The origin of soil organic matter controls its composition and bioreactivity across a mesic boreal forest latitudinal gradient

Running head: *SOM chemistry along a boreal climate transect*

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Abstract

Warmer climates have been associated with reduced bioreactivity of soil organic matter (SOM) typically attributed to increased diagenesis; the combined biological and physiochemical transformation of SOM. Additionally, cross site studies have indicated that ecosystem regime shifts, associated with long-term climate warming, can affect SOM properties through changes in vegetation and plant litter production thereby altering the composition of soil inputs. The relative importance of these two controls, diagenesis and inputs, on SOM properties as ecosystems experience climate warming, however, remains poorly understood. To address this issue we characterized the elemental, chemical (nuclear magnetic resonance spectroscopy and total hydrolysable amino acids analysis), and isotopic composition of plant litter and SOM across a well-constrained mesic boreal forest latitudinal transect in Atlantic Canada. Results across forest sites within each of three climate regions indicated that (1) climate history and diagenesis affect distinct parameters of SOM chemistry, (2) increases in SOM bioreactivity with latitude were associated with elevated proportions of carbohydrates relative to plant waxes and lignin, and (3) despite the common forest type across regions, differences in SOM chemistry by climate region were associated with chemically distinct litter inputs and not different degrees of diagenesis. The observed climate effects on vascular plant litter chemistry, however, explained only part of the regional differences in SOM chemistry, most notably the higher protein content of SOM from warmer regions. Greater proportions of lignin and aliphatic compounds and smaller proportions of carbohydrates in warmer sites' soils were explained by the higher proportion of vascular plant relative to moss litter in the warmer relative to cooler forests. These results indicate that climate change induced decreases in the proportion of moss inputs not only impacts SOM chemistry but

also increases the resistance of SOM to decomposition, thus significantly altering SOM cycling in these boreal forest soils.

1. Introduction

Soil organic matter (SOM) is the largest pool of reduced carbon (C) in terrestrial ecosystems (Jobbágy & Jackson, 2000). Boreal forests hold a significant part of this global C reservoir (Jobbágy & Jackson, 2000; Lal, 2005; Chapin *et al.*, 2009; Scharlemann *et al.*, 2014) and currently act as a C sink (Vanhala *et al.*, 2016), but will undergo pronounced warming over the next century (Price *et al.*, 2013; van Oldenborgh *et al.*, 2013). The fate of SOM under a warming climate remains a major uncertainty in Earth system models, which disagree on whether terrestrial ecosystems will represent a net source or sink of CO_2 in a warmer future (Friedlingstein *et al.*, 2014). Some of this uncertainty is due to the challenge of separating the various ways in which climate influences SOM properties (Luo, 2007). For example, both plant input chemistry and the rate of biological and physiochemical transformation, or diagenesis, are affected by warming and are known to influence SOM properties, including its turnover rate (Quideau et al., 2001; Melillo et al., 2002). Understanding the relative importance of these two processes is important to uncovering controls and timing of soil C-climate feedbacks.

Tightly connected to past and future climate, the chemical, physical, and biological properties of SOM control the rate at which CO_2 is released from soils – an important climate feedback (Waksman & Gerretsen, 1931; Sollins *et al.*, 1996; Leifeld & Fuhrer, 2005). On time scales of weeks to years, respiration rates increase exponentially with temperature. Conversely, on time scales of decades to centuries, SOM properties including respiration rates are themselves determined by the conditions, including climate, under which a given soil has developed (Zech *et al.*, 1989; Franzluebbers *et al.*, 2001; Pisani *et al.*, 2014). SOM formed under a warmer climate or

exposed to prolonged (multi-year) experimental warming, for example, has been found to be less prone to decomposition, as indicated by a lower bioreactivity, the respiration rate at a given temperature (e.g., R_{10} at 10 ˚C) (Luo *et al.*, 2001; Melillo *et al.*, 2002; Fissore *et al.*, 2008; Laganière *et al.*, 2015). Models based on short-term temperature dependence of respiration that don't incorporate the long-term climate effects are therefore prone to overestimate respiration rates under a warmer climate (Luo *et al.*, 2001).

Differences in SOM chemistry, and thus bioreactivity, among soils formed under distinct climate regimes may originate from differences in the extent of diagenetic alteration, i.e., changes in SOM chemistry over time due to the net effects of biological decomposition, root litter deposition, and physiochemical processes like leaching and aggregation. As bioreactivity typically decreases with diagenesis, different rates of diagenesis could explain the difference in bioreactivity observed along climate gradients. In the organic soil horizons of boreal podzols, diagenesis is dominated by microbial decomposition and the leaching of soluble compounds by percolating precipitation. These two processes are potentially affected by climate, as higher temperatures accelerate biological decomposition and greater precipitation can accelerate leaching (Kalbitz et al., 2000). Soils under different climates can thus develop SOM with distinct biological and chemical properties even if they receive the same plant litter inputs. This is best exemplified by warming experiments which manipulate only the below-ground component of an ecosystem. Soil respiration rates typically decrease after multiple years of warming (Melillo *et al.*, 2002), indicating that the prolonged exposure of SOM to a warmer temperature can decrease its bioreactivity. This decrease in bioreactivity was accompanied by a change in SOM chemistry (Feng *et al.*, 2008; Pisani *et al.*, 2015), most notably increased concentrations of cutin derived compounds, and lower concentrations of lignin and carbohydrates. However, in situ experimental

warming in more C-rich forest soils increased soil respiration without reducing SOM bioreactivity (Streit *et al.*, 2014), while still others detected no change in SOM chemistry (Schnecker *et al.*, 2016) suggesting other diagenetic processes such as leaching and root deposition can regulate SOM composition.

The vegetation cover contributing to a soil (plant species composition, physiology, and productivity) represents a second longer-term influence of climate on SOM. Differences in the quantity and composition of litter inputs, in turn, can explain the distinct SOM chemistry of soils that developed under different climate regimes (Quideau *et al.*, 2001; Vancampenhout *et al.*, 2009). The differences in SOM chemistry observed along an elevation gradient (i.e., different proportions of O-Alkyl-C and Alkyl-C), for example, were also observed when plant communities typical of the different altitude zones were planted in close proximity and thereby exposed to the same climate (Quideau *et al.*, 2001). Such chemical differences may explain the stronger effect of forest type relative to climate on SOM bioreactivity (Fissore *et al.*, 2008; Laganière *et al.*, 2013).

Prior to a change in the dominant species or forest type, climate may still affects either the litter chemistry of the dominant species, or the abundance or composition of litter produced by the understory vegetation. In boreal forests, mosses are often the ecosystem component that is most sensitive to anthropogenic disturbance, including moisture, temperature, and N deposition (Gundale *et al.*, 2011, 2014; Lindo *et al.*, 2013). Latitudinal trends of moss and vascular plant net primary production (Gower *et al.*, 2001; Turetsky, 2003; Porada *et al.*, 2013) suggest that the proportion of moss relative to vascular plant litter may decrease with climate warming in boreal forests. As nonvascular plants, mosses exhibit a chemical composition distinct from vascular plants (Hobbie, 1996; Preston *et al.*, 2006; Lang *et al.*, 2009; Philben *et al.*, 2014). Changes in the proportion of moss and vascular plant litter may therefore represent an important mechanism

through which climate influences SOM chemistry in boreal forests, even when dominant vegetation, defined by tree species, remains the same.

While the short to mid-term temperature dependence of respiration has been well characterized in field and laboratory experiments (Sierra *et al.*, 2014), the longer-term climate effects on SOM properties impacting C cycling remain poorly understood. Climate gradient studies in boreal forest regions have highlighted the role of climate in controlling SOM properties providing insight into long-term effects of warming in these ecosystems (Vucetich *et al.*, 2000; Santruckova *et al.*, 2003; Sjögersten *et al.*, 2003; Kane *et al.*, 2005; Meyer *et al.*, 2006; Preston *et al.*, 2006; Cannone *et al.*, 2008; Norris *et al.*, 2011). It remains unclear, however, if this control is due to climate effects on vegetation input chemistry or altered diagenesis. Soil moisture regime, an important consequence of climate, can impact both the vegetation and SOM diagenesis in boreal forests. It is therefore important to control for differences in moisture regimes along climate transects to identify temperature effects on SOM chemistry. For example, an increased alkyl-C:O-alkyl-C ratio observed with climate warming may indicate an increased diagenetic state of SOM likely due to water limitation of plant productivity combined with increased microbial processing of SOM in warmer continental regions (Preston *et al.*, 2006; Norris *et al.*, 2011). However in wetter forests, the elevated alkyl-C:O-alkyl-C could also result from changes in leaching rates or a shift to a greater proportion of vascular relative to non-vascular plant source of SOM with climate change. Distinguishing between these effects is important because they can impact: (1) The timing of changes in SOM properties, such as its bioreactivity, in response to climate change. SOM properties derived from diagenetic alteration would likely occur over time in a linear fashion, whereas SOM properties linked to a shift in litter inputs would exhibit a threshold change; and (2) The interpretation of SOM stocks and turnover using SOM chemistry which depends upon the

origin of that chemistry. The mesic boreal forests of Atlantic Canada feature a climate gradient in which both mean annual temperature (MAT) and precipitation (MAP) decrease with latitude (Table 1, Supporting Information S1), such that greater evaporative loss of soil water at higher temperatures is compensated by greater precipitation (Ziegler *et al.*, 2017). These forests are, therefore, characterized by similarly high soil moisture across a temperature gradient, enabling the study of effects of increasing temperature in the absence of greater water limitation (Supporting Information S2). Previous work in this transect has shown that SOM bioreactivity in these soils decreases from cold to warm climate (Laganière *et al.*, 2015; Podrebarac et al. 2016; Supporting Information S3). The goal of this study was to determine: (1) To what extent variations in SOM chemistry with climate originate from different litter inputs or different degrees of diagenesis; and (2) What SOM chemical attributes relate to the decreasing SOM bioreactivity with warming.

We explore how the chemical composition of SOM from the organic L, F, and H horizons varies along gradients of climate (latitude) and increasing diagenetic alteration (soil depth), and how such variations could explain the observed differences in SOM bioreactivity. The 'decomposition continuum', the gradient of increasing diagenesis often noted in the study of soil profiles (Melillo *et al.*, 1989), is used here determine how SOM chemistry changes with diagenesis. We then applied this forest site-specific understanding of diagenetic indicators to assess drivers of regional variations in organic horizon SOM chemistry to distinguish between climate effects on diagenesis and vegetation. The organic soil horizons contains a substantial fraction (> 1/3) of the total soil profile SOM (Laganière *et al.*, 2013; M. Patrick, pers. comm.), and represents a key source of organic matter to deeper mineral horizons in boreal forest podzolic soils. Due to the absence of a mineral phase, the persistence of SOM in these soil horizons is the net result of litter inputs and losses due to decomposition and leaching, with chemical stability rather

than physical protection against decomposition (Lützow *et al.*, 2006), controlling losses in response to climate change. This approach, however, is not applicable to the underlying mineral soil given the variation in chemical matrix effects associated with the decreasing SOM to mineral content ratios with depth and the variation in parent material across climate regions.

We compiled a dataset of 16 parameters of SOM chemistry (Table 2) and assigned these parameters to six groups based on how they vary by depth and latitude (Fig. 1). The fact that a parameter that does not exhibit any variation by depth or latitude, for example, indicates that this parameter does not change during diagenesis nor vary with litter inputs along the transect (Fig 1a). Similarly, an increasing (or decreasing) trend with latitude in the absence of a change with depth indicates that climate affects a parameter through changes in litter inputs, whereas the same parameter does not change during diagenesis (Fig 1b). Alternatively, a parameter may change with depth but exhibit no difference among climate regions (Fig. 1c), or exhibit added effects on the same parameter where different litter inputs fix initial differences that are noted throughout the profile as it changes with depth due to increased diagenesis (Fig. 1d). We posit that if regional differences in SOM chemistry resulted from different litter inputs, the diagenesis and latitude effects would act independently and affect distinct parameters of SOM chemistry (Fig 1b, 1c). In contrast, if regional differences are acquired via climate driven differences in diagenesis, we would expect that region and depth would affect the same parameters, and that differences among regions would increase with depth (Fig 1e, 1f)

2. Material and Methods

2.1. Field sites

The Newfoundland and Labrador Boreal Ecosystem Latitudinal Transect (NL-BELT) is a boreal climate transect located in Atlantic Canada. We studied forests in three study regions using

three study sites within each region (Table 1). More southern regions were characterized by both higher MAT (0.0 to 5.2 C) and MAP (1040 to 1570 mm a^{-1}), resulting in similar soil moisture across the transect (Supporting Information S2). Warmer forests furthermore exhibited lower C:N in needle foliage, litter, and soils consistent with accelerated nitrogen (N) cycling and greater N availability in the warmer forests (Philben *et al.*, 2016). These trends are consistent with the anthropogenic changes that are predicted to occur in this ecosystem over the next decades, i.e., higher temperatures, precipitation, and allochthonous N inputs (Gruber & Galloway, 2008; Price *et al.*, 2013; van Oldenborgh *et al.*, 2013). The three sites in each region were selected for their similar forest type and successional stage (mature *Abies balsamea* stands), soil properties (well-drained podzols), and disturbance regime (insect outbreak). None of the sites exhibited evidence of having been harvested or afforested (D. Harris pers. comm.). The sites thus represent incarnations of *A. balsamea* dominated forests that developed under different climate regimes, where understory vegetation developed in accordance with the local climate. Climate effects on SOM chemistry of the L, F and H horizons at these sites are therefore isolated to changes in litter inputs and diagenesis.

2.2. Field sampling

We collected soil samples in June 2011 from three replicate plots (10 m diameter) in each site (n = 27) as described in detail in Laganiere et al. (2015). Briefly, 20x20 cm pieces of the entire organic horizon were collected from three random locations in each plot after all living biomass including green mosses had been removed (see Table 1 for depths). These samples were then manually separated into the L, F, and H soil horizons (Oe, Oa, and Oi horizons in the US soil nomenclature) and pooled into one composite sample per soil horizon and plot. These of 81

samples (27 plots x 3 horizons) were further pooled into 27 samples (9 sites x 3 horizons) for total hydrolysable amino acid and nuclear magnetic resonance (NMR) analyses.

Subsamples of the L horizon material were separated into foliar litter, woody material (including cones), and mosses. The dry mass of each fraction was measured or, when the separation of compacted material was not possible, estimated, and reported to the closest 5%, and when present in traces assigned 1%, or as absent (0%). Foliar, woody, and moss litter were then re-combined and all samples were ground for chemical analysis using a Siebtechnik pulverizer.

Litterfall samples were collected between June 2011 and June 2013 as described in (Ziegler *et al.*, 2017). Briefly, 3 litter traps with an area of 0.34 m^2 were installed at each plot (9 per site). The trapped material was collected at least three times per year and sorted into different types of material (green needles, brown needles, deciduous leaves, twigs, cones). Each fraction was dried and weighed separately. Chemical analysis was conducted on pooled samples representing the annual litterfall input at each plot and site.

2.3. Chemical analysis

2.3.1. Soil organic matter

The carbon and nitrogen content (%C, %N) and their stable isotope ratios ($\delta^{13}C$, $\delta^{15}N$) were analyzed as described in Kohl et al. (2015). Briefly, dried and ground samples were analyzed with a Carlo Erba NA1500 Series II elemental analyzer coupled to a DeltaV Plus isotope ratio mass spectrometer (Thermo Scientific).

Cross polarization, magic-angle spin solid-state NMR (CP-MAS NMR) spectra were obtained using a Bruker AVANCE II 600 MHz with a MASHCCND probe. All samples were run at 600.33 MHz (^1H) or 150.96 MHz (^{13}C) and spun at 20 kHz at 298 K. Spectra were deconvoluted using the software 'DM Fit' based on a 19 component model (Massiot *et al.*, 2002). These peaks

were then assigned to 7 functional groups (alkyl-C, methoxy-C, N-alkyl-C, O-alkyl-C, Di-O-alkyl-C, aromatic C, carboxylic-C) based on Wilson (1987) and Preston et al. (2009) and expressed as a percent of the total area resolved via CP-MAS NMR. We furthermore calculated the alkyl:O-alkyl ratio, which typically increases with diagenesis, as alkyl-C/(O-alkyl-C + di-O-alkyl-C + methoxy-C) (Preston *et al.*, 2009). Spectra are provided in Supporting Information S4.

Concentrations of total hydrolysable amino acids (THAA) were retrieved from Philben et al. (2016). We included four parameters describing abundance and composition of THAA, i.e., the fraction of C and N present in the form of THAA (%C as THAA, %N as THAA); the degradation index (DI) which is derived from the first dimension of a principal component analysis of the composition of THAA as described in Philben et al. (2016) and Dauwe et al. (1999); and the relative abundance of glycine (mol% gly). Organic matter diagenesis has been associated with a decrease in DI and %N as THAA and an increase in mol% gly (Dauwe *et al.*, 1999; Philben *et al.*, 2016).

2.3.2. Litterfall

Samples representing the annual litterfall at each plot were analyzed using the same methods as soil samples described above (EA/IRMS, THAA, CP-MAS NMR). For EA/IRMS, fractions of the litterfall (i.e., green needles, brown needles, deciduous litter, twigs, bark, and cones) were analyzed separately from annually weighted pooled samples obtained at the plot level. For CP-MAS NMR and THAA, a pooled sample representing the annual input of the different types of foliar litterfall (green needles, brown needles, deciduous litter) at each site was analyzed.

Litter traps do not collect moss litter inputs to soils. We therefore estimated the chemical composition of the total above-ground litter input including both moss and vascular plant detritus based on the composition of the L-horizon material. We note that as a measure for inputs to soils,

the L layer composition might overestimate the proportion of more slowly decomposed fractions (moss litter and woody material). However, given the consistent pattern between the L layer moss proportion and estimate of moss cover across sites in all three regions (K. Buckeridge unpubl. data), it is likely a good reflection of moss proportion relative to litterfall input. Chemical composition of foliar litter for each site, and mosses collected in two regions of the transect, and where appropriate literature values for woody material were applied to the L layer proportions to estimate chemical composition of the total above-ground litter input (Supporting information S5).

2.4. Bioreactivity of intact LFH profiles

The SOM bioreactivity of field soils was based on the respiration rates of intact cores of the entire organic soil measured in a separate incubation experiment (Podrebarac *et al.*, 2016). We updated the dataset retrieved from Podrebarac and others (2016) to include previously unpublished results from the incubation of soil cores from the mid latitude region of the climate transect (SR) that were conducted as part of the same larger experiment. The complete dataset used here is comprised of the cumulative respiration of 81 soil cores from 27 sites, incubated for 467 days at 5 °C, 10 °C, or 15 °C and 60% water holding capacity, and is provided in Supporting Information S6.

2.4. Data Analysis

2.4.1. Climate and diagenesis effects on SOM chemistry

To characterize the origin of regional differences in SOM chemistry, that is, differences originating from distinct inputs, distinct diagenesis, or their interaction, we conducted a comparative analysis of the individual parameters of SOM chemistry. In general, we use the terms *region* and *latitude* synonymously along with *depth* and *(soil) horizon*. However, *latitude* and *depth* are used to indicate increasing or decreasing trends with these variables, whereas *region* and *(soil) horizon* are used to indicate differences among the different levels that do not necessarily

indicate a consistent trend (e.g. "differs among soil horizons or transect regions"). First, we applied a two-way analysis of variance (ANOVA) to determine if the parameter differed among soil horizons or regions. We then tested if the differences between regions and/or soil horizons detected by ANOVA represented a consistent increase or decrease with depth or latitude (as opposed to merely random differences among regions and/or soil horizons) by calculating the Spearman's correlation coefficient (ρ) of each parameter with both soil depth and latitude. A ρ close to 0 indicates that the parameter varies independently of depth or latitude, whereas a ρ close to -1 or +1 indicates a monotonic decrease or increase with depth or latitude, respectively. We report test metrics (% variance explained and ρ-values, respectively) regardless of statistical significance to allow for a comparison of region/depth effects on both affected and unaffected parameters. The complete results of these analyses are provided in Supporting Information S7.

To test if the proportions of moss, foliar litter, and woody material in the L layer varied among regions, we used the non-parametric Kruskal-Wallis test followed by a Nemenyi post-hoc test as normality and heteroscedasticity could not be assumed.

2.4.2. Relation between SOM bioreactivity and SOM chemistry

We conducted a correlative analysis to evaluate if the regional variations in SOM chemistry among field sites could explain the observed differences in SOM bioreactivity. We included six parameters of SOM chemistry that varied with latitude (%methoxy-C, %O-alkyl-C, %Di-O-alkyl-C, %alkyl-C, %N, %C as THAA) in this analysis. $\delta^{15}N$ and %C also varied with latitude, but were excluded because $\delta^{15}N$ does not represent a chemical property that directly affects bioreactivity and respiration rates were already normalized to %C. For each parameter, we combined the values measured in the individual soil horizons by calculating a weighted average value for the entire organic layer of each site as described in Supporting Information S8. A multiple regression

analysis to distinguish which of these six parameters had the strongest effect on bioreactivity was not possible because the parameters were inter-correlated (Supporting Information S9). We therefore used the first principal component of the six parameters ('PCA1'), representing 79% of their total variance, as a predictor to evaluate their combined effect on bioreactivity. This was accomplished by calculating the regressions between cumulative respiration (log transformed) and PCA1 for each incubation temperature. We also calculated the fraction of site level variance in cumulative respiration in the complete dataset (all temperature treatments) explained by each of the six parameters as well as by PCA1 (Supporting Information S10). All statistical analyses were conducted using the statistical programming environment R version 3.0.2 (R Development Core Team, 2015).

3. Results

3.1. Chemical composition of isolated soil horizons

The analyzed parameters of SOM chemistry exhibited distinct trends with depth and latitude. Soil C content (%C) decreased with depth and somewhat with latitude (highest in most southern relative to other two regions; Fig. 2a), with a similar decrease in all regions. $\delta^{13}C$ values increased with depth but were unaffected by latitude (Fig 2b), however, the southern sites exhibited a greater increase in $\delta^{13}C$ values. In contrast, soil N content and $\delta^{15}N$ increased with depth but also exhibited a decreasing trend with latitude, though these decreases did not differ by region (Figs. 2c, 2d). Three of the functional groups identified via NMR were affected by latitude, not depth; %methoxy-C decreased with latitude whereas %O-alkyl-C and %di-O-alkyl-C increased with latitude, indicative of lower lignin to carbohydrate ratios in colder regions (2e, 2f, 2g). Three other functional groups were affected by depth, but not latitude; %aromatic-C and %N-alkyl-C decreased with depth, whereas %carboxylic-C increased with depth (Figs. 2h,2i,2j). The %alkyl-

C and alkyl:O-alkyl were affected by both latitude and depth with greater values detected in more southern regions and in deeper soil horizons (Figs. 2k,2l). The increase of Alkyl:O-alkyl with depth appeared stronger in more southern forests, but this difference was marginally non-significant ($p = 0.076$, Supporting Information S7). The %N as THAA and the DI decreased with depth but did not differ between regions (Figs. 2m,2n). Mol% gly increased with depth but did not differ among regions (Fig. 2o), whereas %C as THAA decreased with latitude, but did not change with depth (Fig. 2p).

3.2. Categorization of parameters of SOM chemistry by variance with depth and latitude

The parameters included in this study fell into four groups with regard to how the variance was explained by latitude and depth (Fig 3a) enabling our investigation of the potential source of each as described in Fig. 1. Variables that differ by soil horizon and/or regions typically exhibited a monotonous increase or decrease with depth and/or latitude as indicated by significant Spearman correlations (Figs. 3b, 3c). Region and soil horizon explained more than 68% of the variance of all parameters with the exception of %C (46%) and %aromatic-C (39%) (Supporting Information S7).

The three NMR parameters representing the relative carbohydrate and lignin content (%O-alkyl-C, % di-O-alkyl-C, %methoxy-C) were explained by latitude alone (Fig 3a). None of these parameters exhibited a monotonous increase or decrease with depth (Fig 3b), but %O-alkyl-C and %di-O-alkyl-C increased with latitude, whereas %methoxy decreased with latitude (Fig 3c). In contrast, the variations in %carboxylic-C, $\delta^{13}C$, %aromatic, THAA composition (DI and mol% gly), %N as THAA, and %N-alkyl-C were all explained by depth alone. Three of these parameters exhibited a monotonous increase with depth (%carbonyl−C, $\delta^{13}C$, and mol% gly; Fig 3b) and the other four a monotonous decrease (%aromatic-C, DI, %N as THAA, %amino-C; Fig 3b), but none of these parameters increased or decreased with latitude (Fig 3c).

The variances in soil %C, %N, %alkyl-C, $\delta^{15}N$, %C as THAA, and alkyl:O-alkyl were explained by both latitude and depth, but did not exhibit a significant interactive effect of latitude and depth. Four of these parameters exhibited a monotonous increase with depth (%N, $\delta^{15}N$, and alkyl:O-alkyl; Fig 3b) while %C decreased with depth, and all six parameters exhibited a significant decrease with latitude (Fig 3c).

Noteworthy, the latitude and depth interaction (LxD) explained only a small fraction of the total variance of all studied parameters (<14%). Furthermore, only two parameters ($\delta^{13}C$ and DI) exhibited a significant LxD effect (Fig. 1e, 1f), which would indicate that the regional differences in SOM chemistry either become larger (differential diagenetic alteration) or converge with increasing decomposition associated with organic horizon depth. However, only $\delta^{13}C$ exhibited a consistent trend having increased more steeply with depth in the more northern soils. The DI exhibited a steeper decrease from L to F horizons in more southern sites, where as the opposite effect was observed from F to H horizons.

Taken together, the studied parameters thus primarily exhibited the patterns expected if latitude and diagenesis were to affect SOM chemistry independently (Fig. 1b-d), indicating that regional differences in SOM chemistry were largely driven by different inputs to SOM, not by differential diagenesis.

3.3. Evidence for effects of SOM chemistry on its bioreactivity

The first principal component (PCA1) of the six main parameters varying by latitude (%methoxy-C, %O-alkyl-C, %Di-O-alkyl-C, %alkyl-C, %N, %C as THAA) explained 46.7% of the variance in bioreactivity at the site level (Supporting Information 10). This predictor thus explained a similar fraction of variance in SOM bioreactivity as the factor ‘region’ (54.4%). Bioreactivity was negatively correlated to PCA1 for soil cores incubated at 15˚C (R=-0.78,

p=0.014) and 10 °C (R= -0.67, p=0.050). In soil cores incubated at 5˚C, the relation between PCA1 and bioreactivity followed the same trend but did not exhibit a significant correlation (R=-0.48, p=0.190) due to the higher variance among individual soil cores (Fig. 4a). Due to the strong inter-correlation among the six parameters of SOM chemistry that varied by latitude (all R > 0.46; Supporting Information S9), we could not determine which of the parameters may individually explain the differences in bioreactivity. This group of six parameters, however, collectively explained the observed differences in SOM bioreactivity among transect regions.

In contrast to bioreactivity, temperature sensitivity of respiration of intact soil horizons (Q_{10}) did not significantly vary among the transect regions (Supporting Information S6), and Q_{10} values were not correlated with PCA1 (Fig 4b).

3.4. Composition of litter inputs to soils

The litterfall, which included vascular plant litter but not moss litter, did not exhibit significant differences among the three regions for the majority of chemical parameters (%C, $\delta^{13}C$, %N as THAA, DI, mol% gly, and all functional groups in NMR spectra; Fig. 2). In the southern sites, however, litterfall exhibited higher %N, $\delta^{15}N$, and %C as THAA values (Figs. 3d, 2d, 2p) and lower C:N (not shown). Differences in the chemical composition of the litter collected in litter traps thus explained the higher nitrogen and protein abundance, but not the higher relative concentrations of lignin and aliphatic compounds or lower concentrations of carbohydrates in SOM from more southern sites.

The composition of L layer material differed among regions, with greater proportions of foliar litter and smaller proportions of moss litter in warmer compared to colder region soils (Fig. 5). Based on these proportions, we estimated that warmer soils receive total litter inputs (moss, foliar litter, and woody material) with lower proportions of O-alkyl-C and di-O-alkyl-C, and higher

proportions of alkyl-C and methoxy-C, and therefore exhibit higher alkyl:O-alkyl (Total litter in top panel of Figs. 2e, 2f, 2g, 2k, 2l). For %O-alkyl-C, %di-O-alkyl-C, %alkyl-C, and alkyl:O-alkyl, the differences among regions in total litter inputs were similar to those observed in L-horizon SOM. This is despite the higher proportions of O-alkyl-C and lower proportions of alkyl-C observed for litter inputs compared to L-horizon SOM in all regions (Figs. 2f, 2g, 2k, 2l). For %methoxy-C, the difference observed in L-horizon SOM between the two most extreme regions was more than twice our estimate for the difference among total litter inputs across regions. The %methoxy-C in L horizon SOM was 67% higher in the warmest compared to the coolest region, whereas total litter inputs exhibited only 26% higher %methoxy-C in the warmest region; Fig 2e).

Given these litter input results, the parameters describing regional differences in SOM fell into three groups in regards to whether differences in SOM were also reflected in the litter inputs or not. Regional differences in SOM parameters dependent on N concentrations (%N, %C as THAA) and $\delta^{15}N$ could be explained by chemically different vascular plant litter. In contrast, the regional differences in %O-alkyl-C, %di-O-alkyl-C, %alkyl-C, and alkyl:O-alkyl of SOM could be explained by the different proportions of moss and vascular litter. The differences in SOM %methoxy-C, however, were only partially explained by differences in litter chemistry (Fig. 2).

4. Discussion

4.1. SOM chemistry is largely determined by litter inputs, not diagenesis

Our study demonstrated that even in the absence of a change in dominant over-story vegetation, climate-driven changes in SOM properties can be primarily mediated through aboveground processes that lead to different litter inputs, rather than through climate effects on SOM diagenesis. If regional differences in SOM chemistry were to develop over time due to diagenetic alteration under different climatic conditions, as suggested by some *in situ* warming

experiments (Melillo *et al.*, 2002; Feng *et al.*, 2008; Pisani *et al.*, 2015), we would have expected (1) latitude (region) to affect the same parameters of SOM chemistry as diagenesis (depth), and (2) these regional differences to increase with greater diagenetic alteration exhibited from shallow to deeper soil horizons (Fig. 1e, 1f). Most parameters of SOM chemistry that varied with latitude, however, were different from those that varied with diagenesis and signified the major control of litter inputs on climate induced changes in SOM chemistry in these forests (Fig. 3). Of those remaining parameters that did vary with both depth and climate, only two ($\delta^{13}C$ and DI) exhibited a significant depth by latitude interaction. These two parameters though did not consistently indicate increased diagenetic alteration with depth with decreasing latitude. For example, the SOM $\delta^{13}C$ exhibited a greater increase with depth in the highest relative to lowest latitude soils suggesting a greater degree of diagenetic alteration of SOM with depth in the coldest and not the warmest forests. The DI, decreased to a greater extent from L to F horizons in the warmer relative to colder forests, but exhibited the opposite trend from F to H horizons indicating an increased level of diagenetic alteration at lower latitude but isolated to near surface horizons.

Our results are consistent with cross-site studies indicating that differences in vegetation, and thus litter inputs, affect SOM chemistry more strongly than other differences associated with climate (Quideau et al., 2001). This finding bears two important consequences that will improve our understanding of how climate will affect SOM in these mesic forests. First, changes in SOM properties might not happen linearly with temperature, but rather occur at threshold levels driven by changes in vegetation. Second, these changes will occur first in soil horizons that receive fresh plant inputs, and affect deeper soil layers as new SOM is transported down profile.

SOM stocks within underlying mineral soils often respond similar to topsoils to climate (Kane *et al.*, 2005; Hicks Pries *et al.*, 2017) despite having been exposed to diagenesis under

different climates for longer periods. It is, however, important to bear in mind that results from these organic soil horizons (LFH) do not preclude the potential for diagenesis as an important mechanism of climate effects on mineral soil SOM. In particular, the marginally non-significant latitude by depth interaction observed for both di-O-alkyl and alkyl:O-alkyl (Supporting Information S7) in the relatively young organic soil horizons may signify a potential role of diagenetic processes in controlling deeper soil SOM.

We purposefully limited our study to the organic horizons, which represent >1/3 of total SOM in these soil profiles, and are most rapidly affected by a change in climate including altered inputs. Due to this focus, our study did not investigate how climate might affect important processes of SOM diagenesis and stabilization in the underlying mineral horizon like adsorption on mineral surfaces or incorporation into soil aggregates (Lützow et al., 2006). Instead our study covered a range or diagenetic processes that occur in the organic soil horizon including microbial decomposition and leaching. In spite of similar moisture regimes, southern sites were exposed to higher precipitation rates, which could have led to increased leaching of more hydrophilic compounds from soils. This, however, was not supported by our data, as all sites exhibited similar profiles of SOM geochemistry.

The focus on organic soil horizons furthermore enabled us to directly compare chemical parameters by depth and climate region not possible with or among mineral soil horizons due to unresolved matrix effects and low SOC content. Procedures required to isolate SOM from the mineral soil matrix prior to NMR analysis (Schmidt *et al.*, 1997) typically only provide 35-51% of the total SOM, and exhibit much lower signal to noise ratios relative to organic horizon SOM as noted in the mineral soils of these sites (Warren and Ziegler 2017). Future efforts to generate

comparable soil fractions among soil horizons varying in mineral content and composition will aid in the application of the conceptual framework presented herein to deeper soil horizons.

4.2. The diagenetic state of SOM did not vary with climate

The SOM of the mesic forests studied here did not exhibit indices of increased diagenetic alteration with climate warming. This contrast to previous studies of continental boreal forest climate transects (Kane *et al.*, 2005; Norris *et al.*, 2011) reiterates the importance of water availability in controlling the impact of climate warming on SOM. In spite of the different climates in the three regions studied, all chemical parameters of SOM that changed with depth (%C, $\delta^{13}C$, %N, %carboxylic-C, %aromatic, %alkyl-C , %N-alkyl-C, alkyl:O-alkyl, DI, mol% gly, %N and %C as THAA), with the exception of $\delta^{13}C$ and DI, exhibited a similar change with depth in all regions, and most did not differ among regions. In contrast, SOM in soil profiles of more southern, warmer Jack Pine forests in continental Canada exhibited chemical signatures of SOM (low C:N, high $\delta^{13}C$) indicative of increased diagenetic alteration relative to more northern, cooler forests (Norris *et al.*, 2011). Similarly, the decreases in labile fractions accompanied by elevated $\delta^{13}C$ in dense fractions of SOM with MAT in black spruce forests in interior Alaska indicate that a warmer climate led to more diagenetically altered and likely less bioreactive SOM (Kane et al., 2005).

The different response of SOM chemistry and stocks to climate warming between the mesic boreal forests studied here and previously studied continental boreal forests stresses the need for regional understanding (e.g. drier, inland versus mesic, coastal) of forest soil responses to climate change. While continental forest SOM stocks are observed to decrease from colder to warmer climates (Kane *et al.*, 2005; Norris *et al.*, 2011), SOM stocks in mesic boreal forests appear to be retained overall and even increase (Ziegler et al., 2017). It is this balance between inputs and losses in these forests that likely led to the similarity in chemical parameters associated with diagenetic

alteration observed along this transect. Since plant productivity is more sensitive to water limitation than decomposition (Van der Molen *et al.*, 2011), SOM stocks are vulnerable to net losses when warming leads to decreases in tree productivity due to drought, while decomposition continues or even increases due to greater temperature. Changes in SOM associated with this imbalance will occur with chemical indices of greater diagenetic alteration and a decrease in bioreactivity, as more labile SOM components are preferentially decomposed while those more resistant to decomposition accumulate (Norris *et al.*, 2011). The warming response of the mesic forests in our study is different likely because tree productivity is not water limited and is predicted to increase with projected warming for this region in the coming century (Charney et al. 2016; D'Orangeville et al. 2016). Furthermore, nutrient availability to support that productivity appears to increase with warming in these forests (Philben et al. 2016) enabling productivity that compensates for the accelerated decomposition with warming (Ziegler et al. 2017). SOM stocks therefore remain stable in contrast to more dry continental boreal forest ecosystems. Consequently, the decreased SOM bioreactivity observed with warming in these mesic forests was not the result of accelerated diagenesis but rather a shift in vegetation inputs.

The chemical signatures of diagenesis along depth gradients found in this study were consistent with those typically associated with increasing diagenetic alteration. Increases in $\delta^{13}C$ and $\delta^{15}N$ and decreases in C:N with diagenesis are commonly observed in soils and other environments (Nadelhoffer & Fry, 1988). The decrease in %N-alkyl-C with depth and changes in the composition of THAA with depth, observed as decreases in the THAA-based DI and the increase in mol% glycine, have been associated with the microbial processing of organic matter in a range of terrestrial and aquatic ecosystems (Hedges *et al.*, 1994; Dauwe *et al.*, 1999; Shen *et al.*, 2014; Philben *et al.*, 2016). Our results thus suggest that decadal scale changes to SOM chemistry

in the organic horizons of these forests are primarily associated with a change in the soil organic nitrogen (SON) pool. However, the majority of these SON indices (%N as THAA, DI, mol% gly) did not vary with latitude while those that did vary by latitude (%N, $\delta^{15}N$) also exhibited latitude effects in the litter inputs congruent with these trends.

In contrast with SON, most parameters of SOC measured exhibited relatively few observable net changes during diagenesis as signified by a change with depth. However, they did provide congruent evidence for the role of litter inputs in regulating climate effects on SOM chemistry in these forests. The depth increases in %carboxylic C and %alkyl-C observed are congruent, respectively, with the oxidation of functional groups and accumulation of hydrophobic compounds (i.e., plant waxes) during diagenesis (Baldock *et al.*, 1992; Quideau *et al.*, 2000). Accumulation of these functional groups is also consistent with the leaching of more water soluble compounds from the organic layer supported by the large soil dissolved organic C fluxes observed in these precipitation-rich climates (Ziegler *et al.*, 2017). Although some variation in these two measures was explained by climate region no significant climate region by depth interaction was observed indicating little evidence for differential diagenesis with climate. In contrast with %alkyl-C and %carboxylic-C, the relative abundance of C functional groups (%O-alkyl-C, %di-O-alkyl-C, and %methoxy-C) representing lignin and carbohydrates, the most abundant macromolecules in plant litter, did not change with depth. This stands in contrast to the retention of lignin and loss of carbohydrates that typically occurs during litter decomposition (Preston *et al.*, 2009). Instead, the significant effect of latitude on these three parameters further supports the important role of source and composition of litter inputs in regulating climate effects on SOM chemistry in these forests.

4.3. Regional differences in SOM chemistry resulted from differences in moss source and N content of litter

Despite being within a highly constrained transect where sites were selected for the same forest type, climate effects on vegetation had a stronger net effect on SOM chemistry compared to climate effects on soil diagenesis. This underscores the need for delineating soil inputs to understand the response of soil biogeochemistry to a warming climate. Three central mechanisms through which climate and associated N availability likely caused the chemical composition of litter inputs to differ among regions were identified and likely control the changes in SOM chemistry of mesic boreal forests in the future.

(1) **Chemically distinct vascular plant litter.** SOM from colder regions 'inherited' lower protein contents and lower $\delta^{15}N$ values from the vascular plant litter, explaining the lower %N, %C as THAA, and $\delta^{15}N$ values in SOM from colder relative to warmer sites. Higher $\delta^{15}N$ values and lower C:N ratios in SOM from warmer sites, therefore, should not be interpreted as more decomposed SOM. Rather, the decrease in %N with latitude likely resulted from greater foliar N resorption during needle senescence (F. Podrebarac, pers. comm.) in response to lower N availability at the cooler sites (Philben *et al.*, 2016) consistent with a global trend towards greater N limitation in high latitude ecosystems (Zechmeister-Boltenstern *et al.*, 2015).

(2) **Different proportions of vascular plant versus moss litter.** The higher proportion of moss litter relative to needle litter in cooler climate forests (Fig. 5) led to SOM that was chemically more similar to moss litter. Compared to vascular plants, mosses contain higher proportions of carbohydrates and lower proportions of aliphatic compounds (waxes) and no guaiacyl- and syringyl-type lignins (Kögel-Knabner, 2002). Higher proportion of moss inputs thus explained the higher proportions of O-alkyl-C and di-O-alkyl-C, and the lower proportion of alkyl-C in SOM in

the cooler sites. This is furthermore supported by the fact that none of these parameters differed among the needle litter from the different regions (Fig. 2). Greater moss inputs also led to lower lignin contents in the cooler forests, however, the differences in the proportion of moss relative to vascular plant litter could not entirely explain the difference in %methoxy-C observed in SOM among regions (Fig. 2e).

(3) **Distinct changes in litter chemistry during initial litter diagenesis.** The majority of litter mass is lost during initial stages of decomposition, with only a small fraction (20 - 30%) of the litter input incorporated into organic layer SOM (Berg *et al.*, 1996; Prescott, 2010). Environmental conditions affect which chemical components of the initial litter are preferentially decomposed, and which remain to be incorporated into SOM (Wickings *et al.*, 2012). High N availability has been shown to inhibit the degradation of lignin (Jeffries *et al.*, 1981; Melillo *et al.*, 1989); higher N concentrations in southern regions thus could have led to a stronger accumulation of lignin during the initial litter decomposition stage explaining the high proportions of %methoxy-C found in the southernmost region compared to our estimate for total litter inputs in that region. Such effects, however, must have been limited to early litter decomposition, as %methoxy-C values did not exhibit a significant change with depth across the L, F, and H horizons. Furthermore, greater precipitation and soil DOC fluxes (Ziegler et al. 2017), likely results in greater leaching of water soluble compounds in more southern regions, potentially explaining the (non-significant) stronger enrichment of alkyl-C with depth in the warmer forests.

4.4. Moss contributions mediate the climate effect on SOM chemistry and its bioreactivity

Taken together our results suggest that climate-driven differences in litter chemistry determined by the proportion of moss and vascular plant litter had the greatest influence on SOM bioreactivity in these mesic boreal forests. The inter-correlation among these parameters, however,

prevented us from identifying *which* chemical properties are responsible for the increase in bioreactivity with latitude. Instead, we evaluated if this relationship is consistent with the current understanding of the effects of different SOM properties on decomposition.

Consistent with carbohydrates being metabolically favorable compared to that of lignin and plant waxes (Lützow *et al.*, 2006; Moorhead *et al.*, 2013; Kuzyakov *et al.*, 2015), the bioreactivity of SOM increased with the proportion of carbohydrates (%O-alkyl-C and %di-O-alkyl-C) and decreased with the proportion of lignin (%methoxy-C) and aliphatic compounds (%alkyl-C). Surprisingly, bioreactivity decreased with %N and THAA as %C. Elevated N concentrations can alleviate the N limitation of microbial decomposers in organic soil horizons (Mooshammer *et al.*, 2014), and are associated with increased rates of decomposition and therefore SOM bioreactivity (Briones *et al.*, 2014). The opposite trend observed in our study signifies the key role of C chemistry in regulating soil respiratory responses. Despite the lack of variation in Q_{10} of soil respiration in the intact soil cores studied here, previous results indicate that the lower soil bioreactivity observed here in the warmer forests may coincide with higher Q_{10} values relative to the coldest forests (~4 versus ~3, respectively; Podrebarac et al. 2016). Such an increase in Q_{10}, however, would only partially compensate for the 19.4% reduction in soil respiration due to the lower SOM bioreactivity in warmer forests. Under site conditions, respiration rates at a given temperature would remain higher in the coldest than in the warmest region even if Q_{10} values were to increase from 3 to 4 from cold to warm forests (Supporting Information S11).

Our results emphasize that the proportions of nonvascular and vascular plant litter are a key parameter driving the chemical and thereby biological properties of SOM in these forests. SOM was degraded faster, under controlled conditions, if it was derived to a larger extent from moss litter relative to vascular plant litter. This finding stands in contrast to the slower

decomposition rates of fresh moss litter relative to vascular plant litter in both field (litterbag) and laboratory studies (Hobbie, 1996; Lang *et al.*, 2009; Hagemann & Moroni, 2015; S. Butler, pers. comm.). Given what we observed, the moss litter properties responsible for initially slow or inhibited decomposition are likely lost over time. A number of moss species have been shown to produce antimicrobial compounds (Banerjee & Sen, 1979; Basile *et al.*, 1999; Dey & De, 2011; Nikolajeva *et al.*, 2012). Perhaps these compounds are leached out of moss litter during initial decomposition, leaving behind moss-derived SOM that is chemically more labile than vascular plant-derived SOM in later stages of decomposition.

The climate induced changes in moss versus vascular plant inputs and its ramifications for SOM chemistry and bioreactivity stress the importance of accounting for moss litter inputs which are often missed using typical litter trap methods. Moss NPP accounts for on average 20% of the total NPP of upland boreal forests (Turetsky *et al.*, 2010). However, this value varies considerably across forest stands (Bisbee *et al.*, 2001; Gower *et al.*, 2001) in response to humidity, nutrient availability, and vegetation (Vitt, 1990; Lindo *et al.*, 2013; Gundale *et al.*, 2014). Locally, moss NPP can exceed vascular plant NPP (Bonan & Van Cleve, 1992; Frolking *et al.*, 1996; Gower *et al.*, 1997, 2001). Relative to vascular plants, quantifying moss NPP is difficult, labor intensive, and prone to errors (Yuan *et al.*, 2014). Moss litter production therefore remains poorly constrained for most boreal ecosystems (Porada *et al.*, 2013). Moss NPP, however, shows little variation with latitude across mesic boreal ecosystems (Turetsky, 2003; Elbert *et al.*, 2012; Porada *et al.*, 2013), whereas vascular plant NPP in boreal forests strongly decreases with latitude (Gower *et al.*, 2001). It is, therefore, likely that the decrease in proportion of moss litter relative to plant litter with a warmer climate found in this transect is representative of mesic boreal forests in general. Our results show that such a change might cause a decrease in SOM bioreactivity in a warmer future,

representing a mechanism by which soil respiration rates can be reduced following initial short term temperature responses.

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6. Author contributions

LK and SZ designed the study. KE designed and led the litter sampling campaigns and processing, JW coordinated and led the sample analyses. LK analyzed and integrated the datasets supported by MP and FAP. LK and SZ wrote the manuscript with contributions from all co-authors.

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Tables:

Table 1. Location and characteristics of field sites studied herein. Table updated from Kohl *et al.* (2015) and Ziegler *et al.* (2017).

Region	Site	Latitude	Longitude	Elevation	MAT[1]	MAP[1]	PET[1]	Tree species	Litter-fall[2]		Basal area[2]		SOM in LFH[2]		LFH depth[2]		Soil type
				(m)	*(C)*	*(mm a^{-1})*	*(mm a^{-1})*		*(kg ha^{-1} yr^{-1})*		*(m^2 ha^{-1})*		*(kg SOM-C m^{-2})*		*(cm)*		
Eagle River (Cold)	**Muddy Pond (MP)**	53°33'01"N	56°59'13"W	145	0.0	1074	432	*Abies balsamea*	1815		37.2		2.43		9.8		Humo-ferric podzol
	Sheppar's Ridge (SR)	53°03'25"N	56°56'02"W	170	0.0	1074	432	*Abies balsamea*	1992	a	50.1	a	2.16	a	7.9	ab	Humo-ferric podzol
	Harry's Pond (HP)	53°35'12"N	56°53'21"W	136	0.0	1074	432	*Abies balsamea*	2380		38.2		1.95		7.4		Humo-ferric podzol
Salmon River (Mid)	**Hare Bay (HB)**	51°15'21"N	56°8'18"W	31	2.0	1224	489	*Abies balsamea*	4686		45.4		3.13		9.9		Humo-ferric podzol
	Tuckamore (TM)	51°9'51"N	56°0'15"W	16	2.0	1224	489	*Abies balsamea*	3213	ab	39.2	a	3.15	ab	8.7	a	Humo-ferric podzol
	Catch-A-Feeder (CF)	51°5'21"N	56°12'16"W	38	2.0	1224	489	*Abies balsamea*	19421[3]		34.0		2.51		9.7		Humo-ferric podzol
Grand Codroy (Warm)	**Slug Hill (SH)**	48°00'39"N	58°54'16"W	215	5.2	1505	608	*Abies balsamea*	4562		48.3		2.88		8.1		Humo-ferric podzol
	Maple Ridge (MR)	48°00'28"N	58°55'14"W	165	5.2	1505	608	*Abies balsamea*	4007	b	44.7	a	3.23	b	7.9	b	Humo-ferric podzol
	O'Reagan's (OR)	47°53'36"N	59°10'28"W	100	5.2	1505	608	*Abies balsamea*	5374		50.1		2.91		8.3		Humo-ferric podzol

[1]MAT; mean annual temperature; MAP, mean annual precipitation; PET, annual potential evaporation. Meteorological data represent climate normals of 1981-2010 from Cartwright, NL; Main brook, NL; and Doyles, NL weather station and was taken from Environment

Canada (2014). Potential evaporation was calculated according to Xu and Singh (2001) based on monthly temperature and precipitation normals.

[2] Letters indicate significant differences among transect regions. Litterfall was collected from June 2011 to June 2013 as described herein. Soil C stocks from Ziegler *et al.*, (2017).

[3]Field site affected by extreme windfall event.

Table 2: Soil organic geochemical parameters measured in this study.

Method	Abbreviation	Parameter	Unit	Significance	Reference
Elemental Analysis	%C	Carbon content	%		
	$\delta^{13}C$	Stable C isotope value	‰	Typically increases with decomposition	1
	%N	Nitrogen content	%	Typically increases relative to C with decomposition	
	$\delta^{15}N$	Stable N isotope value	‰	Typically increases with decomposition	1
CP-MAS NMR[a]	%Methoxy-C	Relative abundance of methoxy-C	%	Indicative of lignin content	2
	%O-Alkyl-C	Relative abundance of O-alkyl-C	%	Indicative of carbohydrate content	2
	%Di-O-Alkyl-C	Relative abundance of Di-O-alkyl-C	%	Indicative of carbohydrate content	2
	%Aromatic-C	Relative abundance of aromatic C	%	Indicative of aromaticity	2
	%N-Alkyl-C	Relative abundance of N-alkyl-C	%	Indicative of protein content	2
	%Carboxylic-C	Relative abundance of carboxylic-C	%	Indicative of carboxylic acid content	2
	%Alkyl-C	Relative abundance of alkyl-C	%	Indicative of plant waxes and other aliphatic compounds	2
	Alkyl-C:O-Alkyl-C	Alkyl-C to O-alkyl-C ratio		Typically increases with decomposition	2
Total hydrolyzable amino acids (THAA)	%N as THAA	Fraction of N present as amino acid	%	Typically decreases with decomposition	3
	DI	Degradation Index (DI)		Typically decreases with decomposition	3
	Mol% Glycine	Fraction of glycine among all amino acids	mol%	Typically increases with decomposition	3
	%C as THAA	Fraction of C present as amino acid	%	Indicative of bioreactivity	3

References: 1, Nadelhoffer & Fry, 1988; 2, Preston *et al.*, 2000, 2009; 3, Hedges *et al.*, 1994; Dauwe & Middelburg, 1998; Shen *et al.*, 2014; Philben *et al.*, 2016

[a]Note each parameter measured via NMR is only indicative as a relative measure based on total C observed with the technique and therefore not fully quantitative.

Figure captions:

Figure 1. Conceptual figure depicting how a parameter of SOM chemistry would vary with depth and latitude (climate region given as Cold, Mid., Warm) if it was not affected by diagenesis or changing inputs (a), changed with climate due to changes in litter inputs (b) or changed with diagenesis (c). Changing inputs and diagenesis could furthermore independently act on the same parameter (d). Diagenetic alteration might also depend on climate, both in the absence (e) or presence (f) of regionally distinct litter inputs. We posit that if climate region differences result from different inputs, we expect some parameters to be affected by inputs, but not diagenesis, and thus to vary with latitude only (b), while other parameters would be affected by diagenesis and thus vary with depth only (c). Both scenarios allow for parameters that are affected by both depth and latitude (d). Differences acquired during diagenesis would be indicated by regional differences increasing with exposure time (and thus with depth), as indicated by an effect of depth and latitude (e, f).

Figure 2. Depth profiles of parameters of SOM chemistry. (a-d) carbon and nitrogen concentrations and carbon and nitrogen stable isotope values; (e-l) relative abundance of functional groups as determined via CP-MAS NMR; (m-p) parameters describing the concentration and composition of total hydrolysable amino acids (THAA; data from Philben and others (2016)). Colors indicate study region: black indicates northernmost, coldest region; dark grey the middle region; and light grey the southernmost, warmest region. Litterfall refers to the measured litter samples collected in litter traps while total litter refers to the estimate for all surface inputs to SOM chemistry taking into account foliar litter, woody litter, and moss litter (see Supporting Information S5). The L,F,H, organic soil horizons are analogous to the Oi, Oe, and Oa in the U.S. soil classification scheme.

Figure 2. Parameters of soil organic matter chemistry grouped according to how they vary with depth, latitude, or both. Parameters for which these two factors together explained less than 50% of the total variance were excluded. (a) Fraction of variance of each parameter explained by the factors soil horizon (grey), region (black) and their interaction (light grey). Spearman correlation coefficient (ρ) between the parameter and depth (b) or latitude (c) where a ρ close to +1 or -1 indicates a monotonous increase or decrease, respectively, of the parameter with depth or latitude, while a ρ close to 0 indicates independence of the parameter from depth or latitude. Filled bars (black or grey) indicate a significant correlation ($p<0.05$) while open bars signify no significant correlation ($p>0.05$). Abbreviation for glycine (gly), the total hydrolyzable amino acid (THAA) content and the degradation index (DI) based upon THAA are used on the left hand side of the figure.

Figure 3. Effect of SOM chemistry on the bioreactivity (a) and temperature sensitivity of respiration (b) of SOM of intact soil cores of the organic horizon soil from all study sites. PCA1 represents the first principal component of six measured parameters of SOM chemistry that differed with latitude. For each parameter, the weighted mean among L, F, and H horizons was calculated for each site (see Supplemental Information S5). PCA1 explained 79% of the total variance of these six parameters. The regression between PCA and the cumulative respiration was calculated separately for each incubation temperature (open symbols, 5 °C; grey symbols, 10 °C; black symbols, 15 °C). The regions are depicted as circles, cool region; squares, mid region; diamonds, warm region. Note the logarithmic scale of the dependent variable (cumulative respiration). The variables used to generate the PCA and their factor loadings versus PCA1 are stated on top of the figure. Solid lines represent linear regressions where a significant correlation was detected, dashed lines represent linear trends where no correlation was detected.

Figure 4. Composition of L layer material by region. L layer material was separated into foliar litter, woody material and moss litter. Fractions were estimated to the closest 5%. Letters indicate significant differences among regions. Bold vertical lines indicate median values, boxes the interquartile range, and whiskers the minimum and maximum values (n = 9 per region). Open circles indicate outlying values (> 1.5 time the interquartile range difference to lower or upper quartil

Supporting Information captions

Supporting Information S1. Map of field sites.

Supporting Information S2. Soil temperature and volumetric water content.

Supporting Information S3. R10 and Q10 values of isolated soil horizons.

Supporting information S4. CP-MAS NMR spectra of soil organic matter and litter samples.

Supporting information S5. Estimated chemical composition of total litter inputs.

Supporting information S6. Bioreactivity of intact soil cores of L, F, and H horizons.

Supporting information S7. Full results of the statistical analysis presented in Figure 3.

Supporting information S8. Average SOM chemistry of intact soil profiles.

Supporting information S9. Correlation among parameters of litter chemistry used to predict bioreactivity, and cumulative respiration at three temperatures.

Supporting information S10. Evaluation of the effect of regional differences in SOM chemistry on bioreactivity.

Supporting information S11. Potential effects of changes in Q_{10}.

e).