

Direct evidence of CO₂ drawdown through enhanced weathering in soils

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Supplementary Information

The Supplementary Information includes:

- Soil Classification and Soil Evolution in Iceland
- Detailed Field Site Description
- Details of Field Sampling
- Analytical Methods
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Soil Classification and Soil Evolution in Iceland

Iceland is built of volcanic rocks, which are predominantly (80–85 %) of basaltic composition, the remainder being intermediate and silicic volcanics and clastic sediments that are mostly of basaltic composition (Saemundsson, 1979). The oldest exposed rocks are about 15 Myr (McDougall *et al.*, 1984). Iceland was fully covered with glaciers at the Last Glacial Maximum (~20 kyr BP). The ice sheet retreated close to the present coastline around 10.3 kyr BP, and at about 8.0 kyr BP Icelandic glaciers were of similar, or little lesser extent, than at the present (Norðdahl *et al.*, 2008). Hence, all Icelandic soils are of Holocene age younger than ~10 kyr BP (Arnalds, 2008).

Andosols are the dominant soils in Iceland, Vitrisols are present in desert areas and organic-rich Histosols are found in some wetland areas (Arnalds, 2008). Andosols are not common in Europe, but they are widespread in the active volcanic areas of the world (Arnalds, 2008). Two main factors are commonly used to classify Icelandic soils: deposition of aeolian (volcanic) material and drainage (Arnalds, 2004). Aeolian material mostly originates from the sandy desert areas located near active volcanic zones or from glaciofluvial outwash plains. After the settlement in Iceland, around 1076 yr BP, the extent of barren areas that are a source for aeolian material significantly increased (Gísladóttir *et al.*,

2008, Dugmore *et al.*, 2009). Andosols are often found in the wetland areas of Iceland where substantial aeolian input is present, lowering the relative organic content, or where some drainage is present, whereas organic-rich Histosols are found in wetlands with little aeolian input. The progression of soil types with improving drainage conditions from wet to dry follows: Histosols (>20 % C), Histic Andosols (12–20 % C), Gleyic Andosols (>1 to < 12 % C, poorly drained), and Brown Andosols (>1 to <12 % C, freely drained) and Vitrisols with <1 % organic carbon (Arnalds, 2008). This order also reflects the decreasing distance from the volcanic zones and the source of aeolian materials. The transition between these soil types is fluent, and changes in drainage or aeolian input can lead to a change of the soil type. It is postulated that in absence of the volcanic influences, Icelandic wetland soils would largely be organic Histosols, typical of the arctic environments (Arnalds, 2015, 2008). This suggests that applying enhanced weathering EW by the addition of basaltic dust to an organic-rich Histosol can lead to its transition to a more mineral-rich soil such as an Andosol, as found in our study area.

Histosols or peatlands are classified further as *ombrotrophic* or *minerotrophic*, based on the origin and mineral content of the waters feeding them (Rydin and Jeglum, 2013). While *minerotrophic* soils receive mostly ground water that has interacted with the bedrock upstream, leading to an enrichment of the mineral content in the water, *ombrotrophic* soils are dominantly fed by rainwater, and are therefore nearly free of rock derived dissolved constituents (Rydin and Jeglum, 2013). Our studied field site receives mostly rainwater. Therefore, all dissolved constituents in our soil water are assumed to originate from the interaction of rainwater with the embedded dust of our soil, and the decay of organic matter. Based on this assumption, we compare our data (see Fig. 3) with data from other sites reported in the literature as mostly *ombrotrophic*, implying limited interaction with the underlying bedrocks.

Detailed Field Site Description

The field site is located above the source of the Rauðalækur (“Red creek”) river at 63° 53' 42.5" N 20° 21' 15.9" W, 7 km north of the town of Hella, South Iceland. This field site has not been used for agriculture or fertilized for at least the past 10 years prior to this study, hence limited anthropogenic contamination is therefore expected. Based on data from the Icelandic Meteorological Office, the average soil temperature is ~7 °C during the summer (Petersen and Berber, 2018). At 100 cm soil depth, the annual maximum temperature is 9 °C and the annual minimum temperature is 1 °C. The soil can, however, temporarily freeze down to a depth of 50 cm (Petersen and Berber, 2018). The annual rainfall in this area is 1250 ± 200 mm. The average storm yields an average of 15 mm of rain with a maximum duration of 20 hours (www.en.vedur.is/climatology/data). The surface of the studied soil is hummocky, and the vegetation is characterized by graminoids with a clear predominance of Poaceae. The direction of the groundwater flow, estimated based on the surrounding drainage channels, is towards S/SE. Based on field observations, the groundwater table fluctuates near a depth of 50 cm.

The field site is adjacent to a natural escarpment allowing for the characterization of the subsurface soil profile. Several tephra layers were identified within a cleared vertical face of the escarpment. Layers of organic-rich soil



admixed with air-borne basaltic dust separate the tephra layers. The dust in these layers is finer grained than the basalt in the tephra layers. The tephra layers can be assigned to specific volcanic eruptions, as each volcanic eruption in Iceland has its own chemical fingerprint (Dugmore *et al.*, 2009; Grönvold *et al.*, 1995). These allow determination of the soil accumulation rates. As can be seen in Figure 1b, over the last 3300 years about 220 cm of soil has accumulated, averaging to a soil thickening rate of 0.067 cm yr^{-1} . The ‘Settlement layer’, a tephra layer from an eruption of the Vatnaöldur volcanic system at $1079 \pm 2 \text{ BP}$ (Grönvold *et al.*, 1995), which approximately coincides with the initial settlement (Landnám) of Iceland, was barely discernible in the soil profile. Although the exact depth of this Settlement tephra at around 96 cm depth is somewhat uncertain, its location suggests an average soil accumulation rate of 0.086 cm yr^{-1} during the last 1120 years. This is consistent with Gísladóttir *et al.* (2011) who reported that the dust flux over South-Central Iceland increased following the emplacement of the Settlement layer. A detailed description of the soil profile is provided in Table S-1 of the Supplementary Information following the guidelines provided in Schoeneberger *et al.* (2012).

Details of Field Sampling

In situ soil waters were sampled 10 m North from the escarpment in the field with suction cup samplers obtained from Prenart, Denmark. Four suction cup samplers were installed into holes drilled at an angle of 60° at depths of 76, 121, 173, 260 cm on 8 November 2017, following the method of Sigfusson *et al.* (2006). The samplers were left in the field over the winter to allow settling of the soil around the samplers and tubing. The first samples from these suction cup samplers were collected during May 2018 and the last were collected November 2018. The suction cup samplers, which are 95 mm long and 21 mm in outer diameter, consist of a 48/52 % mixture of Polytetrafluorethylene (PTFE) and quartz with an average pore size of $2 \mu\text{m}$. These samplers were connected by 1.8 mm inner diameter Teflon (Fluorinated ethylene propylene) tubing to the surface. Four 60-mL syringes located at the surface were connected *via* 3-way valves and 100 cm long connection polyethylene tubing to the Teflon tubing of the subsurface samplers. The first 30–50 mL of extracted soil water during any sampling was discarded to avoid contamination. It took about 6–8 hours to fill the 60 mL sampling syringes. During the sampling the syringes were kept in a closed cooling box to prevent heating and exposure to sunlight. This approach was adapted to avoid any degassing of the soil solutions and oxidation of the samples. No colour change of the soil solutions due to iron oxidation was observed during the sampling.

Initial sample analysis was performed in the field including sample pH, temperature and Eh measurements, conductivity determination and H_2S titration. Subsamples for major and trace element analysis *via* ICP-OES and ICP-MS as well as for ion chromatography to determine $\text{Fe}^{2+}/\text{Fe}^{3+}$, DOC analysis and alkalinity titration were collected and stabilized on site and analysed later in the lab.



Analytical Methods

The redox potentials (E_{meas}) of the collected fluids were measured directly in the sample syringes in the field using a Microelectrodes Inc MI-800 Micro-ORP Ag/AgCl micro combination redox electrode with a ± 10 mV uncertainty. These values were converted to equivalent potentials for a standard hydrogen electrode (E_{SHE}) using a +199 mV reference potential, E° , for the Ag/AgCl electrode (Sawyer *et al.*, 1995). This calculation was performed using the Nernst equation:

$$E_{\text{SHE}} = E_{\text{meas}} + \ln(10) \cdot (R \cdot T) / F \cdot \text{pH} + E^\circ_{\text{Ag/AgCl}},$$

where R refers to the gas constant, F designates the Faraday's constant, and T symbolizes the temperature in kelvin. Subsequently, ~ 5 mL of each sampled fluid was transferred into 10 mL polypropylene vials for pH temperature, dissolved oxygen, and conductivity measurement. The pH was measured using a Eutech pH 6+ electrode with an uncertainty of ± 0.01 pH units. The dissolved oxygen and conductivity of the samples were measured using a Micro electrodes MI-730 Micro-Oxygen Electrode with an uncertainty of ± 0.5 % and a Eutech COND 6+ with an uncertainty of ± 10 μS , respectively. For major and trace element analysis, 10 mL of each fluid sample was first filtered through 0.2 μm cellulose acetate in-line filters then transferred into acid washed polypropylene bottles. A small quantity of 65 % Merck suprapure HNO_3 was added to acidify these samples to 0.5 % HNO_3 . Samples for iron speciation measurement were first filtered through 0.2 μm cellulose acetate in-line filters then placed into acid cleaned polypropylene bottles. Merck HCl was added to these samples to attain a final acid concentration of 0.5 %. Samples for dissolved organic carbon analysis were collected in acid washed polycarbonate bottles and acidified with 0.5 M suprapure, Merck HCl to a final acid concentration of 3.3 %.

Dissolved hydrogen sulphide, H_2S , was determined in the field by precipitation titration immediately after sampling with an uncertainty of ± 0.7 $\mu\text{mol kg}^{-1}$, using mercury acetate solution $\text{Hg}(\text{CH}_3\text{COO})_2$ of a known concentration as described by Arnórsson (2000). Alkalinity titrations were performed immediately after returning the samples to the laboratory. For each titration, ~ 5 mL of fluid was transferred in a 10 mL vial and titrated to pH 3.3 by addition of 0.1 M HCl while constantly stirring the fluid. The pH of the fluid was recorded using a glass pH electrode together with a pH 110, Eutech instruments millivolt meter. The alkalinity was calculated by the Gran method using the inflection points (Gran, 1952). The final measured alkalinity values are given in meq kg^{-1} with an uncertainty of ± 5 % or less.

Elemental Analysis

Major element compositions of all fluid samples were determined using a Ciros Vision, Spectro Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The instrument was calibrated using the SEL-11 in-house standard, which was referenced to the SPEX CertiPrep commercial standard material. All standards and measured samples were acidified to 0.5 % using suprapure HNO_3 prior to analysis. All measurements were run in duplicate. Blank solutions were measured after every 5 samples and uncertainties were below ± 5 % for each element.



Iron species were determined using a Dionex 3000 ion chromatography system equipped with a Variable Wavelength Detector using the method described by Kaasalainen *et al.* (2016). This method separates Fe^{2+} and Fe^{3+} using pyridine-2,6-dicarboxylic acid (PDCA) as a chelating agent. It detects the distinct Fe cations by post-column derivatization using 4-(2-pyridylazo)resorcinol with a peak absorbance at 530 nm, a detection limit of $\sim 2 \mu\text{g L}^{-1}$ and an uncertainty of $\pm 2 \%$ or less for Fe^{2+} and $\pm 10 \%$ for Fe^{3+} for 200–1000 μL samples.

Dissolved organic carbon concentrations were determined by size exclusion chromatography using a Liquid Chromatography – Organic Carbon Detection system (LC-OCD) obtained from DOC Labor in Karlsruhe, Germany, following the method of Huber *et al.* (2011). The system was calibrated for the molecular masses of humic and fulvic acids using standard material from the Suwannee River, provided by the International Humic Substances Society (IHSS). All DOC measurements have an uncertainty of 5 % or less.

Calculation of Alkalinity Creation and Export in Our Studied Soil

Alkalinity export in our field site was determined by multiplying the mass of water passing through the soil by the alkalinity generated in the soil, taking account the loss of alkalinity as the soil solution interacted with the atmosphere. Any effect of eventual changes in this alkalinity after the fluids arrive in the oceans is not taken into account. The alkalinity of the soil solution after its equilibration with the atmosphere was calculated using the PHREEQC software version 3.4.0 (Parkhurst and Appelo, 1999) together with the minteq.v4 thermodynamic database (Allison *et al.*, 1991; US Environmental Protection Agency, 1998). This alkalinity was determined from the average of all measured major element concentrations, pH and alkalinity in the deepest soil water samplers (see Table S-2). This fluid was equilibrated with atmospheric O_2 concentration. Ferrihydrite is allowed to precipitate at local equilibrium as the fluid oxidized. The resulting fluid was then equilibrated with the 400 ppm CO_2 concentration of the atmosphere to account for fluid degassing.

The mass of fluid passing through the soil was estimated to be equal to the difference between the mean precipitation for the field site minus the evapotranspiration and the direct runoff. The mean precipitation is equal to $1250 \pm 200 \text{ mm yr}^{-1}$, based on the records from the measurement station in Hella located $\sim 7 \text{ km}$ away from the field site operated by the Icelandic Metrological Office Veðurstofa Íslands (<https://en.vedur.is/climatology/data>). The evapotranspiration at the field site was estimated based on Jóhannesson *et al.* (2007) to be equal to 16 % of the precipitation corresponding to 200 mm yr^{-1} . The direct surface runoff is estimated to be 10 %, based on data published by Sigurðsson *et al.* (2004). After subtracting the evapotranspiration and direct surface runoff, approximately $925 \pm 150 \text{ kg m}^{-2} \text{ yr}^{-1}$ of water are estimated to pass through the studied soil annually.

The soil water alkalinity in the deep soil was $2.59 \pm 0.34 \text{ meq kg}^{-1}$ based on the average of the measurements at 260 cm depth. The average alkalinity for the surface waters after oxidation and the precipitation of ferrihydrite calculated with PHREEQC is $1.53 \pm 0.2 \text{ meq kg}^{-1}$. Note that the oxidation from Fe^{2+} to Fe^{3+} releases H^+ . The consequential formation of ferrihydrite from the Fe^{3+} releases additional H^+ , decreasing the pH and alkalinity as well as decreasing



CO₂ solubility. Multiplying this 1.53 ± 0.2 meq kg⁻¹ average alkalinity value by the estimated annual water flux through the soil yields an annual alkalinity export *via* surface waters of 1.45 ± 0.3 eq m⁻² yr⁻¹. Multiplying this number by the atomic weight of carbon yields an annual carbon flux of 17 ± 3.6 g m⁻² yr⁻¹ or 0.17 ± 3.6 t ha⁻¹ yr⁻¹ of C. Note the long-term fate of this captured carbon may evolve once the river water transporting this carbon arrives in the oceans. It should be emphasized that the alkalinity drawn down by the increasing alkalinity could include some contribution from decaying organic material in the soil column. This carbon was originally removed from the atmosphere by photosynthesis, so contributes to the carbon drawdown from the atmosphere as does the direct dissolution of CO₂ from the atmosphere.

To extrapolate the annual mass of carbon drawdown to the gigaton scale, we divided one gigaton of CO₂, which is equal to 2.73×10^8 tons of C by the 0.17 t ha⁻¹ yr⁻¹ of C drawdown in rivers provoked by the addition of basaltic dust to our field site. This yielded a surface area of 1.6×10^9 ha. This surface area is equal to 1.6×10^7 km². This is larger than the surface area of the United States, which is equal to 9.8×10^6 km². The mass of dust needed to be added to 1.6×10^7 km² annually to attain the same $500\text{--}800$ g m⁻² yr⁻¹ of dust added to our study site is obtained by multiplying this flux and surface area. This calculation yields 8 to 13×10^9 t yr⁻¹, which equals 8 to 13 Gt yr⁻¹.

One additional caveat to applying alkalinity generation from enhanced weathering of soils on the continents to global carbon drawdown from the atmosphere is the fate of soil generated alkalinity after its transport in rivers to the oceans. The exact mass of CO₂ removed from the oceans due to alkalinity input is currently debated, but is likely attenuated by carbonate mineral precipitation (Renforth and Henderson, 2017; Moras *et al.*, 2022; Hartmann *et al.*, 2023). Recent estimates suggest a CO₂ uptake efficiency of only 0.6 to 0.8 mol of CO₂ for each mole of alkalinity added to the oceans (He and Tyka, 2023). Such observations suggest that the total carbon drawdown from the atmosphere by alkalinity generation on the continents will depend on the eventual fate of this alkalinity and it is likely decreased by marine processes.

Estimated Organic Carbon Storage Within the Studied Soil

A substantial mass of carbon is stored by soils in organic material. The rate of organic carbon buildup in our studied soil can be estimated by taking account of the rate of soil formation and the organic content of this soil. The average soil formation rate at our study site is estimated to be 0.067 cm yr⁻¹. This estimate is made by dividing the current 2.2 m soil thickness by 3300 years, the time the soil developed (see Fig. 1). The organic carbon content of the studied Histic/Gleyic Andosol is between $\sim 12\%$ and 20% of the dry mass and it has a porosity between 50% and 75% (Snæbjörnsson, 1982; Orradottir *et al.*, 2008). The mass of organic carbon in our studied soil was estimated by considering it is comprised of two parts, an upper part formed after the settlement (1076 yr BP) and a lower part formed from 1076 down to 3300 yr BP (Fig. 1). This separation is based on the report of an increase in dust flux after this time (Gísladóttir *et al.*, 2008; Dugmore *et al.*, 2009). These parts are divided based on the position of tephra layers that allow the direct determination of the net rates of soil accumulation, including the effects of soil erosion, over time. The upper part is a Gleyic Andosol containing



<12 % C by dry weight extending down to ~90 cm, while the lower part is a Histic Andosol containing 12–20 % C by dry weight from ~90 to 218 cm. These maximum soil carbon values of 12 and 20 % were multiplied by the height of each soil section, assuming a porosity between 50 and 75 % (Snæbjörnsson, 1982; Orradottir *et al.*, 2008) to estimate the total carbon present in the studied soil. The combination of this range of carbon content and porosity values yield an estimated total mass of organic carbon stored in this soil equal to 86–172 kg C m⁻². The total mass of carbon estimated in our study area compares well with corresponding estimates of Óskarsson *et al.* (2004), who estimate the C stocks of Histosols in Iceland to be on average 197 kg C m⁻², and the more mineral-rich Histic Andosols in Iceland to be 89 kg C m⁻². Further details of this calculation are provided in Table S-4. Dividing this mass by the 3300-year age of the soil column yields an average organic carbon production rate of 26–52 gC m⁻² yr⁻¹. Note that the mass of carbon in organic material, reported in units of mass of C can be converted to the equivalent mass CO₂ by multiplying the former by the ratios of their respective molar masses: 44/12.

Effect of Basalt on Organic Carbon

The degree to which the addition of basalt increases or decreases the total mass of organic carbon in a soil is currently poorly constrained. Vicca *et al.* (2022) argued that the efficiency of enhanced weathering effort is governed by biologic processes. These authors noted that nutrients released by the addition of ground rocks to soils could enhance plant growth and promote organic carbon storage in soils. They also postulated that the addition of this material could accelerate organic material decay in the subsurface. Goll *et al.* (2021) suggested that the addition of basalt to soils would improve the fertility potentially, enhancing organic carbon storage in soils. Some supporting evidence was reported by Angst *et al.* (2018), who observed that soils derived from a basaltic rock stored more organic carbon than soils derived from sandstone or from loess. This was interpreted by these authors to be due to a combination of a higher clay content and greater availability of nutrients in the basalt derived soils. Similarly, da Silva *et al.* (2016) concluded that the organic carbon content of soils derived from granitic rocks increased with increasing mafic content of the parent rock due to increased clay mineral content. Möckel *et al.* (2021a, 2021b) provided evidence that volcanic mineral dust, and soil and tephra layers hamper organic carbon decomposition in Histosols of natural peatlands in Iceland. In contrast, other studies found that soil parent material and mineral oxide compositions have little effect on the mass of organic carbon in soils (Araujo *et al.*, 2017). One factor that is clearly detrimental to the preservation of soil organic carbon is tilling. Soil tilling has been shown to accelerate greatly soil organic carbon degradation (Wang *et al.*, 2020; Shakoore *et al.*, 2021; Li *et al.*, 2023). Such observations suggest that the way that basaltic dust is added to soil during enhanced weathering efforts may be critical for increasing the net carbon drawdown in these soils. In either case, consideration of the relative rates of carbon drawdown through inorganic compared to organic processes presented in this study suggests that the latter may dominate the net carbon storage in soils due to enhanced weathering. This makes the quantification of the role of basaltic dust on productivity and organic preservation a critical factor in optimizing enhanced weathering efforts.



Supplementary Tables

Table S-1 Description of the soil profile depicted in Figure 1a and 1b. Profile description following Schoeneberger *et al.* (2012). Note that O horizons are here defined as layers with an estimated carbon content $\geq 12\%$.

Horizon	Depth (cm)	Roots (quantity and size) ¹	Boundary (distinctness, topography) ²	Structure (grade, size, type) ³	Mottles (quantity and size) ⁴	Soil colour (moist; Munsell colour code)	Comments
A (O)	0–23	3 vf, 2 f, 2 m	G, S	3, f, sbk	f 1	2.5YR 3/4 7.5YR 2.5/2; colour change towards 2.5YR 4/3 in the lower half of the horizon	41–41.5 cm: dark basaltic tephra At the top 0.5–1 cm: intermixing of dark basaltic tephra
2O1	23–35	3 vf, 2 f, 1 m	C, W	2, f, abk	f 1	Gradual downwards colour change from 10YR 3/3 to 7.5YR 2.5/3	
2O2	35–58	3 vf, 1 f, 1 m	C, W	2, tn, pl	–	7.5YR 2.5/2 (main horizon colour); 7.5YR 4/6 (mottles)	
2O3	58–71	1 vf, very few f, very few co	G, B	t, m, sbk	m 5	7.5 YR 4/6	
2O4	71–96	very few vf, 1 co	A, W	1, m, abk	m 5	7.5YR 2.5/1	100.5–101.5 cm: coarse grey beige coloured tephra
2O5	96–114.5	2 vf, 1 f, 1 co	A, W	2, f, sbk	c 2, c 3	7.5YR 2.5/1	
2O6	116.5–133	3 vf, very few f, 1 co	A, W	2, m, pl	f 1	7.5YR 2.5/1	124.5–125 cm: dark basaltic tephra Layer of rather coarse material; might for instance be from a flooding event
2O7	133–137	3 vf	A, W	2, m, gr	f 2	7.5YR 2.5/2	dark basaltic tephra
3C–T	137–139.5						wood remains in the lower half of the horizon (ø: c. 1.5–4 cm)
4O	139.5–162	3 vf, 1 f, f co	A, W	2, tk, pl	–	7.5YR 2.5/1	
5C–T	162–164.5						very coarse dark-light tephra
6O	164.5–182	3 vf	A, W	1, m, pl	–	7.5YR 2.5/1	wood remains (quite evenly distributed; ø: c. 1.5 cm)
7C–T	182–187.5 187.5–2018 (bottom of the ditch)						dark basaltic tephra
8O		3 vf, 1 f	not applicable, bottom of the ditch	2 tk pl	–	7.5YR 2/2	Wood remains (ø ≤ c. 2cm)

¹ vf-very fine, f-fine, m-medium, co-coarse; ² A-abrupt, C-clear, G-gradual, S-smooth, W-wavy, B-broken; ³ f-fine, tn-fine(thin), m-medium, tk-coarse, sbk-subangular blocky, abk-angular blocky, pl-platy, gr-granular; ⁴ f-few, m-many, c-common.



Table S-2 Soil water compositions measured in the present study.

Sample	Date	Depth (cm)	T (°C)	pH	E _h ^{SHE} (mV)	Alk (meq kg ⁻¹)	DIC (mmol kg ⁻¹)	DOC (µmol kg ⁻¹)	Major element concentrations (µmol kg ⁻¹)									
									Si	Na	K	Ca	Mg	S (tot) ⁻	Cl	Al	Fe ²⁺	Fe ³⁺
LOQ ¹									4.0	11	3.0	1.0	0.2	6.0	28	0.28	0.1	0.1
1*	23	76	9	5.84	233	1.48			678	449	7	420	402	97	402	0.93		
2*	May	121	9	6.27	-9				716	435	13	427	379	102	357	0.99		
3*	2018	173	8.9	6.35	-8				717	390	14	293	233	79	350	1.25		
4*	2018	260	10.1	6.37	-57	2.3			644	441	20	513	535	7	284	2.81		
1a	21	76	19.7	6.02	451	1.41	4.45	247	678	464	<LOQ	380	359	90	404	<LOQ	<LOQ	0.7
2a	June	121	19	6.21	116	1.56	3.72	252	797	427	17	334	261	99	287	2.18	371	10.2
3a	2018	173	19.2	6.2	106	1.53	3.67	344	778	435	<LOQ	384	340	47	322	2.64	460	12.1
4a	2018	260	24.8	6.25	71	2.21	4.75	233	722	448	16	522	527	<LOQ	295	2.57	562	24.9
1b	14	76	16.8	6.06	298	1.5	4.57	381	761	471	0	381	361	71	300	<LOQ	<LOQ	0.7
2b	Aug	121	15.9	6.18	76	1.38	3.50	258	860	446	19	365	314	120	255	2.63	415	25.7
3b	2018	173	15.2	6.28	88	1.59	3.55	265	802	456	16	374	341	29	280	2.62	388**	86.4**
4b	2018	260	15.4	6.41	66	2.13	4.05		740	581	57	486	515	27	462	2.63	464	93.9
1c	18	76	7.6	6	287	1.5	5.47	418	772	482	<LOQ	378	358	111	206	1.70	0.4	0.9
2c	Sep	121	8.9	6.22	123	2.34	5.85	339	887	450	19	422	342	124	254	2.96	412	78.5
3c	2018	173	8.2	6.19	112	2.5	6.53	344	810	463	16	387	348	20	293	2.55	391	74.5
4c	2018	260	7.5	6.28	85	3.02	7.04	331	747	446	22	487	493	<LOQ	282	2.64	451	86.0
1d	29	76	22.5	5.98	439	0.83	2.73	382	566	449	22	330	310	101	583	<LOQ	<LOQ	0.8
2d	Oct	121	22.5	6.13	229	1.56	4.04	488	732	416	20	323	269	77	492	2.13	364	12.0
3d	2018	173	22.5	6.18	224	2.16	5.20	329	807	453	14	383	354	57	332	2.33	465	9.8
4d	2018	260	22.5	6.39	179	2.8	5.20	366	755	444	19	494	499	14	328	2.47	535	24.5
1e	21	76	22.6	5.85	429	1.08	4.40		650	450	17	343	333	106	446	1.54	<LOQ	0.6
2e	Nov	121	22.6	6.11	282	1.21	3.24		668	354	36	229	190	50	368	2.11	246	12.5
3e	2018	173	22.6	6.15	255	2.17	5.45		794	435	17	351	327	44	349	2.76	438	13.6
4e	2018	260	22.6	6.28	190	2.78	5.88		730	423	20	442	451	<LOQ	309	2.53	506	20.7

¹ Limit of Quantification.

* Sample not used for modelling due to missing analysis.

** Fe species calculated from Fe_{tot} and measured Eh.



Table S-3 Literature data included in Figure 3.

pH	Alkalinity (meq kg ⁻¹)	Classification	Reference	Location
3.96 3.93 5.38 5.44 6.28 6.21 6.00 5.93	0 0 0.198 0.371 0.764 0.743 0.623 0.695	Bog Poor fen Forested moderately rich fen Open moderately rich fen	Vitt <i>et al.</i> (1995)	Central Alberta, Canada
5.17 5.33	0.055 0.01	Not specified	Dawson <i>et al.</i> (2002)	NE Scotland, United Kingdom Mid Wales, United Kingdom
5.46 4.68 4.74 4.52	0.5 0.2 0 0	Minerotrophic lawns Ombrotrophic carpets Ombrotrophic lawns Ombrotrophic hummocks	Bragazza <i>et al.</i> (2005)	Wölfl Moor, South Tyrol, Italy
5.04 3.76 3.75 3.68	0.7 0 0 0	Minerotrophic lawns Ombrotrophic carpets Ombrotrophic lawns Ombrotrophic hummocks	Bragazza <i>et al.</i> (2005)	Ryggmossen, Uppsala, Sweden
4.2 4.17 4.66	0.02 0.02 0.076	Bog water	Kulzer <i>et al.</i> (2001)	Western Washington, King County, USA
3.6 6.5	0 1.082	Ombrotrophic bog Groundwater fen	Verry (1975)	Minnesota, USA



Table S-4 Estimates of the carbon stock of the field site and annual accumulation rates with varying porosity.

Depth	75 % porosity		50 % porosity	
	0–90 cm soil	90–218 cm soil	0–90 cm soil	90–218 cm soil
cm of tephra (zero organic carbon)	–	10 cm	–	10 cm
C content	12 %	20 %	12 %	20 %
Soil height	90 cm	118 cm	90 cm	118 cm
Soil mass	225 kg m ⁻²	295 kg m ⁻²	450 kg m ⁻²	590 kg m ⁻²
mass organic carbon	27 kg C m ⁻²	59 kg C m ⁻²	54 kg C m ⁻²	118 kg C m ⁻²
Total C stored	86 kg C m⁻²		172 kg C m⁻²	
Timespan	1140 years	2180 years	1140 years	2180 years
C accumulation rate	0.024 kg C m ⁻² yr ⁻¹	0.027 kg C m ⁻² yr ⁻¹	0.047 kg C m ⁻² yr ⁻¹	0.054 kg C m ⁻² yr ⁻¹



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