Geophysical Research Letters®

RESEARCH LETTER
10.1029/2021GL093392

Organic Matter Chemistry Drives Carbon Dioxide Production of Peatlands

A. E. Normand[1], B. L. Turner[1,2], L. J. Lamit[3], A. N. Smith[4], B. Baiser[5], M. W. Clark[1], C. Hazlett[1], E. S. Kane[6,7], E. Lilleskov[7], J. R. Long[8], S. P. Grover[9], and K. R. Reddy[1]

[1]Soil and Water Sciences, Wetland Biogeochemistry Laboratory, University of Florida, Gainesville, FL, USA, [2]Smithsonian Tropical Research Institute, Ancon, Panama City, Republic of Panama, [3]Department of Biology, Department of Environmental and Forest Biology, Syracuse University, State University of New York College of Environmental Science and Forestry, Syracuse, NY, USA, [4]Department of Chemistry, University of Florida, Gainesville, FL, USA, [5]Wildlife Ecology and Conservation, University of Florida, Gainesville, FL, USA, [6]School of Forest Resources and Environmental Science, Michigan Tech University, Houghton, MI, USA, [7]Northern Research Station, USDA Forest Service, Houghton, MI, USA, [8]Department of Biochemistry and Molecular Biology, University of Florida, Gainesville, FL, USA, [9]Department of Animal, Plant and Soil Sciences, Research Centre for Applied Alpine Ecology, La Trobe University, Agribio, Bundoora, VIC, Australia

Key Points:

- The global variation in soil organic matter chemistry (i.e., specifically the proportion of *O*-alkyl carbon) in peatlands is determined primarily by mean annual temperature
- *O*-alkyl carbon concentration predicts CO_2 production at the global scale across peatlands with contrasting environment and chemistry

Supporting Information:

Supporting Information may be found in the online version of this article.

Correspondence to:

A. E. Normand and K. R. Reddy,
evangelinemaid@gmail.com;
krr@ufl.edu

Citation:

Normand, A. E., Turner, B. L., Lamit, L. J., Smith, A. N., Baiser, B., Clark, M. W., et al. (2021). Organic matter chemistry drives carbon dioxide production of peatlands. *Geophysical Research Letters*, *48*, e2021GL093392. https://doi.org/10.1029/2021GL093392

Received 31 MAR 2021
Accepted 26 JUL 2021

Abstract Peatlands play a critical role in the global carbon (C) cycle, encompassing ~30% of the 1,500 Pg of C stored in soils worldwide. However, this C is vulnerable to climate and land-use change. Ecosystem models predict the impact of perturbation on C fluxes based on soil C pools, yet responses could vary markedly depending on soil organic matter (SOM) chemistry. Here, we show that one SOM functional group responds strongly to environmental factors and predicts the risk of carbon dioxide (CO_2) release from peatlands. The molecular composition of SOM in 125 peatlands differed markedly at the global scale due to variation in temperature, land-use, vegetation, and nutrient status. Despite this variation, incubation of peat from a subset of 11 sites revealed that *O*-alkyl C (i.e., carbohydrates) was the strongest predictor of aerobic CO_2 production. This explicit link provides a simple parameter that can improve models of peatland CO_2 fluxes.

Plain Language Summary Peatlands influence climate, because their soils contain the equivalent of two thirds of the Earth's atmospheric carbon. However, the carbon stored in peatlands is at risk due to climate and land-use changes, which may increase microbial production of carbon dioxide (CO_2) and promote future warming. We found that the chemical composition of soil organic carbon determines the amount of carbon loss from peatlands following drainage. Further, the chemical composition of organic carbon varied among global peatlands based on site characteristics. Therefore, CO_2 emissions from soil due to climate and land-use change vary globally depending on peat carbon chemistry. Information on the chemical composition of soil organic matter will help earth system models improve estimates of CO_2 production from peatlands.

1. Introduction

Peatlands comprise ~3% of the global land area, but store more carbon (C) than any other terrestrial ecosystem (Bridgham et al., 2006; Xu et al., 2018). This organic matter is stabilized by both its chemistry and factors that constrain decomposition, including saturation, temperature, low redox potential, and nutrient availability (Minasny et al., 2019). When these environmental conditions are altered via climate and land-use changes (e.g., rapid warming in northern latitudes and peatland drainage), organic matter is more susceptible to oxidation (Hoyt et al., 2020; Hugelius et al., 2020; Kurnianto et al., 2015; Leifeld et al., 2012; Sjögersten et al., 2016) and the chemical composition of soil organic matter (SOM) becomes a key and potentially rate-limiting constraint on microbial rates of mineralization. As climate and anthropogenic impacts intensify and governments develop policies to preserve peatland C (Evers et al., 2017; Granath et al., 2016; Leifeld & Menichetti, 2018), there is a critical need to understand the controls on SOM stability and model the impact of perturbations on C dynamics and gas fluxes to the atmosphere (Loisel et al., 2020).

Peatlands occur across the globe under a wide range of climate, vegetation, nutrient status, soil pH, and land-use regimes (Frolking et al., 2011; Page et al., 2011; Turetsky et al., 2014; Xu et al., 2018). However, studies of SOM stability have been site-specific and disproportionately focused on northern peatlands, resulting in a lack of an integrated cross-continental understanding on the biogeochemical controls of SOM dynamics, which is needed to improve representation of peatlands in earth system models (Kurnianto et al., 2015; Loisel et al., 2020; Norris et al., 2013; Tfaily et al., 2014). For example, it is typically assumed that the relative proportion of major chemical groups in SOM and their pool sizes and stability are similar in peatlands worldwide, implicit in the use of total C stocks to estimate gas fluxes from peatlands (Lehmann & Kleber, 2015; Todd-Brown et al., 2013; Turetsky et al., 2014). However, this oversimplifies the influence of biogeochemical drivers of SOM dynamics and potentially skews the accuracy of predictive models (Todd-Brown et al., 2013; Zhang et al., 2002). Understanding the variation in peat C chemistry, and its influence on the response of peatlands to perturbation, will therefore improve representation of peat soil decomposition in earth system models.

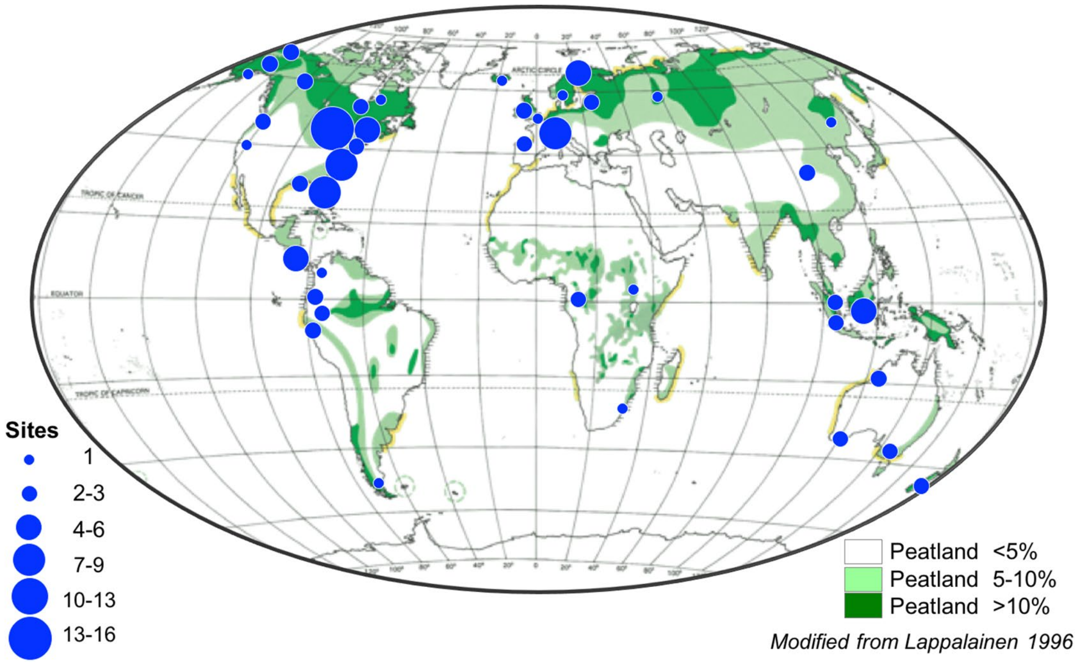
Information on peat chemistry can be obtained by solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy, which identifies SOM composition by classifying ^{13}C nuclei based on differences in bonding environment (Derenne & Tu, 2014; Wilson, 2013). These bonding environments are categorized into C functional groups by resonance frequencies presented using a parts per million (ppm) chemical shift scale: alkyl (0–45 ppm), methoxyl (45–60 ppm), *O*-alkyl (60–110 ppm), aromatic (110–160 ppm), and carboxyl (160–220 ppm, Knicker, 2011). The stability or decomposition potential of specific C functional groups are typically inferred from their behavior in the soil environment (Lehmann & Kleber, 2015). For example, the ratio of alkyl to *O*-alkyl C increases as SOM decomposes and has therefore been used as an index of the degree of decomposition (Baldock et al., 1997; Grover & Baldock, 2012; Tfaily et al., 2014). In addition, ratios that include aromatic C have been used to infer the persistence and resistance of lipid and lignin like plant compounds, or the result of microbial transformations and accumulation of stable byproducts (Bonanomi et al., 2013; Chavez-Vergara et al., 2014; Guéguen et al., 2012; Leifeld et al., 2017). In terms of the consequences of SOM C chemistry for greenhouse gas (GHG) production, some site-specific studies indicate that polysaccharide compounds with oxygenated functional groups correlate with decomposition processes (Leifeld et al., 2012; Sjögersten et al., 2016; Wright et al., 2011), while others suggest that aromatic C regulates soil respiration (Freeman et al., 2004; Hodgkins et al., 2018; Wang et al., 2015). However, there is little broad conceptual understanding of the extent to which variation in SOM chemistry influences GHG production from peatlands (Campbell & Paustian, 2015; Minasny et al., 2019).

We studied 125 global peatlands spanning a wide range of environmental conditions to determine the chemical nature of SOM and performed laboratory incubations using peat from a representative set of 11 sites to determine SOM response to drainage (Figure 1, Table S1, Lappalainen, 1996). We hypothesized that (a) there would be considerable variation in SOM chemical composition across the globe, driven by mean annual temperature (MAT), dominant vegetation inputs (moss, herbaceous, and woody), SOM chemistry (pH and C to nitrogen ratio), and land-use, including drainage. We also hypothesized that (b) peat with higher *O*-alkyl C pools would yield greater aerobic CO_2 production following perturbation by providing readily utilizable C for microbes, whereas greater aromatic and alkyl C would have reduced CO_2 production. Confirmation of these hypotheses would support the suggestion that modelers should refine their generalized assumption of uniform peatland response to climate and land-use changes by incorporating information on SOM chemistry in predictions of CO_2 production (Lehmann & Kleber, 2015; Todd-Brown et al., 2013).

2. Materials and Methods

2.1. Survey and Experimental Methods

Peatland sites included in the global survey were from field sampling (96) or the published literature (29). Figure 1 shows their abundances from different geographical regions. Peat from global survey field sites was sampled from the upper 20 cm of the soil profile, with samples sectioned from 0–10 cm, 10–20 cm, or 0–20 cm depending on the sampling protocol at the particular site. Three or four replicate cores were sampled from each site, then air dried in the laboratory. Composite peat soil samples were analyzed by magic angle spinning (MAS) ^{13}C NMR spectroscopy at the National High Magnetic Field Laboratory (NHMFL). Web of Science was used to identify ^{13}C NMR data from previously published studies of whole peat soil samples from 0 to 20 cm range.



Modified from Lappalainen 1996

Figure 1. Peatland sites included in global survey included 96 sites that were sampled and analyzed and 26 sites with information obtained from the published literature. Peatland sites are identified with circles ($N = 125$) with the number of sites in a geographical region designated by the circle size. Shaded green regions represent the amount of peatland area (bright green 5%–10% and dark green >10% of land area). Figure is modified from Lappalainen (1996) with permission from Global Peat Resources (International Peat Society).

Laboratory incubations were conducted to determine potential CO_2 production on soil samples obtained from 11 peatland sites ranging in MAT, vegetation, and land-use (Table 1). Three replicates soil samples ~4 m apart were collected from each site, except for the PEATcosm samples which were derived from one meter cubed replicate mesocosms at the Houghton Mesocosm Facility (USDA Forest Service, Northern Research Station, Houghton, Michigan). Soil cores were sectioned into 10 cm sections from 0 to 30 cm. Aerobic incubations were prepared by adding soil that was carefully dried from field condition to 60% moisture content by weight into mason jars, which were then sealed and purged with CO_2 free air. Due to design restrictions requiring the need to store gas samples for later analysis, 20 mL of headspace was

Table 1
Location and Properties of Peatland Sites Used in the Incubation Study to Determine the Potential CO_2 Production Rates Under Aerobic Conditions

Site	Location	Vegetation	Land-use	MAT°C	Total C g C kg^{-1}	C/N ratio	pH
Bonanza Creek	Alaska, USA	moss	non impacted	−3.1	394	18	5.2
PEATcosm C	Minnesota, USA	moss	non impacted	3.0	406	52	3.9
PEATcosm L	Minnesota, USA	moss	5 yr drained	3.0	392	45	4.0
Fowlers	Florida, USA	moss	non impacted	20.5	432	22	3.0
Ordway	Florida, USA	herbaceous	non impacted	20.3	469	16	3.0
EAA Virgin	Florida, USA	herbaceous	100 yr drained	23.4	417	13	7.4
EAA Brown Farm	Florida, USA	herbaceous	100 yr farmed	23.4	380	16	7.4
Cerro Muerte	Costa Rica	moss	non impacted	11.0	424	54	4.2
Volcano Poas	Costa Rica	moss	non impacted	12.4	435	98	3.9
San San Pond Sak	Panama	woody	non impacted	25.9	475	19	3.6
Almirante	Panama	woody	non impacted	25.9	472	28	4.4

Note. MAT = mean annual temperature. Soil characteristics correspond to the laboratory analysis of the top 10 cm of the peat profile.

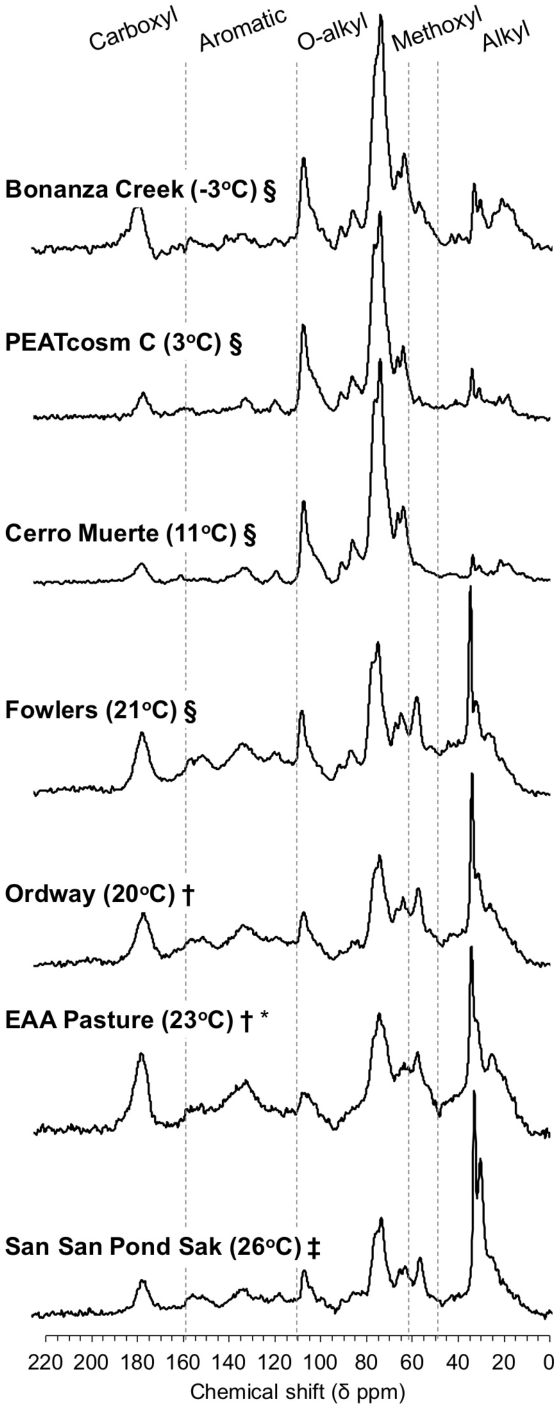


Figure 2. ^{13}C Solid State nuclear magnetic resonance spectra of peatlands varying in mean annual temperature (−3 to 26°C), vegetation type (moss§, herbaceous†, and woody‡), and land-use (nonimpacted and long-term impacted*). Spectral regions corresponding to C functional groups are labeled as alkyl (0–45 ppm), methoxyl (45–60 ppm), *O*-alkyl (60–110 ppm), aromatic (110–160 ppm), and carboxyl (160–220 ppm).

sampled every 2–5 days from incubation jars stored in dark conditions at 20°C then purged again with air for a new time 0 to ensure the headspace did not become anoxic. CO_2 concentrations of each sample period were added together resulting in a 5-point curve of CO_2 production over time (μg C-g^{-1} dw d^{-1}) representing potential CO_2 production rates (Harris & Paul, 1994; Moyano et al., 2013). Further details on methods are provided in the Supporting Information S1.

2.2. Statistical Analysis

Redundancy Analysis (RDA) was used to determine which environmental factors were most important in describing variation in global peatland C chemistry and to better understand how peatlands vary in their C composition. The response data matrix consisted of relative signal intensities for NMR functional groups: carboxyl, aromatic, *O*-alkyl, methoxyl, and alkyl C for each sample. The matrix of predictor variables contained measures of MAT, vegetation type, land-use, C/N, and pH for the sites from which each peat sample was obtained. To better understand the unique contribution of each predictor variable to describing variation in peat carbon chemistry, we conducted variance partitioning. We constructed linear mixed effects models (R package lme4) to model GHG production as a function of C chemistry. We used log-transformed aerobic CO_2 as our response variable, and the following measures of soil C composition as our predictor variables: percent *O*-alkyl C, percent alkyl C, percent aromatic C, alkyl/*O*-alkyl ratio, aromatic/*O*-alkyl ratio, calculated predicted RDA1 scores of each incubation sample, and sample depth. We also tested the quadratic form for each measure of soil C and employed site as a random effect. We then compared the final models using Akaike Information Criteria (AIC) and Bayesian Information Criteria (BIC) to determine the best-fit model. Further explanation of statistical analysis is provided in the Supporting Information S1.

3. Results

3.1. Global Survey

Our comprehensive survey of peatland soils revealed that the chemical nature of SOM determined by ^{13}C NMR spectroscopy varied markedly depending on site and soil characteristics, including land-use, MAT, vegetation type, and stoichiometry of C and N (Figure 2). Although the *O*-alkyl functional group was dominant on average (43 ± 13% of total C, range 17%–70%), the contributions of aromatic C (17% ± 6% of total C, range 6%–41%) and alkyl C (22 ± 7% of total C, range 9%–41%) varied greatly and were sometimes greater than *O*-alkyl C (Table S2).

RDA highlighted distinct differences in SOM composition, explained by MAT, vegetation type, C/N ratio, and land-use ($p = 0.001$), but not pH ($p = 0.1$; Figure 3, Table S3). The first RDA axis (RDA1) described 28.1% of data variation with increased proportions of *O*-alkyl C as RDA1 scores decreased (Figure S2). Generally, peatland SOM with higher proportions of *O*-alkyl C corresponded to soil C/N ratios >40 and developed from moss inputs under cooler climates with low land-use impacts (Figures S3–S6). In contrast, SOM with a high proportion of aromatic C formed from woody litter under warmer climates, or experienced long-term land-use impacts. Variance partitioning showed the unique contribution of MAT (8.1%), land-use (5.8%), vegetation (5.2%), soil C/N

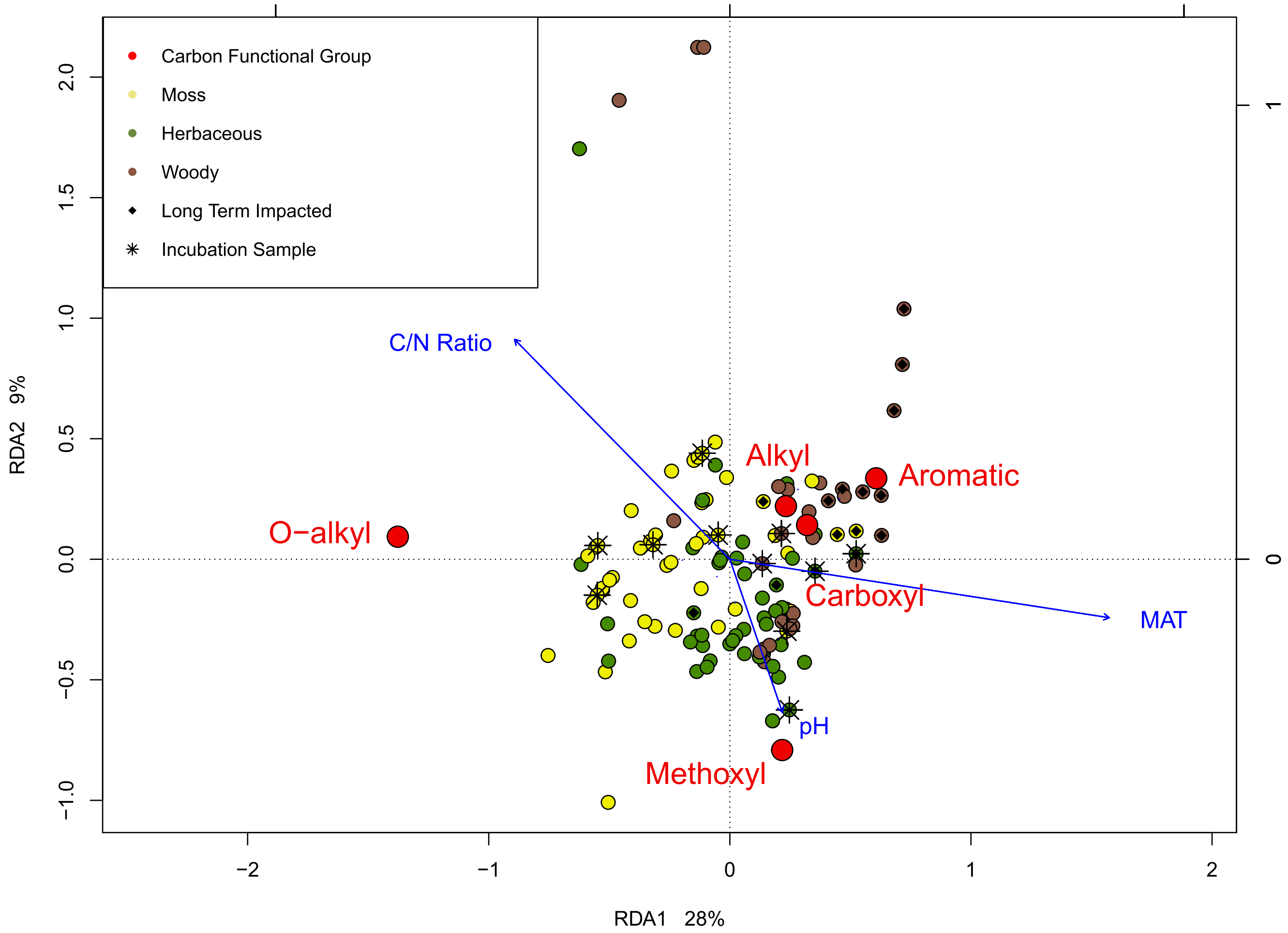


Figure 3. Redundancy analysis of data from 125 peatland sites revealed variation in the prevalence of ^{13}C nuclear magnetic resonance (NMR)functional groups (carboxyl, aromatic, *O*-alkyl, methoxyl, and alkyl C) driven by land-use, C/N ratio, mean annual temperature, and vegetation type. Carbon functional groups determined by NMR are labeled with large red circles, vegetation types are identified by colors of smaller circles (moss - yellow, herbaceous - green, and woody - brown) belonging to each site ($N = 125$), and long term impacted sites are identified with X over circles. The 11 sites that were chosen for the incubation study are indicated with an asterisk.

ratio (3.2%), and pH (1.2%) to variation in SOM chemistry, in addition to shared variation between variables (Table S4).

3.2. Laboratory Incubation Study: Aerobic CO_2 Production

Potential CO_2 production from laboratory incubations varied greatly among 11 peatland sites with a range of MAT, vegetation inputs, and land-use activities (Table 1). The mean CO_2 production (μg C g^{-1} dry weight d^{-1}) ranged from 9 to 455 for 0–10 cm depth, 13 to 368 for 10–20 cm depth, and 9 to 282 for 20–30 cm depth (Table S5). We built a set of mixed effects models for CO_2 production ($n = 33$) with predictor variables representing carbon composition (e.g., percent *O*-alkyl C, percent alkyl C, percent aromatic C, alkyl/*O*-alkyl ratio, aromatic/*O*-alkyl ratio, and a predicted RDA1 score determined by multivariate analysis of the ^{13}C NMR spectroscopy functional groups from the global survey), MAT, and depth (Tables S6–S11). The best-fit model, based on AIC and BIC, included the variables *O*-alkyl C ($t = 7.17$), (O-alkyl C)^2 ($t = -5.63$) and depth ($t = -3.13$ for 10–20 cm and $t = -4.29$ for 20–30 cm; $R^2 = 0.88$; Tables S12 and S13). CO_2 production increased with the proportion of *O*-alkyl C until an asymptote around 50% *O*-alkyl C. Further, CO_2 production decreased at greater depth in the profile (Figure 4).

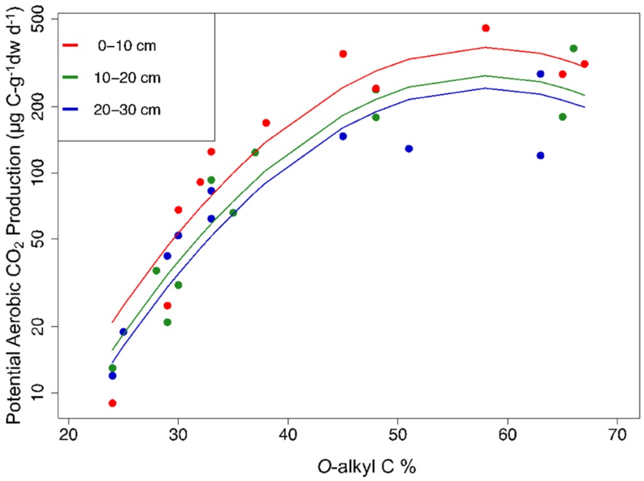


Figure 4. Selected 11 peatland sites were used in the laboratory incubation study conducted at 20°C. Rate of potential aerobic CO_2 production predicted by % *O*-alkyl C ($N = 33$, $R^2 = 0.88$) for sample depths of 0–10 cm, 10–20 cm, and 20–30 cm. The resulting formula is $Potential\ Aerobic\ CO_2\ Production = e^{0.293\, O-alkyl\ C\, -\, 0.003\, O-alkyl\ C^2\, +\, \beta\, -\, 2.534}$ with β corresponding to the coefficient for each depth (0–10 cm = 0.000, 10–20 cm = −0.296, and 20–30 cm = −0.424). The equation for each depth is plotted over dots representing incubation samples (0–10 cm is red, 10–20 cm is green, and 20–30 cm is blue).

4. Discussion

An understanding of global variation in organic matter chemical composition in peatlands and its consequences for soil respiration following perturbation is required to parameterize earth system models that aim to predict future climate scenarios. Our results demonstrate for the first time that at the global scale, strong differences in the chemical composition of organic matter can be predicted by MAT, vegetation, and land-use history, and that this chemistry, in turn, predicts the potential for CO_2 production from peatlands. Differences in peat chemistry and decomposition among peatlands are related to *O*-alkyl and aromatics, of which *O*-alkyls primarily account for differences in gas fluxes. The alkyl/*O*-alkyl ratio has traditionally been assumed to reflect SOM decomposition and stability (Baldock et al., 1997; Grover & Baldock, 2012). The relative unimportance of alkyl C in our study (RDA1 loading score of *O*-alkyl C was six times greater than alkyl C), clarifies that *O*-alkyl C drives the decomposition process compared to alkyl C; therefore, *O*-alkyl C indicates SOM decomposition and stability.

Our study demonstrates that the global variation in *O*-alkyl C is explained by MAT, long term land-use, and the type of vegetation. Higher temperature is associated with greater microbial activity, turnover of *O*-alkyl C, and CO_2 emissions (Hodgkins et al., 2018; Lehmann & Kleber, 2015). In addition, moss is prevalent in peatlands with lower MAT that store larger proportion of total C in the *O*-alkyl C pool contributed by carbohydrates and uronic acids (Harrysson Drotz et al., 2010; Hodgkins et al., 2018; Klingenfuß et al., 2014; Normand et al., 2017). While most peatlands are in arctic and boreal latitudes, 10% of peatlands occur in temperate climates, and the tropical peatland area is potentially much larger than in historic estimates (Frolking et al., 2011; Gumbricht et al., 2017; Page et al., 2011). Forested peatlands, which are prevalent in the tropics, receive more alkyl and aromatic C from above and below ground sources of C-rich lignin and aliphatic compounds like cutin, suberin, and leaf and root waxes (Upton et al., 2018). These compounds preferentially persist in the soil and are deemed recalcitrant and stable due to their complex chemical structure (Di Lonardo et al., 2017; Hodgkins et al., 2018; Hoyos-Santillan et al., 2016; Klingenfuβ et al., 2014; Leifeld et al., 2017; Sjögersten et al., 2016). Long-term drainage for conversion to forestry and agriculture also intensifies degradation via persistent oxygen exposure and increased fire incidence, thus diminishing labile C compounds such as *O*-alkyl C and potentially increasing the relative proportion of aromatic C from recalcitrant compounds and pyrogenic products (Fenner & Freeman, 2011; Hribljan et al., 2017; Klingenfuß et al., 2014; Leifeld et al., 2017; Mastný et al., 2016). Furthermore, our study showed that soil C:N stoichiometry influenced differences in *O*-alkyl, alkyl, and methoxyl C, but not aromatic C, and that surface soil pH plays a limited direct role in regulating C composition.

Carbon dynamics and GHG production in peatlands are regulated by complex interactions between environmental factors that influence soil redox conditions, plant litter production and decay, SOM composition and C:N ratios, pH, microbial and extracellular enzymes activities, and availability of electron acceptors and nutrients (Reddy & DeLaune, 2008). Our study is the first to find that *O*-alkyl C concentration predicts CO_2 efflux at the global scale across peatlands derived from diverse plant communities with fundamentally different chemistry. We predict that the greatest fluxes from peatland drainage will be from undisturbed moss-dominated peatlands at high latitudes or high elevations rich in *O*-alkyl C. Our findings suggest that electron donors do not limit microbial activity and CO_2 production in *O*-alkyl-C-rich peatlands experiencing drained conditions, where oxygen is the primary electron acceptor and abundant.

Previous studies of temperate and boreal peatlands also linked CO_2 production to polysaccharide composition or *O*-alkyl C (Hribljan et al., 2017; Leifeld et al., 2012; Treat et al., 2014; White et al., 2002). Leifeld et al. (2012) presented a strong positive relationship between *O*-alkyl C and aerobic CO_2 production from a temperate peatland, while other studies reported high CO_2 production from arctic peats containing abundant polysaccharides (Treat et al., 2014; White et al., 2002). Our results support and extend these findings to the global scale, but also suggest that peats high in *O*-alkyl C concentrations have more variability in CO_2 production compared to sites with low *O*-alkyl C concentrations, possibly due to other controls such as the type of organic compounds contributing to the *O*-alkyl C signal, limiting resources for microbial activity, or differences in microbial community composition and associated activity. Decreased CO_2 release at deeper peat may be due to previous utilization of the highest quality C compounds, resulting in less favorable *O*-alkyl C substrates (Hodgkins et al., 2018; Sjögersten et al., 2016).

Linking the global peatland survey and complementary laboratory study, we propose that SOM C chemistry, specifically *O*-alkyl C, can be used to predict risk of increased CO_2 emissions from peatlands in response to drainage or decreased water table depth. Global litter decomposition models derived from studies of upland ecosystems currently focus on lignin/N ratios, but our study identifies *O*-alkyl C as the primary indicator of litter mineralization in peatlands as also shown by Bonanomi et al. (2013). Focusing on this class of C compounds provides a simple parameter with the potential to improve models of peat carbon dynamics in the context of climate change.

Data Availability Statement

The authors declare that the data supporting the findings of this study are available within the paper, its supplementary information files, and at https://figshare.com/projects/Organic_matter_chemistry_drives_carbon_dioxide_production_of_peatlands/118407.

Acknowledgments

The authors are grateful for the peat samples contributed by Nate Basiliko, A. Cheesman, C. Richardson, M.M Svenning, A.S. Enriquez, B. Clarkson, C.W. Schadt, C. Hazard, I. Dickie, E.S. Tuittila, J.A. Farmer, T. Larmola, J.M. McLaughlin, R.K. Kolka, L.I. Harris, L. Bragazza, M. Wang, T.R. Moore, P.Q. Thu, R. Andersen, C. McCalley, L. Tedersoo, R. Varner, C.C. Trettin, M.R. Turetsky, M.P. Waldrop, M. Warren, X. Chen, J.B. Yavitt, Z. Wang, J.A. Hribljan, J. Jauhiainen, M. Könönen, J. Rutherford, T. Ontl, A. Kohlenberg, and S. Juutinen. The authors thank Z. Siders, J. Rocca, K. Curtis, J. Hu, F. Ordonez, J. Chanton, L. Theobald, R. Schwartz, A. Bales, C. Bach, T. Behrmann, S. Harttung, E. Hodges, J. Zwart, K. Griffith, K. Beesley, S. Kelso, and L. Potvin for technical assistance. This material is based upon work supported by the National Science Foundation (NSF) Graduate Research Fellowship under Grant No. (GMO2432) including research travel supported by NSF Graduate Research Opportunities Worldwide and NSF Graduate Research Internship Program. A portion of this work was performed in the McKnight Brain Institute at the National High Magnetic Field Laboratory's AMRIS Facility, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490 and the State of Florida. Any opinion, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of NSF. The authors declare no competing financial interests.

References

Baldock, J., Oades, J. M., Nelson, P. N., Skene, T. M., Golchin, A., & Clarke, P. (1997). Assessing the extent of decomposition of natural organic materials using solid-state ^{13}C NMR spectroscopy. *Australian Journal of Soil Research*, *35*, 1061–1084. https://doi.org/10.1071/s97004

Bonanomi, G., Incerti, G., Giannino, F., Mingo, A., Lanzotti, V., & Mazzoleni, S. (2013). Litter quality assessed by solid state ^{13}C NMR spectroscopy predicts decay rate better than C/N and lignin/N ratios. *Soil Biology and Biochemistry*, *56*, 40–48. https://doi.org/10.1016/j.soilbio.2012.03.003

Bridgham, S. D., Megonigal, P. J., Keller, J. K., Bliss, N. B., & Trettin, C. (2006). The carbon balance of North American wetlands. *Wetlands*, *26*, 889–916. https://doi.org/10.1672/0277-5212(2006)26[889:TCBONA]2.0.CO;2

Campbell, E. E., & Paustian, K. (2015). Current developments in soil organic matter modeling and the expansion of model applications: A review. *Environmental Research Letters*, *10*(12), 123004. https://doi.org/10.1088/1748-9326/10/12/123004

Chavez-Vergara, B., Merino, A., Vázquez-Marrufo, G., & García-Oliva, F. (2014). Organic matter dynamics and microbial activity during decomposition of forest floor under two native neotropical oak species in a temperate deciduous forest in Mexico. *Geoderma*, *235–236*, 133–145. https://doi.org/10.1016/j.geoderma.2014.07.005

Derenne, S., & Tu, T. T. N. (2014). Characterizing the molecular structure of organic matter from natural environments: An analytical challenge. *Comptes Rendus Geoscience*, *346*, 53–63. https://doi.org/10.1016/j.crte.2014.02.005

Di Lonardo, D. P., De Boer, W., Klein Gunnewiek, P. J. A., Hannula, S. E., & Van der Wal, A. (2017). Priming of soil organic matter: Chemical structure of added compounds is more important than the energy content. *Soil Biology and Biochemistry*, *108*, 41–54. https://doi.org/10.1016/j.soilbio.2017.01.017

Evers, S., Yule, C. M., Padfield, R., O'Reilly, P., & Varkkey, H. (2017). Keep wetlands wet: The myth of sustainable development of tropical peatlands – Implications for policies and management. *Global Change Biology*, *23*, 534–549. https://doi.org/10.1111/gcb.13422

Fenner, N., & Freeman, C. (2011). Drought-induced carbon loss in peatlands. *Nature Geoscience*, *4*, 895–900. https://doi.org/10.1038/ngeo1323

Freeman, C., Ostle, N. J., Fenner, N., & Kang, H. (2004). A regulatory role for phenol oxidase during decomposition in peatlands. *Soil Biology and Biochemistry*, *36*, 1663–1667. https://doi.org/10.1016/j.soilbio.2004.07.012

Frolking, S., Talbot, J., Jones, M. C., Treat, C. C., Kauffman, J. B., Tuittila, E. S., & Roulet, N. (2011). Peatlands in the Earth's 21st century climate system. *Environmental Reviews*, *19*, 371–396. https://doi.org/10.1139/a11-014

Granath, G., Moore, P. A., Lukenbach, M. C., & Waddington, J. M. (2016). Mitigating wildfire carbon loss in managed northern peatlands through restoration. *Scientific Reports*, *6*. https://doi.org/10.1038/srep28498

Grover, S. P. P., & Baldock, J. A. (2012). Carbon chemistry and mineralization of peat soils from the Australian Alps. *European Journal of Soil Science*, *63*, 129–140. https://doi.org/10.1111/j.1365-2389.2011.01424.x

Guéguen, C., Burns, D. C., McDonald, A., & Ring, B. (2012). Structural and optical characterization of dissolved organic matter from the lower Athabasca River, Canada. *Chemosphere*, *87*, 932–937. https://doi.org/10.1016/j.chemosphere.2012.01.047

Gumbricht, T., Roman-Cuesta, R. M., Verchot, L., Herold, M., Wittmann, F., Householder, E., et al. (2017). An expert system model for mapping tropical wetlands and peatlands reveals South America as the largest contributor. *Global Change Biology*, *23*, 3581–3599. https://doi.org/10.1111/gcb.13689

Harris, D., & Paul, E. A. (1994). Measurement of bacterial growth rates in soil. *Applied Soil Ecology*, *1*(4), 277–290.

Harrysson Drotz, S., Sparrman, T., Schleucher, J., Nilsson, M., & Öquist, M. G. (2010). Effects of soil organic matter composition on unfrozen water content and heterotrophic CO_2 production of frozen soils. *Geochimica et Cosmochimica Acta*, *74*, 2281–2290. https://doi.org/10.1016/j.gca.2010.01.026

Hodgkins, S. B., Richardson, C. J., Dommain, R., Wang, H., Glaser, P. H., Verbeke, B., et al. (2018). Tropical peatland carbon storage linked to global latitudinal trends in peat recalcitrance. *Nature Communications*, *9*, 3640. https://doi.org/10.1038/s41467-018-06050-2

Hoyos-Santillan, J., Lomax, B. H., Large, D., Turner, B. L., Boom, A., Lopez, O. R., & Sjögersten, S. (2016). Quality not quantity: Organic matter composition controls of CO_2 and CH_4 fluxes in neotropical peat profiles. *Soil Biology and Biochemistry*, *103*, 86–96. https://doi.org/10.1016/j.soilbio.2016.08.017

Hoyt, A. M., Chaussard, E., Seppalainen, S. S., & Harvey, C. F. (2020). Widespread subsidence and carbon emissions across Southeast Asian peatlands. *Nature Geoscience*, *13*, 435–440. https://doi.org/10.1038/s41561-020-0575-4

Hribljan, J. A., Kane, E. S., & Chimner, R. A. (2017). Implications of altered hydrology for substrate quality and trace gas production in a poor fen peatland. *Soil Science Society of America Journal*, *81*, 633–646. https://doi.org/10.2136/sssaj2016.10.0322

Hugelius, G., Loisel, J., Chadburn, S., Jackson, R. B., Jones, M., MacDonald, G., et al. (2020). Large stocks of peatland carbon and nitrogen are vulnerable to permafrost thaw. *Proceedings of the National Academy of Sciences*, *117*(34), 20438–20446. https://doi.org/10.1073/pnas.1916387117

Klingenfuß, C., Roßkopf, N., Walter, J., Heller, C., & Zeitz, J. (2014). Soil organic matter to soil organic carbon ratios of peatland soil substrates. *Geoderma*, *235*, 410–417. https://doi.org/10.1016/j.geoderma.2014.07.010

Knicker, H. (2011). Solid state CPMAS ^{13}C and ^{15}N NMR spectroscopy in organic geochemistry and how spin dynamics can either aggravate or improve spectra interpretation. *Organic Geochemistry*, *42*, 867–890. https://doi.org/10.1016/j.orggeochem.2011.06.019

Kurnianto, S., Warren, M., Talbot, J., Kauffman, B., Murdiyarso, D., & Frolking, S. (2015). Carbon accumulation of tropical peatlands over millennia: A modeling approach. *Global Change Biology*, *21*, 431–444. https://doi.org/10.1111/gcb.12672

Lappalainen, E. (1996). *Global Peat Resources*. International Peat Society.

Lehmann, J., & Kleber, M. (2015). The contentious nature of soil organic matter. *Nature*, *528*, 60–68. https://doi.org/10.1038/nature16069

Leifeld, J., Alewell, C., Bader, C., Krüger, J. P., Mueller, C. M., Sommer, M., et al. (2017). Pyrogenic carbon contributes substantially to carbon storage in intact and degraded Northern Peatlands. *Land Degradation & Development*. https://doi.org/10.1002/ldr.2812

Leifeld, J., & Menichetti, L. (2018). The underappreciated potential of peatlands in global climate change mitigation strategies. *Nature Communications*, *9*, 1071. https://doi.org/10.1038/s41467-018-03406-6

Leifeld, J., Steffens, M., & Galego-Sala, A. (2012). Sensitivity of peatland carbon loss to organic matter quality. *Geophysical Research Letters*, *39*. https://doi.org/10.1029/2012GL051856

Loisel, J., Gallego-Sala, A. V., Amesbury, M. J., Magnan, G., Anshari, G., Beilman, D. W., et al. (2020). Expert assessment of future vulnerability of the global peatland carbon sink. *Nature Climate Change*, *11*, 70–77. https://doi.org/10.1038/s41558-020-00944-0

Mastný, J., Urbanová, Z., Kaštovská, E., Straková, P., Šantrůčková, H., Edwards, K. R., & Picek, T. (2016). Soil organic matter quality and microbial activities in spruce swamp forests affected by drainage and water regime restoration. *Soil Use & Management*, *32*, 200–209. https://doi.org/10.1111/sum.12260

Minasny, B., Berglund, O., Connolly, J., Hedley, C., de Vries, F., & Gimona, A. (2019). Digital mapping of peatlands – A critical review. *Earth-Science Reviews*, *196*, 102870. https://doi.org/10.1016/j.earscirev.2019.05.014

Moyano, F. E., Manzoni, S., & Chenu, C. (2013). Responses of soil heterotrophic respiration to moisture availability: An exploration of processes and models. *Soil Biology and Biochemistry*, *59*, 72–85. https://doi.org/10.1016/j.soilbio.2013.01.002

Normand, A. E., Smith, A. N., Clark, M. W., Long, J. R., & Reddy, K. R. (2017). Chemical composition of soil organic matter in a subarctic peatland: Influence of shifting vegetation communities. *Soil Science Society of America Journal*, *81*, 41–49. https://doi.org/10.2136/sssaj2016.05.0148

Norris, C. E., Dungait, J. A. J., Joynes, A., & Quideau, S. A. (2013). Biomarkers of novel ecosystem development in boreal forest soils. *Organic Geochemistry*, *64*, 9–18. https://doi.org/10.1016/j.orggeochem.2013.08.014

Page, S. E., Rieley, J. O., & Banks, C. J. (2011). Global and regional importance of the tropical peatland carbon pool. *Global Change Biology*, *17*, 798–818. https://doi.org/10.1111/j.1365-2486.2010.02279.x

Reddy, K. R., & DeLaune, R. D. (2008). *Biogeochemistry of wetlands: Science and applications*. CRC Press.

Sjögersten, S., Caul, S., Daniell, T. J., Jurd, A. P. S., O'Sullivan, O. S., Stapleton, C. S., & Titman, J. J. (2016). Organic matter chemistry controls greenhouse gas emissions from permafrost peatlands. *Soil Biology and Biochemistry*, *98*, 42–53. https://doi.org/10.1016/j.soilbio.2016.03.016

Tfaily, M. M., Cooper, W. T., Kostka, J. E., Chanton, P. R., Schadt, C. W., Hanson, P. J., et al. (2014). Organic matter transformation in the peat column at Marcell Experimental Forest: Humification and vertical stratification. *Journal of Geophysical Research: Biogeosciences*, *119*, 661–675. https://doi.org/10.1002/2013jg002492

Todd-Brown, K., Randerson, J. T., Post, W. M., Hoffman, F. M., Tarnocai, C., Schuur, E. A., & Allison, S. D. (2013). Causes of variation in soil carbon simulations from CMIP5 earth system models and comparison with observations. *Biogeosciences*, *10*, 1717–1736. https://doi.org/10.5194/bg-10-1717-2013

Treat, C. C., Wollheim, W. M., Varner, R. K., Grandy, A. S., Talbot, J., & Frolking, S. (2014). Temperature and peat type control CO_2 and CH_4 production in Alaskan permafrost peats. *Global Change Biology*, *20*, 2674–2686. https://doi.org/10.1111/gcb.12572

Turetsky, M. R., Benscoter, B., Page, S., Rein, G., Van Der Werf, G. R., & Watts, A. (2014). Global vulnerability of peatlands to fire and carbon loss. *Nature Geoscience*, *8*, 11–14. https://doi.org/10.1038/ngeo2325

Upton, A., Vane, C. H., Girkin, N., Turner, B. L., & Sjögersten, S. (2018). Does litter input determine carbon storage and peat organicchemistry in tropical peatlands? *Geoderma*, *326*, 76–87. https://doi.org/10.1016/j.geoderma.2018.03.030

Wang, H., Richardson, C. J., & Ho, M. (2015). Dual controls on carbon loss during drought in peatlands. *Nature Climate Change*, *5*, 584–587. https://doi.org/10.1038/nclimate2643

White, D. M., Garland, D. S., Dai, X., & Ping, C. L. (2002). Fingerprinting soil organic matter in the arctic to help predict CO_2 flux. *Cold Regions Science and Technology*, *35*, 185–194. https://doi.org/10.1016/s0165-232x(02)00058-7

Wilson, M. A. (2013). *NMR Techniques & Applications in Geochemistry & Soil Chemistry*. Oxford: Pergamon.

Wright, E. L., Black, C. R., Cheesman, A. W., Drage, T., Large, D., Turner, B. L., & Sjoegersten, S. (2011). Contribution of subsurface peat to CO_2 and CH_4 fluxes in a Neotropical peatland. *Global Change Biology*, *17*, 2867–2881. https://doi.org/10.1111/j.1365-2486.2011.02448.x

Xu, J., Morris, P. J., Liu, J., & Holden, J. (2018). PEATMAP: Refining estimates of global peatland distribution based on a meta-analysis. *Catena*, *160*, 134–140. https://doi.org/10.1016/j.catena.2017.09.010

Zhang, Y., Li, C., Trettin, C. C., Li, H., & Sun, G. (2002). An integrated model of soil, hydrology, and vegetation for carbon dynamics in wetland ecosystems. *Global Biogeochemical Cycles*, *16*. https://doi.org/10.1029/2001GB001838

References From the Supporting Information

Aitchison, J. (1982). The statistical analysis of compositional data. *Journal of the Royal Statistical Society: Series B*, *44*(2), 139–177. https://doi.org/10.1111/j.2517-6161.1982.tb01195.x

Barkovskii, A. L., Fukui, H., Leisen, J., Kim, S. H., Marsh, T. L., & Khijniak, A. J. (2009). Rearrangement of bacterial community structure during peat diagenesis. *Soil Biology and Biochemistry*, *41*, 135–143. https://doi.org/10.1016/j.soilbio.2008.10.006

Bates, D., Maechler, M., Bolker, B., Walker, S., Christensen, R. H. B., Singmann, H., et al. (2017). *Linear Mixed-Effects Models using Eigen and S4*.

Dai, X. Y., Ping, C. L., Candler, R., Haumaier, L., & Zech, W. (2001). Characterization of soil organic matter fractions of tundra soils in arctic Alaska by carbon-13 nuclear magnetic resonance spectroscopy. *Soil Science Society of America Journal*, *65*, 87–93. https://doi.org/10.2136/sssaj2001.65187x

Dixon, W. T., Schaefer, J., Sefcik, M. D., Stejskal, E. O., & McKay, R. A. (1982). Total suppression of spinning sidebands in CPMAS C-13 NMR. *Journal of Magnetic Resonance*, *49*, 341–345. https://doi.org/10.1016/0022-2364(82)90199-8

Dodla, S. K., Wang, J. J., & Delaune, R. D. (2012). Characterization of labile organic carbon in coastal wetland soils of the Mississippi River deltaic plain: Relationships to carbon functionalities. *The Science of the Total Environment*, *435–436*, 151–158. https://doi.org/10.1016/j.scitotenv.2012.06.090

Grover, S. P. P., & Baldock, J. A. (2013). The link between peat hydrology and decomposition: Beyond von Post. *Journal of Hydrology*, *479*, 130–138. https://doi.org/10.1016/j.jhydrol.2012.11.049

Hamdan, R., El-Rifai, H. M., Cheesman, A. W., Turner, B. L., Reddy, K. R., & Cooper, W. T. (2012). Linking phosphorus sequestration to carbon humification in wetland soils by ^{31}P and ^{13}C NMR spectroscopy. *Environmental Science & Technology*, *46*, 4775–4782. https://doi.org/10.1021/es204072k

Hijmans, R. J., Cameron, S., Parra, J., Jones, P., Jarvis, A., & Richardson, K. (2005). *WorldClim, version 1.3*. Berkeley: University of California.

Kaal, J., Baldock, J. A., Buurman, P., Nierop, K. G., Pontevedra-Pombal, X., & Martínez-Cortizas, A. (2007). Evaluating pyrolysis–GC/MS and ^{13}C CPMAS NMR in conjunction with a molecular mixing model of the Penido Vello peat deposit, NW Spain. *Organic Geochemistry*, *38*, 1097–1111. https://doi.org/10.1016/j.orggeochem.2007.02.008

Luan, J., Cui, L., Xiang, C., Wu, J., Song, H., & Ma, Q. (2014). Soil carbon stocks and quality across intact and degraded alpine wetlands in Zoige, east Qinghai-Tibet Plateau. *Wetlands Ecology and Management*, *22*, 427–438. https://doi.org/10.1007/s11273-014-9344-8

Oksanen, J., Blanchet, F. G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., et al. (2017). *Community Ecology Package*.

Pontevedra-Pombal, X., Martinez-Cortizas, A., García-Rodeja, E., Buurman, P., et al. (2001). Composición y transformación de la materia orgánica en un histosol de la serra do xistral (norte de galicia) mediante cpmas 13c-nmr. *Edafologia*, *8*(2), 67–79.

Preston, C. M., Shipitalo, S. E., Dudley, R. L., Fyfe, C. A., Mathur, S. P., & Levesque, M. (1987). Comparison of ^{13}C CPMAS NMR and chemical techniques for measuring the degree of decomposition in virgin and cultivated peat profiles. *Canadian Journal of Soil Science*, *67*, 187–198. https://doi.org/10.4141/cjss87-016

Purwanto, B. H., Watanabe, A., Shoon, J. F., Kakuda, K. J., & Ando, H. (2005). Kinetic parameters of gross N mineralization of peat soils as related to the composition of soil organic matter. *Soil Science & Plant Nutrition*, *51*, 109–115. https://doi.org/10.1111/j.1747-0765.2005.tb00013.x

R Core Team. (2016). *R: A language and environment for statistical computing*. Vienna, Austria. R Foundation for Statistical Computing. Retrieved from http://www.R-project.org/

Soil Survey Staff. (1999). *Soil taxonomy: A basic system of soil classification for making and interpreting soil surveysNatural Resources Conservation Service* (2nd ed.). U.S. Department of Agriculture Handbook 436.

Zech, W., Kögel, I., Zucker, A., & Alt, H. (1985). CP-MAS-13C-NMR-Spektren organischer Lagen einer Tangelrendzina. *Z Pflanzenernähr Bodenkd*, *148*, 481–488. https://doi.org/10.1002/jpln.19851480504