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

Susanne Claudia Möckel[1], Egill Erlendsson[1], and Gurún Gísladóttir[1]

[1]University of Iceland

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Abstract

Due to frequent volcanic activity and erosion of dryland soils, magnified by land use after human settlement (c. 870 AD), peatlands in Iceland receive regular additions of mineral aeolian deposits (tephra and eroded material). Hence, their soils may develop not only histic, but also andic characteristics. Yet, mineral aeolian 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 histic and andic soil properties and their relation with C structure. We compare Histosols from three Icelandic peatlands of different degree of exposure to aeolian deposition by evaluating datasets 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, δ^{13}C and δ^{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. The interaction of andic and histic soil properties seems 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 serve as protective barriers. 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.

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Susanne Claudia Möckel[1], Egill Erlendsson[1], and Guðrún Gísladóttir[1,2]

[1]Institute of Life and Environmental Sciences, University of Iceland, Reykjavík, Iceland.

[2]Institute of Earth Sciences, University of Iceland, Reykjavík, Iceland.

Corresponding author: Susanne Claudia Möckel (scm2@hi.is)

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.

Abstract

Due to frequent volcanic activity and erosion of dryland soils, magnified by land use after human settlement (c. 870 AD), peatlands in Iceland receive regular additions of mineral aeolian deposits (tephra and eroded material). Hence, their soils may develop not only histic, but also andic characteristics. Yet, mineral aeolian 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 histic and andic soil properties and their relation with C structure. We compare Histosols from three Icelandic peatlands of different degree of exposure to aeolian deposition by evaluating datasets 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, δ^{13}C and δ^{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. The interaction of andic and histic soil properties seems 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 serve as protective barriers. 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.

1 Introduction

1.1 Role of peatlands in the global C cycle

Most estimates of total soil organic carbon (SOC) in the worlds soils range between 1400-1600 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 towards the high northern latitudes (e.g. Batjes, 2016). Peatlands possess a disproportionate ability to store C. Despite covering only about 3% of terrestrial surface, their organic soils 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 (c. 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 in Iceland is surprisingly small considering its high latitude (between c. 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. 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 aeolian 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., 2011; Gísladóttir et al., 2010; Möckel et al., 2017), owing to more stable conditions for soil formation before the onset of anthropogenic influence c. 870 AD. 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, e.g. only partly decomposed fibric organic material, high C content, and low bulk densities (Arnalds, 2004, 2015). The precise timing of the turning point between stable Histosol formation and more mineral soil layers within soils of mires varies geographically. Generally, it is associated with increased aeolian material being deposited into the mires from severely 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., 2011; Gísladóttir et al., 2010).

1.3 The influence of andic properties on C in mires

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). The positive feedback between allophane and C accumulation has limitations, though. 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 in SOM rich soils (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 mires 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). Yet, research on the interactions between histic and andic soil properties and their impact on C dynamics is still in its infancy. Particularly, questions remain if the mineralogical environment of these soils impacts the stability of their SOC. 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. 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). Furthermore, questions on the potential interaction between andic soil properties and the chemical composition of C in Histosols as derived, for example, by ^{13}C 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 not only governed 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 1990-2018 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. To achieve this aim, the study was based on the following objectives:

a) To determine the development of the structure of SOC throughout profiles of Histosols from three Icelandic peatlands. The peatlands vary in proximity to source areas of aeolian material. We apply robust 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.
b) To evaluate the development of andic properties in Histosols from three Icelandic peatlands. Here, we apply a variety of variables based on selective extractions of Al, Fe and Si with ammonium oxalate and sodium pyrophosphate. The multivariate data are statistically evaluated by robust PCA and cluster analysis.
c) To evaluate if there is a relationship between i) C structure and andic properties and ii) a set of variables, that we refer to here as decomposition proxies (stable isotope ratios δ^{13}C and δ^{15}N, C/N ratio) and andic soil properties. We apply redundancy analysis (RDA) to evaluate if there is a causal relationship between these properties.

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 aeolian material (sparsely vegetated areas in the interior of the country and the active volcanic zones). At each peatland, one soil profile was excavated (Figure 1b). Exact site selection within peatlands was based on unpublished vegetation analysis by the authors, which was conducted at nine quadrats (0.25 m^2) within each peatland along three parallel transects from the margin to the center of each peatland (Figure 1c). For the research presented in this paper, one of the nine sampling points was chosen in each peatland 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 points were chosen: 1c at Torfdalsmýri, 1b at Tindar and 1c at Hrafnabjörg (compare Figure 1c). Pooled bulk soil samples were collected at 10 cm intervals down to a depth of 20 cm below the Hekla 4 tephra layer (Figure 1b). Above and below the Hekla 3 and Hekla 4 tephra layers, the sampling interval was reduced to 2 x 5 cm (see Bonatotzky et al., 2019, 2021). For the determination of dry bulk density (DBD) samples of a predefined volume were cut out from each layer. 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 c. 3 °C in the lowlands and unsheltered coastal areas. Average summer tritherm 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 c. 400-500 mm yr^{-1} is comparatively low, but generally slightly greater in areas close to the sea than the highlands. Average wind speeds range between 3.8 m s^{-1} and 7.4 m s^{-1}, with greatest wind speeds at the highlands and lowest in sheltered lowlands.

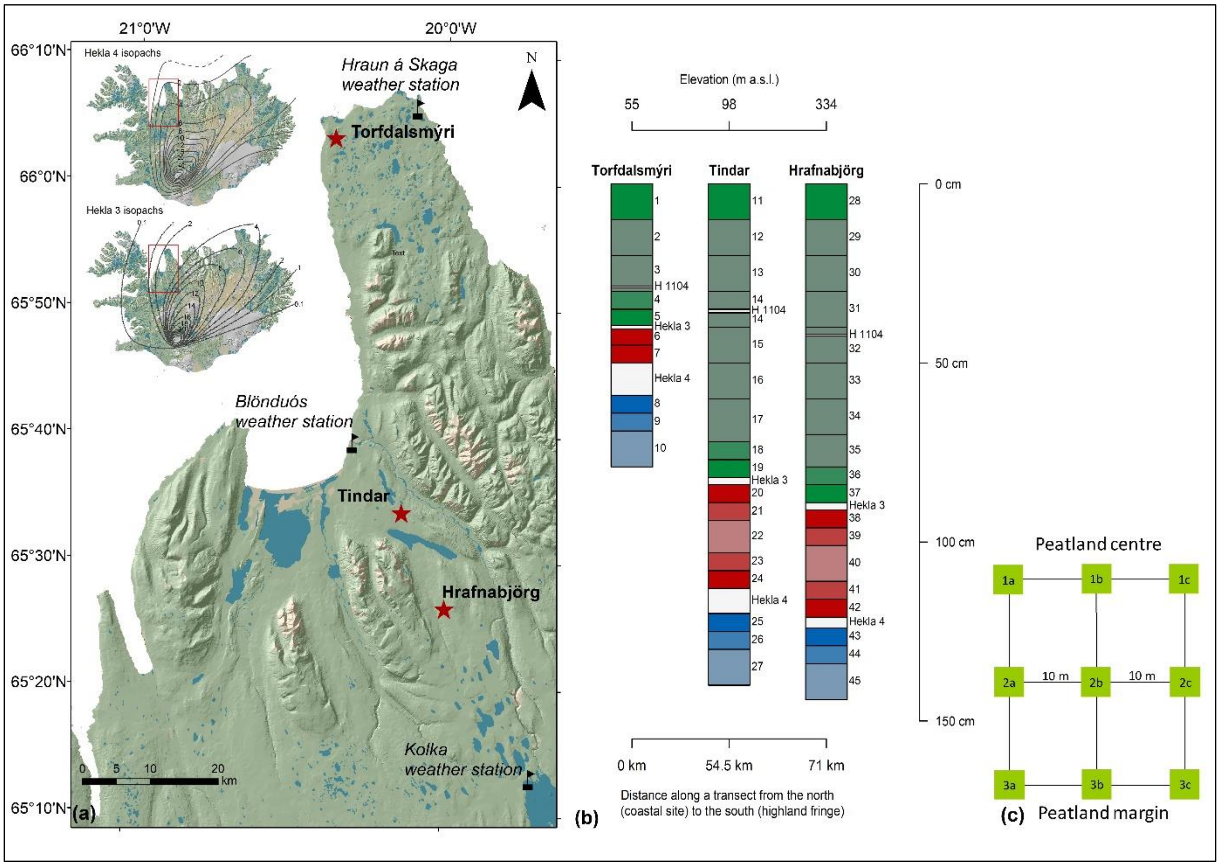

Figure 1. a) The main map shows the research area in Austur Húnavatnssýsla, northwest Iceland, and the location of the three peatland sites Torfdalsmýri, Tindar and Hrafnabjörg, and the weather stations Kolka, Blönduós and Hraun á Skaga. The map insets show the location of the research area in Iceland and Hekla 4 and Hekla 3 isopachs (adapted from G. Larsen & Thorarinsson, 1977). **b)** Soil cores from each peatland. Elevation increases from north to south, toward the interior highlands. 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 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 (G. Larsen & Thorarinsson, 1977) is also shown. This eruption occurred c. 230 years after the settlement of Iceland, and may therefore serve as an approximate demarcation line between prehistorical and historical soil formation. Numbers beside depth intervals resemble the numbering system used for annotation of soil samples throughout the system. The numbers are arbitrary. **c)** Site selection at each peatland was based on unpublished vegetation analysis by the authors.

2.2 Two late Holocene volcanic eruptions – Hekla 4 and Hekla 3

The volcanic eruptions of Hekla 4 (c. 4.35 ka BP; Dugmore et al., 1995) and Hekla 3 (c. 3.06 ka BP; Dugmore et al., 1995) are among the most voluminous silicic Holocene eruptions in Iceland, with an estimated 9 km^3 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 (compare isopachs in Figure 1a), mainly towards the north and northeast as indicated by stratigraphic evidence. 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 higher vegetation of the mire, 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). Moreover, 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 palaeoenvironmental evidence of relatively stable ecosystems with a fair resilience towards tephra deposits before the onset of anthropogenic influence in northwest Iceland, signs of adverse impact by tephra have frequently been reported. In particular, ecosystems in the climatically harsh highland environment were likely more sensitive towards vegetation and soil deterioration induced by large tephra deposits (Eddudóttir et al., 2017; Möckel et al., 2017; Tinganelli et al., 2018).

2.3 Laboratory analyses

2.3.1 Solid state ^{13}C NMR spectroscopy

Solid state ^{13}C NMR spectroscopy was used to determine the structure of soil organic C that contributes to the characteristics of SOM and decomposition processes (Kögel-Knabner, 1997). A cross-polaristion 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 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 (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).

2.3.2 DBD, SOM, %C and %N, stable isotope ratios $\delta^{13}C$ and $\delta^{15}N$

The DBD was determined by mass loss after drying of a known soil volume and SOM was 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 $\delta^{13}C$, $\delta^{15}N$ 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 (Alewell et al., 2011; 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.

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 1N 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_{H2O}) was measured in deionised 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 non-crystalline hydrous oxides of Fe and Al, allophane, and amorphous aluminosilicates (Nanzyo et al., 1993; Wada, 1989). The sum of Al_o + ½Fe_o was calculated, which is 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, 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

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; Filzmoser et al., 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 centred 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 was 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, redundancy analysis (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, δ^{13}C, δ^{15}N) was also investigated by RDA. Only 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 1b), 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 tephra deposits at Torfdalsmýri and Tindar are thicker than isopachs would indicate (2 cm 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 2-4 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.

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 a gradual increase of the A:O/N ratio towards younger soil layers, facilitated by an increase in alkyl C and a decrease in O/N alkyl C. 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 3b). The C structure at Tindar and Hrafnabjörg is similar, but they both differ from Torfdalsmýri with the exception of samples 1, 2 and 10. Cluster one (green) is comprised of all samples from Tindar and Hrafnabjörg and samples 1, 2 and 10 from Torfdalsmýri, whereas cluster two (red) is exclusively composed of the remaining samples from Torfdalsmýri (for goodness of clustering, compare silhouette width plot in Figure 3c).

There are several noteworthy sub-clusters (Figure 3b), which are reflected by the robust PCA (Figure 3a): At Tindar, all soil layers between Hekla 4 and Hekla 3 (numbers 20-24) form one obvious sub-cluster. 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 (numbers 38-42) do not form as clear a sub-cluster, but the sub-cluster also includes several soil layers formed after Hekla 3 (numbers 34, 35, 37). Nevertheless, a shift in C structure after the eruption of Hekla 4 is discernible there too. At Hrafnabjörg and Tindar, the soil layers below Hekla 4 reveal a similar C structure as upper soil layers, namely samples 11-14 (0-40 cm depth) at Tindar and sample 28 (0-10 cm depth) at Hrafnabjörg.

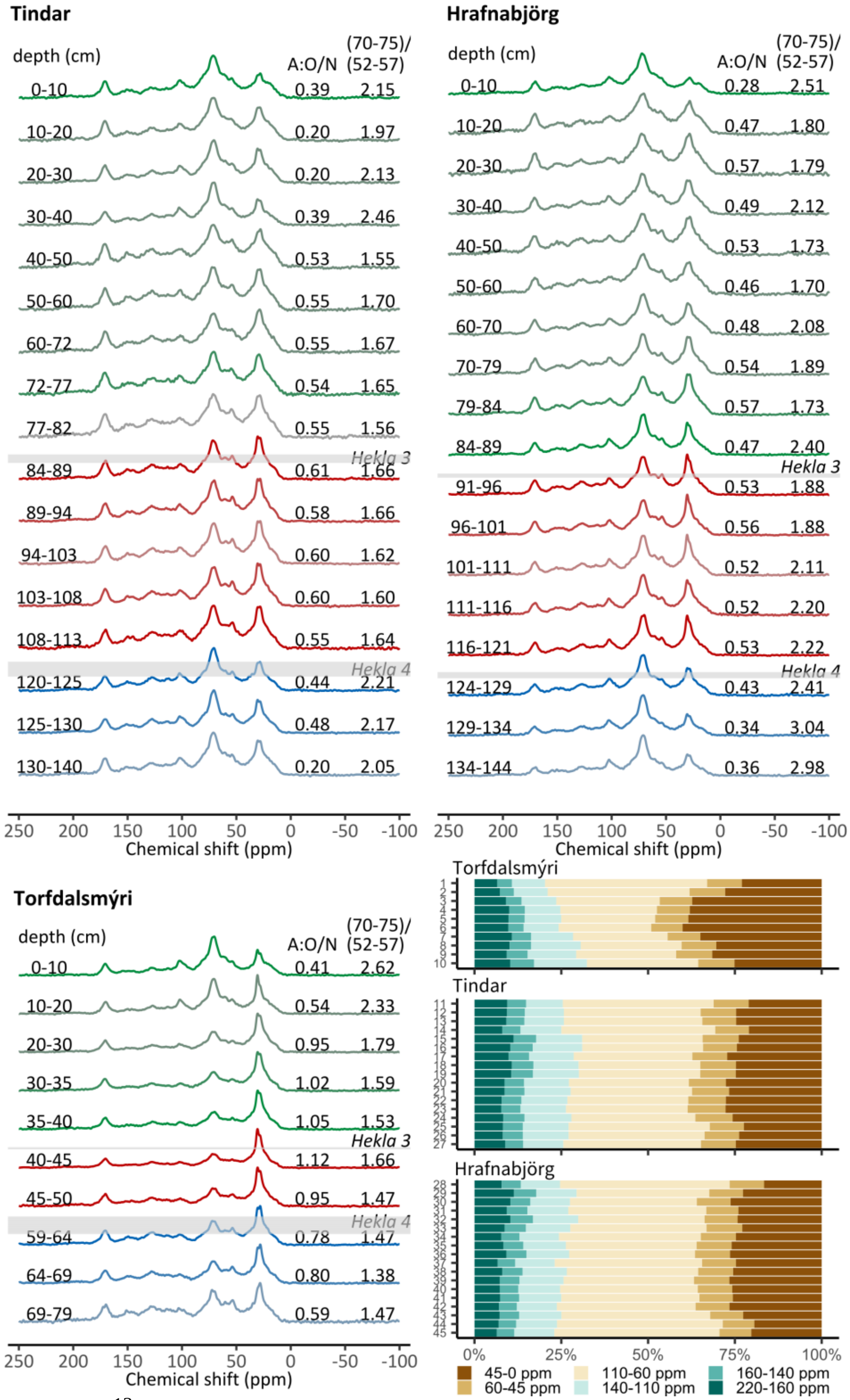

Figure 2. ^{13}C NMR spectra of the three peatlands, including A:O/N and (70-75)/(52-57) ratios. Soil layers formed before Hekla 4 are colored in blue, soils formed between Hekla 4 and Hekla 3 are depicted in red and soils formed after Hekla 3 in green. Darker colors reflect increased influence of aeolian material in the form of either volcanic ejecta (i.e. tephra) or aeolian material from sparsely vegetated or barren areas. Stacked bar charts in the right bottom show the relative

share of the chemical shift regions. For numbers of soil samples used in the bar chart refer the Figure 1b.

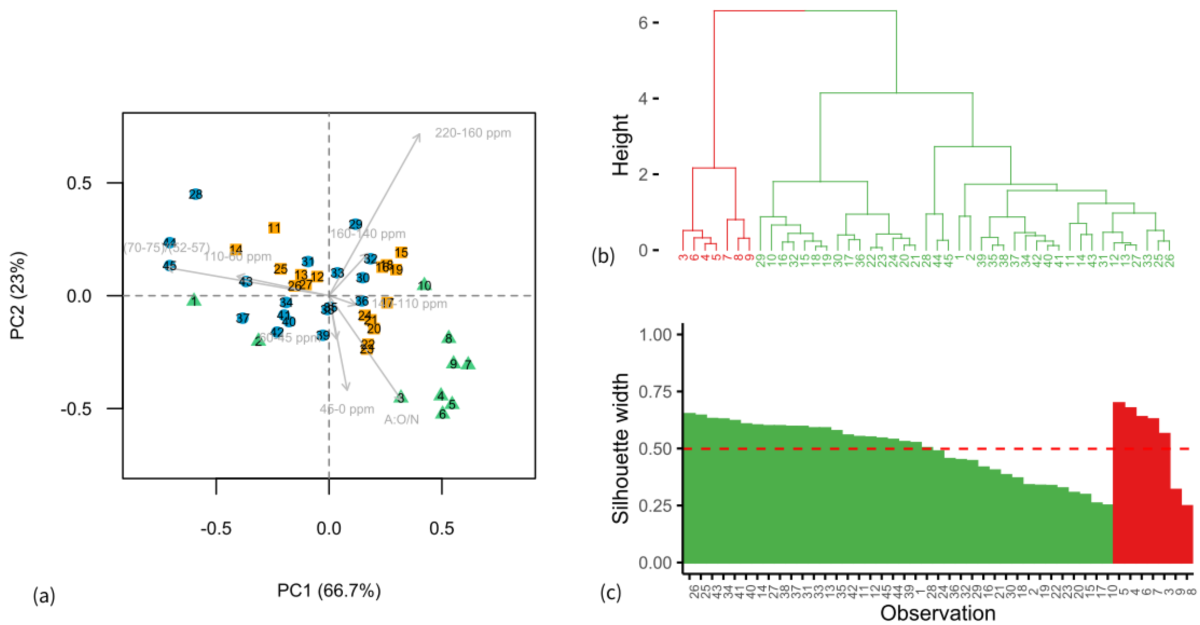

Figure 3. a) Biplot showing loadings of variables and scores of observations of the robust PCA on the ^{13}C NMR data. Observations of different sample sites are depicted by shapes and colors (Torfdalsmýri: green triangle, Tindar: orange square, Hrafnabjörg: blue circle). **b)** Dendrogram based on hierarchical clustering, using manhattan distance and Wards criterion (see Kassambara, 2017) and number of clusters k=2. Cluster one (green) contains all samples from Tindar and Hrafnabjörg and samples 1,2 and 10 from Torfdalsmýri, cluster two (red) is exclusively comprised of samples from Torfdalsmýri. **c)** Silhouette width plot for hierarchical clustering. Average silhouette width = 0.5 (red broken line); Dunn index = 0.298. For position of numbering within soil profiles, refer to Figure 1b.

3.3 Total %C and %N, C/N, SOM and DBD

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.

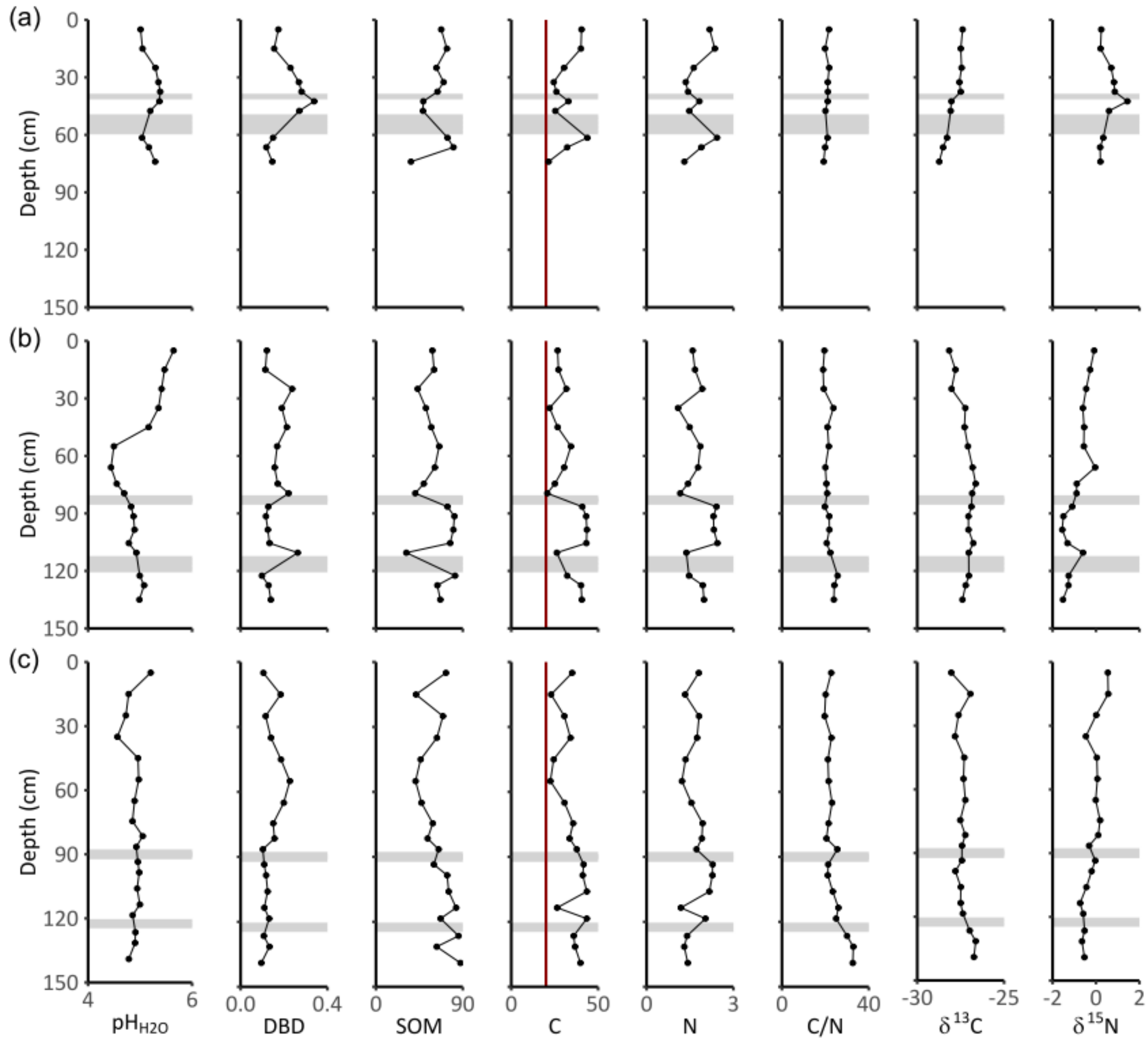

Figure 4. Results of complementary soil properties used in this study at the coastal peatland Torfdalsmýri **(a)**, the lowland Tindar **(b)** and the highland fringe Hrafnabjörg **(c)**. DBD is presented as g cm^{-3}, SOM, C and N are in %, C/N as molar ratio and $\delta^{13}C$ and $\delta^{15}N$ are presented in ‰. Vertical red lines represent the following threshold: C ≥ 20% as diagnostic criterion of Histosols. Shaded grey bars resemble the tephra deposits Hekla 3 and Hekla 4.

3.4 Variation in andic soil properties determined by robust PCA and cluster analysis.

The andic soil properties draw a more diffuse pattern than the C structure (Figure 5). 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 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 6a) and the cluster analysis (Figure 6b). 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 6c). Cluster one (green) contains samples from all three sites, whereas cluster two (red) contains samples from Tindar and Hrafnabjörg only. There is a clear demarcation of the soil layers formed between Hekla 4 and Hekla 3 at Tindar and Hrafnabjörg (Figure 6a and b). Samples 20-23 (Tindar) and 38-42 (Hrafnabjörg) form a clear sub-cluster each.

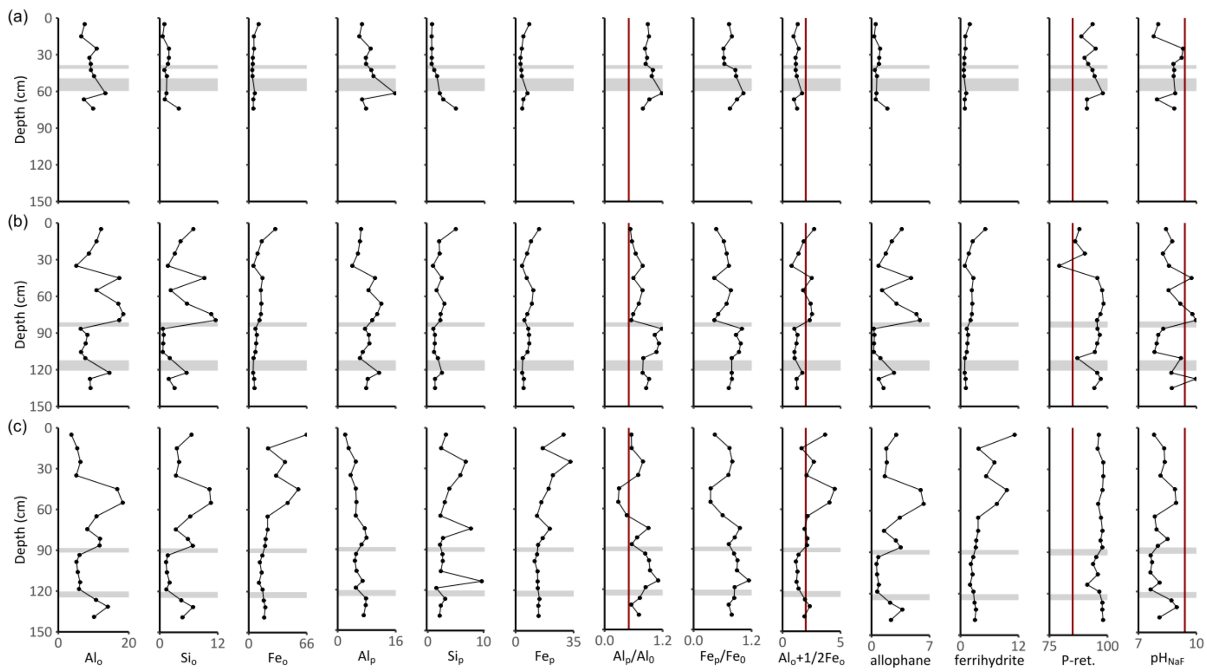

Figure 5. Properties used to reflect andic soil properties in this study: Results of selective dissolution analyses and properties related to amorphous material, and pH_{NaF} and P-retention at the coastal peatland Torfdalsmýri (a), the lowland Tindar (b) and the highland fringe Hrafnabjörg (c). Al_o, Si_o, Fe_o, Al_p, Si_p, Fe_p, and $Al_o+1/2Fe_o$ are presented as g kg_{soil}^{-1}. 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. Shaded grey bars resemble the tephra deposits Hekla 3 and Hekla 4.

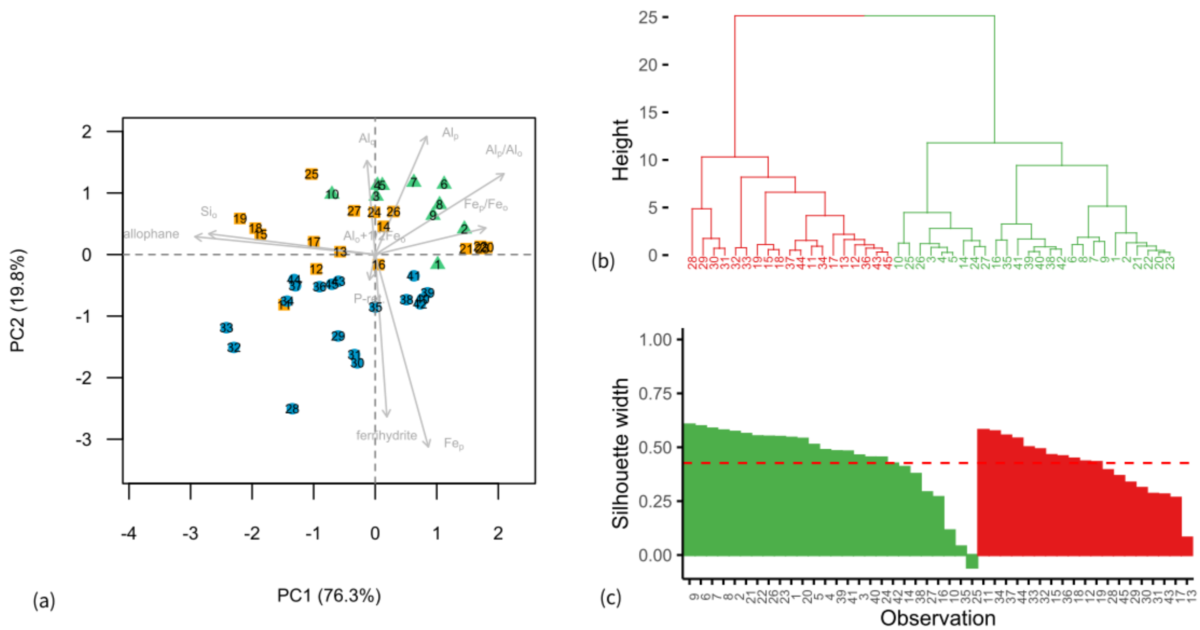

Figure 6. a) Biplot showing loadings of variables and scores of observations of the robust PCA of the compositional andic data, including one external non-compositional variable (arcsine transformed P-retention). Observations of different sample sites are depicted by shapes and colours (Torfdalsmýri: green triangle, Tindar: orange square, Hrafnabjörg: blue circle). **b)** Dendrogram based on hierarchical clustering, using manhattan distance and Wards criterion (see Kassambara, 2017) and number of clusters k=2. Cluster one (green) is comprised of samples from all three sample sites, cluster two (red) is comprised of samples from Tindar and Hrafnabjörg only. **c)** 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 neighbouring clusters. For position of numbers within soil profiles, refer to Figure 1b.

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 c. 95% of the constrained variation are contained within the first two dimensions of the RDA (Figure 7a). Only the effect of the first dimension proved statistically significant (p = .003). Therefore, the effect of Al_p, which contributes mostly to dimension 2, can be neglected. The content of 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 seems 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 are contained within the first two dimensions of the RDA (Figure 7b), both proving significant (p = .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 is 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 $\delta^{15}N$.

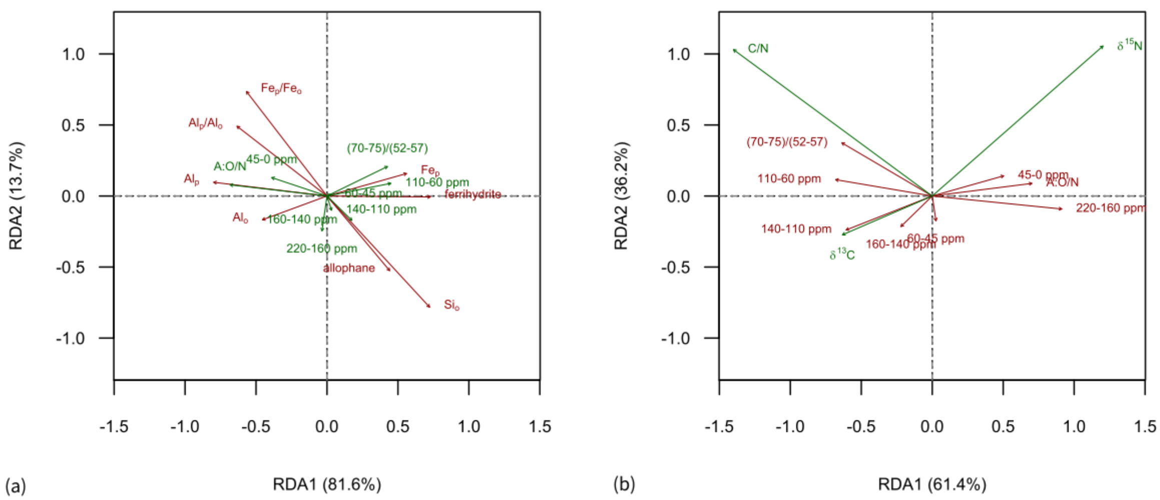

Figure 7. a) Biplot of RDA between C structure (response variables) and andic properties (explanatory variables). Response and explanatory data matrices were transformed to the ilr space prior to performance of RDA, while the results were back transformed to the clr space for ease of graphical illustration and interpretation (van den Boogaart & Tolosana-Delgado, 2013; van den Boogaart et al., 2020). Scaling = type 2. **b)** Biplot of RDA between C/N, $\delta^{13}C$ and $\delta^{15}N$ (response variables) and C structure (explanatory variables). Explanatory data matrices were transformed to the ilr space prior to performance of RDA, while the resulting loadings were back transformed to the clr space. Response variables were normalized. Scaling = type 2.

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} = .553).

4 Discussion

4.1 Soil classification

All three pedons define as Dystric Histosols (IUSS Working Group WRB, 2015), though several layers at Tindar and Hrafnabjörg define as Histic Andosols according to Soil Taxonomy (Soil Survey Staff, 2015).

4.2 Development of C and its structure is impacted by tephra layers

Based upon the relatively 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 lesser, and to link this to inputs of mineral material. The results of our study prove such conclusions hasty. Increased input of mineral aeolian 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). Moreover, relative C content is not necessarily reduced at sites that are more exposed to aeolian deposition, as the peatlands of our study show. Tindar and Hrafnabjörg, which are closer to source areas of aeolian material, contain on average slightly greater %C than Torfdalsmýri. Moreover, the soil accumulation at these two sites is obviously greater than at Torfdalsmýri. There, c. 0.5 m of soil has accumulated since the eruption of Hekla 4 (Figure 1b), whereas at Tindar and Hrafnabjörg, more than 1 m of soil has accumulated during the same time span. Hence, relative C content alone is a poor indicator of the C storage capacity of peatlands in Iceland.

Therefore, we determined the development of C structure of the three peatlands through time (Figure 2) and detected variations that seem to be governed by the occurrence of tephra and other aeolian 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 (Figure 3a and b).

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 towards 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, i.e. the upper 0-10 cm at Hrafnabjörg (sample 28) and the upper 0-40 cm at Tindar (samples 11-14; Figure 3a and b). Though this pattern of first increasing signs of decomposition with depth, and then signs of decreasing decomposition towards even greater depths, is consistent with findings of previous studies (e.g. Möckel et al., 2021; Preston et al., 1987), it is conspicuous that this change coincides with the Hekla 4 tephra layer at Hrafnabjörg and Tindar. Here, other factors than stage of decomposition may contribute to the observed variations in C structure and the stability of the stored C, e.g. 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 e.g. observed by Hotes et al. (2006). At least moderate changes in vegetation composition might have been induced (Eddudóttir et al., 2017, 2020; Eddudóttir et al., 2016). 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).

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 between the two tephra layers stand out from the others with regard to other soil properties than C structure. Total %C and %N are clearly increased (Figure 4). 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. 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 5). 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 (Figure 6a and b). Contrary to what might be expected from soil layers confined 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 content and pH_{NaF} is low. Possibly, the increased %C between the tephra deposits hampers the formation of allophane 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_{H2O} 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 Figure 4 and Figure 5).

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 c. 870 AD (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).

These findings also correspond to a palaeoenvironmental 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, 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 tephra deposits and 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 northern 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 7a) 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 non-histic 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 is 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 (ppm 110-60) in this study is also highest throughout the pedon of Hrafnabjörg (Figure 2 and Figure 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 7a), 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, i.e. to accelerate the reduction of ferric iron (Fe^{3+}) such as in ferrihydrite to the more soluble Fe^{2+} (Vaughan et al., 2009).

The relative similarity of the C structure of soil layers below Hekla 4 and upper soil layers at Hrafnabjörg and Tindar owing to an apparent dominance of O/N alkyl C over alkyl C, is another indicator 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). Likely, the deposit of the Hekla 4 tephra, served as a barrier (see De Vleeschouwer et al., 2008) towards the input of fresh organic material in the years after the eruption and still serve as a barrier towards input of dissolved organic carbon from upper soil layers, thereby hampering microbial activity. During field work, it could indeed be observed at Hrafnabjörg and Tindar, that the compacted Hekla 4 tephra deposits serve as aquifers of limited permeability. At Torfdalsmýri, there is no obvious similarity in C structure between the topsoil and below Hekla 4 subsoil layers. Yet, the tephra layer seems to contribute to protective mechanisms against decomposition as reflected by substantially decreased A:O/N ratios below the tephra deposit (Figure 2).

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 discussed above (Figure 7a).

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 (Figure 2 and Figure 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), and supporting previous evidence of the limitations of C/N ratios as a proxy for decomposition (see Bonanomi et al., 2013; Bonanomi et al., 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 structure, andic soil properties and decomposition proxies, we can draw the following conclusions:

- Relative C contents are insufficient to i) estimate the C storage capacity of peatlands exposed to frequent deposits of volcanic origin and ii) 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 structure in peatlands of different degree of exposition to aeolian 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 are facilitated by mineral deposits of volcanic origin, is less decomposed (or deteriorated) than the SOM of peatlands without notable andic soil properties.
- Thick and compacted tephra layers have the potential to serve as protective barriers. Thus, 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 towards 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 the interaction of andic and histic soil properties, accompanied by the protective role of major tephra deposits, appears to enable an unusual potential for long-term C stabilization in a natural peatland environment, these comparatively undecomposed organic soils may be an even greater source of atmospheric C upon disturbance than anticipated based upon %C only.

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