

We highly appreciate the very helpful and constructive comments of the anonymous referee, which helped us to further improve the manuscript. We tried to consider all of them.

The referee's comments will be shown black. Our response is shown blue, *italic* and tab-indented while changes in the manuscript are in quotation marks and **bold**.

Anonymous Referee #1

The ms describes a study on the influence of changes in plant cover on the decomposition of moss (sphagnum) dominated peat at two peatlands differing in altitude and temperature. The authors investigated a large number of short cores (20 cm) for changes in peat decomposition based on C/N ratios, $\delta^{13}\text{C}$ and changes in organic components derived from pyrolysis GC-MS analyses. The authors found out, that sedges and shrubs litter increases decomposition of moss dominated peat, especially at higher temperature. The effect of vascular plants was more pronounced than that of temperature. Peat decomposition appears to be best reflected by $\delta^{13}\text{C}$, although its application to distinguish source material from decomposition is seen incomplete. C/N and $\delta^{15}\text{N}$ appear to be not specific enough to indicate the effects of vascular plants on moss peat decomposition. The topic and the conclusions are not entirely new, but this is to my knowledge the most comprehensive study on this topic. Especially the combination of stable isotopes, C/N ratios and pyrolysis GC-MS gives new insights into the role of plant cover for initial organic matter degradation in peatlands on a molecular level. The ms is suitable for Biogeosciences and well written and I suggest publication after addressing some issues.

Specific comments: The use of the term decomposition in peatlands is often a bit unspecific and many different methods (compound specific or only operational defined) are used to determine the degree of peat decomposition. Although the authors describe in the ms what C/N, $\delta^{13}\text{C}$ and py-GC-MS can show, but it remains unclear when I see mass loss (C/N and $\delta^{13}\text{C}$) or changes in the molecular composition. The problem here, I think is that e.g. C/N and $\delta^{13}\text{C}$ were used in previous studies to distinguish changes in peat decomposition (here it describes mainly mass loss (polysaccharides), but what the authors investigated in their study is the initial phase of plant material decay (a lot of qualitative changes/ molecular composition) I suggest that the authors make clear what they mean by "peat" and give a clear statement e.g. in their hypotheses what they mean by "decomposition".

Thank you for this suggestion. We will include a sentence what we understand as "decomposition". We will integrate this at the end of the sentence in L.55 as follows:

"We defined decomposition as any changes in properties of the peat relative to its source material, e.g. plant material from *Calluna vulgaris*, *Eriophorum vaginatum*, *Sphagnum* spp. directly after deposition."

We will also include a definition of "peat" at the end of the sentence in L.54:

"Peat was defined as any organic material that accumulates underneath the peatlands surface, including living stems of *Calluna vulgaris*, *Eriophorum vaginatum* and *Sphagnum* spp."

The authors address the importance of oxygen availability, redox conditions and water levels at the time of sampling. They also mention that oxygen transport into the peat via aerenchyma of *E. vaginatum* takes place.

However, redox-conditions (here the availability of oxygen for OM mineralisation) are crucial for peat decomposition. For me it remains unclear how much of the observed changes in decomposition/OM quality are related to redox-conditions/water table depth or oxygen transport via the roots of vascular plants and how much to the presence of plant litter from sedges or shrubs. More shrubs and sedges in peatlands are usually a result of drier conditions. Drier conditions mean lower mean water table and aeration/ increased decomposition of peat, a bit a hen and egg problem. The authors remain unclear about this in their conclusions.

We want to thank the referee for this valuable comment. We agree on the referee's comment that redox conditions are a major control on peat decomposition. This was considered in the sampling design, where we restricted the plot installation to hummocks and peat core sampling to the aerobic zone, the acrotelm. Also we specifically chose locations where sedges and shrubs grew in mixed stands, experiencing similar redox conditions. With this strategy we avoided the "hen and egg problem" as much as possible. However, as addressed to the review provided by Tim Moore, sampling depths in the peat cores are periodically water saturated. Water table measurements 2015/08–2016/07 (three gauges at each site) show that the peat within the sampled 20 cm on the High T site stayed aerated for 117, 360 or 366 days of the year as recorded in the three gauges. On the Low T site, the peat of the top 20 cm was aerated for 137, 138 or 284 days of the year. These measurements underline that beside higher temperature and higher vascular plant proportion, the top 20 cm peat at the High T site stays longer aerated over the year than at the Low T site. This information will be replacing the information of water table depths at the end of the sentence in L. 89 as follows:

"The time during which the top 20 cm of the peat was above the water table was determined with water table measurements between August 2015 and July 2016 at three gauges on each site. At the Low T site, the water table remained below 20 cm for 137, 138 and 284 days of the year; at the High T site, this was 117, 360 and 366 days of the year respectively."

Due to this added information, we will adapt the discussion in L. 308 as follows:

"The altitudinal gradient has been used to reveal potential effects of increasing temperature and associated lower water table on peat decomposition by comparing the decomposition parameters (Table 1) between the High T and Low T site.

Water table and thus aeration did probably not affect peat decomposition under sedges vs. shrubs because our sampling design ensured similar water table between sedges and shrubs at each of our sites. We think that increased peat decomposition as a result of oxygen transportation by the aerenchym of sedges should be more important at the Low T site because of the longer time of water saturation at this site in comparison to the high T site.

We will address this in L. 305 as follows:

"This process is particularly relevant at the Low T site, where the uppermost 20 cm of the peat remained water saturated much longer than at the High T site."

In addition, we will refine our conclusions in L. 348:

"The most important and also surprising result of our study was that vascular plants had a more pronounced impact on peat decomposition than temperature and associated lower water tables together. Potential O₂ transport by the aerenchym of sedges did probably not contribute to enhanced peat decomposition at the High T site, as the top 20 cm peat layer sampled remained above the water table, and thus aerated, for most of the year."

- The authors tend to use general terms such as L 35 alterations in the environment,

We thank the referee for the comment. We will address this in L. 35 as follows:

"Climate change is expected to partly lift these environmental constraints to microbial decomposition by warmer (Karhu et al., 2014) and drier conditions, threatening to release stored organic C as CO₂ to the atmosphere."

L39 plant-soil feedbacks,

We will change the term in L. 39 as follows:

"A systematic change in composition of plant functional types (PFTs) towards vascular plants has a yet unknown potential to accelerate C losses from the stored peat originally dominated by mosses due to increased C input via roots from vascular plants (Bragazza et al., 2013; Gavazov et al., 2018; Robroek et al., 2015), and litter mixing effects (Zhang et al., 2019)."

L66..hydrological conditions. Please be more specific.

We will change the term in L. 66 as follows:

“However, stable isotope patterns are also affected by the water table limiting aerobic decomposition and thus isotopic discrimination in the remaining peat (Krüger et al., 2015) and the plant species forming the litter.”

- Can the authors give an estimate about the ages of their plant/peat samples. Is time an issue here?

Unfortunately, we don't have data on the age of peat in 20 cm depth of both sites. A recent study of two other alpine peatlands at an altitudinal contrast higher than our study (1030 m a.s.l. vs. 1880 m a.s.l.) reported peat ages of 40 and 26 years respectively for the peat in 15-20 cm depth (Gavazov et al., 2018). Assuming these peatlands are similar to ours, the age difference between our sites would be less than 15 years.

The differences between the sites may have affected absolute differences between peat decomposition, but not the impact of shrubs relative to sedges on peat decomposition within sites. Furthermore, differences between the sites were quite small, and we are not able to disentangle the effects of the current temperature and water table on the one hand, and differences in environmental condition during peat formation on the other hand.

Accordingly, we will add information on the estimated age of peat at the end of the sentence in L. 90 in the study site descriptions as follows:

“Furthermore, in peatlands with similar vegetation cover, situated at 1030 m a.s.l. and 1880 m a.s.l. in Switzerland, the age of peat in 15-20 depth was found to be 40 years and 26 year, respectively (Gavazov et al., 2018), meaning that the potential age difference between the peat sampled at our sites is likely less than 15 years.”

- L185-195 The description of Fig. 1 2 and 4 are a bit difficult to decipher. May be distinguish by site.

As suggested, the paragraph in L.185-195 describing the results presented in these figures will be restructured as follows, but Figures 1, 2, and 4 will be maintained as we submitted them:

“Carbon to N ratios and isotopic composition of plant shoots were different between plant tissues, PFTs and to a lesser extent between sites (Fig. 1). Living plant shoots had consistently lower C/N ratios than plant roots irrespective of site or PFT (Fig. 1a). Sedge shoots had significantly lower C/N ratios ($p < 0.001$, Fig. 1a) and were significantly enriched in ^{13}C ($p < 0.001$, Fig. 1b) compared to moss and shrub shoots. Shrub shoots were significantly depleted in $\delta^{15}\text{N}$ compared to sedge and moss shoots ($p < 0.001$, Fig. 1c). Sedge shoots and moss from the High T site were both significantly depleted in ^{13}C compared to Low T site (both $p < 0.01$, Fig. 1b).

Peat C/N ratio and isotopic composition was significantly affected by depth, site and to a lesser extent by PFTs (Fig. 2a, 2b). Carbon to N ratio increased with depth and was higher at the High T site compared to the Low T site (Fig. 2a, Table 2). In the upper 0-2 cm peat layer, C/N ratios and stable isotopes corresponded with values observed for moss (Fig. 1, Fig. 2). Isotopic composition of peat increments was significantly different for depths and PFTs (Table 2). $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of peat increased with depth (Fig. 2b, 2c) and the enrichment in ^{13}C with depth was stronger for sedge-cores than for shrub-cores (i.e. 2.7 ± 0.4 ‰ for sedge-cores and 1.6 ± 0.4 ‰ for shrub cores). The largest enrichment in $\delta^{13}\text{C}$ between the uppermost and lowest depth increment appeared in sedge-cores at the High T site (Fig. 2b; i.e., 3.5 ± 0.5 ‰).”

- Table 1: all reference are from one of the authors (Schellekens). Any independent references available here?

The information on peat pyrolysates is frequently fragmented and scattered in the literature and the identification and/or validation of parameters was mainly demonstrated by these studies of Schellekens et al. However, we fully agree with the reviewer that self-citing is not desired and that the original source publication must be cited too. In order to cite correctly and at the same time avoid repeating the whole reasoning behind the pyrolytic parameters

(that was already published in Schellekens et al.), we have checked the literature once more and we will revise the references accordingly as follows (both in Table 1 and in Section 2.5): Also, note that the reference is given for the interpretation in Sphagnum peat (4th column) and not for the source molecule (3rd column); this was not sufficiently clear and perhaps contributed to the reviewers comment. We will clarify this in the revised manuscript by indicating that interpretation refers to Sphagnum peat; see the heading of the fourth column in Table 1.

Parameter	Unit	Indication	Interpretation in <i>Sphagnum</i> -dominated peat
C/N	-	preferential decomposition of C over N	aerobic decomposition
$\delta^{13}\text{C}$	[‰]	preferential decomposition of ^{12}C over ^{13}C isotope	aerobic decomposition
$\delta^{15}\text{N}$	[‰]	preferential decomposition of ^{14}N over ^{15}N isotope	aerobic decomposition
sum of G and S lignin products	[% TIC ^a]	lignin	vascular plants (van Smeerdijk and Boon, 1987)
sum of <i>n</i> -alkenes and <i>n</i> -alkanes	[% TIC ^a]	cutan, suberan, leaf waxes	ericoid shrubs (Schellekens and Buurman, 2011; van Smeerdijk and Boon, 1987)
C ₃ G/G	-	intact lignin	ericoid shrubs (Schellekens et al., 2012)
4-VG/G	-	ferulic acid	sedges (van Smeerdijk and Boon, 1987; Schellekens et al., 2012)
4-isopropenylphenol (Ph6)	[% TIC ^a]	sphagnum acid	aerobic decomposition of <i>Sphagnum</i> tissues (preferential loss of polyphenols over polysaccharides; Schellekens et al., 2015b)
levoglucosan/sum of polysaccharides	-	cellulose	aerobic decomposition of <i>Sphagnum</i> tissues (preservation of <i>Sphagnum</i> polysaccharides; Schellekens et al., 2015b) ^b

^a total ion current

^b interpretation refers to relatively low values

We will update the paragraph in L. 141ff. as follows:

“Based on the results of previous pyrolysis studies from peatlands a number of pyrolytic parameters reflecting plant species and the degree of **peat** decomposition were extracted (Table 1). A pyrolysis product specific for sphagnum acid (4-isopropenylphenol; Van Der Heijden et al., 1997) has been found to very sensitively reflect aerobic decomposition of *Sphagnum* tissue in *Sphagnum*-dominated peat (**Schellekens et al., 2015b**). Methoxyphenols are unique to lignin, thereby providing a measure for the contribution from vascular plants in peat dominated by *Sphagnum*, because *Sphagnum* contains no lignin (Abbott et al., 2013; Kracht and Gleixner, 2000; **Schellekens et al., 2015c; van Smeerdijk and Boon, 1987**). Since both shrubs and sedges contain lignin, additional parameters were included to distinguish between them. Sedges have large contributions from p-coumaric and ferulic acid (Lu and Ralph, 1999) with typical pyrolysis products 4-vinylphenol (Lg1) and 4-vinylguaiacol (Lg4), respectively (**van der Hage et al., 1993**). Because 4-vinylphenol is also abundant in *Sphagnum* tissue (**van Smeerdijk and Boon, 1987**), the ratio of 4-vinylguaiacol to the summed guaiacyl products (G) **can** be used to reflect sedges (Schellekens et al., 2012). The ratio of C₃-guaiacol to G **usually reflects intact lignin in soils but has been found** indicative for shrubs **in peat** (Schellekens et al., 2012, 2015a). *n*-Alkenes and *n*-alkanes (Al) originate from cutan and suberan present in roots and bark (**Nierop, 1998; Tegelaar et al., 1995**) and leaf waxes (Eglinton and Hamilton, 1967), depending on their chain length, all of which are associated with shrubs in *Sphagnum*-dominated peat (Schellekens and Buurman, 2011; **van Smeerdijk and Boon, 1987**).”

Furthermore, we have checked the whole text for possible reduction of self-citing. In L.73 we will exclude Schellekens et al., 2009 and 2015c.

Further, we will change typography and make other corrections:

Sentence in L. 77 will be changed to:

"In this multi-proxy study, we combined the analytical approaches outlined above to explore the influence of vascular plants on chemical properties and degree of **peat** decomposition in **two** moss-dominated peatlands contrasting in temperature."

We will correct the following references in our manuscript:

- L. 147f where (Lu and Ralph, 2010) will be changed to **Lu and Ralph, 1999**
- L.278 where Schellekens et al., 2015a will be changed to **Schellekens et al., 2015b**
- L.317 where Schellekens et al., 2015c will be changed to **Schellekens et al., 2015b**

Commas will be included in:

- L. 324: "Given the above, ..."
- 4.2.2 too,

Changes to italic will be done in:

- L. 336 *E. vaginatum*
- L. 327 *Sphagnum*-dominated

Grammar in L. 243 will be corrected to:

"Furthermore, the similarity of C/N ratios, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of the uppermost peat increment to those of moss are indicative for moss-dominated peat (Schaub and Alewell, 2009) and **has** been measured likewise in *Sphagnum* peatlands by Kracht and Gleixner (2000)."

We will adjust the sentence in L. 247 as follows:

"**Peat composition under shrubs and sedges is influenced by these species in the studied peat (0-20 cm) as indicated by the molecular parameters for sedge and shrub in the corresponding peat cores (Fig 4b, 4c, 4d).**"

We will make changes in L. 274:

"In addition to changes in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ reflecting the decomposition of the bulk peat (i.e. cumulative effects on all peat components), we examined changes in compounds being indicative for the decomposition of specific plant tissues, i.e. *Sphagnum*-derived peat (**4-isopropenylphenol**)."

We will make changes in L. 295:

"**Because this is not evident from the 4-isopropenylphenol record, it probably reflects a higher contribution of sedge-derived polysaccharides at these depths.**"

The sentence in L. 296f. ("Such a shift...") will be deleted.

We will make changes in L. 298:

"The observed **decomposition** patterns were detected by a parameter describing the whole peat ($\delta^{13}\text{C}$), and were also reflected by compounds indicative for *Sphagnum* material (4-isopropenylphenol)."

The Figure reference in the sentence in L. 302 will be specified:

"Sedge litter is likely to be more readily decomposable compared to shrub litter, caused by its lower C/N ratios (Fig. 1a; Huang et al., 1998; Kařtiovská et al., 2018; Laiho et al., 2003; Limpens and Berendse, 2003).

We will make changes in L. 336:

"On the other hand, Zeh et al. (2019) could show that shrubs translocated more C into the peat at

higher temperatures than sedges, which **could** result in reinforcing effect on peat decomposition with increasing temperature.”

We will add these references to our literature:

- Aerts, R., Callaghan, T. V., Dorrepaal, E., Van Logtestijn, R. S. P. and Cornelissen, J. H. C.: Seasonal climate manipulations result in species-specific changes in leaf nutrient levels and isotopic composition in a sub-arctic bog, *Funct. Ecol.*, 23(4), 680–688, doi:10.1111/j.1365-2435.2009.01566.x, 2009.
- Asada, T., Warner, B. G. and Aravena, R.: Nitrogen isotope signature variability in plant species from open peatland, *Aquat. Bot.*, 82(4), 297–307, doi:10.1016/j.aquabot.2005.05.005, 2005.
- Bragazza, L., Gerdol, R. and Rydin, H.: Effects of mineral and nutrient input on mire bio-geochemistry in two geographical regions, *J. Ecol.*, 91(3), 417–426, doi:10.1046/j.1365-2745.2003.00773.x, 2003.
- Bragazza, L., Limpens, J., Gerdol, R., Grosvernier, P., Hájek, M., Hájek, T., Hajkova, P., Hansen, I., Iacumin, P., Kutnar, L., Rydin, H. and Tahvanainen, T.: Nitrogen concentration and $\delta^{15}\text{N}$ signature of ombrotrophic Sphagnum mosses at different N deposition levels in Europe, *Glob. Chang. Biol.*, 11(1), 106–114, doi:10.1111/j.1365-2486.2004.00886.x, 2005.
- Emmerton, K. S., Callaghan, T. V., Jones, H. E., Leake, J. R., Michelsen, A. and Read, D. J.: Assimilation and isotopic fractionation of nitrogen by mycorrhizal and nonmycorrhizal subarctic plants, *New Phytol.*, 151(2), 513–524, doi:10.1046/j.1469-8137.2001.00179.x, 2001.
- Galloway, J. N., Townsend, A. R., Erisman, J. W., Bekunda, M., Cai, Z., Freney, J. R., Martinelli, L. A., Seitzinger, S. P. and Sutton, M. A.: Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions, *Science* (80-.), 320(5878), 889–892, doi:10.1126/science.1136674, 2008.
- Gebauer, G. and Dietrich, P.: Nitrogen Isotope Ratios in Different Compartments of a Mixed Stand of Spruce, Larch and Beech Trees and of Understorey Vegetation Including Fungi, *Isot. Environ. Heal. Stud.*, 29(1–2), 35–44, doi:10.1080/10256019308046133, 1993.
- Gerdol, R., Siffi, C. and Bombonato, L.: Aboveground production and nutrient status of the vegetation of different mire types in the South-eastern Alps (Italy), *Bot. Helv.*, 120(2), 85–93, doi:10.1007/s00035-010-0077-x, 2010.
- Kohzu, A., Matsui, K., Yamada, T., Sugimoto, A. and Fujita, N.: Significance of rooting depth in mire plants: Evidence from natural ^{15}N abundance, *Ecol. Res.*, 18(3), 257–266, doi:10.1046/j.1440-1703.2003.00552.x, 2003.
- Ménot, G. and Burns, S. J.: Carbon isotopes in ombrogenic peat bog plants as climatic indicators: Calibration from an altitudinal transect in Switzerland, *Org. Geochem.*, 32(2), 233–245, doi:10.1016/S0146-6380(00)00170-4, 2001.
- Nordbakken, J. F., Ohlson, M. and Högberg, P.: Boreal bog plants: nitrogen sources and uptake of recently deposited nitrogen, *Environ. Pollut.*, 126(2), 191–200, doi:10.1016/S0269-7491(03)00194-5, 2003.
- Van Smeerdijk, D. G. and Boon, J. J.: Characterisation of subfossil Sphagnum leaves, rootlets of ericaceae and their peat by pyrolysis-high-resolution gas chromatography-mass spectrometry, *J. Anal. Appl. Pyrolysis*, 11(C), 377–402, doi:10.1016/0165-2370(87)85043-X, 1987.

We will delete these references from our literature:

- Boon, J. J., Wetzel, R. G. and Godshalk, G. L.: Pyrolysis mass spectrometry of some Scirpus species and their decomposition products, *Limnol. Oceanogr.*, 27(5), 839–848, doi:10.4319/lo.1982.27.5.0839, 1982.
- Elmendorf, S. C., Henry, G. H. R., Hollister, R. D., Björk, R. G., Boulanger-Lapointe, N., Cooper, E. J., Cornelissen, J. H. C., Day, T. A., Dorrepaal, E., Elumeeva, T. G., Gill, M., Gould, W. A., Harte, J., Hik, D. S., Hofgaard, A., Johnson, D. R., Johnstone, J. F., Jónsdóttir, I. S., Jorgenson, J. C., Klanderud, K., Klein, J. A., Koh, S., Kudo, G., Lara, M., Lévesque, E., Magnússon, B., May, J. L., Mercado-Díaz, J. A., Michelsen, A., Molau, U., Myers-Smith, I. H., Oberbauer, S. F.,

Onipchenko, V. G., Rixen, C., Martin Schmidt, N., Shaver, G. R., Spasojevic, M. J., Þórhallsdóttir, Þ. E., Tolvanen, A., Troxler, T., Tweedie, C. E., Villareal, S., Wahren, C.-H., Walker, X., Webber, P. J., Welker, J. M. and Wipf, S.: Plot-scale evidence of tundra vegetation change and links to recent summer warming, *Nat. Clim. Chang.*, 2(6), 453–457, doi:10.1038/nclimate1465, 2012.

Hatfield, R. D. and Chaptman, A. K.: Comparing corn types for differences in cell wall characteristics and p-coumaroylation of lignin, *J. Agric. Food Chem.*, 57(10), 4243–4249, doi:10.1021/jf900360z, 2009.

Hobbie, S. E. and Chapin, F. S.: Response of tundra plant biomass, aboveground production, nitrogen, and CO₂ flux to experimental warming, *Ecology*, 79(5), 1526–1544, doi:10.1890/0012-9658(1998)079[1526:TROTPB]2.0.CO;2, 1998.

As already addressed to Tim Moore, in L. 375 the Biester et al. reference occurs twice in the literature of which one will be deleted. Accordingly, Biester et al., 2014a will be changed to Biester et al., 2014.

As already addressed to Tim Moore, in L. 559 the Ward et al. reference will be corrected to:
“Ward, S. E., Ostle, N. J., Oakley, S., Quirk, H., Henrys, P. A. and Bardgett, R. D.: Warming effects on greenhouse gas fluxes in peatlands are modulated by vegetation composition, *Ecol. Lett.*, 16(10), 1285–1293, doi:10.1111/ele.12167, 2013.”

We thank Tim Moore for the very helpful and constructive comments on our work, which helped us to further improve the manuscript. Therefore, we tried to consider all of them.

The referee's comments will be shown black. Our response is shown blue, *italic* and tab-indented while changes in the manuscript are in quotation marks and **bold**.

Referee #2: Tim Moore

This manuscript examines the influence of variations in plant cover on the rate of decomposition in the upper layers of the peat profile, at two sites in the Italian Alps, which vary in their mean annual temperature. The aim is to provide some indication of what may happen if climate change warms peatlands and the vegetation cover of sedges (here *Eriophorum*) and shrubs (here *Calluna*) increases at the expense of *Sphagnum* moss. Peat cores were analyzed for a wide range of properties, related to degree of decomposition, including pyrolysis, which is unusual in peat studies. The results suggested that both temperature (over a 1.4°C range) and vegetation cover influenced decomposition rate of the peat, dominated by residual moss, but that changes in vegetation to sedges and to a lesser shrubs, were more important than the temperature rise, using the two sites as proxies for change.

This contribution is one of several suggesting that changes in vegetation from global change are likely to be more important than simple rises in temperature in affecting the C budget of ecosystems, for example the 'shrubification' of the Arctic. Here, detailed and careful sampling of two sites, with modest differences in air temperature but varying in vascular plant coverage (47 and 77%), provide a suitable analogue to address this issue. The peat samples, and vegetation, have been analyzed by a variety of techniques, some of them common, such as elemental and stable isotopes, and some less common, such as gc/ms pyrolysis. The content of the manuscript is suitable for Biogeosciences and it is generally well written, though I have noted a few errors of the pdf, along with some specific comments.

Some comments for 'discussion':

The sites vary in terms of their mean annual temperature, but is this translated to similar differences in the peat layer undergoing decomposition? Are soil temperature data available to be more precise on the thermal differences in the peat at the two sites? It might be smaller or larger than the 1.4°C.

We thank Tim Moore for this comment. We will give more detailed information on temperature differences in 10 cm depth at the end of the sentence in L. 88 as follows:

"Soil temperature in 10 cm depth between August 2015 and July 2016 was 7.1°C at Lupicino and 5.9°C at Palù Tremole."

Is there an estimate at the rate of peat accretion at the sites? In other words can you estimate over what period the 20 cm of peat have accumulated (e.g. by ²¹⁰Pb dating, perhaps a century?) and what are the changes in the environment over that period? Is what we see now, the same as what it was a century ago, when the current 20 cm peat began to form? For line 263, can you provide an estimate of 'increasing time of exposure'?

As already addressed to referee #1, we don't have data on the age of peat in 20 cm depth of both sites. A recent study of two other alpine peatlands at an altitudinal contrast higher than our study (1030 m a.s.l. vs. 1880 m a.s.l.) reported peat ages of 40 and 26 years respectively for the peat in 15-20 cm depth (Gavazov et al., 2018). Assuming these peatlands are similar to ours, the age difference between our sites would be less than 15 years.

The differences between the sites may have affected absolute differences between peat decomposition, but not the impact of shrubs relative to sedges on peat decomposition within sites. Furthermore, differences between the sites were quite small, and we are not able to

disentangle the effects of the current temperature and water table on the one hand, and differences in environmental condition during peat formation on the other hand.

Accordingly, we will add information on the estimated age of peat at the end of the sentence in L. 90 in the study site descriptions as follows:

“Furthermore, in peatlands with similar vegetation cover, situated at 1030 m a.s.l. and 1880 m a.s.l. in Switzerland, the age of peat in 15-20 depth was found to be 40 years and 26 year, respectively (Gavazov et al., 2018), meaning that the potential age difference between the peat sampled at our sites is likely less than 15 years.”

Do you have any estimates of the input of litter into the sites, based on the vegetation composition, to provide a quantitative context of ‘how much’ is being added? The references cited (lines 41-42) tended to be for Arctic tundra, which is presumably inapplicable to alpine conditions.

We thank the referee for this comment and will specify the information in the sentence in L. 41 based on an applicable reference as follows:

“Vascular plants in alpine peatlands were shown to have up to twice as high net biomass production as mosses (Gerdol et al., 2010) and consequently relatively higher litter inputs.”

I think that careful attention should be given to the water table at the two sites which are reported on line 89. Perhaps the Zeh et al. (2019) ms contains more specific information, but a difference in water table of 30 cm (the minimums reported) would have a profound effect on decomposition rates in the peat cores, the High T site being both warmer and drier... Was August 2015 to July 2016 ‘typical’ in terms of hydrology (i.e. precipitation etc.)? On the other hand, if the highest water table measured was 17 and 15 cm, it means that only the bottom 3 to 5 cm of the 20 cm core were at and under the water table, so we are dealing with decomposition under aerobic conditions, effectively the acrotelm. Perhaps a useful metric would be the proportion of the year in which the water table was within the 20 cm core, especially the 15-20 cm section, to see whether hydrology was significantly different at the two sites. An increased vascular cover, associated with a warming, will likely increase evapotranspiration rates, which in turn will produce a lowered water table, accelerating the vascular ‘invasion’.

We thank Tim Moore for his valuable comment on this topic. As already addressed to referee #1, sampling depths in the peat cores are periodically water saturated. Water table measurements 2015/08–2016/07 (three gauges at each site) show that the peat within the sampled 20 cm on the High T site stayed aerated for 117, 360 or 366 days of the year as recorded in the three gauges. On the Low T site, the peat of the top 20 cm was aerated for 137, 138 or 284 days of the year. These measurements underline that beside higher temperature and higher vascular plant proportion, the top 20 cm peat at the High T site stays longer aerated over the year than at the Low T site. This information will be replacing the information of water table depths at the end of the sentence in L. 89 as follows:

“The time during which the top 20 cm of the peat was above the water table was determined with water table measurements between August 2015 and July 2016 at three gauges on each site. At the Low T site, the water table remained below 20 cm for 137, 138 and 284 days of the year; at the High T site, this was 117, 360 and 366 days of the year respectively.”

Due to this added information, we will adapt the discussion in L. 308 as follows:

“The altitudinal gradient has been used to reveal potential effects of increasing temperature and associated lower water table on peat decomposition by comparing the decomposition parameters (Table 1) between the High T and Low T site.

Eriophorum is arenchymous, with the capacity to oxygenate the peat: would that influence the peat environment in terms of decomposition rate, given that the top 20 cm is above the water table for most of the year?

As already addressed to referee #1, water table and thus aeration did probably not affect differences in peat decomposition under sedges vs. shrubs because our sampling design

ensured similar water table between sedges and shrubs at each of our sites. Water table controlled aeration is a difference between sites though differences in decomposition between PFTs are more pronounced.

We will address this in L. 305 as follows:

“This process is particularly relevant at the Low T site, where the uppermost 20 cm of the peat is water saturated much longer than at the High T site.

And further we will be more precise in our conclusions in L. 348:

“The most important and also surprising result of our study was that vascular plants had a more pronounced impact on peat decomposition than temperature and associated lower water tables together. Potential O₂ transport by the aerenchym of sedges did probably not contribute to enhanced peat decomposition at the High T site, as the top 20 cm peat layer sampled remained above the water table, and thus aerated, for most of the year.”

Line 190: I was surprised to see the large increase in C:N ratio with depth in nearly all the cores, whereas with decomposition one might have expected a decline in the ratio. Is there an explanation for this pattern – I could not see one in the Discussion (cf Table 1). Does atmospheric N deposition play a role here (larger N concentrations in the past few decades)?

We thank Tim Moore for his suggestion and will add this information to the discussion section 4.2 as follows in L. 271:

“Differences in the C/N ratios did not provide a consistent picture regarding changes in peat decomposition. We speculate that the observed increasing C/N ratio with depth might reflect an increasing N deposition in the past decades (Galloway et al., 2008) and an increased contribution of roots (high C/N ratios, Fig. 1a) to peat formation with increasing depth (Sect. 4.1.2). N deposition at the High T site were reported to be 8.2 kg ha⁻¹ y⁻¹ (Bragazza et al., 2005) and for peatlands in norther Italy between 4.2 and > 10 kg ha⁻¹ y⁻¹ (Bragazza et al., 2003, 2005).”

Line 230 I would think that there are major differences in ¹⁵N among the three plant types from zero to -10, which relate back to, I assume, the mycorrhizal dependance of Calluna, the non-mycorrhizal Eriophorum and moss in between

We thank Tim Moore for his suggestion and will include this into the discussion section in L. 226 as follows:

“Properties as C/N ratios, δ¹³C and δ¹⁵N of living plant parts showed significant differences between different PFTs (Fig. 1). C/N ratios of sedge shoots were significantly lower than those of shrubs or mosses, in line with its higher decomposability (Kaštovská et al., 2018; Limpens and Berendse, 2003). ¹³C signature of plant tissue tends to be depleted under warmer and drier conditions (Broder et al., 2012; Gavazov et al., 2016; Skrzypek et al., 2007) explaining the observed δ¹³C depletion of sedge and moss tissues at the High T site compared to Low T site. Shrub shoots were significantly depleted in δ¹⁵N compared to sedge and moss shoots (p < 0.001, Fig. 1c). The depletion of δ¹⁵N in living *C. vulgaris* shoots compared to shoots of *E. vaginatum* and *Sphagnum spp.* is likely related to the symbiotic relationship between *C. vulgaris* and ericoid mycorrhizal fungi (Aerts et al., 2009; Bragazza et al., 2010; Emmerton et al., 2001). The transferred N from mycorrhiza to shrubs occurs to be depleted relative to soil N (Gebauer and Dietrich, 1993). Nevertheless, though differences in δ¹³C and δ¹⁵N between PFT existed, unknown variables influencing δ¹³C and δ¹⁵N in peat, such as various plant species growing in the peat, N deposition history etc. complicated the use of δ¹³C and δ¹⁵N as vegetation proxy.”

As addressed to referee #1, the paragraph in L.185-195 will be restructured as follows, but Figures 1, 2, and 4 will be maintained as we submitted them:

“Carbon to N ratios and isotopic composition of plant shoots were different between plant tissues, PFTs and to a lesser extent between sites (Fig. 1). Living plant shoots had consistently lower C/N ratios than plant roots irrespective of site or PFT (Fig. 1a). Sedge shoots had significantly lower C/N ratios (p < 0.001, Fig. 1a) and were significantly enriched in ¹³C (p < 0.001, Fig. 1b) compared to

moss and shrub shoots. Shrub shoots were significantly depleted in $\delta^{15}\text{N}$ compared to sedge and moss shoots ($p < 0.001$, Fig. 1c). Sedge shoots and moss from the High T site were both significantly depleted in ^{13}C compared to Low T site (both $p < 0.01$, Fig. 1b).

Peat C/N ratio and isotopic composition was significantly affected by depth, site and to a lesser extent by PFTs (Fig. 2a, 2b). Carbon to N ratio increased with depth and was higher at the High T site compared to the Low T site (Fig. 2a, Table 2). In the upper 0-2 cm peat layer, C/N ratios and stable isotopes corresponded with values observed for moss (Fig. 1, Fig. 2). Isotopic composition of peat increments was significantly different for depths and PFTs (Table 2). $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of peat increased with depth (Fig. 2b, 2c) and the enrichment in ^{13}C with depth was stronger for sedge-cores than for shrub-cores (i.e. $2.7 \pm 0.4 \text{ ‰}$ for sedge-cores and $1.6 \pm 0.4 \text{ ‰}$ for shrub cores). The largest enrichment in $\delta^{13}\text{C}$ between the uppermost and lowest depth increment appeared in sedge-cores at the High T site (Fig. 2b; i.e., $3.5 \pm 0.5 \text{ ‰}$)."

I got goggle-eyed looking at the symbols in Figures 1, 2 and 4 and would appreciate some differentiation stronger than washed-out blue and a yukky looking green. Be 'artistic'! Simple black and red would be nice...

We thank the referee for his opinion on the color map. Colors and their effect are indeed very personal. Therefore, we want to keep the colors we used.

4.2.2 is a 45 line 'paragraph' and it might be easier to digest if it was broken down into three paragraphs, each dealing with a specific theme. It is a 'confounding' system with multiple interpretations of results and the strength of the ms is the range of analyses conducted.

We will subset the section into four paragraphs and focus the argumentation as Time Moore suggested:

"The altitudinal gradient has been used to reveal potential effects of increasing temperature and **associated lower water table** on peat decomposition by comparing the suggested decomposition parameters (Table 1) between the High T and Low T site. Increases in $\delta^{13}\text{C}$ with depth were higher at the High T site than at the Low T site (Fig. 2). Therefore, decomposition of the moss-dominated peat is likely to be increased at the High T site compared to the Low T site independent of the vascular plant species.

Depth trends of the *Sphagnum*-specific decomposition parameter (4-isopropenylphenol) do not **reflect**, however, **this increased peat decomposition at higher temperatures**. 4-Isopropenylphenol decreased **less** at the **High T** site compared to the **Low T** site (Fig. 4e). **We might speculate a difference in temperature sensitivity between decomposition of Sphagnum and the whole peat, but such a hypothesis needs to be tested by e.g. temperature controlled incubation experiments. The ratio of levoglucosan to the sum of polysaccharides (Fig. 4f) did not show consistent trends related to temperature again indicating no temperature enhanced degradation of the moss-dominated peat.** Vascular plants and particularly sedges might increasingly contribute to polysaccharides with higher temperatures (see section 4.2.1). These changes from more *Sphagnum*-derived polysaccharides to more sedge-derived polysaccharides could change decomposition dynamics of polysaccharides, since cell walls constituents from *Sphagnum* were found to be less easily decomposable (Hájek et al., 2011). A higher contribution from sedges could therefore superimpose a potential enrichment of *Sphagnum*-derived polysaccharides with depth. Given the above, the higher degree of peat decomposition at the High T site picked up by $\delta^{13}\text{C}$ is probably mediated by higher input rates of easily decomposable vascular plant litter, notably sedges, combined with the warmer and drier conditions favouring aerobic decomposition processes (Biester et al., 2014).

This combined effect of sedges and temperature on peat decomposition has implications for the long-term C storage in *Sphagnum*-dominated peatlands because of projected shifts from sedges to shrubs with climate change (Breeuwer et al., 2009). That change towards less sedges may partly offset temperature driven decomposition processes because of the observed enhancing effect of sedges on peat decomposition. Less sedges (i.e. more shrubs) should result in less peat degradation because (i) the decomposability of available litter (higher contribution of shrub litter) is reduced as its

chemical composition indicates less decomposability (Kristensen and McCarty, 1999; Ward et al., 2015), (ii) an increasing presence of shrubs (*C. vulgaris*) suppresses belowground biota activity and nutrient cycling (Fenner and Freeman, 2011), (iii) *C. vulgaris* associates with mycorrhizal fungi which increase the uptake of organic nutrients leading to an increase of C/N ratio (Read et al., 2004) and thus a decrease in peat decomposition (Ward et al., 2015), (iv) the input of labile C into peat via sedge roots is lower (Crow and Wieder, 2005; Robroek et al., 2015), (v) the transport of oxygen into peat via aerenchym of *E. vaginatum* is lower. On the other hand, Zeh et al. (2019) could show that shrubs translocated more C into the peat at higher temperatures than sedges, which should result in reinforcing effect on peat decomposition with increasing temperature. Obviously, the enhanced C input by shrubs into peat did not coincide with enhanced decomposition of the moss-dominated peat on these sites.”

In the Conclusion, or somewhere in the Discussion, it would be useful to identify the ‘bang for the buck’ in these analyses: some are simple and routine and some, especially the gc/ms pyrolysis, is ‘labour intensive’. Do you have anything to add to the Biester et al. 2014 paper, based on this specific application?

We thank Tim Moore for his comment. The conclusion from Biester et al. (2014) that py-GC/MS is particularly useful in disentangling effects of changes in vegetation composition and decomposition upon changes in environmental conditions (i.e. the hen and egg problem outlined by reviewer 1) is our starting point. In our section “conclusions”, we addressed the advantages/disadvantages of the applied methods (L.343 – 348). As expected (also from Biester et al., 2014), the combination of different methods will result in a more comprehensive picture about peat decomposition. Without py-GC/MS we would not be able to conclude that the moss-dominated peat was more decomposed under sedges than shrubs (i.e. by applying 4-isopropenylphenol to reflect aerobic decomposition of Sphagnum tissue). At the time of the Biester paper (2014), it was not yet known that 4-isopropenylphenol reflects aerobic decomposition of Sphagnum tissue in Sphagnum-dominated peat (Schellekens et al., 2015b).

The central objective of Biester et al 2014 is to compare analytical methods to determine peat decomposition, while our objective is to evaluate the effect of PFT on peat decomposition. We feel that these different themes are clear from the titles, and throughout our manuscript. Therefore, and considering the changes to Section 4.2.2, we do not see the necessity to further enlarge this part of the conclusions.

I provide a copy of the pdf which I have annotated with comments and suggested typographical and other correction. <https://www.biogeosciences-discuss.net/bg-2019-503/bg-2019-503-RC2-supplement.pdf>

Tim Moore

Changes in typography and other suggestions from Tim Moore’s pdf

L. 42 “Vascular plants have a higher biomass production (Hobbie and Chapin, 1998) and consequently relatively higher litter inputs than mosses (Elmendorf et al., 2012).” These (Elmendorf) are results based on work in arctic tundra, whereas your site is alpine, so it is perhaps not very applicable.

As already stated to referee #1, we will specify the information in the sentence in L. 41 based on an applicable reference as follows:

“Vascular plants in alpine peatlands were shown to have up to twice as high net biomass production as mosses (Gerdol et al., 2010) and consequently relatively higher litter inputs.”

L. 70 and range of 15N in Sphagnum?

We will add information about ¹⁵N ranges in Sphagnum at the end of the sentence in L. 70 as follows:

„Sedge leaves were found to be more enriched in ^{13}C and ^{15}N than shrub leaves. **The isotopic ratios for living plant parts found in this study are consistent with the ranges reported in previous studies. Sedge leaves were found to vary in $\delta^{13}\text{C}$ signature between -27.0 to -26.85 ‰ and in $\delta^{15}\text{N}$ between -3.96 to -0.9 ‰; reported ranges for $\delta^{13}\text{C}$ in shrub leaves are -29.2 to -28.83 ‰ and for $\delta^{15}\text{N}$ -10.92 to -9.7 ‰ (Biester et al., 2014; Gavazov et al., 2016; Ménot and Burns, 2001; Nordbakken et al., 2003). *Sphagnum* samples were found to vary in $\delta^{13}\text{C}$ signature between -30.4 and -25.0 ‰ (Bragazza and Iacumin, 2009; Loisel et al., 2009; Preis et al., 2018; Price et al., 1997; Proctor et al., 1992) and in $\delta^{15}\text{N}$ signatures between -7.5 and 2.5 ‰ (Asada et al., 2005; Biester et al., 2014; Bragazza et al., 2005; Kohzu et al., 2003; Ménot & Burns, 2001; Nordbakken et al., 2003).“**

*L. 50 The word “microorganism” will be corrected to the plural:
“microorganisms”*

*In L. 375 the Biester et al. reference occurs twice in the literature of which one will be deleted.
Accordingly, Biester et al., 2014a will be changed to:*

Biester et al., 2014

In L. 559 the Ward et al. reference will be corrected to:

“Ward, S. E., Ostle, N. J., Oakley, S., Quirk, H., Henrys, P. A. and Bardgett, R. D.: Warming effects on greenhouse gas fluxes in peatlands are modulated by vegetation composition, *Ecol. Lett.*, 16(10), 1285–1293, doi:10.1111/ele.12167, 2013.”

Further, we will change typography and make other corrections:

Sentence in L. 77 will be changed to:

"In this multi-proxy study, we combined the analytical approaches outlined above to explore the influence of vascular plants on chemical properties and degree of **peat** decomposition in **two** moss-dominated peatlands contrasting in temperature."

As already addressed to referee #1, we will update the paragraph in L. 141ff. as follows:

"Based on the results of previous pyrolysis studies from peatlands a number of pyrolytic parameters reflecting plant species and the degree of **peat** decomposition were extracted (Table 1). A pyrolysis product specific for sphagnum acid (4-isopropenylphenol; Van Der Heijden et al., 1997) has been found to very sensitively reflect aerobic decomposition of *Sphagnum* tissue in *Sphagnum*-dominated peat (**Schellekens et al., 2015b**). Methoxyphenols are unique to lignin, thereby providing a measure for the contribution from vascular plants in peat dominated by *Sphagnum*, because *Sphagnum* contains no lignin (Abbott et al., 2013; Kracht and Gleixner, 2000; **Schellekens et al., 2015c; van Smeerdijk and Boon, 1987**). Since both shrubs and sedges contain lignin, additional parameters were included to distinguish between them. Sedges have large contributions from p-coumaric and ferulic acid (Lu and Ralph, 1999) with typical pyrolysis products 4-vinylphenol (Lg1) and 4-vinylguaiacol (Lg4), respectively (**van der Hage et al., 1993**). Because 4-vinylphenol is also abundant in *Sphagnum* tissue (**van Smeerdijk and Boon, 1987**), the ratio of 4-vinylguaiacol to the summed guaiacyl products (G) **can** be used to reflect sedges (Schellekens et al., 2012). The ratio of C₃-guaiacol to G **usually reflects intact lignin in soils but has been found** indicative for shrubs **in peat** (Schellekens et al., 2012, 2015a). *n*-Alkenes and *n*-alkanes (Al) originate from cutan and suberan present in roots and bark (**Nierop, 1998; Tegelaar et al., 1995**) and leaf waxes (Eglinton and Hamilton, 1967), depending on their chain length, all of which are associated with shrubs in *Sphagnum*-dominated peat (Schellekens and Buurman, 2011; **van Smeerdijk and Boon, 1987**)."

We will correct the following references in our manuscript:

- L. 147f where (Lu and Ralph, 2010) will be changed to **Lu and Ralph, 1999**
- L.278 where Schellekens et al., 2015a will be changed to **Schellekens et al., 2015b**
- L.317 where Schellekens et al., 2015c will be changed to **Schellekens et al., 2015b**

Commas will be included in:

- L. 324: "Given the above, ..."
- 4.2.2 too,

Changes to italic will be done in:

- L. 336 *E. vaginatum*
- L. 327 *Sphagnum*-dominated

Grammar in L. 243 will be corrected to:

"Furthermore, the similarity of C/N ratios, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of the uppermost peat increment to those of moss are indicative for moss-dominated peat (Schaub and Alewell, 2009) and **has** been measured likewise in *Sphagnum* peatlands by Kracht and Gleixner (2000)."

We will adjust the sentence in L. 247 as follows:

"**Peat composition under shrubs and sedges is influenced by these species in the studied peat (0-20 cm) as indicated by the molecular parameters for sedge and shrub in the corresponding peat cores (Fig 4b, 4c, 4d).**"

We will make changes in L. 274:

"In addition to changes in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ reflecting the decomposition of the bulk peat (i.e.

cumulative effects on all peat components), we examined changes in compounds being indicative for the decomposition of specific plant tissues, i.e. *Sphagnum*-derived peat (4-isopropenylphenol)."

We will make changes in L. 295:

"Because this is not evident from the 4-isopropenylphenol record, it probably reflects a higher contribution of sedge-derived polysaccharides at these depths."

The sentence in L. 296f. ("Such a shift...") will be deleted.

We will make changes in L. 298:

"The observed **decomposition** patterns were detected by a parameter describing the whole peat ($\delta^{13}\text{C}$), and were also reflected by compounds indicative for *Sphagnum* material (4-isopropenylphenol)."

The Figure reference in the sentence in L. 302 will be specified:

"Sedge litter is likely to be more readily decomposable compared to shrub litter, caused by its lower C/N ratios (Fig. 1a; Huang et al., 1998; Kaštovská et al., 2018; Laiho et al., 2003; Limpens and Berendse, 2003).

We will make changes in L. 336:

"On the other hand, Zeh et al. (2019) could show that shrubs translocated more C into the peat at higher temperatures than sedges, which **could** result in reinforcing effect on peat decomposition with increasing temperature."

We will add these references to our literature:

- Aerts, R., Callaghan, T. V., Dorrepaal, E., Van Logtestijn, R. S. P. and Cornelissen, J. H. C.: Seasonal climate manipulations result in species-specific changes in leaf nutrient levels and isotopic composition in a sub-arctic bog, *Funct. Ecol.*, 23(4), 680–688, doi:10.1111/j.1365-2435.2009.01566.x, 2009.
- Asada, T., Warner, B. G. and Aravena, R.: Nitrogen isotope signature variability in plant species from open peatland, *Aquat. Bot.*, 82(4), 297–307, doi:10.1016/j.aquabot.2005.05.005, 2005.
- Bragazza, L., Gerdol, R. and Rydin, H.: Effects of mineral and nutrient input on mire bio-geochemistry in two geographical regions, *J. Ecol.*, 91(3), 417–426, doi:10.1046/j.1365-2745.2003.00773.x, 2003.
- Bragazza, L., Limpens, J., Gerdol, R., Grosvernier, P., Hájek, M., Hájek, T., Hajkova, P., Hansen, I., Iacumin, P., Kutnar, L., Rydin, H. and Tahvanainen, T.: Nitrogen concentration and $\delta^{15}\text{N}$ signature of ombrotrophic *Sphagnum* mosses at different N deposition levels in Europe, *Glob. Chang. Biol.*, 11(1), 106–114, doi:10.1111/j.1365-2486.2004.00886.x, 2005.
- Emmerton, K. S., Callaghan, T. V., Jones, H. E., Leake, J. R., Michelsen, A. and Read, D. J.: Assimilation and isotopic fractionation of nitrogen by mycorrhizal and nonmycorrhizal subarctic plants, *New Phytol.*, 151(2), 513–524, doi:10.1046/j.1469-8137.2001.00179.x, 2001.
- Galloway, J. N., Townsend, A. R., Erisman, J. W., Bekunda, M., Cai, Z., Freney, J. R., Martinelli, L. A., Seitzinger, S. P. and Sutton, M. A.: Transformation of the Nitrogen Cycle: Recent Trends, Questions, and Potential Solutions, *Science* (80-.), 320(5878), 889–892, doi:10.1126/science.1136674, 2008.
- Gebauer, G. and Dietrich, P.: Nitrogen Isotope Ratios in Different Compartments of a Mixed Stand of Spruce, Larch and Beech Trees and of Understorey Vegetation Including Fungi, *Isot. Environ. Heal. Stud.*, 29(1–2), 35–44, doi:10.1080/10256019308046133, 1993.
- Gerdol, R., Siffi, C. and Bombonato, L.: Aboveground production and nutrient status of the vegetation of different mire types in the South-eastern Alps (Italy), *Bot. Helv.*, 120(2), 85–93, doi:10.1007/s00035-010-0077-x, 2010.

- Kohzu, A., Matsui, K., Yamada, T., Sugimoto, A. and Fujita, N.: Significance of rooting depth in mire plants: Evidence from natural ^{15}N abundance, *Ecol. Res.*, 18(3), 257–266, doi:10.1046/j.1440-1703.2003.00552.x, 2003.
- Ménot, G. and Burns, S. J.: Carbon isotopes in ombrogenic peat bog plants as climatic indicators: Calibration from an altitudinal transect in Switzerland, *Org. Geochem.*, 32(2), 233–245, doi:10.1016/S0146-6380(00)00170-4, 2001.
- Nordbakken, J. F., Ohlson, M. and Högberg, P.: Boreal bog plants: nitrogen sources and uptake of recently deposited nitrogen, *Environ. Pollut.*, 126(2), 191–200, doi:10.1016/S0269-7491(03)00194-5, 2003.
- Van Smeerdijk, D. G. and Boon, J. J.: Characterisation of subfossil Sphagnum leaves, rootlets of ericaceae and their peat by pyrolysis-high-resolution gas chromatography-mass spectrometry, *J. Anal. Appl. Pyrolysis*, 11(C), 377–402, doi:10.1016/0165-2370(87)85043-X, 1987.

We will delete these references from our literature:

- Boon, J. J., Wetzel, R. G. and Godshalk, G. L.: Pyrolysis mass spectrometry of some Scirpus species and their decomposition products, *Limnol. Oceanogr.*, 27(5), 839–848, doi:10.4319/lo.1982.27.5.0839, 1982.
- Elmendorf, S. C., Henry, G. H. R., Hollister, R. D., Björk, R. G., Boulanger-Lapointe, N., Cooper, E. J., Cornelissen, J. H. C., Day, T. A., Dorrepaal, E., Elumeeva, T. G., Gill, M., Gould, W. A., Harte, J., Hik, D. S., Hofgaard, A., Johnson, D. R., Johnstone, J. F., Jónsdóttir, I. S., Jorgenson, J. C., Klanderud, K., Klein, J. A., Koh, S., Kudo, G., Lara, M., Lévesque, E., Magnússon, B., May, J. L., Mercado-Díaz, J. A., Michelsen, A., Molau, U., Myers-Smith, I. H., Oberbauer, S. F., Onipchenko, V. G., Rixen, C., Martin Schmidt, N., Shaver, G. R., Spasojevic, M. J., Þórhallsdóttir, P. E., Tolvanen, A., Troxler, T., Tweedie, C. E., Villareal, S., Wahren, C.-H., Walker, X., Webber, P. J., Welker, J. M. and Wipf, S.: Plot-scale evidence of tundra vegetation change and links to recent summer warming, *Nat. Clim. Chang.*, 2(6), 453–457, doi:10.1038/nclimate1465, 2012.
- Hatfield, R. D. and Chaptman, A. K.: Comparing corn types for differences in cell wall characteristics and p-coumaroylation of lignin, *J. Agric. Food Chem.*, 57(10), 4243–4249, doi:10.1021/jf900360z, 2009.
- Hobbie, S. E. and Chapin, F. S.: Response of tundra plant biomass, aboveground production, nitrogen, and CO_2 flux to experimental warming, *Ecology*, 79(5), 1526–1544, doi:10.1890/0012-9658(1998)079[1526:TROTPB]2.0.CO;2, 1998.

Vascular plants affect properties and decomposition of moss-dominated peat, particularly at elevated temperatures

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Abstract. Peatlands, storing significant amounts of carbon are extremely vulnerable to climate change. The effects of climate change are projected to lead to a vegetation shift from *Sphagnum* mosses to sedges and shrubs. Impacts on the present moss-
15 dominated peat remain largely unknown. In this study, we used a multi proxy approach to investigate the influence of contrasting vascular plant types (sedges, shrubs) on peat chemistry and decomposition. Peat cores of 20 cm depth and plant material (*Sphagnum spp.*, *Calluna vulgaris*, *Eriophorum vaginatum*) from two ombrotrophic peatlands in the Italian Alps with a mean annual temperature difference of 1.4 °C were analysed. Peat cores were taken under adjacent shrub and sedge plants growing at the same height above the water table. We used carbon, nitrogen and their stable isotopes to assess general patterns
20 in the degree of decomposition across sampling locations and depths. In addition, analytical pyrolysis was applied to disentangle effects of vascular plants (sedge, shrub) on chemical properties and decomposition of the moss-dominated peat. Pyrolysis data confirmed that *Sphagnum* moss dominated the present peat irrespectively of depth. Nevertheless, vascular plants contributed to peat properties as revealed by e.g. pyrolysis products of lignin. The degree of peat decomposition increased with depth as shown by e.g. decreasing amounts of the pyrolysis product of sphagnum acid and increasing $\delta^{13}\text{C}$ with depth. Multiple
25 parameters also revealed a higher degree of decomposition of *Sphagnum*-dominated peat collected under sedges than under shrubs, particularly at the high temperature site. Surprisingly, temperature effects on peat decomposition were less pronounced than those of sedges. Our results imply that vascular plants affect the decomposition of the existing peat formed by *Sphagnum*,

particularly at elevated temperature. These results suggest that changes in plant functional types may have a stronger impact on the soil carbon feedback in a warmer world than hitherto assumed.

30 **1 Introduction**

Peatland soils store about 550 Gt of carbon (C), which equals one third of all soil organic C while they only cover 3 % of the world's land area (Parish et al., 2008). In contrast to mineral soils, C sequestration in peatlands is not controlled by stabilisation processes related to soil minerals (Schmidt et al., 2011), but is environmentally constrained by low temperatures and prevalent anoxic conditions (high water tables). Climate change is expected to partly lift these environmental constraints on microbial
35 decomposition by warmer (Karhu et al., 2014) and drier conditions, threatening to release stored organic C as CO₂ to the atmosphere. Alterations in the environment will also initiate shifts in vegetation composition, generally favouring vascular plants (sedge, shrub) over *Sphagnum* (moss) (Berendse et al., 2001; Breeuwer et al., 2009; Heijmans et al., 2008; Malmer et al., 1994). A systematic change in composition of plant functional types (PFTs) towards vascular plants has a yet unknown potential to accelerate C losses from the stored peat originally dominated by mosses due to increased C input via roots from
40 vascular plants via changing plant-soil feedbacks (Bragazza et al., 2013; Gavazov et al., 2018; Robroek et al., 2015) and litter mixing effects (Zhang et al., 2019).

Vascular plants in alpine peatlands were shown to have up to twice as high net biomass production as mosses (Gerdol et al., 2010) have a higher biomass production (Hobbie and Chapin, 1998) and consequently relatively higher litter inputs than mosses (~~Elmendorf et al., 2012~~). In addition to litter quantity, the chemical composition differs between PFTs with considerable
45 consequences on decomposition dynamics. *Sphagnum* litter tends to decompose slower than vascular plant litter (Bragazza, 2006; Coulson and Butterfield, 1978; Verhoeven and Toth, 1995; Zhang et al., 2019) due to high carbon to nitrogen (C/N) ratio and decay-inhibiting structural carbohydrates (Coulson and Butterfield, 1978; Hájek et al., 2011; Schellekens et al., 2015b; Turetsky et al., 2008). Within vascular plants, shrub litter differentiates from sedge litter by higher C/N ratio and lower decay rate (Huang et al., 1998; Kaštovská et al., 2018; Laiho et al., 2003; Limpens and Berendse, 2003). Analog to biomass
50 production, shrubs and sedges have higher belowground input of fresh root litter (Schellekens et al., 2011) and C input of living roots in comparison to mosses (i.e. fresh photosynthates; Zeh et al., 2019). Growth and reproduction of microorganisms

are supposed to increase with higher root activity (Bragazza et al., 2015; Ward et al., 2013) which is likely to stimulate peat decomposition. Translating the PFT properties outlined above into consequences for C storage of autochthonous peats where inputs of all species are mixed together remains a challenge, particularly if the impact of recently changing vegetation on the previously formed peat is of interest. This challenge calls for a multi-proxy approach (Biester et al., 2014) for determining the impact of the varying properties of PFTs on peat decomposition *in situ*. Peat was defined as any organic material that accumulates underneath the peatlands surface, including living stems of *C. vulgaris*, *E. vaginatum* and *Sphagnum spp.*

Various analytical approaches exist to assess peat properties and decomposition, each with its own advantages and drawbacks.

We defined decomposition as any changes in properties of the peat relative to its source material, e.g. plant material from *C. vulgaris*, *E. vaginatum*, *Sphagnum spp.* directly after deposition. Carbon to N ratios have been widely used to evaluate decomposition of peat (Biester et al., 2014; Broder et al., 2012; Kuhry and Vitt, 1996; Limpens and Berendse, 2003; Taylor et al., 1989). The microbial mineralisation of C-rich compounds and the subsequent respiration and emission as CO₂ decreases the abundance of C relative to N (Broder et al., 2012). In combination with a high immobilisation of N by microbial biomass, N will be further enriched in the remaining organic material (Damman, 1988). Consequently, C/N ratios are decreasing with increasing decomposition. However, PFTs influence the C/N ratio of peat, too, as their litter differ in C and N contents (Hornibrook et al., 2000).

The stable isotopes ¹³C and ¹⁵N and their vertical trends have been often used alongside C/N ratios (Biester et al., 2014; Broder et al., 2012; Coolen and Orsi, 2015; Krüger et al., 2014, 2015; Novák et al., 1999). Aerobic peat decomposition leads to an enrichment in δ¹³C and δ¹⁵N, due to a preferential use of the lighter isotopes by microorganisms and hence a relative enrichment of ¹³C and ¹⁵N in the remaining organic matter (Alewell et al., 2011; Bragazza et al., 2010; Bragazza and Iacumin, 2009; Kalbitz et al., 2000; Nadelhoffer and Fry, 1988). However, stable isotope patterns are also affected by the water table limiting aerobic decomposition and thus isotopic discrimination in the remaining peat (Krüger et al., 2015) hydrological conditions (Krüger et al., 2014) and the plant species forming the litter. Sedge leaves were found to be more enriched in ¹³C and ¹⁵N than shrub leaves. The isotopic ratios for living plant parts found in this study are consistent with the ranges reported in previous studies. Sedge leaves were found to vary in δ¹³C signature between -27.0 to -26.85 ‰ and in δ¹⁵N between -3.96 to -0.9 ‰; reported ranges for δ¹³C in shrub leaves are -29.2 to -28.83 ‰ and for δ¹⁵N -10.92 to -9.7 ‰ (Biester et al., 2014; Gavazov et

al., 2016; Ménot and Burns, 2001; Nordbakken et al., 2003). (~~Gavazov et al., 2016: sedge: $\delta^{13}\text{C}$: -26.85 ‰, $\delta^{15}\text{N}$: -3.96 ‰ vs shrub: $\delta^{13}\text{C}$: -28.83 ‰, $\delta^{15}\text{N}$: -10.92 ‰~~), while *Sphagnum* samples were found to vary in $\delta^{13}\text{C}$ signatures between ~~-25.30, 4.0~~ and ~~-25.06 ‰~~ (Bragazza and Iacumin, 2009; Loisel et al., 2009; Preis et al., 2018; Price et al., 1997; Proctor et al., 1992) and in $\delta^{15}\text{N}$ signatures between -7.5 and 2.5 ‰ (Asada et al., 2005; Biester et al., 2014; Bragazza et al., 2005; Kohzu et al., 2003; Ménot and Burns, 2001; Nordbakken et al., 2003).

Pyrolysis gas chromatography/mass spectrometry (py-GC/MS) is a powerful but labour intensive tool to characterise the composition of peat, and disentangle the effects of source material from decomposition (Abbott et al., 2013; Huang et al., 1998; McClymont et al., 2011; Schellekens et al., 2009, 2012, 2015a, 2015b, 2015e). Plant specific pyrolysis products which have been used to distinguish vascular plants from *Sphagnum* in peat include lignin-phenols from lignin and 4-isopropenylphenol from sphagnum acid, respectively (Van Der Heijden et al., 1997; McClymont et al., 2011; Schellekens et al., 2009, 2015b, 2015c).

In this multi-proxy study, we combined the analytical approaches outlined above to explore the influence of vascular plants on chemical properties and degree of peat decomposition in two moss-dominated peat at two peatlands contrasting in temperature. We hypothesized that: i) chemical properties of the moss-dominated peat differ under shrub and sedge coverage, (ii) the decomposition of the moss-dominated peat increases with depth and is higher under sedge than shrub coverage, and (iii) increasing temperature is reflected in higher degree of decomposition of the moss-dominated peat, particularly under sedge coverage.

2 Material and Methods

2.1 Study sites

Two ombrotrophic peatlands at different altitude in the north-eastern Alps of Italy were chosen to simulate a climate warming scenario. The peatland at lower altitude, Lupicino, is located at 1290 m a.s.l. and is characterised by a mean annual temperature (MAT) of 6.3°C and a total annual precipitation of 810 mm. The peatland at higher altitude, Palù Tremole, is located at 1700 m a.s.l. with a MAT of 4.9°C and total annual precipitation of 825 mm. Soil temperature in 10 cm depth between August 2015 and July 2016 was 7.1°C at Lupicino and 5.9°C at Palù Tremole. Lupicino will be referred to as High T site and Palù Tremole as Low T site. The time during which the top 20 cm of the peat was above the water table was determined with water table

105 measurements between August 2015 and July 2016 at three gauges on each site. At the Low T site, the water table remained below 20 cm for 137, 138 and 284 days of the year; at the High T site, this was 117, 360 and 366 days of the year respectively. Mean water table depth in August 2015–July 2016, was between 16.7 cm and 28.04 cm at the Low T site and between 14.8 cm and 66.7 cm at the High T site, measured at three gauges respectively (Zeh et al., 2019). Furthermore, in peatlands with similar vegetation cover, situated at 1030 m a.s.l. and 1880 m a.s.l. in Switzerland, the age of peat in 15-20 depth was found to be 40 years and 26 year, respectively (Gavazov et al., 2018), meaning that the potential age difference between the peat sampled at our sites is likely less than 15 years. Vegetation community on both sites is similar and dominated by *Sphagnum spp.*, with contributions from *Calluna vulgaris* and *Eriophorum vaginatum*, representing the three PFTs (bryophyte moss, ericoid shrubs, graminoid sedges). This experimental setup offers a unique opportunity to disentangle impacts of shrubs and sedges on properties and decomposition of a moss-dominated peat. Further detail in biotic and climatic conditions can be found in Zeh et al. (2019).

2.2 Sampling and preparation

115 During the first half of August 2015, we selected 20 hummocks per study site with a closed peat moss cover of at least 95 %, an equal proportion of shrub to sedge cover and a total vascular plant cover of $47 \pm 2 \%$ at Low T site and $77 \pm 2 \%$ at the High T site. The hummocks were located in five groups (blocks) of four hummocks, with maximally 5 m between the hummocks within a block. On each hummock, we took two peat cores: one directly under *C. vulgaris* (shrub-core) and one under *E. vaginatum* tussocks (sedge-core), yielding a total of 40 cores per peatland. Peat cores were sampled with a custom-made metal peat corer with an inside diameter of 5 cm and sampling length of 20 cm. Additionally, photosynthetically active moss tissues from the top 2 cm and plant shoots from *E. vaginatum* and *C. vulgaris* were collected from each hummock. Furthermore, six separate peat cores with 10 cm diameter (three at each site) were randomly sampled for collection of living roots of shrubs and sedges. During the field campaign, peat cores were stored at 8°C within PVC tubes to prevent deformation. Afterwards, they were frozen to -20°C until further sample preparation.

125 Of the collected 80 peat cores, the 20 most representative cores were selected using three criteria: i) peat cores with a minimum length of 20 cm and without physical damages, ii) one shrub-core and one sedge-core from each block and peatland, and iii)

peat cores with the smallest deviation from the mean weight of the respective block. From the active moss tissues, samples were selected corresponding to the chosen peat cores and mixed, if not sampled from the same hummock.

To assess which depth increments are appropriate to characterise changes in peat properties, four cores (one sedge and one shrub from each site) were randomly chosen from the selected 20. These cores were cut into depth increments of 1 cm, except
130 for the topmost increment, which accounted for 2 cm. Carbon and N concentrations were measured as described in Sect. 2.3. The results of these analyses indicated changes in C and N concentrations at 2 cm, 5 cm and 12 cm. Considering these results, the remaining 16 peat cores were cut into four depth increments: 0-2 cm, 2-5 cm, 5-12 cm, 12-20 cm.

Plant and peat material was freeze-dried and then grinded (Fritsch pulverisette 23) before being analysed.

2.3 Total carbon and nitrogen concentration and stable isotope analysis (^{13}C , ^{15}N)

135 Carbon and N concentration were measured with a Vario El III elemental analyser (Elementar Analysensysteme GmbH, Langenselbold, Germany), following standard processing techniques. Carbon and N concentrations were calculated based on total sample weight. The C/N ratio represents the atomic relationship between C and N content of the peat material.

Isotope analysis was done with vario PYRO CUBE coupled to the visION IRMS (Isoprime, Elementar Analysensysteme GmbH, Langenselbold, Germany). Stable C isotope ratios are reported as $\delta^{13}\text{C}$ in [‰] relative to the V-PDB standard and
140 stable N isotope ratios as $\delta^{15}\text{N}$ in [‰] relative to air.

2.4 Pyrolysis gas chromatography/mass spectrometry

To identify characteristics of PFTs and decomposition, representative plant samples for each PFT and one shrub-core and one sedge-core from each peatland were selected to be additionally analysed by py-GC/MS. Plant samples comprised of one root and one shoot sample of shrub and sedge respectively, and one moss tissue sample from each peatland. In total 10 plant samples
145 and four cores were cut into four increments as previously described. They were chosen based on the lowest deviation from the mean in C/N, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analyses. A Pyrolyser EGA/PY-3030D device (Frontier Laboratories, Fukushima, Japan) has been used for analysis. The pyrolysis temperature was set at 600°C, held for 10 s. The pyrolyser was connected with a GC 7890B and MS 5977 (Agilent Technologies, St. Clara, United States). Inlet temperature of the GC was 250°C (split 50:1). The GC oven had an initial temperature of 45°C (held for 4 min), was then heated to 240°C at 4°C min⁻¹ and afterwards heated to

150 300°C at 39°C min⁻¹ (held for 15 min). The GC column, a ZB-5ms (Zebron, Phenomenex Inc., Torrance, United States), had a length of 30 m, a film thickness 0.25 µm, and a diameter of 0.25 mm. The MS was scanning in the range of 50-600 *m/z*.
Pyrolysis product identification and peak integration in pyrograms were performed with Masslab. Based on intensity and frequency on the total ion current (TIC), 57 pyrolysis products were selected for quantification in all 26 samples (A1). Quantification was based on the peak area of characteristic fragment ions (*m/z*) for each product (A1). The relative proportion
155 of each product was expressed as a percentage of the total quantified peak area in one sample (TIC: 100 %). The products were grouped according to chemical similarity and their source into: *n*-alkenes and *n*-alkanes, lignin-derived products, phenols, benzenes and polysaccharides.

2.5 Selection of molecular parameters

Based on the results of previous pyrolysis studies from peatlands a number of pyrolytic parameters reflecting plant species and
160 the degree of peat decomposition were extracted (Table 1). A pyrolysis product specific for sphagnum acid (4-isopropenylphenol; Van Der Heijden et al., 1997) has been found to very sensitively reflect aerobic decomposition of *Sphagnum* tissue in *Sphagnum*-dominated peat (~~Abbott et al., 2013~~; Schellekens et al., ~~2015a~~2015b). Methoxyphenols are unique to lignin, thereby providing a measure for the contribution from vascular plants in peat dominated by *Sphagnum*, because *Sphagnum* contains no lignin (Abbott et al., 2013; Kracht and Gleixner, 2000; ~~Schellekens et al., 2015c~~; ~~van Smeerdijk~~
165 ~~and Boon, 1987~~). Since both shrubs and sedges contain lignin, additional parameters were included to distinguish between them. Sedges have large contributions from p-coumaric and ferulic acid (Lu and Ralph, ~~2010~~1999) with typical pyrolysis products 4-vinylphenol (Lg1) and 4-vinylguaiaicol (Lg4), respectively (~~Boon et al., 1982~~; van der Hage et al., 1993). Because 4-vinylphenol is also abundant in *Sphagnum* tissue (~~van Smeerdijk and Boon, 1987~~), the ratio of 4-vinylguaiaicol to the summed guaiacyl products (G) ~~will can~~ therefore be used to reflect sedges (Schellekens et al., 2012). The ratio of C₃-guaiaicol to G
170 ~~usually reflects intact lignin in soils but has been found~~is indicative for shrubs ~~in peat~~ (Schellekens et al., 2012, 2015a). *n*-Alkenes and *n*-alkanes (Al) originate from cutan and suberan present in roots and bark (~~Hatfield and Chaptman, 2009~~; Nierop, 1998; Tegelaar et al., 1995) and leaf waxes (Eglinton and Hamilton, 1967), depending on their chain length, all of which are associated with shrubs in *Sphagnum*-dominated peat (Schellekens and Buurman, 2011; ~~van Smeerdijk and Boon, 1987~~).

2.6 Statistics

175 All data analysis and visualisation were performed with R, Version 3.6 (R Core Team, 2019). The preliminary four peat cores
which were cut into 1 cm increments were integrated in statistical analysis. For this purpose, the means of C [%], N [%], C/N
ratio, $\delta^{13}\text{C}$ [‰] and $\delta^{15}\text{N}$ [‰] were calculated for each depth increment (2-5 cm, 5-12 cm and 12-20 cm). Linear mixed-effects
models (LMM) were applied to results of C/N ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis to consider the nested structure of peat cores in
180 blocks using packages “lme4” (Bates et al., 2015). Vascular plant effect (shrub vs. sedge), site (Low T vs. High T) and depth
increments were analysed as fixed effect factors, whereby the peat cores nested in blocks were accounted for as random factor
with random intercept structure. If the assumptions of normality in the data and their residuals were met (checked with Shapiro-
Wilk test, histograms and Q-Q plots), a subsequent analysis of variance type II with a Kenward-Roger approximation of degree
of freedom was applied on the linear-mixed models for hypothesis testing using package “lmerTest” (Kuznetsova et al., 2017).
Post-hoc test was accomplished with a pairwise Tukey test applying package “emmeans” (Lenth, 2019). Since data and
185 residuals of C/N ratio, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in shoot materials were not normally distributed, single effects were tested with Wilcoxon
test. Due to limited root sample size, hypothesis tests were neglected.

Principal component analysis (PCA) was applied to the py-GC/MS data. The aim was to reduce the data to a set of uncorrelated,
meaningful components. Each principal component is determined by the largest variance (or largest remaining variance) of all
quantified pyrolysis products and therefore explains a specific percentage of the total variance. They may represent a single
190 effect on peat chemistry, while the abundance of individual pyrolysis products (or other variables) may be influenced by several
environmental factors. Scores indicate to which extend each principal component contributes to a sample. Loadings
demonstrate which individual pyrolysis products are responsible for the patterns in scores. Prior to PCA, the number of
pyrolysis products (variables) was adapted. First, the *n*-alkenes and *n*-alkanes were pooled to a single variable since these
products were large in number (10 and 9, respectively) but in sum only contributed less than 1 % to total abundance.
195 Accordingly, it was avoided that this large set of correlated variables with small abundance was allocated to the first principal
component (Schellekens et al., 2017). Second, key molecular parameters (Sect. 2.5, Table 1) were included as variables to
check their interpretation within the studied plant samples and peat cores. This resulted in a total number of 41 variables for

PCA. To unravel the effects of vascular plants and temperature on peat decomposition in detail, regression analysis and depth records of these molecular parameters are discussed (Sect. 4.1.2, 4.2).

200 **3 Results**

3.1 Carbon to nitrogen ratios and isotopic composition of PFTs and peat

Carbon to N ratios and isotopic composition of plant shoots were different between plant tissues, PFTs and to a lesser extent between sites (Fig. 1). Living plant shoots had consistently lower C/N ratios than plant roots irrespective of site or PFT (Fig. 1a). Sedge shoots had significantly lower C/N ratios ($p < 0.001$, Fig. 1a) and were significantly enriched in ^{13}C ($p < 0.001$, Fig. 1b) compared to moss and shrub shoots. Shrub shoots were significantly depleted in $\delta^{15}\text{N}$ compared to sedge and moss shoots ($p < 0.001$, Fig. 1c). Sedge shoots and moss from the High T site were both significantly depleted in ^{13}C compared to Low T site (both $p < 0.01$, Fig. 1b).

Peat C/N ratio and isotopic composition was significantly affected by depth, site and to a lesser extent by PFTs (Fig. 2a, 2b). Carbon to N ratio increased with depth and was higher at the High T site compared to the Low T site (Fig. 2a, Table 2). In the upper 0-2 cm peat layer, C/N ratios and stable isotopes corresponded with values observed for moss (Fig. 1, Fig. 2). Isotopic composition of peat increments was significantly different for depths and PFTs (Table 2). $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of peat increased with depth (Fig. 2b, 2c) and the enrichment in ^{13}C with depth was stronger for sedge-cores than for shrub-cores (i.e. $2.7 \pm 0.4 \text{ ‰}$ for sedge-cores and $1.6 \pm 0.4 \text{ ‰}$ for shrub cores). The largest enrichment in $\delta^{13}\text{C}$ between the uppermost and lowest depth increment appeared in sedge-cores at the High T site (Fig. 2b; i.e., $3.5 \pm 0.5 \text{ ‰}$). Sedge shoots had significantly lower C/N ratios than moss or shrub shoots ($p < 0.001$, Fig. 1a) and were significantly enriched in ^{13}C and ^{15}N (both $p < 0.001$, Fig. 1b, e) compared to moss and shrub shoots. Site effects were generally small, but moss and sedge shoots from the High T site were both significantly depleted compared to Low T (both $p < 0.01$). Plant shoots had consistently lower C/N ratios than plant roots irrespective of vascular plants (Fig. 1).

Values of C/N ratios and stable isotopes in the upper 0-2 cm peat layer (Fig. 2) corresponded with values observed for moss (Fig. 1, Fig. 2). Carbon to N ratios of peat increments were significantly affected by depth and site, with increasing C/N ratio with depth and higher C/N at the High T site compared to the Low T site (Fig. 2a, Table 2). Depth and vascular plants significantly affected isotopic composition of peat increments (Table 2). $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of peat increased with depth (Fig. 2b,

225 2c) and the enrichment in ^{13}C with depth was stronger for sedge cores than for shrub cores (i.e. $2.7 \pm 0.4\%$ for sedge cores and $1.6 \pm 0.4\%$ for shrub cores, Tukey Test). The largest enrichment in $\delta^{13}\text{C}$ between the uppermost and lowest depth increment appeared in sedge cores at the High T site (Fig. 2b; i.e., $3.5 \pm 0.5\%$, Tukey Test).

3.2 Chemical composition of vascular plants and moss-dominated peat analysed by py-GC/MS

Groups of pyrolysis products are given in Table 3. In the peat samples, polysaccharides (Ps) contributed 56 % - 86 %, and phenols (Ph) 7 % - 30 % to all identified pyrolysis products, while the contribution from lignin-derived products (Lg) was < 15 %. The PCA (Fig. 3) clearly showed differences in the chemical composition of the PFT tissues and peat.

230 Principal components (PC) 1 to 3 explained 75.6 % and hence the major part of the variance in py-GC/MS data. Plotting the scores of PC1 versus PC2 (Fig. 3a) revealed that plant materials of the PFTs as well as peat from different depths clustered based on their pyrolysis products and thus on chemical composition. PC1 separated both shoot and root samples of shrubs and sedges with exclusively positive scores from moss samples with exclusively negative scores. Thus, PC1 distinguished vascular plant samples from moss samples. Peat samples were arranged in between reflecting the contribution of both vascular plants and mosses. The pyrolysis products responsible for the separation of PFTs are reflected in the factor loadings. Most phenols, including the parameter for sphagnum acid (4-isopropenylphenol, Ph6), and some polysaccharides (Ps1, 2, 4, 8, 9) had negative loadings on PC1, corresponding to moss samples (Fig. 3b). Lignin-derived products (sum of guaiacyl and syringyl lignin products, GS) had positive loadings and are indicative for shoot and root tissues of vascular plants (Fig. 3b).

240 Scores of PC2 separate aboveground shoot tissues of the three PFTs and the surface peat (negative scores) from root tissues and the deeper peat increments (positive scores; Fig. 3a); within the peat samples, the deepest increments had the highest positive scores. Levoglucosan (Ps16) and the ratio of levoglucosan to the sum of polysaccharides (L/Ps) had the largest positive loadings, which indicates its relative enrichment with depth.

245 PC3 separates samples based on the two vascular plants, i.e. shrubs and sedges (Fig. 3c). Shrub shoot and root samples had exclusively negative scores. In contrast, all sedge shoot and root samples had positive scores. The peat samples clustered in between (i.e. low scores), but maintained the separation according to vascular plants. Likewise, the parameters selected to reflect the contribution from shrub, i.e. sum of *n*-alkenes and *n*-alkanes (Al, Table 1) and the ratio of C_3 -guaiacol to the sum of guaiacyl products ($\text{C}_3\text{G}/\text{G}$, Table 1) had high negative loading on PC3. The parameter for sedge (the ratio of 4-vinylguaiacol

to the sum of guaiacyl products (4VG/G), Table 1), showed positive loading on PC3 (Fig. 3b). The loadings furthermore suggest that both benzenes and levomannosan (Ps15) were associated to shrub as well, while 2,3-dihydro-5-methylfuran-2-
250 one (Ps3) and guaiacol (Lg2) showed high positive loading and are thus indicative for sedge in this context.

4 Discussion

4.1 Properties of a moss-dominated peat influenced by vascular plants

Testing our hypotheses requires the identification of properties being typical of the different vascular plants. In our study, we were able to apply a set of properties with a different degree of specificity to reveal how shrubs and sedges affect chemical
255 properties of moss-dominated peat.

4.1.1 Different chemical properties of plant materials

Properties as C/N ratios, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of living plant parts showed significant differences between different plant materials/PFTs (Fig. 1). C/N ratios of sedge shoots were significantly lower than those of shrubs or mosses -, in line with its higher decomposability (Kaštovská et al., 2018; Limpens and Berendse, 2003). ^{13}C signature of plant tissue tends to be
260 depleted and thus likely reflect that sedge shoots were more easily decomposable than litter of shrubs or mosses. Carbon isotope signature of plant tissue tends to be depleted in ^{13}C under warmer and drier conditions (Broder et al., 2012; Gavazov et al., 2016; Skrzypek et al., 2007) explaining the observed $\delta^{13}\text{C}$ depletion of sedge and moss tissues at the High T site compared to Low T site. Shrub shoots were significantly depleted in $\delta^{15}\text{N}$ compared to sedge and moss shoots ($p < 0.001$, Fig. 1c). The depletion of $\delta^{15}\text{N}$ in living *C. vulgaris* shoots compared to shoots of *E. vaginatum* and *Sphagnum spp.* is likely related to the
265 symbiotic relationship between *C. vulgaris* and ericoid mycorrhizal fungi (Aerts et al., 2009; Bragazza et al., 2010; Emmerton et al., 2001). The transferred N from mycorrhiza to shrubs occurs to be depleted relative to soil N (Gebauer and Dietrich, 1993). Nevertheless, though differences in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ between PFT existed, unknown variables influencing $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in peat, such as various plant species growing in the peat, N deposition history etc. complicated the use of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ as
270 vegetation proxy. The rather small differences in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ between the plant material in combination with the observed differences between the two sites complicate the use of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ ratios as a vegetation proxy.

By applying PCA to pyrolysates of plant and peat samples, we were able to clearly separate mosses from vascular plants and shrubs from sedges. The pyrolysis product specific for *Sphagnum* (4-isopropenylphenol) and the sum of lignin-derived products indicating vascular plants were particularly useful (Fig. 3a, 3b). Furthermore, the ratio of 4-vinylguaiaicol to the summed guaiacyl products (4VG/G) indeed could be used to reflect sedges (Fig. 3c, 3d). Additionally, the ratio of C₃-guaiaicol to the summed guaiacyl products (C₃G/G) and the sum of *n*-alkenes and *n*-alkanes (Al) could be confirmed as parameters indicative for shrubs (Fig. 3c, 3d).

4.1.2 Effects of vascular plants on chemical properties of the moss-dominated peat

The high contribution of polysaccharides and phenols to peat pyrolysates (Table 3) and a strong positive correlation of the marker for sphagnum acid (4-isopropenylphenol) with the summed phenols (adj. $R^2 = 0.98$; Fig. 5a) indicates that the peat is dominated by *Sphagnum* tissue. The close positions of both peat samples and living *Sphagnum* shoots along PC1 visualise the dominance of *Sphagnum* in the peat. Furthermore, the similarity of C/N ratios, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of the uppermost peat increment to those of moss are indicative for moss-dominated peat (Schaub and Alewell, 2009) and ~~have~~has been measured likewise in *Sphagnum* peatlands by Kracht and Gleixner (2000). Thus, *Sphagnum* tissues dominate the peat of our two sites. Nevertheless, py-GC/MS indicates that the moss-dominated peat has a contribution from vascular plants as lignin-derived products contributed up to 15 % to pyrolysates, particularly in the deeper increments under sedge coverage (Fig. 4a). Peat composition under shrubs and sedges is influenced by these species in the studied peat (0-20 cm) as indicated by the molecular parameters for sedge and shrub in the corresponding peat cores (Fig 4b, 4c, 4d).~~The parameters for sedge and shrub indeed showed generally values in the corresponding peat cores (Fig 4b, 4c, 4d), which indicates that peat composition under shrub and sedge is influenced by these species in the studied peat (0-20 cm).~~ The sedge parameter (i.e. the ratio of 4-vinylguaiaicol to the sum of guaiacols; Table 1) was higher in sedge-core samples than in shrub-core samples (Fig. 4b) illustrating a noticeable contribution from sedge to the peat. The correlation between the sedge parameter and the sum of lignin-derived products (adj. $R^2 = 0.52$, Fig. 5c) indicates a strong contribution from sedges on lignin in sedge-cores. The contribution of shrubs to peat composition, as indicated by the suggested shrub parameter (i.e. the sum of *n*-alkenes and *n*-alkanes; Table 1), seems to be particularly high in the upper three peat increments as this parameter was mostly higher for shrub-core samples than for sedge-

295 core samples in those increments (Fig. 4d). The increasing C/N ratios with depth at both sites could indicate a larger contribution of roots to the moss-dominated peat, since roots had much higher C/N ratios than shoots and moss (Fig. 1, 2a).

By using py-GC/MS we could show that the peat was dominated by *Sphagnum*, and had a contribution from vascular plants; furthermore, we could validate the selected parameters described in the literature to reflect the contribution from sedge and shrub at the two sites.

300 4.2 Decomposition of the moss-dominated peat

Most of the studied parameters changed with depth in the peat cores and might be indicative for the assumed increase in peat decomposition with depth, i.e. with increasing time of exposure to oxygen after peat formation. In all peat cores, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ increased with depth. Since $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ showed a positive correlation (adj. $R^2 = 0.48$, Fig. 5b), their increases with depth may be caused by the same processes. The preferential uptake of lighter isotopes (^{12}C , ^{14}N) for respiration by aerobic

305 decomposers during decomposition causes a relative enrichment of heavier isotopes (^{13}C , ^{15}N) in the remaining organic matter (Krüger et al., 2014, 2015; Nadelhoffer and Fry, 1988; Schaub and Alewell, 2009), suggesting that ^{13}C and ^{15}N depth trends are due to decomposition. Because $\delta^{15}\text{N}$ trends may also be superimposed by N deposition (Novák et al., 2014) and fractionation processes during N fixation (Novák et al., 2016), $\delta^{13}\text{C}$ seems to be a better indicator for peat decomposition in our study. Nevertheless, also $\delta^{13}\text{C}$ peat records might be superimposed by differences in $\delta^{13}\text{C}$ between shoots and roots, plant

310 species, or site specific differences in ^{13}C discrimination (Sect. 4.1.1). Differences in the C/N ratios did not provide any consistent picture regarding changes in peat decomposition. We speculate that the observed increasing C/N ratio with depth might reflect an increasing N deposition in the past decades (Galloway et al., 2008) and an -except for the assumed increased contribution of roots (high C/N ratios, Fig. 1a) for- to peat formation with increasing depth (Sect. 4.1.2). N deposition at the High T site were reported to be $8.2 \text{ kg ha}^{-1} \text{ y}^{-1}$ (Bragazza et al., 2005) and for peatlands in norther Italy between 4.2 and > 10

315 $\text{kg ha}^{-1} \text{ y}^{-1}$ (Bragazza et al., 2003, 2005).

In addition to changes in $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ reflecting the decomposition of the bulk peat (i.e. cumulative effects on all peat components), we examined changes in compounds being indicative for the decomposition of specific plant tissues, i.e., *Sphagnum*-derived peat (4-isopropenylphenol ~~and, to a certain extent, the ratio of levoglucosan to the sum of polysaccharide-derived products~~). *Sphagnum* acid and its pyrolysis product 4-isopropenylphenol have been found to very sensitively reflect

320 aerobic decomposition of *Sphagnum* tissue (Abbott et al., 2013; Schellekens et al., 2015b). The observed decrease of 4-isopropenylphenol with depth occurred in all four peat cores (Fig. 4e) and its negative correlation with ^{13}C (adj. $R^2=0.27$, Fig. 5d), confirms the increase in peat decomposition with depth as indicated by ^{13}C .

The detected increase in polysaccharides with depth (Table 3) likely reflects the relative accumulation of rather resistant polysaccharides of *Sphagnum* cell-walls during aerobic decomposition (Hájek et al., 2011) and the preferential decomposition of *Sphagnum* phenols (Schellekens et al., 2015b). However, the polysaccharide products from the peat samples can have multiple sources, too (e.g. *Sphagnum* cell-walls, or ligno-cellulose from vascular plants; Sarkar et al., 2009). Similarly, the increase with depth of the ratio of levoglucosan to the sum of polysaccharide-derived products (L/Ps) may reflect the relative preservation of *Sphagnum* polysaccharides during aerobic decomposition (Table 1, Fig. 4f). This is confirmed by a strong negative correlation between this ratio and 4-isopropenylphenol (adj. $R^2=0.79$, Fig. 5e), and further by the positive loading of

330 L/Ps on PC2.

4.2.1 Effects of vascular plants on decomposition of moss-dominated peat

We found three indicators that decomposition of moss-dominated peat with depth is boosted by sedge coverage compared to shrub coverage. Increases in $\delta^{13}\text{C}$ with depth were higher for sedge-cores than for shrub-cores (Fig. 2b) and the decrease with depth of 4-isopropenylphenol was mostly stronger in sedge-cores than shrub-cores (Fig. 4e). In general, the L/Ps ratio increased with depth (Fig. 4f). Only in the deepest increment of sedge-cores this ratio decreased. This decrease could indicate that decomposition under sedge coverage in the deepest peat increment is so high that even less decomposable polysaccharides have been decomposed.

~~Because this is not evident from the 4-isopropenylphenol record, it probably reflects a higher contribution of sedge-derived polysaccharides at these depths. Such a shift towards sedge derived cell wall components should result in a higher decomposability of the polysaccharides.~~

340 The observed ~~decomposition~~ patterns were detected by a parameter describing the whole peat ($\delta^{13}\text{C}$), but were also reflected by compounds indicative for *Sphagnum* material (4-isopropenylphenol). The latter suggests that (changes in) vascular plant composition may affect the decomposition of the existing *Sphagnum* peat by changing plant-soil feedbacks (Bragazza et al., 2013; Gavazov et al., 2018; Robroek et al., 2015). The observed higher degree of degradation of peat under sedges than under

345 shrubs may be explained by differences in litter quality or root traits. Sedge litter is likely to be more readily decomposable compared to shrub litter, caused by its lower C/N ratios (Fig. 1a; Huang et al., 1998; Kaštovská et al., 2018; Laiho et al., 2003; Limpens and Berendse, 2003). Furthermore, additional oxygenation by the aerenchym of *E. vaginatum* might trigger further decomposition of moss-dominated peat (Armstrong, 1964; Holzapfel-Pschorn et al., 1986; Roura-Carol and Freeman, 1999). This process is particularly relevant at the Low T site, where the uppermost 20 cm of the peat remained water saturated much longer than at the High T site.

4.2.2 Temperature effects on decomposition of the moss-dominated peat – interactions with vascular plant effects

The altitudinal gradient has been used to reveal potential effects of increasing temperature and associated lower water table on peat decomposition by comparing the suggested decomposition parameters (Table 1) between the High T and Low T sites. Increases in $\delta^{13}\text{C}$ with depth were higher at the High T site than at the Low T site (Fig. 2). Therefore, decomposition of the moss-dominated peat is likely to be increased at the High T site compared to the Low T site independent of the vascular plant species.

Depth trends of the *Sphagnum*-specific decomposition parameter (4-isopropenylphenol) do not align reflect, however, this increased peat decomposition at higher temperatures. 4-Isopropenylphenol decreased more strongly less at the Low-High T site compared to the High-Low T site (Fig. 4e). We might speculate a difference in temperature sensitivity between decomposition of *Sphagnum* and the whole peat, but such a hypothesis needs to be tested by e.g. temperature controlled incubation experiments.

The ratio of levoglucosan to the sum of polysaccharides (Fig. 4f) did not show consistent trends related to temperature again indicating no temperature enhanced degradation of the moss-dominated peat, and the ratio of levoglucosan to the sum of polysaccharides (Fig. 4f) did not show consistent trends related to temperature again indicating no temperature enhanced degradation of the moss-dominated peat. There are several alternative explanations for the contrasting trends observed for the whole peat ($\delta^{13}\text{C}$) and the more *Sphagnum*-derived fraction of the peat: i) decomposition of the *Sphagnum*-derived peat is not enhanced at higher temperatures, and ii) the parameter for *Sphagnum* decomposition may not reflect temperature effects on *Sphagnum*-derived peat. The latter may apply to the ratio of levoglucosan to the sum of polysaccharides (Huang et al., 1998; Schellekens et al., 2015c2015b) because Vascular plants and particularly sedges might increasingly contribute to

370 polysaccharides with higher temperatures (see section 4.2.1). These changes from more *Sphagnum*-derived polysaccharides to
more sedge-derived polysaccharides could change decomposition dynamics of polysaccharides, since cell walls constituents
from *Sphagnum* were found to be less easily decomposable (Hájek et al., 2011). A higher contribution from sedges could
therefore superimpose a potential enrichment of *Sphagnum*-derived polysaccharides with depth. On the other hand, it seems
unlikely that the observed depth trends for the *Sphagnum* specific 4-isopropenylphenol has been affected in a similar way as
375 the less specific ratio of levoglucosan to the sum of polysaccharides. Given the above, the higher degree of peat decomposition
at the High T site picked up by $\delta^{13}\text{C}$ is probably mediated by higher input rates of easily decomposable vascular plant litter,
notably sedges, combined with the warmer and drier conditions favouring aerobic decomposition processes (Biester et al.,
2014).

This combined effect of sedges and temperature on peat decomposition has implications for the long-term C storage in
380 *Sphagnum*-dominated peatlands because of projected shifts from sedges to shrubs with climate change (Breeuwer et al., 2009).

That change towards less sedges may partly offset temperature driven decomposition processes because of the observed
enhancing effect of sedges on peat decomposition. Less sedges (i.e. more shrubs) should result in less peat degradation because
(i) the decomposability of available litter (higher contribution of shrub litter) is reduced as its chemical composition indicates
less decomposability (Kristensen and McCarty, 1999; Ward et al., 2015), (ii) an increasing presence of shrubs (*C. vulgaris*)
385 supresses belowground biota activity and nutrient cycling (Fenner and Freeman, 2011), (iii) *C. vulgaris* associates with
mycorrhizal fungi which increase the uptake of organic nutrients leading to an increase of C/N ratio (Read et al., 2004) and
thus a decrease in peat decomposition (Ward et al., 2015), (iv) the input of labile C into peat via sedge roots is lower (Crow
and Wieder, 2005; Robroek et al., 2015), (v) the transport of oxygen into peat via aerenchym of *E. vaginatum* is lower. On the
other hand, Zeh et al. (2019) could show that shrubs translocated more C into the peat at higher temperatures than sedges,
390 which ~~should~~ could result in reinforcing effect on peat decomposition with increasing temperature. Obviously, the enhanced
C input by shrubs into peat did not coincide with enhanced decomposition of the moss-dominated peat on these sites.

5 Conclusions

The studied plant functional types differed in the chemical composition of their biomass, and therefore in litter quality.
Although both peatlands were moss-dominated, the application of several complementary parameters revealed clear influences

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395 from sedge and shrub litter. Combining data obtained by py-GC/MS and isotopic analysis enabled separating the effects of
PFT and temperature on peat decomposition under field conditions. Whereas changes in $\delta^{13}\text{C}$ depth records reflected the state
of peat degradation, its application to disentangle the effects of source material, decomposition processes, and environmental
factors is incomplete. The C/N ratio and $\delta^{15}\text{N}$ were not specific enough to represent vascular plant effects on decomposition
of the moss-dominated peat. Combining records of molecular parameters and $\delta^{13}\text{C}$ indicated that moss-dominated peat was
400 more decomposed under sedge than under shrub coverage, particularly under high temperatures. The most important and also
surprising result of our study was that vascular plants had a more pronounced impact on peat decomposition than temperature
and associated lower water tables together. Potential O_2 transport by the aerenchym of sedges did probably not contribute to
enhanced peat decomposition at the High T site, as the top 20 cm peat layer sampled remained above the water table, and thus
aerated, for most of the year. Considering that climate change can lead to a shift from *Sphagnum* mosses to vascular plants and
405 from sedges to shrubs (Breeuwer et al., 2009), an increase of sedge coverage may enhance the decomposition of *Sphagnum*
peat in surface layers at elevated temperature. To what extent this increased decomposition may be partly compensated by
growing dominance of shrubs over sedges with climate change deserves further studies in order to link belowground
decomposition to aboveground production.

Data availability

410 The underlying py-GCMS data can be accessed via <http://dx.doi.org/10.25532/OPARA-77>. Carbon to nitrogen (C/N) ratios,
 $\delta^{15}\text{N}$ [‰] and $\delta^{13}\text{C}$ [‰] of shoot and root tissues from the three peat forming plants and of peat increments are available via
<http://dx.doi.org/10.25532/OPARA-78> and <http://dx.doi.org/10.25532/OPARA-79>, respectively.

Author contributions

415 JL, LB and KK designed the study and MTI, LZ, JL, LB and KK collected the samples and data in the field. MTI and LZ
processed the samples and did the analyses. JS contributed to the py-GCMS part of the article, including analysis of the data
and editing on the paper. LZ took the lead in preparing the manuscript, with contributions from all co-authors.

Conflicts of Interest~~mpeting interests~~

The authors declare that they have no conflicts of interest.

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Conflicts of Interest

The authors declare that they have no conflicts of interest.

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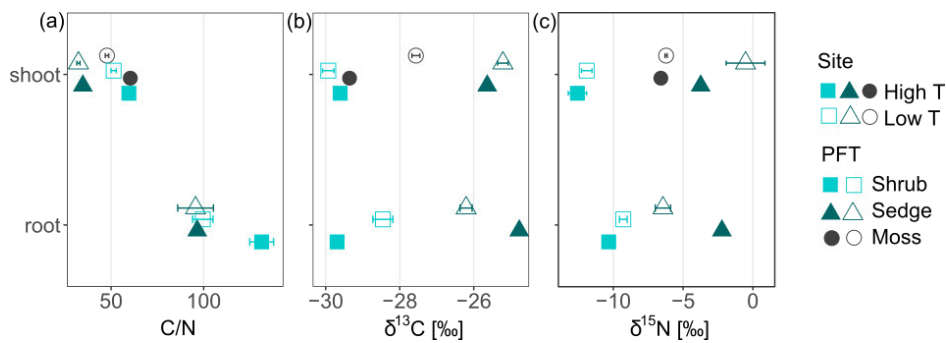
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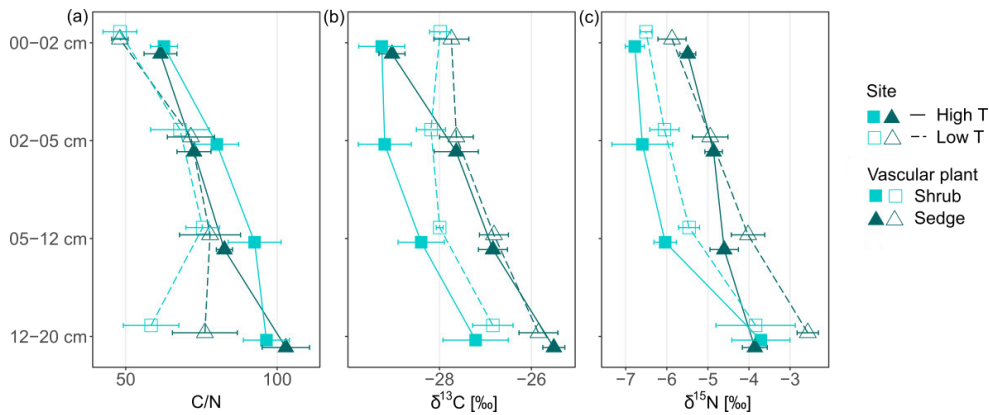
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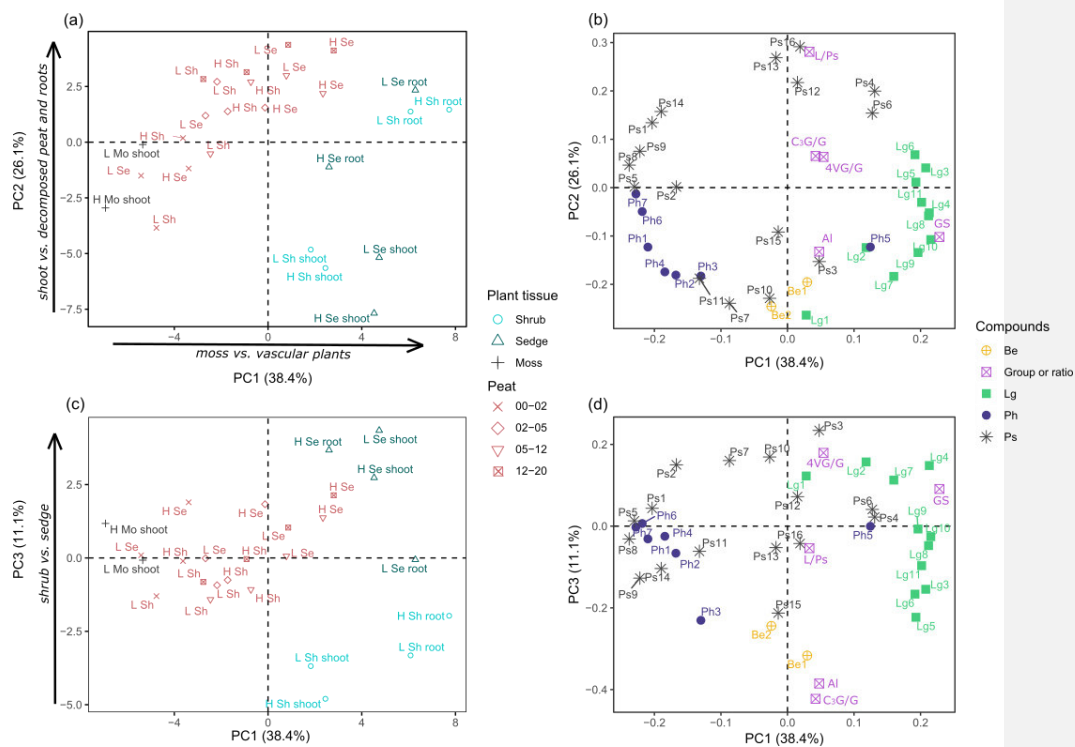
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675 **Figure 1:** Carbon to nitrogen (C/N) ratios, $\delta^{15}\text{N}$ [‰] and $\delta^{13}\text{C}$ [‰] of shoot and root tissues from three plant functional types (PFTs; i.e. mosses, shrubs and sedges) and from two peatlands differing in temperature (high and low temperature indicated by High T and Low T, respectively). Symbols for shoots represent mean values with standard error ($n = 5$), whereas symbols for roots give means of two or a single value (High T sedge root).



680 **Figure 2:** Carbon to nitrogen (C/N) ratios, $\delta^{15}\text{N}$ [‰] and $\delta^{13}\text{C}$ [‰] of peat core increments from two peatlands differing in temperature (high and low temperature indicated by High T and Low T, respectively) and covered by two different vascular plants (shrub and sedge). Symbols represent mean values with standard error ($n = 5$).



685 **Figure 3: Results of the principal component analysis (PCA) of the pyrolysis data to reveal molecular composition of peat and peat forming plants. PC1 to PC2 projections of scores (a) and loadings (b), and PC1 to PC3 projections of scores (c) and loadings (d).**
 Plant samples are labelled by site (H = high temperature; L = low temperature) and plant tissue (shoot, root). Peat samples are named by site and vascular plants (Se = Sedge-peat; Sh = Shrub-peat). The four depth increments are distinguished by symbols. Pyrolysis products correspond to codes that are given in (A1). Abbreviations are according to chemical group: benzenes (Be), lignin products (Lg), phenols (Ph) and carbohydrates (Ps). Additional variables are included into PCA, namely summed *n*-alkenes and *n*-alkanes (Al), 4-vinylguaicol to the summed guaiacyl products (4VG/G), C₃-guaicol to the summed guaiacyl products (C₃G/G), sum of guaiacyl and syringyl lignin products (GS), levoglucosan to summed polysaccharides (L/Ps).
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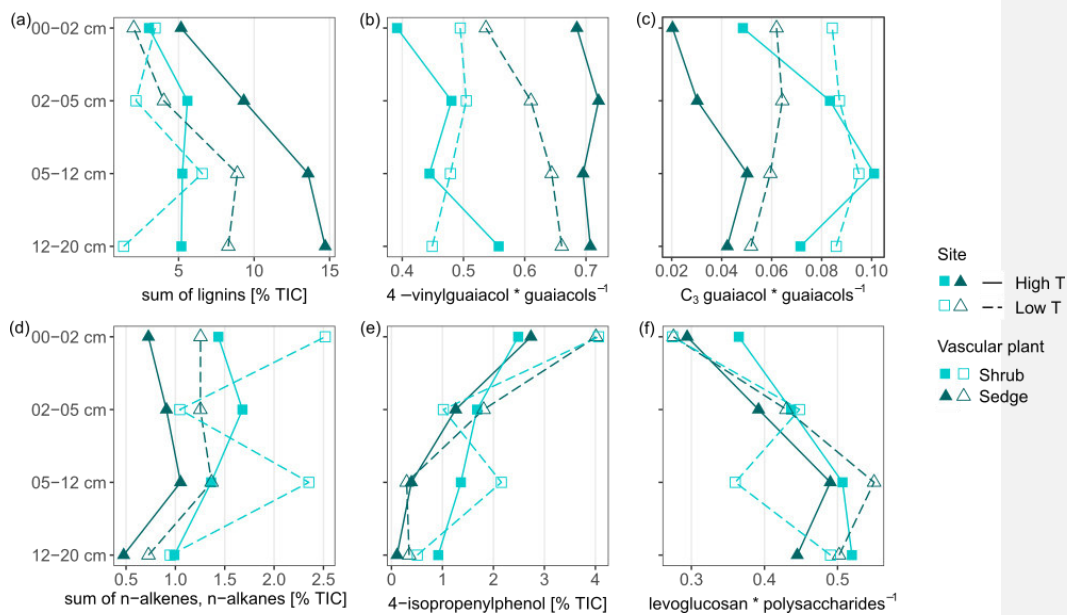
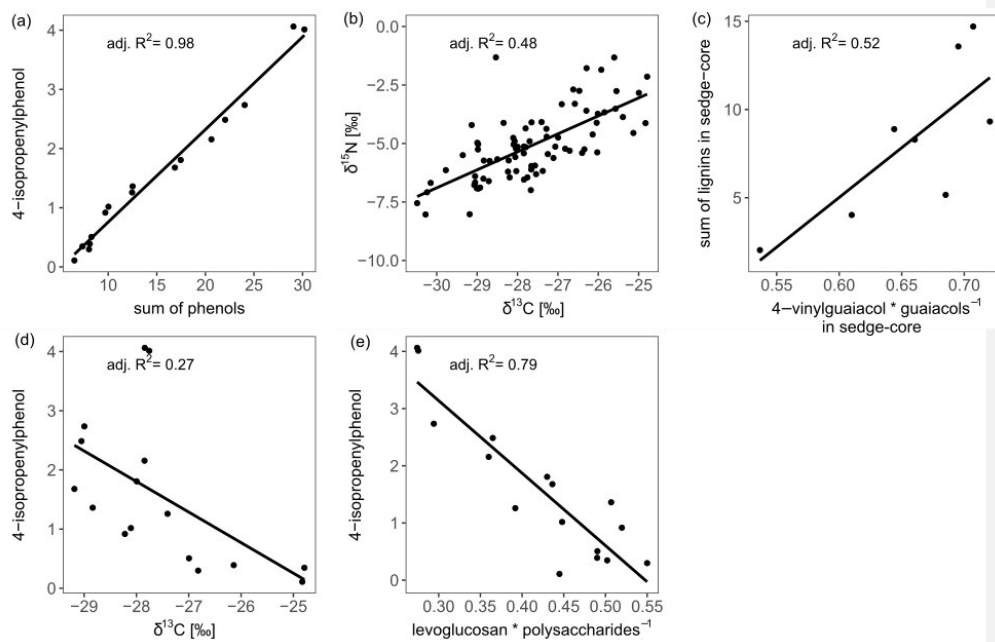


Figure 4: Parameters that reflect vascular plant input in moss-dominated peat (a-d) and decomposition of the moss-dominated peat (e, f) in peat core increments from both sites and given peat cores. Data derived from pyrolysis gas chromatography/mass-spectrometry



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Figure 5: Regression plots between parameters describing decomposition of the moss-dominated peat and the impact of vascular plants on peat properties.

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710 **Table 1: Overview of all parameters used in this study to determine impacts of plant functional types (PFT) on peat properties and decomposition of the moss-dominated peat (for abbreviations of the parameter see legend of Fig. 3).**

Parameter	Unit	Indication	Interpretation in <i>Sphagnum</i> -dominated peat
C/N	-	preferential decomposition of C over N	aerobic decomposition
$\delta^{13}\text{C}$	[‰]	preferential decomposition of ^{12}C over ^{13}C isotope	aerobic decomposition
$\delta^{15}\text{N}$	[‰]	preferential decomposition of ^{14}N over ^{15}N isotope	aerobic decomposition
sum of G and S lignin products	[% TIC ^a]	lignin	vascular plants (van Smeedijk and Boon, 1987)
sum of <i>n</i> -alkenes and <i>n</i> -alkanes	[% TIC ^a]	cutan, suberan, leaf waxes	ericoid shrubs (Schellekens and Blumman, 2011; van Smeedijk and Boon, 1987)
C ₂ G/G	-	intact lignin	ericoid shrubs (Schellekens et al., 2012)
4-X/G/G	-	ferulic acid	sedges (van Smeedijk and Boon, 1987; Schellekens et al., 2012)
4-isopropenylphenol (Ph6)	[% TIC ^a]	sphagnum acid	aerobic decomposition of <i>Sphagnum</i> tissues (preferential loss of polyphenols over polysaccharides; Schellekens et al., 2015b)
leoglucosan/sum of polysaccharides	-	cellulose	aerobic decomposition of <i>Sphagnum</i> tissues (preservation of <i>Sphagnum</i> polysaccharides; Schellekens et al., 2015b) ^b
^a total ion current			
^b interpretation refers to relatively low values			
Parameter	Unit	Indication	Interpretation
C/N	-	preferential decomposition of C over N	aerobic decomposition of organic matter
$\delta^{13}\text{C}$	[‰]	preferential decomposition of ^{12}C over ^{13}C isotope	aerobic decomposition of organic matter
$\delta^{15}\text{N}$	[‰]	preferential decomposition of ^{14}N over ^{15}N isotope	aerobic decomposition of organic matter
sum of G and S lignin products	[% TIC ^a]	lignin	vascular plants (Schellekens et al. 2015b)
sum of <i>n</i> -alkenes and <i>n</i> -alkanes	[% TIC ^a]	cutan, suberan, leaf waxes	ericoid shrubs (Schellekens et al., 2011)
C ₂ G/G	-	intact lignin	ericoid shrubs (Schellekens et al., 2011, 2015a)
4-X/G/G	-	ferulic acid	graminoid sedges (Schellekens et al., 2012)
4-isopropenylphenol (Ph6)	[% TIC ^a]	sphagnum acid	aerobic decomposition of <i>Sphagnum</i> tissues (loss of sphagnum acid; Schellekens et al., 2015b)
leoglucosan/sum of polysaccharides	-	cellulose	aerobic decomposition of <i>Sphagnum</i> tissues (preservation of <i>Sphagnum</i> polysaccharides; Schellekens et al., 2015b)
^a total ion current			

715 **Table 2: Type II analysis of variance with Kenward-Roger's approximation of degree of freedoms applied on carbon to nitrogen (C/N) ratios, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of peat cores ($n = 5$).**

	C/N			$\delta^{13}\text{C}$			$\delta^{15}\text{N}$		
	DF	F-test	<i>p</i>	DF	F-test	<i>p</i>	DF	F-test	<i>p</i>
Vascular plants (VP)	1	0.15	0.69	1	27.05	< 0.001	1	25.79	< 0.001
Site	1	19.04	0.002	1	3.17	0.11	1	1.62	0.24
Depth	3	12.75	< 0.001	3	24.21	< 0.001	3	28.46	< 0.001
VP:Site	1	1.51	0.22	1	1.80	0.18	1	0.01	0.94
VP:Depth	3	0.97	0.41	3	1.90	0.13	3	0.94	0.43
Site:Depth	3	2.40	0.07	3	2.07	0.11	3	0.51	0.68
Site:Depth:VP	3	0.12	0.94	3	0.32	0.81	3	1.26	0.29

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Table 3: Groups of all identified pyrolysis products for all samples: *n*-alkenes and *n*-alkanes (Al), benzenes (Be), lignin products (Lg), phenols (Ph) and polysaccharides (Ps). The contribution of the single products in groups to total ion current were cumulated for each of the respective group.

Sample	PFT	Site	Al	Be	Lg	Ph	Ps
Plant tissue							
Shoot	Sedge	Low T	0.78	2.31	46.57	7.63	42.70
Shoot	Sedge	High T	1.11	4.87	48.89	15.42	29.71
Shoot	Shrub	Low T	3.98	6.63	26.40	21.87	41.12
Shoot	Shrub	High T	5.41	8.72	30.09	19.15	36.63
Shoot	Moss	Low T	1.13	2.83	6.25	25.37	64.42
Shoot	Moss	High T	1.02	3.37	8.76	33.39	53.46
Root	Sedge	Low T	0.77	1.85	32.23	5.50	59.65
Root	Sedge	High T	0.85	1.28	26.57	14.09	57.21
Root	Shrub	Low T	3.53	3.26	23.42	8.90	60.89
Root	Shrub	High T	2.19	1.97	24.71	7.35	63.78
Peat							
00-02 cm	Sedge	Low T	1.25	3.49	9.18	30.18	55.89
00-02 cm	Sedge	High T	0.73	2.63	14.98	24.04	57.62
00-02 cm	Shrub	Low T	2.52	5.64	13.65	29.06	49.13
00-02 cm	Shrub	High T	1.44	2.86	8.77	22.03	64.90
02-05 cm	Sedge	Low T	1.25	2.28	8.99	17.46	70.02
02-05 cm	Sedge	High T	0.91	1.89	18.10	12.46	66.65
02-05 cm	Shrub	Low T	1.04	1.94	4.60	10.03	82.39
02-05 cm	Shrub	High T	1.68	2.31	9.45	16.86	69.70
05-12 cm	Sedge	High T	1.05	1.63	21.69	8.11	67.52
05-12 cm	Sedge	Low T	1.37	2.00	12.27	8.03	76.33
05-12 cm	Shrub	Low T	2.35	3.07	12.72	20.62	61.24
05-12 cm	Shrub	High T	1.36	2.34	7.87	12.51	75.91
12-20 cm	Sedge	Low T	0.73	1.15	11.31	7.35	79.46
12-20 cm	Sedge	High T	0.48	0.85	20.23	6.52	71.92
12-20 cm	Shrub	Low T	0.95	1.59	2.65	8.28	86.53
12-20 cm	Shrub	High T	0.99	1.54	8.19	9.70	79.58

740

745

(A1) Quantified pyrolysis products, their codes, retention time (RT), and specific ion fragments (m/z) used for quantification.

Code	Pyrolysis product	m/z	RT ^c
-	C ₁₉ -C ₂₈ <i>n</i> -alkenes	55, 69	-
-	C ₁₉ -C ₂₉ <i>n</i> -alkanes	57, 71	-
Be1	benzene	78	2.365
Be2	toluene	91, 92	3.86
Lg1	4-vinylphenol	91, 120	20.117
Lg2	guaiacol	109, 124	15.232
Lg3	4-methylguaiacol	123, 138	19.092
Lg4	4-vinylguaiacol	135, 150	23.314
Lg5	C ₃ guaiacol, <i>trans</i>	164	27.73
Lg6	4-acetylguaiacol	151, 166	28.9
Lg7	syringol	139, 154	24.621
Lg8	4-methylsyringol	153, 168	27.687
Lg9	4-vinylsyringol	165, 180	31.239
Lg10	C ₃ syringol, <i>trans</i>	194	35.049
Lg11	4-acetylsyringol	181, 196	35.987
Ph1	phenol	66, 94	11.216
Ph2	C ₁ phenol	107, 108	14.031
Ph3	C ₁ phenol	107, 108	14.819
Ph4	C ₂ phenol	107, 122	18.241
Ph5	catechol	110	19.536
Ph6	4-isopropenylphenol	119, 134	23.039
Ph7	<i>p</i> -hydroxybiphenyl	170	35.33
Ps1	(2 <i>H</i>)furan-3-one	54, 84	4.566
Ps2	2-furaldehyde	95, 96	5.605
Ps3	2,3-dihydro-5-methylfuran-2-one	98	8.826
Ps4	unidentified carbohydrate	55, 86	10.29
Ps5	5-methyl-2-furaldehyde	109, 110	10.328
Ps6	4-hydroxy-5,6-dihydro-(2 <i>H</i>)-pyran-2-one	114	11.648
Ps7	2-hydroxy-3-methyl-2-cyclopenten-1-one	55, 112	12.861
Ps8	dianhydrorhamnose	113, 128	13.324
Ps9	unidentified carbohydrate	128, 72	15.057
Ps10	unidentified carbohydrate	56, 114	16.52
Ps11	1,4:3,6-dianhydro- α -D-glucose	69, 57	19.617
Ps12	1,4-Anhydroxylofuranose	57	21.644
Ps13	1,4-Dideoxy-D-glycero-hex-1-enopyranose-3-ulose	87, 144	22.882
Ps14	levogalactosan	60	25.359
Ps15	levomannosan	60	27.862
Ps16	levoglucosan	60	30.045