilst the H/C and~~
444 ~~O/C ratio are commonly used to infer humification rates. Decreases in H/C ratios and O/C~~
445 ~~ratios are specifically linked to dehydrogenation and decarboxylation respectively.~~ The lack
446 of a significant OR trends is perhaps one of the more unusual observations from this study.
447 Given the classical explanation of peat formation it would be expected that C_{ox} would decline
448 with depth as the peat profile becomes more anaerobic, and therefore an increase in OR
449 would be expected. ~~The classical explanation of peat soils is that they rapidly become~~
450 ~~anaerobic. In peat soils anaerobic conditions result from~~ ~~due to~~ excess organic matter and
451 slow ingress of air due to persistent waterlogged conditions, leading to successive use and
452 exhaustion of redox couples (Reddy and D'Angelo, 1994). However, this succession is noted
453 mainly for inorganic ~~chemical~~ species (e.g. Fe(III)) in soil water and for peat soil water
454 concentrations are often low compared to mineral soils giving them very little buffering
455 capacity with respect to redox conditions meaning that species in solutions are rapidly
456 transformed, e.g. Fe(III) to Fe(II). However, the ~~concentration of inorganic redox species that~~
457 ~~can be reduced is very low~~ ~~amount of reduction occurring is minimal~~ in comparison to the
458 amount of organic matter that could be oxidised and so therefore dramatic changes in
459 ~~inorganic~~ soil solution ~~chemistry~~ are not reflected in the substrate.

460 ~~Thirdly, when examining the variation in organic matter composition a number of~~
461 ~~samples plotted outside of the 3 end member space delineated by humic acid, lignin and the~~
462 ~~high OR end member (Figure 4a). Of particular note is that many of the samples of peat soil~~
463 ~~from the site at Auchencorth plot at values of ΔH_c outside this triangle and this is probably~~

464 ~~due to inputs of silt. Furthermore, some of the vegetation samples also plotted at lower than~~
465 ~~expected OR values. Whatever component lends low OR values to these grass and~~
466 ~~*Sphagnum* samples may be part of the explanation of low OR peat samples from the sites at~~
467 ~~Thorne, Westhay and the Peak District. Equally, the composition of the proposed third end-~~
468 ~~member is not known.~~

469 By considering natural organic carbon reservoirs in a structured survey, this study has
470 examined the variation in OR and it can assess whether the global assessment of OR
471 proposed by Worrall et al. (2013) was appropriate. Firstly, the study has shown that it ~~is was~~
472 possible to distinguish between the naturally-occurring organic matter types (e.g. soil and
473 vegetation) when looking at OR; that is there ~~is are a~~ significant differences between organic
474 carbon pools that are easy to sample and model over large scales.

475 Secondly, Worrall et al. (2013) could only use the data that ~~was were~~ available in the
476 published literature so had little control on the soils orders available and their geographic
477 distribution. This study has been able to take one soil order (Histosols) and compare the OR
478 across a range of locations under similar management in order to assess the relative source of
479 variation in OR. ~~However, the study can show~~ It has shown that there is more variation
480 between carbon pools than between sites but that the variation between carbon pools is
481 independent of the changes between sites, ~~i.e., t~~ This is good statistical justification to support
482 the approach used in Worrall et al. (2013) that as a first approximation, and at large scales,
483 OR is better understood by considering soil and vegetation separately. Thirdly, the study has
484 shown a significant difference between the two soil orders considered by this study (Histosols
485 and Inceptisols) which is an underlying assumption of Worrall et al. (2013) and of the
486 calculation of OR_{soil}^{global} . ~~But as discussed above there was no significant difference but two of~~
487 ~~the biomes directly analysed, i.e. grassland and croplands.~~

488 Fourthly, we can start to address the question of what kind of sample is truly
489 representative of the OR of an environment. Results from the study showed that if OR does
490 not vary with peat depth, then it may be appropriate just to sample the surface peat rather than
491 coring. If peat can be simplified to ~~just~~ surface samples, can the OR of the environment be
492 simplified to ~~just~~ one sample? This study has ~~looked at the vegetation associated with the~~
493 ~~soils and has~~ shown that vegetation and peat samples were not significantly similar to each
494 other to warrant only one sample being taken. Therefore future sampling should concentrate
495 on sampling both the vegetation and soils carbon pools.

496 Finally, this study is a continuation of earlier work (Worrall et al., 2013) ~~that~~
497 ~~calculated a global OR value from a database of OR values. and T~~his study is able to ~~add to~~
498 ~~that database and is able to~~ update the global OR figure accordingly. The peat soils from this
499 study are classified as Histosols ~~in the USDA soil taxonomy. and in~~ Worrall et al. (2013) list
500 Histosols as having an OR of 1.03 (range 0.92 – 1.11) based on 8 studies, 23 locations and
501 345 samples - updating these values with data from this study gives an OR for Histosols of
502 1.08 with an interquartile range of 1.05 - 1.11, based now on 9 studies, 31 locations and 596
503 samples. The mineral soils for this study could be classed as Inceptisols ~~in the review of~~
504 Worrall et al. (2013) the Inceptisols had an OR of 1.07 (range 1.03 to 1.10) based on 2 soils
505 from 1 study this can now be updated to be from 2 studies and 7 sites with 18 samples to give
506 a median value of 1.15 (IQR 1.10 to 1.15). Coupling this information with new estimates for
507 Alfisols (Worrall et al., in review) that updated the OR of 1.10 (range = 1.07 to 1.12) based
508 upon 1 study and 4 soil samples to that of 1.12 (range = 1.08 to 1.19) based upon 2 studies
509 and 2 soils but 84 samples. This would give a new value of $OR_{soil}^{global} = 1.084 \pm 0.002$, where
510 the uncertainty is interquartile range. Similarly, the values for vegetation types can be
511 updated, for grassland the new estimate would be 1.02 with an interquartile range of 1.00 –
512 1.05; croplands would now have a median value of 1.00 (0.99 – 1.05); shrublands with a

513 median value of 1.10 (1.08 to 1.12); and permanent wetlands with a median of 1.02 (0.99 –
514 1.04). This gives an $OR_{veg}^{global} = 1.049 \pm 0.2$ (error as IQR). A new residence time weighted
515 global OR estimate for the terrestrial biosphere (OR_{terra}^{global}) of 1.056 (IQR = 1.054 to 1.058)
516 can be calculated; the previous value of OR_{terra}^{global} was 1.04 ± 0.03 .

517 This study has been able to validate the sampling approach of Worrall et al. (2013)
518 ~~but i.e. sampling the major carbon pools, but this work is able to now suggest that this can be~~
519 ~~improved further.~~ By increasing the level of sophistication and characterising individual
520 components of the carbon pools e.g. lignin vs. cellulose components, active vs. passive soil
521 organic matter, or dissolved organic carbon (DOC) fractions, it may be possible to elucidate
522 the underlying controls on OR in the terrestrial environment. Future research should
523 therefore explore these factors.

524

525 **5. Conclusion**

526 This study has shown that there are significant differences in oxidative ratio (~~OR~~) between
527 mineral soils, peats and vegetation. Whilst there were significant differences in OR between
528 different sites and material types, there was no significant interaction between the factors.
529 ~~Furthermore there was no significant difference in OR with peat depth.~~ This suggests, on a
530 large scale at least, that it the most important factor in OR variation is material type rather
531 than site location and the OR of an environment can be determined by simple sampling of the
532 major terrestrial carbon pools.

533

534 **Acknowledgements**

535 The authors thank the help and support of various land owners, managers and colleagues in
536 allowing access to the various sites and for local site knowledge: Norrie Russell (RSPB
537 Forsinard); Kerry Dinsmore and Mike Billett (CEH Edinburgh); Pippa Chapman (University

538 of Leeds); Tim Kohler (Natural England); Joan Daniels (Natural England Reserve Manager,
539 Whixhall Moss); Mark Blake (Somerset Wildlife Trust); Lauren Parry (University of Leeds),
540 Dan Charman (Exeter University). Thanks to Darren Gröcke and Joanne Peterkin for
541 assistance with CHNO analysis.

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610

611

612 Figure 1. Location of study sites within Great Britain.

613

614 Figure 2. Interval plot of elemental ratios, energy content (MJ/kg), bulk density (g/cm^3) and

615 Oxidative Ratio with peat depth. 95% confidence interval of the mean

616

617 Figure 3. Interval plot of OR for surficial peat samples for each site. 95% confidence interval

618 of the mean

619

620 Figure 4. Plot of OR vs. ΔHc . a) Peat soil samples highlighted; b) Vegetation samples

621 highlighted.

622

623

624 Table 1. Location information for each of the sites

625

626 Table 2. Median values (inter-quartile range in parentheses) for each measured or derived
627 variable for the three material types.

628

629 Table 3. Median values (inter-quartile range in parentheses) for each measured or derived
630 variable for functional plant groups

631

632 Table 4. Median values (inter-quartile range in parentheses) for each measured or derived
633 variable for peat soils by site.

634

635 Table 5. Median values (inter-quartile range in parentheses) for each measured or derived
636 variable for the three standards

637

638 ~~Table 6. One-way ANOVA within vegetation. p = probability of factor being zero, *post hoc*
639 testing where \neq denotes a significant difference between levels.~~

640

641 Table 6. ANOVA for peat samples energy content, C_{ox} and OR values, and bulk density. df =
642 degrees of freedom, p = probability of factor being zero, ω^2 = generalized proportion of
643 variance explained

644 ~~Table 7. ANOVA for peat samples elemental ratios and OR values, energy content and bulk~~
645 ~~density. df = degrees of freedom, p = probability of factor being zero, ω^2 = generalized~~
646 ~~proportion of variance explained~~

647

648 | ~~Table 8. Post hoc testing of site factor from Table 7 (ANOVA) where \neq denotes a~~
649 | ~~significant difference between levels~~

650

651 | Table ~~9~~7. ANOVA for the comparison of surficial peat and mineral soils with vegetation. df
652 | = degrees of freedom, p = probability of factor being zero, ω^2 = generalized proportion of
653 | variance explained

654

655 | ~~Table 10. Post hoc testing of site factor from Table 9 (ANOVA) where \neq denotes a~~
656 | ~~significant difference between levels.~~

Field Code Changed