Assessing changes in carbon stocks of Scottish soils: lessons learnt

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Abstract. Between 1978 and 1988, the soils at 721 locations throughout Scotland were sampled at intervals 10 km apart. They were described, characterised and samples were taken from each of the main horizons. Material not used for analysis was stored in the National Soils Archive. Between 2007 and 2009, 183 of these locations were re-visited (20 km intervals) and fresh samples taken to identify changes in nutrient status, pH and, in particular, soil carbon concentrations and stocks over the 19-31 year period. The archived soil samples from this time were re-analysed alongside those from the recent sampling to determine carbon concentrations. Near Infrared (NIR) spectroscopy was used to estimate their bulk density so that carbon stocks could be calculated as this was not measured at the original sampling. The results showed no statistically significant change in soil carbon stocks to 1 m depth for the main, broad land use types in Scotland apart from a small but significant increase (P=0.035) in soils under woodland. There was approximately 11.5% difference in carbon concentration between the re-analysed, archived soil and values originally obtained, but this was attributed to an artefact of differences in analytical methods. Between the two sampling periods, a decrease in carbon concentration of 2.4 g kg\(^{-1}\) was detected in cultivated soils. However, a significant increase in topsoil thickness of 2.9 cm (P=0.024) was sufficient to compensate for these changes in arable soils such that there was no detectable change in carbon stocks. The work shows the value of soil archives and of measuring horizon thickness.

1. Introduction
The Scottish Government has set ambitious targets to reduce greenhouse gas (GHG) emission to 58% of 1990 levels by 2020 and to 20% of 1990 levels by 2050 as detailed in the Climate Change (Scotland) Act 2009. It is estimated that Scotland’s soils hold around 3000 Mt C and clearly losses of this carbon due to climate or land use change could impact on the Government’s ability to achieve these targets, as well as adversely affecting soil functionality and food security.

In order to establish if Scottish soils were indeed losing soil carbon, the Scottish Government commissioned a research project to evaluate changes in carbon stocks (and other soil properties) across the whole country. This project not only assessed changes but investigated how sampling methods could affect the overall conclusions.

2. Material and Methods
Between 1978 and 1988 an inventory of soils in Scotland was undertaken by locating and describing the soil profile at each 5 km intersection between the easting and northing grid lines. The major soil horizons in each profile were also sampled at each 10 km grid intersection, giving a dataset of 721 sampled profiles. These samples were analysed to determine the concentration of the major exchangeable anions and cations, nitrogen, phosphorus, pH as well as carbon. The results of these
analyses were stored in the Scottish Soil Database and material not used for analysis was stored in the National Soils Archive.

Between 2007 and 2009, 183 of these locations were revisited on a 20 km sample frame, that is, 25% of the original sites. At each location, the sampling position was confirmed by matching site characteristics such as slope, rockiness and aspect with the previous description, and a soil profile similar to the original was identified and each of the major soil horizons was sampled. Composite samples from 0-15 cm were also taken over a 20 × 20 m area using a soil auger and single cores from 0-15 cm and from 0-5 cm were taken from the profile pit at each of the sites.

The subsequent analyses included those done previously as well as bulk density, a key property required in determining carbon stocks. In order to minimise instrument bias, the original archived soils were located and analysed alongside the newly sampled soils in randomised but paired batches. Samples for all analyses were initially air-dried at 30°C and then sieved (<2 mm). Samples for carbon content were further dried at 50°C and those for loss on ignition dried at 105°C. At each stage of subsampling, the soil was riffled to minimise sampling bias. The original, archive samples had also been air-dried at 30°C prior to storage.

Elemental carbon (%) for the original analysis was performed on a Hewlett-Packard CHN 185 analyzer but for the analysis of the new samples and for the reanalysis of archived samples, a Flash EA 1112 Series Elemental Analyser connected via a Conflo III to a DeltaPlus XPisotope ratio mass spectrometer (all Thermo Finnigan, Bremen, Germany) was used. The carbon concentrations were calculated from the area output of the mass spectrometer calibrated against a standard reference material which was analysed with every batch of ten samples [1].

The bulk density was determined for each major horizon in the soil profile for the 2007-9 soil samples, using, wherever possible, three replicates per horizon. Stainless steel cylinders, internal diameter 7.3 cm and height 5 cm, were pushed into the soil and then carefully removed, trimmed to remove excess soil and then extruded into a polythene sample bag, giving a soil volume rounded to 210 cm³. These samples were then dried at 105°C, sieved (<2 mm) to remove stones and any roots and weighed. The bulk density of the fine fraction was obtained after making a correction for the volume of stones and roots.

Figure 1: Distribution of 10 km (a) and 20 km (b) sample locations.
Bulk density was not available for the 1978-88 soil samples so there was a need to estimate the bulk density for these soils in order to estimate carbon stocks. Many pedotransfer functions used to predict bulk density use carbon concentration as a predictor and using these pedotransfer functions would lead to a double reliance on the carbon concentration and subsequent error propagation.

To overcome these issues, Near Infrared (NIR) spectroscopy was used to predict soil bulk density. The measured bulk densities from the 2007-9 samples were used for calibration and subsequent prediction of bulk density values for both datasets to avoid the potential bias of having measured values for one set and predicted values for the other. NIR spectra of the <2 mm soil fraction (that is, the dried and sieved soil from the cores taken to determine bulk density and from the archived soil) were recorded from 1100 – 2500 nm at 2 nm intervals on a FOSS NIRS Systems 5000 spectrophotometer (FOSS NIRSystems, Silver Springs, MD, USA), using a transport module sampling attachment and a quarter cup sample holder. Reflectance mode spectra were collected using Infrasoft International ISiScan Software, Version 2.85.3 (FOSS Analytical AB, Hoganas, Sweden). Infrasoft International WINISI III Software, Version 1.50 E (FOSS Tecator AB, Hoganas, Sweden), was used for the development of calibration equations to predict the unknown bulk densities for the 1978-88 samples as well as predicting bulk densities for the 2007-9 soil samples.

A total of 663 samples had measured bulk densities which were then correlated with the full spectrum of the NIR spectral data to develop an initial equation. A range of pre-processing methods, regression methods and different mathematical treatments were tried in order to obtain the best possible equation, which was validated by cross-validation. As the derived equation did not perform as well for highly organic samples (≥ 37% carbon) as for more mineral soil horizons, two separate regression equations were developed for soils with ≥37% carbon and <37% carbon, respectively [1].

The total profile carbon stock at each site, at each of the two sampling times, was calculated as the sum of the component soil horizon carbon stocks. The stock was calculated to 100 cm unless the profile was restricted by the presence of rock. Soils with flooding could not be sampled to depth. However, if the profile was flooded on one occasion but could be sampled on the other, the carbon stock was also calculated to 100 cm.

For each horizon, the carbon stock was calculated as the product of horizon depth, bulk density and carbon concentration with a correction made for stone content. As both carbon concentration and bulk density were measured on samples taken from the horizon midpoint, there was an assumption that they were representative of the whole horizon. In some cases, two (or three) samples were taken from the horizon, particularly for thick horizons; this was accounted for in the calculation by dividing the horizon into two (or three) equal parts and applying the corresponding sample values.

The comparison of the mean values for carbon concentration, bulk density, soil depth, stone content and carbon stock between soils sampled previously and the newer samples was done using a paired t-test with Genstat 13th edition (VSN International, Hemel Hempstead).

3. Results and discussion
The average time between samples was 25 years (19-31 years) and we found no statistically significant change in soil carbon stocks to 1 m depth over this time period for the main, broad land uses types in Scotland (arable, improved grassland, semi-natural grassland, moorland and bog) apart from a small but significant increase (P=0.05) in soils under woodland (Table 1). However, this change was only apparent when the data for deep (>1 m) peat soils (Histosols) were removed from the analyses. The carbon concentration of Histosols varies little with depth, thus the main determinant in changes in carbon stocks in these soils is the overall thickness. In many cases the actual thickness of these soils could not be determined (the thickness exceeded the depth of the profile pit at around 1m and the additional probing with a 1 m-long soil auger) thus making the detection of change in these soils impossible within the scope of this resampling programme. Including these soils in the overall analyses only increased the mean carbon stocks making those sites where a real difference was detected less significant.
Table 1. Change in mean carbon stocks in Scottish soils over an approximate 25 year period by broad land use type.

| Vegetation type        | 1978-1988 (C t ha⁻¹) | 2007-2009 (C t ha⁻¹) | Change (C t ha⁻¹) | No. sites | P value |
|------------------------|-----------------------|----------------------|-------------------|-----------|---------|
| All                    | 201.7 ± 11.7          | 209.8 ± 13.0         | 8.0               | 149       | 0.175   |
| Arable                 | 111.4 ± 16.5          | 111.5 ± 15.6         | 0.0               | 16        | 0.998   |
| Improved grassland     | 123.5 ± 9.6           | 119.0 ± 9.9          | -4.5              | 32        | 0.343   |
| Semi-natural grassland | 179.7 ± 25.1          | 185.2 ± 27.1         | 5.4               | 26        | 0.709   |
| Woodland               | 163.2 ± 24.1          | 186.7 ± 26.9         | 23.5              | 21        | 0.035   |
| Moorland               | 251.5 ± 20.7          | 257.7 ± 23.4         | 6.2               | 41        | 0.686   |
| Bog                    | 455.0 ± 34.8          | 489.6 ± 44.7         | 34.7              | 13        | 0.286   |

*deep peats (Histosols) and one soil derived from shelly sands removed from analysis.

However, interpreting the results was often far from straightforward and occasionally apparently contradictory. Although there was no change in carbon stocks of soils under arable cultivation, the carbon concentration in the Ap horizon of these soils decreased (36.0 to 33.7 g C kg⁻¹); however, there was a significant increase in topsoil thickness (Table 2) which meant that stocks remained the same (Table 1). Had the soils only been sampled for carbon concentration over 0-15 cm, as has been common in other UK sampling schemes [2, 3], we may have reported a carbon loss.

Table 2. Change in carbon concentration and horizon depth for Ap horizons in arable soils

| Measure               | 1978-1988 | 2007-2009 | Change   | No. sites | P value |
|-----------------------|-----------|-----------|----------|-----------|---------|
| Carbon (g C kg⁻¹)     | 36.0      | 33.7      | -2.4 (-6.6%) | 16       | 0.225   |
| Horizon depth (cm)    | 28.9      | 31.9      | 2.9 (10.2%) | 16       | 0.024   |

Carbon concentrations of the re-analysed, archived soil from the 1978-88 sampling were approximately 11.5 % less than the values obtained by the original analysis. The difference was not due to carbon loss during storage as a similar magnitude of loss was not found when we examined Loss on Ignition data. This suggests that the apparent difference in carbon concentration was due to differences in the protocols and the instrument used at that time (Figure 2a and b). Drying the samples before analyses may be a contributory factor and it is unclear how samples in 1978-88 were dried before analysis. Contemporary samples are dried at 50°C to avoid nitrogen losses. Weight losses after drying at 105°C compared to 50°C were 0.7% and 2.7% for a subset of mineral and organic soils, respectively, suggesting that a difference in drying regime could not explain the observed difference in carbon concentration.
Figure 2: The relationship between the original measured carbon concentrations and the re-analysed soil (a) and the relationship between the original measured loss on ignition values and the re-analysed soil (b).

Having access to the archived material to re-run the analyses was a crucial element of the work, especially given the 11.5% change in carbon concentration that resulted from differences between the instruments used. Had this material not been available and we simply compared the results of the analyses over the two time periods then we would probably have drawn an erroneous conclusion that the carbon stocks of Scottish soils had declined by a considerable amount.

As mentioned, we could not determine carbon stocks fully for some deep peat soils. As the depth to the mineral layer or rock had not been recorded, there was an unknown stock of carbon below 1m, in some cases a considerable one. Hence these were removed from the statistical analyses.

As peat soils have a narrow range of carbon concentrations, the only way to determine changes in carbon stocks for these soils is to determine if the bog is growing or declining. While we were unable to do this for all peat bogs encountered at the sample locations, it is even more difficult to determine changes if the sample depth is 0-15 cm. Indeed, a formerly degraded bog could now be actively growing but as the bulk density of the upper layers would be less than that of amorphous peat, the stock calculation would suggest a decline.

Carbon stocks were calculated on the basis of equivalent volume but several authorities consider equivalent soil mass to be a better basis [4]. Using the equivalent volume may underestimate the true change in carbon, particularly where there is a significant change in bulk density. There is a particular problem in the case of organic soils; any increase in the depth of the organic layer will mean sampling less of the underlying mineral soil and vice versa for a loss of surface layer. However, it can be shown algebraically that even using soil mass (mineral plus organic) can under-estimate the change. Particularly for soils with significant organic content it is preferable to calculate on the basis of equivalent mineral weight. This assumes, of course, that there is no process causing loss or gain of mineral material. The idea is that the mineral material acts an anchor or reference point. We calculated the total mineral stock for our sites at both time periods. The data showed that for the more organic profiles there was an unacceptable degree of variability in the mineral content such that any recalculation based upon equivalent mineral mass would also give very variable carbon stocks. This was particularly applicable to soils under bog, moorland and woodland. For the more mineral soils under arable, improved grassland and most semi-natural grassland, this is an approach worth pursuing. Since our aim was to compare all the soils on an equal basis we have only presented results based upon equivalent volume, excluding the deep peats soils as mentioned above.
Another complicating factor in the analyses was the confounding factor of arable/grass rotations. While it was relatively easy to determine if the site was under continuous arable or permanent grassland, sites that had a mixed arable/grassland system could have been allocated to either arable or permanent grassland, often depending on the age of the grass. Results from an analyses of 2644 topsoils taken from the Scottish soils database, show significant differences ($p<0.01$) in mean carbon concentrations of soils under arable (3.66%), a mixed arable/grassland system (4.45%) and under permanent grassland (5.14%). Thus, the age of the grassland and its position in the rotation will influence the amount of carbon in the soil and its position in the rotation relative to the repeat sample could influence whether a decline or increase in carbon stock was detected. Better recording of land use history would help improve detection of change. Unfortunately, this is not always possible when sampling either randomly or on a grid. Selection of sites based upon known history may select for better overall management and thus bias the results.

Pairing sites gave increased statistical power to the analyses, since it reduced variability due to site differences. However, from a practical point of view, it was sometimes difficult to relocate and replicate the exact soil conditions. While external conditions such as slope, aspect and rockiness could be reasonably well matched, the variability inherent in soils, even over relatively short distances, meant that it could be difficult matching the sequence, thickness and presence of horizons exactly. Alternative approaches such as sampling on an offset grid, for example 1km east and north of the original, would have avoided these problems but would have meant many more sites would have needed to be visited in order to obtain a sufficient sample size. One method used to confirm that the resampled soils were similar to the original was to compare the Fourier Transform Infrared (FTIR) spectra of the mineral component of the soils (Figure 3). While the part of the spectra related to the organic component could change through time, for example, due to a land use change between the two sampling periods, the mineral component should remain the same. By overlaying the FTIR spectra, any differences in the mineralogy could be determined. In all but one case, a good match was found, confirming that these remaining sites were comparable.

![Figure 3](image-url): Example of the use of FTIR to confirm that soil sampled between the two time periods was comparable. The (lower) blue line is from the resampled topsoil (2007) and the (upper) red line is from the original (1987).
4. Conclusions
In conclusion, we were able to demonstrate that there has not been a significant loss in carbon from Scottish soils though interpretation of the results was not straightforward. The sample grid reflected the proportion of land uses in Scotland but also resulted in low sample numbers for some key land uses where carbon losses may be expected, for example, land under arable agriculture. Peat soils also posed a problem where the thickness exceeded the normal sampling depth of 1 m. In these soils, it would have been advantageous to determine a fixed datum such as the top of rock or drift underlying the peat so that changes in thickness could be recorded but even this has problems as bogs can shrink and swell depending on the degree of saturation.

Spectral analyses proved to be useful in both predicting bulk densities and in verifying that the site had been successfully relocated. This would not have been possible had the original samples from the 1978-1988 sampling campaign not been archived. The value of retaining archived material was also demonstrated by the difference in carbon values measured by two different elemental analysers. If the soil had not been available for reanalyses, there was a real danger of inferring that carbon was being lost from Scottish soils.

We have shown that sampling by horizon was superior to sampling by fixed depths particularly for cultivated soils but there is still an assumption that a sample taken from the middle of a horizon is representative of the horizon as a whole. While this may hold true for horizons that are regularly mixed, it may not be true for highly layered soils.

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