Fates of lignin and carbohydrates in Siberian soils

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Referent: Prof. Dr. rer. nat. habil. Georg Guggenberger

Korreferent: Prof. Dr. rer. nat. Birgit Wild

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All things are difficult before they are easy.

Thomas Fuller

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Abstract

Permafrost-affected soils contain a huge reservoir of organic matter (OM) which, in the past, was largely persistent against microbial decomposition as consequence of cool and waterlogged conditions in the active layer, and freezing in the permafrost layer. Knowing the composition and degree of decomposition at molecular level of soil organic matter (SOM) is relevant to assess their vulnerability under impacts of climate change. This thesis investigated two major constituents of SOM, lignin and carbohydrates, across a west-east gradient in northern Siberia (longitudinal transect) and along a north-south gradient in western Siberia (latitudinal transect), aiming at identifying their fate once permafrost is thawing.

The longitudinal transect included three continuous permafrost sites, from Cherskiy (CH) in north-eastern, Logata (LG) in north-central, and Tazovskiy (TZ) in north-western Siberia, which principally differ in active layer thickness and soil mineralogical properties. The latitudinal transect included all major biomes (tundra, taiga, forest steppe and steppe) from arctic to temperate ecosystems, which vary in mean annual temperature (MAT), mean annual precipitation (MAP), vegetation and soil properties. Lignin-derived phenols and neutral sugars within plant and soil samples at each horizon were analysed by CuO oxidation and trifluoroacetic acid (TFA) extraction methods respectively.

Along the longitudinal transect, the stage of lignin degradation, appeared to increase from TZ to CH site. The stronger degradation of lignin and neutral sugars at TZ is supposed to be due to the higher MAT and larger active layer thickness, coinciding with better aeration and/or better mobilization of OM. In addition, the larger contents of Fe and Al (hydr)oxides likely additionally stabilized lignin-derived phenols associated with the mineral phase at these sites. With respect to the latitudinal transect, the stage of lignin degradation appeared to increase from tundra to forest steppe, then decrease to steppe. The increasing degree of lignin decomposition from tundra to forest steppe is likely due to decreasing soil moisture and increasing temperature which might favor the activity and assimilation of lignin-degarded microoragnisms, while drought and high pH are responsible for the restrained lignin decomposition in the steppe biome. The restrained lignin decomposition, in turn impairs the degradation of plant-derived carbohydrates because of a chemical linkage in form of lignocelluloses. It can be expected that increasing soil temperature and consequently increasing active layer thickness as the result of climate warming, which can cause two different soil hydrological scenarios, i.e., warm drier and warm wetter conditions will likely promote lignin and carbohydrate decomposition. This thesis thus contributes to a better understanding of the impact of permafrost thaw on OM stabilization in high latitude, and a magnitude in the realease of greenhouse gases into the atmosphere under global warming.

Keywords: Permafrost, soil organic matter, lignin, carbohydrates, density fractionation, climate change.

Zusammenfassung

Permafrostböden bilden einen bedeutenden Speicher für organische Substanz (OM), der in der Vergangenheit als Folge von Wasserstau in der aktiven Zone und des gefrorenen Zustands der Permafrostzone weitgehend resistent gegenüber mikrobieller Zersetzung war. Im Zuge des Klimawandels sind Kenntnis über Zusammensetzung und Abbaugrad der organischen Substanz auf molekularer Ebene für die Abschätzung der Vulnerabilität gegenüber Abbau relevant. Die vorliegende Dissertation untersucht den Effekt der Permafrostdegradation auf zwei OM-Hauptkomponenten, Lignin und Kohlenhydrate, entlang eines W-E-Gradienten (Longitudinaltransekt) im nördlichen Sibirien und eines N-S-Gradienten (Lagtidudinaltransekt) im westlichen Sibirien.

Der Longitudinaltransekt umfasst mit Chersky (CH) im nordöstlichen Sibirien, Logata (LG) im nördlichen Zentralbereich Sibiriens und Tazovskiy (TZ) im nordwestlichen Sibirien drei durchgängige Permafrostgebiete, die sich hauptsächlich in der Dicke der aktiven Zone und den mineralogischen Eigenschaften unterscheiden. Der Latitudinaltransekt umfasst von der arktischen bis zur gemäßigten Klimazone alle Hauptbiome (Tundra, Taiga, Waldsteppe, Steppe), die in mittlerer Jahrestemperatur (MAT), mittlerem Jahresniederschlag (MAP), Vegetation und Bodeneigenschaften variieren. Lignin- basierte Phenole und Neutralzucker der Boden- und von Pflanzenproben wurden über CuO-Oxidation und Trifluoressigsäureextraktion gewonnen analysiert.

Entlang des Longitudinaltransekts nahm das Stadium des Ligninabbaus, von der TZ zur CH-Seite ab, Der stärkere Abbau von Lignin und Neutralzuckern von TZ ist vermutlich auf eine höhere MAT, eine mächtigere aktive Zone und in diesem Zusammenhang bessere Durchlüftung und die Mobilisierung von OM zurückzuführen. Dazu haben hier die höheren Al- und Fe-(Hydr)Oxidgehalte vermutlich zusätzlich mit der Mineralphase assoziierte Lignin-basierte Phenole stabilisiert. Im Bereich des Latitudinaltransekts nahm der Ligninabbau von der Tundra zur Waldsteppe zu und dann zur Steppe ab. Der zunehmende Grad des Ligninabbaus von der Tundra zur Waldsteppe ist wahrscheinlich auf abnehmende Bodenfeuchtigkeit und steigende Temperatur zurückzuführen, die die Aktivität und Assimilation von Lignin-degardierten Mikroorganismen favorríieren könnten, während Trockenheit und hoher pH für verlangsamten Ligninabbau im Steppenbiom verantwortlich sind.

Der eingeschränkte Ligninabbau behindert umgekehrt den Abbau Pflanzen-basierter Kohlenhydrate, da beide Komponenten über Lignocellulose chemisch verbunden sind. Es kann erwartet werden, dass ansteigende Bodentemperaturen und eine dadurch zunehmende Dicke der aktiven Zone als Folge der globalen Erwärmung den Lignin- und Kohlenhydratabbau fördert, was sich mit zwei hydrologischenen Szenarien erklären lässt, warm-trockener und warm-nasser. Die vorliegende Dissertation trägt zu einem besseren Verständnis des Effekts von Permafrostdegradation auf die Destabilisierung der organischen Substanz in den hohen Breiten bei, die zu einer Magnitude in der Freisetzung von Treibhausgasen führen und zur globalen Erwärmung beitragen kann.

Stichwörter: Permafrost, organische Bodensubstanz (OM), Lignin, Kohlenhydrate, Dichtefraktionierung, Klimawandel

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Abbreviations

$(Ad/Al)_V$	Mass ratios of vanillic acid over vanillin
$(Ad/Al)_S$	Mass ratios of syringyl acid over syringylaldehyde
BP	Before present
C	Carbon
CH	Cherskiy
dw	Dry weight
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
GC	Gas chromatography
GC-FID	Gas chromatography-flame ionization detector
GC-MS	Gas chromatography-mass spectroscopy
GHG	Greenhouse gases
HF	Heavy fraction
LF	Light fraction
LG	Logata
MAT	Mean annual temperature
MAP	Mean annual precipitation
N	Nitrogen
OC	Organic carbon
OM	Organic matter
SOC	Soil organic carbon
ALT	Active layer thickness
TFA	Trifluoroacetic acid
TZ	Tazovskiy
VSC	Sum of vanilyl, syringyl, and coumaryl units

1. Introduction and objectives

1.1. Soil organic carbon and the global carbon cycle

Soil organic carbon (OC) is an important part in the C cycling of soil, vegetation, ocean, and the atmosphere (Fig. 1). The soil OC pool represents an estimated 2400 Pg C in the first meter of soil (Stockmann et al., 2013), which is approximately three time as much as the atmospheric carbon (C) pool (Oelkers and Cole, 2008) and four times larger than terrestrial vegetation (FAO and ITPS, 2015). Primary sources of soil OC are plants, comprising of above-ground plant litter, including leaves/needles, twigs, buds and fruits and below-ground litter, root residues and root exudates as well as photo- and chemo-autotrophic microorganisms which incorporate atmospheric CO_2 into organic material by photosynthesis. Uptake of methane (CH_4) in soil occurs via oxidation by specialized aerobic bacteria – methanotrophs (Hanson and Hanson, 1996).

After die-off, the organic material is decomposed and incorporated into the soil by the action of soil organisms, and by sorption of dissolved organic carbon (DOC) to soil minerals. Soil OC is subsequently mineralized by heterotrophic organisms to CO_2 and CH_4, which is emitted back into the atmosphere. The mean residence time of OC in the soil can range from hours to millennia (Schmidt et al., 2011; Trumbore, 2000). In addition to losses by CO_2 and CH_4, OC is partly exported to rivers and oceans as DOC. If more C is released from soil as greenhouse gas (CO_2, CH_4) than is incorporated by residues of C-fixing organisms such as plants and phototrophic microbes, the impact of soil OC on atmospheric greenhouse gases and thus on climate warming is positive, and vice versa. Hence, understanding the decomposition and transformation of soil OC is crucial for assessing the greenhouse gas balance under changing climatic conditions.

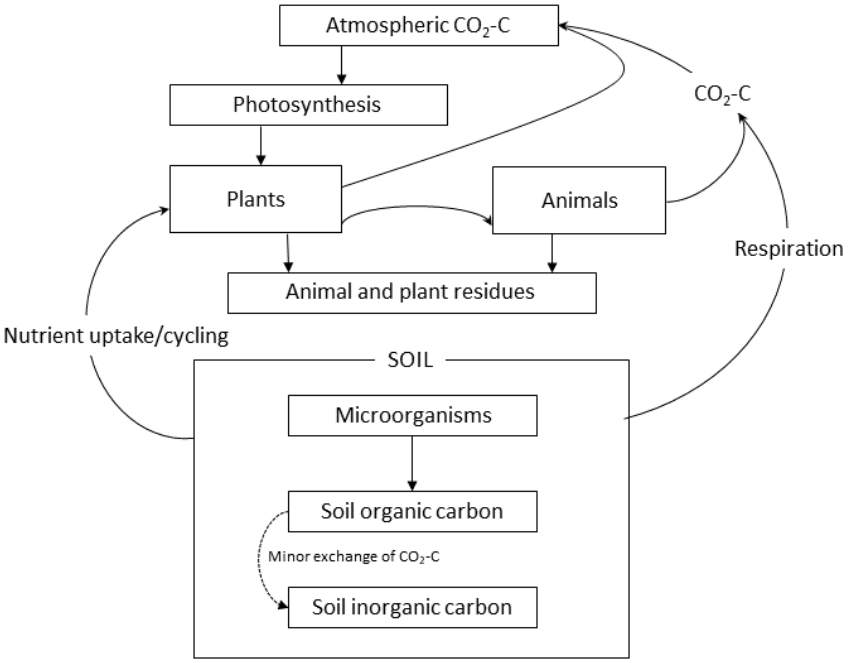

Fig. 1: The terrestrial carbon cycle (Follett et al. 2011)

1.2. Soil organic matter

Soil organic matter (OM) is defined as plant and animal residues in soil at various stages of decomposition, and their re-synthesized products (Baldock and Skjemstad, 2000). It is a heterogeneous mixture of organic components, containing ca. 50-60% of carbon. The parent OM has undergone decomposition/humification processes, through the action of animals and microorganisms, resulting in a mixture of identifiable organic compounds and morphologically unstructured humic compounds. Microbial biomass additionally contributes to the soil OM pool, which are considerably lesser extent than plants throughout entire soil profile (Kassim et al., 1981) but they can contribute a significant part of OM in mineral soils in form of amino sugars and protein-derived amino acids (Mikutta et al. 2019).

Traditionally, the stability of soil OM is assessed on the basis of intrinsic properties of the chemical composition, and has been partitioned into “labile” (easy-to-decompose) vs. “recalcitrant” (hard-to-decompose) forms (Kleber and Johnson, 2010; von Lützow et al., 2006). More recently, it was recognized that OM persists not because of the intrinsic properties of their structure, but rather because of environmental controls on soil OM including soil temperature, moisture content, microbial community composition, and several other physical factors such as mineral-associated protection (Schmidt et al., 2011; Lehmann and Kleber, 2015. For instance, the intrinsically easily degradable “labile” SOM such as sugars can persist not only for weeks, but for decades, and the intrinsically “recalcitrant” SOM such as lignin or plant lipids is found to be degraded faster than bulk organic matter (Dignac et al., 2005; Heim and Schmidt, 2007; Lehmann and Kleber, 2015) or bulk litter (Sanaullah et al., 2010; Klotzbücher et al., 2011). Therefore, it remains unclear which chemical structures will be preferentially decomposed or stabilized. A fundamental study that examines the molecular composition of SOM and its behavior in a given region, thus, will be important for understanding its potential response to global warming. On the one hand, lignin represents biomacromelucles that have been considered as relatively stable and is not re-synthesized by microorganisms. On the other hand, carbohydrates are known to be quite easily degraded. They can be examples for the decomposition and stabilization of the two types of organic matter, i.e. easily available plant sources and more stable plant sources.

1.2.1. Lignin

Lignin encompasses to soil exclusively from plant litter and root input, and is considered to play an important role in controlling litter decomposition in soils (Hobbie 1996, Hobbie et al., 2006). Lignin is derived from the Latin term “lignum”, which means “wood” (Sarkanen and Ludwig., 1971). In plant tissues, lignin is covalently bonded with hemicelluloses, which in turn are bound to cellulose via hydrogen bonding, forming complexes, i.e. lingocelluloses (Kirk and Colling, 1984; Kirk and Farrell,

1987). Thereby, lignin becomes a barrier preventing decomposition of (hemi)-celluloses (Kirk and Colling, 1984).

Lignin is a random, three-dimensional, highly-branched polymer (Fig. 2a), playing an important role in providing mechanical support to bind fibers together in the transport of water and nutrients (Hedges and Ertel, 1982; Kögel, 1986). Lignin structurally is comprised of three different phenylpropanes, or monolignols (vanillyl, syringyl, coumaryl; abbreviated as V, S, C respectively) (Fig. 2b). The lignin concentration and composition differ between plant species. The VSC content make up 20-36 % of dry weight (dw) in woody trees (Zhu and Pan, 2011), 12-18 % in grasses (Winterfeld et al. 2015), but only 4-8 % in non-vascular plants (e.g. mosses) and lichens (Winterfeld et al. 2015).The gymnosperms are dominated by V, while angiosperms are richer in S and grasses in C-units (Hedges and Mann, 1979; Kögel et al., 1988). The mass ratios of acids over aldehydes, i.e. $(Ac/Al)_V$ and $(Ac/Al)_S$ reflects stage of oxidative lignin degradation in soils (Hedges and Ertel, 1982; Kögel, 1986).

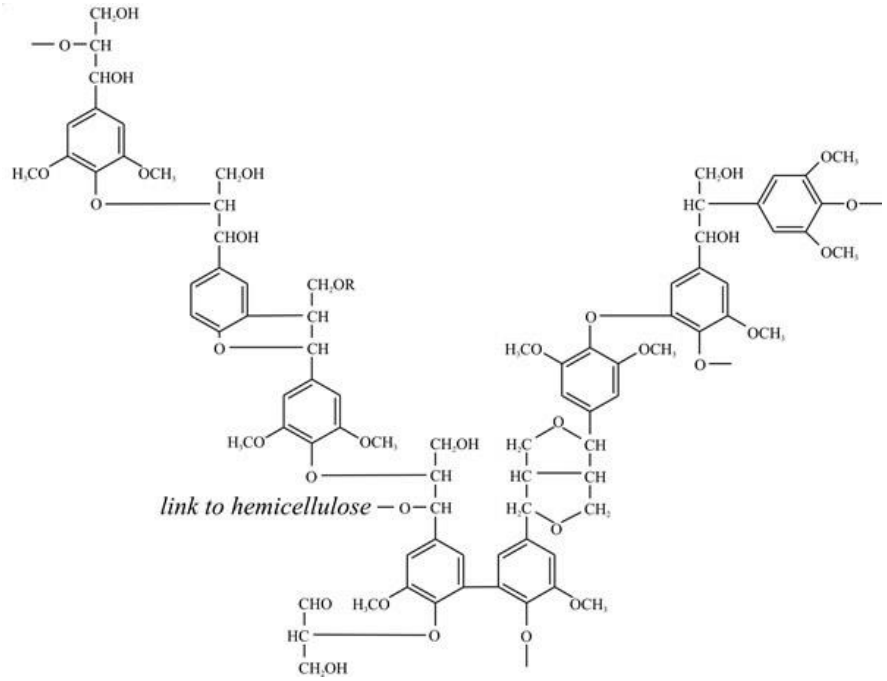

Fig. 2a: Schematic formula of the polymer structure of angiosperm lignin (Moore et al., 2000).

The occurrence of lignin in soil is a result of litter input and the loss with microbial mineralization and leaching, which are regulated by various factors, such as vegetation, soil properties and microbial community (Otto and Simpson, 2006; Haritash and Kaushik 2009; Thevenot et al. 2010). White-rot fungi are the most effective bio-degraders of lignocellulosic biomass (e.g., *Phanerochaete*

chrysosporium) and can degrade lignin faster than other microorganisms (Kirk et al. 1976; Haider, 1986).

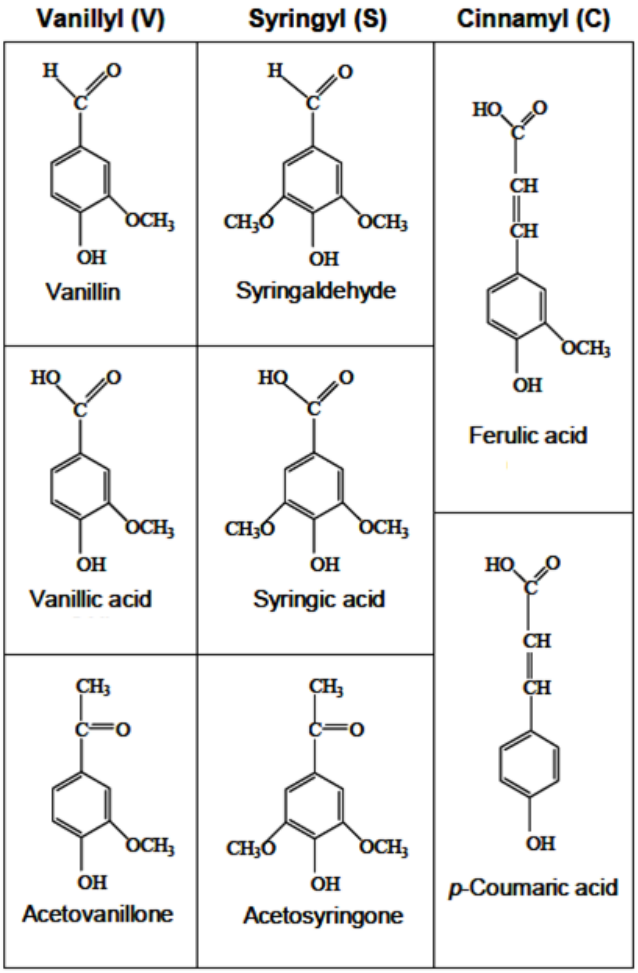

Fig. 2b: Structure of lignin-derived phenols isolated by CuO oxidation (Thevenot et al., 2010)

They are able to produce a number of extracellular enzymes such as laccases, phenolxylase, peroxidases that directly attack lignin, cellulose, and hemicellulose of the plant cell wall to decompose it. The brown-rot fungi are less efficient in degrading lignin compared to white-rot, and can partially degrade lignin (Trojanowski, 1969; Kirk et al., 1976; Haider, 1992).

Although fungi are reported to be more potent in lignin degradation, many soil bacteria such as Actinomycetes are also capable of solubilizing and mineralizing polymeric lignin and lignin-related compounds. The potential lignin-degrading bacteria are mostly in the taxa of Alphaproteobacteria, Gammaproteobacteria, and Actinomycetes (Bugg et al. 2011), with the best-characterized being *Streptomyces viridosporus* (Ramachandra et al., 1988). Phenol-degrading bacteria such as Kocuria and Staphylococcus (DeRito et al. 2005), peroxidase-producing *Flavobacterium meningosepticum* (Koga et al., 1999), and bacterial degraders of polyaromatic hydrocarbons (Peng et al 2008) also have a natural ability for degrading lignin derived from decomposing plant biomass. The fungi are largely

absent in anaerobic soils such as deeper mineral soils or water-logging soils whereas these conditions favor decomposition by bacteria (Kellner and Vandenbol, 2010), which are the most likely lignin-degraders when oxygen is limited (Faix, 1991; Wong, 2008; Parthasarathi et al., 2011). Lignin degradation is in general oxygen dependent, though anaerobic lignin degraders have been reported as well (DeAngelis et al., 2011), which are being much retarded in their lignin decomposition (Gittel et al., 2015).

Distribution of lignin in different soils has been broadly discussed for different soil environments (Guggenberger et al. 1994; Otto and Simpson, 2006). The OC-normalized lignin contents generally decrease with soil profile in temperate and tropical soils as result of progressive lignin degradation (Dignac et al., 2002; Feng and Simpson, 2011; Rumpel et al., 2004). However, in a few cases, lignin appeared to be selectively preserved in deeper horizons of peat (Bourdon et al., 2000; Bambalov, 2007) and permafrost soils (Gundelwein et al., 2007), where the oxygen availability is low. An increase in these ratios is found from organic to mineral horizon. Furthermore, lignin phenols in association with minerals are considered to be protected against microbial decomposition, regardless of oxygen availability (Eusterhues et al., 2014; Riedel et al., 2013).

The quality of substrates additionally affects lignin degradation as it is a co-metabolic process, at which easily decomposable C sources can stimulate lignin degradation (Klotzbücher et al., 2011), while nitrogen availability may inhibit lignin degradation (reviewed by Thevenot et al., 2010). Soil pH can affect lignin degradation as it influences the activity of lignin-degrading fungi and bacteria, which are at their optimum at pH of around 5 and 8.5, respectively (reviewed by Thevenot et al., 2010). The proportion of lignin to OC generally are higher in the coarse than the fine fraction of soil while the $(Ac/Al)_{V,S}$ ratios increase with decreasing particle size and are highest in the clay fraction (Guggenberger et al. 1994; Monreal et al. 1995; Schöning et al. 2005).

The transformation of lignin has been investigated intensively in temperate soils (Kögel et al., 1988; Guggenberger et al., 1994; Spielvogel et al., 2007), tropical soils (Guggenberger et al., 1995; Möller et al., 2002), tropical wetlands (Tareq et al., 2004), and peat soils (Bourdon et al., 2000; Bambalov, 2007). Despite of its molecular recalcitrance, lignin turnover studies in temperate and tropical soils have produced conflicting results, most of them suggesting that large proportions of plant-residue lignin decompose within a year of incorporation into soils (Dignac et al., 2005; Heim and Schmidt, 2007). However, the lignin decomposition was less pronounced in the wet soils such as peat and bogs. The understanding of lignin transformation in permafrost soils is still scarce. Thus, here we focused on lignin decomposition in partitioning of OM between particulate and mineral-associated OM of permafrost soils.

1.2.2. Carbohydrates

Non-cellulosic carbohydrates (e.g., hemicelluloses) in soils consist of relatively short, mainly branched heteropolymers, which originate from plant tissues and are also synthesized during

microbial neoformation (Fig. 3). Carbohydrates are the most dominant component in plant tissues (50-70% dw) (reviewed by Gunina and Kuzyakov, 2015), and consist of various pentoses and hexoses, with more abundance of arabinose and xylose, while lichens and mosses contain significant amounts of galactose and mannose (Sariyildiz and Anderson, 2003; Schaedel et al., 2010). Root tissues contain 2-3 times more carbohydrates than green leaves (Zhang et al., 2014). Glucose is the most dominant sugars in root exudates (40-50%), whereas arabinose and ribose are nearly absent (Grayston and Campbell, 1996; Hutsch et al., 2002).

Soil microbes can synthesize sugars from the sugar C or other C-containing substances derived from plant litter. Microbially-derived sugars are primarily hexose (e.g., galactose, mannose, fucose, rhamnose) (Cheshire, 1979; Moers et al., 1990; Murayama, 1984). Carbohydrates are themselves easily-degradable compounds, which have a residence time of a few weeks to months (Martin et al., 1974), if they are not protected by stabilization mechanisms. Carbohydrates are degraded by a wide range of bacterial polysaccharidases and glycosidases to smaller oligomers and their component sugars, by using exoenzymes under both aerobic and anaerobic conditions, which are subsequently fermented to short chain fatty acids, H_2, CO_2, and a variety of other acidic and neutral end products (MacFarlane et al., 1995).

Sugars are crucial substrates for microbial maintenance and growth, which in turn stimulate further exoenzyme production, thus accelerating the decomposition of SOM (Gunina and Kuzyakov, 2015). Microbially-derived sugars preferentially bind to clay-sized particles (Guggenberger et al., 1994; Spielvogel et al., 2007). Fine soil particles, thus, often show higher ratios of microbial sugars to plant-derived sugars than coarser particles, e.g., in temperate (Guggenberger et al., 1994; Spielvogel et al., 2007; Kiem and Kögel-Knabner, 2003) and tropical (Guggenberger et al., 1995) soils.

The degree of carbohydrates alteration, i.e. microbial degradation of plant-derived carbohydrates and synthesis of microbial ones as relatively indicated by increasing ratios of microbially-derived over plant-derived sugars ((galacose + mannose)/(arabinose + xylose); GM/AX), generally increases with soil depth in temperate (Guggenberger et al., 1994) and tropical (Nacro et al., 2005) soils. However, in peatland, plant-derived carbohydrates have been found to degrade only in surface horizons and to remain roughly unaltered at larger depths (Bourdon et al., 2000; Bambalov, 2007). Since carbohydrates are to some extent chemically bound to lignin in form of lignocelluloses, the understanding of the fate of SOM is more pronounced if they are studied together, considering carbohydrates and lignin.

1.2.3. Biomarker analysis

Biomarker analysis is a molecular-level based analysis SOM constituents, which yields highly specific molecular information about the source and degradation stage of SOM (Feng and Simpson, 2011). Although biomarker methods are only able to extract and measure a small portion of total

SOM, the method is sensitive for analyzing specific SOM components, i.e. lignin, lipids, carbohydrates, *etc*., and their transformation during OM decomposition processes.

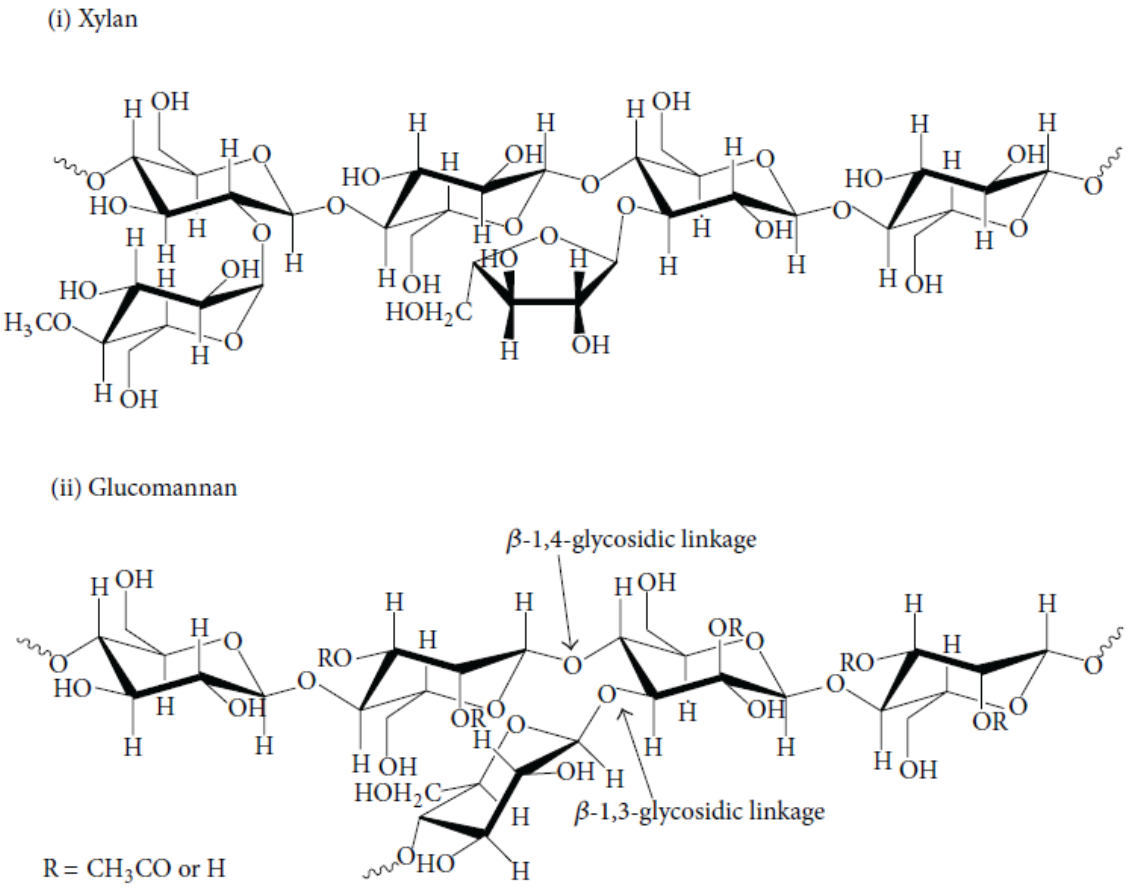

Fig. 3: Schematic formula of the polymer structure of hemicelluloses (i) xylan, (ii) glucomannan (Lee et al., 2014)

Biomarker analysisis usually undergone by variety of analytical steps such as solvent extraction, acid hydrolysis, base hydrolysis and CuO oxidation, and identified by chromatography technique (Otto and Simpson, 2007). Especially, biomarker methods are highly advantageous for understanding SOM responses to global climate change (Feng and Sipmson, 2011).

There are several methods for quantitative analysis of lignin, i.e, the Klason, acetyl bromide, thioacidolysis, and CuO-oxidation methods (Fagerstadt et al. 2015). Klason is a gravimetric method do not physically isolate lignin, but describe lignin within the original sample (Dence, 1992). The acetyl bromide method is based on the formation of acetyl derivatives in non-substituted OH groups and bromide replacement of the Cα-OH groups to produce a complete solubilization of the cell wall material (Moreira-Vilar et al., 2014). However, Klason and acetyl bromide methods do not provide compositional information on lignin.

Alkaline CuO is a technique commonly used to analyze the composition of lignin in complex sample matrixes, such as soils and sediments (Hedges and Ertel, 1982; Kögel and Bochter, 1985). The

oxidation with CuO induces cleavage of β-O-4 ether bonds in lignin, and retains the three carbons of the side chain of the phenol (Hedges and Ertel 1982; Kuo et al., 2008; Kaiser and Brenner, 2012). The CuO method yields phenolic products with aldehydic, ketonic and acidic side chains which can be identified by gas chromatography/mass spectrometry (GC/MS) or liquid chromatography/mass spectrometry (LC/MS) (Fagerstedt et al. 2015). The CuO method, thus, is a promising method to study the monomeric composition of lignin (Fagerstedt et al. 2015).

Traditionally, neutral sugars in soil are released from non-cellulosic saccharides by H_2SO_4 (Cheshire, 1979), but it has been reported that TFA is the most efficient method in quantification of neutral sugars in soils since TFA can be evaporated directly (Amelung et al., 1996). Neutral sugars can be derivatised by silylation (Larre-Larrouy and Feller, 1997), transformation into oximes (Amelung et al., 1996; Nierop, 2001) or acetylation of alditols acetate (Rumpel and Dignac, 2006). However, silylation and oximation produce complicated chromatograms with more than one peak per sugar due to syn and anti isomer differentiation, especially for low OC contents-containing mineral soils. Acetylation of alditols eliminates the anomeric centre and therefore simplifies the chromatograms dramatically as most sugars produce one chromatographic peak (Zhang et al., 2007). Another advantage of this derivatisation procedure is that the hydrolysed sugar solution do not need to be purified, as they are solvent extractable after transformation into alditols.

1.3. Controlling factors of organic matter dynamics in soil

1.3.1. Role of soil microorganisms

Soil microorganisms comprise bacteria, fungi and archaea, including autotrophs or heterotrophs. Autotrophs use energy from sunlight or inorganic compounds (e.g. Fe^{2+}, nitrate, nitrite) to fix atmospheric CO_2 to produce carbohydrates, fats and proteins, whereas heterotrophs use organic carbon compounds as a source of carbon and energy (Aislabie and Deslippe, 2013). Microorganisms excrete extracellular enzymes, which are able to break down high molecular weight into low molecular weight substances through hydrolytic or oxidative pathways, e.g., enzymatic depolymerization. Microorganisms further assimilate the soluble, low molecular weight compounds (Sinsabaugh et al., 2009; Sinsabaugh, 2010), producing adenosine triphosphate (ATP) and releasing CO_2. In soil, fungi initiate the decomposition of fresh organic residues by softening organic debris and making it easier for other organisms to join in the decomposition process. Fungi, hence, are important in degrading chemically recalcitrant compounds such as lignin. Fungi usually are active in the presence of oxygen and weakly acidic environments (Aislabie and Deslippe, 2013). Likewise, at high pH levels, the Actinomycetes, a large group of bacteria, are important in degrading chemically non-easily degradable compounds, such as lignin, cellulose, and chitin (Aislabie and Deslippe, 2013). Although most bacteria require oxygen for assimilation, some others (e.g., archaea) are able to use alternative electron acceptors including nitrate and sulphate (Aislabie and Deslippe, 2013).

Soil microorganisms are not only a driver of soil OM decomposition but also contribute to the formation of SOM pools (Condron et al., 2010). Upon cell death, materials that are synthesized in the course of microbial anabolism are released into the soil, where they are subject to further degradation (Lehmann and Kleber, 2015). Modern analytical tools for the characterization of biomolecules in microbial cells and soils suggest a direct and rapid contribution of microbial cell walls to soil organic matter protected by interaction with minerals (Miltner et al., 2012; Schurig et al., 2013).

1.3.2. Stabilization by formation of organo-mineral associations and soil aggregation

The physiochemical protection of soil OM is addressed by either the association of OM with soil minerals such as (hydr)oxides of Fe and Al and with clay particles, or the occlusion of the organic substrate within soil aggregates. The associations between soil OM and soil minerals reduce the availability of decomposable OM substrates (Sollins et al., 1996; Six et al., 2002). Studies of agricultural soils showed that the turnover of free, bioaccessible OM compounds are roughly 3-4 times faster than those of the same compounds found in association with minerals (Marschner et al., 2008). At a molecular scale, OM interacts with mineral surfaces via multiple binding processes, including ligand exchange, polyvalent cation bridges, hydrophobic interaction, hydrogen bonding, complexation, van der Walls forces, and charge interaction (Mortland, 1970). Mikutta et al (2006) showed that OM bound to minerals by mainly ligand exchange was more resistant against mineralization than OM held by van der Waals forces and cation bridges. Likewise, enzymes can be protected by interaction with soil minerals, producing enzyme-organo-mineral interaction (Nannipieri et al., 1996; Merino et al., 2016), and enzyme-clay interaction (Gianfreda and Bollag, 1994). Intrinsic characteristics of soil OM, for instance, the degree of cyclization and existence of polar functionalities, enhance the sorption rate by promoting strong bonding (Ahmat et al., 2016). Organic matter with higher molecular weight, acidity, and aromaticity tends to be preferentially absorbed to soil minerals (Kaiser and Zech, 1997). Such physical association with (hydr)oxides and clay minerals makes the OM in soils less available and less vulnerable to microbial decomposition (Baldock and Skjemstad, 2000; Kalbitz and Kaiser, 2008).

One such parameter is the presence of reactive iron (Fe) minerals (defined here as iron minerals that are reductively dissolved by the chemical reductant sodium dithionite, e.g. ferrihydrite or goethite), which are known to stabilize OM by sorption and co-precipitation (Kleber et al., 2015; Kogel-Knabner et al., 2008). Fe-bound carbon can be protected by soil structural conditions (such as aggregate formation, macro-scale shifts in fluid flow paths), thus be less accessible to decomposer organisms (Asano and Wagai, 2014). At the same time, oxygen (O_2) diffusion is hindered further favoring soil organic matter (OM) preservation rather than decomposition (Asano and Wagai, 2014). Thus, Fe–OM associations are thought to significantly influence long-term carbon storage in numerous environments (Kleber et al., 2005; Riedel et al., 2013). Several studies already identified poorly crystalline Fe-OM associations in the field or produced them in the lab, and demonstrated that

they are resistant to microbial or chemical reduction (Eusterhues et al., 2014; Coward et al., 2014). The inventory of reactive iron minerals in humid climates is highly dynamic as they precipitate and dissolve in response to changing redox conditions. Mineral soil slurry incubations previously showed OM protection by iron only under static oxic conditions (Chen et al., 2015). However, iron(III) mineral reduction and dissolution under oxygen limitation led to anaerobic mineralization of dissolved OM and soil OM by 74% and 32–41%, respectively. When mineral dissolution occurs, iron and carbon mobilization, increased carbon lability/bioavailability, and increased gaseous carbon loss as CO_2 and CH_4 follow (catalyzed by heterotrophic and methanogenic microorganisms) (Herndon et al., 2015; Turetsky et al., 2008).

Soil aggregates consist of soil particles that bind to each other more strongly than to adjacent particles. The interaggregate pores provide space for retention and exchange of air and water, and enables growth and the movement of soil microorganisms and microbial communities (Wilpiszeski et al., 2019). These respond to and act on the architecture of the soil, so allowing the development of a high level of biological diversity, which spreads and forms changing distribution patterns reflecting the interaction between microorganisms and the soil (Young and Crawford, 2004). Nevertheless, aggregates might physically protect soil OM by forming physical barriers between microorganisms and their enzymes and the substrate, by limiting the spatial accessibility of the substrate, since the interaggregate pores are too small to be passed by microbes (Elliott and Coleman, 1988; Six et al., 2002).

Up to 90% of the organic matter in soil is tightly bound to minerals, particularly in deeper soil layers (Rumpel and Kögel-Knabner et al., 2010; Bischoff et al., 2016). The stabilization of soil OM by mineral-organic associations can be studied by density fractionation. Density fractionation is frequently applied to separate soil OM according to the degree and the mode of interaction with minerals. Density fractions are operationally defined by density cut-off and sonication intensity to separate OM pools into light and heavy fractions (LF vs. HF) that differ in structure and function (Cerli et al., 2012; Lavallee et al., 2019). The LF ($\leq$1.6 g mL^{-1}) contains mainly particulate OM (POM), and the HF (>1.6 g mL^{-1}) comprises mostly mineral-associated OM (MOM). The LF is considered to be primarily particulate OM (i.e., plant residues), not or only loosely attached to soil minerals, whereas the heavy fraction contains more decomposed OM and/or microbial residues absorbed on soil mineral surfaces (Kanazawa and Filip, 1986; Jocteur Monrozier et al., 1991). Two general pathways of MOM formation have been advocated, either the sorption of microbial assimilates or the sorption of plant-derived compounds (Kalbitz and Kaiser, 2008; Cotrufo, et al., 2013, Mikutta el al., 2019). The adsorption of simple low-molecular weight OM such as aliphatic and aromatic carboxylates, amino acids, hydroxamate ligands, or phospholipids has been extensively studied for variable-charge metal oxide surfaces (reviewed by Kleber et al., 2015). Microorganisms (bacteria and archaea as well as most protozoa, fungi, and algae) interact with soil minerals in a variety of ways, including the microbially mediated formation and dissolution of minerals, the

formation of MOM through the deposition of microbial products on mineral surfaces, and finally the acquisition and utilization of organic materials in MOM for microbial metabolism (reviewed by Kleber et al., 2015). Mikutta et al. (2019) studied the pathways of the formation of MOM in soil profiles along a 120-ky ecosystem gradient that developed under humid climate from the retreating Franz Josef Glacier in New Zealand, indicating that litter quality had little effect on the accumulation of mineral-associated carbon and that plant-derived carbon bypassed microbial assimilation at all soil depths. Overall, MOM formation is not monocausal but involves various mechanisms and processes, with reactive minerals being effective filters capable of erasing chemical differences in OM inputs (Mikutta et al., 2019). Up to 90% of the organic matter bound to minerals; understanding of mineral stabilized-OM is important.

1.3.3. Impact of abiotic conditions

Temperature

It is commonly accepted that reaction rates in the decomposition process follows the Arrhenius equation given by

$$k = Aexp\left(\frac{-E}{RT}\right) (1)$$

where A is the pre-exponential factor, E is the activation energy, R is the universal gas constant, and T is the absolute temperature (Arrhenius, 1889).

The equation implies that rates of chemical, physiochemical and biochemical reactions in soil OM decomposition increase with temperature. This relation will increase with the higher activation energy (i.e., the minimum energy that is required to activate atoms or molecules to undergo a chemical reaction) (Conant et al., 2011). The assumption indicates that increasing soil temperature will stimulate the decomposition of low-quality substrates to a larger extent than that of high-quality substrates (Davidson and Janssens, 2001).

Temperature also controls the magnitude of organo-mineral association, and consequently controls substrate availability (Kögel-Knabner et al. 2008). The binding between soil OM and mineral surfaces is a chemical or phyochemical process, its rate, thus, depends on temperature following the kinetic theory (Kögel-Knabner et al. 2008). Similarly, desorption of organic matter from mineral surfaces is temperature-dependent. The soil OM is preferentially released from organo-mineral complexes with increasing temperature (Hamaker and Thompson, 1972; Pignatello, 2000). Alternatively, the temperature also increases diffusion and dissolution, both of which increase substrate availability to soil microbes and leaching losses of soil OM (Xu and Saiers, 2010). Hence, temperature controls directly and indirectly the soil OM stabilization by regulating the rates of decomposition reactions, the OM availability, the size of enzymes and microorganisms, and the microbial efficiency (Conant et al., 2011).

Moisture

In addition to temperature, soil moisture is one of the most important abiotic variables in soil OM decomposition (Oechel et al., 1998; Shaver et al., 2006; Oberbauer et al., 2007; Lawrence et al., 2015). As discussed in Koven et al. (2015), the effect of soil moisture is even stronger in controlling soil OM decomposition than that of temperature. Warming and drying of wet soils lead to higher soil respiration rates than warming alone (Oberbauer et al., 2007, Natali et al., 2015). Soil moisture principally depends on precipitation, drainage and water evaporation. Soil moisture affects the amount and activity of microbial biomass, controls the availability of oxygen for microorganisms, creates periods of water stress for microbes, and may also destabilization the SOM, which results in a greater availability of carbon for soil microorganisms (Tulina et al., 2009). Excessive moistening causes a drop in aerobic respiration and the CO_2 diffusion rate in the soil. For instance, incubation experiments of arable soils and straw wheat at different water contents (10, 25, and 40 wt %) indicated that the easily mineralizable fraction of SOM was most sensitive to changes in the soil moistening, which was most optimal at 25% of water contents (Tulina et al., 2009). Either drying up or moistening of soils caused a declined mineralization of the straw wheat (Tulina et al., 2009). The long-term soil dryness may slow down the rate of the SOM mineralization from retarding the number and activity of microbes (Tulina et al., 2009). For example, several studies indicated that the intensity of microbial respiration increases upon the rise in the soil water content from the dry state to the normal moistening but decreases upon excessive soil moistening (Edwards, 1975; Kowalenko et al., 1978; Wu et al., 2006). Therefore, research increasingly focuses on understanding the potential effect of changing soil moisture on OM stabilization.

1.4. Climate change in high latitude

Projections indicate that global temperatures will increase by 1.3 – 1.8 °C by 2100 (Schaefer et al., 2018). In high-latitude regions of the Earth, temperatures could rise twice as fast as the global average (e.g. 0.6 °C per decade over the last 30 years) (Schuur et al., 2015). Permafrost areas are expected to be reduced by 60%, responding to 120 ± 85 Gt of carbon emissions by 2100 (Schaefer et al. 2014). The RCP model (representative concentration pathways) of Nitzbon et al. (2020) estimated that by 2100 thaw-affected carbon of northeast Siberian arctic lowlands could be up to three-fold under moderated warming RCP 4.5 and twelve-fold under strong warming RCP 8.5 (refers to the concentration of carbon that delivers global warming at an average of 4,5 and 8.5watts per square meter across the planet, respectively). Such thawing of permafrost facilitates the microbial decomposition of OM (Schuur et al. 2015). For examples, study of yedoma areas in north-eastern Siberia indicated that an active layer deepening of about 100 cm will increase organic C availability in a seasonally thawed state by 5.8 Tg (13.2 kg C m^{-2}) (Fuchs et al. 2017). Auxiliary effects of climate change such as wildfires further increase permafrost degradation and active layer deepening (Tas et

al., 2014). Active layer detachment and permafrost collapse due to thawing further expose formerly buried permafrost and also increase microbial activity and degradation of previously unavailable soil organic matter (Pautler et al., 2010) and conversion of SOC into greenhouse gasses. Warmer conditions and increased atmospheric CO_2 will enhance plant growth that will remove some CO_2 from the atmosphere (Friedlingstein et al., 2006), but this may only partially compensate for the much greater carbon losses from thawing permafrost (Schaefer et al. 2014). The permafrost degradation, hence, amplifies surface warming, representing a positive feedback effect that may accelerate climate change. Thus, studies are needed which address the potential effect of climate change on the quantity and quality of OM in permafrost soils.

1.5. Permafrost soils

Permafrost is defined as ground (soil or rock included ice or organic material) that remains at or below 0 °C for at least two consecutive years (Harris et al., 1988), is found primarily in the Arctic, sub-Arctic, and Antarctic regions, as well as in alpine regions, for example in the Qinghai-Tibet Plateau, South America, and Sweden (Bockheim and Munroe, 2014). The arctic permafrost zone occupies about 65% of the territory of the Russian Federation, 24% of the Northern Hemisphere, and 9 % of the landmass of the earth, storing huge amounts of OC (1.035 Pg, Hugelius et al., 2014), equal to ca. 50% of the globally terrestrial OC (Tarnocai et al., 2009; McGuire et al., 2009; European Commission, 2015). The portion of the soil above perennially frozen permafrost that thaws and freezes seasonally is called active layer (Harris et al., 1988), the depth of which is dependent on air temperature, moisture content, vegetation, and snow cover (Tarnocai, 1980). The lower portion remains perennially frozen and is called permafrost layer. The upper limit of the permafrost layer is referred to as permafrost table. Soils which are affected by permafrost, further referred to as permafrost-affected soils, are classified as Cryosols according to the World Reference Base (2014) or as Gelisols according to the Soil Survey Staff (2014). Permafrost thickness can be hundreds of meters (e.g., over 500 m in Siberia), while the active layer thickness is from a few tens of centimeters to several meters (Tarnocai, 1980). The permafrost layer immediately underneath the active layer is characteristically ice-rich, which acts as an impermeable barrier to drainage, therefore permafrost terrain is regularly wet. The ice-rich zone is the reason why permafrost terrain is considered to be sensitive to disturbance such as deepening of the active layer and accelerated SOM degradation as the ice melts (Osterkamp and Burn, 2003).

A permafrost profile generally includes organic topsoil, mineral topsoil, subsoil, buried topsoil, and the permafrost layer (Fig. 4). Cryoturbation is a dominant process in many permafrost soils in response to repeated freeze-thaw cycles, leading to the mixing of soil layers, and burial of soil OC compounds from the topsoil layers (O and A horizon) into the lower subsoil horizons (B and C horizon) (Van Vliet-Lanoë, 1998; 2004), namely buried horizons. Although buried materials locate at subsoil horizons, they exhibit a C and nitrogen (N) content similar to that of the present topsoil

horizons (Kaiser et al. 2007). Radiocarbon dating revealed, however, that the mean age of C in the buried layer was three times higher (~1300 years BP) than that of C in the A horizon (~400 years BP), suggesting that the decomposition in the buried layer is delayed (Kaiser et al. 2007; Gentsch et al. 2015a). Cryoturbation, hence, may contribute to long-term storage of C in soils of northern latitudes, and may be indicative of former permafrost (Bockheim and Tarnocai, 1998).

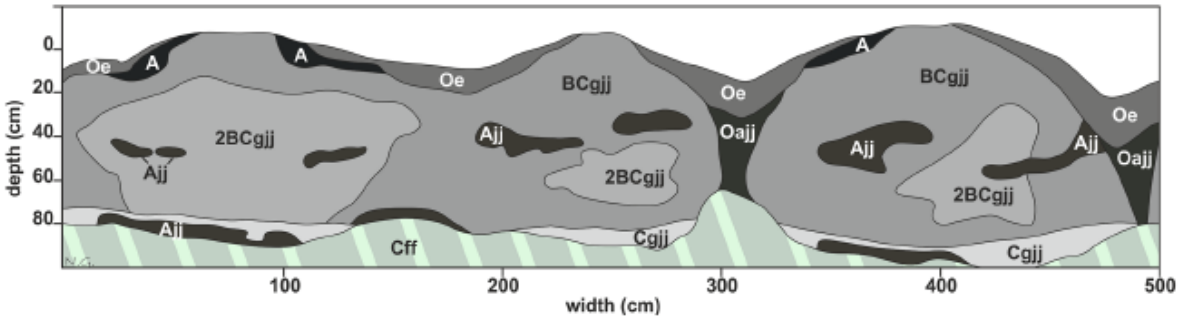

Fig. 4: Typical profile of a permafrost soil in North-Eastern Siberia, showing organic topsoil (Oe), mineral topsoil (A), buried topsoil (Ajj), mineral subsoil (BCgjj, 2BCgjj, Cgjj), as well as the upper part of the permafrost horizon (Cff) (Gentsch et al., 2015a).

Because the underlying permafrost impedes subsurface drainage permafrost soils are often wet, which greatly affects OM decomposition, and other biogeochemical processes by low redox potentials. The associated low degree of OM decomposition have led to the accumulation of large stores of organic carbon in the active layer and underlying permafrost. The OM will be exposed to decompose once the soils become dryer as result of global warming. Considering the 1,035 Pg of arctic soil carbon (Hugelius et al. 2014), such an additional stimulation of OM decomposition beyond the climate change effect can accelerate net ecosystem C losses, and amplify the positive feedback to global warming.

1.6. Features of organic matter stabilization in permafrost soils

Permafrost-affected soils have accumulated vast pools of OC (about 1,035 Pg, Hugelius et al. 2014). The degradation of OM in permafrost is affected by the degradability of the permafrost itself. An increase in active layer stimulates the biogeochemical C cycling and decomposition (Rui et al., 2011). The active layer deepening can unlock frozen OM and activate microbes, make them more easily accessible to decomposition. The active layer deepening also promotes plant rooting as well as the downward transport of water, nutrients, oxygen and microorganisms into the subsoils (Lawrence et al., 2015; St Jaques and Sauchyn, 2009; Schuur and Mack, 2018), and thus will accelerate soil OM decomposition in deep soil layers and increase carbon losses to the atmosphere (Fontaine et al., 2007; Gocke et al., 2010, Schuur et al., 2015; Wild et al., 2016).

The kinetic theory implies that rates of soil OM decomposition increase with increasing temperature (Conant et al. 2011). The impact of temperature on OM decomposition is more pronounced for ecosystems of low temperature such as permafrost soils. As temperature sensitivity of OM decomposition itself increases with component complexity, recalcitrant compounds such as lignin are therefore expected to exhibit relatively high-temperature sensitivity. The OM degradation in permafrost soils is also sensitive to hydrothermal changes, which affect the redox potentials and oxygen availability (Wu et al., 2012). Absence of oxygen, created by water-logged conditions can retard aerobic oxidation of OM (McLatchey and Reddy, 1998) but may promote anaerobic oxidation via multiple anaerobic pathways (e.g., hydrolysis, fermentation, and methanogenesis) (Keller and Bridgham, 2007; Sutton-Grier et al., 2011; Wilson et al., 2017).

Most plants growing in permafrost-affected soils are nonvascular species with lower quality litter (Chapin et al., 1995). N availability is positively related to biomass growth rate – consistent with growth limitation under low N conditions. A key characteristic of arctic vegetation is the high spatial heterogeneity in plant abundance and functional type. The dominant vegetation can vary from prostrate evergreen heath to tussock sedges, to deciduous woody shrubs over distances of just a few metres. Plant biomass varies greatly between these communities, as does the dominant mycorrhizal association: from ericoid heath to deciduous shrubs, and arbuscular or nonmycorrhizal tussock sedges. Spatial variation in tundra plant communities is linked to topography and hydrology, which play an important role in determining soil nutrient availability. Saturated soils are common in tundra because permafrost impedes drainage, and nutrient turnover is inhibited where anoxia develops. However, after water is moving down slope or along water tracks, nutrient delivery to plant roots increases. Surface water flow is an important factor in determining plant abundance in arctic landscapes (Rastetter et al., 2004; Mekonnen et al., 2021b. So even in soils with apparently higher N availability, N limitation appears to have increased over time. Soil state factors, such as topography and parent material, as well as plant N acquisition strategy and mycorrhizal association, will influence spatial patterns of plant N limitation. The future state of vegetation will play an important role in determining ecosystem function in the tundra biome, including potential feedbacks on climate via the carbon cycle and surface energy balance. Warming generally increases arctic vegetation growth (Bjorkman et al., 2018a), thereby augmenting the relative importance of water and nutrient sources, primarily nitrogen (N) (Chapin et al., 2005; Shaver et al., 2006).

The most abundant groups of microbes in permafrost are Actinobacteria, Bacteroidetes, Proteobacteria, Firmicutes, Chloroflexi, and Acidobacteria (Steven et al., 2008; Yergeau et al., 2010; Deng et al., 2015; Stackhouse et al., 2015). Archaea and fungi are also present, but about 200–1000 times lower in abundance (Yergeau et al. 2010; Stackhouse et al. 2015; Frey et al. 2016). Gittel et al. (2014) studied Siberian permafrost and found that bacterial abundances in cryoturbated topsoils were as high as in non-cryoturbated topsoils. In contrast, fungal abundances decreased with depth and were significantly lower in cryoturbated than in non-cryoturbated topsoils. The OM decomposition in

Siberian permafrost soils thus is likely more facilitated by bacteria than by fungi. However, microbial composition is sensitive to soil temperature and moisture. Increasing temperature and decreasing moisture of permafrost soils are expected to increase abundance and activity of microorganisms, especially fungal community (Li et al., 2017; Zhang et al., 2018). The study of Baumann et al. (2009) showed that soils with low C and N contents have lower microbial abundance (Wang et al., 2011).

The microbial decomposer communities thus in the permafrost soils are considered to be limited by low C and N availability. Wild et al. (2015) indicated different controlling factors for C and N pools between soil horizon in Siberian permafrost. They suggested a C limitation for microbial decomposers in organic and mineral horizons, while cryoturbated materials might be limited by low N availability. Hence, OM in mineral horizons might be vulnerable to changes in the availability of additional C sources, for example by increased plant growth and subsequently increased allocation of plant-derived compounds to the soil with global warming, while microbial decomposers in cryoturbated horizons are constrained by N limitation, contributing to the persistence of cryoturbated materials in arctic permafrost soils (Wild et al. 2016).

Despite of slow physicochemical weathering, mineral transformation and formation of exchangeable metal ions and secondary Fe-Al-oxide has been shown to be significant in permafrost soils (Gentsch et al., 2015a). These minerals can potentially bind with OC, producing mineral associated OM (MOM). Using density fractionation, Gentsch et al. (2015a) showed that 81% of total OC was stored in subsoil horizons, and the mineral-associated OM represented 55% of the OC in the permafrost soils. Likewise, Prater et al. (2020) revealed nearly 40% of the OC stock in the fractions of clay-sized mineral-associated OM in arctic permafrost soils. Although the proportion of OM in association with mineral to entire OM pool in permafrost soils is lower than those of temperate soils (ca. 90%, Rumpel and Kögel-Knabner et al., 2010), they still contribute a crucial role in OM stabilization in permafrost affected soils. The OC is associated to minerals through various mechanisms, including aggregation, adsorption and/or complexation or co-precipitation processes (Kaiser and Guggenberger, 2003). However, in permafrost soils the impact of aggregation in SOM stabilization is considerably smaller, because thawing following freezing, with the attendant liquid water, causes destabilization of aggregates (Dagesse 2013). There is growing concern about the implications of impact of reactive mineral with C cycling in permafrost soils. Such minerals of concern are soil clay and Fe oxides, which have a high sorption affinity (Kaiser and Guggenberger, 2000; Kaiser and Zech, 2000). Wang et al. (2021) studied permafrost peatland and showed that the concentration of organic carbon was significantly negatively correlated with soil clay content, while it was significantly positively correlated with iron oxides, indicating that soil clay and iron oxides play an important role in stabilizing organic carbon in the permafrost soils (Wang et al., 2021). The moist and acidic conditions of permafrost peatlands increase the adsorption capacity of organic matter to iron oxide (Wagai and Mayer, 2007). Degradation of permafrost can influence the soil Fe balance, with Fe oxides disappearing and Fe forming complexes with carboxyl groups (Fe-CO) (Riedel et al.,

2013). After such a reaction, degradation of OM is prevented, which results in a stable Fe-CO complex (Salvadó et al., 2015). Similarly, Prater et al. (2020) found that OM occluded in associated with clay-sized minerals may be less mobilized with deepening of the active layer. However, thawing along with formation of water-logging and reducing conditions could also unlock carbon associated with metastable Fe phases due to the activity of Fe(III)-reducing bacteria (Patzner et al., 2020). Hence, it is crucial to gain more insight of the relevance of mineral-organic associations for the current OC storage and their possible attenuating effect on the permafrost carbon feedback.

To predict how permafrost soils will respond to climate change in terms of releasing greenhouse gases, it is necessary to know the chemical composition and stabilization mechanisms of SOM. Since arctic soils store with more than 80% of OC in horizons deeper than 30 cm and 55% of that in association with soil minerals (Gentsch et al. 2015), understanding the controls over soil OM decomposition and its response to permafrost degradation in differently separated soil OM pools (particular OM and mineral associated-OM) of whole soil profile is crucial. This thesis used biomarker analysis to access the source and degradation stage of two most predominant compounds of soil OM, i.e. lignin and carbohydrates for predicting carbon losses from arctic ecosystems in the future climate warming.

1.7. Motivation and hypothesis

Organic matter in arctic permafrost soils contains higher C contents than that currently present in the atmosphere. Climate change is particularly stronger in the Arctic, and could cause a considerable part of the OM in permafrost to thaw out, get decomposed, and be released as greenhouse gases; further enhancing global warming. However, the factors regulating the decomposition and transformation of soil OM in permafrost soils remain uncertain. This thesis focuses on the concentration and degree of decomposition of lignin (as more stable plant biomacromolecule) and carbohydrates (as more labile plant and microbial-derived molecules) in functionally different soil fractions of permafrost regions with different active layer thickness, and explores the factors involving in the stabilization of these compounds under climate change.

Studies measuring soil OM composition have reported a high spatial variability, with soil OM decomposition depending not only on soil conditions, but also on vegetation types and topographic positions. As observed along a latitudinal transect in boreal Canada, ecosystem shifts, associated with long-term climate warming, can affect soil OM properties through changes in vegetation and plant litter production, soil conditions thereby altering the composition and activities of microbial decomposers (Kohl et al., 2018). In this thesis, I addressed the concentration and stabilization mechanisms of lignin and carbohydrates by CuO oxidation and TFA hydrolysis at three permafrost regions from north to west of northern Siberia (Cherskiy, Logata and Tazovskiy) respectively, which characterizes a continentality gradient. Permafrost soils were density fractionated before biomarker analysis in order to identify the role of mineral-protected mechanisms. I further determined soil lignin

patterns along a latitudinal gradient stretching along a north-south gradient from (Tazovskiy) to steppe biomes (Fig. 5). The study thus addresses the vulnerability of lignin and carbohydrates in permafrost soils upon thawing and vegetation shift as result of climate warming.

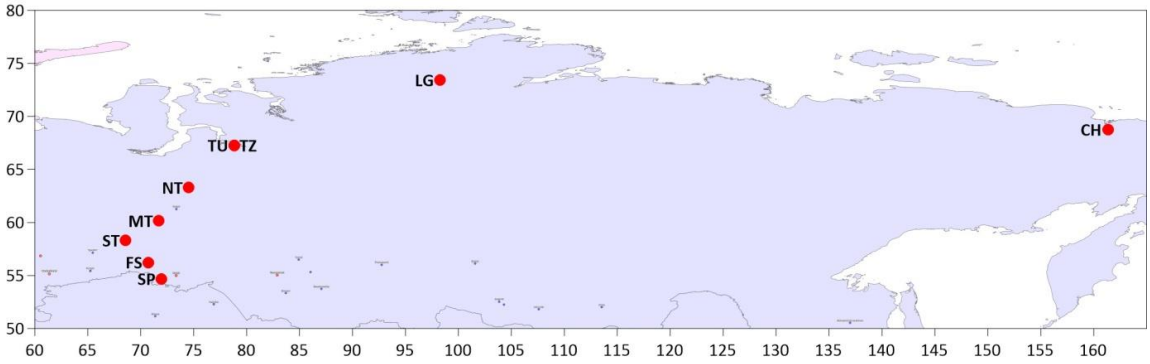

Fig. 5: Study area and location of sites (CH: Cherskiy, LG: Logata, TZ: Tazovskiy, TU: Tundra, NT: Northern taiga, MT: Middle taiga, ST: Southern taiga, FS: Forest steppe, SP: Steppe)

Based on the theoretical background above, I addressed the following general research hypotheses:

H1: Lignin is stabilized in permafrost soils, especially in the subsoil. Because of association in lignocelluloses, carbohydrates also accumulate in permafrost subsoils.

H2: Low temperature and anaerobisis are important mechanisms stabilizing lignin and carbohydrates in permafrost soils. The stabilization of these compounds is accentuated by the microbial community structure, the OM quality, the accessibility of OM to the decomposers and the formation of mineral-organic associations.

H3: Both direct and indirect climatic impact control lignin decomposition along a soil climosequence in western Siberia from tundra to steppe biomes.

H4: The context-protected lignin and carbohydrates will quickly decompose if permafrost thaws under climate warming.

The thesis used a “space-for-time” substitution to explore the pathways of lignin and carbohydrate transformation in Siberian soils, and predict the potential consequences of climate change for OM decomposition especially in permafrost soils.

These objectives and hypotheses are addressed by three individual studies and an integrative analysis of the entire data set across all sites:

I. Fate of carbohydrates and lignin in north-east Siberian permafrost soils

Study I was conducted to assess the contributions of lignin and carbohydrates to the soil OM pool and their decomposition state in a soil profile of permafrost affected soils in the north-eastern Siberia, thus testing **H1**. Separation of functionally different OM fractions was done in order to address the

distribution of lignin and sugar components at free-state or in association with soil minerals, thus contributing to **H2**.

II. Lignin preservation and microbial carbohydrate metabolism in permafrost soils

Study II aimed at evaluating the degree of lignin and carbohydrate decomposition of three permafrost soils from east to west of northern Siberia differing in mean annual temperature, active layer thickness, thus testing **H2**. Separation of functionally different OM fractions was done in order to assess the stability of mineral associated OM, thus contributing to **H2**. Global warming will increase permafrost temperature and thawing, the effects of these patterns on lignin and carbohydrates were investigated, thus contributing to **H4**.

III. Direct and indirect climatic impact on lignin decomposition as studied along a soil climosequence in western Siberia

Study III investigated the factors controlling the variability of lignin concentration and decomposition in the western Siberia by studying 6 different latitudinal biomes, from the tundra to the steppe, testing **H3.**

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2. Study I

Fate of carbohydrates and lignin in north-east Siberian permafrost soils

Contribution: I conducted most of the analysis in the laboratory, collected and evaluated the data, compiled the tables and figures, and wrote the manuscript.

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Fate of carbohydrates and lignin in north-east Siberian permafrost soils

Thao Thi Dao[a,*], Norman Gentsch[a], Robert Mikutta[b], Leopold Sauheitl[a], Olga Shibistova[c,a], Birgit Wild[d,e,f], Jörg Schnecker[d,e,g], Jiří Bárta[h], Petr Čapek[h], Antje Gittel[i,k], Nikolay Lashchinskiy[l], Tim Urich[e,m,n], Hana Šantrůčková[h], Andreas Richter[d,e], Georg Guggenberger[a,c]

[a]Institute of Soil Science, Leibniz University Hannover, Germany
[b]Soil Science and Soil Protection, Martin Luther University Halle-Wittenberg, Germany
[c]VN Sukachev Institute of Forest, Krasnoyarsk, Russia
[d]Department of Microbiology and Ecosystem Science, University of Vienna, Vienna, Austria
[e]Austrian Polar Research Institute, Vienna, Austria
[f]Department of Environmental Science and Analytical Chemistry, Stockholm University, Stockholm, Sweden
[g]Department of Natural Resources and the Environment, University of New Hampshire, Durham, NH, USA
[h]Department of Ecosystem Biology, University of South Bohemia, České Budějovice, Czech Republic
[i]Department of Biology, Centre for Geobiology, University of Bergen, Bergen, Norway
[k]Department of Bioscience, Center for Geomicrobiology, Aarhus, Denmark
[l]Central Siberian Botanical Garden, Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russia
[m]Department of Ecogenomics and Systems Biology, University of Vienna, Vienna, Austria
[n]Institute of Microbiology, Ernst-Moritz-Arndt University, Greifswald, Germany

*** Corresponding author.**
E-mail address: thao@ifbk.uni-hannover.de (T.T. Dao).
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Abstract

Permafrost soils preserve huge amounts of organic carbon (OC) prone to decomposition under changing climatic conditions. However, knowledge on the composition of soil organic matter (OM) and its transformation and vulnerability to decomposition in these soils is scarce. We determined neutral sugars and lignin-derived phenols, released by trifluoroacetic acid (TFA) and CuO oxidation, respectively, within plants and soil density fractions from the active layer and the upper permafrost layer at three different tundra types (shrubby grass, shrubby tussock, shrubby lichen) in the Northeast Siberian Arctic. The heavy fraction (HF; >1.6 g mL^{-1}) was characterized by a larger enrichment of microbial sugars (hexoses *vs.* pentoses) and more pronounced lignin degradation (acids *vs.* aldehydes) as compared to the light fraction (LF; <1.6 g mL^{-1}), showing the transformation from plant residue-dominated particulate OM to a largely microbial imprint in mineral-associated OM. In contrast to temperate and tropical soils, total neutral sugar contents and galactose plus mannose to arabinose plus xylose ratios (GM/AX) decreased in the HF with soil depth, which may indicate a process of effective recycling of microbial biomass rather than utilizing old plant materials. At the same time, lignin-derived phenols increased and the degree of oxidative decomposition of lignin decreased with soil depth, suggesting a selective preservation of lignin presumably due to anaerobiosis. As large parts of the plant-derived pentoses are incorporated in lignocelluloses and thereby protected against rapid decomposition, this might also explain the relative enrichment of pentoses with soil depth. Hence, our results show a relatively large contribution of plant-derived OM, particularly in the buried topsoil and subsoil, which is stabilized by the current soil environmental conditions but may become available to decomposers if permafrost degradation promotes soil drainage and improves the soil oxygen supply.

1. Introduction

Arctic permafrost-affected soils store around 1,300 Gt carbon (Hugelius et al., 2014), which accounts for approximately 50% of the global soil organic carbon (OC) pool. Organic matter (OM) in permafrost soils has been protected from microbial decomposition by the climatic conditions at high-latitudes, i.e., by being perennially frozen in the permafrost exposed to seasonally frozen conditions in the active layer as well as by the frequent soil water saturation (Chapin et al., 1980, Schuur et al., 2008). However, increasing temperatures and changing precipitation pattern will likely promote permafrost loss, changes in plant productivity, species composition and plant-soil C allocation, and soil organic matter (SOM) decomposition, which likely facilitate either directly or indirectly further carbon release to the atmosphere and a possibly positive feedback to global warming (Schuur et al., 2011; Runyan et al., 2012; Gentsch et al., 2015b; Wild et al., 2016).

The chemical composition and accumulation of OM in different soil horizons of a particular ecosystem reveals the state of OM decomposition, which is an integral result of both biotic and abiotic soil conditions. Carbohydrates entering the soil system with plant rhizodeposits, roots and aboveground litter as well as products of microbial and faunal metabolism represent a major energy source for heterotrophic soil microbial communities (Cheshire, 1979; Murayama, 1984; Gunina and Kuzyakov, 2015). Plant-derived carbohydrates in soils are represented by relatively greater proportions of pentoses (e.g., arabinose and xylose), whereas sugars of microbial origin are relatively richer in hexoses (e.g., galactose and mannose) and deoxysugars (e.g., fucose and rhamnose) (Murayama, 1984; Oades, 1984). While plant-derived sugars are reported to decompose rapidly in soil (Martin and Haider, 1986), microbially synthesized sugars can contribute to older SOM fractions when stabilized physically or chemically (Tsutsuki and Kuwatsuka, 1989; Guggenberger et al., 1994; Rumpel et al., 2010) or upon their continuous recycling by microorganisms (Sauheitl et al., 2005; Derrien et al., 2006).

Unlike carbohydrates, lignin is exclusively derived from plants. This aromatic biopolymer contains resistant C bonds, e.g., C-O-C and C-C between the monomeric phenylpropanoid units, and is intimately associated with celluloses and hemicelluloses, i.e., lignocelluloses. The degradation of lignin is primarily driven by fungi. White-rot fungi are most efficient in lignin degradation and mineralization (Haider and Trojanowski, 1980; Arora and Sharma, 2010) while brown-rot fungi preferentially degrade celluloses and hemicelluloses, and modify lignin only to a limited extent (Highley and Illman, 1991). In addition to fungi, three groups of bacteria *actinomycetes, α-proteobacteria, and γ-proteobacteria* (Zimmermann, 1990; Bugg et al., 2011) are also partly involved in lignocellulose degradation. As most microbial lignolytic enzymes, e.g., peroxidases and laccases, are mainly active under presence of oxygen, complete lignin degradation is basically restricted to aerobic soil conditions (Kirk and Farrell, 1987; Bugg et al., 2011). Due to its biochemical resistance and limited abundance of ligninolytic degraders in soils, lignin has been considered in the literature to be slowly degradable in soils and to represent the slower C-cycling fraction of plant litter (Haider et

al., 1975; Stevenson, 1994). However, the rate of lignin decomposition in soil is still under debate. For example, Kiem and Kögel-Knabner (2003) used CuO oxidation to determine soil lignin contents and composition in fertilized land *vs.* bare fallow, and found no evidence for long-term stabilization of lignin in soil. Furthermore, compound-specific isotope analysis of lignin phenols derived from CuO oxidation indicated that lignin turnover can be as fast or even faster than that of bulk SOM (Dignac et al., 2005; Heim and Schmidt, 2007) or bulk litter (Sanaullah et al., 2010; Klotzbücher et al., 2011).

The fate of carbohydrates and lignin has been investigated intensively in temperate soils (Kögel et al., 1988; Guggenberger et al., 1994; Spielvogel et al., 2007), tropical soils (Guggenberger et al., 1995; Möller et al., 2002), tropical wetlands (Tareq et al., 2004), and tropical and European peat soils (Bourdon et al., 2000; Bambalov, 2007). However, the understanding of OM transformation in permafrost soils is still scarce. Gundelwein et al. (2007) determined acid insoluble lignin, i.e., Klason lignin, of a few permafrost soil samples from central Siberia and suggested a restrained degradation of lignin in the lower parts of the active layer in permafrost soils. Höfle et al. (2013) applied ^{13}C-NMR spectroscopy and lipid analysis of permafrost soils and reported that the chemical composition and inherent decomposability of organic substances play a more important role in OM stabilization than the formation of mineral-organic association, which contrasts findings for temperate soils (Marschner et al., 2008). Likewise, Gentsch et al. (2015b) used ^{13}C-NMR and X-ray photoelectron spectroscopy to show a progressive alteration of OM composition with increasing soil depth. However, these spectroscopic techniques only provide an overview of the total OM composition, and lipid analysis might reflect the origin of OM rather than its degradation state.

To characterize the detailed composition and transformation of OM in permafrost soils and its potential vulnerability to climate warming, we investigated the carbohydrate and lignin signatures of plants and soil samples from the active layer (seasonal thawing) and the upper permafrost layer in north-eastern Siberia by using chemolytic methods. Since on landscape level, tundra vegetation is highly heterogeneous (Fletcher et al., 2010), we included three tundra types (shrubby grass, shrubby tussock, shrubby lichen) in our study to examine their impact to SOM quality and transformation. As the majority of OM in permafrost soils resides in mineral-organic associations (Gentsch et al., 2015a), which is considered relatively stable against biodegradation (Torn et al., 1997; Kalbitz et al., 2005; Mikutta et al., 2006), we applied density fractionation to separate the light fraction (LF; <1.6 g mL^{-1}), containing mainly particulate OM (POM), from the heavy fraction (HF; >1.6 g mL^{-1}), comprising mostly mineral-associated OM (MOM). We hypothesized that (i) lignin decomposition is restrained in deeper soil horizons because of the low temperature and frequent anoxic conditions and (ii) plant-derived carbohydrates decline with soil depth, as they represent an easily available carbon and energy source also under anoxic conditions. Hence, permafrost-affected soils with their unfavorable environmental conditions for microbial decomposition may be relatively enriched in lignin-derived components, particularly at larger soil depth.

2. Materials and methods

2.1. Soil and vegetation samples

The study was carried out at three different tundra types (shrubby grass, shrubby tussock and shrubby lichen) along the lower Kolyma river near the settlement Cherskiy, Russia (Table 1), within the zone of continuous permafrost (Brown et al., 1998). According to WorldClim database, the mean annual precipitation is 160 mm and the mean annual temperature is -12.7 °C (Hijmans et al., 2005). All soils in the study area were classified as Gelisols with intensive cryoturbation. Three 5-m wide soil profiles per each tundra type were excavated and soil horizons from active layer and the upper permafrost (up to 45 cm depth below the permafrost table) were sampled at the end of summer in August 2010, when the active layer had reached its maximal depth. Soil horizons were classified as organic topsoil (O), mineral topsoil (A/AB), buried topsoil (Ojj/Ajj), mineral subsoil (BCg/Cg) and permafrost (Cff) horizons as described in Gentsch et al. (2015a). Directly after sampling, all living roots were removed, and soils were dried at 50 °C and homogenized by sieving to <2mm. The soils are characterized by high OC contents with slight difference between the tundra types, mostly weakly acidic pH (6.08 ± 0.94, mean ± SD), and silty-clay texture (Table 2; Gentsch et al., 2015b). The dominating plants are dwarf shrubs, graminoids, lichens and mosses, and specific species are reported in Table 1. Aboveground (leaves, stems) and belowground (roots exclusively lichens and mosses) biomass of the dominating species was taken randomly with 5 replicates. Like soil samples, plant samples were dried (40 °C) and ground before analyzing neutral sugar and lignin contents.

Table 1: Sampling sites, vegetation and soil classification (Gentsch et al., 2015b)

Tundra type	Latitude	Longitude	Dominant plants	Active layer depth	Soil classification and texture*
Shrubby grass tundra	N69^0 26' 15.5"	E161^0 42' 36.4"	*Betula exilis, Salix sphenophylla, Carex lugens, Calamagrostis*	30-70	Ruptic-Histic Aquiturbel, fine silty
Shrubby tussock tundra	N69^0 26' 46.0"	E161^0 45' 5.5"	*Eriophorum vaginatum, Carex lugens, Betula exilis, Salix pulchra.,*	35-60	Ruptic-Histic Aquiturbel, clayey to fine silty
Shrubby lichen tundra	N68^0 44' 51.9"	E161^0 35' 40.5"	*Betula exilis, Vaccinium uligonosum, Flavocetraria nivalis,*	35-90	Ruptic-Histic Aquiturbel, fine silty to loam-skeletal

* *Soil Survey Staff (2014).*

2.2. Density fractionation

For the analysis we used soil density separates provided by Gentsch et al. (2015b), who fractioned soil samples according to Golchin et al. (1994) with some modifications. Two density fractions were isolated by sodium polytungstate solution, i.e., the light fraction (LF) with a density <1.6 g mL^{-1} and the heavy fraction (HF) with a density >1.6 g mL^{-1}. The LF mainly consists of free and unprotected plant residues; occluded POM is considered minor given the limited aggregation of the studied Gelisols and was thus not separated. The HF comprises mineral-associated OM formed by coprecipitation with multivalent cations (Al, Fe) and adsorption of OM to pedogenic minerals (Gentsch et al., 2015a).

2.3. Organic carbon, total nitrogen content, and $\delta^{13}C$ ratio

Organic carbon (OC), total nitrogen (TN) contents and the $\delta^{13}C$ ratio of plant materials, bulk, LF and HF soils were measured by Gentsch et al. (2015b) in duplicates using an Elementar IsoPrime 100 IRMS (IsoPrime Ltd., Cheadle Hulme, UK) coupled to an Elementar Vario MICRO cube EA C/N analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). These authors tested randomly 20 samples for inorganic carbon with about 2% of samples containing concentrations of ≤1wt%. Thereafter, carbonate was removed from all samples before analysis by acid fumigation as described in Harris et al. (2001). Hence, reported carbon contents refer to OC.

2.4. Carbohydrate analysis

Non-cellulosic sugars were released from plant and soil samples by acid hydrolysis according to Amelung et al. (1996), while the purification of the hydrolysate followed a modified procedure of Rumpel and Dignac (2006) and Eder et al. (2010).

Briefly, neutral sugar monomers were released from plant and soil samples equivalent to 3-5 mg OC by means of acidic hydrolysis at 105 °C for 4 h using trifluoroacetic acid (TFA). Thereafter, filtered hydrolysates were purified according to Eder et al. (2010), i.e., released iron was complexated using EDTA. While these authors used 0.1 mL of the hydrolyzed sample, we increased the amount to 1.0 mL due to the low carbohydrate contents of the HF. We further improved the clean up procedure to increase the recovery. We freeze-dried samples prior to derivatization to remove residual water, and neutralized remaining TFA by adding some drops of 2M NH_3 solution. These changes improved the average recovery to 85 ± 5%. The following derivatization to sugar alditol acetates followed the procedure described by Rumpel and Dignac (2006).

Identification and quantification of sugar-monomers was based on calibration with pure standard solutions. Myo-inositol was added to samples before hydrolysis as a first internal standard for compensation of losses during the clean-up procedure, while recovery standard D-allose was derivatized to alditol acetates and added to samples prior to gas chromatograph analysis. Sugars were separated and detected using a gas chromatograph (7890A, Agilent, USA) equipped with a flame ionization detector (FID) according to Spielvogel et al. (2007).

Additionally, the ratios of galactose + mannose to arabinose + xylose (GM/AX) and of rhamnose + fucose to arabinose +xylose (RF/AX) were calculated. Previously, these ratios were used as indicators for estimating the plant *vs.* microbial source of the sugar in soil (Murayama, 1984; Oades, 1984), but recently this is considered ambiguous because some plant species contain a relevant amount of hexoses (reviewed by Gunina and Kuzyakov, 2015).

Table 2: Organic carbon (OC), total nitrogen (N), C/N ratio and stable ^{13}C isotopic composition ($\delta^{13}C$) of the different horizons of the bulk soils and the respective LF and HF for all tundra types (Gentsch et al., 2015b).

	Bulk				LF				HF			
Soil horizon	**OC (%)**	**TN (%)**	**C/N**	**$\delta^{13}C$ (‰)**	**OC (%)**	**TN (%)**	**C/N**	**$\delta^{13}C$ (‰)**	**OC (%)**	**TN (%)**	**C/N**	**$\delta^{13}C$ (‰)**
Organic topsoil	**23.8±1.69**	**1±0.06**	**24±1.39**	**-28.2±0.15**								
Grass	20.6 ± 2.47	0.93±0.05	21.8±1.99	-27.9±0.31								
Tussock	26.2±2.57	1.14±0.07	23.6±3.14	-28.3±0.21								
Lichen	23.6±3.42	0.92±0.12	25.8±1.39	-28.5±0.26								
Mineral topsoil	**3.42±1.04**	**0.22±0.06**	**14.4±0.96**	**-26.8±0.18**	**34.4±2.7**	**1.07±0.14**	**34.5±3.07**	**-28.6±0.32**	**1.73±0.39**	**0.14±0.03**	**12.1±0.78**	**-26.5±0.12**
Grass	2.81±1.47	0.21±0.09	12.5±1.06	-26.5±0.17	39.8±0.47	1.43±0.33	32.0±6.38	-28.1±0.64	1.88±1.08	0.15±007	10.3±1.36	-26.2±0.19
Tussock	4.72±2.56	0.28±0.14	16.1±0.6	-27.4±0.09	32.3±6.73	0.92±0.1	34.2±6.2	-28.9±0.43	1.33±0.26	0.1±0.01	12.2±0.67	-27±0.12
Lichen	2.5±0.85	0.16±0.03	14.6±3.13	-26.5±0.41	29.8±3.02	0.78±0.09	38.1±1.99	-28.8±0.67	1.93±0.25	0.14±0.006	14.3±1.14	-26.5±0.08
Burried topsoil	**10.1±1.00**	**0.60±0.05**	**16.1±0.37**	**-27.5±0.08**	**36.6±0.41**	**1.43±0.02**	**25.6±0.42**	**-27.9±0.1**	**8.2±0.84**	**0.62±0.08**	**13.7±0.52**	**-26.6±0.1**
Grass	11±1.7	0.64±0.07	16.5±0.6	-27±0.05	35.8±0.73	1.51±0.03	23.8±0.47	-27.8±0.09	7.34±0.89	0.72±0.15	11.6±0.72	-26.7±0.06
Tussock	15.5±1.77	0.84±.09	18.5±0.24	-27.6±0.22	36.7±0.85	1.45±0.03	25.3±0.55	-28±0.12	12.2±1.71	0.74±0.1	16.6±0.23	-27.2±0.11
Lichen	6.76±0.92	0.45±0.06	14.6±0.31	-27.7±0.06	37.2±0.61	1.36±0.02	27.3±0.58	-27.8±0.22	6.17±0.91	0.45±0.06	13.6±0.26	-26.1±0.03
Mineral subsoil	**1.31±0.10**	**0.11±0.00**	**11.5±0.37**	**-26.3±0.17**	**40.5±0.74**	**1.29±0.07**	**32.9±1.38**	**-27.6±0.14**	**0.89±0.08**	**0.09±0.004**	**9.76±0.4**	**-26.1±0.15**
Grass	1.04±0.09	0.1±0.005	10.9±0.49	-26.2±0.1	40.1±056	1.42±0.14	29.8±2.8	-27.4±0.21	0.73±0.04	0.08±0.004	8.69±0.54	-26.1±0.11
Tussock	1.65±0.16	0.13±0.01	12.7±0.45	-27.2±0.21	38.7±0.72	1.07±0.08	37.4±2.12	-28.4±0.11	1.23±0.16	0.1±0.008	11.6±0.54	-26.9±0.08
Lichen	1.2±0.21	0.1±0.01	10.7±0.8	-25.4±0.18	42.9±1.9	1.32±0.06	32.4±0.76	-27.1±0.17	0.63±0.06	0.07±0.04	8.64±0.32	-25.3±0.1
Permafrost	**1.97±0.38**	**0.15±0.02**	**11.7±0.84**	**-26.4±0.16**	**39.6±0.37**	**1.71±0.1**	**25.4±1.5**	**-27.5±0.13**	**1.17±0.23**	**0.11±0.01**	**9.51±0.61**	**-26.2±0.14**
Grass	0.90±0.05	0.10±0.00	9.2±0.27	-25.8±0.08	39.9±0.33	2.2±013	19.7±2.47	-27.1±0.19	0.58±0.05	0.08±0.009	7.1±0.56	-25.7±0.13
Tussock	2.56±0.70	0.16±0.24	13.3±1.72	-26.9±0.25	40.1±0.72	1.42±0.08	29.1±1.62	-27.9±0.16	1.23±0.22	0.11±0.01	10.3±0.87	-26.5±0.2
Lichen	2.90±1.17	0.20±0.07	13.2±0.80	-26.6±0.51	37.8±0.71	1.28±0.08	29.8±1.81	-27.2±0.26	1.9±1.05	0.15±0.07	11±1.05	-26±0.23

Values are mean values (± standard error)

2.5. Lignin analysis

The amount of lignin-derived phenols and its degree of oxidative degradation in plant and soil samples were determined using alkaline CuO oxidation following the method of Hedges and Ertel (1982) with modifications of Kögel and Bochter (1985). Briefly, lignin was oxidized with CuO in teflon vessels in the presence of ammonium iron sulfate hexahydrate [$Fe(NH_4)_2(SO_4)_2.6H_2O$], glucose and 2 M NaOH to release lignin-derived phenols. The vessels were sealed and heated for 3 h at 170 °C. The lignin-derived monomers were purified using preconditioned C_{18} column (Bakerbond) and converted to trimethylsilyl (TMS) derivatives by reaction with (N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) in pyridine. The derivatized lignin-derived monomers were identified and quantified using gas chromatography-mass spectrometry (450-GC, ion trap 220MS Varian, USA) using a capillary column (FactorFour™ VF-5ms, 30 m, 0.25 mm I.D., 0.25 µm film thickness). The oven temperature was programmed from 100 °C to 160 °C at a rate of 10 °C min^{-1}, from 160 °C to 250 °C at 20 °C min^{-1}, and finally at 50 °C min^{-1} to 300 °C. Calibration was based on measurement of the dominant mass fragments of eight different analyzed substances using ten concentration levels of standards. The first internal standard (ethylvanillin) was added before CuO oxidation, while the second internal standard (phenylacetic acid) was added prior to derivatization. The recovery of ethylvanillin during the procedure was on average 78 ± 15%. Vanillyl (V) and syringyl (S) units were calculated as the sum of their ketone, aldehyde and carboxylic acid forms; cinnamyl (C) units were the sum of ferulic acid and p-coumaric acid. Total lignin-derived phenols were defined as the sum of individual units (VSC = V + S + C). Mass ratio of syringyl to vanillyl (S/V) and cinnamyl to vanillyl (C/V) units reflect the origin of major plant groups (gymnosperm vs. angiosperm) with smaller ratios being indicative for gymnosperms (Hedges and Mann, 1979). Mass ratios of acids over aldehydes of vanillyl $(Ac/Al)_V$ units were used to follow the degree of lignin degradation (Hedges and Ertel, 1982; Kögel, 1986).

2.6. Statistics

One-way ANOVA, followed by Tukey's HSD post-hoc testing and two-way ANOVA were used to determine the differences in neutral sugar and lignin phenol composition between horizons and between tundra types at a significance level of $p \leq 0.05$. Pearson correlation coefficients were applied to describe linear relationships between parameters. All variables were tested for normal distribution and log transformed if necessary. Non-metric multidimensional scaling (NMDS) was used to visualize variation in sugar and lignin composition according to differences in sites, plant species and soil horizons. NMDS analysis was conducted on the basis of Euclidean distance matrix using the "metaMDS" function in the "vegan 2.4-0" package of R version 3.2.2 (Oksanen et al., 2016). The objects that are ordinated closer to one another are more similar than those further apart. The ellipses show 95% confidence interval (CI), indicating the probability of containing the population mean. Axes are arbitrary and scaled in units of Euclidean distance. ADONIS (Permutational Multivariate

Analysis of Variance Using Distance Matrices) and post hoc-ADONIS (pairwise-ADONIS) in the vegan package of R were used to test the significant differences of sugar and lignin community within horizons (McArdle and Anderson, 2001; Anderson, 2001). Statistical analyses, calculations and plots were performed and created in R version 3.2.2 (R Core Team, 2015) and Sigma Plot 10 (Systat Software, San Jose, USA).

3. Results

3.1. Carbohydrate composition and distribution

Plant samples

The OC-normalized neutral sugar contents of plant tissues varied between 200 and 480 g kg^{-1} OC, and decreased in the order mosses/lichens (450.0 ± 7.1) >~ graminoids (413.0 ± 9.6) > dwarf shrubs (220 ± 9.8 g kg^{-1} OC, mean ± SE; Table 3), which are consistent with data obtained for plant communities of Alpine tundra (Prietzel et al., 2013). The largest relative proportion of glucose on total hydrolysable carbohydrates was observed for dwarf shrubs (77.0 ± 4.0 g kg^{-1} OC, mean ± SE), while graminoids were particularly rich in xylose (184.0 ± 23.5 g kg^{-1} OC), and mosses/lichens were characterized by a larger proportion of galactose and mannose (222.0 ± 48.0 g kg^{-1} OC). Almost all types of plants contained small amounts of galactose and mannose, and thus had small GM/AX values (Table 3), which fit to the findings of Prietzel et al. (2013). Exceptionally, lichens and mosses had a larger amount of these hexoses, resulting in a higher GM/AX and RF/AX ratios compared to dwarf shrubs and graminoids (Table 3).

Table 3: Carbohydrate and lignin patterns of plant source materials

Plant species	Total neutral sugar (g kg^{-1} OC)	GM/AX	RF/AX	VSC (g kg^{-1} OC)	S/V	C/V	$(Ac/Al)_V$
Dwarf shrub (n = 7)	220 ± 10	0.47 ± 0.06	0.08 ± 0.008	28.5 ± 3.7	0.70 ± 0.05	0.74 ± 0.05	0.38 ± 0.07
Graminoid (n = 4)	413 ± 10	0.18 ± 0.03	0.01 ± 0.0025	61.3 ± 9.2	1.50 ± 0.3	1.78 ± 0.70	0.15 ± 0.03
Moss (n = 1)	440	3.44	0.23	8.20	0.50	0.46	0.60
Lichen (n = 1)	454	6.24	0.29	0.70	0.40	0.35	1.50

Values are mean values (± standard error)

Soil fractions

In soil, OC-normalized contents of neutral sugars accounted for 210 ± 15.6 g kg^{-1} OC (mean ± SE) in O horizons (n = 11, all sites), 160 ± 7.0 g kg^{-1} OC in the LF (n = 49, all sites), and 150 ± 7.0 g kg^{-1} OC in the HF (n = 60, all sites). In comparison with covering plants, the O horizons and the fractionated mineral soils (LF and HF) had significantly smaller OC-based contents of neutral sugars released upon acid hydrolysis and higher GM/AX ratios (one way-ANOVA, $p < 0.001$).

In the LF of mineral soils, a one-way ANOVA on OC-normalized total neutral sugar contents showed no significant difference between tundra types in respective soil horizons (Fig. 1a; Supplementary Table 1). The GM/AX ratio of the organic topsoil at shrubby lichen tundra was significantly higher than at the two other sites (Fig. 1b; Supplementary Table 1). In contrast, the

GM/AX ratio of the LF at the shrubby lichen tundra did not differ from those of the shrubby grass and shrubby tussock tundra. The OC-normalized total neutral sugar contents in the LF appeared to slightly decline with soil depth at the shrubby lichen tundra, while no trend was observed for the shrubby grass and shrubby tussock tundra (Fig. 1a). A similar trend was observed when the abundance of neutral sugars was presented with respect to dry mass of soil fraction (Supplementary Figure 1a). This went along with a general decline in the GM/AX ratios (Fig. 1b). For all pooled sampling sites, Tukey's HSD indicated that total neutral sugar contents in permafrost layers were smaller than in organic topsoil and buried topsoil horizons, whereas no significant differences were found between organic topsoil, mineral topsoil and mineral subsoil horizons (Supplementary Table 2). In contrast to plant tissues, the glucose content was not predominant in the O horizon and the LF (data not shown), which were relatively richer in arabinose, and xylose ($p < 0.01$). The RF/AX ratio of the LF showed a similar trend as the GM/AX ratio, i.e., it also decreased with soil depth and was significantly higher in O horizons than in the LF ($p < 0.001$).

Like for the LF, a one-way ANOVA revealed no significant difference in OC-normalized neutral sugar contents in the HF between tundra types in respective soil horizons (Fig. 1c; Supplementary Table 1). Normalized to OC, the HF had similar averaged hydrolysable carbohydrate contents as the LF but a clearer tendency of decreasing contents with soil depth (Fig. 1c). Total carbohydrate in the HF decreased steeply under shrubby grass tundra (from 197 ± 15 to 109 ± 14 g kg^{-1} OC, mean ± SD) and shrubby tussock tundra (from 304 ± 62 to 131 ± 18 g kg^{-1} OC), while this decline was less pronounced under shrubby lichen tundra (from 228 ± 15 to 159 ± 7 g kg^{-1} OC). The variability of sugar contents related to dry mass was the same except for buried horizons across all tundra types, which had considerably higher total neutral sugar contents compared to non-buried materials (Supplementary Figure 1b).

Compared to the LF, the HF exhibited larger GM/AX ratios (0.93 ± 0.31 vs. 0.55 ± 0.15, mean ± SD), which likewise decreased with increasing soil depth, at all tundra types ($p < 0.001$; Fig. 1d). This trend was caused by the decrease of galactose and mannose (Supplementary Fig. 2b), and the decrease of glucose also was found (62 ± 12 g kg-1 OC at mineral topsoil vs. 29 ± 13 g kg-1 OC at deeper horizons, mean ± SD) with soil depth. The rhamnose signal in the HF appeared as double-peak, so that no valid RF/AX ratio could be calculated. However, the small signal intensities suggest only low rhamnose concentrations, so that the total sugar contents were not strongly influenced by the lack of rhamnose quantification.

The NMDS analysis of OC-normalized neutral sugars revealed that the individual neutral sugars differed quite prominently between the O horizons and the LF of the mineral soils and the respective plant source materials (Fig. 2a; ADONIS: $p < 0.001$). Likewise, the statistical analysis revealed differences in sugar composition between soil horizons in both LF and HF (Fig. 2a, b; ADONIS: $p < 0.001$). Pair-wise ADONIS comparisons, subsequently, showed significant differences in individual neutral sugars between organic topsoil, mineral subsoil and permafrost layer, whereas no

significant difference was observed between topsoil and buried topsoil (Supplementary Table 3). The analysis also confirms that the neutral sugar composition in the O horizon and the LF was specific for certain soil horizons, which appeared as clusters: Higher concentrations of mannose, fucose, rhamnose and glucose occurred in organic and mineral topsoil horizons, while arabinose and xylose were stored more dominantly in subsoil horizons and permafrost layers. Similarly to the LF, also in the HF pentoses contributed more to subsoil and permafrost horizons whereas hexoses appeared more abundantly in the topsoil and buried topsoil horizons.

3.2. Lignin phenol concentration and distribution

Plant samples

The CuO-digestible lignin (VSC) contents of graminoids were higher than those of dwarf shrubs (61.3 ± 9.2 *vs.* 28.5 ± 3.7 g kg^{-1} OC; mean ± SE; Table 3). Also lichen and green moss contained smaller contents of lignin-like compounds (0.7 and 8.2 g kg^{-1} OC, respectively). Vascular plants contained relatively equivalent amounts of V and S units (0.7 ± 0.2, mean ± SD), as is expected for angiosperm vegetation (Hedges and Ertel, 1982). *Carex lugens* and *Eriophorum vaginatum* had particularly high C/V ratios (1.3 and 3.2, respectively), reflecting a high abundance of coumaryl compounds which is typical for grasses (Iiyama et al., 1990; Lam et al., 2001; Otto and Simpson, 2006).

Soil fractions

Organic carbon-normalized contents of lignin-derived phenols accounted for 25 ± 1.7 g kg^{-1} OC (mean ± SE) in O horizons (n = 11, all sites), 34 ± 1.2 g kg^{-1} OC in the LF (n = 58, all sites), and 20 ± 0.8 g kg^{-1} OC in the HF (n = 55, all sites). The contents of lignin-derived phenols in the organic topsoil were thus smaller than in the covering vascular plants.

A comparison of the different tundra types showed that in organic topsoil, the yield of VSC was smaller at shrubby lichen tundra than at shrubby grass and shrubby tussock tundra, but no significant difference was observed for the LF (Fig. 3a; Supplementary Table 1). Interestingly, the LF materials exhibited a relatively higher yield in VSC than the organic topsoil horizons of the respective tundra types (Fig. 3a), and the Tukey's HSD for all tundra revealed that the LF of the permafrost horizon contained significantly more VSC than the LF from buried topsoil and subsoil horizons (Fig. 3a; Supplementary Table 2). The same trend was obtained when the abundance of VSC was presented according to dry mass of LF materials (Supplementary Figure 3a).

Likewise, the HF showed no significant differences in the OC-normalized VSC content among tundra types, whereas for all pooled sampling sites, VSC appeared to differ between horizons with higher concentrations in mineral subsoil and permafrost horizons than in mineral and buried topsoils (Fig. 3b; Supplementary Fig. 4b). Based on dry mass, VSC was generally constant with soil depth, except for buried horizons, which had substantially higher values (Supplementary Figure 3b). In

comparison with the LF, the HF contained smaller OC-normalized VSC contents in the respective horizons (two-way ANOVA, $p < 0.05$).

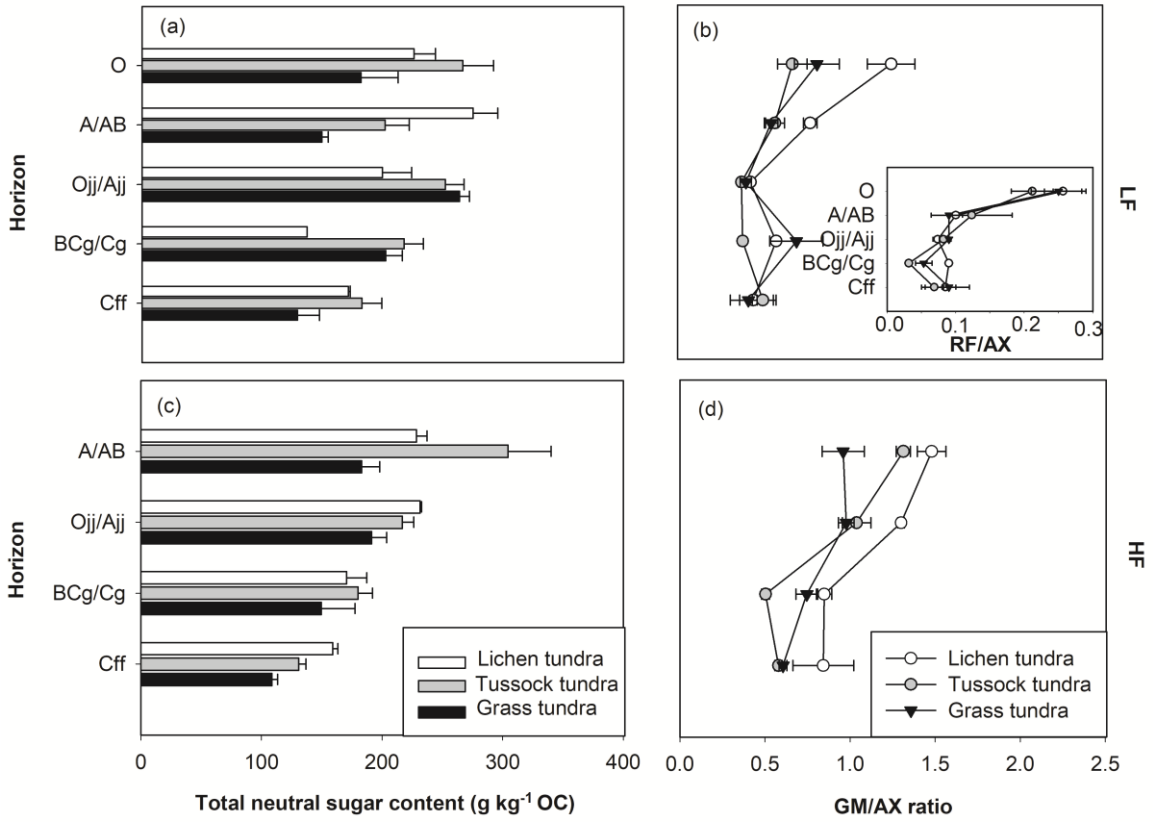

Fig. 1: Total carbohydrate patterns within soil profiles of three tundra types, displaying the carbohydrate contents of (a) O horizons and the light fraction (LF), and (c) the heavy fraction (HF), as well as GM/AX and RF/AX ratios (b and d). Error bars are given as SE.

The indicator for oxidative decomposition of lignin, the $(Ac/Al)_V$ ratio was significantly higher in O materials and the HF of permafrost horizons at the shrubby grass tundra than at the two other sites (Fig. 3c and d; Supplementary Table 1). In the LF, $(Ac/Al)_V$ did not show a consistent trend with soil depth, but was significantly higher in buried topsoil than in mineral topsoil horizons (Supplementary Table 2). The $(Ac/Al)_V$ ratios of the HF did not show any significant differences with soil depth. With respect to differences between soil fractions, the $(Ac/Al)_V$ ratio was significantly higher in the HF than in the LF (two-way ANOVA; $p < 0.001$).

The NMDS plot and pair-wise ADONIS revealed that OC-normalized individual lignin-derived phenols of the O horizons and the LF in the active layers were significantly different from permafrost layers. In contrast, in the HF differences existed mainly between the buried topsoil in comparison to the subsoil and permafrost horizons (Fig. 4b; Supplementary Table 3).

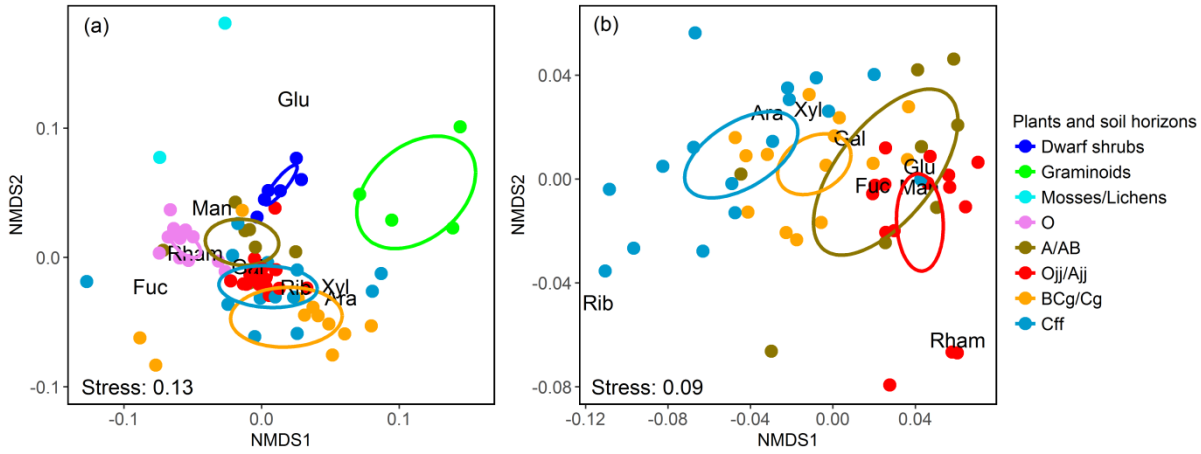

Fig. 2: NMDS plot of total carbohydrate and individual sugar contents (Rham: rhamnose, Fuc: fucose, Rib: ribose, Ara: arabinose, Xyl: xylose, Man: mannose, Gla: galactose, Glu: glucose) from individual plant and soil samples over all tundra types for (a) the plants, O horizons and light fraction (LF) and (b) the heavy fraction (HF).

3.3. Comparison of hydrolysable carbohydrates, CuO lignin, C/N ratio, and δ ^{13}C ratio

For the LF, no correlation between OC-normalized total sugars or galactose plus mannose (GM) with C/N or $\delta^{13}C$ was detected. For the HF, the decreasing OC-normalized contents of total sugar and GM, i.e., microbially-derived sugars, with soil depth went along with decreasing C/N and increasing $\delta^{13}C$ values (Fig. 5). Further, increasing OC-normalized VSC contents with soil depth tended to be related to decreasing C/N ratios and increasing $\delta^{13}C$ ratios in the HF, and no clear relationship between these parameters were observed for the LF (Fig. 5). Over all sites, OC-normalized contents of the pentoses, arabinose and xylose were slightly but significantly correlated with VSC in both LF and HF (Fig. 6; $r^2 = 0.15$, $p < 0.001$, $n = 38$; $r^2 = 0.27$, $p < 0.001$, $n = 42$, respectively).

4. Discussion

4.1. Carbohydrate transformation in permafrost soils

There are a number of studies employing GM/AX and RF/AX ratios to assess the microbial decomposition of plant-derived sugars, which are considered to be enriched in arabinose and xylose, and subsequent production of microbial sugars, being enriched in galactose, mannose, rhamnose, and fucose (Cheshire et al., 1979; Murayama, 1984; Oades, 1984). The predominance of hexoses in mosses and lichens which is consistent with reports by Olafsdottir and Ingólfsdottir (2001) and Stark et al. (2012) implies that these plants provide an input signal to soil that may blur this concept (Nierop et al., 2001; Prietzel et al., 2013) and questions the usefulness of the GM/AX ratios as indicator for microbially-synthesized sugars. At the other tundra types, despite a small extent of green moss covering, the high proportion of arabinose and xylose as well as narrow GM/AX and RF/AX ratios of

most plants, organic topsoil and LF materials confirmed a high contribution of plant-derived sugars to SOM (Oades, 1984; Guggenberger et al., 1994).

Density fractionation has been frequently used to separate plant residues in the mineral soils into the LF, whereas microbially transformed organic matter is enriched in the HF (Golchin et al., 1994; Grünewald et al., 2006). As reported for temperate (Guggenberger et al., 1994; Spievogel et al., 2007, Kiem and Kögel-Knabner, 2003) and tropical (Guggenberger et al., 1995) soils, also in the investigated permafrost soils, higher GM/AX ratios were observed in the HF than in the LF. This is indicative of a larger abundance of microbially-derived sugars in the HF. The selective accumulation of microbial sugars in the HF is in line with smaller C/N and less negative $\delta^{13}C$ ratios in the HF as compared to the LF (Table 2; Gentsch et al., 2015a,b). While inorganic N contributed only marginally to total N in bulk samples (Gentsch et al., 2015b), the lower C/N ratios of the HF typically are associated with a higher relative contribution of OM of microbial origin (Waksman, 1933; Dignac et al. 2002; Rumpel and Kögel-Knabner, 2011), which is underpinned by the microbially-induced enrichment of the ^{13}C isotope. Hence, in the mineral-associated OM, products of microbial resynthesis preferentially accumulate also in permafrost soils. This might be ascribed to the preferential location of microbial biomass at mineral surfaces (Marsh et al., 2012). As well, this may point to microorganisms which use Fe(III) and Mn(IV) from the soil minerals as alternative electron acceptors for their katabolic functions, leading to the degradation of OC sources to carbon dioxide under anaerobic conditions (Lovley et al., 2004; Kappler and Straub, 2005; Weber et al., 2006). For the soil samples investigated in our study, Gittel et al. (2014) indeed found sulfur-and metal-reducing *Desulfuromonadales* in the deeper soil horizons showing that mineral surfaces are a preferential habitat for microbes. On the other hand, microorganisms exudate extracellular polymeric substances, which are rich in polysaccharides and can sorb well to mineral phases (Kleber et al., 2015). Also after death, microbial remains may reside on the mineral surfaces (Miltner et al., 2012), and microbially-derived sugars consequently accumulate in the HF. When looking at the changes in the pattern of neutral sugars in the two density fractions with soil depth, however, the investigated permafrost soils showed relative enrichment of plant-derived sugars relative to OC as well as to dry mass with increasing soil depth (Supplementary Fig. 1a and 2a), which contrasts studies of temperate (Spielvogel et al., 2007) and tropical soils (Möller et al., 2002; Navarrete and Tsutsuki, 2008). A continuous rejuvenation of plant residues in soil by root litter input, cryogenic processes, and a slow decomposition of the LF might be responsible for the observed lack of change in total neutral sugar contents and arabinose plus xylose with depth.

However, due to mostly anaerobic conditions only very few roots were visible in the subsoil, as was also reported by Iversen et al. (2015). Since the ^{14}C ages of the LF are old, i.e. in the range of 3060-8560 years BP (Gentsch et al., 2015b), we rather suggest that the decomposition of the LF is not

much proceeded, especially with respect to the pentoses. It seems to be also true for the HF, where the concentrations of pentoses relative to OC were similarly constant with soil depth.

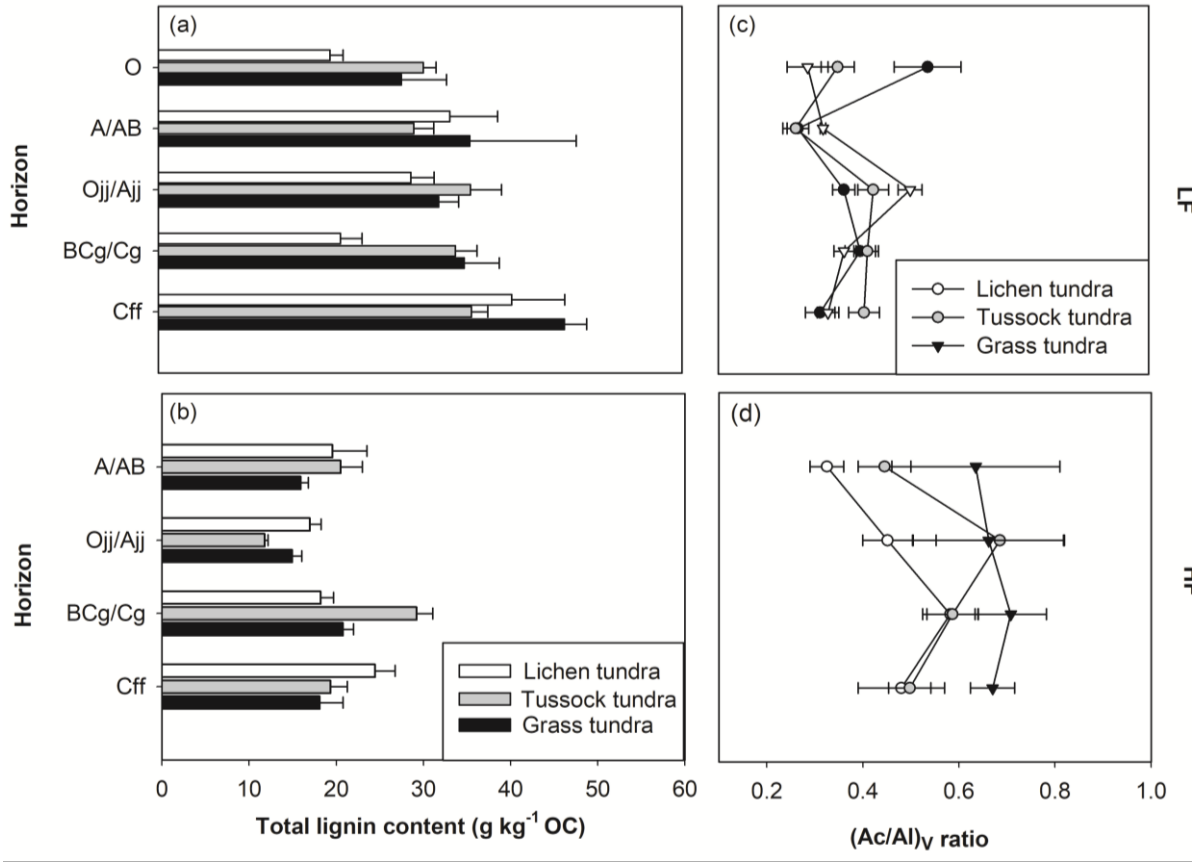

Fig. 3: CuO oxidation-derived lignin patterns within soil profiles of three tundra types, displaying contents of vanillyl, syringyl, and cinnamyl units (VSC) of (a) O horizons and the light fraction (LF), and (b) the heavy fraction (HF), as well as $(Ac/Al)_V$ ratios (c and d). Error bars are given as SE.

We hypothesized that plant-derived carbohydrates would decline with soil depth, as they represent an easily available carbon and energy source for microorganisms, however, our findings contrast this hypothesis. According to Seelenfreund et al. (1990), arabinose and xylose are enriched in lignocellulose where sugars are chemically bound to lignin moieties. This is confirmed here by the significantly ($p < 0.001$) positive correlation between the OC-normalized contents of the pentoses arabinose and xylose with VSC in both LF and HF (Fig. 6). A similar pattern of sugar composition with soil depth has been also found for peat layers (Bourdon et al., 2000) and bogs (Jia et al., 2008). This chemical bonding of pentoses to lignin moieties couples the sugar decomposition to that of lignin, and may drastically reduce the microbial availability of plant derived sugars (Moran et al., 1989; Moran and Hodson, 1989). In fact, the contents of lignin-derived phenols in the LF were high and even increased with soil depth, so that an impregnation of plant-derived sugars by lignin appears to be plausible.

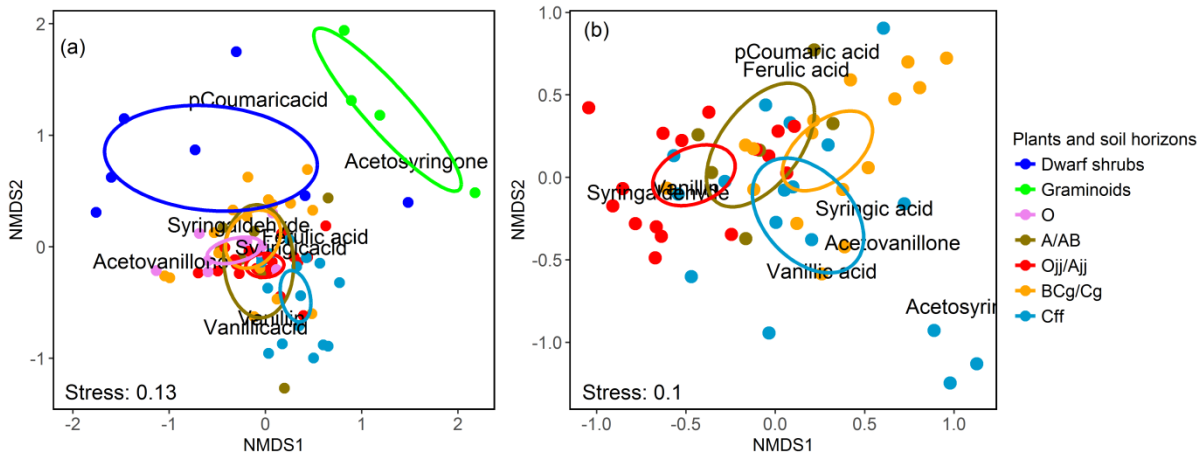

Fig. 4: NMDS plot of contents of individual phenols and phenolic acids from individual plant and soil samples over all tundra types for (a) the plants, O horizons and light fraction (LF) and (b) the heavy fraction (HF). The data were log-transformed to get smaller stress values.

A constant decrease of OC-normalized total sugar and GM contents in the HF with soil depth (Fig. 1d; Supplementary Fig. 2b), indicates a depletion of microbial-derived carbohydrates, which contrasts the observations in temperate (Spielvogel et al., 2007) and tropical soils (Möller et al., 2002). This might suggest a pronounced recycling of microbial-derived sugars in permafrost soils. Despite relatively low abundances of microorganisms in the deeper part of the active layer (Čapek et al., 2015), Gittel et al. (2014) identified the abundance of phyla *Chloroflexi*, *Gemmatimonadetes* and *Firmicutes in* buried topsoil and subsoil. Under frozen conditions microorganisms in permafrost soils are confined to thin water films (Rivkina et al., 2000), and by that possibly separated from organic substrates. As a consequence, microorganisms might favor an effective recycling of microbial necromass (i.e., dead biomass residues) that is spatially closer than plant OC sources. This behavior could be responsible for the decreasing total sugar contents of the HF, and particularly of mannose and galactose, supposedly of microbial origin. Such pronounced sugar decomposition and recycling along with a relative enrichment of N within microbial biomass and metabolites leads to the observed smaller C/N ratios with soil depth and is indicative of microbial SOM transformation (Waksman, 1933; Dignac et al. 2002, Rumpel and Kögel-Knabner, 2011).

4.2. Lignin transformation in permafrost soils

The CuO-digestible lignin contents (VSC) of arctic vascular plants are in the range of plants growing on northern peat soils (Williams et al., 1998), temperate peat soils (Bambalov, 2007), semi-arid grasslands (Otto and Simpson, 2006) and the Lena River delta (Winterfeld et al., 2015). The small content of VSC in lichen and moss was consistent with several reports (Erickson and Miksche, 1974; Winterfeld et al., 2015), which described a minor content of lignin-like compounds in nonvascular plants. The relatively smaller VSC contents in O horizons of lichen tundra as compared to those of the other tundra types is thus most likely caused by the larger contribution of lichen litter to SOM.

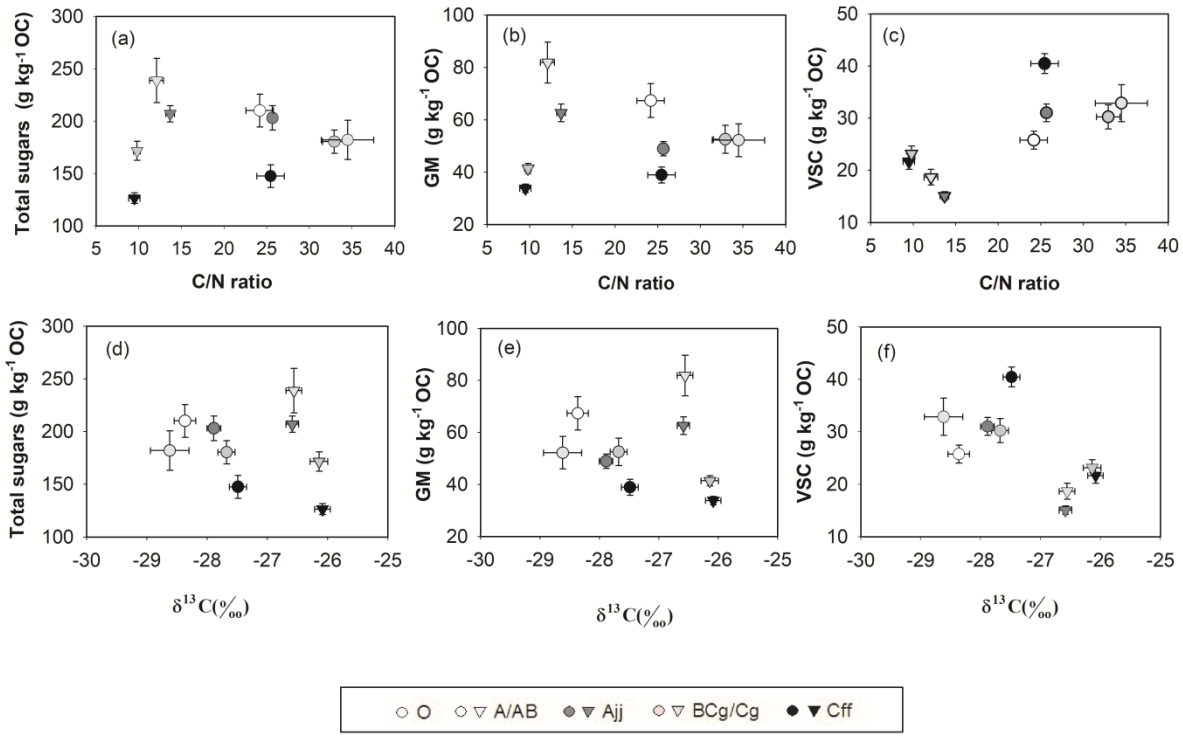

Fig. 5: Relationships of total neutral sugar contents, galactose plus mannose (GM), as well as lignin-derived phenols (VSC) with C/N ratios (a, b, c) and $\delta^{13}C$ values (d, e, f), of the LF (circles) and the HF (triangles). Mean values and error bars (SE) from horizons of soil profiles in all tundra types are given. All correlations are not statistically significant ($p > 0.05$).

As compared to the plant sources, the organic horizons showed smaller contents of VSC and higher $(Ac/Al)_V$ ratios, indicating a progressive lignin degradation already at the early stages of the decomposition of plant residues as it is also known from temperate soils (Kögel et al., 1988; Zech et al., 1994). In the mineral soil horizons, LF and HF clearly showed a very different lignin pattern, with the former being much richer in lignin-derived phenols and having a lower degree of oxidative decomposition.

This result is consistent with reports from temperate soils, showing that lignin is less decomposed in coarse size fractions, containing primarily POM, than in OM associated with clay- and silt-sized particles (Guggenberger et al., 1995; Thevenot et al., 2010). As a result of non-complete lignin decomposition of plant residues, water-soluble lignin-degraded products are produced and released into soil solution (Kaiser et al., 2004). Those water-soluble lignin degradation products have a strong affinity towards charged soil minerals (Guggenberger and Zech, 1994; Kaiser et al., 2004), which might cause the selective accumulation of particular acidic lignin components in the HF (Grünewald et al., 2006; Hernes et al., 2007).

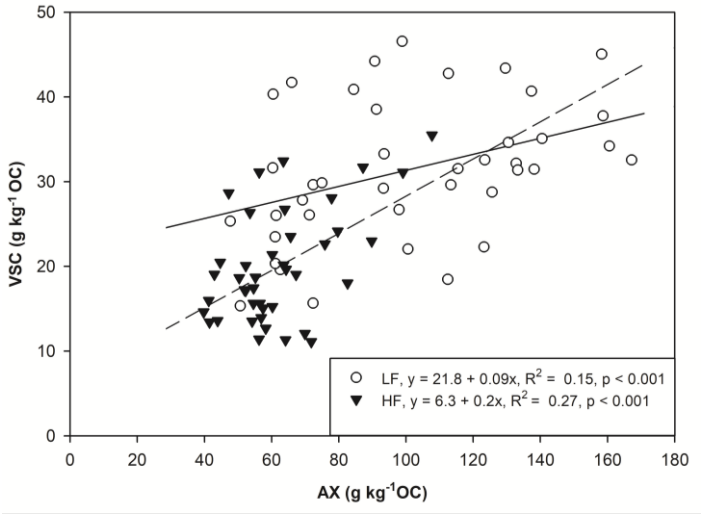

Fig. 6: Relationship between lignin-derived phenols (VSC) and the sum of arabinose plus xylose (AX) of the LF (solid line) and HF (dashed line) from all tundra types.

Independent of this fractionation of differently decomposed lignin between LF and HF, constant or even increasing contents of lignin-derived phenols along with low $(Ac/Al)_V$ values with soil depth, in both fractions indicated low ligninolytic activity and relative enrichment of lignin-derived substances in the subsoil including the permafrost layer. This is in strong contrast to studies investigating lignin decomposition in temperate (Spielvogel et al., 2007), semi-arid grassland (Otto and Simpson, 2006), and tropical soils (Möller et al., 2002). In all these studies, strongly decreasing VSC values along with increasing $(Ac/Al)_V$ ratios indicate pronounced lignin decomposition as lignin is not considered as recalcitrant in terrestrial mineral soils (Marschner et al., 2008). Nonetheless, the lignin pattern in the investigated permafrost soils is similar to a tropical peaty marsh (Bourdon et al., 2000), a tropical wetland (Tareq et al., 2004), an ombrotrophic peat (Schellekens et al., 2015), and central Siberian subarctic soils (Gundelwein et al., 2007), where lignin decomposition is also hampered. This pattern is supported by increasing contents of aryl-C and methoxyl-C with soil depth at our study sites as assessed by ^{13}C-NMR spectroscopy (Gentsch et al., 2015b). In line with a preservation of lignin in deeper horizons of permafrost soils, previous studies have found mostly young lignin derived from litter and surface soils in dissolved organic carbon and sediments of arctic rivers (Amon et al., 2012; Feng et al., 2013; Feng et al., 2015a; Feng et al., 2015b).

Lignin preservation at our study sites might be attributed to the fact that lignin degradation by filamentous fungi is impaired under the largely anaerobic conditions in the permafrost soils. As a complete degradation of lignin is based on the action of oxidative enzymes such as peroxidases and laccases, oxygen is required (Kirk and Farrell, 1987), which is lacking in most parts of the waterlogged permafrost soil profiles. Although previous authors revealed that *actinobacteria* and other lignolytic bacteria can grow in oxygen-depleted environments (Geib at al., 2008) and in frozen soils (McMahon et al., 2011), they employ oxygen-requiring peroxidases to degrade lignin (Bugg et

al., 2011) and thus require at least temporarily oxic conditions. The lacking decreasing trend of normalized-OC lignin contents with soil depth went along with a decrease in the C/N ratio. This might be assigned to the fact that lignin is less prone to microbial degradation compared to other SOM compounds, leading to the enrichment of lignin. On the other hand, high N content may inhibit lignin degradation by suppressing the synthesis of ligninolytic enzymes (Li et al., 1994; Dignac et al., 2002), even for microbes that can grow under oxygen-limited conditions. In consequence, lignin decomposition has been strongly slowed down.

4.3. Stabilization of carbohydrates and lignin in buried materials

On basis of dry HF mass, total neutral sugars and lignin-derived phenols of buried topsoil were higher than that of mineral topsoil. This may be attributable to the fact that the cryoturbated materials are derived not only from mineral topsoil but also from organic topsoil which have higher OM contents. The higher mass-based abundances of sugars and lignin in the buried topsoil than mineral topsoil and the concurrently comparable OC-normalized contents within the density fractions of buried and non-buried horizons (Supplementary Fig. 1 and 3), suggest that the OM degradation in buried topsoils is generally impaired. This conclusion is also supported by a high ^{14}C age of the SOM within buried horizons of up to 2300 years (Gentsch et al., 2015b). Gittel et al. (2014) and Schnecker et al. (2014) used molecular techniques and PLFA analysis for the studied soils and reported that the microbial community in the buried topsoil samples was rather similar to the surrounding subsoil and differed from those of the mineral topsoil. This is in contrast to the resemblance of the sugar pattern in the buried topsoil to that of the parent topsoil materials. Hence, different physicochemical soil conditions (i.e., anaerobic conditions) associated with a different microbial community might contribute to the centennial to millennial stabilization of SOM-enriched topsoil materials translocated to the subsoil. This is consistent with a broken link between microbial biomass, enzymes and nutrient availability as documented by Čapek et al. (2015).

5. Conclusions

Our study delivered insights into the contents and decomposition patterns of carbohydrates and lignin in permafrost-affected soils. The impact of vegetation was seen most prominently in the organic horizon, where in the lichen tundra the highest GM/AX ratios and lowest VSC contents were observed due to the large contribution of lichens as OM source. The lack of decreasing trends of OC-normalized lignin phenols with soil depth clearly indicates the restrained lignin decomposition in the permafrost soils mainly due to anaerobic conditions, which are unfavorable for lignin-degrading microorganisms. A similar trend was observed for plant-derived sugars, which are possibly stabilized in soil due to an impregnation by lignin (i.e., lignocellulose). These findings are in contrast to terrestrial temperate and tropical mineral soils, where aerobic conditions prevail, and concentrations of plant-derived organic substances decrease with soil depth. As water saturation and anaerobiosis in

permafrost soils are caused by the water-logging effect of the permafrost table, we expect that climate warming will improve aeration in arctic soils which would accelerate lignin degradation. This, in turn, would release plant-derived sugars as good substrates for katabolic functions and microbial biomass production, but will potentially lead to nitrogen deficiency as sugars are free of nitrogen. This in turn will stimulate further lignin degradation. We thus conclude that upon permafrost degradation and improved soil drainage the system will switch from a low C-input / C-availability and highly effective internal recycling system to a high C-input / C-availability system with high turnover rates and gaseous C losses.

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Supplementary material – Study I

Supplementary Table 1: Significance of differences in neutral sugar and lignin contents between tundra types of each horizon, with different letters indicating significant differences at $p < 0.05$.

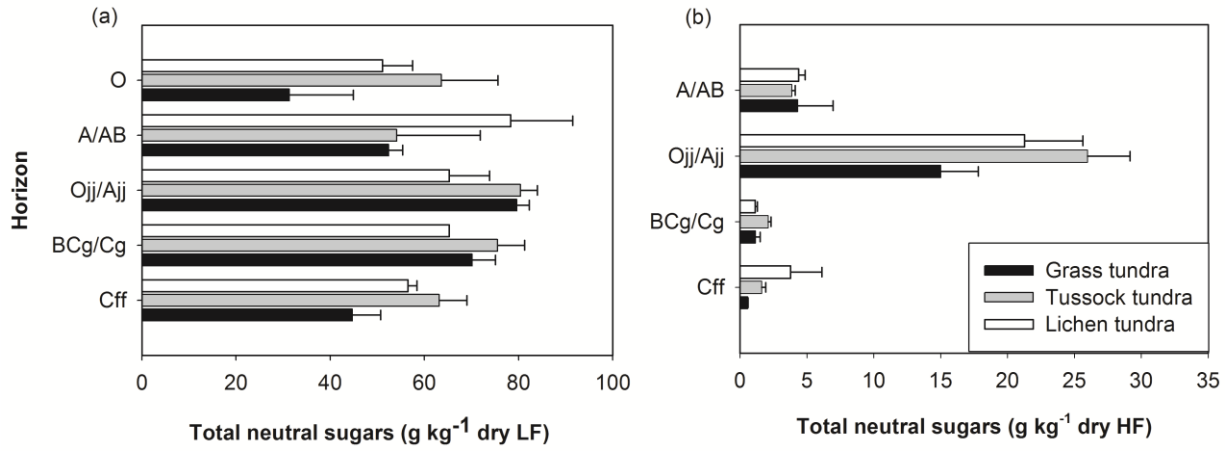
Tundra type	LF																				HF											
	Total neutral sugar (g kg^{-1}OC)					GM/AX ratio					Total lignin content (g kg^{-1}OC)					$(Ac/Al)_V$ ratio					Total neutral sugar (g kg^{-1}OC)				GM/AX ratio				Total lignin content (g kg^{-1}OC)				$(Ac/Al)_V$ ratio			
	O	A/AB	Ajj	B/C	Cff	O	A/AB	Ajj	B/C	Cff	O	A/AB	Ajj	B/C	Cff	O	A/AB	Ajj	B/C	Cff	A/AB	Ajj	B/C	Cff	A/AB	Ajj	B/C	Cff	A/AB	Ajj	B/C	Cff	A/AB	Ajj	B/C	Cff
Shrubby grass	a	ab	a	a	a	a	a	a	ab	a	a	a	a	a	ab	a	a	ab	a	a	ab	a	a	a	a	a	a	a	a	a	a	a	a	a
Shrubby tussock	a	a	a	a	a	a	a	a	ac	a	a	a	a	a	ac	b	a	a	a	a	ac	a	a	a	b	a	b	a	a	ab	b	a	a	a	a	b
Shrubby lichen	a	ac	a	b	a	b	a	a	a	a	b	a	a	b	a	b	a	ac	a	a	a	a	a	a	b	a	a	a	a	ac	a	a	a	a	a	b

Supplementary Table 2: Significance of differences in neutral sugar and lignin contents between soil horizons of each tundra type, with different letters indicating significant differences at $p < 0.05$

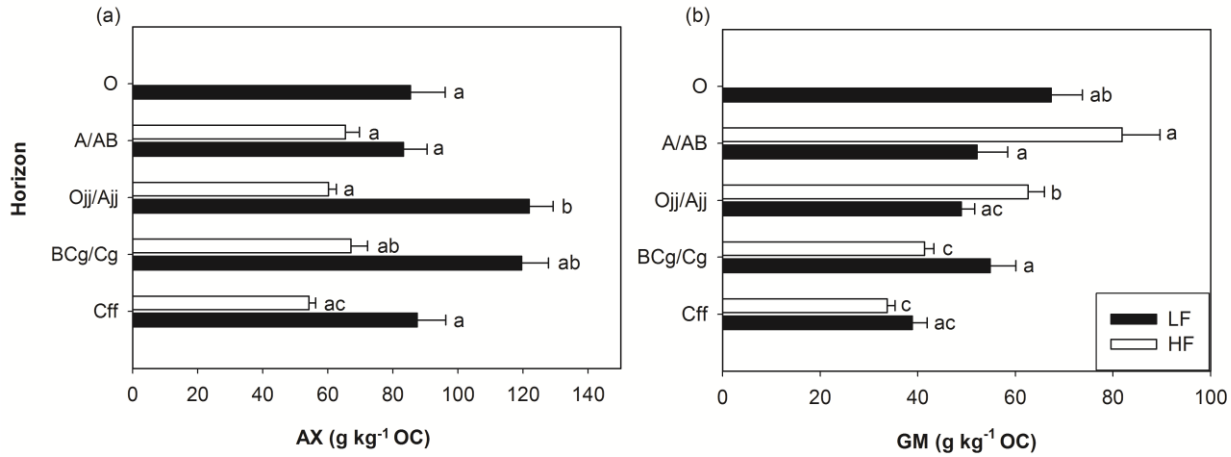
Soil horizon	LF																				HF											
	Total neutral sugar (g kg^{-1} OC)					GM/AX ratio					Total lignin content (g kg^{-1} OC)					$(Ac/Al)_V$ ratio					Total neutral sugar (g kg^{-1} OC)				GM/AX ratio				Total lignin content (g kg^{-1} OC)				$(Ac/Al)_V$ ratio			
	O	A/AB	Ajj	B/C	Cff	O	A/AB	Ajj	B/C	Cff	O	A/AB	Ajj	B/C	Cff	O	A/AB	Ajj	B/C	Cff	A/AB	Ajj	B/C	Cff	A/AB	Ajj	B/C	Cff	A/AB	Ajj	B/C	Cff	A/AB	Ajj	B/C	Cff
Shrubby grass	a	a	b	ac	ad	a	a	a	a	a	ab	a	ab	a	ac	ab	ac	ac	a	ac	a	a	a	b	ab	ab	a	ac	a	ab	a	ac	a	a	a	a
Shrubby tussock	ab	a	a	a	ac	ab	a	ac	ac	a	a	a	a	a	a	a	a	a	a	a	a	b	c	d	a	b	c	c	a	ab	ac	ab	a	a	a	a
Shrubby lichen	a	a	a	a	a	a	bc	bd	b	b	ab	a	a	ab	ac	ac	ab	ac	ab	abd	ab	ab	a	ac	a	a	b	b	a	a	a	a	a	a	a	a
All sites	a	ab	a	ab	b	a	b	b	b	b	a	ab	a	a	b	a	ab	ac	a	a	a	a	b	c	a	b	c	c	ab	b	a	a	a	a	a	a

Supplementary Table 3: p-values of pair-wise ADONIS analysis of carbohydrates and lignin composition in terms of contents (g kg^{-1} OC) between different horizons. Asterisks indicate significant differences (***p < 0.001; **p < 0.01; *p < 0.05).

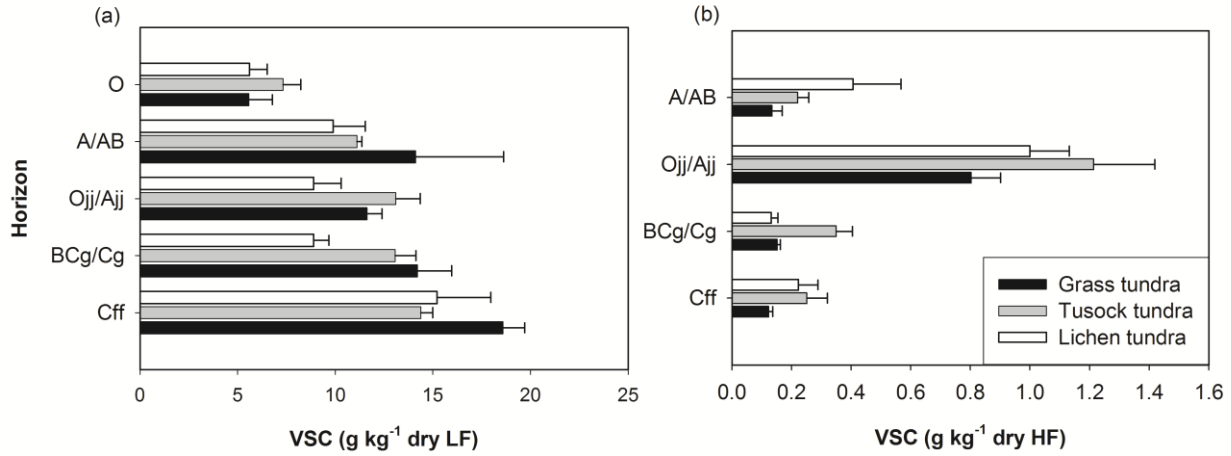
Soil fraction	Horizon	p-value	
		Carbohydrate	Lignin
LF	O *vs.* Ajj	0.120	0.066
	Ajj *vs.* BCg/Cg	0.175	0.547
	A *vs.* Ajj	0.131	0.316
	Ajj *vs.* Cff	0.001**	0.001**
	O *vs.* BCg/Cg	0.02*	0.163
	O *vs.* A	0.281	0.039*
	O *vs.* Cff	0.002*	0.001**
	A *vs.* BCg/Cg	0.124	0.242
	BCg/Cg *vs.* Cff	0.034*	0.001**
	A *vs.* Cff	0.068	0.049*
HF	Ajj *vs.* Cff	0.001**	0.001**
	Ajj *vs.* BCg/Cg	0.001**	0.001**
	A *vs.* Ajj	0.073	0.051
	BCg/Cg *vs.* Cff	0.001**	0.167
	A *vs.* Cff	0.001**	0.32
	A *vs.* BCg/Cg	0.001**	0.098



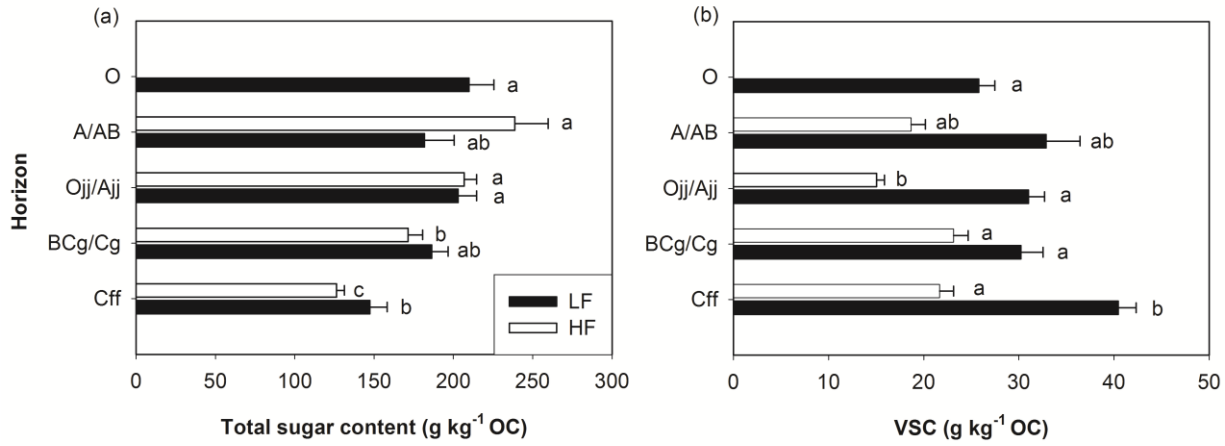
Supplementary Fig. 1. Total contents of neutral sugars relative to dry fraction in the LF (a), and in the HF (b) within soil profiles of each tundra types. Error bars are given as SE.



Supplementary Fig. 2: Total contents of arabinose plus xylose (AX) (a), and of galactose plus mannose (GM) (b) within soil profiles of all tundra types. Error bars are given as SE. Small letters indicate significant differences between horizons of each fraction at $p < 0.05$.



Supplementary Fig. 3: Total contents of lignin-derived phenols (VSC) relative to dry mass of LF (a), and of HF (b) within soil profiles of each tundra types. Error bars are given as SE.



Supplementary Fig. 4: Total contents of neutral sugars (a), and of VSC (b) within soil profiles of all tundra types. Error bars are given as SE. Small letters indicate significant differences between horizons of each fraction at $p < 0.05$.

3. Study II

Lignin preservation and microbial carbohydrate metabolism in permafrost soils

Contribution: I conducted most of the analysis in the laboratory, collected and evaluated the data, compiled the tables and figures, and wrote the manuscript.

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Lignin preservation and microbial carbohydrate metabolism in permafrost soils

Thao Thi Dao[a,*], Robert Mikutta[b], Leopold Sauheitl[a], Norman Gentsch[a], Olga Shibistova[a,c], Birgit Wild[d,e,f], Jörg Schnecker[d], Jiří Bárta[g], Petr Čapek[g], Antje Gittel[h,i], Nikolay Lashchinskiy[k], Tim Urich[l], Hana Šantrůčková[g], Andreas Richter[d,m], Georg Guggenberger[a,c]

[a] Institute of Soil Science, Leibniz Universität Hannover, Germany

[b] Soil Science and Soil Protection, Martin Luther University Halle-Wittenberg, Germany

[c] VN Sukachev Institute of Forest, Krasnoyarsk, Russia

[d] Department of Microbiology and Ecosystem Science, University of Vienna, Vienna, Austria

[e]Department of Environmental Science and Analytical Chemistry, Stockholm University, Stockholm, Sweden

[f] Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden

[g] Department of Ecosystem Biology, University of South Bohemia, České Budějovice, Czech Republic

[h] Department of Biology, Centre for Geobiology, University of Bergen, Bergen, Norway

[i] Department of Bioscience, Center for Geomicrobiology, Aarhus, Denmark

[k] Central Siberian Botanical Garden, Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russia

[l] Institute of Microbiology, Ernst-Moritz-Arndt University, Greifswald, Germany

[m] Austrian Polar Research Institute, Vienna, Austria

*** Corresponding author:** Thao Thi Dao (email: thao@ifbk.uni-hannover.de)

Key words: lignin, carbohydrate, permafrost soils, density fractionation, soil organic matter decomposition, mineral-associated organic matter

Plain language summary

Permafrost thawing and subsequent decomposition of large parts of the soil organic carbon (OC) currently stored in the northern circumpolar permafrost region are projected to cause a positive feedback on global warming. To understand the potential consequences of climate change for organic matter (OM) decomposition in permafrost soils, we determined the concentration and degree of decomposition of two dominating constituents of soil OM, lignin and non-cellulosic carbohydrates by using CuO oxidation and TFA hydrolysis, respectively, in density fractionated soils covering a longitudinal gradient of northern Siberia (from east to west: Cherskiy; Logata; Tazovskiy). We found a stronger degradation of lignin and neutral sugars at Tazovskiy with its shallower active layer, probably due to better aeration, as compared to the other sites. Our study, hence, suggests that climate-induced degradation of permafrost soils will promote lignin and carbohydrate transformation and carbon loss. In addition, larger contents of clay and Fe and Al oxides at the Cherskiy site with appear to favor accumulation of lignin and neutral sugars, likely suggesting the extent of OM transformation is further modulated by soil mineralogical properties.

Main point #1:

The deepening of active layer favors the decomposition of lignin and plant-derived sugars in permafrost soils.

Main point #2:

Soil clay and mineral phases appear to favor accumulation of lignin and neutral sugars in permafrost soils.

Main point #3:

Magnitude of climate-induced degradation of lignin and carbohydrates will depend on soil texture and mineralogical properties.

Abstract

Permafrost-affected soils in the northern circumpolar region store more than 1,000 Pg soil organic carbon (OC), and are strongly vulnerable to climatic warming. However, the extent to which changing soil environmental conditions with permafrost thaw affects different compounds of soil organic matter (OM) is poorly understood. Here, we assessed the fate of lignin and non-cellulosic carbohydrates in density fractionated soils (light fraction, LF *vs.* heavy fraction, HF) from three permafrost regions with decreasing continentality, expanding from east to west of northern Siberia (Cherskiy, Logata, Tazovskiy, respectively). In soils at the Tazovskiy site with thicker active layers, the LF showed smaller OC-normalized contents of lignin-derived phenols and plant-derived sugars and a decrease of these compounds with soil depth, while a constant or even increasing trend was observed in soils with shallower active layers (Cherskiy and Logata). Also in the HF, soils at the Tazovskiy site had smaller contents of OC-normalized lignin-derived phenols and plant-derived sugars along with more pronounced indicators of oxidative lignin decomposition and production of microbial-derived sugars. Active layer deepening, thus, likely favors the decomposition of lignin and plant-derived sugars, i.e. lignocelluloses, by increasing water drainage and aeration. Our study suggests that climate-induced degradation of permafrost soils may promote carbon losses from lignin and associated polysaccharides by abolishing context-specific preservation mechanisms. However, relations of OC-based lignin-derived phenols and sugars in the HF with mineralogical properties suggest that future OM transformation and carbon losses will be modulated in addition by reactive soil minerals.

1. Introduction

Arctic soils store about 1,035 Pg of organic carbon (OC) (Hugelius et al., 2014), which is currently protected from microbial decomposition as consequence of low temperature, poor drainage, and frequent anoxic conditions (Hobbie et al., 2000; Ping et al., 2015), as well as cryoturbation caused by seasonal freeze-thaw processes (reviewed by Ping et al., 2015). Most atmosphere circulation models predict amplified Arctic warming by the late 21st century and beyond (IPCC 2019) that is expected to stimulate permafrost thaw and deepening of the seasonally thawed active layer (Anisimov et al., 1999; Nelson et al., 2001; Schuur et al., 2008; Mueller et al., 2015; Prater et al., 2020). The deepening of the active layer will increase oxygen availability (Lawrence et al., 2015; St Jaques and Sauchyn, 2009), promoting plant rooting as well as the downward transport of water, nutrients, and microorganisms into the subsoils (Schuur and Mack, 2018). These patterns may accelerate soil organic matter (OM) decomposition in deep soil layers and increase carbon losses to the atmosphere (Fontaine et al., 2007; Gocke et al., 2010, Schuur et al., 2015; Wild et al., 2016).

Understanding the potential consequences of climate change for OM decomposition in permafrost soils and predicting the response of global carbon budgets requires knowledge on the behavior of individual OM constituents, and their interaction with the mineral matrix under different environmental conditions (Koven et al., 2015; Ping et al., 2015). This study focuses on two most predominant compounds of soil OM, lignin (as more stable plant biomacromolecule) and carbohydrates (as more labile plant and microbial-derived molecules). Lignin is a high-molecular-weight phenolic biopolymer that constitutes up to 30% of dry wood mass (Higuchi, 1981). It is not susceptible to hydrolytic attack but is readily degradable by oxidative enzymes (Kirk and Farrell, 1987). Thus oxygen availability is an important factor for lignin degradation. For instance, temperate soils typically exhibit a decrease of OC-normalized lignin concentrations with depth as result of progressive lignin degradation (Dignac et al., 2002; Feng and Simpson, 2011; Rumpel et al., 2004). Conversely, lignin appeared to be selectively preserved in deeper horizons of peat (Bourdon et al., 2000; Bambalov, 2007) and permafrost soils (Gundelwein et al., 2007; Dao et al., 2018), where the oxygen availability is low as result of high soil moisture.. Furthermore, lignin phenols in association with minerals are considered to be protected against microbial decomposition, regardless of oxygen availability (Eusterhues et al., 2014; Hall et al. 2016; Riedel et al., 2013).

Non-cellulosic carbohydrates (e.g., hemicelluloses) in soils consist of relatively short, mainly branched heteropolymers, which originate from plant tissues and are also synthesized during microbial neoformation (reviewed by Gunina and Kuzyakov, 2015). Plant-derived carbohydrates are to some extent chemically bound to lignin through cinnamic acid ester linkages and form the so-called lignocelluloses (Decker et al., 2008; Fengel and Wegener, 1984). In consequence, plant-derived carbohydrate degradation can be constrained by slow lignin degradation (Benner et al., 1984). Carbohydrates, especially of microbial origin, can also be stabilized in soils by sorption to soil

minerals (Derrien et al., 2006). Fine soil particles, thus, often show higher ratios of microbial sugars to plant-derived sugars than coarser particles, e.g., in arable soils (Kiem and Kögel-Knabner, 2003), peat bogs (Comont et al., 2006), and also in permafrost soils (Dao et al., 2018). The extent of carbohydrate alteration (i.e. microbial degradation of plant-derived carbohydrates and synthesis of microbial ones) generally increases with soil depth in temperate (Guggenberger et al., 1994) and tropical (Nacro et al., 2005) soils, whereas such a pattern was not observed in northeastern Siberian permafrost soils (Dao et al., 2018).

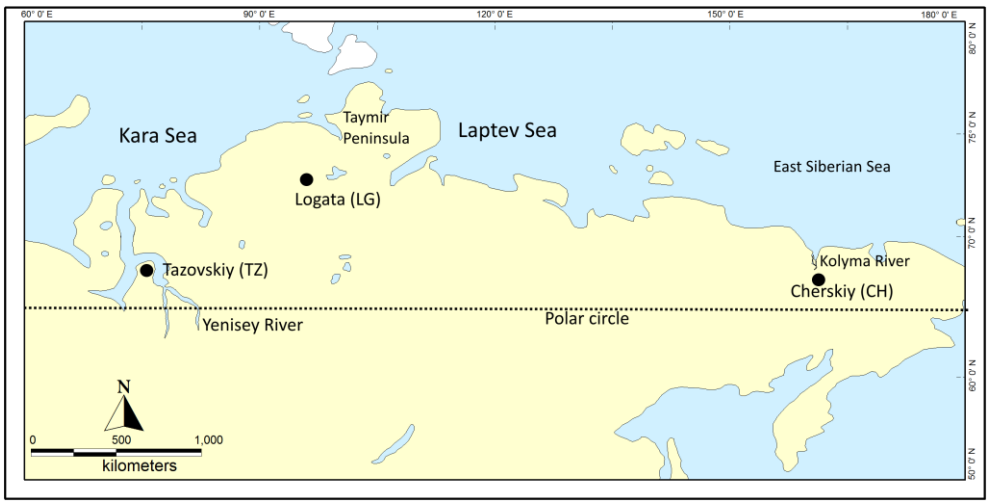

Figure 1: Study area and location of sites.

The protection of soil OM by forming associations with soil minerals is well known for temperate and tropical soils (Kleber et al., 2015, Kögel-Knabner et al., 2008). Recently, this process has also been considered as key control in the stabilization of OM in permafrost soils and its temperature response (Gentsch et al., 2018; Prater et al., 2020; Patzner et al., 2020). Soil density fractionation into light and heavy fractions (LF *vs.* HF) yields distinct soil OM pools that differ in structure and function (Lavallee et al., 2019), i.e. non or partly decomposed plant residues *vs.* microbially transformed organic molecules stabilized against fast microbial decomposition by associations with minerals such as iron (Fe) and aluminum (Al) oxides or clay minerals (Golchin et al., 1994, 1995; Herold et al., 2014; Kögel-Knabner et al., 2008). Prater et al. (2020) underlined that with deepening of the active layer in permafrost soils the large and rather undecomposed OM pool becomes accessible to microorganisms, while OM occluded in aggregates or associated with clay-sized minerals may be less mobilized. However, thawing along with formation of water-logging and reducing conditions could also unlock carbon associated with metastable Fe phases due to the activity of Fe(III)-reducing bacteria (Patzner et al., 2020).

Despite of the high vulnerability of OM in permafrost soils to climatic change, several studies used fractionation approaches to investigate the distribution and composition of OM pools in

permafrost-affected soils (Dao et al., 2018; Diochon et al., 2013; Gentsch et al., 2015b; Höfle et al., 2013; Mueller et al., 2015; Xu et al., 2009). Nevertheless, most of them used spectroscopic and isotopic techniques, which provided an overview of the total but not on the more detailed molecular OM composition. In order to delineate the possible consequences of active layer deepening on OM composition, we analyzed the molecular composition and microbial transformation of lignin and carbohydrates in the density fractionated soils (LF *vs.* HF) along a longitudinal gradient in northern Siberia. We hypothesized that permafrost soils in the western part of northern Siberia with a warmer climate and deeper active layer show a higher degree of lignin and carbohydrate transformation than regions of colder climate and shallower active layer, particularly in the subsoil horizons. We expected that these differences are more pronounced in the LF than in the HF, as the latter is more protected by association with minerals. We further assumed that differences in the mineral composition among sites also affect the composition and transformation of lignin and carbohydrates in the HF, as the presence of reactive mineral phases may control the formation of mineral-associated OM in the active layer.

2. Materials and methods

2.1. Site description, plant and soil sampling

Samples were collected from three sites in northern Siberia along a longitudinal gradient, from Cherskiy in the Kolyma region in the east to Logata on the Taymyr peninsula, in the center, to Tazovskiy in the Siberian Plain in the west (Figure 1). According to WorldClim database (Hijmans et al., 2005), the mean annual temperature (MAT) and mean annual precipitation (MAP) were relatively similar in Cherskiy (-12.7°C; 160 mm) and Logata (-13.5°C; 270 mm), but higher at Tazovskiy (-8.2°C; 454 mm) (Table 1). The continentality index (K) was calculated after Gorczynski (Blüthgen and Weischet, 1980), based on the annual temperature amplitude (difference of highest and lowest mean monthly temperature) and the latitude, and Werchojansk (east Siberia) being considered to represent 100% continentality. Continental indexes of Cherskiy 67.8, Logata 60.8, and Tazovskiy 56.5, respectively, demonstrate decreasing degree of continentality from the east to the west Siberian sampling sites, which potentially affects active layer thickness (May and Gerya, 2021). However, active layer thickness was similar for Cherskiy and Logata (30-85 cm *vs.* 30-70 cm, respectively), while a deeper active layer was observed for Tazovskiy (100-150 cm) (Table 1). All sites are in regions with continuous permafrost and comprise forest-tundra and tundra biomes with different plant associations (Table 1). Soils were predominantly classified as Aquiturbels (Gentsch et al., 2015a) according to USDA Soil Taxonomy (Soil Survey Staff, 2014). Strong reducing conditions were however only observed close to the permafrost surface, as indicated by color hues between 5G and 10BG and low Munsell color values (≤4) and chroma (2). Redoximorphic soil features were less prominent at Tazovskiy with its deeper active layer than at the other two sites.

Table 1: Characterization of sampling sites (data for Cherskiy are from Dao et al., 2018 and those for Logata and Tazovskiy from Gentsch et al., 2015a).

Site	Coordinates	MAT (°C)	MAP (mm)	Continentality index	Vegetation type	Soil type	Active layer (cm)	Dominant plant species
Cherskiy	68°45'N, 161°20'E	– 12.7	160	68	Shrubby grass tundra	Ruptic-Histic Aquiturbel	30–70	*Betula exilis, Salix sphenophylla, Carex lugens, Calamagrostis holmii, Aulacomnium turgidum*
					Shrubby tussock tundra	Ruptic-Histic Aquiturbel	35–60	*Eriophorum vaginatum, Carex lugens, Betula exilis, Salix pulchra, Aulacomnium turgidum*
					Shrubby lichen tundra	Typic Aquiturbel	60–85	*Betula exilis, Vaccinium uligonosum, Flavocetraria nivalis, Flavocetraria cucullata*
Logata	73°25'N, 98°16'E	– 13.5	270	61	Dryas tundra	Typic Aquiturbel	35–70	*Dryas punctata, Rhytidium rugosum, Hylocomium splendens*
					Grassy moss tundra	Typic Aquiturbel	30–65	*Betula nana, Carex arctisibirica, Hylocomium splendens, Tomentypnum nitens*
Tazovskiy	67°16'N, 78°50'E	– 8.2	454	57	Shrubby lichen tundra	Typic Aquiturbel	100–120	*Empetrumnigrum, Ledum palustre, Betulanana, Cladonia rangiferina,Cladonia stellaris*
					Forest tundra	Typic Aquiturbel	130–150	*Larix sibirica, Ledum palustre, Betula nana, Vaccinium uligonosum, Cladonia rangiferina, Cladonia stellaris*

Mean annual temperature (MAT) and mean annual precipitation (MAP) were derived from the WorldClim database (Hijmans et al., 2005); soil description follows the USDA Soil Taxonomy (Soil Survey Staff, 2014). Active layer depth was determined at the time of sampling.

Sampling was done at the end of summer in 2010 (Cherskiy), 2011 (Logata), and 2012 (Tazovskiy), respectively, ensuring maximum annual thawing depth at the date of sampling. At each study site, three (Cherskiy) or two (Logata, Tazovskiy) tundra vegetation types were identified, and dominating plants of the main tundra vegetation types collected. For each vegetation type, we excavated three soil profiles as replicates. Soil profiles were dug as 5 × 1 m trenches down to the permafrost surface to obtain a representative cross section through micro-topographic features (hummocks, patterned ground) and irregular cryoturbation pattern. Because of hummocks and irregular cryoturbation patterns, soil horizons were heterogeneously distributed. We collected all diagnostic horizons including cryoturbated topsoil materials at various positions within the soil profile but at comparable depth. For that, about 20 subsamples per diagnostic horizon were sampled at random and bulked. We additionally sampled the upper part of the permafrost in three replicates using a steel corer, to a maximum depth of 30 cm from the permafrost table.

Following Gentsch et al. (2015a), the active layer horizons were categorized into organic topsoil (O), mineral topsoil (A/AB), buried topsoil, i.e., topsoil material that was buried in deeper horizons by cryoturbation (Ojj/Ajj), mineral subsoil (BCg/Cg), and the upper part of the permafrost layer (Cff). Directly after sampling, living roots and visible soil fauna were removed and soil samples were dried at 50°C and ground in the laboratory before further analyses. Data from Cherskiy were previously published by Dao et al. (2018).

2.2. Density fractionation, organic carbon and total nitrogen, soil texture, and soil mineralogy

The separation of particulate and mineral-associated OM was achieved by density separation, knowing that this physical separation method is operationally defined (Cerli et al., 2012). Soil density fractions were obtained by separation of a light fraction (LF; < 1.6 g mL^{-1}) from a heavy fraction (HF; > 1.6 g mL^{-1}) using a sodium polytungstate solution as described in Gentsch et al. (2015a, b). Organic carbon and total nitrogen (TN) contents and the $\delta^{13}C$ value of OM in the organic topsoil, LF, and HF were measured in duplicates (Gentsch et al., 2015a, b) using an Elementar IsoPrime 100 IRMS (IsoPrime Ltd., Cheadle Hulme, UK) coupled to an Elementar Vario Isotope cube EA C/N analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) after removing traces of carbonates by acid fumigation (Harris et al., 2001).

Contents of pedogenic Fe and Al in bulk soils were determined using extractions with 0.2 M ammonium oxalate and sodium dithionite-citrate-bicarbonate (Mckeague and Day, 1966). Oxalate-extractable Fe (Fe_o) and Al (Al_o) represent poorly crystalline oxide phases and organic complexes, while dithionite-extractable Fe (Fe_d) includes Fe-organic complexes, poorly crystalline as well as crystalline Fe oxides (Cornell and Schwertmann 2003). The extraction solutions were analyzed for Fe and Al by inductively coupled plasma optical emission spectroscopy (ICP-OES; Varian 725-ES, Palo Alto, California). More details are reported in Gentsch et al. (2015a). The data are presented in Table 2.

2.3. Lignin analysis

Concentrations of lignin-derived phenols and their degree of oxidative alteration in soil were determined using alkaline CuO oxidation following the method of Hedges and Ertel (1982) with modifications of Amelung et al. (1999). Lignin-derived phenols were released by oxidation with CuO in the presence of $Fe(NH_4)_2(SO_4)_2.6H_2O$, glucose and 2 M NaOH at 170°C for 3 h. The lignin-derived monomers were purified using a conditioned C18 column (Bakerbond) and converted to trimethylsilyl (TMS) derivatives by reaction with (N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) in pyridine. Thereafter, derivatized-lignin monomers were identified and quantified using gas chromatography-mass spectrometry (Varian 450-GC with ion trap 220MS, Palo Alto, USA). Ethylvanillin and phenylacetic acid were used as internal and recovery standard, respectively. Analyzed lignin-derived phenols were vanillin, acetovanillone, vanillic acid, syringaldehyde, acetosyringone, syringic acid, ferulic acid, and p-coumaric acid. Vanillyl (V) and syringyl (S) units were calculated as the sum of their aldehyde, ketone and carboxylic acid forms, and cinnamyl units (C) are the sum of ferulic acid and p-coumaric acid. The acid to aldehyde ratios of vanillyl $(Ac/Al)_V$ and syringyl units $(Ac/Al)_S$, were used to assess the degree of lignin alteration (Hedges and Ertel, 1982). The concentration of lignin-derived C was defined as the sum of C in the eight lignin-derived phenols normalized to the OC content (g kg^{-1} OC). The lignin-derived phenol contents of bulk soils were calculated by combining

the values of two density fractions, based on the efficiency of fractionation (Gentsch et al., 2015a). The lignin stock was reported based on the directly measured lignin-derived phenols (VSC) per square meter soil (kg m^{-2}), using the bulk density values reported in Gentsch et al. (2015a).

Table 2: Basic characteristics related to organic matter in bulk soils, the light fraction (LF) and heavy fraction (HF) along with pH, soil texture, and iron (Fe) and aluminum (Al) contents originating from pedogenic metal oxide phases within the soil profiles (n=3) of each sampling site (data are from Gentsch et al., 2015a).

Soil horizon	Bulk soil									LF			HF		
	OC	C/N	$\delta^{13}C$	pH	Clay	Silt	Fe_o	Fe_d	Al_o	OC	C/N	$\delta^{13}C$	OC	C/N	$\delta^{13}C$
	(g kg^{-1}		(‰)		(%)	(%)	(g kg^{-1}	(g kg^{-1} dw)	(g kg^{-1}	(%)		(‰)	(%)		(‰)
Organic															
Cherskiy	239 ±	24.0 ±	-28.3 ±	5.1 ±			n.d.	n.d.	n.d.						
Logata	195 ±	22.9 ±	-28.4 ±	5.7 ±			n.d.	n.d.	n.d.						
Tazovskiy	236 ±	33.2 ±	-26.6 ±	4.8 ±			n.d.	n.d.	n.d.						
Mineral															
Cherskiy	34 ±	14.4 ±	-26.8 ±	5.6 ±	19.3 ±	73.2 ±	6.3 ±	11.9 ±	1.6 ± 0.6	34.4 ±	34.5 ±	-28.6 ±	1.7 ±	12.1 ±	-26.6 ±
Logata	70 ±	16.0 ±	-27.9 ±	5.5 ±	22.7 ±	48.7 ±	4.0 ±	5.9 ±	0.8 ± 0.3	33.6 ±	26.7 ±	-29.1 ±	5.6 ±	15.0 ±	-27.7 ±
Tazovskiy	3.5 ±	16.9 ±	-25.8 ±	5.3 ±	26.8 ±	66.6 ±	3.8 ±	5.6 ±	1.8 ± 0.7	36.3 ±	40.1 ±	-27.4 ±	2.7 ±	14.1 ±	-26.9 ±
Burried															
Cherskiy	101 ±	16.1 ±	-27.5 ±	5.8 ±	28.7 ±	66.7 ±	10.5	12.9 ±	2.6 ± 0.6	36.6 ±	25.7 ±	-27.9 ±	7.8 ±	13.7 ±	-26.6 ±
Logata	84 ±	17.0 ±	-27.4 ±	6.4 ±	25.7 ±	62.3 ±	5.1 ±	6.8 ±	0.8 ± 0.2	32.4 ±	22.2 ±	-28.2 ±	5.8 ±	15.0 ±	-27.0 ±
Tazovskiy	42 ±	16.1 ±	-25.8 ±	5,9 ±	28.9 ±	64.5 ±	4.7 ±	6.2 ±	1.9 ± 1.1	39.8 ±	36.7 ±	-26.9 ±	3.0 ±	13.0 ±	-26.1 ±
Mineral															
Cherskiy	13 ± 5	11.5 ±	-26.3 ±	6.1 ±	17.0 ±	76.1 ±	6.3 ±	10.5 ±	1.2 ± 0.2	40.5 ±	32.9 ±	-27.7 ±	0.9 ±	9.4 ±	-26.1 ±
Logata	18 ± 7	13.9 ±	-26.3 ±	6.7 ±	29.1 ±	67.3 ±	5.3 ±	8.4 ±	0.9 ± 0.2	34.6 ±	26.8 ±	-27.6 ±	1.6 ±	11.4 ±	-26.4 ±
Tazovskiy	3 ± 1	9.0 ±	-24.1 ±	6.6 ±	19.1 ±	74.2 ±	2.8 ±	4.7 ±	0.9 ± 0.3	26.7 ±	34.7 ±	-26.0 ±	0.3 ±	6.4 ±	-24.7 ±
Permafros															
Cherskiy	20 ±	11.7 ±	-26.5 ±	7,1 ±	16.7 ±	78.5 ±	7.0 ±	9.7 ±	1.1 ± 0.3	39.7 ±	25.5 ±	-27.5 ±	1.1 ±	8.2 ±	-26.1 ±
Logata	15 ±	12.2 ±	-24.6 ±	6,9 ±	24.8 ±	74.9 ±	4.3 ±	8.5 ±	0.6 ± 0.1	39.1 ±	29.2 ±	-26.3 ±	1.0 ±	10.6 ±	-24.4 ±
Tazovskiy	2 ± 1	7.3 ±	-23.7 ±	7,3 ±	13.4 ±	60.9 ±	2.4 ±	4.5 ±	0.6 ± 0.1	20.4 ±	29.4 ±	-25.5 ±	0.1 ±	4.8 ±	-24.6 ±

Values are mean ± SD, n.d.: not determined. Feo, Alo: Oxalate-extractable Fe and Al, Fed: dithionite-extractable Fe.

2.4. Carbohydrate analysis

Neutral sugars were analyzed following the method of Amelung et al. (1996) with modifications of Rumpel and Dignac (2006), Eder et al. (2010), and Dao et al. (2018) for purification and derivatization steps. After hydrolysis with 4 M trifluoroacetic acid (TFA) at 105°C for 4 h, neutral sugars were derivatized using $NaBH_4$ solution (20 mg L^{-1}) and acetic anhydrite. Derivatized compounds were extracted with dichloromethane before injection into a gas chromatograph equipped with a flame ionization detector (Agilent 7890A, Palo Alto, USA). Myo-inositol and D-allose were used as internal and recovery standard, respectively. Analyzed neutral sugars were rhamnose, fucose, arabinose, ribose, xylose, mannose, galactose and glucose. While the pentoses arabinose (A) and xylose (X) are mainly of plant origin, the hexoses galactose (G) and mannose (M) and the deoxyhexoses rhamnose (R) and fucose (F) are largely formed by microbial biomass (Murayama 1984; Oades 1984) and some lower plant groups, e.g. lichens and mosses (Olafsdottir and Ingólfsdottir, 2001). The ratios of GM/AX and RF/AX are, hence, widely used to trace the origin of carbohydrates in soils (Murayama, 1984).

2.5. Statistics

One-way ANOVA, followed by Tukey's HSD post-hoc test, was used to test for significant differences in lignin-derived phenol and neutral sugar contents between sites and between horizons at a significance level of $p < 0.05$. All variables were tested for normal distribution and log transformed if necessary. The effect of soil properties and pedogenic minerals on lignin and sugar patterns was examined using Pearson correlation. Non-metric multidimensional scaling (NMDS) was used to visualize the variation of lignin and neutral sugar contribution between in sites and soil horizons. The ellipses show 95% confidence intervals, axes are arbitrary and scaled in units of Euclidean distance (Oksanen et al., 2016). Permutational multivariate analysis of variance using distance matrices (ADONIS) and post hoc-ADONIS (pairwise-ADONIS) in the vegan package of R were used to test for significant differences of sugar and lignin composition within sites and horizons (Anderson, 2001; McArdle & Anderson 2001).

Table 3: Total OC-normalized lignin-derived phenol and neutral sugar carbon contents of dominant plant species at each sampling site.

Plant species	Total lignin-derived phenol g C kg^{-1} OC				Total neutral sugar g C kg^{-1} OC			
	Cherskiy	Logata	Tazovskiy	All	Cherskiy	Logata	Tazovskiy	All
Dwarf shrub	21.1 ± 10.0	22.0 ±8.0	20.3 ± 3.1	20.9 ± 7.3	88.7 ± 10.6	127.4 ±	100.6 ± 11.5	94.6 ± 12.1
Graminoid	38.5 ± 10.0	38.0 ± 4.8	n.d	36.0 ± 4.5	165.5 ± 7.7	211.8 ±	n.d	176.4 ± 21.0
Lichen	0.7	n.d	0.6 ± 0.4	0.7 ± 0.4	276.0	n.d	411.0 ± 130.4	316.4 ± 37.7
Moss	8.2	5.2	n.d	6.7 ± 2.1	183.0	266.8	n.d	224.9 ± 59.2

Values are mean ± SD, n.d.: not determined due to no appearance. Mean values without SD are not replicated.

The effect of soil properties and mineral phases on NMDS ordination was examined using environmental fitting tests in the envfit function in vegan, and the significance of vectors was tested with 999 permutations. For statistical analyses, calculations, and plots we used R version 3.2.2 (R Core Team, 2015) and Sigma Plot 10 (Systat Software, San Jose, CA, USA).

3. Results

3.1. Lignin and carbohydrate compositions of arctic plants

The contribution of lignin-derived phenols to OC, as assessed by the CuO oxidation method, accounted for 36.02 ± 4.53 g C kg^{-1} OC (mean ± SD) in arctic graminoids, 20.94 ± 7.28 g C kg^{-1} OC in dwarf shrubs, and 2.84 ± 2.77 g C kg^{-1} OC in lichen/moss (Table 3). The averaged OC-normalized contents of lignin-derived phenols of plant tissues were slightly higher in shrubby grass tundra and shrubby tussock tundra than tundra types with smaller lichen/moss contents (Table 4). The OC-normalized of neutral sugar contents were highest in lichen and mosses with 261,7 ± 57,4 g C kg^{-1} OC, followed by graminoids (176,4 ± 21.0 g C kg^{-1} OC), and dwarf shrubs (94.6 ± 12.1 g C kg^{-1} OC; Table 3). The averaged neutral sugar contents of plant tissues were higher in shrubby lichen and moss

tundra than other tundra types (Table 4). Overall, dwarf shrubs and graminoids showed higher percentages of arabinose and xylose and smaller percentages of mannose and galactose compared to lichens and mosses, and all plants were characterized by small fucose and negligible ribose contents (Table S1).

3.2. Lignin and carbohydrate contents and stocks in bulk soils

The OC-normalized lignin-derived phenol content of the organic topsoils were smaller in shrubby lichen tundra compared with other tundra types at Cherskiy, and in grassy moss tundra compared to dryas tundra at Logata, while they were similar between tundra types at Tazovskiy, following the lignin contents of the parent plant materials (Table 4). In comparison of all tundra types at each site, the lignin-derived phenol contents in bulk soils ranged from 5.5 ± 2.9 to 41.9 ± 33.2 g C kg^{-1} OC and tended to be largest in Cherskiy followed by Logata and Tazovskiy, and did not show a clear trend with soil depth (Table 5). On a soil mass basis, lignin-derived phenol contents ranged from 1.7 ± 1.3 to 24.2 ± 20.5 g kg^{-1} dry weight (dw) (Table 5), which translates to stock values in the entire examined soil profiles ranging from 0.11 ± 0.06 to 0.56 ± 0.22 kg lignin-derived phenol m^{-2} (Table 6). Cherskiy and Logata tended to show the largest stocks of lignin-derived phenols in the mineral subsoils and permafrost layers, followed by the organic topsoils and the mineral and buried topsoils (Table 6). In contrast, Tazovskiy showed the largest stocks of lignin-derived phenols in the organic topsoil compared to deeper horizons (Table 6). Integrated over all soil horizons, soils from Cherskiy and Logata stored more lignin-derived phenols than those from Tazovskiy.

The OC-normalized neutral sugar content of the organic topsoils were similar between tundra types at Logata and Tazovskiy, while they showed a higher value in shrubby lichen tundra compared with other tundra types at Cherskiy, which likewise followed the contents of the parent plant materials (Table 4).

Table 4: Total OC-normalized lignin-derived phenol and neutral sugar carbon contents of representative plant species at each tundra type.

	Cherskiy				Logata			Tazovskiy		
	Shrubby grass tundra	**Shrubby tussock tundra**	**Shrubby lichen tundra**	**All**	**Dryas tundra**	**Grassy moss tundra**	**All**	**Shrubby lichen tundra**	**Forest tundra**	**All**
C/N	31.3 ± 3.6	33.7 ± 7.2	34.1 ± 30.5	34.3 ± 28.5	49.8 ± 6.2	35.8 ± 12.6	37.7 ± 15.3	49.6 ± 42.3	35.8 ± 48.25	58.2 ± 40.9
$\delta^{13}C$ (‰)	-28.4 ± 6.1	-28.8 ± 5.0	-29.6 ± 2.9	-28.6 ± 1.7	-30.1 ± 1.0	-29.1 ± 1.1	-29.5 ± 1.2	-28.8 ± 2.0	-28.4 ± 1.2	-26.6 ± 2.2
VSC (g C kg^{-1} OC)	37.5 ± 11.0	35.9 ± 9.9	27.2 ± 18.2	34.0 ± 15.0	15.8 ± 4.7	43.3 ± 15.2	39.3 ± 13.0	27.6 ± 8.2	30.1 ± 9.6	27.6 ± 9.1
Neutral sugar (g C kg^{-1} OC)	110.8± 44.0	113.1± 47.4	158.1± 91.9	142.8± 52.7	193.0 ± 104.3	188.7 ± 71.3	174.8 ± 54.5	128.3 ± 84.9	143.6 ± 99.9	110.2 ± 146.1

Values are mean ± SD.

Considering all tundra types at each site, the neutral sugar contents of OM in bulk soils ranged from 50.0 ± 24.3 to 177 ± 51.0 g C kg^{-1} OC with only clear difference between organic topsoil of Cherskiy and Tazovskiy was observed, and tended to decrease with soil depth at all sites (Table 5). On a soil mass basis, neutral sugar contents ranged from 15.3 ± 11.0 to 111.5 ± 61.0 g kg^{-1} dw (Table 5). There were no differences between organic topsoil horizons, but in the mineral topsoil contents were highest at Cherskiy followed by that at Tazovskiy and Logata. Expressed as stock values, soils contained from 2.4 ± 0.6 to 5.5 ± 1.5 kg neutral sugar m^{-2} for the total examined depth (Table 6). In general, at all three sites, organic topsoil and mineral subsoils stored more neutral sugars than the mineral topsoil and buried topsoil horizons, while at Cherskiy and Logata also permafrost horizons comprised large stocks of neutral sugars (Table 6).

3.3. Lignin in soil density fractions

For the LF, OC as well as soil dw-normalized contents of lignin-derived phenols tended to increase towards the permafrost layer at Cherskiy and Logata (Figure 2a, Figure S1a, Table S2), but no clear trend was observed for the $(Ac/Al)_V$ and $(Ac/Al)_S$ ratios (Figure 2b, 2c; Table S2). In contrast, at Tazovskiy the LF showed a significant decrease in OC and soil dw-normalized lignin-derived phenol contents (Figure 2a, Figure S1a, Table S2) and increasing $(Ac/Al)_V$ ratios with soil depth, including the buried topsoils (Figure 2b; Table S2).

Although a similar lignin-derived phenol content was observed for organic topsoils at all three sites, over all mineral soil horizons the LF showed smaller OC- and soil dw-normalized lignin-derived phenol contents and higher $(Ac/Al)_V$ ratios at Tazovskiy than at Logata and Cherskiy ($p < 0.0001$) (Figure 2a, 2b; Figure S1a).

Table 5: Lignin-derived phenol and neutral sugar contents normalized to OC and dry weight (dw) in bulk soils.

Site / horizon	Lignin-derived phenols		Neutral sugars	
	g C kg^{-1} OC	g kg^{-1} dw	g C kg^{-1} OC	g kg^{-1} dw
Cherskiy				
O	16.4 ± 3.6	6.2 ± 1.9	85.0 ± 20.8	54.3 ± 25.6
A/AB	25.1 ± 11.5	13.0 ± 7.1	109.6 ± 27.2	79.6 ± 28.2
Ojj/Ajj	10.1 ± 5.5	4.2 ± 3.5	56.1 ± 11.5	31.7 ± 13.9
BCg/Cg	18.6 ±13.2	9.0 ± 7.8	55.0 ± 21.2	40.1 ± 36.8
Cff	41.9 ± 33.2	24.2 ± 20.5	60.9 ± 34.6	45.3 ±35.8
Logata				
O	14.9 ± 5.4	4.4 ± 1.1	148.3 ± 10.4	75.8 ± 29.2
A/AB	10.0 ± 3.4	1.7 ± 1.3	86.4 ± 15.0	21.6 ± 8.4
Ojj/Ajj	9.6 ± 2.9	2.2 ± 2.0	59.4 ± 10.4	19.2 ± 8.5
BCg/Cg	12.3 ± 5.4	4.2 ± 2.6	67.6 ± 8.6	25.0 ± 15.5
Cff	27.4	n.d.	n.d.	n.d.
Tazovskiy				
O	13.0 ± 0.9	4.9 ± 1.8	177.8 ± 51.0	111.5 ± 61.0
A/AB	10.6 ± 7.4	5.2 ± 4.2	89.5 ± 29.3	42.4 ± 23.9
Ojj/Ajj	5.5 ± 2.9	2.3 ± 2.3	50.0 ± 24.3	15.3 ± 11.0
BCg/Cg	11.8 ± 5.8	6.7 ± 4.7	55.2 ± 27.5	40.8 ± 27.5
Cff	n.d.	n.d.	40.5	1.8

Values are mean ± SD;, n.d.: not determined due to lack of samples; (*): not included Cff horizons due to lack of sample materials.

The NMDS and subsequent pairwise-ADONIS showed distinct clusters of individual lignin-derived phenols relating to OC and soil dw as well across sites (Figure 3a, 3b; Table S3). Also here, Tazovskiy tended to show a smaller abundance of lignin-derived phenols in the LF than the two other sites.

The HF contained less lignin-derived phenols normalized to OC than the LF, and no clear trend was observed for $(Ac/Al)_V$ und $(Ac/Al)_S$ ratios (Figure 2). For the HF, the contribution of lignin-derived phenols tended to increase towards the permafrost layer at the Cherskiy but to decrease at Logata and Tazovskiy (Figure 2d; Figure S1b, Table S2). The $(Ac/Al)_V$ and $(Ac/Al)_S$ ratios of the HF tended to increase with soil depth at the Cherskiy and Logata sites, whereas no trend was observed for Tazovskiy (Figure 2e, 2f; Table S2). However, the ANOVA followed by Tukey's HSD showed no significant differences in lignin-derived phenol contents as well as $(Ac/Al)_V$ and $(Ac/Al)_S$ ratios between soil horizons at all sites (Table S2), except for contents of lignin-derived phenols between Ojj/Ajj and deeper horizons at the Cherskiy site. Comparing the HF between sites, Tazovskiy had smaller amounts of OC-based lignin-derived phenols than Logata and Cherskiy (Figure 2d). The NMDS and subsequent pairwise-ADONIS showed distinct clusters of individual lignin-derived phenols as related to OC and soil dw as well across sites (Figure 4a, 4b; Table S3). Confirming the ANOVA results, Tazovskiy tended to show the smallest abundance of lignin-derived phenols in the HF, which increased over Logata to Cherskiy.

3.4. Carbohydrates in soil density fractions

For the LF, the contents of OC and soil dw-normalized total neutral sugars decreased from organic topsoils to mineral subsoils at Tazovskiy (Figure 5a, Figure S2a, Table S2). A similar, but less pronounced pattern was observed at Logata, whereas concentrations were relatively constant at Cherskiy. Comparing the LF between sites, OC- and soil dw-normalized neutral sugar contents were larger at Tazovskiy than at the other sites ($p < 0.001$) in organic topsoil horizons, while they were smaller in the mineral subsoils and buried topsoils ($p < 0.01$; Figure 5a; Figure S2a). Like for lignin, the NMDS and subsequent pairwise-ADONIS showed distinct clusters of individual neutral sugars related to OC and soil dw as well across sites (Figure 3c, 3d; Table S3). Cherskiy tended to show a higher abundance of arabinose and xylose, while Logata and Tazovskiy soils showed a higher abundance of mannose, rhamnose, and fucose (Figure 3c, 3d). The GM/AX ratios in the organic topsoils and the LF of other genetic horizons were larger at Tazovskiy for the whole soil profiles than at the other sites (Figure 5d).

The HF had higher OC-normalized neutral sugars contents and higher GM/AX ratios than the LF (Figure 2). For the HF, all sites showed a decrease of OC- and soil dw-normalized total neutral sugar contents with soil depth (Table S2). The GM/AX ratios also decreased with soil depth at Cherskiy and Tazovskiy while no clear trend was observed for Logata (Figure 5e, 5h). Comparing the HF between sites, no significant difference in neutral sugars contents related to OC was observed, but Tazovskiy and Logata showed higher GM/AX ratios than Cherskiy (Figure 5h). The NMDS and

subsequent pairwise-ADONIS revealed distinct clusters of individual OC-based neutral sugars between the three sites, while no significant difference in soil dw-based neutral sugars was observed between Cherskiy and Tazovskiy (Figure 4c, 4d; Table S3).

3.5. Lignin and carbohydrate contents related to soil properties

For the LF of all sites, OC- and soil dw-normalized lignin-derived phenol contents were positively correlated with pH while neutral sugar contents exhibited a negative correlation (Table 7). Further, the lignin-derived phenols and neutral sugar contents on basis of OC and soil dw were negatively correlated with active layer thickness while a positive correlation was observed for $(Ac/Al)_V$ and GM/AX ratios. Environmental vector fitting on NMDS of LF showed a strong significant relationship between the distribution of lignin phenols and neutral sugars with active layer thickness (Figure 3, Table S4). It also revealed a significant relation with pH, C/N, and $\delta^{13}C$, but in poorer significance compared to active layer thickness.

For the HF of all sites, pH shows a negative correlation with soil dw-based lignin-derived phenols, and a positive one with $(Ac/Al)_V$ and $(Ac/Al)_S$ ratios (Table 7). At the same time, pH was negatively correlated with OC- and soil dw-normalized neutral sugar contents and with the GM/AX ratio. Lignin derived-phenol contents on basis of OC and soil dw decreased with increasing active layer depth, while no such correlation was observed for oxidative indicators of lignin degradation.

Table 6: Stocks of lignin-derived phenols and neutral sugars in organic topsoil (O) horizons and the light fraction (LF), heavy fraction (HF), and the bulk soil for different sampling sites and soil horizons (0-100 cm).

Horizon	O horizon and LF			HF			Bulk soil		
	Lignin-derived phenols (kg m^{-2})								
	Cherskiy	Logata	Tazovskiy	Cherskiy	Logata	Tazovskiy	Cherskiy	Logata	Tazovskiy
O	0.11 ± 0.12	0.05 ± 0.03	0.08 ± 0.06				0.11 ± 0.12	0.05 ± 0.03	0.08 ± 0.06
A/AB	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.01 ± 0.01	0.04 ±	0.01 ± 0.01	0.02 ± 0.02	0.05 ± 0.03	0.01 ± 0.01
Ojj/Ajj	0.03 ± 0.00	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.00	0.02 ±	0.02 ± 0.01	0.05 ± 0.005	0.04 ± 0.02	0.02 ± 0.01
BCg/Cg	0.02 ± 0.01	0.05 ± 0.02	0.01 ± 0.00	0.11 ± 0.06	0.13 ±	0.02 ± 0.01	0.17 ± 0.007	0.18 ± 0.07	0.02 ± 0.01
Cff	0.06 ± 0.05	0.04 ± 0.03	n.d.	0.11 ± 0.07	0.04 ±	n.d.	0.21 ± 0.15	0.10	n.d.
Total	0.22 ± 0.19	0.10 ± 0.02	0.09 ± 0.03	0.28 ± 0.12	0.20 ±	0.03 ± 0.01	0.56 ± 0.22	0.35 ± 0.08	0.11 ± 0.06
	Neutral sugars (kg m^{-2})								
	Cherskiy	Logata	Tazovskiy	Cherskiy	Logata	Tazovskiy	Cherskiy	Logata	Tazovskiy
O	1.16 ± 1.08	1.02 ± 0.77	1.23 ± 0.82				1.16 ± 1.08	1.02 ± 0.77	1.23 ± 0.82
A/AB	0.04 ± 0.03	0.09 ± 0.08	0.05 ± 0.08	0.11 ± 0.1	0.54 ± 0.29	0.24 ±	0.17 ± 0.21	0.63 ± 0.36	0.30 ± 0.36
Ojj/Ajj	0.20 ± 0.10	0.09 ± 0.07	0.02 ± 0.04	0.39 ± 0.1	0.36 ± 0.18	0.48 ±	0.62 ± 0.06	0.46 ± 0.23	0.50 ± 0.41
BCg/Cg	0.10 ± 0.04	0.27 ± 0.08	0.02 ± 0.02	0.64 ± 0.44	1.85 ± 0.64	0.47 ±	0.75 ± 0.21	1.75 ± 1.02	0.48 ± 0.14
Cff	0.19 ± 0.14	0.32 ± 0.55	n.d.	0.71 ± 0.62	1.45 ± 1.09	n.d.	1.02 ± 0.77	3.75	n.d.
Total	1.52 ± 1.05	2.80 ± 0.84	1.18 ± 0.21	1.80 ± 0.88	4.76 ± 1.76	1.25 ±	3.72 ± 0.89	5.50 ± 1.52	2.35 ± 0.58

Values are mean ± SD; n.d.: not determined due to the large active layer thickness in the western Siberian soils,where no permafrost appeared within the examined soil depth.

Neutral sugar contents did not show a clear correlation with active layer thickness, whereas GM/AX showed a positive one (Table 7). The soil dw-based lignin-derived phenol and neutral sugar contents were also positively correlated with clay, Fe_d, Fe_o, and Al_o contents but negatively with silt contents. The $(Ac/Al)_V$ and $(Ac/Al)_S$ ratios showed only a positive correlation with silt contents. In contrast, GM/AX ratios were positively correlated with clay contents but negatively correlated with silt contents as well as with Fe_d and Fe_o contents.

Environmental vector fitting for HF revealed that pH, active layer thickness, contents of clay as well as of Fe_d, Fe_o, and Al_o were significantly correlated with both lignin-derived phenol and neutral sugar patterns. However, the effect of mineral contents was stronger than that of pH on lignin patterns, while the opposite was observed for the neutral sugar patterns (Figure 4, Table S4).

4. Discussion

4.1. Lignin and carbohydrate contents in permafrost environments versus other ecosystems

The arctic graminoids showed generally smaller CuO oxidation lignin contents than those in peatlands (Bourdon et al., 2000), in grasslands (Otto and Simpson, 2006), in forest (Prietzel et al., 2013) and in mangrove soils (Opsahl and Benner, 1995) (Table 8). The lignin-derived phenol contents of dwarf shrubs

Table 7: Pearson correlation table between lignin-derived phenol (VSC) and neutral sugar contents, lignin oxidation indicators, and GM/AX ratios with environmental parameters and soil properties (n = 100-120) of all sites. Significance level: * $p < 0.05$, ** $p < 0.01$. AL denotes active layer.

	LF							HF						
	VSC (g kg^{-1} dw)	**VSC (g kg^{-1} OC)**	**$(Ac/Al)_V$**	**$(Ac/Al)_S$**	**Neutral sugars (g kg^{-1} dw)**	**Neutral sugars (g kg^{-1} OC)**	**GM/AX**	**VSC (g kg^{-1} dw)**	**VSC (g kg^{-1} OC)**	**$(Ac/Al)_V$**	**$(Ac/Al)_S$**	**Neutral sugars (g kg^{-1} dw)**	**Neutral sugars (g kg^{-1} OC)**	**GM/AX**
C/N	-0.29*	-0.29	0.20*	-0.28*	0.12	-0.07	0.18*	0.62**	-0.23*	-0.34*	-0.31	0.64**	0.17	0.42**
$\delta^{13}C$	0.18	-0.07	0.22*	0.03	-0.38**	-0.29	0.36**	-0.52**	-0.45**	0.19*	0.14	-0.55**	-0.27*	-0.11
pH	0.41**	0.41	0.04	0.20*	-0.36**	-0.45	-0.2*	-0.34*	0.09	0.26*	0.23*	-0.45**	-0.48	-0.32**
AL thickness	-0.59**	-0.64**	0.49**	-0.44**	-0.32**	-0.22*	0.44**	-0.41**	-0.70**	0.00	0.06	-0.21*	0.12	0.72**
Clay (%)								0.37*	-0.24*	-0.1	-0.25*	0.63**	0.31*	0.37**
Silt (%)								-0.53**	0.17*	0.41**	0.35*	-0.63**	-0.48**	-0.37**
Fe_d (g kg^{-1} dw)								0.18	0.26*	0.13	0.03	0.33**	-0.19*	-0.35**
Fe_o (g kg^{-1} dw)								0.35*	0.21*	0.10	-0.03	0.48**	-0.21*	-0.32**
Al_o (g kg^{-1} dw)								0.31*	-0.18*	0.12	-0.03	0.03		0.09

were also smaller than those of pine needles (Otto and Simpson, 2006; Kuo et al., 2008; Opsahl and Benner, 1995), while the observed lignin phenol contents of lichen and mosses were higher than those reported in the study of Zavarzina et al. (2015) (Table 8). The observed OC-normalized lignin-derived

phenol contents of organic topsoil horizons, ranging from 12 to 19 g C kg^{-1} OC, were smaller than in the surface layer of peatlands (Bourdon et al., 2000) and organic topsoil of grasslands (Otto and Simpson, 2006), and either smaller or comparable to lignin concentrations reported for organic layers of forest soils (Rumpel et al. 2002, Spielvogel et al., 2007), while being higher than report of Feng and Simpson (2007) for grassland. In the studied permafrost soils, the OC-normalized contents of lignin-derived phenols declined in the organic topsoil relative to the parent plants, mirroring the degradation of lignin in the organic surface layer of tundra soils. The OC-based lignin-derived phenol contents in bulk soil showed no clear trend with soil depth (Table 5), being consistent with peat soils (Williams et al., 1997), whereas in many studies of grasslands and forests the contents decreased from the topsoil to deeper horizons (Feng and Simpson, 2007; Rumpel et al., 2002; Wiesmeier et al., 2009). As a consequence, OC-normalized lignin contents in permafrost subsoils were larger than those in subsoils of the temperate zones by factors of 2 to 7 (Feng and Simpson, 2007; Rumpel et al., 2002), while they were smaller than in subsoil horizons of peat (Bourdon et al., 2000) (Table 8). We, hence, suggest that lignin decomposition in the bulk mineral subsoils of permafrost-affected soils appears to be restrained.

The arctic graminoids and dwarf shrubs showed lower TFA-hydrolyzable sugar contents than those of Alpine (Prietzel et al., 2013) and of mangrove soils (Opsahl and Benner, 1999). These contents of moss and lichen, in contrast, were higher than reported for peatbog (Comont et al., 2006) (Table 8). The OC-normalized content of neutral sugars in the organic topsoils of the studied permafrost soils was generally larger than that of Alpine soils (Prietzel et al., 2013), and of temperate forest soils (Spielvogel et al., 2007), but smaller than the upper section of a peat core (Comont et al., 2006). The observed decrease of neutral sugar contents with soil depth in the study soils was in line with the observation of a peat core (Comont et al., 2006) and temperate soils (Navarrete and Tsutsuki, 2008; Spielvogel et al., 2007). Hence, in contrast to the decomposition of lignin, the transformation of carbohydrates in bulk soils appears to be similar in permafrost compared to temperate soils.

4.2. Decomposition pathways in functional organic matter fractions

Lignin and neutral sugars in light fraction materials

In combination of all tundra types there was no significant difference in OC-normalized lignin contents in plants and organic horizons between sites (Table 4; Figure 2). This suggests that the source of lignin entering the mineral soil was not a factor explaining the difference in lignin content and degradation along soil profiles between sites. The LF in mineral soils derives from plant residues and root detritus, and more LF is generally present in topsoils, as they receive more aboveground litter and represent the main rooting zone with higher belowground litter inputs than in deeper soil horizons (Gentsch et al., 2015a).

Table 8: Contents of lignin-derived phenols and neutral sugar (g C kg^{-1} OC) of plants and soils from reference studies. Abbreviations are O, organic topsoils; A, mineral topsoils; B/C, mineral subsoils; Cff, permafrost horizons.

Nr.	Location	Land-use	MAT (°C)	MAP (mm)	Graminoid		Dwarf shrub/woody plant		Lichen/moss		O	A	B/C	Cff	O	A	B/C	Cff
					VSC	Neutral sugar	VSC	Neutral sugars	VSC	Neutral sugars	VSC				Neutral sugars			
1	Siberia	Permafrost	-12.7 – -8.2	57-68	20.9	94.6	36	176.4	0.7-6.7	316.4	15.1	15.9	16.5	24	121.5	94.1	59.5	59.0
2	Canada	Permafrost	-6.8	298								6.9*		1.5				
3	Russia	Artic mountain	0	1600					0.4-4.4									
4	Madagascar	Peaty marsh	16	1600	90						50	33.4	20.0-32.0					
5	France	Peatbog	7-8	1349		48-80				110-176					197	122	90	
6	Canada	Grassland	1.7 – 3.3	413-452	70		128				33.8							
7	Germany	Forest	6.3 – 11.0	700-1250							21.6	13.5	7.0					
8	Alberta	Grassland	1.7-5.0	413-452							3,6	3.2	2.5					
9	USA	Forest	18.3	813	96		90											
10	Austria	Alpine soils	5.5	2109		257-354		267-444		193					69			
11	Germany	Forest	5.7	1150-1300							24	19			88.5	62.3		
12	USA	Mangrove		62.3	60.1	230	60.1	90-275										
13	Brazil	Grassland	14,5	1800-2000	2.7		5.9				0.9	0.4	0.38					

*1. This study; 2. Bröder et al. 2021; 3. Zavarzina et al. 2015; 4. Bourdon et al. 2000; 5. Comont et al. 2006; 6. Otto and Simpson, 2006; 7. Rumpel et al. 2002; 8. Feng and Simpson, 2007; 9. Kuo et al. 2008; 10. Prietzel et al. 2013; 11. Spielvogel et al. 2007; 12. Opsahl and Benner 1995, 1999; 13. Wiesmeier et al., 2009, * value of whole active layer.*

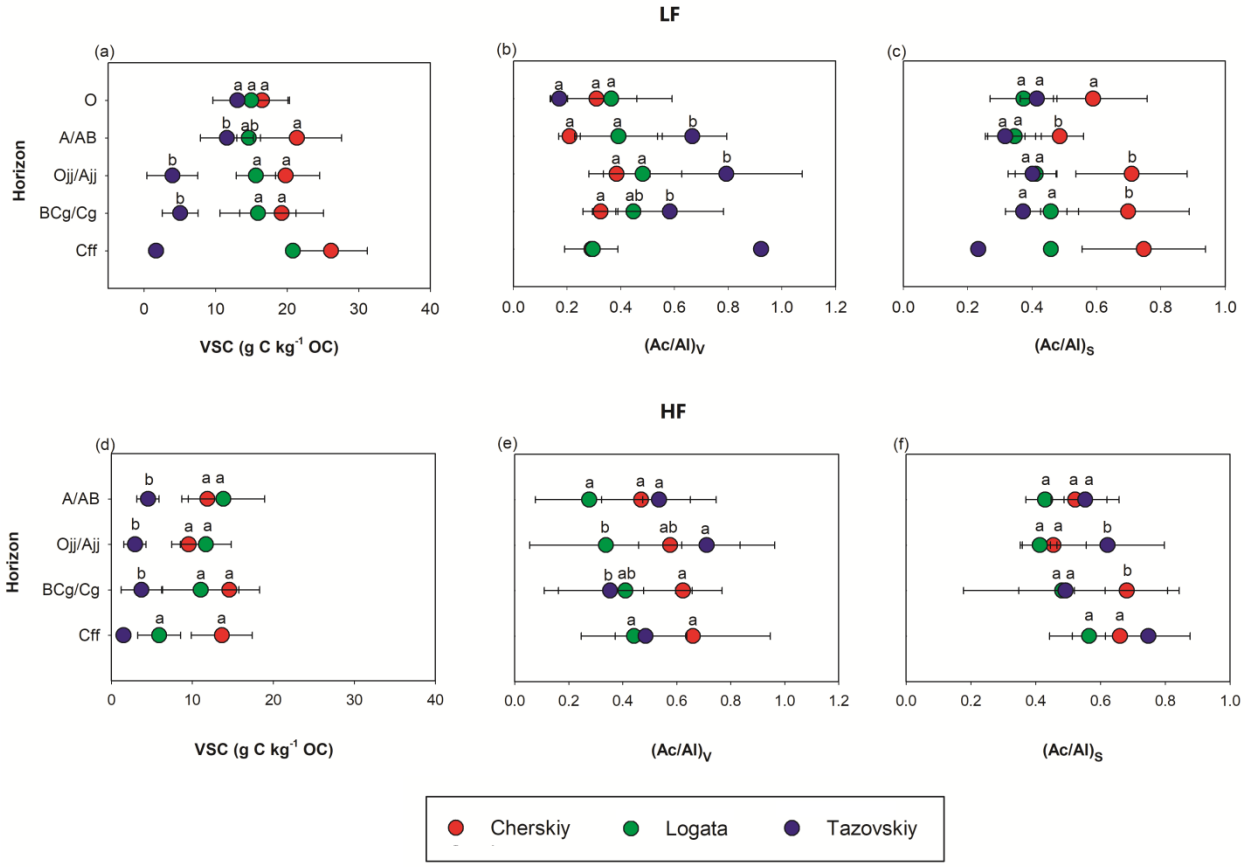

Figure 2: Contents of lignin-derived phenols (VSC) along with $(Ac/Al)_V$ and $(Ac/Al)_S$ ratios in organic topsoil (O) horizons and the light fraction, LF (a-c) and heavy fraction, HF (d-f) of mineral soil horizons. Error bars represent standard deviations. The different letters indicate significant differences between sites for each horizon. Since the present study followed several other investigations (e.g., Gentsch et al. 2015a, b), the amount of available material did not allow replicate analyses for both fractions of the permafrost Cff horizon from the Tazovskiy site.

However, also cryoturbation may cause the translocation of LF material to the deeper mineral soil. At the colder sites Cherskiy and Logata with their shallow active layer, the contributions of lignin-derived phenols and plant-derived sugars to LF fraction (on both, OC and soil dw basis) were constant or even increased with soil depth. At the same time, the ratios of $(Ac/Al)_V$ and $(Ac/Al)_S$ were constant or even decreased in all mineral soil horizons. These findings indicate that lignin-derived phenols and neutral sugars in the LF in the subsoils of these two sites are hardly degraded, which is supported by relatively constant values of C/N and $\delta^{13}C$ in this fraction with depth (Table 2). The retarded degradation is additionally supported by high ^{14}C ages of LF material at the Cherskiy site, ranging from 3060 to 8560 years (Gentsch et al. 2015b), while LF material from temperate forest soils is usually much younger, e.g., 60-100 years at Spanish Pyrenees (Leifeld et al., 2015).

In contrast, the western site Tazovskiy with a deeper active layer exhibited decreasing contents of lignin-derived phenols and plant-neutral sugars from topsoil to deeper horizons, including the buried topsoil. These results suggest that the LF material becomes progressively altered with soil depth (Otto and Simpson, 2005; Rumpel et al., 2002), which for lignin is also reflected by increasing $(Ac/Al)_V$ ratios and for sugars by generally higher GM/AX ratios. The more advanced decomposition of LF-lignin and neutral sugars at Tazovskiy as compared to Logata and Cherskiy is also in line with generally higher $\delta^{13}C$ values in the LF of Tazovskiy (Table 2). Given the comparable $\delta^{13}C$ values of source plants of all sites (Table 3), the higher $\delta^{13}C$ values in the LF of Tazovskiy than Cherskiy and Logata reflect the preferential respiratory loss of the isotopically light carbon during microbial decomposition of soil OM (Wang et al., 1996). This pattern was also supported by decreasing C/N ratios with soil depth at Tazovskiy but not at Cherskiy and Logata (Table 2).

The concurrent transformation patterns of lignin and neutral sugars with soil depth hint to their presence as lignocellulose (Seelenfreund et al., 1990), with ongoing decomposition causing the parallel alteration of both structural components. At Cherskiy and Logata, such impregnation of saccharides by lignin may protect them from rapid microbial utilization (Moran and Hodson, 1989), while the accelerated lignin decomposition at Tazovskiy also unlocks the plant-derived sugars. This finding was supported by a positive correlation between VSC and AX for LF materials of each site (Figure 6a).

The enhanced LF degradation at the western Tazovskiy site may be caused by higher MAT and probably more available oxygen as a result of the deeper active layer than at Cherskiy and Logata. The deeper active layer at Tazovskiy may increase drainage and enhance oxygen transport into subsoils, as it has been shown for northeast Siberian polygonal tundra soils (Walz et al., 2017). When combining the three sites, we further found significant negative correlations between active layer thickness and lignin and sugar contents, and a positive one with $(Ac/Al)_V$ and GM/AX ratios (Table 7). Also in the NMDS plots active layer thickness showed the greatest effect (expressed by the length of fitting arrows, Figure 3) on the lignin and sugar contents of organic topsoils and LF of the mineral soils (Figure 3). All the data indicate a larger degree of lignin and carbohydrate transformation with increasing active layer thickness, suggesting active layer thickness and the zone of aeration as important control in the turnover of OM in permafrost soils.

Lignin and neutral sugars in the heavy soil fraction

The presence of plant and microbial compounds in the HF indicates that formation of mineral-organic associations in permafrost soils occurs via two distinct pathways (Sokol et al., 2019): First, the microbial community processes plant residues and then microbial assimilates become sorbed to minerals (Cotrufo et al., 2015). Second, dissolved OM, either leached from topsoils or liberated in mineral horizons by desorption and microbial processes (Liebmann et al., 2020), is directly sorbed to minerals without preceding microbial assimilation of plant-derived carbon (Mikutta et al., 2019).

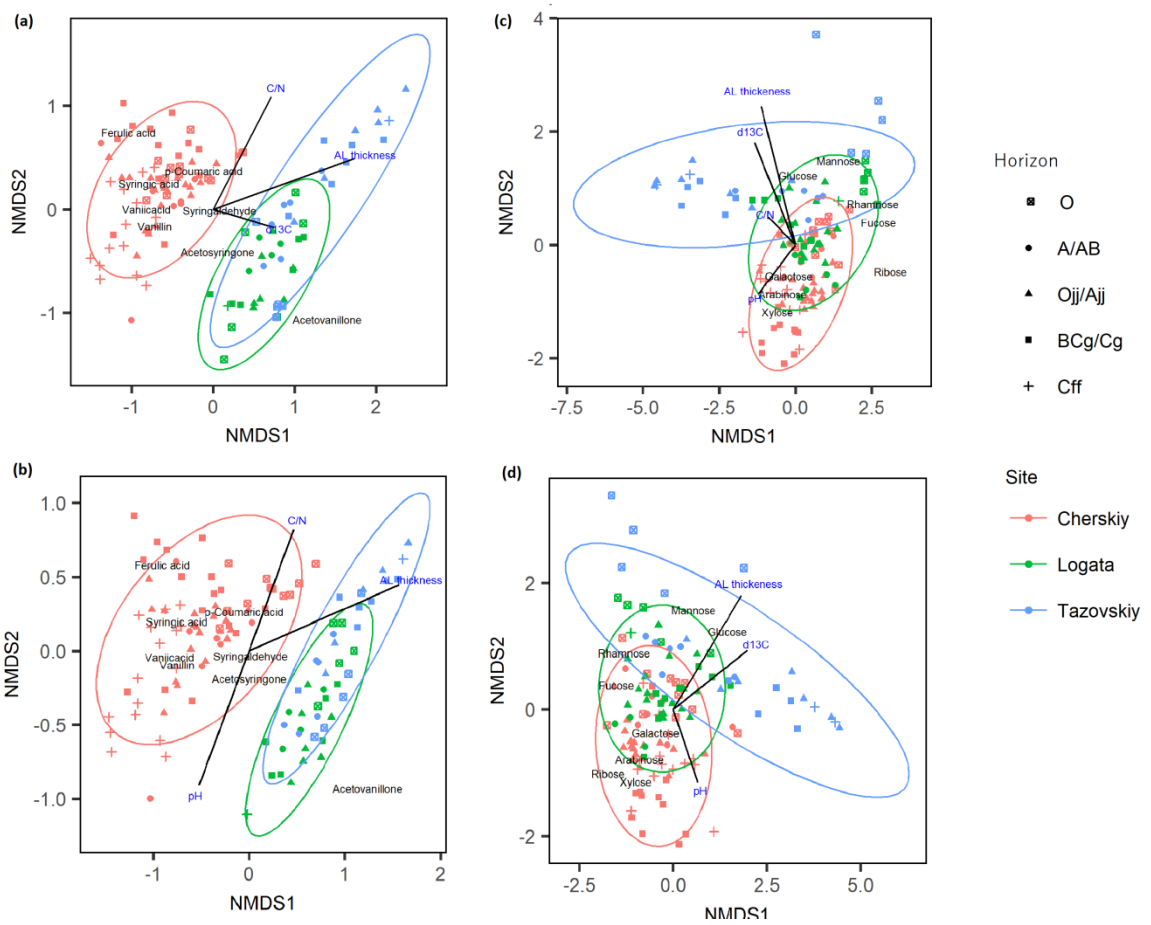

Figure 3: Nonmetric multidimensional scaling analysis (NMDS) plots of contents of individual lignin-derived phenols and neutral sugars on basis of OC (g C kg^{-1} OC) (a, c) and of soil dw (g kg^{-1} dw) (b, d) and from individual soil samples over all sites for organic topsoil (O) horizons and the light fraction. The significant fitting vectors refer to the correlations between active layer (AL) thickness, soil pH, C/N, and $\delta^{13}C$ of the LF, and contents of individual lignin-derived phenols. Arrow lengths refer to the strength of correlation. The data were log-transformed to reduce stress values.

As lignin is not favorably used for microbial assimilation, lignin accumulation is best explained by the second pathway. In comparison to HF of other soils, soil dw-based contents of lignin-derived phenols in the topsoil were somewhat smaller than in humid tropical Hawaiian soils (Mikutta et al., 2009) but in the range of New Zealand soils under humid temperate climate (Mikutta et al., 2019). Comparing all study sites, Tazovskiy showed smaller OC- and soil dw-normalized contents of lignin-derived phenols compared to Cherskiy and Logata. In addition, lignin contents in Tazovskiy slightly decreased from mineral topsoil to mineral subsoil, which was in general agreement with some studies of clay- and silt-sized mineral-associated in forest soils (Rumpel et al., 2004, 2012; Vancampenhout et al., 2012, Mikutta et al. 2009).

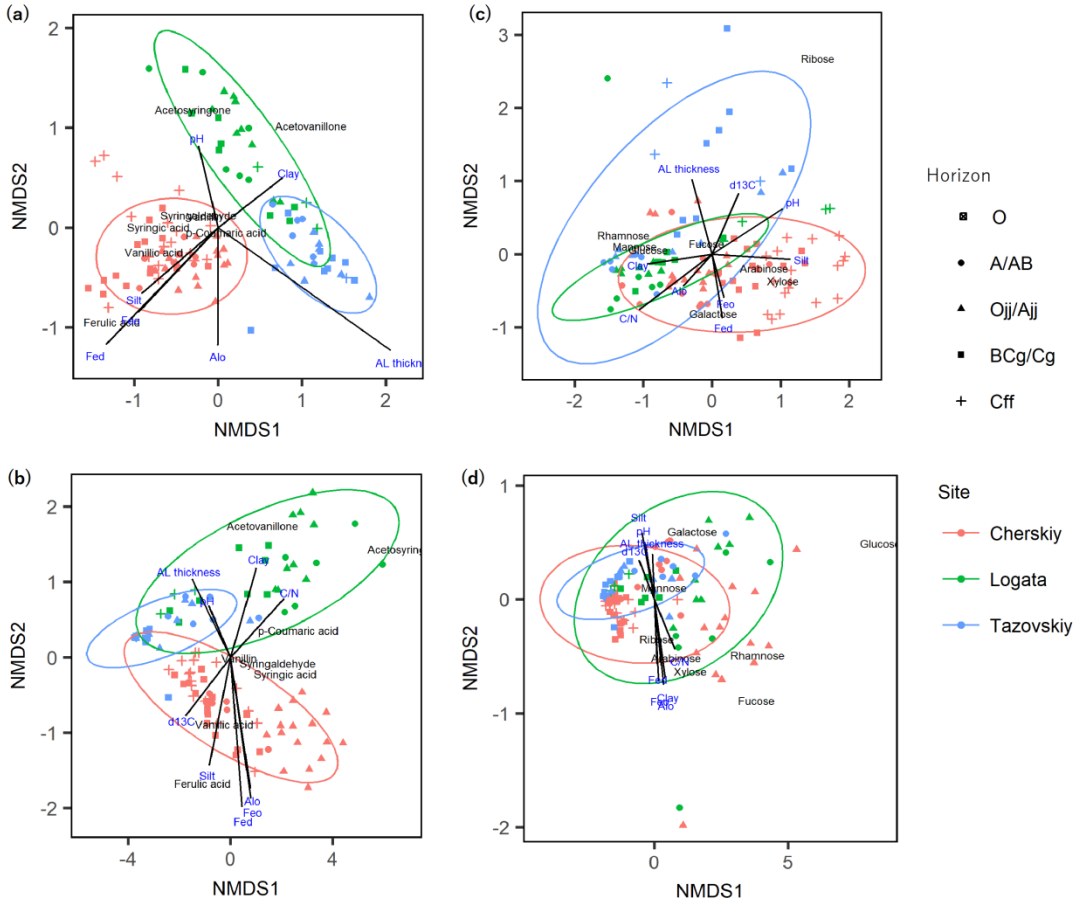

Figure 4: Nonmetric multidimensional scaling analysis (NMDS) plots of contents of individual lignin-derived phenols and neutral sugars on basis of OC (g C kg^{-1} OC) (a, c) and of soil dw (g kg^{-1} dw) (b, d) from individual soil samples over all sites for the heavy fraction. The significant fitting vectors refer to the correlations between active layer (AL) thickness, C/N, and $\delta^{13}C$ of the HF, pH, contents of oxalate-extractable Fe and Al (Fe_o, Al_o), and dithionite-extractable Fe (Fe_d) (g kg^{-1} dw). Arrow lengths refer to the strength of correlation. The data were log-transformed to reduce stress values.

The decrease of lignin contents with depth was explained by preferential sorption of lignin to mineral surfaces when dissolved OM moves down the soil profile (Kaiser et al., 2001; Kaiser and Zech, 2000; reviewed by Angst et al. 2021). In contrast, the OC-normalized lignin contents in the HF of Cherskiy and Logata soils tended to remain unchanged from topsoil to subsoil. We speculate that the comparable lignin content in the subsoil HF could also be explained by sorption processes. In permafrost soils, seasonal thawing creates pulses of melting water, draining faster to larger depth than in non-permafrost soils (Ostroumov, 2004). However, the shallower active layer at Logata and Cherskiy may impair the fast drainage, thus enhancing the opportunity for dissolved OM interactions with soil minerals.

Unlike lignin, neutral sugars derive not only from plants but also from microbial assimilates. The abundance of neutral sugars in the HF, hence, is due to sorption of both dissolved OM and microbial residues. The contents of mainly plant-derived neutral sugars (i.e., xylose and arabinose) in

the HF (10 to 26 g C kg^{-1} OC) have exceeded those of lignin (3 to 14 g C kg^{-1} OC), which is consistent with temperate forest soils (Córdova et al., 2018; Guggenberger et al., 1995; Kiem and Kögel-Knabner, 2003). The plant-derived sugar contents were slightly smaller at Tazovskiy than at Cherskiy and Logata, while no difference between the three sites was observed for microbially-derived sugars as well as the GM/AX ratios (Figure 5). The HF of permafrost soils contained either a similar proportion of neutral sugars as humid tropical Hawaiian soils (Mikutta et al., 2009) and even a three-fold higher share as soils under deciduous and coniferous stands in the temperate zone (Rumpel et al., 2010), suggesting that neutral sugars might be an integral component of stabilized OM in permafrost soils (Angst et al., 2021).

When normalized to OC, neutral sugar contents of all three sites decreased with soil depth. This trend was consistent to those of temperate forest (Rumpel et al., 2012) and steppe soils (Bischoff et al., 2018), but was in contrast to Spielvogel et al. (2008) who reported an increasing proportion of neutral sugars in the HF of acidic forest soils with depth. Further, the GM/AX ratios of HF in permafrost soils generally decreased from topsoil to deeper horizons, while it increased in forest soils (Rumpel et al., 2010). The lower GM/AX ratios and C/N ratios in the HF of mineral subsoil and permafrost layer than in topsoil and buried topsoil rather suggest a more effective microbial recycling, with preferential use of microbial necromass by microorganisms. Effective recycling of microbial necromass leads to a loss of carbon by respiration whereas N is efficiently recycled, thus also explaining the depth trends in C/N ratios. This finding is supported by the studies at the same soils by Wild et al. (2014) and Capek et al. (2015), who showed increasing respired substrate-derived carbon and decreasing microbial carbon from mineral topsoil to mineral subsoil horizons.

The relatively larger contribution of lignin moieties and associated plant sugars in the HF of subsoil horizons at Cherskiy and Logata is also likely due to the negative impact of frequently anaerobic conditions on the lignin-degrading microbial community. Although Gittel et al. (2013) showed for the Cherskiy soils that actinobacteria abundance increases with soil depth, actinobacterial lignin degradation activity is apparently lower than fungal activity, due to smaller biomass, lower cell-specific enzyme activities, and absence of hyphae structures (Gittel et al., 2014). Gentsch et al. (2015b) used ^{13}C nuclear magnetic resonance spectroscopy and X-ray photoelectron spectroscopy to demonstrate an increasing proportion of aromatic and aliphatic carbon with soil depth in the HF of the Cherskiy soils, suggesting an enrichment of less oxidized carbon forms of plant and microbial origin in the mostly anaerobic deep active layer of permafrost soils.

4.3. Controls on lignin and carbohydrate transformation in permafrost soils

At the western site Tazovskiy, with its quite favorable soil environment, lignin appears to be well decomposable, as has also been shown for temperate soils (von Lützow et al., 2006). In contrast to Tazovskiy, the OC-normalized contents of lignin-derived phenols increased at eastern Cherskiy and middle Logata sites with depth while the degree of oxidative alteration remained at a low level. This indicates that the stage of lignin decomposition is low under the cold and frequently anaerobic

conditions in the active layer und the upper permafrost at Cherskiy and Logata. In the absence of oxygen, the decomposition of compounds with a low nominal oxidation state, primarily lipids but also lignin, is strongly restrained since it is thermodynamically ineffective (Boye et al., 2017; Keiluweit et al., 2016).

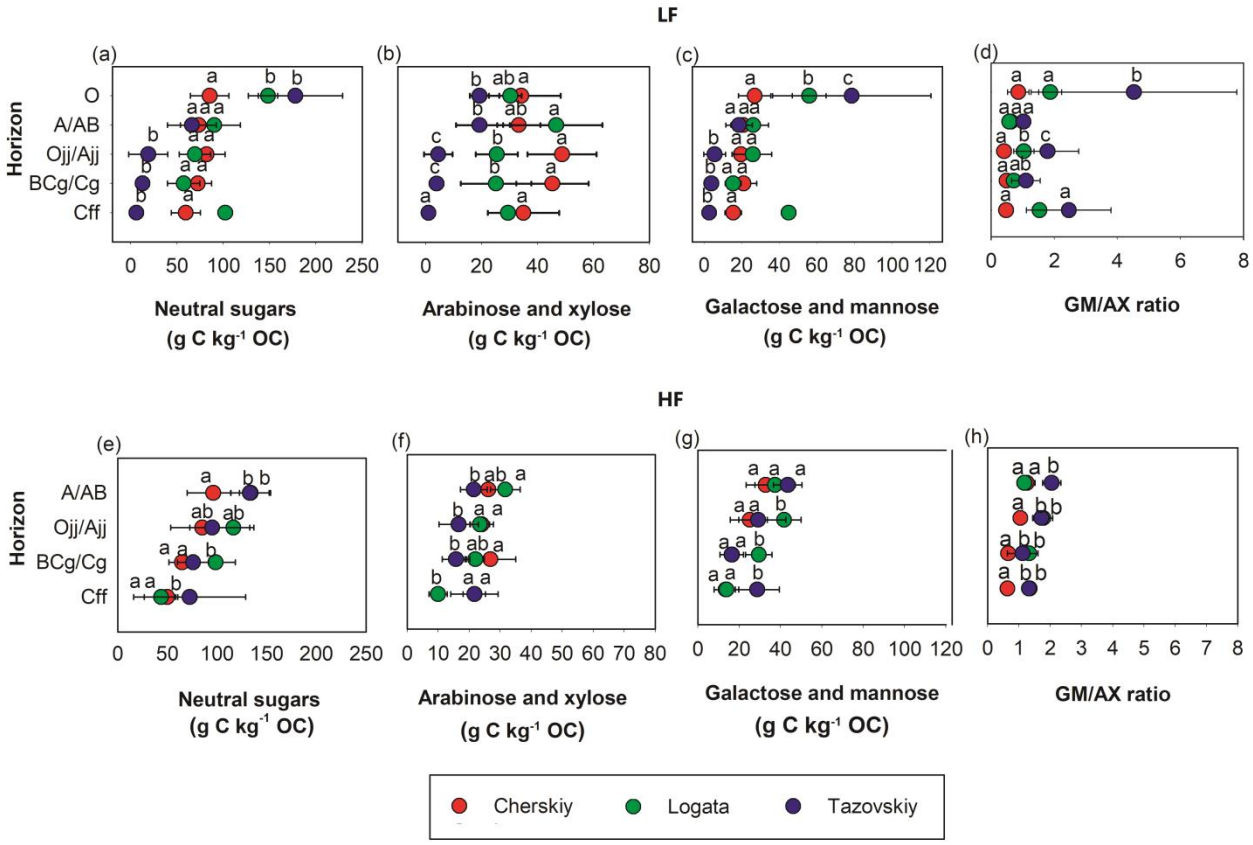

Figure 5: Contents of total neutral sugars, primarily plant-derived sugars arabinose plus xylose, and primarily microbially-derived sugars galactose plus mannose along with GM/AX ratios within soil profiles of all sampling sites in the organic topsoil (O) horizons and the light fraction, LF (a-d), and heavy fraction, HF (e-h) of mineral soil horizons. Error bars represent the standard deviation. The different letters indicate significant differences between sites for each horizon. GM/AX stands for (galactose + mannose)/(arabinose + xylose). Since the present study followed several other investigations (e.g., Gentsch et al. 2015a, b) the amount of available material did not allow replicate analyses of the LF from the Cff horizon of the Logata site.

According to Keiluweit et al. (2017), the less efficient anaerobic metabolism selectively preserves otherwise bioavailable reduced organic compounds from decomposition. A shift from anaerobic to aerobic conditions of bulk soils in contrast can increase mineralization rates 10-fold (Keiluweit et al., 2017). Hence, at Cherskiy and Logata lignin in the LF appears to be preserved by a context-specific persistence. As a large part of plant-derived sugars are incorporated in lignocelluloses, this context-specific persistence also protects plant sugars from decomposition in both fractions of Cherskiy and Logata, as supported by a significant, positive regression between OC-normalized VSC and AX in the LF and HF of Cherskiy and Logata (Figure 6b). In contrast,

lignocellulose is well decomposed in the much less hydromorphic Tazovskiy soils, possibly additionally facilitated by the higher MAT at this site.

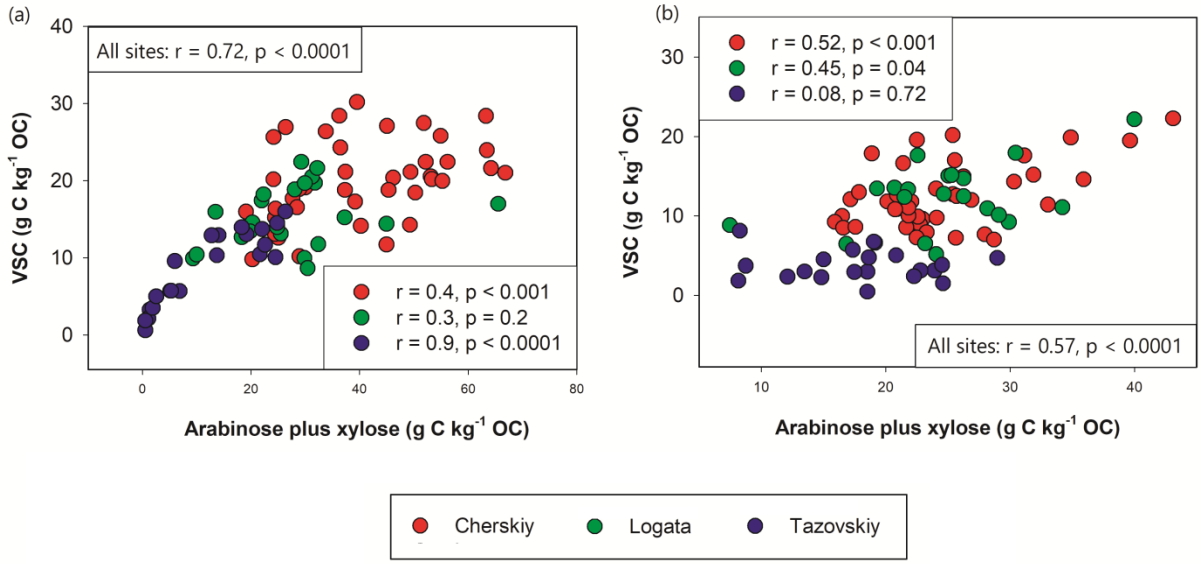

Figure 6: Relationship between total lignin-derived carbon and the sum of arabinose plus xylose carbon in the (a) light fraction (b) and heavy fraction of mineral soil horizons from the three study sites.

When analyzing the decomposition patterns of lignin and carbohydrates in the HF of the three permafrost sites, not only climatic factors and associated soil physical conditions must be considered, but also soil mineralogy. The HF contained smaller amounts of OC-normalized lignin-derived phenols and neutral sugars of assumed plant origin at Tazovskiy than at Logata and Cherskiy. Concurrently, the degree of oxidative decomposition of the remnant lignin and the relative proportion of microbial sugars were higher at Tazovskiy than at Logata and Cherskiy. At first glance, this observation can be similarly explained as for the LF. The lower soil moisture along with the higher mean annual temperature might have contributed to the more advanced decomposition of plant residues and formation of microbial metabolites (Davidson and Janssens, 2006). However, also the texture and mineralogical composition differed between the sites, which might have an impact not only on OC storage (see Gentsch et al., 2015a) but also on OM composition. The effect of mineralogical properties was revealed by a positive correlation between soil dw-normalized lignin and neutral sugar contents with clay, Fe_d, Fe_o, and Al_o contents across all sites (Table 7). Hence, differences in the mineralogical composition, with highest contents in pedogenic Fe oxides in Cherskiy, might determine the sorption capacity and thus the accumulation of lignin and neutral sugars in the HF, decreasing in the order Cherskiy > Logata > Tazovskiy. However, we also found indications that biomarker compounds were selectively associated with certain mineral phases. In relation to clay contents, the negative regression of OC-based lignin-derived phenols *vs.* positive regression of neutral sugars in the HF provides evidence for the selective association of neutral sugars with clay minerals.

In contrast, the positive regression of lignin-derived phenol contents with Fe contents *vs.* a negative regression of neutral sugars pointed at selective lignin retention by Fe oxides. These findings are in agreement with Kawahigashi et al. (2004), who reported preferentially retained aromatic dissolved OM in the Fe oxide-enriched horizons of central Siberian permafrost soils. Moreover, these patterns were in line with studies of non-permafrost soils that demonstrate the preferential adsorption of OM rich in aromatic moieties and carboxyl groups on Fe oxides (Biber and Stumm, 1994; Gu et al., 1994; Kaiser and Zech, 2000; Kaiser, 2003; Korshin et al., 1997) and of neutral sugars on clay minerals (Kaiser and Zech, 2000). Recently, Patzner et al. (2020) suggested that permafrost thaw may foster the release Fe and associated carbon due to the activity of Fe(III)-reducing bacteria. Such a process, principally depending on anaerobic conditions, could also partly explain the relatively low Fe_o contents and the more advanced lignin and carbohydrate decomposition at the Tazovskiy site with its larger active layer thickness.

Lignin-derived phenol contents showed no significant relationship to pH when normalized to OC, but a significant negative correlation when expressed by soil dw. This contrasts with the previously observed stimulation of microbial lignin degradation at decreasing soil pH (Thevenot et al., 2010). At the same time, pH was negatively correlated also with neutral sugar contents and GM/AX, indicating a lower contribution of microbially-synthesized sugars at higher pH values. Thus, pH might not control microbial lignin and carbohydrate degradation activity, but rather affect the sorption of these substances to mineral phases, since the sorption of anionic compounds is usually greater at lower pH because of the greater protonation and formation of positively charged mineral surfaces (van Bergen et al., 1997, Pierzynski et al., 2005).

5. Conclusions

Density fractionation together with biomarker analysis was used to assess the contents and decomposition of lignin and carbohydrates in permafrost soils in northern Siberia as influenced by climatic conditions and mineral properties. In comparison to many non-permafrost environments, the OC-normalized contents of lignin-derived phenols in bulk soils were smaller, while neutral sugars contents were comparable or even higher. The strongest degradation of lignin and neutral sugars in the LF was observed at Tazovskiy, which may be due to the highest MAT and largest active layer thickness, coinciding with better aeration, as compared to the other sites. These factors might also have contributed to the relatively weak decomposition status of lignin in the HF of soils at Cherskiy and Logata. In addition, the larger contents of Fe and Al oxides likely additionally stabilized lignin-derived phenols associated with the mineral phase at these sites. Our study suggests that the stabilization of lignin and polysaccharides associated with lignin (lignocelluloses) is context-dependent, and climate-induced degradation of permafrost soils, i.e. increasing active layer thickness, will promote carbon losses by microbial degradation of lignin and associated polysaccharides. However, the magnitude of future OM losses from permafrost soils will strongly depend on texture

and mineralogical properties, either assisting or hampering the turnover of OM in the HF. These findings confirm our initial assumption that, in addition to climatic constraints, soil mineralogy is a decisive factor variegating the transformation of organic matter also in permafrost. Here, generally more knowledge is required about mineralogical soil properties of high-latitude ecosystems, including the transformation of mineral phases under changing environmental conditions.

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Data available statement

The data that support the findings of this study are openly available in the EarthChem Library repository at https://doi.org/10.26022/IEDA/112204. Data of soil properties are publicly available at Gentsch et al. 2015a [DOI: 10.5194/bgd-12-2697-2015]. Neutral and lignin data from Cherskiy site are publicly available at Dao et al. 2018 [DOI: 10.1016/j.soilbio.2017.10.032].

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Supplementary material – Study II

Table S1: Total OC-normalized neutral sugar C content and contribution of individual neutral sugars to total sugar content (%) of dominant plant species.

	Total neutral sugar C	Rhamnose	Fucose	Ribose	Arabinose	Xylose	Mannose	Galactose	Glucose
	(g kg^{-1} OC)			%					
Dwarf shrub	104.0± 21.0	4.3 ± 2.2	0.6 ± 0.4	0.3 ± 0.2	16.1 ± 4.0	24.5 ± 8.3	3.2 ± 1.3	15.3 ± 4.2	35.8 ± 8.3
Graminoid	185.4 ± 28.0	1.1 ± 0.6	0.1 ± 0.1	0.4 ± 0.3	18.6 ± 5.0	43.6 ± 8.0	1.8 ± 0.8	7.8 ± 1.6	26.6 ± 10.7
Lichen	377.4 ± 125.8	2.0 ± 1.7	0.0 ± 0.0	0.4 ± 0.2	3.0 ± 1.1	0.3 ± 0.2	34.0 ± 28.0	17.2 ± 9.0	44.0 ± 32.0
Moss	225.0	6.8	0.9	0.2	10.9	7.2	21.4	33.6	19.0

Values are mean ± SD.

Table S2. Results of one-way ANOVA to test for significant differences in contents of lignin-derived phenols and neutral sugars between horizons for each site. Significant differences are indicated by different letters at $p < 0.05$. The data are shown in Figures 2 and 5.

Soil	Site	Neutal sugars (g C kg^{-1} OC)					AX (g C kg^{-1} OC)					GM (g C kg^{-1} OC)					VSC (g C kg^{-1} OC)					$(Ac/Al)_V$					$(Ac/Al)_S$				
		O	A/AB	Ojj/Ajj	BCg/Cg	Cff	O	A/AB	Ojj/Ajj	BCg/Cg	Cff	O	A/AB	Ojj/Ajj	BCg/Cg	Cff	O	A/AB	Ojj/Ajj	BCg/Cg	Cff	O	A/AB	Ojj/Ajj	BCg/Cg	Cff	O	A/ AB	Ojj/Ajj	BCg/Cg	Cff
O horizon and LF	**Cherskiy**	a	a	a	a	a	a	a	b	ab	a	ab	a	ac	a	ac	a	a	a	a	b	a	ab	ac	a	ab	ab	b	a	a	a
	Logata	a	bc	b	bd	ab	a	ab	ac	ac	ac	a	bc	b	bd	ab	a	a	a	a	n.d.	a	a	a	a	n.d.	a	a	a	a	n.d.
	Tazovskiy	a	bc	b	bd	b	a	a	b	b	b	a	b	b	b	b	a	a	b	b	n.d.	a	b	b	b	n.d.	a	a	a	a	n.d.
HF	**Cherskiy**		a	a	b	c		a	a	ab	ac		a	b	c	c		ab	a	b	b		a	a	a	a		ab	a	b	b
	Logata		a	ab	b	c		a	b	b	c		a	a	b	c		a	a	a	a		a	a	a	a		a	a	a	a
	Tazovskiy		a	b	c	abc		a	a	a	a		a	b	c	abc		a	a	a	a		a	a	a	a		a	a	a	a

n.d.: not determined because of missing replicates, AX: sum of arabinose and xylose, GM: sum of galactose and mannose, VSC: sum of vannilyl, syringyl, coumaryl units, LF: light fraction, HF: heavy fraction.

Table S3: Results of pairwise-ADONIS test to analyze for differences in NMDS plots of carbohydrates and lignin contents in the light fraction (LF) and heavy fraction (HF) between sites (p-values).

	Carbohydrates				Lignin			
	g kg^{-1} dw		g C kg^{-1} OC		g kg^{-1} dw		g C kg^{-1} OC	
	LF	HF	LF	HF	LF	HF	LF	HF
Cherskiy vs. Logata	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Cherskiy vs. Tazovskiy	0.001	0.107	0.001	0.001	0.001	0.001	0.001	0.001
Tazovskiy vs. Logata	0.001	0.001	0.001	0.008	0.001	0.001	0.001	0.001

Table S4: Correlation coefficients of the active layer (AL) thickness, pH, C/N and $\delta^{13}C$ ratios, contents of oxalate-extractable Fe and Al (Fe_o, Al_o) and dithionite-extractable Fe (Fe_d) on two axes of NMDS plots visualizing OC-normalized lignin-derived phenol and neutral sugar contents for each fraction for the O horizon and the light fraction (LF), and the heavy fraction (HF), respectively. Note: correlation coeffecients of mineral parameters with the OC-normalized lignin-derived phenol and neutral sugar contents are given for HF only. Significance level: * $p < 0.05$, ** $p < 0.01$.

	Lignin-derived phenol contents						Neutral sugar contents					
	g C kg^{-1} OC			g kg^{-1} dw			g C kg^{-1} OC			g kg^{-1} dw		
	NMDS1	NMDS2	r^2	NMDS1	NMDS2	r^2	NMDS1	NMDS2	r^2	NMDS1	NMDS2	r^2
O and LF												
AL	0.96	0.26	0.71***	0.96	0.27	0.42***	-0.41	0.90	0.58***	0.71	0.70	0.53**
pH	n.d.	n.d.	0.05	-0.49	-0.86	0.17**	-0.84	-0.53	0.16**	0.53	-0.84	0.13**
C/N	0.53	0.84	0.27**	0.41	0.90	0.16**	-0.91	0.40	0.07*	n.d.	n.d.	0.01
$\delta^{13}C$	0.99	-0.07	0.09*	n.d.	n.d.	0.03	-0.59	0.80	0.39**	0.90	0.42	0.38**
HF												
AL thicness	0.85	-0.51	0.63***	-0.82	0.57	0.36**	-0.27	0.96	0.28**	-0.19	0.98	0.09*
pH	-0.27	0.96	0.06*	-0.7	0.7	0.14**	0.85	0.50	0.32**	-0.94	-0.33	0.2**
C/N	n.d.	n.d.	0.01	0.97	0.22	0.55***	-0.80	-0.59	0.43**	0.91	0.41	0.53**
$\delta^{13}C$	0.48	-0.87	0.08*	n.d.	n.d.	0.01	0.44	0.89	0.22**	-0,99	-0.09	0.39**
Clay (% w)	0.95	0.29	0.07*	0.79	0.60	0.15**	-0.99	-0.05	0.17**	0.99	0.17	0.
Silt (% dw)	-0.59	0.80	0.18**	-0.46	-0.88	0.38***	0.99	0.06	0.30**	-0.73	-0.67	0.38**
Fe_d (g kg^{-1}	-0.73	-0.68	0.36***	0.18	-0.98	0.46***	0.27	-0.96	0.18**	0.24	-0.97	0.19*
Fe_o (g kg^{-1}	-0.73	-0.67	0.19**	0.31	-0.94	0.43***	0.39	-0.92	0.09*	0.28	-0.95	0.
Al_o (g kg^{-1}	-0.04	-0.99	0.19**	0.30	-0.95	0.40***	n.d.	n.d.	0.05	0.50	-0.85	0.44**

Significant level: * P-value < 0.05, ** P-value < 0.01, *** P-value < 0.001; n.d.: not determined because of insignificance.

4. STUDY III

Lignin decomposition along a soil climosequence in western Siberia

Contribution: I carried out the analysis in the lab. I collected and evaluated the data, compiled the tables and figures, and wrote the manuscript.

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Lignin decomposition along a soil climosequence in western Siberia

Thao Thi DAO[a,*], Robert MIKUTTA[b], Birgit WILD[c,d,e], Leopold SAUHEITL[a], Norman GENTSCH[a], Olga SHIBISTOVA[a,f], Jörg SCHNECKER[c], Nikolay LASHCHINSKIY[h], Andreas RICHTER[c,g], Georg GUGGENBERGER[a,f]

[a] Institute of Soil Science, Leibniz Universität Hannover, Germany
[b] Soil Science and Soil Protection, Martin Luther University Halle-Wittenberg, Germany
[c] Department of Microbiology and Ecosystem Science, University of Vienna, Vienna, Austria
[d] Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden
[e] Department of Environmental Science, Stockholm University, Stockholm, Sweden
[f] VN Sukachev Institute of Forest, SB RAS, Krasnoyarsk, Russia
[g] Austrian Polar Research Institute, Vienna, Austria
[h] Central Siberian Botanical Garden, SB RAS, Novosibirsk, Russia

***Corresponding Author:**

Dao Thi Thao; thao@ifbk.uni-hannover.de

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Abstract

Lignin is one of the most abundant components of vascular plants and represents a major carbon source in soils. Due to climate change a northward shift of biomes can be observed in high latitude regions. In order to elucidate the combined effect of climate and soil characteristics on the decomposition pattern of lignin, we investigated lignin contents and its degree of oxidative decomposition within soil profiles along a climosequence in western Siberia. Soil samples were collected from organic topsoil to mineral subsoil at six sites along a 1,500-km latitudinal transect, stretching from tundra, through taiga and forest steppe to typical steppe. The stage of lignin degradation, as mirrored by decreasing lignin contents normalized to organic carbon and increasing oxidative alteration of the remnant lignin within soil horizons, increased from tundra to forest steppe and then decreased to the steppe. The different state of lignin degradation between horizons related well to the activity of phenoloxidase and peroxidase, the enzymes involved in lignin depolymerization that are were considered to be produced by both bacterial and fungal communities. The low microbial lignin decomposition in the tundra was likely due to low temperature and high soil moisture which might favor bacteria over fungi. Increasing temperature and decreasing soil moisture, facilitating a higher abundance of fungi, led to increased fungal lignin decomposition towards the south. However, drought and high pH might be responsible for the reduced lignin decomposition in the steppe. We infer that a shift of biomes to the north, driven by climate change, might promote lignin decomposition in the northern parts, whereas in the south a further retardation might be likely.

1. Introduction

Most biomes on Earth will be affected by global warming (Dillon et al. 2010; Pereira et al. 2010), potentially altering the carbon balance between terrestrial ecosystems and the atmosphere (Bond-Lamberty and Thomson, 2010). Expected changes include a shift of biomes particularly at high latitudes (Schepaschenko et al. 2013; Jiang et al. 2012), likely leading to a northward greenness expanse at high latitudes. This will increase the input of aboveground and belowground litter to soils, modify the litter chemical composition, and alter microbial community composition and activity (Grosse et al. 2011). Likewise, changing environmental conditions such as in temperature and precipitation may affect soil organic matter (SOM) decomposition and stabilization, with a direct impact on the release of greenhouse gases to the atmosphere (McGuire et al. 2006; Grosse et al., 2011; Schepaschenko et al. 2013; Conant et al. 2011).

Lignin is the second most important plant constituent, entering the soil via plant litter and roots, and is considered to play an important role in controlling litter decomposition (Hobbie, 1996; Hobbie et al. 2006). Lignin structurally comprises the three different phenylpropanes or monolignols vanillyl (V), syringyl (S), and cinnamyl (C), and has long been thought to be more stable against microbial decomposition than other major components of plant litter, i.e. cellulosic and noncellulosic polysaccharides and proteins (Martin et al. 1980; Haider, 1992). The concentration of the V + S + C units (VSC) varies between different plant taxa and decreases in the order coniferous trees (Sterjiades and Erikson, 1993; Raich et al., 2007), deciduous trees (Vivanco and Austin, 2008; Devi and Yadava, 2007), shrubs (Laishram and Yadava, 1988), and graminoids, mosses, and lichens (Winterfeld et al. 2015; Dao et al. 2018). The stage of lignin degradation, as mirrored by decreasing lignin contents normalized to organic carbon and increasing oxidative alteration of the remnant lignin.

The best understood mechanism for lignin degradation is associated with fungi, particularly white-rot fungi such as basidiomycetes (Kirk et al. 1976; Haider, 1986). However, bacteria are also known to potentially degrade lignin such as alphaproteobacteria, gammaproteobacteria, and actinomycetes (Bugg et al. 2011), with the best-characterized bacterium being Streptomyces viridosporus (Ramachandra et al. 1988). In soil, microbial lignin decomposition is generally performed by biologically mediated, oxidative reactions which use free oxygen or ferric iron-bearing minerals as terminal electron acceptors for environments lacking oxygen (Peng et al. 2008, Patzner et al. 2020).

Temperature frequently affects turnover rates of SOM (Davison and Janssens, 2006; Connant et al. 2011) by generally following three basic theories of decomposition kinetics: (1) when substrate availability and enzyme activity do not constrain reaction rates, decomposition rates increase with temperature (Arrhenius, 1889), (2) increases in decomposition rates with warming temperature should be greatest at cold temperatures (Lloyd and Taylor, 1994), and (3) organic substrates with high activation energies (i.e. slow rates) experience greater proportional increases in decomposition with increasing temperature than those with low activation energy (Davidson and Janssens, 2006). As

lignin has a high activation energy, it might be strongly affected by temperature changes, especially in cold climates. For examples, an increase of 2°C has been suggested to accelerate the decomposition of chemically recalcitrant carbon by 21%, compared with only 10% for chemically labile carbon (Davidson and Janssens, 2006). Furthermore, soil temperature affects lignin decomposition indirectly by controlling substrate availability for microorganisms as lignin decomposition is co-metabolic process (Conant et al. 2011). Warming can also promote plant root exudation and generally increase labile SOM forms (Yin et al. 2013), which in turns can accelerate the degradation of old and recalcitrant SOM in high latitude soils (Keuper et al. 2020; Mau et al. 2018; Wild et al. 2016).

In addition to temperature, soil moisture is one of the most important abiotic variables controlling SOM decomposition (Oechel et al. 1998; Shaver et al. 2006; Oberbauer et al. 2007; Lawrence et al. 2015; Koven et al. 2015). Warming and drying of wet soils lead to higher soil respiration rates than warming alone (Oberbauer et al. 2007, Natali et al. 2015). In general, moisture affects the amount and activity of microbial biomass, controls the substrate diffusion and oxygen supply for microorganisms, and may also destabilize SOM particularly under reductive conditions (Patzner et al. 2020), which results in a greater availability of carbon for soil microorganisms (Tulina et al. 2009; Patzner et al. 2020). On the other hand, long-term soil dryness may slow down the rate of SOM mineralization by reducing microbial biomass and activity (Tulina et al., 2009). Several studies, for examples, indicated that microbial respiration increases with soil water content from the dry state to normal moisture but decreases if water content further increases (Edwards, 1975; Kowalenko et al., 1978; Wu et al., 2006).

Many studies of lignin in temperate and tropical soils indicated decreasing lignin contents and increasing acid-to-aldehyde ratios of V and S units [(Ac/Al)V and (Ac/Al)S] with soil depth as result of a continuous degradation of lignin (Rumpel et al. 2002; Wang et al. 2018). In some cases, lignin has been shown to preferentially accumulate in the subsoil, either due to input of fresh root litter (Angst et al. 2016), low microbial decomposition (Bourdon et al. 2000; Tareq et al. 2004; Dao et al. 2018), or by sorption on mineral surfaces (Kaiser et al. 1997; Klotzbücher et al. 2016). Soil pH additionally exerts a control on lignin degradation, with an optimal pH for lignin degrading-fungi around 5 and for lignin degradation by Streptomyces around 9.5 (reviewed by Thevenot et al. 2010).

Uncertainty remains regarding the interplay between the varying controls on lignin degradation in soil and on the contribution of lignin to SOM in different biomes and soil depths. Here, we investigated the dependency of lignin decomposition on biotic and abiotic soil parameters under natural conditions. To that end, we used a 1,500 km long, latitudinal bioclimatic transect in western Siberia, stretching from the Arctic to the steppe biome. We hypothesized that soil temperature and moisture are decisive drivers being responsible for a different state of lignin decomposition in soils along the climosequence. We further assumed that soil pH, carbon and nitrogen (N) availability and microbial community composition additionally affect the degree of lignin decomposition. We approached our hypotheses by investigating the contents of lignin-derived phenols and their degree of

oxidative degradation using the CuO oxidation method at different depths of soil profiles along the climosequence and related the state of lignin decomposition to climatic parameters, dominating vegetation, soil pH, carbon and N availabilities as assessed by soil C/N ratio, phenoloxidase and peroxidase activities, and phospholipid fatty acid (PLFA) patterns as a proxy for bacterial and fungal abundance.

2. Materials and methods

2.1. Sampling sites

Soil samples were collected from six biomes along a 1,500-km latitudinal transect (67°16'N to 54°41'N) in western Siberia, including tundra, northern taiga, middle taiga, and southern taiga, forest steppe, and typical steppe (Fig. 1). Mean annual temperature (MAT) increased southward, ranging from -7.6°C to 1.0°C, while mean annual precipitation (MAP) was highest in the middle taiga (438 mm) and lowest in the steppe (309 mm) (Stolbovoi and McCallum, 2002; Table 1). Concurrently, the length of the growing season with daily mean temperatures above 5°C increased towards the southern biomes. Dryness of biome, expressed as aridity index and defined as the ratio of potential evaporation to precipitation (reviewed by Walton 1969 and Stadler, 2005), increased from north (0.44 in tundra) to south (1.30 in steppe) (Schnecker et al. 2015). Dominant vegetation varied among biomes, i.e. tundra was characterized by shrubs and lichens, taiga by coniferous trees, the forest steppe was richer in deciduous trees and herbaceous, and steppe showed abundant herbaceous perennials (Table 1).

Soils were sampled in August 2012 during the late growing season at the respective sites. At all sites, three dominant soil horizons of three replicate soil pits were sampled. Soil horizons were designated according to World Reference Base for Soil Resources (IUSS Working Group World Reference Base, 2015).

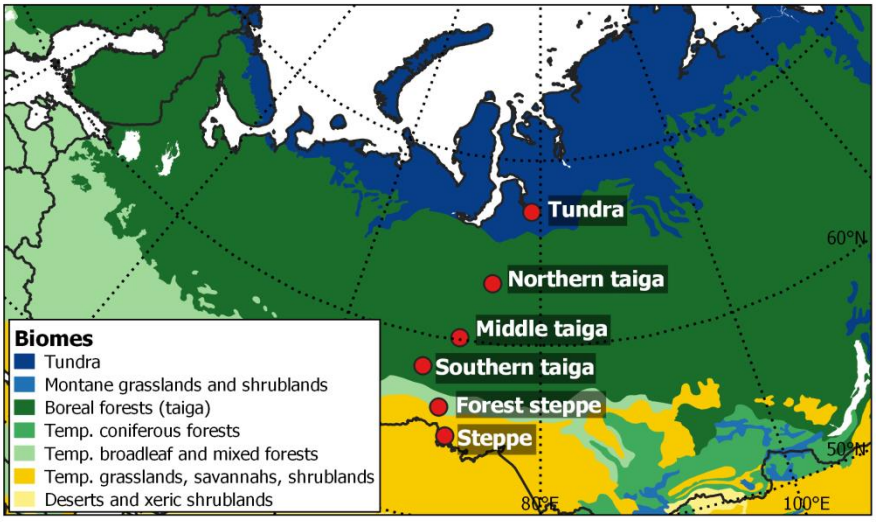

Fig 1: Map of sampling sites along the climosequence in western Siberia.

Following Wild et al. (2015), the O and OA horizons were referred to as organic topsoil, the A, AE, and EA horizons as mineral topsoil, and the E, B, and BC horizons as mineral subsoil (Table 1). Directly after sampling, living plant roots were manually removed, and soil samples were sieved to <2 mm, except for the tundra soil, where samples were too moist for sieving and instead homogenized by hand.

2.2. Lignin analysis

Concentrations of lignin-derived phenols (vanillin, acetovanillone, vanillic acid, syringaldehyde, acetosyringone, syringic acid, ferulic acid, and *p*-coumaric acid) were determined using alkaline CuO oxidation following the method of Hedges and Ertel (1982) with modifications by Kögel and Bochter (1985). In brief, lignin-derived phenols were released by oxidation with CuO in the presence of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, glucose, and 2 M NaOH at 170°C for 3 h. The lignin-derived monomers were purified using a conditioned C_{18} column and converted to trimethylsilyl (TMS) derivatives by reaction with N,O-bis-(trimethylsilyl)-trifluoroacetamide (BSTFA) in pyridine. Thereafter, derivatized-lignin monomers were identified and quantified using gas chromatography-mass spectrometry (450-GC, ion trap 220MS Varian, Palo Alto, CA, USA). Ethylvanillin was used as recovery standard, and added prior to the CuO-oxidation, while phenylacetic acid was used as internal standard, and added prior to derivatization. Vanillyl and S units were calculated as the sum of their aldehyde, ketone and carboxylic acid forms, and C units are the sum of ferulic acid and *p*-coumaric acid. The $(Ac/Al)_V$ and $(Ac/Al)_S$ ratios were used to assess the degree of lignin alteration (Hedges and Ertel, 1982). The concentration of total lignin was defined as the sum of the eight lignin-derived phenols (VSC) normalized to the soil dry weight (g VSC kg^{-1} soil) or normalized to the organic carbon (OC) content of the soil and the C content of the individual lignin-derived phenols (g VSC-C kg^{-1} OC).

2.3. Soil parameters

The data on soil pH, OC and total N (TN) contents, and the $\delta^{13}C$ ratio of SOM were taken from Wild et al. (2015). Data on phenoloxidase and peroxidase activity and the bacteria/fungi ratio of the microbial community are from Schnecker et al. (2015). The pH was determined potentiometrically in 1 M KCl extracts. Organic C and TN contents as well as the $\delta^{13}C$ ratio were analyzed by elemental analysis-isotope ratio mass spectrometry (EA-IRMS), consisting of a Carlo Erba EA 1110 elemental analyzer coupled to a Finnigan MAT DeltaPlus IRMS with a Finnigan MAT ConFlo II Interface (Thermo Fisher Scientific, Waltham, MA, USA). Mineral topsoil and subsoil at both forest steppe sites and all horizons of the steppe site contained traces of carbonate, which were removed by acidification with HCl before EA-IRMS analysis (Prommer et al. 2014). The C/N ratios of soil samples were calculated based on OC and TN masses. Phenoloxidase activities were measured using L-3,4-dihydroxyphenylalanine (DOPA) as substrate in a photometric assay (Schnecker et al. 2015). Phospholipid fatty acids were determined according to Frostegard et al. (1991) with the modification

by Kaiser et al. (2010). The bacteria/fungi ratio of the microbial community was estimated by the ratios of PLFAs assigned to bacteria and fungi (for more details see Schnecker et al. 2015).

Table 1: Characterization of sampling sites along the climosequence in western Siberia.

Site	Coordinates	MAT (°C)	MAP mm	Aridity index	Dominant plant species	Soil type	Organic topsoil		Mineral topsoil		Mineral subsoil	
							Horizon	Depth (cm)	Horizon	Depth (cm)	Horizon	Depth (cm)
Tundra	67°16'N 78°50'E	-7.6	392	1.3	*Betula nana, Cladonia* spp.	Turbic Cryosol	O	0-6	A	2-13	Bg, BCg	6-57
Northern taiga	63°17'N 74°32'E	-4.6	430	1.06	*Picea obovata, Larix sibirica*	Histic Podzol	Oi, Oe	0-22	AE,EA	8-30	Bg	14-47
Middle taiga	60°09'N 71°43'E	-2.2	438	0.89	*Abies sibirica, Picea obovata*	Endogleyic Regosol	Oi	0-6	A,AE, EA	6-14	E, EA	12-55
Southern taiga	58°18'N 68°35'E	-0.5	396	0.71	*Picea obovata, Abies sibirica*	Albic Podzol	Oi	0-7	A,AE	4-18	E, EA	15-59
Forest steppe-forest	56°14'N 70°43'E	0.7	340	0.53	*Populus tremula, Betula pendula*	Haplic Phaeozem	O, Oa	0-10	A	7-46	B	57-109
Forest steppe-meadow	56°14'N 70°43'E	0.7	340	0.53	*Calamagrotis epigeios, C. arundinacea*	Luvic Phaeozem	Oa	0-7	A	4-35	Bt	26-84
Steppe	54°41'N 71°38'E	1.0	309	0.44	*Stipa capillata,Festuca valesiaca*	Calcic Kastanozem	Oa	0-12	Ak	8-37	Bk	27-109

MAT is mean annual temperature; MAP is mean annual precipitation. Aridity index is defined as the ratio of potential evaporation to precipitation and has a threshold for drylands at 0.65 (Maestre et al. 2012). The data were reported in Wild et al. (2015) and Schnecker et al. (2015).

2.4. Statistics

One-way analysis of variance (ANOVA) followed by Tukey's HSD post-hoc test was used to test for significant differences in lignin-derived phenol contents and indicators of oxidative lignin alteration between sites and horizons at a significance level of $p \leq 0.05$. Two-way ANOVA was used to test the effect of site and horizon and their interactions. All variables were tested for normal distribution and log transformed if needed. The strength of correlation between parameters was calculated with the Pearson correlation coefficient. Principal component analysis (PCA) was performed to reduce the multivariate matrix into a bidimensional space in order to analyze the relationship between lignin patterns and biotic and abiotic parameters using the "ggbiplot" package in R 4.0.3. Structural equation modeling (SEM) was used as multivariate statistical method to estimate the relative relationships between observed variables, which include exogenously observed variables (i.e., MAT and aridity), endogenously observed variables (i.e., soil pH, C/N, enzyme activity, bacteria/fungi ratio), and latent variables (i.e., OC-normalized VSC-C, $(Ac/Al)_V$, and $(Ac/Al)_S$) (Kline, 2015). The latent variables were assessed to predict the term "stage of lignin decomposition". Some of the variables were log-transformed to achieve normal distribution. Linear relationships between variables were calculated with some of the variables first requiring rescaling to achieve approximately equal variances for all variables. The SEM was implemented in R 4.0.3 using the "lavaan" package (Rosseel, 2012).

Table 2: Basic soil characteristics of the study sites. All values are means with standard deviation in brackets (Wild et al., 2015 and Schnecker et al. 2015).

	Tundra			Northern taiga			Middle taiga			Southern taiga			Forest steppe-forest			Forest steppe-meadow			Steppe		
	Organic topsoil	Mineral topsoil	Mineral subsoil	Organic topsoil	Mineral topsoil	Mineral subsoil	Organic topsoil	Mineral topsoil	Mineral subsoil	Organic topsoil	Mineral topsoil	Mineral subsoil	Organic topsoil	Mineral topsoil	Mineral subsoil	Organic topsoil	Mineral topsoil	Mineral subsoil	Organic topsoil	Mineral topsoil	Mineral subsoil
OC (g kg^{-1} dw)	303.0 (69.30)	28.51 (6.30)	4.22 (1.30)	452.10 (12.00)	37.00 (7.00)	7.10 (2.60)	408.20 (67.80)	63.30 (33.50)	16.70 (8.40)	393.90 (57.30)	43.40 (8.10)	4.70 (0.80)	257.20 (19.80)	45.60 (10.10)	5.30 (0.20)	201.30 (71.70)	24.50 (3.50)	5.80 (0.80)	33.90 (11.30)	20.10 (6.10)	7.20 (1.80)
C/N	31.96 (5.65)	16.00 (1.50)	10.95 (1.57)	34.99 (1.38)	27.35 (4.45)	14.89 (1.07)	23.82 (0.74)	20.52 (4.70)	16.29 (3.81)	26.59 (0.69)	13.96 (1.79)	9.39 (0.47)	16.22 (0.84)	12.88 (0.56)	9.75 (0.42)	14.67 (0.15)	13.05 (0.29)	10.69 (0.49)	10.99 (0.36)	10.84 (0.58)	9.15 (0.40)
$\delta^{13}C$ (‰)	-26.54 (0.46)	-25.69 (0.10)	-24.57 (0.23)	-28.27 (0.46)	-27.13 (0.59)	-25.79 (0.11)	-29.14 (0.32)	-26.94 (0.61)	-26.54 (0.56)	-28.38 (0.53)	-26.80 (0.08)	-25.24 (0.19)	-27.80 (0.21)	-25.71 (0.53)	-25.27 (0.33)	-27.63 (0.19)	-26.15 (0.16)	-25.91 (0.08)	-25.38 (1.13)	-25.09 (0.61)	-24.87 (0.18)
pH	3.73 (0.12)	3.70 (0.08)	3.88 (0.13)	2.80 (0.10)	3.06 (0.11)	3.77 (0.06)	3.67 (0.06)	3.25 (0.10)	3.48 (0.11)	4.23 (0.31)	3.62 (0.16)	3.73 (0.17)	7.03 (0.78)	4.26 (0.13)	4.08 (0.10)	5.70 (0.62)	4.14 (0.05)	4.02 (0.16)	4.59 (0.10)	5.08 (0.11)	7.92 (0.91)
Phenoloxidase (mmol h^{-1} g^{-1} C_{mic})	1.03 (0.39)	5.32 (2.31)	23.95 (7.29)	1.39 (0.68)	17.11 (9.26)	8.99 (1.93)	0.89 (0.23)	9.44 (5.88)	17.,43 (8.15)	1.23 (1.12)	5.02 (0.58)	11.30 (4.27)	0.30 (0.07)	3.91 (1.97)	8.34 (1.85)	0.19 (0.03)	3.82 (1.69)	6.23 (2.11)	1.94 (1.21)	3.47 (0.88)	7.66 (2.13)
Bacteria/Fungi[a]	1.49 (0.59)	1.87 (0.23)	6.04 (2.69)	1.28 (0.08)	3.78 (1.50)	4.82 (0.79)	1.20 (0.41)	3.,56 (1.02)	4.65 (0.67)	1.90 (0.08)	3.58 (1.50)	4.17 (0.79)	2.27 (0.46)	4.84 (0.49)	2.84 (0.63)	2.16 (0.38)	3.00 (0.88)	2.35 (0.31)	3.40 (0.07)	2.95 (0.66)	2.58 (0.48)

[a] *Bacteria/Fungi indicates the ratio of phospholipid fatty acids (PLFA) assigned to bacteria and fungi according to Frostegård et al. (1991).*

3. Results

Contents of lignin-derived phenols are reported on the basis of soil dry weight (dw) and also normalized to OC. While the former informs on storage of lignin-derived phenols, the latter is suitable to assess the relative enrichment or depletion of lignin-derived phenols during SOM transformation with increasing soil depth (Kögel-Knabner, 1993).

3.1. Lignin patterns in the surface layers

For surface layers, concentrations of lignin-derived phenols were lowest in the steppe (0.7 ± 0.3 g VSC kg^{-1} soil dw) and highest in the southern taiga (11.5 ± 4.9 g VSC kg^{-1} soil dw) (Fig. 2). Normalized to OC, lignin-derived phenols ranged from 5.2 ± 2.1 to 14.7 ± 4.5 g VSC-C kg^{-1} OC (Fig. 3). The OC-normalized lignin-derived phenol contents were lowest for organic topsoil of the tundra and tended to increase towards the south, but differences were not statistically significant (Fig. 3). The $(Ac/Al)_V$ ratios were significantly higher in the organic topsoil of forest steppe and uppermost layer of steppe than those of the northern sites, while the $(Ac/Al)_S$ ratios did not show clear differences between sites (Fig. 3). Similarly, S/V ratios were higher in the forest steppe and the steppe than in the taiga and tundra, while no significant difference between sites was observed for the C/V ratios (Fig. 3).

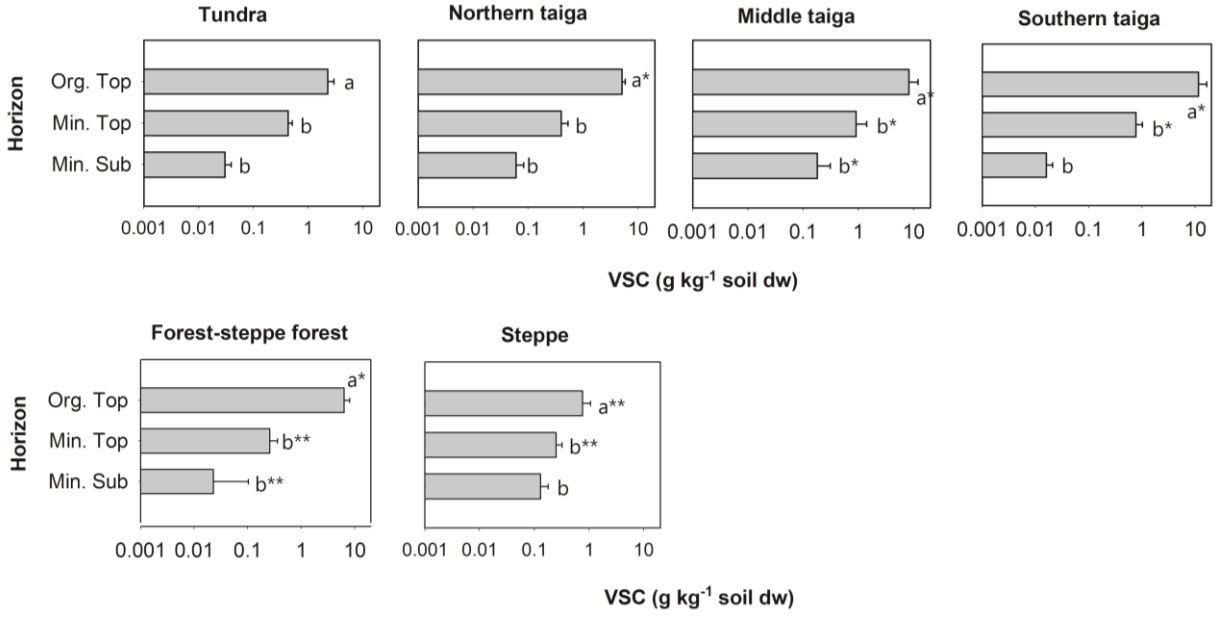

Fig. 2: Total lignin-derived phenol contents (vanillyl, syringyl, and cinnamyl units; VSC) normalized to soil dry weight (dw) within soil profiles at each site (note the log-scale). Error bars represent standard deviations with n=3. The letters indicate significant differences between horizons of each site, and the symbols * indicate significant differences between sites for each horizon with a significance level $p < 0.05$. Abbreviations are: Org. Top, organic topsoils; Min. Top, mineral topsoils; Min. Sub mineral subsoils.

Table 3: F statistics for bi-factorial ANOVA, testing the effects of site and horizon lignin patterns (*p < 0.05, **p<0.01, ***p<0.001)

Lignin patterns	F values
VSC (g kg^{-1}dw)	
Site	7.6***
Horizon	191.8***
Site × Horizon	18.8***
VSC (g VSC-C kg^{-1}OC)	
Site	9.3***
Horizon	37.5***
Site × Horizon	6.8***
$(Ac/Al)_V$	
Site	11.0***
Horizon	14.8***
Site × Horizon	2.2*
$(Ac/Al)_S$	
Site	20.9***
Horizon	10.3***
Site × Horizon	1.9*

3.2. Lignin patterns in the mineral soils

In the mineral topsoil, lignin-derived phenols accounted for 0.2 ± 0.01 to 0.9 ± 0.5 g VSC kg^{-1} soil dw (Fig. 2). Concentrations were highest in the middle and southern taiga, and lowest in the steppe. Mineral subsoil horizons exhibited 0.03 ± 0.002 to 0.2 ± 0.1 g VSC kg^{-1} soil, with lowest contents at the southern taiga and the forest steppe sites (Fig. 2). On an OC basis, lignin-derived phenol contents in the mineral topsoil range from 5.5 ± 3.4 to 11.6 ± 2.6 g VSC-C kg^{-1} OC, and were lowest in the forest steppe, while no difference was observed for the other sites (Fig. 3). In the mineral subsoil, the lignin-derived phenol contents ranged from 2.7 ± 0.8 to 12.3 ± 6.1 g VSC-C kg^{-1} OC, with largest values in the steppe (Fig. 2). The $(Ac/Al)_V$ of mineral topsoils and subsoils appeared to increase from north to south. Values of $(Ac/Al)_S$ in the mineral topsoil and subsoil exceeded those of $(Ac/Al)_V$ at most sites, and generally increased from the tundra to the southern taiga, and then declined to the steppe (Fig. 3).

3.3. Variability in lignin patterns between horizons

Two-way ANOVA indicates that lignin-derived phenol contents normalized to soil dry weight and OC differed more strongly with soil horizons than with sites (Table 3). Similarly, soil horizons had a larger impact on $(Ac/Al)_V$ than sites. In contrast, $(Ac/Al)_S$ was more variable between sites than soil horizons. Figure 4 reveals the depth-dependent changes of the OC-normalized lignin-derived phenol content and $(Ac/Al)_V$, which are given as mean difference between the upper and lower horizons. Negative mean differences of OC-normalized lignin-derived phenol contents between the mineral topsoils and the organic topsoils reflect the selective depletion of SOM in lignin from the organic topsoil to the mineral topsoil, except for the tundra (Fig. 4a,b,c). These differences tended to increase

from the northern taiga to the forest steppe, but slightly decreased in the steppe. The difference between mineral subsoils and mineral topsoils were also negative, with the exception of the steppe. However, the differences were smaller than those between organic topsoil and mineral topsoil, and did not show a clear latitudinal trend. Due to cumulative effects, largest mean differences were observed between mineral subsoils and organic topsoils and were strongest at the forest steppe-forest site.

A positive mean difference of $(Ac/Al)_V$ between mineral topsoils and organic topsoils as well as between mineral subsoils and mineral topsoils was observed, indicating increasing oxidative alteration of lignin with soil depth (Fig. 4). However, the mean differences of $(Ac/Al)_V$ between the horizons showed no clear trends between sites (Fig. 4). At the basis of the whole soil profile, the largest relative increase of $(Ac/Al)_V$ was observed for the middle and southern taiga sites (Fig. 4f). The similar trend was also found for $(Ac/Al)_S$ ratios, but not shown.

3.4. Lignin patterns in relation to biotic and abiotic parameters

The PCA indicates that soil dw- and OC-normalized contents of lignin-derived phenols were negatively related to $(Ac/Al)_V$ and $(Ac/Al)_S$ (Fig. 5). There was a positive relation of $(Ac/Al)_V$ and $(Ac/Al)_S$ with phenoloxidase activities, bacteria/fungi ratios, and $\delta^{13}C$. The PCA plot exhibited decreasing VSC contents (both based on soil dry weight and OC) and increasing $(Ac/Al)_V$ and $(Ac/Al)_S$ values with soil depth. Further, the different sites were clustered following the north-south gradient. The SEM reveals a complex impact of climatic and soil parameters on the stage of lignin decomposition (Fig. 6). Of the climatic variables, while aridity data were not involved in the SEM, MAT tended to have a positive impact on lignin decomposition. Phenoloxidase activity was significantly positively related to the stage of lignin degradation, and also the bacteria/fungi ratio exerted a positive impact on lignin decomposition (Fig. 6). In contrast, the C/N ratio and soil pH showed a negative effect on lignin decomposition in soils along the climosequence.

4. Discussion

4.1. Vegetation effects on organic layer lignin properties

Lignin content and chemical composition in the organic layer samples of the tundra, taiga, and forest steppe and the uppermost layer of the steppe reflected the wide variety of vegetation types along our 1,500 km latitudinal transect. The average lignin contents of the organic horizons along the climosequence ranged from 2.0 ± 0.4 to 14.7 ± 4.0 g VSC-C kg^{-1} OC corresponding to 3.1 ± 0.6 to 22.9 ± 6.3 g VSC kg^{-1} OC. This range mirrors well that of 2.3–59.4 g VSC kg^{-1} OC reported in a review of Thevenot et al. (2010). We observed the significantly lowest lignin contents in the organic layers of the tundra, both related to soil dry weight and OC (Fig. 2, 3).

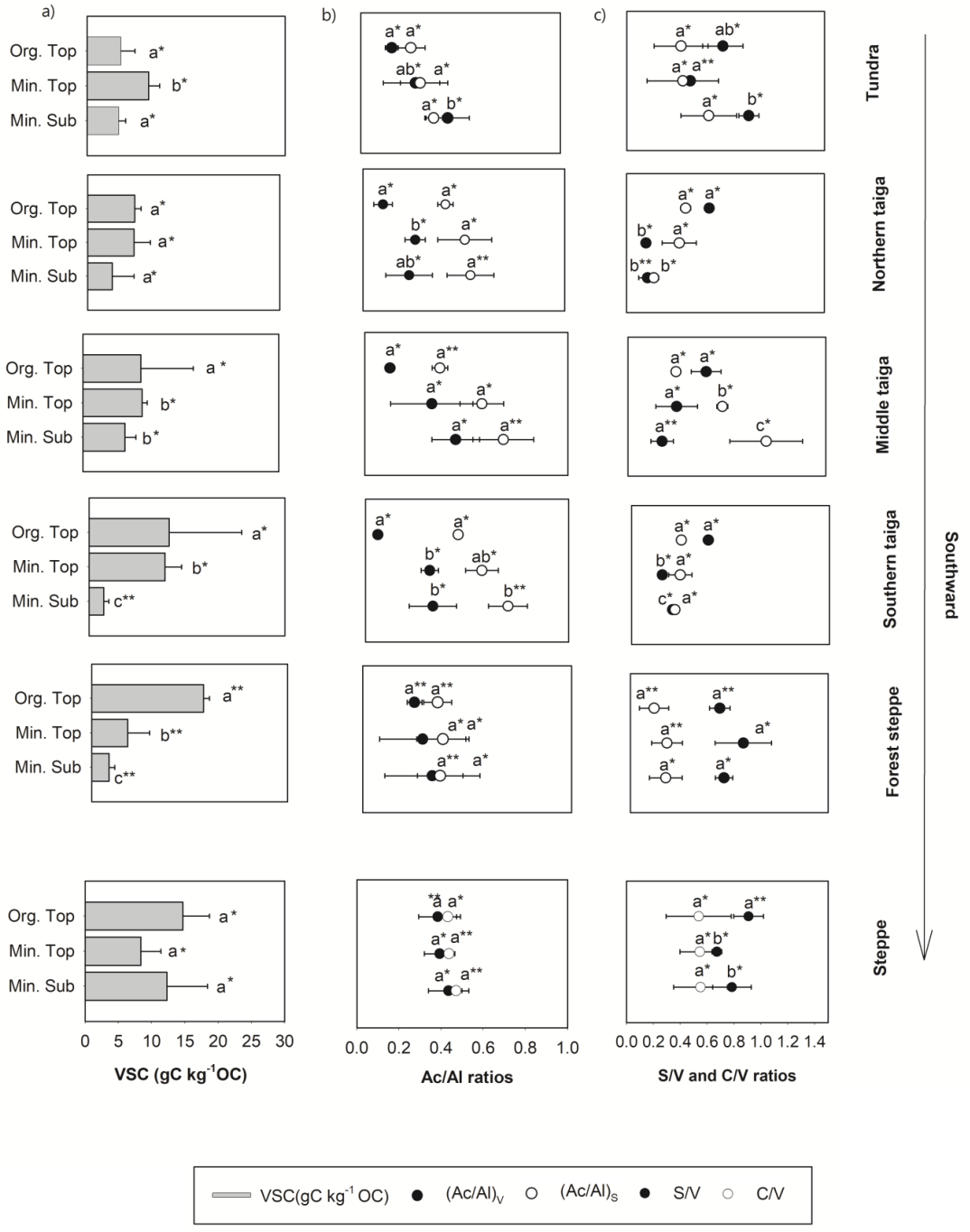

Fig. 3: Total lignin-derived phenol contents (VSC-C) normalized to organic carbon (OC) within soil profiles at all sampling sites (a) along with ratios of vanillic acid to vanillin [$(Ac/Al)_V$] and syringic acid to syringaldehyde [$(Ac/Al)_S$] (b), syringyl units to vanillyl units (S/V), and cinnamyl units to vanillyl units (C/V) (c). Error bars represent standard deviations with n=3. The letters indicate significant differences between horizons of each site, and the symbols * indicate significant differences between sites for each horizon with a significance level $p < 0.05$. Abbreviations are: Org. Top, organic topsoils; Min. Top, mineral topsoils; Min. Sub mineral subsoils.

Tundra vegetation is mainly composed of lichens, mosses, and shrubs (Table 1), with only minor production of aboveground litter (Fu et al. 2017). Low litter input rates along with a small

contribution of lignin-derived phenols in plant tissues (0.4–20.7 g VSC-C kg^{-1} OC; Dao et al., 2018) might have contributed to the low lignin contents of tundra organic layers.The general southward increase in OC-normalized lignin-derived phenols in the organic topsoil from tundra to forest steppe was likely driven by a growing proportion of vascular plants relative to moss litter, as observed along a latitudinal transect in boreal Canada (Kohl et al., 2018).

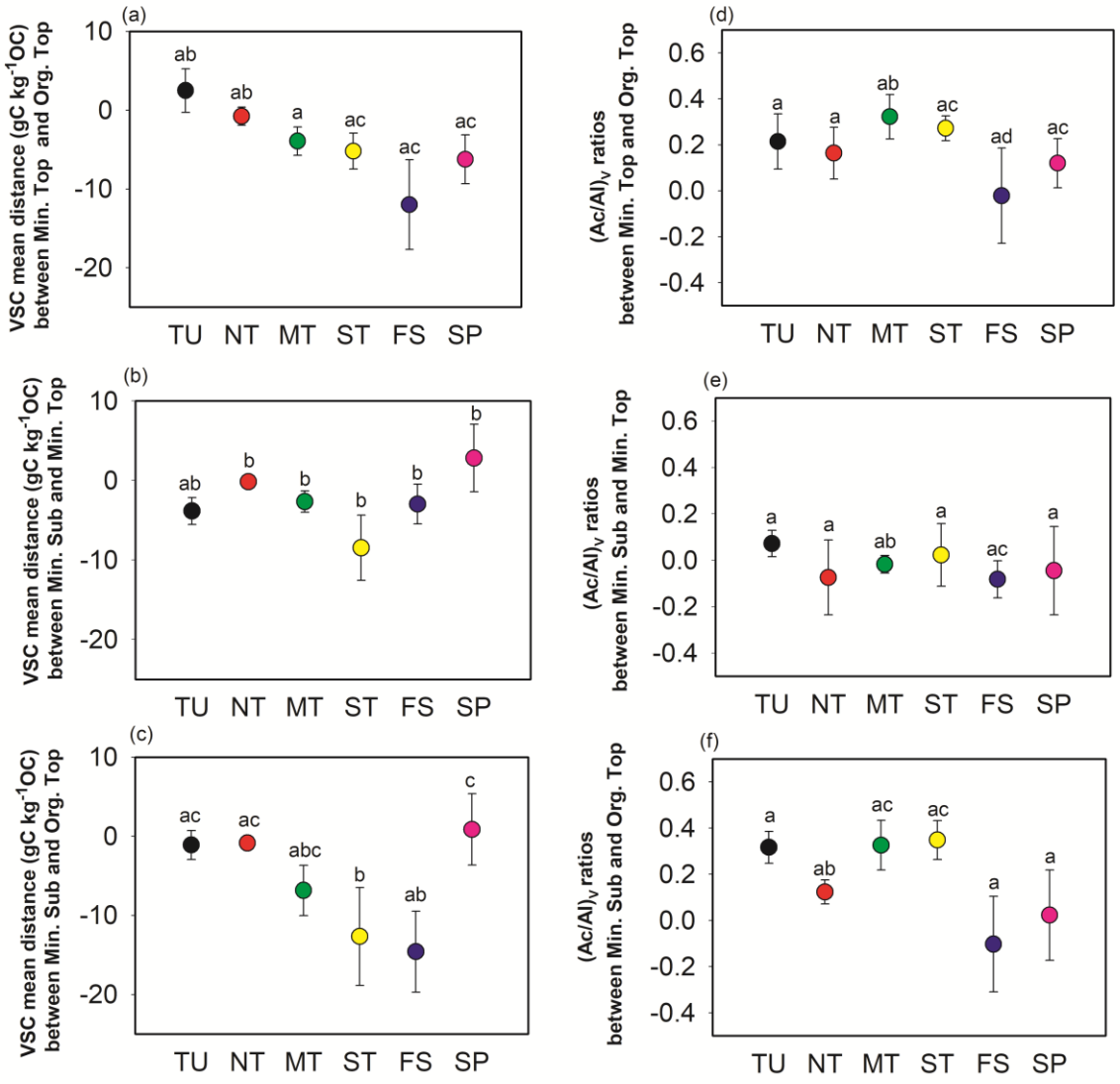

Fig. 4: Mean differences of OC-normalized lignin contents (a, b, c) and $(Ac/Al)_V$ ratios (d, e, f) between upper and lower horizons. Error bars are standard deviations with n=3. The letters indicate significant differences between sites. Abbreviations are: Org. Top, organic topsoils; Min. Top, mineral topsoils; Min. Sub mineral subsoils; TU, tundra; NT, northern taiga; MT, middle taiga; ST, southern taiga; FF, forest steppe-forest; FM, forest steppe-meadow; SP, steppe.

The effect of different vegetation on lignin is also reflected in the relative contribution of the V, S, and C units in the organic topsoil. The trend of increasing S/V ratios from the taiga to the forest steppe

likely reflects the higher proportion of lignin derived from angiosperms as related to gymnosperms (Hedges and Mann, 1979; Kögel-Knabner et al. 1988). Similarly, as lignin in grass litter is more enriched in C units (Iiyama et al. 1990; Lam et al. 2001), the C/V ratios in the uppermost layer of the steppe were higher than at the other sites. Hence, the lignin signature in the organic layer reflects the prevailing vegetation along the climosequence.

4.2. Lignin decomposition dynamics within the soil profiles

Decreasing OC-normalized lignin contents and increasing oxidative alteration of lignin indicate progressing lignin decomposition with soil depth. The change in lignin decomposition state between horizons increased along the transect from tundra to forest steppe and then decreased to steppe. This is indicated by the mean differences of lignin contents, and $(Ac/Al)_V$ and $(Ac/Al)_S$ ratios between deeper and shallower horizons. In the tundra soils, the OC-normalized VSC-C contents showed no clear trend with depth, while $(Ac/Al)_V$ and $(Ac/Al)_S$ increased. A previous comparison of three Siberian tundra sites indicated that lignin appeared to progressively decompose with soil depth in western Siberia, but was selectively preserved in central and eastern Siberia, where a shallow active layer and anaerobiosis restrained lignin decomposition (Dao et al. 2022). The increasing (Ac/Al) values with depth in the tundra of this study mirror the increasing oxidative decomposition of lignin in the subsoil, which is consistent with the study of Dao et al. (2022). Since tundra is characterized by vegetation with no (e.g. mosses, lichens) or shallow roots (Iversen et al. 2015), lignin input from fresh roots into mineral horizons is restrained.

The sites from the northern taiga to the forest steppe showed decreasing OC-normalized lignin contents together with increasing $(Ac/Al)_V$ and $(Ac/Al)_S$ ratios with soil depth, reflecting progressive lignin degradation. The varying mean differences of lignin contents between deeper and upper horizons were likely more pronounced in the southern taiga and forest steppe than in the northern sites, suggesting an increase in lignin decomposition from tundra to forest steppe. However, the difference in $(Ac/Al)_V$ and $(Ac/Al)_S$ between horizons was less pronounced in the southern taiga and forest steppe than in the northern sites which may be due to the difference in sorption ability by soil minerals (Kaiser et al. 2004; Hernes et al. 2007).

The higher OC-normalized lignin contents in the mineral topsoils compared to organic topsoils in the tundra may thus be due to interactions with the mineral matrix (e.g., by sorption or physical stabilization of particulate OM) which stabilize some parts of the lignin, which over time is then getting enriched in the A horizon. On the other hand, the higher contribution of lignin in mineral topsoil may be due to cryoturbation which causes a mixing of particulate OM (POM) from organic topsoil to mineral topsoil. Although the buried materials were not included in the study, the cryoturbative processes seemingly also affected non-buried topsoil horizons.

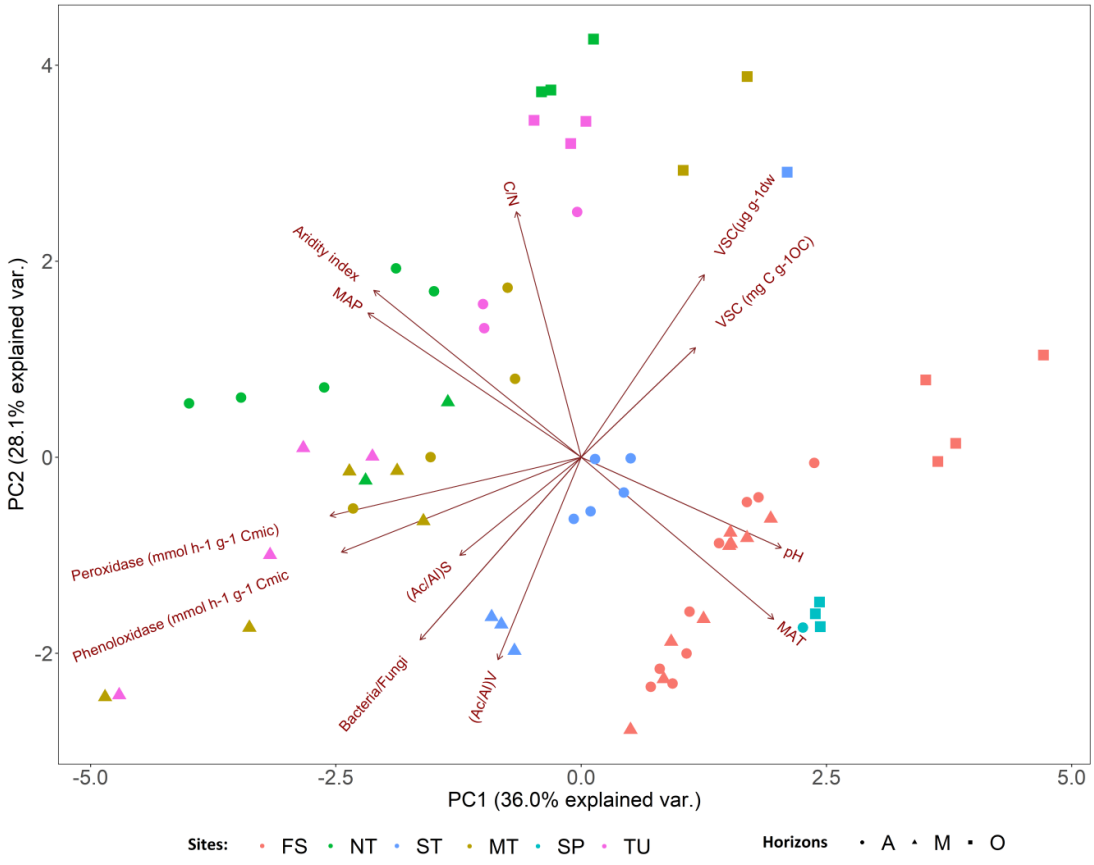

Fig. 5: Biplot of the first two PCA axes of lignin patterns (VSC, $(Ac/Al)_V$, $(Ac/Al)_S$), environmental factors (MAT, aridity index), biological factors (phenoloxidase activity, bacteria/fungi ratio) and soil and SOM factors (soil pH, C/N ratio) for all horizons of all sites. Abbreviations are O, organic topsoils; A, mineral topsoils; M, mineral subsoils; TU, tundra; NT, northern taiga; MT, middle taiga; ST, southern taiga; FS, forest steppe, SP, steppe.

This argument was supported by Gentsch et al. (2015) who indicated that the POM-C contents in tundra A horizons is about one-third of bulk OC. Lignin degradation was significantly related to MAT as shown in PCA and SEM (Figs. 5, 6), which indicates enhanced lignin degradation with increasing temperature. The kinetic theory implies that rates of SOM decomposition increase with temperature (Conant et al. 2011). The increasing temperature from tundra to forest steppe explained for increasing degree of lignin decomposition.

In addition to temperature, soil moisture is one of the most important abiotic variables in SOM decomposition (Oechel et al., 1998; Shaver et al., 2006; Oberbauer et al., 2007; Lawrence et al., 2015). Moisture controls oxygen availability for microorganisms, affecting microbial community composition and enzyme activity (Tulina et al. 2009). Phenoloxidases and peroxidases have been shown to play an important role in the oxidative depolymerization and transformation of a broad spectrum of aromatic compounds (Sinsabaugh, 2010). Using the same set of samples as this study, Schnecker et al. (2015) showed that phenoloxidase and peroxidase activity differed more strongly between soil horizons than between biomes. Similarly, we here found that also lignin contents and

$(Ac/Al)_V$ ratios were more different between horizons rather than sites. The increasing degree of lignin degradation with depth was significantly positively related to the activities of phenoloxidase enzymes and the bacteria/fungi ratio (Figs. 5 and 6). These findings indicate that lignin degradation was related to oxidative enzyme activity and microbial composition. The bacteria/fungi ratio increased with soil depth in the tundra and taiga but it declined in the forest steppe and steppe (Schnecker et al., 2015). In the high-latitude soils with high moisture levels, lignin degradation is probably induced rather by bacteria than fungi. For example, Tao et al. (2020) reported that in tundra soils β-*Proteobacteria* account for 95% of total abundance of potential lignin decomposers. In fact, actinobacteria and filamentous bacteria may partly take over the role of fungi and produce phenoloxidases and peroxidases (de Boer et al. 2005; DeAngelis et al. 2011; Bugg et al. 2011) to oxidize the dominant beta aryl ether linkage between phenylpropane units, and a variety of dioxygenases to remove methoxy groups and cleave rings (Masai et al., 2007). There is also some evidence indicating that bacterial decomposition of oligomeric lignin is a ubiquitous process in soils of various forest types in North America, with the potential to occur in deeper soil layers following early stages of litter decomposition (Wilhelm et al. 2019).

Compared to the northern biomes, southern taiga and forest steppe were drier, which favors a higher abundance of fungi and fungal lignin decomposition in these sites. In the steppe, no trend of VSC contents as well as $(Ac/Al)_V$ and $(Ac/Al)_S$ were observed with depth, likely indicating a restrained lignin decomposition in the subsoils, or reflecting the fact that our surface soil layer was quite mineral and that caused a weaker gradient in soil properties than at the other sites. Snowmelt and rain events in southern Siberian steppe soils usually moisten only the first 60-80 cm, hence, the subsoil often remains dry (Guggenberger, own observation). The steppe soils thus are characterized by low soil moisture, expressed by a low aridity index (0.44 and 0.53 respectively, Table 1), which is in the range of a semiarid climate (Middleton and Thomas, 1997). Low soil moisture reduces microbial activities in general (Gill and Burke, 2002; Liu et al. 2009; Klotzbücher et al. 2016) and also restricts the availability of substrates to microorganisms (Amelung et al. 1999; Moyano et al. 2013), finally leading to declined SOM degradation, including that of lignin. Further, slower lignin degradation in subsoil horizons of the steppe could additionally be favored by the slightly alkaline pH (8.0 ± 1.0, Table 2), which might impair the activity of lignin-degrading enzymes (reviewed by Thevenot et al. 2011). Hence, both soil moisture and pH might contribute to the lower lignin degradation at this site, which is supported by the negative correlations between lignin decomposition and aridity index and pH (Figs. 5 and 6). These findings are also consistent with the study of Kayler et al. (2018) who found a faster SOM turnover in the southern taiga than in the steppe soils.

The SEM indicated a decreasing state of lignin degradation with increasing C/N ratio of SOM (Fig. 6). In fact, the organic topsoil of tundra and northern taiga had higher C/N ratios but less pronounced lignin degradation than other sites, which contrasts the observation that lignin in forest soils with wide C/N ratios is more decomposed (reviewed by Thevenot et al. 2011). We speculate that

the colder and wetter conditions in the tundra and northern taiga which may prevail lignin degradation rather than effect of SOM quality, i.e., higher C/N ratios.

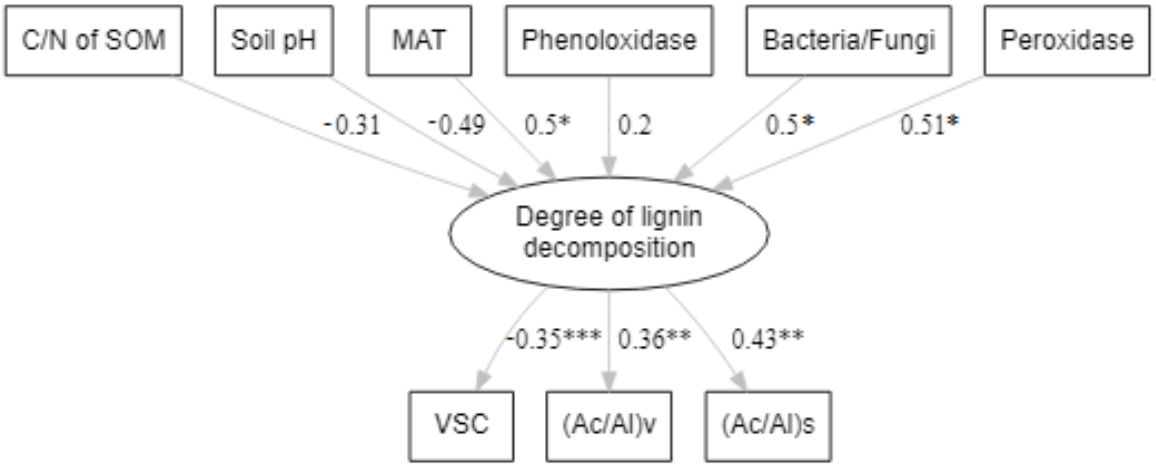

Fig. 6: Structural equation model showing the effects of mean annual temperature (MAT) and soil parameters (phenoloxidase activity, bacteria/fungi, C/N, pH) on the stage of lignin decomposition in soils along the climosequence, which is described by decreasing OC-normalized lignin derived phenols (VSC-C) and increasing $(Ac/Al)_V$ and $(Ac/Al)_S$ ratios of all studied sites. Numbers on arrows depict standardized path coefficients with their significance indicated as ***P < 0.001, **P < 0.01, and *P < 0.05.

4. Conclusions

Our study revealed that the pattern of decomposition and preservation of lignin along a climosequence in western Siberia depends on a complex interaction of direct and indirect effects of environmental parameters. In the organic topsoil, climate influenced lignin contents via vegetation type. In the mineral soil, the state of lignin degradation appeared to increase with warmer and drier climate from tundra to forest steppe and to decrease to the arid steppe biome. In high-latitude soils, bacteria are likely primary drivers in lignin degradation rather than fungi as high moisture levels are more favorable for bacteria. The mid-latitude soils, i.e. southern taiga and forest steppe, were characterized by drier soil conditions that favored the abundance of fungi leading to a higher degree of lignin degradation. These findings suggest that warmer and drier conditions with climate change could accelerate lignin decomposition at high latitudes. However, drought and high pH were responsible for low lignin decomposition in the steppe soils. An expansion of the steppe biome towards the southern taiga may thus lead to a retardation of lignin decomposition in these areas. Such changes may also have an impact on the overall long-term development of soil organic carbon stocks.

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5. Synthesis

5.1. *Lignin and carbohydrate contents in permafrost environments versus other ecosystems*

Arctic graminoids showed generally smaller CuO oxidation lignin contents than plants in peatlands (Bourdon et al., 2000), in grasslands (Otto and Simpson, 2006), in forest (Prietzel et al., 2013) and in mangrove soils (Opsahl and Benner, 1995). The lignin-derived phenol contents of dwarf shrubs were also smaller than those of pine needles (Otto and Simpson, 2006; Kuo et al., 2008; Opsahl and Benner, 1995), while the observed lignin phenol contents of lichen and mosses were higher than those reported in the study of Zavarzina et al. (2015). The smaller OC-normalized lignin contents in organic topsoil were observed than that of peatlands (Bourdon et al., 2000) and grasslands (Otto and Simpson, 2006), and forest soils (Rumpel et al., 2002, Spievogel et al., 2007), while being higher than reported by Feng and Simpson (2007) for a temperate grassland. In the studied permafrost soils, the OC-normalized contents of lignin-derived phenols declined in the organic topsoil relative to the parent plants, mirroring the degradation of lignin in the organic surface layer of tundra soils. The OC-based lignin-derived phenol contents in bulk soil showed no clear trend with soil depth, being consistent with peat soils (Williams et al., 1998), whereas in many studies of grasslands and forests the contents decreased from the topsoil to deeper horizons (Feng and Simpson, 2007; Rumpel et al. 2002; Wiesmeier et al., 2009). As a consequence, OC-normalized lignin contents in permafrost subsoils were larger than those in subsoils of the temperate zones (Feng and Simpson, 2007; Rumpel et al., 2002) by factors of 2 to 7, while they were smaller than in subsoil horizons of peat (Bourdon et al., 2000). Hence, lignin decomposition in the bulk mineral subsoils of permafrost-affected soils appears to be restrained.

Arctic graminoids and dwarf shrubs showed lower TFA-hydrolyzable sugar contents than those of alpine (Prietzel et al., 2013) and of mangrove soils (Opsahl and Benner, 1999). In contrast, the sugar contents of mosses and lichens were higher than those growing in peatbog (Comont et al., 2006). The OC-normalized content of neutral sugars in the organic topsoils of the studied permafrost soils was generally larger than that of alpine soils (Prietzel et al., 2013), and of temperate forest soils (Spielvogel et al., 2007), but smaller than the upper section of a peat core (Comont et al., 2006). The observed decrease of neutral sugar contents with soil depth in the study soils was in line with the observation of a peat core (Comont et al., 2006) and temperate soils (Navarrete and Tsutsuki, 2008; Spielvogel et al., 2007). Hence, in contrast to the decomposition of lignin, the transformation of carbohydrates in bulk soils appears to be similar in permafrost compared to temperate soils.

5.2. Low temperature and anaerobisis primarily causes the stabilization of lignin and carbohydrates in permafrost soils.

The stage of lignin degradation is characterized by a decrease in the lignin content normalized to OC and increase in the oxidative alteration of the remnant lignin $(Ac/Al)_V$ and $(Ac/Al)_S$ within soil

horizons (Hedges and Ertel, 1982; Kögel, 1986). Similarly, the increasing stage of carbohydrates degradation is reflected by increasing proportion of microbial sugars over plant-derived ones (GM/AX) (Cheshire, 1979; Murayama, 1984). In the eastern (Cherskiy) and central (Logata) Siberian permafrost locations under study, OC-normalized lignin and plant-derived sugars contents were relatively constant with soil depth in both light and heavy soil fractions (LF and HF). At the same time, the ratios of $(Ac/Al)_V$ and $(Ac/Al)_S$ were constant or even decreased in all mineral soil horizons, indicating a selective preservation of these biomarkers. In contrast, the western site Tazovskiy exhibited decreasing contents of lignin-derived phenols and plant-neutral sugars from topsoil to deeper horizons, including the buried topsoil. These results suggest that lignin and carbohydrates become progressively altered with soil depth (Otto and Simpson, 2005; Rumpel et al., 2002), which for lignin is also reflected by increasing $(Ac/Al)_V$ ratios and for sugars by generally higher GM/AX ratios. However, GM/AX ratios decreased with soil depth especially in HF for all studied permafrost sites, reflecting a recycling of microbial necromass (i.e., dead biomass residues). This trend was in contrast to Spielvogel et al. (2008) who reported an increasing proportion of neutral sugars in the HF of acidic forest soils with depth. Under frozen conditions microorganisms in permafrost soils are confined to thin water films (Rivkina et al., 2000), and by that possibly separated from organic substrates. As a consequence, microorganisms might favor an effective recycling of microbial necromass (i.e., dead biomass residues) that is spatially closer than plant OC sources. This behavior could be responsible for the decreasing total sugar contents of the HF, and particularly of mannose and galactose, supposedly of microbial origin.

The enhanced lignin and carbohydrate degradation at the western Tazovskiy site may be caused by higher MAT and probably more available oxygen as a result of the deeper active layer than at Cherskiy and Logata. Temperature has been frequently shown to affect turnover rates of SOM (Davison and Janssens, 2006; Connant et al., 2011). The effect of temperature on SOM decomposition increases with environmental temperature (Arrhenius, 1889). Each SOM pool consists of a continuum of soil carbon substrates of varying chemical complexity and such an approach may also conceal the kinetic characteristics of individual SOM structures (Davidson and Janssens, 2006). Macromolecular lipids and aromatic structures are usually considered to be recalcitrant because they are much more resistant to microbial attack in comparison to easily degradable compounds such as proteins and carbohydrates (Gleixner et al., 2001; Melillo et al., 2002). Generally, lignin is considered to be more resistant to biodegradation due to their aromaticity (Melillo et al., 1982; Gleixner et al., 2001), it would strongly affected by temperature change. Similarly, chemically bound or mineral-associated SOM is more stable than SOM in a “free” form (Baldock and Skjemstad, 2000). Furthermore, future temperature increases associated with climate change are predicted to be greatest in high latitudes, where are characterized by cold temperature and high OC contents (Chapman and Walsh, 1993; Lloyd and Taylor, 1994). A number of studies have suggested rising mean annual air temperatures particularly led to higher temperature of permafrost soils during spring and summer (Frauenfeld et al.,

2004; Chudinova et al., 2006; Qian et al., 2011). According to the Worldclim database (Hijmans et al. 2005), mean maximum air temperature was higher at TZ than at LG and CH (17.2 °C; 14.4 °C and 14.0 °C; respectively). This difference presumably leads to a warmer soil temperature at TZ than other sites during spring and summer. Snow cover additionally influences permafrost soil temperature because snow can act as an insulator or thermal blanket, inhibiting the penetration of cold into the soil (Reiger, 1983). The thicker and prolonged snow cover, thus, likely increases winter soil temperature (Chudinova et al., 2001) and delays the active layer freeze-up date (Zhang, 2005). Long-term snow depth measurements for different regions in Northern Eurasia indicated that western Siberia was characterized by thicker and prolonged snow cover than eastern Siberia (0.082 vs. 0.047 cm/year; 0.211 vs. 0.143 day/year; respectively) (Lemke and Jacobi, 2012). Greater snow cover, hence, may characterize TZ rather than CH, possibly resulting in higher winter soil temperature and delay of freeze-up within the season at TZ. Assuming a small variability in soil temperature between Tazovskiy and Cherskie and Logata may lead to more advanced lignin and carbohydrate decomposition in the former.

The stabilization of lignin at Cherskiy and Logata might also be attributed to the largely anaerobic conditions in the permafrost soils. As a complete degradation of lignin is based on the action of oxidative enzymes such as peroxidases and laccases, oxygen is required (Kirk and Farrell, 1987), which is lacking in most parts of the waterlogged permafrost soil profiles. Although previous authors revealed that Actinobacteria and other lignolytic bacteria can grow in oxygen-depleted environments (Geib at al., 2008) and in frozen soils (McMahon et al., 2011), they employ oxygen-requiring peroxidases to degrade lignin (Bugg et al., 2011) and thus require at least temporarily oxic conditions. Hence, lignin is less prone to microbial degradation compared to other SOM compounds under these environmental conditions, leading to the retarded lignin decomposition under such water-logging permafrost soils. Although Gittel et al. (2013) showed for the Cherskiy soils that Actinobacteria abundance increases with soil depth, actinobacterial lignin degradation activity is apparently lower than fungal activity, due to smaller biomass, lower cell-specific enzyme activities, and absence of hyphae structures (Gittel et al., 2014). In consequence, lignin has been enriched in the subsoils. The deepening of active layer can improve water flow to the deeper layers, leading to reduction in water content in the whole volume of active layer, which may enhance the oxygen diffusion. According to Keiluweit et al. (2017), the less efficient anaerobic metabolism selectively preserves otherwise bioavailable reduced organic compounds from decomposition. A shift from anaerobic to aerobic conditions of bulk soils in contrast can increase mineralization rates 10-fold (Keiluweit et al., 2017). These patterns improve aerobically microbial activity, and stimulate the aerobic decomposition of SOM, which is responsible for the higher degree of lignin and carbohydrate decomposition in the site of deeper active layer Tazovskiy compared to Logata and Cherskiy.

Sugars are usually an easily available carbon source. However, in plant cell walls, neutral sugars are chemically bound to lignin moieties in terms of lignocellulose (Seelenfreund et al., 1990),

with ongoing decomposition causing the parallel alteration of both structural components. At Cherskiy and Logata, such impregnation of saccharides by lignin may protect them from rapid microbial utilization (Moran and Hodson, 1989), while the accelerated lignin decomposition at Tazovskiy unlocks and exposes the plant-derived sugars to microbial decomposition. The study indicates a larger degree of lignin and carbohydrate transformation with increasing active layer thickness, suggesting active layer thickness and the zone of aeration as important control in the turnover of OM in permafrost soils.

5.3. Further crucial factors in soil OM stabilization are likely the microbial community structure and the formation of mineral-organic associations in permafrost soils.

The microbial community structure and the accessibility of soil OM to the decomposer community are thought to be crucial factors in the process of OM accumulation and storage in soils (Schmidt et al., 2011; Dungait et al., 2012). The positive relationship between bacteria/fungi ratio as estimated by the pattern of phospholipid fatty acids (PLFA) and the stage of lignin in high latitude soils, including tundra, taiga and forest suggests a preferred role of bacteria over fungi in lignin degradation. It was indicated that arctic terrestrial environments are generally nitrogen limited (Shaver and Chapin, 1980; Martineau et al., 2010) and show low fungal abundances (Waldrop et al., 2000; Zak and Kling, 2006; Yergeau et al., 2010). On the basis of qPCR quantification of the unamplified DNA, Yergeau et al. (2010) found well adapted bacteria to the conditions occurring in permafrost habitats, such as Actinobacteria, Betaproteobacteria. Gittel et al. (2014) showed for the Cherskiy soils that Actinobacteria abundance increases with soil depth. Actinobacteria and filamentous bacteria are also able to produce phenoloxidases and peroxidases (de Boer et al., 2005; DeAngelis et al., 2011; Bugg et al., 2011). On the other hand, dehydrogenases and dioxygenases which are produced by bacteria can cleave the dominant β-aryl ether linkage between phenylpropane units and remove methoxy groups (Masai et al., 2007). These findings evidence the preferential lignin decomposition by bacteria in high latitude soils of Siberia, which was consistent with a process in deeper soil horizons of forest in North America (Wilhelm et al., 2019). The role of fungi is diminished in the high latitude soils because of frequent anaerobic soil conditions (Silver et al., 1999). However, fungal communities within cryoturbated OM were more susceptible to environmental change and some taxa may shift their role, which may lead to accelerate the fungal decomposition OM in permafrost-affected soils after warming (Varsadiya et al., 2021).

Density fractionation has been frequently used to separate plant residues in the mineral soils into the LF, whereas microbially transformed organic matter is enriched in the HF (Golchin et al., 1994; Grünewald et al., 2006). In permafrost soils, the $(Ac/Al)_{V,S}$ as well as the GM/AX ratios were higher in the HF than in the LF, showing a less decomposed lignin and sugar in coarse size fractions, containing primarily particular OM, than in OM associated with clay- and silt-sized particles

(Guggenberger et al., 1995; Kiem and Kögel-Knabner, 2003), which is similar to observations in non-permafrost soils (Guggenberger et al., 1994; Spievogel et al., 2007, Kiem and Kögel-Knabner, 2003). Because of having a strong affinity towards charged soil minerals (Guggenberger and Zech, 1994; Kaiser et al., 2004), the water-soluble acidic lignin and microbially-derived sugars components selectively accumulated in the HF (Grünewald et al., 2006; Hernes et al., 2007). It is thus concluded that mineralogy plays an important role in the OM stabilization of permafrost soils.

At the western site Tazovskiy, lignin appears to be well decomposed with increasing soil depth in the HF fraction. The HF contained lower amounts of OC-normalized lignin-derived phenols and neutral sugars of assumed plant origin at Tazowskiy than at Logata and Cherskiy. Concurrently, the degree of oxidative decomposition of the remnant lignin and the relative proportion of microbial sugars were higher at Tazovskiy than at Logata and Cherskiy. At first glance, this observation can be explained with its more favorable soil environment in the Tazovskiy. The drier soil conditions along with the higher mean annual temperature might have contributed to more advanced decomposition of plant residues and formation of microbial metabolites (Davidson and Janssens, 2006). However, also the texture and mineralogical composition differed between the sites, which might have an impact not only on OC storage (see Gentsch et al., 2015a) but also on OM composition. The effect of mineralogical properties was revealed by a positive correlation between soil soil dry weight-normalized lignin and neutral sugar contents with pedogenic minerals, i.e. clay, Fe_d, Fe_o, and Al_o contents, across all sites. Hence, differences in the mineralogical composition, with highest contents in pedogenic Fe oxides in Cherskiy, might determine the sorption capacity and thus the accumulation of lignin and neutral sugars in the HF, decreasing in the order Cherskiy > Logata > Tazovskiy. These minerals are known to form strong and preferential complexes of carboxyl- and aromatic-C forms with Al and Fe oxides via ligand exchange, divalent cation bridging (Kaiser & Guggenberger, 2003; Kleber et al., 2015) and physical sorption of OM on mineral surface via van der Waals interactions, electrostatic or hydrophobic bonding (Feng et al., 2005; Mikutta et al., 2007). Alternatively, higher abundance of chlorites at TZ and LG than CH might result in a depleted surface area, and consequently reduce the sorption capacity with SOM in the former (De Kimpe et al., 1979). Recently, Patzner et al. (2020) suggested that permafrost thaw may foster the release Fe and associated carbon due to the activity of Fe(III)-reducing bacteria. Such a process, principally depending on anaerobic conditions, could also partly explain the relatively low Fe_o contents and the more advanced lignin and carbohydrate decomposition at the Tazovskiy site with its larger active layer thickness.

5.4. Implications for the fate of lignin and carbohydrates under the impact of climatic change

Anaerobisis, low temperature, and mineral protection strongly impact the OM degradation in the high arctic soils. The climate warming is prone to increase permafrost degradation, and thus increase active

layer thickness, which strongly influences soil hydrology as the permafrost horizons largely prevent water movement (Panikov, 2009). The increasing drainage improves the transport of nutrients, oxygen as well as microbial biomass to deeper soil layers. Under anaerobic conditions, some bacteria were found to be able to produce lignin-degrading enzymes. The decreasing soil moisture and subsequently increasing oxygen availability of wet soils can promote the activities of these enzymes, which can increase degree of lignin decomposition. Moreover, increasing oxygen and nutrients through soil depth can increase abundance and activity of fungal communities (Carney et al., 2007; Drissner et al., 2007), which can further promote lignin degradation (Classen et al., 2015a, b). At the same time, lateral groundwater flow as result of increasing permafrost degradation is observed to significantly increase ground temperatures, and can accelerate microbial activity, especially that of fungi which are more sensitive to temperature than bacteria (Dutta et al. 2016). Alternatively, the permafrost melting can activate the dormant microbial community (Weiman 2015), leading to stimulate soil OM decomposition. Lignin, thus, will be decomposed more strongly, if they are exposed to warmer conditions. Because sugars are chemically bound to lignin moieties, i.e. lignocelluloses (Seelenfreund et al., 1990), ongoing lignin decomposition causes the parallel alteration of carbohydrates. For instance, Svoboda (2015a) found a production of proteins and enzymes from bacteria that break down large molecules like plant cellulose into simpler sugars during thawing process that in turns can serve as source of energy for growing of the microorganisms.

However, permafrost thaw can also increase soil moisture in lowland regions or as a result of localized ground slumping that results from melting ground ice. Even in upland areas that may experience large-scale soil drying, localized ground subsidence can result in collapsed areas that are saturated, interspersed with adjacent unsubsided and drier areas (Jorgenson et al., 2001, O'Donnell et al., 2012, Vogel et al., 2009). With continued thawing, thus, the wetland with complete water saturation can expand in some areas, where can get more reducing conditions. It has been shown that reactive soil minerals, specifically iron(III) (oxyhydr)oxides, can trap organic carbon in soils overlying intact permafrost, and may limit carbon mobilization and degradation as it is observed in other permafrost environments (Patzner et al., 2020). During permafrost thaw, water-logging and O_2 limitation lead to reducing conditions and an increase in abundance of Fe(III)-reducing bacteria which favor mineral dissolution and drive mobilization of both iron and carbon along the thaw gradient by using the reactive Fe as terminal electron acceptor (Patzner et al., 2020). When mineral dissolution occurs, OM protected by minerals becomes more available for decomposition, leading to increasing microbial decomposition of OM. For instance, mineral soil slurry incubations previously showed that iron(III) mineral reduction and dissolution under oxygen limitation led to anaerobic mineralization of dissolved OM and soil OM by 74% and 32–41%, respectively (Chen et al. 2020). Such a process, principally depending on anaerobic conditions, could also partly explain the relatively low Fe_o contents and the more advanced lignin and carbohydrate decomposition when permafrost thaws.

Furthermore, global warming may change SOM decomposition patterns by altering the soil microbial community structure and activity through increased carbon inputs (Pendall et al., 2004). Global warming is predicted to increase vegetation productivity, litterfall, and root exudates in the northern biomes (Cramer et al., 2001), and shift vegetation communities which can further act as a feedback for decomposition of OM (Hobbie et al., 2001; Cornelissen et al., 2007). For example, warming is leading to rapid replacement of Canadian tundra by boreal forest (Danby and Hik, 2007) and pan-arctic shrub encroachment in arctic tundra (Epstein et al., 2004), or increases in the dominance of evergreen shrubs in the arctic (Cornelissen et al., 2007). A previous study indicated that increased root exudates and litter production accumulate more new soil carbon (e.g., sugar and lipids) but decompose more old carbon (e.g., lignin) (Jia et al., 2019). The northern biomes such as tundra and taiga are characterized by low N availability, with higher C/N ratio (Post et al., 1985; Xu et al., 2013; Wild et al., 2015), inducing the limitation of OM decomposition. The increased availability of substrate and nutrients can alter C and N availability, and subsequently alter microbial community and activity. More specifically, the elevated fresh C inputs likely promoted soil fungal community that may enhance lignin oxidation (Feng et al., 2008). Wild et al. (2014) predicted that C losses from arctic permafrost soils with global change differ at soil horizons. Microbial OM decomposition in mineral subsoils might be vulnerable to an increase in the availability of additional energy sources, such as to increased allocation of plant-derived compounds to the deeper soil with global warming. The decomposition of cryoturbated organic matter, in contrast, might be affected by changes in N availability, for example as a consequence of generally higher decomposition rates with global warming (Hobbie, 1996; Nadelhoffer et al., 1991; Schaeffer et al., 2014; Schimel et al., 2004).

My study suggests that the stabilization of lignin and polysaccharides associated with lignin (lignocelluloses) is context-dependent, and climate-induced degradation of permafrost soils, i.e. increasing temperature, active layer thickness, and vegetation shifts will promote microbial degradation of lignin and associated polysaccharides, further increase C losses into the atmosphere. However, the magnitude of future OM losses from permafrost soils will strongly depend on texture and mineralogical properties, either assisting or hampering the turnover of OM. These findings confirm our initial assumption that, in addition to climatic constraints, soil mineralogy is a decisive factor variegating the transformation of organic matter also in permafrost.

6. Conclusions

My thesis addresses the contents and decomposition state of two major soil OM components, lignin and carbohydrates, at individual horizons of density fractions of arctic permafrost soils. Further it investigates the fate of lignin in soils along a latitudinal gradient, reaching from tundra, through taiga and forest steppe to steppe. By following a space-for-time approach and studying whole soil profiles, this thesis aimed at identifying the decomposition and stabilization processes of lignin and sugars depending on environmental conditions, primarily driven by the permafrost patterns.

The permafrost soils in the west of northern Siberia (Tazovskiy) show an elevated decomposition of lignin and carbohydrates in both density fractions compared to Cherskiy and Logata. The reason is firstly ascribed for warmer soil temperature in Tazovskiy which was resulting from higher mean annual air temperature and probably thicker snow cover. Secondly, it is induced by soil hydrology with two different soil hydrological scenarios: dry and oxic or wet and reducing conditions which were caused by the deepening of the active layer thickness. An increasing active layer thickness can improve water moving and subsequently oxygen availability, which further can stimulate activity of lignolytic decomposers and consequently accelerate lignin decomposition. During permafrost thaw, water-logging and O_2 limitation lead to reducing conditions and an increase in abundance of Fe(III)-reducing bacteria which favor mineral dissolution and drive mobilization of both iron and carbon along the thaw gradient by using the reactive Fe as terminal electron acceptor (Patzner et al., 2020). When mineral dissolution occurs, OM protected by minerals becomes more available for decomposition, leading to increasing microbial decomposition of OM. Both two scenarios are supported the relatively low Fe contents and the more advanced lignin and carbohydrate decomposition in the Tazovskiy than in the Logata and Cherskiy.

The decomposition mechanisms of lignin were verified by studying six biomes along the latitudinal gradient, from tundra to steppe. The stage of lignin degradation appeared to increase with warmer and drier climate from tundra to forest steppe and to decrease to the arid steppe biome. The trend of lignin decomposition with depth was consistent with the activity of phenoloxidase and peroxidase, and microbial composition (Schnecker et al., 2015). In high latitude soils, bacteria are likely primary drivers in the lignin degradation rather than fungi as high soil hydrology is favorable for bacteria rather than for fungi. The middle latitude soils, i.e. southern taiga and forest steppe, were characterized by drier soil conditions that favored more abundance of fungi leading to higher degree of lignin degradation. However, drought and high pH in the steppe soils caused the decreased lignin decomposition. An expanding steppe area under climate change may thus likely lead to a retardation of lignin decomposition in the parts of the latitudinal gradient.

Permafrost thawing is likely the most important natural process that may translocate carbon (C) from terrestrial ecosystems to the atmosphere as response to global warming, thus initiating a positive feedback to climate change. Depending on ice richness and soil drainage, permafrost degradation can result in wetter or drier conditions. The thesis implied that either warm wetter or

warm drier condition upon permafrost degradation accelerates soil OM decomposition. The warm drier probably appears in the upland when thawing can improve soil drainage, oxygen and nutrients. This will cause a shift of the microbial community towards higher proportion of fungi and foster the activity of lignin-degrading enzymes and thus stimulate lignincelluloses decomposition, especially for particulate OM. The warm wetter probably appears in lowland regions or as a result of localized ground slumping that results from melting ground ice (Lawrence et al. 2015). The reducing conditions may accelerate Fe(III)-reducing bacteria activity and subsequently release OM which was bound by Fe to microbial metabolism (Patzner et al., 2020).

My thesis implies that the warming climate will accelerate lignin and carbohydrate decomposition in high latitude soils. However, the texture and mineralogical composition have an impact on OM decomposition in permafrost soils. Here, generally more knowledge is required about mineralogical soil properties of high-latitude ecosystems, including the transformation of mineral phases under changing environmental conditions.

References Synthesis & Conclusions

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CV

Thi Thao Dao **Email: thao@ifbk.uni-hannover.de**

Personal details

Date of birth	25.09.1981
Nationality	Vietnam

Education

09/2011-	PhD student at the Institute of Soil Science Leibniz University Hannover Supervisor: Prof. Dr. Georg Guggenberger
2004 – 2006	Master studies in Organic Chemistry Graduation: Master of Science Hanoi University of Science, Vietnam
1998 – 2003	Bachelor studies in Chemistry Graduation: Bachelor of Science Hanoi University of Science, Vietnam
1995 – 1998	High school Vinh Bao, Hai Phong, Vietnam

Work experience

2003-2003	Research assistant at the Centre of Environment and Sustainable Development Hanoi University of Science. Project: “Residues and movements of some conventional pesticides on rice and vegetable crops in Northern Vietnam”
2004 – 2006	Tutor at the Faculty of natural science at Haiphong University Tutorial of environmental chemistry and analytical chemistry
2006 – 2011	Lecturer at the Faculty of natural science at the Electric Power University Lecture of general Chemistry and environmental chemistry

Publications

Dao, T., Mikutta, R., Sauheitl, Leopold, S., Gentsch, N, Shibistova, O., Wild, B., Schnecker, J., Barta, J., Capek, P., Gittel, A., Lashchinskiy, N., Urich, T., Santruckova, H., Richter, A., Guggenberger, G., 2022. Lignin preservation and microbial carbohydrate metabolism in permafrost soils. Journal of Geophysical Research: Biogeosciences. 127. 10.1029/2020JG006181.

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