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Interactive comment on "Comparison of different methods to determine the degree of peat decomposition in peat bogs" *by* H. Biester et al.

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Bg-2013-444 Final Response to referee comments:

We thank the reviewers for their constructive comments and suggestions which we believe will improve the manuscript.

Referee #1 This paper aims to evaluate peat decomposition proxies as indicators for decompositionprocesses in two ombrotrophic mires. They characterize and compare severalmeasures of decomposition proxies in depth profiles of these mires, including pyrolysis-GC-MS, C/N ratios, stable isotopes of C and N, FTIR spectroscopy, Rock Eval oxygenand hydrogen indices, and humic acid UV adsorption. This study is an impressive and comprehensive comparison of different methods usedto quantify OM de-

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composition. The authors highlight that depth profiles of many ofthese indices are both affected by decomposition processes, vegetation changes, andpossibly other external and internal factors (e.g., N deposition and recycling). A particularstrength of this study is the use of molecular analysis using GC-MS attemptto differentiate between these processes and discuss the performance of each thedecomposition proxies in regards to molecular tracers. As mentioned, this is a verycomprehensive characterization of biogeochemical decomposition measures in peatbogs with high relevance for climate reconstruction and characterization of historic depositioninputs of trace elements. The analyses, although I am not fully familiar with allof the techniques used, seem very sound, are well described, and seem to have appropriatequality control measures. Overall, this is a highly suitable paper for publicationin Biogeosciences. The introduction is very well written, clearly lays out the issues withmany of these decomposition proxies, and is very well referenced – in short, it does anexcellent job to highlight the need and importance of this study.

My major concern with the paper is the current structure of the results and discussionsections which makes it very difficult for the reader to understand the analysis, comparisons,and their respective interpretations. One reason for this may be that the paper isextremely dense and comprehensive, and as such presents a vast amount of data andchemical analysis which are difficult to fully absorb. However, I had to read the resultsand discussion sections many times in order to understand the direction and interpretationof all analysis performed. I strongly suggest that these two sections need to becomprehensively restructured for the readers to be able to follow the arguments madeby the authors – see section below for some suggestions. In particular section 4.3. and the following subsections (4.3.1 through 4.3.5) are extremelycumbersome to follow. I think the main reason is the introduction of the PrincipalComponent Analysis (PCA) and the two factors F1 and F2 that represent watertable heights and degradation of vascular plants based on analysis of GC-MS data. While this is very elegant analysis to compare decomposition measures to moleculartracers, the authors need to prepare the reader much earlier and more directly for thisapproach. For example, they should

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make it a specific goal in the introduction thattheir evaluation of decomposition proxies is based in large parts on molecular analysisand PCA factors, and clearly state that the factors allow to differentiate betweenprocesses contributing to changes in decomposition proxies (i.e., water table height affecting species abundance and decomposition, and decomposition of vascular plants).

A: We agree with the reviewer that the manuscript contains a lot of data and high information density and that some restructuring as proposed by the reviewer might help to improve the readability of the manuscript. We restructured the manuscript following the reviewer's suggestions. First we described at the end of the introduction section that peat structural information obtained by pyrolysis-GC-MS was used as the basis for the interpretation of the peat decomposition indicators. We also added a sentence on how PCA was used to decipher biogeochemical processes related to peat decomposition and vegetation changes. We have also moved the description of pyrolysis-GC-MS results to the beginning of the result section to give the molecular composition of the peat first.

R: If this is clearly laid out in the introduction, and the results and discussion section alsoput an emphasis on this approach, it will be much easier to follow comparison of otherdecomposition proxies to this approach. Similarly, figures should be re-arranged in away to help this restructuring. For example, Figure 4 introducing the two main factorsshould be very early in the manuscript and be discussed early in results and discussionsections. Currently, figure 3 and many text sections show and discuss PCA factors F1and F2 before they are clearly discussed and interpreted.

A: We have now moved the interpretation and discussion of the pyrolysis-GC-MS results to the beginning of the discussion section so that this information is now available for further discussion of the other decomposition proxies. According to this new structure, Fig.1 is now showing the results (depth profiles) of pyrolysis-GC-MS, followed by two figures showing the results (depth profiles) of the decomposition proxies. The discussion section is starting now with the figure showing the interpretation of the

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pyrolysis-GC-MS results (distribution of factor loading of proxies and pyrolysis products).

R: Then, I suggest that a morestructured comparison of decomposition proxies to these factors should be done; forexample, in Figure 5 only one regression is shown relating decomposition proxies toF1 (i.e., for C/N), but large parts of sections 4.3.1 through 4.3.5. specifically discuss relationshipsto F1 and F2 to decomposition proxies without showing these relationships.To help this, the correlation matrix between factors F1/F2 and decomposition proxiescurrently shown in Suppl. Table S3 could be moved to the main text. Other figures ofthe manuscript (e.g., Fig. 1, Fig. 2, and possibly Figure 3) could possibly be movedfrom the main manuscript to the supplemental information.

A: We agree that some more of the relationships (correlations) between decomposition proxies and F1 and F2 factors should be shown. We decided to add this information to Figure 5 because we think that a correlation matrix with large amounts of proxies in the main text is even more difficult to follow.

R: While I do not insist on restructuring the manuscript exactly the way I mentioned above,I need to re-emphasize the need to restructure the results and discussion section. Thisis really a great dataset with unique and elegant analysis and interpretations, but Ithink in its current form many readers will be overwhelmed and not be able to followthe reasoning of the authors without repeated reading.

A: We agree on that, however, we doubt that it is possible to thoroughly understand a data set like this without repeated reading, whatever the structure might be.

R: Other comments: Page 17352: Abstract: what is missing in the abstract is the entireapproach using PCA analysis and PCA factors based on molecular characterizationand their relationships to decomposition proxies. This is one of the main aspects indiscussion and should be clearly mentioned and described in the abstract. Has been added

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Page 17352, line 8: “if not misleading” – clarify what is meant here or reword, why/whatis misleading?

Has been removed

Page 17352, line 17: define abbreviation “UV-ABS” when first mentioned

Has been added

Page 17352, line 25: “showed less variation” – less than what, doe they mean theywere stable through the profile?

Has been added

Page 17352, line 28: “reasonable information despite their bulk nature” clarify what is meant and reword

Has been changed

Page 17353, line 21: “has been reported recently” delete recently as these studies areover 10 years ago now.

Has been removed

Page 17354, line 16: add reference

Has been added

Page 17354, line 17: write out versus

Has been changed

Page 17355, line 11: add reference about the impact of fire incidence.

Has been changed

Page 17355, line 19: “more narrow” I assume they mean lower C/N ratios indicative ofmore decomposed peat material?

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Has been changed

Page 17357, line 4: reword the entire sentence starting with “Unless the fact that. . ..”

Has been changed

Page 17357, line 20, the authors use H/C and O/C indices earlier in the manuscript andhere use HI and OI (I guess they mean hydrogen and oxygen indices) – they shouldbe consistent with the terminology through the manuscript and in figures.

A: This was correct because with mentioning the H/C and O/C ratios we intend to indicate what the HI and OI indices actually show.

Page 17359, line 22: define GC-TCD

Has been added

Page 17362: Results: a very important component of the discussion is based on PCAand comparison of decomposition proxies to factors F1 and F2. This should be presentedin the results section, which will make the discussion easier to follow.

Has been restructured

Page 17362, line 12-18; and Table 1 and 2: the authors should show stdev in Table1, and discuss if d13C and d15N are statistically different instead of stating “slightlylighter”

Has been changed

Page 17362, line 23: “a similar trend of increasing values. . .”: the authors should quantify the similarities of trends, e.g., by referring to the correlation matrix or perform consistent scatterplots/regressions between different proxies.

A: We did not quantify the trend, but refereed to the correlation matrix now

Page 17363, line 2: “seem to show inverse relationship. . .” same as above, please quantify.

A: We refereed to the correlation matrix now.

Page 17363, line 24: “a remarkable sharp decrease. . .” this was also observed in the KK profile at about 43 cm depth, why not mention and discuss that also for the KK profile?

Has been added

Page 17363, line 12: “do not correspond to those of any other decomposition proxy”– as mentioned above, the correlations/correlation matrix should be done for all proxy-comparison to quantify similarities/differences between proxies.

A: This information is in the correlation matrix, reference added.

Page 17364, line 3: for that reason, molecular component were only determined in the KK core” I have no problem that molecular composition was only determined in onecore, but I would remove the justification given – as mentioned above, some of thetraditional decomposition proxies show differences between the cores.

A: We think we should keep this explanation, otherwise the reader will probably not understand why the KRB core has not been analyzed.

Page 17365 and 17366: section 3.2.1.and 3.2.2. The reason for presenting thesevegetation markers and molecular characterization becomes only clear later in the discussionsection and the use of these markers in Figure 4. It would help tremendouslyif the reader is prepared for the use of these makers in the PCA analysis and theirfactors, maybe make a separate results section how the markers are used to developfactors F1 and F2 which will then be compared systematically to traditional decompositionproxies.

A: As described above, we changed the structure of the manuscript to make the role of the pyrolysis-GC-MS data and the PCA clearer. We think that PCA should not be a part of the results, but we moved it to the beginning of the discussion section, so that the information of F1 and F2 is now available for discussing the other proxies.

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Page 17366 and following: The discussion should start with a detailed description ofthe use of PCA and Factors 1 and 2, and their interpretation, and then systematicallyinterpret all traditional decomposition proxies in regards to this analysis. This wouldgreatly help to follow the manuscript.

Has been restructured (see comments above).

Page 17366 section 4.1; This section would be much clearer to follow if analysis of molecular tracers was done first and the authors already discuss relationships to factorsF1 and F2 although it is not clear yet what these mean.

Has been restructured (see comments above).

Page 17373, lines 4: “the fact that in our KK peat not lignin. . .” reword

Has been changed

Page 17374, line 12: A comparison of the FTIR intensity. . .is given in Suppl Fig S4). This should probably be mentioned earlier in this discussion section, why introducenew results at the end of a discussion section?

Has been changed

Section 4.3.3. Be consistent with theuse of O/C and H/C and OI and HI.

Has been modified

Page 17378, line 7 reflecting change in mass lo loss and ARE related. . .

Sentence has been correct

Page 17378, line 10 : change “sand” to and

Has been corrected

Page 17378, line 18: change “despites” to despite

Has been corrected

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Page 17379, line 13: change “correlates” with correlate

Has been corrected

Page 17379, line 22, remove comma before changes

Has been changed

Referee #2 General Comments This manuscript has interest because it makes comparison betweenseveral techniques that might be used to investigate past changes in peat decomposition.It is based on studies on two peat cores from one locality – Harz Mountains– and the authors' general conclusions are drawn inductively from this particularlocation. However, whether it is possible to extrapolate from these specific findings towider general application elsewhere is not known (and to an extent, this is acknowledgedin the Conclusions). Indeed, because of the constituents of the peat from thislocation, the choice of mires for making these comparisons between techniques maylimit applicability of the findings. For example, it is somewhat unfortunate that the authors chose mires in which Eriophorumremains are present in the peat, because this taxon is known to produce erraticand potentially erroneous values using one of the techniques reviewed (the colorimetricmethod), owing to the strong contrast in relative decay between unhumifiedEriophorumfibres and the more humified peat matrix. Markedly different results can be obtainedfrom the same analysed horizon in the peat, depending upon which of these fractionshappens to predominate in any 0.2 g sub-sample (Chambers et al., 2011). So, it isperhaps not surprising that the UV-ABS method used on these Harz Mountain peatsproduced results that are different from some of the other techniques applied (this ispartly admitted on p. 17377, lines 16–19, but the specific problem of Eriophorum is notmentioned).

A: We consider the choice of a peatland that has contributions from Eriophorumas representative, as most Sphagnum-dominated peatlands have contributions from this graminoid. Thus, the fact that the colorimetric method is influenced by vascular plants, such asEriophorum, says more about the shortcomings of the method than the selec-

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tion of the peatland. Our data do not indicate that the proposed mechanism influenced the method.

Specific Comments: The review of the literature is not complete. In places, these omissionshave led inadvertently to inaccuracies. For example, on p. 17355 the authorsstate that“Blackford and Chambers (1993) introduced an alkaline extraction (NaOH) procedurecombined with UV absorption measurements to determine differences in the degree ofpeat humification based on the leachate’s color intensity.” It would be more complete to say that“Aaby and Tauber (1975) used Bahnson’s (1968) alkaline extraction (NaOH) procedurecombined with UV absorption measurements to determine differences in the degree ofpeat humification based on the leachate’s color intensity, and related this to bog surfacewetness at the time of peat formation. Blackford and Chambers (1993) comparedthis colorimetric ‘determination of peat humification’ for reconstructing past bog surfacewetness with various other simple methods (such as fibre content; von Post visual humificationscale, etc.), and considered fibre content and the colorimetric technique tobe superior. However, because ‘percentage peat humification’ is a dubious concept,they recommended that results from colorimetry should instead be reported using percentagelight transmission values. A revised protocol for this colorimetric method waspublished recently by Chambers et al. (2011).”

Aaby, B. &Tauber, H. (1975) Rates of peat formation in relation to degree of humificationand local environment, as shown by studies of a raised bog in Denmark. Boreas,4, 1–14.

Bahnson, H. (1968) Kolorimetriskebestermmelserafhumificeringstal i højmosetørvfraFuglsømosepåDjursland (Colorimetric determination of humification for bog peatfrom Fuglsø Mire in Jutland). Meddelelserfra Dansk GeologiskFørening, 18, 55–63.

Chambers, F.M., Beilman, D.W. & Yu, Z. (2011) Methods for determining peat humificationand for quantifying peat bulk density, organic matter and carbon content for-

palaeostudies of climate and peatland carbon dynamics. Mires and Peat, 7, Article 07,1–10.

A: We appreciate this comment and have re-written this section according to the reviewer's suggestion. We also included the suggested references.

p. 17377, lines 22–55. There is no mention here of the work of Morgan et al. (2005),who used size-exclusion chromatography and showed, inter alia, that humic and fulvicacid compounds were being extracted from peats through alkali digestion; there wereimplications about their structures and molecular masses. Morgan, T.J., Herod, A.A.,

Brain, S.A., Chambers, F.M. and Kandiyoti, R. (2005) Examination of soil contaminatedby coal-liquids by size-exclusion chromatography in 1-methyl-2-pyrrolidinone solutionto evaluate interference from humic and fulvic acids and extracts from peat. Journal ofChromatography, 1095, 81–88

A: We suggest avoiding these references as they are focused solely on the chemical characteristics of NaOH extracted humic and fulvic acids, which is not the topic of our manuscript.

Nowhere in the manuscript are there cited any of the several relevant papers onproxy-climate methods from peats that were published in Mires and Peat, vol 7: http://www.mires-and-peat.net/mpj3.html#Vol7 It is important to cite some of these becausethey represent state-of-the-art laboratory protocols for various proxy-climatemethods from peats, including those of testate amoebae, peat geochemistry, pollenand non-pollen microfossils, peat humification, etc., and they are more up-to-date thanother papers regarding specific techniques (e.g. analysis of testate amoebae) that arecited by the authors. Some of the papers (in that volume of Mires and Peat) were publishedin 2010; others in 2011. It is unclear also whether the field-sampling protocol ofDe Vleeschouwer et al. (2010; in that same volume) was followed by the authors whenthey sampled the Harz mires.

A: We have cited two references from Mires and Peat (Chambers, Klavins) which we think are relevant for this manuscript on peat decomposition. Our study does not include testate amoebae, pollen or non-pollen microfossils which are climate proxies but no specific proxies for peat decomposition; we therefore decide not to cite them here. Our peat cores were extracted in 2008 prior to the publication of the field-sampling protocol of De Vleeschouwer et al. (2010). We also think that this protocol is not crucial here, as it is predominately designed for trace element analysis and not validated for decomposition studies. We also believe that we gained sufficient experience during the past 15 years to extract representative peat samples.

p.17367 The comment that “Changes in humic acids may thus reflect more a signalof vegetation changes than of changes in humification or decomposition alone” is nota new finding. That there is a ‘species’ signal in peat humification records using theNaOH colorimetric technique was recognised by Chambers et al. (1995). This findingwas also mentioned by Yelloff&Mauquoy, but the first recognition was in the following:Chambers, F.M., Barber, K.E., Maddy, D. and Brew, J. (1997) A 5500-year proxyclimateand vegetational record from blanket mire at Talla Moss, Peebleshire, Scotland.The Holocene, 7, 391–399.

References has been added

Technical (text-drafting) corrections Several times, sentences begin ‘Due to’. In allthese instances, what was meant was ‘Owing to’. There might also be occasions when‘due to’ (= caused by) was used within sentences when ‘owing to’ (= because) mightbe better. See advice in Booth, V. Communication in Science: Writing and Speaking,CUP, Cambridge.p.

Has been changed according to the reviewer’s suggestion.

17352, line 20, p. 17353, line 10, 17357, line 16 and p. 17368, line 3: change‘extend’ to ‘extent’

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Has been changed

p. 17358, line 8: change ‘present day’ to ‘present-day’

Has been changed

p. 17371, line 6: change ‘dryer’ to ‘drier’

Has been changed

p. 17361 lines 17-18 I wonder whether ‘was adopted by Blackford and Chambers(1993)’ should instead be ‘of Blackford and Chambers (1993) was adopted’ [Note alsothat this paper has been superseded by Chambers et al. (2011).]

p. 17362, line 15: hyphenate ‘peat forming’: ‘peat-forming’

Has been changed

p. 17374, line 9. Write ‘FTIR data, however, confirm’ [not ‘confirms’]

Has been changed

p. 17375, line 14. Re-word the end of this sentence: ‘discussed controversial’ does notread well.

Has been changed

p. 17376, lines 17-18 ‘present day increase in grasses on the bogs surface’ Thereare two things to change here: (i) hyphenate ‘present day’ (to ‘present-day’); (ii) dosomething about the missing apostrophe in ‘bogs surface’. It is not clear whether thissentence refers to one or to two bogs. If two, then place an apostrophe after the sin bogs. Or, can avoid an apostrophe altogether by writing as follows: ‘present-dayincrease in grasses on the bog surface’

Has been changed

p. 17377, lines 16-17. Change ‘due to the fact that’ to ‘because’

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Has been changed

p. 17379. Change ‘Moreover, the amount of UV-absorbing aromatic compounds whichare e.g. abundant in lignin also depend on changes in vegetation, which does notnecessarily correlates with’ to ‘Moreover, the amount of UV-absorbing aromatic compoundsthat are abundant in lignin, for example, also depend on changes in vegetation,which do not necessarily correlate with’.

Has been changed

Interactive comment on Biogeosciences Discuss., 10, 17351, 2013.