Carbon Storage in Peatlands within an Ever-changing Environment

Soil Organic Matter Dynamics in the Context of Active Volcanism

Susanne Claudia Möckel

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Dissertation submitted in partial fulfillment of a
Philosophiae Doctor degree in Geography

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Abstract

In the wake of increasing awareness of global warming, peatland conservation and restoration receive impetus by efforts to sequester carbon. Peatlands comprise a significant component of the global carbon cycle as they store up to 30% of global soil carbon. Carbon accumulation in Histosols, the most common organic soils of peatlands, is usually directed by hydrology and vegetation characteristics and the chemical composition of organic carbon. Mineral soil constituents, an important contributor for carbon accumulation and stability in mineral soils, are usually not considered important in Histosols. However, there is a growing body of evidence regarding the importance of mineral material in the volcanic ejecta for the carbon dynamics of peatlands in volcanic regions. Windborne volcanic ejecta certainly affect Histosols in Iceland. The island is one of the most active volcanic places in the world, and amongst the most dynamic of aeolian environments due to strong winds and a globally unmatched extent of volcaniclastic deserts. The aim of this PhD thesis was to investigate carbon dynamics in Icelandic Histosols under the varying impact of windborne mineral material. The research provides evidence for the co-importance of vegetation and carbon characteristics, and mineral soil constituents, for carbon dynamics in Icelandic peatlands. Particularly interesting is the positive relationship between minerals like allophane and ferrihydrite and certain carbon groups as well as shifts in carbon structure and stability around thick tephra deposits. This should be taken into consideration in projections of the effects of pressure such as by climate change and drainage on carbon cycling within peatland ecosystems.

Útdráttur

Á undanförnum árum hefur vitund almennings um loftslagshlýnun aukist. Í tengslum við það hefur verndun og endurheimt mýra til þess að auka bindingu kolefnis notið vaxandi meðbyrs. Mýrar, eða nánar tiltekið mómýrar, geyma allt að 30% kolefnis jarðvegs á heimsvísu og eru því mikilvægur hlekkur í kolefnishringrás. Helstu áhrifaþættir kolefnisuppsöfnunar í mójörð (lífrænn jarðvegur mómýra) eru að jafnaði vatnsbúskapur, gróðurfarseinkenni og efnasamsetning kolefnis. Steinefni sem eru mikilvægir þættir uppsöfnunar og stöðugleika kolefnis í steinefnajarðvegi, eru venjulega ekki talin móta bindingu kolefnis í mójörð. Nýlegar rannsóknir benda þó til þess að steinefni í formi gjósku og annarra gosefna hafi áhrif á ferli kolefnis í mómýrum á eldvirkum svæðum. Vindborin gosefni hafa því áhrif á mójörð á Íslandi enda er eldvirkni þar með því mesta sem gerist í heiminum. Auk þess eru á landinu óvenju mikil foksvæði þar sem saman fer samspil sterkra vinda og óvenju mikilla auðna sem gjarnan eru þakin fokefnum af eldfjallauppruna. Markmið þessa doktorsverkefnis var að rannsaka ferli kolefnis í íslenskri mójörð undir mismiklum áhrifum vindborinna steinefna. Niðurstöður rannsóknarinnar benda sterklega til þess að samspil af gróðurfarseinkennum, efnasamsetningu kolefnis og steinefnum í jarðvegi móti ferli kolefnis í íslenskum mómýrum. Jákvæð fylgni milli steinefna á borð við allófan og ferrihýdrít og ákveðinna hópa kolefnis er sérstaklega athyglisverð. Einnig eiga sér stað áberandi breytingar á efnasamsetningu og stöðugleika kolefnis samhliða því að þykk gjóskulög leggjast yfir mómýrar. Mikilvægt er að taka tillit til áhrifa steinefna á ferli kolefnis í mómýrum á eldvirkum svæðum þegar spáð er fyrir um afleiðingar umhverfisbreytinga á borð við loftslagsbreytingar og framræslu á hringrás kolefnis í þessum vistkerfum.

List of Papers

Paper I

Möckel, S. C., Erlendsson, E., Prater, I., & Gísladóttir, G. (2021). Tephra deposits and carbon dynamics in peatlands of a volcanic region: Lessons from the Hekla 4 eruption. *Land Degradation & Development*, *32*(2), 654-669. https://doi.org/https://doi.org/10.1002/ldr.3733

Paper II

Möckel, S. C., Erlendsson, E., & Gísladóttir, G. (2021). Andic Soil Properties and Tephra Layers Hamper C Turnover in Icelandic Peatlands. *Journal of Geophysical Research: Biogeosciences*, *126*(12), e2021JG006433. https://doi.org/https://doi.org/10.1029/2021JG006433

Paper III

Möckel, S. C., Erlendsson, E., & Gísladóttir, G. Beyond the obvious – the impact of mineral aeolian deposits on carbon characteristics over the last millennium in Icelandic Histosols. Manuscript submitted to the Journal of *International Soil and Water Conservation Research (ISWCR).*

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Abbreviations

%Ash	Soil inorganic content
%C	Total carbon
%N	Total nitrogen
Al	Aluminium
Al_o, Fe_o, Si_o	Ammonium oxalate extractable Al, Fe and Si
Al_p, Fe_p	Sodium pyrophosphate extractable Al and Fe
C	Carbon
DBD	Dry bulk density
EUNIS	European Nature Information System
Fe	Iron
Fe(II)	Ferrous iron
Fe(III)	Ferric iron
LULUCF	Land use, land-use change and forestry
NMDS	Non-metric multidimensional scaling
NMR	Nuclear magnetic resonance
OM	Organic matter
PCA	Principal component analysis
pH_{H2O}	Soil pH determined in deionised water
pH_{NaF}	Soil pH determined in 1N NaF solution
P-retention	Phosphate retention
RDA	Redundancy analysis
Si	Silicon
WRB	World Reference Base for Soil Resources

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As the journey of this PhD is coming to an end, I would like to spend some words on people, which contributed to this work and which deserve recognition. Above all, this research would not have been possible without my great PhD committee, Guðrún Gísladóttir, Egill Erlensson and Rattan Lal.

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1 Introduction

1.1 The Term *Peatland*

In order to avoid confusion or misunderstandings, it is necessary to define how the term *peatland* will be applied in this thesis. There is not a universally accepted definition of peatlands and their material *peat* (e.g. Xu et al., 2018). Generally accepted is the rather loose definition of peatlands being "an area with or without vegetation with a naturally accumulated peat layer at the surface" (Joosten et al., 2002). However, there is a lack of consensus about the minimum peat thickness at a site to be defined as a peatland, and about the minimum content of organic material required for a substrate to be defined as peat. Joosten et al. (2002) base their work on a minimum peat depth of 30 cm, while pointing out that the minimum peat thickness required for peatlands varies between country and discipline, ranging from 20 to 70 cm. They define peat as material, which contains ≥ 30% of organic matter (OM) based on dry mass, a common value in the literature. However, requirements as low as 5% and as high as 65% OM may be encountered. Then, diagnostic thresholds of organic carbon (C) content of Histosols, common soils of peatlands and often simply called *peat* or *peat soils*, differ between soil classification systems. Soil Taxonomy (Soil Survey Staff, 2014a) requires Histosols to contain 12-18% C, depending on clay content, whereas the World Reference Base for Soil Resources (WRB; IUSS Working Group WRB, 2015) puts the threshold at 20% C content, while the Canadian System of Soil Classification (Soil Classification Working Group, 1998) requires more than 17% C for organic soils resembling Histosols. The Icelandic Soil Classification (Arnalds, 2015; Arnalds & Óskarsson, 2009) uses the threshold of > 20% C used by the WRB for Histosols, which Arnalds (2015) refers to as "true peat soils".

In Iceland, the term peatland is widely used for ecosystems with waterlogged soils, even though many of these areas may not fulfil the definition of a peatland being an area with or without vegetation with a naturally accumulated peat layer *at the surface* (e.g. Joosten et al., 2002; Rydin & Jeglum, 2013). Following the definitions of Histosols in WRB (IUSS Working Group WRB, 2015) and the Icelandic Soil Classification (Arnalds, 2015; Arnalds & Óskarsson, 2009), many of the so called peatlands of the island actually ceased to accumulate peat centuries ago, long before the widespread impact of mechanized drainage. Hence, peat layers (referred to hereon as Histosols) are not found precisely at the surface in all but only just over 1% of soils in Iceland, despite 7.8% - 9% of the island classifying as wetlands (Arnalds, Gudmundsson, et al., 2016; Ottósson et al., 2016). However, many of these wetlands used to be more organic. Soils fulfilling the > 20% C threshold are more widespread in pre-settlement subsoil layers i.e. in soil layers formed before c. 870 AD (Arnalds, 2015; Gísladóttir et al., 2011; Gísladóttir et al., 2010; Möckel et al., 2017), in areas where the surface soils of wetlands are now dominated by mineral soils. The reasons for the recession of Histosols in surface layers will be outlined later in this thesis. For means of simplicity, I will use the term *peatland* both for wetlands, where Histosols (using > 20% C threshold) are found in the surface layers, and for wetlands, in which a shift towards more mineral soils likely took place centuries ago, but where Histosols can probably be found in subsoil layers. Last, I would like to clarify that the three peatlands, which are at the core of the research presented in this thesis, do indeed comprise Histosols in their surface layers according to the definition presented above (> 20% C). They are in fact mires, i.e. peatlands where peat (or Histosol) is currently being accumulated (Joosten et al., 2002; Rydin & Jeglum, 2013).

Following, a brief discourse on the land-use history of peatlands, their ambiguous reputation and the pressures that they have been, and still are, facing is given. Then, an overview of C storage in Histosols in peatlands of non-volcanic and volcanic regions follows, which eventually leads to the aim and objectives of the study here introduced.

1.2 Peatlands - Troublesome Obstacles, Valuable Resources and Versatile Ecosystems

In many countries where mires or peatlands are common, they have (or have had) a profound impact on the daily life of people, particularly in pre-industrial societies. While they may have formed a tedious obstacle to travellers (Flint & Jennings, 2020; Schulz et al., 2019), or even dangerous, and potentially deadly terrain (Byg et al., 2020; Huijbens & Pálsson, 2009; Meredith, 2002; Þorbergsson, 1906), the livelihoods of people also depended on this vital resource (Joosten, 2016; Steindórsson, 1936, 1964). For example, according to a study by Sigurmundsson et al. (2021) in southeast Iceland, wetland meadows served as an important source of hay, and as winter grazing grounds in pre-industrial times. Indeed, wetlands are still an important resource for some rural communities (Byg et al., 2020; Lassila, 2021; Schulz et al., 2019).

The goods and benefits derived from peatlands are diverse and can vary between areas of the globe. Peatlands can provide grazing for domestic animals, and important hunting grounds as habitats for game species (Byg et al., 2017; Lassila, 2021; Schulz et al., 2019). They can provide building material and fuel in the form of peat while wild plant species can provide timber, food for humans and livestock (fodder), and the raw materials required for textiles (see also Chapman et al., 2003). Peatlands also impact upon resources of other ecosystems, such as on fish stocks in lakes and rivers (Schulz et al., 2019; Turetsky & St. Louis, 2006). More recently, interest in peatlands for recreational purposes is growing in some countries (Byg et al., 2020; Flint & Jennings, 2020), but considering the profound impact on the daily life of people in some places, it comes to no surprise that peatlands also bear cultural meaning (Schulz et al., 2019) and importance for place identity (Lassila, 2021). In many cultures, mythical stories are attached to peatlands (e.g. Schulz et al., 2019), and peatlands provide invaluable witness of the past by preserving archaeological remains and palaeoecological records (e.g. Coles, 2004; Flint & Jennings, 2020).

1.3 Peatlands in the 20th and 21st Centuries

1.3.1 Drainage and Surface Sealing of Peatlands

The multiple benefits derived from peatlands reflect their versatile ecosystem services, such as their importance for biodiversity, their function for water quality, flood regulation and drought buffering, their importance for climate regulation through their great potential to store C (Joosten et al., 2016; Minayeva et al., 2016; Stoneman et al., 2016; Yu et al., 2010), and their role for landscape connectivity and the intactness of other ecosystems (Minayeva et al., 2016). This array of ecosystem services provided by peatlands could in themselves be reason enough to acknowledge the importance of protection and regeneration efforts aimed at them. But despite their multi-functional significance, perception of peatlands remains ambiguous. According to Joosten (2016) a prevalent perception of peatlands as wastelands has rendered them a ready target of increasing infrastructure development and surface sealing under the pressure of growing population numbers. Furthermore, as heavy machinery became more widely available, new technologies led to the extensive drainage of peatlands for agriculture and forestry, and in many places, they were destroyed beyond recognition (Chapman et al., 2003; Coles, 2004; Flint & Jennings, 2020; Joosten, 2016). Especially in densely populated areas in Europe, but also in less densely populated areas of Scandinavia, draining was ubiquitous for a great part of the second half of the 20th century. Despite population densities of rural areas in Iceland being the lowest in Europe (Eurostat, 2021; Statistics Iceland, 2021b) and similar as in Canada, Alaska and Siberia (Statista, 2021; Yuri, 2016), the share of degraded peatlands there is in line with European averages of nearly 44% (Joosten, 2016). Between the early Forties and late Sixties of the twentieth century up to 70% of the expense incurred by the digging of ditches was state-subsidized (Geirsson, 1975), leading to approximately 47% of inland wetlands in Iceland being impacted by drainage for agriculture (Arnalds, Gudmundsson, et al., 2016).

1.3.2 The Struggle for Peatland Protection

Despite the ambiguous reputation of peatlands, their protection has been urgently emphasized for decades in national and international agreements (Barthelmes et al., 2015; Coles, 2004; Ramsar, 2002; Stoneman et al., 2016). In Iceland, from about the 1970s on, a slow shift from the perception of mires as inconvenient land, that should be moulded according to agricultural needs, towards ecosystems worth protecting, was tangible (Garðarsson, 1974, 1975; JG, 1976; Náttúruverndarsamtök Austurlands, 1973). This was in line with conservation efforts occurring elsewhere. In 1971, the Ramsar Convention on Wetlands was held, with a handful of nations adopting the convention a few years later. In 1976, the Council of Europe launched the European Wetlands Campaign (Matthews, 1993). Then, Iceland, as a Ramsar signatory began to initiate peatland and more generally wetland conservation and restoration actions from the mid-1990’s (Garðarsson et al., 2006; Magnússon, 1998), largely driven by bird conservation. But restoration efforts since have been of limited extent (Aradóttir et al., 2013; Óskarsson et al., 2020), as exemplified by an average annual restoration rate of 45 ha yr^{-1} in the years 2016-2018 (Stjórnarráð Íslands, 2019).

Further degradation of peatlands for the sake of resource exploitation continues (e.g. Turetsky & St. Louis, 2006). In many countries, peat is increasingly used for horticulture, and draining of peatlands to facilitate commercial afforestation still affects large areas. Also, the recent global race to exploit mineral resources in the Global North poses an aggravated threat to many peripheral peatlands (Lassila, 2021). In Iceland and elsewhere (Joosten, 2016; Rochefort & Lode, 2006; Turetsky & St. Louis, 2006), the great expansion of hydroelectric power generation has taken and continues to take its toll on peatlands. From the early 1950's peat ceased to appear in the official statistics of Iceland as a source of energy (Statistics Iceland, 2021a). However, the great increase of hydroelectric power production and the associated construction of reservoirs and connected infrastructure inevitably adversely affects, or destroys many ecosystems (Egilsson et al., 2001; Magnússon et al., 2001).

1.3.3 Impetus for Peatland Protection and Restoration

Despite the ongoing anthropogenic pressure faced by peatlands, there has long been some awareness of the impact of different types of land cover and ecosystems upon climate. For instance, "If all wetlands of the country [Iceland] would be perfectly drained, the climate would get warmer and *better*" (translated from Icelandic in Halldórsson, 1896; p. 9) was stated in the Icelandic farming magazine *Búnaðarrit* more than a century ago. Meanwhile, the projections of Alexander von Humboldt already more than two hundred years ago were less enthusiastic, but he worried about human-induced climate change as a consequence of land use practices such as forest clearance and draining wetlands ("Humboldt's legacy," 2019; Wulf, 2015). Yet, it is only rather recently that peatland conversation and restoration has received some impetus through efforts to sequester C (Chapman et al., 2003; Schulz et al., 2019) in the wake of increasing awareness of global warming. Today, peatland restoration as a means to combat climate change is also gaining more governmental attention in Iceland (Verkefnisstjórn aðgerðaáætlunar í loftslagsmálum, 2020), but of the 48 measures to reduce emissions or sequester C introduced by the Climate Action Plan of the country until 2030, two are aimed at wetland protection and wetland restoration. The intermediate goal is to reach more than a tenfold increase of annual wetland restoration within the four years between 2019 and 2022 (see also Stjórnarráð Íslands, 2019), i.e. to reach an annual restoration of 500 ha yr^{-1} by the year 2022.

1.4 Carbon Storage in Histosols

1.4.1 Formation of Histosols and their Carbon Stocks

Histosols are organic soils of peatlands (IUSS Working Group WRB, 2015). Usually, climate and topography are considered to shape the preconditions for Histosol formation, which depends on the slow decomposition and associated accumulation of OM due to anaerobic conditions (Clymo, 1987; Joosten, 2016). As such, peatlands can form anywhere given that preconditions for a high groundwater table prevail, i.e. sufficient precipitation in interaction with favourable topography. However, most extensive areas of peatlands occur at high northern latitudes where ample precipitation and high ground water tables in interaction with cold temperatures form excellent preconditions for the accumulation of OM. Uncertainties remain about the extent of peatlands, both regionally and globally. For instance, according to a recent estimate by Hugelius et al. (2020), northern peatlands cover 3.7 ± 0.5 million km^2, which is up to ~ 1 million km^2 more than indicated by the global peatland map PEATMAP presented only two years earlier by Xu et al. (2018). Estimates of the total C pools of northern peatlands also vary between studies, not least due to uncertainties of peatland cover (e.g. Xu et al., 2018), but also due to variability or inaccuracy in the determination of factors used to estimate soil organic C contents, such as soil bulk densities and depth estimates, and inconsistent definitions of peat (Köchy et al., 2015). For instance, Turunen et al. (2002) estimated a total C pool of 273 Pg in northern peatlands based on C accumulation in Finnish peatlands. The approach was later criticised as a likely underestimate by Yu (2012), who pointed out that the C stock of Finish peatlands was too small a share of all northern peatlands to be a suitable basis for global extrapolation. Later estimates of 547 Pg by Yu et al. (2010) are about twice as high as those by Turunen et al. (2002), similar to an earlier estimate of 455 Pg by Gorham (1991). A more recent and considerably higher estimate of 1,055 Pg by Nichols and Peteet (2019) has been argued unrealistic by Ratcliffe et al. (2021) and Yu et al. (2021), and also refuted by another recent estimate of 415 ± 150 Pg by Hugelius et al. (2020). The latter estimate is also in line with a review of northern peatlands C stocks by Yu (2012) ten years ago, which argues that despite considerable uncertainty and variability between estimates of C stocks in northern peatlands, C stocks of northern peatlands likely range around 500 ± 100 Pg. This amounts to approximately 25 – 30% of the estimated global soil C store in the upper two meters of soil (2060 ± 215 Pg carbon) as derived from the global soil map WISE30sec (Batjes, 2016). Hence, despite uncertainties about the total geographic extent and C storage of peatlands, it is manifest that these ecosystems constitute an important store of C and represent a significant component of the global C cycle. Pristine peatlands, where biomass production and accumulation exceed decomposition, are long-term C reservoirs (e.g. Turunen et al., 2002), but Alexandrov et al. (2020) estimate the maximum C storage potential of northern peatlands until the end of the current interglacial at 875 ± 125 Pg, i.e. about an another 300 Pg C could be sequestered in addition to the ca. 500 Pg already stored. However, when subject to degradation, such as by drainage, extraction, conversion to agricultural use, flooding for hydroelectric reservoirs, peatlands can become net sources of C emissions.

Indeed, degraded peatlands exert an unusually strong influence on the global C cycle, even though about 80% of peatlands worldwide are still in a relatively natural state (Joosten, 2016). According to a report by Joosten (2009) more than a decade ago, degraded peatlands were responsible for about 5% of anthropogenic CO_2 emissions. This disproportionate contribution of disturbed peatlands to greenhouse gas emissions worldwide is exemplified by the emission trends of greenhouse gases in Iceland, where net emissions between 1990-2018 from the land use, land-use change and forestry (LULUCF) sector are estimated to be more than double the combined emissions from all other sectors (The Environment Agency of Iceland, 2020). By far the greatest part of the emissions from the LULUCF sector in Iceland is ascribed to the drainage of organic wetland soils. Importantly, however, these estimates are based upon Tier 1 of the IPPC guidelines (IPCC, 2014; The Environment Agency of Iceland, 2020), which are based on research of boreal peatlands elsewhere than Iceland. The estimation of C emissions from drained organic soils based on non-regional coefficients may comprise considerable uncertainty. The circumstances of peatland formation and hence, C dynamics in these ecosystems in Iceland, differ from those of other regions at similar latitudes, as will be described in the following sections.

1.5 Soil Organic Carbon Stabilization

1.5.1 Carbon Stabilization in Mineral Soils

The potential to sequester C differs considerably between soil groups. As summarized in a review by Kögel-Knabner and Amelung (2021) the interaction between various factors modifies the C storage capacity of different mineral soil groups, including climatic conditions, soil chemical properties like the formation of organo-mineral complexes facilitated by reactive surfaces of minerals, soil physical properties (e.g. aggregation), as well as other pedogenic processes. Kramer and Chadwick (2018) estimate that about 600 Pg of soil organic C is globally retained by reactive minerals of the clay-size fraction. However, stabilization capacity differs between clay-sized minerals (Rasmussen et al., 2018). Highly reactive, short range order (more recently also called nanocrystalline) silicates and metal oxides, and metal-humus complexes, have been observed to be of greater C stabilization importance than crystalline phyllosilicates and crystalline pedogenic oxides in humid acid soils (Kleber et al., 2005; Kögel-Knabner et al., 2008; Rasmussen et al., 2018). Also, as pointed out in a review by Kögel-Knabner et al. (2008) stabilization of soil organic matter differs between organic chemical components. They observed that alkyl C and O/N-alkyl C compounds dominate in organo-mineral associations, whereas other compounds were of minor importance. As mineral weathering is climate dependent, stabilization of C by minerals is also observed to be highly dependent on climate, but Kramer and Chadwick (2018) found a strong positive impact of soil moisture and flux of water through soils on the amount of C stabilized by organo-mineral associations. However, under anoxic conditions, the protective role of some minerals such as short range order or nanocrystalline iron oxides may be reversed (Chen et al., 2020). While organo-mineral complexes probably dominate stabilization mechanisms in mineral subsoils, several co-dominant factors may shape C dynamics in surface soils (e.g. Kramer & Chadwick, 2018; Kögel-Knabner et al., 2008).

1.5.2 Carbon Storage in Andosols

Andosols, soils of volcanic regions, are known for their exceptionally high C storage capabilities (Kögel-Knabner & Amelung, 2021; Takahashi & Dahlgren, 2016; Wada, 1985), but they contain the highest contents of C of all mineral soils. This is related to their mineral constituents, which form from volcanic ejecta and exert a strong impact on soil forming processes (Nanzyo et al., 1993). The weathering of the volcanic parent material leads to abundant precipitation of aluminium (Al), iron (Fe) and silicon (Si), which favours the formation of highly active nanocrystalline minerals like the aluminosilicate allophane and the Fe-hydroxide ferrihydrite (Bonatotzky et al., 2021; Hewitt et al., 2021; Shoji et al., 1993; Wada, 1989). As previously stated, these clay-sized mineral constituents play a particularly strong role for the C accumulation of humid acid soils (Kleber et al., 2005; Kögel-Knabner et al., 2008; Rasmussen et al., 2018). Hence, formation of Al/Fe-humus complexes, and organo-mineral complexes facilitated by nanocrystalline minerals is particularly prominent in soils formed from volcanic ejecta (e.g. Asano & Wagai, 2014; Bonatotzky et al., 2021; Inagaki et al., 2020; Wada, 1989) and mainly responsible for their elevated C storage capacities. Burial of topsoil by fresh tephra layers may additionally prevent C loss from underlying soil layers (Kögel-Knabner & Amelung, 2021).

1.5.3 Carbon Storage in Organic Histosols

It is widely accepted, that the dominant processes of C stabilization in mineral soils, organo-mineral complexation and aggregation, are of minor importance in organic wetland soils such as Histosols (Kögel-Knabner & Amelung, 2021; Leifeld et al., 2012), but the hydrological conditions and chemical characteristics of OM are the predominant impact factors of C dynamics in these soils (e.g. Kayranli et al., 2010; Kögel-Knabner & Amelung, 2021; Zhaojun et al., 2011). However, there is still some lack of understanding about the driving factors behind regional differences in C sequestration in these soils (Amendola et al., 2018). Just as with any other reference soil group (IUSS Working Group WRB, 2015) or soil order (Soil Survey Staff, 2015), Histosol is the hypernym of a great diversity of soils that share some common diagnostic criteria, but vary with regard to more refined characteristics. There can be great differences in the vegetation composition serving as parent material (Joosten, 2016), ranging from tropical peatlands formed in rain forests (e.g. Page et al., 2006), restiad peatlands in New Zealand (e.g. Clarkson et al., 2004), bryophyte dominated peatlands common to, but not restricted to, peatlands of the boreal zones (e.g. Clarkson et al., 2017; Clymo, 1987; Joosten, 2016), and peatlands dominated by vascular plants such as sedges and grasses, mostly found in temperate and subtropic regions (Joosten, 2016). Vegetation type has a great influence on the characteristics of the peatlands soils (Joosten, 2016; Leifeld et al., 2012; Rezanezhad et al., 2016; Rydin & Jeglum, 2013) including structure and hydrology, decomposability and density, and consequently, C dynamics.

For instance, the chemical composition of the vegetation from which the OM in peatlands is derived is known to influence its sensitivity towards temperature changes, but labile forms of OM with a simpler structure are generally observed to be relatively less sensitive towards temperature increases than recalcitrant forms (e.g. Conant et al., 2011; Mikan et al., 2002). In a study of six peatlands in Switzerland (each with different history of drainage and management) Leifeld et al. (2012) found a strong positive relationship between C mineralization rates and polysaccharide content, concluding that the chemical composition of the peat was an important driver of decomposition rates and C loss - when disturbed e.g. through drainage or climate change. Research evidence on the influence of the vegetation composition of peatlands on C storage is not unequivocal. For example, when comparing the C accumulation rates of vascular plant dominated fen peat and *Sphagnum* dominated bog peat in southern Patagonia, Loisel and Bunsen (2020) found considerably larger soil C stocks and greater C accumulation rates in the bogs than fens. However, in continental Canada, Yu (2006) observed an opposite trend with greater C accumulation rates arising in fens rather than bogs.

There are indications that organo-mineral complexes also play a role for C dynamics in peatlands. Fe compounds have been observed to be of particular importance for the cycling of various elements in peatlands, including C. Curtinrich et al. (2022) found evidence for the importance of ferric iron (Fe(III)) for C stabilization even in mineral-poor peatlands. Moore and Clarkson (2007) observed links between Fe concentration and C stability in Peatlands in New Zealand, as indicated by comparatively little dissolved organic carbon (DOC) in the catchment waters of Fe rich peatlands. This may result in the release of C as the reduction of the Fe(III) to ferrous iron (Fe(II)) increases with rising temperatures (see also Knorr, 2013).

There is evidence that the chemical composition of the C is also linked to the formation and stability of Fe-C compounds. For instance, phenolic compounds derived from *Sphagnum* mosses, are considered to promote OM accumulation through different trajectories, e.g. by hampering microbial activity (Freeman et al., 2001; Zhao et al., 2021), and by quenching OM degrading radicals such as $^{\bullet}OH$, but also by enhancing the formation of poorly crystalline Fe(III) such as in ferrihydrite and its complexation with organic compounds (Zhao et al., 2021). Hence, in peatlands which are dominated by *Sphagnum* mosses, the chemical composition of the vegetation may shape the decomposability of the OM directly, but also indirectly by promoting a stabilizing effect through the formation of organo-mineral complexes. In a study on a subalpine Chinese peatland, Zhao et al. (2019) found that up to nearly one fifth of the C was Fe-bound, with the highest values derived from *Sphagnum* dominated plots, and a stabilizing role of poorly crystalline Fe compounds. Nevertheless, interactions between Fe and C have mainly been studied in mineral soils, and studies in peatlands remain underrepresented (Curtinrich et al., 2022).

Vegetation characteristics can also influence soil aeration by oxygen leakage from roots (radial oxygen loss) regardless of water level (e.g. Yarwood, 2018), but the extent of radial oxygen loss differs between plant species of a peatland (e.g. Lai et al., 2011). This may then affect redox-reactions in the soils, including oxidation and reduction of metal elements, the mineralogical properties of the soil (Yarwood, 2018) and the formation of organo-mineral complexes. Different plant species will also shape decomposition processes and the oxidation state of metal elements by affecting the soil microbial composition through provision of different root exudates (e.g. Yarwood, 2018).

1.5.4 Carbon Storage in Histosols in Iceland

Recently, there is emerging research evidence for the role of volcanic ejecta for peatland C dynamics. For example, several studies report increased C accumulation following tephra deposition (Ratcliffe et al., 2020; Zhang et al., 2022), likely driven by elevated phosphorus levels derived from the volcanic material. In a study of a peatland on the Japanese island of Hokkaido, Hughes et al. (2013) detected a more complex pattern. They observed a temporary decrease in C accumulation following tephra deposition, probably as a result of a vegetation shift from *Sphagnum* to monocotyledon dominated plant communities and a concomitant increase in decomposition rates. The decrease in C accumulation was soon offset by an even greater increase in C accumulation rates once the *Sphagnum* re-established itself and likely experienced a phase of invigorated growth due to the fertilizing effect of nutrient leachates of underlying tephra layers. Loisel and Bunsen (2020) observed that the majority of 58 southern Patagonian peatlands, which today are *Sphagnum* dominated bogs, experienced a transition from fens dominated by vascular plants (e.g. sedges, grasses and rushes) to *Sphagnum* dominated bogs following tephra deposition around 4200 cal yr. BP. They argue that while hydrologic changes driven by climate cooling (see also Mayewski et al., 2004) probably also disturbed the equilibrium of the fens, the tephra deposition most likely facilitated the final transition from fens to bogs. The potential impact of tephra deposits on vegetation succession is important, but as previously described, the vegetation as a source of OM impacts the peatlands soil properties, not least their C dynamics. Furthermore, while the hydrology of peatlands is mostly governed by climate, compacted tephra layers may impede vertical movement of water within the peat column (Arnalds, 2015; De Vleeschouwer et al., 2008), which presumably affects C dynamics.

Windborne volcanic ejecta is an important impact factor of peatland soils in Iceland as the island experiences one of the highest rates of volcanic activity in the world, with an average of c. twenty volcanic eruptions per century during the Holocene (Thordarson & Hoskuldsson, 2008). However, distinct depositional events during volcanic eruptions are not the only major contributor of aeolian material to Icelandic peatlands. Glacial outwash plains and eroded dryland soils represent another steady source of windborne mineral material of volcanic origin. The causes and initiation of the widespread erosion of dryland soils and ecosystem degradation in Iceland has found ample reflection in the scientific literature (e.g. Dugmore et al., 2009; Eddudóttir et al., 2020; Gísladóttir et al., 2011; Gísladóttir et al., 2010; Streeter et al., 2015). Most research provides good agreement that barren areas serving as dust sources were certainly not uncommon before the human settlement in ca. 870 AD; however, owing to a combination of a harsh climate and a dynamic landscape shaped by active volcanism and glacial processes, their extent increased rapidly after the settlement (e.g. Arnalds, Dagsson-Waldhauserova, et al., 2016; Dugmore et al., 2009; Eddudóttir et al., 2020; Tinganelli et al., 2018). There is strong evidence that the island's ecosystems were relatively resilient in the absence of anthropogenic pressure, able to recover quickly from environmental pressure driven by climate changes and volcanic activity (Eddudóttir et al., 2020; Eddudóttir et al., 2016; Möckel et al., 2017; Streeter et al., 2015). The onset of land use after the settlement led to rapid land degradation by vegetation destruction and shifts in vegetation communities, with consequent decline of soil quality and the fatal erosion of the erosion prone Andosols, leading to a rapid increase in barren areas serving as dust sources after the settlement (e.g. Arnalds, Dagsson-Waldhauserova, et al., 2016; Dugmore et al., 2009; Óskarsson et al., 2004). Today, the potent interaction of sparse vegetation cover, low resilience of the remaining Andosols, harsh climatic conditions with frequent strong winds (Einarsson, 1984) and a globally unparalleled area of volcaniclastic deserts (Arnalds, Dagsson-Waldhauserova, et al., 2016), places Iceland amongst the most active aeolian environments worldwide.

Therefore, mineral material of volcanic nature is not only deposited into the peatlands in form of distinct tephra layers during volcanic eruptions, but in form of recurring fluxes of windborne dust from aeolian source areas. The location of peatlands with respect to the major dust sources is reflected in a wide range in the mineral and organic content of their soils. Farthest from the active volcanic zones, sparsely vegetated, and barren areas, organic Histosols (> 20% C; Arnalds, 2015; Arnalds & Óskarsson, 2009; IUSS Working Group WRB, 2015) occur (Figure 1.1). Only a comparatively small share of soils in Iceland comprise Histosols as surface soils, despite an estimated share of 7.8% - 9% of wetlands in the country (Arnalds, Gudmundsson, et al., 2016; Ottósson et al., 2016). Overall, c. 1% of surface soils exhibit Histosols (Arnalds, 2004). The distribution of so-called Histic Andosols (compare Icelandic Soil Classification; Arnalds & Óskarsson, 2009; Óskarsson et al., 2004) with >5% is considerably greater, but these soils contain with 12-20% C a greater share of mineral constituents than Histosols. Closest to the dust sources, Gleyic Andosols dominate in surface soils of wetlands. They are estimated to comprise > 2% of all soils and contain a considerable share of mineral material, with C contents between 1% and 12%. The destabilization of the environment after the settlement probably induced a shift towards more mineral rich wetland soil, but more C rich subsoil layers are frequently found below relatively mineral surface soil layers in wetlands in Iceland (Arnalds, 2015; Gísladóttir et al., 2011; Gísladóttir et al., 2010; Möckel et al., 2017). However, even soils that fulfil the > 20% C criterion of Histosols often exhibit a mixture of histic, andic and vitric properties

(Bonatotzky et al., 2019), and average C contents (Bonatotzky et al., 2019; Möckel et al., 2017) are below the northern peatland averages of 46-51% C reported by Loisel et al. (2014).

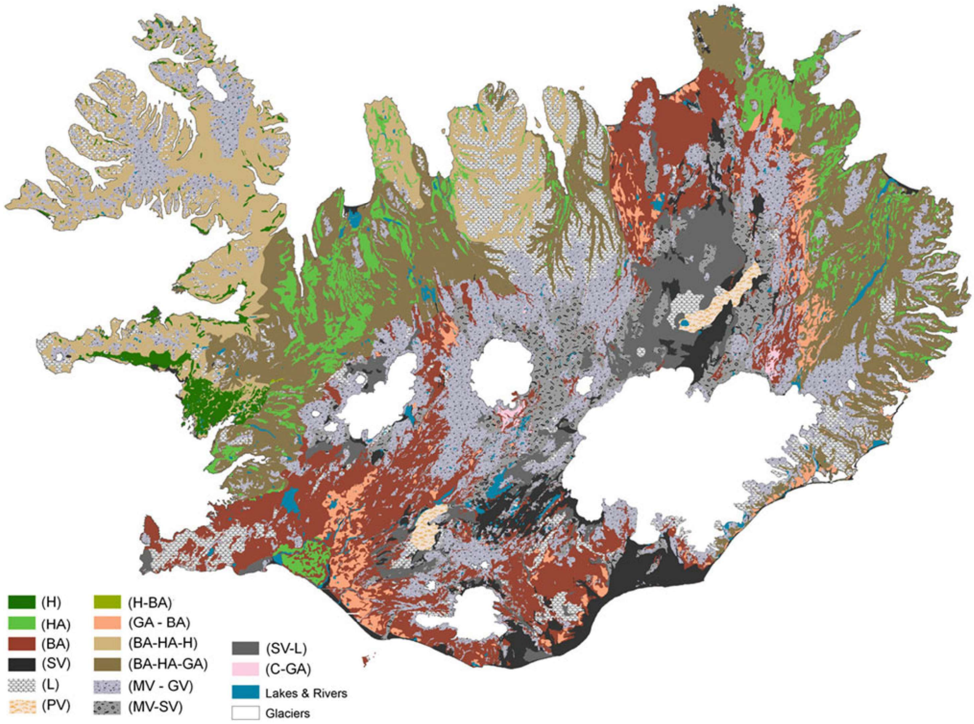

Figure 1.1: Soil Map of Iceland derived from Arnalds (2015), based on Arnalds and Óskarsson (2009). H = Histosol, HA = Histic Andosol, BA= Brown Andosol, SV =Arenic Vitrisol, L = Leptosol, PV = Pumice Vitrisol, GA = Gleyic Andosols, MV/GV = Cambic Vitrisol, C = Cryosol.

Besides obviously lowering the relative C content of peatlands in Iceland, uncertainties remain about the impact of the inorganic aeolian deposits on C dynamics. An easily visible effect of the dust depositions on peatlands in Iceland is their vegetation characteristics, which certainly impact C characteristics. Contrary to the majority of peatlands of other subarctic regions (Clymo, 1987; Joosten, 2016), vascular plants dominate the Icelandic ones (Steindórsson, 1936, 1964). Bryophytes, including *Sphagnum*, occur, but are not dominant. Due to the volcanic nature of the aeolian deposits, questions arise if stabilization processes similar to Andosols may be of importance, i.e. the formation of organo-mineral complexes facilitated by nanocrystalline minerals and metal-humus complexes (e.g. Asano & Wagai, 2014; Bonatotzky et al., 2021; Inagaki et al., 2020; Wada, 1989).

1.6 Research Aims and Objectives

The principal aim of this research was to investigate the impact factors of C dynamics in Icelandic Histosols subject to the varying impact of windborne mineral material from volcanic eruptions and the aeolian deposition of mineral constituents of a volcanic nature derived from other major dust sources. The focus is on the stability of the C, its decomposition, and the associated influence of environmental and pedogenic variables. To achieve the research aim, the following objectives were at the core of the study:

1. To investigate the impact of vegetation composition and C characteristics on the stability and decomposition of C in Icelandic Histosols as opposed to the potential influence of mineral soil constituents **(Papers I, II** and **III)**.

2. To determine if distinct tephra deposits impact C dynamics of Histosols, i.e. the C structure, C decomposition and stability of the C **(Papers I** and **II)**, and its temperature sensitivity **(Paper I)**.

3. To investigate interactions between andic soil properties and characteristics of C in Histosols in pre-settlement subsoils **(Paper II)**.

4. To investigate interactions between andic soil properties and characteristics of C in post-settlement surface soils **(Papers II** and particularly **III)**.

5. To determine if increased mineral content of peatlands leads to decreased absolute C storage capacity **(Papers II** and **III)**.

Histosols from three peatlands in northwest Iceland, each with differing degree of exposure to aeolian deposition, were compared. All three peatlands were subject to tephra deposits from the volcanic eruptions Hekla 4 and Hekla 3 (erupted ca. 4.25 ka BP and 3.06 ka BP, respectively; Dugmore et al., 1995). With an estimated 9 and 12 km^3 of tephra ejected respectively, these two eruptions range among the most voluminous silicic Holocene eruptions in Iceland (Larsen & Thorarinsson, 1977). Three sets of soil samples were used, with one set at the core of one paper each (detailed descriptions of the soil samples are provided in the methods sections). Various data sets were evaluated, including:

- The peatlands vegetation characteristics
- The Histosols C stability based on laboratory CO_2 respiration at 5 °C, 15 °C and 25 °C
- The Histosols C structure derived by ^{13}C nuclear magnetic resonance (NMR) spectroscopy
- Andic soil properties based on selective extractions of Al, Fe, and Si
- Decomposition proxies C/N, $\delta^{13}C$, and $\delta^{15}N$
- Various complementary soil properties (e.g. OM content, dry bulk density (DBD), pH etc.).

Thereby, the study provides novel insight into factors underlying C dynamics of Histosols impacted by mineral aeolian deposition of volcanic nature.

2 Methodology

2.1 Research Area and Study Sites

The research area of this study is located in northwest Iceland, Austur Húnavatnssýsla district (Figure 2.1). Three sloping fen peatlands were selected which form a transect from the northern coast of the Skagi peninsula, southwards through the lowlands of Svínadalur valley to the highland fringe south of Svínadalur. The coastal site, *Torfdalsmýri* (ca. 40-55 m a.s.l.), is located at the northwestern tip of Skagi peninsula, about 1 km from the sea. Situated farthest from centres of volcanic activity and sparsely vegetated or barren dust source areas in the interior of the country, Torfdalsmýri is relatively sheltered from aeolian deposition. The site at the highland fringe, *Hrafnabjörg* (ca. 330 m a.s.l.), is located closest to dust source areas and active volcanic zones, and is about 26 km from the sea. The plateau Auðkúluheiði, an area affected by severe soil erosion (e.g. Arnalds et al., 2001; Eddudóttir et al., 2016) is only about 10 km south of the Hrafnabjörg peatland. The lowland peatland at *Tindar* (ca. 100-110 m a.s.l.), is located within a broad section of Svínadalur valley, about 15 km north of Hrafnabjörg, and 11 km from the sea to the north.

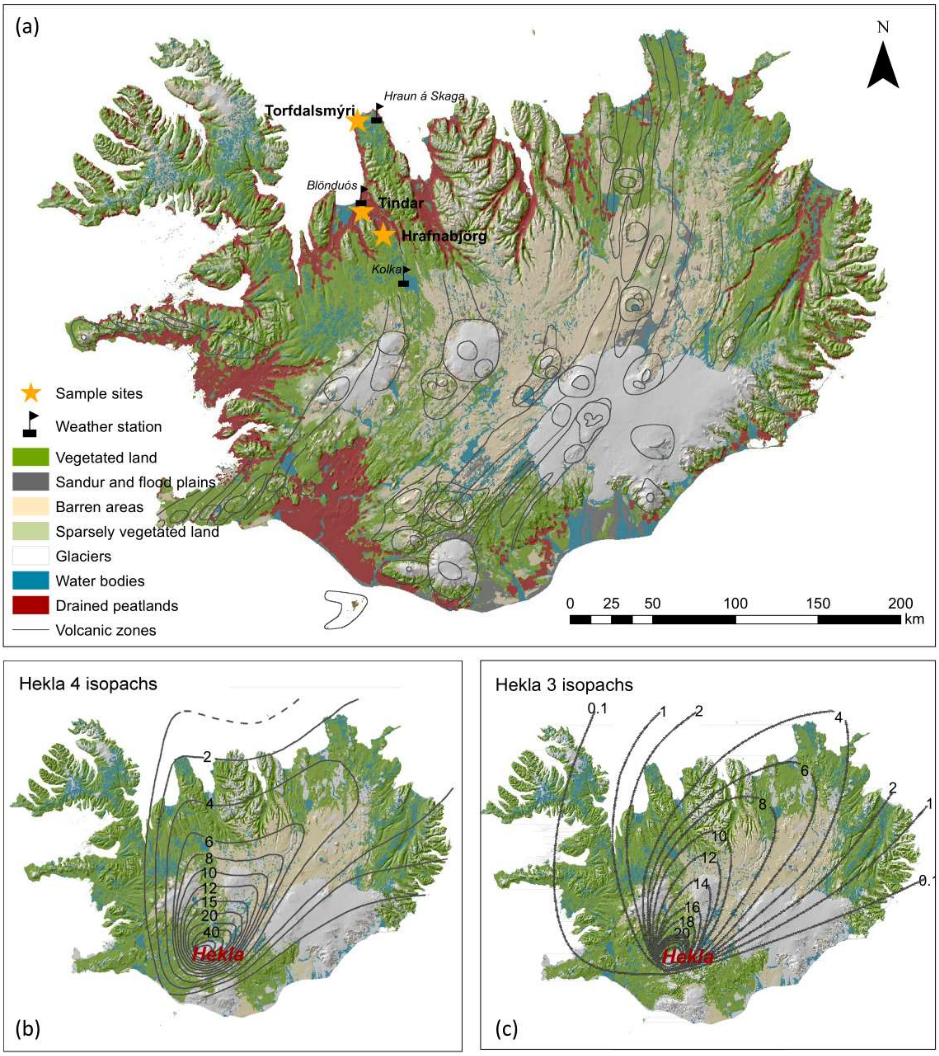

Figure 2.1 The map in (a) shows the location of the sample sites with respect to source areas of aeolian mineral material, i.e. sparsely vegetated or barren areas and the active volcanic zones. Drained peatlands are depicted in red, and volcanic zones with grey lines. The maps in (b) and (c) show the Hekla 4 and Hekla 3 isopachs (adapted from Larsen & Thorarinsson, 1977). Map source: IS50 V database of the National Land Survey of Iceland (LMI, n.d.; map produced by Susanne C. Möckel)

The oceanic climate of Iceland is characterized by mild winters and cool summers (Einarsson, 1984), and is influenced greatly by its situation at the border of warm and cold ocean currents and at the frontier of warm and cold air masses. Winds are strong, precipitation considerable and weather changes are frequent. The mountainous nature of the island is greatly responsible for variations in climate patterns between regions, not least variations in precipitation. Areas in the Southeast and South experience the highest annual precipitation (up to > 4000 mm yr^{-1}), whereas in North and Northeast Iceland annual precipitation between 400 mm and 600 mm is common. Located in northwest Iceland, the annual precipitation in the research area of this study is relatively low (400-500 mm; Table 2.1; IMO, n.d.-a), with higher amounts at the coast than further inland. Likewise, colder average air temperatures are recorded at weather stations in the highlands than in coastal lowlands. For a summary of main climate characteristics at weather stations within the research area, see Table 2.1.

Table 2.1 Main climate characteristics at weather stations within the research area. Data are available for the following time spans: Hraun á Skaga: 1956 – 2015; Blönduós: 1949 – 2001; Kolka: 1994 –2015 (IMO, n.d.-a, n.d.-b). The summer tritherm in Iceland comprises the months June – August, the autumn tritherm comprises September – October. The winter tritherm lasts from December – February and spring tritherm lasts from March – May. For information about the sampling locations in relation to the position of each weather station compare Figure 2.1.

Weather station	**Hraun á Skaga**	**Blönduós**	**Kolka**
Elevation (m a.s.l.)	3	8	506
Mean annual temperature (°C)	2.94	3.05	0.64
Mean summer tritherm temperature (°C)	7.9	9.1	7.8
Minimum summer tritherm temperature (°C)	6.3	7.4	6.3
Maximum summer tritherm temperature (°C)	10.2	10.4	9.3
Mean winter tritherm temperature (°C)	-1.0	-1.6	-4.7
Mean autumn tritherm temperature (°C)	3.6	3.4	0.6
Mean spring tritherm temperature (°C)	1.3	1.7	-1.3
Mean annual precipitation (mm)	512	480	352
Mean annual windspeeds (m s^{-1})	5.7	3.8	7.4

2.2 Soil Sampling and Vegetation Analysis

Three sets of soil samples were taken from each peatland. Each set of soil samples formed the basis of one of the three papers presented in this thesis:

For **Paper I**, soil samples obtained for a previous project (Möckel et al., 2017) were used. At each peatland, one pedon was cleared and bulk samples collected per soil horizon (Figure 2.2). The Hekla 4 tephra formed a well-defined stratum within each soil profile, with tephra thicknesses of 5 cm at Torfdalsmýri, 6 cm at Tindar and 1 cm at Hrafnabjörg. Laboratory analyses (C mineralization, ^{13}C NMR spectroscopy, content of nitrite, nitrate and ammonium) were conducted on selected horizons (Figure 2.2), i.e. the very surface horizon and the horizons above and below the Hekla 4 tephra deposits. The results of the laboratory analyses were also discussed in context of various soil variables considered in Möckel et al. (2017).

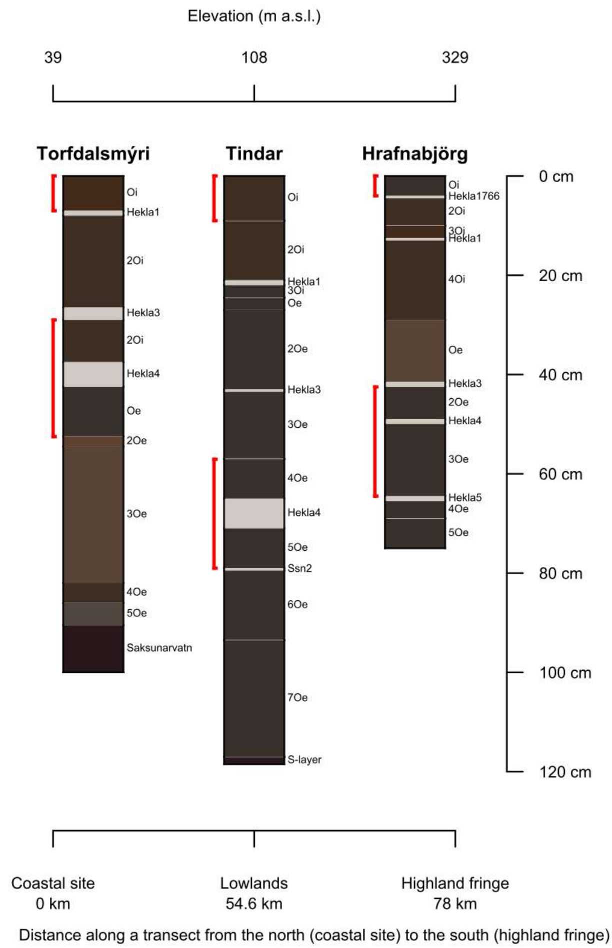

Figure 2.2: Soil profiles used in Paper I of this study. Profiles were taken from three peatlands (Torfdalsmýri, Tindar and Hrafnabjörg) along a north-south transect, with elevation increasing southwards towards the highlands. Soil horizons analysed in Paper I are indicted by red brackets. Division of profiles into horizons and the location of tephra layers is shown. Colours of the soil profiles resemble Munsell soil colours. A thorough description of soil morphological properties is available in Möckel et al. (2017). The figure was produced with the R package Aqp (Beaudette et al., 2020).

For **Paper II**, one soil profile was excavated at each peatland (Figure 2.3). Exact site selection within peatlands was based on two criteria: it should be located in the centre of the peatland ecosystem, and it must contain well preserved tephra deposits from the Hekla 3 and Hekla 4 eruptions (Dugmore et al., 1995; Larsen & Thorarinsson, 1977). The Hekla 3 and Hekla 4 tephra formed well-defined strata, with Hekla 4 tephra thicknesses of 9 cm at Torfdalsmýri, 7 cm at Tindar, and 3 cm at Hrafnabjörg, and Hekla 3 tephra thicknesses of < 0.5 cm at Torfdalsmýri, 2 cm at Tindar and 2 cm at Hrafnabjörg. Hekla 4 deposits at Torfdalsmýri and Tindar are thicker than isopachs would indicate (2 cm and 4 cm, respectively; Figure 2.1; Larsen & Thorarinsson, 1977), but thinner than isopachs would suggest at Hrafnabjörg (4-6 cm). Hekla 3 tephra layers are all thinner than isopachs for the area indicate (2 cm at Torfdalsmýri, between 2-4 cm at Tindar and Hrafnabjörg). Where tephra deposits are thinner than expected, this might be a result of post-eruption redistribution by wind rather than reflecting initial thicknesses. Pooled bulk soil samples were collected at 10 cm intervals down to a depth of 20 cm below the Hekla 4 tephra layer. Above and below the Hekla 3 and Hekla 4 tephra layers, the sampling interval was reduced to 2 x 5 cm (Bonatotzky et al., 2019, 2021).

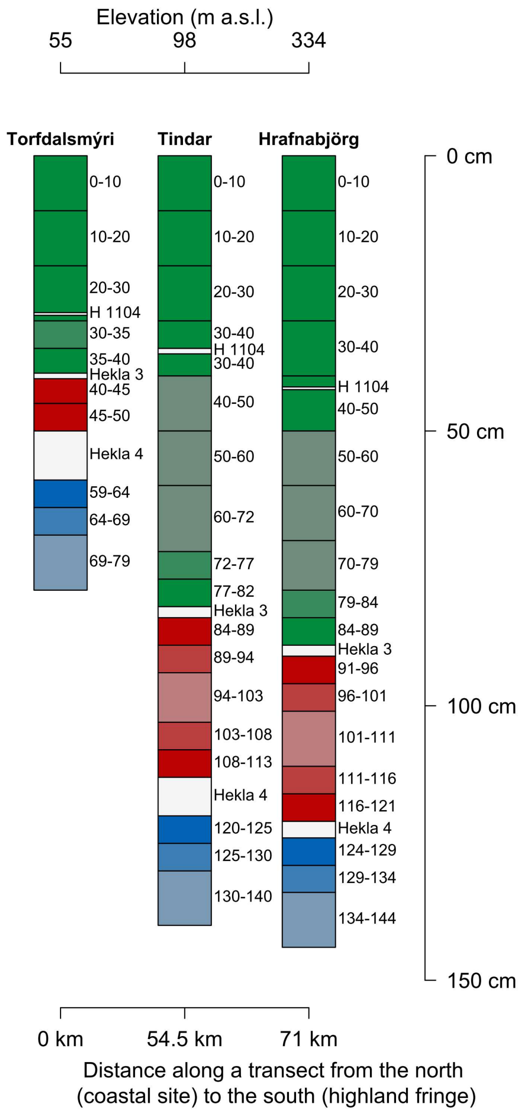

Figure 2.3: Soil cores used in Paper II, showing depth intervals used during sampling. White layers represent tephra deposits within the soil column. Blue layers reflect pre-Hekla 4 soil layers. Soils formed between the eruptions of Hekla 4 and Hekla 3 are depicted in red and post-Hekla 3 layers are in green. Darker colours reflect increased influence of aeolian material in the form of either volcanic ejecta (i.e. tephra) or aeolian material from sparsely vegetated or barren areas. The tephra deposit from an eruption of the volcano Hekla in 1104 AD (Larsen & Thorarinsson, 1977) is also shown. This eruption occurred c. 230 years after the settlement of Iceland, and serves as an approximate demarcation line between pre-settlement and post-settlement soil formation. Soil layers formed after Hekla 1104 are assumed to be subject to greater aeolian deposition due to increased soil erosion after the settlement (Dugmore et al., 2009; Gísladóttir et al., 2011; Gísladóttir et al., 2010), particularly after 1100 in the study area (Bates et al., 2021; Tinganelli et al., 2018). The figure was produced with the R package Aqp (Beaudette et al., 2020).

For **Paper III**, soil samples were collected from nine quadrats at each peatland, along three parallel transects (transects a, b, c; Figure 2.4). Each transect extended from the margin to the centre of each peatland. Along each transect, three quadrats were sampled as follows: one at the margin (1), one at the centre (3) and one between the margin and the centre (2) of the peatland. At each quadrat, vegetation was characterized according to the relevé method by Braun-Blanquet (Dombois & Ellenberg, 1974). Soil samples were collected from the upper 30 cm (divided into three intervals: 0-5 cm, 5-15 cm, 15-30 cm). This depth is defined as the surface tier in non-sphagnum dominated Histosols by Soil Taxonomy (Soil Survey Staff, 2014a), and spans the main rooting depth at biomes of the boreal and arctic regions (Jackson et al., 1996). Also, soils of this depth range at the peatlands most likely formed exclusively during post-settlement times (judging from core chronology in Paper II).

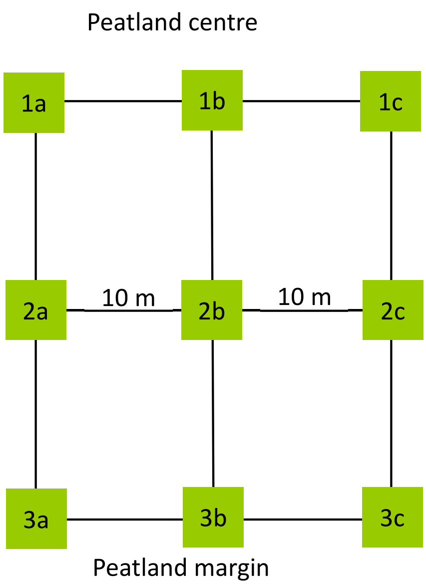

Figure 2.4: Sampling approach used in Paper III. Vegetation analysis and soil sampling was conducted at nine quadrats (0.25 m^2) at each peatland, along three parallel transects from the margin to the centre of each peatland.

2.3 Laboratory Analyses

2.3.1 Total Carbon and Nitrogen Content and Stable Isotope Ratios $\delta^{13}C$, $\delta^{15}N$

Determination of total carbon (%C) and nitrogen (%N) by dry combustion (Soil Survey Staff, 2014b; Papers I, II and III) and of the stable isotope ratios $\delta^{13}C$, $\delta^{15}N$ (**Papers II and III**) as an indicator of degradation state and the hydrology of peatlands (e.g. Alewell et al., 2011; Krüger et al., 2014), was conducted by the Cornell Isotope Laboratory in the USA. Due to the absence of carbonate minerals in Icelandic soils (Bonatotzky et al., 2021; Mankasingh & Gísladóttir, 2019; Vilmundardóttir et al., 2014), soil organic C was assumed to be equivalent to %C. As a proxy for decomposition (e.g. Kuhry & Vitt, 1996; Malmer & Holm, 1984), the molar C/N ratio was calculated. However, while C/N may prove satisfying for the determination of decomposition of peatlands with a homogeneous vegetation history, this is not always the case for peatlands that undergo frequent vegetation changes such as in Iceland. Previous research there (e.g. Möckel et al., 2017) and elsewhere (e.g. Hoorens et al., 2003; Hornibrook et al., 2000; Lawson et al., 2014) provides a strong indication that changes in the C/N of peatlands do not always reflect changes in decomposition as the vegetation that serves as the parent material of Histosols also impacts C/N ratios. In order to understand and describe decomposition processes and C degradability in these peatlands, the support of more than one proxy is essential. Hence, in order to give a holistic account of C characteristics, its chemical composition by ^{13}C NMR spectroscopy was also determined.

2.3.2 Carbon Structure Based on ^{13}C NMR Spectroscopy (Papers I, II and III)

Determination of C structure by ^{13}C NMR spectroscopy was chosen above other techniques (i.e. those that involve the extraction of OM) in order to include the total OM (Kögel-Knabner, 1997). Integration of the chemical shift (Table 2.2) was based on Knicker et al. (2005), modified by Leifeld et al. (2012).

Table 2.2 Integration of the chemical shift based on Knicker et al. (2005), modified by Leifeld et al. (2012). Signal intensities for the chemical shift regions 70–75 ppm and 52–57 ppm were used to calculate the (70-75)/(52-57) ratio, which Bonanomi et al. (2013) observed to correlate positively with decay rates. As a proxy for decomposition, the alkyl C to O/N-alkyl C (A:O/N) ratio was calculated (Baldock et al., 1997).

Chemical shift region (ppm)	Assignment	
220-160	carboxyl/carbonyl/amide C	
160-140	O/C-aryl C	
140-110	C/H-aryl C	
110-60	O-alkyl C	O/N-alkyl C
60-45	N-alkyl C	
45-0	alkyl C	
70-75	O-alkyl C of carbohydrates	
52-57	methoxyl C of lignin	
*90-60	polysaccharides	

* The chemical shift region for polysaccharides was only integrated in Paper I.

Information on the share of the different C types in soils is a key to understanding decomposition processes and to determine the stage of decomposition of the C (Conte et al., 2004; Kögel-Knabner, 1997). Research on various soil types has revealed that changes in the share of the different C types are a good indicator of decomposition of OM (Baldock et al., 1997; Conte et al., 2004; Kögel-Knabner, 1993, 1997; Leifeld et al., 2012). For instance, the share of alkyl C increases with decomposition, at the same time as the share of O/N-alkyl C decreases (Baldock et al., 1997). Consequently, the alkyl C:O/N-alkyl C ratio (A:O/N) can be used as a proxy for decomposition, whereas increasing ratios indicate advancing decomposition. The ratio of O-alkyl C of carbohydrates/methoxyl C of lignin ((70–75 ppm)/(52–57 ppm)) was recommended by Bonanomi et al. (2013) as an indicator for decay rates. They observed the ratio to be positively related to decay rates.

2.3.3 Carbon Mineralization as Indicator of Carbon Stability (Paper I)

Determination of C mineralization by measurements of CO_2 respiration were originally used as a proxy for biological soil fertility (e.g. Haney et al., 2008). In recent years, measurements of CO_2 efflux from soil have increasingly been used to gauge OM decomposition and C dynamics in soils (e.g. Kuzyakov, 2006). Here, laboratory measurements of CO_2 emissions were conducted via incubation of soils and NaOH traps in closed jars at stable temperatures (5 °C, 15 °C and 25 °C), using back titration to determine the CO_2 captured by the NaOH traps (Alef & Nannipieri, 1995; Isermeyer, 1952). By using laboratory incubations at stable temperature, the focus was on the effect of temperature on C stability regardless of other environmental impact factors, such as emissions of living plants (Kuzyakov, 2006).

2.3.4 Andic Soil Properties (Papers II and III, and Unpublished Data of Soil Samples of Paper I)

Selective dissolution of Al, Fe and Si with ammonium oxalate and sodium pyrophosphate was conducted following Soil Survey Staff (2014b; methods 4G2 and 4G3, respectively). The Al, Fe and Si extracted with ammonium oxalate (Al_o, Fe_o, Si_o) is indicative of the active forms of Al and Fe of organic complexes (Al/F-humus complexes), nanocrystalline hydrous oxides of Fe and Al, and nanocrystalline aluminosilicates like allophane (Nanzyo et al., 1993; Wada, 1989). Active Fe and Al extracted with sodium pyrophosphate (Fe_p, Al_p) is associated with organic compounds. Based on the selective dissolutions, ferrihydrite content was determined (%ferrihydrite = %Fe_o x 1.7; Childs, 1985), and the sum of Al_o + ½Fe_o calculated (≥ 2% as diagnostic criterion of andic soil properties; IUSS Working Group WRB, 2015). Allophane or allophane-like constituents were estimated by the equation proposed by Mizota and van Reeuwijk (1989), based on Parfitt and Wilson (1985). Unlike Mizota and van Reeuwijk (1989), who recommend to use only Al/Si ratios (derived from (Al_o-Al_p)/Si_o) between 1.0 and 2.5, Al/Si ratios < 1 which can occur in allophane (Parfitt & Kimble, 1989) were used in this research. Phosphate retention (P-retention) as a diagnostic criterion of andic soil properties (≥ 85%; IUSS Working Group WRB, 2015; Papers II and III) and the pH in 1N NaF solution (pH_{NaF}) as an indicator of amorphous material ($pH_{NaF} \geq 9.4$) was determined following Blakemore et al. (1987).

2.3.5 Complementary Soil Properties (All Three Papers if not otherwise indicated)

The DBD of the soils and field water content was determined by mass loss after drying of a known soil volume. Content of OM and inorganic material (%Ash) was measured by loss on ignition at 550 °C (Heiri et al., 2001). Soil acidity was measured in deionised water (pH_{H2O}) using a soil:water ratio of 1:10 (Blakemore et al., 1987; Rayment & Lyons, 2011). Based on DBD and %C, C density (kg m^{-3}) was calculated for each depth interval in **Papers II and III**. For **Paper I**, contents of nitrite (NO_2^-), nitrate (NO_3^-) (Shand et al., 2008) and ammonium (NH_4^+) (Nelson, 1983) were determined spectrophotometrically using a

GENESYS 10S Series UV - Visible Spectrophotometer and 2 M KCl soil extracts (Blakemore et al., 1987; Carter & Gregorich, 2007) of an air-dried soil:liquid ratio of 1:10.

2.3.6 Statistical Data Evaluations

Differences in soil mineralization between soil horizons and between temperatures (**Paper I**) were evaluated by one-way ANOVA, and Tukey's HSD test (R package Agricolae; De Mendiburu, 2020; Quinn & Keough, 2002), using an alpha level of 0.05. Relationships between C mineralization and selected indicators of C structure (**Paper I**) were determined by exponential regression, which were chosen based on the comparison of Akaike information criteria corrected for small sample size (AICc; Burnham & Anderson, 2004).

Variations in vegetation characteristics between peatlands (**Paper III**) were analysed by non-metric multidimensional scaling (NMDS; function metaMDS, R package vegan; Oksanen et al., 2019; Podani, 2006) after recoding the categories of the Braun-Blanquet cover scale (0, r, +, 1, 2, 3, 4, 5; Dombois & Ellenberg, 1974) according to van der Maarel (0, 1, 2, 3, 5, 7, 8, 9; van der Maarel, 1966 in Camiz et al., 2017).

Variations in C structure (**Papers II** and **III**) as reflected by the six ^{13}C NMR chemical shift regions and the A:O/N and (70–75)/(52–57) ratio, and variations in andic soil properties, were investigated by robust principal component analysis (PCA) for compositional data (function pcaCoDa, R package robCompositions; Filzmoser et al., 2009; Filzmoser et al., 2018) and hierarchical clustering (R package factoextra, function eclust; Kassambara, 2017).

In order to investigate the impact of variations in andic soil properties on variations in C structure (**Papers II** and **III**), redundancy analysis (RDA; R package vegan; Oksanen et al., 2019) was conducted. The influence of andic properties and C structure on decomposition proxies (C/N, δ^{13}C, δ^{15}N; **Papers II** and **III**) was also investigated by RDA. Spearman rank correlations (**Paper II**) and Pearson correlations (**Paper III**) were conducted in order to evaluate if there is a relationship between %C, %Ash, DBD, and C density (R package GGally, function ggpairs; Quinn & Keough, 2002; Schloerke, 2021). All statistical analyses were carried out using the software R, versions 3.5.2 (**Paper I**) and 4.0.2 (**Papers II** and **III**).

3 Results

In following chapters, the results of the three papers will be summarized. First, an overview of the pattern of the vegetation characteristics and the pedogenic environment at each of the three peatlands is given. Then, interrelations between different sets of variables are described.

3.1 Vegetation Characteristics (Paper III)

Despite having several species in common, vegetation characteristics show distinct differences between the sites. In particular, Torfdalsmýri differs in its plant composition from the other two sites, while Tindar and Hrafnabjörg bear more resemblance to each other. At Torfdalsmýri, the vegetation is dominated by *Eriophorum angustifolium,* and resembles the habitat type of *D2.26 Common cotton-grass fens* following the European Nature Information System (EUNIS; EEA, 2019; Ottósson et al., 2016). At Tindar, *Carex nigra* is the most dominant species, while various flowering plants and dwarf shrubs are also common, e.g. *Betula nana*, *Empetrum nigrum* and *Vaccinium uliginosum*. The vegetation composition at this site is similar to two habitat types, i.e. *D3.162 Boreal black sedge-brown moss fens* and *D4.163 Icelandic black sedge-brown moss fens*. At Hrafnabjörg, vegetation is most similar to the habitat type *D2.332 Basicline bottle sedge quaking mires*, with *Carex rostrata* clearly dominating, while *Equisetum palustre, Vaccinium uliginosum* and *Betula nana* are also common.

3.2 The Pedogenic Environment of the Sites (Papers I, II, III)

3.2.1 Total %C, %Ash, DBD, Carbon Density, and Carbon Stocks

On average, all sites meet the ≥ 20% C criterion of Histosols (IUSS Working Group WRB, 2015). However, at Tindar and Hrafnabjörg, the criterion is not fulfilled by several surface soil samples (0-30 cm), particularly in the upper 0-5 cm of soils.

Surface Soils (**Paper III**)

In surface soils, total %C contents are on average highest at Torfdalsmýri, and lowest in Hrafnabjörg, except for 15-30 cm depth, in which average %C are slightly lower at Tindar than at Hrafnabjörg. The ranges and means ($\overline{x}$) of %C contents within the upper 30 cm are as follows: 21-41%, $\overline{x}$ = 31% at Torfdalsmýri, 17-35%, $\overline{x}$ = 26% at Tindar and 14 – 34 %, $\overline{x}$ = 24% at Hrafnabjörg. The total mineral content (%Ash) in surface soils draws a pattern opposite to %C. Average DBD is rather similar in surface soil at all sites and relatively stable with depth, except for a noticeable increase at 15-30 cm depth at Tindar. Ranges are as follows: 0.12-0.34 g cm^{-3}, $\overline{x}$ = 0.18 g cm^{-3} at Torfdalsmýri, 0.11-0.34 g cm^{-3},

$\overline{x}$ = 0.21 g cm^{-3} at Tindar and 0.08 – 0.33 g cm^{-3}, $\overline{x}$ = 0.19 g cm^{-3} at Hrafnabjörg. The C density, just as %C, is overall highest at Torfdalsmýri and lowest at Hrafnabjörg, and increases with depth at all three sites.

Subsoils (**Paper II**)

In subsoils, %C is overall greater at Tindar and Hrafnabjörg than at Torfdalsmýri. In particular, between the tephra deposits of Hekla 3 and Hekla 4, the two sites experience elevated %C, with values > 40% being most common. Torfdalsmýri, on the other hand, experiences a drop in %C above Hekla 4. Above the Hekla 3 deposit, %C decrease at all sites, with values < 30% frequently observed. At Torfdalsmýri, %C recovers eventually towards values as high as 40% in the upper 20 cm. Content of %Ash in subsoils describes an opposite trend to %C. Overall, DBD is low until shortly after Hekla 3 at Tindar and Hrafnabjörg, above which it increases slightly. At Torfdalsmýri, DBD experiences a noticeable peak between the two tephra deposits. Generally, DBD at Torfdalsmýri is considerably greater than at the other two sites, with values well above 0.2 g cm^{-3} frequently observed. This translates into overall highest C density at Torfdalsmýri, and a more uniform development of C density than %C at Tindar and Hrafnabjörg. Despite Torfdalsmýri revealing the greatest C densities, total C stocks that accumulated since the Hekla 4 eruption are with 560 and 557 t ha^{-1} notably higher at Tindar and Hrafnabjörg, respectively, than at Torfdalsmýri (361 t ha^{-1}). This is a result of elevated soil accumulation during that period at Tindar and Hrafnabjörg, where 113 cm and 121 cm of soil accumulated, respectively, compared to 50 cm at Torfdalsmýri.

3.2.2 Decomposition Proxies C/N Ratio, $\delta^{13}C$ and $\delta^{15}N$

The C/N ratio is very stable throughout the soil profile at Torfdalsmýri, with values fluctuating between 19 and 22. At Tindar and Hrafnabjörg, C/N ratios increase with depth and are noticeably higher below Hekla 4 than above, particularly at Hrafnabjörg where values as high as 33 are reached (**Paper II**). In surface soils (**Paper III**) C/N ratios are on average lowest at Torfdalsmýri and very alike at Tindar and Hrafnabjörg. Stable isotope ratios $\delta^{13}C$ are rather stable with depth in soil layers above Hekla 3 at Torfdalsmýri, whereas in soil layers below Hekla 3, they decrease (**Paper II**). At Tindar, $\delta^{13}C$ increases down to Hekla 3, but slightly decreases again thereafter. At Hrafnabjörg, $\delta^{13}C$ fluctuate, only experiencing an increasing trend below Hekla 4. Stable isotope ratios $\delta^{15}N$ experience a clear peak between the two tephra layers at Torfdalsmýri, and are generally highest at the coastal site. At Tindar and Hrafnabjörg, $\delta^{15}N$ decrease with depth.

3.2.3 Carbon Structure by ^{13}C NMR Spectroscopy

The C structure was determined by ^{13}C NMR spectroscopy for each paper. In **Paper I** and **Paper II**, it was measured for all soil samples (compare subchapter "2.2 Soil Sampling and Vegetation Analysis"). For **Paper III**, C structure was only determined for soil samples of transect *b* (Figure 2.4).

Generally, C structure at Torfdalsmýri differs from the more comparable C structure of Tindar and Hrafnabjörg, particularly in subsoils (**Papers I and II**). Overall, the C structure at Torfdalsmýri is characterized by C groups reflective of more degraded material. The A:O/N ratios are relatively high, facilitated by a high share of alkyl C and comparatively low O/N alkyl C contents. The (70-75)/(52-57) ratios are relatively low in most subsoil layers at

Torfdalsmýri in **Paper II**, particularly in comparison with Hrafnabjörg. In subsoil layers of **Paper I**, however, all sites show relatively similar (70-75)/(52-57) ratios in the soil horizons formed above and below Hekla 4. The C structure at Tindar and Hrafnabjörg is generally indicative of relatively less degraded material than at Torfdalsmýri as reflected by a higher share of O/N alkyl C at the expense of akyl C, which translates into comparatively low A:O/N ratios.

In the younger surface soils, the differences between sites are very pronounced in **Paper I** and similar as described for subsoils in the previous paragraphs. In **Papers II and III**, however, the differences between the sites are subtler. There, the C structure of the surface layers (0-5 cm) is similar at all sites, with a characteristic predominance of O/N alkyl C over alkyl C, leading to low A:O/N ratios, and accompanied by high (70-75)/(52-57) ratios. Toward deeper soil layers (5-15 cm and 15-30 cm in **Paper III**), there is a relative increase of alkyl C at the expense of O/N alkyl carbon, which is responsible for an increase of A:O/N ratios with depth. At the same time, (70-75)/(52-57) ratios are decreasing. Other C groups than alkyl C and O/N alkyl C do not show as clear a pattern with depth. The relative increase of alkyl C at the relative expense of O/N alkyl carbon and accompanied increase of A:O/N ratios with depth is more pronounced at Torfdalsmýri than at Tindar and Hrafnabjörg.

3.2.4 Andic Soil Properties

In **Paper I**, andic soil properties were not included, but results of dissolution for soil samples used in **Paper I** are available in Figure 3.1. The findings of **Paper I** will be discussed in the context of these results in this thesis.

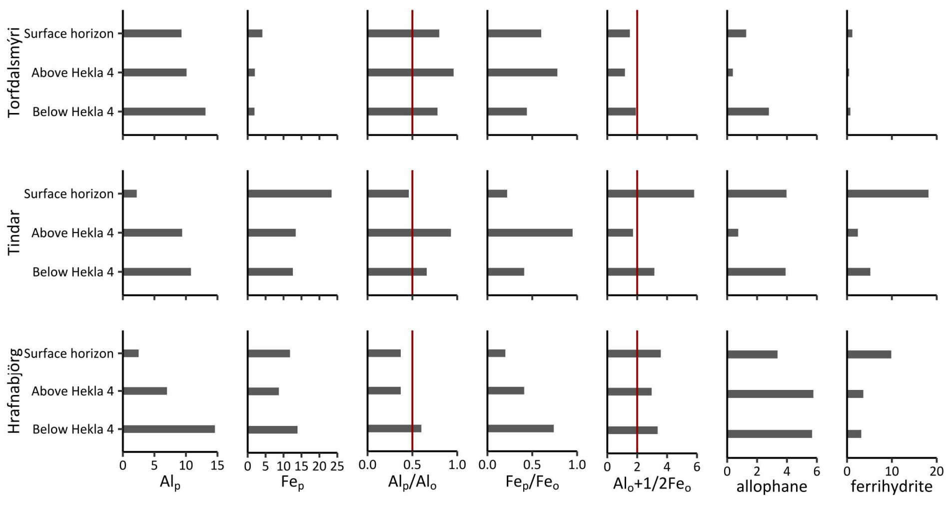

Figure 3.1: Variables based on selective dissolutions of Al, Fe and Si of soil samples used in Paper I. Al_p and Fe_p, are presented as g kg_{soil}^{-1}, Al_o+1/2Fe_o, allophane and ferrihydrite are presented in %. Vertical red lines represent the following thresholds: $Al_p/Al_o = 0.5$ as demarcation of allophanic and non-allophanic Andosols (0.1-<0.5 → allophanic Andosols; 0.5-1.0 → nonallophanic Andosols), $Al_o+1/2Fe_o \geq 2\%$ as diagnostic criterion of andic soil properties.

Overall, andic soil properties are stronger at Tindar and Hrafnabjörg than at Torfdalsmýri (**Papers II and III**), both in surface soils and in subsoils. This is particularly manifested by comparatively high levels of allophane in conjuction with low Al_p/Al_o ratios and $Al_o + ½Fe_o$ values, several of them fulfilling the ≥2% diagnostic criterion of andic soil properties (IUSS Working Group WRB, 2015). Ferrihydrite contents are also comparatively high at the two sites, with increasing values toward younger soil layers above Hekla 3, particularly at Hrafnabjörg. Interestingly, the tephra deposits again form demarcation lines, inducing a shift in andic soil properties. At both Tindar and Hrafnabjörg, the soil layers formed between the tephra deposits of Hekla 4 and Hekla 3 form a clear subcluster characterized by a sharp decrease in andic properties, i.e. low allophane and ferrihydrite contents, high Al_p/Al_o ratios and $Al_o + ½Fe_o$ values < 2%. Note that Al_p/Al_o and Fe_p/Fe_o ratios are > 1 in several instances, which might be due to an overestimation of Al_p and Fe_p and/or an underestimation of Al_o and Fe_o (e.g. Childs, 1985; Mizota & van Reeuwijk, 1989). P-retention was above the 85% criterion of andic soil properties (IUSS Working Group WRB, 2015) in most subsoil (**Paper II**) and surface soil samples (**Paper III**), with exception of a few samples at Torfdalsmýri and Tindar showing values < 85%. Only few surface and subsoil samples reached the threshold of $pH_{NaF} \geq 9.4$ (IUSS Working Group WRB, 2015).

3.3 Relation Between Vegetation Composition and Carbon Characteristics (Paper III)

At first glance, differences in vegetation characteristics between sites seem to be reflected in patterns of C structure. Both sets of data clearly show that Tindar and Hrafnabjörg bear more resemblance to each other than Torfdalsmýri. Nevertheless, C characteristics of the upper 0-5 cm of soils at Torfdalsmýri share more common characteristics with Tindar and Hrafnabjörg than vegetation characteristics imply. At all sites, these very youngest soil layers are characterized by comparatively high contents of labile O/N alkyl C and a relatively small share of the more recalcitrant alkyl C. Only in the deeper soil layers (5-15 cm and 15-30 cm) do C characteristics at Torfdalsmýri become more distinct, due to a quicker shift towards a greater share of alkyl C and higher A:O/N ratios than observed at Tindar and Hrafnabjörg.

3.4 Effect of Distinct Tephra Deposits on Carbon Dynamics

3.4.1 Carbon Structure around Tephra Deposits

There are several interesting patterns in C structure adjacent to distinct tephra deposits (**Papers I and II**). Firstly, the C structure of the very oldest soil layers below Hekla 4 at Hrafnbjörg and Tindar (**Paper II**) is conspicuously similar to the C structure of upper and much younger soil layers, i.e. 0-40 cm at Tindar and 0-10 Hrafnabjörg. Second, there is a clear change in C structure after the deposition of the Hekla 4 tephra, particularly at Tindar and Hrafnabjörg (this is particularly clear in **Paper II**, but also indicated in **Paper I**). This shift is characterized by a decrease in the (70–75)/(52–57) ratios above the tephra deposit, an increase in alkyl C, and a decrease in O/N-alkyl C, leading to elevated A:O/N ratios.

Third, at Tindar, the Hekla 3 tephra (**Paper II**) seems to induce another shift in C structure, again towards lower A:O/N ratios facilitated by a decrease in alkyl C, and an increase in O/N-alkyl C. At this lowland site, the soil layers formed between the two tephra deposits form a clear subcluster.

3.4.2 Carbon Stability (Paper I)

Overall, C mineralization rates increase toward the highlands and the active volcanic zones, and decrease with soil depth. The lowest rates come from the soil horizons of the costal peatland of Torfdalsmýri, but the difference compared to the other two sites is particularly manifest in the surface horizon. There are only minor differences in C mineralization of the surface horizon at Tindar and Hrafnabjörg, while a more variable pattern is drawn by the horizons above and below Hekla 4. The most prominent difference in C mineralization between Tindar and Hrafnabjörg appears in the soil horizon below Hekla 4. There, C mineralization rates are approximately twice as high at Tindar than at Hrafnabjörg at all temperatures ($p = 0.012$ at 5 °C, $p < .001$ at 15 and 25 °C). At 15 and 25°C, C mineralization rates from the layer above Hekla 4 at Tindar exceed those at Hrafnabjörg slightly. At 5 °C the contrary is the case.

Differences in C mineralization of soil horizons above and below Hekla 4 vary between sites and temperatures. At Torfdalsmýri and Hrafnabjörg, there is no difference in emissions from the two layers at 5 °C, but at 15 and 25 °C, C emissions are moderately higher from the layers above Hekla 4. At Tindar, C emissions from below Hekla 4 at 5 °C and 25 °C are clearly greater than from above ($p < 0.001$), but differences are insignificant at 15 °C ($p = 0.255$). The $Q_{10}15/5$ decrease with time of the experiment, whereas $Q_{10}25/15$ are more stable. While $Q_{10}15/5$ values of the surface horizon and below Hekla 4 are alike towards the latter stages of the experiment, $Q_{10}15/5$ values above Hekla 4 are consistently higher than those of the other layers, particularly at Tindar where a $Q_{10}15/5$ value as high as 5.3 is detected after 400 days of C mineralization.

3.5 Relationship Between Andic Soil Properties and Carbon Characteristics

In surface soils (**Paper III**), a rather strong relationship between andic soil properties (explanatory data matrix) and C structure (dependent variables) is indicated by RDA (unadjusted $r^2 = 0.65$, adjusted $r^2 = 0.49$). Alkyl C shows a positive relationship to the ratios Fe_p/Fe_o, Al_p/Al_o, and content of Al_p and Al_o. The latter two also show a positive relationship with A:O/N ratios. Ferrihydrite, $Al_o + ½Fe_o$ and Fe_p appear negatively related to alkyl C and A:O/N ratios, but positively to O/N alkyl. Allophane and Si_o content are negatively related to Alkyl C, but positively related to carboxyl/carbonyl/amide C, O/C-aryl C and C/H-aryl C. At large, similar relationships between mineral soil constituents and C groups are detected in subsoils (**Paper II**). However, the share of the variation of C structure, which is constrained by andic soil properties is lower in subsoils (unadjusted $r^2 = 0.41$, adjusted $r^2 = 0.29$). In both cases, only the effect of the first dimension proved statistically significant ($p = 0.001$), but a share as high as 73% (subsoils) and 75% (surface soils) of constrained variance was described by the first dimension.

Decomposition proxies C/N, $\delta^{13}C$, and $\delta^{15}N$ are less constrained by andic soil properties than the C structure in surface soils (**Paper III**, unadjusted r^2 = 0.49, adjusted r^2 = 0.26), particularly as again only the effect of the first dimension proved statistically significant. Nevertheless, a positive relationship between content of Si_o, Fe_p, allophane, ferrihydrite and Al_o+ ½Fe_o, with C/N ratio is indicated. The same variables do not seem to affect $\delta^{13}C$, but have a slight negative impact on $\delta^{15}N$. In **Paper II**, there was no significant relationship between andic soil properties and decomposition proxies.

3.6 Relationship Between Content of Mineral Soil Constituents and Absolute Carbon Storage

Both in surface soils of **Paper III** and subsoil dominated samples of **Paper II**, relative contents of mineral soil constituents (%Ash) have no effect on absolute C storage per volume increment of soil (C density) as shown by low and insignificant correlation coefficients of Pearson (**Paper III**) and Spearman rank correlations (**Paper II**). The lack of a relationship between %Ash and C density despite a significant negative effect of %Ash on relative C contents (%C) may be explained by a relatively strong positive relationship between %Ash and DBD and between DBD and C density.

4 Discussion

4.1 Carbon dynamics Partly Governed by Vegetation and Carbon characteristics

In a very broad sense, differences in vegetation characteristics between sites (**Paper III**) are reflected by the pattern of C structure. The C structure of surface soils (particularly **Paper III,** but also **Papers I** and **II**) and subsoils (**Papers I and II)** at Tindar and Hrafnabjörg is more alike than compared with Torfdalsmýri. Likewise, vegetation characteristics at Tindar and Hrafnabjörg bear more resemblance to each other than compared with Torfdalsmýri (**Paper III**). Evidently, vegetation characteristics influence C characteristics and C dynamics in the peatlands of this study, similar as has been observed in previous research (e.g. Leifeld et al., 2012; Loisel & Bunsen, 2020; Malmer & Wallén, 2004). Overall, the C structure at Torfdalsmýri is characterized by C groups indicative of more degraded material, with a comparatively large share of alkyl C at the expense of O/N-alkyl C. This is reflected by lower C mineralization rates at this site.

Importantly, of all soil layers it is the majority of the very youngest surface soils (0-5 cm, **Paper III**, but see **Paper I**) at Torfalsmýri, which share more common characteristics in C structure with corresponding layers at Tindar and Hrafnabjörg than differences in vegetation characteristics would imply. At all three peatlands, the C structure of these young soil layers is characterized by comparatively high contents of labile O/N alkyl C and a relatively small share of more recalcitrant alkyl C. Only in the deeper layers of the surface tier (5-15 cm and 15-30 cm) and the subsoil layers (**Paper I** and **II**) does C structure at Torfdalsmýri become more distinct. The expected shift towards more recalcitrant C groups with depth (Leifeld et al., 2012; Tfaily et al., 2014), reflective of more decomposed OM, is quicker at Torfdalsmýri than at the other two sites. One possible explanation might be differences in the prevalence of *Sphagnum* mosses between the sites. *Sphagnum* derived phenolic compounds have frequently been observed to inhibit decomposition through several pathways; for instance by suppressing microbial activity (Freeman et al., 2001; Zhao et al., 2021), but also by enhancing the formation of Fe-mineral complexes and by quenching degrading radicals such as •OH. As bryophytes were not determined at species level in this study, strong conclusions cannot be drawn here. However, **Paper III** reveals that bryophytes in general, including *Sphagnum* mosses, are more dominant at Tindar and Hrafnabjörg. Hence, it is possible that the comparative lack of *Sphagnum* derived phenolic compounds at Torfdalsmýri enhances decomposition processes there. Indeed, Torfdalsmýri shows a slightly smaller share of phenolic compounds (160-140 ppm) than the other two sites, particularly in surface soils (**Paper III**), but also in many subsoil layers (**Paper II**). The share of phenolics ranges between ca. 4% and 7% in all soil samples, though, and it is likely that this small relative difference in contents of these C compounds can only partially be held responsible for differences in C dynamics.

Exponential regressions between accumulated C mineralization after 400 days of incubation, and chosen C groups derived from the ^{13}C NMR spectra, and ratios based thereupon, indicate similar patterns as indicated by research elsewhere (**Paper I**). For instance, this study corroborates observations by Leifeld et al. (2012) and Preston et al. (1987) that certain labile C groups, such as O/N-alkyl C, and more specifically polysaccharides, are particularly sensitive to biodegradation, and therefore positively related to C mineralization. As described by Bonanomi et al. (2013), this study finds that (70-75)/(52-57) ratios are a good predictor of decay rates, with higher C mineralization found in soils with high (70-75)/(52-57) ratios. The negative relationship between A:O/N ratios and C mineralization is in agreement with e.g. Baldock et al. (1997), that higher A:O/N ratios are indicative of more advanced decomposition, and hence, more recalcitrant OM. Hence, C mineralization at Tindar and Hrafnabjörg is noticeably higher than at Torfdalsmýri, at least partly arising from a higher share of labile C groups, and a comparatively small share of more recalcitrant C such as alkyl C (e.g. Dungait et al., 2012; Preston et al., 1989), leading to low A:O/N ratios and high (70-75)/(52-57) ratios.

While the chemical composition of the C is one driving factor of C stability and the C mineralization of the Histosols in this study, there are suspicious irregularities and outliers in C mineralization, which are not explained by C structure. For instance, mineralization rates in the soil horizon below Hekla 4 at Tindar are higher than that of all other subsoil layers at Tindar and Hrafnabjörg, despite only minor differences in C structure. Evidently, C stability in these soil horizons is not only driven by the chemical composition of the C.

4.2 Evidence for the Impact of Mineral Soil Constituents on Carbon Dynamics

In the following subchapters, evidence for factors other than vegetation shaping C characteristics, and for factors other than C characteristics alone being responsible for the stability of the C in the peatlands will be discussed. The results indicate that the C dynamics of the peatlands of this study are affected by the mineral soil constituents, in form of distinct tephra layers and pedogenic minerals derived from inorganic material (such as aeolian dust fluxes from eroding and sparsely vegetated or barren drylands; e.g. Arnalds, Dagsson-Waldhauserova, et al., 2016; Dugmore et al., 2009). Most likely there are differing stabilization and decomposition processes taking place at the three sites. Presumably, this causes the OM in subsoils at Torfdalsmýri to be more decomposed and to hold more recalcitrant C compounds than at Tindar and Hrafnabjörg. Differences in stabilization processes likely also explain conspicuous fluctuations in C structure with depth within sites; also, they are probably responsible for the notable differences in C mineralization rates and differences in temperature sensitivity of C mineralization between subsoils at Tindar and Hrafnabjörg. Tephra layers are accompanied by a shift in C structure and seem to alter the temperature sensitivity of decomposition

4.2.1 Effect of Tephra Deposits on Carbon Mineralization

Torfdalsmýri experiences lower C mineralization (**Paper I**) in its subsoils compared with those of Tindar and Hrafnabjörg, readily explained by differences in C structure (e.g. Leifeld et al., 2012) but C mineralization also differs between the subsoil layers of Tindar and Hrafnabjörg. For example, the C emissions of the soil horizon below Hekla 4 at Tindar clearly exceed that of all other subsoil layers at Tindar and Hrafnabjörg. Furthermore,

$Q_{10}15/5$ values of the soil horizon above Hekla 4 are consistently higher than those of the other layers, particularly at Tindar, indicating greater sensitivity to temperature changes. These patterns cannot be explained by differences in C structure. Contrary to a shift in C structure observed around the Hekla 4 tephra in soil cores of **Paper II**, no noteworthy shift in C structure is indicated by the ^{13}C NMR spectra in this part of the study (**Paper I**). However, there are shifts in other soil properties around the tephra layer which are indicative of instabilities in the pedogenic environment. At both sites, DBD increases, and OM decreases. At Hrafnabjörg, %C also decreases considerably (from 33% before the eruption to 16% after the eruption), but at Tindar %C increases (from 37% to 42%). This leads to an intriguing change in OM/C ratio at the two sites. While the ratio increases from 1.45 to 2.00 at Hrafnabjörg, it decreases from 1.64 to 1.18 at Tindar. Strong conclusions about potential vegetation changes cannot be drawn based on OM/C ratios as there is no information available about these values for Icelandic Histosols. However, research elsewhere (Klingenfuß et al., 2014; Pribyl, 2010) shows that OM/C ratios are not least shaped by substrate, i.e. they are an indicator of vegetation characteristics and decomposition. In a study on German peatlands, Klingenfuß et al. (2014) found higher OM/C ratios in *Sphagnum* peat (2.05 ± 0.09) than in vascular plant derived peat (1.73 ± 0.09). The OM/C ratio in the soil horizon above Hekla 4 at Hrafnabjörg is in line with that of *Sphagnum* peat by Klingenfuß et al. (2014). Given that this indicates an increase in the prevalence of *Sphagnum* mosses at this site after the volcanic eruption, one might expect indicators of decomposition such as A:O/N ratios and (70-75)/(52-57) ratios to reflect that too. As described above, *Sphagnum* derived phenolic compounds have frequently been observed to inhibit decomposition through several pathways, such as by suppressing microbial activity (Freeman et al., 2001; Zhao et al., 2021), but also by enhancing the formation of Fe-mineral complexes and by quenching degrading radicals such as $^{\bullet}OH$. However, decomposition proxies are not supportive of a decreased breakdown of OM above Hekla 4 at Hrafnabjörg. Moreover, ^{13}C NMR spectra do not show an elevated share of phenolic compounds in that horizon. Summarized, this confirms evidence of previous studies (e.g. Moinet et al., 2018) that C stability, and the temperature sensitivity of decomposition, is not only a function of intrinsic characteristics of the OM itself, but also dependent on substrate availability.

4.2.2 Impact of Andic Soil Properties on Carbon Stability

As described, Histosols in Iceland often develop andic properties (e.g. Bonatotzky et al., 2019) due to the intermixture of inorganic aeolian material of volcanic origin. In **Paper I**, andic soil properties were not investigated, but it was hypothesized that the mineral constituents in the Histosols might facilitate the formation of minerals like allophane and ferrihydrite, leading to abundant precipitation of free Al and Fe and hence, promote the physical protection of C through the formation of organo-mineral and Fe/Al-humus complexes (e.g. Kögel-Knabner & Amelung, 2021; Kögel-Knabner et al., 2008; Mikutta et al., 2006; Takahashi, 2020). Differences in the predominance of andic soil properties might then explain the observed pattern in C mineralization (Moinet et al., 2018). Consequently, the C in the subsoil horizons at Hrafnabjörg, with its lower C mineralization, should physically be better protected than at Tindar. Also, the horizons above Hekla 4 at Tindar and Hrafnabjörg should be less protected by mineral constituents than the horizons below Hekla 4, explaining the elevated $Q_{10}15/5$ values, particularly at Tindar.

Data on selected dissolutions of Al, Fe and Si (Figure 3.1) indicate that differences in abundances of mineral phases between the subsoil horizons may contribute to the observed irregularities in C mineralization. First, the horizon above Hekla 4 at Tindar is the only subsoil horizon which does not fulfil the diagnostic threshold of andic soil properties of $Al_o + 1/2Fe_o \geq 2\%$ (IUSS Working Group WRB, 2015) with low allophane and ferrihydrite content and low levels of Al_p and Fe_p, both indicative of limited amounts of organically bound Al and Fe. In light of a recent study by Moinet et al. (2018) which observed a significant decrease in the temperature sensitivity of OM decomposition upon adding allophane to soils, the very low allophane content at Tindar above Hekla 4 (< 1% allophane) deserves attention. At Hrafnabjörg, allophane and ferrihydrite content above and below Hekla 4 are comparable (> 5% and > 3%, respectively), but Al_p and Fe_p are higher in the horizon below the tephra layer. Generally, the horizons below Hekla 4 at Tindar and Hrafnabjörg show clear andic soil properties. However, that Al_p and Fe_p is higher at Hrafnabjörg may indicate that more C is stabilized in Al/Fe-humus complexes there (Takahashi, 2020) and possibly explains why C emissions are lower than from the corresponding horizon at Tindar. Furthermore, the bonding of C to mineral soil constituents is a function of factors other than the mere presence of mineral constituents. The pH_{H2O} is comparatively low below Hekla 4 at Hrafnabjörg (4.8 in contrast to 5.1 at Tindar), and the formation of Al-humus complexes predominantly occurs at pH <5 (e.g. Adams et al., 2000; Shoji & Fujiwara, 1984). The C/N ratio has also been shown to affect the stabilization of OM by organo-mineral complexes, but a recent study by Kopittke et al. (2020) observed a low C/N ratio to facilitate the complexation of organic free minerals with OM. This might serve as another explanation for the higher C mineralization rates below Hekla 4 at Tindar, which reveals a comparatively high C/N ratio (24).

4.2.3 Shifts in Carbon Structure Coincide with Tephra Layers

Contrary to our observations in **Paper I**, several variations in C structure, which are likely shaped by tephra deposits were detected in **Paper II**. At first, decomposition unsurprisingly increases with depth at the three peatlands (Leifeld et al., 2012; Malmer & Holm, 1984; Preston et al., 1987; Tfaily et al., 2014), as indicated by a relative increase of recalcitrant C forms toward deeper soil layers. The share of alkyl C increases at the relative expense of O/N-alkyl C, leading to increasing A:O/N ratios (Baldock et al., 1997; Preston et al., 1989). At the same time, (70-75)/(52-55) ratios follow a decreasing trend with depth. However, there is a shift in C structure around the Hekla 4 tephra deposit at all sites, but in soil layers below Hekla 4 the trend of C structure indicative of increasing decomposition is reversed (**Paper II**). This is particularly prominent at Tindar and Hrafnabjörg, where the C structure of the very oldest soil layers below Hekla 4 is conspicuously similar to that of much younger, and rather undecomposed surface soil layers, characterized by a surprisingly small share of recalcitrant alkyl C and a high share of more labile O/N alkyl C. While a reversal from increasing decomposition with depth toward decreasing decomposition at greater depth has been observed in previous studies (e.g. Preston et al., 1987), the co-occurrence of the shift in C structure with the Hekla 4 tephra layer is salient.

Several interacting trajectories are conceivable here. First, the similarity of the C structure of the oldest subsoils and the young surface soils at Hrafnabjörg and Tindar may indicate that other factors of the pedogenic environment than the chemical composition of the C are shaping its decomposition and stability. As for instance observed by De Vleeschouwer et al. (2008), tephra deposits may function as a physical barrier. Such barriers can impede the vertical movement of water within the peat column and hinder the input of fresh OM (both in the form of litter during the years following eruption, and as DOC derived from upper soil layers), and thereby hamper microbial activity. Such a trajectory is in agreement with observations made during field work, but the compacted Hekla 4 tephra deposits clearly showed limited permeability. Second, the shift in C structure might also reflect a shift in vegetation characteristics at the peatlands induced by or coinciding with the tephra deposit, rather than being solely indicative of different stages of decomposition. Shifts in vegetation composition serving as parent material of Histosols may be induced by environmental factors such as climate change and/or the deposition of tephra from volcanic eruptions (Blackford et al., 2014; Eddudóttir et al., 2017, 2020; Hughes et al., 2013; Loisel & Bunsen, 2020). Palaeoenvironmental studies on lake sediments derived in relatively close proximity to the peatlands of this study (Eddudóttir et al., 2017, 2020; Eddudóttir et al., 2016) show that the Hekla 4 tephra might have indeed induced some moderate changes in vegetation composition, which may then explain the sudden shift in C structure. Deteriorating climatic conditions could explain why the peatland vegetation was not as resistant to tephra fall of moderate extent as described for instance by Hotes et al. (2006). The Hekla 4 tephra deposit does coincide with an episode of cooling (e.g. Eddudóttir et al., 2016; Geirsdóttir et al., 2013; Larsen et al., 2012).

Evidently, the Hekla 3 tephra deposit does not serve as a physical barrier in the same way as the Hekla 4 tephra deposit at the peatlands of this study. The thickness of Hekla 3 is less than the thickness of Hekla 4 at all sites, and Hekla 3 was not observed to be as impermeable as Hekla 4. Nevertheless, while being less prominent than the Hekla 4 tephra layer, the Hekla 3 tephra also coincides with some variations in C structure. At Tindar, the soil layers between Hekla 4 and Hekla 3 form a clear sub-cluster with regard to C structure. At Hrafnabjörg, there are also indications of subcluster formation between the tephra layers, however this is less clear than at Tindar, due to a subtler shift in C structure around Hekla 3 at this site. Overall, the soils between tephra deposits at Tindar and Hrafnabjörg reflect very stable conditions, and there is hardly any change in C structure with time and depth between Hekla 3 and Hekla 4.

4.3 Interactions Between Andic Soil Properties and Carbon Characteristics

Distinct tephra deposits are not the only mineral constituents in the pedons of this study that can affect C characteristics. Aeolian inorganic material derived from eroding drylands (e.g. Arnalds, Dagsson-Waldhauserova, et al., 2016; Dugmore et al., 2009) and pedogenic minerals formed thereof (Bonatotzky et al., 2021; Nanzyo et al., 1993; Shoji et al., 1993; Wada, 1989) also play a role. The geographical location of the three peatlands (Figure 2.1) with respect to major source areas of inorganic aeolian material is well reflected by the differing prevalence of mineral soil constituents in general, and andic soil properties in particular. Tindar and Hrafnabjörg, which are closer to the aeolian dust sources, contain more %Ash and less %C in the upper soil layers (**Papers II** and **III**) than the more distant Torfdalsmýri. This is reflected by more pronounced andic soil properties, such as higher contents of allophane and ferrihydrite, lower Al_p/Al_o ratios, and a sum of $Al_o+½Fe_o$ frequently ≥ 2.

By means of RDA analyses (**Paper II** and **Paper III**), this study indicates that C structure is partly constrained by andic soil properties. The most notable pattern is that non-allophanic Histosols, with low ferrihydrite content, high Al_p/Al_o and Fe_p/Fe_o ratios (compare t.d. Mizota

& van Reeuwijk, 1989) are characterized by C structure indicative of more degraded or recalcitrant material (i.e. comparatively high alkyl C contents and high A:O/N ratios). High contents of ferrihydrite are associated with C groups indicative of undecomposed material, reflected by high O/N alkyl contents and high ratios of (70-75)/(52-57). Allophane and Si_o are positively related to carboxyl/carbonyl/amide C and H/C-aryl C. While broadly the same pattern is observed in **Paper II** and **Paper III**, it is notably stronger in **Paper III**, which investigates surface soils only. The RDA between andic soil properties as an explanatory data matrix and C structure as dependent data matrix in **Paper II** reveals an adjusted $r^2 = 0.29$, compared with the adjusted $r^2 = 0.49$ in **Paper III**. This difference is likely due to increasing contents of mineral material and a stronger prevalence of andic soil properties at a shallower soil depth (see also **Paper II**); a consequence of increased mineral transport of volcanic origin into the peatlands after the expansion of barren and eroding areas after the settlement (Arnalds, Dagsson-Waldhauserova, et al., 2016; Dugmore et al., 2009; Gísladóttir et al., 2011; Gísladóttir et al., 2010). This, in conjunction with better oxygenation (Chesworth et al., 2006; Vaughan et al., 2009), probably facilitates the development of stronger andic properties in surface soils of peatlands than in subsoils, explaining the elevated contents of allophane and ferrihydrite (Dahlgren et al., 1993).

The increased aeolian redistribution of mineral material after the settlement probably also explains why a significant effect (adjusted $r^2 = 0.26$) of andic soil properties on the decomposition proxies C/N ratio, $\delta^{13}C$ and $\delta^{15}N$ was found in the surface soils examined in **Paper III**. There, a positive relationship between ferrihydrite, allophane and $Al_o+½Fe_o$ and C/N ratios was found, while the same variables were negatively related to $\delta^{15}N$. In contrast, in **Paper II**, which is mainly based on pre-settlement subsoils, C/N ratio, $\delta^{13}C$ and $\delta^{15}N$ were not constrained by andic soil properties (adjusted $r^2 = 0.01$, $p_{model} = 0.553$).

4.4 Impact of Mineral Aeolian Deposits on Absolute Carbon Storage (Papers II and III)

While the relative C contents in this research are well below the averages of 46-51% reported for northern peatlands by Loisel et al. (2014), DBD values range around or even exceed the higher values reported by Loisel et al. (2014). They are also well above averages reported by other studies on boreal and subarctic peatlands (e.g. Turunen et al., 2002). This has implications, but as Köchy et al. (2015) emphasized, even a small increase or decrease of DBD has a great effect on absolute C storage in organic soils, much more so than in mineral soils. This is well illustrated here. Particularly in upper portions of the peat columns, a trend of comparatively low %C in conjunction with elevated DBD is prominent (**Paper II** and **III**), especially in post-settlement soil layers (**Paper III**). However, no significant effect of changes in relative contents of mineral soil constituents on absolute C storage capacity was found in surface soils (**Paper III**) or subsoils (**Paper II**), with correlations between %Ash and C density found to be insignificant. Naturally, relative C content (%C) decreased in response to increasing %Ash, but as there was also a strong positive correlation between %Ash and DBD, the absolute C storage capacity of the peatlands of this study was not impeded by increased %Ash.

4.5 Reflections on Carbon Dynamics of Peatlands under the Influence of a Warming Climate and Increased Dust Deposition

This study intimates the importance of soil mineral constituents for C stabilization in many Histosols in Iceland, in addition to the importance of hydrological conditions, and the chemical characteristics of OM (e.g. Kayranli et al., 2010; Kögel-Knabner & Amelung, 2021; Zhaojun et al., 2011). This resembles the processes recognized in mineral soils (e.g. Kögel-Knabner & Amelung, 2021; Kögel-Knabner & Kleber, 2011; Marschner et al., 2008). This is contrary to observations made elsewhere, where the dominant processes of C stabilization in mineral soils, organo-mineral complexation and aggregation, are of minor importance in organic wetland soils like Histosols (Kögel-Knabner & Amelung, 2021; Leifeld et al., 2012).

Some of the findings are clearly distinct from the results of studies on stabilization processes in mineral soils, while other observations are more consistent with them. Contrary to studies on mineral soils (Dahlgren et al., 1993; Kögel-Knabner & Amelung, 2021; Kögel-Knabner & Kleber, 2011; Matus et al., 2014; Takahashi & Dahlgren, 2016), this study does not find a preferential formation of Al/Fe-humus complexes by complexation of Al and Fe with carboxyl C, but rather a preferential formation of Al-humus complexes with alkyl C, and of Fe-humus complexes with O/N-alkyl C. It remains open to question as to whether or not the observed positive relationship between Al_p and alkyl C indicates a causal relationship, or if the relative accumulation of these C compounds results from processes other than the formation of metal-humus complexes in non-allophanic soils of volcanic regions. Possibly, toxic levels of exchangeable Al might retard microbial breakdown specifically of these C compounds, resulting in their relative accumulation (Tonneijck et al., 2010).

Carboxyl/carbonyl/amide C in particular, but also O/C-aryl C and C/H-aryl C correlate positively with allophane in our study, which supports findings by Parfitt et al. (1999) of a preferential stabilization of carboxyl groups by allophane in poorly drained Podzols in New Zealand. In conjunction with observations that phenolics (O/C-aryl C) may have an inhibiting effect on decomposition processes (Freeman et al., 2001; Hättenschwiler & Vitousek, 2000; Zhao et al., 2021), the positive relationship between allophane and these compounds is of particular interest. The positive relationship between polysaccharide-type OM (O/N-alkyl C) and Fe_p, and to a lesser extent with ferrihydrite, is also in agreement with previous studies. Miltner and Zech (1998) observed reduced decomposition rates of polysaccharides in beech litter upon the addition of selected oxides such as ferrihydrite. A study by Schöning et al. (2005) on four different non-volcanic mineral soil types also indicated a positive effect of Fe-oxides on relative O/N alkyl C content.

The importance of organo-mineral complexes for C dynamics of the peatlands of this study should be considered in projections of potential changes in C dynamics of these ecosystems under the interacting influence of a warming climate and aggravated dust deposition. Albeit, estimates of net C emissions from organic soils in Iceland are based on Tier 1 of the IPPC guidelines (IPCC, 2014; The Environment Agency of Iceland, 2020), which are based on research of boreal peatlands neither affected by tephra deposits nor andic soil properties.

Changes in climate pattern such as increased temperatures and changes in moisture may enhance the reduction of the Fe(III) in ferrihydrite to more soluble Fe(II), which can also lead to increased C losses (Curtinrich et al., 2022; Knorr, 2013) via DOC and as CO_2. Elevated levels of Fe(II) may in turn affect OM degradation rates. Upon oxidation of dissolved Fe(II), highly degrading $^{\bullet}OH$ radicals are produced (Trusiak et al., 2019; Zhao et al., 2021), which potentially accelerate the degradation of the DOC. Another factor, which may impact the formation and stability of Fe-organo complexes, as well as decomposition processes, and which will likely be affected by both climate change and aeolian mineral deposition, are vegetation changes (Eddudóttir et al., 2020; Ireland et al., 2014; Loisel & Bunsen, 2020; Lyons et al., 2020; Norby et al., 2019). For instance, changes in redox cycling of Fe could themselves alter vegetation characteristics, but Fe redox cycling has also been shown to affect the availability of nutrients such as P, Ca and Mg (Curtinrich et al., 2022; Zhaojun et al., 2011). Some studies (e.g. Lyons et al., 2020; Norby et al., 2019) suggest that *Sphagnum* abundances will decline upon climate warming, due to changes in soil moisture and a shift towards the greater dominance of vascular plants. The peatlands of our study are already dominated by vascular plants which raises the question as to whether or not *Sphagnum* mosses in such vascular plant dominated sites will be particularly sensitive towards the effects of climate warming. If this is the case, the enhancing effect of *Sphagnum* species on the formation of Fe-organo complexes might be diminished, at the same time as formation of $^{\bullet}OH$ radicals might be enhanced due to the lack of a quenching effect of *Sphagnum* derived phenolic compounds on $^{\bullet}OH$ radicals upon oxidation of Fe(II) (Zhao et al., 2021). As the production of $^{\bullet}OH$ radicals greatly depends on Fe(II) concentration and, hence, on the presence of Fe containing mineral material (Trusiak et al., 2019), increased production of CO_2 by $^{\bullet}OH$ oxidation of DOC may be particularly relevant at peatlands closer to source areas of mineral aeolian material. Vegetation changes may also be induced by tephra deposition, or by a steady flux of aeolian dust. While many studies indicate only temporary changes in vegetation composition, such as a temporary decline of *Sphagnum* in favour of vascular plants following tephra deposition (e.g. Hotes et al., 2004; Hughes et al., 2013; but see Loisel & Bunsen, 2020), questions arise if recovery of declining plant species after several years or decades as proposed by these studies would be delayed or even impeded by the additional effects of changes in climatic pattern and steady dust fluxes from barren drylands. Increased levels of deposition of mineral aeolian material into the Histosols most likely also leads to elevated pH (e.g. Arnalds, Gudmundsson, et al., 2016) towards surface soils. Such changes in pH induced by dust deposition may further reduce the stability of organo-mineral associations (e.g. Inagaki et al., 2020; Varadachari et al., 1994). Grybos et al. (2009) observed that under reducing conditions in wetlands, increases in pH enhance the desorption of OM, particularly from Fe- and Mn-hydroxides. Garrido and Matus (2012) found a significant negative correlation between pH and Al_p (and also Fe_p), confirming observations of previous studies that the formation and stability of metal-humus complexes (particularly that of Al-humus complexes) predominantly occurs at $pH < 5$ (Adams et al., 2000; Shoji & Fujiwara, 1984). On the other hand, allophane formation is favoured above a threshold of $pH \geq 5$ (e.g. Garrido & Matus, 2012; Matus et al., 2014; Shoji et al., 1993; Wada, 1989). Hence, the importance of this highly reactive mineral for the stabilization of OM may increase with elevated pH.

5 Conclusions

While vegetation characteristics and the chemical composition of the C certainly play a role for C dynamics in undrained peatlands in the volcanic environment of Iceland, mineral soil constituents are also of importance, more so than in peatlands of less dynamic environments. All peatlands of this study contain clearly defined tephra deposits, but the two peatlands, which are closer to sources of mineral aeolian material also bear clear signs of andic properties.

C dynamics in peatlands that receive frequent inputs of windborne mineral material of volcanic origin appear only partly governed by vegetation and C characteristics. While the C structure of the very youngest surface soil layers at the three sites closely resemble each other (despite differences in vegetation characteristics), the C at Torfdalsmýri (the site least impacted by mineral material) reveals decomposition trajectories distinct from the other two sites. Subsoils of peatlands which are more exposed to aeolian deposition reveal a C structure indicative of more labile and less degraded material than more sheltered sites. This is probably due to the interaction of different factors, including vegetation characteristics and soil mineral content.

One explanation may be found in seemingly small, but important differences in relative content of key C groups. For instance, the share of phenolics ranges between ca. 4% - 7% in all soil samples. While this comprises only a minor part of the whole soil C, with seemingly little difference between soil samples, it could still be partially responsible for differences in C trajectories. *Sphagnum* derived phenolic compounds are known to be an important inhibitor of OM decomposition through several pathways. This study does not provide detailed information about the cover of *Sphagnum* mosses, but it indicates a greater prevalence of *Sphagnum* at those sites which comprise less decomposed C and, on average, a slightly greater share of phenolics. Hence, it is possible that *Sphagnum* mosses play a greater role for C dynamics of Icelandic peatlands than usually anticipated based on their relatively small share in these vascular plant dominated ecosystems. Future studies should put more emphasis on the occurrence of *Sphagnum* species in Icelandic peatlands, and their potential fate under environmental pressures like a warming climate and dust deposition. This could be of particular importance in peatlands that receive regular inputs of Fe containing mineral material, as one pathway by which *Sphagnum* derived phenolic compounds inhibit decomposition is by enhancing the formation of Fe-organo complexes.

This study finds evidence of interactions between C groups and soil minerals, some of which bear a resemblance to stabilization processes in mineral soils. Particularly interesting is the positive relationship between labile O/N alkyl C and active Fe and ferrihydrite, indicative of a stabilizing effect of these mineral constituents, also observed in mineral soils. Furthermore, there is evidence of a stabilizing effect of allophane on carboxyl/carbonyl/amide C, similar to studies on allophanic podzols in New Zealand. A positive relationship between allophane and C/N ratios, and allophane and O/C aryl C, supports previous studies on European temperate forest soils where the share of these C compounds decreases with increasing decomposition.

Projections of the effects of climate change and other disturbances such as by drainage on C cycling in Icelandic peatlands should not only take interactions between climatic variables (e.g temperature and precipitation), hydrology, vegetation characteristics and C characteristics into consideration, but also the effects of mineral soil constituents. Changes in temperature and hydrology will likely impact peatlands in Iceland in several interacting ways. Changes in vegetation composition and dominant species may affect the chemical composition of OM, with concomitant effects on decomposability of the substrate itself, but also with likely effects on the formation and stability of organo-mineral associations. Soil C mineralization at 5 °C, 15 °C and 25 °C showed clearly that C of subsoils lacking andic soil properties like allophane, ferrihydrite and Al/Fe humus complexes was much more sensitive towards temperature increases than C with a very similar C structure of a soil environment with andic soil properties. This indicates that reactive minerals and active Fe and Al, typical for volcanic dryland soils, do play a stabilizing role in the Histosols of volcanic regions. However, the stability of organo-mineral complexes and metal-humus complexes may change as a consequence of warming and changes in hydrology. A possible scenario is that the stability of Fe-bound OM may be threatened, while complexation of allophane with OM may gain importance, particularly if soil pH increases under increased pressure from aeolian deposition.

Questions arise on the potential effects of future major tephra deposits on peatland ecosystems. This study shows clear shifts in C structure and C stability around pre-settlement tephra deposits. However, while these eruption events evidently imposed at least a temporary equilibrium shift in the pre-settlement peatland environments, the pedogenic environment between the tephra layers is indicative of surprisingly stable conditions (characterized by little sign of reworked mineral material, a conspicuous lack of andic soil properties, and comparatively decomposed, but high relative C contents). To use these observations of the pre-settlement subsoils in order to draw conclusions about the impact of tephra fall on the present day peatlands in Iceland is however doubtful. There are strong indications of destabilizations in the pedogenic environment towards post-settlement surface soils. Today, the peatlands are located in a more dynamic environment than several thousand years ago, due to the far greater extent of eroding drylands and the aggravated severity of dust deposition and reworking of mineral material. Considering the degraded state of Icelandic soils and vegetation today, not only in the highlands, but also in widespread lowland areas, it is conceivable that a tephra deposit of similar thickness as Hekla 4 would today impose more severe and prolonged imbalances of C dynamics of peatlands than it did over 4,000 years ago when ecosystems were likely more resilient to volcanic eruptions of such magnitude.

Increased relative mineral contents in Icelandic peatlands naturally lead to decreased relative C contents. However, this must not lead to the misconception that the absolute C storage capacity of the Histosols was likewise negatively affected. Elevated levels of mineral soil constituents usually go hand in hand with increased bulk density of the soils, higher than average values observed in northern peatlands. Consequently, C densities do not necessarily decrease as relative C contents decrease. In this study, no correlation was detected between contents of mineral soil constituents and C density. That does not preclude that windblown mineral material may have a significant effect on C storage capacities in other settings.

While on average containing less relative C content than Histosols of other northern peatlands, Icelandic Histosols are still organic soils with more than 20% C. However, as explained in the introduction of this thesis, the greater share of soils of Icelandic wetlands do not (anymore) belong to the soil type of Histosols, but count as Andosols (Histic and Gleyic), due to an even greater impact of mineral soil constituents than in the soils of this study. In many areas, where Histic and Gleyic Andosols are found in surface soils today, Histosols may be found in deeper subsoil layers of pre-settlement age. After the settlement aeolian deposition in an increasingly disturbed environment reached levels high enough to impose a shift in soil type. Future research should not only focus on the effect of mineral deposition on Histosols, but also on these relatively less organic wetland soils.

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Paper I

Tephra deposits and carbon dynamics in peatlands of a volcanic region: Lessons from the Hekla 4 eruption

Author’s contribution:

Susanne Claudia Möckel (SCM), Guðrún Gísladóttir (GG) and Egill Erlendsson (EE) planned the study and applied for research funding. Field work was conducted by SCM, GG, EE, Ólafur Eggertsson, Scott John Riddell and Sigrún Dögg Eddudóttir. Laboratory work was conducted by SCM, but ^{13}C NMR measurements were conducted at the Chair of Soil Science of the Technical University of Munich, under guidance of Isabel Prater (IP) and with assistance of Franziska Fella. SCM conducted the data analysis and wrote the manuscript. The co-authors (EE, GG, IP), and two anonymous reviewers provided useful comments to the manuscripts.

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RESEARCH ARTICLE

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Tephra deposits and carbon dynamics in peatlands of a volcanic region: Lessons from the Hekla 4 eruption

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Abstract

Interactions between tephra deposits from volcanic eruptions and peatland carbon (C) dynamics are poorly understood despite the significant extent of peatlands influenced by tephra worldwide. Tephra falls can affect peat accumulation within a radius of at least 1,000 km. In Iceland, volcanic activity is amongst the highest in the world and it might even increase due to pressure release on subglacial volcanoes. A potent combination of sparse vegetation, low cohesion of Andosols, and frequent strong winds, facilitates the regular input of mineral aeolian material from eroded areas into peatlands in Iceland, in addition to tephra deposits. We present results of a study on the impact of a major tephra deposit, the Hekla 4 tephra, on C dynamics in Icelandic peatlands. We investigated three sites at differing distances from the active volcanic zones and major erosion areas in the interior of the country. A combination of variables was applied, including laboratory C mineralization at 5, 15 and 25°C and C structure obtained by solid-state ^{13}C NMR spectroscopy. Tephra deposits seem to affect C dynamics. Differences in C mineralization can only be partially explained by C structure. The C mineralization from soils with conspicuously similar C structure differs by a factor of up to 2.7. Temperature sensitivity of decomposition after the tephra deposition increases by a factor of up to 2.2. Changes in inorganic matter and the ratio of soil organic matter to soil organic carbon by a factor of up to 1.3 and 1.4, respectively, were also observed.

KEYWORDS

^{13}C NMR spectroscopy, C mineralization, carbon dynamics, peatlands, tephra deposits

1 | INTRODUCTION

1.1 | Carbon dynamics in volcanically influenced peatlands—What do we know?

Vast areas of peatland worldwide are located within active volcanic regions and, hence, within tephra-receiving areas (Payne & Blackford, 2008), for example, in Alaska and Western Canada, Kamchatka, Patagonia, the tropical and subtropical Andes, Japan, Indonesia and Iceland (Ayris & Delmelle, 2012; Chimner & Karberg, 2008; Hotes, Poschlod, & Takahashi, 2006; Payne & Blackford, 2008; Yu, 2006). Based on a number of real-time, in-situ studies following volcanic eruptions, for example, Mount St. Helens (USA) in 1980 (Antos & Zobel, 1985; Harris, Mack, & Maurice, 1987), Mount Koma (Japan) in 1996 (Tsuyuzaki & Hase, 2005), and others reviewed by Ayris and Delmelle (2012), the immediate impact of tephra deposits is relatively well known. Field observations following the Mount St. Helens eruption of 1980 (Antos & Zobel, 1985) revealed that a tephra cover of 150 mm was sufficient to kill nearly all herbaceous plants while 45 mm was enough to eliminate most bryophytes. Most research on vegetation responses to tephra deposits has been conducted on dryland plant communities, leaving less certainty about the impact on wetland vegetation (Ayris & Delmelle, 2012).

According to Ayris and Delmelle (2012) about 1% of peatland is located within 20 km of known Holocene volcanoes, and approximately another 1% lies within 200 km. However, the impact range of distal tephra deposits can be far greater than 200 km. Blackford, Payne, Heggen, de la Riva Caballero, and van der Plicht (2014) found clear evidence of a profound impact on vegetation and peat accumulation imposed by tephra from the mid-Holocene eruption of the Alaskan Aniakchak volcano (Aniakchak II) in a peatland located more than 1,000 km from the volcano. There, tephra layers of 3–12 mm thickness were preserved. Therefore, the extent of peatlands influenced by tephra fall worldwide is clearly significant (cf. Payne & Blackford, 2008). Despite that, and the growing knowledge on the role of peatlands in the global carbon (C) cycle (Leifeld & Menichetti, 2018; Mitsch et al., 2013; Yu, Loisel, Brosseau, Beilman, & Hunt, 2010), our understanding of the interactions between tephra deposits and C dynamics in peatlands remains fragmentary, aggravated by the contradictory findings of the few studies conducted so far (Ayris & Delmelle, 2012). It has frequently been suggested that tephra deposits may affect peat accumulation through the impact on vegetation characteristics and hydrological conditions. Nutrient leaching from tephra deposits favours the dominance of vascular plants over bryophytes such as *Sphagnum*, and leads to increased decomposition by enhancing microbial activity (Biester, Martinez-Cortizas, Birkenstock, & Kilian, 2003; Broder, Blodau, Biester, & Knorr, 2012; Damman, 1988; Tsutsuki & Kondo, 1997). In some cases, tephra deposition has led to a shift in vegetation towards assemblages typical not only of more nutrient rich, but also of drier ecosystems, for example, a shift from Cyperaceae-dominated to Poaceae-dominated vegetation assemblages (Blackford et al., 2014; Erlendsson, Edwards, & Buckland, 2009). Other studies provide evidence of decreased decomposition below fine-grained, semi-impermeable tephra layers, which presumably promote anaerobic conditions (Hotes, Poschlod, Takahashi, Grootjans, & Adema, 2004). In the decades after tephra deposition, C sequestration may be impeded due to vegetation destruction or increased aerobic decomposition (Blackford et al., 2014). The results from these studies demonstrate inconsistent evidence for the immediate short-term impact of volcanic emissions on C dynamics, and even less clarity on the long-term impact of tephra on C dynamics in peatlands.

The need to decipher C dynamics in volcanically influenced peatlands is obvious; (a) globally, considering the C storage capacity of peatlands and the considerable extent of these ecosystems within the range of volcanic emissions, and (b) not least more locally in Iceland. The frequency of volcanic eruptions in Iceland has been amongst the highest in the world during the Holocene (every 5 years on average; Thordarson & Hoskuldsson, 2008) and might even increase with warming climate and the consequent pressure release on subglacial volcanoes (Sigmundsson et al., 2010). A factor aggravating the impact of tephra deposition on peatland C dynamics in Iceland may be the frequent aeolian redistribution of minerogenic material from sparsely vegetated or barren areas. In particular, the human colonisation of Iceland c. 870 AD and concomitant introduction of livestock led to a widespread alteration of vegetation communities and induced erosion, and thereby, diminishing the capability of ecosystems to withstand the conventional influences of volcanism and climate (Dugmore, Gisladóttir, Simpson, & Newton, 2009; Eddudóttir, Erlendsson, Tinganelli, & Gísladóttir, 2016; T. Einarsson, 1961; Hallsdóttir, 1987). Desert-like areas are, to the best of our knowledge, not found elsewhere close to peatlands influenced by volcanism. The potent combination of sparse vegetation cover, the nature of Andosols (cf. IUSS Working Group WRB, 2015), the volcanic dryland soils characterized by low cohesion (Arnalds, 2008) and frequently occurring strong winds (M. A. Einarsson, 1984) facilitates the input of mineral aeolian material into peatlands in Iceland. The deterioration of the Histosols (cf. IUSS Working Group WRB, 2015) of the Icelandic peatlands, due to the redeposition of aeolian material from eroded areas, is readily observed, for example, a rise in bulk density and the decline of moisture content and organic C (Gísladóttir, Erlendsson, & Lal, 2011; Gísladóttir, Erlendsson, Lal, & Bigham, 2010; Möckel, Erlendsson, & Gísladóttir, 2017). This decreases their resilience towards disturbances (Arnalds, 2015) like those imposed by tephra deposits from volcanic eruptions.

1.2 | The Hekla 4 eruption and its ecologic implications

The Hekla 4 event ranks amongst the most productive of Icelands Holocene eruptions. It generated an estimated 9 km^3 of tephra (Larsen & Thorarinsson, 1977) at c. 4.25 ka BP from the volcano Hekla (Dugmore et al., 1995) in South Iceland. Stratigraphic evidence of the eruption is found in c. three-quarters of Iceland, but the main deposition direction was towards the north and northeast (Figure 1; Larsen & Thorarinsson, 1977). In our study area, the tephra is relatively fine-grained with a dominantly silicic chemical composition, but includes intermediate portions and basaltic andesites (cf. Sverrisdottir, 2007). The deposits towards the north and northeast contain mainly light-coloured silicic tephra. Today, the average thickness of tephra layers found in soils and sediments in North Iceland at a distance of c. 180–230 km from the source volcano is about 2–4 cm (Figure 1; Larsen & Thorarinsson, 1977), but thicknesses of 6 cm (Möckel et al., 2017) and even up to 8 cm (Eddudóttir et al., 2017) have been reported. The original thickness of the freshly fallen, uncompacted deposits may have been far greater, as much as twice as thick as that observed in stratigraphies today (cf. Sarna-Wojcicki, Shipley, Dzurisin, & Wood, 1981).

Contrary to ecosystems in Iceland today, which are the artefact of large-scale vegetation changes, vegetation destruction and soil erosion after the human settlement (Dugmore et al., 2009; Eddudóttir et al., 2016), ecosystems at the time of the Hekla 4 eruption were relatively stable (Eddudóttir et al., 2016; Eddudóttir, Erlendsson, & Gísladóttir, 2015). Yet, an investigation of the effects of the Hekla 4 tephra on vegetation in Northwest Iceland by Eddudóttir et al. (2017) revealed aggravated disturbance in ecosystems close to the highlands. Tinganelli et al. (2018) supported these findings by detecting increased dry bulk density, magnetic susceptibility and C/N ratios in lake

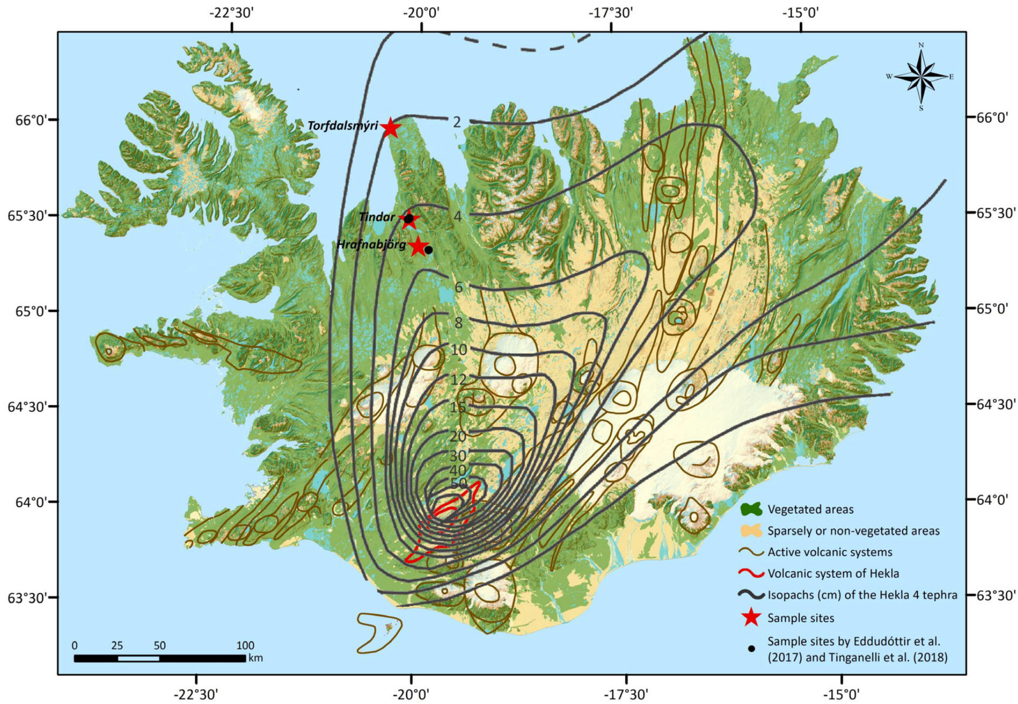

FIGURE 1 The research area is located in Northwest Iceland, Austur Húnavatnssýsla district. Three peatlands were investigated along a north–south transect from the coast (Torfdalsmýri) over the inland lowlands (Tindar) to the highland fringe (Hrafnabjörg). The sites are located between the 2 and 6 cm isopachs of the Hekla 4 tephra deposits; isopachs are based on Larsen and Thorarinsson (1977). The coastal site Torfdalsmýri is located farthest from the active volcanic zones and from sparsely or non-vegetated areas in the interior of the country, while the southernmost site of Hrafnabjörg at the highland fringe is located closest to both. Sample sites of previous studies in the area (Eddudóttir, Erlendsson, & Gísladóttir, 2017; Tinganelli, Erlendsson, Eddudóttir, & Gísladóttir, 2018) are also depicted [Colour figure can be viewed at wileyonlinelibrary.com]

sediments close to the highlands. In contrast to the lowland ecosystems, the more vulnerable ecosystems at the highland fringe did not recover from the disturbances (Eddudóttir et al., 2017; Tinganelli et al., 2018).

The studies by Eddudóttir et al. (2017) and Tinganelli et al. (2018) conform to the findings of work in Northwest Iceland by Möckel et al. (2017), which this study builds upon. There, evidence indicated the importance of geographic location on soil properties in Icelandic peatlands and pointed to changes induced by allochthonous mineral material. Patterns in several soil variables reflected disturbance following the Hekla 4 tephra deposition at a peatland at the highland fringe (Hrafnabjörg) to an extent not observed in a lowland peatland (Tindar) or a peatland close to the open sea (Torfdalsmýri; Figure 1 and Table 1). For instance, dry bulk density (DBD) increased, soil organic matter (SOM) and soil organic carbon (SOC) decreased and the soil morphology changed from woody sedge peat to silty sediments.

1.3 | Study focus

This study focuses on the impact of tephra deposition on C dynamics in peatlands to address the hypothesis that, tephra deposits alter the C stability of Histosols. This can take place through the following trajectories:

1. Previous studies indicate that tephra deposits of a certain thickness may alter vegetation of peatlands (Blackford et al., 2014; Eddudóttir et al., 2017; Erlendsson et al., 2009; Möckel et al., 2017). We expect that such vegetation changes should be reflected in changes in C structure (measured by ^{13}C NMR), which, in turn, should be reflected in altered C mineralization.
2. Tephra deposits can alter soil properties such as nutrient content, pH and content of soil inorganic material (IOM), which can impact C mineralization.

We apply a combination of several variables; (a) C mineralization reflected by CO_2 respiration measured by laboratory incubations at 5, 15 and 25°C, (b) C structure obtained by solid state ^{13}C NMR spectroscopy and (c) nitrite (NO_2^-), nitrate (NO_3^-) and ammonium (NH_4^+) content. The findings are also discussed in the context of data on C/N and SOM/SOC ratio, base cation content and pH measured in water, which are based on a previous publication (cf. Möckel et al., 2017;

TABLE 1 Summary table of selected soil properties from Möckel et al. (2017)

	DBD	SOM	IOM	N	C	C/N	SOM/SOC	pH	$cmol_c\ kg^{-1}$ Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	CEC	ost H-value	Sediment description built upon Troel-Smith
Torfdalsmýri															
Surface horizon	0.24	45.5	54.5	1.955	33.88	20	1.34	4.8	4.31	2.83	1.01	0.19	8.34	H4	Ag2, Th1, Sh1, Ga+
Above Hekla 4	0.20	82.4	17.6	2.149	50.98	28	1.62	4.5	7.71	4.42	1.37	0.04	13.54	H3	Th2, Sh1, Ag1, Ga+
Below Hekla 4	0.24	71.8	28.2	1.844	41.46	26	1.73	4.6	8.43	4.10	1.18	0.04	13.75	H5	Th1, Sh1, Ag1, As1, Ga+
Tindar															
Surface horizon	0.15	51.8	48.2	1.677	30.21	21	1.72	5.4	32.49	10.39	1.18	1.48	45.55	H3	Th3, Ag1, Sh+, Ga+
Above Hekla 4	0.22	50.0	50.0	2.405	42.45	21	1.18	4.2	50.34	15.50	0.98	0.10	66.92	H6	Dl2, Sh1, Ag1, Th+
Below Hekla 4	0.18	61.0	39.0	1.827	37.28	24	1.64	5.1	52.42	17.96	1.36	0.13	71.87	H6	Ag2, Th1, Sh1, Dl+, Dg+
Hrafnabjörg															
Surface horizon	0.23	46.5	53.5	1.903	29.98	18	1.55	5.6	52.53	17.10	1.04	1.42	72.09	H3	Th2, Sh2, Ag+, Ga+, Gs+
Above Hekla 4	0.39	32.8	67.2	0.995	16.41	19	2.00	5.1	15.75	5.07	0.36	0.00	21.18	H7	Ag3, Sh1, Th+, Ga+
Below Hekla 4	0.29	48.1	51.9	2.120	33.18	18	1.45	4.8	32.01	9.54	0.50	0.00	42.05	H6	Ag2, As1, Th1, Sh+, Ga+, Dl+

Note: Dry bulk density (DBD; g cm^{-3}), soil organic matter (SOM; %) and soil inorganic matter (IOM; %) was determined by loss on ignition (Heiri, Lotter, & Lemcke, 2001), total nitrogen (N; %) and total carbon (C; %) by dry combustion (USDA, 2014), CEC and base cations by extraction with ammonium acetate (USDA, 2014). Due to the absence of carbonate minerals, soil organic carbon (SOC) = C. For the von Post Humification Scale see, for example, Clymo (1983), for sediment description based upon Troels-Smith refer to Aaby and Berglund (1986) and Troels-Smith (1955).

Table 1). To elucidate the impact of tephra deposition on C dynamics, we concentrate on soil horizons adjacent to the Hekla 4 tephra layer.

2 | METHODS

2.1 | Sampling approach and research area

The research area is located in the Austur Húnavatnssýsla district in Northwest Iceland. Soil samples were collected from three peatlands along a north–south transect from the coast (Torfdalsmýri; 39 m a.s.l), via the inland lowlands (Tindar; 108 m a.s.l) to the highland fringe (Hrafnabjörg; 329 m a.s.l; Figure 1). The three peatlands differ in their distance from the major erosion areas in the interior of the country and from the active volcanic zones (Figure 1). At each site, one soil pit was dug and a pooled bulk soil sample of each horizon was collected (Figure 2). The Hekla 4 tephra formed a well-defined stratum within each soil profile, with tephra thicknesses of 5 cm at Torfdalsmýri, 6 cm at Tindar and 1 cm at Hrafnabjörg. Tephra deposits at Torfdalsmýri and Tindar are thicker than isopachs for the area indicate

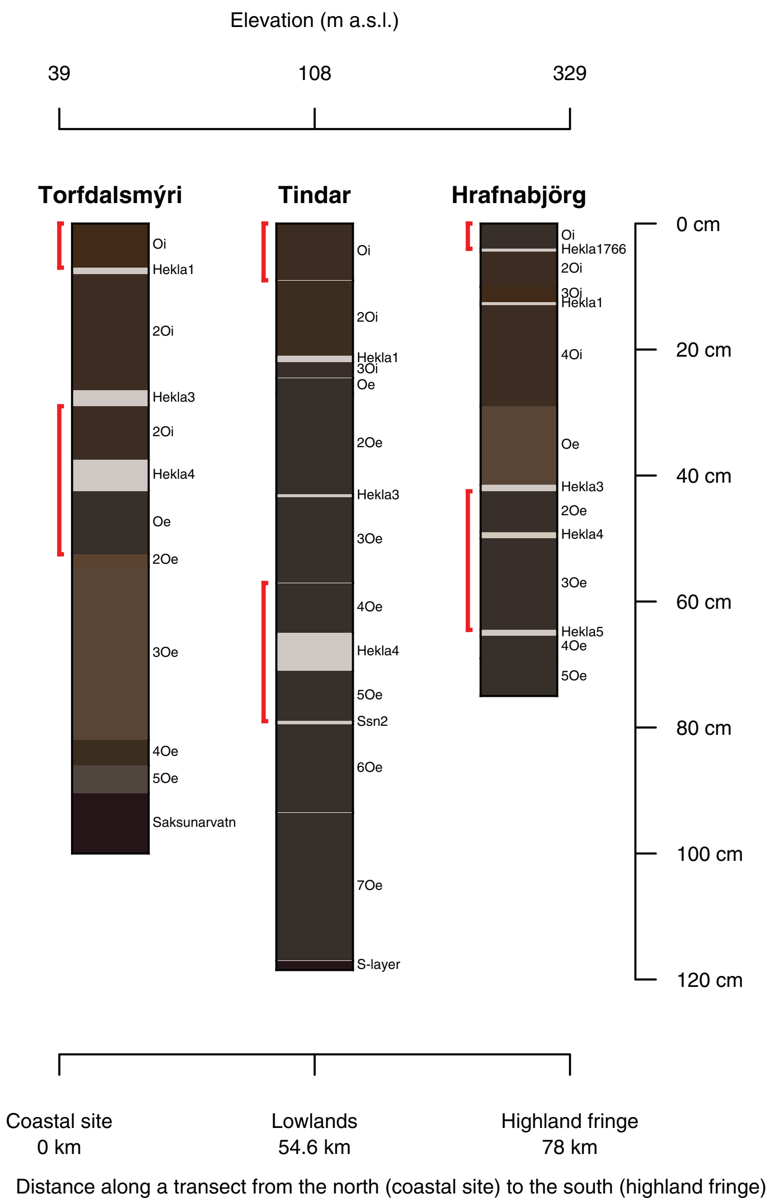

FIGURE 2 Soil profiles taken from three peatlands (Torfdalsmýri, Tindar, Hrafnabjörg) along a north–south transect, with elevation increasing southwards towards the highlands. Soil horizons analysed in this study are indicated by red brackets. Soil horizon designations are based on the USDA soil survey manual (USDA, 2017). Other designations refer to tephra layers. For a thorough description of soil morphological properties, see Möckel et al. (2017). The figure was produced with the R package Aqp (Beaudette, Roudier, & Brown, 2020) and colours of the soil profiles resemble Munsell soil colours [Colour figure can be viewed at wileyonlinelibrary.com]

(2 and 4 cm isopachs, respectively; Figure 1), but thinner than isopachs would suggest (4–6 cm) at Hrafnabjörg. The thin tephra layer at Hrafnabjörg might be a result of post-eruption redistribution by wind and probably does not reflect initial thickness. The thicknesses of the tephra deposits were probably not lethal for most higher vegetation, but might well have been for bryophytes (Antos & Zobel, 1985). Analyses were conducted on soil samples from the surface horizons and those above and below the Hekla 4 tephra deposit (Figure 2).

Annual precipitation in the area is relatively low (c. 400–-500 mm yr^{-1}; IMO, n.d.) and decreases from the open sea towards the highlands. Mean annual air temperatures range from 0.7°C at the Kolka weather station in the highlands, to c. 3°C at the Blönduós weather station for lowlands and the Hraun á Skaga weather station at the coast. Average wind speeds are highest close to the highlands (7.4 m s^{-1}) and lowest in the lowlands sheltered from the open sea (3.8 m s^{-1}).

2.2 | Laboratory analyses

2.2.1 | Soil C mineralization

We determined C mineralization by CO_2 respiration via long-term incubation experiments at 5, 15 and 25°C. Triplicates of the <2 mm size fraction of each bulk sample were subsampled and rewetted to field moisture content (cf. Möckel et al., 2017) for a time period of 400 days using closed jars and NaOH traps (Alef & Nannipieri, 1995; Isermeyer, 1952). Time intervals between changes of the NaOH traps were adjusted to respiration activity, with more frequent changes during the first weeks of the experiment than in the later stages. To assure constant soil water content, samples were weighed regularly during the incubation (cf. Fierer, Craine, McLauchlan, & Schimel, 2005). Respired CO_2-C was calculated and normalized to C content (cf. Möckel et al., 2017). Q_{10} coefficients were determined after 7, 21, 100, 200 and 400 days of incubation.

2.2.2 | Solid state ^{13}C NMR spectroscopy

Solid state ^{13}C NMR spectroscopy was used to determine the structure of soil organic C, which contributes to the characteristics of SOM and decomposition processes (Kögel-Knabner, 1997). We applied a cross-polarization magic angle spinning technique (CPMAS) with a Bruker DSX 200 spectrometer (Billerica/USA) with a proton resonance frequency of 50.32 MHz and a spinning speed of 6.8 kHz. To circumvent spin modulation during the Hartmann-Hahn contact, a ramped ^{1}H-pulse was used during a contact time of 1 ms. Pulse delays of 0.8 s were used for all samples and between 3,601 and 12,178 scans were accumulated during each measurement. A line broadening of 25 Hz was applied. The ^{13}C chemical shifts were calibrated relative to tetramethylsilane that was equalized to 0 ppm.

Integration was based on Knicker, Totsche, Almendros, and González-Vila (2005), modified by Leifeld, Steffens, and Galego-Sala (2012). The signal intensity was integrated into seven chemical shift regions in order to determine the relative share of the different C compounds: 220–160 ppm (carboxyl/carbonyl/amide C), 160–140 ppm (O/C-aryl C), 140–110 ppm (C/H-aryl C), 110–60 ppm (O/N-alkyl C), 95–60 ppm (polysaccharides), 60–45 ppm (O/N-alkyl C) and 45–0 ppm (alkyl C). Additionally, signal intensities for 70–75 ppm (O-alkyl C of carbohydrates) and 52–57 ppm (methoxyl C of lignin) were determined in order to calculate the (70–75)/(52–57) ratio, which Bonanomi et al. (2013) observed to correlate positively with decay rates. As a proxy for decomposition, we calculated the alkyl C to O/N-alkyl C (A:O/N) ratio, with higher ratios indicating a more advanced decomposition (Baldock et al., 1997).

2.2.3 | NO_3^-, NO_2^- and NH_4^+

Soil NO_2^-, NO_3^- (Shand, Williams, & Coutts, 2008) and NH_4^+ (Nelson, 1983) were determined spectrophotometrically using a GENESYS 10S Series UV–Visible Spectrophotometer and 2 M KCl soil extracts (Blakemore, Searle, & Daly, 1987; Carter & Gregorich, 2008) with an air-dried soil:liquid ratio of 1:10.

2.3 | Statistical evaluations

The soil mineralization data were tested for homogeneity of variances with the Fligner-Killeen test. Differences in mean soil mineralization between soil layers were then analysed for each temperature separately on log transformed data (skewness of non-transformed data >1) by one-way ANOVA, followed by the Tukey's HSD test (Quinn & Keough, 2002). In the same way, differences between temperatures as represented by Q_{10} values were analysed for each soil layer separately on non-transformed data ($-0.5 < \text{skewness} < 0.5$). An alpha level of .05 was used for all statistical tests.

The relation between C mineralization and C structure was evaluated by exponential regressions between selected indicators of C structure (O/N-alkyl C, polysaccharides, A:O/N ratio and (70–75)/(52–57) ratio) and C mineralization at 5, 15 and 25°C. Exponential regressions were chosen based on the comparison of Akaike information criteria corrected for small sample size (AICc; cf. Burnham & Anderson, 2004) of three models (linear, second order polynomial, exponential).

All statistical analyses were carried out using the software R version 3.5.2. The Tukey's HSD test was conducted using the CRAN package Agricolae (De Mendiburu, 2020), the AICc by using the package AICcmodavg (Mazerolle & Linden, 2019). Regression figures were produced using the package Ggplot2 (Wickham, 2016).

3 | RESULTS

3.1 | Soil C mineralization

3.1.1 | Between-site and within-site differences

There are clear between-site differences in C mineralization, with overall rates increasing towards the highlands and the active volcanic zones at all incubation temperatures (Figure 3; Supporting information S1). The C emissions from all layers at Torfdalsmýri are lower than at the other sites, this being especially conspicuous for the surface horizon ($p < .001$; Supporting information S1; Figure 3 and Table 2). Mineralization rates from the surface horizon at Hrafnabjörg are only slightly higher than from the surface horizon at Tindar. The most prominent difference in mineralization between Tindar and Hrafnabjörg is detected for the layer below Hekla 4, with mineralization rates at Tindar being approximately twice as high as those at Hrafnabjörg at all temperatures ($p = .012$ at 5°C, $p < .001$ at 15 and 25°C; Figure 3 and Table 2). At 15 and 25°C, mineralization rates from the layer above Hekla 4 at Tindar exceed those at Hrafnabjörg slightly. At 5°C the contrary is the case (Table 2).

Within each site, the highest C mineralization rates occur in the surface horizon (Figure 3; Supporting information S1). Differences between the layers above and below Hekla 4 vary between sites and temperatures (Table 2). At Torfdalsmýri and Hrafnabjörg, there is no difference in emissions from the two layers at 5°C, but at 15 and 25°C emissions are moderately higher from the layers above Hekla 4. At Tindar, emissions from below Hekla 4 at 5 and 25°C are clearly greater than from above ($p < .001$).

3.1.2 | Q_{10} coefficients

At all sites, Q_{10} coefficients for a temperature increase from 5 to 15°C (Q_{10}15/5) are higher and less consistent through time than for a temperature increase from 15 to 25°C (Q_{10}25/15; Table 3). Overall, Q_{10}15/5 are higher during earlier stages of the experiment than latter. The Q_{10}15/5 values of the surface horizon and below Hekla 4 are similar towards the latter stages of the experiment, while Q_{10}15/5 values above Hekla 4 are consistently higher than those of the other layers. This is particularly pronounced at Tindar. The same pattern does not occur for Q_{10}25/15 coefficients, which show less variability between layers and through time than Q_{10}15/5.

3.1.3 | ^{13}C NMR spectroscopy

The chemical structure of soil organic C at Torfdalsmýri differs noticeably from that at Tindar and Hrafnabjörg (Figure 4; Supporting information S2). At Torfdalsmýri, the proportion of alkyl C is higher in all layers than at the other two sites and the proportions of polysaccharides and O/N alkyl C of the signal range 110–60 ppm is lower. Differences between Tindar and Hrafnabjörg are minor. Generally, A:O/N

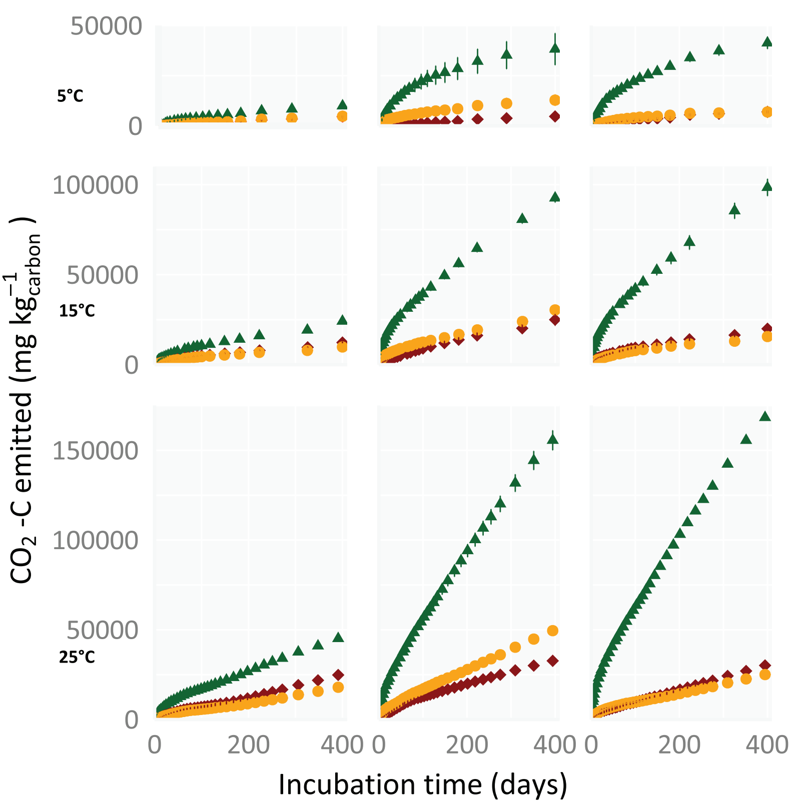

FIGURE 3 Cumulative soil C mineralization at 5, 15 and 25°C at the coastal site (Torfdalsmýri), the lowland site (Tindar) and the highland fringe site (Hrafnabjörg). Colours depict the different horizons: green = surface horizon, red = above Hekla 4, yellow = below Hekla 4 [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Relative between-site differences in C mineralization at 5, 15 and 25°C presented as the following ratios: Tindar/Torfdalsmýri, Tindar/Hrafnabjörg, Hrafnabjörg/Torfdalsmýri as well as differences between the layers below and above Hekla 4 within each site

	5°C		15°C		25°C	
	Relative difference (ratio)	***p* (Tukey's HSD)**	**Relative difference (ratio)**	***p* (Tukey's HSD)**	**Relative difference (ratio)**	***p* (Tukey's HSD)**
Tindar/Torfdalsmýri						
Surface horizon/surface horizon	3.8	*<.001*	3.8	*<.001*	3.4	*<.001*
Above Hekla 4/above Hekla 4	1.0	*>.999*	2.0	*<.001*	1.3	*.002*
Below Hekla 4/below Hekla 4	2.7	*<.001*	3.1	*<.001*	2.7	*<.001*
Tindar/Hrafnabjörg						
Surface horizon/surface horizon	0.9	*.999*	0.9	*.996*	0.9	*.836*
Above Hekla 4/above Hekla 4	0.7	*.274*	1.3	*.169*	1.1	*.849*
Below Hekla 4/below Hekla 4	1.9	*.012*	1.9	*<.001*	2.0	*<.001*
Below Hekla 4/above Hekla 4	1.8	*.024*	1.5	*.001*	1.6	*<.001*
Above Hekla 4/below Hekla 4	0.7	*.442*	1.6	*<.001*	1.3	*.002*
Hrafnabjörg/Torfdalsmýri						
Surface horizon/surface horizon	4.2	*<.001*	4.1	*<.001*	3.7	*<.001*
Above Hekla 4/above Hekla 4	1.5	*.195*	1.6	*<.001*	1.2	*.039*
Below Hekla 4/below Hekla 4	1.4	*.464*	1.6	*<.001*	1.4	*<.001*
Below Hekla 4/above Hekla 4						
Torfdalsmýri	1.0	*>.999*	0.8	*.113*	0.7	*<.001*
Tindar	2.7	*<.001*	1.2	*.255*	1.5	*<.001*
Hrafnabjörg	1.0	*>.999*	0.8	*.093*	0.8	*.047*

ratios are highest at Torfdalsmýri. Within each sample site, the maximum A:O/N ratio is observed in the layer above Hekla 4. The (70–75)/(52–57) ratio of the surface horizon at Torfdalsmýri is lower than that at Tindar and Hrafnabjörg. The respective ratio of the layers above and below Hekla 4 differs only slightly between sites.

Regarding differences within each site, it is most conspicuous that differences in C structure between the layers above and below the Hekla 4 tephra are only minor at all sites. Besides that, each site is characterized by an overall increase in alkyl C and an overall decline in O/N-alkyl C with depth. A steady decline in polysaccharides and O/N-alkyl C with increased depth takes place at Torfdalsmýri in contrast to Tindar and Hrafnabjörg, where slightly higher values are observed below Hekla 4 than above. The increase of alkyl C with depth is not linear, that is, it is lower below Hekla 4 than above at all sites (Supporting information S2). The A:O/N ratio generally increases with depth, but while ratios are nearly equal above and below Hekla 4 at Torfdalsmýri, slightly higher ratios occur above Hekla 4 than below at Tindar and Hrafnabjörg. The (70–75)/(52–57) ratio declines steadily with depth at Torfdalsmýri, but less so at Tindar and Hrafnabjörg, where somewhat lower ratios occur above Hekla 4 than below.

3.1.4 | NO_3^-, NO_2^- and NH_4^+

Only the horizon above Hekla 4 at Hrafnabjörg yielded NO_3^- above the detection limit (Table 4). The contents of NO_2^- and NH_4^+ are above the detection limit in all layers at all sites, but NH_4^+ contents are much greater than NO_2^- contents and Torfdalsmýri contains the most NH_4^+. At Torfdalsmýri and Tindar, NH_4^+ and NO_2^- contents are

TABLE 3 Q_{10} values after 7, 21, 100, 200 and 400 days of incubation

	Q_{10} 15/5						Q_{10} 25/15					
Incubation time (days)	**7**	**21**	**100**	**200**	**400**	***p (Tukey's HSD)***	**7**	**21**	**100**	**200**	**400**	***p (Tukey's HSD)***
Torfdalsmýri												
Surface horizon	7.1	2.5	2.4	2.2	2.4	*<.001*	1.8	1.7	1.6	1.8	1.9	*<.001*
Above Hekla 4	8.1	5.2	3.5	3.0	2.7	*<.001*	1.4	1.5	1.4	1.6	2.0	*<.001*
Below Hekla 4	9.1	4.0	2.7	2.2	2.1	*.035*	1.7	1.3	1.3	1.4	1.9	*.003*
Tindar												
Surface horizon	3.1	2.1	1.7	2.0	2.4	*<.001*	1.3	1.2	1.4	1.6	1.7	*<.001*
Above Hekla 4	4.5	11.1	6.6	5.4	5.3	*<.001*	1.4	1.3	1.4	1.3	1.3	*.021*
Below Hekla 4	3.6	1.9	1.9	1.9	2.4	*<.001*	1.0	1.1	1.4	1.6	1.6	*<.001*
Hrafnabjörg												
Surface horizon	4.2	2.0	1.9	2.0	2.4	*<.001*	1.4	1.4	1.5	1.6	1.7	*<.001*
Above Hekla 4	15.2	3.8	3.0	2.7	2.9	*<.001*	0.8	1.0	1.0	1.3	1.5	*<.001*
Below Hekla 4	6.6	2.4	1.9	1.9	2.3	*.004*	1.4	1.4	1.3	1.3	1.6	*.002*

Note: p-Values of Tukey's HSD test for Q_{10} values after 400 days of incubation are also presented.

greater above the tephra layer than below, whereas the opposite holds true at Hrafnabjörg.

4 | DISCUSSION

We hypothesised that tephra deposits alter the stability of C in Histosols by altering vegetation composition and, hence, C structure, and/or by altering various soil properties (e.g., nutrient content, pH, IOM, etc.).

The results reveal no profound changes in ^{13}C NMR spectra after the deposition of the Hekla 4 tephra, with minor differences between the layers below and above Hekla 4 at all sites (Figure 4; Supporting information S2). The C structure at Torfdalsmýri differs profoundly from the other two sites, which is reflected in lower C respiration (Supporting information S1; Table 2). Despite an overall similarity in C structure at Tindar and Hrafnabjörg, C mineralization differs between subsoil layers. The C mineralization of the soil below Hekla 4 at Tindar clearly exceeds that of the other subsoil layers. The most profound change in C stability induced by the tephra deposition is reflected by Q_{10}15/5 values, which are highest above Hekla 4 at all sites (Table 3).

At Torfdalsmýri, other soil properties were not adversely affected by the Hekla 4 tephra deposit. On the contrary, SOM and SOC increase after the volcanic eruption, while DBD and von Post humification decrease (Table 1). At Tindar and Hrafnabjörg, the inverse development is observed, with the exception of SOC at Tindar, which increase slightly despite a simultaneous decrease in SOM. Overall, changes in soil properties at Hrafnabjörg are the clearest, indicating a development towards a more mineral soil. Of intrigue is the change in SOM/SOC, which increases greatly at Hrafnabjörg, but decreases at Tindar. Content of NH_4^+ and NO_2^- at Tindar and Torfdalsmýri is higher in the soils formed after the eruption, whereas the opposite is observed at Hrafnabjörg (Table 4). Likewise, a decrease in CEC is seen at Hrafnabjörg after the eruption, but less so at Tindar and Torfdalsmýri (Table 1).

4.1 | Impact of the Hekla 4 tephra on C structure

Our hypothesis that tephra deposits affected C structure is not supported by the ^{13}C NMR spectra (Figure 4; Supporting information S2). The absence of profound changes in C structure does not necessarily suggest that the peatlands were not experiencing vegetation changes of some kind in the years after the eruption (cf. Möckel et al., 2017). Besides vegetation characteristics, the stage of decomposition impacts C structure (Leifeld et al., 2012). It is also conspicuous, that despite considerable differences in present vegetation characteristics between sites (Torfdalsmýri is dominated by *Eriophorum angustifolium*, Hrafnabjörg by *Carex rostrata* and Tindar is co-dominated by several vascular plants, including *Carex nigra* and various flowering plants and dwarf shrubs; Möckel, Erlendsson and Gísladóttir, unpublished data), the ^{13}C NMR spectra of the surface horizons at Tindar and Hrafnabjörg are very similar. Some changes in SOM and SOC properties certainly take place around the Hekla 4 tephra deposits, the most prominent being a change in SOM/SOC ratios (Table 1; cf. Möckel et al., 2017). At Tindar, the ratio decreases from 1.64 to a very low ratio of 1.18, facilitated by a drop in SOM at the same time as SOC increases. At Hrafnabjörg, the post-eruption SOM/SOC ratio is high (2.00), greater than the pre-eruption value of 1.45. A vegetational interpretation of our SOM/SOC ratios lacks scientific information on this variable in the Icelandic peatland environment, but research on German peatlands (Klingenfuß, Roßkopf, Walter, Heller, & Zeitz, 2014) and various other soil types (Pribyl, 2010) indicates that the SOM/SOC ratio is, amongst others, a function of substrate and, hence, vegetation characteristics and stage of decomposition. In the study by Klingenfuß et al. (2014), *Sphagnum*

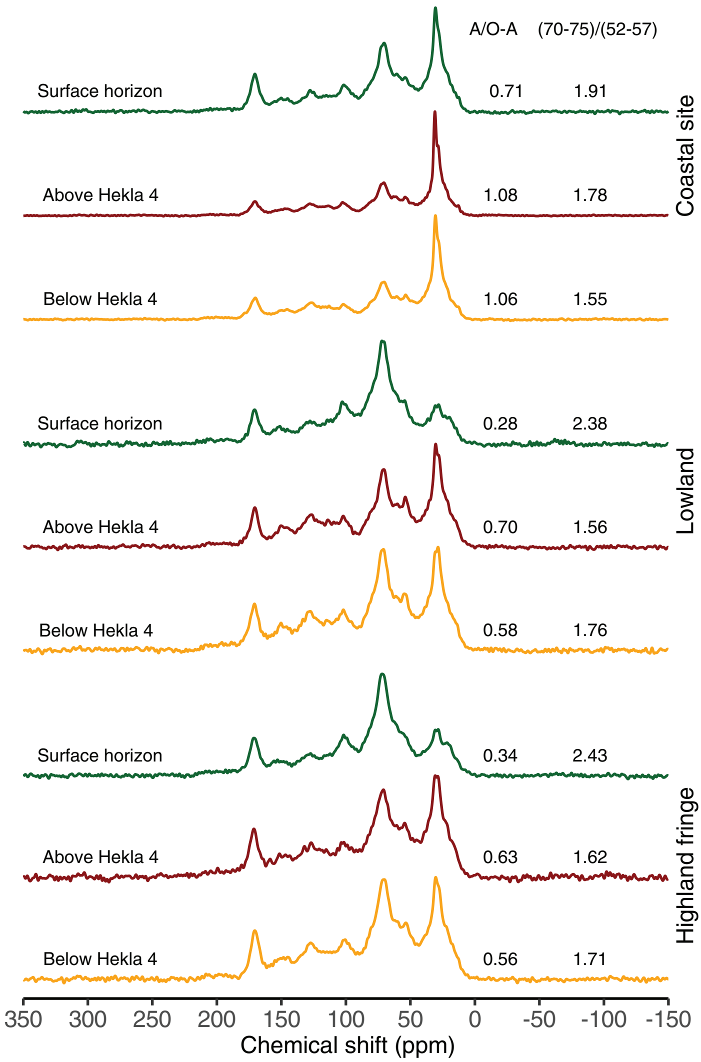

FIGURE 4 The ^{13}C NMR spectra for the surface horizon and the soil horizons above and below Hekla 4 at the coastal site (Torfdalsmýri), the lowland site (Tindar) and the highland fringe (Hrafnabjörg) [Colour figure can be viewed at wileyonlinelibrary.com]

peat showed higher SOM/SOC ratios than peat substrate derived from vascular plants (2.05 ± 0.09 vs. 1.73 ± 0.09, respectively).

4.2 | Relation between C structure and C mineralization

We proposed alterations in C mineralization facilitated by changes in C structure induced by the Hekla 4 tephra. As discussed, there were only minor changes in C structure and only minor differences between the ^{13}C NMR spectra from Tindar and Hrafnabjörg (Figure 4; Supporting information S2). To explore if, and to what extent, C mineralization is modified by C structure, exponential regressions between cumulative CO_2-C (mg kg_{carbon}^{-1}) and chosen C groups and ratios were conducted (Figure 5). Of course, the number of samples investigated is not sufficient to draw strong conclusions from inferential statistics. Yet, correlations between variables can still serve as a guide to detect major influences on C dynamics and to discover trends and patterns that the investigated variables can otherwise not explain. The regressions indicate that overall, O/N-alkyl C, polysaccharides and the (70–75)/(52–57) ratio are positively related to C mineralization, while the A:O/N ratio shows negative correlation (Figure 5). These findings accord with previous research. Leifeld et al. (2012) found a clear relation between C mineralization and content of polysaccharides and O/N-alkyl C in Histosols and Preston et al. (1987) reported that polysaccharides are especially sensitive to biodegradation. Bonanomi et al. (2013) found the (70–75)/(52–57) ratio to be a good predictor of decay rates,

TABLE 4 NO_2^-, NO_3^- and NH_4^+ contents at the coastal site (Torfdalsmýri), the lowlands (Tindar) and the highland fringe (Hrafnabjörg)

	Nitrite [mg kg_{soil}^{-1}]		Nitrate [mg kg_{soil}^{-1}]		Ammonium [mg kg_{soil}^{-1}]	
	Mean[a]	*SD*	Mean[a]	*SD*	Mean[a]	*SD*
Torfdalsmýri						
Surface horizon	0.059	*0.028*	<LOD		55.066	*2.332*
Above Hekla 4	0.107	*0.065*	<LOD		78.616	*1.512*
Below Hekla 4	0.055	*0.014*	<LOD		50.017	*1.645*
Tindar						
Surface horizon	0.267	*0.008*	<LOD		44.307	*0.885*
Above Hekla 4	0.509	*0.067*	<LOD		40.525	*0.386*
Below Hekla 4	0.106	*0.008*	<LOD		29.339	*0.450*
Hrafnabjörg						
Surface horizon	0.333	*0.032*	<LOD		47.942	*0.785*
Above Hekla 4	0.100	*0.018*	0.950	*0.094*	23.193	*0.058*
Below Hekla 4	0.238	*0.020*	<LOD		45.291	*0.329*
LOD	*0.004*		*0.538*		*0.214*	

[a]Mean of three replicates.

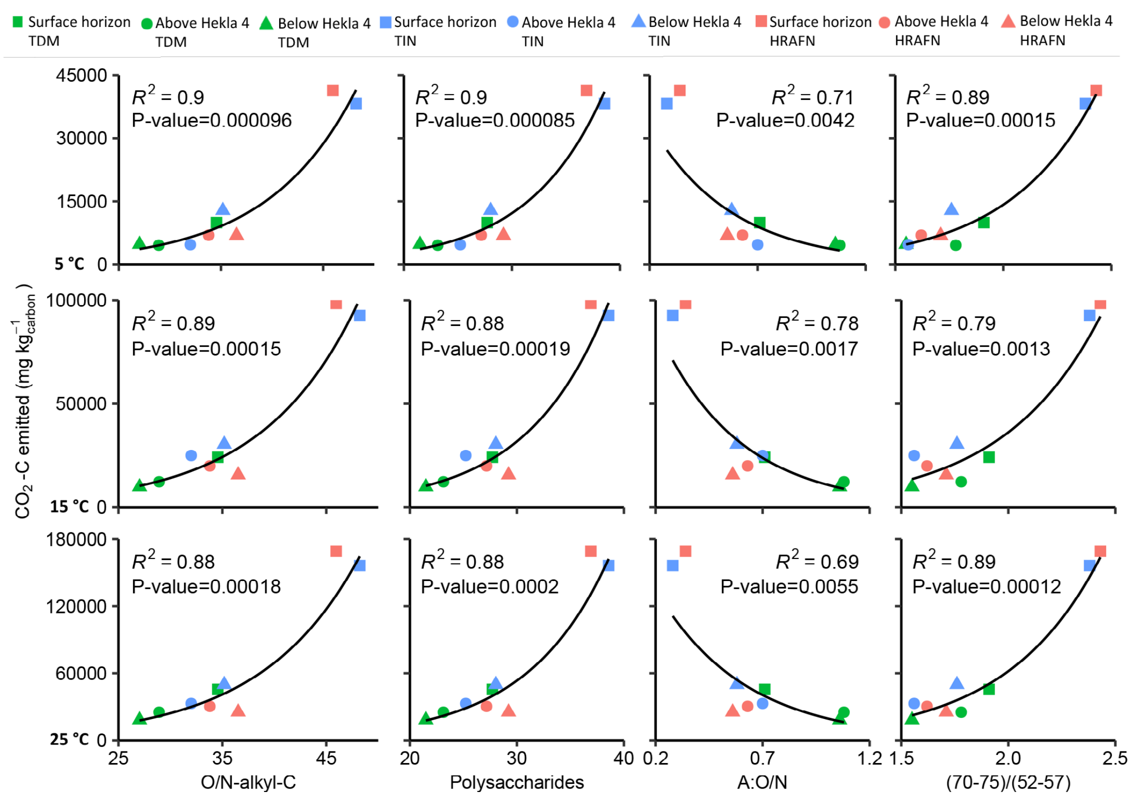

FIGURE 5 Exponential regression graphs showing cumulative CO_2-C (mg kg_{carbon}^{-1}) emitted at 5, 15 and 25°C after 400 days of incubation at the coastal site (Torfdalsmýri), the lowland site (Tindar) and the highland fringe (Hrafnabjörg) as a function of O/N-alkyl C (110–60 ppm), polysaccharides (95–60 ppm), A:O/N and (70–75)/(52–57) ratio. Colours represent the different sample sites (red = Hrafnabjörg (HRAFN), green = Torfdalsmýri (TDM), blue = Tindar (TIN)) and shapes represent different soil horizons (square = surface horizon, circle = above Hekla 4, triangle = below Hekla 4) [Colour figure can be viewed at wileyonlinelibrary.com]

with higher rates expected from soils with a higher (70–75)/(52–57) ratio.

The conspicuous similarity of the ^{13}C NMR spectra of the surface horizons at Tindar and Hrafnabjörg is reflected in only minor differences in C mineralization (Supporting information S1; Table 2). At those sites, the abundance of O-alkyl C, in particular polysaccharides, and a rather low alkyl C content, are mirrored in a low A:O/N ratio and a high (70–75)/(52–57) ratio (Figure 4; Supporting information S2), indicating high-quality, easily decomposable C (Leifeld et al., 2012; Preston et al., 1987). At Torfdalsmýri, the NMR spectrum of the surface horizon indicates C of lower quality, which is expected to be less easily decomposed. The A:O/N ratio is considerably higher, reflected also in less abundant polysaccharides. Indeed, C mineralization of the surface horizon at Torfdalsmýri with rather low quality C, a high proportion of hydrophobic, and hence recalcitrant alkyl C (Dungait, Hopkins, Gregory, & Whitmore, 2012; Preston et al., 1989) is considerably lower than mineralization from Tindar and Hrafnabjörg (Figure 3 and Table 2; Supporting information S1). The (70–75)/(52–57) ratio of the surface horizon at Torfdalsmýri is lower than at the other two sites and therefore predicts the low mineralization there (cf. Bonanomi et al., 2013).

The chemical composition of the litter parent material and the soil organic C evidently plays a role in C stability and C mineralization, but cannot solely account for the observed variations. Despite rather strong coefficients of determination (Figure 5), there are irregularities in C mineralization which cannot be attributed to the chemical composition of the C (cf. Baldock et al., 1997; Bonanomi et al., 2013; Leifeld et al., 2012). In contradiction to the similarities in C structure (Figure 4; Supporting information S2), mineralization rates in the layer below Hekla 4 at Tindar far exceed those of all other subsoil layers at Tindar and Hrafnabjörg (Supporting information S1; Table 2). This indicates that the stability of C in these subsoil layers is impacted by other soil properties than C structure alone.

4.3 | Relation between soil properties other than C structure and C mineralization

We proposed that tephra deposits would not only alter the C structure, but also other soil properties and, by that, modify C mineralization. A conspicuous property of Icelandic Histosols is that they often develop andic soil properties due to comparatively high IOM in form of volcanic deposits and aeolian material from eroded Andosols. As it is widely accepted that the association of SOM with mineral particles influences its stability (Kögel-Knabner et al., 2008; Mikutta, Kleber, Torn, & Jahn, 2006; Thornley & Cannell, 2001), changes in IOM content might influence the stability of the C in Histosols. In soils with andic properties, two processes are mainly responsible for mineral protection of SOM: the bonding of SOM with allophane clay, and bonding with metal ions such as Al^{3+} and Fe^{3+} (Arnalds, 2015; Mankasingh & Gísladóttir, 2019). Hence, it could be expected that SOM in the subsoil layers at Hrafnabjörg, with its higher IOM (Table 1), should be physically better protected than SOM at Tindar. The lower C mineralization rates at Hrafnabjörg below Hekla 4 than at Tindar support this assumption, but C mineralization rates above Hekla 4 oppose this argument. The layer above Hekla 4 at Hrafnabjörg contains the least SOC (16%) and the most IOM (67%). Despite that, C mineralization at 15 and 25°C is even a little higher than below Hekla 4 at Hrafnabjörg (Supporting information S1; Table 2).

Of course, the bonding of SOM to minerals is a function of various factors and is not fully understood (Hassink, Whitmore, & Kubát, 1997; Kopittke et al., 2020; Mayer & Xing, 2001; Varadachari, Mondal, Dulal, & Ghosh, 1994). Certainly, pH plays a role in facilitating or hampering the formation of organo-mineral complexes. For instance, the formation of aluminium-humus complexes, an important mechanism of soil organic C stabilization in non-allophanic soils with andic properties (Bäumler & Zech, 1994; Bonatotzky, Ottner, Erlendsson, & Gísladóttir, 2019; Matus et al., 2008; Matus, Amigo, & Kristiansen, 2006; Takahashi & Dahlgren, 2016), predominantly occurs at pH <5 (Adams, Hawke, Nilsson, & Powell, 2000; Shoji & Fujiwara, 1984). Generally, bonding of SOM to clay particles has been observed to correlate negatively with pH (Hassink et al., 1997; Mayer & Xing, 2001; Varadachari et al., 1994). The relatively high pH of 5.1 above Hekla 4 at Hrafnabjörg and below Hekla 4 at Tindar (Table 1) might therefore limit stabilization of SOM by organo-mineral complexes. Of course, pH has likely varied since the formation of the soils. Past soil acidity might either have enhanced or inhibited the formation of organo-mineral complexes in a way not reflected by current pH.

The C/N ratio might also influence the formation of organo-mineral complexes. A recent study by Kopittke et al. (2020) indicates that binding of organic matter to formerly organic free minerals is facilitated by a low C/N ratio. This might provide some explanation for the high C mineralization rates below Hekla 4 at Tindar, with a C/N ratio of 24, higher than the other subsoil layers at Hrafnabjörg and Tindar (Table 1).

Finally, intermixing of mineral material with organic material of Histosols might even have a destabilizing effect on SOC by affecting their macro- and microstructure, hydraulic properties and availability of nutrients (Rezanezhad et al., 2016; Strack, Kellner, & Waddington, 2005; Walczak, Rovdan, & Witkowska-Walczak, 2002). The supply of cations by weathering of tephra and aeolian material of volcanic origin (cf. Jakobsson, Jónasson, & Sigurdsson, 2008; Möckel et al., 2017) might enhance C mineralization (cf. Curtin, Campbell, & Jalil, 1998; Xu & Qi, 2001). The impact of different N levels on C turnover is debated. For instance, Ramirez, Craine, and Fierer (2010) observed an ubiquitous decrease in soil respiration following N additions in form of NH_4^+ and NO_3^-. Currey et al. (2010) observed a decline in C mineralization of more recalcitrant C compounds, but an increase for more labile C compounds. In summary, the comparatively high cation content at Tindar (Table 1), in interaction with rather low NH_4^+ content below Hekla 4 (Table 4), might contribute to the increased C mineralization in that layer. Meanwhile, the layer above Hekla 4 at Hrafnabjörg was the only layer that revealed a NO_3^- content above detection limit, possibly explaining the only marginally greater C mineralization than below Hekla 4 despite lower NH_4^+ content. Also, the mere occurrence of NO_3^- in that layer might indicate increased aeration of the soil after the tephra deposition (cf. Rydin & Jeglum, 2013).

4.4 | Impact of the tephra deposit on temperature sensitivity of C mineralization

The greatest impact of the Hekla 4 tephra can be seen in the temperature sensitivity of the SOM. The response of SOM decomposition to temperature changes has widely been observed to depend on SOM chemistry, with more labile SOM being less sensitive to temperature changes than recalcitrant forms (Conant et al., 2011). Mikan, Schimel, and Doyle (2002), for instance, observed an inverse relation between Q_{10} respiration coefficients and SOM quality of thawed arctic tundra soils, indicating that the decomposition of SOM or, more specifically, SOC, with a more complex structure is more sensitive to temperature than SOC with a simpler structure and, according to the commonly used definition, higher quality (Bosatta & Ågren, 1999; Fierer et al., 2005; Mikan et al., 2002).

Our results challenge the proposed inverse relation between temperature dependance of C mineralization and SOM quality. Long-term Q_{10}15/5 values exhibit an inconsistent pattern with depth (Table 3) and changes in SOM quality. Long-term Q_{10}25/15 values indicate a positive relationship between temperature dependance of C mineralization and SOM quality, but Q_{10}25/15 values of the surface horizon are in the majority of the layers higher than or equal to the subsoil layers. In addition, only Q_{10}25/15 values indicate a slightly greater temperature sensitivity at Torfdalsmýri than the other two peatlands, despite its overall more complex C structure. Possibly, the true temperature sensitivity of the SOM is blurred by the influence of the aeolian mineral deposits in the Histosols. The temperature dependence of mineralization increases after deposition of the Hekla 4 tephra, as indicated by consistently higher Q_{10}15/5 values above Hekla 4 than below (Table 3). The absence of the same pattern in Q_{10}25/15 might be explained by adaptation of the microbial communities to lower temperatures at these latitudes (cf. Frey, Lee, Melillo, & Six, 2013; Mikan et al., 2002; von Lützow & Kögel-Knabner, 2009). Also, higher sensitivity of decomposition to temperature changes within the lower temperature range has also been observed elsewhere (Kirschbaum, 1995; Lloyd & Taylor, 1994).

5 | CONCLUSIONS

This study demonstrates that tephra deposits are an important factor influencing C dynamics in peatlands within the vicinity of active volcanoes. Even though the low number of samples does not allow for strong conclusions built upon inferential statistics, hypotheses can be drawn from the ecological interpretation of the results of this study.

- Deposition of tephra has the potential to impact C dynamics, depending on various site-specific factors. This impact is not necessarily reflected in absolute C mineralization rates or C structure of soils after several thousand years since the eruption, but other soil properties indicate that the ecosystems and pedogenic processes were affected by the eruption. In this study, such changes are particularly prominent at the peatlands closer to the highlands and the active volcanic zones, that is, at Tindar and Hrafnabjörg. We observed, for instance, a decrease in SOM by a factor of 1.2 at Tindar and 1.5 at Hrafnabjörg. The SOM/SOC ratio decreased at Tindar and increased at Hrafnabjörg, both by a factor of 1.4.
- Moreover, input of mineral material impacts the temperature dependence of C mineralization more than the recalcitrance of the organic material itself. We observe a positive relationship between the temperature dependence of C mineralization and SOM quality, contrary to the findings of numerous previous studies. The Q_{10}5/15 values of the soils at Torfdalsmýri are either equal to, or lower than, at Tindar and Hrafnabjörg (up to two times lower), despite their relatively high content of recalcitrant C compounds. Also, we consistently observe greatest Q_{10}5/15 values in the layers above the Hekla 4 tephra deposit, up to 2.2 times as high as below Hekla 4, despite negligible differences in C structure. This is important as the frequency of extreme weather events and the number of hot and dry summer days is likely to increase in the future.
- Considering the degraded state of Icelandic soils and vegetation today, not only in the highlands, but also in widespread lowland areas, it is likely that a tephra deposit of similar thickness as Hekla 4 would have a greater impact on C dynamics today than it did over 4,000 years ago when ecosystems were presumably more resilient to volcanic eruptions of such magnitude.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

The authors confirm that data supporting the findings of this study are available within the article and the Supporting Information section. Further information about raw data can be made available from the corresponding author upon request.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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Paper II

Andic Soil Properties and Tephra Layers Hamper C Turnover in Icelandic Peatlands

Author's contribution:

Susanne Claudia Möckel (SCM), Guðrún Gísladóttir (GG) and Egill Erlendsson (EE) planned the study and applied for research funding. Field work was conducted by SCM, EE and Theresa Bonatotzky. Laboratory work was conducted by SCM, but ^{13}C NMR measurements were conducted at the Chair of Soil Science of Technical University of Munich, under guidance of Isabel Prater (IP) and with assistance of Franziska Fella. SCM conducted the data analysis and wrote the manuscript. The co-authors (EE, GG), and two anonymous reviewers provided useful comments to the manuscripts.

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Key Points:

- Andic soil properties impact the carbon structure of Histosols of volcanic regions and their carbon storage capacity
- Andic soil properties and thick tephra deposits appear to enhance long-term carbon stabilization in undisturbed peatlands
- Relatively undecomposed Histosols with andic properties may be a greater source of atmospheric carbon upon disturbance than anticipated

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Andic Soil Properties and Tephra Layers Hamper C Turnover in Icelandic Peatlands

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Abstract Due to frequent volcanic activity and erosion of dryland soils, magnified by land use after human settlement (ca. 870 CE), peatlands in Iceland receive regular additions of mineral eolian deposits. Their soils may develop not only histic but also andic characteristics. Yet, mineral eolian deposition as an environmental determinant of peatlands in Iceland is still poorly understood, not least with regard to the peatlands carbon (C) stores. This study advances our understanding of the impact of tephra deposition on Histosols by elucidating interactions between C characteristics and andic soil properties. We compare Histosols from three Icelandic peatlands of different degrees of exposure to eolian deposition by evaluating data sets of their C structure derived by ^{13}C NMR spectroscopy, andic soil properties based on selective extractions of Al, Fe, and Si, and decomposition proxies C/N, $\delta^{13}C$, and $\delta^{15}N$. By applying multivariate statistical methods, we are able to present several important patterns. Soil organic matter of Histosols with andic properties is less decomposed than that of Histosols without notable andic properties. Andic soil properties seem to impact their C structure by facilitating the formation of organo-mineral complexes, which particularly hamper the decomposition of chemically more labile C groups. Tephra layers appear to hamper microbial activity in deeper soil layers by preventing input of fresh organic matter. The interaction of andic and histic soil properties and the protective role of major tephra deposits may enable an unusual potential for long-term C stabilization in a natural peatland environment.

Plain Language Summary Peatlands belong to the greatest terrestrial carbon stores worldwide. Their organic soils possess exceptional capacities for long-term carbon storage. Peatlands in Iceland are unusual as they receive comparatively great amounts of windborne mineral material from volcanic eruptions or sparsely vegetated and eroded drylands. These mineral additions of volcanic origin to the otherwise organic substrate of the peatlands shape their soil characteristics and set them apart from similar soils in neighboring countries. On the one hand, they bear characteristics typical for organic soils in Nordic peatlands, on the other hand they possess characteristics of mineral soils of volcanic regions. Little is known about the impact of interactions between these characteristics on the peatlands carbon stores. This study increases our knowledge on carbon storage of peatlands in volcanic regions. We compare soils from three peatlands in northwest Iceland and shed light on interactions between their mineral and organic constituents, with a particular focus on soil organic carbon. We find strong indications that decomposition processes are slower in soils with stronger characteristics of mineral volcanic soils. In undisturbed (anaerobic) peatlands, this seems to impact long-term carbon storage positively, but in disturbed (aerobic) peatlands, it might pose a threat of accelerated carbon emissions.

1. Introduction

1.1. Role of Peatlands in the Global C Cycle

Most estimates of total soil organic carbon (SOC) in the world range between 1,400 and 1,600 Pg within the upper 1 m of soil only (Batjes, 1996, 2016; Schlesinger, 1977). Hence, SOC amounts to at least twice the amount of carbon (C) in the atmosphere (Lehmann & Kleber, 2015). Its distribution is far from even, but SOC increases toward the high latitudes (e.g., Batjes, 2016). Peatlands, wetlands with organic soils (Histosols), possess a disproportionate ability to store C. Despite covering only about 3% of terrestrial surface, they store a great part of SOC worldwide. Yu et al. (2010) estimate that peatlands accumulated approximately 612 Pg of C during the Holocene, while the bulk of this C (ca. 547 Pg) is stored in boreal and subarctic peatlands. The great C storage capacity of peatlands and its implications for the global C cycle is of growing research interest (e.g., Loisel et al., 2014; Nichols & Peteet, 2019; Page et al., 2011; Yu et al., 2010), not least its fate under increasing land use pressure and climate change. Our study augments the existing pool of research by focusing on relatively poorly investigated peatlands in Iceland, which are representative of peatlands of volcanic regions.

1.2. The Icelandic Wetland Soil Environment

The surface cover of Histosols, the organic soils of peatlands, is about 1,090 km^2 (Arnalds, 2004), surprisingly small for Iceland considering the high latitude (between ca. 63°N and 66°N), high precipitation, and the total extent of wetlands in the country which is estimated to be 7.800 km^2 (Ottósson et al., 2016) to 9.000 km^2 (Arnalds et al., 2016), around 7.8%–9% of the island. Hence, only about 12%–14% of wetlands in Iceland define as peatlands, while it is estimated that peatlands comprise at least one third of global wetlands (Parish et al., 2008). Located in an active volcanic environment, the soils of the Icelandic wetlands comprise a wide range of mineral and organic content (Arnalds, 2004; Bonatotzky et al., 2019; Möckel et al., 2017) and exhibit a mixture of histic, andic, and vitric properties (Bonatotzky et al., 2019). What properties dominate depends mainly on location of the wetlands with respect to the major eolian source areas. Only about 1.2% of the surface soil cover in Iceland meets the ≥20% C criterion of Histosols required by the Icelandic soil classification system (Arnalds, 2004; Arnalds & Óskarsson, 2009) and that of the WRB (IUSS Working Group WRB, 2015). The soils that do fulfill the ≥20% criterion for Histosols rarely reach the average of 46% C (e.g., Arnalds et al., 2016; Bonatotzky et al., 2019; Möckel et al., 2017) reported for northern peatlands by Loisel et al. (2014). The subsurface distribution of Histosols is certainly greater than 1.2%. More C rich subsoil layers are frequently found below more mineral surface soil layers of wetlands in Iceland (Arnalds, 2015; Gísladóttir et al., 2010, 2011; Möckel et al., 2017). This indicates a once greater distribution of peatlands, owing to more stable conditions for soil formation before the onset of anthropogenic influence ca. 870 CE. So called Histic Andosols comprise approximately 5.5% of surface soils in Iceland, which contain between 12% and 20% C (Arnalds, 2004). While the andic dominance of these soils places them in the major soil group of Andosols as defined by the Icelandic classification system (Arnalds, 2004; Arnalds & Óskarsson, 2009), they do bear strong histic properties, for example, only partly decomposed fibric organic material, high C content, and low bulk densities (Arnalds, 2004, 2015). The precise turning point between the formation of Histosols and more mineral soil layers within soils of wetlands varies geographically. Generally, it is associated with increased eolian material being deposited into the wetlands from eroded drylands, facilitated by a potent combination of vegetation destruction, livestock grazing, deteriorating climatic conditions, and volcanic activity (Dugmore et al., 2009; Gísladóttir et al., 2010, 2011).

1.3. The Influence of Andic Properties on C in Peatlands

Mineral soils of volcanic regions, Andosols, also possess great potential to store C (Kögel-Knabner & Amelung, 2021; Takahashi & Dahlgren, 2016; Wada, 1985), which is related to the mineral constituents of these soils. The main parent material is volcanic ejecta, which exerts an unusually strong impact on soil forming processes (Nanzyo et al., 1993). The weathering of this material leads to abundant precipitation of Al, Fe, and Si and to the preferential formation of short-range ordered (SRO) minerals like allophane and, (to a lesser extent) imogolite, the formation of Fe-hydroxides (i.e., ferrihydrite), as well as the development of Al/Fe-humus complexes (Bonatotzky et al., 2021; Shoji et al., 1993; Wada, 1989). The effect of SRO minerals, ferrihydrite, and other active forms of Al and Fe on C accumulation has been under investigation for several decades. Al and Fe are known to stimulate C accumulation by forming bonds with humus resulting in Al/Fe-humus complexes and organo-mineral complexes facilitated by SRO minerals and ferrihydrite (Asano & Wagai, 2014; Bonatotzky et al., 2021; Inagaki et al., 2020; Wada, 1989). In very organic soils, soil organic matter (SOM) is recognized to hinder allophane formation (Nanzyo et al., 1993; Wada, 1989) due to the preferential complexation of Al with humus and the consequent unavailability of Al for allophane formation (Dahlgren et al., 1993; Nanzyo et al., 1993). Rendering phosphorus unavailable for plants is another consequence of the high content of active Al and Fe (Nanzyo et al., 1993) through the formation of Al/Fe-phosphate compounds.

Soils of Icelandic peatlands are arguably important terrestrial C stores, not least in light of comparatively high bulk densities, even within the most organic ones (e.g., Arnalds, 2004; Bonatotzky et al., 2019; Gísladóttir et al., 2011; Loisel et al., 2014; Möckel et al., 2017). Despite rarely reaching relative C contents of other northern peatlands of nonvolcanic regions, their carbon stocks are in line with or even higher than global averages of 1,125 t ha^{-1} in peatlands reported by Joosten et al. (2016). According to Óskarsson et al. (2004), C stocks of Histosols in Iceland are on average 1,975 t ha^{-1}, while C stocks of the more mineral Histic Andosols comprise

891 t ha^{-1}. Yet, research on the interactions between histic and andic soil properties and their impact on C dynamics is still in its infancy. Several studies have detected increased decomposition of SOM adjacent to tephra layers (Broder et al., 2012; Mathijssen et al., 2019). Tephra layers are also regularly observed to induce changes in vegetation characteristics of peatlands (e.g., Blackford et al., 2014; Eddudóttir et al., 2017; Payne & Blackford, 2008), which, in turn, may impact the chemical composition and stability of their SOC (Kögel-Knabner, 1997; Leifeld et al., 2012). Questions remain if the mineralogical environment of soils of peatlands in volcanic regions impacts the stability of their SOC. This might, for instance, occur by the formation of organo-mineral complexes otherwise not found in organic soils, and by impacting the chemical composition of the SOC (Takahashi & Dahlgren, 2016). The simultaneous occurrence of active volcanism and peatlands is not as rare as this sparse research implies (Payne & Blackford, 2008). Besides Iceland, it may be found in regions as diverse as the tropical and subtropical Andes, Japan, Indonesia, New Zealand, Alaska, Western Canada, Kamchatka, and Patagonia (Ayres et al., 2006; Buytaert et al., 2007; Chimner & Karberg, 2008; Hotes et al., 2006; Payne & Blackford, 2008; Ratcliffe et al., 2020; Yu, 2006). In order to understand C cycling in the peatlands of these regions, and associated C cycle–climate feedbacks, it is necessary to disentangle the interplay between andic and histic soil properties, that is, the interactions between mineral constituents typical for andic soils and the chemical characteristics of SOC of histic soils. Buytaert et al. (2007) found a strong indication that Al-humus complexes in organic soils in Ecuador play a role in C accumulation. But the majority of studies on C dynamics of volcanically affected peatlands does not encompass an investigation of andic properties (e.g., Chimner & Karberg, 2008; Hribljan et al., 2016; Ratcliffe et al., 2020). Questions on the potential interaction between andic soil properties and the chemical composition of C in Histosols as derived, for example, by ^{13}C nuclear magnetic resonance (NMR) spectroscopy have only rarely been addressed (Matus et al., 2014). A recent study by Möckel et al. (2021) provides evidence for the impact of major tephra layers on C mineralization of Icelandic Histosols and its temperature sensitivity without inducing a major shift in ^{13}C NMR spectra. This indicates that the stability of SOC of Histosols in volcanic regions is governed not only by the chemical structure of the SOC and hydrology (e.g., Kögel-Knabner & Amelung, 2021) but also by other factors of the soil environment, not least soil mineral constituents and tephra deposits.

1.4. Research Aim and Objectives

It is essential to disentangle interactions between histic and andic soil properties to understand C storage in peatlands of volcanic regions. The immense potential of intact peatlands to act as a net C sink (Gorham, 1991; Yu et al., 2010) goes hand in hand with the threat of disturbed peatlands being a net source of atmospheric C (Leifeld et al., 2019). This is exemplified by the emission trends of greenhouse gases in Iceland, where net emissions between 1990 and 2018 are estimated to be highest from the land use, land use change, and forestry sector (LULUCF). Most of this emission is ascribed to the drainage of organic wetland soils (The Environment Agency of Iceland, 2020). The aim of this study was to advance understanding of the impact of tephra deposition on soil development in peatlands with a focus on interactions between histic and andic properties and their impact on SOC characteristics and SOC storage. To achieve this aim, the study was based on the following objectives:

1. To determine if increased mineral content of peatlands leads to decreased C storage capacity. Therefore, we evaluate by Spearman rank correlation if there is a relation between relative contents of C (%C), mineral material (%Ash), dry bulk density (DBD), and C density.
2. To determine the development of the structure of SOC throughout profiles of Histosols from three Icelandic peatlands through time and under varying impact by tephra deposition. The peatlands vary in proximity to source areas of eolian material. We apply robust principal component analysis (PCA) and cluster analysis of ^{13}C NMR spectra, with a particular focus on potential variations around two tephra deposits, Hekla 4 and Hekla 3.
3. To evaluate the development of andic properties in Histosols from three Icelandic peatlands through time and under varying impact by tephra deposition. We apply a variety of variables, including Al and Fe of Al/Fe-humus complexes, allophane and ferrihydrite content based on selective extractions of Al, Fe, and Si with ammonium oxalate and sodium pyrophosphate, and P-retention. The multivariate data are statistically evaluated by robust PCA and cluster analysis.
4. To evaluate if there is a relationship between (a) C structure and andic properties and (b) a set of variables, that we refer to here as decomposition proxies (stable isotope ratios $\delta^{13}C$ and $\delta^{15}N$, C/N ratio) and andic soil

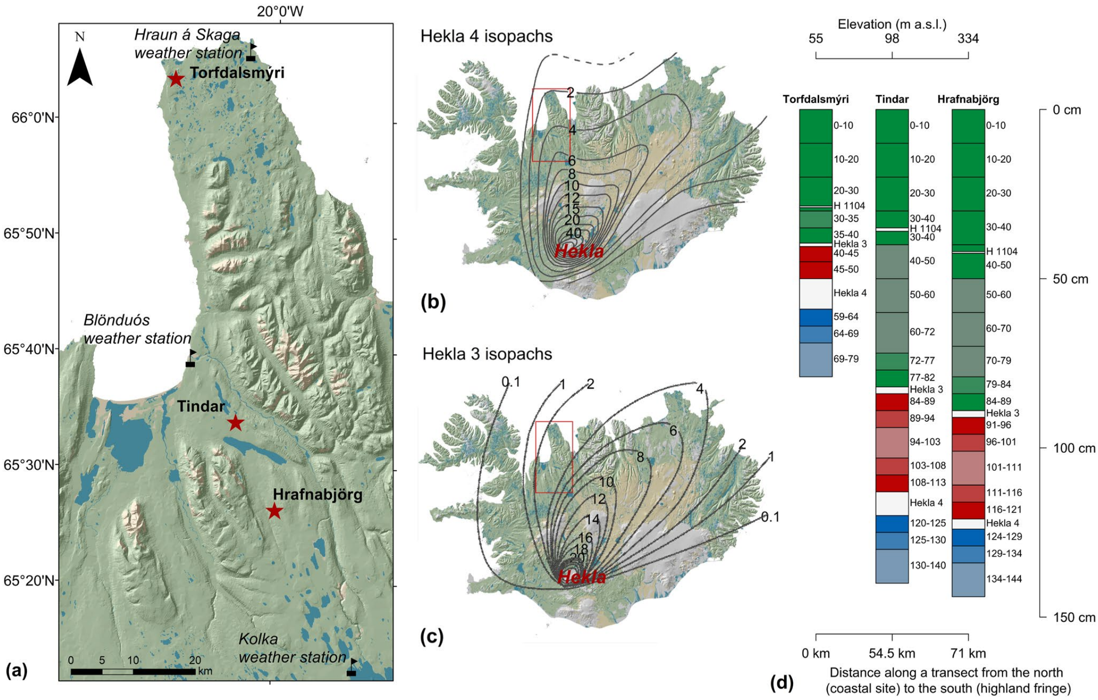

Figure 1. (a) The map shows the research area in Austur Húnavatnssýsla, northwest Iceland, the location of the three peatland sites Torfdalsmýri, Tindar, and Hrafnabjörg and the weather stations. The maps in (b) and (c) show the location of the research area in Iceland and Hekla 4 and Hekla 3 isopachs (adapted from G. Larsen & Thorarinsson, 1977). (d) Soil cores from each peatland showing depth intervals used during sampling. White layers represent tephra deposits within the soil column. Blue layers reflect pre-Hekla 4 soil layers. Soils formed between the eruptions of Hekla 4 and Hekla 3 are depicted in red and post-Hekla 3 layers in green. Darker colors reflect increased influence of eolian material in the form of either volcanic ejecta (i.e., tephra) or eolian material from sparsely vegetated or barren areas. The tephra deposit from an eruption of the volcano Hekla in 1104 CE (G. Larsen & Thorarinsson, 1977) is also shown. This eruption occurred ca. 230 years after the settlement of Iceland and serves as an approximate demarcation line between prehistorical and historical soil formation. Soil layers formed after Hekla 1104 are assumed to be subject to greater eolian deposition due to increased soil erosion after the settlement (Dugmore et al., 2009; Gísladóttir et al., 2010, 2011), particularly after 1100 in the study area (Bates et al., 2021; Tinganelli et al., 2018).

properties. We apply redundancy analysis (RDA) to evaluate if variations in C structure may be explained by variations in andic soil properties, and if variations in andic soil properties are reflected by variations in decomposition proxies.

2. Methods

2.1. Research Area and Sampling Approach

The research area is in Austur Húnavatnssýsla in northwest Iceland (Figure 1a). Soil samples were collected from three peatlands along a north-south transect from the coast (Torfdalsmýri), via the lowlands (Tindar) to the highland fringe (Hrafnabjörg). The peatlands differ in their distance from the major source areas of eolian material (sparsely vegetated areas in the interior of the country and the active volcanic zones). At each peatland, one soil profile was excavated (Figure 1d). Exact site selection within peatlands was based on two criteria: it should be located in the middle of the peatland ecosystem, and it must contain well preserved tephra deposits from the Hekla 3 and Hekla 4 eruptions (described in the next subchapter). The following sampling locations were chosen: N66°03.276′ W020°22.651′ at Torfdalsmýri, N65°34.732′ W020°07.359′ at Tindar, and N65°26.266′ W019°59.573′ at Hrafnabjörg. Pooled bulk soil samples were collected at 10 cm intervals down to a depth of 20 cm below the Hekla 4 tephra layer (Figure 1d). Above and below the Hekla 3 and Hekla 4 tephra layers, the sampling interval was reduced to 2 × 5 cm (see Bonatotzky et al., 2019, 2021). All soil samples were subsequently stored at 4°C.

Weather observations are available from the following weather stations: Hraun á Skaga (1956–2015) for Torfdalsmýri, Blönduós (1949–2001) for Tindar and Blönduós, and Kolka (1994–2015) for Hrafnabjörg (Figure 1a; IMO, n.d.-a, n.d.-b). Mean annual temperatures range from 0.7°C in the highlands to about 3°C in the lowlands and unsheltered coastal areas. Average summer tritherm (June–August) temperatures are 7.8°C and 7.9°C in the highlands and unsheltered coastal areas, and 9.1°C at more sheltered sites in the lowlands. The annual precipitation of about 400–500 mm $year^{-1}$ is comparatively low, but generally slightly greater in areas close to the sea than the highlands. Average wind speeds range between 3.8 and 7.4 m s^{-1}, with greatest wind speeds at the highlands and lowest in sheltered lowlands.

2.2. Two Late Holocene Volcanic Eruptions: Hekla 4 and Hekla 3

The volcanic eruptions of Hekla 4 (ca. 4.35 ka BP; Dugmore et al., 1995) and Hekla 3 (ca. 3.06 ka BP; Dugmore et al., 1995) are among the most voluminous silicic Holocene eruptions in Iceland, with an estimated 9 and 12 km^3 of tephra ejected, respectively (G. Larsen & Thorarinsson, 1977). While the volcano Hekla is located in South Iceland, the tephra of the two eruptions was spread over great parts of Iceland, mainly toward the north and northeast as indicated by stratigraphic evidence (Figures 1b and 1c). The average thickness of the compacted tephra deposits in the research area of this study is about 2–6 cm (G. Larsen & Thorarinsson, 1977) for both tephra layers, but Hekla 4 tephra deposits may even be thicker (Eddudóttir et al., 2017). The thicknesses of the tephra deposits were probably not necessarily lethal for the vascular plants of the peatland, but might have been so for bryophytes (e.g., Antos & Zobel, 1986). Also, they might at least have put pressure on some vascular plants and induced a shift in dominant species (Hotes et al., 2006). Initial thicknesses might have been greater and were probably later altered by redistribution by wind and water (Eddudóttir et al., 2020; Möckel et al., 2021) and compaction. Despite several studies (Eddudóttir et al., 2017; Möckel et al., 2017; Tinganelli et al., 2018) providing paleoenvironmental evidence of relatively stable ecosystems with a fair resilience toward tephra deposits before the onset of anthropogenic influence in northwest Iceland, some signs of adverse impact by tephra have been reported by the same studies. In particular, ecosystems in the climatically harsh highland environment were likely more sensitive toward vegetation and soil deterioration induced by large tephra deposits.

2.3. Laboratory Analyses

2.3.1. Solid-State ^{13}C NMR Spectroscopy

Solid-state ^{13}C NMR spectroscopy was used to determine the chemical composition or structure of SOC that impacts the characteristics of SOM and decomposition processes (Kögel-Knabner, 1997). A cross-polarization magic angle spinning technique (CPMAS) with a Bruker DSX 200 spectrometer (Billerica/USA) was applied with a proton resonance frequency of 50.32 MHz and a spinning speed of 6.8 kHz. To circumvent spin modulation during the Hartmann–Hahn contact, a ramped ^1H-pulse was used during a contact time of 1 ms. Pulse delays of 0.8 s were used for all samples and between 2,736 and 11,325 scans were accumulated per measurement. A line broadening of 25 Hz was applied. The ^{13}C chemical shifts were calibrated relative to tetramethylsilane that was equalized to 0 ppm.

Integration was based on Knicker et al. (2005). The signal intensity was integrated into six chemical shift regions in order to determine the relative share of the different C compounds: 220–160 ppm (carboxyl/carbonyl/amide C), 160–140 ppm (O/C-aryl C), 140–110 ppm (C/H-aryl C), 110–60 ppm (O/N-alkyl C), 60–45 ppm (O/N-alkyl C), and 45–0 ppm (alkyl C). Additionally, signal intensities for 70–75 ppm (O-alkyl C of carbohydrates) and 52–57 ppm (methoxyl C of lignin) were determined in order to calculate the so called (70–75)/(52–57) ratio. Bonanomi et al. (2013) observed this ratio to correlate positively with decay rates, which is ascribed to the relatively higher content of the labile O-alkyl C of carbohydrates than the more recalcitrant methoxyl C of lignin as (70–75)/(52–57) ratios increase. As a proxy for decomposition, we calculated the alkyl C to O/N-alkyl C (A:O/N) ratio. Higher ratios indicate a more advanced decomposition, which is characterized by relatively greater content of recalcitrant alkyl C than the more labile O/N-alkyl C (Baldock et al., 1997).

2.3.2. DBD, SOM, %C and %N, and Stable Isotope Ratios $\delta^{13}C$ and $\delta^{15}N$

The DBD was determined by mass loss after drying of a known soil volume; SOM and %Ash were measured by loss on ignition at 550°C (Heiri et al., 2001). Determination of total carbon (%C) and nitrogen (%N) by dry combustion (Soil Survey Staff, 2014b) and of the stable isotope ratios $\delta^{13}C$ and $\delta^{15}N$ was conducted by the Cornell Isotope Laboratory in the USA. Due to the absence of carbonate minerals in Icelandic soils, SOC is equivalent to %C (Bonatotzky et al., 2021; Mankasingh & Gísladóttir, 2019; Vilmundardóttir et al., 2014). Natural $\delta^{13}C$ and $\delta^{15}N$ in Histosols provide information on the degradation and the hydrology of peatlands (e.g., Alewell et al., 2011; Andersson et al., 2012; Drollinger et al., 2019; Krüger et al., 2014). An increase of $\delta^{13}C$ and $\delta^{15}N$ with depth indicates aerobic decomposition of SOM and a higher state of degradation. Stable or decreasing $\delta^{13}C$ and stable $\delta^{15}N$ values indicate anaerobic decomposition. Based on DBD and %C, C density (kg m^{-3}) was calculated for each sampling interval. C stocks (t ha^{-1}) were calculated for three time intervals at each site: Hekla 3 to present, Hekla 4 to Hekla 3, and before Hekla 4. Note that basal ages of soil layers formed before Hekla 4 are not known.

2.3.3. Phosphate Retention and pH in DiH_2O and NaF

Phosphate retention as a diagnostic criterion of andic soil properties (≥85%; IUSS Working Group WRB, 2015) was measured by spectrophotometrical absorbance at 466 nm after color reaction with nitric vanadomolybdate acid reagent (Blakemore et al., 1987). The pH in 1 N NaF solution (pH_{NaF}) was determined following Blakemore et al. (1987) and Soil Survey Staff (2014b). While pH_{NaF} is not a diagnostic criterion of andic properties (Childs, 1985; IUSS Working Group WRB, 2015), it is routinely used as an indicator of amorphous material, common in soils of volcanic regions. High abundance of amorphous material results in $pH_{NaF} \geq 9.4$. Soil acidity (pH_{H_2O}) was measured in deionized water (DiH_2O), using a soil:water ratio of 1:10 (Blakemore et al., 1987; Rayment & Lyons, 2011). This unusually small ratio is mainly used for organic soils such as Histosols.

2.3.4. Selective Dissolution of Al, Fe, and Si

Extraction of Al, Fe, and Si with ammonium oxalate (0.2 M, pH 3.0) was carried out with a SampleTek mechanical vacuum extractor as described in Soil Survey Staff (2014b; method 4G2). The Al, Fe, and Si thus extracted (Al_o, Fe_o, Si_o) is indicative of the active forms of Al and Fe of organic complexes and of noncrystalline hydrous oxides of Fe and Al, allophane, and amorphous aluminosilicates (Nanzyo et al., 1993; Wada, 1989). The sum of $Al_o + 1/2Fe_o$ was calculated, which is a diagnostic criterion of andic soil properties (≥2%; IUSS Working Group WRB, 2015). Ferrihydrite was estimated as %ferrihydrite = %Feo × 1.7 (Childs, 1985). Sodium pyrophosphate was used to extract the part of active Fe and Al (Fe_p, Al_p), which is associated with organic compounds (Al/Fe-humus complexes; Soil Survey Staff, 2014b; method 4G3). Allophane or allophane-like constituents were estimated by the equation proposed by Mizota and van Reeuwijk (1989), based on Parfitt and Wilson (1985). While Mizota and van Reeuwijk (1989) recommend to use only Al/Si ratios (derived from $(Al_o - Al_p)/Si_o$) between 1.0 and 2.5 for the calculation of allophane, we also use Al/Si ratios <1, which may occur in allophane (Parfitt & Kimble, 1989).

2.4. Statistical Evaluations

Spearman rank correlations were determined in order to evaluate if there is a relation between %C, %Ash, DBD, and C density (R package GGally, function ggpairs; Quinn & Keough, 2002; Schloerke, 2021).

In order to disentangle the development of the C structure through time, the data set of the six ^{13}C NMR chemical shift regions and the A:O/N and (70–75)/(52–57) ratio was investigated by robust PCA and hierarchical clustering. Robust PCA was chosen due to several multivariate outliers (R package robCompositions, function outCoDa; de Sousa et al., 2020; Filzmoser & Hron, 2008; Filzmoser et al., 2018). The robust PCA was conducted by the function pcaCoDa from the R package robCompositions (Filzmoser et al., 2009, 2018). This function opens compositional data such as those derived from ^{13}C NMR by isometric logratio transformation (ilr) and back-transforms the loadings and scores into centered logratio (clr) space to facilitate graphical illustration and interpretation of the results.

The clustering tendency of the ilr transformed ^{13}C NMR data set (see van den Boogaart & Tolosana-Delgado, 2013; van den Boogaart et al., 2020) was investigated by the Hopkins statistic and a dissimilarity matrix (R packages factoextra and clustertend; Kassambara, 2017; Kassambara & Mundt, 2020; YiLan & RuTong, 2015).

The clustering approach was chosen based on comparison of internal measures and stability measures of hierarchical, *k*-means, and pam clustering (see Kassambara, 2017). The optimal number of clusters was determined by comparison of the elbow, silhouette, and gap statistic method and by assessing the goodness of different clustering approaches by silhouette width plots (R packages factoextra and NbClust; Charrad et al., 2014; Kassambara, 2017; Kassambara & Mundt, 2020). Consequently, hierarchical clustering with two clusters was conducted using Ward's minimum variance method and Manhattan distance, which is less sensitive to outliers than Euclidean distance (R package factoextra, function eclust; Kassambara, 2017).

Similarly, robust PCA and cluster analysis were conducted in order to evaluate the variability of andic soil properties. Compositional variables based on selective extractions were used, and arcsine transformed P-retention as external variable (see Kynčlová et al., 2016).

In order to investigate the impact of variations in andic soil properties on variations in C structure, RDA (R package vegan; Oksanen et al., 2019) was conducted. P-retention and $Al_o + 1/2Fe_o$ were omitted due to low loadings of these variables in the robust PCA. The matrices of response variables and explanatory variables were transformed to the ilr space for performance of RDA and the results back transformed to the clr space for ease of interpretation (R package compositions; van den Boogaart & Tolosana-Delgado, 2013; van den Boogaart et al., 2020).

The impact of andic properties and C structure on decomposition proxies (C/N, $\delta^{13}C$, $\delta^{15}N$) was also investigated by RDA. The explanatory data matrices (andic soil properties and C structure) were transformed to the ilr space while the response variable matrix (decomposition proxies) was normalized prior to performance of RDA. All statistical analyses were carried out using the software R, version 4.0.2.

3. Results

3.1. Hekla 3 and Hekla 4 Tephra Deposits

The Hekla 3 and Hekla 4 tephra formed well-defined strata (Figure 1d), with Hekla 4 tephra thicknesses of 9 cm at Torfdalsmýri, 7 cm at Tindar, and 3 cm at Hrafnabjörg, and Hekla 3 tephra thicknesses of <0.5 cm at Torfdalsmýri, 2 cm at Tindar, and 2 cm at Hrafnabjörg. Hekla 4 deposits at Torfdalsmýri and Tindar are thicker than isopachs would indicate (2 and 4 cm, respectively; Figure 1a; G. Larsen & Thorarinsson, 1977), but thinner than isopachs would suggest at Hrafnabjörg (4–6 cm). Hekla 3 tephra layers are all thinner than isopachs for the area indicate (2 cm at Torfdalsmýri, between 2 and 4 cm at Tindar and Hrafnabjörg). Where tephra deposits are thinner than expected, this might be a result of posteruption redistribution by wind rather than reflecting initial thicknesses.

3.2. Variation in C Structure Derived by Robust PCA and Cluster Analysis

Changes in C structure are discernible around the Hekla 4 tephra deposits (Figure 2). At Torfdalsmýri, these changes are subtle and characterized by an initial increase of the A:O/N ratio toward younger soil layers, facilitated by an increase in alkyl C, and a decrease in O/N-alkyl C. This trend is reversed in the upper 30 cm, where A:O/N ratios decrease again. At Tindar and Hrafnabjörg, the changes are more pronounced and characterized by a decrease in the (70–75)/(52–57) ratio, an increase in alkyl C, and a decrease in O/N-alkyl C (110–60 ppm). These changes are supported by the robust PCA (Figure 3a) and the cluster analysis (Figure 3c). The C structure at Tindar and Hrafnabjörg is similar, but they both differ from Torfdalsmýri with the exception of samples from the depths 0–10, 10–20, and 69–79 cm. Cluster 1 (green) is composed of all samples from Tindar and Hrafnabjörg and depths 0–10, 10–20, and 69–79 cm from Torfdalsmýri, whereas cluster 2 (red) is exclusively composed of the remaining samples from Torfdalsmýri (for goodness of clustering, compare silhouette width plot in Figure 3b).

There are several noteworthy subclusters (Figure 3c), which are reflected by the robust PCA (Figure 3a): at Tindar, all soil layers between Hekla 4 and Hekla 3 (84–113 cm) form one obvious subcluster. Clearly, there is a shift in C structure after the eruption of Hekla 4. At Hrafnabjörg, the layers formed between Hekla 4 and Hekla 3 (91–121 cm) do not form as clear a subcluster, but the subcluster also includes several soil layers formed after Hekla 3. Nevertheless, a shift in C structure after the eruption of Hekla 4 is discernible. At Hrafnabjörg and Tindar, the soil layers below Hekla 4 reveal a similar C structure as upper soil layers, that is, the upper 0–40 cm at Tindar and 0–10 cm at Hrafnabjörg.

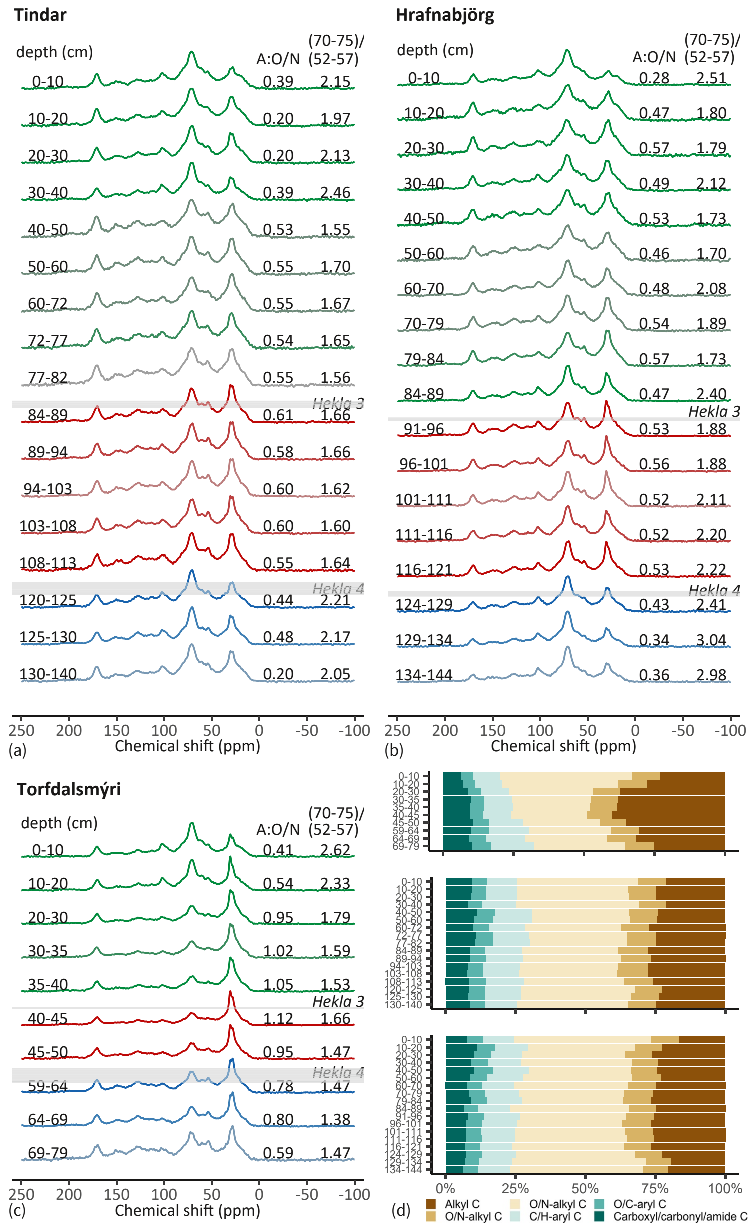

Figure 2. (a–c) ^{13}C nuclear magnetic resonance (NMR) spectra of the three peatlands, including A:O/N and (70–75)/(52–57) ratios. Soil layers formed before Hekla 4 are colored in blue, soils formed between Hekla 4 and Hekla 3 are depicted in red, and soils formed after Hekla 3 in green. Darker colors reflect increased influence of eolian material in the form of either volcanic ejecta (i.e., tephra) or eolian material from sparsely vegetated or barren areas. Soil layers formed after Hekla 1104 (see Figure 1d) are assumed to be subject to greater eolian deposition due to increased soil erosion after the settlement (Dugmore et al., 2009; Gísladóttir et al., 2010, 2011). Stacked bar charts in (d) show the relative share of the chemical shift regions.

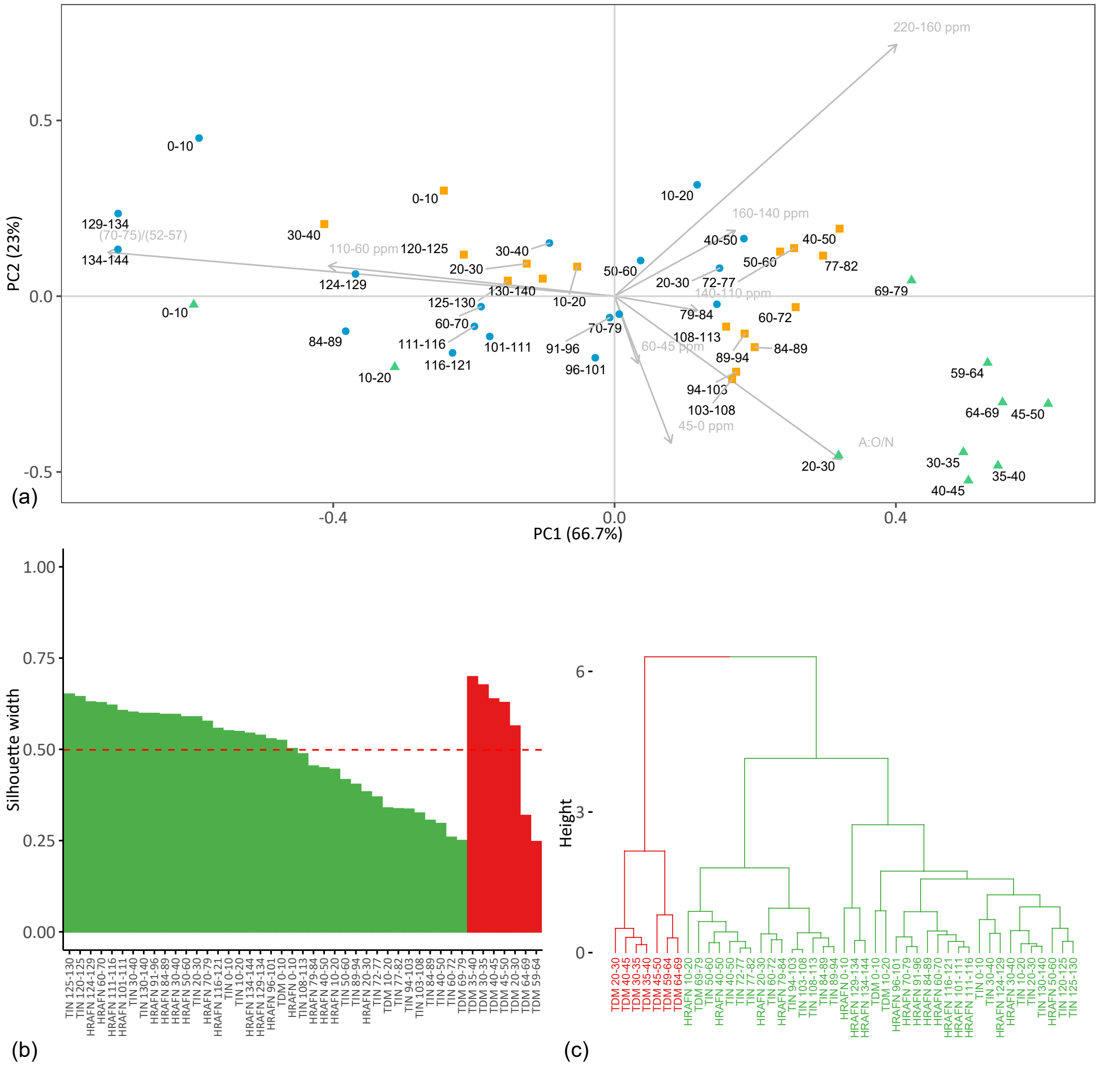

Figure 3. (a) Biplot of the robust principal component analysis on the ^{13}C NMR data. Observations of different sample sites are depicted by shapes and colors (Torfdalsmýri [TDM]: green triangle, Tindar [TIN]: orange square, and Hrafnabjörg [HRAFN]: blue circle). (b) Silhouette width plot for hierarchical clustering. Average silhouette width = 0.5 (red broken line); Dunn index = 0.298. (c) Dendrogram based on hierarchical clustering, using Manhattan distance and Wards criterion (see Kassambara, 2017) and number of clusters $k = 2$.

3.3. Total %C and %N, C/N, SOM DBD, C Density, and C Stocks

Total %C and %N content at Tindar and Hrafnabjörg is highest between tephra layers, apart from one outlier at each site (Figure 4). This is accompanied by high SOM levels at Tindar, but comparatively lower SOM levels at Hrafnabjörg. At Torfdalsmýri, the same variables conspicuously decrease between tephra layers. The DBD is overall low until shortly after Hekla 3 at Tindar and Hrafnabjörg but experiences a peak between tephra deposits at Torfdalsmýri. The C/N ratio is very stable throughout the soil profile at Torfdalsmýri, but at Tindar and Hrafnabjörg it increases with depth and is noticeably higher below Hekla 4 than above. C density is overall highest at Torfdalsmýri. However, soil accumulation at Tindar and Hrafnabjörg since the Hekla 4 tephra deposition is 113

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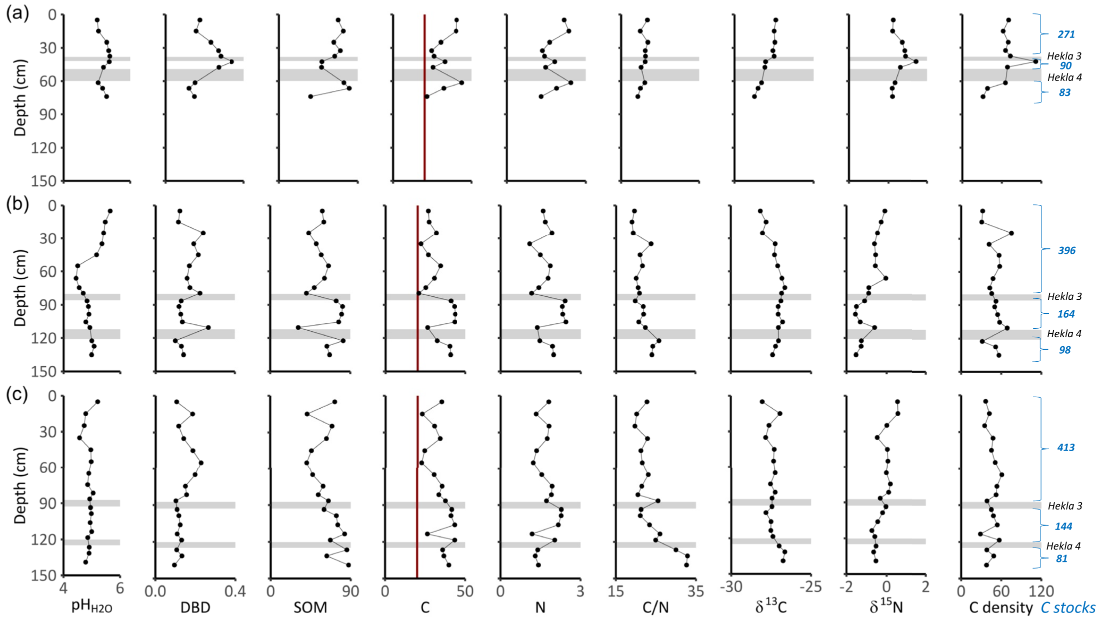

Figure 4. Results of complementary soil properties used in this study at Torfdalsmýri (a), Tindar (b), and Hrafnabjörg (c). Dry bulk density (DBD) is presented as g cm^{-3}, soil organic matter (SOM), C, and N are in %, C/N as molar ratio, $\delta^{13}C$ and $\delta^{15}N$ are presented in ‰, and C density in kg m^{-3}. Included are also total C stocks (t ha^{-1}, blue numbers) for the following time spans: Hekla 3 to present, Hekla 4 to Hekla 3, and before Hekla 4. Note that basal ages of soil layers formed before Hekla 4 are not known. Vertical red lines represent the following threshold: C ≥ 20% as diagnostic criterion of Histosols. Shaded gray bars indicate the tephra deposits Hekla 3 and Hekla 4.

and 121 cm, respectively, compared to only 50 cm at Torfdalsmýri. Consequently, total C stocks that accumulated since the Hekla 4 eruption are with 560 and 557 t ha^{-1}, respectively, notably higher at these two sites than at Torfdalsmýri (361 t ha^{-1}).

Spearman rank correlation between %C, %Ash, DBD, and C density (Figure 5) indicates a statistically significant inverse relation between %C and DBD ($\rho = -0.52$, $p < 0.001$) and %C and %Ash ($\rho = -0.65$, $p < 0.001$). Albeit, there is a significant positive relation between DBD and C density ($\rho = 0.7$, $p < 0.001$). The slight positive relation between %Ash and C density proved statistically insignificant ($\rho = 0.16$, $p = 0.3$).

3.4. Variation in Andic Soil Properties Determined by Robust PCA and Cluster Analysis

The andic soil properties (Figure 6) draw a more diffuse pattern than the C structure. Yet, some changes that seem to be related to the occurrence of the tephra layers can be discerned at Tindar and Hrafnabjörg. There, the soils are comparatively allophanic, accompanied by low Al_p/Al_o ratios and high Al_o and $Al_o + 1/2Fe_o$ values, which frequently fulfill the ≥2% diagnostic threshold of andic soil properties (IUSS Working Group WRB, 2015). Between the Hekla 3 and Hekla 4 tephra deposits, the opposite is true. While pH_{NaF} rarely exceeds the ≥9.4 threshold, it is particularly low between tephra layers at Tindar and Hrafnabjörg. Contents of Fe_o, Fe_p, and ferrihydrite are most pronounced at Hrafnabjörg, with highest abundances recorded above the Hekla 3 tephra deposit.

This pattern is supported by the robust PCA (Figure 7a) and the cluster analysis (Figure 7c). Some grouping according to peatlands is discernible, but there is also considerable overlap between sites. Within-site variability is lowest at Torfdalsmýri. For some samples, the allocation to clusters is diffuse (compare silhouette width plot in Figure 7b). Cluster 1 (green) contains samples from all three sites, whereas cluster 2 (red) contains samples from Tindar and Hrafnabjörg only. There is a clear demarcation of the soil layers formed between Hekla 4 and Hekla 3

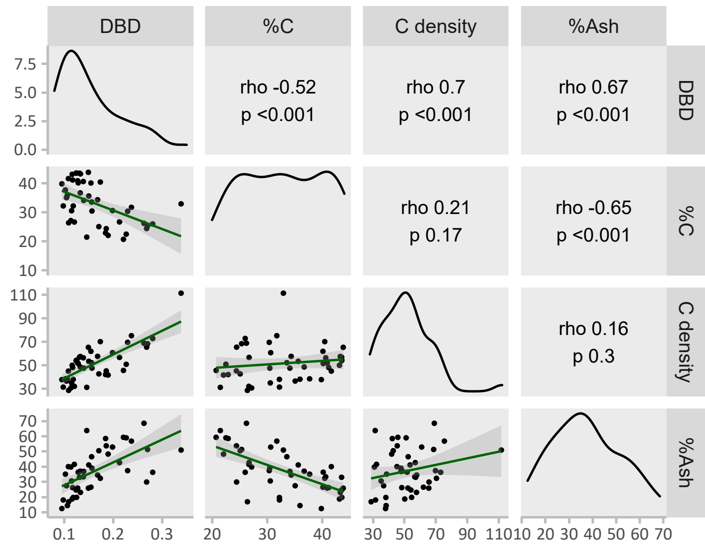

Figure 5. Matrix of scatterplots and Spearman rank correlation coefficients (ρ) and probability value (p) between %C, %Ash, DBD, and C density.

at Tindar and Hrafnabjörg. Soils between 84 and 108 cm depth at Tindar and 91 and 121 cm depth at Hrafnabjörg form a clear subcluster each.

3.5. Impact of Andic Soil Properties on Variations in C Structure by RDA

A moderate share of the variation of C structure is constrained by andic soil properties (unadjusted $r^2 = 0.41$, adjusted $r^2 = 0.29$), and about 95% of the constrained variation is contained within the first two dimensions of the RDA (Figure 8a). Only the effect of the first dimension (73% of constrained variation) proved statistically significant ($p = 0.001$). The contents of Al_p, Al_o, Al_p/Al_o, and Fe_p/Fe_o seem to be positively related to alkyl C and the A:O/N ratio, while their impact on other C groups is little or negative. Fe_p, Si_o, and allophane seem strongly negatively correlated with alkyl C and A:O/N ratio. Content of Fe_p is positively related to O/N-alkyl C (110–60 ppm) and (70–75)/(52–57) ratio. Allophane and Si_o are positively related to carboxyl/carbonyl/amide C and H/C-aryl C.

3.6. Impact of C Structure on Decomposition Proxies (C/N, $\delta^{13}C$, $\delta^{15}N$) by RDA

A moderate share of the variation of the decomposition proxies C/N, $\delta^{13}C$, and $\delta^{15}N$ is constrained by C structure (unadjusted $r^2 = 0.54$, adjusted $r^2 = 0.45$), and nearly 98% of the constrained variance is contained within the first two dimensions of the RDA (Figure 8b), both proving significant ($p = 0.001$). The C/N ratio appears positively related to the (70–75)/(52–57) ratio and O/N-alkyl C (110–60 ppm), but negatively to carboxyl/carbonyl/amide C, A:O/N, and alkyl C. On the other hand, carboxyl/carbonyl/amide C, A:O/N, and alkyl C are positively related to $\delta^{15}N$, but negatively to $\delta^{13}C$. The C groups of C/H-aryl C and O/C-aryl C, in turn, are positively related to $\delta^{13}C$ and negatively to $\delta^{15}N$.

3.7. Impact of Andic Soil Properties on Decomposition Proxies by RDA

The direct impact of andic soil properties on the decomposition proxies C/N, $\delta^{13}C$, and $\delta^{15}N$ proved marginal (unadjusted $r^2 = 0.15$, adjusted $r^2 = 0.01$) and not significant ($p_{model} = 0.553$).

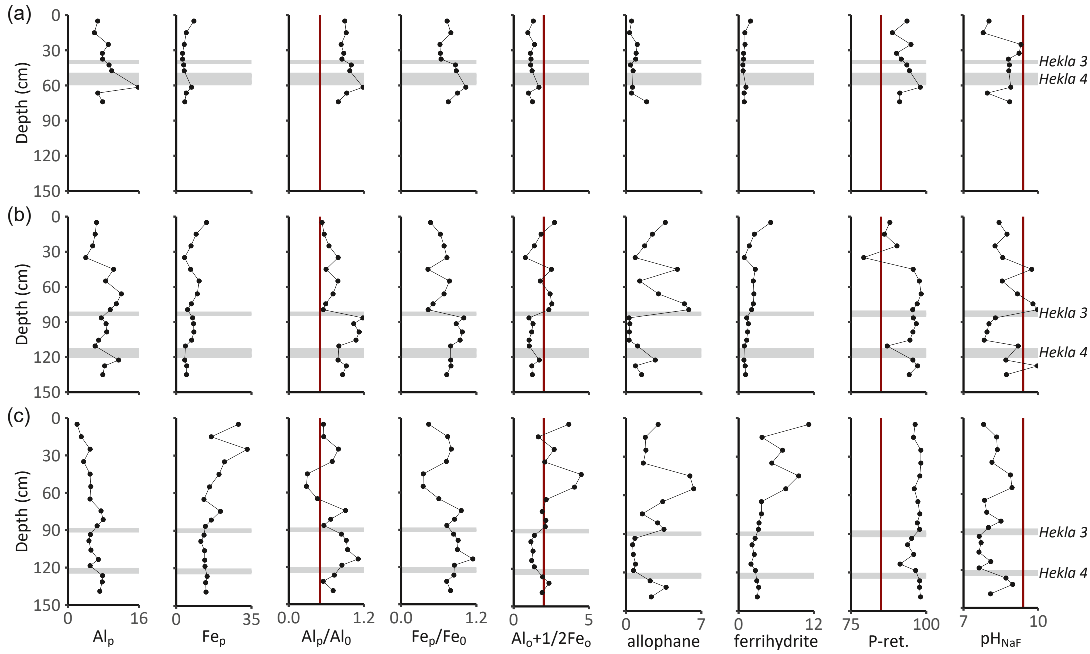

Figure 6. Variables based on selective dissolution analyses, and pH_{NaF} and P-retention at the coastal peatland Torfdalsmýri (a), the lowland Tindar (b), and the highland fringe Hrafnabjörg (c). Al_p and Fe_p, are presented as g kg_{soil}^{-1}; $Al_o + 1/2Fe_o$, allophane, ferrihydrite, and P-retention are presented in %. Vertical red lines represent the following thresholds: $Al_p/Al_o = 0.5$ as demarcation of allophanic and nonallophanic Andosols (0.1 to <0.5 → allophanic Andosols; 0.5–1.0 → nonallophanic Andosols), $Al_o + 1/2Fe_o \geq 2\%$ as diagnostic criterion of andic soil properties, P-retention ≥ 85% as diagnostic criterion for andic soil properties, and $pH_{NaF} \geq 9.4$ indicating high abundance of amorphous material. Shaded gray bars indicate the tephra deposits Hekla 3 and Hekla 4.

4. Discussion

4.1. Increased Mineral Content Does Not Hamper C Storage Capacity of Peatlands

Based upon the lower %C content of Histosols in Iceland in comparison to other Nordic peatlands (Loisel et al., 2014), it might seem obvious to conclude that the C storage capacity of peatlands in Iceland is decreased, due to inputs of mineral material. The results of our study refute such simple inference. Increased contents of mineral eolian material may indeed lead to decreased relative C content, but soil accumulation rates and/or DBD are often also notably increased at sites where this is the case (e.g., Gísladóttir et al., 2010; Möckel et al., 2017). While we detect a significant negative correlation between %Ash and %C, and DBD and %C, C density at the peatlands of this study is positively related to DBD and not significantly impacted by mineral contents (Figure 5). Interestingly, accumulated C stocks at Tindar and Hrafnabjörg since the eruption of Hekla 4 are greater than at Torfdalsmýri despite overall higher C density at Torfdalsmýri. This is related to the greater soil accumulation at Tindar and Hrafnabjörg. While about 0.5 m of soil has accumulated since the eruption of Hekla 4 at Torfdalsmýri (Figure 1d), more than 1 m of soil has accumulated during the same time span at Tindar and Hrafnabjörg. Mineral contents are overall not greater at Hrafnabjörg and Tindar. However, they are more characterized by mineral constituents typical for andic soils (Figures 6 and 7). While the three pedons of this study overall define as Dystric Histosols (IUSS Working Group WRB, 2015), several layers at Tindar and Hrafnabjörg bear andic soil properties (Figure 6; IUSS Working Group WRB, 2015; Soil Survey Staff, 2015), which is not the case at Torfdalsmýri. Generally, relative C content alone seems to be a poor indicator of the C storage capacity of peatlands in Iceland, and an increase of mineral content does not necessarily impact their C storage capacity. However, the nature of the mineral constituents seems to play a role for C storage.

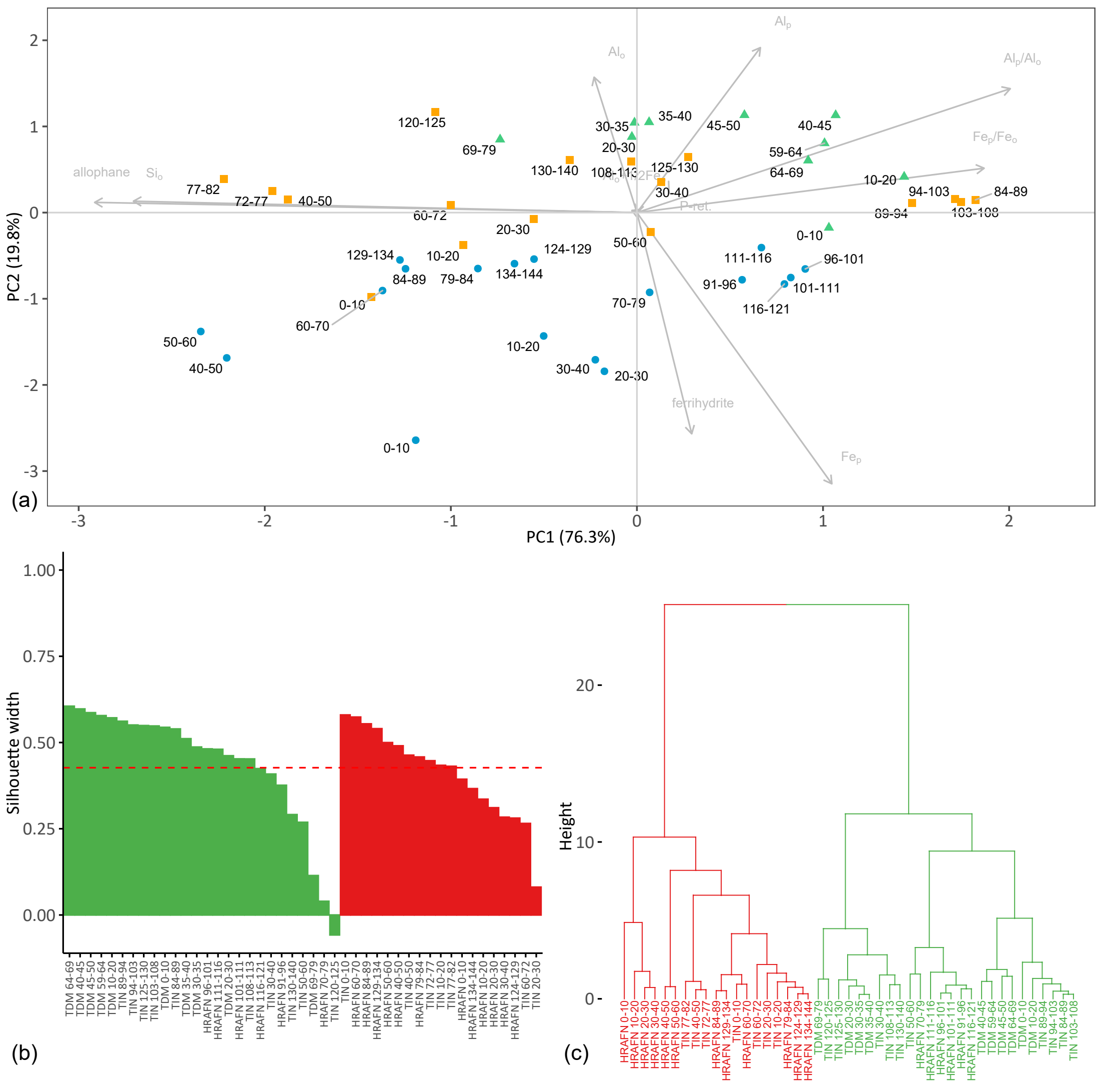

Figure 7. (a) Biplot of the robust principal component analysis of the compositional andic data, including one external noncompositional variable (arcsine transformed P-retention). Observations of different sample sites are depicted by shapes and colors (Torfdalsmýri [TDM]: green triangle, Tindar [TIN]: orange square, and Hrafnabjörg [HRAFN]: blue circle). (b) Silhouette width plot for hierarchical clustering. Average silhouette width = 0.43 (red broken line); Dunn index = 0.221. Observations with a silhouette width close to zero indicate proximity to neighboring clusters. (c) Dendrogram based on hierarchical clustering, using Manhattan distance and Wards criterion (see Kassambara, 2017) and number of clusters $k = 2$.

4.2. C Characteristics Are Impacted by Tephra Layers

As relative C content alone is a poor indicator of the C storage capacity of peatlands in Iceland, we determined the development of C structure of the three peatlands through time (Figure 2), with a particular focus on variations around tephra layers. Indeed, we detected variations that seem to be governed by the occurrence of tephra and other eolian deposits. Two characteristics are the most conspicuous: a shift in C structure around the Hekla 4 tephra deposit, and the formation of a subcluster of soil layers formed between Hekla 3 and Hekla 4 at Hrafnabjörg and Tindar, which is characterized by relatively increased contents of recalcitrant alkyl C in conjunction

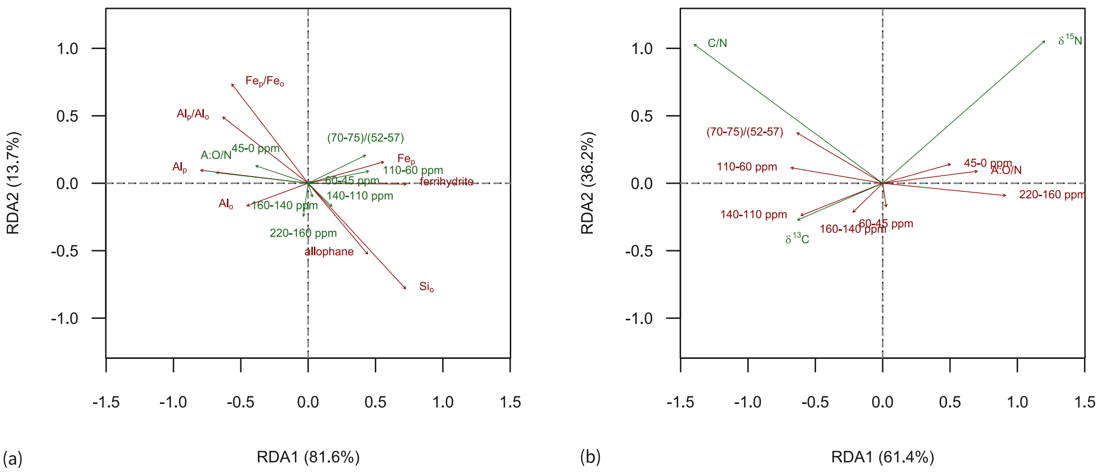

Figure 8. (a) Biplot of RDA between C structure (response variables) and andic properties (explanatory variables). Scaling = type 2. (b) Biplot of RDA between C/N, $\delta^{13}C$, and $\delta^{15}N$ (response variables) and C structure (explanatory variables). Scaling = type 2.

with increased A:O/N ratios (Figures 2, 3a, and 3c). These soil layers also stand out from the others with regard to other soil properties than C structure, but total %C and %N are clearly increased (Figure 4).

Through the greater part of the profiles, decomposition unsurprisingly increases with depth (see Malmer & Holm, 1984; Tfaily et al., 2014), with more recalcitrant C forms increasing in quantities toward deeper layers (e.g., Leifeld et al., 2012; Tfaily et al., 2014). This is indicated by a relative accumulation of alkyl C, a depletion of O/N-alkyl C (particularly 110–60 ppm), and, hence, by increasing A:O/N ratios (Baldock et al., 1997; Möckel et al., 2021; Preston et al., 1989), and by overall decreasing (70–75)/(52–55) ratios (Bonanomi et al., 2013; Möckel et al., 2021). Beneath the Hekla 4 tephra deposits, this development is interrupted or even reversed (Figure 2). Particularly at Hrafnabjörg and Tindar, lower A:O/N ratios, facilitated by a relative decrease of the more recalcitrant alkyl C and accumulation of the more labile O/N-alkyl C, resemble much younger and less decomposed soil layers, that is, the upper 0–10 cm at Hrafnabjörg and the upper 0–40 cm at Tindar (Figures 3a and 3c). Although an initial trend of increased decomposition with depth and a reversal to decreased decomposition at greater depth is consistent with findings of previous studies (e.g., Möckel et al., 2021; Preston et al., 1987), it is conspicuous that the reversal coincides with the Hekla 4 tephra layer. Here, other factors than stage of decomposition may contribute to the observed variations in C structure and the stability of the stored C, for example, the characteristics of the local vegetation serving as parent material of the Histosols. Vegetation characteristics, in turn, are subject to changes induced by environmental disturbances such climate change (e.g., Leifeld et al., 2012) and/or major tephra deposits following volcanic eruptions (Blackford et al., 2014; Eddudóttir et al., 2017, 2020). The change in C structure after the Hekla 4 event might be an indicator of peatland vegetation less resilient to tephra deposition of moderate extent as for example, observed by Hotes et al. (2006). At least, moderate changes in vegetation composition might have been induced (Eddudóttir et al., 2016, 2017, 2020). Also, the Hekla 4 tephra deposits serve as a stratigraphic boundary of an episode of cooling climate (Eddudóttir et al., 2016; Geirsdóttir et al., 2013; D. J. Larsen et al., 2012).

The relative similarity of the C structure of soil layers below Hekla 4 and upper soil layers at Hrafnabjörg and Tindar might also indicate that the chemical structure of the SOC is not the sole driver of its stability (Ahrens et al., 2015; Fontaine et al., 2007; Kögel-Knabner & Kleber, 2011; Marschner et al., 2008; Miltner & Zech, 1998). Possibly, the Hekla 4 deposits served as a barrier (see De Vleeschouwer et al., 2008) toward the input of fresh organic material in the years after the eruption and may still serve as a barrier toward input of dissolved organic carbon from upper soil layers, thereby hampering microbial activity. During field work at Hrafnabjörg and Tindar, we could observe the compacted Hekla 4 tephra deposits to serve as aquifers of limited permeability. At Torfdalsmýri, there is no obvious similarity in C structure between the topsoil and subsoil layers below Hekla 4. The tephra layer still seems to contribute to protective mechanisms against decomposition as reflected by substantially decreased A:O/N ratios below the tephra deposit (Figure 2).

Despite the lack of a similar shift in C structure after the Hekla 3 event, this tephra deposit also serves as a demarcation line at Hrafnabjörg and Tindar. The soil layers above Hekla 3 are indicative of increased environmental instability as indicated by greater variations in SOM and DBD, overall decreased SOM, %C, and % N, and increased DBD. This conforms to observations on lake sediments by Eddudóttir et al. (2020) and Tinganelli et al. (2018) and may be ascribed to increased disturbances by reworked tephra and climate cooling (e.g., Boygle, 1999; Geirsdóttir et al., 2013; Mayewski et al., 2004).

4.3. Andic Soil Properties Indicate Stable Conditions Between Tephra Layers

At Torfdalsmýri, no distinct pattern of andic soil properties could be detected (Figure 6). Generally, andic properties are only weakly developed there. At Hrafnabjörg and Tindar, the differentiation of the soil layers between Hekla 4 and Hekla 3 from the other soil layers is even clearer than based on changes in SOM properties (Figures 7a and 7c). Contrary to what might be expected from soil layers demarcated by two prominent tephra deposits, their andic properties are the least developed; $Al_o + 1/2Fe_o$ is far below the diagnostic threshold of 2% (IUSS Working Group WRB, 2015; Soil Survey Staff, 2014a), allophane, Al_o, and Si_o contents and pH_{NaF} are low. The increased %C between the tephra deposits is an unlikely explanation in our organic soils, despite C being known to hamper allophane formation in mineral soils by complexation of Al with humus (Dahlgren et al., 1993; Nanzyo et al., 1993; Wada, 1989). Yet, %C content is also relatively high in the other layers at Hrafnabjörg and Tindar, often coincident with high allophane content (see Bonatotzky et al., 2019). The pH_{H_2O} of the soils also fails to serve as an explanation. Allophane formation is favored by high pH and impeded by pH < 5 (Matus et al., 2014; Shoji et al., 1993; Wada, 1989). Indeed, the pH of the soils between tephra layers at Tindar and Hrafnabjörg is exclusively ≤5. But this applies to several other soil layers with considerably higher allophane content too (compare Figures 4 and 6).

Another interesting feature is the obvious increase in andic soil properties above Hekla 3. The increase of ferrihydrite content with decreasing soil depth at all sites, but particularly at Hrafnabjörg, is likely associated with enhanced input of inorganic material in a frequently disturbed environment as early as two millennia before the settlement in ca. 870 CE (Eddudóttir et al., 2020; Möckel et al., 2017) and higher redox potentials in surface soils than subsoils (Chesworth et al., 2006; Vaughan et al., 2009). Eventually, the ecosystems ability to return to equilibrium was lost after the onset of anthropogenic influence (e.g., Dugmore et al., 2009; Eddudóttir et al., 2020). The consequent increased input of mineral material, of predominantly basaltic origin (Arnalds et al., 2001), is a likely premise for increased allophane and ferrihydrite formation (Dahlgren et al., 1993), accompanied by more frequent oxygenation following water saturation fluctuations, which facilitates ferrihydrite formation (Chesworth et al., 2006; Vaughan et al., 2009). Several volcanic eruptions might also have contributed mineral material in form of thin tephra deposits to the soils of this study after the settlement (e.g., Hekla 1104; Figure 1d and Hekla 1766; G. Larsen & Thorarinsson, 1977; Möckel et al., 2017; Þórarinsson, 1968). However, work by Möckel et al. (2017) at the same peatlands provides evidence for increased input of mineral material predominantly due to anthropogenic influence as indicated by increased magnetic susceptibility of the soils even in the absence of tephra layers.

Our findings correspond to a paleoenvironmental study on lake sediments close to our research area by Eddudóttir et al. (2020). There, a stable depositional environment between Hekla 4 and Hekla 3 tephra layers is demonstrated, followed by a decrease in stability after the deposition of Hekla 3 tephra (see also Boygle, 1999), which also coincided with climate cooling in the Northern Hemisphere (e.g., Geirsdóttir et al., 2013; D. J. Larsen et al., 2012; Mayewski et al., 2004).

4.4. Impact of Andic Soil Properties on C Structure

It is clear that an inherent characteristic of Histosols is their great potential to accumulate and store C, facilitated by anaerobic conditions, and enhanced by a cool climate in regions at high latitudes such as Iceland. The impact of tephra deposits and andic soil properties on C dynamics of Histosols has hitherto gained only little attention. Hence, it is interesting that there is a clear positive relationship between alkyl C and A:O/N on the one hand and Al_p/Al_o, and Al_p on the other hand (Figure 8a) in the soils of this study. This indicates enhanced formation of metal-humus complexation with increasing decomposition (Takahashi & Dahlgren, 2016) by preferential formation of Al-humus complexes with aliphatic C groups. This is contrary to several previous studies on nonhistic soil types. Barbera et al. (2008), for instance, detected little interaction between poorly crystalline Al and alkyl C in soils developed on basaltic material in Italy. Instead, a preferential formation of metal-humus complexes with carboxylic functional groups is frequently suggested (e.g., Dahlgren et al., 1993; Kögel-Knabner & Amelung, 2021; Kögel-Knabner & Kleber, 2011; Takahashi & Dahlgren, 2016). Allophane and Si_o are positively related to carboxyl/carbonyl/amide C and H/C-aryl C, supporting, a preferential accumulation of carboxyl C and phenolic C in the presence of allophane (see Kögel-Knabner & Amelung, 2021). The positive relation of Fe_p and ferrihydrite predominantly with O/N-alkyl C of 110–60 ppm indicates a preferential complexation of active Fe with O/N-alkyl C, which is in agreement with previous studies (e.g., Miltner & Zech, 1998; Schöning et al., 2005). This, in turn, would support the hypothesis that stabilization of C is related to its association with mineral soil components rather than its chemical recalcitrance (e.g., Kögel-Knabner & Kleber, 2011), which is also interesting in light of previous studies at the same peatlands (see Möckel et al., 2021). There, C stability as indicated by soil C respiration was greater at Hrafnabjörg than Tindar despite even slightly higher content of carbohydrates at Hrafnabjörg. Indeed, content of active Fe and of carbohydrates (110–60 ppm) in this study is also highest throughout the pedon of Hrafnabjörg (Figures 2 and 5). This clearly indicates that stability of SOC in Histosols of volcanic regions is not only governed by the chemical structure of the SOC and hydrology but also by the mineralogical environment of the soils.

In summary, the relation between andic properties and C types indicates that alkyl and O/N-alkyl C are the major groups in organo-mineral associations of the Histosols in this study (Figure 8a), similar as detected for various mineral soils (Kögel-Knabner et al., 2008). This gives rise to questions about the fate of these organo-mineral associations under changing climatic conditions, which may both impact soil temperature and aeration and, hence, soil redox conditions (Knorr, 2013; Vaughan et al., 2009). Knorr (2013), for instance, observed a positive relation between transport of dissolved organic carbon from riparian wetlands and dissolved ferrous iron (Fe^{2+}), while temperature increases are known to enhance reducing conditions in soils, that is, to accelerate the reduction of ferric iron (Fe^{3+}) such as in ferrihydrite to the more soluble Fe^{2+} (Vaughan et al., 2009).

4.5. Decomposition Is Affected by Andic Soil Properties Despite Insignificance of RDA

Despite the statistical insignificance of the RDA between andic soil properties and the decomposition proxies C/N, $\delta^{13}C$, and $\delta^{15}N$, care should be taken to conclude that andic soil properties do not impact decomposition. Instead, their effect is probably indirect through its influence on C structure, as discussed above (Figure 8a).

The negative relation between $\delta^{13}C$ on the one hand and A:O/N ratio and alkyl C on the other hand is in agreement with common observations that recalcitrant forms of C, which are depleted in ^{13}C, become enriched as decomposition proceeds (e.g., Alewell et al., 2011). The relatively uniform $\delta^{13}C$ depth pattern at Tindar and Hrafnabjörg, as opposed to a declining depth pattern at Torfdalsmýri, is resembled by their ^{13}C NMR spectra, but at Tindar and Hrafnabjörg, the C composition is indicative of slower decomposition than at Torfdalsmýri (Figures 2 and 3a; Alewell et al., 2011; Krüger et al., 2014). The positive relation between $\delta^{15}N$ on the one hand and A:O/N ratio and alkyl C on the other hand conforms to previous evidence of higher $\delta^{15}N$ characteristic of more degraded peatlands (Drollinger et al., 2019). Hence, the comparatively high $\delta^{15}N$ are, again, supportive of more advanced decomposition at Torfdalsmýri. Unexpectedly, we observed no correlation between $\delta^{15}N$ and C/N ratios, which is contrary to observations of previous studies (e.g., Drollinger et al., 2019), but supports previous evidence of the limitations of C/N ratios as a proxy for decomposition (see Bonanomi et al., 2013, 2019; Möckel et al., 2017).

5. Conclusions

The aim of this study was to advance understanding of the impact of tephra deposition on soil development in peatlands with a focus on interactions between histic and andic soil properties and their impact on C dynamics. Based on multivariate analysis of data sets of C characteristics, andic soil properties, and decomposition proxies, we can draw the following conclusions:

- Relative C contents are insufficient to (a) estimate the C storage capacity of peatlands exposed to frequent deposits of volcanic origin and (b) to estimate the amount of greenhouse gasses emitted from these peatlands upon disturbance. This is indicated by profound differences in soil accumulation rates and C stocks in peatlands of different degrees of exposition to eolian material in Iceland, accompanied by conspicuous differences in C structure and andic soil properties.

- Andic soil properties impact the C structure of Histosols of volcanic regions, and hence their C storage capacity. The interaction of andic and histic soil properties leads to the formation of organo-mineral complexes, which particularly hamper the decomposition of chemically more labile C groups. Hence, SOM of Histosols of peatlands, where the formation of andic properties is facilitated by mineral deposits of volcanic origin (i.e., Tindar and Hrafnabjörg), is less decomposed (or deteriorated) than the SOM of peatlands without notable andic soil properties (e.g., Torfdalsmýri).
- Thick and compacted tephra layers have the potential to serve as protective barriers. They hamper microbial activity and decomposition of SOM; in the short term by preventing the input of fresh organic material in the years after a tephra deposition into deeper soil layers, and in the long term by serving as a barrier toward input of dissolved organic carbon from upper soil layers. Consequently, when protected by major tephra layers, subsoils in peatlands of volcanic regions may resemble younger surface soils.
- While andic soil properties, accompanied by the protective role of major tephra deposits, appear to enable an unusual potential for long-term C stabilization in a natural peatland environment, these comparatively undecomposed organic soils, which contain relatively great amounts of labile C compounds, may be an even greater source of atmospheric C upon disturbance than anticipated based upon %C only.

Data Availability Statement

The data, on which this research is based, are accessible through the Dryad Digital Repository (https://datadryad.org/stash/share/2Qy-XTFwnR18CacSvtE4_YVczvfQmk7ooVFqlNYlucA, doi:10.5061/dryad.tmpg4f502).

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Paper III

Beyond the obvious – the impact of mineral aeolian deposits on carbon characteristics over the last millennium in Icelandic Histosols

Author's contribution:

Susanne Claudia Möckel (SCM), Guðrún Gísladóttir (GG) and Egill Erlendsson (EE) planned the study and applied for research funding. Field work was conducted by SCM and GG. Laboratory work was conducted by SCM, but ^{13}C NMR measurements were conducted by the staff at the Chair of Soil Science of Technical University of Munich, under guidance of Jörg Prietzl. SCM conducted the data analysis and wrote the manuscript. The co-authors (EE, GG) provided useful comments to the manuscripts.

Beyond the obvious – the impact of mineral aeolian deposits on carbon characteristics over the last millennium in Icelandic Histosols

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Abstract

The visual effects of just over a millennium of heavy erosion of dryland soils (Andosols) are ubiquitous in the Icelandic landscape. While lushly vegetated peatlands may appear like pristine oases of resilience in an otherwise degraded landscape, they are impacted by the surrounding soil erosion. Iceland has one of the most active aeolian environments worldwide, and there is emerging evidence that windborne volcanic deposits in peatlands influence their carbon dynamics. In this study the impact of increased dust deposition after the settlement of Iceland in c. 870 AD on the mineral pedogenic environment and its interaction with carbon characteristics of Histosols is investigated. The research uses surface soils of Histosols from three peatlands, which receive varying amounts of mineral deposition. We analyse datasets of the peatland vegetation characteristics, their carbon structure as derived by ^{13}C NMR spectroscopy, andic soil properties based on selective extractions of Al, Fe, and Si, and other complementary soil properties. While differences in vegetation characteristics are to some extent reflected by differences in carbon characteristics, the mineral pedogenic environment also seems to play a role here. We find a stronger relation between andic soil properties and carbon characteristics than previously observed in pre-settlement Histosols. Decomposition of soil organic matter in Histosols which are strongly influenced by andic properties seems to be relatively slow, with carbon characteristics dominated by labile carbon compounds, opposed to more rapid degradation of soil organic matter and comparatively great accumulation of recalcitrant carbon compounds in Histosols without notable andic properties.

1 Introduction

1.1 Hidden side effects of dryland soil erosion

Human induced vegetation destruction and its effects on soil quality in Iceland, leading to fatal erosion of dryland soils, are widely discussed in the scientific literature (e.g. Dugmore et al., 2009; Eddudóttir et al., 2020; Óskarsson et al., 2004). While environmental conditions driven by climate changes and volcanic activity regularly caused alterations in vegetation and soil dynamics before the human settlement of the island c. 870 AD (e.g. Eddudóttir et al., 2020; Eddudóttir et al., 2016; Möckel et al., 2017; Streeter et al., 2015), there is evidence that the ecosystems were generally resilient and recovered quickly from environmental disturbance in the absence of anthropogenic pressure. Human settlement more than on thousand years ago led to rapid land degradation, manifested by vegetation destruction and shifts in vegetation communities, and the consequent severe erosion of the erosion prone Andosols (the soils of the Icelandic drylands). While barren areas and potential dust sources were certainly not uncommon before the settlement, owing to a combination of a harsh climate and a dynamic landscape shaped by active volcanism and glacial processes, their extent increased rapidly following the settlement (e.g. Arnalds, Dagsson-Waldhauserova, et al., 2016; Dugmore et al., 2009). Due to the detrimental combination of sparse vegetation cover, sensitivity of the remaining Andosols towards erosion, a harsh climate with frequent strong winds (Einarsson, 1984) and the globally unmatched extent of volcaniclastic deserts (Arnalds, Dagsson-Waldhauserova, et al., 2016; Einarsson, 1984), Iceland today is one of the most active aeolian environments in the world.

The visual effects of just over a millennium of heavy erosion of dryland soils are ubiquitous in the landscape, especially in areas where remnants of vegetation and soils of once mature ecosystems are present in an otherwise barren landscape. Particularly striking is the occurrence of lushly vegetated peatlands or wetlands, surrounded by sparsely vegetated, or even barren, and eroding drylands. Ostensibly, these wetlands can appear like pristine oases of resilience in an otherwise degraded landscape. However, the dust-receiving ecosystems like the wetlands are also subject to disturbances, but it is well known that dust fluxes have widespread ecological consequences, such as redistribution of nutrients and perturbations of hydrologic and biogeochemical cycles (Field et al., 2010; Okin et al., 2011). Dust fluxes are a natural process and can be an important contributor to ecosystem functioning, e.g. by providing nutrients to otherwise nutrient depleted ecosystems such as highly weathered tropical soils (Field et al., 2010). However, the share of human induced dust load has significantly increased with intensified land use, which can have palpable consequences, particularly at local or regional scales (Arnalds, Dagsson-Waldhauserova, et al., 2016; Neff et al., 2008). Even in eastern North America, in an environment with considerably less aeolian activity than Iceland, the effects of land clearances on drylands are often discernible by changes in nearby peatlands, e.g. by increased input of mineral material and associated nutrients into the organic soils of peatlands and resulting vegetation changes (Ireland et al., 2014). Yet, as pointed out by Field et al. (2010), the ecological consequences of dust redistribution are often neglected in many ecological studies.

1.2 Impact of dust deposition on carbon cycling in peatlands receives little attention

The soils of mires are the greatest terrestrial carbon (C) store (Joosten et al., 2016) despite covering less than 3% of the global terrestrial surface area (Hugelius et al., 2020). Degraded peatlands therefore have an exceptionally adverse effect on the global C cycle. With the mechanisation of agriculture the extensive drainage of mires for agricultural purposes led to their widespread degradation, and in many places, they were destroyed beyond all recognition (Joosten, 2016). Especially in densely populated areas in Europe, but also in less densely populated areas of Scandinavia, draining was ubiquitous for a great part of the second half of the 20th century. According to a report by Joosten (2009) more than a decade ago, disturbed peatlands were responsible for about 5% of anthropogenic CO_2 emissions, while only covering about a mere 0.3% of the global land area (see also Joosten, 2016). Despite population densities of rural areas in Iceland being the lowest in Europe (Eurostat, 2021; Statistics Iceland, 2021), the share of degraded peatlands there is in line with the European average of nearly 44% (Joosten, 2016). More specifically, according to Arnalds, Gudmundsson, et al. (2016), approximately 47% of inland wetlands in Iceland are impacted by draining for agricultural purposes. Mechanized drainage of peatlands in Iceland was particularly common between the early 1949's and late 1960's, when up to 70% of the cost to dig the ditches was state-subsidised (Geirsson, 1975). From the 1970's, a slow shift in the perception of mires as inconvenient land, that should be moulded according to agricultural needs, towards ecosystems worth protecting, was tangible in Iceland (Garðarsson, 1974; JG, 1976; Náttúruverndarsamtök Austurlands, 1973). Despite this, peatland restoration efforts have been limited (Aradóttir et al., 2013; Óskarsson et al., 2020), as exemplified by an average annual restoration rate of 45 ha yr^{-1} in the years 2016-2018 (Stjórnarráð Íslands, 2019). Furthermore, destruction of peatlands has not ceased despite newly applied didges for agricultural purposes not being common anymore. Other measures, such as the great increase of hydroelectric power production and the construction of reservoirs and associated infrastructure, adversely affect or destroy many peatlands and other ecosystems (Egilsson et al., 2001; Magnússon et al., 2001).

Overall, the disproportionate contribution of disturbed peatlands to greenhouse gas emissions worldwide is exemplified by the emission trends of greenhouse gases in Iceland. Net C emissions between 1990-2018 from the Land use, land-use change, and forestry sector (LULUCF) are estimated to be more than double the combined emissions from all other sectors (The Environment Agency of Iceland, 2020). By far the greatest part of the emissions from the LULUCF sector is ascribed to the drainage of organic wetland soils. The estimates of net C emissions from organic soils in Iceland are based on Tier 1 of the IPPC guidelines (IPCC, 2014; The Environment Agency of Iceland, 2020), which are based on research of boreal peatlands not affected by volcanic ejecta or dust fluxes from eroding drylands. However, new research evidences that windborne deposits of volcanic origin in Icelandic peatlands impact their C dynamics (Möckel, Erlendsson, & Gísladóttir, 2021; Möckel, Erlendsson, Prater, et al., 2021).

1.3 Impact of dryland soil erosion on peat accumulating ecosystems in Iceland

Usually, inorganic material is not considered a primary impact factor for C characteristics in Histosols (Kögel-Knabner & Amelung, 2021; Leifeld et al., 2012), the organic soils of peatlands. In Iceland, aeolian inorganic material does certainly impact upon the formation and characteristics of these soils. First, vegetation characteristics are shaped by the input of windborne mineral material of volcanic origin. Contrary to many peat forming ecosystems of other subarctic regions (Clymo, 1987; Joosten, 2016), Icelandic peatlands are widely characterized by vascular plants (Steindórsson, 1936, 1964). Bryophytes, including *Sphagnum*, also occur, but are not dominant. It is well known that the type of vegetation will influence the characteristics of the peatlands soils (Joosten, 2016; Leifeld et al., 2012; Rezanezhad et al., 2016; Rydin & Jeglum, 2013), not least their structure and hydrologic characteristics, decomposability, density and, consequently, their C characteristics.

While the term peatland is widely used for ecosystems with waterlogged soils in Iceland, many peatlands actually ceased to accumulate Histosols centuries ago, notably before the introduction of mechanised drainage. The extent of Histosols in surface layers is only just over 1%, though 7.8% - 9% of the island's terrestrial surface classifies as wetlands (Arnalds, Gudmundsson, et al., 2016; Ottósson et al., 2016); many of which that used to be peat-accumulating ecosystems. Hence, while Histosols provide only a small part of surface soils in Iceland, more C rich subsoil layers are often found in pre-settlement subsoil layers (Arnalds, 2015; Gísladóttir et al., 2011; Gísladóttir et al., 2010; Möckel et al., 2017) in regions where surface soils of wetlands today are dominated by less organic Histic or Gleyic Andosols (see Arnalds, 2015; and Arnalds & Óskarsson, 2009 for information about the Icelandic soil classification). This is a consequence of the destabilization of the environment after the onset of anthropogenic influence c. 870 AD, resulting in the dispersal of eroded material from dryland ecosystems. Therefore, many wetland soils in Iceland comprise a mixture of histic, andic and vitric soil properties. Histosol surface layers occur only in settings with comparatively little aeolian influence, i.e. farthest from the active volcanic zones, and far from the most extensively eroded areas in the highlands. Even the Histosols commonly contain some andic and vitric properties (Bonatotzky et al., 2019; Möckel, Erlendsson, & Gísladóttir, 2021).

1.4 C turnover in peatlands of volcanic regions

There is emerging evidence that aeolian mineral deposits impact upon the C dynamics of Histosols, in addition to hydrology and the chemical composition of the soil organic carbon, which are usually considered the predominating factors of C turnover in peatlands (e.g. Leifeld et al., 2012). For instance, a positive feedback between metal elements like Al and Fe and C accumulation has been observed (Amendola et al., 2018; Möckel, Erlendsson, & Gísladóttir, 2021). Furthermore, Möckel, Erlendsson, Prater, et al. (2021) and Möckel, Erlendsson and Gísladóttir (2021) provide evidence that the mineral deposits affect the stability of the C in peatlands. The mineral material within the peat column seems to affect the temperature sensitivity of C mineralization. Contrary to the results of various previous studies in non-volcanic regions (e.g. Conant et al., 2011; Mikan et al., 2002), Möckel, Erlendsson, Prater, et al. (2021) observe higher temperature sensitivity of soil organic carbon dominated by labile C compounds than of soil organic carbon dominated by recalcitrant forms. This is particularly interesting in light of a conspicuous co-occurrence of the accumulation of labile C compounds, andic soil properties and tephra deposits (Möckel, Erlendsson, & Gísladóttir, 2021; Möckel, Erlendsson, Prater, et al., 2021). The high temperature sensitivity of labile C compounds in Histosols of volcanic regions, combined with their relative prominence within soil organic carbon of these soils, may then pose an increased risk of C emissions from the same peatlands upon disturbance.

1.5 Research aim

The studies of Möckel, Erlendsson, Prater, et al. (2021) and Möckel, Erlendsson and Gísladóttir (2021) focus mainly on processes in subsoils and on the impact of tephra deposits on C dynamics, i.e. the impact of distinct depositional events. Hence, the aim of this study is to advance understanding on the pedogenic environment for soil organic carbon storage in the post-settlement surface soils of Icelandic peatlands which are subject to constant, but variable, inputs of aeolian mineral deposits from eroded drylands. The following objectives are at the core of this study:

- To determine variations in the vegetation characteristics of three Icelandic peatlands in differing geographical settings and to evaluate if variations in vegetation characteristics are reflected in variations in C structure.

- To examine the potential relation between C structure and andic soil properties, and to evaluate if mineral content (%Ash) has an impact on absolute soil organic carbon contents (kg m^{-3}).
- To examine the potential relation between C structure, andic soil properties, and decomposition.

Our results will also be discussed in the context of similar studies on mineral soils. We work with datasets of vegetation analysis conducted in the field, C structure derived by ^{13}C NMR spectroscopy, andic soil properties based on selective dissolutions with ammonium oxalate and sodium pyrophosphate, P-retention and pH measured in NaF (pH_{NaF}), and several proxies reflecting decomposition (C/N, $\delta^{13}C$, $\delta^{15}N$ and A:O/N ratio), accompanied by complementary soil properties, e.g. pH measured in water (pH_{H2O}), dry bulk density and soil organic matter content.

2 Methods

2.1 Research area, vegetation analysis and soil sampling

Our research area is in Austur Húnavatnssýsla in northwest Iceland (Figure 1a), where Histosols are comparatively common in the surface soils of wetlands (Arnalds, 2015; Arnalds & Óskarsson, 2009). Soil samples were collected from three peatlands along a north-south transect from the coast (Torfdalsmýri), via the lowlands (Tindar) to the highland fringe (Hrafnabjörg). Soil forming factors differ between the sites with regard to climate (see Table 1) and their distance from primary source areas of allochthonous mineral material (tephra from volcanic eruptions and mineral material from major erosion areas in the interior of the country). At each peatland, systematic vegetation analysis and soil sampling was conducted at nine quadrats (0.25 m^2) along three parallel transects from the margin to the centre of each peatland (Figure 1b). Vegetation assessment was conducted by the Relevé Method by Braun-Blanquet (Dombois & Ellenberg, 1974). Plant species were identified using Kristinsson (2010). At each quadrat, bulk soil samples were taken from the rooting zone (top 30 cm of the soil; see Iversen et al., 2015), subdivided into three intervals: 0-5 cm, 5-15 cm and 15-30 cm. Based upon a previous study at the same sample sites (Möckel, Erlendsson, & Gísladóttir, 2021), we assume the upper 30 cm of soils were formed after the human settlement of Iceland in c. 870 AD. For the determination of dry bulk density and field water content, samples of a predefined volume were cut out from each layer. All soil samples were subsequently stored at 4°C until further processing.

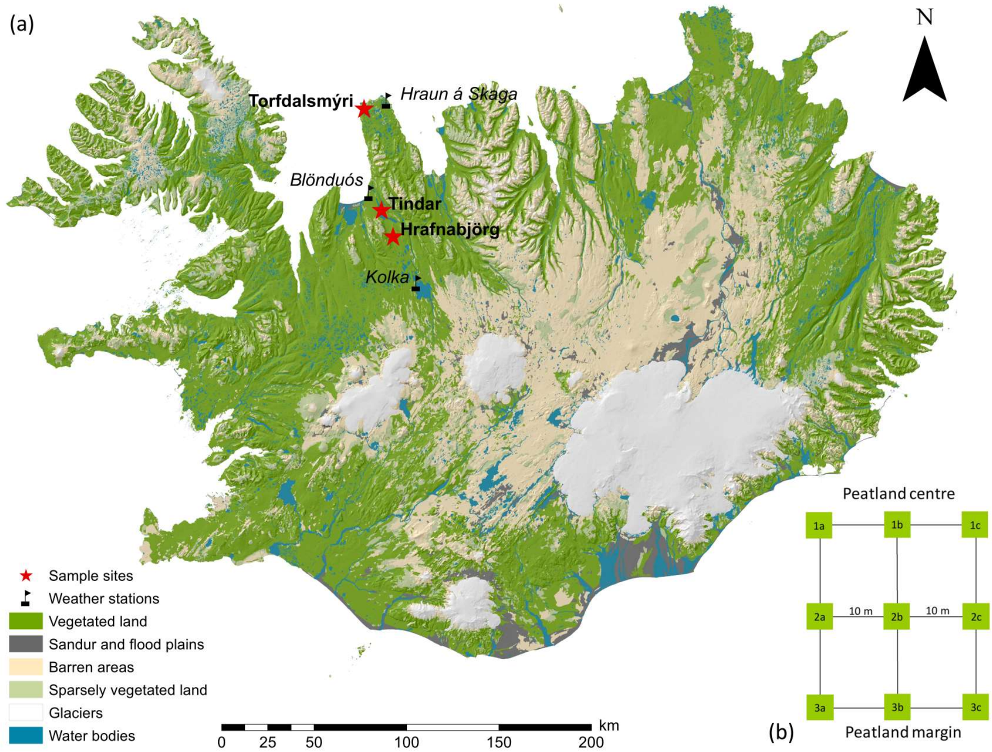

Figure 1: (a) The map shows the location of the three peatlands in relation to source areas of mineral aeolian material, i.e. sparsely vegetated or barren areas. Map source: IS50 V database of the National Land Survey of Iceland (LMI, n.d.). Figure (b) shows the sampling approach: vegetation analysis and soil sampling was conducted at nine quadrats (0.25 m^2) at each peatland, along three parallel transects from the margin to the centre of each peatland.

Table 1: Meteorological data for the research area derived from three weather stations. Data are available for the following time spans: Hraun á Skaga: 1956 – 2015; Blönduós: 1949 – 2001; Kolka: 1994 –2015 (IMO, n.d.-a, n.d.-b). The summer tritherm in Iceland comprises the months June – August, the autumn tritherm comprises September – October, winter tritherm lasts from December – February and spring tritherm lasts from March – May. For information about the sampling locations in relation to the position of each weather station refer to Figure 1a.

Weather station	Hraun á Skaga	Blönduós	Kolka
Elevation (m a.s.l.)	3	8	506
Mean annual tempearture (°C)	2.94	3.05	0.64
Mean summer tritherm temperature (°C)	7.9	9.1	7.8
Minimum summer tritherm temperature (°C)	6.3	7.4	6.3
Maximum summer tritherm temperature (°C)	10.2	10.4	9.3
Mean winter tritherm temperature (°C)	-1.0	-1.6	-4.7
Mean autumn tritherm temperature (°C)	3.6	3.4	0.6
Mean spring tritherm temperature (°C)	1.3	1.7	-1.3
Mean annual precipitation (mm)	512	480	352
Mean annual windspeeds (m s^{-1})	5.7	3.8	7.4

2.2 Laboratory analyses

2.2.1 C structure by solid state ^{13}C NMR spectroscopy

The structure of soil organic C was determined by solid state ^{13}C NMR spectroscopy. Here, only soil samples from transect *b* (Figure 1b) in each peatland were analysed, i.e. nine samples from each site. A cross-polarisation magic angle spinning technique (CPMAS) with a Bruker DSX 200 spectrometer (Billerica/USA) was applied with a proton resonance frequency of 50.32 MHz and a spinning speed of 6.8 kHz. To circumvent spin modulation during the Hartmann-Hahn contact, a ramped ^{1}H-pulse was used during a contact time of 1 ms. Pulse delays of 0.8 s were used for all samples and between 1031 and 10362 scans were accumulated per measurement. A line broadening of 25 Hz was applied. The ^{13}C chemical shifts were calibrated relative to tetramethylsilane that was equalized to 0 ppm.

Integration was based on Knicker et al. (2005). The signal intensity was integrated into six chemical shift regions in order to determine the relative share of the different C compounds: 220–160 ppm (carboxyl/carbonyl/amide C), 160–140 ppm (O/C-aryl C), 140–110 ppm (C/H-aryl C), 110-45 ppm (O/N-alkyl C) divided into 110–60 ppm (O-alkyl C), 60–45 ppm (N-alkyl C), and 45–0 ppm (alkyl C). Additionally, signal intensities for 70–75 ppm (O-alkyl C of carbohydrates) and 52–57 ppm (methoxyl C of lignin) were determined in order to calculate the (70–75)/(52–57) ratio, which Bonanomi et al. (2013) observed to correlate positively with decay rates. As a proxy for decomposition, we calculated the alkyl C to O/N-alkyl C (A:O/N) ratio, with higher ratios indicating a more advanced decomposition (Baldock et al., 1997).

2.2.2 Andic soil properties: Selective dissolution of Al, Fe and Si, P-retention and pH_{NaF}

Selective dissolution of Al, Fe and Si with ammonium oxalate and sodium pyrophosphate was conducted on soil samples from transects *b* (compare Figure 1b) in each peatland, i.e. on nine samples from each peatland. Extraction of Al, Fe and Si with ammonium oxalate (0.2 M, pH 3.0), was carried out following Soil Survey Staff (2014; method 4G2). The Al, Fe and Si thus extracted (Al_o, Fe_o, Si_o) is indicative of the active forms of Al and Fe of organic complexes (Al/F-humus complexes), nanocrystalline (previously referred to as non-crystalline) hydrous oxides of Fe and Al, and nanocrystalline (previously referred to as amorphous or non-crystalline) aluminosilicates like allophane (Nanzyo et al., 1993; Wada, 1989). The sum of $Al_o + ½Fe_o$ was calculated as a diagnostic criterion of andic soil properties (≥ 2%; IUSS Working Group WRB, 2015). Ferrihydrite was estimated as %ferrihydrite = $\%Fe_o$ x 1.7 (Childs, 1985). Sodium pyrophosphate was used to extract the part of active Fe and Al (Fe_p, Al_p), which is associated with organic compounds (Al/Fe-humus complexes; Soil Survey Staff, 2014; method 4G3). Allophane or allophane-like constituents were estimated by the equation proposed by Mizota and van Reeuwijk (1989), based on Parfitt and Wilson (1985). While Mizota and van Reeuwijk (1989) recommend to use only Al/Si ratios (derived from $[Al_o-Al_p]/Si_o$) between 1.0 and 2.5 for the calculation of allophane, we use Al/Si ratios < 1 which may also occur in allophane (Parfitt & Kimble, 1989).

Phosphate retention (P-retention) as a diagnostic criterion of andic soil properties (≥ 85%; IUSS Working Group WRB, 2015) and the pH in 1N NaF solution (pH_{NaF}) as an indicator of nanocrystalline material (previously referred to as amorphous) was determined following Blakemore et al. (1987). High abundance of nanocrystalline material, common in soils of volcanic regions, results in $pH_{NaF} \geq 9.4$.

2.2.3 Dry bulk density, field water content, soil organic matter, pH_{H2O}, and decomposition proxies C/N and stable isotope ratios $\delta^{13}C$ and $\delta^{15}N$

The dry bulk density and field water content was determined by mass loss after drying of a known soil volume. Content of soil organic matter and inorganic material (%Ash) was measured by loss on ignition at 550 °C (Heiri et al., 2001). Soil acidity was measured in deionised water (pH_{H2O}) using a soil:water ratio of 1:10 (Blakemore et al., 1987; Rayment & Lyons, 2011). Determination of total carbon (%C) and nitrogen (%N) by dry combustion (Soil Survey Staff, 2014) and of the stable isotope ratios $\delta^{13}C$, $\delta^{15}N$ as an indicator of degradation state and the hydrology of peatlands (e.g. Alewell et al., 2011; Krüger et al., 2014), was conducted by the Cornell Isotope Laboratory in the USA. Due to the absence of carbonate minerals in Icelandic soils (Bonatotzky et al., 2021; Mankasingh & Gísladóttir, 2019; Vilmundardóttir et al., 2014), we assume soil organic carbon to be equivalent to %C. As a proxy for decomposition (e.g. Kuhry & Vitt, 1996; Malmer & Holm, 1984) we calculated the molar C/N ratio. Based on dry bulk density and %C, we calculated the C density (kg m^{-3}) for each depth interval.

2.2.4 Statistical evaluations

Categories of the Braun-Blanquet cover scale (0, r, +, 1, 2, 3, 4, 5; Dombois & Ellenberg, 1974) were recoded according to van der Maarel (0, 1, 2, 3, 5, 7, 8, 9; van der Maarel, 1966 in Camiz et al., 2017). Then, nonmetric multidimensional scaling (NMDS; function metaMDS, R package vegan; Oksanen et al., 2019; Podani, 2006) was used to discern variations in vegetation characteristics between the sites. Variations in C structure as reflected by the six ^{13}C NMR chemical shift regions and the A:O/N and (70–75)/(52–57) ratio were investigated by robust principal component analysis (PCA) for compositional data (function pcaCoDa, R package robCompositions; Filzmoser et al., 2009; Filzmoser et al., 2018) and hierarchical clustering (R package factoextra, function eclust; Kassambara, 2017). For the cluster analysis, the compositional ^{13}C NMR data were isometric logratio (ilr) transformed (van den Boogaart & Tolosana-Delgado, 2013; van den Boogaart et al., 2020). The clustering tendency was investigated by the Hopkins statistic and a dissimilarity matrix (R packages factoextra and clustertend; Kassambara, 2017; Kassambara & Mundt, 2020; YiLan & RuTong, 2015). The clustering approach (hierarchical clustering) was chosen based on comparison of internal measures and stability measures of hierarchical, k-means and pam clustering (see Kassambara, 2017). The optimal number of clusters ($k = 2$) was determined by comparison of the elbow, silhouette and gap statistic method and by assessing the goodness of different clustering approaches by silhouette width plots (R-packages factoextra and NbClust; Charrad et al., 2014; Kassambara, 2017; Kassambara & Mundt, 2020). The variability of andic soil properties was likewise determined by robust PCA and hierarchical clustering ($k = 4$). In order to investigate the impact of variations in andic soil properties on variations in C structure, redundancy analysis (RDA; R package vegan; Oksanen et al., 2019) was conducted. The impact of andic properties on decomposition proxies (C/N, $\delta^{13}C$, $\delta^{15}N$) was also investigated by RDA. Pearson correlations were determined in order to evaluate if there is a relation between %C, %Ash, dry bulk density, and C density (R package GGally, function ggpairs; Quinn & Keough, 2002; Schloerke, 2021). All statistical analyses were carried out using the software R, version 4.0.2.

3 Results

3.1 Vegetation Characteristics

At Torfdalsmýri, the vegetation is dominated by *Eriophorum angustifolium;* at Tindar, *Carex nigra* is the most dominant, but various flowering plants and dwarf shrubs are also common, e.g. *Betula nana*, *Empetrum nigrum* and *Vaccinium uliginosum*; at Hrafnabjörg, vegetation is clearly dominated by *Carex rostrata*, but *Equisetum palustre, Vaccinium uliginosum* and *Betula nana* are also common (Table 2, Figure 2). Following the European Nature Information System (EUNIS; EEA, 2019; Ottósson et al., 2016), vegetation characteristics at Torfdalsmýri resemble the habitat type of *D2.26 Common cotton-grass fens*. Vegetation at Tindar is similar to two habitat types, i.e. *D3.162 Boreal black sedge-brown moss fens* and *D4.163 Icelandic black sedge-brown moss fens.* Vegetation characteristics at Hrafnabjörg are similar to *D2.332 Basicline bottle sedge quaking mires.*

Table 2: Major plant functional groups and their associated species encountered. Abbreviations of plant species used in the NMDS (Figure 2) are given to the left of the species name in grey colour. Abbreviations in brackets denote the occurrence within the respective peatlands: TDM = Torfdalsmýri, TIN = Tindar and HRAFN = Hrafnabjörg. When marked bold, the species are prominent at the site (i.e. they reach at least cover scale category "1" at a minimum of four quadrats). When marked grey, occurrence of the species at the site is only minor (i.e. [i] the species is only existent in a maximum of four quadrats, never reaching more than cover scale category "+"; or [ii] the species was detected in only one quadrat, not exceeding cover scale category "1"). The nomenclature follows Kristinsson (2010) and the Panarctic Flora (PAF, n.d.).

	Sedges/Rushes		**Grasses**		**Deciduous woody plants**
CxCn	*Carex canescens* (TDM)	AO	*Anthoxanthum odoratum* (TIN, HRAFN)	BN	*Betula nana* (TDM, **TIN, HRAFN)**
CxCa	*Carex capillaris* (TIN, HRAFN)	CN	*Calamagrostis neglecta* (TDM)	SA	*Salix arctica* **(TDM,** HRAFN)
CxCh	*Carex chordorrhiza* (TIN, **HRAFN**)	FR	*Festuca rubra ssp. richardsonii* (TIN)	SH	*Salix herbacea* (TDM)
CxL	*Carex lyngbyei* (HRAFN)	PP	*Poa pratensis* (TIN)	SP	*Salix phylicifolia* **(TDM,** HRAFN)
CxN	*Carex nigra* (TDM, **TIN, HRAFN**)			VU	*Vaccinium uliginosum* **(TDM, TIN, HRAFN)**
CxRa	*Carex rariflora* (TDM, TIN, **HRAFN**)		**Forbs**		
CxRo	*Carex rostrata* (TIN, **HRAFN**)	BA	*Bartsia alpina* (TIN)		**Evergreen woody plants**
CxS	*Carex saxatilis* (TDM)	BV	*Bistorta vivipara* (TDM, TIN, HRAFN)	EN	*Empetrum nigrum* **(TDM,** TIN, **HRAFN)**
EA	*Eriophorum angustifolium* (**TDM**, HRAFN)	CaP	*Cardamine pratensis ssp. angustifolia* (TDM, TIN, HRAFN)		
JA	*Juncus arcticus* (TIN)	CoP	*Comarum palustre* (TDM, **TIN**)		**Pterydophytes**
LM	*Luzula multiflora* (TIN, HRAFN)	GV	*Galium verum* (TIN)	EP	*Equisetum palustre* (TDM, **TIN, HRAFN)**
LS	*Luzula sudetica* (HRAFN)	PV	*Pinguicula vulgaris* (HRAFN)	SS	*Selaginella selaginoides* (TIN)
		TA	*Thalictrum alpinum* (TDM, **TIN,** HRAFN)		
		VP	*Viola palustris* (TDM)	BRY	***Bryophyta* (TDM, TIN, HRAFN)**

Despite several common species (Table 2), the NMDS on the vegetation community data shows that vegetation characteristics at the coastal site Torfdalsmýri are quite distinct from Tindar and Hrafnabjörg, whereas vegetation characteristics at Tindar and Hrafnabjörg bear a greater resemblance to each other.

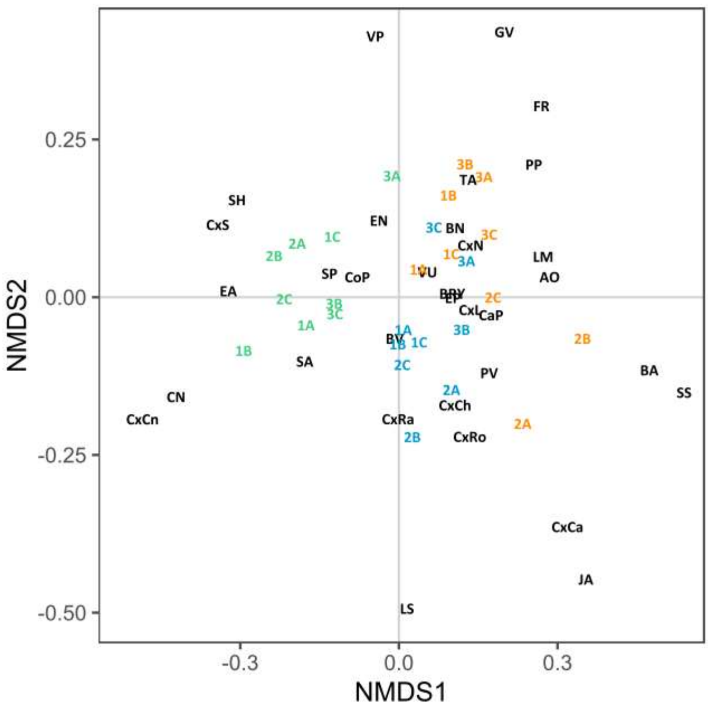

Figure 2: Vegetation characteristics at the three peatlands shown by NMDS. Quadrats of each peatland are depicted by different colours: green at Torfdalsmýri, orange at Tindar and blue at Hrafnabjörg. Species are indicated in black colour. For species abbreviations, refer to Table 2.

3.2 Patterns of C structure derived by robust PCA and cluster analysis

Raw ^{13}C NMR spectra (including A:O/N and (70-75)/(52-57) ratios) and stacked bar charts showing the share of the six integrated chemical shift regions are shown in Figure 3. Overall, all sample plots reveal a somewhat similar and expected development of C structure with depth: in the upper 0-5 cm of soils, there is a characteristic predominance of O/N alkyl C over alkyl C, which leads to low A:O/N ratios, accompanied by high (70-75)/(52-57) ratios. In progressively deeper soil layers (5-15 cm and 15-30 cm), there is a relative increase of alkyl C at the relative expense of O/N alkyl C, which is responsible for an increase of A:O/N ratios with depth. At the same time, (70-75)/(52-57) ratios are decreasing. Other than alkyl C and O/N alkyl C, C groups do not show as clear a pattern with depth. Despite the ubiquitous trend of a gradual increase of recalcitrant alkyl C at the expense of more labile O/N alkyl C (which leads to considerable overlap of sample sites in the robust PCA and cluster analysis), there are some noteworthy differences between sites (Figure 3, Figure 4a and Figure 4c). The relative increase of alkyl C at the expense of O/N alkyl carbon, accompanied by increased A:O/N ratios with depth, is stronger at Torfdalsmýri than at Tindar and Hrafnabjörg (Figure 3, Figure 4c). While the clustering tendency of the samples is not very strong (compare silhouette width plot in Figure 4b), the cluster analysis (Figure 4a) supports the pattern shown in Figure 4c, that the C structure of the deeper soil layers at Tindar and Hrafnabjörg is more alike each other than the C structure at Torfdalsmýri.

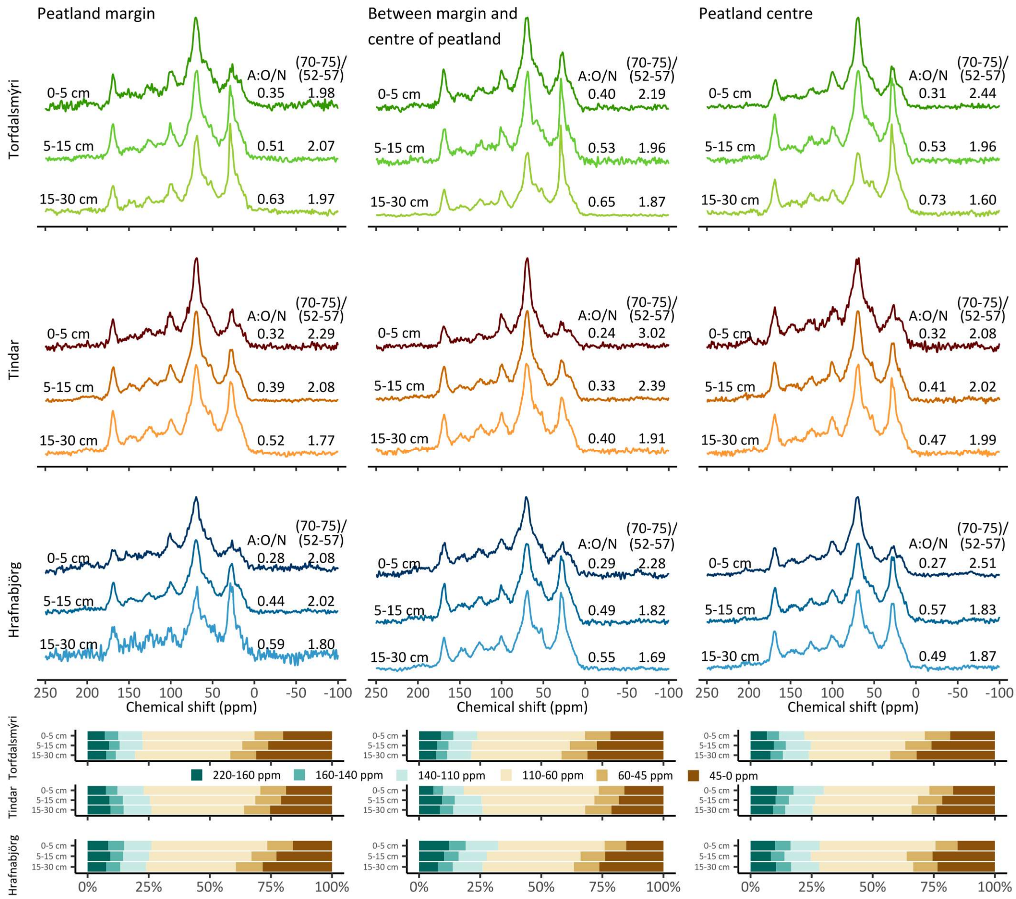

Figure 3:The C structure of the three peatlands shown by ^{13}C NMR spectra, including A:O/N and (70–75)/(52–57) ratios.

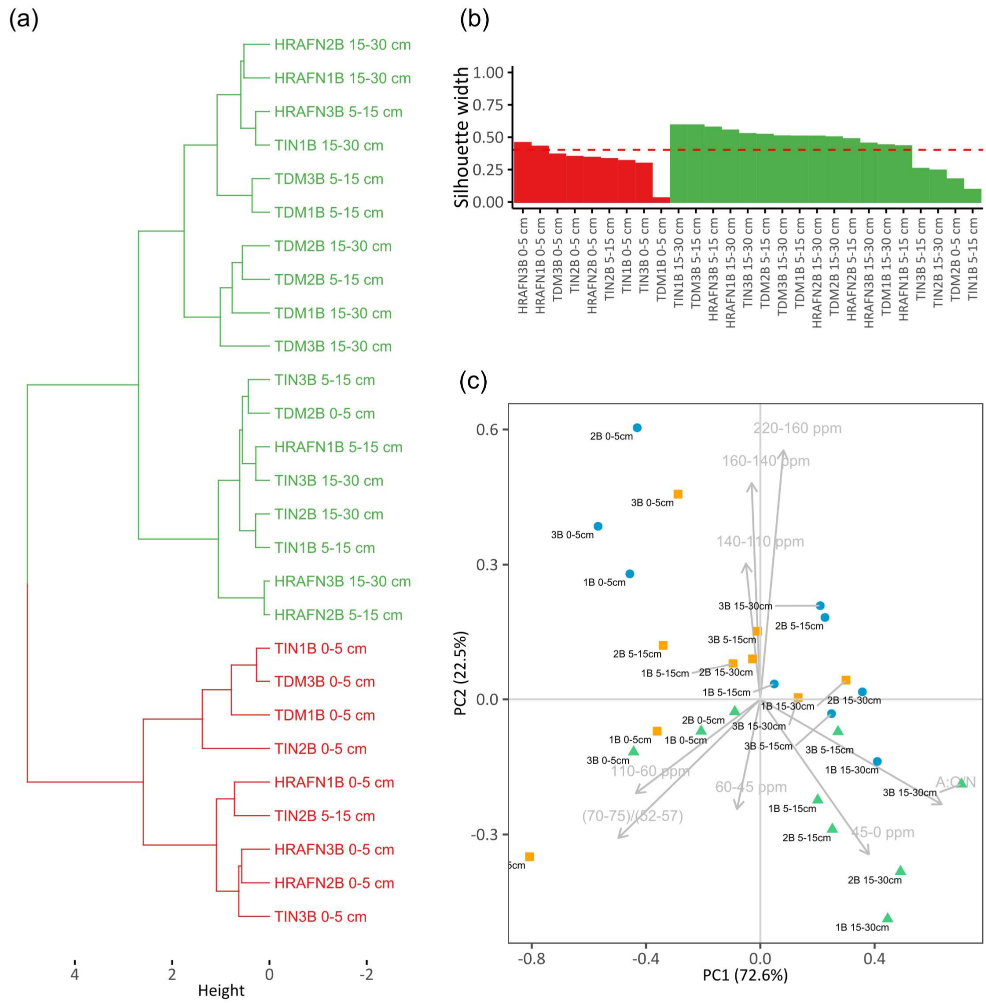

Figure 4: Variations in C structure by ^{13}C NMR based on hierarchical clustering and robust PCA. (a) Dendrogram based on hierarchical clustering, using Manhattan distance and Wards criterion (Kassambara, 2017) and number of clusters k=2; Dunn index = 0.269.(b) Silhouette width plot for hierarchical clustering. Average silhouette width for hierarchical clustering with two clusters = 0.4. (c) Biplot of the robust principal component analysis on the ^{13}C NMR data. Observations of different sample sites are depicted by shapes and colours (Torfdalsmýri [TDM]: green triangle, Tindar [TIN]: orange square, and Hrafnabjörg [HRAFN]: blue circle).

3.3 Pattern of andic soil properties derived by robust PCA and cluster analysis

The andic soil properties (Figure 5) do not show the ubiquitous trends with depth as revealed by the ^{13}C NMR spectra (Figure 3). However, the robust PCA (Figure 6c) and cluster analysis (Figure 6a) reveal some general differences between samples sites despite a not very strong clustering tendency (compare silhouette width plot in Figure 6b). Again, Torfdalsmýri provides different results to the more similar Tindar and Hrafnabjörg. At these two sites, the andic properties are more developed than at the coastal site Torfdalsmýri. This is particularly manifested by comparatively high levels of allophane in conjunction with low Al_p/Al_o ratios and Al_o + ½ Fe_o values, several of them fulfilling the ≥2% diagnostic criterion of andic soil properties (IUSS Working Group WRB, 2015). Ferrihydrite contents are also comparatively high at the two sites, particularly at Hrafnabjörg. Note that at Torfdalsmýri, Al_p/Al_o and Fe_p/Fe_o ratios are > 1 in several instances, which might be due to an overestimation of Al_p and Fe_p and/or and underestimation of Al_o and Fe_o (e.g. Childs, 1985; Mizota & van Reeuwijk, 1989).

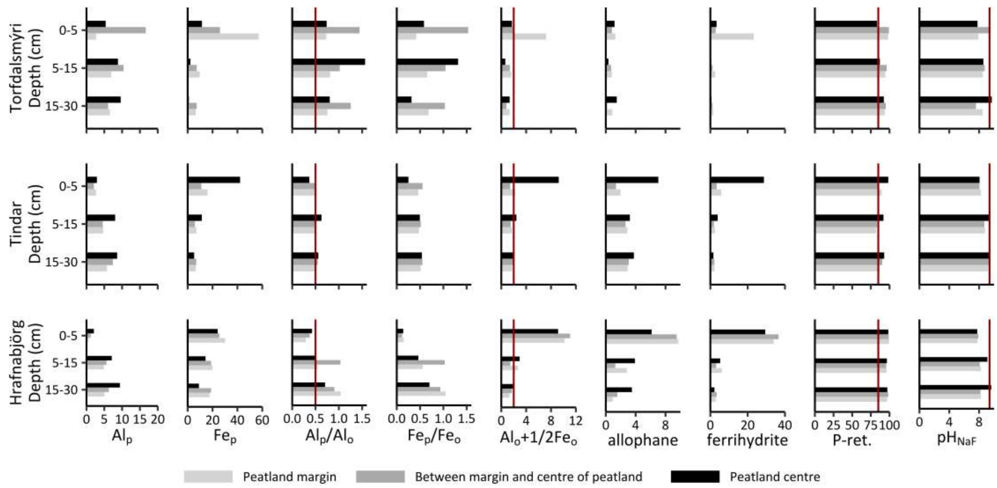

Figure 5: Andic soil properties derived from selective dissolution analyses, and pH_{NaF} and P-retention at the coastal peatland Torfdalsmýri, the lowland Tindar and the highland fringe Hrafnabjörg. Al_p and Fe_p, are presented as g kg_{soil}^{-1}, $Al_o+1/2Fe_o$, allophane, ferrihydrite and P-retention are presented in %. Vertical red lines represent the following thresholds: Al_p/Al_o = 0.5 as demarcation of allophanic and non-allophanic Andosols (0.1-<0.5 → allophanic Andosols; 0.5-1.0 → nonallophanic Andosols), $Al_o+1/2Fe_o \geq 2\%$ as diagnostic criterion of andic soil properties, P-retention ≥ 85% as diagnostic criterion for andic soil properties and $pH_{NaF} \geq 9.4$ indicating high abundance of amorphous material.

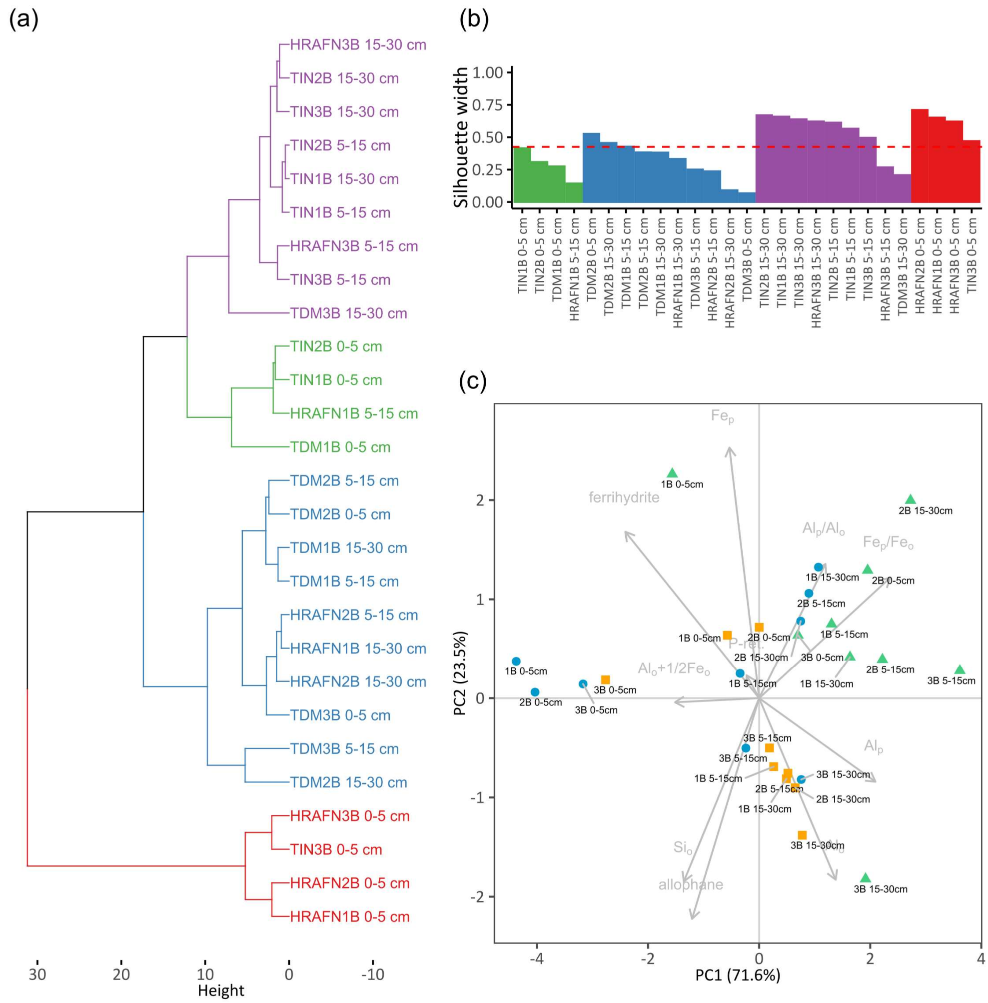

Figure 6: Variations in andic soil properties based on hierarchical clustering and robust PCA. (a) Dendrogram based on hierarchical clustering, using Manhattan distance and Wards criterion (Kassambara, 2017) and number of clusters k=4; Dunn index = 0.254. (b) Silhouette width plot for hierarchical clustering. Average silhouette width for hierarchical clustering with four clusters = 0.43. (c) Biplot of the robust principal component analysis of the compositional andic data, including one external non-compositional variable (arcsine transformed P-retention). Observations of different sample sites are depicted by shapes and colours (Torfdalsmýri [TDM]: green triangle, Tindar [TIN]: orange square, and Hrafnabjörg [HRAFN]: blue circle).

3.4 C/N, stable isotope ratios $\delta^{13}C$ and $\delta^{15}N$ and various complementary soil properties

Average dry bulk density is similar at all sites in 0-5 cm and 5-15 cm of soils, but in 15-30 cm of soils, it is noticeably higher at Tindar than at the other two sites (Figure 7). On average, total %C and %N content is highest at Torfdalsmýri. In the upper 0-5 cm, Tindar contains on average more %C and %N than Hrafnabjörg. However, this difference between the two sites is noticeably decreased in 5-15 cm, and negligible, or even slightly reversed, in 15-30 cm. On average, all sites and soil depths meet the ≥ 20% C criterion of Histosols (IUSS Working Group WRB, 2015). However, at Tindar and Hrafnabjörg, the criterion is not fulfilled by several samples, particularly in the upper 0-5 cm of soils. C density describes a similar pattern as %C and %N except at depths of 15-30 cm. Here, average C density at Tindar is noticeably higher than that of Hrafnabjörg, which may be attributable to the increased average dry bulk density of Tindar's soils at that depth. The content of %Ash roughly describes an opposite pattern to %C and %N, with lowest %Ash contents at Torfdalsmýri, higher contents of %Ash at Tindar than Hrafnabjörg in 0-5 cm and 5-15 cm of soils, but slightly lower contents of %Ash at Tindar than Hrafnabjörg in 15-30 cm of soils. While %Ash content at Torfdalsmýri is on average greatest in the upper 0-5 cm of soils, the same does not hold true at Tindar and Hrafnabjörg. However, variability in %Ash content does increase towards upper soils layers at the two sites, resulting in increased frequency of comparatively high %Ash contents. Pearson correlation (Figure 8) revealed that while there is a strong negative relation between %Ash and %C (r = - 0.86, p < 0.001), %Ash content does not have an effect on C density (r = 0.05, p = 0.65). The lack of a relation between %Ash and C density goes hand in hand with a relatively strong positive relation between %Ash and dry bulk density (r = 0.66, p < 0.001) and between dry bulk density and C density (r = 0.69, p < 0.001).

Average stable isotope ratios $\delta^{13}C$ (Figure 7) are comparatively stable with depth at Torfdalsmýri, while they show an increasing trend with depth at Tindar and Hrafnabjörg. Average stable isotope ratios $\delta^{15}N$ are comparatively stable with depth at Torfdalsmýri and Tindar, but show a decreasing trend with depth at Hrafnabjörg. C/N ratios are on average lowest at Torfdalsmýri but similar at Tindar and Hrafnabjörg. The pH_{H2O} was on average > 5 in all soil depths at all sites. Generally, it was lowest at Torfdalsmýri, and highest at Tindar, while being highest in the upper 0-5 cm at all sites; values > 6.5 were detected at Tindar and Hrafnabjörg. Only a few soil samples reached the threshold of ≥ 9.4 of pH_{NaF} (IUSS Working Group WRB, 2015) indicating andic soil properties. Average P-retention was above the 85% criterion of andic soil properties (IUSS Working Group WRB, 2015) in all depths at all sites, despite some replicates at Torfdalsmýri and Tindar showing values < 85%.

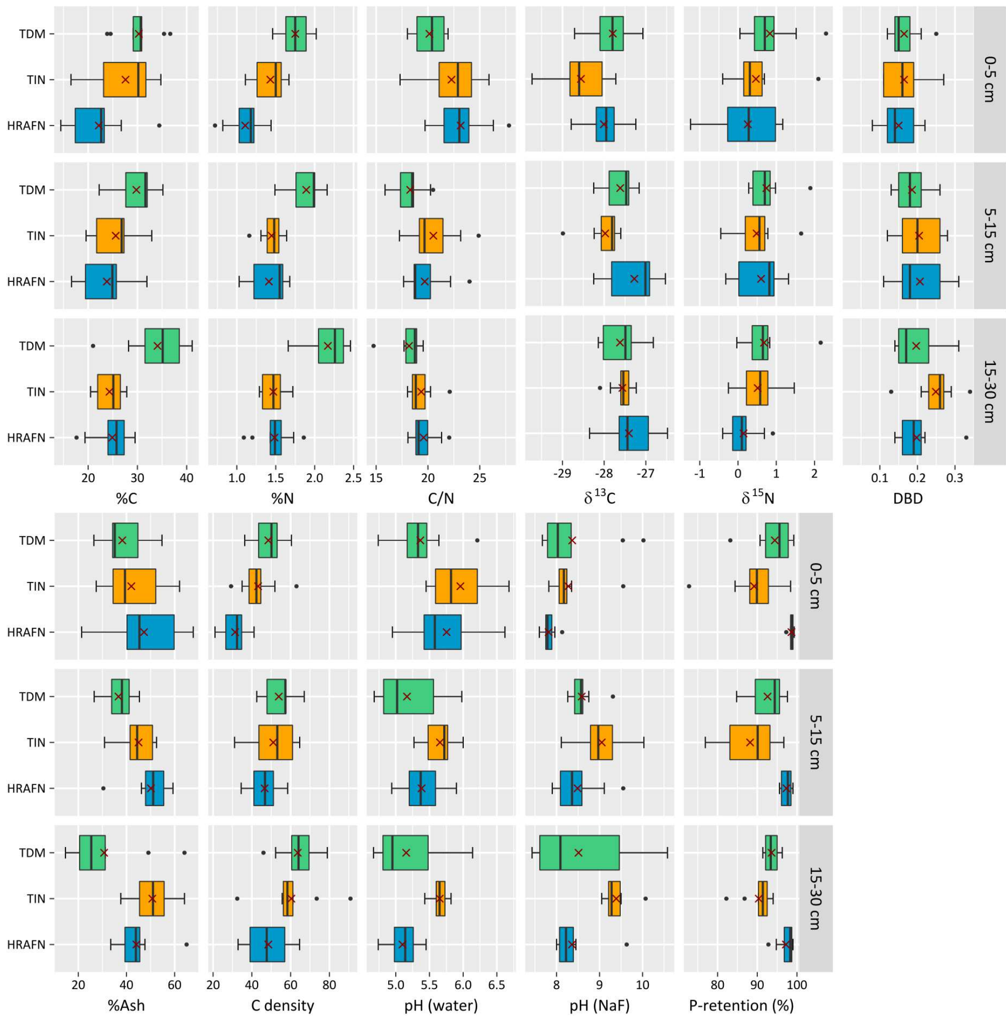

Figure 7: Complementary soil properties used in this study at Torfdalsmýri (TDM), Tindar (TIN) and Hrafnabjörg (HRAFN) using boxplots. Means are also depicted by a red x. %Ash, %C and %N, and P-retention are presented in %, C/N as molar ratio, $\delta^{13}C$ and $\delta^{15}N$ are presented in ‰, C density in kg m^{-3}. Dry bulk density (DBD) is presented as g cm^{-3}.

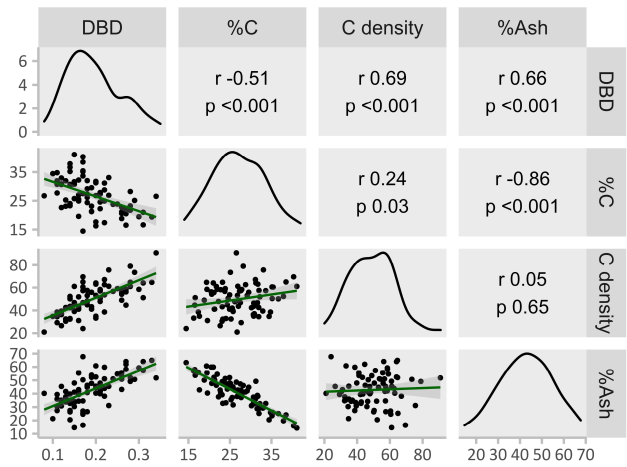

Figure 8: Correlation between %Ash, dry bulk density (DBD), C density and %C at the three peatlands derived by Pearson correlation. The figure shows the matrix of scatterplots, Pearson correlation coefficients (r) and probability values (p).

3.5 Possible relations between various soil properties as indicated by RDA

The RDA between andic soil properties as explanatory data matrix and C structure as dependent variables (Figure 9a) shows a rather strong relation between the two data sets (unadjusted $r^2 = 0.65$, adjusted $r^2 = 0.49$). However, only the effect of the first dimension (75% of constrained variation) was statistically significant based on an alpha value of 0.05 ($p_{RDA1} = 0.001$, $p_{RDA2} = 0.164$). Alkyl C (45-0 ppm) seems to be positively related to the ratios Fe_p/Fe_o, Al_p/Al_o, and content of Al_p and Al_o. The latter two also seem to have a clear positive relation with A:O/N ratios. Ferrihydrite, $Al_o + ½Fe_o$ and Fe_p seem to be negatively related to alkyl C and A:O/N ratios, but positively to O/N alkyl C (110-60 ppm and 60-45 ppm). Allophane and Si_o content are negatively related to Alkyl C, but positively related to carboxyl/carbonyl/amide C (220–160 ppm), O/C-aryl C (160-140 ppm) and C/H-aryl C (140-110 ppm).

The RDA between andic soil properties as explanatory variables and decomposition proxies C/N, $\delta^{13}C$, and $\delta^{15}N$ as dependent variables (Figure 9b) indicates a moderate relation (unadjusted $r^2 = 0.49$, adjusted $r^2 = 0.26$). Again, only the effect of the first dimension proved statistically significant ($p_{RDA1} = 0.016$, $p_{RDA2} = 0.716$). A positive relation between content of Si_o, Fe_p, allophane, ferrihydrite and Al_o+ $½Fe_o$ with C/N ratio is indicated, while the same variables do not seem to impact $\delta^{13}C$, but have a slight negative impact on $\delta^{15}N$.

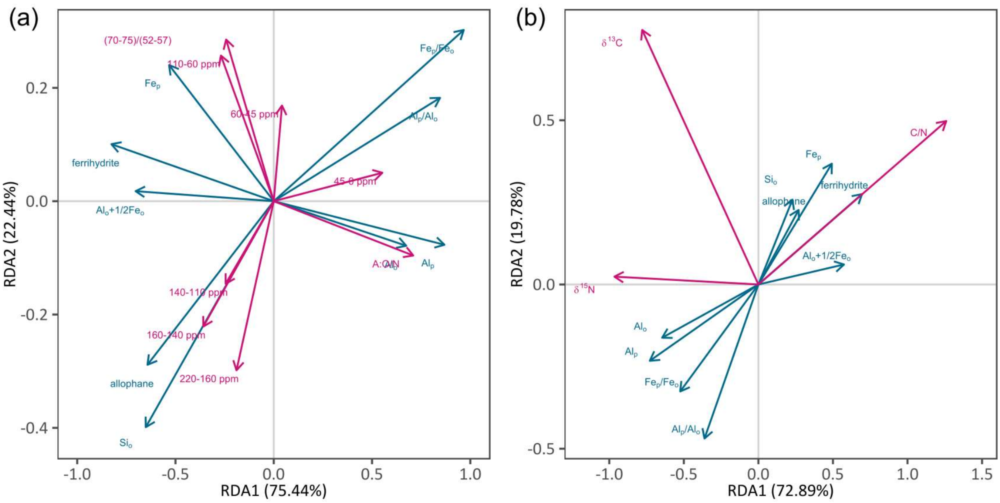

Figure 9: (a) Relation between C structure (response variables) and andic properties (explanatory variables) depicted by biplot of RDA. Unadjusted $r^2 = 0.65$, adjusted $r^2 = 0.49$, $p_{RDA1} = 0.001$, $p_{RDA2} = 0.164$. (b) Relation between C/N, $\delta^{13}C$, and $\delta^{1}N$ (response variables) and andic properties (explanatory variables) depicted by biplot of RDA. Unadjusted $r^2 = 0.49$, adjusted $r^2 = 0.26$, $p_{RDA1} = 0.016$, $p_{RDA2} = 0.716$.

4 Discussion

4.1 Increased mineral deposition does not decrease C storage of peatlands

As Möckel, Erlendsson and Gísladóttir (2021) pointed out, one cannot make the simple inference that comparatively high mineral contents of many Histosols in Iceland, in conjunction with relatively low %C contents (Loisel et al., 2014), result in a decreased absolute C storage capacity. This is because increased deposition of windborne mineral material also often leads to increased soil accumulation rates and increased dry bulk densities (see also Bonatotzky et al., 2019; Gísladóttir et al., 2010; Möckel et al., 2017). In the study by Möckel, Erlendsson and Gísladóttir (2021), there was a negative correlation between %Ash and %C, but a positive correlation between %Ash and dry bulk density and no significant relation between %Ash and C density. Arguably, the absence of an effect of increased mineral contents on absolute C contents in their study might be due to a dominance of prehistorical subsoils, i.e. of soils which formed before human induced expansion of eroding drylands and barren areas (e.g. Arnalds, Dagsson-Waldhauserova, et al., 2016; Dugmore et al., 2009; Gísladóttir et al., 2011; Gísladóttir et al., 2010). Hence, we tested for effects of %Ash on %C, dry bulk density and C density in post-settlement surface soils. The results were strikingly similar to Möckel, Erlendsson and Gísladóttir (2021; Figure 8), with our dry bulk densities being considerably higher (Figure 7) than mean dry bulk density detected by previous studies on Histosols of boreal and subarctic mires elsewhere (e.g. Turunen et al., 2002). Here, we provide further evidence that despite decreased relative C contents in peatlands with enhanced mineral deposition, a decrease in absolute C storage per volume of soil is not induced, as mineral deposition increases the density of the soils. As this study does not provide basal dates for the investigated soils, we were not able to calculate annual soil and C accumulation rates. However, it is a valid question if increased amounts of mineral deposition after the settlement impact C accumulation rates per time increment, not least as Möckel, Erlendsson and Gísladóttir (2021) detected considerable differences between C accumulation of pre-settlement soils at the same peatlands. Also, despite no evidence for an impact of mineral deposition on absolute C storage per volume of soil, the more refined C characteristics differ between the peatlands (Figure 3 and 4). In the next two subchapters, potential impact factors of C characteristics will be discussed.

4.2 Differences in vegetation characteristics impact C characteristics

In a very broad sense, our results show that patterns of vegetation differences between peatlands (Figure 2) are reflected by variations in C structure (Figure 4a and 4c). The NMDS (Figure 2) demonstrates that vegetation characteristics at Torfdalsmýri are rather distinct from Tindar and Hrafnabjörg, while the latter two sites bear more of a resemblance to each other. A similar pattern is shown by the cluster analysis (Figure 4a) and PCA (Figure 4c) on the C structure. This is in general agreement with the commonly accepted knowledge that vegetation characteristics have a significant impact on C characteristics in peatlands (e.g. Leifeld et al., 2012). However, a closer look reveals that the C characteristics at Torfdalsmýri share more common characteristics with Tindar and Hrafnabjörg than vegetation characteristics imply. For instance, the upper 0-5 cm of soils at Torfdalsmýri are rather similar to their 0-5 cm counterparts at Tindar and Hrafnabjörg, characterized by comparatively high contents of labile O/N-alkyl C and a relatively small share of more recalcitrant alkyl C (Figure 3, Figure 4c). In the deeper soil layers (5-15 cm and 15-30 cm), C characteristics at Torfdalsmýri become more distinct. Generally, the expected shift towards more recalcitrant C groups with depth (Leifeld et al., 2012; Möckel, Erlendsson, & Gísladóttir, 2021; Tfaily et al., 2014), reflective of more decomposed organic matter is quicker at Torfdalsmýri than at the other two sites, particularly in comparison with Tindar (Figure 3, Figure 4c). This is in agreement with previous studies at the same sites (Möckel, Erlendsson, & Gísladóttir, 2021; Möckel, Erlendsson, Prater, et al., 2021). While these studies focused on subsoil C characteristics, they also investigated the C characteristics of one very topsoil sample (0- $\leq$ 10 cm depth) at each site. Again, despite clear vegetation differences, the C characteristics were rather similar at all sites to start with, but evidently underwent different stabilization and decomposition processes thereafter and consequently, the C characteristics in subsoils at Torfdalsmýri are indicative of notably more decomposed, i.e. more recalcitrant C compounds.

4.3 Interactions between andic soil properties and C characteristics

Our study supports previous results that C stability in Histosols of volcanic regions is driven by more factors than C structure (Möckel, Erlendsson, & Gísladóttir, 2021) and vegetation characteristics. Möckel, Erlendsson and Gísladóttir (2021) investigated if andic soil properties could partly explain the observed different development of C structure with depth in peatlands. By means of RDA, they found that a moderate share (adjusted r^2 = 0.29) of C structure was constrained by andic properties. The most notable pattern described was that non-allophanic Histosols, with low ferrihydrite content (i.e. with high Al_p/Al_o and Fe_p/Fe_o ratios) were characterised by C structure indicative of more degraded or recalcitrant material (i.e. comparatively high alkyl C contents and high A:O/N ratios). High ferrihydrite content was associated with C groups indicative of undecomposed material, reflected by high O/N alkyl contents and high ratios of (70-75)/(52-57). Allophane and Si_o were positively related to carboxyl/carbonyl/amide C and H/C-aryl C. Overall, the results presented here reflect the pattern described previously by Möckel, Erlendsson and Gísladóttir (2021; Figure 9a). However, we detect a notably stronger relation between andic soil properties and C structure (adjusted r^2 = 0.49). This probably reflects increased mineral transport of volcanic origin into the peatlands after the rapid expansion of barren and eroding areas after the settlement (Arnalds, Dagsson-Waldhauserova, et al., 2016; Dugmore et al., 2009; Gísladóttir et al., 2011; Gísladóttir et al., 2010). This, in conjunction with better oxygenation (Chesworth et al., 2006; Vaughan et al., 2009), would lead to more developed andic properties in surface soils of peatlands than in subsoils, particularly higher allophane and ferrihydrite content (Dahlgren et al., 1993). It may be expected that this is more strongly expressed in peatlands located closer to the dust sources (Figure 1). As expected, Tindar and Hrafnabjörg, contain relatively more %Ash and less %C (Figure 7) than the more sheltered Torfdalsmýri, going hand in hand with stronger andic properties (Figure 5), i.e. higher allophane and ferrihydrite content, lower Al_p/Al_o ratios, and a sum of $Al_o+½Fe_o$ frequently ≥ 2.

The increased aeolian redistribution of mineral material after the settlement might also explain why Möckel, Erlendsson and Gísladóttir (2021) detected no direct significant relation between andic soil properties and the so-defined decomposition proxies C/N ratio, $\delta^{13}C$ and $\delta^{15}N$, while we detect a moderate relation (adjusted r^2 = 0.26, Figure 9b). We see a positive relation between ferrihydrite, allophane and $Al_o+½Fe_o$ and C/N (Figure 9b), while the same variables are negatively related to $\delta^{15}N$. This confirms that andic soil properties facilitate the accumulation of relatively undecomposed material (see Figure 9a).

4.4 Relation between C structure and mineral soil constituents in organic Histosols in comparison with mineral soils

Our study indicates an important effect of soil mineral constituents on C stabilization in Histosols in Iceland, not unlike the processes recognized for mineral soils (e.g. Kögel-Knabner & Amelung, 2021; Kögel-Knabner & Kleber, 2011; Marschner et al., 2008). This is contrary to many observations elsewhere, that the dominant processes of C stabilization in mineral soils, organo-mineral complexation and aggregation, are of minor importance in organic wetland soils such as Histosols (Kögel-Knabner & Amelung, 2021; Leifeld et al., 2012). Similar to Möckel, Erlendsson and Gísladóttir (2021), some of our results are distinct from the results of previous studies on stabilization processes in mineral soils, while other of our observations bear resemblance to mineral soils. Various previous studies provide evidence for the formation of Al/Fe-humus complexes, primarily with carboxylic functional groups (Dahlgren et al., 1993; Kögel-Knabner & Amelung, 2021; Kögel-Knabner & Kleber, 2011), which Matus et al. (2014) and Takahashi and Dahlgren (2016) corroborate in their reviews on C stabilization processes and the role of aluminum-humus complexes in volcanic soils. However, our RDA (Figure 9a) does not indicate a particular relation between Al/Fe-humus complexes and carboxyl C, but rather a preferential formation of Al-humus complexes with alkyl C, and of Fe-humus complexes with O/N-alkyl C. However, despite the observed positive relation between Al_p and alkyl C in our study, it may be a matter of debate if this indicates a causal relationship. Other processes than the formation of metal-humus complexes may lead to the relative accumulation of these C compounds in non-allophanic soils in volcanic regions. In a study on non-allophanic volcanic ash soils in Ecuador, Tonneijck et al. (2010) suggest that toxic levels of exchangeable Al might retard the microbial breakdown of these specific C compounds, resulting in their relative accumulation. Indeed, acidity might also explain the relative accumulation of alkyl C in our soils, but the pH_{H2O} at Torfdalsmýri is overall lower than at Tindar and Hrafnabjörg (Figure 7).

Carboxyl/carbonyl/amide C in particular, but also O/C-aryl C and C/H-aryl C, seem positively associated with allophane in our study. Parfitt et al. (1999) also found indications of a preferential stabilization of carboxyl groups by allophane in poorly drained Podzols in New Zealand. In conjunction with observations that phenolics (O/C-aryl C) may have an inhibiting effect on decomposition processes (Freeman et al., 2001; Hättenschwiler & Vitousek, 2000), the positive relation between allophane and these compounds is of particular interest. Our observed positive relation between O/N-alkyl C and Fe_p, and to a lesser extent ferrihydrite, is in agreement with previous studies. In an incubation study by Miltner and Zech (1998), for instance, decomposition rates of polysaccharides (O-alkyl C) in beech litter were observed to be reduced with the addition of selected oxides, including ferrihydrite. A study by Schöning, Knicker, et al. (2005) on four different non-volcanic mineral soil types from temperate forests also indicated a positive effect of Fe-oxides on relative O/N alkyl content. In a further related study, Schöning, Morgenroth, et al. (2005) found, similar to us, a positive relation between O/C-aryl C and C/N ratios, indicative of a decreased share of these C compounds as decomposition proceeds.

4.5 Potential implications of climate warming on peatlands with andic soil properties

The importance of organo-mineral complexes for C dynamics in peatlands with andic soil properties should be recognized where potential changes in C dynamics of the ecosystems, subject to climate change and aggravated dust deposition, are being modelled. For instance, the importance of Fe compounds for C dynamics of peatlands effected by volcanic emissions may pose an increased thread of carbon loss from their soils upon warming. This might be particularly pertinent with regard to surface soils which are more prone to the impact of temperature and hydrologic changes than subsoils. Changes in climate patterns such as increased temperatures and changes in moisture may enhance reduction of the ferric iron (Fe(III)) in ferrihydrite to more soluble ferrous iron (Fe(II)), and therewith lead to increased carbon loss (Chen et al., 2020; Curtinrich et al., 2022; Knorr, 2013), e.g. as dissolved organic carbon and as CO_2. As pointed out by Kramer and Chadwick (2018), even slight changes in effective soil moisture can have a significant effect on the amount of C stabilized by reactive minerals. For example, under anoxic conditions the C stabilizing role of Fe may be reversed (Chen et al., 2020). Questions therefore arise on the possible effect of elevated levels of Fe(II) on soil organic matter degradation. Upon oxidation of dissolved Fe(II), highly degrading $^{\bullet}OH$ radicals are produced (Trusiak et al., 2019; Zhao et al., 2021), which may then accelerate the degradation of the dissolved organic carbon.

Vegetation characteristics are another factor, which will likely be affected by climate change (Eddudóttir et al., 2020; Ireland et al., 2014; Loisel & Bunsen, 2020; Lyons et al., 2020; Norby et al., 2019), and which may impact the formation and stability of Fe-mineral complexes, and decomposition processes. For instance, changes in redox cycling of Fe could not only alter decomposition and stabilization of soil organic matter, but also alter vegetation characteristics by affecting the availability of nutrients such as P, Ca and Mg (Curtinrich et al., 2022; Zhaojun et al., 2011). Some studies (e.g. Lyons et al., 2020; Norby et al., 2019) suggest that *Sphagnum* abundances could decline upon warming, due to changes in soil moisture and a shift towards the greater dominance of vascular plants. *Sphagnum* derived phenolic compounds have frequently been observed to inhibit decomposition, for instance by suppressing microbial activity (Freeman et al., 2001; Zhao et al., 2021), but also by enhancing the formation of Fe-mineral complexes and by quenching degrading radicals such as $^{\bullet}OH$. Therefore, climate warming might not only enhance the reduction of Fe(III) to more soluble Fe(II) and an associated release of Fe-bound C directly through altered hydrology and temperature (Curtinrich et al., 2022), but may also affect Fe species by its effect on vegetation compositions. While we did not determine bryophytes at species level in this study, Figure 2 shows that bryophytes in general, including *Sphagnum* mosses, are more dominant at Tindar and Hrafnabjörg, i.e. the two peatlands with higher levels of ferrihydrite and Fe-humus compounds (Figure 5 and Figure 6), as well as a greater prevalence of phenolic compounds (Figure 4). The potentially negative effect of climate warming upon *Sphagnum* mosses may be particularly quick in peatlands already dominated by vascular plants as in this study. Vegetation changes such as a temporary decline of *Sphagnum* in favour of vascular plants may also be induced by tephra deposition (e.g. Hotes et al., 2004; Hughes et al., 2013; but see Loisel & Bunsen, 2020). Questions arise if recovery of declining plant species after several years or decades after the eruption might be delayed or even impeded by the additional effects of changes in climatic pattern and steady dust fluxes from barren drylands. Increased incorporation of redeposited dust into Histosols may also lead to elevated pH (e.g. Arnalds, Gudmundsson, et al., 2016), as can be seen in the surface soils examined in this study (Figure 7). Such changes in pH may reduce the stability of organo-mineral associations (e.g. Inagaki et al., 2020; Varadachari et al., 1994). Grybos et al. (2009) observed that under reducing conditions in wetlands, increases in pH enhance the desorption of soil organic matter, particularly from Fe- and Mn-hydroxides. Garrido and Matus (2012) found a significant negative correlation between pH and Al_p (and also Fe_p), confirming observations of previous studies that the formation and stability of metal-humus complexes (particularly that of Al-humus complexes) predominantly occurs at pH < 5 (Adams et al., 2000; Shoji & Fujiwara, 1984). On the other hand, allophane formation is favoured by pH $\geq$ 5 (e.g. Garrido & Matus, 2012; Matus et al., 2014; Shoji et al., 1993; Wada, 1989). Hence, the importance of this highly reactive mineral for the stabilization of soil organic matter of Histosols with andic soil properties will possibly increase with elevated pH.

5 Conclusions

By analysing data sets of vegetation cover, C characteristics, andic properties and various complementary soil properties derived from three Icelandic peatlands, we provide indications of several interesing patterns in post-settlement Histosols. While vegetation characteristics and the chemical composition of the soil organic carbon evidently play a role for C dynamics in undrained peatlands in the volcanic environment of Iceland, mineral soil constituents seem to be of greater importance than in peatlands of less dynamic environments.

The C characteristics of the very youngest surface soils (0-5 cm) of all three peatlands are similar despite clear differences in vegetation characteristics, but the development of the C structure with depth differs between them. Overall, decomposition seems to proceed more slowly at peatlands with notable andic properties than at peatlands that reveal no or weak andic properties. A number of factors may be at play here. For instance, as *Sphagnum* derived phenolic compounds are recognized as an inhibitor of soil organic matter decomposition through several pathways, seemingly small differences in the relative content of this C group may partly be responsible for differences in C trajectories. While not providing detailed information about abundances of *Sphagnum* mosses, this study indicates a greater dominance of *Sphagnum* at the sites with less decomposed soil organic carbon and an overal greater share of phenolics. Future studies should put more emphasis on the occurrence of *Sphagnum* species in Icelandic peatlands as *Sphagnum* mosses might play a greater role in the C dynamics of Icelandic peatlands than usually thought based upon their relatively limited presence within these vascular plant dominated ecosystems.

Another explanation for the differing decomposition trajectories might be interactions between C groups and soil minerals, some of which bear a resemblance to stabilization processes in mineral soils. Particularly interesting is the positive relation between labile O/N alkyl C and active Fe and ferrihydrite, indicative of a stabilizing effect on labile C groups as observed in mineral soils. Also, we find indications of a stabilizing effect of allophane on carboxyl/carbonyl/amide C, similar to studies on allophanic podzols in New Zealand. The positive relation between allophane and C/N ratios, and allophane and O/C aryl C supports previous studies on European temperate forest soils where the share of these C compounds decreases with increasing decomposision. Projections of the effects of environmental pressure, such as a warming climate, on C cycling in Icelandic peatlands should therefore not only consider interactions between climatic variables like temperature and precipitation, and vegetation- and C characteristics, but also interactions with mineral soil constituents.

Finally, the share of inorganic contents (%Ash) in post-settlement Histosols increases with decreasing distance to the most extensive dust sources in the interior of the country. Inevitably, relative contents of soil organic matter and C decline as the share of inorganic contents increases. Importantly however, absolute C contents per volume increment of soils are overall not affected by increased aeolian deposition. This is explained by the greater soil bulk densities of the more mineral soils. As this study does not provide basal dates for the investigated soils, we were not able to calculate annual soil and C accumulation rates. Therefore, future studies should investigate whether or not varying amounts of mineral deposition impact C accumulation rates per time increment. Also, windblown mineral material may in some cases have a significant effect on C storage capacities of wetland soils. Future research should therefore not only focus on the effect of mineral deposition on Histosols, but also on the relatively less organic Histic and Gleyic Andosols common in surface soils of Icelandic wetlands.

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