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**Discussions**

# Are C-loss rates from drained peatlands constant over time? The additive value of soil profile based and flux budget approach

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Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

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Are C-loss rates from drained peatlands constant over time?

J. Leifeld et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀◀ | ▶▶

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Are C-loss rates from drained peatlands constant over time?**

J. Leifeld et al.

Title Page

| Abstract | Introduction |
| Conclusions | References |
| Tables | Figures |

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Are C-loss rates from drained peatlands constant over time?**

J. Leifeld et al.

## Abstract

Drained peatlands are $CO_2$ hotspots and lose important soil functions over time. In contrast to mineral soils, their high carbon density induces long lasting and high emissions. These emissions can be estimated using various approaches which cover different system boundaries in time and space. Here we compare 5 years flux measurements from manual chambers with a soil profile based method to estimate carbon losses from two temperate fens under different management intensity drained at the end of the 19th century. According to the flux measurements, both grassland sites currently lose significant amounts of carbon as $CO_2$ in the order of 7.1 and 9.1 t $CO_2$-C ha$^{-1}$ a$^{-1}$ when managed non-intensively or intensively, respectively. Profile based estimates, which make use of the difference in ash concentration along the soil profile, reveal a total of 284 and 619 t C ha$^{-1}$ since the onset of drainage. These substantial losses are accompanied by a sharp decrease in peat quality as measured by NMR spectroscopy, confirming that a large part of former topsoil material is already mineralized. On average, the profile based estimate converts to smaller annual loss rates of 2.2 (non-intensive) and 4.8 t $CO_2$-C ha$^{-1}$ a$^{-1}$ (intensive) management. Our data, together with historical flux measurements at this site, provide evidence that peat decomposition rates increased over time, despite declining organic matter quality. We suggest that higher management intensities (i.e., higher fertilization and changes in carbon export from the field), including drainage, and increased mean annual temperature may be important factors for higher emissions today. These two methods are complementary in terms of time horizon and system boundary and, in conjunction, confirm the long-term emission potential of temperate drained organic grassland soils.

## 1 Introduction

The carbon budget of drained peatland soils is of high relevance given the important role of peatlands for soil carbon storage globally and their potential to emit $CO_2$ to the

atmosphere at high annual rates and over long periods of time once drained (Joosten, 2010; Leifeld, 2013). In the temperate region, a peat deposit drained for agriculture with a thickness of 2 m, a bulk density of $0.1\,\mathrm{g\,cm^{-3}}$ composed of peat with a carbon fraction of 0.5 reveals a total emission potential of $1000\,\mathrm{t\,C\,ha^{-1}}$ which, considering a mid-range emission factor of $5\,\mathrm{t\,CO_2\text{-}C\,ha^{-1}\,a^{-1}}$ (IPCC, 2014), converts to an average emission of these $5\,\mathrm{t\,CO_2\text{-}C\,ha^{-1}\,a^{-1}}$ over a period of 200 years. Because of the longevity and magnitude of net $CO_2$ emissions from drained organic soils, which by far exceeds that for mineral soils, suitable methods for estimating their historical and future carbon losses are needed in order to develop and establish site specific mitigation measures.

Different methods exist to estimate the carbon budget of drained peatland systems. Direct measurements of the $CO_2$ and $CH_4$ fluxes by eddy covariance or chamber techniques in conjunction with quantification of other ecosystem carbon imports and exports deliver quite accurate data (Ojanen et al., 2012). They are, in the case of chambers, restricted to small areas and often are employed only over a few years, a comparably short period of time considering that drained peatlands may emit $CO_2$ for centuries. A second type of methods make use of the subsidence taking place after peatland drainage to track back the carbon loss (Couwenberg and Hooijer, 2013; Grønlund et al., 2008). With subsidence data the volumetric loss must be converted to a peat loss which requires a valid estimate of the contribution from oxidation to the total subsidence. Thirdly profile-based methods, which estimate previous soil carbon stocks, peat thickness and thus carbon losses, have been suggested by various authors (e.g., Leifeld et al., 2011a, b; Rogiers et al., 2008; Schothorst, 1972). They are typically based on a comparison of top- and subsoil characteristics e.g., carbon concentration, bulk densities and ash contents. These attributes tend to change systematically after lowering of the groundwater table (Kluge et al., 2008; Simola et al., 2012). Profile based methods rely on conditions referring to undisturbed peatland, and the corresponding property values are often assumed to be found in the permanently water saturated subsoil of a profile. Because of the different system boundaries, assump-

tions and time spans considered, a comparison of approaches is needed in order to crosscheck emission estimates from shorter and longer time intervals and to identify possible method-specific biases. Here we compare, for the first time, the carbon budget of drained temperate fens which were measured (i) over five years by means of manual chambers and (ii) by using a time-integrative profile based method that uses peat ash contents, bulk densities, and carbon concentrations in upper and deeper layers of the peat deposit for estimating pre-drainage and current peat carbon densities. Our aim is to thoroughly examine the suitability of the profile based method for deriving long-term soil C loss by comparing it with results from chamber measurements as well as with chemical peat properties, and to provide new estimates for the long-lasting peat carbon loss for drained temperate peatlands managed as grasslands.

## 2  Sites and methods

The studied sites are located at fields of the ZALF research station in Paulinenaue (Brandenburg, Germany 52.687° N, 12.721° E). They are embedded into a huge mire complex, so-called "Havelländisches Luch", which were formed in the Warsaw–Berlin ice marginal valley of the last glaciation (Weichsel). Glaciofluvial, mainly sandy sediments are overlain by Late Pleistocene to Holocene peat layers of 0.3 to 3 m thickness. The climate is characterized by a mean annual air temperature of 9.2 °C and a mean annual precipitation of 530 mm (period 1982–2012). Although being drained for centuries the area still shows groundwater level near to the surface (0.1–1.5 m). The recent soil pattern reveals a very high local soil heterogeneity as indicated by spatial correlation lengths (soil organic matter [SOM] stocks, soil types) lower than 30 m. However, the spatial distribution of soils is not random, but strongly related to (micro-)relief showing Arenosols developed from aeolian sands at microhighs and a shift from Gleysols to Histosols in a continuum towards microlows (differences in height < 1 m).

## 2.1 Land use and amelioration history

The margins of the "Havelländisches Luch" were first drained at the beginning of the 14th century (Behrendt, 1988). A systematic amelioration for the entire "Luch" started 1718 and was completed 1724. Ditches and dams were constructed to drain the formerly swampy terrain and to get access to the land. Grasslands with hay production dominated the "Luch" at that time. The drainage ditches closest to our sites were established in 1882 (Fig. S1 in supplement). In order to prevent repeated flooding and to increase grassland productivity, a second amelioration with deeper drainage ditches took place between 1907 and 1925. A substantial increase in ditch lengths occurred between 1958 and 1961, when approx. 1000 km of new ditches were established in the area (Behrendt, 1988). The next huge effort to increase productivity started in the early 1970s by the so-called "Komplexmelioration", which lastet until the late 1980s. The basic idea was to establish a system of pumping stations and related ditches in order to increase and lower the groundwater level dynamically over the vegetation period – related to the actual plants' water demand. In addition fertilizer application rates, including organic manure, increased and the acreage of arable land doubled at the expense of grassland. After re-unification of Germany in 1989 a substantial de-intensification took place. Arable land was re-converted into grassland, fertilizer rates dropped, and hydraulic, technical devices felt into disrepair due to economic reasons.

## 2.2 Site selection and management, soil sampling and analysis

We studied two sites, P1 and P4, both classified as Hemic Histosol (WRB, 2006), but differing in the management intensity. Site P1 stands for a non-intensively managed meadow. It is dominated by *Festuca arundinacea*, annually fertilized with 125 kg K ha$^{-1}$ and 35 kg P ha$^{-1}$, and cut once per year. Site P4 represents an intensively managed meadow for that region. It is dominated by *Phalaris arundinacea*, annually fertilized with 70 kg N, 125 kg K ha$^{-1}$ 35 kg P ha$^{-1}$, and cut thrice per year. The distance from the center of the chamber plots to the next drainage ditch was 53 m for P1 and 17 m for P4.

Soils were sampled in July 2011. At each site four replicated soil cores were taken at the corners of a virtual quadrat of 2.8 m × 2.8 m. Sampling points were close to the chamber positions. The upper 0.3 m were excavated using a soil auger with plastic inlet of 7.5 cm diameter. Below that depth the peat was of lower density and a Belorussian peat corer (diameter 5.1 cm) was used. Maximum peat thicknesses was 0.8 and 0.4 m (P4 and P1, respectively). Underneath the peat layers organic horizons gradually changed towards mineral horizons. Soil cores were placed in halved plastic tubes, wrapped with plastic foil, brought to the lab and cut there into 3 cm slices. A total of 141 samples was retrieved.

Soil material was dried at 105 °C, ground and milled in a ball mill. Soil bulk density was calculated from the ratio of dry soil per segment volume. Contents of organic carbon (OC) of all samples were quantified by elemental analysis (Euro EA, Hekatech, Germany). Because carbonates were visible by eye in some samples, all samples were pre-treated with HCl to remove carbonate before elemental analysis and NMR spectroscopy. A subset of 60 samples was measured for loss-on-ignition by thermogravimetry at 600 °C (prepAsh, Precisa, Switzerland). The difference to the total sample weight equals its ash content. The organic matter and ash content of all other samples was estimating using the close linear relationship between organic carbon and loss-on-ignition ($r = 0.97$).

Solid-state $^{13}$C NMR spectra from seven soil samples were taken at the NMR facility of the Technical University of Munich, Germany. The cross-polarization magic angle spinning (CPMAS) technique with a $^{13}$C-resonance frequency of 50.32 MHz and a spinning speed of 6.8 kHz was applied. A ramped 1H-pulse starting at 100 % to 50 % of the initial power was used during a contact time of 1 ms to circumvent spin modulation during the Hartmann–Hahn contact. Pulse delays between 400 and 800 ms were used for all spectra. Preliminary experiments confirmed that the pulse delays were long enough to avoid saturation. Depending on the C contents of the samples, between 2200 and 3500 scans were accumulated and no line broadening was applied. The $^{13}$C chemical shifts were calibrated relative to tetramethylsilane (0 ppm). The relative contributions of

the various C groups were determined by integration of the signal intensity in their respective chemical shift regions according to Knicker et al. (2005). The region from 220 to 160 ppm was assigned to carbonyl (aldehyde and ketone) and carboxyl/amide-C. Olefinic and aromatic C were detected between 160 and 110 ppm. O-alkyl and N-alkyl-C signals were found from 110 to 60 ppm and from 60 to 45 ppm. Resonances of alkyl C were assigned to the region from 45 to −10 ppm. For the current study, two spectral subregions were of particular interest: resonances from 60 to 90 ppm were used as a quantitative indicator of polysaccharides, and resonances from 110 to 160 ppm were taken as a quantitative indicator for the presence of aromatic moieties.

## 2.3 Calculation of soil carbon loss from peat cores

Profile-based methods for estimating previous soil carbon densities and thus carbon losses through drainage are typically based on the comparison of soil profile properties, namely carbon concentrations, bulk densities, and ash contents, with a reference. For the latter often undisturbed subsoil is used as, also in our case, no pristine reference site could be sampled nearby. The basic assumption behind profile-based methods is that the undisturbed deeper layers resemble the characteristics of the upper soil horizons before commencement of peatland drainage.

Here we apply a new method that combines two previously published approaches which were based on soil subsidence and changes in soil bulk density (Leifeld et al., 2011a) and changes in the soil's ash content (Rogier et al., 2008; Leifeld et al., 2011b). The method is related to the one published by Schothorst (1977) but differs in its calculation of secondary subsidence. We call it combined method.

According to Schothorst (1977) and Kasimir-Klemedtsson (1997), the peat's volumetric loss after drainage is owing to a combination of physical (primary consolidation due to the loss of pore water pressure and peat shrinkage, hereafter referred to as primary subsidence) and chemical (oxidative loss of organic matter or secondary subsidence) processes. For calculating soil carbon losses only the latter is of relevance, but changes in bulk density contribute to the overall change in profile properties.

Primary subsidence [m] is calculates as

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

with

$$V_i = \mathrm{Bd}_{\mathrm{OS}i} / \mathrm{Bd}_{\mathrm{OSr}} \times T_i \tag{2}$$

Where $V_0$ is the pre-drainage thickness of layer $i$ [m], $\mathrm{Bd}_{\mathrm{OS}i}$ is organic matter density in layer $i$, $\mathrm{Bd}_{\mathrm{OSr}}$ 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. $\mathrm{Bd}_{\mathrm{OS}}$ 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 $2.65\,\mathrm{t\,m^{-3}}$.

Secondary subsidence is calculated from the pre-drainage thickness $T_{0i}$ [m] attributable to organic matter oxidation

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

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

$$C_{di} = T_d \times C_r / T_r \tag{4}$$

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 as

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

Volumetric and carbon losses were calculated separately for each soil core and results are presented as means and 95 % confidence interval ($n = 4$ per site). As reference layers all organic layers of site P4 above the mineral sediment were included that varied

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

in ash content by relative less than 13 % within a core. This cut-off value separated ash-poor layers from those located directly above. The latter were often characterized by relatively abrupt increases in ash content. For site P1, ash contents of reference layers from P4 were used owing to the already high ash concentrations and the shallow thickness of peat at P1, both indicating that no undisturbed reference layer was left.

The major difference of the combined method to previously published profile-based approaches is that changes in soil bulk density, caused not only by peat oxidation but also by compaction due to e.g. farm machinery, are not used to calculate organic matter losses. Ash ratios are based on concentrations rather than on densities to avoid interference with changes in bulk density through compaction which mainly occur in the upper soil layers. Primary subsidence is not required for estimating soil carbon losses, but together with secondary subsidence these values are valuable plausibility indicators and can be used for a direct comparison when soil subsidence is measured in the field. They also deliver the proportion of subsidence attributable to either physical compaction or organic matter oxidation.

## 2.4   Gas exchange and calculation of soil carbon balance

Gas exchange was measured during May 2007 and April 2012. The measurements based on the use of a manual chamber system (from transparent or white PVC, bottom size 0.56 m$^2$, volume 0.296 m$^3$, 3 replicates per study site). Biweekly measurements of $CH_4$ emissions were conducted by a static closed chamber approach (Livingston and Hutchinson, 1995), whereas campaigns for $CO_2$ flux measurements were compiled all three to four weeks, using a dynamic closed chamber approach described by Drösler (2005). Transparent chambers were used for the measurement of net ecosystem exchange (NEE, resulting from gross primary production and ecosystem respiration) and opaque (white) chambers for the measurement of ecosystem respiration ($R_{eco}$, sum of autotrophic and heterotrophic respiration). Gross primary production (GPP, net photosynthesis) was calculated from the difference between NEE and $R_{eco}$. To cover a broad variance of air and soil temperatures and photosynthetic active radiation (PAR) at each

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

campaign, continuously measurements were conducted over the course of one to two bright days, starting before sunrise. An R© program script was used for stepwise data processing of measured $CO_2$ concentrations (Hoffmann et al., 2014). The program (i) calculates measured $CO_2$-fluxes, (ii) parameterizes $R_{eco}$ and GPP, (iii) facultative computes an adaptive temperature model and finally (iv) model NEE, $R_{eco}$ and GPP as individual values and sums over the turn of the measurement period. $CH_4$ fluxes were calculated, using the R package FLUX (Jurasinski et al., 2014). A detailed description of the gas flux measurements can be found in the supplement.

For calculating soil carbon balance, the difference of $C_{input}$ (e.g. manure, fertilizer and seed) and $C_{output}$ (harvest) is added to the net gaseous C exchange ($CO_2$ and $CH_4$).

$$\Delta SOC_i = \sum_{i=1}^{n} [CO_{2\text{net exchange (NEE)}} + CH_{4\text{net exchange}} + (C_{input} - C_{output})_i] \tag{6}$$

Where a positive $\Delta SOC$ stands for soil carbon loss, $CO_{2\text{net exchange}}$ is the sum of $R_{eco}$ and GPP, and $CH_{4\text{net exchange}}$ represents the balance of $CH_4$ emissions and uptake by the soil.

Together with the gas exchange, permanently installed groundwater probes were installed at both sites. Groundwater level was monitored biweekly and modeled half-hourly.

## 3 Results

### 3.1 Soil properties and reference layers

Figures 1–3 provide the key parameters used for calculations according to equations 1–5. Soil ash contents were mostly above values of $200\,\mathrm{mg\,g^{-1}}$ apart from layers below 0.6 m depth in profile P4. In the shallow profile P1 ash concentrations did not drop below $200\,\mathrm{mg\,g^{-1}}$ soil. Table 1 provides the ash data used for calculating the soil carbon

losses. Soil carbon concentrations revealed just the opposite pattern to ash and increased with depth. Soil bulk densities partially reached values higher than $0.4\,\mathrm{g\,cm^{-3}}$ in the upper 0.2 m of soil and declined to values of below $0.2\,\mathrm{g\,cm^{-3}}$ below 0.6–0.8 m (P4). The dot product of carbon concentrations and soil bulk densities revealed organic carbon densities for the upper 0.3 m soil of 352 (P1) and 317 (P4) $\mathrm{t\,C\,ha^{-1}}$ and total carbon stocks in peat of 415 and 662 $\mathrm{t\,C\,ha^{-1}}$ for P1 and P4.

## 3.2  Soil carbon losses

Soil organic carbon and volume losses as estimated by the combined method applying equations 1–5 are given in Table 2 together with the soil carbon budget measured by gas exchange. Profile-based estimates reveal total soil carbon losses from these drained fens of 284 and 619 $\mathrm{t\,C\,ha^{-1}}$ for P1 and P4. The losses integrate on average over 0.34 (P1) and 0.65 m (P4).

These losses convert to annual rates of 2.2 ($\pm0.6$, 95 % CI) and 4.8 t ($\pm1.9$) C $\mathrm{ha^{-1}}$, if we assume peat oxidation mainly to occur since first drainage of P1 and P4 in 1882 (129 years ago). For both sites the variability in these data reflect spatial heterogeneity. The conversion from natural peatland to agricultural management induced a total subsidence of 0.8–1.4 m with more than half of it attributable to peat oxidation. Chamber measurements for P1 and P4 revealed annual net carbon losses of 7.1 ($\pm2.0$) and 9.1 ($\pm6.6$) $\mathrm{t\,C\,ha^{-1}}$, respectively, for the period 2007–2012. Here the variability is more pronounced compared to the profile-based method and mainly reflects year-to-year variability induced by interannual variations in GPP, Reco, and harvest export (Table S1 in supplement). In both cases annual losses are smaller with the profile based estimate. The overlaps of confidence intervals between methods indicate no significant difference for P4 whereas calculated loss rates are significantly smaller at P1 when using the combined method.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

### 3.3 Organic carbon composition

The composition of soil organic matter measured by $^{13}$C NMR spectroscopy showed pronounced and significant changes within the soil profile (Figs. 4 and 5). In topsoils O-alkyl carbon contents were at maximum 31 % of OC and aromatic contents were between 12 and 13 % of OC. Whereas there is a general decline in O-alkyl carbon with depth in these peat profiles ($r = -0.95$; $p < 0.01$), the aromatic content significantly increases ($r = 0.83$, $p < 0.05$, Pearson's).

### 3.4 Long-term trends in climate, drainage intensity, and hay yield

The 120 years record from the weather station in Potsdam, ca. 40 km apart, reveal an increase in mean annual air temperature since the 1990s (Fig. 6a). Precipitation did not change systematically but was highly variable (Fig. 6b). During the time of chamber measurements, rainfall variability measured at the site coincided with variability in groundwater levels (Table S1). Ditch lengths density in the area of Paulinenaue increased from below 1.5 km km$^{-2}$ at the end of the 18th century to more than 3 km km$^{-2}$ nowadays (Fig. 6c). Overall management intensification is indicated by increasing hay yields for the federal state of Brandenburg (Fig. 6d).

## 4 Discussion

Our results indicate that agricultural management of Histosols at Paulinenaue induced a substantial, long-lasting and still ongoing loss of carbon from these soils. This finding is in line with the long recognized understanding of drained organic soils as hot spots for CO$_2$ (Kasimir-Klemedtsson et al., 1997). The two methods for estimating carbon losses from drained peatlands reveal loss rates of the same order of magnitude. The overall range of between 2 and 9 t C ha$^{-1}$ a$^{-1}$ for sites P1 and P4 compares well with current estimates on CO$_2$ emission factors (Höper et al., 2008; Byrne et al., 2004; IPCC 2013) for temperate systems under grassland use. With either method site P4 tends

Are C-loss rates from
drained peatlands
constant over time?

J. Leifeld et al.

to lose carbon at a higher rate than P1. This might be due to an accelerated turnover of organic material as a result of the intensive management at P4 (higher mowing frequency, regular application of N fertilizer) compared to P1. A different distance to the drainage ditch seems, however, not an important factor in controlling $CO_2$ release considering groundwater levels which were similar for P1 and P4 (Table S1, Supplement). Generally, the 5-years annual carbon loss rates, measured directly as flux, tend to be more variable and systematically higher compared to the profile-based method which integrates over more than one century. In the following, possible reasons for these findings are discussed.

## 4.1  Random variation

At both sites the variability between replicates is higher with the flux based method and reflects both, variability in space and time. The spatial variability is owing to the locally different position of the three chambers in the field. This spatial variability is similar to that of the soil cores taken for the combined method. Temporal variability, however, can be seen only in the flux based method. Carbon dioxide exchange over former peatlands is highly and directly sensitive to annual or interannual changes in water table, vegetation season lengths, and weather conditions in general (Augustin et al., 1996; Jacobs et al., 2007). This in line with variations observed during the measurement period 2007–2012 (Table S1 in Supplement). The flux method gives detailed information on contemporary C budgets and provides relationships to the important drivers. On the contrary, the profile based methods mimics the whole period of drainage, in our case roughly one century, and hence integrates periods of higher and lower emissions. Its only source for variability is spatial heterogeneity between sampling points which is, in our case, rather small.

## 4.2 Methodological limitations and systematic effects

Beside random variation systematic, methodological differences have to be taken into account as well. Either method implicitly operates with different system boundaries in time and space. In case of the chamber approach, it is not clarified finally, if microclimatological conditions due to chamber deployment cause ecophysiological disturbances, which in turn result in biased C flux rates (Juszczak et al., 2012; Lai et al., 2012; Langensiepen et al., 2012; Kutzbach et al., 2007). This concerns even more the effect of measurement frequency and its distribution over the year as well as the underlying model assumptions for C flux rates (Hoffmann et al., 2014; Beetz et al., 2013; Lai et al., 2012; Janssens and Pilegaard, 2003). The profile method is also based on various assumptions, particularly the representativeness of the reference layer for the pre-drainage conditions in the layers above and thus a relative homogeneous pattern of bulk density as well as ash and SOC content throughout the peat profile at onset of drainage. Hence a major concern refers to the representativeness of reference layers, both, under a horizontal (spatial heterogeneity) and vertical perspective (temporal variability during peat formation). Contrary to mineral soils (mass balance approaches, e.g., Sommer et al., 2000) any peat profile reflects a clear chronostratigraphy with depth, including temporal changes in vegetation type, productivity and decomposability as well as layers of mineral admixtures by dust influx or flooding events.

The two selected methods for quantifying the soil C budget differ systematically also in the completeness of C flux capture. Flux measurements give an estimate of net biome productivity which corresponds closely to the soil's carbon budget if other important carbon import and export fluxes are quantified, as in our case. However, also fluxes of dissolved C from organic soils in either organic or inorganic form can be an important pathway for soil carbon export from peatlands (Fiedler et al., 2008; Roulet et al., 2007; Strack et al., 2008; IPCC, 2013). These fluxes are not captured by the flux based approach, but are accounted for by the profile based method. Hence with

all other factors being equal, the latter method would report higher carbon losses from soil.

## 4.3  Does peat quality explain our findings?

Not only the above mentioned difference in C flux capture, but also measured peat quality parameters using NMR spectroscopy would be expected to result in higher C losses when applying the profile based method. Soil polysaccharide content is a measure for the peat's intrinsic decomposability (Leifeld et al., 2012; Tfaily et al., 2014). They have been shown to reveal a typical depth pattern in peat deposits and are considered an important factor in controlling organic carbon losses in degrading peatlands. In pristine mires peat in the upper horizons contains up to 80 % of its carbon as polysaccharides, resembling the composition of the plant material it is composed of (Schellekens and Buurman, 2011). Low topsoil polysaccharide contents of around 25–30 % at Paulinenaue indicate that the material had resided in much deeper peat layers before drainage because polysaccharide contents steadily decline with depth in intact mires. Hence, peat nowadays exposed to the surface is depleted in easily degradable polysaccharides and this is similar to the pattern found for other organic soils with a long-lasting drainage history (Leifeld et al., 2012). The NMR data indicate that P1 and P4 must have lost substantial amounts of peat carbon, in line with the measured carbon budget. The peat quality points toward a poor degradability of the material which makes up the topsoil today compared to a presumably better degradability of peat many decades ago.

## 4.4  Indications for increasing C-loss rates over time

The reasoning above suggests that (i) the difference in system boundary captured by the two methods leads to smaller C loss rates using chamber measurements and (ii) a declining topsoil peat quality over time results in smaller C-loss rates today. Both arguments would let us expect smaller losses using current-day chamber flux mea-

surements which are in apparent contradiction to the measured relatively high current emission rates. This leads us to suggest a non-linear increase in C-loss rates over time.

We argue that decadal or centennial changes in external drivers of peat degradation may explain why annual C-loss rates switched towards higher rates in more recent times. We regard climate change, farming practices as well as amelioration, like a setup of drainage systems, as the most important factors.

One important factor for shifts in C-loss rates might be climate change, mainly a decadal increase in temperature or changes in precipitation. Looking at the regional situation, indeed, mean air temperatures (MAT) in Potsdam increased in a non-linear mode – about 1 °C since the 1990s (Fig. 6a, compare Cubasch and Kadow, 2011). Consequently, plant growth (NPP) might have been stimulated in the last two decades as well as shoot/root respiration and microbial respiration (Reco). For annual precipitation, however, no decadal or centennial trend was found (Fig. 6b). Instead, year-to-year variability in rainfall rate is very high. Together, increasing MAT may shift C-loss rates towards higher values whereas we exclude rainfall-driven topsoil moisture, which is an important factor for peat decomposition (Fenner and Freeman, 2011), to be related to the decadal, probably non-linear increase in C-loss rates.

Vegetation productivity and agricultural management via harvest and fertilization are important drivers for soil organic matter input and decomposition and hence the multi annual C budget of the system (Beetz et al., 2013; Elsgaard et al., 2012; Kandel et al., 2013; Drösler et al., 2013). For example, nitrogen fertilizer inputs to agricultural soils in Germany roughly doubled between 1961 and today (FAO, 2013) which resulted in an increase in productivity and yields, but may, at the same time, have also accelerated organic matter decomposition. NPP export exerts an important control on the carbon balance of organic soils (Drösler et al., 2013), hence higher C export (yields) will probably shift the carbon budget towards a stronger $CO_2$ source. The long-term trend of hay yields in Brandenburg confirms the postulated increase in biomass export (Fig. 6d), though discontinuously in four distinct periods: (i) Before 1890, hay yields varied between 2 and $3\,\mathrm{t\,ha^{-1}\,a^{-1}}$, (ii) between 1900 and 1965 a rather stable yield

level of 3.5–4.5 t hay ha$^{-1}$ a$^{-1}$ is reported, (iii) a clear increase, almost a doubling of hay yields, occurred during the period of "Komplexmelioration" (1970 to 1989), and, (iv) finally a drop in yields can be seen after 1989. Nevertheless the rather stable level of 5–6 t hay ha$^{-1}$ a$^{-1}$ after 1989 is still higher compared to the period before 1970. By trend the increase in biomass exports corresponds to the postulated increase in C-loss rates over time as well as the different biomass production of non-intensively managed P1 (5.9 t ha$^{-1}$ a$^{-1}$) and intensively managed P4 (12.7 t ha$^{-1}$ a$^{-1}$).

The suggested increase in C-loss rates over time is supported by the findings of Mundel (1969), who applied a profile-based method to Gleysols and Histosols – for the first time to our knowledge. In his seminal work he studied 515 pairs of surficial soils and adjacent buried soils under dams of known ages ("Luchdämme" constructed 1718–24, and a railway dam constructed in 1882). He assumed minor changes of SOM stocks in buried soil profiles due to a reduced oxygen supply and exclusion of management effects starting with the time of dam construction, i.e. burial of soils. Next he calculated the difference in SOM stocks between a surficial soil (so-called "cultural soils") and its neighboring, buried soil under a dam (so-called "natural soils") in a pairwise manner. Mundel (1969) found a linear relationship between SOM stocks of surficial soils in 1966 and the SOM changes over time (Fig. S2 in supplement). Where SOM stocks (1966) were larger than 45 kg m$^{-2}$ ("Luchdämme") or 70 kg m$^{-2}$ (railway dam), respectively, SOM losses occurred and increased linearly with SOM stocks (compare Bellamy et al., 2005). Importantly, when taking into account the different burial ages, SOM-/C-loss rates increased by a factor 2–3 from 1720 to 1882 compared to the period 1882 to 1966. This increase in SOM decomposition over time coincides with an almost doubling of ditch length densities around 1880 as calculated from historical maps (Fig. 6c). The resulting systematically lower groundwater level led to an enhanced oxygen supply in a larger soil volume, hence an increase in C-loss rates. Figure 6c shows that ditch lengths density further increased since Mundels work, thereby eventually triggering even faster peat decomposition in most recent times. Early CO$_2$ exchange studies at lysimeters – performed during 1968–1970 – confirm the relationship be-

tween groundwater depth and $CO_2$ emission in a quantitative manner. Mundel (1976) found significant, non-linear relationships between groundwater depth, peat thickness, and $CO_2$ emission rate (Fig. S3 in supplement). When the historical data from Mundel (1969) are put into context with our measurements, the resulting time-series strongly indicates increasing C-loss rates over time at the Paulinenause sites (Table 3). In consequence, any chronological extrapolation of current day emission measurements on organic soils must be exercised with caution, given systematic changes of important drivers such as climate, drainage, and management intensity over time.

## 5 Conclusions

The comparison of five-year C flux measurements and profile-based C loss estimates that integrate over time periods of decades to more than one century indicates that, under conditions of continuous agricultural use, these temperate grassland soils do not lose their C emission function over time until the whole peat deposit is exhausted. Whereas flux based measurements provide insight into the contemporary carbon budget of the fields, profile based methods integrate over much longer periods of time. The profile based method reveals emission factors which are on average smaller although of the same order of magnitude as the flux measurements. For the profile based method, management history is only weakly constrained which makes the conversion of cumulated losses to annual average emission rates uncertain, because drivers for soil-derived carbon emissions change over time. Peat quality declines with ongoing decomposition but this factor seems to be outweighed by intensified management and drainage and perhaps also climate drivers that accelerate peat decomposition today. Together, the two methods are complementary in terms of time horizon and system boundary and, in conjunction, confirm the long-term emission potential of temperate drained organic grassland soils.

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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Are C-loss rates from drained peatlands constant over time?

J. Leifeld et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Are C-loss rates from drained peatlands constant over time?**

J. Leifeld et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◄◄ | ►►

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Table 1.** Ash reference values (mg ash g$^{-1}$ soil) (1 SD) and number of 3 cm-layers per site ($n$) that were included for the calculation of the reference value. The corresponding soil depth is between 0.71 and 0.76 m.

|  | P1[1] | P4 |
| --- | --- | --- |
| Ash content | 134 (10) | 134 (10) |
| $n$ | 14 | 14 |

[1] Values for P1 were taken from site P4 because no reference horizons could be retrieved due to the direct transition from degraded organic horizons to the underlying mineral sediment.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Table 2.** Overview of carbon losses calculated from soil profiles (C-loss soil) and from gas flux measurements (C-loss chambers), soil volume lost (total and contribution from peat oxidation), soil carbon stocks in the topsoil and in the whole peat profile. Carbon losses are given as mean and 95 % confidence interval. Carbon stocks are given as mean (1 SD).

|  | P1 | P4 |
|---|---|---|
| C-loss soil ($t\,ha^{-1}$) | 284 (78) | 619 (247) |
| C-loss soil per year ($t\,C\,ha^{-1}\,a^{-1}$) | 2.2 (0.6) | 4.8 (1.9) |
| Soil volume loss (m) | 0.79 | 1.35 |
| Fraction volume lost from oxidation | 0.56 | 0.71 |
| C-loss chambers ($t\,C\,ha^{-1}\,a^{-1}$) | 7.1 (2.0) | 9.1 (6.6) |
| C stock 0–0.3 m ($t\,ha^{-1}$) | 352 (14) | 317 (6) |
| C stock whole peat profile ($t\,ha^{-1}$) | 414 (76) | 662 (31) |

**Table 3.** A comparison of carbon loss rates from drained fens at Paulinenaue. Values in Mundel (1969) are given as soil organic matter and were converted to carbon by assuming a peat carbon fraction of 0.5. For further details, see text and Supplement.

| Measurement period | Method | Average C loss rate ($t\,C\,ha^{-1}\,a^{-1}$) | source |
|---|---|---|---|
| 1722–1966 | paired plot | 0.8[1] | Mundel (1969) |
| 1882–1966 | paired plot | 1.6[1] | Mundel (1969) |
| 1882–2011 | profile based | 2.2/4.8[2] | this study |
| 2008–2011 | chambers | 7.1/9.1[2] | this study |

[1] Calculated for a SOM stock of $130\,kg\,SOM\,m^{-2}$ as measured for site P4.
[2] Site P1/P4.

**Figure 1.** Soil organic carbon concentrations at two drained peatland sites. Error bars are one SD ($n = 4$). Solid line – P1, dashed line – P4.
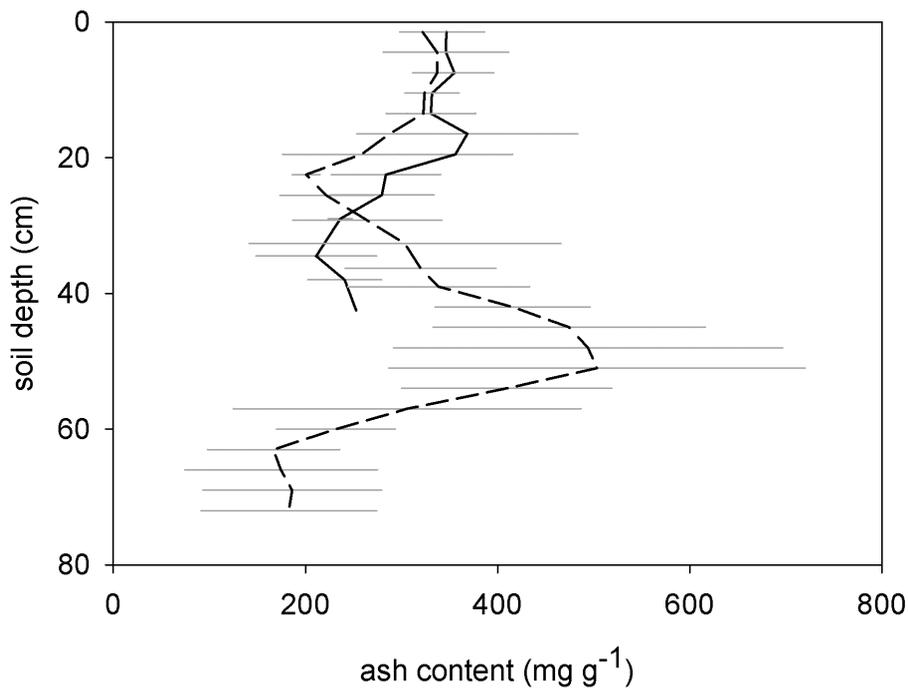
**Figure 2.** Soil ash concentrations at two drained peatland sites. Error bars are one SD ($n = 4$). Solid line – P1, dashed line – P4.
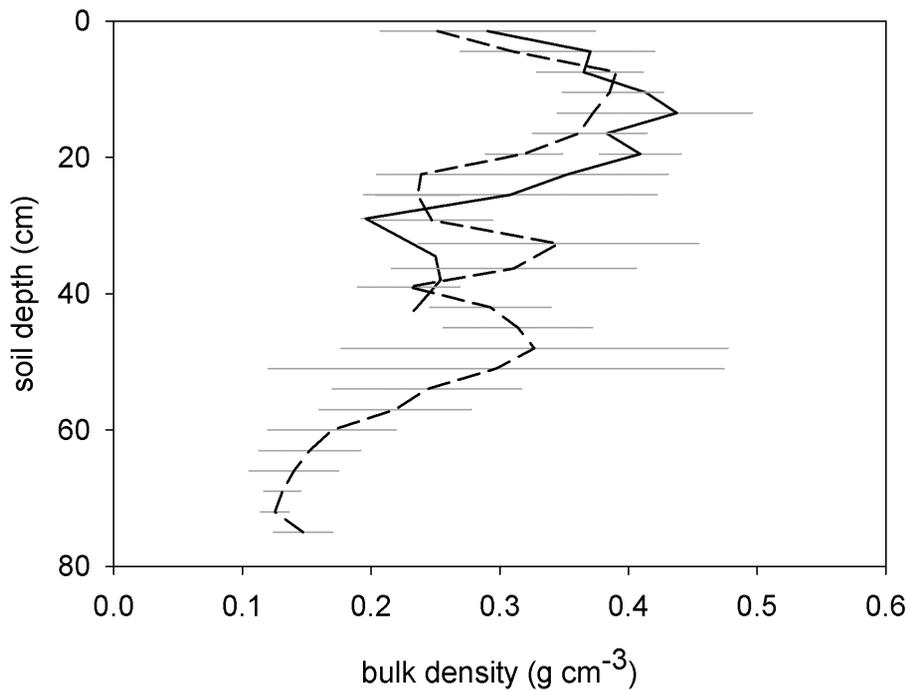
**Figure 3.** Soil bulk densities at two drained peatland sites. Error bars are one SD ($n = 4$). Solid line – P1, dashed line – P4.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
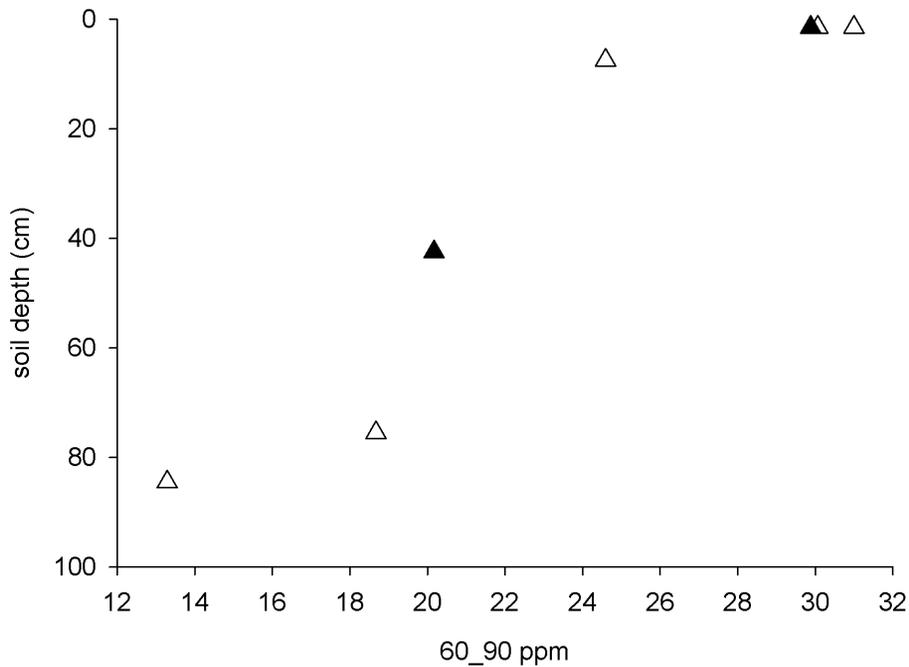
**Figure 4.** O-alkyl-C contents (% of SOC) from NMR spectra as a function of soil depth (closed symbols: P1, open symbols: P4).

**Are C-loss rates from drained peatlands constant over time?**

J. Leifeld et al.

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

◀ | ▶|

◀ | ▶

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
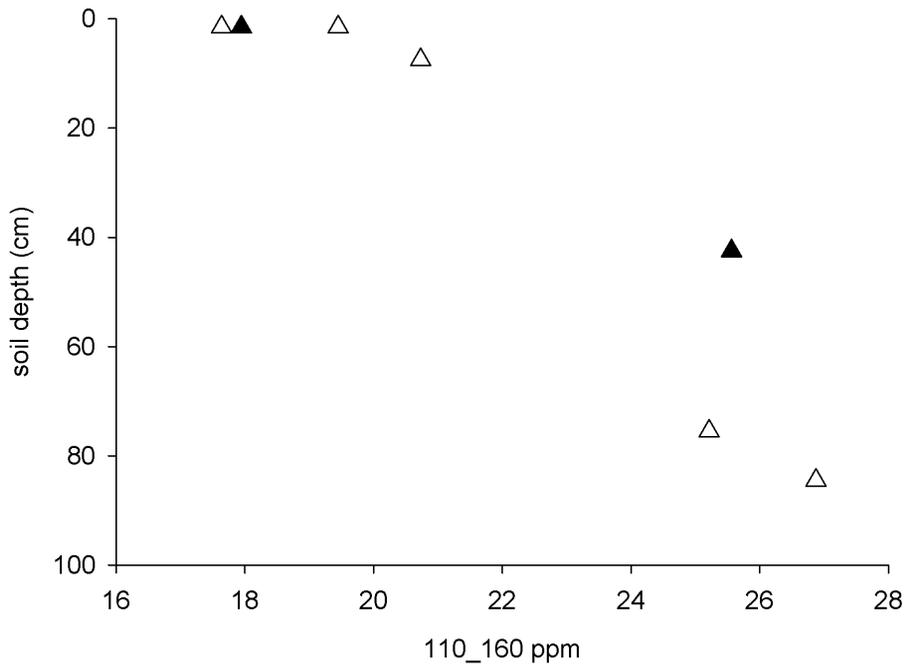
**Figure 5.** Aromatic-C contents (% of SOC) from NMR spectra as a function of soil depth (closed symbols: P1, open symbols: P4).

Full Screen / Esc

Printer-friendly Version

Interactive Discussion
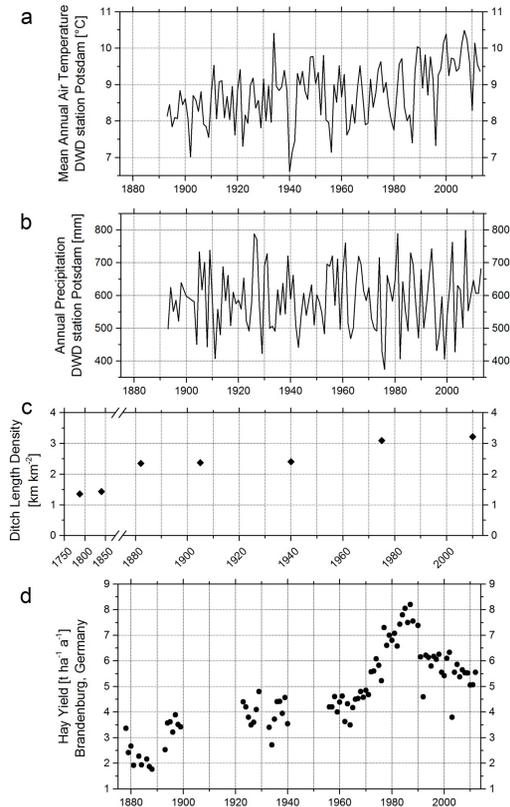
**Figure 6.** Synoptic compilation of long-term trends in potential drivers of non-linear C-loss rates; **(a)** air temperature **(a)**, annual precipitation **(b)**, data from DWD station Potsdam, approx. 40 km E of Paulinenaue ("Climate Data Center" at http://www.dwd.de/); **(c)** ditch length densities calculated by GIS ArcView using historical maps in a 7 km × 6 km window (Fig. S1 in supplement); **(d)** hay yields (t dry matter ha$^{-1}$) in Brandenburg (Agricultural Statistics of Prussia, Deutsches Reich, and Federal State of Brandenburg).

Title Page

Abstract | Introduction

Conclusions | References

Tables | Figures

|◄ | ►|

◄ | ►

Back | Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion