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Biogeochemical indicators of peatland degradation – a case study of a temperate bog in northern Germany

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Abstract

Peatlands store a great proportion of the global soil carbon pool and can loose carbon via the atmosphere due to degradation. In Germany, most of the greenhouse gas 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 (GE) to an intensively managed grassland site (GI), all formed in the same bog complex in northern Germany. Vertical depth profiles of δ^{13}C, δ^{15}N, ash content, C/N ratio, bulk density, as well as radiocarbon ages were studied to identify peat degradation and to calculate carbon loss. At all sites, including the near-natural site, δ^{13}C depth profiles indicate aerobic decomposition in the upper horizons. Depth profiles of δ^{15}N differed significantly between sites with increasing δ^{15}N values in the top layers with increasing intensity of use, indicating that the peat is more decomposed. At both grassland sites, the ash content peaked within the first centimeter. In the near-natural site, ash contents were highest in 10–60 cm depth. This indicates that not only the managed grasslands, but also the near-natural site, is influenced by anthropogenic activities, most likely due to the drainage of the surrounding area. However, we found very young peat material in the first centimeter 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 δ^{13}C and ash content depth profiles. Based on the enrichment of ash content and changes in bulk density, we calculated carbon loss from these sites in retrograde. As expected land use intensification leads to a higher carbon loss which is supported by the higher peat ages at the intensive managed grassland site. All investigated biogeochemical parameters together indicate degradation of peat due to (i) conversion to grassland, (ii) historical drainage as well as recent development and (iii) land use intensification.

1 Introduction

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

GHG emissions from peatlands under grassland use for the temperate zone average 6.1 $\mathrm{t\,C\,ha^{-1}\,a^{-1}}$ for deeply drained and 3.6 $\mathrm{t\,C\,ha^{-1}\,a^{-1}}$ for shallowly drained peatlands (IPCC, 2013). Ranked by land-use intensity, intensively managed grasslands emit 28.3 $\mathrm{t\,CO_{2eq}\,ha^{-1}\,a^{-1}}$, extensively managed grasslands between 2.2 and 20.1 t $\mathrm{CO_{2eq}\,ha^{-1}\,a^{-1}}$ (depending on the water table), near-natural bogs are almost climate-neutral, but dry bogs emit up to 9.6 $\mathrm{t\,CO_{2eq}\,ha^{-1}\,a^{-1}}$ (Drösler et al., 2013).

To study soil degradation in different environments, stable 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, the δ^{13}C is almost constant, because in water saturated soils the oxygen availability is low, decomposition of organic material is limited, and therefore the fractionation is small (Clymo and Bryant, 2008; Skrzypek et al., 2008; Alewell et al., 2011). Alternatively, under anaerobic conditions with anaerobic decomposition, the depth profile may show a slight decrease with depth because of an relative enrichment of ^{13}C depleted lignin (Benner et al., 1987; Alewell et al., 2011). Under aerobic conditions, decomposers preferentially use the lighter ^{12}C for respiration. Hence the heavier ^{13}C accumulates in the remaining organic matter and the δ^{13}C value increases with depth (Nadelhoffer and Fry, 1988; Ågren et al., 1996). Increasing δ^{13}C values with depth are typical for well drained or mineral soils (Nadelhoffer and Fry, 1988; Alewell et al., 2011). Together, peatland drainage induces a change from a uniform δ^{13}C depth profile to increasing δ^{13}C values with depth (Fig. 1).

Because atmospheric N is the primary source of N in the system, δ^{15}N values in natural bogs are assumed to scatter around 0 ‰ (Fig. 1) (Jones et al., 2010; Broder et al., 2012). However, plant species in intact peatlands show a high variability of δ^{15}N signatures from −11.3 to +2.7 ‰ (Asada et al., 2005b), which could influence the δ^{15}N signature of the remaining peat material. Nitrogen isotope fractionation during decomposition processes leads to an enrichment of ^{15}N in the remaining material and an increase of soil ^{15}N with depth and age (Nadelhoffer and Fry, 1988; Nadelhoffer et al., 1996). Therefore, δ^{15}N values in (wet) oxic soils increase with depth (Fig. 1) with lower δ^{15}N values in the upper horizon and higher δ^{15}N values in deeper horizons (Nadelhoffer et al., 1996; Kohzu et al., 2003). Consequently, we assume that in drained and/or degraded peatlands, δ^{15}N values are increasing with depth, owing to the above mentioned process (Fig. 1). In intensively managed ecosystems, the application of mineral and/or organic fertilizer, with their different isotopic signals (Bateman and Kelly, 2007), could additionally alter the stable nitrogen isotope signature in soil.

Another indicator of organic matter decomposition is the C/N ratio of the peat (Malmer and Holm, 1984; Kuhry and Vitt, 1996). 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.

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., 2008; Leifeld et al., 2011a), based on the premise of an accumulation of mineral matter (or “ash”) with peat oxidation. In a pristine state of a bog, where the mineral input solely derives from the atmosphere, we assume a relative homogeneous ash depth profile. Drainage induces peat oxidation and net CO_2 emission, leading to peat subsidence and a relative enrichment of ash content in the upper layers, where decomposition is strongest. A so-called combined method (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 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, how stable isotopes of carbon and nitrogen can be used as indicators of peatland degradation along a gradient of land use and drainage intensity and weather 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:

1. The $\delta^{13}C$ depth profile changes from a constant signal under near-natural conditions to increasing $\delta^{13}C$ values with depth in degrading peatlands.
2. Higher decomposition of the peat in the degraded sites leads to an increase of $\delta^{15}N$ values in the upper layers.
3. C losses are higher in the intensively managed compared to the extensively managed grassland.

Analysis of other indicators, such as radiocarbon age, ash content and C/N ratio, will be used for validation of the interpretation of the stable isotope depth profiles.

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2 Material and methods

2.1 Site description

The study area is located in, Lower Saxony, north western Germany, close to the North Sea 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 average annual precipitation of 925.7 mm and an average annual temperature of 8.5 °C (reference period 1961–1990; German Weather Service, 2010). Bog formation started at about 6000 years BP on a former fen area (Schneekloth, 1970). Since the late 17th century, peat was extracted at the edges of the bog. Intensive drainage started at the beginning of the 20th century, and land use was intensified in the middle of the 20th century (Ahrendt, 2012). Industrial peat extraction at the Ahlen–Falkenberger peatland began in 1957 (Schneekloth, 1981) and was terminated in the 1990s, when conservation area was established (Beckmann and Krahn, 1991; Beller et al., 1994). About 60 % of the remaining area is currently used as grassland, and only a small area in the centre of the peat bog complex (approx. 5 %) was never drained or cultivated and remains as a natural peat bog today (Höper, 2007). In this area, vegetation is dominated by 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 wetland (NW) as unmanaged. Further, we studied two former areas of the bog which are drained and nowadays managed as grassland: The extensive grassland (GE) is neither fertilized nor manured and only cut once per year. The intensive grassland (GI) is cut 4–5 times per year and fertilized with mineral fertilizer and manure. GI is drained with pipes as well as drainage ditches whereas GE is only drained by ditches which were closed in 2003/04. At the NW site, the water table was around the soil surface in 2012 and fluctuated between the surface and 80 cm depth (GI) and between surface and 40 cm depth (GE) (Frank et al., 2014). Across the former bog complex, thicknesses of peat range from 330 cm in cultivated to 515 cm in uncultivated, near-natural areas (Beetz et al., 2013). Current GHG flux measurements at the Ahlen–Falkenberger peatland (2007–2009) indicate a carbon source at GI of about 5–8 tC ha^{-1} a^{-1}. The Net ecosystem carbon balance was positive in one and negative in the following year at GE (Beetz et al., 2013). Site NW was C neutral in one year and accumulated C in the other year (Beetz et al., 2013).

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 ($n = 3$). 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 δ^{13}C in [‰] relative to the V-PDB standard. Stable nitrogen isotope ratios are reported as δ^{15}N in [‰] relative to the atmospheric nitrogen standard. The analytical standard deviation is 0.15 % and 0.1 % for δ^{15}N and δ^{13}C, respectively.

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

2.3 Radiocarbon analyses

Radiocarbon (^{14}C) analysis was performed with accelerator mass spectrometry (AMS) at the Laboratory of for the Analysis of Radiocarbon with AMS (LARA) at the University of Bern (Szidat et al., 2014). For each site, three depths were selected for radiocarbon dating and samples at these depths were investigated for each individual core. Samples were selected after evaluation of stable isotope and ash content depth profiles and were taken where a clear change in depth pattern was indicated. 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 CArbon DAting System MICADAS (Synal et al., 2007). Sample homogeneity and measurement reproducibility was proven by double analysis of 8 random samples, whereas general accuracy and precision was reported earlier (Szidat et al., 2014). ^{14}C ages were calibrated using the IntCal13 dataset (Reimer et al., 2013). Samples with bomb signature were dated using the Bomb13 NH1 dataset (Hua et al., 2013). Results of the individual measurements are shown in Tab. S1.

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

The integrated calculation of carbon loss of the peatland since the beginning of drainage is based on the simplified assumption of a constant ratio between carbon to ash content during accumulation of peat and that ash content before drainage is the same at all depths. After drainage, peat starts to oxidize and carbon is lost as CO_2 (Rogiers et al., 2008). Additionally, 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 (Leifeld et al., 2011a). The carbon loss was calculated separately for each core.

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.

The *primary subsidence* [m] is calculated as follows (Leifeld et al., 2014):

$$V_{0i} - T_i \tag{1}$$

with

$$V_{0i} = \mathrm{Bd\,OS}_i / \mathrm{Bd\,OS}_\mathrm{r} \times T_i \tag{2}$$

Where V_{0i} is the pre-drainage thickness of layer i [m], Bd OS_i is organic matter density in layer i, Bd OS_r is organic matter density of the reference layer [$\mathrm{t\,m^{-3}}$], and T_i is the thickness of layer i [m] at time of sampling. Bd OS 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 $\mathrm{t\,m^{-3}}$.

The *secondary subsidence* is calculated from the pre-drainage thickness T_{0i} [m] attributable to organic matter oxidation (Leifeld et al., 2014):

$$T_{0i} = T_i \times \mathrm{ash}_i / \mathrm{ash}_\mathrm{r} \tag{3}$$

with T_i the thickness of layer i [m], ash_i the ash concentration of layer i, ash_r the ash concentration of the reference layer and the amount of soil carbon in any single layer $C_{d\,i}$ [$\mathrm{t\,m^{-2}}$] lost by oxidation given as

$$C_{d\,i} = T_d \times C_\mathrm{r} / T_\mathrm{r} \tag{4}$$

with C_r the soil carbon stock of the reference layer [$\mathrm{t\,m^{-2}}$], T_r the thickness of the reference layer [m] and the volumetric loss due to peat oxidation T_d [m] given

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

Carbon losses are displayed as $\mathrm{t\,C\,ha^{-1}}$ and loss rates as $\mathrm{t\,C\,ha^{-1}\,a^{-1}}$ by dividing the carbon loss by the number of years passed since the peatland was drained.

The NW site could not be used as a reference for the calculation of C loss, because of the influence of drainage activities of surrounding areas, indicated by higher ash contents at 10–50 cm depth. We used the deeper layers of the grassland sites as a reference, similar to the approach taken in previous studies (Rogiers et al., 2008; Leifeld et al., 2011a).

2.5 Statistical analyses

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

3 Results and discussion

3.1 Stable carbon isotopes

In both grassland soils, δ^{13}C values increase from about −30 ‰ in the upper centimeter to about −25 ‰ in deeper layers (Fig. 2). This increase of δ^{13}C values with depth indicates aerobic conditions in the peat profile, as aerobic decomposition selectively uses the lighter isotope ^{12}C for respiration and the heavier ^{13}C is enriched in the remaining organic material of the soil (Nadelhoffer and Fry, 1988; Ågren et al., 1996). This δ^{13}C depth pattern was also found at site NW, indicating degradation also at this site (Fig. 2). In general, natural peatlands are expected to show a uniform δ^{13}C depth profile (Clymo and Bryant, 2008; Skrzypek et al., 2008) or a trend towards slightly lower values, caused by an enrichment of recalcitrant substances depleted in ^{13}C (Benner et al., 1987; Krull and Retallack, 2000; Alewell et al., 2011). An increase of δ^{13}C values 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 oxic grassland soils (Accoe et al., 2003). In northern peatlands, increases of δ^{13}C with depth were found in dry hummocks in contrast to uniform depth profiles in water saturated hollows (Alewell et al., 2011; Krüger et al., 2014).

Depth profiles of δ^{13}C values are apparently compressed in the upper part of both grasslands compared to site NW (Fig. 2). A linear regression analyses with δ^{13}C vs. depth results in deepest slopes of δ^{13}C vs. depth at site GI (Table 1), which might point to a higher peat loss there compared to GE. Below this point the δ^{13}C values of all profiles are more or less constant throughout the profile, indicating low decomposition with limited fractionation (Clymo and Bryant, 2008).

3.2 Stable nitrogen isotopes

The δ^{15}N values first increase and then decrease with depth at the NW site (Fig. 3). The inversion is located at ca. 20–40 cm depth, corresponding to δ^{15}N values of −2.0 to −4.0 ‰. At the grassland sites, δ^{15}N values decrease in the upper part of soil and remain constant in the deeper profile. At GE, δ^{15}N values are slightly positive in the upper few centimetres of the profile and reach values of around −4.0 ‰ below 20 cm. At GI, on the other hand, δ^{15}N values are positive in the upper centimetres (up to 4.0 ‰) and decrease to up to −10.5 ‰ in deeper layers. The values at GI are more variable and reach more negative δ^{15}N values in the deeper part as compared to GE.

The δ^{15}N values of a natural peatland should be rather constant at around 0.0 ‰, because atmospheric N is the primary source of N (Jones et al., 2010; Broder et al., 2012). However, peat plant species show a wide range of δ^{15}N values from below −11 to above +2 ‰ (Asada et al., 2005b), and this may influence the δ^{15}N values of the remaining peat material. Incubation of peat mosses have shown a ^{15}N enrichment with time with an increase of δ^{15}N with depth (Asada et al., 2005a). Human activities have a great influence on δ^{15}N values in mosses by different atmospheric depositions and their N sources and are not simply related to the total N deposition (Bragazza et al., 2005). Low δ^{15}N values were reported in areas with high local ammonia emissions from livestock during animal husbandry, manure storage and spreading (Asman et al., 1998) with very low δ^{15}N values in wet (NH_4) and dry (NH_3) deposition (Bragazza et al., 2005). Sphagnum mosses are depleted in ^{15}N compared to the atmospheric nitrogen and have lower δ^{15}N values in areas affected by agricultural activities (Bragazza et al., 2005). The δ^{15}N depletion in the upper part of NW profiles may be assignable to the very low δ^{15}N values of e.g. *Calluna vulgaris*, which might have mean δ^{15}N value as low as −9.0 ‰ (Nordbakken et al., 2003; Bragazza et al., 2010), and is nowadays one of the dominating species at this site. Atmospheric N deposition, as discussed above, may be another reason. Below approximately 20 cm, δ^{15}N values are less negative and in the range of nitrogen isotope values typical for mosses (Asada et al., 2005b).

δ^{15}N depth profiles of our drained sites show a completely different depth pattern as hypothesized in our theoretical concept for drained peatlands (Fig. 1) with decreasing instead of increasing δ^{15}N values with depth (Fig. 3). High δ^{15}N of the topsoil in our grassland sites (Fig. 3) most likely indicate increased microbial activity, caused by drainage, in conjunction with effects from organic fertilizer application at GI. Decomposition is often linked to an enrichment of ^{15}N, because of preferential use of ^{14}N (Högberg, 1997; Novak et al., 1999; Kalbitz et al., 2000). Increased microbial activity in the upper centimeter of the drained peatland leads to increased turnover of N which results in an enrichment of ^{15}N (Kalbitz et al., 2000), especially in the first centimetres. Organic fertilizer may be enriched in ^{15}N (Watzka et al., 2006), which may explain higher δ^{15}N values in the topsoil of GI. A study of nitrogen isotopes from mineral and organic fertilizer demonstrated that organic fertilizer has a mean δ^{15}N value of +8.5 ‰ (Bateman and Kelly, 2007). However GE, which does not receive any fertilizer, is also enriched in ^{15}N in the upper part. We therefore assign the (smaller) ^{15}N enrichment at GE to ongoing oxidative peat decomposition and the (stronger) ^{15}N enrichment at GI to the combined effect of peat decomposition and organic fertilizer applications.

3.3 C/N ratio

At both grassland sites, C/N ratios are narrow 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). 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).

3.4 Correlations between stable isotopes and soil C/N

Decomposition affects both stable δ^{13}C and δ^{15}N by an enrichment of the heavier isotopes in the remaining soil organic matter as well as the C/N ratio. A linear correlation 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).

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

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

3.5 Ash content and bulk density

Ash content and bulk density are indicators for peat decomposition (Clymo, 1984). At NW, ash contents are enriched between 10 and 60 cm depth at NW (Fig. 4). Bulk density increases at this depth and is higher compared to deeper parts of the profiles (Fig. S1). Higher ash content in these depths compared to the deeper layers suggest an increase of decomposition of the peat (Engel et al., 2010). We interpret this accumulation as being the result of drainage activities in the vicinity of NW during formation of these peat layers. Above and below this depth, the ash content is small, indicating less decomposition of the peat. At both grassland sites, ash content (Fig. 4) and bulk density (Fig. S1) increase strongly in the upper centimetres of the profiles, referring to recent and ongoing peat oxidation. In deeper layers of GI and GE, ash contents are constant and very low (Fig. 4) and in the range of natural peatlands (Clymo, 1984). Thus we used these data as reference layers to calculate the amount of carbon lost since onset of peatland drainage.

3.6 Carbon loss

Carbon losses as induced by drainage are highest at GI, and intermediate at GE. The mean (± SD) C losses are 429 (±109) and 188 (±28) tC ha^{-1} for GI and GE, respectively. These results are in accordance with higher current GHG emissions in GI than in GE (Beetz et al., 2013). In general, the net GHG emission from extensively managed grasslands is smaller than from intensively managed grasslands (Drösler et al., 2013). The total carbon loss at these sites since the onset of drainage is similar to drained peatlands in Switzerland under extensive management (Leifeld et al., 2011a). Site NW had also lost carbon in the magnitude of 115 (±63) tC ha^{-1}. This C loss may be attributed to the intensive 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, 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 at this site with an accompanying increase of the water 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 degradation stage (Ellenberg, 1954) with historical anthropogenic influences.

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 and 81 cm depth are an indicator for undisturbed peat layers in this depth.

At both grassland sites, high calibrated radiocarbon ages in the upper centimetres are taken as an indicator for peat degradation and carbon loss. We found > 500-year-old peat in the upper centimeter at these sites. In 14 to 19 cm depth at GE and 27 to 34 cm depth at GI the peat is 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 BC at GE and GI, respectively. The higher ages at the intensively managed grassland profile 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 comparison to site NW, peat ages in deeper parts of the grassland sites are up to 1500 years older. The grassland sites have lost almost all peat that has been accumulated in the last several centuries.

3.8 Indicators for peatland degradation and quantification of C loss

All parameters (δ^{13}C, δ^{15}N, ash content, C/N ratio, bulk density, and radiocarbon ages) indicate a degradation of the former bog when managed as grassland (GE and GI) at the Ahlen–Falkenberger peatland. All those data could be used as indicators for peatland degradation, but not all in a quantitative manner (Table 3). Peat loss as well as carbon loss is higher when the grassland is used more intensively as shown by the depth profiles of δ^{13}C and ash content. These results are in accordance with the higher peat ages of the deeper parts of the intensively compared to the extensively managed grassland.

At site NW, both depth profiles of stable carbon isotopes and ash content indicate degradation processes by increasing δ^{13}C signatures with depth and a relative enrichment of ash in 20–60 cm depth, respectively. From about 65 cm depth the δ^{13}C signatures at NW are almost constant indicating a natural peat which is supported by the small differences in the mean radiocarbon ages of 65 and 81 cm depth. Above the uniform depth trend the δ^{13}C 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 the first centimetres provide evidence for contemporary peat accumulation with young peat material formed in the last decades. Correspondingly, stable carbon isotopes signatures are constant in the first ten centimetres, indicating the development of growing conditions without disturbance.

Furthermore, the radiocarbon ages indicate that the disturbance at NW shown by δ^{13}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.

4 Conclusions

Depth profiles of different biogeochemical parameters together provide a detailed insight into peatland formation and the effects of management on peat degradation. δ^{13}C, δ^{15}N, ash content, C/N ratio, bulk density, as well as radiocarbon ages in peat depth profiles indicate degradation of all peatlands, but to very different degrees. 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, also bogs considered semi-natural were impaired by anthropogenic activities, at least in the past.

1. Increasing δ^{13}C values with depth indicate aerobic decomposition of the peat material at all sites. We found no absolute differences in the δ^{13}C patterns, but could show that the slopes of the δ^{13}C depth profiles differ significantly, as a result of peat degradation.
2. With conversion to grassland (extensive (GE) and intensive (GI)), δ^{15}N depth profiles change significantly compared to a semi-natural situation. Both, increasing peat decomposition and fertilizer application systematically changed the δ^{15}N signature of the soil. The δ^{15}N values in the upper soil profiles reflect the decomposition degree of the peat material and show a completely different depth pattern as hypothesized.
3. The three sites lost carbon in the order $\mathrm{NW} < \mathrm{GE} < \mathrm{GI}$. Higher losses under intensive management are supported by higher peat ages at this site as well as the steeper slopes of δ^{13}C 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.

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Table 1. Slope and coefficient of determination of regression analyses between δ^{13}C and depth until the δ^{13}C value of −25.0 ‰ was reached in the depth profile. Three profiles of each site, near-natural (NW), extensive managed grassland (GE) and intensive managed grassland (GI) site from the Ahlen–Falkenberger peatland are presented.

Site/core	slope	R^2	p	n
NW1	0.26	0.97	0.0004	7
NW2	0.07	0.92	0.0000	17
NW3	0.08	0.94	0.0000	17
GE1	0.13	0.92	0.0023	6
GE2	0.09	0.74	0.0015	10
GE3	0.11	0.92	0.0022	6
GI1	0.21	0.96	0.0008	6
GI2	0.14	0.89	0.0016	7
GI3	0.20	0.90	0.0146	5

Table 2. Correlation coefficient between δ^{13}C, δ^{15}N and C/N ratio at the near-natural (NW), extensive managed grassland (GE) and intensive managed grassland (GI) site at the Ahlen–Falkenberger peatland.

Site/core	δ^{13}C vs. δ^{15}N	δ^{13}C vs. C/N	δ^{15}N vs. C/N
NW 1	$0.21^{\text{n.s.}}$	$0.40^{\text{n.s.}}$	$-0.41^{\text{n.s.}}$
NW 2	$-0.16^{\text{n.s.}}$	0.60^{b}	-0.52^{b}
NW 3	$0.35^{\text{n.s.}}$	0.46^{a}	-0.49^{a}
GE 1	$-0.26^{\text{n.s.}}$	0.49^{a}	-0.81^{c}
GE 2	-0.69^{c}	0.70^{c}	-0.85^{c}
GE 3	-0.56^{b}	$0.32^{\text{n.s.}}$	-0.74^{c}
GI 1	-0.71^{c}	0.61^{b}	-0.78^{c}
GI 2	-0.48^{a}	0.68^{c}	-0.75^{c}
GI 3	-0.56^{b}	$0.32^{\text{n.s.}}$	-0.74^{c}

n.s. = not significant, [a] $p < 0.05$, [b] $p < 0.01$, [c] $p < 0.001$.

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Table 3. Biogeochemical parameters from the Ahlen–Falkenberger peatland profiles as indicators for peatland degradation as well as peat and carbon loss.

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
^{14}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

* For bogs and assuming homogeneous atmospheric input.

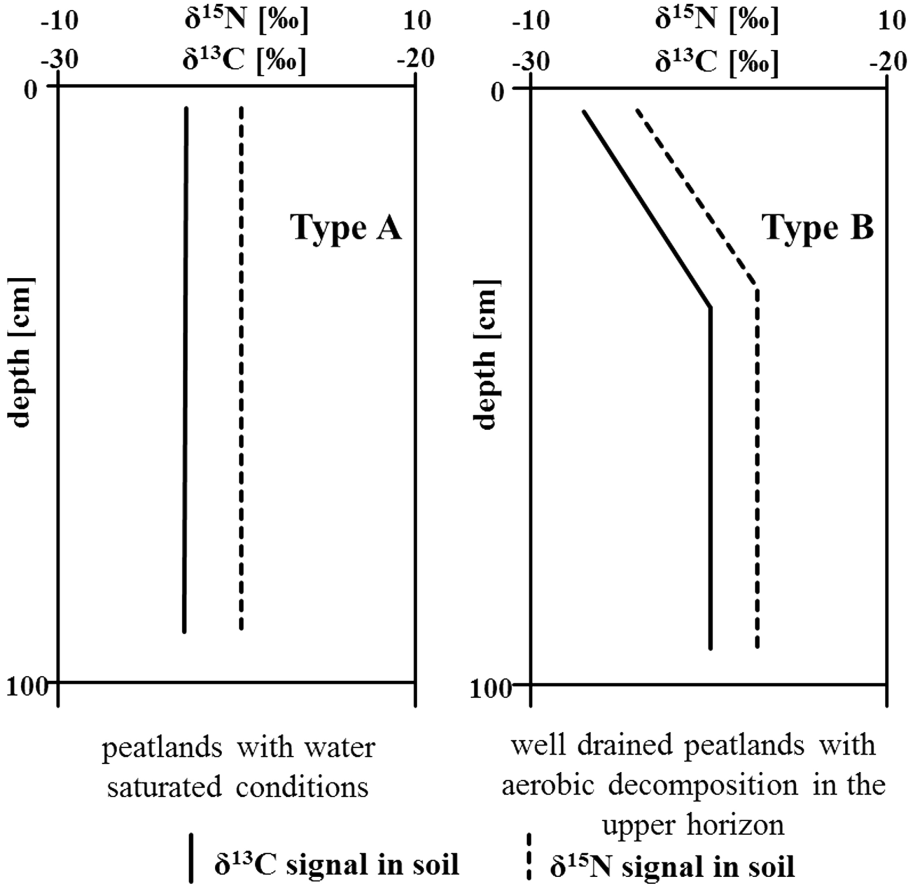

Figure 1. Theoretical concept of δ^{13}C and δ^{15}N depth profiles in natural (left) and degraded (right) peatlands.

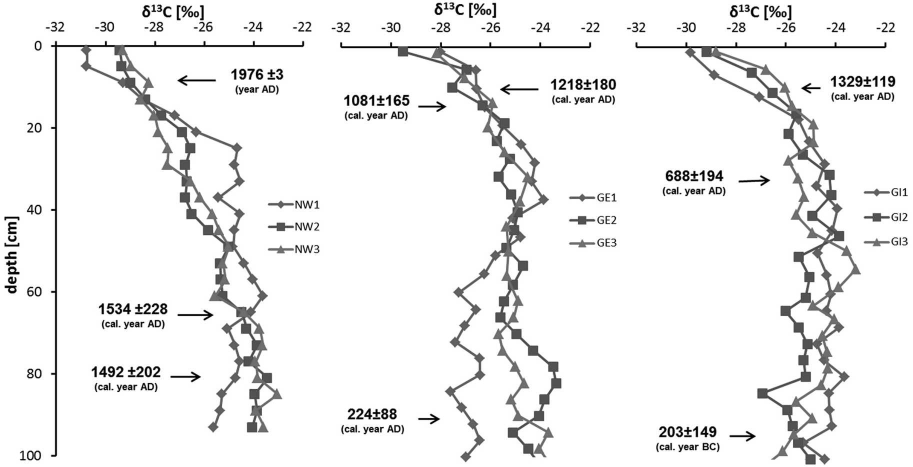

Figure 2. δ^{13}C depth profiles at the near-natural site (NW), extensive used grassland site (GE) and intensive used grassland site (GI) at the Ahlen–Falkenberger peatland. Calibrated radiocarbon ages are displayed as mean calendar ages with 1 SD ($n = 3$) at their corresponding depth.

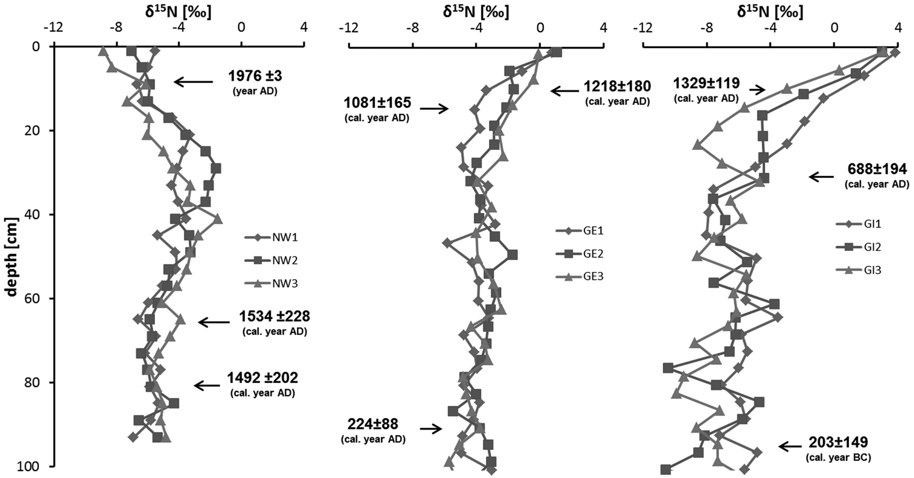

Figure 3. δ^{15}N depth profiles at the near-natural site (NW), extensive used grassland site (GE) and intensive used grassland site (GI) at the Ahlen–Falkenberger peatland. Calibrated radiocarbon ages are displayed as mean calendar ages with 1 SD ($n = 3$) at their corresponding depth.

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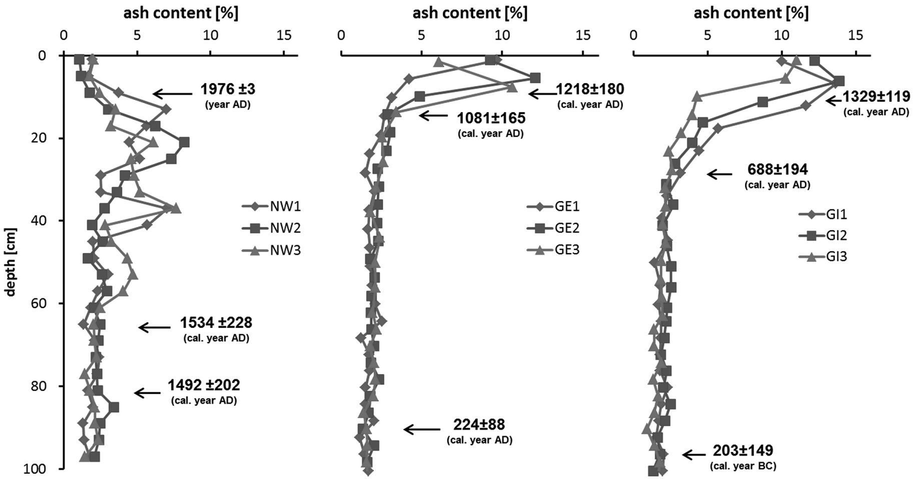

Figure 4. Ash content depth profiles at the near-natural site (NW), extensive used grassland site (GE) and intensive used grassland site (GI) at the Ahlen–Falkenberger peatland. Calibrated radiocarbon ages are displayed as mean calendar ages with 1 SD ($n = 3$) at their corresponding depth.