1 Dear Editor,

we appreciate the comments by W. Bleuten, E. Hobbie and four anonymous reviewers for providing useful and constructive comments that have helped us to improve the manuscript. Following their suggestions, we have revised the manuscript carefully. Below you can find our detailed responses (bold) to the comments. The pages and lines mentioned in our responses refer to the pages and lines in the revised manuscript.

7 Best Regards

- 8 Jan Paul Krüger (on behalf of all authors)
- 9
- 10

11 Short comment by E. Hobbie

This is an interesting approach and a good use of ash content. The Suess effect will probably contribute some to low d13C values in the uppermost peat layers, since the d13C of atmospheric CO2 has dropped by 1.7 per mil since 1850 (most rapidly since 1950).

15 Reply: Thank you! That is true, the Suess effect could have contributed to the low  $\delta^{13}$ C 16 values in the uppermost layer of the near-natural site. But the further increase of  $\delta^{13}$ C 17 (more than 5 per mil) with depth shows the aerobic decomposition of the peat at this 18 site. We will include a short discussion of this aspect in the revised manuscript.

- 19
- 20

21 Anonymous Referee #1

The topic of the manuscript is relevant for Biogeosciences. The paper present important additions to our knowledge on the peatland biogeochemistry. The language of the manuscript is very good except one misprint in the abstract (see below). However, I recommend some revisions before final consideration of this paper for publication.

26 General comments:

1. The plots for natural peatlands are somewhat inconsistent between Figs. 1 and 2. In the former Figure,  $\delta^{13}C$  does not depend on depth. The relevant arguments are provided in Sect. 1. However, in Fig. 2, all three NW ('near-natural') plots show significant dependence of 1  $\delta^{13}$ C on depth. The difference of  $\delta^{13}$ C in these plots between the near-surface layer and the 2 depth of  $\approx 1$  m (the deepest data presented in the paper) for the NW plots is even larger than 3 the corresponding differences for the GE and GI sites. I guess, that this inconsistency should 4 be addressed before considering the paper for publication in Biogeosciences.

Reply: The figure 1 is the theoretical concept for natural and degraded peatland based 5 on literature research. In figure 2 the results of the  $\delta^{13}$ C measurements of the three 6 investigated sites are presented. The results show, that the  $\delta^{13}$ C depth profiles of the NW 7 8 site are different to the expected depth profile of natural peatlands in the theoretical concept (Fig. 1). This indicates a degradation of the NW site. The differences of  $\delta^{13}$ C 9 values between the near-surface layer and the deepest investigated layer are higher for 10 the NW profiles compared to the grassland sites, which is mainly due to the lower  $\delta^{13}$ C 11 values in the first 6 cm at the NW site compared to the grassland sites. The lower  $\delta^{13}$ C 12 13 values of the NW site are probably due the Suess effect (please see reply to short comment by E. Hobbie) due to the fact that these ecosystem has bound more C into the 14 15 soil than the grassland sites.

16 2. An additional inconsistency is found between Figs. 1 and 3 is due to  $\delta^{15}$ N for managed sites 17 (GI and GE). In the conceptual Fig. 1  $\delta^{15}$ N changes from negative values in the near-surface 18 peat layer to the positive values at greater depths. However, the respective plots in Fig. 3 19 show an opposite dependence on depth. Again, this matter should be resolved before 20 publication.

21 Reply: As described in the reply to the first general comment the figure 1 is a theoretical 22 consideration for the expected depth profiles of natural and degraded peatlands and the 23 figure 3 presents the results of our measurements at the three different sites.

- 24 Specific and technical comments:
- 25 1. p. 16826, line 15: please remove comma after 'near-natural site';
- 26 2. Table 2: I would suggest to remove the superscript 'n.s.' and type the numbers with p < p
- 27 0.05 (and with smaller p) in boldface; 3. I would suggest to break all Figures in parts (a, b, c,

etc.). It would simplify reference to these parts in the body of the text.

## 29 Reply: We will change the specific and technical comments in the revised manuscript.

30

#### 1 <u>Reviewer 3</u>

The manuscript is actually an extended case study of the previous one (Alewell et al. 2011 Biogeosciences. 8:1769.). However, the authors in this study appear to over-interpret the results. The author indeed can carefully read the previous paper and discuss the results in a more balanced manner.

6 Reply: We think there is a misunderstanding here. Our manuscript deals with 7 biogeochemical indicators of peatland degradation along a land use gradient in 8 temperate bogs. Temperate bogs and subarctic palsa peatlands are completely different 9 ecosystems. Also we use a large number of indicators to detect human-induced changes 10 in the peat profile. The current study is therefore not an extension of Alewell et al. 11 (2011) but an application of the Alewell et al. approach to a complete new situation in a 12 different ecosystem context.

13

(1) The title. The title is relatively vague. The authors claim that 'Biogeochemical indicators
of peatland degradation – a case study of a temperate bog in Northern Germany'. One could
not understand what are biogeochemical indicators and how precisely these indicators could
represent environmental disturbances. The new title is apparently needed in a straightforward
manner.

19 Reply: Our title already gives precise information about the set-up. The specific 20 indicators are described in the abstract. Stable isotopes, C and N concentrations as well 21 as ash content are well known biogeochemical soil parameters which have the potential 22 to indicate disturbance of ecosystems and their biogeochemical cycles.

23

(2) The conclusion. The authors conclude that 'All investigated biogeochemical parameters
together indicate degradation of peat due to conversion to grassland, (ii) historical drainage as
well as recent development and land use intensification. These statements are pretty vague
and could be imagined without experimentation.

Reply: Our aim was to test if these parameters, particularly stable isotopes of carbon and nitrogen, are suitable indicators for peatland degradation and hence human disturbance. We selected a peatland with known land-use history and clear differences between the study sites to investigate the soil parameters and to test our hypotheses. With this newly gained knowledge about the indicators these methods can be applied to
 other peatlands where only little information on previous or ongoing disturbance is
 available.

4

5 (3) Peatland degradation as the theme is not appropriate. It appears there is no solid evidence 6 in support peat degradation in this study. As the authors mentioned, aerobic and/or 7 decomposition can occur in peatland, leading to degradation. However, the indicators, rather 8 than solid evidence of peatland degradation were investigated. It remains uncertain whether 9 these indicators could accurately reflect what is going on in peatland. In addition, it was said 10 that the highest carbon loss was observed in the intensively managed grassland (GI). However, only the carbon in soils was concerned. It seems that a large amount of 11 12 aboveground biomass will be removed by grazing. What will happen if this was taken into account? 13

14 Reply: We disagree with reviewer 3: Peatland degradation is the focus of our study. We 15 could show (significant) differences of the biogeochemical indicators between the two 16 managed (degraded) sites on the one hand and the near-natural site on the other. The managed sites are degraded due to drainage and land use activities. We calculated C loss 17 18 using the combined method (described in Leifeld et al. 2014) which is a time-integrative 19 profile approach that integrates soil parameters (bulk density, ash content and C 20 concentration) to calculate carbon loss since the onset of drainage. These calculations 21 clearly show that the profiles lost substantial amounts of carbon since onset of drainage, 22 i.e., these soils are degraded. Our aim was to estimate the total C loss of the soil to the 23 atmosphere, whether it comes from peat oxidation or indirectly via harvesting of the 24 aboveground biomass. For this type of calculation, harvest does not need to be included 25 in the equations of the combined method. We agree that the observed carbon losses may have been caused by both, oxidation and smaller plant-derived residue inputs, but this 26 does not change the total carbon budget of the soil. The cuts and manuring for the years 27 2007/08 and 2008/09 are presented in table 3 in Beetz et al. (2013). 28

29

(4) The authors seem to draw no solid conclusion for the usefulness of isotope techniques as
indictors of peatland degradation. One point that is interesting I guess is the slope of 13C with
depth. This slope appears to be a better predictor, and the authors can relate it to previous

studies (Alewell et al., 2011). In fact, the current manuscript needs to be presented in a
 manner similar to previous study by Alewell et al. 2011.

Reply: We could show that even the near-natural site is influenced by the surrounding 3 drainage activity which is displayed in the  $\delta^{13}$ C profiles as well as in the C loss 4 calculation by the combined method. Hence, also bogs considered as near-natural or 5 6 even natural could potentially be impaired by anthropogenic activities, at least in the past. Furthermore, the  $\delta^{15}N$  profiles show significant differences between the three 7 investigated sites with both, increasing peat decomposition and fertilizer application 8 systematically changing the  $\delta^{15}$ N signature of the soil. With this we concluded the 9 usefulness of stable isotopes in bulk samples to detect peatland degradation. We again 10 emphasize that slopes of  $\delta^{13}$ C vs. depth are included in our analysis. We put our results, 11 at several places, into context with those of Alewell et al. (2011) but, at the same time, 12 stress that we are dealing with a very different type of ecosystem in the present 13 14 manuscript.

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- 16

#### 17 Anonymous Referee #5

This is a concise and clearly presented paper that draws upon a number of biogeochemical 18 19 indicators to consider peat degradation at three sites of contrasting management history, in northern Germany. The research is generally described well, and although the results are 20 21 presented in a descriptive manner, they illustrate the potential to use this approach more widely when assessing peatland degradation. However, it would have been useful if the 22 23 authors had reflected more on this latter point in the paper (specifically the wider significance of this research). While I feel that the paper is very close to publishable quality already, I 24 25 suggest that the authors consider the following suggestions to improve the manuscript further: Throughout the manuscript the authors refer to increases (or decreases) in isotopic 26 composition. I would prefer to see isotopic compositions described as enriched (or depleted). 27

28 Reply: Thank you. We will alter the conclusion and reflect more on the potential to use 29 the approaches. The increase (and decrease) of isotope values refers to the depth profiles 30 and the change of  $\delta^{13}$ C or  $\delta^{15}$ N with depth. So what is really meant is a "increase in enrichment" or a "decrease in enrichment". We will be clearer on this point and will
 either state the development of enrichment or trend of depth profile.

Site Description: In the light of subsequent comments on the importance of drainage, it would
be helpful to see a fuller description of the 'intensive drainage' that occurred (page 16830;
line 10);

# Reply: We will go back to the literature and present a more detailed description of the drainage that occurred at the Ahlen-Falkenberger peatland.

- A location figure would be helpful to identify the (9) points where samples were located –
  and the relative size and distribution of the three categories of peatland (wetland; extensively
  managed grassland; intensively managed grassland);
- 11 Reply: Sampling points are the same locations where other investigations were done

12 which are described in Beetz et al. (2013) and Frank et al. (2014). We will add a figure

13 with the study site to the supplementary material (Fig. S1).

- 14 Soil sampling and analysis: Why were samples only collected to 50cm depth; and how close
- 15 were the replicate samples collected at each plot?
- 16 Reply: Samples were collected down to approximately 100 cm depth (Page 6; line 10).
- 17 All three replicates were sampled within about 5m radius close to the investigations plot
- 18 of Beetz et al. (2013) and Frank et al. (2014).
- 19 What depths were selected for radiocarbon dating ? (page 16832; line 4)
- 20 For each site, three depths were selected for radiocarbon dating and samples at these
- 21 depths were investigated for each individual core. Samples for radiocarbon analyses
- 22 were selected after evaluation of ash content and stable isotope depth profiles and were
- 23 taken where a clear change in depth pattern was indicated (Page 6; line 31).
- Minor points: Abstract: line 21: 'in retrograde' should this be 'retrospectively'? Page
  16829: line 12: 'a posterior' rephrase. Page 16839: line 24: remove 'been'.
- 26 **Reply: done**
- 27
- 28
- 29

1 Anonymous Referee #6

2 General Comments

In this paper, Kruger et al report the results of a study investigating the depth profile of various biogeochemical markers in peatlands. These markers are examined for their suitability in determining both qualitatively and quantitatively the level of peatland degradation. This paper is clearly appropriate for Biogeoscience, providing a useful assessment of the varying degrees to which stable isotopes, bulk density, C/N ratios, radiocarbon age, and ash content can be used to assess peatland health in the past and present. I believe the paper is suitable for publication, provided the authors address the issues brought up in the review process.

The authors may wish to consider rearranging the Results and Discussion section so that section 3.7 (radiocarbon age) appears before the other sections. This would allow them to make explicit linkages between peat age and the other biogeochemical markers. For example, in section 3.5, there is a inference of drainage activities owing to the enhanced ash content in the NW site between 10 and 60 cm. If the radiocarbon ages were presented earlier, this presumed drainage period could be linked to an actual date, and discussed in the context of the historical record.

17 Reply: The section 3.7 (radiocarbon age) will be presented earlier in the Results and

# 18 Discussion part. We will discuss the enhanced ash content in the NW site between 10 and

19 **60 cm in the context of the radiocarbon ages.** 

In some places, the units were a little different than elsewhere in the literature. For example,
p2L24 (and others) use t C ha- 1 a- 1. Consider using kg or Mg, and yr instead of a. This
may be a convention for Biogeoscience, though.

## 23 **Reply:** We will change the units into kg C $m^{-2}$ yr<sup>-1</sup>.

When the authors reference GHG emissions, it is a little unclear whether this refers to just CO emissions from the soil or to a fuller assemblage of GHGs including methane, N 2 O, etc. For example, on P5 it discusses " Current GHG flux measurements", but then presents the actual fluxes in terms of NEP, which implies CO 2 fluxes only. Be clear about the types of emissions you are describing; if it's CO 2 flux measurements, say that so readers don't assume methane/N 2 O were also being measured.

### **30** Reply: Fluxes will be presented in a clear defined way.

1 It might be helpful to have a concluding sentence in the abstract guiding readers as to which 2 biogeochemical makers, based on this study, seem most useful for determining peatland 3 degradation. Based on your results, it seems like ash content, in combination with radiocarbon 4 age, presents a much clearer picture than either of the stable isotope profiles (especially 5 nitrogen.)

# Reply: An additional sentence with the most useful biogeochemical indicator(s) of peatland degradation will be added to the abstract.

In several places (P8L20, P10L12, P12L29) there is reference to the " upper centimeter" of the soil. Does that actually refer to the soil sample from 0-1 cm, or is it meant to convey soils in the upper horizon? Whichever it is, it needs to be made more explicit; i.e., " In the top 1 cm of the soil" or " From 0-10 cm). The paper could benefit from a close editing for English usage; there were some issues of clarity throughout the paper. I have noted some of them in the " Specific Comments" section.

# Reply: In the whole manuscript depths will be presented in a clear manner. We will change "upper centimeter" in the whole manuscript to precise depths.

- 16
- 17 Specific Comments
- 18 P1L16 " lose carbon to the"

## 19 Reply: changed

20 P1L25 based on your results, the enhanced  $\delta$ 15 N is due to both decomposition and fertilizer

21 application (in the GI case); the fertilizer application should be mentioned here as well.

## 22 **Reply: we will add the fertilizer application in this sentence.**

P1L27... "This indicates that not only the managed..." It is a little unclear which marker is being described here. It could be read as just the ash marker (from previous sentence), or the whole panel of biogeochemical makers. If you are meaning to refer to the ash content only, saying "These ash profiles, not only in the managed grasslands but in the natural wetlands, indicate that all the sites were influenced by anthropogenic activities either currently in the past, most likely through drainage."

## 29 Reply: changed

- 1 P2L3-5 "... we calculated carbon loss from these sites in retrograde" reads a little 2 awkwardly. Perhaps you could explicitly state the time frame for which you calculated C loss.
- 3 Reply: we calculated the total C loss form these soils since the peatland was influenced

4 by anthropogenic activities. The calculated C loss by the combined method presents the

- 5 total C loss since the peatland was affected by drainage.
- 6 P2L21 " GHGs from organic soils comprise 5.1% of Germany's national total emissions"

#### 7 Reply: changed

- 8 P2L23-28 Keep units consistent! Either use C or CO 2 to trace emissions so readers don't
  9 have to scale on the fly.
- 10 Reply: We would like to do so, but the CO<sub>2</sub> emissions are presented as CO<sub>2eq</sub> which
- 11 includes the  $N_2O$  emissions from these sites and are only presented in this way in the
- 12 literature.
- 13 P3L3 " almost constant with depth"

#### 14 **Reply: changed**

15 P3L7 " show a slight decrease in  $\delta$ 13 C with depth"

#### 16 **Reply: changed**

- 17 P3L21 I don't understand the " (wet) oxic soils" formulation. Is it different if the oxic soils are
- 18 dry? Is this an important distinction to be made?
- 19 **Reply: no, sorry to be unclear, we will delete (wet).**
- P3L29-30 Rather than "wider" C/N ratios, use "larger". Substitute "smaller" for "
  narrower". I think this is a more common way to express these ratios; check for other
  occurrences later in the text.

# Reply: we will change in the whole text wider into larger and narrower into smaller. Please see also our reply to reviewer W. Bleuten.

- 25 P4L3 " aa" can be deleted
- 26 **Reply: changed**
- 27 P4L14 " weather "whether
- 28 **Reply: changed**

1 P4L28 remove comma: " The study area is located in Lower Saxony"

## 2 **Reply: changed**

3 P4L29 remove quotes around peatland name

## 4 **Reply: changed**

5 P5L7 " when conservation area" " when a conservation area"

## 6 **Reply: changed**

- P5L13-25 Here you present a bunch of information on your 3 sites. It would be good if you could keep the sites in the same order throughout. Here you present GE before GI when talking about cut/fertilizer schedule, GI before GE when talking about drainage, and GI, GE, then NW when talking about carbon balances. It will be easier for readers to keep track of the
- 11 differences between the sites if they are presented the same way each time.

## 12 **Reply: We will keep the sites in the same order and revise the site description chapter.**

13 P5L23-25 Either give the actual NEP values for all 3 or for none; here you give the exact

- 14 values for GI but no numbers for GE or NWP.
- 15 **Reply: We will add the information to the manuscript**
- 16 P4L23 " The Net ecosystem" " The net ecosystem"

## 17 **Reply: changed**

- 18 P9L6-7 A more in depth explanation of how the different slopes point to different peat loss
- 19 rates might be helpful. I understand how the overall pattern of  $\delta 13$  C indicates relative levels
- 20 of degradation, but it's harder to link the slopes to peat loss.

## 21 Reply: We will add a more detailed explanation to this part of our manuscript.

22 P9L7 " Below this point" - clarify. Below which depth?

## 23 **Reply: changed in the revised version.**

24 P9L14 " decrease in the upper" " decrease with depth in the upper"

## 25 **Reply: changed**

- 26 P9L20 delete " rather"
- 27 **Reply: changed**

1 P10L14 " Organic fertilizer may be" " Organic fertilizer may also be"

# 2 **Reply: changed**

3 P10L23 " C/N ratios are narrow" " C/N ratios are smaller"

# 4 **Reply: changed**

5 P10L26 you could add that these typical values indicate lower levels of microbial activity.

# 6 Reply: added

7 P10L30 " as well as the C/N ratio" " as well as decreasing the C/N ratio"

# 8 **Reply: changed**

- 9 P11L28 Include all sites in the first sentence: Carbon losses as induced by drainage are
- 10 highest at GI and lowest at NW, as estimated by the combined bulk density and ash content
- 11 method."

# 12 **Reply: changed**

- 13 P11L30 " higher current GHG emissions" " higher measured GHG emissions". Also, make
- 14 sure that GHG emissions is correct; do you really mean CO 2 emissions?

# 15 **Reply: changed**

- 16 P12L7 " nowadays a C sink" " nowadays is a C sink"
- 17 **Reply: changed**
- 18 P12L22 check GHG vs CO 2 flux
- 19 Reply: the net ecosystem carbon balance of the NW site shows that this site is a C sink
- 20 during the investigated years (Beetz et al. 2013).
- 21 Table 2: Is the  $\delta 15$  N vs  $\delta 13$  C column really necessary?
- 22 Reply: no, we will delete this column from Table 1 in the revised manuscript.
- 23
- 24
- 25 W. Bleuten (Referee)
- 26 General comments

The article present an interesting attempt to define decomposition of peat in three different 1 2 land unit types by radio isotopes of N and C and classical methods (ash content, C/N, Bulk 3 Density, 14C ). The results of the different methods have been compared and combined in order to find clues for determination of peat decomposition rates related to land use. The 4 5 "semi-natural" type (NW), according to the vegetation composition obviously has been degraded. The question rise if the top "soil" of this NW type can be compared to the grassland 6 7 types, which both are drained heavily. There is no information about the application level of 8 manure, fertilizer and or lime, nothing mentioned about cattle grazing (and dropping) yes or 9 no. Liming, if occurred, will strongly influence the Carbon and ash content of the top layers 10 and therefore effect the conclusions from the analyses. The location of the cores and the 11 surrounding drainage system development over time could be found in Leifeld et al. (BGD-11-12341-2014 Supplement: Fig S1). It should have been much better if this Figure was 12 13 included in this paper (I could not find/open any supplement of the article).

14 Reply: We used stable isotope ratios of carbon and nitrogen as well as ash content, C/N 15 ratio, bulk density and 14-C to indicate peatland degradation. We give an overview of the application of fertilizer and mowing (Page 5; line 21). For detailed description see 16 Beetz et al. (2013) and Frank et al. (2014). Our sites were neither limed nor grazed. We 17 18 will add a sentence to this aspect to the study site description (Page 5; line 24). The study 19 sites from Leifeld et al. (BGD-11-12341-2014) are not the same as studied here. Study 20 sites from Leifeld et al. (2014) are situated in Paulinenaue, Brandenburg, Germany 21 whereas our study sites are placed near Cuxhaven, Lower Saxony, Germany. We will 22 add a figure with the study sites in the revised manuscript (see Fig. S1). There is a 23 supplement to this article available online at the Biogeosciences homepage 24 (http://www.biogeosciences-discuss.net/11/16825/2014/bgd-11-16825-2014-

25 supplement.pdf).

Specific comments Definition of catotelm as used in this paper is missing. What is the top of the soil: top moss heads, top of acrotelm? That is important for interpretation of decomposition: in acrotelm always rather high.

Reply: We will delete the term catotelm in the revised manuscript, because it is only usable in pristine peatlands. For C loss calculations by the combined method we used the data from depth below the lowest water table throughout the year (Frank et al., 2014) in the profiles as reference layer for the C loss calculation. This was done in a 1 similar way in the paper by Leifeld et al. (2014). The top of the soil is the vegetation of

2 **the site.** 

- 3 No C-concentration data are presented, only ash content
- 4 Reply: C concentrations for each sample are presented in the supplementary table
- 5 (http://www.biogeosciences-discuss.net/11/16825/2014/bgd-11-16825-2014-
- 6 supplement.pdf).
- 7 Depth in Table 1 is missing: regressions refer to different depths?
- 8 Reply: We will add the depths to which the regression analyses were done to table 1.
- 9 It is not clear which peat layer(s) of the NW cores are used as reference peat
- 10 Reply: We used the samples from the lowest 30 cm of our profiles (i.e. 70-100 cm depth)

11 of the NW cores as references. These samples show no enrichment of ash content. We

- 12 will add a sentence in the revised manuscript.
- 13 Technical corrections
- 14 P3: 6-7 Alternatively, under anaerobic conditions with anaerobic decomposition the depth
- 15 profile may show a slight decrease with depth because of an relative enrichment of 13C
- 16 depleted lignin Not clear what is meant here. Maybe better use instead of "alternatively":
- 17 "However," And what is "13C depleted lignin"?

# 18 Reply: We will use however instead of alternatively. It should be ... because of a relative 19 enrichment of <sup>13</sup>C depleted substances like lignin.

- 20 12-13 Together, peatland drainage induces a change from a uniform  $\delta$ 13C depth profile to 21 increasing  $\delta$ 13C values with depth. That is valid for catotelm layers, not for acrotelm.
- Reply: This is the description of our theoretical concept about the effect of drainage on  $\delta^{13}$ C depth profile. We used the depth patterns of  $\delta^{13}$ C profiles from the literature and from our own investigations for our theoretical concepts. A water saturated peat soil has a uniform depth profile of  $\delta^{13}$ C values (Clymo and Bryant, 2008; Alewell et al., 2011; Krüger et al., 2014) throughout the whole profile and in oxic soils the  $\delta^{13}$ C values increase with depth (Nadelhoffer and Fry, 1988). Please see additionally our response to reviewer 1.

25-27 In intensively managed ecosystems, the application of mineral and/or organic fertilizer,
 with their different isotopic signals, could additionally alter the stable nitrogen isotope
 signature in soil Also by droppings from cattle and by atmospheric deposition N balance will
 be influenced, the latter not only in intensively used peatland.

5 Reply: Our sites were not grazed (we will add this information in the revised 6 manuscript). Yes, not only the intensively used grassland site is influenced by 7 atmospheric N deposition. We discussed the influence of atmospheric N deposition (Page 8 10; line 23) on the  $\delta^{15}$ N values in the soil as well as peat vegetation (Page 10; line 14) in 9 chapter 3.2 in our manuscript.

29-31 Little decomposed peat has wider C/N ratios, reflecting the former plant material,
whereas the ratio becomes narrower in strongly decomposed peat owing to a preferential loss
of C over N during microbial decomposition. "wider" and "narrower": low and high?
Expected is depletion of N by microbial decomposition and therefore increase of C/N ratio.

Reply: changed to: Little decomposed peat has larger C/N ratios, reflecting the former plant material, whereas the ratio becomes lower in strongly decomposed peat owing to a preferential loss of C over N during microbial decomposition. Please see also our reply to reviewer 6.

- P 5 11-12 .. vegetation is dominated by cross-leaved heath (Erica tetralix L.), flat-topped bog
  moss 11 (Sphagnum fallax Klinggr.), and common cotton grass (Eriophorum angustifolium
  Honck.). On p10:1 Calluna vulgaris is mentioned to be one of the dominant species.
  Typically, the presence of heather points at some drainage.
- Reply: The vegetation of the near-natural site indicates a mild degradation of this
  peatland (please see page 13; line 25).
- 24 Where were the cores taken? 16 (GI type)

25 **Reply: Cores were taken close to the former study sites (see study site location in Beetz** 

- 26 et al. 2013 and Frank et al. 2014).
- 27 ...fertilized with mineral fertilizer and manure. What about cattles droppings, liming?

28 Reply: Liming and cattle grazing was not performed on these sites. We will add a

29 sentence to this aspect in the revised manuscript (Page 5; line 24).

- 1 16-17 GI is drained with pipes as well as drainage ditches whereas GE is only drained by
  2 ditches Depth of drainage?, depths of ditches? Distances of drains and ditches to the core
  3 sites?
- 4 Reply: A detailed description of drainage ditch depth and drainage pipes can be found
  5 in Frank et al. (2014).
- 6 18 At the NW site, the water table was around the soil surface What is meant with "around"?7 Needs specification.
- 8 Reply: The water table was close to the soil surface with a variation of -10 cm to 5 cm 9 during the sampling period by Frank et al. (2014). We will change this in the revised 10 manuscript (Page 5; line 26).
- 11 28-29... three peat cores per site were collected in the Ahlen-Falkenberger peatland at NW,
- 12 GE and GI (n=3). No details of the core sites location properties. Is it expected that the 3 land
- 13 unit types are homogenous spatially?
- 14 Reply: We took three cores per site. The cores of each site show a similar stratigraphy, 15 consequently we expect some spatially homogeneity between the three land unit types.
- 16 The management of the grassland sites has not changed for more than 20 years (Frank 17 et al. 2014).
- P6 13-14 The material remaining after heating is defined as the ash content of the sample. The
  presence of lime (naturally and or applied for agriculture) is included in Carbon content?
  Results of Organic Matter or Carbon content and of Bulk Density are not presented in this
  article which is an omission.
- Reply: The sites were never limed. Results of all biogeochemical parameters for every single soil sample are presented in a table in the supplementary material of the manuscript. The results represent the organic carbon content of the peat samples. Additionally, the results of bulk density as well as C/N ratio are presented in figures in the supplementary material (http://www.biogeosciences-discuss.net/11/16825/2014/bgd-11-16825-2014-supplement.pdf).
- P7 5-7 we assume that the ash content in the catotelm is not affected by drainage and ash from the oxidized peat remains at the site and accumulates in the upper layer. The ash content of the catotelm of each individual core is taken as a reference value Not clear what is meant here with "catotelm". Usually it is dedicated to the permanently saturated peatlayers of pristine

bogs. In the bogs described here the lower water table is -40 to -80 cm below the "soil"surface, which means that at least part of the original catotelm fall dry as a result of artificial drainage. What is meant with the "upper layer"? Is that catotelm? Or top of catotelm? It is advisable to avoid the usage of the term catotelm for this study.

5 Reply: We used the deepest samples of our cores as references. All samples we used as 6 reference are deeper than 80 cm below the soil surface. That's right the term catotelm in 7 case of degraded peatlands is not usable. We will revise the ash content part and replace 8 the word catotelm. The term "upper layer" will be defined in more detail.

9 P8: 20-25, p9: 4-5 The interesting differences in d13C increase with depth between the 10 grasslands and the NW type is related to drainage even in the NW site. However, in the 11 (limited) description of the site the water level is said to be "near the surface". The top layers 12 of the NW site differ substantially to the grassland sites, but this cannot be verified as the 13 article does not give details of the core. Most probably, the top layers of the NW site consists 14 of fresh organic material (acrotelm thickness can be up to 40 cm). In contrary, the top layers 15 of the grasslands consists of already partly decomposed peat (see 14C ages in Fig 2).

Reply: Today the water table at NW is high, but could have been lower in the past due 16 17 to a stronger influence of drainage activities of the surrounding area. Since the 1990s the 18 NW site is a nature reserve (page 5; line 14) and may thus be more protected against 19 drainage influence. Yes, the top layers of the NW site differ to the top layers of the 20 grassland sites. The NW site consist of fresh organic material and the grassland site are 21 already more stronger decomposed due to aerobic decomposition. Furthermore, the 22 grassland sites have lost peat deposits from almost 1000 years, which is indicated by the 23 radiocarbon ages at the grassland sites.

In Table 1 the regressions coefficients and slopes between the core sites are compared but for
the NW site to a depth of ca. -0.5 m and for the GE and GI sites ca. -0.3 m (depth of -25 0/00,
deducted from fig 1).

# 27 Reply: We will add the depth used for regression analyses to every single core in table 1. 28 As we described in section 2.5 (page 9; line 2) the regression analyses were done until the 29 $\delta^{13}$ C value of -25.0 ‰ was reached.

30 P9: 20 - p10:20 (3.2 Stable nitrogen isotopes) Here, also the differences between NM and 31 grassland sites are described solely from the analyses. The peat material, in particular of the upper layers are different between NW and grassland sites, which influence the value of theconclusions.

3 Reply: The results of the stable nitrogen isotope values are presented and discussed in 4 the chapter 3.2 for each land use type. In this part we discuss the influence of the present 5 vegetation types on the stable nitrogen isotope signal (Page 10; line 14). The material in 6 the upper layers is certainly different between the near-natural and both grassland sites. 7 We found stronger decomposed peat material in the upper layers at the grassland sites 8 (indicated by low C/N ratios (Fig. S2), higher bulk densities (Fig. S3), high ash content 9 (Fig. 4)) compared to the near-natural site. Furthermore, we could show with the 10 radiocarbon ages that the grassland sites have lost a substantial amount of peat and that the near-natural site has organic matter fixed during the second half of the last century. 11

P11 (3.5 Ash content and bulk density) 15-16 (Fig. 4). Bulk density increases at this depth 12 and is higher compared to deeper parts of the profiles and 18-19 We interpret this 13 14 accumulation as being the result of drainage activities in the vicinity of NW during formation of these peat layers There is no information about the presence of charcoal within the peat as 15 16 indicators of fires at or near the core sites. Fires may explain the peaks in ash content about ca 17 1880 and ca 1780 (estimated from Fig 4). Also by deposition of mineral soil material spread 18 from arable land by wind may explain the peaks. The conclusion that any increase in ash 19 content result from drainage can be doubtful. 20-21 At both grassland sites, ash content (Fig. 20 4) and bulk density (Fig. S1) increase strongly in the upper centimeters Could not find Fig S1

Reply: We found no charcoal layer in the peat profiles. The history of the peatland is 21 22 well documented and there is no mention of fires. While it is true that we have no proof 23 that there were no fires, we are quite confident that we would know if there had been 24 fires. It is, however possible that ash particles from other burning peatlands in the vicinity may have been deposited. In the late 19th century, peat burning was quite 25 26 common. If mineral soil material would have been deposited on top of the organic soils, 27 we would expect a stronger ash signal also for the natural site, which we didn't find. 28 Hence, it is reasonable to assume that the ash accumulation stems primarily from a 29 preferential loss of organic matter via oxidation although atmospheric deposition cannot 30 be fully excluded as a contributing process. At both grassland sites, ash content (Fig. 4) and bulk density (Fig. S3) are very high in the upper centimetres compared to the lower 31 32 parts of the profiles. Figure S3 is in the supplementary material of the manuscript

- 1 (http://www.biogeosciences-discuss.net/11/16825/2014/bgd-11-16825-2014-
- 2 **supplement.pdf**).
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# **1** Biogeochemical indicators of peatland degradation – a case study

- 2 of a temperate bog in Northern Germany
- 3

4

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## 15 Abstract

16 Organic soils in Ppeatlands store a great proportion of the global soil carbon pool and can 17 loose carbon via the atmosphere due to degradation. In Germany, most of the greenhouse gas 18 (GHG) emissions from organic soils are attributed to sites managed as grassland. Here we investigated a land- use gradient from near-natural wetland (NW) to an extensively managed 19 (GE) to an intensively managed grassland site (GI), all formed in the same bog complex in 20 northern Germany. Vertical depth profiles of  $\delta^{13}$ C,  $\delta^{15}$ N, ash content, C/N ratio, bulk density, 21 as well as radiocarbon ages were studied to identify peat degradation and to calculate carbon 22 loss. At all sites, including the near-natural site,  $\delta^{13}C$  depth profiles indicate aerobic 23 decomposition in the upper horizons. In the topsoil,  $\delta^{15}$ N increased in the order NW<GE<GI 24 owing to differences in peat decomposition and fertilizer application. Depth profiles of  $\delta^{15}N$ 25 differed significantly between sites with increasing  $\delta^{15}N$  values in the top soil layers with 26 parallel to an increasing increase in land use intensity of use., indicating that the peat is more 27 28 decomposed. At both grassland sites, the ash content peaked within the first centimeters. In 29 the near-natural site, ash contents were highest in 10-60 cm depth. The ash profiles, is

indicates that not only at the managed grassland sites, but also at the near-natural site indicate 1 2 that all sites were influenced by anthropogenic activities either currently or in the past, most 3 likely due to drainage., is influenced by anthropogenic activities, most likely due to the drainage of the surrounding area. Based on the enrichment of ash content and changes in bulk 4 5 density, we calculated total carbon loss from the sites since the peatland was influenced by anthropogenic activities. Carbon loss increased in the order NW<GE<GI. Radiocarbon ages 6 7 of peat in the topsoil of GE and GI were hundreds of years, indicating loss of younger peat 8 material. In contrast, peat in the first centimeters of the NW was only a few decades old, 9 indicating recent peat growth. It is likely that the NW site accumulates carbon today but was 10 perturbed by anthropogenic activities in the past. Together, all biogeochemical parameters 11 indicate degradation of peat due to (i) conversion to grassland with historical drainage and (ii) land use intensification. However, we found very young peat material in the first centimeter 12 13 of the NW, indicating recent peat growth. The NW site accumulates carbon today even though it is and probably was influenced by anthropogenic activities in the past indicated by 14  $\delta^{13}$ C and ash content depth profiles. Based on the enrichment of ash content and changes in 15 bulk density, we calculated carbon loss from these sites in retrograde. As expected land use 16 intensification leads to a higher carbon loss which is supported by the higher peat ages at the 17 intensive managed grassland site. All investigated biogeochemical parameters together 18 19 indicate degradation of peat due to (i) conversion to grassland, (ii) historical drainage as well as recent development and (iii) land use intensification. 20

21

### 22 **1** Introduction

23 Peatlands are comprise the most important soil organic carbon (C) pool, and storinge more than 600 Pg carbon-C (Yu et al., 2011; Jungkunst et al., 2012). In these water saturated soils, 24 anoxic conditions hinder organic matter decomposition and favour peat accumulation (Clymo, 25 26 1984). Drainage of peatlands induces oxic conditions and causes increasing carbon dioxide 27 emissions (Maljanen et al., 2001) and resulting in a net loss of carbon to the atmosphere. Over 28 the last century, more than 50 % of the peatland area in Europe has been converted mainly to 29 agriculture or forestry (Byrne et al., 2004). In Germany, 75 % of the greenhouse gas (GHG) 30 emissions from organic soils are attributed to agricultural use (Höper, 2007) and more than 31 half of the GHG emissions from managed peatlands originate from grassland sites managed as grasslands (Drösler et al., 2008). Together, GHG's from organic soils contribute comprise
 5.1 % to of Germanys' national total emissions (Drösler et al., 2013).

In the temperate zone\_GHG emissions from peatlands under grassland use for the temperate zone-average 0.6.1 t-kg C m<sup>-2</sup> yr<sup>-1</sup> C ha<sup>-1</sup>-a<sup>-1</sup> for deeply drained and 0.4 3.6 kg C m<sup>-2</sup> yr<sup>-1</sup> t-C ha<sup>-1</sup>-a<sup>-1</sup> for shallowly drained peatlands (IPCC, 2013). Ranked by land\_-use intensity, intensively managed grasslands emit 2.8.3 kg CO<sub>2eq</sub> m<sup>-2</sup> yr<sup>-1</sup> t-CO<sub>2eq</sub>-ha<sup>-1</sup>-a<sup>-1</sup>, and extensively managed grasslands between 0.2.2 and 2.0.1 kg CO<sub>2eq</sub> m<sup>-2</sup> yr<sup>-1</sup> t-CO<sub>2eq</sub>-ha<sup>-1</sup>-a<sup>-1</sup> (depending on the water table) (Drösler et al., 2013), nearNear-natural bogs are almost climate-neutral, but dry bogs emit up to 1.09.6 kg CO<sub>2eq</sub> m<sup>-2</sup> yr<sup>-1</sup> t-CO<sub>2eq</sub>-ha<sup>-1</sup>-a<sup>-1</sup> (Drösler et al., 2013).

To study soil degradation in different environments, stable <u>carbon and nitrogen</u> isotopes are a useful tool (Schaub and Alewell, 2009; Alewell et al., 2011; Conen et al., 2013; Meusburger et al., 2013; Krüger et al., 2014). In two recent studies in the subarctic region, stable carbon isotope depth profiles were shown to be a meaningful indicator of peatland degradation as well as of the uplifting by permafrost (Alewell et al., 2011; Krüger et al., 2014).

In a natural peatland with low decomposition rates, the  $\delta^{13}$ C signature is almost constant with 15 depth, because in water saturated soils the oxygen availability is low, decomposition of 16 17 organic material is limited reduced, and therefore the isotopic fractionation is small (Clymo and Bryant, 2008; Skrzypek et al., 2008; Alewell et al., 2011). AlternativelyHowever, under 18 anaerobic conditions with of anaerobic decomposition, the depth profile may show a slight 19 decrease  $\delta^{13}$ C may slightly decrease with depth because substances like lignin, which require 20 aerobic conditions for their decomposition, are relatively enriched in <sup>13</sup>Cof an relative 21 enrichment of <sup>13</sup>C depleted lignin (Benner et al., 1987; Alewell et al., 2011). Under aerobic 22 conditions, decomposers preferentially use the lighter <sup>12</sup>C for respiration. Hence the heavier 23 <sup>13</sup>C accumulates in the remaining organic matter and the  $\delta^{13}$ C value increases with depth 24 (Nadelhoffer and Fry, 1988; Ågren et al., 1996). Increasing  $\delta^{13}$ C values with depth are typical 25 for well drained or mineral soils (Nadelhoffer and Fry, 1988; Alewell et al., 2011). With a 26 27 switch from anaerobic to aerobic conditions, peatland drainage is suggested to Together, peatland drainage induces a change from a uniform  $\delta^{13}C$  depth profile to increasing  $\delta^{13}C$ 28 29 values with depth (Fig. 1).

30 Because atmospheric N is the primary source of N in thenatural terrestrial ecosystem,  $\delta^{15}$ N 31 values in natural bogs are assumed to scatter around 0 ‰ (Fig. 1) (Jones et al., 2010; Broder 32 et al., 2012). However, plant species in intact peatlands <u>vary substantially show a high</u>

variability of in their  $\delta^{15}$ N signatures from -11.3 % to +2.7 % (Asada et al., 2005b), which 1 2 could influence the  $\delta^{15}N$  signature of the remaining peat material. A second source of variability comes from nitrogenNitrogen isotope fractionation during decomposition, 3 processes leadings to an enrichment of <sup>15</sup>N in the remaining material and an increase of soil 4 <sup>15</sup>N with depth and age (Nadelhoffer and Fry, 1988; Nadelhoffer et al., 1996). Therefore,  $\delta^{15}$ N 5 values in (wet) oxic soils increase with depth (Fig. 1) with lower  $\delta^{15}$ N values in the upper 6 horizon and higher  $\delta^{15}$ N values in deeper horizons (Nadelhoffer et al., 1996; Kohzu et al., 7 2003). Consequently, we We assume hypothesize that also in drained and/or degraded 8 peatlands, owing the above mentioned processes,  $\delta^{15}N$  values are increasing increase with 9 depth, owing to the above mentioned process (Fig. 1). In intensively managed ecosystems, the 10 11 application of mineral and/or organic fertilizer, with their different isotopic signals (Bateman 12 and Kelly, 2007), could additionally alters the stable nitrogen isotope signature in soil.

In natural peat profiles the radiocarbon signature shows an increasing age with depth (Shotyk
et al., 1998) due to peat accumulation in the course of time. Owing to the loss of peat which

15 has been accumulated in the last several hundreds or thousands of years a degrading peatland,

with a loss of the younger, more recently accumulated C of the upper layers to the
 atmosphere, changes the <sup>14</sup>C depth profile towards higher ages near the peat surface.

18 Another indicator of organic matter decomposition is tThe C/N ratio indicates the degree of 19 decomposition of the peat material of the peat (Malmer and Holm, 1984; Kuhry and Vitt, 20 1996). Little decomposed peat has wider larger C/N ratios, reflecting the former plant 21 material, whereas the ratio becomes narrower smaller in strongly decomposed peat owing to a 22 preferential loss of C over N during microbial decomposition.

23 A simple but reliable estimate of C loss from cultivated peatlands can be obtained based on differences in ash content throughout the peat profile (Grønlund et al., 2008; Rogiers et al., 24 25 2008; Leifeld et al., 2011a)., These methods based on the premise of aa-accumulation of mineral matter (or 'ash') with peat oxidation, i.e. preferential loss of organic vs. mineral 26 27 matter. In a pristine state of a bog, where the mineral input solely derives from the 28 atmosphere, we assume a relative homogeneous ash depth profile. Drainage induces peat 29 oxidation and net CO<sub>2</sub> emission, leading to peat subsidence and a relative enrichment of ash 30 content in the upper layers, where decomposition is strongest. A so-called combined method 31 (Leifeld et al., 2014) makes use of differences in bulk density and ash content in the profile, in order to estimate not only C-loss-estimates, but also volumetric changes of the peat. It 32

distinguishes between primary (settling) and secondary (oxidation) subsidence of the peat
 after drainage (Ewing and Vepraskas, 2006).

The main goal of our study was to test, <u>how-whether</u> stable isotopes of carbon and nitrogen can be used as indicators of peatland degradation along a gradient of land use and drainage intensity and w<u>h</u>eather we could estimate carbon loss a posterior. We apply the above concepts to a typical and well-studied peatland complex, the Ahlen-Falkenberger peatland, in northern Germany. Our hypotheses are:

- 8 (I) The  $\delta^{13}$ C depth profile changes from a constant signal under near-natural conditions to 9 increasing  $\delta^{13}$ C values with depth in degrading peatlands.
- 10 (II) Higher decomposition of the peat in the degraded sites leads to an <u>increase enrichment of</u> 11  $\delta^{15}$ N values in the upper layers.
- (III) C losses are higher in the intensively managed compared to the extensively managedgrassland.
- Analysis of other indicators, such as radiocarbon age, ash content and C/N ratio, will be usedfor validation of the interpretation of the stable isotope depth profiles.
- 16

### 17 2 Material and Methods

#### 18 **2.1 Site description**

19 The study area is located in, Lower Saxony, north western Germany, close to the North Sea 20 coast. The peat bog complex called "Ahlen-Falkenberger peatland" (53°41'N, 8°49'E) is one of the largest peat bog complexes in northern Germany. The climate is humid Atlantic with an 21 22 average-mean annual precipitation of 925.7 mm and an average-mean annual temperature of 23 8.5°C (reference period 1961–1990; German Weather Service, 2010). Bog formation started 24 began at about 6000 years BP on a former fen area (Schneekloth, 1970). Since the late 17th 25 century, peat was extracted at the edges of the bog. Intensive dDrainage activities started at 26 the beginning of the 20th century, and In the middle of the 20th century over 50 homesteads were established in the Ahlen-Falkenberger peatland and land use was intensified in the 27 middle of the 20<sup>th</sup> century (Ahrendt, 2012). Industrial peat extraction at the Ahlen-28 Falkenberger peatland began in 1957 (Schneekloth, 1981) and was terminated in the 1990s, 29 when a conservation area was established (Beckmann and Krahn, 1991; Beller et al., 1994). 30

About 60 % of the remaining former bog area is currently used as grassland, and only a small 1 area in the centre of the peat bog complex (approx. 5 %) was never drained or cultivated and 2 remains as a natural peat bog today (Höper, 2007). In this area, vegetation is dominated by 3 4 cross-leaved heath (Erica tetralix L.), flat-topped bog moss (Sphagnum fallax Klinggr.), and common cotton grass (Eriophorum angustifolium Honck.). We consider this near-natural 5 6 wetland (NW) as unmanaged. Further, we studied two former areas of the former bog which 7 are drained and nowadays managed as grassland: The extensive grassland (GE) is neither 8 fertilized nor manured and only cut once per year., The the intensive grassland (GI) is cut 4-5 9 times per year and fertilized with mineral fertilizer and manure (see details for the years 10 2008/2009 in Beetz et al. 2013). Liming and cattle grazing was never performed on these 11 sites. GI is drained with by pipes as well as drainage ditches whereas GE is only drained by ditches which were closed in 2003/2004. At the NW site, the water table was around the soil 12 13 surface with a variation of -10 cm to 5 cm -in 2012 and fluctuated between the surface and  $\frac{80}{100}$ 40 cm depth (GIGE) and between surface and 40-80 cm depth (GEGI) (Frank et al., 2014). 14 Across the former bog complex, peat thicknesses of peat range from 330 cm in cultivated to 15 515 cm in uncultivated, near-natural areas (Beetz et al., 2013). Current-Recent GHG flux 16 17 measurements at the Ahlen-Falkenberger peatland (2007-2009) indicate site NW was C neutral in one year (-0.002 kg C m<sup>-2</sup> yr<sup>-1</sup>) and accumulated C in the other year (-0.124 kg C m<sup>-2</sup> 18 <sup>2</sup> yr<sup>-1</sup>) (Beetz et al., 2013), a carbon source at GI of about 5-8 t C ha<sup>-1</sup>yr<sup>-1</sup>. The Net net 19 ecosystem carbon balance at site GE was positive in one (0.088 kg C  $m^{-2}$  yr<sup>-1</sup>) and negative in 20 the following year (-0.147 kg C m<sup>-2</sup> yr<sup>-1</sup>) at GE (Beetz et al., 2013). GI was a carbon source 21 for both years with C loss of about 0.548 to 0.817 kg C m<sup>-2</sup> yr<sup>-1</sup> (Beetz et al., 2013). Site NW 22 23 was C neutral in one year and accumulated C in the other year (Beetz et al., 2013).

24

### 25 **2.2 Soil sampling and analyses**

In November 2012, three peat cores per site were collected in the Ahlen-Falkenberger peatland at NW, GE and GI (n=3) (Fig. S1). We took our cores close to the same locations from earlier studies by Beetz et al. (2013) and Frank et al. (2014). Peat samples were taken in the first 50 cm with a soil corer (Giddings Machine Company, US) and in deeper parts with a Russian peat corer (Eijkelkamp, Netherlands) down to approximately one meter. Cores were embedded in plastic shells, wrapped with plastic foil and transported directly to the lab. Cores were cut into 2 cm sections and oven-dried at 40-50°C for 72 h. All samples were ground and homogenised in a vibrating ball mill (MM 400, Retsch, Germany). Stable carbon and stable nitrogen isotopes as well as C and N content were measured by combined mass spectrometry coupled to a SL elemental analyser (Integra2, Sercon, UK). The C/N ratio represents the mass relationship between carbon and nitrogen content of the bulk peat material. Stable carbon isotope ratios are reported as  $\delta^{13}$ C in [‰] relative to the V-PDB standard. Stable nitrogen isotope ratios are reported as  $\delta^{15}$ N in [‰] relative to the atmospheric nitrogen standard. The analytical standard deviation is 0.15 % and 0.1 % for  $\delta^{15}$ N and  $\delta^{13}$ C, respectively.

8 The ash content was determined by thermogravimetry (prepAsh, Precia, Switzerland), using 9 0.5-1.0 g sample material. A pre-drying at 130°C was used to correct the dry mass and to 10 evaporate the residual moisture. The sample was than heated to 600°C in air until no 11 significant mass change (constant mass) could be measured (see detailed description of the 12 method by Leifeld et al. (2011a)). The material remaining after heating is defined as the ash 13 content of the sample.

14

### 15 2.3 Radiocarbon analyses

Radiocarbon (<sup>14</sup>C) analysis was performed with accelerator mass spectrometry (AMS) at the 16 Laboratory of for the Analysis of Radiocarbon with AMS (LARA) at the University of Bern 17 18 (Szidat et al., 2014). For At each site, three depths were selected for radiocarbon dating and the <sup>14</sup>C content of samples at from these depths were investigated was measured for each 19 individual core. Samples were selected after evaluation of stable isotope and ash content 20 21 depth profiles. Segments where stable isotope and ash contents clearly changed were selected 22 for radiocarbon analysis. and were taken where a clear change in depth pattern was indicated. 23 The ground and homogenised material was combusted, transformed into solid targets using an automated graphitisation equipment (AGE) (Nemec et al., 2010), and measured with the MIni 24 25 CArbon DAting System MICADAS (Synal et al., 2007). Sample homogeneity and measurement reproducibility was proven by double analysis of 8 random samples, whereas 26 general accuracy and precision was reported earlier (Szidat et al., 2014). <sup>14</sup>C ages were 27 calibrated using the IntCal13 dataset (Reimer et al., 2013). Samples with bomb signature were 28 dated using the Bomb13 NH1 dataset (Hua et al., 2013). Results of the individual 29 measurements are shown in Tab. S1. 30

Radiocarbon ages are presented for each site and selected depth as means (n=3) with 1 SD in
 cal. years AD or cal. years BC. Results of the individual measurements are shown in Tab. S1.

1

#### 2 **2.4** Calculation of carbon loss by the ash content and bulk density (combined method)

3 The integrated calculation of carbon loss of the peatland since the beginning of drainage is 4 based on the simplified assumption of a constant ratio between carbon to ash content during 5 accumulation of peat and that ash content before drainage is the same at all depths. After 6 drainage, peat starts to oxidize and carbon is lost as CO<sub>2</sub> (Rogiers et al., 2008). Additionally, 7 we assume that the ash content in the catotelm deeper parts of the profile is not affected by 8 drainage. and aAsh from the oxidized peat remains at the site and accumulates in the upper 9 layer of the profile. Differences in soil properties of bulk density, ash content and organic C 10 content between the topsoil and undisturbed subsoil can be used to infer pre-drainage soil 11 thickness and C stocks. The mean ash content of the deeper parts of the profiles, where 12 samples show no enrichment of ash, in our case below 80 cm depth<del>catotelm</del> of each individual core is-was taken as a reference value (Leifeld et al., 2011a). The carbon-C loss 13 was calculated separately for each core. 14

The method of Leifeld et al. (2014) combines two previously published methods which were based on changes in bulk density (Leifeld et al., 2011b) and changes in ash content (Rogiers et al., 2008; Leifeld et al., 2011a) in peat profiles. This so-called combined method (Leifeld et al., 2014) estimates the physical primary subsidence due to the loss of pore water and peat shrinkage, and the chemical secondary subsidence due to the oxidative loss of organic matter.

20 The <u>primary subsidence</u>  $\underline{S_p}$  [m] is calculated as follows (Leifeld et al., 2014):

$$21 \qquad S_P = PT_{0i} - PT_i \tag{1}$$

22 with

$$23 \qquad PT_{0i} = Bd_{OSi} / Bd_{OSr} \times PT_i \tag{2}$$

Where  $\underline{PTV}_{0i}$  is the pre-drainage thickness of layer i [m], Bd-<sub>OSi</sub> is organic matter density in layer i, Bd-<sub>OSr</sub> is organic matter density of the reference layer [t m<sup>-3</sup>], and  $\underline{PT}_i$  is the thickness of layer i [m] at time of sampling. Bd-<sub>OS</sub> is calculated from the soil mass of per unit soil volume minus the ash mass and the ash volume of the same soil volume, assuming a specific density of ash particles of 2.65 t m<sup>-3</sup>.

29 The <u>secondary subsidence</u>  $\underline{S}_{\underline{s}}$  is calculated from the pre-drainage thickness  $\underline{S}T_{0i}$  [m] 30 attributable to organic matter oxidation (Leifeld et al., 2014):

$$1 \qquad ST_{0i} = ST_i \times F_{ashi} / F_{ashr}$$

with  $\underline{S}T_i$  the thickness of layer i [m],  $\underline{F}_{ashi}$  the ash concentration of layer i,  $\underline{F}_{ashr}$  the ash concentration of the reference layer.

$$S_s = ST_{0i} - ST_i$$
(4)

5 Before drainage, any layer  $ST_{oi}$  contained the same amount of carbon per soil volume as the 6 contemporary undisturbed reference layers  $ST_r$  in the deeper soil profile. and tThe amount of 7 soil carbon in any single layer  $C_{di}$  [tkg m<sup>-2</sup>] lost by oxidation is given as

$$8 \quad C_{di} = S_s \times C_r / ST_r \tag{54}$$

9 with  $C_r$  the soil carbon stock of the reference layer [t m<sup>-2</sup>],  $\underline{S}T_r$  -the thickness of the reference 10 layer [m] and the volumetric loss due to peat oxidation  $\underline{T}_d \underline{S}_s$  [m]-given.

$$11 \qquad T_d = T_{0i} - T_i \tag{5}$$

Beside the carbon loss, total peat subsidence [m] can be calculated by the combined method. Carbon losses are displayed as  $t \pm kg C = ham^{-4} - 2$  and loss rates as  $t \pm kg C = ham^{-4} - 2 = ayr^{-1}$  by dividing the carbon loss by the number of years passed since the peatland was drained.

The NW site could not be <u>used\_taken\_as</u> a reference for the calculation of C loss<u>for the</u> managed sites because it was also influenced by drainage activities in surrounding areas as, because of the influence of drainage activities of surrounding areas, indicated by higher ash contents at 10-50\_cm depth. We <u>instead</u> used the deeper layers (samples below 80 cm depth) of the grassland sites as a reference, similar to the approach taken in previous studies (Rogiers et al., 2008; Leifeld et al., 2011a).

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#### 22 2.5 Statistical analyses

Spearman correlation analyses were used to identify the relationship between  $\delta^{13}$ C,  $\delta^{15}$ N and C/N. Regression analysis of  $\delta^{13}$ C and depth was carried out with the software R2.15.1. At each individual core  $\delta^{13}$ C values against depth were used from the uppermost sample down until  $\delta^{13}$ C reaches a value below -25.0 ‰.

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### 1 **3 Results and Discussion**

### 2 **3.1 Stable carbon isotopes**

In both grassland soils,  $\delta^{13}$ C values increase from about -30 ‰ in the upper centimeters to 3 about -25 ‰ in deeper layers (Fig. 2b, Fig. 2c). This increase of  $\delta^{13}$ C values with depth 4 indicates aerobic conditions in the peat profile, as aerobic decomposition decomposers 5 selectively uses the lighter isotope  ${}^{12}C$  for respiration and whereas the heavier  ${}^{13}C$  is enriched 6 in the remaining organic material of the soil (Nadelhoffer and Fry, 1988; Ågren et al., 1996). 7 This  $\delta^{13}$ C depth pattern was also found at site NW, indicating also aerobic degradation also at 8 this site (Fig. 2a). In general, natural peatlands are expected to show a uniform  $\delta^{13}C$  depth 9 profile (Clymo and Bryant, 2008; Skrzypek et al., 2008) or a trend towards slightly lower 10 values, caused by an enrichment of recalcitrant substances depleted in <sup>13</sup>C (Benner et al., 11 12 1987; Krull and Retallack, 2000; Alewell et al., 2011). The Suess effect could have contributed to the low  $\delta^{13}$ C values in the uppermost layer of the near-natural site, but the 13 further increase of  $\delta^{13}$ C with depth is connected to peat material much older than the Suess 14 effect and is very likely owing to aerobic decomposition of the peat. An increase of  $\delta^{13}C$ 15 16 values with depth by about 4.0 to 5.0 ‰ is typical for well drained mineral soils (Becker-Heidmann and Scharpenseel, 1986; Nadelhoffer and Fry, 1988) and are in accordance with 17 oxic grassland soils (Accoe et al., 2003). In northern peatlands, increases of  $\delta^{13}$ C with depth 18 were found in dry hummocks in contrast to uniform depth profiles in water saturated hollows 19 (Alewell et al., 2011; Krüger et al., 2014). 20

In the upper layers of both grassland sites  $\mathbf{D}$  depth profiles of  $\delta^{13}$ C values are apparently 21 compressed in the upper part of both grasslands compared to site NW (Fig. 2). A linear 22 regression analyses with  $\delta^{13}$ C vs. depth revealsresults in d a tendency towards steepest slopes 23 of  $\delta^{13}$ C vs. depth at GI followed by GE and NW at site GI (Tab. 1), ). which might point to a 24 higher peat loss there compared to GE However, we do not regard this pattern as a 25 <u>quantitative indicator</u>. Below the <u>inversion at depth where -25.0 %</u> this point the  $\delta^{13}$ C values 26 of all profiles are-remain more or less constant throughout the deeper profile, indicating low 27 decomposition with limited fractionation (Clymo and Bryant, 2008). 28

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30 **3.2 Stable nitrogen isotopes** 

The δ<sup>15</sup>N signal in peat soils is mainly driven by following processes: vegetation input,
 decomposition, N deposition and fertilizer application. The δ<sup>15</sup>N values of a natural bog
 should be constant at around 0.0 ‰, because atmospheric N is the primary source of N (Jones
 et al., 2010; Broder et al., 2012).

At NW T the  $\delta^{15}$ N values first increase and then decrease with depth at the NW site (Fig. 3a). 5 The inversion is located at ca. 20-40 cm depth, corresponding to  $\delta^{15}$ N values of -2.0 to -4.0 6 7 %. At the grassland sites, stable nitrogen isotopes decrease with depth in the upper partfirst 20 cm of the soil and remain constant with no further clear trend in the deeper parts of the 8 profile. In the first few centimeters of the GE profileAt GE,  $\delta^{15}$ N values are slightly positive 9 in the upper few centimetres of the profile and reach values of around -4.0% below 20 cm 10 (Fig. 3b). At GI, on the other hand,  $\delta^{15}N$  values are positive in the upper-uppermost 11 12 centimetres (up to 4.0 ‰) and a decrease to updown to -10.5 ‰ in deeper layers (Fig. 3c). Compared to GE  $\delta^{15}$ N is The values at GI are more variable at GI and reaches more negative 13  $\delta^{15}$ N-values in the deeper part of the soil profile-as compared to GE. 14

The  $\delta^{15}$ N values of a natural peatland should be rather constant at around 0.0 %, because 15 atmospheric N is the primary source of N (Jones et al., 2010; Broder et al., 2012). At natural 16 peatlands, like NW, However, peat plant species show a wide range of  $\delta^{15}$ N values from 17 below -11.0 to above +2.0 % (Asada et al., 2005b), and this which may influence the  $\delta^{15}N$ 18 values of the remaining peat material in the profile. The  $\delta^{15}N$  depletion in the upper part of 19 NW profiles may be assignable to the very low  $\delta^{15}$ N values of the vegetation (Nordbakken et 20 al., 2003; Bragazza et al., 2010). Sphagnum mosses are depleted in <sup>15</sup>N compared to the 21 atmospheric nitrogen and have even lower  $\delta^{15}N$  values in areas affected by agricultural 22 activities (Bragazza et al., 2005). Incubation of peat mosses have shown a <sup>15</sup>N enrichment 23 with time resulting in with an increase of  $\delta^{15}$ N values with depth in the near surface (Asada et 24 al., 2005a). Below approximately 20 cm,  $\delta^{15}$ N values are less negative and in the range of 25 26 nitrogen isotope values typical for mosses (Asada et al., 2005b). Human activities greatly influence  $\delta^{15}N$  values in mosses beyond triggering decomposition via atmospheric N 27 28 depositions. The various N sources vary in their isotopic signatureHuman activities have a great influence on  $\delta^{15}$ N values in mosses by different atmospheric depositions and their N 29 sources and are not simply related to the total N deposition (Bragazza et al., 2005). Low  $\delta^{15}$ N 30 31 values were reported in areas with high local ammonia emissions (from livestock during 32 animal husbandry, manure storage and spreading) (Asman et al., 1998) owing to the with-very

low  $\delta^{15}$ N values in wet (NH<sub>4</sub>) and dry (NH<sub>3</sub>) deposition (Bragazza et al., 2005). Sphagnum 1 mosses are depleted in <sup>15</sup>N compared to the atmospheric nitrogen and have lower  $\delta^{15}$ N values 2 in areas affected by agricultural activities (Bragazza et al., 2005). The  $\delta^{15}$ N depletion in the 3 upper part of NW profiles may be assignable to the very low  $\delta^{15}$ N values of e.g. Calluna 4 vulgaris, which might have mean  $\delta^{15}$ N value as low as 9.0 % (Nordbakken et al., 5 2003;Bragazza et al., 2010), and is nowadays one of the dominating species at this site. 6 Atmospheric N deposition, as discussed above, may be another reason. Below approximately 7 20 cm,  $\delta^{15}$ N values are less negative and in the range of nitrogen isotope values typical for 8 mosses (Asada et al., 2005b). 9

 $\delta^{15}N$  depth profiles of our drained sites show a completely different depth pattern as 10 hypothesized in our theoretical concept for drained peatlands (Fig. 1) and with decreaseing 11 instead of increasing  $\delta^{15}$ N values rather than increase with depth (Fig. 3). High  $\delta^{15}$ N of the 12 topsoil in our grassland sites (Fig. 3) most likely indicate increased microbial activity, caused 13 14 by drainage, in conjunction with effects from organic fertilizer application at GI. Decomposition is often linked to an enrichment of <sup>15</sup>N, because of preferential use of <sup>14</sup>N 15 (Högberg, 1997; Novak et al., 1999; Kalbitz et al., 2000). Increased microbial activity in the 16 upper-first centimeters of the drained peatland leads to increased turnover of N which results 17 18 in an enrichment of <sup>15</sup>N (Kalbitz et al., 2000), especially in the first 2-5 centimetrers. It can therefore be postulated that decomposition of peat material results in an enrichment of <sup>15</sup>N. 19 This is one possible explanation for the higher  $\delta^{15}$ N values at GE and GI as compared to NW. 20 Atmospheric N deposition, as discussed above, could additionally influence the  $\delta^{15}$ N signal in 21 these profiles, however we do not see any effect at site NW. Organic fertilizer may also be 22 enriched in <sup>15</sup>N (Watzka et al., 2006), which may contribute to explain higher  $\delta^{15}$ N values in 23 the topsoil of GI. A study of nitrogen isotopes from mineral and organic fertilizer 24 demonstrated that organic fertilizer has a mean  $\delta^{15}$ N value of +8.5 % (Bateman and Kelly, 25 2007). However GE, which does not receive any fertilizer, is also enriched in<sup>15</sup>N in the upper 26 partfirst centimeters of the profile. We therefore assign the (smaller) <sup>15</sup>N enrichment at GE to 27 ongoing oxidative peat decomposition and the (stronger) <sup>15</sup>N enrichment at GI to the 28 29 combined effect of peat decomposition and organic fertilizer applications.

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1 Radiocarbon signatures from the upper peat layers (8-10 cm depth) of site NW indicate the presence of bomb carbon and organic matter fixed during the second half of the last century. 2 This recent C accumulation of almost 1.0 kg C  $m^{-2}$  in the last approximately 50 years at NW 3 is in accordance with the current GHG flux measurements (Beetz et al., 2013), showing that 4 5 the bog has been sequestering carbon during recent years. In deeper parts (65-81 cm depth) of NW, mean peat ages range between 1328 and 1796 cal. years AD. The small differences 6 7 between the mean radiocarbon ages at 65 cm and 81 cm depth at NW are an indicator for 8 undisturbed peat. They point to an average 16 cm of peat growth in approximately 62 years. 9 At both grassland sites, calibrated radiocarbon ages in the upper centimeters are much higher 10 than at NW. This finding can be taken as an indicator for peat degradation and carbon loss. Drainage-induced carbon loss starts from the top, selectively removing younger peat and 11 12 exposing older peat to the surface. We found >500-year-old peat in the upper 14 centimeters at these sites. In 14 to 19 cm depth at GE and 27 to 34 cm depth at GI the peat is almost 1000 13 and 1300 years old, respectively. Peat in deeper parts of the grassland profiles show calibrated 14 mean ages of 165 to 325 cal. years AD and 313 to 34 cal. years BC at GE and GI, 15 respectively. The higher ages in the upper parts of the profile at GI indicate higher peat and C 16 losses compared to the GE, when similar conditions in the peat profiles before onset of 17

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## 22 3.3-4\_C/N ratio

At both grassland sites, C/N ratios are <u>narrow-smaller</u> in the upper layers of the soil profile
(Fig. S2), indicating strong microbial transformation of the peat (Malmer and Holm, 1984;
Kuhry and Vitt, 1996) and possible influence of fertilization (GI). In most of samples from
NW and in deeper layers of GI and GE, C/N ratios are in the range considered as typical for
ombrotrophic peatlands (Kuhry and Vitt, 1996) and indicate low microbial activity.

drainage are assumed. In comparison to NW, peat ages in deeper parts of the two grassland

sites are up to 1500 years older. The grassland sites have lost almost all peat that has

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# 29 **3.4-5** Correlations between stable isotopes and soil C/N

accumulated in the last several centuries.

30 Decomposition affects both stable  $\delta^{13}$ C and  $\delta^{15}$ N by an enrichment of the heavier isotopes in 31 the remaining soil organic matter as well as <u>decreasing the-</u>C/N ratio. A linear correlation

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between these parameters is expected if the material is influenced by strong decomposition
during peat formation or post-sedimentation (Wynn, 2007; Engel et al., 2010). However, no
correlation between the above mentioned parameters will be found in well-preserved peat
(Engel et al., 2010; Jones et al., 2010).

5 Stable isotopes and C/N ratio correlate weakly positive Correlation analyses of isotopes and 6 C/N ratio show a weak positive (r = 0.40 to 0.60) and weakly negative correlation (r = -0.41 7 to -0.52) between  $\delta^{13}$ C and C/N ratio and  $\delta^{15}$ N and C/N ratio, respectively, for theat NW for 8  $\delta^{13}$ C and  $\delta^{15}$ N, respectively (see Tab. 2), indicating that the peat is not strongly decomposed 9 and/or that decomposition did not alter the original isotope signal (Sharma et al., 2005). 10 Zaccone et al. (2011) also found a positive, albeit not significant correlation between  $\delta^{13}$ C and 11 C/N in a well-preserved peat bog in the Swiss Jura mountains.

12 At our grassland sites,  $\delta^{13}$ C and C/N ratio correlate positively (r = 0.32 to 0.70) and  $\delta^{15}$ N and 13 | C/N ratio negatively (r = -0.74 to -0.85), indicating that its the peat is strongly decomposed.

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# 15 **3.5-6** Ash content and bulk density

Ash content and bulk density are indicators for peat decomposition (Clymo, 1984). At NW, 16 17 ash content s are is enriched between 10 and 60 cm depth at NW (Fig. 4a). Bulk density 18 increases at this depth and is higher compared to deeper parts of the profiles (Fig. S1S3). 19 Higher ash content in these depths compared to the deeper layers suggest an increase of 20 decomposition of the peat (Engel et al., 2010). We interpret this ash accumulation as being the result of drainage activities in the vicinity of NW during formation of these peat layers. The 21 22 peat layers with the enriched ash content at the NW site are on average between 50 and 500 years old, which corresponded to the beginning of first land use intensification in this 23 24 peatland. Above and below this depth, the ash content is small, indicating less decomposed 25 ition of the peat. High ash contents (Fig. 4b, Fig. 4c) and bulk densities (Fig. S3) in the first centimeters of the profile at both grassland sites indicate peatland degradation and refer to 26 recent and ongoing peat oxidation. At both grassland sites, ash content (Fig. 4) and bulk 27 density (Fig. S1) increase strongly in the upper centimetres of the profiles, referring to recent 28 and ongoing peat oxidation. In deeper layers of GI-GE and GEGI, ash contents are constant 29 and very low (Fig. 4) and in the range of natural peatlands (Clymo, 1984) and also in the 30 31 range of deeper, undisturbed layers at NW. Thus we used these data as reference layers to calculate the amount of carbon lost since onset of peatland drainage. 32

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## 3.6-7 Carbon loss and peat subsidence

3 Carbon losses estimated by the combined method as induced by drainage are highest at GI. and-intermediate at GE and lowest at NW. The mean (±SD) C losses are 11.5 (±6.3), 18.8 4  $(\pm 2.8)$  and 42.9  $(\pm 10.9)$  kg C m<sup>-2</sup> 931  $(\pm 167)$  and 555  $(\pm 190)$  t C ha<sup>-1</sup> for NW, GE and GI, 5 respectively and GE, respectively. The C loss at site NW may be attributed to the intensive 6 7 drainage and peat extraction activities of the surrounding area in the last century, which may also have impaired the hydrology of this remaining bog. However, in recent years/decades, 8 9 peat at NW is again accumulating C (Beetz et al., 2013) and can therefore nowadays be 10 considered a C sink. This is attributed to the current designation of restoration activities in the frame of a nature conservation area at this site with an accompanying increase of the water 11 12 table (Beckmann and Krahn, 1991; Beller et al., 1994). The heath vegetation at NW, as it is common for peat bogs in Germany, suggests a mild degradational stage (Ellenberg, 1954) 13 14 with likely historical anthropogenic influences. These results carbon loss of the grassland sites determined in this study are in accordance with higher <del>current</del> measured GHG emissions in at 15 site GI than in-at site GE (Beetz et al., 2013). In general, the net GHG emission from 16 extensively managed grasslands is smaller than from intensively managed grasslands, owing 17 18 to a combination of smaller C exports and higher water tables (Drösler et al., 2013). The total 19 carbon loss at these sites since the onset of drainage is similar comparable to drained 20 peatlands in Switzerland under extensive management (Leifeld et al., 2011a). Site NW had also lost carbon in the magnitude of 234 (±38) t C ha<sup>-1</sup>. This C loss may be attributed to the 21 intensive drainage and peat extraction activities of the surrounding area in the last century, 22 23 which may also have impaired the hydrology of this remaining bog. However, in recent 24 years/decades, peat at NW is again accumulating C (Beetz et al., 2013) and therefore nowadays a C sink. This is attributed to the current designation of a nature conservation area 25 at this site with an accompanying increase of the water table (Beckmann and Krahn, 1991; 26 Beller et al., 1994). The heath vegetation at NW, as it is common for peat bogs in Germany, 27 suggests a mild degradation stage (Ellenberg, 1954) with historical anthropogenic influences. 28

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## 30 **3.7 Radiocarbon ages**

Radiocarbon signatures from the upper peat layers (8-10 cm depth) of site NW indicate the
 presence of bomb carbon and thus accumulation of organic matter fixed during the second

half of the last century. This recent accumulation is in accordance with the current GHG flux
 measurements (Beetz et al., 2013), which indicate that the bog has been sequestering carbon
 during the recent years. In deeper parts (65-81 cm depth) of NW, mean peat ages range
 between 1328 and 1796 cal. years AD. The small differences between the mean radiocarbon
 ages at 65 cm and 81 cm depth are an indicator for undisturbed peat layers in this depth.

6 At both grassland sites, high calibrated radiocarbon ages in the upper centimetres are taken as 7 an indicator for peat degradation and carbon loss. We found >500-year-old peat in the upper 8 centimeter at these sites. In 14 to 19 cm depth at GE and 27 to 34 cm depth at GI the peat is 9 almost 1000 and 1300 years old, respectively. Deeper parts of the grassland profiles show calibrated mean ages of peat material with 165 to 325 cal. years AD and 313 to 34 cal. years 10 BC at GE and GI, respectively. The higher ages at the intensively managed grassland profile 11 12 indicate higher peat and C losses from this site compared to the extensively managed grassland site, assuming similar conditions in the peat profiles before onset of drainage. In 13 14 comparison to site NW, peat ages in deeper parts of the grassland sites are up to 1500 years 15 older. The grassland sites have lost almost all peat that has been accumulated in the last several centuries. 16

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### 18 **3.8 Indicators for peatland degradation and quantification of C loss**

19 All parameters ( $\delta^{13}$ C,  $\delta^{15}$ N, ash content, C/N ratio, bulk density, and radiocarbon ages) 20 indicate a degradation of the former bog <u>at the Ahlen-Falkenberger peatland</u> when managed 21 as grassland (GE and GI) at the Ahlen-Falkenberger peatland. <u>All of these parameters might</u> 22 <u>be usefulAll those data could be used as</u> indicators for peatland degradation, but not all in a 23 quantitative manner (Tab. 3).

24 Stable carbon isotope depth profiles indicate degradation at all sites at the peatland. At NW in the upper 10 cm and below 65 cm depth as well as in deeper parts of the grassland sites  $\delta^{13}$ C 25 is constant with depth indicating a natural peat. Stable nitrogen isotope, ash content, C/N ratio 26 27 as well as bulk density depth profiles show a higher decomposition of the peat material in the upper part at the grassland sites as well as in 20-60 cm depth at NW. The  $\delta^{15}$ N signal in the 28 peat profiles is mainly driven by decomposition (GE and GI) and fertilizer application (GI). 29 Radiocarbon ages,  $\delta^{13}$ C as well as ash content in the first centimeter of the NW depth profiles 30 provide evidence for contemporary peat accumulation with young peat material formed in the 31 last decades. Peat from topsoil segments of both grassland sites is much older than peat from 32

deeper segments of the NW site. These data illustrate the consequences of peatland drainage
 that induces loss of peat material which has been accumulated over the last centuries. The ash
 content in combination with bulk density and C content (combined method) gives reasonable
 estimates of C loss since the onset of drainage activities in this peatland.

Soil ash content and radiocarbon signatures have the potential to provide quantitative
estimates on peatland carbon loss whereas changes in stable isotope patterns and C/N ratios
serve as qualitative indicators and support the understanding of processes and mechanisms
involved.

9 Peat loss as well as carbon loss is higher when the grassland is used more intensively as 10 shown by the depth profiles of  $\delta^{13}$ C and ash content. These results are in accordance with the 11 higher peat ages of the deeper parts of the intensively compared to the extensively managed 12 grassland.

At site NW, both depth profiles of stable carbon isotopes and ash content indicate degradation 13 processes by increasing  $\delta^{13}$ C signatures with depth and a relative enrichment of ash in 14 20-60 cm depth, respectively. From about 65 cm depth the  $\delta^{13}$ C signatures at NW are almost 15 constant indicating a natural peat which is supported by the small differences in the mean 16 radiocarbon ages of 65 cm and 81 cm depth. Above the uniform depth trend the 813C 17 18 signatures increase indicating a degradation of the peatland since 1534±228 cal. years AD. However, in the upper soil profiles of NW, radiocarbon ages as well as low ash contents in 19 the first centimetres provide evidence for contemporary peat accumulation with young peat 20 21 material formed in the last decades. Correspondingly, stable carbon isotopes signatures are constant in the first ten centimetres, indicating the development of growing conditions 22 23 without disturbance.

Furthermore, the radiocarbon ages indicate that the disturbance at NW shown by δ<sup>13</sup>C as well
as ash content depth profiles is not displayed in both grassland sites, because this peat
material has been lost due to peat oxidation. The peat material in both grassland sites is much
older than at the deeper parts of the NW site and shows the consequences of peatland drainage
with peat loss which has been accumulated over the last centuries.

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## 1 4 Conclusions

2 Depth profiles of different biogeochemical parameters together provide a detailed insight into peatland formation and the effects of management on peat degradation.  $\delta^{13}C$ ,  $\delta^{15}N$ , ash 3 content, C/N ratio, bulk density, as well as radiocarbon ages in peat depth profiles indicate 4 5 degradation of all peatlands, but to very different degrees. Peat and C loss could be quantified 6 by the combination of ash content and bulk density and is supported by the radiocarbon ages. 7 At the near-natural site (NW), stable carbon isotopes and ash contents indicate degradation due to the drainage of the surrounding area, which affected the NW site in the past. Hence, 8 also bogs considered semi-natural were impaired by anthropogenic activities, at least in the 9 10 past.

- 11 (I) Increasing  $\delta^{13}$ C values with depth indicate aerobic decomposition of the peat material at all 12 sites. We found no absolute differences in the  $\delta^{13}$ C patterns, but could show that the slopes of 13 the  $\delta^{13}$ C depth profiles differ significantly, as a result of peat degradation.
- (II) At the near-natural site (NW), stable carbon isotope and ash content depth profiles as well
  as radiocarbon dating indicate moderate degradation due to the drainage of the surrounding
- area in the past. Hence, also bogs considered semi-natural were impaired by anthropogenic
   activities. Recent organic matter accumulation, as indicated by the <sup>14</sup>C values, indicates
   rehabilitation of the peatland.
- 19 (III) With conversion to grassland increasing peat decomposition and fertilizer application 20 systematically alter the  $\delta^{15}N$  signature of the soil. With conversion to grassland (extensive 21 (GE) and intensive (GI)),  $\delta^{15}N$  depth profiles change significantly compared to a semi-natural 22 situation. Both, increasing peat decomposition and fertilizer application systematically 23 changed the  $\delta^{15}N$  signature of the soil. The  $\delta^{15}N$  values in the upper soil profiles reflect the 24 decomposition degree of the peat material and show a completely different depth pattern as 25 hypothesized.
- 26 (IV) Based on ash accumulation calculations the three sites lost carbon in the order NW < GE 27 <br/>
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- 29 (III) The three sites lost carbon in the order NW < GE < GI. Higher losses under intensive 30 management are supported by higher peat ages at this site as well as the steeper slopes of  $\delta^{13}$ C 31 with depth. To quantify the carbon losses from the soil due to the degradation of the peatland,

the applied combined method gives reasonable C losses since the onset of human
 intervention.

Biogeochemical soil parameters of peat profiles are applicable to detect peat degradation and
to determine the order of quantitative peat and C loss. Solely one parameter in soil depth
profiles is often not enough to detect peat degradation but with the combination of different
biogeochemical parameters in a high resolution it is possible to detect the degradation.

7

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1 Tab. 1: Slope, <u>depth</u> and coefficient of determination of regression analyses between  $\delta^{13}$ C and 2 depth until the  $\delta^{13}$ C value of -25.0 ‰ was reached in the depth profile. Three profiles of each

3 site, near-natural (NW), extensive managed grassland (GE) and intensive managed grassland

4 (GI) site from the Ahlen-Falkenberger peatland are presented. <u>'n' refers to number of soil</u>

5

segments per site and replication included in the regression.

Site/core	<u>depth (cm)</u>	slope	$R^2$	р	n
NW1	<u>25.0</u>	0.26	0.97	0.0004	7
NW2	<u>65.0</u>	0.07	0.92	0.0000	17
NW3	<u>65.0</u>	0.08	0.94	0.0000	17
GE1	<u>23.7</u>	0.13	0.92	0.0023	6
GE2	<u>40.3</u>	0.09	0.74	0.0015	10
GE3	<u>31.7</u>	0.11	0.92	0.0022	6
GI1	<u>28.4</u>	0.21	0.96	0.0008	6
GI2	<u>31.0</u>	0.14	0.89	0.0016	7
GI3	<u>18.7</u>	0.20	0.90	0.0146	5

6

- 1 Tab. 2: Correlation coefficient and p value (p<0.05 in boldface) between  $\delta^{13}C_{,,,\delta^{15}N}$  and C/N
- 2 ratio <u>as well as between  $\delta^{15}$ N and C/N ratio for the whole profiles</u> at the near-natural (NW),
- 3 extensive managed grassland (GE) and intensive managed grassland (GI) site at the Ahlen-
- 4 Falkenberger peatland.

Site/core	$\delta^{13}$ C vs. C/N	$\delta^{15}$ N vs. C/N			
NW 1	$0.40^{\frac{\text{n.s.}(0.051)}{2}}$	-0.41 <sup>n.s.(0.051)</sup>			
NW 2	0.60 <sup>**(0.002)</sup>	-0.52 <sup>**(0.010)</sup>			
NW 3	0.46 <sup>*(0.022)</sup>	-0.49 <sup>*(0.016)</sup>			
GE 1	0.49 <sup>*(0.012)</sup>	-0.81 <sup>***(0.000)</sup>			
GE 2	$0.70^{\frac{***}{(0.000)}}$	-0.85 <sup>***(0.000)</sup>			
GE 3	0.32 <sup>n.s.(0.000)</sup>	-0.74 <sup>****<u>(0.002)</u></sup>			
GI 1	0.61 <sup>**(0.002)</sup>	-0.78 <sup>(0.000)</sup> ***			
GI 2	0.68 <sup>(0.000)***</sup>	-0.75 <sup>(0.000)****</sup>			
GI 3	0.32 <sup>n.s.(0.109)</sup>	-0.74 <sup>(0.000)****</sup>			
<sup>n.s.</sup> = not significant, <sup>*</sup> p< 0.05, <sup>**</sup> p< 0.01, <sup>***</sup> p<					

Parameters	Reliable indicator for peat degradation?	Quantification of C loss possible?	
$\delta^{13}C$	yes	no	
$\delta^{15}N$	yes	no	
Ash content	yes*	yes	
<sup>14</sup> C age	yes	(yes)	
C/N	(yes)	no	
Bulk density	(yes)	(yes with ash content)	
Correlation between $\delta^{13}$ C, $\delta^{15}$ N and C/N	yes	no	

Tab. 3: Biogeochemical parameters from the Ahlen-Falkenberger peatland profiles as
 indicators for peatland degradation as well as peat and carbon loss.

3 \* for bogs and assuming homogeneous atmospheric input

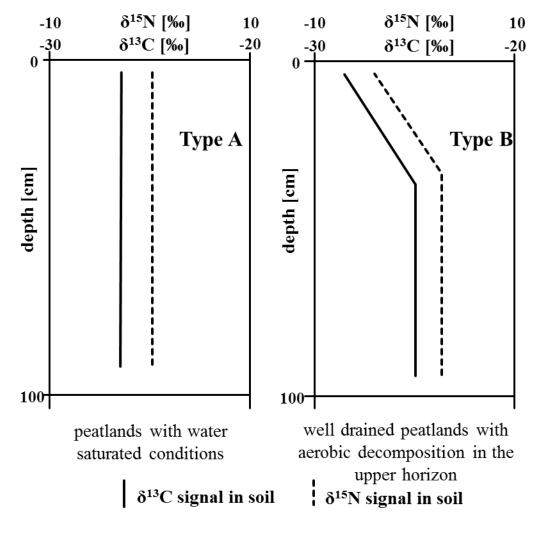


Fig. 1: Theoretical concept of  $\delta^{13}$ C and  $\delta^{15}$ N depth profiles in natural (left) and degraded (right) peatlands.

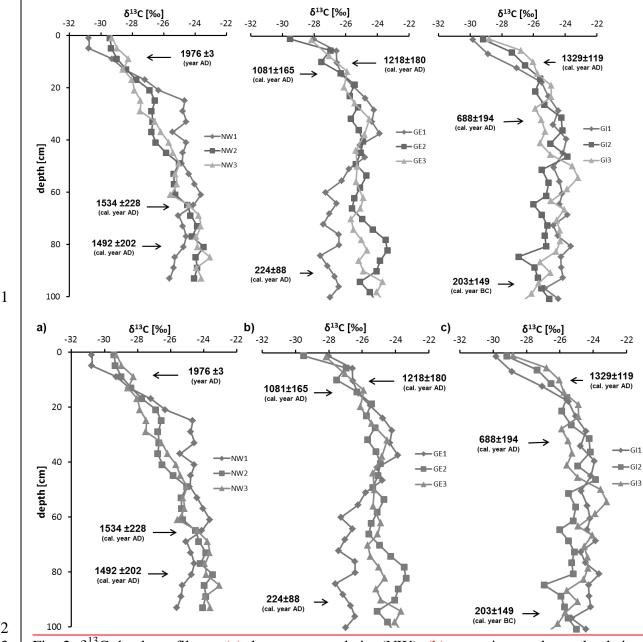


Fig. 2:  $\delta^{13}$ C depth profiles at (a) the near-natural site (NW), (b) extensive used grassland site (GE) and (c) intensive used grassland site (GI) at the Ahlen-Falkenberger peatland. Calibrated radiocarbon ages are displayed as mean calendar ages with 1 standard deviation (n=3) at their corresponding depth.

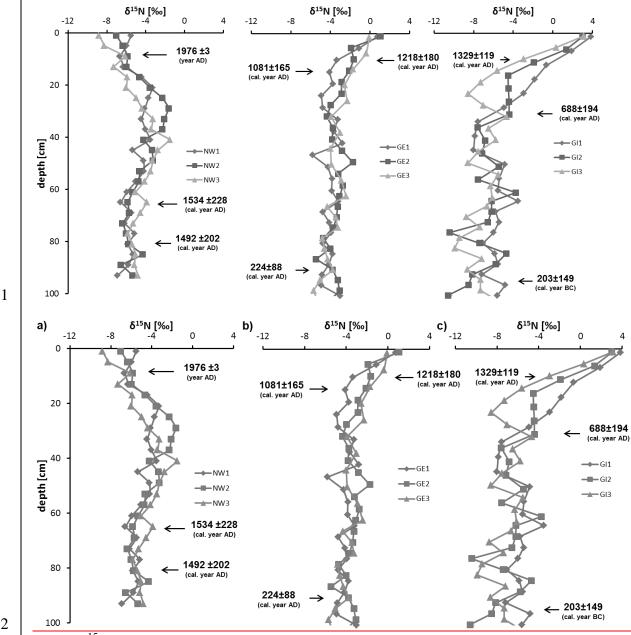




Fig. 3:  $\delta^{15}$ N depth profiles at (a) the near-natural site (NW), (b) extensive used grassland site (GE) and (c) intensive used grassland site (GI) at the Ahlen-Falkenberger peatland. Calibrated radiocarbon ages are displayed as mean calendar ages with 1 standard deviation (n=3) at their corresponding depth.

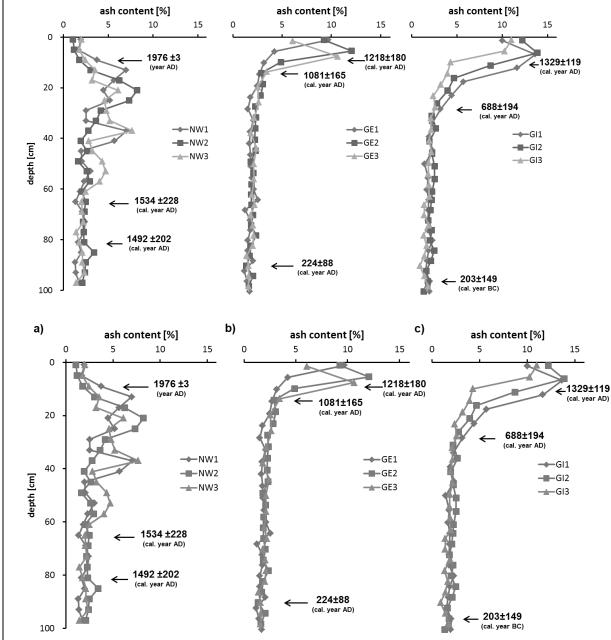


Fig. 4: Ash content depth profiles at (a) the near-natural site (NW), (b) extensive used grassland site (GE) and (c) intensive used grassland site (GI) at the Ahlen-Falkenberger peatland. Calibrated radiocarbon ages are displayed as mean calendar ages with 1 standard deviation (n=3) at their corresponding depth.