Investigating glacial sediment provenance in Northern Ireland using principal component analysis of Tellus soil geochemical data

Geological Survey of Northern Ireland (GSNI)

Open Report OR/10/017

BRITISH GEOLOGICAL SURVEY

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Keywords

Tellus, soil geochemistry, Quaternary, ice flow, glacial deposits, Armoy Moraine.

Front cover

Section through a sequence of glaciofluvial deposits in Northern Ireland.

Bibliographical reference

SCHEIB, A.J., DUNLOP P. AND COOPER, M.R. 2010. Investigating glacial sediment provenance in Northern Ireland using principal component analysis of Tellus soil geochemical data. *British Geological Survey Internal Report*, OR/10/017. 28pp.

Keyworth, Nottingham British Geological Survey 2010

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Foreword

This report is the outcome of a preliminary and collaborative study by the British Geological Survey (BGS), Geological Survey of Northern Ireland (GSNI) and the School of Environmental Sciences, University of Ulster, Coleraine (UU) into the application of soil geochemical baseline data to interpret and characterise glacial deposits and morphological features from two different ice flow events across north Northern Ireland.

Acknowledgements

The authors acknowledge the efforts of all student samplers and BGS/GSNI staff involved during the Tellus geochemical sampling campaigns, sample preparation, analysis and data processing. Further we would like to thank Mike Young (GSNI) for his support and for his valuable comments on this study.

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Summary

This report describes results of a preliminary study using Tellus soil geochemical baseline data to investigate the character and spatial variation of glacial deposits located north and south of the Armoy Moraine which marks the limit of two different ice flow events in north Northern Ireland.

The first part of the report introduces the study area and describes the regional glacial geomorphology and soil geochemical and geological data

The second part of this report discusses the multivariate analysis used to interrogate the soil geochemical data with the aims of a) establishing element associations for the different glacial deposits, b) ascribing these geochemical signatures to potential source bedrock and, as a result of these c) reconstructing ice flow trajectories.

This preliminary study has established that there are distinct geochemical variations in soils derived over glacigenic sediments and related landforms in the area north and south of the Armoy Moraine, which supports the case that they have been formed by ice flowing from different directions. .

Indicator elements for soils formed north of the Armoy Moraine in the area glaciated by an ice advance made by the Scottish ice sheet, that flowed onshore and created the Armoy Moraine, are rare earth elements (REE) Ce and La, as well as Nb As, Th and Rb.

Soils south of the Armoy Moraine that formed over glacial sediments and landforms that were generated by ice flowing northwards out of the Lough Neagh basin are dominated by the geochemistry of major oxides and base metals. Key indicator elements are Co, Ni, V, Fe_2O_3, MgO and Cr, which tie them to basalts of the Antrim Lava Group of the Antrim plateau.

This study shows that geochemical baseline data is an an important tool for investigating glacial sediments and geomorphological features formed by glacial ice advances and offers real potential to help unravel former ice sheet histories

1 Introduction

The glacial landforms and sediments that cover large parts of Ireland record a complex history of ice sheet advance and retreat during different phases of the last Irish Ice Sheet (e.g. Greenwood and Clark, 2008). A clear example of such complexity is located in County Antrim where landform assemblages have been generated by ice flowing from both Scotland and Ireland and are separated by a large moraine complex known as the Armoy Moraine.

Due to this complexity glacial sediments are extremely heterogeneous in their make-up; their composition of size fraction can vary from clay to cobbles due to several factors, including ice flow velocity and the source material which has been incorporated. For this reason glacial sediments, such as tills are the most difficult superficial deposits to describe and classify, but are crucial to the reconstruction of former glaciations and the understanding of ice sheet behaviour and past climates (Evans, 2007). A significant challenge of working with data from the geological record is gathering enough evidence over a wide area to provide a regional-scale perspective of the ice mass. Several research programs have attempted to address this issue using remote sensing techniques which have the advantage of providing imagery of former ice sheet beds at a regional or national scale which allow widespread mapping of glacial landform assemblages (e.g. Clark and Meehan, 2001; Dunlop and Clark, 2004; Greenwood and Clark, 2008). Such studies rely on satellite imagery, Digital Terrain Models (DTM) and offshore multibeam bathymetry data to reconstruct palaeo ice sheet activity and have been applied in both Britain and Ireland and on the continental shelf west of these landmasses (Bradwell et al., 2008; Greenwood and Clark, 2008; O Cofaigh et al., in press). An alternative approach to this method is to examine the spatial variation in the composition and provenance of regionally extensive till sheets in order to reconstruct former ice flow paths (Larson and Mooers, 2005). Such approaches require a high density and spatial distribution of data points, and have been widely employed for drift prospecting in mid- and high-latitude regions formerly glaciated by the Laurentide and Scandinavian ice sheets (McClenaghan et al., 1992; Klassen, 2001; Sarala, 2005).

Traditionally, geochemical mapping has been carried out for two main purposes; firstly, for mineral exploration studies and secondly for application in environmental management However, Scheib et al. (2009a,b) have evaluated the application of regional-scale soil geochemical baseline data for glacigenic sediment provenancing in central England. This study utilised high-density (1 sample per 2 km^2) geochemical soil data from the Geochemical Baseline of the Environment (G-BASE) project from sites collected over Middle Pleistocene till deposits of the Anglian glaciation. The use of multivariate analytical techniques showed distinct geochemical signatures within soils formed over these till deposits. Linking these signatures to potential source material allowed the successful reconstruction and testing of several ice flow models across central and eastern England.

High resolution geochemical baseline data collected by the Geological Survey of Northern Ireland's (GSNI) Tellus survey in Northern Ireland (NI) allows the approach described by Scheib et al. (2009a; in press) to be applied in this region. This study used Tellus soil geochemical data at a resolution of 1 sample per 2 km^2 in combination with glacial geomorphological and superficial sediment maps to classify the geochemical separation and characterisation of glacial regions and features in the area of the Armoy Moraine, north County Antrim.

1.1 STUDY AREA

The study area is situated in the region of the Bann river valley that stretches from the shores of Lough Neagh in the centre of Northern Ireland to the North Antrim coastline on the north coast of Northern Ireland (Fig. 1). The site spans a wide corridor that that measures approximately 35 km wide by 65 km and covers an area ca. 2200 km^2. This study area was chosen as a test site to investigate the geochemical signatures of tills in this region to establish whether this technique might be useful to help unravel ice sheet history in Ireland. This region is a prime area to test the technique because it is known to contain tills that were formed by two different ice flow events during the last glacial period (McCabe and Dunlop, 2006; McCabe, 2008). One was formed by ice that flowed northwards along the Bann valley out of the Lough Neagh Basin creating a prominent drumlin swarm that runs the length of the valley. The other flowed southwards from Scotland into north Antrim and created a prominent moraine ridge known as the Armoy Moraine that separates both ice flow events (McCabe and Dunlop, 2006). If it can be established that the tills generated by the separate ice flow events have unique or statistically separable geochemical signatures then the technique might be useful in helping to unravel ice flow histories in other parts of Ireland where the flow patterns are more complex and interpretations remain controversial. High resolution geomorphological and geochemical data already exists for the region which will be used for this study. The data consists of i) over 600 individually drumlins that straddle both sides of the Armoy Moraine that have been mapped from a GSNI 5 m DTM and ii) a geomorphological map of the Armoy Moraine (both provided by the UU) and iii) high-density soil geochemical baseline data from the Geological Survey of Northern Ireland's (GSNI) Tellus project.

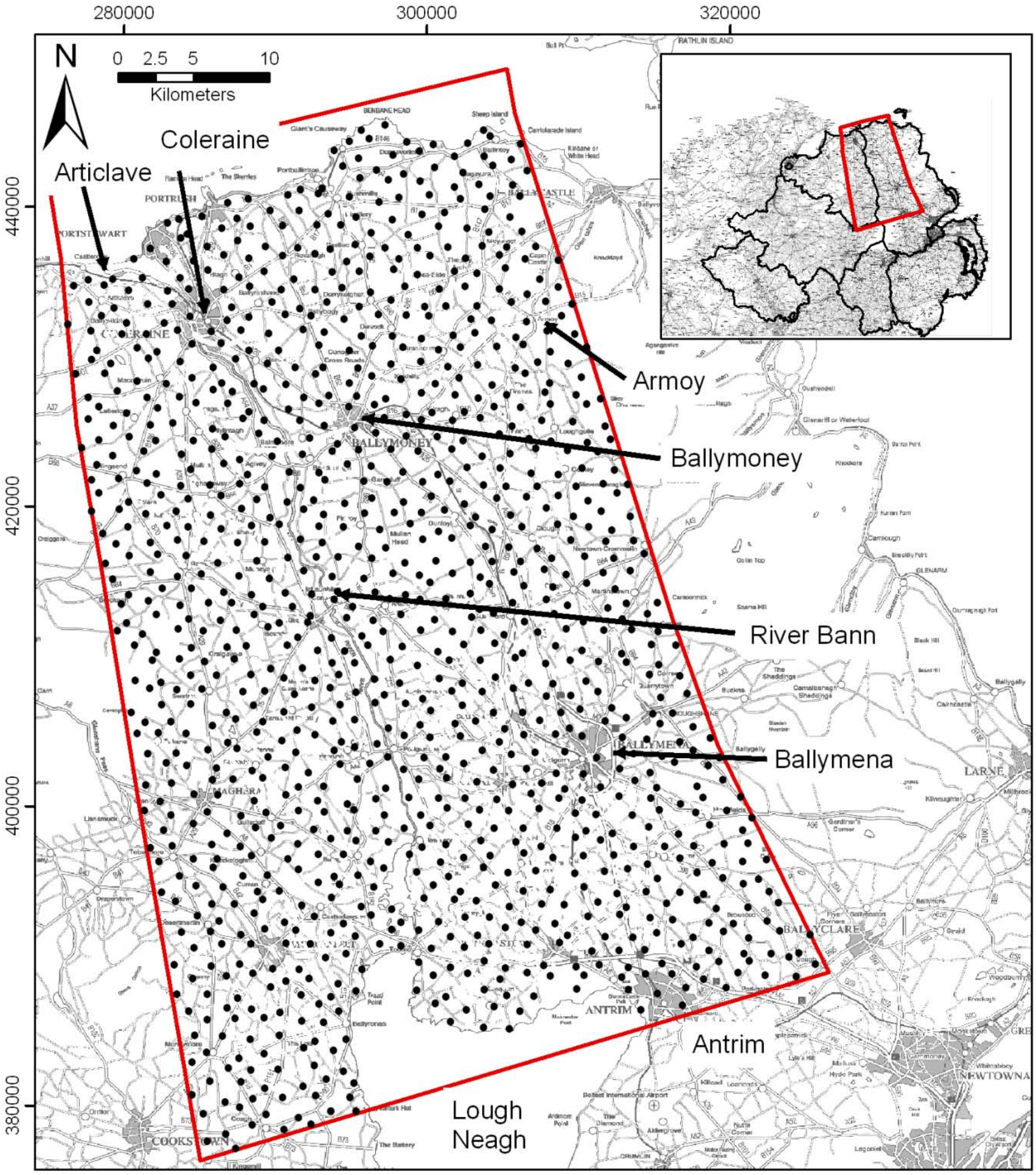


Figure 1: The study area and main places discussed in the text. Black dots indicate Tellus soil sample sites which are at an average density of 1 per 2 km^2.

1.2 GEOLOGY AND GLACIAL HISTORY OF THE STUDY AREA

This section provides a brief summary of the main bedrock geology as well as the glacial history and related deposits across the study area. The area shown in Figure 1 has been exposed to a sequence of glacial and climatic events that occurred in northeast Ireland during the Late Devensian period between 17 kyr and 13 kyr before present (McCabe and Dunlop, 2006).

1.2.1 Bedrock Geology

Figure 2b displays the bedrock geology of the study area. The dominant bedrock rocks are Palaeocene basalts of the Upper and Lower Basalt Formation that form the Antrim Plateau. A small area to the northeast is underlain by Dalradian Schists. Outcrops in the southwest consist of a sequence of limestone, sandstone and mudstone rocks of the Carboniferous and Permian-Triassic, which are separated by a small Ordovician granite intrusion.

A Palaeogene intrusive rhyolite complex, which forms the Tardree Mountains, is indicated by the yellow circle on Figure 2 as it is not shown by the 1:250 000 bedrock geology map.

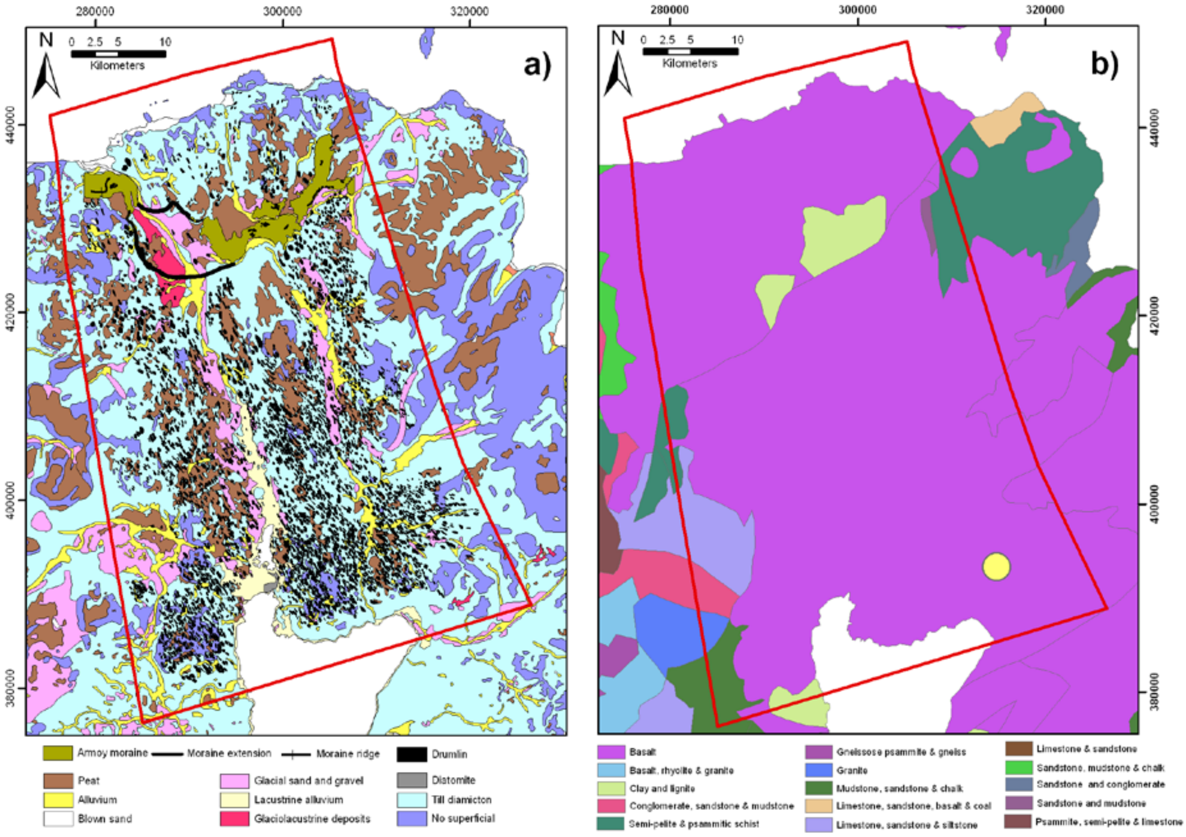


Figure 2: (a) 250k superficial geology and (b) simplified 250k bedrock geology map of the study area. Superficial geology includes over 600 mapped drumlin polygons (black) and the Armoy Moraine to the north (data by P Dunlop).

Both the Tardree complex and the Basalt formations are part of the Antrim Lava Group with an age of 62 to 58 Ma.

1.2.2 Quaternary deposits

The superficial geology map (Fig. 2a) shows a heterogeneous pattern of sedimentary deposits covering the entire study area. The most dominant are glacigenic deposits such as tills (diamictons) and glaciofluvial sand and gravel deposits. However, more recent Hollocene alluvium and peats occur in the region. The most prominent glacial feature in the Bann valley is a large drumlin swarm of over 600 drumlins (Fig. 2a) (Spagnolo et al., 2010). The drumlins all have the same north-northwest alignment that gives the landscape a streamline appearance. The orientation clearly indicates that this drumlin field was generated by a northwards advance of Irish Ice that came from the Lough Neagh Basin and flowed northwards towards the north Antrim coastline (Fig. 3) (McCabe and Dunlop, 2006). This advance has not been dated radiometrically, but is of similar strength to those of the Killard Point Re-advance that peaked between 13.9 ±105 and 13.7±115 ^{14}C ka BP (16.7 and 16.4 cal ka BP) (AA22820, AA22821) (McCabe, 2008).

The other major glacigenic feature in the region is the prominent belt of moraine ridges (< 5km wide and 40 km long) stretching from Armoy in the east to Articlave in the west and which is convex southwards. This is the Armoy Moraine, which stratigraphically overlies the Bann valley drumlin field (Fig. 3). The moraine system is known to contain erratics of Scottish provenance and has glaciotectonic structures created by ice pressures from the north (Fig. 3). It consists of a nested series of linear ridges with discrete crest lines. The moraine is mostly intact except in places where melt water erosion along the channel of the River Bann has removed sediment and cut through the structure (McCabe and Dunlop, 2006). The clast content of the moraine deposits consists of mainly locally derived basalts, but also includes coarse grained granite, Cretaceous chalk and flint, quartzite and other metamorphic rocks including a far-travelled erratic of Ailsa Craig microgranite from the Firth of Clyde (McCabe and Dunlop, 2006). Based on these erratics of northeastern provenance, glaciotectonic structures within the moraine deposits as well as an ice-toe depression (Garry Bog) immediately north of the moraine, supports the proposition that the ridge building was caused by a Scottish Ice sheet that flowed onshore from Scotland in a southwesterly direction into the Antrim lowlands (Fig. 3) (McCabe and Dunlop, 2006). This moraine postdates the earlier Killard Point Re-advance and marks the limit of a later ice advance that emanated from Scotland and reached its maximum limits ~14.7 cal ka BP (McCabe 2008). AMS ^{14}C dates from the northern part of the Irish Sea Basin show that the final ice advance at 14.7 ^{14}C ka BP was followed by rapid ice sheet wastage which was completed by 14 cal ka BP according to dated organic deposits from the base of Sluggan Bog, County Antrim (Lowe et al., 2004).

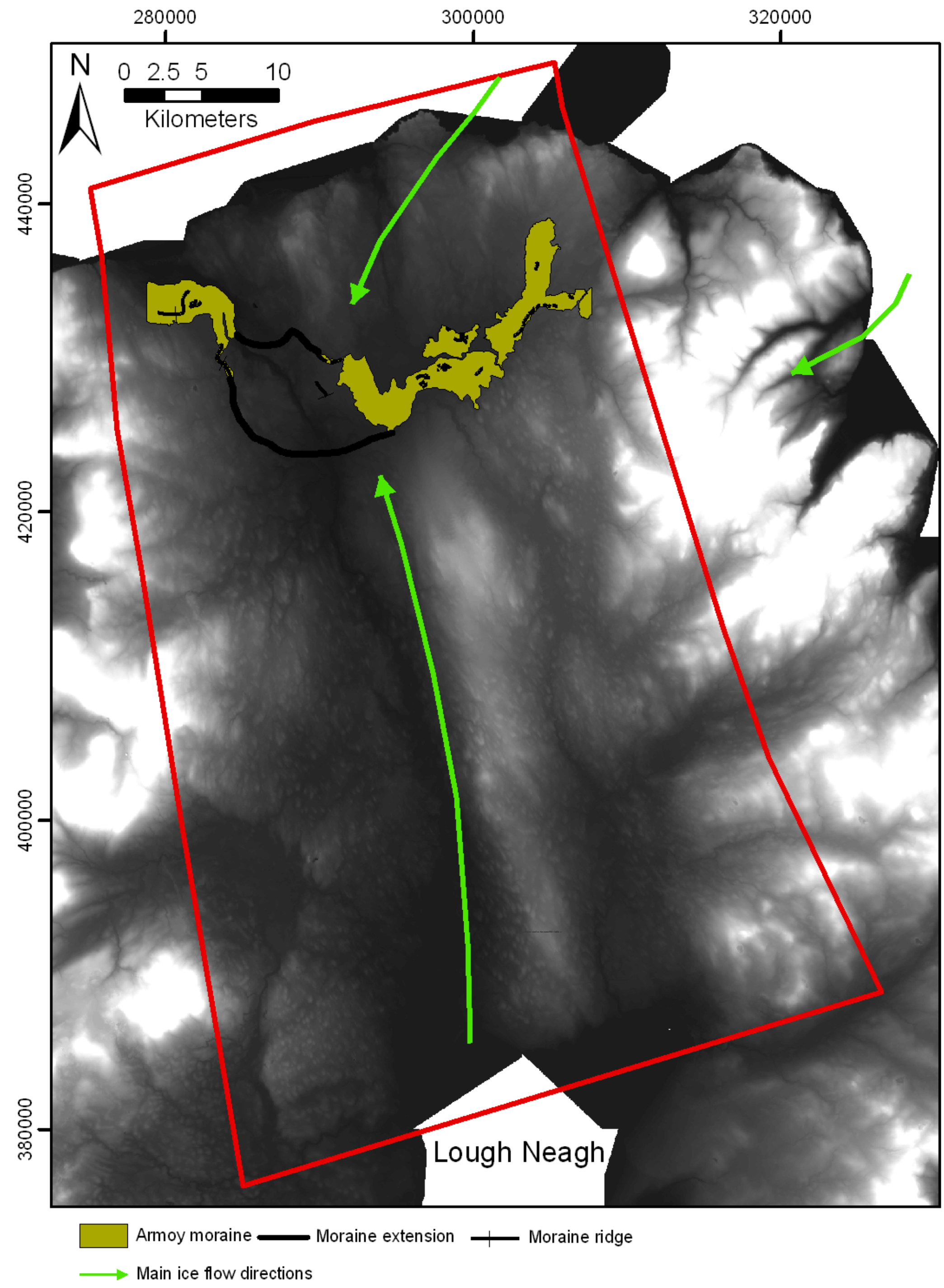


Figure 3: 5 m Digital terrain model (DTM) of the study area showing the extent of the Armoy Moraine (data by Paul Dunlop, UU) and generalised main ice flow trajectories that formed the Bann valley drumlin field and the Armoy Moraine (based on McCabe and Dunlop, 2006).

2 Materials and Methods

2.1 SOIL GEOCHEMICAL BASELINE DATA: SAMPLING, PREPARATION AND ANALYSIS

This study uses data from the Tellus survey of Northern Ireland that was carried out between 2005 and 2007. The survey comprised airborne geophysics and a high-density geochemical survey of the environment, collecting stream sediments, stream waters and soil. Across Northern Ireland almost 6900 soil samples were collected at a regular grid at a density of 1 sample per 2 km^2. Sampling procedures were adapted from the G-BASE project (Johnson et al., 2005) two soil samples were collected at each sample site from standard depths, a surface (5 to 20 cm) and a profile (35 to 50 cm) sample using a handheld auger. Each sample is a composite of five sub-samples taken from the corners and centre of a 20 by 20 m square. The sub-samples were then homogenised and transferred into paper Kraft® bags forming one surface and one profile sample from each site (Johnson et al., 2005). Following collection, surface soil samples were transported to British Geological Survey's laboratories in Keyworth, Nottingham, England, for sample preparation and analysis by X-ray fluorescence spectrometry (XRFS). First, the soil samples were dried at below 30^{o} C then sieved to < 2 mm. The sieved samples were then homogenised, coned and quartered and a 30 g sub-sample ground in an agate planetary ball mill until 95 % are < 53 µm before analysis by XRFS. This provides analytical data of total concentration for elements Ag, Al_2O_3, As, Ba, Bi, Br, CaO, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe_2O_3, Ga, Ge, Hf, I, In, K_2O, La, MgO, MnO, Mo, Na_2O, Nb, Nd, Ni, P_2O_5, Pb, Sb, Sc, Se, SiO_2, Sm, Sn, SO_3, Sr, Ta, Te, Th, TiO_2, Tl, U, V, W, Y, Yb, Zn and Zr. Additional to the analytical procedures, pH and loss on ignition (LOI) were also measured on each soil sample.

Prior to presentation and interpretation the analytical data undergo rigorous quality assurance procedures, which involve the verification, quality control and data levelling processes that are necessary to make the data fit for the purpose (Johnson et al., 2008).

Information on the Tellus survey and geochemical baseline data including maps can be found online at http://www.bgs.ac.uk/gsni/tellus/geochemical_survey/index.html.

2.2 INITIAL GEOCHEMICAL DATA ASSESSMENT

The initial dataset for the study area comprises XRFS data for a total of 1074 topsoil samples. Geochemical data for each sample site was, in the first instance, spatially joined with several spatial datasets including the 1:250 000 Superficial Geology of Northern Ireland, drumlin and Armoy Moraine data (based on intersects within 20 m). This was carried out using the spatial join tool in ArcGIS v9.2. Additionally, each site was classed based on whether it was collected to north of the Armoy Moraine (group 1), within the moraine (group 2) or to the south of the moraine (group 3).

In the first instance, we excluded sites from the dataset that were located directly over bedrock based on the 1:250 000 Bedrock Geology, unless they fell within a drumlin feature that was mapped in that area. In a further step we excluded data for peaty soils based on LOI values greater than 50 % as high organic carbon content in soils can significantly influence the levels of, for example base metals, such as Cr or Pb due to either dilution effects or accumulation through atmospheric fall-out from anthropogenic sources (Scheib, 2010). As a result of these exclusions the total topsoil data were reduced to 904 sites from the original 1074.

This dataset was further assessed by calculating descriptive statistics and generating probability plots to exclude data for elements that either have issues with the lower limits of detection or are potentially influenced by anthropogenic activities.

Based on the above, the study used the following elements Al_2O_3, As, Ba, CaO, Ce, Co, Cr, Cu, Fe_2O_3, Ga, Hf, K_2O, La, MgO, MnO, Nb, Ni, Rb, Sc, Se, SiO_2, Sr, Th, TiO_2, U, V, Zn and Zr.

2.3 MULTIVARIATE DATA ANALYSIS – PCA

Principal Component Analysis (PCA) is a multivariate analytical technique and a commonly used tool in geochemistry to investigate and manipulate large datasets of multi-element geochemical data. It has also been widely used in Quaternary studies to identify key variables within a dataset, and to determine how different variables inter-relate (Richards, 1998, 2002; Lee, 2003; Scheib et al., 2009a).

PCA was used to examine the relationship between the different geochemical elements and in relation to glacial features. However, because the element geochemical data of most elements was non-normally distributed and PCA is sensitive to non-normalised data, the dataset for the 904 samples was log-transformed prior to analysis (Pison et al., 2003).

PCA extracts a smaller number of uncorrelated variables from a large set of data. The goal is to explain the maximum amount of variance with the fewest number of principal components (PC). It was carried out in Minitab v15©, using a correlation matrix and varimax rotation. Firstly, the the number of variables is reduced to form a small number of independent principal components (PC) representing the main variability of the data. Secondly, more interpretable combined variables are created.

Results of a PCA are given as a number of PC, which are linear combinations of variables that account for the maximum variance within the set (Dunteman, 1989). The programme calculates several PCs until 100 % of the variance is explained. Component loadings (or coefficients) of each element will indicate how much each element is represented by each PC. It also computes eigenvalues and the proportion of variance for each PC. The eigenvalue represents the sum of the squared component loading and the variance (%) is calculated by dividing this eigenvalue with the number of variables used (in this case n = 25) and multiplied by ten (Johnston, 1978).

Additionally, we calculated component or loading scores, which are a linear combination of the individual soil site data and the component loadings, for each individual sample site. The scores were also calculated for each of the principal components and are greatest, if both the reported concentrations of element as well as their loading are high (Johnston, 1978). In the results section, this component score distribution will help to interpret the different PCs in a spatial context.

3 Results – Soil geochemical signatures

The focus of this results section will be to describe and establish geochemical signatures in soils derived over different glacial deposits and in relation to the two different ice advances. To compare these signatures with the overall baseline geochemistry of the study area, we included a summary of descriptive statistics of the Tellus soil geochemical data for the selected elements and sites within the study area (Table 1).

Table 1. Summary statistics of soil geochemical data from 28 elements selected for this study (n=904).

Element	Minimum	Mean	Median	Maximum	Skewness	StDev
Al_2O_3	5.9	12.6	12.8	16.5	-0.87	1.85
As	0.5	6.0	5.8	29.1	1.79	2.42
Ba	158	313	309	1193	3.64	85.4
CaO	0.4	1.8	1.8	4.8	0.43	0.66
Ce	16.0	29.1	28.0	82.0	2.79	7.32
Co	2.0	32.8	33.6	64.8	-0.32	12.4
Cr	29.1	249	237	816	0.95	108
Cu	3.6	78.8	75.9	216	0.52	34.8
Fe_2O_3	0.8	8.0	8.2	14.1	-0.50	2.47
Ga	3.4	15.2	15.7	31.1	-0.74	3.40
Hf	2.3	4.9	4.8	12.7	1.12	0.96
K_2O	0.3	0.9	0.8	3.7	1.90	0.46
La	8.0	15.1	14.0	40.0	2.42	4.11
MgO	0.5	2.0	1.9	4.1	0.38	0.64
MnO	0.0	0.1	0.1	0.8	1.44	0.07
Nb	6.4	9.8	9.5	26.1	1.97	1.89
Ni	5.8	106	104	280	0.25	48.5
Rb	5.4	25.6	23.4	88.2	1.25	13.3
Sc	2.5	19.9	20.1	35.4	-0.35	5.94
Se	0.1	0.9	0.8	2.7	1.45	0.33
SiO_2	25.8	45.9	44.8	78.8	1.02	7.98
Sr	18.3	93.6	87.2	293	1.39	36.1
Th	0.2	2.9	2.7	9.7	1.48	1.31
TiO_2	0.3	1.1	1.2	2.0	-0.71	0.28
U	0.0	1.6	1.6	6.3	1.34	0.54
V	26.8	181	186	384	-0.46	56.3
Zn	13.3	103	105	247	-0.06	33.3
Zr	61.4	155	149	666	2.21	48.6

3.1 ELEMENT ASSOCIATIONS IN RELATION TO GLACIAL AREAS AND FEATURES

This section describes a first attempt to establish the geochemical variability in soils from areas influenced by the different glacial events and ice sheets (described in section 2.1). Therefore, the geochemical data were separated into three groups. Group 1 includes soil data for the area north of the Armoy Moraine, Group 2 data from within the Armoy Moraine and Group 3 the largest, southerly area between the Armoy Moraine and Lough Neagh.

Soil geochemical data of the 28 selected elements are displayed as boxplots below (Fig. 4), displaying the middle 50 % of the data indicated by a grey box and the upper and lower 25 % of the data indicated by whiskers. For improved inter-comparison, we included a median connect line in each graph. Data distribution show that median elements concentrations of As, Ga, Nb , Sr, Th, U are highest within Group 1, the area that was affected by a Scottish ice sheet. Median values of the these elements, as well as Ba, Ce, Hf, K_2O, La, Rb, SiO_2 and Zr, are amongst the highest in soils collected within the Armoy Moraine (Group 2). Concentrations of remaining analytes comprising major oxides and base metals are highest in soils collected within Group 3, the area that was glaciated and covered by an ice sheet originating from Lough Neagh.

This simple break-up of the data shows a definite change in soil geochemistry from glacial areas 1 and 2 to Group 3. Glacial deposits north of the Armoy Moraine and the moraine itself are compositionally linked.

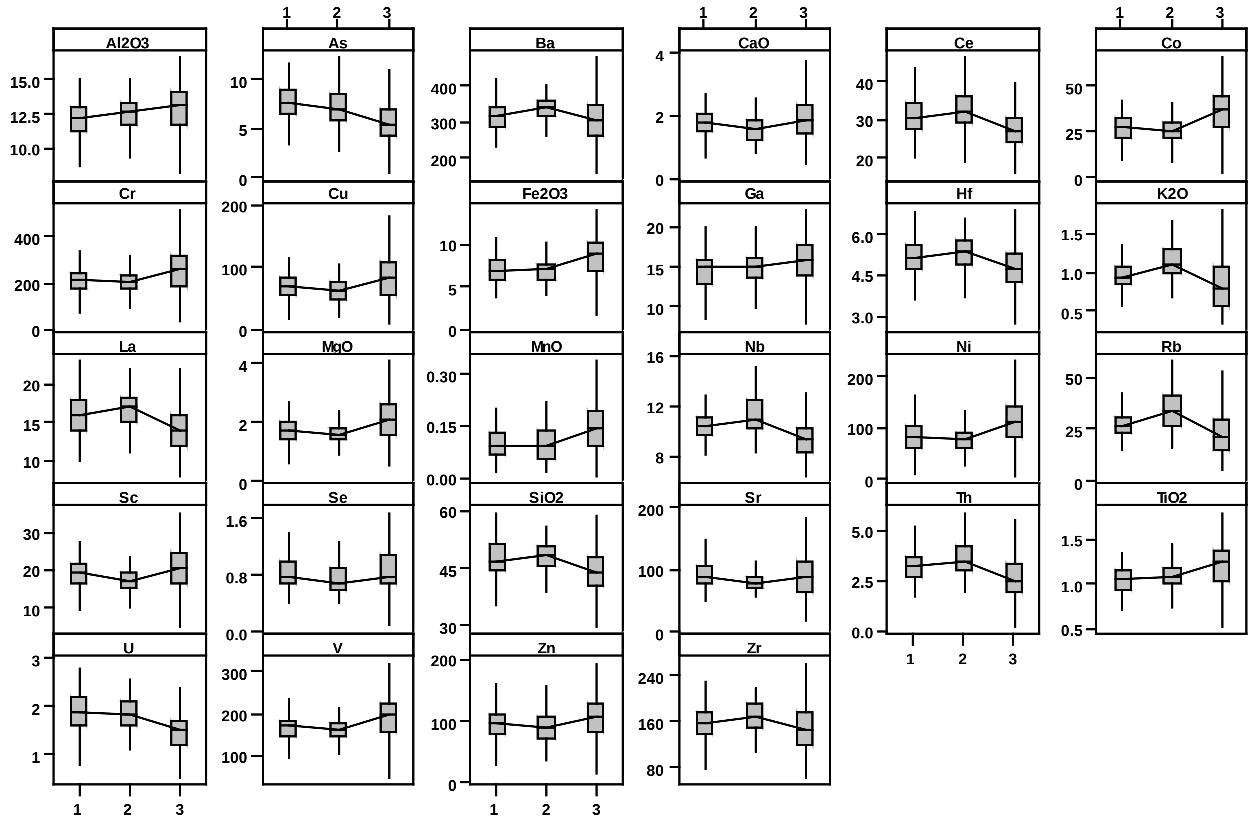


Figure 4: Box plots displaying concentration ranges for 28 elements and compounds in topsoils collected within glacial Group 1 (n=109), Group 2 (n=70) and Group 3 (n=725). Graphs present the middle 50% of the data as an interquartile range box and the upper and lower 25 % as whiskers.

Figure 5 displays box plots of soil geochemical data only for sample points that fell in a mapped drumlin feature (see Fig. 2) in an attempt to establish soil geochemical signatures in morphological features and landforms within the three glacial areas.

Generally, the trend seen in Fig. 4 is still the same. Especially, concentrations of base metals and major oxides are higher in drumlins within Group 3. Plots for Group 1 and 2 have changed slightly. Most median concentrations of those elements that were highest in Group 1 are now higher for Group 2 and vice versa. However, these results should be treated with care as they are based on a very low number of samples.

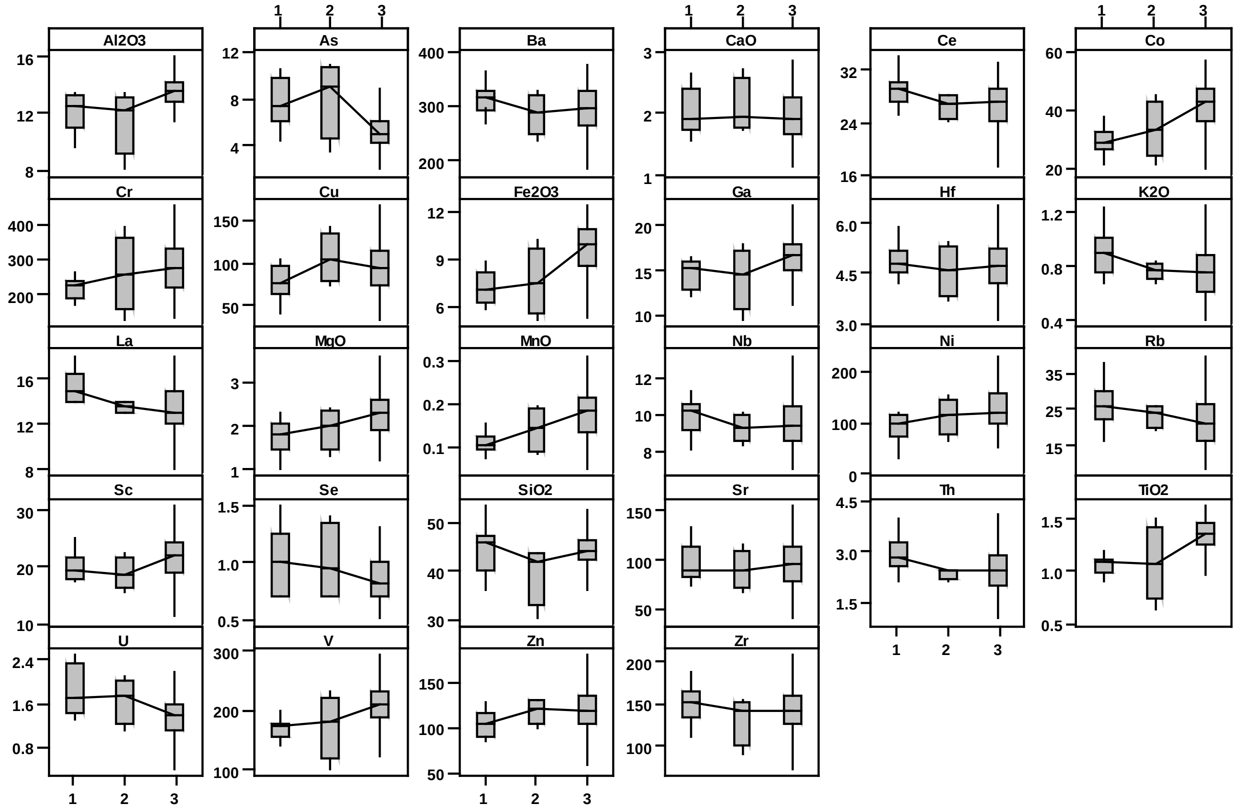


Figure 5: Box plots displaying concentration ranges for 30 elements in soils collected within drumlins of Group 1 (n=9), Group 2 (n=4) and Group 3 (n=150). Graphs present the middle 50% of the data as an interquartile range box and the upper and lower 25 % as whiskers.

3.2 PCA RESULTS – ELEMENT ASSOCIATIONS

The previous section presented the geochemical data for each element in relation to three broad glacial areas. Here, the PCA results of the main element associations are presented across the study area within the geochemical dataset to see if these correspond to particular glacial areas.

PCA calculated a total of 28 PCs until 100% of the variance within the data were explained. The PCs receiving highest eigenvalues, and comprising variables with high factor loadings, were assumed to be the variables that best represent the geochemical characteristics and element associations within the data. Figure 6 shows a typical eigenvalue plot as produced by PCA that indicates the significance of the derived PCs (Grunsky and Smee, 1999). The plot shows a sharp decline of eigenvalues within the first three PCs, which means that most of the data variation is explained by these components. In fact, PCs with eigenvalues < 1.0 were excluded from further interpretation, as suggested by Mandal et al. (2008).

The first four PCs (PC1 to PC4) have eigenvalues > 1 and represent 82 % of the total variance. Figure 7 displays the element loadings for the first four PCs as bar charts accompanied by a table listing their actual loading values. The higher the individual element loading the stronger its association to the repsective component.

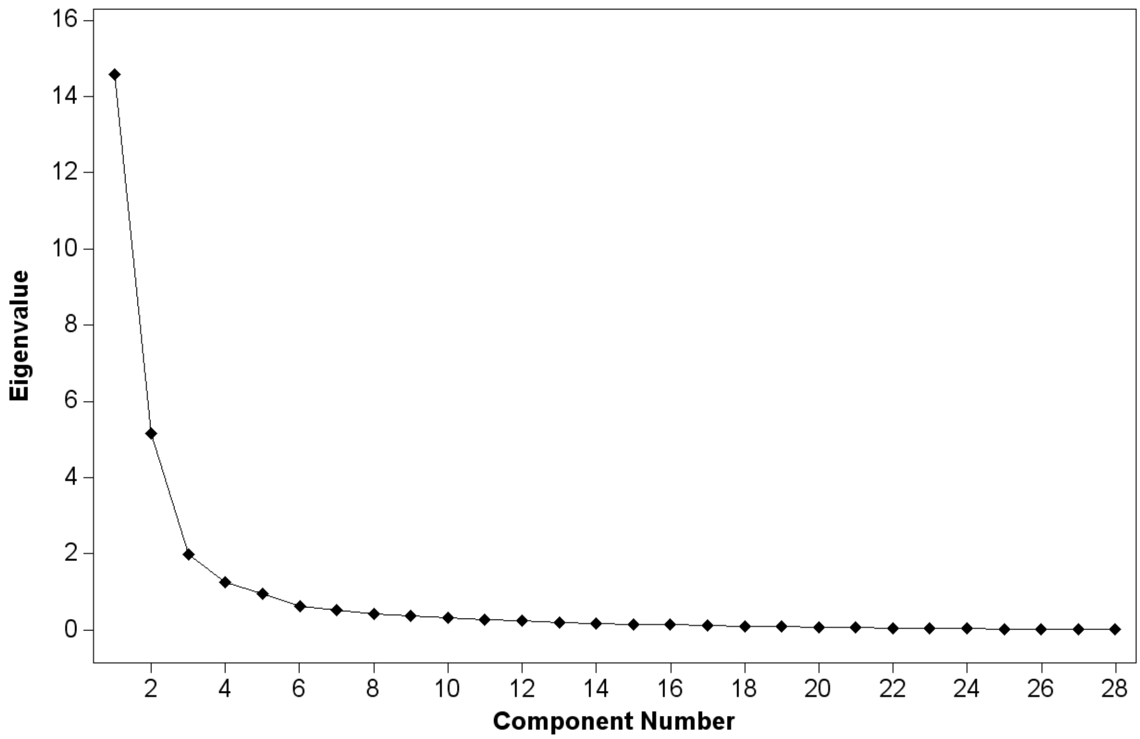


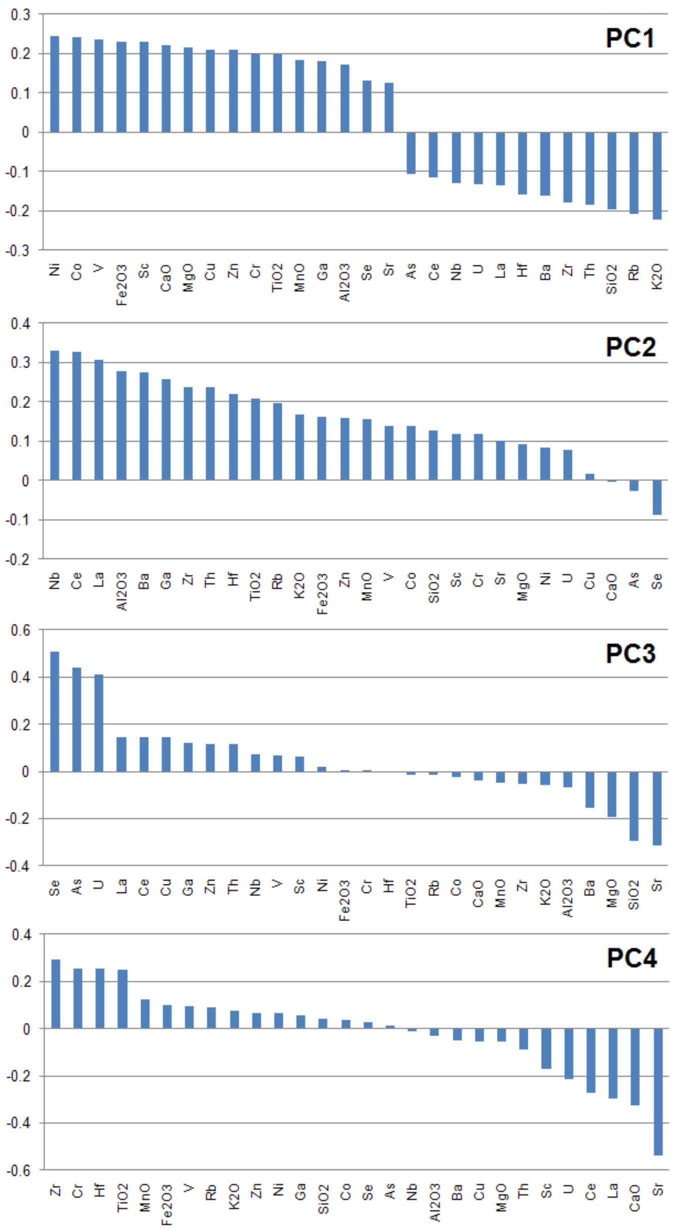
Figure 6. Eigenvalue plot produced by PCA.

The most dominant component, with an eigenvalue of 14.6, is PC1 representing a variance of nearly 52 % of the data. Almost all major oxides and base metals are associated in this component, with strongest, positive loadings (>0.2) from CaO, Co, Cr, Cu, Fe_2O_3, MgO, Ni, Sc, TiO_2, V and Zn. In relation to these, PC1 also displays a negative related asociation of Hf, K_2O, Rb, SiO_2, Th and Zr (loadings < -0.2)

PC2, with an eigenvalue of 5.2, accounts for 18.4 % of the data and represents a positive element association of Al_2O_3, Ba, Ce, Ga, Hf, La, Nb, Rb, Th, TiO_2 and Zr with loadings > 0.2. Some of the elements associated in PC1 have positive loadings at around 0.1.

These first two PCs account for over 70 % of the variance within the dataset. A good way of visualising the element associations and relations is in a loading plot (Fig. 8). It shows a distinct separation of the elements into two halves. Al_2O_3 and Ga for example have strong loadings in both PC1 and PC2, whereas loadings of Cu and CaO are only strongest in PC1. On the other hand, strong loadings of elements of PC2, for example Rb and K_2O are negatively related to PC1.

PC3 accounts for 7.1 % of the data variance and has an eigenvalue of 2.0. Elements associated are As, Se and U, with strong negative loadings of SiO_2, Sr and MgO. PC4 accounts for a further 4.5 % of the variance with an eigenvalue of 1.3. Elements associated in PC4 are Cr, Hf and Zr with strong negative loadings for CaO, Ce, La, Sr and U. Most elements with strong positive loadings in PC2, 3 and 4 are negative in PC1.



Variable	PC1	PC2	PC3	PC4
Al_2O_3	0.17	0.28	-0.07	-0.03
As	-0.11	-0.03	0.44	0.02
Ba	-0.16	0.28	-0.16	-0.05
CaO	0.22	0.00	-0.04	-0.33
Ce	-0.11	0.33	0.15	-0.27
Co	0.24	0.14	-0.03	0.04
Cr	0.20	0.12	0.00	0.26
Cu	0.21	0.02	0.16	-0.05
Fe_2O_3	0.23	0.16	0.00	0.10
Ga	0.18	0.26	0.12	0.06
Hf	-0.16	0.22	0.00	0.26
K_2O	-0.22	0.17	-0.06	0.08
La	-0.13	0.31	0.15	-0.30
MgO	0.22	0.09	-0.20	-0.06
MnO	0.18	0.16	-0.05	0.13
Nb	-0.13	0.33	0.07	-0.01
Ni	0.25	0.08	0.02	0.06
Rb	-0.21	0.20	-0.01	0.09
Sc	0.23	0.12	0.06	-0.17
Se	0.13	-0.09	0.51	0.03
SiO_2	-0.20	0.13	-0.30	0.04
Sr	0.13	0.10	-0.31	-0.54
Th	-0.19	0.24	0.11	-0.09
TiO_2	0.20	0.21	-0.01	0.25
U	-0.13	0.08	0.41	-0.21
V	0.24	0.14	0.07	0.09
Zn	0.21	0.16	0.12	0.07
Zr	-0.18	0.24	-0.05	0.30
Eigenvalue	14.6	5.2	2.0	1.3
Variance (%)	52.0	18.4	7.1	4.5

Figure 7. Bar chart of element loadings for PC1, PC2, PC3 and PC4 and table of actual loading values including the eigenvalues and proportion of variance in % (n=904)

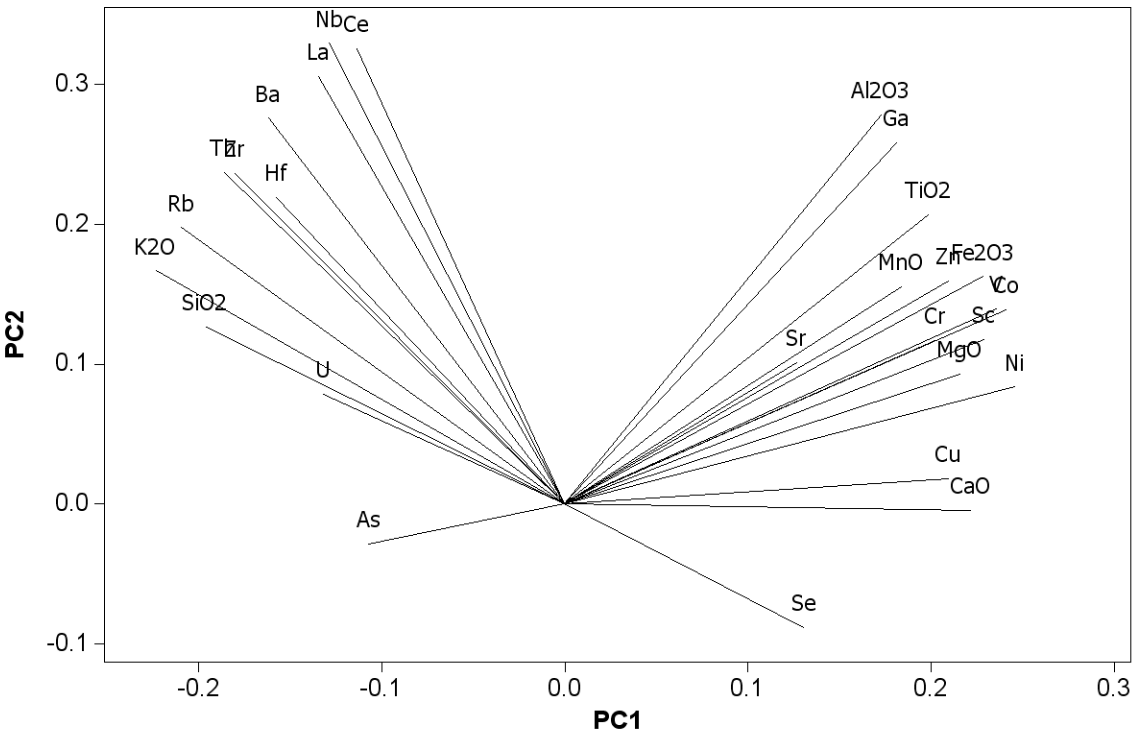


Figure 8: Loading plot for PC1 and PC2

3.3 PCA RESULTS – SPATIAL LOADING SCORE DISTRIBUTION

PC scores were also calculated as part of the PCA, which are used to spatially interpret and identify the element associations, described in the previous section. These scores, which are a linear combination of the individual sample data and the component loading, were calculated for each PC and each individual sample site. The basic rule is, the higher the concentration of an element that also has a high loading in a particular component, the larger the score will be (Johnston, 1978). Scores for PCs 1 to 4 are plotted as graduated colour dot maps seen below (Fig. 9).

3.3.1 Score distribution of PC1

The map of PC1 scores is geochemically most distinct. Highest PC1 scores that represent elevated levels of base metals and some of the major oxides are dominant within the eastern half of the study area.

Sites with highest negative scores that relate to elements with strong negative loadings such as K_2O, Rb and SiO_2, are located in the lower western corner of the study area. The latter area corresponds to mainly sedimentary strata of Carboniferous to Cretaceous age, including a smaller Ordovician intrusive inlayer.

The Armoy Moraine seems to form, especially its eastern half, a geochemical boundary, as the dominant geochemical signatures representing PC1 only reach as far as the southern edge of the moraine. Geochemical data of soil samples collected within and beyond (north of) the Armoy Moraine, do not represent element associations highlighted by PC1.

This is evidence of glacial deposits formed by a different glacial ice advance and source material in this area. The lack of a PC1 geochemical signature in soils east of the Armoy Moraine also suggests an influence of a different ice advance.

A strong geochemical signature of negative PC1 scores can be seen in the southeast of the study area which can be closely linked to bedrock lithology of the Tardree complex.

3.3.2 Score distribution of PC2

In comparison to the map of PC1 scores, the spatial patterns in PC2 are less distinct and show only a few areas with spatial geochemical variation. The highest PC2 scores were calculated for sample sites in the southeast of the study areas near Ballymare (Fig.1), which closely relate to the Tardree ryholite complex. Other high positive scores are located within the Armoy Moraine as well as further north towards the coast. The eastern half of the study area, particularly between the Armoy Moraine and Ballymare, which was dominated by high scores of PC1, displays low to negative scores for PC2. Overall, PC2 suggest a reverse score distribution to PC1, which corresponds with the component loadings shown in Fig. 7.

3.3.3 Score distribution of PC3 and 4

Scores for PC3 scatter rather randomly across the study area. However, most of the higher scores tend to be located in the northern half of the study area, with the low to negative scores being more abundant in the south of the study area.

The most interesting feature of PC 3 and 4 are high scores of PC4 that represent an element association of Cr, Hf, Zr and TiO_2. These plot mainly along the western edge of the study area. This group of elements is interesting as these have been used elsewhere to identify aeolian deposits, such as loess and coversands (Scheib and Lee, 2010; Taylor et al., 1983).

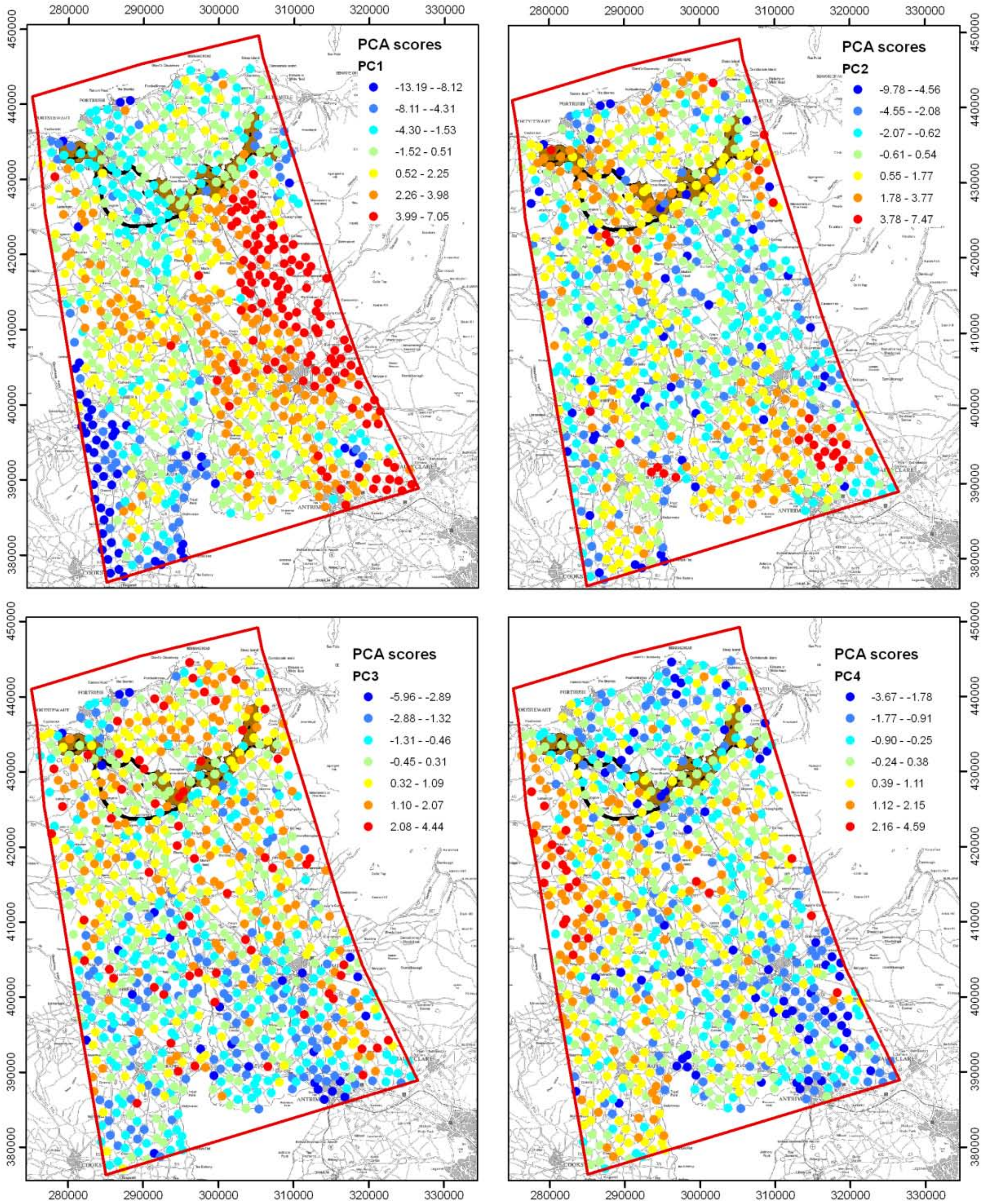


Figure 9: Principal component scores for PC1, PC2, PC3 and PC4.

4 Discussion

This section discusses some interesting element associations within the dataset that suggest geochemically distinct zones within the study area. This section discusses the main findings and their relation to bedrock geology and the glacial events that affected the soil geochemistry.

Separating the study area into regions based on their different glacial events showed a variation in element concentrations. Almost the entire study area is underlain by the same bedrock geology (Fig. 3), which suggests that differing soil geochemical signatures and element concentrations have to some degree been influenced by superficial and glacigenic deposits. Results of the PCA will help to distinguish the main element associations and their spatial relation to bedrock and glacial history in the study area.

The element association and distribution of scores for PC1 suggest a strong bedrock signature in soils. This especially is the case over the elevated areas of the eastern part of the study area (glacial area 3), where we identified a strong basaltic signature of base metals and major oxides in these soils. These signatures, although slightly weaker, can also be seen on the western side of the River Bann. Another subtle feature of negative PC1 scores seems to coincide with sample sites along the River Bann south of the Armoy Moraine. This signal could relate to alluvial outwash material and glacial sand and gravel (Fig. 2).

Further southwest the strong positive signature is absent and indicates instead negative loading scores (Figs. 6 and 8). This area is underlain by sedimentary strata of Carboniferous to Permian age as well as an Ordovician granitic intrusion (Fig. 2), which seem to have a strong influence of the soil geochemistry in this particular area.

We established that the dominant features of PC1 are bedrock related. However, the basaltic feature disappears abruptly at the southern limit of the Armoy Moraine. The latter together with glacial area 1 beyond and north of the moraine, displays a much weaker even a non-existent basaltic geochemical signature despite being located over basaltic bedrock. This geochemical indifference suggests that the soil geochemistry to the north must have been influenced by another, geochemically different source material. This is also suported by data shown in Figs. 4 and 5, where base metals and major oxides concentations, related to basalts, are much lower in Groups 1 and 2.

The spatial distribution of scores for PCs 2 to 4 display much weaker spatial patterns. In PC2 the strongest loadings relate to rare earth elements Ce and La followd by Nb, Ba and Ga. Their high scores plot mainly within the Armoy Moraine and towards the coast related to Group 1. This clearly suggests that material deposited in this area has no geochemical signal related to the underlying basalts and is therefore more likely to be associated with the Scottish Ice advance.

Another area of high PC2 scores, that in turn calculated negative score values for PC1, is southeast of Ballymare. Soils in this area are strongly influenced by the underlying Tardree rhyolites of the Upper Basalt Formation, which are geochemically distinct from soils over the basalts of the same formation. This area also displays high scores of PC3 associating As, Se and U.

The geochemical signature shown by PC4 is not related to material deposited directly by one of the last ice advances, but may relate to aeolian sediments deposited under periglacial conditions. Its associated elements Hf, Zr and Ti are known indicators for these type of deposits (Scheib and Lee, 2009; Taylor et al., 1983). The enrichment of Zr and Hf in the silty to sandy fraction of aeolian sediments is due primarily to the resistant nature and the high density (4.6-4.7) of zircon mineral grains. Such minerals can withstand chemical and physical weathering over long geological periods and their density leads to preferential accumulation during wind-related sorting processes (Scheib and Lee, 2010). The occurrence of Cr, also a resitant mineral, could suggest that wind blown material had its source in the east, picking up material of ground and weathered basalts off the Antrim plateau. Wind then transported material in a westerly direction, where it accumulated.

The discussion has so far highlighted several elements, which are either distinct for soils with strong bedrock signatures or may allow us to attribute glacial deposits to different source materials.

- Co, Ni, V, Fe_2O_3, MgO, Cr are indicators for soils in glacial area 3 that formed from superficial deposits with strong basalt signatures.
- Nb, Ce, La, Th and (As) are indicators for soils formed on superficial deposits in glacial areas 1 and 2. These are areas that have not been influenced by the Lough Neagh ice sheet and subsequently incorporated basaltic material. The source of these deposits is most likely the Scottish Ice sheet.

- Rb and K_2O are indicators for soils and their superficial parent material from the south west of the study area, which have strong bedrock signatures from Carboniferous to Permian sedimentary rocks.
- Hf, Zr, Cr and TiO_2 are indicators for resistant minerals accumulated in soils, most likely due to aeolian sediments, which appear to be located along the western edge of the study area.

5 Conclusion

This study has established that there are distinct geochemical variations in soils derived over glacigenic sediments and related landforms in the area north and south of the Armoy Moraine and are due to the glacial activities of two different ice advances.

Indicator elements for soils formed in the area glaciated by the Scottish ice sheet, which flowed onshore and deposited the Armoy Moraine, are the REEs Ce and La, as well as Nb As, Th and Rb.

Soils south of the Armoy Moraine that formed over glacial sediments and landforms of the ice sheet that flowed out of Lough Neagh towards the Armoy Moraine are dominated by the geochemistry of major oxides and base metals. Key indicator elements are Co, Ni, V, Fe_2O_3, MgO and Cr, which ties them to the basalts of the Antrim plateau.

We can conclude that soil geochemical baseline data can be an important and valuable asset in the investigation and interpretation of glacial sediments and morphological features formed by glacial ice advances. This study however, is ony a preliminary attempt and research should be carried out in more depth.

We recommend including a more targeted approach in collecting soil geochemical data, for example, from 1) areas where soils are directly underlain by potential source bedrock. This will help to establish a soil-bedrock signature to enable a more accurate provenancing of glacial sediments, and from 2) areas where soils lie upon specific morphological features such as drumlins and ribbed moraines. This is especially important for areas where both glacial features occur side by side but with different orientations.

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