

29. Carbon sequestration in the soils of Northern Ireland: potential based on mineralogical controls

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Complex relationships between soil organic carbon (SOC), mineralogy, land-use and climate may exist in the soils of Northern Ireland. Greater understanding of these interactions can improve the effectiveness of SOC sequestration and management strategies. Mineralogy and SOC concentrations in soils derived from four different parent rocks (sandstone, shale, basalt and granodiorite) were characterised and indicate that soil mineralogy and geochemistry play an important role in determining the concentration of SOC. This primarily depended on the absence or presence of high surface area clay and iron oxide minerals and on the soil pH. Soil mineralogy did not appear to have a major impact on the composition of soil organic matter (SOM) with depth. The results suggest that when carbon sequestration practices in Northern Ireland are considered, soils derived from basalts are likely to acquire greater carbon concentrations than soils from other lithologies.

INTRODUCTION

Soils are a major terrestrial sink for organic carbon. Global estimates suggest that soils contain at least 1500 Gt of organic carbon (Jobbágy and Jackson, 2000). The potential of soils to sequester carbon may have significant effects on climate change mitigations and is accountable under the Kyoto Protocol (Freibauer *et al.*, 2004). Thus the ability of soils to maintain and enhance SOC levels is of key interest. However, there is still uncertainty regarding the distribution and dynamics of SOC reservoirs (Torn *et al.*, 1997). In natural ecosystems, rainfall and temperature are major controls on the net primary productivity (NPP) and the rate at which the microbial biomass decomposes SOC (Lal,

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2004). In managed soils, carbon storage is also dependent on the farming system and soil management strategies.

While climate and land-use determine NPP and carbon input, soil properties such as texture, mineralogy and structure have been identified as important factors in SOC storage. Aggregate formation is known to protect SOC from microbial decomposition (Baldock and Skjemstad, 2000; Lützow *et al.*, 2006), while the molecular structure of some carbon compounds and their supposed resistance to decomposition have been considered essential to SOC storage. However, a study by Schmidt *et al.* (2011) suggested that even compounds considered particularly persistent (e.g. lignin) could decompose at the same rate as, or more quickly than, bulk SOM. Thus other mechanisms may be important in limiting the decomposition of compounds that make up the SOC store. These mechanisms may include the absence of a compound needed for the metabolism of certain organic components or the specific micro-environmental conditions in the soil which may restrict the access to or activity of decomposer enzymes (e.g. hydrophobicity, acidity or sorption to surfaces).

With respect to the sorption of SOM to mineral surfaces, differences in soil mineralogy may be an important factor in the protection of SOC. Variations in the surface properties of different clay minerals and oxides control the available surface area SOM can bind to, while the pH of the soil influences the surface charge of the mineral and its ability to adsorb organic compounds (Kaiser *et al.*, 1997; Saïdy *et al.*, 2013). Iron oxides in particular have been recognised as a major sorptive surface (Kaiser and Zech, 2000) and their concentration in soils may have a large impact on SOC protection. Specific compound classes that are most persistent in soil include aromatics and lipids (Haritash and Kaushik, 2009), although lignin and tannins are also reasonably persistent. These persistent compounds are likely to represent the SOC that is stored for longest periods, aided by decreasing microbial biomass with increasing depth (Eilers *et al.*, 2012). The impact of different soil mineralogies, however, on the protection of specific compounds and the likely effect on the SOC pool, is unclear (Lützow *et al.*, 2006).

The soils of Northern Ireland represent an excellent opportunity to examine the combined potential effects of lithology, land-use and climate on soil carbon storage for several reasons, including: (i) Northern Ireland covers a relative small area with a highly diverse geology in close proximity; (ii) the soils are all of similar age (at least biologically) because Northern Ireland was covered by the British–Irish Ice Sheet (BIIS) up to 15 kyr BP (Clark *et al.*, 2012); (iii) the soils from the different lithologies have experienced a relatively consistent climate since their inception; and (iv) the land-use history for all soils has been broadly similar, in that the deforestation of land followed by agricultural use was completed by 1750. In this work, we combine data from a recent study (Ashton, 2014) with published and archive data on Northern Ireland soils (Cruickshank, 1997) to assess the potential mineralogical and geochemical properties of soils that can help determine carbon storage and stability. This information can be used in maximising management strategies

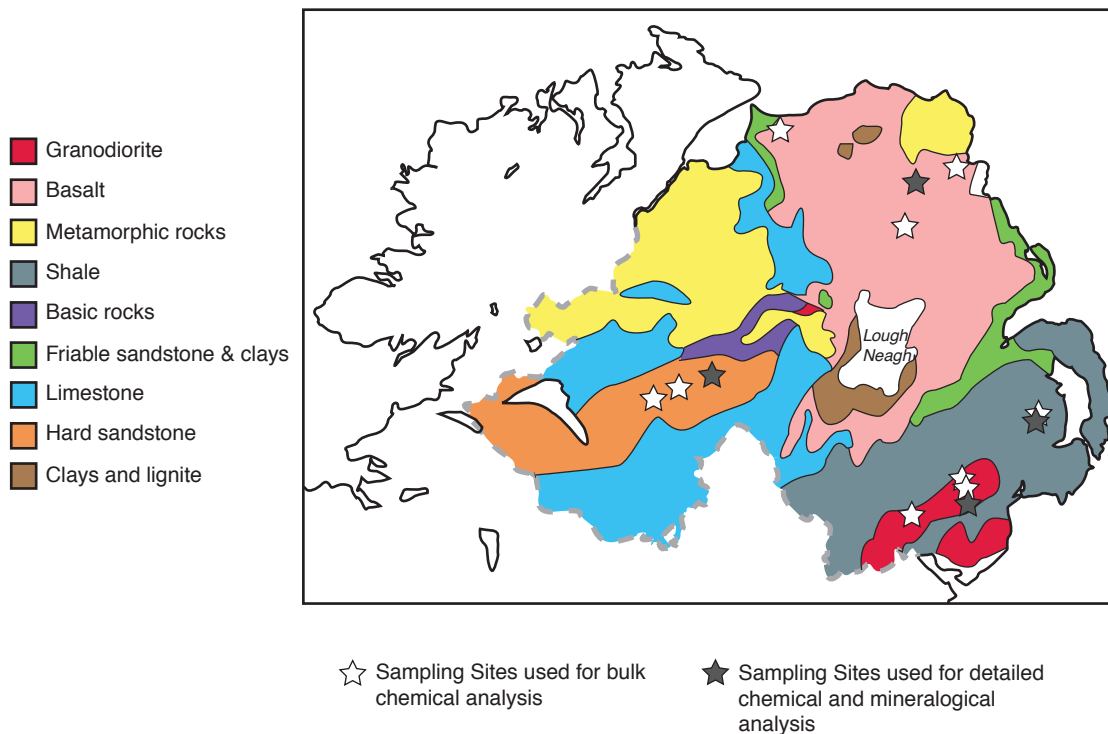


Figure 29.1. Simplified geological map of Northern Ireland displaying the site locations of soil profiles taken during this study.

or enhancing carbon sequestration in soils through schemes such as re-forestation or conversion to long-term pasture (Lal, 2004; Smith, 2008).

MATERIALS AND METHODS

Site selection

All soil samples analysed during this study were collected as part of a research project (Ashton, 2014) that examined the development of soils above different lithologies (sandstone, granodiorite, basalt and shale) across Northern Ireland (Fig. 29.1). The sites were chosen using the detailed metadata collected during the Tellus survey to ensure that the soils analysed had developed above bedrock, had similar land-use and were unlikely to be contaminated. Table 29.1 describes the soil properties at the sites sampled. Importantly, all samples are considered to be well drained, being rankers, brown earths, podzols or surface water gleys, with the exception of sample site M on the basalt. The land-use histories for the site locations were examined using topographic maps dating back to 1860, which showed that these sites had not been forested since at least that time. Previous studies have suggested that the indigenous forest in Ireland was mostly cleared by 1750 (Kaplan *et al.*, 2009; O'Hanlon, 2012) and that approximately 95% of all current forest in Ireland was planted post 1950.

TABLE 29.1. CHARACTERISTICS OF SOILS SAMPLED, INCLUDING THE SUGGESTED SOIL SERIES BASED ON DANI SOIL SURVEY AT I:250K

| Sample | Parent material | Altitude (m) | Precipitation (mm) | Irish soil series 1:250k | % C 0–30 cm | Depth (cm) | Field notes |
|--------|-----------------|--------------|--------------------|--------------------------|-------------|------------|--|
| BB | Basalt | 160 | 800–1200 | Surface water gley | 11.8 | 75 | Improved pasture; well drained; no sign of gleying; sample taken on gentle slope |
| M | Basalt | 300 | 1200–1600 | Humic ranker | 12.2 | 40 | Rough grazing; sample had impeded drainage at 40 cm |
| GB | Basalt | 300 | 800–1200 | Brown ranker | 13.6 | 40 | Rough grazing; sample taken on semi-steep slope; well drained |
| SL | Basalt | 260 | 800–1200 | Humic ranker | 11.4 | 40 | Rough grazing; no evidence of string humic layer; more of a brown ranker |
| V | Granodiorite | 140 | 800–1200 | Brown podzol | 4.41 | 55 | Improved pasture; well drained; no evidence of podzolisation; sample taken on gentle slope |
| GG | Granodiorite | 140 | 800–1200 | Brown podzol | 3.47 | 50 | Improved pasture; well drained; no evidence of podzolisation; sample taken on gentle slope |
| TU | Granodiorite | 170 | 800–1200 | Brown ranker | 5.8 | 50 | Rough pasture; well drained; no evidence of podzolisation; sample taken on gentle slope |
| N | Granodiorite | 220 | 800–1200 | Brown podzolic | 4.1 | 40 | Improved pasture; well drained; no evidence of podzolisation; sample taken on gentle slope |
| CAA | Shale | 80 | 800–1200 | Surface water gley | 7.02 | 40 | Improved pasture; well drained; no evidence of podzolisation; sample taken on gentle slope |
| CAB | Shale | 80 | 800–1200 | Surface water gley | 4.5 | 40 | Improved pasture; well drained; no evidence of podzolisation; sample taken on gentle slope |
| FO | Sandstone | 210 | 800–1200 | Shallow brown podzol | 12.1 | 30 | Rough pasture; no evidence of podzolisation; well drained; sample taken on gentle slope |
| SE | Sandstone | 190 | 800–1200 | Surface water gley | 8.77 | 70 | Improved pasture; no evidence of gleying; well drained; sample taken on gentle slope |
| COB | Sandstone | 120 | 800–1200 | Surface water gley | 4.8 | 60 | Improved pasture; no evidence of gleying; well drained; sample taken on gentle slope |

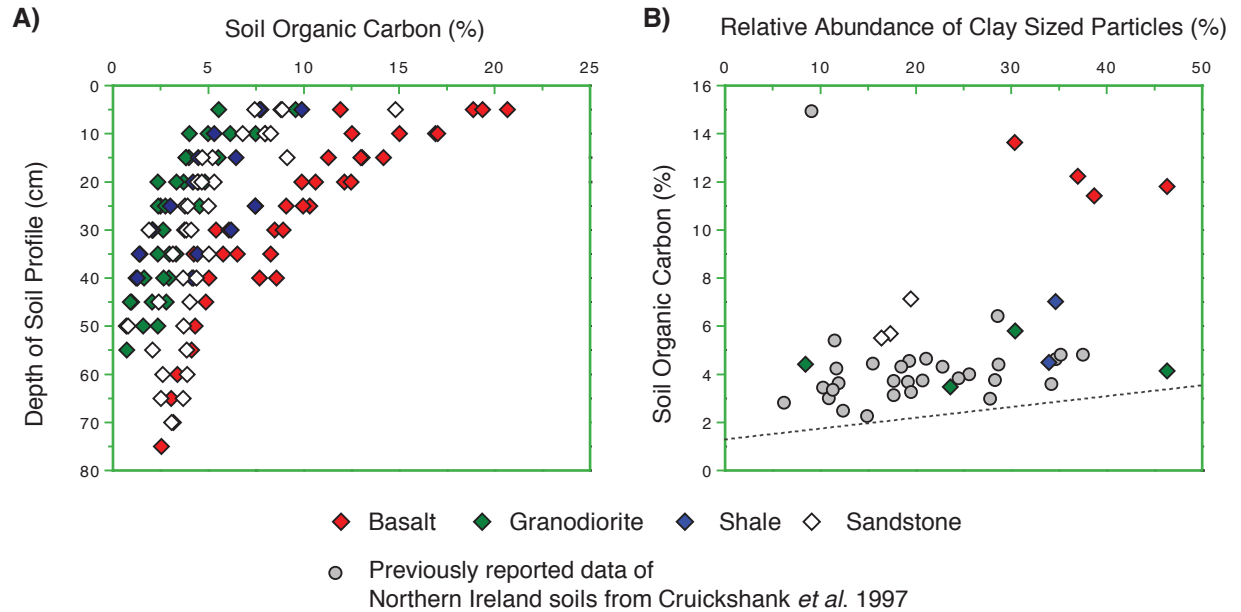


Figure 29.2. (A) SOC versus depth for the soil profiles taken from the different lithologies, with details in Table 29.1. (B) Average SOC values from the top 30 cm of the soil profiles plotted against the concentration of clay sized particles. The lithologies sampled in this study are indicated by filled diamonds colour coded according to parent lithology. Additional SOC values for these horizons for Northern Ireland soils are taken from Cruickshank (1997) (grey circles). The dashed line in panel B (not fitted) suggests a minimum value of SOC with increasing clay content based on the work of Milne *et al.* (2006).

Major inputs of SOC into these soils will have started with the development of Holocene vegetation after the retreat of the BIIS. Results from previous ^{14}C dating analysis of two soil profiles from Dartmoor and Glen Dye in the UK by Parry (2012) determined maximum ^{14}C dates of 10,221 and 4393 years BP. Both studies determine the ^{14}C age to be in line with the retreat of the BIIS. Thus, it is likely the initiation of large-scale carbon inputs into the soil profiles analysed during this study would have occurred between these dates. A further constraint on carbon storage in the profiles examined is the change of land-use from forest to a range of agricultural uses. This would have been broadly similar across what is now Northern Ireland and largely complete by 1750.

Sampling and analysis

Soil pits were dug and sampled in 5 cm sections from the surface to bedrock. SOM was determined using loss-on-ignition at 375°C for 16 hours and converted to SOC using a conversion factor of 0.58 (Rowell, 1994). Total element concentrations were determined using XRF analysis and normalised against volatile content using loss-on-ignition at 1000°C for 1 hour. Broad soil mineralogy assessments were completed on four full soil profiles (locations shown in Fig. 29.1), one from each parent lithology. Freeze-dried subsamples from the soil profiles were pyrolysed at 700°C for 10 s using a CDS (Chemical Data Systems) 5200 series pyroprobe pyrolysis unit interfaced to the Agilent 7890A GC and Agilent 5975C MSD Mass Spectrometer to assess changes in the composition of pyrolysed organic matter. Full details of the sampling and experimental methodology can be found in Ashton (2014).

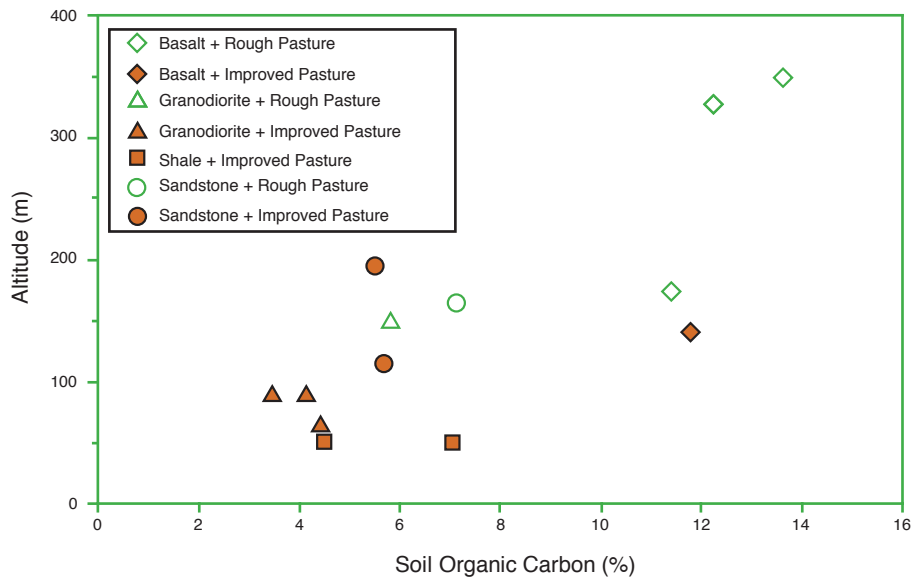


Figure 29.3. Relationship between SOC (0–30 cm) formed on different lithologies, altitude and land-use.

RESULTS AND DISCUSSION

Soil carbon content

In the soils analysed during this study, the concentration of organic carbon exhibited a decrease with depth across all lithologies, with soils derived from the basalts having the greatest wt% concentration (Fig. 29.2a). The steepest decline was found within the top 30 cm for all profiles. Concentrations (wt%) of SOC within this section of the profiles varied between 3 and 13 wt%, and are compared with previously reported values by Cruickshank (1997) in Fig. 29.2b, where they are plotted against % clay. No consistent increase in SOC concentration with clay content was found, although clay particles play a key role in aggregation, thus protecting soil SOC. However, Milne *et al.* (2006) demonstrated that while no direct correlation may be found between SOC and clay content, a minimum value of SOC with increasing clay content may be found. Within the combined data set (Fig. 29.2b) it is possible to visualise a lower limit of SOC with an increasing percentage of clay, although we have too few data points to be able to define a lower limit of SOC.

Rawlins *et al.* (2009) suggested that the inclusion of altitude improved the prediction of soil carbon concentration in mineral, organo-mineral and peat soils in Northern Ireland, possibly due to a shorter growing season and slower decomposition. Testing this hypothesis with our data set (Fig. 29.3) showed that for soils (0–30 cm) below 200 m, no trend with altitude was found. However, the concentration of SOC was approximately 4% higher in soils formed from basalts. The results also found that samples from rough pasture had a greater wt% SOC than those from improved pasture. This may partly account for

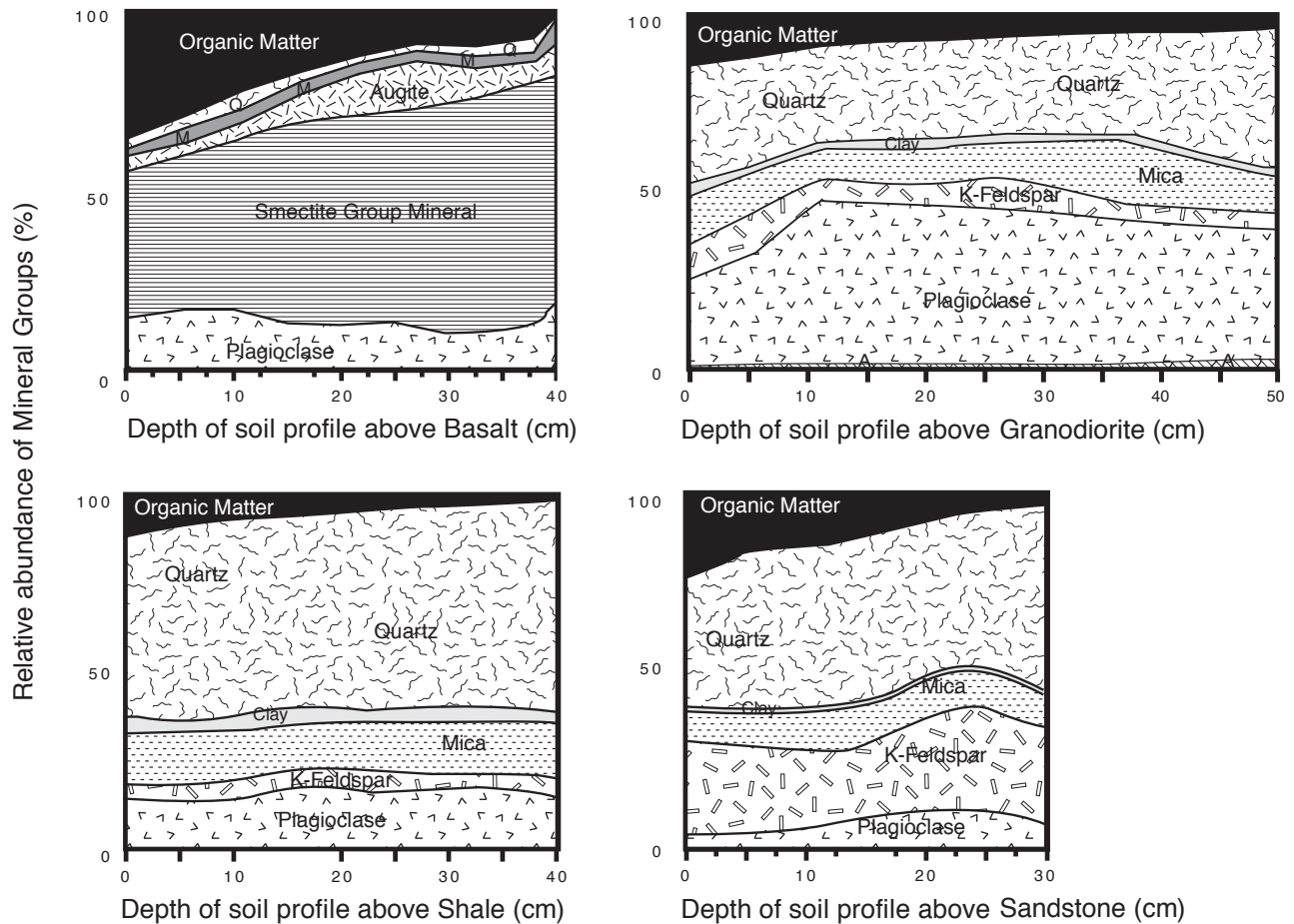


Figure 29.4. Whole soil mineralogy of soil profiles taken from basalt (SL), granodiorite (TU), shale (CAB) and sandstone (FO) lithologies in Northern Ireland (details in Table 29.1). M = magnetite; Q = quartz.

the slightly higher SOC contents found for soils M and GB (Table 29.1) on the basalt lithology at altitudes greater than 300 m. Considering the potential combined influences of altitude, drainage, pasture type and lithology, there is evidence that carbon concentrations are higher in soils where basalt was the parent material.

Soil mineralogical composition

Broad assessments of soil mineralogy were completed on one profile from each lithology (Fig. 29.4). The soil mineralogy above basalt parent rock was dominated by plagioclase (11–16%), augite (pyroxene; <5–15%) and 2:1 aluminosilicate clay (smectite; 40–70%), as well as smaller concentrations of quartz and magnetite. In contrast, the soil mineralogy above granodiorite bedrock was dominated by quartz, plagioclase and potassium-feldspar, with mica and clay minerals contributing <17% to the overall mineralogy. The soil mineralogy of the profiles above shale and sandstone was similar to the granodiorite profile although the relative mineral abundances varied (Fig. 29.4). Clay minerals contributed

TABLE 29.2. BROAD ASSESSMENT OF CLAY MINERALOGY IN NORTHERN IRELAND SOILS BASED ON ANALOGOUS SOIL PARENT TYPES IN SCOTLAND AND ON WORK BY WILSON *et al.* (1984) AND MITCHELL (1955)

| NI soil parent material | Clay type | Clay composition | | | | % FeO _D * | |
|-------------------------|--------------------|------------------|-------|-------------|-------|----------------------|--|
| | | Dominant | Major | Subordinate | Minor | | |
| Devonian red sandstone | Illite | | | | | 0.5–1% | |
| | Kaolinite | | | | | | |
| | Illite-vermiculite | | | | | | |
| Silurian shale | Illite | | | | | <1% | |
| | Kaolin | | | | | | |
| | Chlorite | | | | | | |
| Granodiorite | Illite | | | | | <1.5% | |
| | Kaolin | | | | | | |
| | Vermiculite | | | | | | |
| Basalts | Illite | | | | | ~3% | |
| | Kaolin | | | | | | |
| | Montmorillonite | | | | | | |
| | Vermiculite | | | | | | |

*Data taken from Cruickshank (1997) for dithionite extractable iron oxides.

less than 5% to the mineralogy of the shale- and sandstone-derived soils (20% and 13%, respectively when all phyllosilicates were included).

While more in-depth analysis has been undertaken on clay mineralogy on the basaltic rocks in Northern Ireland and the UK generally (Bain *et al.*, 1980; Smith, 1957), high-resolution analyses of clay composition on other soil types from Northern Ireland are limited. Kiely (1991) previously stated that soil parent material was the principal factor in determining the soil mineralogy; for example, soils formed from Old Red Sandstone,

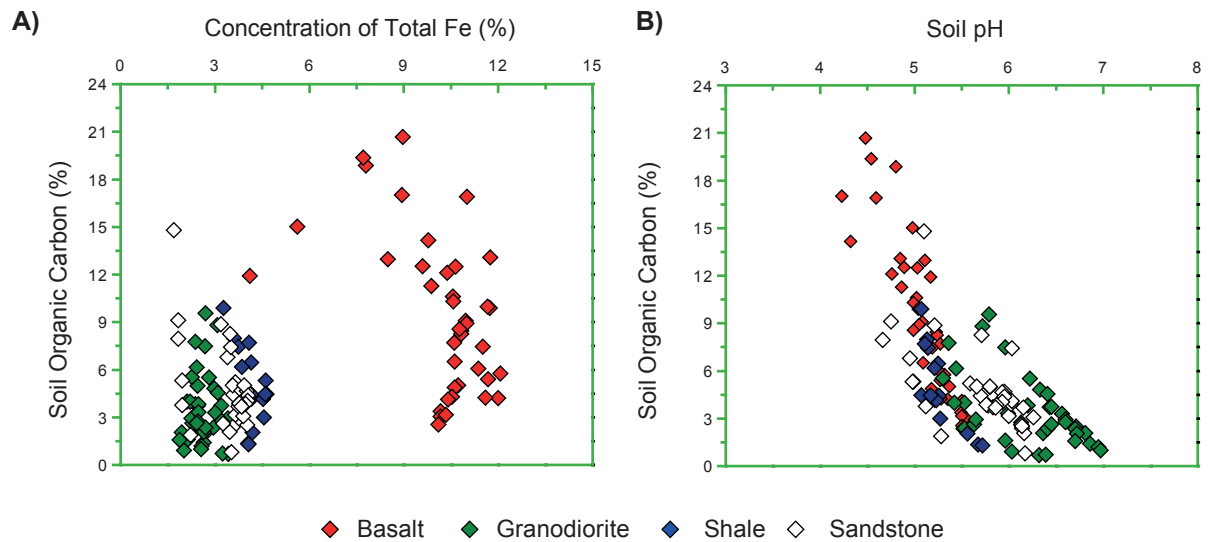
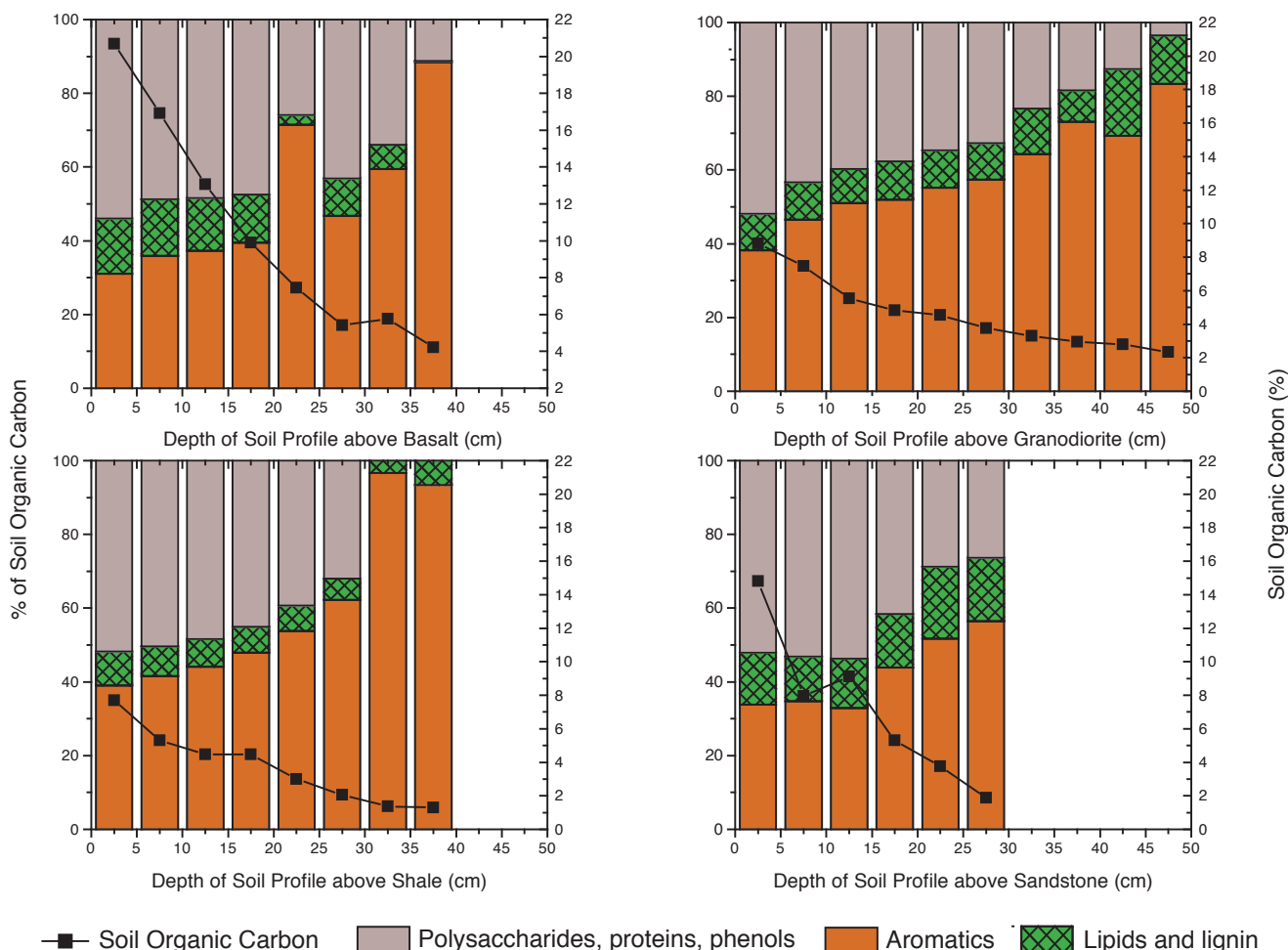


Figure 29.5. (A) Iron concentration versus SOC; (B) soil pH versus SOC in soil cores taken from sites across Northern Ireland. The lithologies are indicated by filled diamonds colour coded according to parent lithology.

Lower Carboniferous shale, Silurian shale and Ordovician shale had high levels of mica in their fine silt and clay fractions. As Northern Ireland has a similar geology to Scotland, where more work on soil clays has been undertaken (Wilson *et al.*, 1984; Mitchell, 1955), we can use information from these soils to describe likely clay compositions in these Northern Ireland soils. Comparison with these analogous soils, summarised in Table 29.2, indicates that illite is likely the dominant clay mineral for those soils which have not developed over basalt.

Soil geochemistry

Total iron concentrations, as determined by XRF, were significantly higher in the soils above basalt (up to 12 wt %) compared to soils above the other lithologies (Fig. 29.5a). The soils above shale, granodiorite and sandstone have relatively similar carbon and iron concentrations (Fig. 29.5a). However, these iron concentrations include not only iron oxide phases but also iron-bearing silicates. Iron oxide data from Cruickshank (1997) are included in Table 29.2 and show that soils derived from basalts are likely to have at least twice the concentration of dithionite extractable iron oxides compared with the other soil types. This is further confirmed by the presence of approximately 5% magnetite in the basalt-derived soils as identified by XRD (Fig. 29.4). Thus, it is likely that the higher proportion of iron oxides in the soils derived from basalts plays a major role in the retention of higher organic carbon. In particular, non-crystalline iron oxides, produced from the weathering of iron-bearing minerals in the basalt, will provide significant surface area for organic carbon sorption. A reduction in soil pH decreases negative charges on the clay and/or oxide particles which, in turn, increases sorption of SOC. Soil pH in the basalt soils was generally the lowest of all soils analysed (Fig. 29.5b) and this will further enhance the



sorption of SOC, compared with other lithologies. For the other soils, where soil mineralogy was similar, a small pH influence on SOC concentrations was identified. Soil pH generally increased in the order basalt < shale < sandstone < granodiorite, whereas the percentage SOM decreased in the order granodiorite < sandstone < shale < basalt.

Composition of organic carbon

The long-term storage of SOC depends not only on concentration but also on the persistence of compounds in the soil profile. Molecular composition analysis was completed to assess changes between profiles and with depth, using pyrolysis gas chromatography mass spectrometry (Py-GCMS). These results, reported in Ashton (2014), revealed changes in the relative abundance of compound classes with depth (Fig. 29.6). Combined, the relative proportion of the persistent organic compounds (aromatics, lipids and lignin) increased with depth within each of the profiles. In particular, the relative proportion of aromatics

Figure 29.6. SOC and soil composition as % of total SOC as determined by py-GCMS, in soil profiles taken from basalt (SL), granodiorite (TU), shale (CAB) and sandstone (FO) lithologies in Northern Ireland (details in Table 29.1).

increased substantially with depth (Fig. 29.6). While in the top 15 cm of each soil profile the relative abundance of the aromatics varied between 30% and 50% of the pyrolysed SOM, this increased to up to 97% at the base of the profiles. This supports the assumption that certain compounds in SOM appear to be more persistent within the soil environment and make up larger proportions of SOC at depth.

IMPLICATIONS FOR SOIL MANAGEMENT

The data set used in this study demonstrates that land-use (pasture type) along with environmental (e.g. altitude) factors may influence carbon concentration and storage. However, soil mineralogy and pH also appear to play an important role. The factors explored were broadly similar for soils developed above sandstone, granodiorite and shale where SOC analyses suggest that carbon has accumulated at approximately similar rates. In comparison, SOC contents in the soils derived from basalt indicate that carbon has accumulated at broadly double that rate, even where environmental and land-use factors were broadly similar to those of the different lithologies (e.g. Samples BB and SL). The major differences in the basalt-derived soils are the dominance of the high surface area vermiculite and montmorillonite clays (Table 29.2), higher CEC and concentrations of iron oxides, and a slightly lower soil pH. While the increased surface area of clays minerals formed from the basalt rock may increase SOC sorption (Saidy *et al.*, 2013), the increase in iron oxides is thought to be of greater importance as they can adsorb more SOC than smectitic clays (Tombácz *et al.*, 2004). The sorption of SOC on hydrous iron oxides is also pH-dependent, with sorption favouring acidic conditions, similar to those found in the basalt soils analysed, due to a greater negative charge (Jardine *et al.*, 1989). These geochemical and mineralogical differences may explain the higher carbon accumulation in the basalt soils.

Despite the differences in geochemistry and mineralogy, examination of the molecular composition of carbon with depth between the different profiles revealed a relatively consistent pattern, suggesting that mineralogy was less important in determining the molecular composition of SOM with depth. This is likely a consequence of similar vegetation inputs and the time scale over which the soils have been receiving carbon inputs (Kögel-Knabner, 2002). In all profiles aromatics dominated the pyrolysed SOM at depth, these often being found to be more persistent in soils (Kalbitz *et al.*, 2005; Mikutta *et al.*, 2009). The mechanisms through which these aromatic structures are preserved at depth are not fully understood, but work by Fontaine *et al.* (2007) suggests that priming bacterial communities with labile carbon enhances their degradation. Thus low concentrations of fresh labile organic carbon at depth may be a limiting factor on aromatic decomposition with depth. The findings suggest that the increase of SOC in the basalt-derived soils, if compared with the other lithologies, is not due to interactions of specific compounds with the dominant mineralogy found in these soils. Instead, the results indicate that the controlling factor is more dependent on the abundance of sorption sites and surface charge to capture leached and root deposited organic carbon (Schmidt *et al.*, 2011; Torn *et al.*, 1997).

Understanding the complex relationships between carbon and the soil properties (mineralogy, pH) that help sequester carbon is important when considering management options. It is recognised that increases in carbon sequestration can be achieved through conversion of arable land to either pasture or forestry (Ostle *et al.*, 2009; West, 2011) and information from this study may encourage effective planning of soil-based carbon sequestration. The Woodland Carbon Code (Forestry Commission, 2014) used by the Northern Ireland Forest Service recognises that the carbon benefits associated with woodland creation are generally greatest on soils with lower organic matter content such as mineral soils. From this work it can be seen that sequestration on basalt-derived soils may be of greatest value, particularly as forest soils tend to acidify with time.

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