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The Holocene

Contemporary carbon fluxes do not reflect the long-term carbon balance for an Atlantic blanket bog

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Contemporary carbon fluxes do not reflect the long-term carbon balance for an Atlantic blanket bog

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Abstract

Peatlands are one of the largest terrestrial stores of carbon. Carbon exchange in peatlands is often assessed solely by measurement of contemporary fluxes, however these fluxes frequently indicate a much stronger sink strength than that measured by the rate of C accumulation in the peat profile over longer timescales. Here we compare profile based measurements of C accumulation with the published net ecosystem C balance for the largest peatland area in Britain, the Flow Country of northern Scotland. We estimate the long-term rate of C accumulation to be 15.4 g C m^{-2} yr^{-1} for a site where a recent eddy covariance study has suggested contemporary C uptake more than six times greater (99.37 g C m^{-2} yr^{-1}). Our estimate is supported by two further long-term C accumulation records from nearby sites which give comparable results. We demonstrate that a strong contemporary C sink strength may not equate to a strong long-term sink and explore reasons for this disparity. We recommend that contemporary C sequestration should be viewed in the context of the long-term ecological drivers, such as fires, eco-hydrological feedbacks, and the changing quality of litter inputs.

A Introduction

Peatlands store more carbon (C) in a given area than any other terrestrial biome (Dise and Phoenix, 2011). They cover only 2-3% of the global land area, but are estimated to store 612 GtC (Yu, 2011); equivalent to greater than half the CO_2 currently stored in the atmosphere (Dise, 2009). On a global scale, peatlands have been a persistent sink for atmospheric CO_2 throughout the Holocene (Yu, 2011), resulting in a net climatic cooling effect for all but the first few centuries of their initiation (Frolking and Roulet, 2007).

Peatlands are unusual in that they can store C over geological timescales, yet this C is located close to the surface, and is vulnerable to climatic and anthropogenic disturbances (Frolking et al., 2011). Globally, degraded peatlands are thought to be emitting more than 1400 Mt tonnes of CO_2 annually (Joosten, 2009), more than international aviation and marine transport combined (Cames et al., 2015). In Scotland, our study area, degraded peatlands could be responsible for as much as 15% of national greenhouse gas emissions (Smith et al., 2009) and it is estimated that restoration of peatlands could provide up to 2.7 Mt CO_2-eq savings per year (Chapman et al., 2012). The capacity of restored peatlands to halt losses and to store and sequester C in the future has been recognised as a key criterion when prioritising areas for restoration (Artz et al. 2013, Artz et al. 2014). However, for many peatlands there are no reliable baseline C accumulation rates against which to assess losses and gains. These uncertainties are even more acute at the regional scale and for certain peatland types, such as blanket bogs (Lindsay, 2010). As a consequence, peatland C is rarely included in global climate models, despite the potential for strong climatic feedbacks (Limpens et al., 2008).

The two most widely used approaches to assessing C sequestration in peatlands involve measuring contemporary C fluxes to quantify the net ecosystem C budget (NECB), and determining the C accumulated over time in peat profiles. Flux studies focus on quantifying the key inputs and outputs of C from the system. Studies typically involve chamber or eddy covariance (EC) measurements of net CO_2 and CH_4 emission or uptake, combined with measurements of aquatic C fluxes. Such studies have the advantage of quantifying the different components of the C budget, with their differing greenhouse warming potentials. Eddy covariance towers allow the recording of fluxes from a relatively large footprint, but have the important disadvantage of being highly resource-intensive. Therefore such records are relatively rare, only span the recent past and frequently omit some elements of the C budget such as methane or aquatic C. The longest published flux record for any peatland, the Canadian raised bog Mer Bleue, only spans the last 15 years (Humphreys et al., 2014) and, Auchencorth Moss, the longest record in the UK, only covers 11 years (Helfter et al., 2015) .

To place these relatively short-term NECB records into their long-term context, it is necessary to consider the long-term accumulation of C in peatlands. Carbon accumulation studies combine analyses of the C content of the peat with a chronology of peat accumulation to quantify how much C a peatland has accumulated over time. Such studies have the advantage of longer temporal reach, but there are also disadvantages, in that they cannot distinguish amongst C fluxes and can only assess the C which is accumulated by the peatland and *retained* in the peat. As such, net loss of C will always appear as a slowdown in accumulation, or a hiatus in peat growth; negative values are not possible. The latter is an important caveat, as factors such as fire or drought may cause peatlands to abruptly lose C which had previously been retained for hundreds of years (Frolking et al., 2014). Actuo and palaeo C flux/sequestration methods are seldom used in combination (Roulet et al., 2007), and when they are, they have not been in agreement (Table I)

INSERT TABLE I HERE

While C accumulation profiles are globally quite numerous (Charman et al., 2013; Korhola et al., 2010; Turunen and Turunen, 2003; van Bellen et al., 2011; Yu, 2011, 2006a), they are relatively rare in some otherwise well-studied regions such as the UK (Lindsay, 2010). Many published profile records have been dated at low resolution, sometimes with only a single dating point (Lindsay 2010). Without a robust chronology, profile studies reveal relatively little about the processes driving C dynamics. In Scotland, three published high-resolution (with four or more evenly spaced dates) C accumulation profiles are available, which span the entire period of bog development (Anderson 2002). Several short profiles do exist for other sites (Billett et al., 2010; Yang et al., 2001), but these have mostly been for the relatively undecomposed acrotelm peat close to the surface, and as such are not representative of either long-term relative C accumulation (LORCA), or indeed the contemporary NECB which includes C exchange across the whole profile, not just the acrotelm.

Theoretically, measurements of NECB and LORCA should converge as NECB is measured over longer time scales (Frolking and Roulet, 2007; Frolking et al., 2014; Yu, 2012), yet the timescale over which this will occur is relatively unknown (Yu, 2012). A convergence of rates was seemingly apparent in the long record from Mer Bleue (Roulet et al 2007), however recent updates to the NECB record now suggest a contemporary C sequestration rate more than double that implied by peat cores (Roulet et al., 2016).

A six year EC record of C exchange has recently been published for a site in the Flow Country of Scotland, Cross Lochs (Levy & Gray, 2015), making it the third longest published record for C flux over Atlantic blanket bog (Artz et al., 2015) and arguably the only published EC record from a near pristine site (Levy and Gray, 2015). Incorporated in the C balance are measurements of CO_2, CH_4 and DOC. Non CO_2 losses of C accounted for 13% of the total NECB and were mainly through DOC export. The site was presented as a strong and consistent sink for C over the six years, with a reported average NECB of -99.37 g C m^{-2} yr^{-1}.

Using either the contemporary flux or the profile approach in isolation provides an incomplete picture of the processes driving C dynamics. In this study, we produced three C accumulation profiles to complement C exchange measurements for the Flow Country of Caithness and Sutherland. We then used a detailed chronology to assess whether the contemporary NECB at the Cross Lochs eddy covariance site is representative of long-term C accumulation. Finally, we discuss the factors driving C exchange over different timescales.

A Site description

INSERT FIGURE 1 HERE

We collected and dated cores from three sites in the Flow Country peatlands of Caithness and Sutherland (Figure 1). Our key site was Cross Lochs (OS National Grid reference: NC 85095 44154), which is the site of the eddy covariance tower considered by Levy & Grey (2015). This site is located within the RSPB Forsinard Flows National Nature Reserve, north west of one of the pool systems which are characteristic of the Flow Country (Lindsay et al., 1988). The coring site was on a gentle slope with vegetation dominated by *Sphagnum spp.* (incl. *S. cuspidatum, S. papillosum* and *S. fallax*), *Calluna vulgaris, Trichophorum germanicum* and *Eriophorum angustifolium* and a peat depth of 3.68 m. The peat was dominated by *Sphagnum spp*. and sedge remains with birch macrofossils towards the base. Humification varied down core below the acrotelm alternating between H4 and H8 on the von post scale.

To assess the variability of LORCA across the Flow Country blanket bogs, we also sampled two other sites further to the east.

Catanach (OS National Grid reference: ND 00605 48769) is also located within the RSPB Forsinard Flows National Nature Reserve, approximately 16 km north east of Cross Lochs. The vegetation community was similar to Cross Lochs including *Sphagnum spp.,* along with *Calluna vulgaris*, *Betula nana* and *Arctostaphylos uva-ursi,* the peat was shallower (1.76 m) and the stratigraphy showed a mixture of *Sphagnum* and sedge peat which was more humified than at the other sites, typically H7 or above in the catotelm peat.

Bad a' Cheo (OS National Grid reference: ND 16500 50174) is the easternmost sampling site, located in an area which has been enclosed from grazing, except by deer, since 1968, close to the A9 road. The vegetation is dominated by *Sphagnum spp*., with *Calluna vulgaris* and *Eriophorum spp.* present, but less abundant than in the other sites. The peat depth at this site was 4.46 m. *Sphagnum spp.* remains were more abundant in the core stratigraphy compared to the previous sites; however, layers of sedge peat were also present. Birch wood was found in the bottom section of the core and humification was low, H4-H6, in the catotelm peat and the vegetation composition was disenable even close to the base of the core.

A Methods

B Coring strategy

Cores were taken in October 2013 using a 7 cm diameter, 1 m long Russian peat corer (Belokopytov & Beresnevich 1955 in: Jowsey 1966). Sampling was carried out from the midpoint between hummock and hollow microforms down to the mineral substrate, using the twin borehole method with 10 cm overlaps in order to minimise the risk of core compression, as outlined by De Vleeschouwer et al. (2010). The two boreholes were no more than 0.3 m apart. In the Cross Lochs site the coring point was selected to be towards the centre of the EC tower footprint. Cores were transported and stored horizontally to avoid compression and refrigerated until analysis.

B Bulk density, loss on ignition and carbon content analysis

Bulk density (ρ) measurements were carried out at 1 cm resolution for the Cross Lochs core and at 5 cm resolution for the other cores. Only a single sample was analysed for the uppermost 5 cm of the Cross Lochs core, due to the fibrous nature of the peat. Sample volume was determined using the water displacement method (Chambers et al., 2011). Wet peat samples, approximately 10-20 cm^3 in size, were carefully removed from the cores and placed into a volumetric cylinder and water volume displaced recorded. Samples were dried overnight at 105°C, and ground sub-samples incinerated at 550°C for 4 hours. The difference in weight before and after incineration was used to calculate loss on ignition.

C and N content was determined using an elemental analyser (Carol Erba 1108, University of Stirling), calibrated for each run using rice flour standards with standard checks every 10 to 12 samples. Loss on ignition and C content was measured at 5 cm resolution and values for a small number of missing segments (for instance due to low sample size in low density peat) were interpolated.

B Tephrochronology

Cryptotephrochronology offers the potential for high-precision dating, but at the expense of the time-consuming process of locating tephra shards (Gehrels et al., 2008). However, advances in multi-sensor core scanning offers the opportunity to speed up this process. The use of an 'ITRAX' scanner, which combines X-ray fluorescence (XRF) and X-radiography, has been shown to be effective for locating cryptotephra in lake sediments (Kylander et al., 2011). X-radiography has previously shown good potential for locating larger cryptotephra layers in the north of Scotland (Dugmore and Newton, 1992)

Multi-sensor core scanning was carried out using the ITRAX core scanner (Cox Analytical Systems) at the University of Aberystwyth. High-resolution (0.2 mm) X-radiographs were produced for all cores. XRF elemental profiles were produced at 0.2 mm resolution for Cross

Lochs and 2 mm for the other sites. Tephra layers were identified by: 1) visible black bands in the X-radiographs; 2) peaks in key elements such as Fe, Ca, Ti and Mn in the XRF-profiles, and 3) distinct troughs in the loss on ignition data. Where at least one of these features was apparent, 1 cm thick samples spanning the zone of interest were sub-sampled. Samples were incinerated in a muffle furnace at 550°C for 4 hours, when necessary they were soaked in 10% HCl to remove coloration from the ash and mounted on a slide for analysis as described by Pilcher and Hall (1992). These samples were examined microscopically at ×400 magnification and tephra shards identified by their distinctive morphology.

A total of four tephra layers were found which contained quantities of shards sufficient for geochemical analysis. In order to link these tephra deposits to eruptions of known age they were geochemically analysed by electron probe microanalysis (EPMA). Peat samples containing tephra from the relevant horizons were acid digested following Dugmore et al. (1992), and thin sections were prepared by mounting the shards in resin, grinding to a thickness of 75 μm and polishing until smooth using 6 μm and 1 μm diamond pastes (Dugmore et al. 1995).

Shards were analysed using Wavelength Dispersive Spectrometry (WDS) on a Cameca SX100 electron microprobe at the School of Geosciences, University of Edinburgh (see supplementary data). The microprobe was set to an accelerating voltage of 15 kV, with a beam current of 2 nA (Na, Mg, Al, Si, Ca, Fe, and K) and 80 nA (Ti, Mn and P). A beam diameter of 5 μm was used to prevent mobilisation of sodium. Standards of basaltic (USGS BCR2g) and rhyolitic (Lipari obsidian) glasses were measured alongside the tephra to assess analytical performance. Full details of the settings are presented in Hayward (2012).

Tephra layers were linked to known eruptions through comparison with published elemental data from Tephrabase (Newton et al., 2007) with a particular focus on the Hekla-4 and Glen

Garry tephras which were both expected to be found in our sites (Newton et al., 2007). Based on the recommendations in Dugmore et al. (1995), distinctive oxide ratios of FeO and TiO_2 were primarily used in the identification of Hekla 4 while CaO and MgO ratios were used for Glen Garry.

B Radiocarbon dating

Macrofossils of above-ground and near surface material were located within the peat core and cleaned in preparation for radiocarbon analysis. Samples selected for ^{14}C dating comprised *Sphagnum austinii* leaves, *Molinia caerulea* rhizomes, woody twigs of *Betula spp.,* stems of unidentified brown mosses and charcoal fragments. Eleven samples were dated from the full length of the Cross Lochs core and one sample each from the base of each of the Catanach and Bad a' Cheo cores (Table II). Samples were dated at the Poznan Radiocarbon Laboratory (Poznan, Poland) and DirectAMS (Washington, USA).

B Age-depth models and carbon accumulation

Age-depth models were constructed using the Bayesian modelling package BACON (Blaauw and Christen, 2011), using a combination of tephra and AMS radiocarbon dates. The calibrated age of the Hekla 4 eruption had a much lower chronological error associated with the calendar age and was therefore particularly useful in constraining the model. BACON uses prior information such as plausible accumulation rates and the law of superposition to reduce uncertainty and produce a more realistic model (Blaauw and Christen, 2011). Priors for accumulation mean, accumulation shape and memory mean were set at default values based on the compilation of Goring (2012). Data on bulk density and C content were combined with the BACON age-depth models to produce reconstructions of C accumulation which incorporate temporal uncertainty.

A

RESULTS

B

Tephrochronology

Four identifiable tephra layers were found. Two in the Bad a' Cheo core, BADO 134.3 and BADO 200.1, and one each in Catanach and Cross Lochs cores, CATO 116.7 and CRSLO 165.6 respectively. Geochemical analyses produced results which strongly correlated with the Hekla 4 eruption (c. 4287 ± 58 cal. BP; Pilcher et al. (1996)) for three of the tephra layers: BADO 200.1, CATO116.7 and CRSLO 165.6 (Figure 2), and the Glen Garry eruption (c. 2176 ± 244 cal. BP; Barber et al., (2008)) for the remaining layer: BADO 134.3 (Figure 3; Supplementary material). These four tephra layers were used in the age/depth models. An additional tephra layer with geochemistry strongly matching that of the Lairg A eruption was also found in analysable quantities at 2.28 m depth, in a core taken 200 m away from Bad a' Cheo within a conifer plantation (Ratcliffe, 2015). Three more potential tephra layers were detected in the Cross Lochs core, but due to the low density of shards we were unable to correlate them to an eruption using EPMA. More details of these can be found in (Ratcliffe, 2015).

INSERT FIGURE 2 HERE

INSERT FIGURE 3 HERE

B Radiocarbon dating

Radiocarbon dates ranged from 1885 ± 30 to 9287 ± 32 BP (Table II) and generally had low error, with a mean uncertainty of ± 127 years in the 1σ calibrated age. All dates conformed to the law of superposition, with one exception. Poz-62766 was much younger than expected, and this date is suspected of being inaccurate. The radiocarbon lab noted that Poz-62766 contained less than the minimum advisable weight of C. It was included in the age-depth modelling; but the preferred model does not pass through it. Radiocarbon dating suggests peat initiation at 9491-9558 1σ cal BP for Cross Lochs, 5745-5910 1σ cal. BP. for Catanach, and 8455-8855 1σ cal. BP. for Bad a' Cheo (Table II).

INSERT TABLE II HERE

B Age-depth models

An age-depth model was produced for each site (Figure 4) to show the estimated uncertainty in the age of peat throughout the profile. The Cross Lochs core is better constrained, with less uncertainty for peat age at a given depth compared to Bad a' Cheo and Catanach. The time period from 2 ka to 4 ka cal. BP. is perhaps the best constrained, whereas uncertainty is higher for both the last 2 ka and for the early Holocene.

INSERT FIGURE 4 HERE

B Carbon accumulation

Peat has accumulated throughout the Holocene, with no evidence for any hiatuses (Figure 5). Accumulation rates varied between 8 and 32 g C m^{-2} yr^{-1}. Cross Lochs had an average C accumulation rate of 15.43 ± 5.06 g C m^{-2} yr^{-1} while for Catanach it was 16.47 ± 4.20 g C m^{-2} yr^{-1} .The average C accumulation rate for the Bad a' Cheo profile was 17.43 ± 4.90 g C m^{-2} yr^{-1}.

At Cross Lochs, the C accumulation rate was generally slightly higher than average in the early Holocene, and decreased rapidly at c. 6030 cal. BP. Carbon accumulation began to increase again just before c. 4570 cal. BP. and peaked around c. 2890 ka cal. BP. before decreasing rapidly. There was then a slow increase in C accumulation up to the boundary with the acrotelm (Figure 5).

Results for the Catanach site imply that carbon accumulation was most rapid in the first 2560 years after initiation, with rates in the region of 16-20 g C m^{-2} yr^{-1}, followed by a decrease down to 12-15 g C m^{-2} yr^{-1} which persisted until c. 940 cal BP (Figure 5) and the transition zone to acrotelm peat.

INSERT FIGURE 5 HERE

Bad a' Cheo also had relatively higher carbon accumulation rates during the early Holocene, with a decrease around 6520 cal BP. Carbon accumulation was fairly stable until just before c 4 ka cal. BP. when it declined and remained low until around 2 ka cal. BP. There was then a rapid increase in the average rate of carbon accumulation similar to levels recorded between c. 6-4 ka cal. BP. (Figure 5).

Carbon accumulation rates in the Cross Lochs and Bad a'Cheo cores during the early to mid-Holocene were consistently above the long-term averages for these sites and both decreased around 6.5-6 ka cal. BP. At that time, the younger Catanach peatland commenced peat formation. Changes in C accumulation rates for the late Holocene are more contradictory, with the period of c. 4-2.5 ka cal. BP. representing the highest accumulation rates for the Cross Lochs core, the lowest for Bad a' Cheo, and intermediate values for Catanach. Carbon accumulation rates between 2 ka – 750 cal. BP. years for Bad a' Cheo and Catanach were close to the long-term mean, while at Cross Lochs accumulation rates were amongst the lowest seen since bog development was initiated. However, interpretation of the Bad a'Cheo and Catanach records is limited by the available dating points.

A Discussion

B Carbon accumulation and climate in peatlands of northern Scotland

LORCA for the three sites in our study was 16.44 g C m^{-2} yr^{-1}, slightly lower than the value of 21.3 g C m^{-2} yr^{-1} reported for three sites in the North West Highlands by Anderson (2002) However, these rates are very similar to the mean rate of 18.6 g C m^{-2} yr^{-1} estimated for northern peatlands globally (Yu, 2011). Our values include C stored across the whole profile including the acrotelm, as do the majority of published values for LORCA. However, long-term peat accumulation depends on the transfer of organic material from the acrotelm to the catotelm (Wieder, 2001) and the proportion of primary production which actually reaches the catotelm is highly variable (Yu et al., 2001). This proportion depends on factors such as litter quality, litter turnover and acrotelm (water table) depth (Bauer, 2004). Thus, the inclusion of the acrotelm will overestimate the long term C accumulation rate as younger peats have undergone relatively less decomposition than older peats (Clymo et al., 1998) . It is difficult to predict what proportion of organic matter in the acrotelm will be transferred to the catotelm. For example, the recent rate of C accumulation (RERCA) for Scottish peats has been found to be 35-209 g C m^{-2} yr^{-1} over the last 150 years (Billett et al., 2010), which for our cores would represent approximately the top 0.1 m of the profile, or the upper half of the acrotelm. It is difficult to say how much of this RERCA will be *retained* in the peat over a given time period without considering the individual ecohydrological properties of the peatland. In a review of several thousand peat profile measurements, RERCA was found to be poorly correlated to LORCA (Turunen, 2003).

Initiation of peat development was not uniform across sites. Peat formation at Cross Lochs and Bad a' Cheo commenced in the early Holocene, which was a period of both rapid lateral expansion and C accumulation for northern peatlands globally (Yu et al., 2009). Whilst at Catanach peat accumulation did not occur until the mid-Holocene at 5.7-5.9 ka cal. BP, and coincided with a decline in tree cover and an increase in Calluna pollen at the regional scale between 6.8 and 4.6 ka cal. BP (dates published in Charman., (1994) and calibrated here for comparative purposes using Oxcal) which may be linked to bog expansion (Charman, 1994, 1992). At all three sites in this study, the peat was directly underlain by bedrock or glacial till and no evidence of lake mud was found, indicating that paludification, rather than terrestrialisation was the dominant process in peatland initiation.

Perhaps the most dramatic change in Holocene C accumulation rates (Figure 5) occurred at approximately 4.4 ka cal. BP. During this time, *Pinus sylvestris* colonised a large area of Scottish blanket bog in response a drying of the climate, which may have been induced by a migration of the jet stream northwards (Gear and Huntley, 1991). About four centuries later, the regional climate became wetter and colder (Anderson et al., 1998), triggering the regional extinction of *P. sylvestris* located on blanket bog (Gear and Huntley, 1991). In a nearby pollen core, the pollen assemblage shows a rise in *Empetrum nigrum* immediately prior to the sudden and short-lived peak in *P. sylvestris*, supporting the hypothesis of drier regional conditions at this time (Charman, 1990).

Only the core chronology for Cross Lochs is detailed enough at this point in the stratigraphy (Table 2) to interpret sub-millennial changes, which may explain the differing response in C accumulation seen for Catanach and Bad a' Cheo. There was a moderate increase in C accumulation at Cross Lochs during the dry period between 4.3-3.9 ka cal. BP followed by a much greater increase in the wet period from 3.9 - 3.3 ka cal. BP. Carbon assimilated as leaf litter is particularly sensitive to climate for a period of decades to centuries after fixation, while it is stored in the aerobic acrotelm (Frolking et al., 2014). Therefore it is important to note that the better preservation conditions of the wet period may have resulted in better preservation of the C fixed during the preceding dry period.

These findings are in agreement with those for the same time period published in Anderson (2002), but are somewhat contradictory to when compared to other findings from later time periods. Changes in solar activity and the length of growing season have been found to be the dominant drivers of C accumulation at the centennial scale during the late Holocene (Charman et al., 2013; Mauquoy et al., 2008, 2002). However, as the response of peatland C to changes in climate and hydrology is often non-linear (Laiho, 2006; Swindles et al., 2012), fair comparisons cannot be made unless the same time period, and therefore the same climatic drivers, are being compared. Our results and those of Anderson (2002) indicate some of the most dramatic changes in Holocene peatland C accumulation have occurred in the mid-Holocene, around the time of the temporary expansion of *P. sylvestris* on to blanket bog. Therefore, we suggest this may be one of the most interesting periods to study environmental drivers of peatland C accumulation.

B The potential utility of core scanning

A major limitation to producing more records of Holocene C accumulation is the cost of dating date peat cores at high resolution (Payne et al., 2016). Tephrochronology offers the potential for precise dates, but at the expense of time-consuming analyses. We found that core scanning was capable of rapidly locating cryptotephras. Denser layers, such as CRSLO165.6, were immediately obvious, showing up as dark bands on the X-radiograph, similar to those reported by Dugmore & Newton (1992) and producing distinguishable peaks across a range of elements. However, these were not found to be representative of the more detailed geochemistry recorded in Figures 2 & 3. Smaller layers such as BADO134.3 induced a more subtle response, with no visible band on the X-radiograph and element peaks barely visible above background levels. All peaks in the elemental data needed to be verified for the presence of tephra using optical microscopy and many false positives were found, but the reduction in labour was still considerable. We therefore believe that wider adoption of core scanning may encourage the greater use of tephrochronology in peatland palaeoecological research. The core scanner also revealed several distinct cryptotephra layers in the Cross Lochs core which had shard concentrations too low to be successfully analysed. However, chronostratigraphic matching indicates that the layer located at 1.383 m might have originated from the Hekla-S/Kebister eruption, and the layer at 2.520 m from Lairg A. The presence of at least 14 identifiable cryptotephra layers in Scotland (Swindles et al., 2011) demonstrates the potential of tephrochronology for contributing to the chronology of future profile-based estimates of C accumulation.

B

Comparison of core-based and EC flux-based carbon accumulation rate estimates

The LORCA calculated for Cross Lochs, 15.43 g C m^{-2} yr^{-1}, is much lower than that of the NECB of 99.37 g C m^{-2} yr^{-1} published in Levy & Grey (2015). Such differences between LORCA and contemporary NECB seem to be the norm rather than the exception (Table I), although the number of sites for which both data are available is admittedly small. Lac la Biche, Moanatuatua and Moor House (Table I), show particularly large differences in C accumulation derived from the two approaches, with NECB approximately three to six times greater than LORCA. This is despite having inter-annual flux datasets and allowing for measured, or realistic estimates, of non-CO_2 fluxes. For example C losses through CH_4 emissions from bogs, which constitute all sites in Table 1 with the exclusion of Lac la Biche, typically do not exceed 8 g C yr-1 (Roulet et al., 2007). For fens, of which Lac la Biche is an example, CH_4 emissions may be higher but would not typically exceed 35 g C yr-1 (Bäckstrand et al., 2009). The export of DOC from intact peatlands is typically 10-20 g C m^{-2} yr^{-1} (Baird et al., 2009) but may be as high as 25-40 g C m^{-2} yr^{-1} for drained peatlands (Billett et al., 2004; Dinsmore et al., 2010; Strack and Zuback, 2013). Consequently, non-CO_2 fluxes would need to be unrealistically high to explain the discrepancy between contemporary and long-term C balance for the three sites in Table 1 which do not include DOC and CH_4. As such contemporary C accumulation is clearly greater than long-term C accumulation at a range of sites across the world, despite the slowdown in C accumulation which might be expected as peatland ecosystems mature (Clymo et al., 1998). Possible explanations for this may be found in the operational time scales of different drivers of peatland C dynamics (Yu, 2006b). The drivers of C accumulation over centennial to millennial timescales should not be expected to be the same as those driving inter-annual variation (Frolking et al., 2014).

For example, the flux density of photosynthetically available radiation (PAR) usually drives fluxes at daily or shorter timescales, through the impact on plant photosynthesis. While PAR is highly variable from day to day and also century to century (Mauquoy et al., 2008), inter-annual variability in PAR can be quite low (Strachan et al., 2016). As such, at the inter-annual scale precipitation and temperature may be better predictors of C dynamics (Peichl et al., 2014; Strachan et al., 2016). This is not because precipitation and temperature are fundamentally more important to peatland C balance, but because they tend to show greater variance than PAR over that interval. Similarly variance in other divers of peatland C accumulation, such as vegetation type, fire and low-frequency changes in climate (Frolking et al., 2014; Turetsky et al., 2002) will be close to zero over the intervals eddy covariance can practically measure, but could become a significant, or even dominant, source of variance over longer intervals. The environmental drivers of C dynamics in peatlands, over a given time period, will be strongly influenced by the variance in drivers that occurs over that period. Lack of variance over the timescales measured means some important drivers of the C balance simply cannot be accounted for.

Fire is known to be a particularly important component of long term C dynamics (Pitkanen et al., 1999) and plays a prominent role in the functioning of the majority of northern peatlands (Turetsky et al., 2015). However, including fires in the contemporary peatland C balance is impractical as they occur only intermittently. At Cross Lochs, fire has been common since the early Holocene (Charman, 1992; Robinson, 1987) and charred *Calluna* remains have been found in the surface peat not far from the EC site (Charman 1990). A single fire event may release C accumulated over a century or more (e.g. 140 years; Pitkanen et al., 1999), and may reduce C uptake in peatlands by as much as 85% over their developmental history (Turetsky et al., 2002). This lost C, and associated peat depth, will cause an apparent slowing of the long-term C accumulation rate. Contemporary C sink strength can then be increased for up to 75 years following a fire as vegetation recovers (Harden et al., 1997; Trumbore and Harden, 1997; Ward et al., 2007; Wieder et al., 2009). Depending on the timing of measurements, this may result in a situation where C losses from fire are not recorded in the contemporary C balance, but increased C sequestration after the fire is recorded. If this occurs then the contemporary C sink would be expected to be greater than the long term C accumulation rate.

The relationship between environmental variables and C dynamics becomes increasingly complex over longer timescales and strong relationships recorded over inter-annual timescales cannot always be assumed to stand up over longer time periods. The indirect effects of environmental drivers on peatland C dynamics will be moderated through ecohydrological feedbacks operating over many decades (Laiho, 2006; Waddington et al., 2015). These feedbacks can result in either an amplification, or a dampening, of the influence of an environmental conditions on peatland C dynamics (Laiho, 2006; Swindles et al., 2012; Waddington et al., 2015). For example, feedbacks between water table, decay and peat hydraulic conductivity may cause decay rates to be relatively insensitive to changes in precipitation over long periods of time (Swindles et al., 2012; Waddington et al., 2015). Yet alternatively, positive feedbacks may enhance the impact of changes in precipitation on C balance through changes in vegetation, modification of transpiration rates and further lowering of the water table (Waddington et al., 2015). Thus thresholds of peatland ecohydrological response, i.e. whether negative or positive feedbacks will be dominant, and over what timescale, are an important considerations to be made when assessing the environmental drivers of peatland C balance (Limpens et al., 2008).

Carbon sequestration rates close to 100 g C m^{-2} yr^{-1} in ombrotrophic bogs are likely to be unsustainable in the long-term, as values of C accumulation inferred from profile measurements rarely come close to 100 g C m^{-2} yr^{-1} and have only ever been recorded for peatlands in the early stages of initiation (Page et al., 2004; Pendea and Chmura, 2012) or for fen peats in response to rapid changes in hydrology (Yu et al., 2003). Litter inputs into peatlands typically undergo comparatively rapid decay in the acrotelm for a period of decades to centuries (Malmer and Wallén, 2004) before passing into the relatively stable catotelm. The portion of the photosynthetically-fixed C which re aches the catotelm will depend on the amount of decay this material undergoes. This is controlled by factors such as mean position and variability of the water table depth, along with temperature and the properties of the litter inputs (Bauer, 2004; Clymo et al., 1998). Short-term increases in C accumulation can actually represent changes in acrotelm thickness, rather than any change in input to the relatively stable catotelm (Belyea and Clymo, 2001). This could be expected in bogs where vascular plant cover is increasing, resulting in higher, but more easily decomposable, litter inputs (Malmer et al., 2005; Waddington et al., 2015). For example, the primary production in sedge-dominated fens is usually much higher than in *Sphagnum* bogs, yet C accumulation is on average lower for fen peats due to differences in litter quality (Rydin et al., 2006; Turunen, 2003). The stability of C added to the acrotelm, and the portion of it which ultimately reaches the long-term store in the catotelm, should be considered when assessing the sink strength of a peatland based on the contemporary NECB.

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It has been hypothesised that environmental change has caused an increase in NECB, relative to Holocene C accumulation rates, across northern peatlands (Yu, 2012) and this could be the case at Cross Lochs. The specific drivers of this change could include lengthening of the growing season, increased nitrogen deposition, and CO_2 enrichment, all of which have been predicted to cause an increase in peatland C accumulation rates (Charman et al. 2013). Nitrogen deposition for Forsinard has been estimated at 6.3 kg N ha^{-1} yr^{-1}, a value which is lower than much of the UK, but is high enough to impact on many peatland vegetation communities (Payne, 2014). The growing season has increased by more than five weeks relative to 1961 (Sniffer, 2014). CO_2 enrichment has been demonstrated to increase primary production in forests by as much as 25% (DeLucia et al., 1999). While the effects of CO_2 enrichment on nutrient poor peatlands appear to be small (Hoosbeek et al., 2001). However the combined effects of increased N deposition and CO_2 enrichment have seldom been explored (Siegenthaler et al., 2010). Modelling of peatland C processes is required to 'bridge the gap' between NECB and LORCA (Bauer, 2004) and can be used to forecast the fate of recently fixed C. This has proved to be challenging thus far because of the numerous interacting processes and feedbacks involved in peatland ecohydrology (Waddington et al., 2015) and the lack of good palaeo and contemporary data on C accumulation and ecological parameters at the site level, such as decay and productivity rates. Locating palaeoecological work at flux sites, and conversely locating new flux sites in peatlands with a well studied palaeoecology, such as those outlined in Payne et al., (2016) may facilitate better modelling in the future.

A Conclusion

Large discrepancies exist between contemporary and long-term C accumulation rates across a number of peatlands globally, including in our blanket bog site, Cross Lochs, in the north of Scotland. Long term C accumulation rates provide a measure for C which has been *retained* in the deeper catotelm peat but provide a poor measure of current C accumulation rates. NECB provides a measure of a peatlands current C balance, however we argue that when considered in isolation NECB may provide a poor indicator of peatland ecosystem C dynamics over intermediate and longer time scales. The context provided by long-term C accumulation rates, published here and in other studies, would suggest that contemporary C accumulation rates at or greater than 100 g C yr^{-1} are not sustainable in the medium to long-term in ombrotrophic bogs. While productivity dominates the variance in peatland C accumulation over short time scales, this becomes progressively less so over longer time periods. C fixed through primary production will be most vulnerable to fire and microbial decay over the following period of acrotelm residence time, typically a period of decades to centuries. Thus decay and disturbance become more important when considering progressively longer timescales.

Changes in vegetation communities over the period of acrotelm residence preceding flux measurements may result in contemporary CO_2 fluxes which compare the primary production of the contemporary vegetation community with the heterotrophic respiration of litter dominated by former communities. For instance, a peatland which has seen a recent shift from Sphagnum towards vascular species may have higher rates of primary productivity associated with vascular plants. However, low rates of heterotrophic respiration associated with *Sphagnum* litter, which may still be the dominant source of heterotrophic respiration, may be retained. Such a site would show strong C sink activity for a temporary period, until the acrotelm litter composition changes to become representative of the current community.

Thus when NECB is used as an assessment of C balance, and especially when extrapolating to the regional scale, peatland C flux measurements should be considered together with how representative the current vegetation community is of the down core acrotelm litter. Equally important when extrapolating data over longer time scales, is the amount of decay that recently fixed C is likely to undergo before it reaches the relatively stable catotelm. While site productivity derived from contemporary fluxes is relatively straightforward to interpret, heterotrophic respiration will be strongly influenced by the palaeoecology of the individual site, therefore we recommend that future studies of peatland C balance should combine contemporary and palaeo approaches. This would have the advantage of producing data with which to parameterise and validate site level models of C accumulation, which are ultimately needed to better predict future peatland C dynamics.

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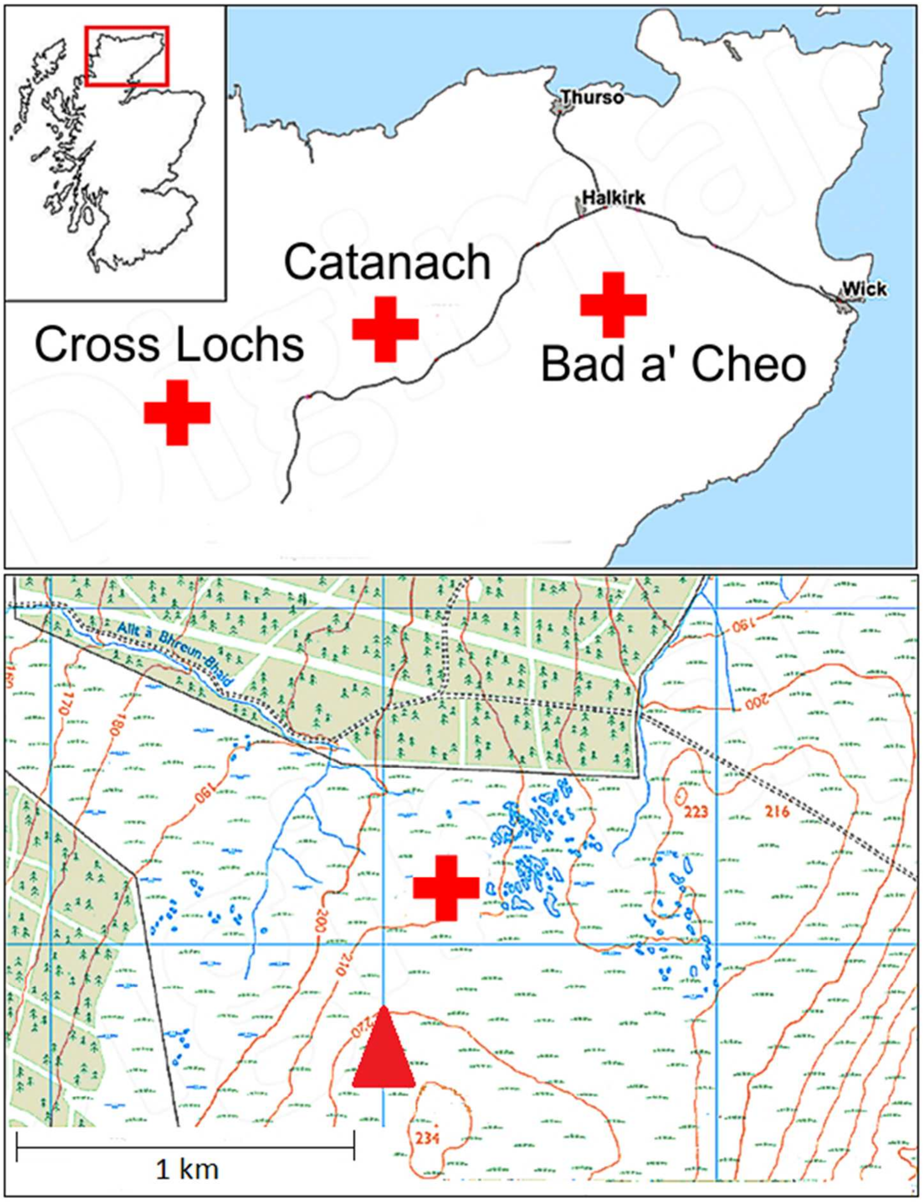
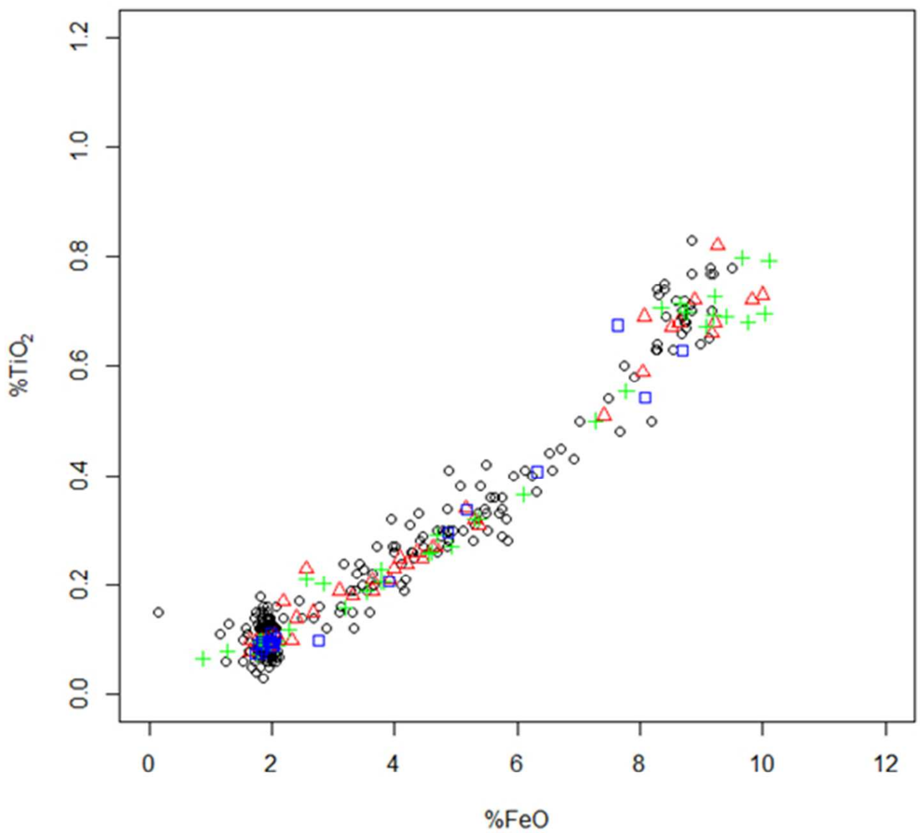


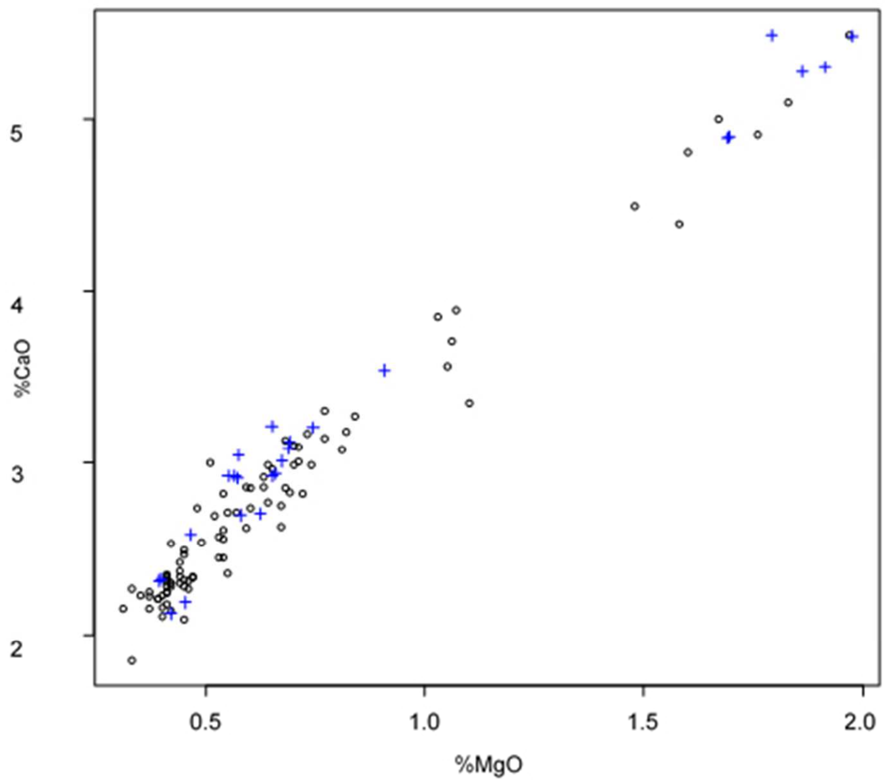
map of site locations in the north of Scotland marked by crosses b) detailed location of the Cross Lochs core, marked by a cross and the eddy covariance tower, marked as a triangle. © Crown Copyright and Database Right 2016 Ordnance Survey (Digimap Licence)

160x208mm (96 x 96 DPI)



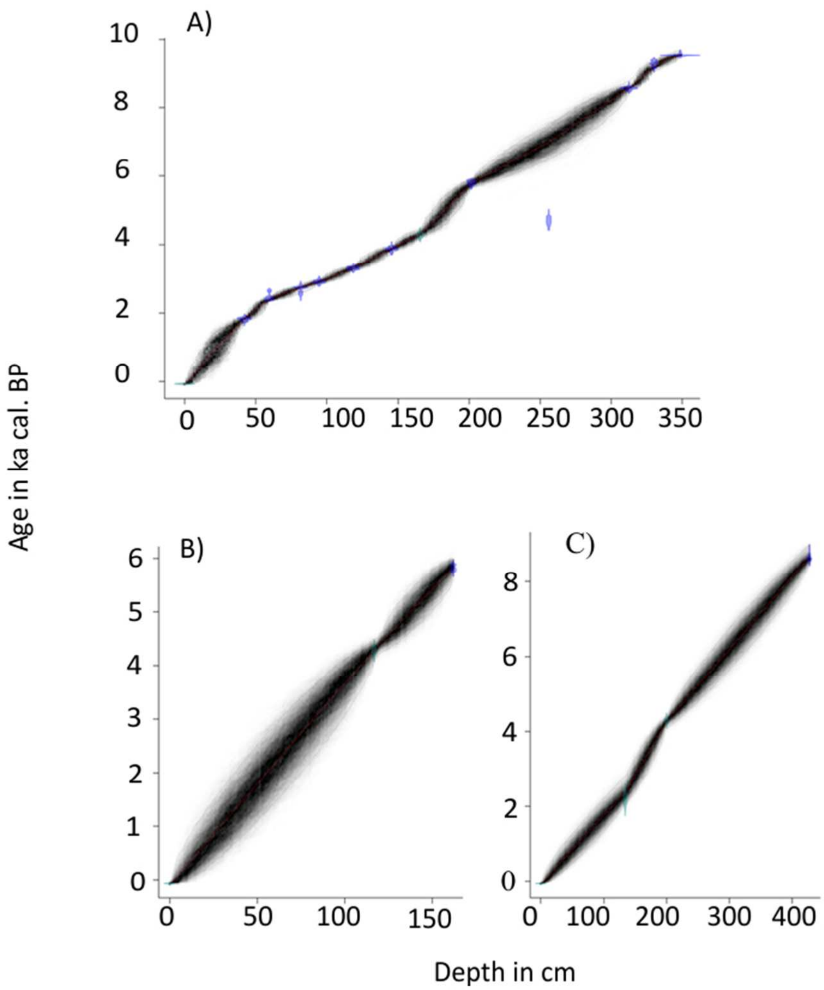
% TiO and FeO of reference Hekla 4 shards from Tephrabase (Newton et al., 2007), displayed as black circles, Compared with shards from Cross Lochs, red triangles and Catanach, green crosses and Bad a' Cheo, blue squares.

164x144mm (96 x 96 DPI)



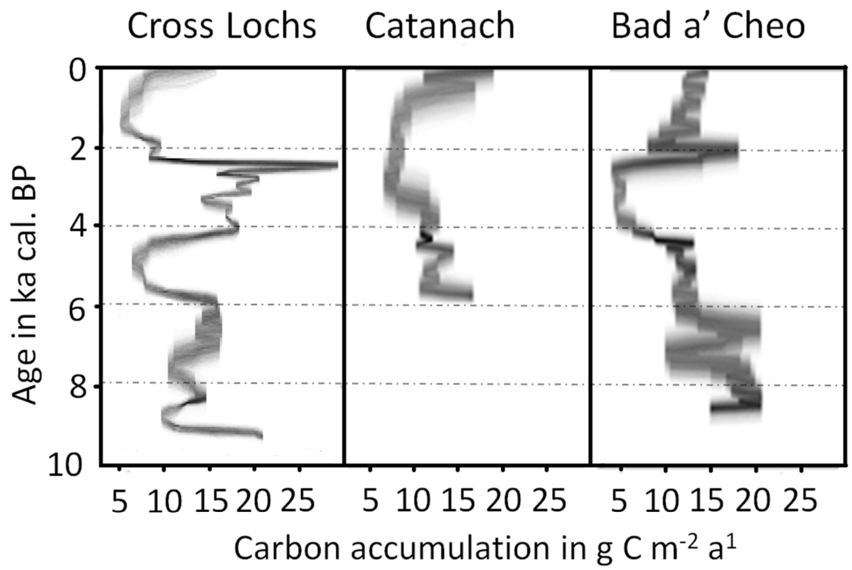
Calcium and magnesium oxide concentration of BADO134 shards, blue crosses, compared with reference material for the Glen Garry eruption obtained from Tephrabase (Newton et al., 2007), black circles.

140x121mm (96 x 96 DPI)



Age-depth models produced in BACON for a) Crosslochs b) Catanach and C) Bad a 'Cheo. Thickness of the plot represents the uncertainty in the age

220x250mm (96 x 96 DPI)



Long term carbon accumulation rates over time for Cross Lochs, Catanach and Bad a' Cheo. Thickness of the plot represents the uncertainty in age.

345x216mm (96 x 96 DPI)

Site	Fluxes included In contemporary carbon balance	Contemporary carbon balance in g C m^{-2} yr^{-1}	Long term carbon accumulation in g C m^{-2} yr^{-1}	References
Mer Bleue, Canada	CO_2,CH_4,DOC,	32 ± 40.0	14-21.9	(Roulet et al., 2016, 2007)
'Wesern peatland' Lac la Biche, Canada	CO_2	~189 ± 47	19-24	(Flanagan and Syed, 2011)
Moanatuatua, New Zealand	CO_2	~234	34.2	(Campbell et al., 2014; Schipper et al., 2002)
Forsinard/Cross Lochs, Scotland	CO_2, CH_4, DOC	99.4 ± 9.5	15.4-17.5	(Levy and Gray, 2015); this publication
Moor House, Pennines, England	CO_2, DOC, POC, CH_4	134.3 ± 32	27	(Garnett, 1998; Lloyd, 2010)
Lac Le Caron, Canada	CO_2	~76	22.6	(Strachan et al., 2016; van Bellen et al., 2011)

Site:	Lab no.	Mid-point depth (cm)	Material selected for dating	Radiocarbon date (BP)	Best estimate (cal BP)	1σ Calibrated age range (cal.BP)
Cross Lochs	Poz-62862	42	Charcoal	1885 ± 30	1834	1731-1890
Cross Lochs	Poz-62861	59.5	Charcoal	2405 ± 30	2426	2349-2682
Cross Lochs	Poz-62858	81.5	*Sphagnum austinii leaves*	2600 ± 50	2735	2495-2844
Cross Lochs	Poz-62863	94.5	Charcoal	2805 ± 30	2907	2804-2995
Cross Lochs	D-AMS 006128	118.5	*Molinia caerulea rhizome*	3092 ± 25	3296	3234-3370
Cross Lochs	Poz-62864	145.5	Charcoal	3580 ± 30	3882	3777-3977
Cross Lochs	Poz-62860	201.5	*Molinia caerulea* Rhizome	5040 ± 35	5815	5664-5902
Cross Lochs	Poz-62766	256	*Molinia caerulea rhizome*	4170 ± 80	4694	4446-4862
Cross Lochs	D-AMS 006126	330	*Molinia caerulea rhizome*	8279 ±32	9287	9136-9405
Cross Lochs	D-AMS 006127	312.5	*Molinia caerulea rhizome*	7787 ± 32	8568	8460-8632
Cross Lochs	D-AMS 006125	348.5	*Betula* stem	8567 ± 33	9535	9491-9558
Bad a' Cheo	Poz-62859	427.5	Brown moss stems	7830 ± 50	8614	8455-8855
Catanach	Poz-62866	162	Charcoal	5080 ± 35	5816	5745-5910

Table I:

Sites for which with published long-term and contemporary rates of C accumulation. Sites which do not have multiple years of eddy covariance data and those with only long term or contemporary measurements have been excluded. Contemporary C accumulation rates are listed as approximate for those sites where the carbon balance is missing either DOC or CH_4. DOC is an abbreviation of dissolved organic carbon and POC is particulate organic carbon.

Table II:

Radiocarbonage, depth, calibrated age and 1σ Calibrated age range for the AMS radiocarbon dates used in the age depth models

Figure 1: map of site locations in the north of Scotland marked by crosses b) detailed location of the Cross Lochs core, marked by a cross and the eddy covariance tower, marked as a triangle. © Crown Copyright and Database Right 2016 Ordnance Survey (Digimap Licence)

Figure 2:

% TiO and FeO of reference Hekla 4 shards from Tephrabase (Newton et al., 2007), displayed as black circles, Compared with shards from Cross Lochs, red triangles and Catanach, green crosses and Bad a' Cheo, blue squares.

Figure 3:

Calcium and magnesium oxide concentration of BADO134 shards, blue crosses, compared with reference material for the Glen Garry eruption obtained from Tephrabase (Newton et al., 2007), black circles.

Figure 4:

Age-depth models produced in BACON for a) Crosslochs b) Catanach and C) Bad a 'Cheo. Thickness of the plot represents the uncertainty in the age

Figure 5:

Long term carbon accumulation rates over time for Cross Lochs, Catanach and Bad a' Cheo. Thickness of the plot represents the uncertainty in age

SUPPLEMENTARY MATERIAL

Geochemistry from electronprobe microanalysis of tephra shards at 164cm in the Cross Lochs core, Identified as Hekla 4

Shard	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Total
1	70.74	0.23	14.96	3.99	0.16	0.04	2.22	4.90	2.51	0.01	99.75
2	62.47	0.73	14.65	10.00	0.29	0.77	4.59	4.61	1.67	0.23	100.01
3	63.58	0.72	14.40	8.90	0.28	0.56	4.31	4.80	1.68	0.21	99.43
4	61.98	0.82	14.33	9.26	0.29	0.87	4.59	4.34	1.66	0.25	98.40
5	63.45	0.68	14.21	8.63	0.31	0.65	4.67	4.32	1.78	0.23	98.93
6	64.27	0.51	14.18	7.42	0.26	0.31	3.94	5.09	1.90	0.11	97.99
7	68.56	0.27	14.16	4.67	0.19	0.09	2.72	5.26	2.27	0.03	98.21
8	62.52	0.66	14.06	9.18	0.29	0.62	4.29	4.84	1.76	0.21	98.44
9	62.48	0.72	14.01	9.82	0.32	0.74	4.58	4.45	1.66	0.24	99.04
10	64.84	0.69	13.97	8.07	0.28	0.54	4.07	4.71	1.82	0.19	99.17
11	71.07	0.21	13.90	3.64	0.14	0.04	2.34	4.48	2.46	0.01	98.29
12	68.06	0.34	13.88	5.17	0.20	0.13	2.95	4.87	2.20	0.06	97.86
13	62.95	0.68	13.86	9.22	0.32	0.66	4.56	4.35	1.63	0.20	98.44
14	69.55	0.25	13.57	4.45	0.17	0.07	2.57	4.98	2.37	0.03	98.01
15	62.10	0.67	13.54	8.51	0.29	0.60	4.32	4.75	1.81	0.19	96.80
16	68.24	0.32	13.51	5.31	0.21	0.12	3.09	4.98	2.26	0.03	98.07
17	71.73	0.19	13.42	3.10	0.14	0.02	2.20	5.17	2.56	0.01	98.55
18	68.95	0.25	13.31	4.08	0.17	0.06	2.68	4.73	2.47	0.02	96.74
19	67.98	0.31	13.29	5.38	0.21	0.09	2.96	4.85	2.10	0.04	97.21
20	63.85	0.59	13.19	8.05	0.28	0.48	3.70	4.70	1.86	0.17	96.87
21	70.03	0.21	13.16	3.93	0.16	0.04	2.21	4.75	2.43	0.01	96.93
22	72.19	0.18	13.15	3.32	0.15	0.00	2.15	5.08	2.54	0.02	98.79
23	69.15	0.24	13.04	4.20	0.17	0.10	2.69	4.86	2.36	0.02	96.82
24	73.74	0.10	13.01	2.33	0.08	0.02	1.29	3.51	3.45	0.00	97.55
25	69.63	0.26	12.97	4.36	0.15	0.10	2.61	4.48	2.35	0.04	96.96
26	71.21	0.19	12.73	3.64	0.13	0.04	2.10	4.83	2.55	0.02	97.45
27	73.84	0.09	12.72	1.99	0.08	0.03	1.30	5.13	2.87	0.01	98.06
28	73.10	0.17	12.69	2.19	0.08	0.12	1.37	4.83	2.85	0.00	97.39
29	72.46	0.11	12.67	2.04	0.07	0.00	1.27	4.86	2.78	0.01	96.26
30	71.65	0.15	12.60	2.67	0.11	0.02	1.70	4.80	2.64	0.01	96.35
31	72.27	0.14	12.52	2.39	0.07	0.10	1.68	5.16	2.44	0.00	96.78
32	75.02	0.08	12.48	1.64	0.07	0.04	1.38	3.93	2.79	0.01	97.42
33	73.88	0.10	12.43	1.65	0.09	0.02	1.32	4.58	2.85	0.02	96.94
34	74.10	0.09	12.38	1.91	0.08	0.02	1.22	4.77	2.93	0.00	97.50
35	73.47	0.09	12.29	1.94	0.08	0.01	1.31	4.70	2.99	0.01	96.89
36	72.95	0.10	12.28	2.13	0.08	0.03	1.27	4.63	2.94	0.00	96.41
37	73.90	0.09	12.27	1.93	0.08	-0.01	1.38	4.67	2.90	0.01	97.22
38	73.34	0.09	12.26	1.94	0.08	0.04	1.49	4.99	2.82	0.01	97.06
39	73.38	0.10	12.26	1.94	0.09	0.03	1.32	4.48	2.95	0.01	96.58
40	72.22	0.23	12.16	2.56	0.12	0.04	0.58	4.96	4.21	0.00	97.07
41	68.01	0.27	12.05	4.62	0.18	0.10	2.66	4.99	2.16	0.04	95.07
42	72.69	0.10	12.05	1.75	0.08	0.03	1.37	4.49	2.83	0.00	95.38

43	76.80	0.09	11.98	1.77	0.09	0.01	1.14	4.32	3.00	0.00	99.20
44	73.60	0.09	11.79	1.75	0.07	0.04	1.33	4.60	2.92	0.01	96.20
45	74.98	0.09	11.78	1.92	0.09	0.03	0.92	3.42	3.29	0.00	96.54
46	73.04	0.09	11.58	1.76	0.07	0.00	1.18	4.77	2.84	0.00	95.33
47	74.74	0.10	11.54	1.84	0.09	0.04	0.91	3.79	3.48	0.01	96.52

Geochemistry from electronprobe microanalysis of tephra shards found in the Bad a' Cheo core at 200.1cm, Identified as Hekla 4

Shard	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Total
1	71.41	0.09	12.63	2.04	0.08	0.02	1.27	4.93	2.75	0.01	95.24
2	72.41	0.09	12.66	2.00	0.09	0.05	1.35	4.83	2.72	0.01	96.20
3	64.69	0.41	13.76	6.33	0.24	0.21	3.38	5.20	2.07	0.09	96.37
4	72.57	0.08	12.61	1.85	0.09	0.02	1.27	5.00	2.91	0.01	96.42
5	72.68	0.11	13.08	1.98	0.08	0.02	1.37	4.74	2.72	0.01	96.79
6	73.20	0.10	12.71	1.84	0.09	0.01	1.28	4.97	2.85	0.00	97.04
7	73.64	0.10	13.33	1.97	0.08	0.01	1.43	4.71	2.84	0.01	98.12
8	73.53	0.09	13.24	2.03	0.08	0.04	1.36	4.96	2.88	0.01	98.21
9	73.40	0.09	13.52	1.79	0.08	0.04	1.33	5.13	2.83	0.01	98.23
10	67.59	0.34	14.77	5.18	0.20	0.19	3.02	5.03	2.08	0.06	98.45
11	74.66	0.09	13.04	1.96	0.08	0.01	1.41	4.91	2.68	0.02	98.87
12	74.11	0.10	13.41	1.82	0.08	0.02	1.33	5.19	2.87	0.00	98.93
13	74.20	0.09	13.15	2.03	0.08	0.00	1.40	5.45	2.86	0.01	99.27
14	74.93	0.10	13.30	1.97	0.07	0.01	1.39	4.78	2.98	0.01	99.55
15	74.30	0.09	13.62	1.82	0.08	0.02	1.45	5.49	2.78	0.01	99.65
16	74.16	0.09	13.61	2.03	0.08	0.00	1.46	5.31	2.90	0.01	99.66
17	73.11	0.10	13.85	2.76	0.10	0.06	1.85	5.66	2.32	0.01	99.81
18	68.97	0.30	15.29	4.88	0.20	0.09	2.84	5.18	2.11	0.04	99.90
19	70.80	0.21	14.60	3.92	0.15	0.04	2.31	5.47	2.38	0.01	99.90
20	64.96	0.54	14.53	8.08	0.30	0.39	3.95	5.20	1.91	0.13	99.99
21	74.83	0.10	13.58	1.94	0.07	0.00	1.44	5.40	2.78	0.01	100.15
22	76.12	0.08	13.05	1.82	0.08	0.05	1.34	4.87	2.92	0.01	100.32
23	64.28	0.63	14.46	8.69	0.29	0.50	4.41	5.09	1.80	0.16	100.33
24	74.92	0.10	13.79	2.05	0.07	0.00	1.41	5.28	2.85	0.02	100.49
25	66.00	0.67	15.22	7.64	0.24	0.49	3.79	5.48	1.94	0.21	101.68
26	76.40	0.08	14.28	1.74	0.08	0.03	1.37	5.04	2.85	0.01	101.87

Geochemistry from electronprobe microanalysis of tephra shards found in the Catanach core at 116cm, Identified as Hekla 4

Shard	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Total
1	61.19	0.79	13.73	10.10	0.30	0.83	4.44	4.45	1.68	0.32	97.83
2	61.44	0.67	14.34	9.07	0.30	0.67	4.14	4.92	1.78	0.24	97.56
3	62.08	0.80	15.04	9.67	0.31	0.97	4.43	4.74	1.66	0.29	99.98
4	62.10	0.73	14.05	9.22	0.29	0.72	4.44	4.21	1.65	0.25	97.67
5	62.20	0.68	14.44	9.76	0.29	0.67	4.51	4.36	1.65	0.23	98.78
6	62.50	0.70	14.79	10.03	0.29	0.62	4.33	4.62	1.80	0.21	99.89

7	62.59	0.69	14.31	9.20	0.28	0.71	4.34	4.56	1.75	0.22	98.66
8	62.78	0.69	14.03	9.41	0.30	0.71	4.62	4.55	1.67	0.21	98.98
9	62.90	0.70	14.96	8.72	0.28	0.69	4.26	4.49	1.79	0.23	99.01
10	62.95	0.70	14.02	8.77	0.30	0.60	4.23	4.59	1.73	0.23	98.12
11	63.19	0.55	12.98	7.78	0.28	0.39	3.85	4.80	1.82	0.15	95.79
12	63.75	0.71	13.87	8.66	0.27	0.69	4.05	4.65	1.71	0.23	98.60
13	64.01	0.71	14.05	8.34	0.30	0.56	4.00	4.57	1.71	0.22	98.47
14	65.92	0.50	14.15	7.27	0.24	0.32	3.49	4.96	1.98	0.11	98.94
15	66.65	0.37	13.24	6.10	0.23	0.16	3.03	4.80	2.13	0.07	96.77
16	67.54	0.27	13.18	4.93	0.15	0.07	2.58	4.75	2.24	0.03	95.74
17	67.85	0.26	14.46	4.60	0.18	0.07	2.68	5.04	2.35	0.04	97.51
18	67.89	0.32	13.51	5.30	0.19	0.12	2.91	4.75	2.24	0.05	97.29
19	68.33	0.29	13.38	4.70	0.18	0.11	2.82	4.93	2.27	0.04	97.07
20	68.48	0.32	13.46	5.38	0.20	0.14	2.93	5.12	2.16	0.05	98.25
21	69.16	0.21	12.94	3.79	0.15	0.06	2.22	4.73	2.40	0.02	95.67
22	69.49	0.21	13.69	2.56	0.15	0.10	3.19	5.48	1.71	0.03	96.61
23	69.73	0.26	14.65	4.55	0.16	0.27	2.78	5.42	1.47	0.06	99.36
24	70.40	0.23	13.67	3.79	0.14	0.06	2.28	4.79	2.43	0.02	97.81
25	70.47	0.16	11.90	3.20	0.12	0.02	1.96	4.66	2.63	0.01	95.13
26	70.97	0.21	12.90	3.83	0.15	0.02	2.29	4.85	2.44	0.03	97.68
27	71.02	0.20	12.02	2.83	0.13	0.04	1.87	4.75	2.63	0.03	95.52
28	71.26	0.19	13.17	3.54	0.13	0.03	2.12	4.50	2.55	0.01	97.52
29	72.37	0.12	13.38	2.28	0.10	0.03	1.44	4.85	2.60	0.02	97.18
30	72.53	0.10	13.14	1.97	0.08	-0.01	1.30	4.86	2.77	0.01	96.76
31	72.54	0.10	12.18	1.84	0.08	0.00	1.25	4.71	2.75	0.01	95.45
32	72.97	0.10	13.02	1.82	0.08	0.01	1.28	5.05	2.77	0.00	97.09
33	73.03	0.10	12.68	2.08	0.08	-0.01	1.28	4.84	2.80	0.00	96.87
34	73.04	0.09	12.15	2.10	0.09	0.02	1.29	4.87	2.74	0.00	96.40
35	73.19	0.08	12.67	1.75	0.09	0.01	1.21	4.40	2.83	0.01	96.24
36	73.20	0.10	12.23	1.79	0.07	0.02	1.28	4.59	2.86	0.01	96.14
37	73.35	0.07	11.06	0.88	0.06	0.01	0.65	3.82	5.28	0.01	95.20
38	73.56	0.09	12.65	1.98	0.08	0.04	1.29	4.65	2.82	0.01	97.16
39	73.97	0.10	11.84	1.99	0.09	0.01	1.37	4.78	2.81	0.01	96.96
40	74.42	0.10	12.85	1.88	0.07	0.00	1.29	5.12	2.60	0.00	98.33
41	74.90	0.08	12.55	1.76	0.07	0.02	1.33	4.39	2.85	0.02	97.95
42	75.41	0.08	12.76	1.28	0.07	0.03	1.41	4.18	2.78	0.01	98.01

Geochemistry from electronprobe microanalysis of tephra shards from Bad a' Cheo at 124cm, Identified as Glen Garry:

Shard	SiO2	TiO2	Al2O3	FeO	MnO	MgO	CaO	Na2O	K2O	P2O5	Total
1	71.84	0.69	13.50	5.04	0.12	0.66	2.94	4.46	1.88	0.15	101.27
2	64.61	1.30	14.05	7.09	0.16	1.70	4.90	4.24	1.40	0.45	99.91
3	72.64	0.65	13.65	4.65	0.11	0.57	2.93	4.52	1.94	0.14	101.80
4	74.38	0.59	13.95	3.72	0.10	0.46	2.58	4.39	1.99	0.14	102.31
5	64.80	1.29	13.18	6.90	0.14	1.69	4.89	4.57	1.46	0.37	99.30
6	71.86	0.69	13.11	4.59	0.11	0.65	2.93	4.85	1.92	0.15	100.86
7	64.29	1.11	13.40	7.01	0.15	2.25	5.34	4.20	1.42	0.24	99.41
8	70.51	0.72	12.63	5.16	0.13	0.67	3.01	4.93	1.76	0.16	99.69

9	62.54	1.42	13.54	7.74	0.17	1.91	5.30	4.14	1.29	0.45	98.50
10	68.32	0.85	12.94	5.48	0.15	0.91	3.54	4.51	1.74	0.23	98.66
11	69.08	0.71	13.15	4.58	0.12	0.57	3.04	4.68	1.71	0.15	97.81
12	72.71	0.10	13.07	2.02	0.08	-0.01	1.38	5.32	2.74	0.02	97.44
13	73.94	0.07	13.03	1.49	0.07	0.01	0.73	4.32	5.21	0.00	98.87
14	73.24	0.64	12.69	4.50	0.12	0.62	2.71	4.48	1.93	0.11	101.05
15	63.05	1.28	12.39	7.47	0.17	2.50	5.93	4.01	1.31	0.28	98.40
16	64.98	1.40	14.65	8.18	0.17	1.79	5.49	4.15	1.33	0.40	102.52
17	70.59	0.68	13.05	4.71	0.13	0.65	3.21	4.53	1.82	0.13	99.49
18	70.19	0.73	13.23	5.01	0.15	0.69	3.12	4.33	1.79	0.12	99.36
19	60.15	1.31	14.21	8.27	0.18	3.97	7.35	3.54	0.96	0.21	100.14
20	71.93	0.65	13.68	4.30	0.10	0.55	2.93	4.76	1.92	0.11	100.92
21	72.17	0.68	13.88	4.47	0.13	0.57	2.91	4.05	1.82	0.13	100.81
22	63.71	1.43	14.39	7.76	0.18	1.86	5.28	4.00	1.34	0.40	100.35
23	72.93	0.50	12.84	3.73	0.09	0.39	2.32	4.65	2.11	0.06	99.62
24	59.67	1.38	13.82	8.66	0.18	3.77	7.29	3.80	1.00	0.21	99.78
25	70.68	0.51	12.74	3.49	0.09	0.45	2.19	4.50	1.91	0.07	96.63
26	70.39	0.65	12.58	4.46	0.13	0.58	2.70	4.35	1.88	0.10	97.81
27	62.69	1.55	13.85	8.31	0.18	1.98	5.48	3.94	1.17	0.43	99.56
28	73.66	0.52	12.35	3.85	0.10	0.40	2.33	4.62	1.95	0.08	99.84
29	71.87	0.72	13.34	5.20	0.12	0.69	3.09	4.62	1.78	0.14	101.56
30	74.03	0.56	12.90	4.12	0.10	0.42	2.12	4.41	2.23	0.09	100.98
31	71.61	0.76	13.57	5.01	0.14	0.74	3.21	4.66	1.85	0.16	101.71