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REGULAR ARTICLE

Carbon storage change and $\delta^{13}C$ transitions of peat columns in a partially forestry-drained boreal bog

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Abstract
Background and aims In forestry-drained peatlands, drying leads to changes in C cycling which could affect peat $\delta^{13}C$. Furthermore, the $\delta^{13}C$ profile of the entire peat column may reveal effects of earlier climatic periods.
Methods We measured peat $\delta^{13}C$ and C inventories in adjacent peat profiles, two collected from undrained and two from the drained side of a bog that was partially ditch-drained 37 years earlier. The cores were sliced into 10-cm subsamples for analyses; matching of the profiles based on surface levelling, peat stratigraphic correlation and a horizontal ash layer found in both profiles.
Results Surface subsidence of 30 cm was observed in the dried site and the uppermost 160 cm in the undrained site contained an excess of 5.9 kg m^{-2} of C compared with the corresponding strata of the ditch-drained site. The $\delta^{13}C$ values increased but markedly only in the thin surface layer of the drained site, indicating low $\delta^{13}C$ of the missing C (ca. –30‰). In the deeper strata, dating to Mid-Holocene, high dry bulk density, C%, N%, humification index and low C/N ratio were connected to low $\delta^{13}C$ of peat.
Conclusions Drainage of 37 years increased $\delta^{13}C$ values in the upper peat profile of the drained bog and led to the selective loss of ^{13}C depleted C. Results indicate that C balance studies can be aided by C isotope analyses. Low $\delta^{13}C$ values in the peat profile indicate the existence of a wet fen stage during the moist and warm period during Mid-Holocene.

Keywords Biogeochemistry · *Sphagnum* · Suess effect · Bog · Carbon cycle · Carbon-13 · Diagenesis · Drainage · Isotope ecology

Introduction

In a peat-forming ecosystem, decay of fresh plant material effectively occurs in the uppermost, predominantly

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aerobic stratum, acrotelm, while deeper down, in the catotelm, persistently anoxic conditions below the water table promote peat preservation (Ingram 1978). Mesotelm is defined as the intermediate zone, through which C is transferred from acrotelm to catotelm (Clymo and Bryant 2008). In reality, these zones are somewhat arbitrary and their vertical position may change over time by changing hydrological regime and aeration conditions at the site. Fens formed in depressions are fed by groundwater, and thus tend to be influenced by minerogenic nutrients. Fens develop into bogs when the surface grows above the reach of groundwater. The water and nutrient sources of bog vegetation depend on the precipitation and snow, leading to *Sphagnum* dominance. *Sphagnum* peat dominated bogs are ^{13}C-enriched compared to fens, where vascular plants dominate (Andersson et al. 2012; Krüger et al. 2016; Nykänen et al. 2018). In addition to the primary atmospheric CO_2 source, secondary CO_2 sources also affect peat $^{13}C/^{12}C$ ratios (denoted as $\delta^{13}C$). Reuse of ^{13}C-depleted respired CO_2 will deplete the fresh biomass (Jones et al. 2014; Nykänen et al. 2018). The same way, ^{13}C-depleted CO_2 derived from methane oxidation by methanotrophic symbionts in *Sphagnum* mosses leads to the formation of ^{13}C-depleted peat C (Raghoebarsing et al. 2005, Larmola et al. 2010). Furthermore, the Suess effect, anthropogenic ^{13}C-depletion of atmospheric CO_2 (Rubino et al. 2013) also affects the $\delta^{13}C$ values of the uppermost peat strata (Esmeijer-Liu et al. 2012). Aerobic and anaerobic decay processes affect differently the peat $\delta^{13}C$ values. In general, aerobic microbial decomposition increases $\delta^{13}C$ in the resulting peat (Ågren et al. 1996), while anaerobic decay preserves or decreases the bulk peat $\delta^{13}C$ values (Alewell et al. 2011; Krüger et al. 2014, 2015).

Water source and water table levels are the main factors determining the peatland type and vegetation. Furthermore, water saturation is an important factor in the peatland C balance. Thus, both water source and water levels determine $\delta^{13}C$ values of the developing peat deposit. We have studied the effects of drainage-enhanced decomposition on peat $\delta^{13}C$ values and especially the ^{12}C and ^{13}C balances, by comparing adjacent, well correlated but contrasting peat profiles, two from undrained and two from the drained side of a partially ditch-drained bog. The peat material we analyzed consists of stored samples collected during an earlier and more extensive study (Pitkänen et al. 2013), which demonstrated the marked effects of ditch drainage on the total peat C balances at this particular bog. Our analyses for $\delta^{13}C$, C% and N% of the two profiles aims to address three research questions: firstly, to determine the effects of drainage-induced surface peat decomposition on C isotope balance; secondly, to determine the long term changes in the stable C isotopes by analysing each of the consecutive 10-cm samples of the complete profiles, and thirdly, by comparing the isotope signatures on sequences of the contrasting profiles, to substantiate their comparability and to assess the reproducibility of the analysis methods (while lack of more replicates prevents any actual statistical analyses of the data).

The Rahesuo bog site provides exceptionally favourable conditions to study the effects of artificial drainage, because the large excentric bog has been partially ditch-drained along the natural water flow direction. As a consequence, the effects of drainage are seen at the border of the undrained and drained parts as surface subsidence and vegetation changes in the latter. Pitkänen et al. (2013) investigated this study setting by analyzing peat bulk C dynamics in seven pairs of matching peat profiles collected from either side of the marginal ditch. In the present study, we have used material stored from two pairs of those profiles.

Materials and methods

Study site

The ombrotrophic Rahesuo peatland is a large raised bog complex (750 ha) situated in Ilomantsi, eastern Finland (62°52′ N, 31°10′ E, Fig. 1a). The annual average temperature at the nearest weather station at Lieksa (distance 76 km) is 2.0 °C and precipitation 711 mm for the period of 1981–2010 (Pirinen et al. 2012). The warmest and wettest month is July (16.0 °C, 92 mm) and the coldest is February (−10.7 °C). There is usually snow cover from November to the end of April. The age of the basal peat layer of the drained site is 10,200 cal. Yrs. B.P. this to form cal yr BP (Mäkilä and Goslar 2008). Details of the study site are shown in Table 1. Rahesuo has been earlier studied by Tolonen (1967) and Geological Survey of Finland (Geological Survey of Finland peatland database and unpublished material in the peat inventory archive of GSF).

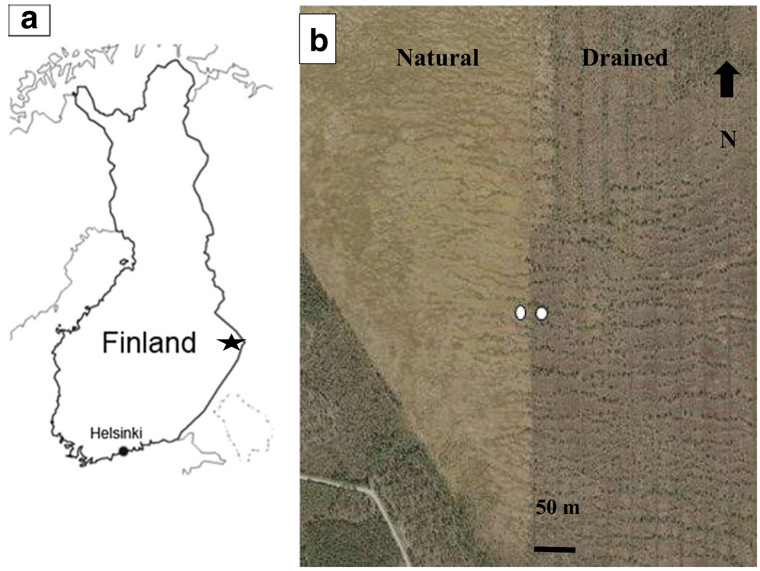

Fig. 1 Location of Rahesuo in Finland marked by a star (**a**) and location of sampling points in aerial map of Rahesuo by white dots (**b**) (Copyright Maanmittaushallitus)

While the bog complex is largely ditch-drained, there is an undrained section of 30 ha in its western part (Fig. 1b). Determined by land ownership borders, the margin between undrained and drained parts runs parallel to the natural water flow; the slope of the bog surface is about 2.5 m per 1000 m along the marginal ditch. Most of the bog was ditched by 40 m ditch intervals during winter 1971–1972. Thus, there was 37 full growing seasons prior to peat sampling in June 2009. At the drainage border, drying appears to have affected the undrained side only within a few meters from the marginal ditch (Pitkänen et al. 2013). The main indicator species of the bog hollows of the undrained side, such as *Sphagnum balticum*, *Carex limosa* and *Scheuchzeria palustris* are replaced by *Mylia anomala* and *Polytrichum strictum* on the drained side. Surface subsidence of the drained side is evident along the entire drainage margin. Surface levelling in the hollow where the sampling was done, indicated a 30 cm subsidence on the drained side. In contrast, only slight sloping of the surface towards the marginal ditch was observed, and only within the nearest 10 m from it. As judged by peat stratigraphy, marked loss of surface peat is evident on the drained side, but deeper down the stratigraphies appear quite similar and occur consistently at the same horizontal levels (e.g. an *Eriophorum vaginatum* – rich stratum at 52–58 cm in the undrained side and at corresponding depth of 22–28 cm in the drained side profile).

Peat sampling

In Pitkänen et al. (2013), two complete peat profiles from the undrained (UNDR) and drained (DRA) sites were sampled from the same hollow. The distance between the two replicate profiles at both sites was 1 m and continuous samples were taken at 10 cm intervals. The locations of both sites were approximately 7 m from the ditch (Fig. 1b). Samples were collected with a box corer to a depth of 1 m and with a Russian type side-cutting peat corer from the deeper peat layers. Dry BD and ash content were determined (Pitkänen et al. 2013). Drying of the samples took place at 105 °C and homogenized samples were stored in paper bags at room temperature. For the present study, we analyzed samples from two full profiles from undrained and drained sites.

Stratigraphic depths are expressed as depth below the peat surface. The individual 10-cm samples are indicated by their mid-point depth, so $_{\mathrm{DRA}}225$ cm refers to the sample from 220 to 230 cm on the drained side, whereas $_{\mathrm{UNRA}}5 - {}_{\mathrm{UNDR}}145$ cm refers to the uppermost 0–150 cm of the undrained (natural) side. In Pitkänen et al. (2013), the marked downward increase of ignition residue, observed consistently at $_{UNDR}245$ cm and $_{DRA}215$ cm were taken as a common base level for profile comparisons and inventory calculations. A synchronous charcoal layer at $_{UNDR}165$ cm and $_{DRA}135$ cm was used as an additional marker level for the profiles. The profile matching of Pitkänen et al. (2013) was slightly modified in the present study: 10 cm layers above the **S**ynchronous **C**harcoal **L**ayer at $_{UNDR}155$ cm and $_{DRA}125$ cm (**SCL**$_{UNDR}155/_{DRA}125$) was used in the C balance and δ^{13}C calculations. Similarly, the profile base level based on the **S**ynchronous increased **A**sh content **L**ayer (Pitkänen et al. 2013) was elevated by 10 cm to $_{UNDR}235$ cm and $_{DRA}205$ cm (**SAL**$_{UNDR}235/_{DRA}205$). This change to the synchronous layer positions was done to avoid any over or underestimation of C store because the exact location of the synchronous charcoal layer within each 10 cm sample was unknown.

Analyses of δ^{13}C, C% and N% from peat

In 2014, subsamples (2–4 mg) of the original peat samples were weighted in tin cups and analysed for δ^{13}C, C% and N%. Analyses were done with Elementar Cube (Elementar, Hanau, Germany) coupled with Isoprime 100 (Isoprime Limited, Cheadle Hulme, UK) isotope ratio mass spectrometer. A certified birch leaf standard (Elementar Microanalysis, UK) was used as a reference for C% and N% and also as an internal isotopic standard on Lsvec - LSB-19 scale (Coplen et al. 2006). Peat samples were not acidified based on Nykänen et al. (2018), where acidification did not change the peat δ^{13}C values. The birch leaf standard was analyzed

Table 1 Major features of the study site

	Unrained site	Drained site
Tree stand volume$^{(1)}$ (m^{-3} ha^{-1})	0	< 10
Peat thickness$^{(1)}$ (cm)	265	245
Water table below surface$^{(1)}$ (cm)	2–10	5–15
Subsidence compared to undrained side$^{(1)}$ (cm)	0	-30
Peat BD$^{(2)}$ (g dm^{3}) (0–10 cm)	25.6	53.6
C (%)$^{(2)}$, 0–10 cm	45.5	45.5
N (%)$^{(2)}$, 0–10 cm	0.64	0.82

Rahesuo data is from [1] Pitkänen et al. 2013, and from [2] this study

for δ^{13}C, C% and N% after each 5 peat samples to correct for the analyzer drift, while linearity was checked in every run with variable concentration of C and N in standards corresponding to C and N amount of the samples. Standard deviation for the repeated standard runs was: <0.15 for δ^{13}C, <0.3 for C% and < 0.03 for N%.

Stable isotope compositions were expressed in the delta notation as a ‰ deviation of the heavy-to-light isotope abundance ratio in the sample from that of a standard, VPDP for C. The results are reported relative to the standard scale.

$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right) sample}{\left(\frac{^{13}C}{^{12}C}\right) standard} - 1 \right) * 1000 \tag{1}$$

The total C mass of each sample was calculated based on the known volume, measured dry BD and C% of peat sample. In order to calculate the masses of ^{12}C and ^{13}C of samples, delta notation (Eq. 1) was converted back to the atom percent (at%) by formula (Fry 2006):

$$at\% = \frac{\delta^{13}C + 1000}{\delta^{13}C + 1000 + \frac{1000}{0.0118}} * 100 \tag{2}$$

Where: δ^{13}C = δ^{13}C value of the sample, 0.0118 = ratio of VPDB standard and at% = atomic percent.

Pitkänen et al. (2013) estimated the total C inventories for the undrained and drained Rahesuo profiles above the respective base levels **SCL**$_{UNDR}165$ and **SCL**$_{DRA}135$. The C mass change was taken as the difference of C inventories between the two sites. In their study, C concentration was estimated to be 50% of the dry mass (Pitkänen et al. 2013). In this study, the total C inventories of the peat profiles were calculated by summing up C masses in each 10-cm sample above the synchronous basal layers by using C%, known sample volume and bulk density to calculate C masses for each sample. We also calculated the C masses of the corresponding 90-cm peat profiles from **SCL**$_{UNDR}155$ to **SAL**$_{UNDR}235$ and from **SCL**$_{DRA}125$ to **SCL**$_{DRA}205$. The ratio of ^{13}C and ^{12}C masses were converted to δ^{13}C values by eq. 1.

The variance of each profile pair on undrained and drained site C mass and δ^{13}C is expressed as mean ± standard error. Missing or gained C error estimate comes from possible combinations on undrained and drained site (undrained site profiles 1 and 2 and drained site profiles 1 and 2). $\delta^{13}C$ values for missing or gained C were determined by calculating the mass weighted means of missing or gained C and $\delta^{13}C$ combinations for undrained and drained site and thus error estimate is shown as range of all possible combinations. Mass weighted average with range of individual profiles of $\delta^{13}C$ for the $_{UNDR}5$ – $_{UNDR}80$ cm and $_{DRA}5$ – $_{DRA}50$ cm of the uppermost peat layer were used to compare the current peat upper layer $\delta^{13}C$ values affected by drainage to historical ones deeper down in the peat column.

The Long Term Average Rate of Carbon Accumulation (LORCA) was calculated by dividing the total C mass of 250 cm long peat profiles from the undrained site by basal peat age (10,220 yr) from (Mäkilä and Goslar 2008). Similarly, $LOR^{12}CA$ and $LOR^{13}CA$ were calculated to get an estimate for the annual addition of ^{12}C and ^{13}C in the peat profiles.

Statistical analysis

Pearson correlation and regression analyses were done to the peat profiles $_{UNDR}5$ – $_{UNDR}235$ cm and $_{DRA}5$ – $_{DRA}205$ cm to study the relationships between $\delta^{13}C$ and C%, N%, C/N-ratio and dry BD. The effect of drainage (undrained vs. drained) on $\delta^{13}C$, C%, N% and C/N of surface peat was tested using a t-test. Analyses were done with IBM SPSS Statistics version 25.

Results

Peat constitutes and $\delta^{13}C$, C%, N% and C/N-ratio stratigraphy

The peat column inventory done by the Geological Survey of Finland, conducted at a site different from ours, but showing rather similar stratigraphic features, showed that undrained peat surface was composed mostly of *Sphagnum* and aquatic herbs (Fig. 2g). Deeper in the peat column, the proportion of *Eriophorum* and sedges increased, and peat material was dominated by sedges from 205 to 245 cm. In basal peat, shrubs also appeared (Fig. 2g). According to the GSF data, the peat humification index (von Post H1–10) rapidly increases below the poorly humified 0–60 cm surface layer (H2–3); maximum value (H8) was found from 150 to 190 cm. Below 190 cm, the von Post values decreased again (Fig. 2g). LORCA was 11.7 ± 0.2 g C m^{-2} yr^{-1} (mean ± SE), and it could be divided into 11.56 g m^{-2} yr^{-1} of ^{12}C and 0.13 g m^{-2} yr^{-1} of ^{13}C.

Original data of $\delta^{13}C$, C%, N%, C/N-ratio and bulk density is in Sup. 1. In the top 10 cm of peat, the $\delta^{13}C$ values were statistically significantly ($t(2) = -6.73$, $p = 0.02$) higher on the drained side ($\delta^{13}C$ −25.9 ± 0.24‰) compared to $\delta^{13}C$ −27.6 ± 0.09‰ in the undrained site (Fig. 2a). Mass weighted average of $\delta^{13}C$ values for the 50 cm of the current surface peat on drained site were 0.76‰ (0.60–0.91‰) (mean + range) enriched compared to the undrained site 80 cm values.

In both the undrained and drained profile, there is a marked peak of $\delta^{13}C$ immediately below the uppermost surface peat layer; peak values of −24.9 ± 0.39‰ and −24.0 ± 0.46‰ were found at $_{UNDR}25$ cm and $_{DRA}15$ cm, respectively (Fig. 2a). Deeper down there is a rapid decrease to about −28‰ in both profiles and then a steadier decline rather uniformly in both site profiles, from $_{UNDR}75$ to $_{UNDR}185$ cm at the undrained site and from $_{DRA}45$ to $_{DRA}155$ cm on the drained site. The most depleted $\delta^{13}C$ was found at $_{UNDR}185$ cm (−29.0 ± 0.15‰) and $_{DRA}155$ cm (−29.0 ± 0.04‰). Thus, the minimum $\delta^{13}C$ values in the UNDR and DRA peat profiles were showing a similar depth difference (30 cm) as the synchronous ash layers between the undrained and drained sites, and conformed to the surface subsidence. $\delta^{13}C$ values decreased below $_{UNDR}215$ and $_{DRA}185$ cm towards the boundary of the basal peat-mineral soil and increased in the undrained site but not on the drained site (Fig. 2a).

At the drained site, there was more variation in the C concentration (Fig. 2b) than on the undrained site. The C% was lower at the drained site to a depth of $_{DRA}75$ cm, but it increased in the deeper peat layers from $_{DRA}105$ cm to $_{DRA}205$ cm (Fig. 2b). On the drained side, C% peaked at depth layers from $_{DRA}165$ cm to $_{DRA}205$ cm.

Drainage decreased the uppermost peat N% down to a depth of $_{DRA}55$ cm (Fig. 2c). However, the N% increased in the deeper peat layers from $_{DRA}65$ – $_{DRA}155$ cm, and also in the basal peat layers from

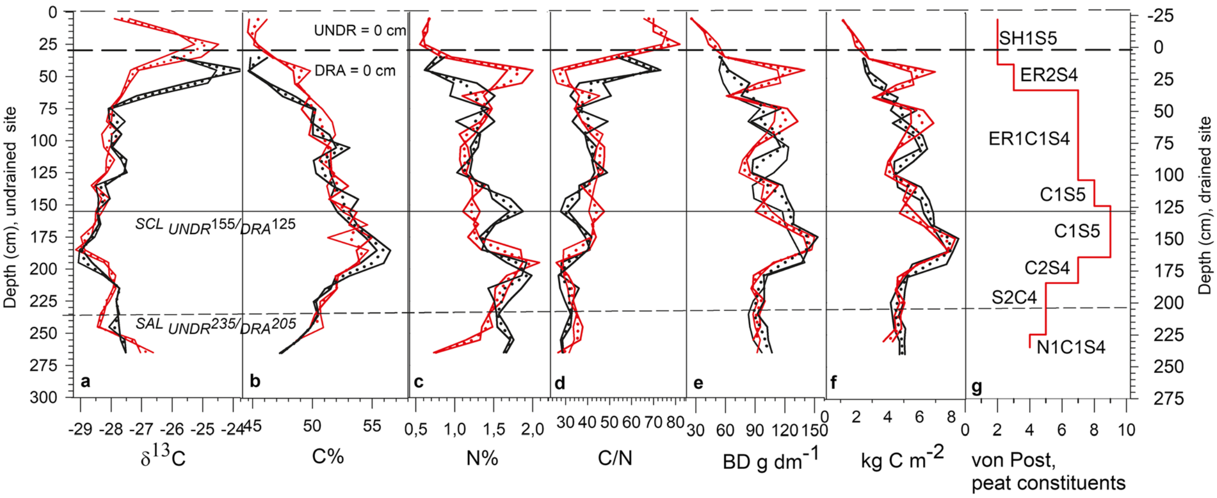

Fig. 2 Rahesuo stratigraphy of undrained site (dotted red line is mean, solid red lines show individual profiles) and drained site (dotted black line is mean, solid black lines show individual profiles). Surface and synchronous levels are marked with vertical lines. δ^{13}C (‰) (**a**), C% (**b**), N% (**c**), C/N-ratio (**d**), BD (**e**), amount of C m^{-2} (**f**) and peat humification on von Post scale and peat constituenst (**g**). Surface for undrained site (UNDR = 0 cm) and drained site (DRA = 0 cm). Upper synchronous layer line (**SCL$_{\mathbf{UNDR}}$155/$_{\mathbf{DRA}}$125**) used in calculations is 10 cm above detected synchronous charcoal layer at $_{\mathrm{UNDR}}$165 cm and $_{\mathrm{DRA}}$135 cm. Lower synchronous layer line (**SAL$_{\mathbf{UNDR}}$235/$_{\mathbf{DRA}}$205**) is elevated 10 cm above ash amount increase determined as transfer layer from peat to mineral subsoil border at depth of $_{\mathrm{UNDR}}$245 cm and $_{\mathrm{DRA}}$215 cm. Peat constituents on six grade scale portions: SH = *Scheuchzeria* (aquatic herbs), ER = *Eriophorum* (cotton grass), S = *Sphagnum* (moss), C = *Carex* (sedge), N=Nanolignidi (shrubs)

$_{\mathrm{DRA}}$175 – $_{\mathrm{DRA}}$245 cm and in the mineral subsoil (Fig. 2c). At both the undrained and drained sites, the C/N ratio was largest in the surface peat layers, peaked similarly as δ^{13}C at $_{\mathrm{UNDR}}$25 cm (~78) and at $_{\mathrm{DRA}}$15 cm (~71) and decreased to 30–40 below $_{\mathrm{UNDRA}}$45 cm and $_{\mathrm{DRA}}$25 (Fig. 2e). C/N ratio was at a minimum (27.3) 10 and 20 cm below the depth where δ^{13}C had minimum value on undrained and drained sites, respectively. Variation in N% was larger compared to C%, and thus the C/N ratio was a mirror image of N% (Fig. 2c, d).

In the uppermost 0–50 cm of both of the profiles, there appeared to be no correlation between the δ^{13}C values with the other measured variables and these samples did not fit with the regressions established between δ^{13}C and C% in the samples $_{\mathrm{UNDR}}$45 to $_{\mathrm{UNDR}}$235 and $_{\mathrm{DRA}}$45 to $_{\mathrm{DRA}}$205 level (Fig. 3). In the peat profile $_{\mathrm{UNDR}}$45 to $_{\mathrm{UNDR}}$235 and $_{\mathrm{DRA}}$45 to $_{\mathrm{DRA}}$205, the δ^{13}C decreased with depth (Fig. 2a). However, a significant negative correlation between δ^{13}C and sampling depth was found only at the undrained site (Table 2). At the undrained site, the δ^{13}C had a negative correlation with the dry BD. The C% correlated positively with sampling depth at the undrained site and with BD at the undrained and drained site. N% correlated positively with the depth at the drained site (Table 2), but not on the undrained site. A significant negative correlation was found between C/N-ratio and peat depth at the drained site (Table 2).

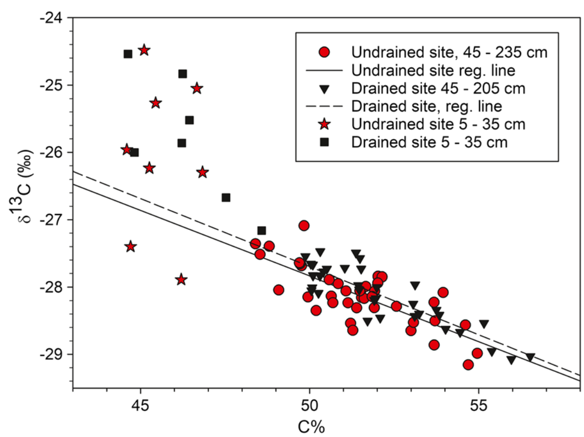

Fig. 3 Regression line between δ^{13}C and C%. Undrained site, depths 45–235 cm: $\delta^{13}C = -0.20 * C\% - 18.08$, $p < .0001$, F = 52.4, $r^2 = 0.58$, $n = 38$; drained side, depths 45–205 cm: $\delta^{13}C = -0.20 * C\% - 17.57$, $p < .0001$, F = 96.7, $r^2 = 0.75$, $n = 32$

Table 2 Correlation matrix for undrained (depths 45–235 cm) and drained (depths 45–205 cm) sites of Rahesuo bog

	Bulk density		C/N-ratio		N%		C%		Depth	
	UNDR	DRA	UNDR	DRA	UNDR	DRA	UNDR	DRA	UNDR	DRA
δ^{13}C	−.390	**-.733**[b]	**-.349**[a]	.238	.264	−.361	**-.761**[b]	**-.867**[b]	**-.527**[b]	−.237
Depth	.019	−.004	−.123	**-.548**[b]	.260	**.594**[b]	**.568**[b]	.297	1	1
C%	**.344** [a]	**.774**[b]	–	–	−.029	.197	1	1		
N%	.277	.084	–	–	1	1				
C/N	−.237	−.015	1	1						
BD	1	1								

[a] Correlation is significant at the 0.05 level (2-tailed)

[b] Correlation is significant at the 0.001 level

$n = 40$ for undrained side and $n = 34$ for drained side

Carbon deficit

The total C deficit in the drained side profile was 4.2 ± 3.0 kg C m^{-2} or 114.0 ± 81.5 g C m^{-2} yr^{-1}, compared with the undrained one (total C inventories above **SAL**$_{\mathrm{UNDR}}$235/$_{\mathrm{DRA}}$205; Table 3). The missing C was ^{13}C-depleted, [δ^{13}C, −31.2 (−4.3 - −31.3) ‰] compared to the corresponding average of the undrained site peat C (δ^{13}C -28.0 ± 0.03‰) (Table 3).

For the peat sequences above the **SCL**$_{\mathrm{UNDR}}$155/$_{\mathrm{DRA}}$125 layer, the C deficit was 5.9 ± 1.1 kg C m^{-2} due to drainage (Table 3), which when divided by the post-ditching number of years, translates to an average annual C loss of 159.0 ± 1.1 g C m^{-2} yr^{-1}. The peat profile above **SAL**$_{\mathrm{UNDR}}$155/$_{\mathrm{DRA}}$125 had quite similar δ^{13}C values above the synchronous ash layer both in the undrained (δ^{13}C -27.7 ± 0.04‰) and drained (δ^{13}C -27.5 ± 0.01‰) sites. The missing C [δ^{13}C −30.0 (−29.1‰ − −32.4‰)] was ^{13}C-depleted compared to the corresponding δ^{13}C average of the undrained site peat C (-27.7 ± 0.04‰) (Table 3).

When comparing the deeper parts of the profiles, the C mass was larger in the sequence $_{\mathrm{DRA}}$105 − $_{\mathrm{DRA}}$185 than in the corresponding part in the undrained one (Fig. 2f). Thus, the 90 cm peat section between the $_{\mathrm{DRA}}$125 − $_{\mathrm{DRA}}$205 showed a 3.0 ± 1.9 kg m^{-2} excess in the C mass at the drained compared to $_{\mathrm{UNDR}}$155 − $_{\mathrm{UNDR}}$235 peat columns (Table 3). The additional C [δ^{13}C −27.8 (−25.4‰ - −31.6‰)] was ^{13}C-enriched compared to the corresponding δ^{13}C average of the undrained site peat C (-28.4 ± 0.01‰) (Table 3).

Discussion

Using peat δ^{13}C values as an indicator of changed environmental conditions

Andersson et al. (2012) and Esmeijer-Liu et al. (2012) studied the δ^{13}C stratigraphy of natural peatlands connected to different climatic periods or peatland development stages. The effect of water table lowering on the δ^{13}C profiles has been studied on peatlands where the water table was lowered due to peat uplifting caused by permafrost formation (Krüger et al. 2014), drainage for agriculture (Krüger et al. 2015) and forestry (Krüger et al. 2016; Nykänen et al. 2018). A new approach in this study was the calculation of the absolute amounts of ^{13}C and ^{12}C by the same methods used earlier in C balance calculations (Minkkinen et al. 1999; Pitkänen et al. 2013; Krüger et al. 2016).

The calibrated age of the basal peat of Rahesuo bog was 10,220 yr B.P. (Mäkilä and Goslar 2008). Thus, the studied peat profiles have stored the history of the whole Holocene climatic periods on peat C and also the effects of natural diagenetic processes on δ^{13}C values. Also, the natural succession of vegetation due to peat surface elevation in relation to the mineral water source is stored in the peat profiles. Furthermore, water-table level change

Table 3 Rahesuo carbon stores, $\delta^{13}C$ values and $\delta^{13}C$ of carbon gained or missing

	kg C m^{-2}, $\delta^{13}C$ (‰)		kg C m^{-2}, $\delta^{13}C$ (‰)	g C m^{-2} yr^{-1}
	UNDR	DRA	Balance	
Above	68.2 ± 1.85	62.3 ± 0.58	−5.9 ± 1.12	−159.5 ± 0.03
$SCL_{UNDR}155/_{DRA}125$	−27.7 ± 0.04	−27.5 ± 0.01	−30.0 (−29.1 - −32.4)	
Above	114.8 ± 1.41	110.5 ± 3.41	−4.2 ± 3.01	−114.0 ± 81.5
$SAL_{UNDR}235/_{DRA}205$	−28.0 ± 0.03	−27.9 ± 0.03	−31.2 (−4.3 - −31.3)	
$_{UNDR}155–235/$	51.8 ± 0.94	54.8 ± 3.13	+3.0 ± 1.89	n/a
$_{DRA}125–205$ cm	−28.4 ± 0.01	−28.4 ± 0.01	−27.8 (−25.4 - −31.6)	

Negative values in masses indicate loss, while positive values indicate gain. *n* = *2* per treatment. In ″Balance“ column mass weighted mean $\delta^{13}C$ value of missing C and minimum and maximum $\delta^{13}C$ values of individual column pair comparisons in parentheses

induced by drainage has altered the balance between C uptake and release on the drained side during the last several decades. Thus, this study demonstrates that the analysis of $\delta^{13}C$ values in depth profiles is a useful tool to identify the effect of water table lowering on $\delta^{13}C$ values as well as comparing it to the $\delta^{13}C$ values of natural state peatland in similar climatic conditions. Furthermore, synchronous layers in the nearby peat columns offered a possibility to quantify the carbon stocks and to calculate actual ^{12}C and ^{13}C amounts and show changes in $\delta^{13}C$ values quantitatively.

The changes (above) reflected in peat $\delta^{13}C$ values are mainly connected to changes in hydrology, while ^{13}C depletion (^{13}C-Suess effect) of atmospheric CO_2 and increase of CO_2 concentration are affecting C supply and its $\delta^{13}C$ imprint. In general, most of the annual C exchange and formation of the initial $^{12}C/^{13}C$ ratios in peat occurs in the surface layer facing the atmosphere. However, the bulk $\delta^{13}C$ values are measured from the stored peat of different ages. As an example, on a boreal ombrotrophic *Sphagnum fuscum* bog hollow, 10 km from Rahesuo bog, 188 g C m^{-2} yr^{-1} was captured in photosynthesis and 198 g C m^{-2} was respired during an exceptionally dry summer, while 30 g C m^{-2} was lost through respiration during the winter, with a total loss of 62 g C m^{-2} yr^{-1} when also leaching (loss 7 g C m^{-2} yr^{-1}) and CH_4 flux (loss 15 g C m^{-2} yr^{-1}) were included (Alm et al. 1999). Compared to these carbon flows, the recent apparent rate of C accumulation during the 100 years for Rahesuo (26.3 g C m^{-2} yr^{-1}) (Mäkilä and Goslar 2008) is also relatively small compared to the mean $LORCA_{100}$ values of bogs in Finland (Turunen et al. 2002). In addition to this, the LORCA for the whole peat column in Rahesuo is smaller (11.7 g C m^{-2} yr^{-1}) than that of the Larsson et al. (2017) average (13.7 ± 5.5 (SD) g m^{-2} yr^{-1}) for a Swedish oligotrophic fen. Furthermore, the LORCA for Rahesuo was only half of the average of 127 northern peatland sites (23 ± 2 (SE) g C m^{-2} yr^{-1}) as given by Loisel et al. (2014). In any case, $\delta^{13}C$ values in peat profile are always measured from highly processed peat, which is only a fraction from the originally captured C.

Before distinctive changes in bulk peat $\delta^{13}C$ values can occur, there must be environmental changes in active processes that lead to a $^{12}C/^{13}C$ ratio change. In general, if both C uptake and release will decrease by the same amount, there will be no change in ^{13}C-values stored in peat. However, if C uptake remained the same but respiration increased, it will lead to a peat ^{13}C-enrichment. e.g. when water-table decreases due to increasing hummock height. Furthermore, the amounts of stored ^{12}C and ^{13}C in peat profiles depend on many processes, which can have opposite effects on the final bulk $\delta^{13}C$ values. Also, diagenetic processes decrease the original $\delta^{13}C$ values of peat, since anaerobic microbes preferentially use isotopically heavier compounds instead of more recalcitrant lignin that has a lower $\delta^{13}C$ value (Benner et al. 1987). Thus, processes leading to an increase in lignin fraction in bulk peat have a major role in depleting the stored peat $\delta^{13}C$ values.

Peat $\delta^{13}C$ values of the undrained site

In this study, the basal peat layer, consisting of shrubs, sedges and *Sphagnum* mosses was relatively ^{13}C-

enriched compared to the peat layer above it and also had a low humification index, comparable to the peat profile study from East European Russian Arctic (Andersson et al. 2012).

The most ^{13}C-depleted peat layer was found at $_{\mathrm{UNDR}}185$ and $_{\mathrm{DRA}}155$ cm, i.e. exactly at the same level taking into account the surface subsidence at the drained site. The same depth layer also had the maximum C%. Maximum nitrogen content and minimum C/N ratio was 10 and 20 cm below the most depleted layer on undrained and drained sites, respectively. Bulk density was highest at the same depth as the δ^{13}C minimum on undrained side and 10 cm over the δ^{13}C minimum at drained site. Furthermore, humification index and the volumetric amount of C was largest at these same depth layers. Similarly, Kaislahti Tillman et al. (2010) found that peat with higher C% and lower C/N ratio, as indications of degradation, was also most depleted in ^{13}C.

In the Rahesuo bog, the mean peat growth was 0.25 mm yr^{-1} (Mäkilä and Goslar 2008) and the most negative δ^{13}C values of the peat profile originated approximately from 7400 to 7600 years BP. Thus, these peat layers were probably formed during the warm and moist period of the Mid-Holocene 7950–6750 years B.P. (Seppä and Birks 2001). One possible explanation for the ^{13}C-depleted peat may be the increased amount of more ^{13}C-depleted vascular plant material instead of *Sphagnum* mosses during the warm climatic period. In the GSF peat inventory, remains of sedges in depth layers between 155 and 245 cm were abundant. In addition to vascular plants ^{13}C-depletion, *Sphagnum* peat can become ^{13}C-depleted during a warm and moist climate due to increased methanogenesis (Jones et al. 2010). Furthermore, recycling of C during the wet fen stage can lead to vegetation ^{13}C-depletion (Jones et al. 2014).

In addition to the initial formation of ^{13}C-depleted wet fen stage peat, decay also leads to further peat ^{13}C-depletion. July temperatures were ~3 °C warmer during Mid-Holocene compared to the present day (Seppä and Birks 2001), thus promoting a higher decay rate. Vascular plants are mainly composed of lignocellulose, whereas *Sphagnum* mosses are primarily composed of cellulose (Benner et al. 1987; Kracht and Gleixner 2000). Both aerobic and anaerobic decay of peat containing lignin is known to cause ^{13}C-depletion (Fernandez et al. 2003). In this study, the most ^{13}C-depleted peat and the highest concentrations of C and N were found at the same depths. This was likely due to a faster decay rate of organic matter of vascular plants compared to bryophytes, leading to higher C%, N%, and smaller C/N ratio (Andersson et al. 2012). Furthermore, active microbes throughout the peat profile enable continuing slow decay through the whole peat profile. Putkinen et al. (2009) found active archaeal communities in deep peat layers, while Mpamah et al. (2017) showed that there were considerable amounts of viable microbes throughout the peat profile, mainly in the surface and basal layers but also in the middle section of the peat profile.

In the Rahesuo bog, the anaerobic catotelm layer had a negative correlation between δ^{13}C and C%, and the corresponding slope in our equation: $\delta^{13}\mathrm{C}\ (\mathrm{peat}) = -0.20 * \mathrm{C\%}\ (\mathrm{peat}) - 18.1$, was between those of Larsson et al. (2017) for *Sphagnum* spp. and *Eriophorum* spp. peat. Thus, diagenetic processes in peat containing *Sphagnum* spp. and vascular plants decreased the peat δ^{13}C (above) and, possibly also amplified the effect of already ^{13}C-depleted vegetation cover effect on peat δ^{13}C.

Above the most ^{13}C-depleted peat layer, peat ^{13}C-enrichment begins, possibly due to the cooling and drying of the climate leading gradually to an increased proportion of *Eriophorum vaginatum* and to a decrease in N% and humification index. These changes possibly indicate a major decrease in water flow thus ending the fen stage. In an otherwise ^{13}C-enriching peat profile, there is a 0.4‰ shift to more negative δ^{13}C values at a depth of 135 cm on undrained site, and also a small increase in N%. The climatic period or change in hydrology leading to this shift is unknown. Overall, the peat δ^{13}C profile of the undrained side followed the main vegetation assemblages comparable to the results of Andersson et al. (2012). Changes in vegetation type were a consequence of past climatic periods and possibly from a change in hydrology when the peat surface grew above the minerogenic water sources.

Effect of artificially lowered water table on peat ^{13}C/^{12}C-ratios

Most of the 15 Mha of peatlands drained for forestry, are found in the boreal and temperate zones of Russia and Fennoscandia (Joosten and Clarke 2002). Globally, the peatland area drained for forestry, cropland or grassland is ca. 50.9 Mha (Leifeld and Menichetti 2018).

To compare the effects of lowering water table on carbon balance and peat ^{13}C/^{12}C-ratios, the studied sites have to be originally similar, with a long lasting water table lowering and hydrology affected so that the water table drop due to ditching is affecting only the drained site. In the original study (Pitkänen et al. 2013), Rahesuo was chosen since the border ditch runs along the natural water flow direction of the bog. Since the natural upper margin of the bog is intact, the natural water flow regime is minimally affected on the undrained side, whereas effects of drainage are seen right up to the marginal ditch. Thus, comparable profiles for the undrained and drained conditions were available close to each other from either side of the marginal ditch from the same original hollow.

Drainage of Rahesuo bog for forestry 37 years before sampling, resulted in a lowered water table level, increased dry BD, subsided peat surface, changed vegetation composition and led to C loss, but did not markedly enhance tree growth on the drained side (Pitkänen et al. 2013). In this study, the average C loss based on mass difference inventories from the whole peat column was clearly larger, 114 g C m^{-2} yr^{-1} compared to the contemporary net ecosystem C balance of Alm et al. (1999), whose study was conducted during an exceptionally dry summer at a nearby natural bog. It is not clear which CO_2 flux component, CO_2 uptake or respiration most affected the C balance at our site. In a natural bog, an early and prolonged drought period decreased carbon uptake, while a short drought period increased respiration (Lund et al. 2012). In any case, respiration increases in drained peatlands (Silvola et al. 1996). In general, isotopic fractionation during decomposition and respiration increases the $\delta^{13}C$ values of remaining C (Ågren et al. 1996). The upper parts of peat profiles of both the undrained and drained sites of Rahesuo were the most ^{13}C enriched sections of the studied peat columns and drying further increased the $\delta^{13}C$ of the surface peat. While respiration leading to preferred release of ^{12}C may be the most important factor in peat ^{13}C-enrichment, CH_4 production and methanotrophy are known to decrease when the water table drops (Urbanová et al. 2013), which can also cause ^{13}C-enrichment of aerobic peat layers.

The C mass in the topmost 10 cm of the Rahesuo bog was 1163 g C m^{-2} in the undrained site and 2468 g C m^{-2} in the drained site. Based on the actual rate of C accumulation during the last 100 years ($ARCA_{100}$), dry BD and C% for the surface peat, approximately 8.4 cm of new peat has accumulated on the undrained site surface during the last 37 years. Thus, only the top 10 cm of the surface peat got most of the newly formed ^{13}C-depleted plant C material. At the drained site, surface peat $\delta^{13}C$ value increased ~1.7 ‰ in the top 10 cm. This indicates that the peat surface C balance has changed: ^{13}C-enrichment due to respiration has been clearly larger than the C uptake in photosynthesis counteracting ^{13}C enrichment. Opposite to the drained Rahesuo bog site, the top 9 cm of the drained peat surface of the *Sphagnum fuscum* pine bog at the Lakkasuo peatland was ~2.0 ‰ depleted (Krüger et al. 2016). This ^{13}C depletion probably followed from the C addition to the surface layer from new vegetation and also from the litter falling from the trees, C input being there jointly larger than the amount of released C from decaying peat. The different response in the $^{13}C/^{12}C$-ratio to the water level lowering between these two drained and natural bog pairs was mostly due to differences in their development after drainage. Primarily, in Lakkasuo the original water flow was perpendicular to the ditches, and thus drainage possibly affected the undrained site hydrology, whereas in Rahesuo, water flow was parallel to the ditches. This difference is linked to their C balance estimate measured by the C mass comparison method: in this study and in the original study (Pitkänen et al. 2013), the Rahesuo bog acted as a C source (114.0 ± 81.5 g C m^{-2} yr^{-1}), while the drained bog at Lakkasuo was a C sink of 70 g C m^{-2} yr^{-1} in an earlier study (Minkkinen et al. 1999) and even a bigger sink in recent study (179 ± 83 g C m^{-2} yr^{-1}) (Krüger et al. 2016) when compared to its undrained pair.

Another factor leading to differences between Lakkasuo and Rahesuo surface $\delta^{13}C$ values is the addition of vascular plants containing lignin (Fernandez et al. 2003), being more distinct in Lakkasuo (Krüger et al. 2016) compared to the Rahesuo bog (Pitkänen et al. 2013). In Rahesuo, $\delta^{13}C$ of the missing C from the layer above the synchronous ash layer was lower ($\delta^{13}C$, −30‰) than peat $\delta^{13}C$ on the undrained site and clearly lower than the atmospheric CO_2 ($\delta^{13}C$, ~ −8 ‰, Rubino et al. 2013). Thus, when respiration increases, the amount of ^{13}C-depleted CO_2 released from decaying peat increases in photosynthesis compared to atmospheric CO_2 ($\delta^{13}C$ ~ − 8‰), leading to further ^{13}C-depletion of vegetation and surface peat (Nykänen et al. 2018). However, this effect was not visible in Rahesuo.

Clear ^{13}C-enrichment at the peat surface "turning point" was found both in the undrained and drained sites of the Rahesuo bog. Both on the undrained and drained sites of the Rahesuo peat profiles, C% and N% had their minimum values and biggest C/N ratio at the same layers ($_{UNDR}25$, $_{DRA}15$) where $\delta^{13}C$ values peaked. Thus, it would be logical to locate the $\delta^{13}C$ turning point to the original mesotelm. The mesotelm is defined as a metabolically active interface between the oxic acrotelm and anoxic catotelm. However, the mesotelm is also a horizon that is mainly anoxic but periodically oxic (Clymo and Bryant 2008). Thus, microbial processes can change in the mesotelm from aerobic to anaerobic due to changes in water saturation. Furthermore, both respiration and leaching are active at this depth.

Similar enrichment in $\delta^{13}C$ values near the surface was initially found from the uplifted palsa peat profiles formed due to frost upheave ca. 2500 cal yr BP (Andersson et al. 2012) or palsa uplifting leading to drying of formerly wet peat 155–671 years earlier (Alewell et al. 2011). However, the turning point was not found in peatlands drained for agriculture (Krüger et al. 2015) or forestry (Krüger et al. 2016) even though these practices lead to a drastic decrease in the water table levels and to increased C loss. Turning point $\delta^{13}C$ enrichment was 0.8‰ larger and C% 0.5% smaller on the drained site, thus indicating increased C loss from the peat surface compared to the undrained site. Due to subsidence the maximum $\delta^{13}C$ value was closer to the current peat surface on the drained site than on the undrained site, thus indicating that this $\delta^{13}C$ maximum was there before artificial drainage.

$\delta^{13}C$ Suess effect and peatland carbon exchange

$\delta^{13}C$ of atmospheric CO_2 has decreased 1.6‰ from 1850 to 2002, to the current ~ –8‰ (Rubino et al. 2013). At the same time, the concentration of CO_2 in the atmosphere has increased from preindustrial values of ~280 ppm to ~390 ppm (Rubino et al. 2013). In the Rahesuo bog, ^{13}C-depleted atmospheric CO_2 has been used by the surface vegetation since 1850 and thus the surface peat to a depth of ~25 cm has used the progressively depleting CO_2 based on $ARCA_{100}$, peat dry BD and C concentration. In the Rahesuo bog, ^{13}C depletion of the surface peat due to ^{13}C-Suess effect was not clear or different compared to the deeper peat profile, as it was in a 30 cm long surface *Sphagnum* peat column studied in northern Finland (Esmeijer-Liu et al. 2012). In this study, ^{13}C depletion was not detected, since respiration, CO_2 reuse, CH_4 production and flux, and methanotrophy have all affected the peat $\delta^{13}C$ values both on the undrained and drained sites in the same depth layers as the ^{13}C-depleted atmospheric CO_2. In addition to this, the increase of CO_2 concentration is not affecting peat $\delta^{13}C$ values, since $^{13}C/^{12}C$ fractionation in plants is independent of natural CO_2 concentration variation (Kohn 2010).

Carbon (^{12}C and ^{13}C) storage change

In this study, the actual masses of ^{12}C and ^{13}C in whole peat profiles were calculated. The splitting of C to ^{12}C and ^{13}C masses was possible, since gravimetric and volumetric C masses were known with their $\delta^{13}C$ values. To our knowledge, this was the first time that this kind of calculation was done. The close proximity of the sites, vegetation pattern, composition of peat and similarity of C%, N% and $\delta^{13}C$ profiles strongly support the presumption that at least the upper half of the undrained and drained site peat profiles were similar before drainage, and thus the differences of $\delta^{13}C$ values in peat were due to differences in C flows as affected by drainage. The calculated C loss was 5.9 ± 1.1 kg m^{-2} for the upper peat profile, and for the whole peat profile 4.2 ± 3.0 kg m^{-2}. In other Finnish undrained and drained bog pairs studied by similar methods, a clear increase in C amount following drainage has been detected (eg. Minkkinen et al. 1999; Krüger et al. 2016). However, further discussion of reasons leading to these fundamental differences are beyond this MS, but probably related to factors that explain differences in ^{13}C-depletion in Lakkasuo and ^{13}C-enrichment in Rahesuo bog surface peat.

Drainage affects mostly the upper peat layers, thus the smaller C loss for the whole profile C balance calculation was due to a larger C mass below the synchronous ash layer at the drained site. The 90 cm peat section below the synchronous ash layer had 3.0 ± 1.9 kg m^2 more C on the drained site. One 10 cm slice of peat contains 4–7 kg C m^{-2}, thus increased peat compaction cannot explain this addition, since marker layers remained at the same levels on undrained and drained sites. Leaching of DOC is one possible explanation for C addition since unlike CO_2 and CH_4, DOC is retained and captured in the peat samples used for C mass and $\delta^{13}C$ analyses. In a 2 m deep pristine bog, ^{14}C analyses showed that part of the DOC in the whole peat column originated from the newly formed surface peat (Wilson et al. 2016). However, an increase of downward DOC leaching is not effective enough to move 3 kg C m^{-2} in 37 years from the upper peat profile to the deeper peat profile. Thus, it is also possible that the larger amount of C was due to original differences in the deep peat layers between the sites.

Drainage as an analog of past dry periods

In general, the positive shift in the peat $\delta^{13}C$ values indicates drier conditions, even though Lakkasuo bog $\delta^{13}C$ data shows that vegetation development can lead to decreased $\delta^{13}C$ values in the upper peat profile (Krüger et al. 2016). The upper peat profile on the undrained and on the drained site was also the most ^{13}C-enriched section of the whole peat column. Drainage led to a peat C loss, dry bulk density increase, and to ~1.9‰ ^{13}C-enrichment of the surface peat. However, the increase was only 0.76‰ when $\delta^{13}C$ of the corresponding surface peat layers ($_{UNDR}$80 cm to $_{DRA}$50 cm) were compared. Drained peatlands have been used as analogs to climate change induced drying and concomitant changes in vegetation and C flows (Laine et al. 1996), even though factors leading to natural permanent water table decrease oblige changes also in precipitation and air temperature. According to the results of this study, the effects of artificial lowering of the water table on $\delta^{13}C$ could be comparable to the effects of the earlier severe dry periods values in peat columns. In general, $\delta^{13}C$ values of surface peat layers decrease from their original values via diagenetic processes. In this study, the decrease in $\delta^{13}C$ values was 0.20‰ per one % increase of C% (Fig. 3 equation). Therefore, earlier positive (or negative) shifts in $\delta^{13}C$ values of ancient surface peat are noticeable in peat profiles as changes in $\delta^{13}C$ value trends, but the change is probably smaller than the difference in $\delta^{13}C$ values between undrained and drained sites in this study.

Conclusions

On both the undrained and drained sites, the most depleted $\delta^{13}C$ values were at the same depths as the maximum peat dry BD, C%, N% and the minimum C/N ratio. This indicates the existence of a wet fen stage during the moist and warm period and diagenetic processes further accelerating ^{13}C-depletion in the peat layer. Drainage and 37 years of water table decrease led to the loss of ^{13}C depleted C and to increased $\delta^{13}C$ values in the drained Rahesuo bog surface. The drained site was a source of ^{13}C depleted CO_2 to the atmosphere. The increased value of $\delta^{13}C$ in the peat column due to an artificial lowering of the water table can be compared to earlier severe dry periods as a positive shift in $\delta^{13}C$ values in the peat column accompanied by an increase in BD and C%. Analysis of $\delta^{13}C$ can be used as an additional tool to follow current and past C flows in the peat columns. The method used here to calculate ^{13}C and ^{12}C balances in a known peat profile may be useful when studying the environmental changes in peat or lake sediment profiles when accurate ^{14}C-datings and depth levels are available.

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