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Methods used in the Tellus Geochemical Mapping of Northern Ireland

Tellus Geochemistry Programme

Open Report OR/07/022

BRITISH GEOLOGICAL SURVEY

TELLUS GEOCHEMISTRY PROGRAMME

OPEN REPORT OR/07/022

Methods used in the Tellus Geochemical Mapping of Northern Ireland

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Keyworth, Nottingham   British Geological Survey   2007

Keywords

Tellus; Geochemistry; Soil; Stream sediment; Stream water; G-BASE.

Irish Grid Reference

SW corner 190000,310000
Centre point 280000,382500
NE corner 370000,455000

Map

Sheet: Northern Ireland, 1:250 000 scale, Geological Map of Northern Ireland

Front cover

Soil sampling in Co. Fermanagh, 2004.

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BRITISH GEOLOGICAL SURVEY

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Foreword

This report presents the sampling and analytical methodologies employed in the G-BASE and Tellus regional and urban geochemical surveys of Northern Ireland conducted in the periods 1994 – 1996 (G-BASE) and from 2004 – 2007 (Tellus). Detailed accounts of the sampling methodology are presented together with information relating to the analysis of inorganic parameters (i.e., major and minor oxides, trace elements, anions), quality control procedures employed both in the field and during analysis for both the G-BASE and Tellus surveys. The report contains material from the British Geological Survey G-BASE regional geochemistry atlases together with new information specific to the Tellus regional geochemistry program.

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Contents

ACRONYMS

ANOVA	Analysis of variance
BGS	British Geological Survey
CRM	Certified reference material
DARD	Department of Agriculture and Rural Development
DETI	Department of Enterprise, Trade and Investment
DFP	Department of Finance and Personnel
DOC	Dissolve organic carbon
ED-XRF	Energy dispersive X-ray fluorescence
ES	Emission spectrometry
G-BASE	Geochemical Baseline Survey of the Environment
GSNI	Geological Survey of Northern Ireland
GTK	Geological Survey of Finland
ICP-AES	Inductively coupled plasma atomic emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICS	Instrument controlled software
IDW	Inverse Distance Weighting
LIMS	Laboratory information management system
LLD	Lower limit of detection
NPOC	Non-purgeable organic carbon
OSNI	Ordnance Survey of Northern Ireland
PGE	Platinum group elements
PMT	Photo-multiplier tube
RESI	Resource and Environment Survey of Ireland
RM	Reference material
SRM	Secondary reference material
SRW	Secondary reference water
SVOC	Semi-volatile organic carbon
TOC	Total organic carbon
WD-XRFS	Wavelength dispersive X-ray fluorescence spectrometry

FIGURES

TABLES

Summary

The Geological Survey of Northern Ireland (GSNI) and the British Geological Survey (BGS) have completed geochemical surveys of Northern Ireland in three phases of sampling and analysis. Sampling and quality control were undertaken according to the G-BASE protocol of BGS, as follows:

- Stream sediment and stream waters surveys in 1994-96 (2,908 sites in the west) and in 2004-06 (2,966 sites in the east). The sampling distribution averaged one site per 2.4 km^2.
- Soil sampling surveys of rural areas and of selected urban areas in 2004-06. 6,862 sites were sampled at an average of one site per 2 km^2. Two samples were collected at each site, from depths of 5-20 cm and 35-50 cm.
- Soil sampling of the urban areas of Belfast and Londonderry, at 1,315 sites at a distribution of four sites per km^2.

Analyses were undertaken by laboratories (including BGS), selected by open tender, for a range of inorganic compounds and trace elements, as follows:

- Stream sediment and shallow soil samples were analysed by X-ray fluorescence (XRF) spectrometry.
- Shallow and deep soil samples were analysed by inductively coupled plasma (ICP) spectrometry.
- Deep soil samples were analysed for selected elements by fire-assay;
- Stream water samples were analysed by ICP and ion-chromatography.

One quarter of the urban soil samples (one site per km^2) were analysed for a range of semi-volatile organic carbons (SVOCs).

Digital databases and images of the results have been produced.

1 Introduction

The Tellus project comprises an integrated airborne geophysical survey and ground geochemical survey of Northern Ireland. The project was implemented to provide high resolution regional baseline datasets to underpin government and private body policy decisions concerning sustainable economic development, social infrastructure, environment and human health. The project provides datasets and knowledge in support of;

i). Natural environmental baseline- assisting agriculture, water management, pollution mapping and environmental health.

ii). Mineral resource development- recognition of regional anomalies and structural controls, metallogenic provinces.

iii). Geological mapping- improving the knowledge of subsurface geology and structure to support infrastructure development.

The Tellus project was originally conceived as part of an all-Ireland project known as the Resource and Environment Survey of Ireland (RESI). It was intended that RESI would be completed by the Geological Survey of Northern Ireland (Belfast) and the Geological Survey of Ireland (Dublin) under separate government funding bodies. CSA Group Ltd. was appointed to complete a detailed scoping, implementation and costing exercise on the Northern Ireland component of RESI by the Department of Enterprise, Trade and Investment (DETI) for Northern Ireland. This scoping document was completed in October 2003 (O'Neill, 2003).

PricewaterhouseCoopers (PwC) were commissioned by DETI in January 2004 to undertake the Economic Appraisal of the Northern Ireland component of the RESI project using the Northern Ireland Civil Service Green Book guidelines (DFPNI, 2003; H.M. Treasury, 2003). Funding for the Northern Ireland component of RESI was achieved in March 2004 after a successful cost benefit analysis. This report details the sampling and analytical methodology, quality control, data presentation and interpretation parameters of the geochemistry component of Tellus.

The Tellus sampling programme utilised the staff, procedures and practices of the British Geological Survey's G-BASE (Geochemical Baseline Survey of the Environment) programme. A brief summary of the sampling methodology is presented as part of this report. A more comprehensive account of the G-BASE sampling methodology is presented in Johnson (2005). Additional information describing differences to the G-BASE methodology implemented by the Geological Survey of Northern Ireland (GSNI) for the Tellus survey is presented in this report.

2 Previous Geochemical Surveys

At the time of commencement of the Tellus geochemistry survey in 2004 several regional type geochemical programmes had been conducted in Northern Ireland. Previous surveys had been undertaken for a variety of end-purposes, e.g., agriculture, mineral exploration. In each case the surveys had yielded detailed and valuable geochemical information concerning the natural environment of Northern Ireland. Despite the existence of these datasets each contained inherent limitations which prevented their application for a variety of end-uses. The surveys and their characteristics are detailed below;

2.1 IMPERIAL COLLEGE SURVEY

The Imperial College (London) completed a survey between 1967 and 1973 by the Applied Geochemistry Research Group at Imperial College. This survey analysed 18 elements in 4,832 stream sediment samples (Webb et al, 1973). Sample sites were located near road intersections. The average sampling density was 1 site per square mile. Composite samples (100 g) were collected from two locations 50 ft apart. Samples were collected from streams where the upstream catchment did not exceed 10 square miles. Sample preparation comprised oven-drying the sediments and sieving them to a -80 mesh (c.200 µm) fraction. The sediments were analysed for Al, Ba, Ca, Co, Cr, Cu, Fe, Ga, K, Mg, Mn, Ni, Pb, Sc, Si, Sr, V and Zn using an ARL 2900B Quantometer (40 channel automatic emission spectrometer). Element distributions were plotted as a series of greyscale maps, some subtractive colour maps were also produced.

2.2 GEOLOGICAL SURVEY OF NORTHERN IRELAND

This survey was undertaken between 1973 and 1976 for mineral reconnaissance purposes. Sampling focused on the Dalradian Supergroup. Three phases of survey were completed; 1) reconnaissance drainage survey; 2) a detailed drainage survey; and 3) a soil survey. The reconnaissance drainage survey sampled stream sediments, waters and pan concentrates at a density of 1 site per 0.5 to 0.8 km of stream length (equivalent to 1 sample per 2 km^2 of drainage basin). A detailed drainage survey at 100 m sample spacing was completed over some anomalies identified in the interpretation of the reconnaissance survey. The soil survey was conducted at two localities, samples were collected at 100 m intervals along east-west traverses 200 m apart. Samples were analysed for Ag, As, Ba, Co, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Sn, V, and Zn by a combination of atomic absorption spectrometry (AAS), colorimetry, and emission spectrometry (ES). Semi-quantitative results were obtained for Ba, Cu, Pb and Zn in a subset of the heavy mineral concentrates.

2.3 DEPT. OF AGRICULTURE & RURAL DEVELOPMENT (DARD) SOIL ATLAS OF NORTHERN IRELAND

Soil sampling took place between 1987 and 1997 (Jordan et al, 2000) for the purposes of agricultural research. Lowland soils (<200 m elevation) were the primary focus of research. Upland areas outside of the area of enclosure were sampled at a density of 1 per 5 km^2. A total of 6,138 soil samples were collected at a density of 1 per km^2. Samples were collected from the 0 to 25 cm horizon. Fifteen elements (Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, and Zn) were analysed in an aqua regia digest of the -2 mm fraction. Analysis was completed by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry). The “extractable” concentration of elements was also determined (plus sulphur) on a subset of the samples (1,100 samples) using a EDTA (ethylenediaminetetraacetic acid) extractant.

2.4 NORTHERN IRELAND G-BASE SURVEY

Fieldwork was conducted in summer periods between 1994 and 1996 (Flight et al, 1995, 1998). Stream sediment (<150 µm fraction), pan concentrates and water samples were collected at 2,908 sites in the western part of Northern Ireland, achieving an average sample density of 1 site per 2.15 km^2. Sites were located on first and second order streams. The sediments were analysed by XRF for 33 determinands, Ag, As, Ba, Bi, CaO, Cd, Ce, Co, Cr, Cu, Fe2O3, Ga, K2O, La, MgO, MnO, Mo, Nb, Ni, P2O5, Pb, Rb, Sb, Se, Sn, Sr, Th, TiO2, U, V, Y, Zn, and Zr. A separate fire assay for Au, Pd and Pt was completed at Acme Analytical Laboratories (Vancouver). 42 parameters were measured in water, including bicarbonate, chloride, fluoride, nitrate and a trace element suite, using a combination of ion chromatography, ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry) and ICP-MS (Inductively Coupled Plasma Mass Spectrometry) instrumentation.

3 Sampling Overview

During the Tellus geochemistry programme different sample types were collected at alternate time periods. This was due in part to preparation logistics, staff availability and the fact that previous sampling by the G-BASE programme in the mid-90's had collected stream sediment and water samples (but not soil samples) for the western part of Northern Ireland. The need to undertake autumn and spring fieldwork phases precluded the sampling of stream sediments, waters and heavy mineral concentrates on the basis of health and safety and difficulty/ practicality in obtaining samples, i.e., streams in flood and low ambient temperature. G-BASE protocol also advised collection of water samples at baseflow conditions to reduce variability of stream geochemistry due to overland flow and short-term fluctuation due to input from rain showers and other ephemeral sources.

Daily tasks were completed by field staff at base camp, these included such items as;

1. Assigning sites

   On any given day field staff assigned sites to sampling pairs for the following day's workload. The number and location of sites was assigned on the basis of the sample types to be collected and the terrain to be traversed. In general, soil only sampling maintained an average of 10 sites per day per sampling pair. Combined soil and stream site sampling reduced the number of sites that could be sampled per day. The prevalence of smaller field enclosures in Northern Ireland reduced the daily sampling rate in some areas.

2. Location maps

   Field maps showing the sampling area for each pair of samplers were prepared the day before sampling by the Tellus field staff. Ordnance Survey of Northern Ireland (OSNI) 1:50 000 "Discoverer Series" maps were used. The field area and 1 km sampling blocks were marked on each location map by the field staff using the criteria of terrain, access and distance to sampling region. The choice of sample site within each kilometre square was at the discretion of the fieldworkers using G-BASE sample acquisition guidelines. Location maps were given to each pair of samplers the evening before to allow them to examine the terrain and devise potential walking routes between sites. As part of the biosecurity protocol farm-holdings with notified disease were marked on the location maps and avoided. Due to the lack of published 1:25 000 scale topographic maps in Northern Ireland it was necessary to use 1:10 000 map data for the urban survey programme of Greater Belfast and Londonderry.

3.1 OVERVIEW OF SAMPLE TYPES

Sample types collected as part of the Tellus survey are itemised in Table 1. These sample types are also collected by the British Geological Survey G-BASE program, however, additional analytical tests are performed on Tellus soil samples (Figure 11).

Table 1: Summary of sample types collected by Tellus.

Sample Type	Sample Code	Description
Stream Sediment	C	Fine stream sediment wet sieved at site to <150µm. Collected from low order (i.e. smallest) streams, e.g., 1st or 2nd order.
Heavy Mineral Concentrate	P	<2mm sediment from drainage site panned in a wooden Malaysian-type dulang pan at site. A 3 - 5 kg sample is panned until 20 – 40 g of heavy mineral concentrate remains. Inspected at site for bulk mineralogical identification. Not routinely analysed.
Stream Water	W	Collected from site of "C" and "P" samples. Water samples collected for analysis of; (*i*) pH; (*ii*) alkalinity and conductivity; (*iii*) anions and NPOC; and (*iv*) trace element suite by ICP-AES/ ICP-OES and ICP-MS.
Surface Soil	A	A composite sample of five auger flights collected at corner points and centre of a 20 x 20 m square. A 5 to 20 cm depth interval is sampled using a hand-held Edelman soil auger. The surface organic litter and root-zone (0 - 5 cm) is removed where present (e.g. grassland). Dried, disaggregated and sieved in the laboratory to <2 mm. Routinely analysed by XRF and by aqua regia ICP-OES/ MS. Loss on ignition and pH determined on every sample.
Deep Soil	S	A composite sample of five auger flights collected at corner points and centre of a 20 x 20 m square. A 35 to 50 cm depth interval is sampled using a hand-held Edelman soil auger (using same auger holes as "A" sample). Dried, disaggregated and sieved in the laboratory to <2 mm. Analysed by aqua regia ICP-OES/ MS and "near-total" ICP-OES/ MS. Au, Pd and Pt also obtained by fire assay ICP-MS. Sulphate determined by hydrochloric acid digest/ ICP-MS.

Note: in urban areas only soils were collected, at a density of 4 samples per km^2

3.2 SAMPLING EQUIPMENT

There were two primary sets of equipment carried by each pair of samplers, a stream sampling kit (Figure 1) and soil sampling kit (Figure 2). The soil kit comprised an Edelman auger, sample bags and soil observation field cards. The stream sampling kit comprised two sieves (2 mm and 150 µm nylon mesh on wooden frame), a dulang pan for producing heavy mineral concentrates, a plastic dish for sediment storage during sieving and stream site observation field cards. A metal spade was also carried for extracting sediment from each stream bed. Two syringes and a set of disposable 0.45 µm cellulose filters were carried for stream water sampling as well as several 250 mL polypropylene bottles for collecting water samples from sites rich in suspended sediment, such samples were filtered back at field base.

Figure 1: Stream sediment sampling

For each stream site a “site bag” was assembled by the field staff and issued to the samplers. A Tellus “site bag” comprised a sediment sample bag and a heavy mineral concentrate bag, one 60 mL Nalgene™ bottle for trace element analysis (analysed at the Geological Survey of Finland), one 30 mL Nalgene™ bottle for anion analysis (analysed at ALcontrol, Holland), a 10 mL plastic sample bottle for pH and a 250 mL Nalgene™ bottle for collecting water to determine alkalinity and conductivity. Each sampling pair carried heavy duty polypropylene bags for collecting sediment from dry stream beds. Where dry sediment sites were encountered c.5 kg of the dry sediment was collected and subsequently sieved at the next site, or alternatively at field base.

Figure 2: Soil sampling

3.3 PEAT SAMPLING PROCEDURES

In Northern Ireland approximately 13 to 17 % of the land surface is classified as peat substrate (van Dam, 2006, pers.com.). Peat areas are generally located in mountainous terrain. Sites classified as peat required a special protocol (Ander et al, 2005) in order to obtain sufficient sample for analysis. The high organic content and waterlogged nature of peat sites necessitated the collection of a larger field sample due to the considerable reduction in volume during the drying process.

To accommodate the larger sample the following procedures were adopted;

1. At peat sites two sets of ‘A’ and ‘S’ sample bags were collected. The bags were labelled “A1” and “A2” and “S1” and “S2” corresponding to the “A” and “S” samples respectively.
2. The samples were collected in the same manner as normal soil samples with the exception that a set of adjacent sample holes were collected 15 cm from each primary auger hole.
3. On the field checklists two additional columns were labelled “A2” and “S2” to identify sites were two bags of sample were collected for each “A” and “S” sample. This allowed samples to be tracked from the field to the laboratory.

4 Urban Inorganic Soil Sampling

The Tellus urban inorganic (trace element) survey (Figure 3) was based on the procedures and sampling protocols of the G-BASE urban programme and has been described by Knights (2007).

1. Three sample sites were initially collected per 1 km block within the Belfast Metropolitan Area and Londonderry City boundary. Each kilometre square was sub-divided into 4 quadrants, each quadrant represented a 500 m x 500 m square. The south-east quadrant of each kilometre block was not sampled as part of the main urban inorganic sampling phase. The target sample location was at the centre of each 500 m sided square, where practical. Samples were collected from areas of undisturbed ground where available. In many instances samples were collected from gardens, road verges, central reservations, recreational ground and public land. In all cases the most representative sample for that locality was collected and point source contamination was avoided.
2. The sampling protocol was identical to the regional soils programme for both standard and duplicate sample sites. Two samples labelled “A” and “S” were collected at each site, corresponding to the 5 to 20 cm and 35 to 50 cm soil depth intervals respectively. Sample observation details were recorded in a similar manner to regional soil samples.
3. A different procedure to the regional sampling programme was employed to record site location details in urban areas. Where samples were collected near houses or business premises the address of the house was recorded for the site location details, or the company name and address in the case of commercial premises. In church grounds the name of the church was recorded.

Figure 3: Urban inorganic soil sampling

5 Urban Organic Soil Sampling

The first phase of urban sampling collected three soil samples for inorganic analysis in each kilometre block (i.e., the NW, NE and SW quadrants). On completion of phase one urban sampling the phase two organic sampling programme commenced. The organic programme collected one site per kilometre block. The site was located in the south-east quadrant of each kilometre block. At each site separate organic and inorganic samples were collected. This facilitated the completion of the urban inorganic survey whilst also permitting organic samples to be collected at the same location.

The protocol for organic sampling (Appendix I) was devised by Dr. Rory Doherty from Queen's University, Belfast. As part of the protocol samplers were required to wear nitrile rubber gloves to prevent contamination of samples. Gloves were worn at all stages of the process from initial sampling to placing samples in the cool box and washing the auger. Personnel were advised on potential methods of sample contamination, e.g., use of deodorants and cosmetics. In contrast to the G-BASE urban sampling protocol which collects two duplicate pairs in every 100 samples the Tellus urban organic programme collected twelve duplicate pairs for every 70 organic samples.

At each organic site one sampler collected the organic sample using a separate auger which was washed in detergent and water (as described in the organic sampling protocol). Five auger holes were collected, similar to the inorganic sampling protocol. Organic auger samples were placed into a large glass dish and mixed using a stainless steel trowel. After several minutes of mixing the sample was then transferred to an amber coloured glass jar, as supplied by ALcontrol (Chester, England), the analytical contractor.

Each jar was pre-numbered with the unique site identification number and date, as well as the samplers initials (card writer initials first). Soil was placed in the jar using the trowel. When the jar was full it was gently tapped to remove trapped air, additional sample was then added until the jar was full. The lid was then carefully replaced and secured making sure that no soil particles were present on the rim of the glass jar that could prevent a fully airtight seal. Each jar had a unique barcode number assigned to it by the analytical contractor. The barcode serial number was written on the top of the field card.

Filled sample jars were then placed inside a cool box which contained frozen ice blocks. The temperature of the cool box was noted and the cool box secured inside the van. An optimum temperature of 4°C was preferred.

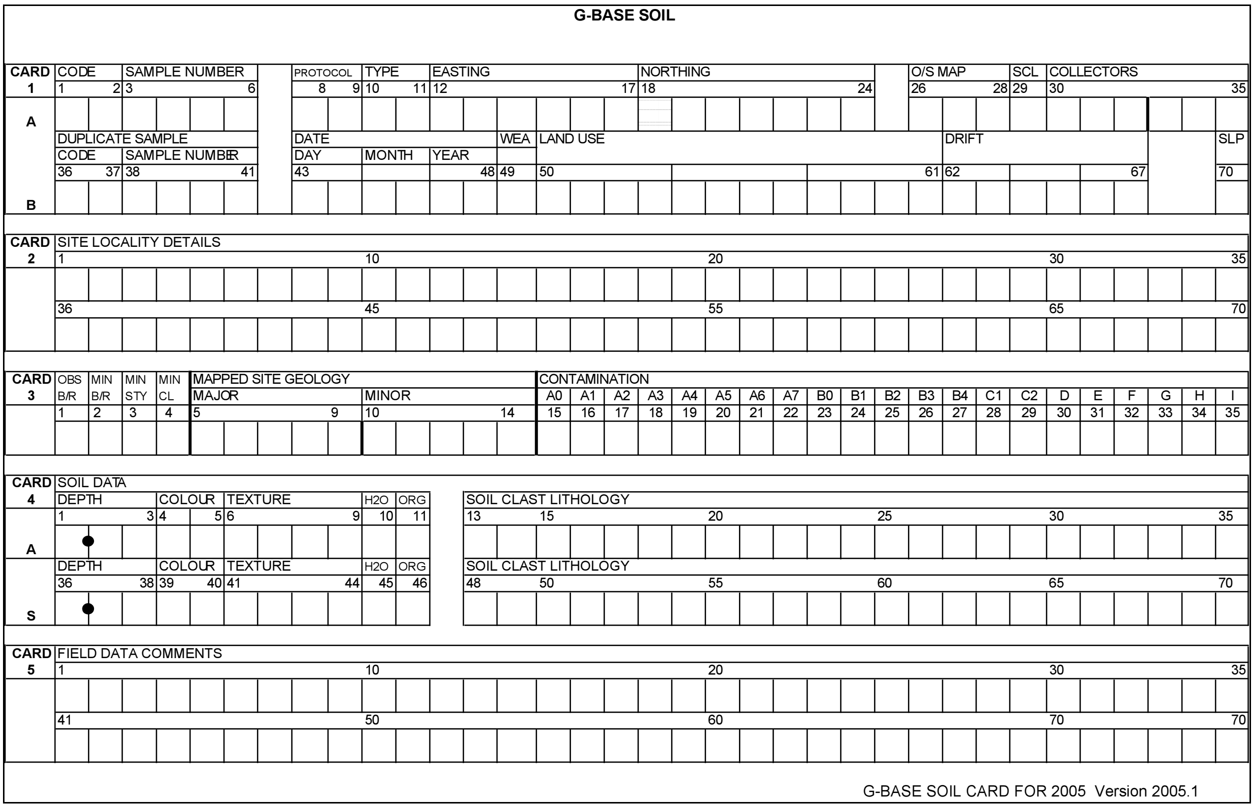
The organic sampling auger was then washed in cold water and detergent using a nylon brush, as prescribed in the sampling protocol. The auger was rinsed with cold water and placed inside a self seal bag for use at the next site.

At the end of the sampling day the organic samples were transferred from the cool box to a dedicated fridge at the field base. The samples were stored at 4°C until the next morning when they were packed in cool boxes containing ice blocks for collection by the ALcontrol courier. The samples were collected between noon and 1pm and then transported to Dublin. They were then flown to ALcontrol's Chester laboratory for analysis (arriving at the Chester laboratory the following morning). Details pertaining to the urban organic analytical parameters are not reported in this document. Full specifications are given in ALcontrol (2006) and ALcontrol (2007).

6 Recording of Site Information

6.1 FIELD OBSERVATION CARDS

A printed field card was the primary method of recording field observations relating to site and sample characteristics. Examples of the soil and stream site observation cards are shown in Figures. 4 and 5.



G-BASE SOIL

CARD 1
A
CODE 1 2 | SAMPLE NUMBER 3 6 | PROTOCOL 8 9 | TYPE 10 11 | EASTING 12 17 | NORTHING 18 24 | O/S MAP 26 28 | SCL 29 | COLLECTORS 30 35
B
DUPLICATE SAMPLE CODE 36 37 | SAMPLE NUMBER 38 41 | DATE DAY MONTH YEAR 43 48 | WEA 49 | LAND USE 50 61 | DRIFT 62 67 | SLP 70

CARD 2
SITE LOCALITY DETAILS 1 10 20 30 35
36 45 55 65 70

CARD 3
OBS B/R 1 | MIN B/R 2 | MIN STY 3 | MIN CL 4 | MAPPED SITE GEOLOGY MAJOR 5 9 | MINOR 10 14
CONTAMINATION

A0	A1	A2	A3	A4	A5	A6	A7	B0	B1	B2	B3	B4	C1	C2	D	E	F	G	H	I
15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35

CARD 4
SOIL DATA
A
DEPTH 1 3 | COLOUR 4 5 | TEXTURE 6 9 | H2O 10 | ORG 11 | SOIL CLAST LITHOLOGY 13 15 20 25 30 35
S
DEPTH 36 38 | COLOUR 39 40 | TEXTURE 41 44 | H2O 45 | ORG 46 | SOIL CLAST LITHOLOGY 48 50 55 60 65 70

CARD 5
FIELD DATA COMMENTS 1 10 20 30 35
41 50 60 70 70

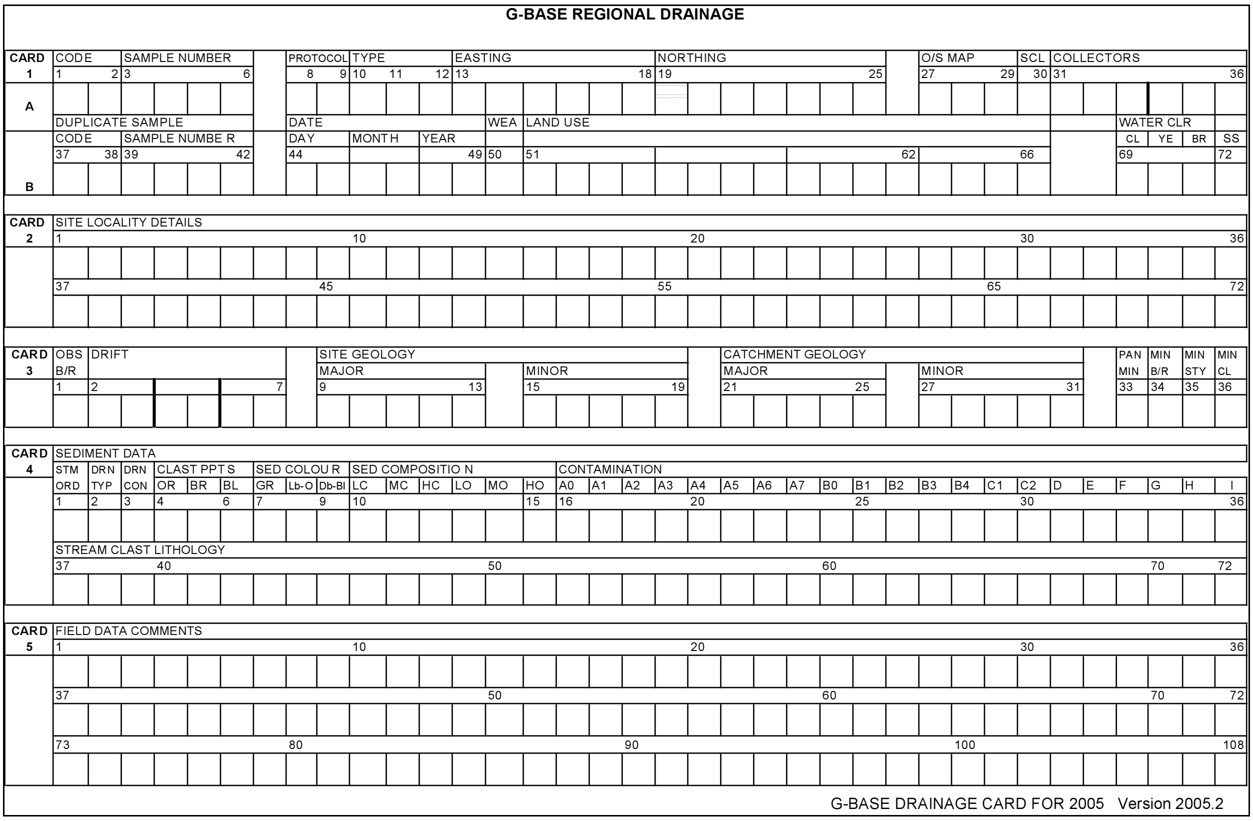
G-BASE SOIL CARD FOR 2005 Version 2005.1

Figure 4: Soil field observation card

Observations from field cards were entered into a digital Access2000™ database after they underwent a field quality control process. The quality control process involved checking that the correct codes had been recorded on field cards and that GPS coordinates recorded on the card matched those in the GPS unit for each site. Maps showing the location of sample sites were also produced as part of this process. The process of completing a printed card and producing a digital database of observations allowed both a traditional paper archive of observations to be maintained as well as the construction of a computerised database which could be made available to numerous end-users. Field cards were used as follows;

1. Each batch of 100 field cards was numbered using one of four random number lists. Each list contained 100 randomised numbers. The first two digits of a sample number (forming the area code) were pre-allocated. For Northern Ireland, “55”, “56” and “57” were utilised as the first two digits according to British Geological Survey (BGS) Geochemistry Database (Lister et al, 2005) protocol. Although collected using a random numbering system, samples were later analysed in numerical order.

Randomisation of the unique sample numbers during collection allowed consecutive sample numbers to be sampled from non-adjacent field localities, in effect randomising samples prior to analysis. This process facilitated identification of carry-over during analysis or contamination of samples during any of the post-collection procedures.



G-BASE REGIONAL DRAINAGE

CARD 1

A: CODE 1–2 | SAMPLE NUMBER 3–6 | PROTOCOL 8–9 | TYPE 10 11 12 | EASTING 13–18 | NORTHING 19–25 | O/S MAP 27–29 | SCL 30 | COLLECTORS 31–36

B: DUPLICATE SAMPLE: CODE 37–38, SAMPLE NUMBE R 39–42 | DATE: DAY 44, MONTH, YEAR –49 | WEA 50 | LAND USE 51 62 66 | WATER CLR: CL YE BR SS 69–72

CARD 2

SITE LOCALITY DETAILS 1 10 20 30 36

37 45 55 65 72

CARD 3

OBS B/R 1 | DRIFT 2–7 | SITE GEOLOGY: MAJOR 9–13, MINOR 15–19 | CATCHMENT GEOLOGY: MAJOR 21–25, MINOR 27–31 | PAN MIN 33 | MIN B/R 34 | MIN STY 35 | MIN CL 36

CARD 4

SEDIMENT DATA

STM ORD 1 | DRN TYP 2 | DRN CON 3 | CLAST PPT S: OR BR BL 4–6 | SED COLOU R: GR Lb-O Db-Bl 7–9 | SED COMPOSITIO N: LC MC HC LO MO HO 10–15 | CONTAMINATION: A0 A1 A2 A3 A4 A5 A6 A7 B0 B1 B2 B3 B4 C1 C2 D E F G H I 16 20 25 30 36

STREAM CLAST LITHOLOGY 37 40 50 60 70 72

CARD 5

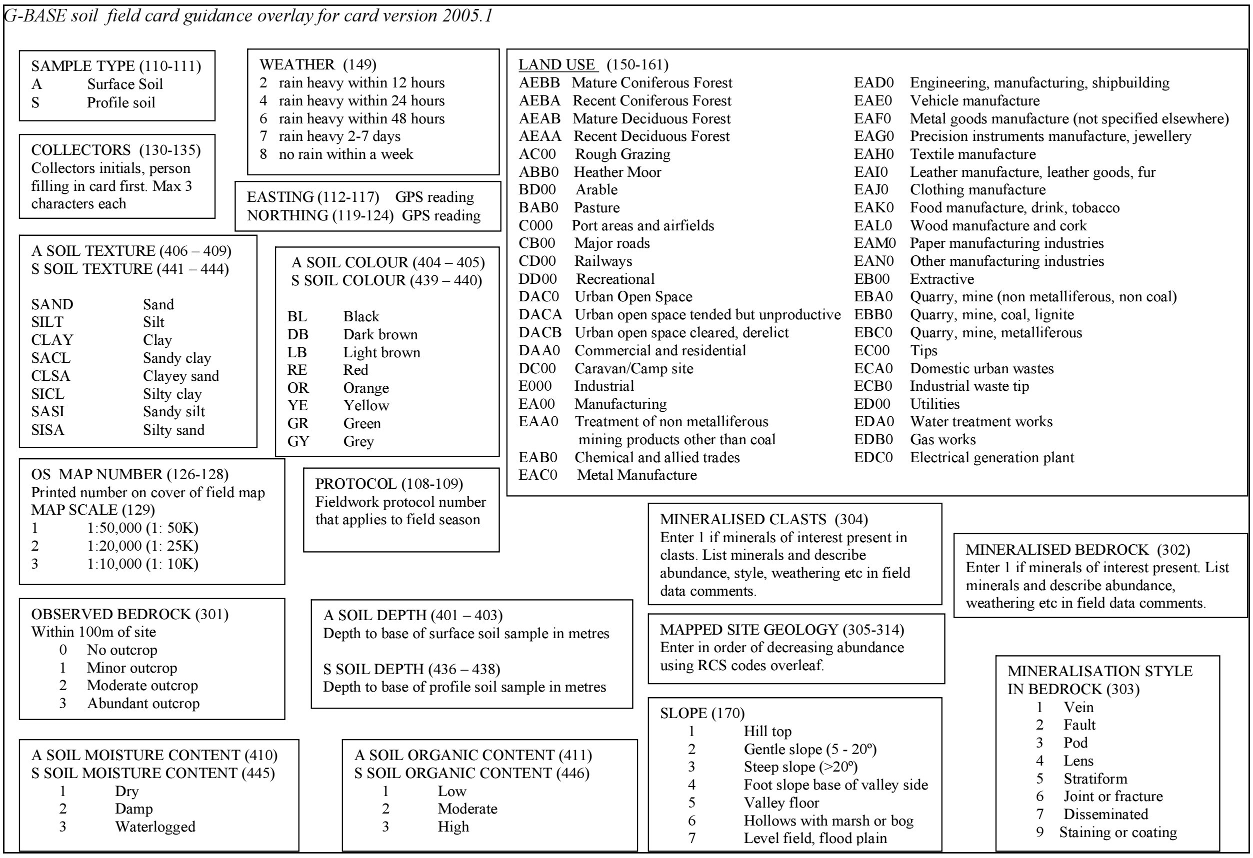
FIELD DATA COMMENTS 1 10 20 30 36

37 50 60 70 72

73 80 90 100 108

G-BASE DRAINAGE CARD FOR 2005 Version 2005.2

Figure 5: Drainage site field observation card.



G-BASE soil field card guidance overlay for card version 2005.1

SAMPLE TYPE (110-111)

A	Surface Soil
S	Profile soil

COLLECTORS (130-135)
Collectors initials, person filling in card first. Max 3 characters each

WEATHER (149)

2	rain heavy within 12 hours
4	rain heavy within 24 hours
6	rain heavy within 48 hours
7	rain heavy 2-7 days
8	no rain within a week

EASTING (112-117) GPS reading
NORTHING (119-124) GPS reading

A SOIL TEXTURE (406 – 409)
S SOIL TEXTURE (441 – 444)

SAND	Sand
SILT	Silt
CLAY	Clay
SACL	Sandy clay
CLSA	Clayey sand
SICL	Silty clay
SASI	Sandy silt
SISA	Silty sand

A SOIL COLOUR (404 – 405)
S SOIL COLOUR (439 – 440)

BL	Black
DB	Dark brown
LB	Light brown
RE	Red
OR	Orange
YE	Yellow
GR	Green
GY	Grey

LAND USE (150-161)

AEBB	Mature Coniferous Forest	EAD0	Engineering, manufacturing, shipbuilding
AEBA	Recent Coniferous Forest	EAE0	Vehicle manufacture
AEAB	Mature Deciduous Forest	EAF0	Metal goods manufacture (not specified elsewhere)
AEAA	Recent Deciduous Forest	EAG0	Precision instruments manufacture, jewellery
AC00	Rough Grazing	EAH0	Textile manufacture
ABB0	Heather Moor	EAI0	Leather manufacture, leather goods, fur
BD00	Arable	EAJ0	Clothing manufacture
BAB0	Pasture	EAK0	Food manufacture, drink, tobacco
C000	Port areas and airfields	EAL0	Wood manufacture and cork
CB00	Major roads	EAM0	Paper manufacturing industries
CD00	Railways	EAN0	Other manufacturing industries
DD00	Recreational	EB00	Extractive
DAC0	Urban Open Space	EBA0	Quarry, mine (non metalliferous, non coal)
DACA	Urban open space tended but unproductive	EBB0	Quarry, mine, coal, lignite
DACB	Urban open space cleared, derelict	EBC0	Quarry, mine, metalliferous
DAA0	Commercial and residential	EC00	Tips
DC00	Caravan/Camp site	ECA0	Domestic urban wastes
E000	Industrial	ECB0	Industrial waste tip
EA00	Manufacturing	ED00	Utilities
EAA0	Treatment of non metalliferous mining products other than coal	EDA0	Water treatment works
		EDB0	Gas works
EAB0	Chemical and allied trades	EDC0	Electrical generation plant
EAC0	Metal Manufacture		

OS MAP NUMBER (126-128)
Printed number on cover of field map
MAP SCALE (129)

1	1:50,000 (1: 50K)
2	1:20,000 (1: 25K)
3	1:10,000 (1: 10K)

PROTOCOL (108-109)
Fieldwork protocol number that applies to field season

MINERALISED CLASTS (304)
Enter 1 if minerals of interest present in clasts. List minerals and describe abundance, style, weathering etc in field data comments.

MINERALISED BEDROCK (302)
Enter 1 if minerals of interest present. List minerals and describe abundance, weathering etc in field data comments.

OBSERVED BEDROCK (301)
Within 100m of site

0	No outcrop
1	Minor outcrop
2	Moderate outcrop
3	Abundant outcrop

A SOIL DEPTH (401 – 403)
Depth to base of surface soil sample in metres

S SOIL DEPTH (436 – 438)
Depth to base of profile soil sample in metres

MAPPED SITE GEOLOGY (305-314)
Enter in order of decreasing abundance using RCS codes overleaf.

MINERALISATION STYLE IN BEDROCK (303)

1	Vein
2	Fault
3	Pod
4	Lens
5	Stratiform
6	Joint or fracture
7	Disseminated
9	Staining or coating

SLOPE (170)

1	Hill top
2	Gentle slope (5 - 20º)
3	Steep slope (>20º)
4	Foot slope base of valley side
5	Valley floor
6	Hollows with marsh or bog
7	Level field, flood plain

A SOIL MOISTURE CONTENT (410)
S SOIL MOISTURE CONTENT (445)

1	Dry
2	Damp
3	Waterlogged

A SOIL ORGANIC CONTENT (411)
S SOIL ORGANIC CONTENT (446)

1	Low
2	Moderate
3	High

Figure 6: Soil field card 'crib-sheet'.

2. Sampling pairs were allocated a quantity of pre-numbered field cards each day corresponding to the number of sites they were expected to sample. At each site the next card in the sequence was used and the samples were allocated the unique identification number on the field card.

Sample characteristics and site observations were recorded using pre-determined lists of observations with associated codes for each variable, shown in Figure 6. These lists were known as 'crib-sheets'. Additional details relating to the completion of field cards can be found in Johnson (2005).

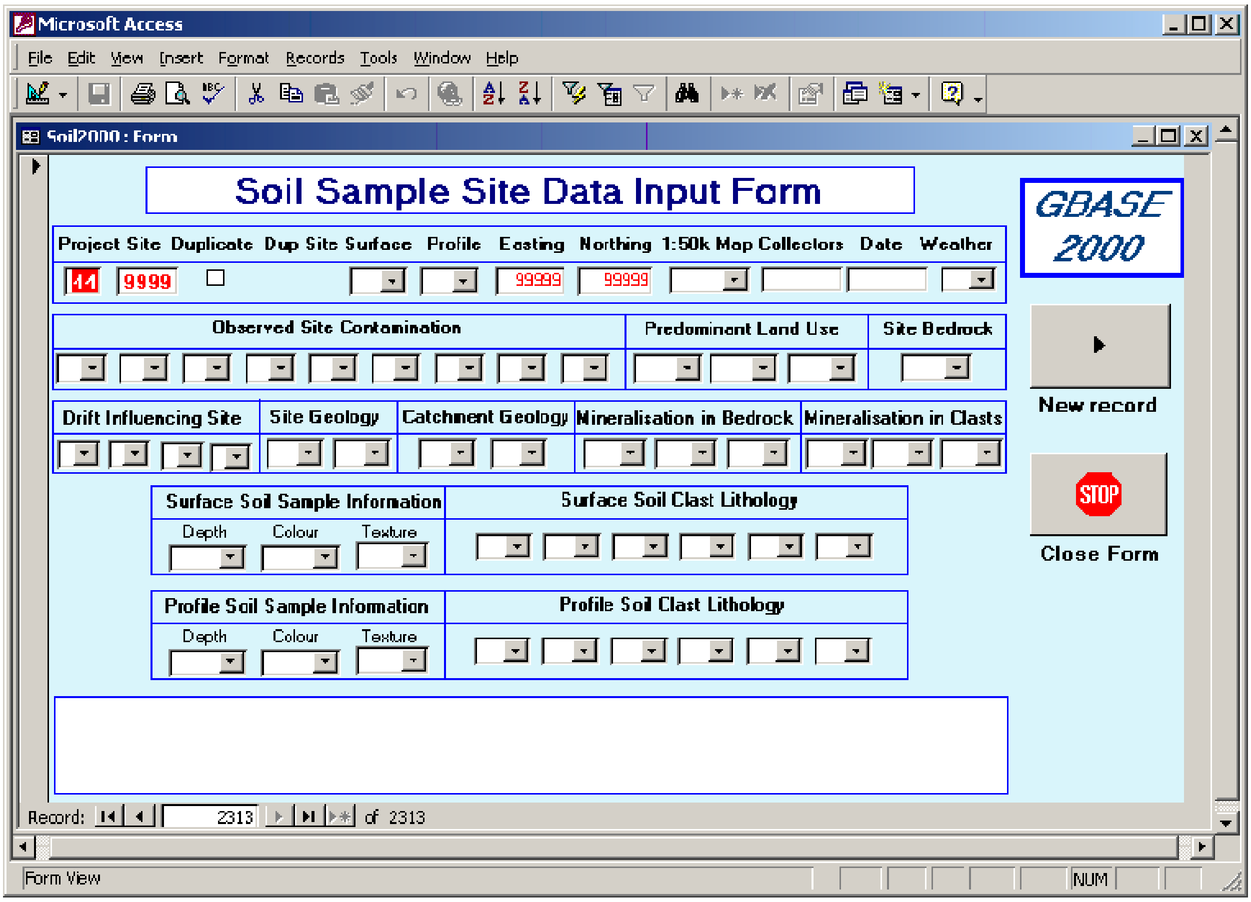

Project 44
Site 9999
Duplicate ☐
Easting 99999
Northing 99999
Record: 2313 of 2313

Figure 7: Digital field database soil data entry screen.

6.2 DIGITAL FIELD DATABASE

The G-BASE field database design was used for Tellus sampling. This Access2000™ database (Lister et al, 2005) was used to store information from the field cards. Separate data input screens were used for soil and sediment sites (Figure 7) and extensive use of drop-down menus facilitated data capture. The programming of rules into the database prevented accidental duplication of information, such as inputting the same sample number twice or the same geographic coordinates. The database was also modified to allow Irish grid coordinates to be entered.

7 Underweight Sediment Samples

During sample preparation at the laboratories of the British Geological Survey a number of sediment samples were found to have insufficient weight to accomplish all of the proposed analytical tests. The following reasons are proposed for the presence of underweight samples;

i). Sediment Drying- sediments were collected wet and remained waterlogged for several days to weeks after collection, particularly during periods of prolonged wet weather. It was thus difficult to obtain an accurate weight of sample until the full drying process was complete.

ii). Stream Bedrock- many of the stream sites were located in mountainous terrain where streams and rivers flowed over exposed bedrock. These sites contained only minor quantities of fine sediment. At these sites the samplers persevered and obtained a sample. However, due to the waterlogged nature of samples it was difficult to judge if sufficient sample was obtained.

iii). Coarse Sediments- many of the streams had very coarse sediments which made it more difficult and time consuming to obtain sufficient quantity of fine sediment.

iv). Peat Substrate- near mountain tops many of the streams flowed through and over peat bogs. Sediments collected at such sites were very organic-rich. The abundance of organic matter in the sediment samples resulted in a greater reduction in mass during drying in comparison to "normal" samples. This resulted in many of these samples reporting below the required sample weight.

Overall, the presence of underweight sediment samples was a result of the nature of the terrain and the unique stream conditions that made it very difficult to obtain sediment samples without the need for excessive sampling time. When plotted on maps the locations of underweight samples confirmed that it was primarily a feature of mountainous terrain in particular localities and that there was no systematic problem with sampling methodology.

To counteract the potential impact of the underweight sediments on the fire assay (Au, Pd, Pt) analytical programme it was decided to implement a procedure whereby the sediment XRF pellets could be utilised for the fire assay. This was done in close consultation with the British Geological Survey and with the analytical sub-contractor, Acme Analytical Laboratories (Vancouver). This entailed the destruction of the XRF pellet by milling and the submission of the "disaggregated" pellet material to the sub-contractor for fire assay. Discussion of this procedure with the sub-contractor revealed no significant problems with this methodology. The only requirement was that the weights of sediment and binder in each pellet needed to be known in order to produce the final PGE values. A total of 342 pellets were disaggregated in this manner. Ten samples of the binder material were also sent to Acme Analytical Laboratories to assess the Au, Pd, and Pt content of the binder and any likely contribution to the reported values.

A sediment re-sampling programme was implemented in spring and summer 2006 to collect sediment from sites where there was not sufficient material for analysis. A total of 170 sites were sampled, 30 in the spring and the remaining 140 in the summer.

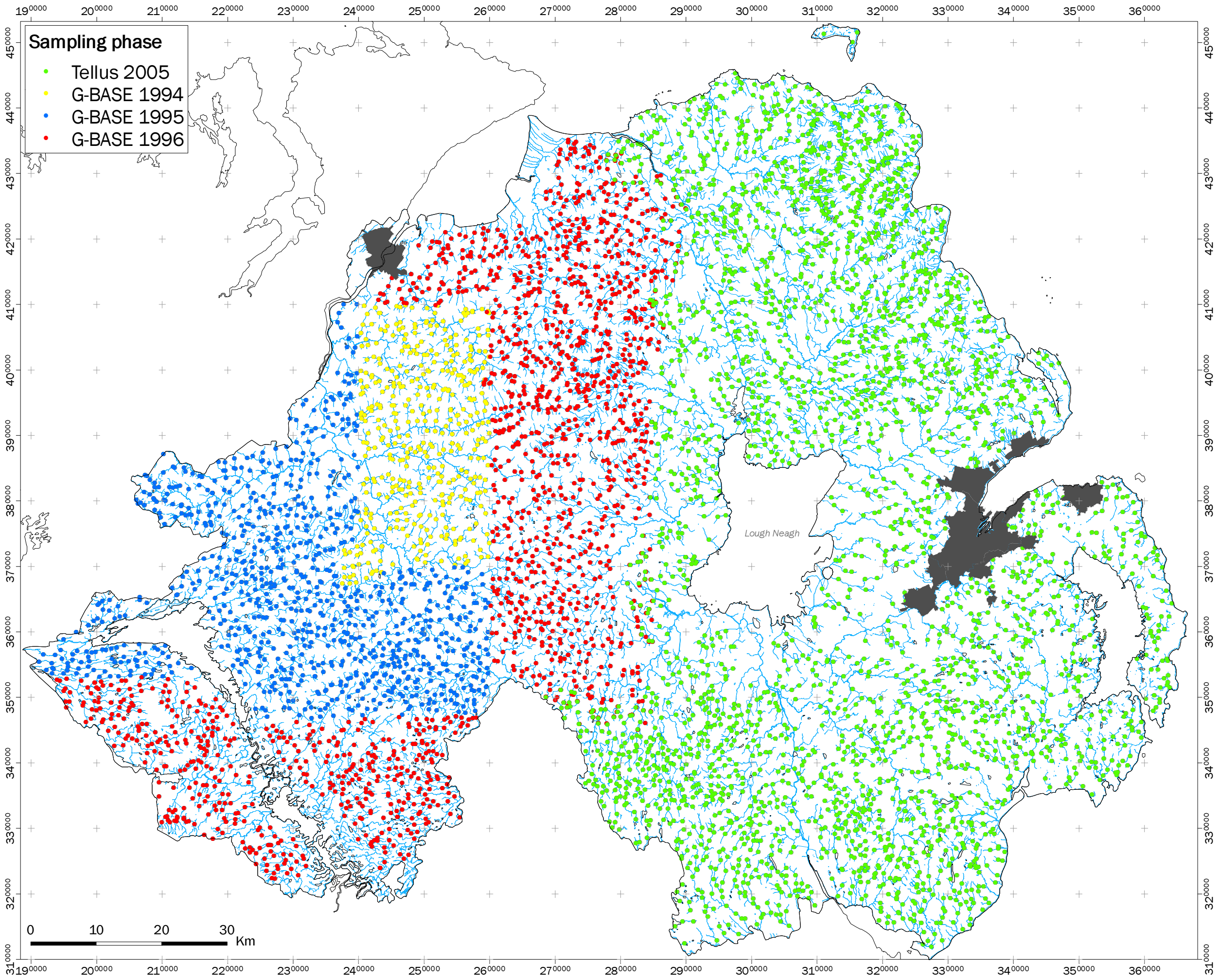


Figure 8: G-BASE and Tellus drainage sampling sites.

8 Sample Collection Timetable and Analysis Overview

Stream sediments, waters and heavy mineral concentrates were collected (Figure 8) from first and second order streams of river catchments (Figure 9) during two discrete sampling campaigns corresponding to the G-BASE and Tellus surveys. A total of 2,908 stream sites were sampled in the west of Northern Ireland in the period 1994 to 1996 as part of the G-BASE Survey.

Stream sites on the eastern side of Northern Ireland were sampled (2,966 stream sites) by the Tellus programme in the summers of 2005 and 2006. The vast majority of Tellus stream sites were sampled in the period July to September 2005. Supplementary stream sediment sampling was completed in the summer of 2006 for sites which had proved difficult to sample during the main 2005 phase. Sample types and field sampling procedures were similar for both the G-BASE and Tellus surveys. The combined G-BASE and Tellus stream datasets have an average sampling density of 1 site per 2.4 km^2. Soils were collected during a single phase of sampling during the Tellus survey from July 2004 to March 2006. Soil sampling was undertaken all year round with samplers traversing terrain on foot during the main summer sampling phase and by car and foot during the period late autumn to late spring.

Analysis of stream sediment and water samples collected during the G-BASE programme was completed at the laboratories of the British Geological Survey (Keyworth, Nottingham). Sediment Au, Pd, Pt and Rh were analysed at Acme Analytical Laboratories (Vancouver). Laboratories for the analysis of Tellus stream sediment, stream water and soil samples were chosen by a competitive tender process. Analysis contracts were awarded by the Department of Enterprise, Trade and Investment (DETI) for Northern Ireland to the following successful candidates;

- British Geological Survey (Keyworth, Nottingham)

Stream sediment preparation and XRF analysis with sub-contracting of Au, Pd, Pt and Rh fire assay/ ICP-MS analysis to Acme Analytical Laboratories (Vancouver). Soil preparation and XRF analysis. Soil pH and loss on ignition.

- SGS Laboratories (Toronto)

Aqua regia digest/ ICP-MS, “near-total” digest/ ICP-MS, Au, Pd and Pt fire assay/ ICP-MS analysis of soil samples. Sulphate by hydrochloric acid.

- ALcontrol Laboratories (Holland)

Anion analysis of stream waters with trace element analysis sub-contracted to the Geological Survey of Finland (GTK).

- ALcontrol (Chester)

Analysis of organic parameters in urban soils, e.g., PCB's (polychlorinated biphenyls), PAH’s (polycyclic aromatic hydrocarbons).

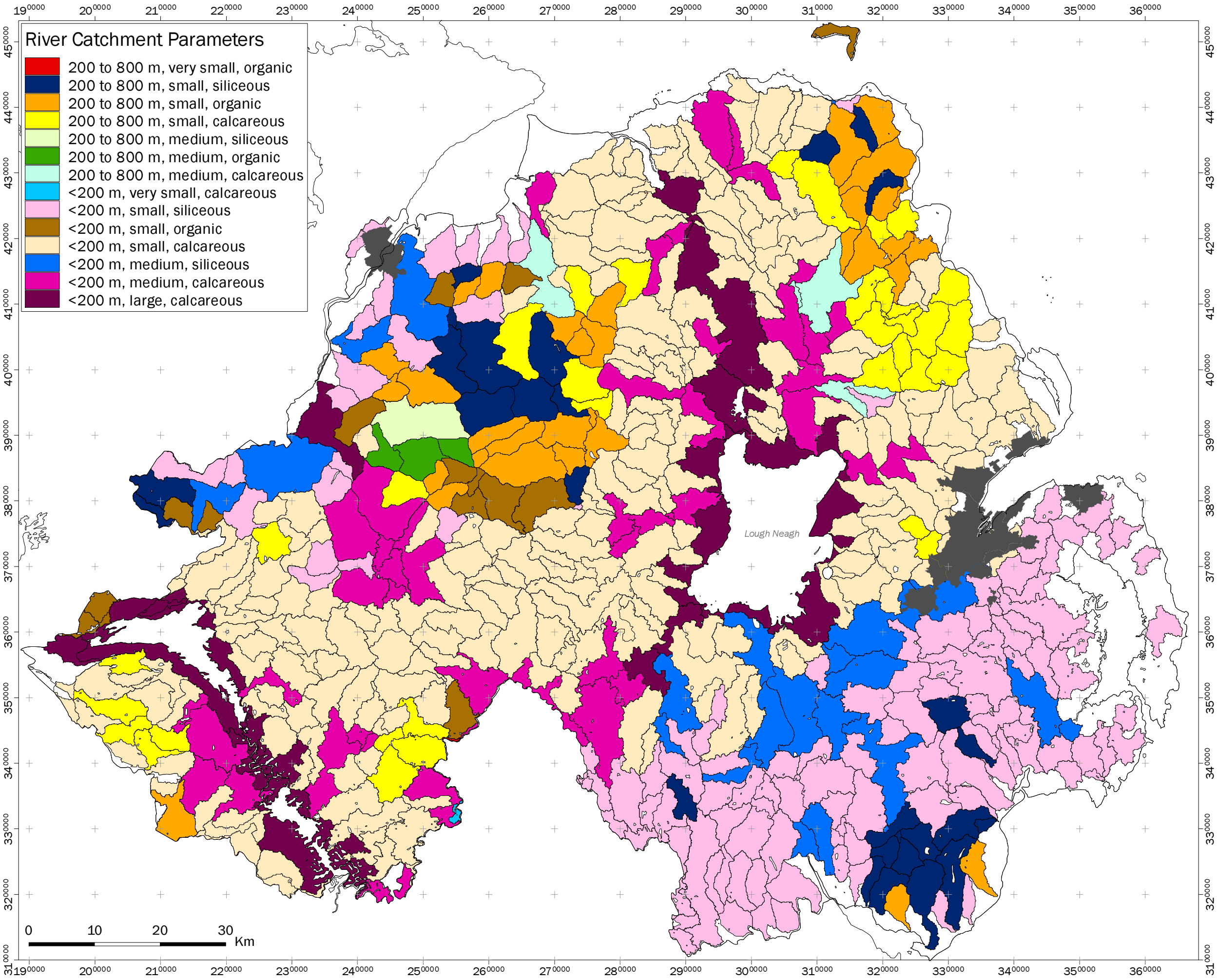


Figure 9: Stream water catchments of Northern Ireland.

Data reproduced by kind permission of the Environment & Heritage Service, Northern Ireland.

9 Sample Preparation

9.1 STREAM SEDIMENTS

The generic sampling and analytical methodologies for the stream sediment (Figure 10), stream water and soil samples were those subsequently recommended as international standards for geochemical mapping (Darnley et al., 1995). The geochemical data therefore conform to the standards set by International Geological Correlation Programme (IGCP) 360 for the preparation of internationally compatible regional geochemical maps.

In 2005 Tellus samples were collected by two field sampling teams, each consisting of approximately ten university students led by staff from the British Geological Survey (BGS). One team was based in the north-eastern part (e.g., Co. Antrim) of Northern Ireland and the other in the south-eastern part (e.g. Co. Down). Sampling and data recording procedures were taught to field samplers with practical demonstration and assessment of sampling methodology by experienced British Geological Survey staff. A training week for staff involved in the project was held in the Mourne Mountains in Spring 2005. Students worked in pairs but were interchanged daily to reduce the potential for the introduction of sampling bias by adoption of individual procedures. The methods used in collecting the stream sediment samples were those recommended by Plant and Moore (1979), who also described the procedures on which the organisation of the sampling programme and sample preparation were based. Sampling procedures were based on those described by Plant (1971). As far as possible, samples were collected from active sediment, upstream of any potential source of contamination, such as habitation, industrial activity or any road or track crossing.

The sediment sample was collected after removal of the oxidised surface material and was wet-screened on site using a method devised by B.A. Toms (Department of Chemistry, University of Birmingham). This method uses a minimum of water to collect a <150 µm sediment fraction. Approximately 100 g of material was collected in a Kraft™ paper bag. A heavy-mineral concentrate was obtained at each site by screening the stream sediment through a 2 mm nylon sieve and panning 2 - 3 kg of this sieved material using the method described by Leake and Aucott (1973). There were subtle differences between the sample preparation procedures employed in the G-BASE and Tellus surveys. In the G-BASE survey stream sediment samples were freeze-dried and then ground to <50 µm at a field laboratory. During the Tellus field campaign air-drying was undertaken prior to dispatch of batches of 100 samples to the Tellus store at Carrickfergus. Further air-drying was completed at Carrickfergus to a level that would allow samples to be packaged for onward transport to the British Geological Survey (BGS) laboratories at Keyworth. On arrival at the BGS laboratories samples were checked against shipping lists prior to assigning laboratory batch numbers in the BGS UKAS Quality Assurance System. If necessary, the dried Tellus sediment samples were disaggregated by hand in a mortar and pestle. The mortar and pestle were thoroughly cleaned using warm tap water and rinsed with reverse osmosis (RO) water after the disaggregation of a sample. Tellus sediment samples were freeze dried under reduced pressure within a pre-set temperature range of -30°C to 30°C for a minimum of 24 hours. Samples were then transferred to a trace level sample preparation laboratory. Transposition of sample numbers and cross contamination of samples was prevented by preparing each sample individually.

Figure 10: Stream sediment sampling during the Tellus survey.

This image shows the process of sieving the <150 µm fraction.

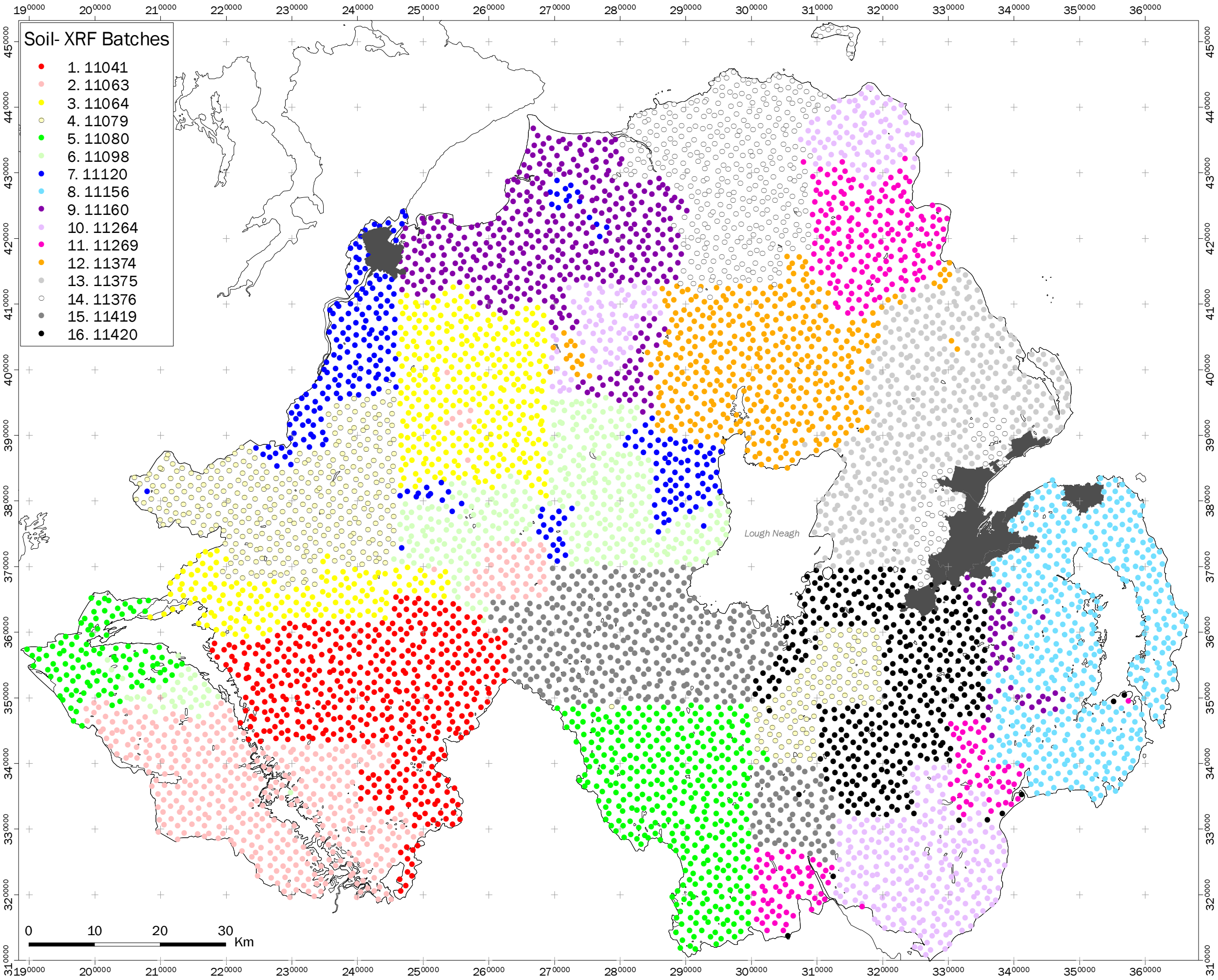


Figure 11: Tellus soil sample sites classified by XRF analytical batches.

The sediment sample was then sub-sampled to provide a representative 30 ± 2 g sub-sample suitable for agate ball milling. Replicate samples were also prepared at this stage of processing, by riffle splitting the coarse powder in half. Replicates were made from each of the duplicate sample pairs. The 30 g sub-sample of coarse powder was placed into a clean agate ball mill vessel and milled at 350 rpm for 40 minutes. On completion of milling a sub-sample (11.0 - 11.5 g) of milled powder was then removed from the milling vessel and placed into a labelled container for dispatch to the sub-contractor for Au, Pd, Pt, and B analysis. An additional sub-sample (approximately 7.0 ± 1.0 g) was retained for future reference. From the remaining powder, a sub-sample (12.00 ± 0.05 g) was weighed out and placed back into the agate mill. To this powder an aliquot 3g (±0.05g) of Elvacite 2013 (n-butyl methacrylate copolymer, DuPont & Co) was added and the sample/ binder mix was milled for four minutes at 300 rpm. Tellus XRF pellets utilised a binder comprising two blended synthetic waxes of 90% EMU 120 FD wax and 10% Ceridust (both waxes are styrene based co-polymers). On completion of binder milling prepared powders were placed into tamper evident plastic sample tubes for temporary storage prior to pellet preparation. Each sample was pressed on a calibrated Herzog semi-automatic pellet press at 25 kN to produce a 40 mm diameter pellet.

Prior to analysis certified reference materials and secondary reference materials were inserted into the sample batches for Au, Pd, and Pt analysis by fire assay. Full details are given in the quality control section of this report. Secondary reference materials used in the previous G-BASE survey were also submitted in Tellus sample batches for both fire assay and pressed pellet XRF analysis. All reference materials were concealed in the sample batches sent for analysis at both Acme Laboratories and BGS Laboratories.

9.2 STREAM WATERS

Water samples were collected several metres above the stream sediment site to avoid contamination by disturbed sediment or pore water. Great care was taken during the sampling procedure to avoid any other sources of contamination. The methods used for collecting water samples were tested by the British Geological Survey in a pilot study in North Wales in 1988 and correspond to those now recommended as international standards for geochemical mapping (Darnley et al., 1995). The geochemical data therefore conform to the standards set by International Geological Correlation Programme (IGCP) 360 for the preparation of internationally compatible regional geochemical maps. Sample preservation procedures employed during these studies correspond to recommendations made by the British Standards Institute and International Standards Organisation (BSI, 1986, Guidance on the preservation and handling of samples, BS 6068, Section 6.3; ISO 5667/3-1985).

A total of 2,846 stream-water samples were collected (Figure 8) by the G-BASE survey in the mid-1990's, coincident with stream sediment sites. The Tellus survey collected 3,063 stream water sites in the summer of 2005. The combined G-BASE and Tellus stream water datasets have a sample density of 1 site per 2.3 km^2 (total sampling area 13,741 km^2). Identical sampling methodologies were employed for both surveys, analytical methods varied between the two surveys.

Stream water samples collected during the G-BASE survey;

1) Multi-element sample- a 30 mL field filtered (0.45 µm Millipore® cellulose disposable filter) water sample collected in a 30 mL polystyrene Sterilin® vial. Acidified at field-base to 1% v/v using ultrapure AristarTM-grade concentrated nitric acid. Sample analysed by ICP-AES/ ICP-MS.

2) Chloride and nitrate sample- a 30 mL field filtered (0.45 µm Millipore® cellulose disposable filter) water sample collected in a 30 mL polystyrene bottle. Not acidified. Sample analysed by ion chromatography.

3) Total Organic Carbon (TOC) sample- a 30 mL field filtered (0.45 µm Millipore® cellulose disposable filter) water sample collected in a 30 mL polyethylene Nalgene® bottle. Not acidified. Analysis was performed on 50% of samples.

4) Fluoride sample- a 30 mL unfiltered water sample collected in a 30 mL polythene bottle. Not acidified. Sample analysed at a field laboratory using an ion selective electrode connected to a high impedance meter.

5) pH/ conductivity sample- a 30 mL unfiltered sample collected in a 30 mL polythene bottle. Parameters determined each evening on return to field base.

6) Total alkalinity sample- a 250 mL unfiltered sample collected in a polyethylene bottle with watertight cap. Parameter determined at field base the day after collection.

Stream water samples collected during the Tellus survey;

1) Trace elements sample- a 60 mL field filtered (0.45 µm Millex™ disposable filter) water sample collected in a 60 mL high-density 'Nalgene'™ bottle with watertight polyethylene cap. Sample analysed by ICP-AES/ MS.

2) Anions sample- a 30 mL field filtered (0.45 µm Millex™ disposable filter) water sample collected in a 30 mL high-density 'Nalgene'™ bottle with watertight polyethylene cap. Not acidified. Sample analysed by ion chromatography.

3) pH sample- a 30 mL unfiltered sample collected in a 30 mL polyethylene bottle with black watertight cap. Parameter determined each evening on return to field base.

4) Total alkalinity and conductivity sample- a 250 mL unfiltered sample collected in a polyethylene 'Nalgene'™ bottle with watertight cap. Parameters determined at field-

base. Conductivity was determined on the evening of collection, alkalinity the day after collection.

All containers were rinsed with stream water prior to sample collection. Particular care was taken with the pH and alkalinity samples to eliminate air bubbles and hence minimise degassing. The trace element and anion sample containers were rinsed with filtered water from the site prior to collection of the actual sample. Samples for ICP-AES and ICP-MS analysis were acidified each evening at field-base to 1% v/v using ultrapure Aristar™-grade concentrated nitric acid. Water pH was determined each evening using a temperature-compensated glass combination electrode connected to a high-performance pH meter (Radiometer Model PHM 80), and conductivity was determined using a standard 1 cm path-length cell in conjunction with a conductivity bridge. The pH and conductivity meters were calibrated using stock solutions prior to and at the end of each daily analytical run. Alkalinity was determined by titration the day after sample collection using a Hach digital titrator with sulphuric acid (0.8 M or 0.08 M) and bromocresol green indicator. The results are presented as mg/L HCO_3^-.

Prior to dispatch to the analytical contractor a certified reference water was inserted into each batch of 100 samples. A minimum of two secondary reference waters were also inserted into batches of 100 samples. Full details are given in the quality control section of this report. All reference materials were concealed in the sample batches sent for analysis at ALcontrol Laboratories (The Netherlands) and their subcontractor, GTK (Finland).

G-BASE and Tellus samples were stored in a cool, dark location (e.g., domestic refrigerator at 4°C) until dispatched to the laboratory/ sample facility, where they were also stored at 4°C. Tellus samples were dispatched to a sample store at Carrickfergus prior to collection in two main phases (14th September; 19th October, 2005) by the analytical contractor, ALcontrol (Holland).

Samples were bar-coded by ALcontrol staff and loaded into trays during collection from the Tellus store at Carrickfergus. Sample batches were transported to Holland in a refrigerated van with an ambient temperature of 4°C. A temperature data logger was transported with both batches to record the ambient air temperature. On arrival at ALcontrol Laboratories the samples were checked, scanned and logged into the ALcontrol laboratory information management system (Figure 12). Samples for the analysis of trace elements were transported to the laboratories of the Geological Survey of Finland (GTK) by ALcontrol Laboratories within a few days of arrival in Holland. A temperature controlled refrigerated van was used for this transport.

Figure 12: Tellus water samples for anion analysis.

9.3 SOILS

Soils were exclusively sampled during the Tellus program. Two separate sampling programs were conducted, a ‘regional’ survey (Figure 11) and an ‘urban’ survey. The ‘regional’ sampling programme encompassed all of Northern Ireland, except the urban areas of Belfast and Bangor. The Metropolitan Urban Areas of Belfast, Bangor, Carrickfergus, Carryduff, Castlereagh, Greenisland, Holywood, Lisburn, Newtownabbey, and the Londonderry Urban Area were sampled during the ‘urban’ survey at an increased sample density of 4 sites per km^2 (1,172 sites). Regional soil samples were collected on a systematic basis from rural areas across Northern Ireland. Soil samples were collected from alternate 1 km grid squares of the Irish grid coordinate system. The methods used for urban soils were similar except that; 1) the sample density was higher, at four sites per square kilometre, and 2) the sample sites corresponded closely to a predefined grid and did not avoid areas of human influence.

For the soil survey the choice of sampling location within each kilometre square was random, subject to the avoidance wherever possible of roads, tracks, railways, overhead electricity lines, human habitation and other disturbed ground. At each site two composite samples of five auger flights were collected, each composite sample comprised approximately 750 g of unsieved material. Samples were collected using a hand auger with a 20 by 5 cm flight from a standard depth interval of 5 – 20 cm for designated 'A' samples, referred to subsequently as “surface soils”, and at 35 – 50 cm for designated 'S' samples (nominally the B horizon), referred to subsequently as “deep soils”. Some 6,862 regional soil sites were sampled (Figure 13) and analysed. Resulting in an average regional sampling density of 1 site per 2 km^2 (total sampling area 13,741 km^2). Observations of soil colour, depth, clast lithology and abundance were recorded at site. The samples were classified into five textural groups (sand, sand-silt, silt, silt-clay and clay).

Figure 13: Tellus regional soil sampling.

Image shows the Edelman auger and sample bags for collecting sample. Note: an additional small sample bag is shown in the photograph, this sample was collected in the first period of regional soil sampling as a reserve sample for soil pH analysis. This procedure was discontinued shortly after and the samples were not utilised.

At each sample site, information pertaining to the location, site geology, catchment geology, contamination, land use, and other features required for data interpretation was recorded on a data card in a standard BGS format. The location was also plotted on a field copy of the 1:50 000 Ordnance Survey of Northern Ireland (OSNI) Discoverer Series map. Soils were initially air-dried at the field-base prior to transport to the sample store at Carrickfergus where they were dried in a dedicated temperature controlled oven at 30°C for approximately 2 - 3 days. At the end of each field campaign samples were checked against field sheets prior to packing for transport to the laboratories of the British Geological Survey at Keyworth, Nottingham. Shipping logistics and transport of samples was arranged by the Tellus Geochemistry Manager and BGS Transport Manager. On arrival at the BGS laboratories samples were checked against shipping lists prior to assigning laboratory batch numbers in the BGS UKAS Quality Assurance System. The "A" and "S" soils were prepared in the same manner in a trace-level sample preparation laboratory.

Samples were disaggregated prior to sieving to a <2 mm fraction using nylon mesh (Figure 14). Replicate samples were prepared by riffle splitting each of the duplicate samples. Soil pH and loss on ignition (LOI) was determined on "A" samples only. Soil pH and LOI was determined for every "A"/ surface soil sample. A representative 30 g (± 2 g) sub-sample was obtained by cone and quartering. This sub-sample was then milled in an agate ball mill at 300 rpm for 30 minutes. Different analytical procedures were employed for the surface and deep soils. Pressed pellet production and XRF analysis were completed by BGS laboratories on surface soils only.

Sub-samples of milled soil were weighed and placed into tamper evident plastic sample tubes by BGS laboratory staff and dispatched to other analytical contractors on behalf of GSNI/ DETI. The XRF pressed pellet was prepared by adding an aliquot (3 g ±0.05 g) of two blended synthetic waxes comprising 90% EMU 120 FD wax and 10% Ceridust (both waxes are styrene based co-polymers) to 12 g (± 0.05 g) of milled material. This mixture was milled for 4 minutes at 300 rpm. On completion of the binder milling the prepared powders were placed into tamper evident plastic sample tubes for temporary storage prior to pellet preparation. Pellets (40 mm) were pressed using a calibrated Herzog semi-automatic pellet press at 25 kN.

Figure 14: Equipment used for soil disaggregation and sieving.

(Photograph ©NERC).

Prior to analysis certified reference materials and secondary reference materials were inserted into the sample batches sent for analysis at SGS Laboratories (Toronto). Secondary reference materials were inserted into sample batches sent for XRF analysis at BGS Laboratories. All reference materials were concealed in the sample batches sent for analysis at both laboratories. Full details pertaining to the insertion of reference materials are given in the quality control section of this report.

9.4 ROCK SAMPLING

A reconnaissance rock sampling programme was completed after the main phase of Tellus fieldwork (Figure 15). A total of 114 samples were collected. Samples were collected randomly from outcrops across Northern Ireland (Appendix II).

Several donated samples of mineralisation from Curraghinalt (gold bearing base metals), South Armagh (base-metal) and Whitespots (lead mineralisation) were incorporated into the lithogeochemical program. In all cases only fresh unaltered material was collected/ analysed. At each site a c.15 kg representative sample of each outcrop was collected. Samples were prepared at the laboratories of the British Geological Survey, Keyworth, Nottingham. Preparation consisted of an initial thorough washing of the sample to remove any rock or soil debris. Samples were then chipped and 100 g of material was milled in an agate ball-mill to a specification identical to that for the soils. The rock powders were dried overnight at 105°C before loss on ignition (L.O.I.) and fused bead production. Any samples with visible mineralisation were prepared in a similar manner but in a separate facility dedicated to higher-grade materials. The fused bead XRFS analysis was completed at the laboratories of the British Geological Survey.

All other analytical tests were completed at SGS Laboratories (Toronto). The analytical methods and detection limits for the lithogeochemical trace element suite are presented in Table 2. The parameters of lithogeochemical analyses were as follows;

1. **Fused bead XRF-** for major oxides.
2. **Loss of ignition-** determined after 1 hour at 1050°C.
3. **Au, Pd, Pt Fire Assay/ ICP-MS-** a 30 g sample was analysed. SGS Laboratories method code FAM303.
4. **Multi-element suite by sodium peroxide fusion-** completed on a 0.5 g sample with analysis by ICP-MS. SGS Laboratories method code ICM90A.
5. **F by Specific Ion-** completed on a 0.5 g sample. SGS Laboratories method code ISE07A.
6. **C by Leco-** completed on a 0.5 g sample. SGS Laboratories method code CSA01V.
7. **S by Leco-** completed on a 0.5 g sample. SGS Laboratories method code CSA06V.
8. **Hg by Cold-Vapour Atomic Absorption Spectrometry-** completed on a 0.6 g sample. SGS Laboratories method code CVA14C.

Prior to analysis certified reference materials and secondary reference materials were inserted into the sample batches. All reference materials were concealed in the sample batches sent for analysis. Chinese lithogeochemical certified reference materials GSR-1 to GSR-6 were used for all analytical tests (China National Analysis Center for Iron and Steel, 1986), except Au, Pd and Pt by fire assay.

The parameters of the GSR-1 to 6 reference materials are as follows;

GSR-1	Grey medium-grained biotite granite sample from Qianlishan rock body in Chenzhou, Hunan. Also referred to as GBW07103.
GSR-2	Mesozoic quartz hornblende andesite from the vicinity of the Meishan iron mine in Nanjing, Jiangsu. Also referred to as GBW07104.
GSR-3	Cenozoic alkali-olivine basalt from Zhangjiakou, Hebei. Also referred to as GBW07105.
GSR-4	Light and dark arkosic quartz-sandstone from Group Wutong, Silurian system in Tongling, Anhui. Also referred to as GBW07106.
GSR-5	Shale from Group Chuanlinggou, Sinian system in Jixian, Tianjin. Also referred to as GBW07107.
GSR-6	Banded argillaceous limestone, Triassic system in Tongling, Anhui. Also referred to as GBW07108.

Table 2: Lithogeochemical analytical parameters and analytes.

Method	Element	Unit	Detection Limit		Element	Unit	Detection Limit
WD-XRFS Fused Glass Bead	SiO_2	%	0.01		[2]SO_3	%	0.01
	TiO_2	%	0.01		Cr_2O_3	%	0.01
	Al_2O_3	%	0.01		SrO	%	0.01
	[1]Fe_2O_3	%	0.01		ZrO_2	%	0.02
	Mn_3O_4	%	0.01		BaO	%	0.02
	MgO	%	0.05		[3]NiO	%	0.01
	CaO	%	0.01		[3]CuO	%	0.01
	Na_2O	%	0.05		[3]ZnO	%	0.01
	K_2O	%	0.01		[3]PbO	%	0.01
	P_2O_5	%	0.01		-	-	-
Sodium Peroxide Fusion/ ICP-MS	Ag	mg/kg	1.00		Mg	%	0.01
	Al	%	0.01		Mn	mg/kg	10.00
	As	mg/kg	5.00		Mo	mg/kg	2.00
	B	mg/kg	10.00		Nb	mg/kg	1.00
	Ba	mg/kg	0.50		Nd	mg/kg	0.10
	Be	mg/kg	5.00		Ni	mg/kg	5.00
	Bi	mg/kg	0.10		P	%	0.01
	Ca	%	0.01		Pb	mg/kg	5.00
	Cd	mg/kg	0.20		Pr	mg/kg	0.05
	Ce	mg/kg	0.10		Rb	mg/kg	0.20
	Co	mg/kg	0.50		Sb	mg/kg	0.10
	Cr	mg/kg	10.00		Sc	mg/kg	5.00
	Cs	mg/kg	0.10		Sm	mg/kg	0.10
	Cu	mg/kg	5.00		Sn	mg/kg	1.00
	Dy	mg/kg	0.05		Sr	mg/kg	0.10
	Er	mg/kg	0.05		Ta	mg/kg	0.50
	Eu	mg/kg	0.05		Tb	mg/kg	0.05
	Fe	%	0.01		Th	mg/kg	0.10
	Ga	mg/kg	1.00		Ti	%	0.01
	Gd	mg/kg	0.05		Tl	mg/kg	0.50
	Ge	mg/kg	1.00		Tm	mg/kg	0.05
	Hf	mg/kg	1.00		U	mg/kg	0.05
	Ho	mg/kg	0.05		V	mg/kg	5.00
	In	mg/kg	0.20		W	mg/kg	1.00
	K	mg/kg	0.01		Y	mg/kg	0.50
	La	mg/kg	0.10		Yb	mg/kg	0.10
	Li	mg/kg	10.00		Zn	mg/kg	5.00
	Lu	mg/kg	0.05		Zr	mg/kg	0.50
Fire Assay/ ICP-MS							
	Au	µg/kg	1.00				
	Pd	µg/kg	1.00				
	Pt	µg/kg	1.00				
Leco	F	mg/kg	20.00				
	C	%	0.01				
	S	%	0.01				
CV-AA							
	Hg	µg/kg	5.00				

[1] represents total iron expressed as Fe_2O_3. [2] SO_3 represents sulphur retained in the fused bead after fusion at 1200°C. [3] not included in the UKAS Accreditation schedule.

Figure 15: Tellus reconnaissance rock sampling.

Due to the health and safety risks involved in obtaining rock samples additional personal protective equipment was worn. In this example a hard hat with shatterproof face shield was worn. Goggles were also worn beneath the face shield for additional protection. Photograph courtesy L.M. Stockdale.

For the analysis of Au, Pd, and Pt by fire assay the following CANMET Reference Materials (RMs) were used; TDB-1, WPR-1, and WGB-1. Separate insertions of the CANMET RM's were also analysed and reported by SGS as part of the fire assay analysis. All GSR series and CANMET RMs were inserted into their respective batches at a rate of three samples per 87 field samples. Four field duplicate pairs were collected per field batch (100 samples). Secondary reference soils Antbas, Dal, LwrPala and S13B were inserted in rotation at a rate of two samples per field batch. Due to the unavailability of lithogeochemical secondary reference materials it was not possible to matrix match SRMs to the survey.

All analyses at SGS Laboratories were completed by a combination of ICP-OES and ICP-MS instrumentation. Data were reported as censored and uncensored datasets.

10 Chemical Analysis

The following analytical tests were completed on the rural and urban soil samples;

10.1 SURFACE SOIL/ "A" SAMPLE

Samples from the 5 - 20 cm depth. These samples were analysed in the following manner;

1. Pressed pellet XRF- completed at the laboratories of the British Geological Survey (BGS), Keyworth, Nottingham. Major oxides and trace elements on a pressed powder pellet.
2. Aqua regia digest- completed at SGS Laboratories (Toronto). Aqua regia digestion of a 1 g sub-sample, trace element analysis by ICP-OES and ICP-MS.
3. pH- a sub-sample (10 g ±2 g) of the <2 mm fraction (obtained by cone and quartering), slurried with 0.01M $CaCl_2$ solution, with a soil/solution ratio of 1:2.5. Soil pH was measured using a calibrated pH meter.
4. Loss on ignition- 1 g of milled sample was dried in an oven at 105°C for a minimum of 4 hours. The sample was then heated in a furnace at 450°C for 4 hours. Loss on ignition was calculated using the weight loss between the sample heated at 450°C and dried at 105°C.

10.2 DEEP SOIL/ "S" SAMPLE

Samples from the 35 - 50 cm depth. These samples were analysed in the following manner;

1. Aqua regia digest- completed at SGS Laboratories (Toronto). Aqua regia digestion of a 1 g sub-sample, trace element analysis by ICP-OES and ICP-MS.
2. "Near-total" digest- completed at SGS Laboratories (Toronto). Multi acid (HF-$HClO_4$-HCl-HNO_3) digestion, trace element analysis by ICP-OES and ICP-MS.
3. Au and PGE by fire assay- completed at SGS Laboratories (Toronto). Lead fire assay of a 10 g sub-sample of milled material followed by Au, Pd and Pt analysis by ICP-MS.
4. Sulphate by dilute hydrochloric acid leach- completed at SGS Laboratories (Toronto). Hydrochloric acid digestion of a 1 g sub-sample followed by sulphate analysis by ICP-OES.

10.2.1 Soil and stream sediment X-ray fluorescence spectrometry

Major oxides and trace elements in stream sediment and soil samples were primarily analysed by wavelength-dispersive X-ray fluorescence spectrometry (Ingham and Vrebos, 1994). Stream sediments were analysed in two phases, the first phase from 1994 to 1996 corresponding to the G-BASE survey and a second phase between 2005 and 2006 corresponding to the Tellus survey. For both sediment analytical phases sample types and procedures were identical. Sample preparation and XRF analysis were completed at the laboratories of the British Geological Survey at Keyworth, Nottingham. Advances in XRF analysis at BGS (Figure 16) in the intervening period between the two surveys facilitated a greater range of determinands and lower detection limits for the more recent Tellus samples. Details of sediment XRF analysis for both phases are presented. The following instrumentation was used during the Tellus stream sediment and soil analysis.

Wavelength Dispersive X-Ray Fluorescence (WD-XRF) Spectrometers

Instrumentation comprised:

1). One PANalytical Axios Advanced, 4 kW Rh tube, automatic x-y-z sample changer (purchased in 2005).

2). One Philips MagiX-PRO, 4 kW Rh tube, automatic x-y-z sample changer (purchased in 2002).

3). One Philips PW2400, 3 kW Rh tube, automatic sample changer (purchased 1993).

Figure 16: X-ray Fluorescence spectrometry instrumentation.

Photograph taken at the laboratories of the British Geological Survey, Keyworth, Nottingham. (Photograph ©NERC)

A second Philips PW2400 spectrometer (purchased 1992) was used for the first phase of the Tellus analysis. This was upgraded to the Axios Advanced spectrometer in 2005. All spectrometers were controlled using PANalytical SuperQ application software including the Pro-Trace calibration package and standards.

Energy Dispersive (Polarised) X-Ray Fluorescence Spectrometer (ED-XRF)

Instrumentation comprised:

1). Two PANalytical Epsilon 5 spectrometers (ED-P-XRF), 100 kV Gd tube, automatic x-y-z sample changer with proprietary application software package.

For major element analysis, a wide range of Reference Materials (e.g., GSD-7, GSS-1, LKSD-1, LKSD-4) were used for calibration purposes and to determine background and spectral interference correction factors. The PANalytical calibration algorithm was used to fit calibration curves, applying matrix correction by influence coefficients. Calibrations were validated by analysis of a sub-set of Reference Materials (RMs).

For trace element analysis, a set of synthetic standards (Pro-Trace) was used to calibrate the instruments and to determine background, spectral interference and matrix correction factors. The PANalytical Pro-Trace calibration algorithm was used to fit calibration curves, applying matrix correction by mass absorption coefficients. The calibrations were validated by analysis of a wide range of Reference Materials.

For the Tellus samples Energy Dispersive Polarised X-Ray Fluorescence (ED(P)-XRF) spectrometers were used to analyse those elements for which the WD-XRF spectrometers were insufficiently sensitive (Table 4). Certified Reference Material standards were used to calibrate the instruments. The PANalytical software was used for spectral deconvolution and to fit calibration curves, applying matrix correction by internal ratio Compton correction method. The calibrations were validated by analysis of a wide range of Reference Materials. The detectors were calibrated weekly. All backgrounds and peaks were corrected for instrument drift using two external ratio monitors, when required. Quality control was maintained by regular analysis of two glass monitor samples containing 47 elements at nominally 30 mg/kg and 300 mg/kg. Results were presented as run charts for statistical analysis using statistical process control software (SPC).

Table 3: XRF analyses – compounds

llus data, 2005			BASE data, 1994		
nalyt	LD (%	Method	nalyt	LD (%	Method
Al_2O_3	0.2	WD-XRFS			
CaO	0.30	WD-XRFS	CaO	0.032	WD-XRFS
Cl	0.05	WD-XRFS			
Fe_2O_3	0.05	WD-XRFS	Fe_2O_3	0.590	WD-XRFS
K_2O	0.10	WD-XRFS	K_2O	0.129	WD-XRFS
MgO	0.3	WD-XRFS	MgO	0.068	WD-XRFS
MnO	0.010	WD-XRFS	MnO	0.010	WD-XRFS
Na_2O	0.3	WD-XRFS			
P_2O_5	0.05	WD-XRFS	P_2O_5	0.013	WD-XRFS
SiO_2	0.1	WD-XRFS			
SO_3	0.5	WD-XRFS			
TiO_2	0.020	WD-XRFS	TiO_2	0.034	WD-XRFS

The analytes determined and lower limits of detection (LLD) for both the G-BASE and Tellus stream sediment samples are listed in Table 3 and Table 4. The lower limits of detection are theoretical values for the concentration equivalent to three standard deviations (99.7% confidence interval) above the background count rate for the analyte in an iron-rich alumino-silicate matrix. For silicate matrices the practical detection limits for most elements approach the theoretical values due to high instrumental stability. LLD's were calculated from a matrix blank and the 'synthetic' Pro-Trace standards using Equation 1.

Equation 1: The theoretical lower limit of detection.

$$\text{L.L.D.} = \frac{3}{m}\sqrt{\frac{R_b}{T_b}}$$

Where:

m = sensitivity (counts per second per %)

R_b = the background count rate (counts per second)

T_b = the counting time on the background (s)

Table 4: XRF analyses - trace elements

Tellus data, 2004-6			G-BASE data, 1994-6		
Analyte	**LLD mg/kg**	**Method**	**Analyte**	**LLD mg/kg**	**Method**
Ag	0.5	ED-XRFS	Ag	1.9	WD-XRFS
As	0.9	WD-XRFS	As	1.7	WD-XRFS
Ba	1.0	ED-XRFS	Ba	10	WD-XRFS
Bi	0.3	WD-XRFS	Bi	1.1	WD-XRFS
Br	0.8	WD-XRFS			
Cd	0.5	ED-XRFS	Cd	1.0	WD-XRFS
Ce	1.0	ED-XRFS	Ce	4.7	WD-XRFS
Co	1.5	WD-XRFS	Co	0.8	WD-XRFS
Cr	3.0	WD-XRFS	Cr	8.4	WD-XRFS
Cs	1.0	ED-XRFS	Cs	3.2	WD-XRFS
Cu	1.3	WD-XRFS	Cu	5.2	WD-XRFS
Ga	1.0	WD-XRFS	Ga	2.1	WD-XRFS
Ge	0.5	WD-XRFS			
Hf	1.1	WD-XRFS			
I	0.5	ED-XRFS			
In	0.5	ED-XRFS			
La	1.0	ED-XRFS	La	2.8	WD-XRFS
Mo	0.2	WD-XRFS	Mo	1.0	WD-XRFS
Nb	0.9	WD-XRFS	Nb	0.8	WD-XRFS
Nd	3.6	WD-XRFS			
Ni	1.4	WD-XRFS	Ni	4.2	WD-XRFS
Pb	1.3	WD-XRFS	Pb	3.9	WD-XRFS
Rb	1.0	WD-XRFS	Rb	1.3	WD-XRFS
Sb	0.5	ED-XRFS	Sb	1.9	WD-XRFS
Sc	2.7	WD-XRFS			
Se	0.2	WD-XRFS	Se	0.4	WD-XRFS
Sm	3.0	WD-XRFS			
Sn	0.5	ED-XRFS	Sn	2.1	WD-XRFS
Sr	1.1	WD-XRFS	Sr	12.8	WD-XRFS
Ta	1.1	WD-XRFS			
Te	0.5	ED-XRFS			
Th	0.7	WD-XRFS	Th	1.6	WD-XRFS
Tl	0.5	WD-XRFS			
U	0.5	WD-XRFS	U	0.2	WD-XRFS
V	2.9	WD-XRFS	V	8.4	WD-XRFS
W	0.6	WD-XRFS	W	2.0	WD-XRFS
Y	1.1	WD-XRFS	Y	11.5	WD-XRFS
Yb	1.4	WD-XRFS			
Zn	1.2	WD-XRFS	Zn	6.3	WD-XRFS
Zr	1.2	WD-XRFS	Zr	65.8	WD-XRFS

Individual results are not reliable below the quoted lower limits, but reliable estimates of the average or typical values over an area may be obtained at lower levels of concentration; meaningful distribution patterns may thus be recognised for some elements at levels lower than the LLD.

During analysis the XRF pellet was irradiated with X-rays, inducing secondary X-ray fluorescence of the atoms within the sample. This secondary radiation was collimated onto a diffraction crystal and its intensity at selected peak and background positions in the X-ray spectrum was measured using a detector mounted onto a goniometer. The net intensity at each of the peak positions was calibrated against known synthetic standards and Reference Materials (RMs).

The calibration lines were established using numerous RMs, placing the slope to give the best fit through the average of the predominantly silicate RMs. Where a sample composition differs widely from this average it may produce erroneous results, e.g., peat substrates. Elements such as Ba, Cu, Ni, Pb, Sr, Ti, Zn and Zr which are usually present at trace levels, will cause interference if they are present at concentrations above c. 0.5%, leading to uncorrected errors in most analytes.

10.3 SOIL AND STREAM SEDIMENT AU AND PGE BY FIRE ASSAY/ ICP-MS

Tellus soil samples were analysed (SGS method code FAM303) in a single phase at SGS Laboratories (Toronto). Stream sediments were analysed at Acme Analytical Laboratories Ltd. (Vancouver) in two phases (Acme method code 3B-MS). G-BASE stream sediment samples were analysed in early 2002 and Tellus stream sediment samples in a single phase in the winter of 2006/ 2007. For soils, gold, palladium and platinum were determined on deep soil samples (35 - 50 cm depth). For both sample types (sediment, soil) 10 g sub-samples of milled material were prepared and dispatched to the analytical contractors by BGS laboratories. A standard lead fire assay process was completed on samples in both laboratories. Soil samples were fired for 60 minutes (Figure 17) with a flux mixture containing lead oxide (litharge) in a gas furnace at 1050℃ ±100℃. Sediment samples were fired for 40 minutes. Silver was added in order to alloy the precious metals and produce a bead at the end of the cupellation process. On completion of the firing the resulting lead button was separated from the borosilicate slag and subsequently heated in a MnO cupel for 1 hour. This removed the lead and produced a silver bead containing Au, Pt and Pd (and Rh).

For the soil analysis the bead was digested in 0.5 mL of 1:1 nitric acid and 0.5 mL of hydrochloric acid and then diluted to 5 mL with water. For sediments the bead was digested with 1 mL of hot nitric acid (HNO_3) and then 10 mL of hydrochloric acid (HCl). In both laboratories a portion of the digested silver bead was aspirated into the ICP-MS where the concentrations of Au, Pd and Pt were determined against calibration standards. A semi-quantitative analysis of rhodium was obtained in stream sediment samples. Soil samples were analysed on a PerkinElmer Sciex Elan 9000 ICP-MS Spectrometer and sediment samples on a Perkin Elmer Elan 6000 ICP-MS Spectrometer. Quoted detection limits for soil and sediment analysis are shown in Table 5. For soils the calibration curve consisted of four points: blank, 10, 25 and 50 µg/L for each of gold, palladium and platinum in solution. An independent check solution at 10 µg/mL was analysed after the calibration, a ±10 % tolerance had to be met before analysis commenced.

Table 5: Quoted detection limits for Au, Pt, Pd (and Rh) in soil and stream sediments.

Element	Soil Quoted Detection Limit (µg/kg)[4]	Sediment Quoted Detection Limit (µg/kg)[5]
Au	[2]1.0	1.0
Pt	[2]0.5	0.1
Pd	[2]1.0	0.5
[1]Rh	[3]na	0.05

[1] semi-quantitative analysis. [2] subsequently revised, see Table 28. [3] not analysed

[4] SGS Laboratories (Toronto). [5] Acme Laboratories (Vancouver).

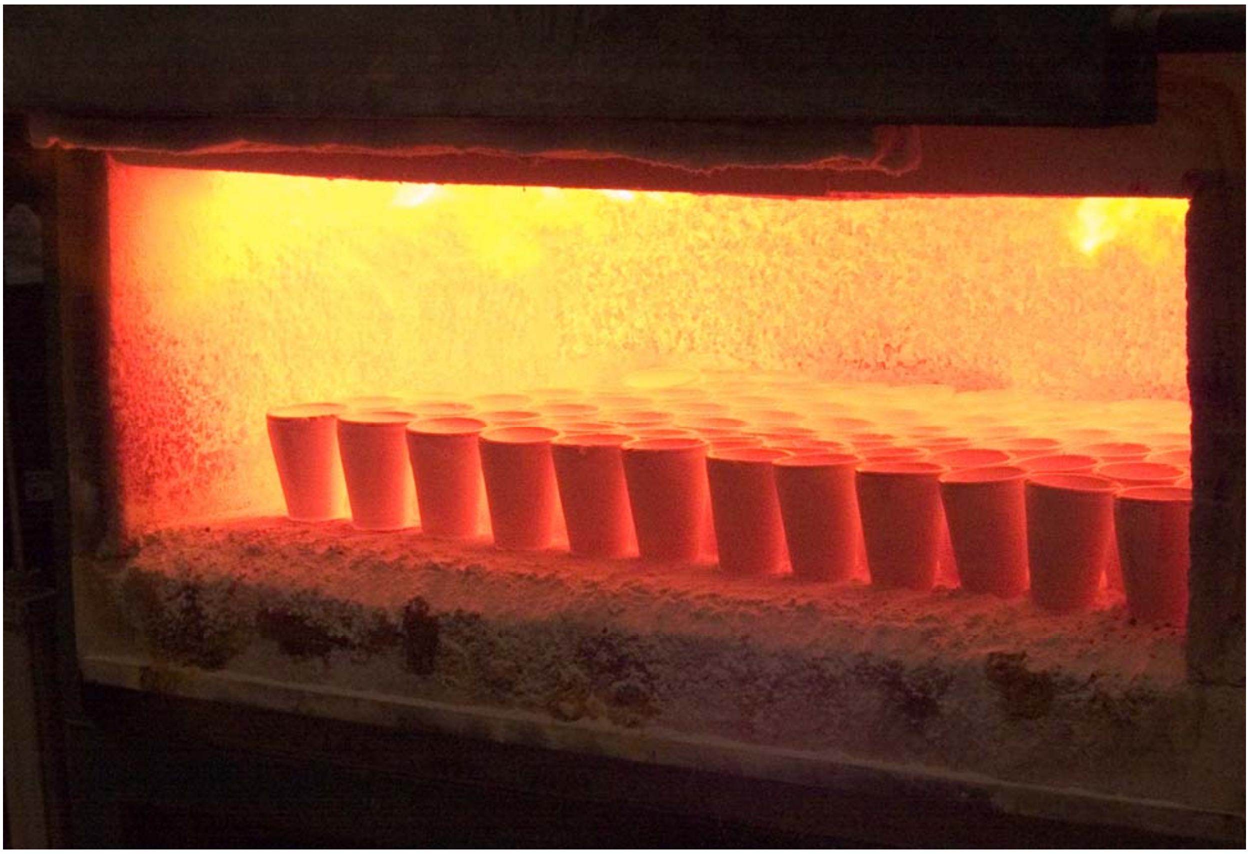


Figure 17: Fire assay of Tellus soil samples at SGS Laboratories (Toronto).

A calibration check was performed after every 48 samples to ensure that the calibration stayed within the ±10 % limit. Solution concentrations were converted to raw concentration in the sample and exported to the laboratory information management system (LIMS) where a weight correction was automatically applied. Upon assessment and successful completion of the quality control criteria the results were validated and the final data files prepared for dispatch to the Tellus Geochemistry Manager.

At SGS Laboratories an analytical batch comprised 80 samples. A 10 g sample of a CANMET reference material and a blank were analysed (and reported) every 48 samples by SGS Laboratories. CANMET reference materials WGB-1 (CANMET, 1997), WMG-1 (CANMET, 2004a), WMS-1, WPR-1 (CANMET, 2004b) and TDB-1 (CANMET, 1994) were analysed in rotation. Analysis of reference material WMS-1 was discontinued after the first phase of analysis due to the high concentration of Au, Pd and Pt and inconsistency of values with respect to those likely to be encountered in a regional baseline survey. Palladium values in CANMET reference material TDB-1 were treated as “provisional”. All reference materials and blanks were reported as part of the data file. Laboratory detection limits (D.L.) were determined according to CAN-P-1579 (Standards Council of Canada, 2001). Certified reference materials were not reported in the G-BASE sediment sample batches sent to Acme Laboratories (Vancouver) for fire assay and boron analysis. For the Tellus stream sediments Acme Laboratories analysed and reported a blank on average every 20 samples, a CANMET standard (WMG-1, TDB-1) every 50 field samples, an internal secondary reference material on average every 17 samples (FA-100S) and every 33 samples (G1- granite) for both the fire assay (Au, Pd, Pt, Rh) and sodium peroxide (boron) analyses.

10.4 STREAM SEDIMENT BORON DETERMINATION

Two phases of boron analysis (Acme method code Group 2A) contemporaneous with the fire assay were performed at Acme Analytical Laboratories Ltd. (Vancouver). A 0.10 g sub-sample of milled sediment was weighed into a zirconium crucible and mixed with 1.5 g Na_2O_2 and 0.5 g NaOH. Analysis was completed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) using a single spectrometer (ICP13) in the case of Tellus samples. The quoted detection limit was 2 mg/kg. Internal laboratory quality control was completed in accordance with the procedures outlined for the Acme Laboratories fire assay analysis. Quality control of G-BASE samples was monitored using internal standard LIB-10. For Tellus samples quality control was monitored using internal standards C3, FA-100S and LIBF200.

10.5 SOIL AQUA REGIA DIGEST (HCL, HNO_3) AND ICP-OES/ MS ANALYSIS

Upon receipt at SGS Laboratories (Toronto) samples were logged into the laboratory information management system (LIMS) and workorder numbers generated for each analytical batch (c.80 samples). The detection limits and analytical methodology for the aqua regia digest suite of elements is presented in Table 6. The aqua regia digest (SGS method code ICM12B) was performed on both the “surface” and “deep” soil samples. For each sample 1 ±0.005 g was weighed into a 50 mL centrifuge tube and logged into the LIMS. To each sample 8 mL of HNO_3 was added and the sample agitated prior to placement into a water bath at 80 - 90°C for thirty minutes. The sample was then allowed to cool slightly before the addition of 4 mL of HCl. The sample was further agitated and placed into a heated water bath for two hours. During this time the sample was agitated every thirty minutes. The sample was then cooled to room temperature and diluted to 50 mL with deionised water. The centrifuge tube was then capped and shaken. The digest was analysed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) and ICP MS.

For the ICP-OES analyses (Table 7) the instrument (Optima 5300DV ICP-OES, PerkinElmer Life and Analytical Sciences, USA) was calibrated using a blank and either a 5 mg/kg standard for trace elements, or a 50 mg/kg standard for the major elements (Al, Ca, Fe, K, Mg, Na, P, S, and Ti). A calibration check standard was analysed after every 24 samples to ensure that the calibration remained within a ±10% tolerance. The ICP instruments were calibrated at the beginning of each analytical run (approximately 300 samples). Lutetium at 5 mg/kg was used as an internal standard for all standards and soil samples to allow for plasma variations due to the different sample types.

SGS Laboratories analysed an internal secondary reference material (XRAL01A) approximately every 47 samples. Expected values for XRAL01A are reported in Table 9. Results were converted to parts per million (ppm) in the solid sample and exported to the LIMS for final weight correction, data analysis and validation prior to reporting.

For the ICP-MS analyses (Table 8) a portion of the sample was diluted with a solution of 1 % HNO_3 containing Rh and Re as internal standards. Analysis was conducted using a PerkinElmer Sciex Elan 9000 ICP-MS Spectrometer (PerkinElmer Sciex, Canada). The calibration curve consisted of four points; 0, 10, 25 and 50 µg/L (1, 2.5 and 5.0 µg/L for Ag, Au, Pd, Pt and Hg) for each of the ICP-MS elements. A calibration check at 10 µg/L was completed after every 48 soil analyses to ensure that there was no analytical drift. The instrument was calibrated before every analytical run (approximately 200 to 300 samples). The results were converted to mg/kg in the solid and exported to the LIMS for final weight correction, data analysis and validation prior to reporting.

Table 6: Elements, detection limits and analysis method for aqua regia digest ICP-OES/ MS analysis of soil at SGS Laboratories.

Element	Detection limit (mg/kg)	Method		Element	Detection limit (mg/kg)	Method
Ag	0.01	ICP-MS		Na	0.01%	ICP-OES
Al	0.01%	ICP-OES		Nb	0.05	ICP-MS
As	0.10	ICP-MS		Ni	0.50	ICP-MS
Au	0.10	ICP-OES		P	50.00	ICP-OES
B	10.00	ICP-OES		Pb	0.20	ICP-MS
Ba	5.00	ICP-OES		Pd	0.50	ICP-MS
Be	0.10	ICP-MS		Pt	0.10	ICP-MS
Bi	0.02	ICP-MS		Rb	0.20	ICP-MS
Ca	0.01%	ICP-OES		S	0.01%	ICP-OES
Cd	0.01	ICP-MS		Sb	0.05	ICP-MS
Ce	0.05	ICP-MS		Sc	0.10	ICP-MS
Co	0.10	ICP-MS		Se	1.00	ICP-MS
Cr	1.00	ICP-OES		Sn	0.30	ICP-MS
Cs	0.05	ICP-MS		Sr	0.50	ICP-OES
Cu	0.50	ICP-OES		Ta	0.05	ICP-MS
Fe	0.01%	ICP-OES		Tb	0.02	ICP-MS
Ga	0.10	ICP-MS		Te	0.05	ICP-MS
Ge	0.10	ICP-MS		Th	0.10	ICP-MS
Hf	0.05	ICP-MS		Ti	0.01%	ICP-OES
Hg	0.01	ICP-MS		Tl	0.02	ICP-MS
In	0.02	ICP-MS		U	0.05	ICP-MS
K	0.01%	ICP-OES		V	1.00	ICP-OES
La	0.10	ICP-MS		W	0.10	ICP-MS
Li	1.00	ICP-OES		Y	0.05	ICP-MS
Lu	0.01	ICP-MS		Yb	0.10	ICP-MS
Mg	0.01%	ICP-OES		Zn	1.00	ICP-OES
Mn	5.00	ICP-OES		Zr	0.50	ICP-OES
Mo	0.05	ICP-MS		-	-	-

Table 7: ICP-OES: instrumentation and typical operating conditions for Tellus soil samples at SGS Laboratories.

Parameter	Typical operating conditions
Instrument	Optima 5300DV ICP-OES
Spectrometer	Echelle grating with Charge Coupled Device Detector
Spray chamber	Baffled cyclonic
Nebuliser	Burgener Mira Mist
Torch	Single slot
Autosampler	Cetac EXR-8
RF power	1300 W
RF frequency	40 MHz
Viewing height	Dual viewing
Coolant gas	15 L/min
Plasma gas	0.2 L/min
Nebuliser gas	0.65 L/min
Solution uptake	1.5 mL/min
Pump	Internal

Table 8: ICP-MS: instrumental and analytical parameters for Tellus soil analyses at SGS Laboratories.

Parameter	Typical operating conditions
Forward power	1000 W
Coolant gas flow	13 L/min
Auxiliary gas flow	0.5 L/min
Nebuliser gas flow	0.9 L/min
Integration time	2 x 400 msec
Nebuliser	Cross flow
Spray chamber	Ryton double pass
Spray chamber temperature	Ambient
Mass range	6 – 238 atomic mass units
Mode of acquisition	Peak Hopping
Type of detector	Simulscan Dual Stage
Detector mode	Dual

Table 9: Expected values for SGS Laboratories SRM XRAL01A analysed by SGS method code ICM12B.

Element	Unit	Detection Limit	Expected Value
Ag	mg/kg	0.01	2.18
Al	%	0.01	0.53
As	mg/kg	1.00	1081.00
B	mg/kg	10.00	12.86
Ba	mg/kg	5.00	3539.80
Be	mg/kg	0.10	0.39
Bi	mg/kg	0.02	11.71
Ca	%	0.01	1.91
Cd	mg/kg	0.01	2.82
Ce	mg/kg	0.05	14.64
Co	mg/kg	0.10	6.48
Cr	mg/kg	1.00	123.25
Cs	mg/kg	0.05	1.84
Cu	mg/kg	0.50	105.00
Fe	%	0.01	1.91
Ga	mg/kg	0.10	1.68
Ge	mg/kg	0.10	0.10
Hf	mg/kg	0.05	0.19
Hg	mg/kg	0.01	4.63
In	mg/kg	0.02	0.21
K	%	0.01	0.16
La	mg/kg	0.10	8.00
Li	mg/kg	1.00	3.50
Lu	mg/kg	0.01	0.11
Mg	%	0.01	0.27
Mn	mg/kg	5.00	304.70
Mo	mg/kg	0.05	9.79
Na	%	0.01	0.01
Nb	mg/kg	0.05	0.05
Ni	mg/kg	0.50	41.52
P	mg/kg	50.00	700.00
Pb	mg/kg	0.20	72.43
Rb	mg/kg	0.20	7.23
S	%	0.01	0.18
Sb	mg/kg	0.05	118.38
Sc	mg/kg	0.10	2.88
Se	mg/kg	1.00	4.05
Sn	mg/kg	0.30	2.39
Sr	mg/kg	0.50	62.39
Tb	mg/kg	0.02	0.30
Te	mg/kg	0.05	0.13
Th	mg/kg	0.10	2.73
Tl	mg/kg	0.02	4.72
U	mg/kg	0.05	3.57
V	mg/kg	1.00	225.50
W	mg/kg	0.10	12.40
Y	mg/kg	0.05	9.38
Yb	mg/kg	0.10	0.74
Zn	mg/kg	1.00	179.20
Zr	mg/kg	0.50	6.50

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10.6 SOIL "NEAR-TOTAL" (HCL, HNO_3, $HCLO_4$, HF) DIGEST AND ICP-OES/ MS ANALYSIS

At SGS Laboratories (Toronto) samples were logged into the LIMS and workorder numbers generated for each analytical batch (c.80 samples). The detection limits and analytical methodology for the suite of elements is presented in Table 10. The "near-total" digest (SGS method code ICM40B) was performed on the "deep" ("S", 35 to 50 cm depth) soil samples only.

A 0.20 g ±1.0 mg sample was weighed into a 50 mL Teflon dish. Then 2 mL each of nitric, hydrochloric and hydrofluoric acids were added to each sample dish, plus 1 mL of perchloric acid. The inner wall of the dish was then rinsed with deionised water and the dish heated at 200-250°C until dry. The dish was allowed to cool, then 1.0 mL of perchloric acid was added, the dish was then re-heated to dryness at the same temperature. The dish was cooled again and 2 mL of hydrochloric acid and 1 mL of nitric acid were added. The dish was allowed to stand for a few minutes before the addition of approximately 10 mL of deionised water, the dish was then heated to dissolve the salts. The solution was transferred to a graduated plastic centrifuge tube and diluted to 12 mL with deionised water. The centrifuge tube was then covered with parafilm and agitated.

Samples were analysed by a combination of ICP-OES and ICP-MS. The ICP-OES instrument (Optima 5300DV ICP-OES, PerkinElmer Life and Analytical Sciences, USA) was calibrated using a blank and either a 5 mg/kg standard for trace elements, or a 50 mg/kg standard for the major elements (Al, Ca, Fe, K, Mg, Na, P, S, and Ti). A calibration check standard was analysed after every 24 soil samples to ensure that the calibration remained within a ±10% tolerance. The instrument was calibrated at the beginning of each analytical run (approximately 300 samples). Lutetium at 5 mg/kg was used as an internal standard for all standards and soil samples to allow for plasma variations due to different sample types. The results were converted to mg/kg in the solid sample and exported to the LIMS for final weight correction, data analysis and validation prior to reporting.

For the ICP-MS analysis a portion of the sample was diluted with a solution of 1% HNO_3 containing Rh and Re as internal standards. Analysis was conducted using a PerkinElmer Sciex Elan 9000 ICP-MS Spectrometer (PerkinElmer Sciex, Canada). The calibration curve comprised four points; 0, 10, 25 and 50 µg/L (1, 2.5 and 5.0 µg/L for Ag, Au, Pd, Pt and Hg) for each of the ICP-MS elements. A calibration check at 10 µg/L was analysed after every 48 soil analyses to ensure that there was no analytical drift. The instrument was calibrated before every analytical run (approximately 200 to 300 samples). Results were converted to parts per million (ppm) in the solid and exported to the LIMS for final weight correction, data analysis and validation prior to reporting.

A 0.20 g ±1.0 mg sample of CANMET certified reference material (CRM) SO-3 (CANMET, 1979) was analysed approximately every 48 samples. The reference material is a calcite and dolomite bearing grey brown luvisol soil collected near Guelph (Ontario, Canada).

Table 10: Elements, detection limits and analysis method for the "near-total" digest ICP-OES/ MS analysis of soil at SGS Laboratories.

Element	Detection limit (mg/kg)	Method		Element	Detection limit (mg/kg)	Method
Ag	0.02	ICP-MS		Na	0.01%	ICP-OES
Al	0.01%	ICP-OES		Nb	0.10	ICP-MS
As	1.00	ICP-MS		Ni	0.50	ICP-MS
Ba	5.00	ICP-OES		P	50.00	ICP-OES
Be	0.10	ICP-MS		Pb	0.50	ICP-MS
Bi	0.04	ICP-MS		Rb	0.20	ICP-MS
Ca	0.01%	ICP-OES		S	0.01%	ICP-OES
Cd	0.02	ICP-MS		Sb	0.05	ICP-MS
Ce	0.05	ICP-MS		Sc	0.10	ICP-MS
Co	0.10	ICP-MS		Se	2.00	ICP-MS
Cr	1.00	ICP-OES		Sn	0.30	ICP-MS
Cs	5.00	ICP-MS		Sr	0.50	ICP-OES
Cu	0.50	ICP-OES		Ta	0.05	ICP-MS
Fe	0.01%	ICP-OES		Tb	0.05	ICP-MS
Ga	0.10	ICP-MS		Te	0.05	ICP-MS
Ge	0.10	ICP-MS		Th	0.20	ICP-MS
Hf	0.02	ICP-MS		Ti	0.01%	ICP-OES
In	0.02	ICP-MS		Tl	0.02	ICP-MS
K	0.01%	ICP-OES		U	0.10	ICP-MS
La	0.10	ICP-MS		V	1.00	ICP-OES
Li	1.00	ICP-OES		W	0.10	ICP-MS
Lu	0.01	ICP-MS		Y	0.10	ICP-MS
Mg	0.01%	ICP-OES		Yb	0.10	ICP-MS
Mn	5.00	ICP-OES		Zn	1.00	ICP-OES
Mo	0.05	ICP-MS		Zr	0.50	ICP-OES

10.7 SOIL SULPHATE (SO_4) BY HYDROCHLORIC ACID (HCL) DIGEST ICP-OES ANALYSIS

Sulphate analysis on a hydrochloric acid digest was performed on the "deep" soil samples only (SGS method code CHAY50). The digestion procedure was as follows;

1. 0.1 g of soil sample was weighed into a test tube.
2. 2 mL of distilled water was added to the test tube.
3. The sample was then agitated and heated to boiling point for a few minutes.
4. 1 mL of concentrated hydrochloric acid was then added and the sample heated to boiling point. Heating was continued for 15 to 20 minutes.
5. The sample was then cooled and diluted to 20 mL with distilled water.

The digested sample solution was then aspirated into the ICP-OES instrument (Varian Vista Pro Radial, Varian Inc., Melbourne, Australia). Instrument parameters are presented in Table 11.

Table 11: ICP-OES: instrumentation and typical operating conditions for soil sulphate analysis.

Parameter	Typical operating conditions
Instrument	Varian Vista Pro Radial
Spectrometer	Echelle Grating with Vista Chip Charge Coupled Device Detector
Spray chamber	Baffled cyclonic
Nebuliser	Burgener T2100
Torch	-
Autosampler	Cetac ASX-510
RF power	1300 W
RF frequency	40 MHz
Viewing height	9 mm above the coil
Coolant gas	15 L/min
Plasma gas	1.5 L/min
Carrier gas	0.7 L/min
Solution uptake	1.5 mL/min
Pump	Internal

The instrument was calibrated at the start of each analytical run (c.300 samples) using a 50 mg/kg standard and a blank. A calibration check standard was analysed after every 24 soil samples to ensure that the calibration remained within a ±10 % tolerance. A 0.1 g sample of CANMET certified reference material (CRM) PD-1 (CANMET, 1981) was analysed (and reported) approximately every 48 samples. The reference material is a composite of non-ferrous dusts from the Hudson Bay Mining and Smelting Company Ltd. (Manitoba, Canada). Analytical results were exported to the LIMS where data analysis and validation were completed. The sulphate was calculated from the sulphur. The detection limit was 0.05 % SO_4.

10.8 STREAM WATERS

The stream water results from the G-BASE and Tellus surveys, although produced more than a decade apart, integrate surprisingly well. The main differences between the two datasets can be attributed to improvements in analytical methodology. Tellus water samples have been analysed with generally better lower limits of detection and for a greater range of elements. The complete Northern Ireland stream water data set can be used with the confidence that element variability is attributable to natural or anthropogenic factors.

10.8.1 G-BASE Stream water analysis

10.8.1.1 INDUCTIVELY COUPLED PLASMA ATOMIC-EMISSION SPECTROMETRY (ICP-AES) OF G-BASE WATER SAMPLES

ICP-AES was used to determine 14 elements in G-BASE stream waters between 1994 and 1996. Details of the equipment and operating conditions are given in Table 12. In routine operation, samples were loaded in racks on an ARL Plasma Autosampler (Thermo Electron Corporation). Each rack holding up to 64 samples, the autosampler could hold up to three racks. The instrument used was a Fisons Instruments ARL 3580 with mini torch. This size of torch allowed less gas and power to be used than a standard ICP torch but facilitated the same power density and comparable detection limits. The instrument incorporated two spectrometers, simultaneous and sequential, based on identical 1 m Paschen Runge concave grating systems. These analyses used the simultaneous spectrometer which had 45 fixed channels. The light path from the torch to the spectrometers was partly enclosed in an argon-flushed tube to minimise the absorption of low-wavelength lines by the atmosphere. The image of the torch was positioned onto the photomultiplier tubes (PMT's) by moving the entrance slit to the spectrometer and determining the slit position which gave the maximum peak intensity. This position varied from one PMT to another, so an average, compromise position was calculated. The sensitivity of the PMT's could be adjusted to suit the wide concentration range of elements in solution by manual adjustment of the links on a resister network.

Table 12: ICP-AES: instrumentation and typical operating conditions for G-BASE water samples.

Parameter	Typical operating conditions
Instrument	Fisons ARL 3580 Quantometer
Spectrometer	1 m Paschen Runge with purged light path. 45 fixed channels
Spray chamber	Conical 45 mL minimum volume with impact bead
Nebuliser	Meinhardt glass concentric, TR-30-K3
Torch	Quartz mini torch
Autosampler	ARL plasma autosampler
RF power	650 W
RF frequency	27.12 MHz
Viewing height	9 mm above the coil
Coolant gas	7.5 L/min
Plasma gas	0.8 L/min
Carrier gas	0.8 L/min
Solution uptake	2.0 mL/min
Pump	Gilson Minipuls 3

The elements determined, detection limits and units are listed in Table 13. The detection limits were based on five times the standard deviation of the blank and give a conservative value based on data merged from three years of operation. The ICP and autosampler were controlled using the manufacturer's PlasmaVision software, which incorporated instrument-control software (ICS). The ICS provided microprocessor control of the instrument and analytical procedure. An IBM PS/2 Model 70 personal computer was used to run the PlasmaVision software and was connected to a printer and the local area network (LAN), this allowed high-speed transmission of data for off-line data processing.

Table 13: ICP-AES: elements determined, detection limits and units for G-BASE water analyses.

Determinant	Detection Limit	Units
Al	14	µg/L
B	11	µg/L
Ba	2	µg/L
Ca	13	µg/L
Fe	4	µg/L
K	38	µg/L
Mg	18	µg/L
Mn	1	µg/L
Na	12	µg/L
P	61	µg/L
Si	10	µg/L
SO_4	64	µg/L
Sr	1	µg/L
Zn	7	µg/L

The spectrometer was calibrated by aspirating multi-element standard solutions and plotting emission intensity against concentration using the PlasmaVision software (Tait and Ault, 1992). Standard solutions were prepared by serial dilution of stock standard solutions. The stock standard solutions for Al, Ba, Be, Cd, Co, Cr, Cu, Fe, La, Mn, Mo, Ni, Pb, Si, Sr, V, Y, Zn and Zr were prepared from single-element standard solutions purchased from commercial suppliers. For B, Ca, K, Li, Mg, Na, P, and SO_4^{2-} standard solutions were prepared from the dissolution of pure solids, usually Specpure® metals and chemicals from Johnson Matthey Chemicals. Total sulphur was reported as sulphate, as described by Miles and Cook (1982). On-line spectral interferences were investigated by aspirating a high-purity solution of the interfering element and measuring the intensity of emission at the wavelength of the interfered element. Mathematical correction factors were then incorporated into the software.

Quality control during the ICP-AES analyses was maintained by means of drift-correction standards, in-house quality-control standards, and participation in the Aquacheck inter-laboratory testing scheme. The results from the drift-correction standards were used to adjust the calculated concentration for changes in instrument response during the analytical run (Ault, 1993). Two in-house QC standard solutions were analysed several times in random positions within every batch of one hundred samples. Data from these solutions were assessed against a running mean and two sigma limits (approximately 95% confidence) for every determinand. If QC data were consistently outside these limits, data for the corresponding samples were rejected and the samples reanalysed.

10.8.1.2 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS) OF G-BASE WATER SAMPLES

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was used to determine 23 trace elements in stream waters (Table 14). The quadrupole ICP-MS instrument used was a VG Plasmaquad PQ 2+ in combination with a Gilson 222 autosampler. The system was controlled by a PC through dedicated software. A summary of typical instrument operating conditions for the analysis of aqueous solutions is shown in Table 15.

Table 14: ICP-MS: elements determined, detection limits and units for G-BASE water samples.

Determinant	**Detection Limit** (µg/L)	**Determinant**	**Detection Limit** (µg/L)
Ag	0.08	Ni	0.6
Al	1.53	Pb	0.05
As	0.46	Rb	0.06
Be	0.03	Sb	0.06
Cd	0.02	Se	2.52
Ce	0.02	Tl	0.01
Co	0.05	U	0.05
Cr	0.35	V	0.14
Cu	0.13	Y	0.01
La	0.01	Zn	0.77
Li	0.22	Zr	0.03
Mo	0.03		

The ICP-MS instrument comprised an inductively coupled plasma to provide a source of positively charged ions and a quadrupole mass spectrometer to detect these ions, linked together by an interface. Liquid samples were pumped through a nebuliser, the resulting sample aerosol and argon mixture passed through a water-cooled spray chamber, to remove the larger droplets, before injection into the central channel of the ICP torch. Energy transfer processes in the plasma resulted in rapid desolvation, atomisation and ionisation of the sample aerosol.

The positively charged ions were extracted from the plasma into the vacuum system of the mass spectrometer. The ions passed through a sampling orifice of 1 mm diameter into a mechanically pumped vacuum system where a supersonic jet formed. The central section of this jet was extracted through the skimmer orifice of 0.7 mm diameter and was then focussed by a series of electrostatic ion lenses into the quadrupole mass analyser. DC and RF voltages were applied to opposite pairs of the four rods of the quadrupole. These voltages were varied such that only ions of a given mass: charge (m/z) ratio had a stable path through the rods and emerge from the other end. By varying the DC and RF voltages rapidly the mass spectrometer was able to sweep across the mass range from 0 to 300 mass units in less than a second. Although the quadrupole analyser had a relatively low resolving power (<400), it was sufficient to separate ion m/z from ion (m/z) +1 but not from a polyatomic ion with a very similar m/z.

Table 15: ICP-MS: instrumental and analytical parameters for G-BASE water analyses.

Parameter	Typical operating conditions
Forward power	1350 W
Coolant gas flow	13 L/min
Auxiliary gas flow	0.5 L/min
Nebuliser gas flow	0.95 L/min
Integration time	3 x 60 sec
Nebuliser	Meinhardt concentric
Spray chamber	Scott double pass
Spray chamber temperature	6 °C
Mass range	6 – 240 atomic mass units
Mode of acquisition	Scanning
Type of detector	Channeltron
Detector mode	Pulse counting

The ions transmitted by the quadrupole were detected using a dynode electron multiplier. Counts for a particular mass were accumulated for a number of sweeps across the mass range and were proportional to the concentration of the element in the aspirated solution. The response at any mass was calibrated against standards containing known concentrations of the element of interest.

Jarvis (1997) presents a simplified description of the instrumentation. Montaser (1998) contains a comprehensive review of the technique and background theory. Detection limits were based on three standard deviations of a large number of 1% nitric acid blanks inserted throughout all the analytical runs of G-BASE waters. The instrument was calibrated at the beginning of every analytical run using standards prepared from certified Spex® ICP-MS multi-element solutions in the range 0 to 50 µg L-1. In addition, mixed element standards at 10 µg L-1 were inserted at regular intervals throughout the analysis run and used to correct for any drift in instrument sensitivity. In order to obtain the best detection limits and minimise contamination from other sources water samples with conductivities less than 2000 µS were analysed neat, without any dilution or addition of internal standard. Any samples with conductivities greater than 2000 µS were diluted with 1% high purity nitric acid to reduce conductivity to below this value. Multi-element quality control (QC) check standards containing the elements of interest at 5 µg L-1 were analysed after at most every 15 samples. All QC data were examined to check that the difference between the QC standard and its nominal value was less than 10 %. Each analytical run was independently verified by a different analyst, including post processing of the data for drift, dilution and collation. In addition, the samples were plotted in run order to check for any step changes between runs, changes in blank values or any anomalous results. As with the ICP-AES method, accuracy was monitored by regular participation in the Aquacheck inter-laboratory proficiency testing scheme for waters, in which approximately 350 laboratories participate worldwide.

10.8.1.3 CHLORIDE AND NITRATE IN G-BASE WATER SAMPLES BY ION CHROMATOGRAPHY

Instrumentation

A Bran+Luebbe Analyzing Technologies AutoAnalyzer 3 continuous segmented flow system fitted with an xyz autosampler was used for the analysis of chloride (Cl^-) and nitrate (NO_3^-) in G-BASE stream waters. The instrument was connected to a dedicated PC installed with AACE (AutoAnalyzer Control and Evaluation) software for interpretation and quantification of the results. Analysis was completed at the laboratories of the British Geological Survey (Keyworth, Nottingham).

Analytical methodology

Five prepared standards were used to calibrate the instrument at the start of each analytical run. The calibration standards had a concentration range of 5 to 100 mg/L for Cl^-, and 2.5 to 50 mg/L for NO_3^-. Quality control samples and blanks were analysed at the start and end of each analytical run and after a maximum of 20 field samples. Measurements were obtained by an automated computerised process which compared sample peak heights with those for standard solutions. Dilution of samples was employed to bring the analyte concentration within the range of concentration covered by the standards.

Chloride and nitrate (as total oxidisable nitrogen) were determined in each water sample using an air-segmented flow colorimetric technique. This methodology required a filtered (<0.45 mm) water sample. Successive water samples were fed into a carrier stream into which air bubbles were injected, thereby isolating successive samples and avoiding cross contamination. The use of a high precision peristaltic pump facilitated the measurement of an exact volume of reagent and sample for each segment, thereby aiding reproducibility. Parallel streams of reagent and sample were injected into a glass helical mixing coil. The reagent reacted with the determinand to form a coloured complex which was then passed into a colorimeter containing a flowcell and appropriate filter. The absorbance of each sample solution was measured continuously in an optical cell. The analyte concentration was determined by comparing the absorbance peaks for samples with peaks for known standard solutions. Chloride was determined using the quantitative displacement of thiocyanate from a colour reagent containing mercuric thiocyanate and ferric nitrate (Equation 2). Thiocyanate was liberated by the reaction of chloride in the water sample with mercuric thiocyanate in the reagent, producing soluble mercuric chloride and thiocyanate ions. A highly coloured ferric thiocyanate is formed. The absorbance of the ferric thiocyanate is proportional to the original chloride concentration of the water sample. The absorbance was measured at 480 nm.

Equation 2: Chemical reaction for the quantification of chloride in stream water

$$2Cl^- + Hg(SCN)_2 + 2Fe^{3+} \rightarrow HgCl_2 + 2[Fe(SCN)]^{2+}$$

Nitrate was measured using a technique which reduced nitrate to nitrite in the presence of hydrazine. The procedure employed a dialysing membrane to eliminate interference from dirty or coloured samples. Segmented nitrate flowed on one side of the membrane while the reduced nitrite which had passed through the membrane flowed on the other side. The segmented nitrite flow underwent a diazotisation reaction when combined with a stream of sulphanilamide. The resulting diazonium ion reacted with N-(1-napthyl)-ethylenediamine to form a reddish purple azo dye which absorbs at 520 nm. The period from sample collection to analysis was short in order to minimise any change in anion chemistry in response to microbial activity. The technique determined total oxidised nitrogen, as such any pre-existing nitrite (NO_2^-) in the sample contributed to the final nitrate concentration, thus introducing a small positive bias to the G-BASE nitrate measurements. All data for this method fall outside the scope of the British

Geological Survey UKAS accreditation. The detection limits (Table 16) were 1.0 and 0.2 mg/L for Cl^- and NO_3^-, respectively.

Table 16: Anions and other parameters, detection limits for G-BASE water samples.

Anion	**Symbol**	**Detection limit**
Fluoride	F^-	0.02 mg/L
Chloride	Cl^-	1.0 mg/L
Nitrate	NO_3^-	0.2 mg/L
Bicarbonate	HCO_3^-	0.1 mg/L
Conductivity	SO_4^{2-}	10 µs/cm
DOC	-	0.5 mg/L

10.8.1.4 FLUORIDE IN G-BASE WATER SAMPLES BY ION SELECTIVE ELECTRODE

Fluoride was determined using an Orion Model 94-09 fluoride ion selective electrode with an Orion Model 90-01 single-junction reference electrode connected to an Orion Model 420A ISE meter (Cook and Miles, 1980). The fluoride electrode was calibrated with a series of standards, ranging from 10 to 10 000 µg/L fluoride. The standards were run at regular intervals to check the calibration. The lowest quantifiable concentration was 10 µg/L. Total Ionic Strength Adjustment Buffer (TISAB) was added to all standard and sample solutions to maintain a high and constant ionic strength relative to the variable concentrations of fluoride. Samples and standards were equilibrated to the same temperature and mixed with TISAB at a 30:3 (mL sample:TISAB) ratio. The solutions were stirred by a magnetic stirrer prior to measurement.

10.8.1.5 NON-PURGEABLE ORGANIC CARBON IN G-BASE STREAM WATERS (NPOC)

Analysis of non-purgeable organic carbon (NPOC) in a filtered water sample determines the dissolved organic carbon (DOC) content. Analysis for NPOC was conducted using a Shimadzu TOC 5000 analyser (Serial No. 28604210) with associated ASI 5000 auto-sampler (Serial No. 29D07360). Samples were automatically pre-treated by the addition of a small volume of 10 % HCl and sparged with inert gas to remove any inorganic carbon in the sample. Technically, any organic species that are volatile on acidification are also removed - although such species are rare in natural waters.

The remaining organic carbon in the sparged sample was then combusted in a furnace, evolved carbon dioxide was measured using a non-dispersive infra-red (NDIR) gas analysis system. Samples were calibrated against a series of standards and the method was subject to stringent quality control and proficiency testing regimes. The determination of NPOC was accredited by UKAS.

10.8.1.6 TELLUS STREAM WATER ANALYSIS

Analysis for anions and NPOC was completed at ALcontrol Laboratories in Hoogvliet, The Netherlands (Figure 18). The ICP trace element analysis was conducted at the laboratories of the Geological Survey of Finland (GTK) in Espoo. Samples were analyzed for trace elements by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Anions were analysed by ion chromatography. Operating parameters for ICP-AES and ICP MS instrumentation are detailed in Tables 17 and 18 respectively.

Figure 18: ALcontrol Laboratories, Hoogvliet, The Netherlands.

(*Photograph courtesy of ALcontrol. ©ALcontrol, 2007*)

At GTK the samples were stored in a cool environment (4ºC) away from sunlight. Calibration standards were prepared in a clean room. Analytical detection limits were calculated as the average plus six times the standard deviation of seven reagent blanks. Instruments were calibrated using certified multi-element calibration standards. Each element was calibrated using a blank and one calibration standard. The calibration was verified using independent certified calibration standards.

In each batch of 100 samples the quality assurance of analytical methods was monitored with the inclusion of two analyses of three certified reference water samples, namely, NIST-1640 (National Institute of Standards and Technology, 2006), SLRS-4 (National Research Council Canada, 1998) and SPS-SW2 (Spectrapure Standards, 2006). Two reagent blanks and six laboratory duplicates were also analysed. Statistical process control charts (e.g., Shewhart Plots) were used to monitor the accuracy of reference materials. Analytical duplicates were plotted using X-Y plots as a means of monitoring precision.

Table 17: ICP-AES: instrumentation and typical operating conditions for Tellus water samples.

Parameter	**Typical operating conditions**
Instrument	Iris Advantage Duo High Resolution
Spectrometer	Axial and radial, detector: CID (Charge Injection Device)
Spray chamber	Cyclonic (glass)
Nebuliser	Meinhardt glass concentric
Torch	Concentric, glass
Autosampler	AS 300 (TJA)
RF power	950 W
RF frequency	27.12 MHz
Viewing height	Axial and radial view (fixed height)
Coolant gas	16.0 L/min
Plasma gas	1.0 L/min
Carrier gas	0.56 L/min
Solution uptake	1.4 mL/min
Pump	Peristaltic

Table 18: ICP-MS: instrumental and analytical parameters for Tellus water analyses.

Parameter	**Typical operating conditions**
Forward power	1000 W
Coolant gas flow	15 L/min
Auxiliary gas flow	0.8 L/min
Nebuliser gas flow	0.83 - 0.88 L/min
Integration time	1000 msec
Nebuliser	Cross-flow
Spray chamber	Scott
Mass range	7 - 238 atomic mass units
Mode of acquisition	Peak hopping
Type of detector	Electron multiplier
Detector mode	Dual

Table 19: ICP-AES: element suite, emission wavelengths and detection limits for Tellus water samples.

Element	Wavelength (nm)	Detection limit (mg/L)
Ca	315.8	0.1
Fe	239.5	0.01
Fe	248.4	0.01
K	766.5	0.5
Mg	279.0	0.1
Mg	285.2	0.1
Na	589.5	0.2
P	185.9	0.05
S	182.0	0.3 (as SO_4^{2-})
Si	243.5	0.06
Si	251.6	0.06

10.8.1.7 ICP-AES OF TELLUS WATERS

Analysis was undertaken on a Thermo Jarrel Ash IRIS Advantage AP-HR-DUO at GTK Laboratories (Finland). The element suite, wavelengths and detection limits are shown in Table 19. Multiple wavelengths were quantified for some elements (e.g., Fe) in order to ascertain the signal to background contrast and to assess sensitivity of individual wavelengths. Analyses were accredited to the ISO/IEC 17025 specification.

10.8.1.8 ICP-MS OF TELLUS WATERS

Analysis was undertaken on a PerkinElmer Sciex Elan 6000 at GTK Laboratories (Finland). The mass and detection limit for each element is shown in Table 20. For some elements (e.g., Cr) two masses were quantified in order to calculate known interferences and check for inter-element interferences.

Table 20: ICP-MS: element suite, mass and detection limits for Tellus water samples.

Element	Mass	DL (µg/L)	Element	Mass	DL (µg/L)
Ag	106.905	0.01	Mo	94.906	0.02
Al	26.982	0.5	Mo	97.906	0.02
As	74.922	0.05	Ni	59.933	0.05
[1]*Au*	*196.967*	*0.1*	P	30.994	10
B	11.009	0.5	Pb	207.977	0.05
Ba	136.905	0.05	[1]*Pd*	*105.903*	*0.1*
Be	9.012	0.05	[1]*Pd*	*107.904*	*0.1*
Bi	208.980	0.02	[1]*Pt*	*194.965*	*0.02*
Br	78.918	10	Rb	84.912	0.01
Cd	110.904	0.02	[1]*Rh*	*102.905*	*0.01*
Cd	113.904	0.02	Sb	120.904	0.02
Co	58.933	0.02	Se	81.917	0.5
Cr	51.941	0.2	Sn	119.902	0.05
Cr	52.941	0.2	Sr	85.909	0.1
Cs	132.905	0.01	Th	232.038	0.01
Cu	62.930	0.1	Ti	46.952	0.5
[1]*Hg*	*201.971*	[2]*no DL*	Tl	204.975	0.01
[1]*Ho*	*164.930*	*0.001*	U	238.050	0.01
K	38.964	10	V	50.944	0.05
La	138.906	0.001	W	183.951	0.01
Li	7.016	0.02	[1]*Y*	*88.905*	*0.001*
Mn	54.938	0.02	Zn	65.936	0.2
			[1]*Zr*	*89.904*	*0.03*

[1] *not within accreditation protocol* [2] *no quoted detection limit, semi-quantitative measurement*

Analyses were accredited to the ISO/IEC 17025 specification, except for Au, Ho, Pd, Pt, Rh, Y and Zr which were not within the accreditation protocol.

10.8.1.9 ANALYSIS OF ANIONS IN TELLUS WATER SAMPLES

Anion analysis was conducted using a Metrohm 861 Compact Ion Chromatography System at ALcontrol Laboratories (Hoogvliet, The Netherlands). Analytes and associated detection limits are shown in Table 21. Anions were analyzed in accordance with ISO 10304-1 (International Organization for Standardization, 1992).

Table 21: Anions and detection limits for Tellus water samples.

Anion	Symbol	Detection limit (mg/L)
Fluoride	F^-	0.01 mg/L
Chloride	Cl^-	0.05 mg/L
Bromide	Br^-	0.02 mg/L
Nitrite	NO_2^-	0.01 mg/L
Nitrate	NO_3^-	0.02 mg/L
Phosphate	P	0.1 mg/L
Sulphate	SO_4^{2-}	0.05 mg/L
NPOC	-	0.5 mg/L

Anions were determined by liquid chromatographical separation using an analytical separating column. After separation, the anions were measured using a conductivity detector. The conductivity detector was used in combination with a cation exchanger in order to convert the separated anions to their corresponding acids. In the separation column a low capacity anion exchanger was used as the stationary phase and a solution of sodium carbonate and sodium bicarbonate as mobile phase (eluent). In order to achieve a greater degree of linearity for low concentration anions a small amount of oxalic acid was added. Anions were analyzed in the following order; fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulphate.

Calibration standard solutions were made from the potassium salt of the ion. A calibration curve was established on a weekly basis using 6 calibration solutions. Daily checking of the calibration curve was undertaken using 2 of the 6 standard solutions. Samples were analysed in a cyclical sequence of standard solutions, blank, 20 field samples, check standard solutions, blank, 20 samples, etc. An independent reference sample was made of the sodium salt of the ions. Quality control results were monitored on a statistical process control chart. ALcontrol was accredited for the analysis of Br, Cl, NO_2, NO_3, SO_4 by ion chromatography, for fluoride by ion-selective electrode and for nitrite and HPO_4 by spectrophotometric method.

10.8.1.10 ANALYSIS FOR NON PURGEABLE ORGANIC CARBON (NPOC) IN TELLUS WATER SAMPLES

Non-purgeable organic carbon (NPOC) is the total content of NPOC attached to dissolved or suspended solids. Cyanates, elementary carbon and thiocyanate are included in this measurement. The analysis was conducted in accordance with NEN-EN-1484, accredited by RvA Netherlands (Dutch Accreditation Council). Samples were acidified using phosphoric acid and purged with nitrogen gas to remove inorganic and purgeable carbon. Each sample was then injected into a FormacsHT (high temperature) TOC/ TN Analyser made by Skalar Analytical B.V. The sample was heated to 800°C. Carbon present within the sample was oxidised to CO_2 and carried using an oxygen gas flow into an IR-detector. The absorption of infrared light at 4.2 µm wavelength was used as a measure of the amount of CO_2 produced by the sample and hence the NPOC. Samples were analysed using instrumentation dedicated to water analysis only. A detection limit of 0.50 mg/L was achieved.

Potassium hydrogen phthalate was used for calibration. A reference sample comprising acetanilide solution and a check solution made from cellulose were analysed. In each analytical batch of 20 field samples a sequence of calibration solutions, blanks, and control samples were analysed. Results for reference materials were plotted on statistical process control charts.

11 Quality Control

Similar sampling and analytical protocols were employed in the G-BASE and Tellus surveys in order to minimise sampling and analytical errors and reduce the analytical uncertainty of the results. The use of contractors as part of the Tellus survey required the use of additional certified reference materials to those commonly utilised as part of the overall quality assurance of the G-BASE survey. Similar protocols were utilised in the insertion of secondary reference materials (SRM) into both the G-BASE and Tellus surveys. The methods of Plant et al (1975) were employed to monitor potential variance throughout the geochemical program, from collection through preparation to analysis. A method based on randomised sample numbers (Plant, 1973) was used to identify any systematic error in field sampling and analysis. Although soil and stream sediment preparation and XRF analyses were undertaken at BGS laboratories (Keyworth) separate facilities and staff members for preparation and analysis maintained the principle that samples were 'blind' to the analysts, both in terms of sample location and position of quality control samples in the analytical stream. Internal BGS quality control procedures are discussed in Johnson et al (in press).

11.1 COLLECTION AND PREPARATION OF SOIL SECONDARY REFERENCE MATERIALS

Five bulk soil samples (c.30kg) were collected in 2004 for use as SRMs in the Tellus soil programme (Table 22). The locations of the SRM sites were chosen to be representative of the four main geological quadrants of Northern Ireland, i.e., Dalradian meta-sediments in the north-west (SRM Dal), the Tertiary Antrim basalts of the north-east (SRM Antbas), the Lower Palaeozoic shale and greywacke of the south-east (SRM LwrPala, Figure 19) and the Carboniferous limestones and shales of the south-west (SRM Carb).

Figure 19: Collection of the LwrPala secondary reference material.

At each site a consistent B-horizon soil was sampled, except for the Curr sample which was azonal. The five bulk soil samples were prepared at the laboratories of the British Geological Survey, Keyworth, Nottingham. Preparation comprised sieving to a <2mm fraction followed by milling in an agate ball-mill (as to standard Tellus soil specification) followed by blending of milled materials. Ten sub-samples of the prepared material were analysed by XRF to test homogeneity. Tellus SRM 'Carb' and 'Curr' were not routinely analysed. In the case of 'Curr' a high water content prevented its use as a XRF secondary reference material. However, it was used sporadically in wet chemical techniques. Material S13B was included in the Tellus analytical programme in order to facilitate a comparison of datasets with the remainder of the United Kingdom where S13B is routinely analysed as a secondary reference material by the British Geological Survey G-BASE program.

Table 22: Tellus soil secondary reference material parameters.

SRM	Easting	Northing	Soil type/ geology
Antbas	303512	405707	Mineral gley on Lower Basalt Formation
Carb	262562	406923	Mineral gley on Ballyshannon Limestone Formation
Curr	256770	386072	Peat on Mullaghcarn Formation
Dal	262562	406923	Mineral gley on Claudy Formation
LwrPala	299357	335362	Mineral gley on Gala 6 Group
[1]S13B	383900	519600	Mineralised Carboniferous limestone, UK

[1] British Geological Survey G-BASE internal SRM, <150µm bulk stream sediment from an area of mineralised Carboniferous limestone, grid reference in British National Grid.

11.2 COLLECTION AND PREPARATION OF TELLUS STREAM WATER SECONDARY REFERENCE MATERIALS

As part of the Tellus stream survey three secondary reference stream waters were collected for inclusion at a rate of 2 samples per field batch (Table 23). Sites were chosen to be representative of the geology of the Tellus stream survey field area. At each site a single 25 litre sample of stream water was collected. This sample was filtered using a 0.45 µm Millex™ disposable filter. Approximately 15 litres of the sample was decanted to a separate container and acidified at field-base to 1% v/v (with ultrapure analytical grade nitric acid). The remaining 10 litres was decanted to a separate container, it was not acidified. Both samples were stored in Nalgene™ containers at 4ºC. The acidified sample was used for the F/A trace element analysis and the unacidified sample for the F/UA anions and NPOC analysis.

Table 23: Stream water secondary reference material parameters.

SRM	Easting	Northing	Land-use/ Geology
Armoy	307948	431724	Agricultural pasture. Antrim basalt.
CarWat	316535	313979	Forest stream. Tertiary gabbro and Lower Palaeozoic sediments.
PalWat	295463	335372	Agricultural pasture. Lower Palaeozoic sediments.

11.3 MONITORING OF QUALITY CONTROL USING REFERENCE MATERIALS, DUPLICATES AND REPLICATES

Stream sediment, stream water and soil samples were collected in batches of 100 samples, designated as a "field batch". Each field batch had an assigned sheet of randomised numbers (Appendix III) issued sequentially on a daily basis. In each field batch two numbers were allocated to secondary reference materials, two numbers to a field duplicate pair and two numbers to replicates. The G-BASE stream sediment replicates were generated in a field laboratory. Tellus soil and stream sediment replicates were generated as part of the sample preparation process at the BGS laboratories. Water replicates were generated at field base from the duplicate pair of each field batch. In both the G-BASE and Tellus water sampling programs two numbers were allocated for "blank waters", typically deionised or reverse osmosis water. Secondary reference waters were not routinely inserted for the G-BASE waters program.

During the G-BASE stream sediment survey long-term analytical shifts were monitored by analysing the SRMs. CRMs and SRMs were used to monitor long-term analytical drift for Tellus stream sediment samples. Time-versus-concentration plots for each of the CRM (in the case of Tellus) and SRM samples were used to identify shifts in the analytical data, simple arithmetic factors were calculated to enable the data to be normalised for systematic drift (Lister & Johnson, 2005).

In the G-BASE stream sediment and water surveys a value of half the detection limit was substituted for analyses reporting below the lower limit of detection. This arbitrary procedure was necessary prior to statistical treatment of the data, as discussed by Albert and Horowitz (1995) to deal with non-qualitative results. For the Tellus stream (sediment, water) and soil surveys the reporting of uncensored analytical data reduced the need to substitute below detection limit analyses with a value of half the detection limit. As part of the Tellus geochemistry programme a lower limit of detection was determined for each analytical parameter using calibration standards and repeat analyses of certified materials. Detection limits quoted by contractors were verified and utilised to censor data presented as maps. As part of the quality control process levelling of individual datasets was completed for low-level instrumental and temporal drift using certified reference materials and secondary reference materials in association with their certified and provisional values respectively. Analyses reporting below zero after quality control were replaced with a value of 'zero'. SRMs and protocols for the G-BASE and Tellus surveys were as follows;

11.3.1 X-ray fluorescence spectrometry of G-BASE and Tellus stream sediment samples

A suite of reference materials were analysed before and after each batch of Tellus sediment samples. Details of these reference materials are shown in Table 24. One sample of each reference material was analysed before and after each batch.

Two SRMs were inserted into each field batch of 100 samples for both the G-BASE and Tellus surveys. Secondary reference materials S13, S15, S24, and S3B were used in sequence throughout the duration of analysis (Table 25). Sub-samples of bulk SRMs were prepared by sample preparation staff of the British Geological Survey and submitted blindly to the XRF laboratory.

Table 24: Reference materials analysed before and after Tellus stream sediment and soil XRF batches.

RM	**Matrix**	**Source**
[1]GSD-7	Stream sediment from mica schist geology, Liaoning, China	China National Analysis Centre for Iron and Steel
[1]GSS-1	Dark brown podzolic soil from Heilongjiang, China	Institute of Geophysical and Geochemical Exploration, China
[2]LKSD-1	Lake sediment. Mixture of lots from Joe Lake and Brady Lake (Ontario)	Canadian Certified Reference Materials Project, CANMET, Canada
[2]LKSD-4	Lake sediment. Composite from Big Gull Lake (Ontario) and Key and Sea Horse Lakes (Saskatchewan)	Canadian Certified Reference Materials Project, CANMET, Canada

[1] *element values are certified* [2] *element values are provisional (Lynch, 1990)*

Certified reference material GSD-7 (China National Analysis Center for Iron and Steel, 1998a) is also known as NCS DC 73317 and as GBW07307; GSS-1 (China National Analysis Center for Iron and Steel, 1998b) is also known as NCS DC 73319 and as GBW07401.

Table 25: Stream sediment secondary reference materials for G-BASE and Tellus analyses.

[1]S13	-150µm bulk stream sediment	Carboniferous Limestone
[1]S15	-150µm bulk stream sediment	Sandstone
[1]S24	-150µm bulk stream sediment	Mineralised Slate
[1]S3B	-150µm bulk stream sediment	Granite
[2]STSD-1	CANMET stream sediment	Lavant Creek, Ontario

[1] Internal British Geological Survey SRM [2] Tellus stream sediment programme only

In the Tellus stream sediment survey a number in each field batch was reserved for a sample of CANMET standard STSD-1 (Lynch, 1990). This material was considered a secondary reference material for the purposes of the Tellus analysis.

11.3.2 X-ray fluorescence spectrometry of Tellus soil samples

A suite of reference materials were analysed in the same manner as the Tellus stream sediment batches, i.e. one sample of each reference material before and after each analytical batch. Details of these reference materials are provided in Table 24. Secondary reference materials Antbas, Dal, LwrPala and S13B (British Geological Survey) were used in the soil XRF analysis (Table 22). Secondary reference materials were inserted in sequence at a rate of two insertions per field batch (100 samples).

11.3.3 ICP-MS of Tellus soil samples: Aqua regia digest/ "Near-total" digest/ SO_4 hydrochloric acid digest

The Tellus soil SRMs were submitted blindly in sample batches of "surface" and "deep" soils to SGS Laboratories (Toronto). Identical secondary reference materials to those used in the soil XRF analysis were inserted at the same reserved sample numbers. A 1 g sub-sample of SRM was weighed for each insertion. CANMET "TILL" series (Lynch, 1996) reference materials (Table 26) were inserted at a rate of two samples per field batch.

Table 26: CANMET "TILL" series attributes.

Sample	Matrix	Location
TILL-1*	Soil	25 km NW of Lanark, Ontario, Canada
TILL-2	Till	Scission's Brook, New Brunswick, Canada
TILL-3*	Soil	8 km E of Cobalt, Ontario, Canada
TILL-4	Till	Scission's Brook, New Brunswick, Canada

** sample represents combined "B" and "C" horizons.*

A 1 g sample of each reference material was inserted in sequence, i.e., TILL-1, TILL-2, TILL-3, TILL-4. In the first season these samples could not be inserted blindly and so were given a -1/ -2/ -3/ -4 suffix to a pre-existing sample number. Subsequently the samples were inserted blindly using a pre-allocated position on the random number list. Reported concentration values for CANMET Till materials were treated as 'provisional' values. Sporadic samples of 'Curr' were included in batches of samples. This sample was not inserted blindly and was given a '-curr' suffix.

11.3.4 Fire assay ICP-MS of Tellus soil samples

The Tellus soil SRMs (Table 22) were submitted blindly in sample batches of "deep" soils for determination of Au, Pd, and Pt by fire assay at SGS Laboratories (Toronto). Identical SRMs to those used in the soil XRF analysis were inserted at the same reserved sample numbers. A 10 g sub-sample of SRM was weighed for each insertion. CANMET reference materials (Table 27) TDB-1, WPR-1, WGB-1 and WMG-1 were inserted at a rate of two samples per field batch. A 10 g sample of each reference material was inserted in sequence, i.e., TDB-1, WPR-1, WGB-1, WMG-1. In the first season these samples could not be inserted blindly and so were given a -1/ -2/ -3/ -4 suffix to a pre-existing sample number. Subsequently the samples were inserted blindly using a pre-allocated position on the random number list.

Table 27: CANMET platinum group reference material parameters.

Sample	Type	Location
TDB-1	Diabase rock	Tremblay Lake, Saskatchewan, Canada
WPR-1	Altered Peridotite	Wellgreen Complex, Yukon Territory, Canada
WGB-1	Gabbro	Wellgreen Complex, Yukon Territory, Canada
WMG-1	Mineralised gabbro	Wellgreen Complex, Yukon Territory, Canada

Analysis of the data for blanks inserted into the fire assay batches revealed that the detection limits needed to be higher than those quoted in Table 5 for the soil dataset. Revised detection limits were based on Shewhart plots of blank data. A value of three times the standard deviation of the blank analyses was used to establish the revised limit of detection for Au, Pd and Pt. Intricate analysis of raw data revealed instances of carryover from certified reference materials affecting blanks. These carryover effects were removed from the dataset facilitating a lowering of detection limits to a conservative value. Carryover effects were primarily confined to the blanks due to the procedure of analysing blanks after certified reference materials. The revised detection limits are shown in Table 28.

Certified reference materials were not incorporated into the G-BASE sample batches sent to Acme Laboratories (Vancouver) for analysis. One 10 g sub-sample of a secondary reference material (S3B, S26) was inserted into each G-BASE field batch (100 samples).

Table 28: Quoted and revised detection limits for Au, Pt and Pd in soil samples.

Element	Soil Quoted Detection Limit (µg/kg)	Soil Revised Detection Limit (µg/kg)
Au	1.0	2.0
Pt	0.5	1.2
Pd	1.0	1.1

11.3.5 Fire assay/ ICP-MS and boron by Na_2O_2 fusion/ ICP-MS in G-BASE and Tellus stream sediment samples

Tellus sediment batches contained the secondary reference materials Antbas, LwrPala and S3B in rotation, at a rate of two SRM per field batch. A 10 g sample of TDB-1, WPR-1 or WMG-1 was also inserted into each Tellus field batch. Due to the absence of certified values for Au, Pd, Pt and Rh in certain CANMET reference materials, analyses for these reference materials were treated as equivalent in status to a secondary reference material. It was not possible to replicate the G-BASE SRM suite for the Tellus analytical programme because of limited stocks of these materials, however, sufficient quantity of S3B was available to facilitate its use in the Tellus analysis and in the levelling of the G-BASE and Tellus datasets. The use of soil SRM materials in a sediments programme was negated by virtue of the total analysis of the fire assay, thereby reducing the necessity to matrix match secondary reference materials.

11.4 STREAM WATER SAMPLES

Procedures operated by both the G-BASE and Tellus sampling programs facilitated monitoring of quality control within these individual surveys. During each survey two sample numbers within each field batch of 100 samples were reserved for the insertion of blank waters from a stock supply of deionised water. Blank water samples were inserted in the field during sample collection for all analytical tests conducted in the G-BASE and Tellus surveys (except for pH, conductivity and alkalinity). Blank waters for ICP-AES and ICP-MS samples were acidified with 1% v/v Aristar-grade concentrated nitric acid. Time-series plots of the blank water data were generated as an aid to the identification of small background shifts in analytical instrumentation or possible low-level contamination of the samples.

Secondary reference waters (SRW) were not routinely inserted in field batches during the G-BASE survey. Three SRWs (Armoy, CarWat and PalWat) were inserted into each field batch of Tellus samples for both trace element (F/A sample) and anions (F/UA sample) analysis (Table 23). All Tellus SRW sub-samples were prepared during a single phase of decanting immediately prior to the first shipment of samples to ALcontrol. The 'CarWat' and 'PalWat' samples were inserted blindly into field batches. The 'Armoy' SRW was assigned a suffix (-A) to a pre-existing sample number and as such was not submitted blindly. A sample of certified reference water SLRS-4 (National Research Council of Canada) was also incorporated blindly into both the trace element and anions analysis. In the case of the anions analysis the acidified nature of the sample and over-range values for SLRS-4 proved a useful quality control check.

11.4.1 Integration of G-BASE and Tellus stream sediment and water datasets

The collection of soil samples during a single time period coupled with the judicious use of certified and secondary reference materials facilitated both the quality control and batch to batch levelling of this particular dataset (Lister & Johnson, 2005).

11.4.1.1 STREAM SEDIMENT DATASET INTEGRATION

The sampling of drainage sites over two different periods of time was subject to a range of variables which impacted on the completion of identical quality control procedures and levelling for the two different surveys (Lister, 2006a, Lister, 2006b). During each phase of sampling sufficient quality control procedures were in place to facilitate the assessment of the quality of each individual dataset and the production of quality controlled datasets. The two phases of sediment analysis were subject to different circumstances;

- Instrumentation

  Although all sediment XRF analysis was completed at the laboratories of the BGS several of the XRF instruments had been replaced at the time of commencement of the Tellus analysis. Due to the calibration procedures employed by BGS and high level of quality control monitoring conducted by this laboratory the impact of instrumentation differences is minimal. Data variance as a consequence of instrumentation changes was reduced to a minimum by analysis of an identical suite of SRM for both the G-BASE and Tellus surveys.

- Element suite

  The addition of XRF-ED instrumentation resulted in the analysis of a larger trace element suite for the Tellus survey. A total of 33 determinands were analysed in the G-BASE samples compared with 52 in the Tellus samples. The following determinands were not analysed in the G-BASE sediments, Al_2O_3, Na_2O, SiO_2, SO_3, Br, Cl, Cs, Ge, Hf, I, In, Nd, Sc, Sm, Ta, Te, Tl, W, and Yb. Only the Tellus survey area contains data for these elements in stream sediments (Figure 8).

- Detection limits

  The new XRF equipment enabled lower detection limits to be achieved for the majority of elements in Tellus sediment samples.

- Certified reference materials

  The use of CRMs in the Tellus programme facilitated a higher degree of quality control and potential integration with other surveys. The absence of routine CRM analyses in the G-BASE survey did not reduce the quality of the dataset due to the calibration and quality control procedures employed in the XRF analysis. The use of an identical suite of secondary reference materials for both the G-BASE and Tellus surveys compensated for the lack of routine CRM analyses in the G-BASE survey.

The routine analysis of CRM in the Tellus survey facilitated a levelling of datasets and an assessment of accuracy and precision across all sediments datasets when used in conjunction with secondary reference materials. The disparity of detection limits between the two surveys was counteracted by presenting datasets for the whole of Northern Ireland using the G-BASE detection limits. Datasets produced for the eastern part of Northern Ireland as part of the Tellus survey may be plotted separately to take advantage of the lower detection limits in this survey.

11.4.1.2 STREAM WATER DATASET INTEGRATION

The levelling of the G-BASE and Tellus water datasets (Ander, 2006) ultimately proved a more difficult task in comparison to the stream sediment datasets. Despite the temporal difference in sampling it was possible to merge the datasets for the vast majority of analytes, only As, Cr and NO_3 were presented as separate datasets for both the G-BASE and Tellus surveys. There was a range of factors which may have contributed variance to datasets, including:

- Temporal variation

  The results may be subject to temporal fluctuation. Seasonality is counteracted within each survey time period by the daily collection of a water sample from a "monitor site" near each field base location. Although the trend of seasonality may be similar from year to year the variance introduced by sampling approximately 10 years apart cannot be accounted for, however, the majority of analytes for the G-BASE and Tellus datasets were successfully merged (Ander, 2006).

- Analytical Laboratories

  The G-BASE water samples were analysed in the BGS laboratories. The Tellus water samples were analysed at two laboratories. ALcontrol Laboratories (The Netherlands) analysed anions in Tellus samples and trace elements were analysed by GTK Laboratories (Finland). A minimum of two laboratories were used for every anion and trace element determined. Different analytical quality control procedures were employed in both laboratories. However, the high standard of analysis and quality control in all three laboratories reduced the likely variance introduced by laboratories to a practical minimum level. All three laboratories were accredited and operated analytical procedures and protocols to ISO standard.

- Instrumentation

  Differences in ICP-MS instrumentation and separate calibration protocols between laboratories resulted in a disparity in detection limits for many analytes.

Table 29: Comparison of G-BASE and Tellus anion detection limits.

Analyte	G-BASE Detection Limit	Tellus Detection Limit
Chloride	1.00 mg/L	0.05 mg/L
Nitrate	0.20 mg/L	0.02 mg/L
Fluoride	0.02 mg/L	0.01 mg/L

The difference was most notable in the anions analysis, with an order of magnitude difference in some instances, e.g., nitrate, 0.20 mg/L G-BASE, 0.02 mg/L Tellus.

- Certified reference waters

  A single reference water (SLRS-4) was inserted blindly into every field batch of Tellus samples. This reference water was also used by the GTK laboratory for ICP-MS calibration and subsequent monitoring of quality control. The use of this reference water both in field batches and within the GTK laboratory permitted an assessment of the quality of data over the course of analysis and a micro-levelling between analytical batches (if required). Certified reference waters were not used routinely in G-BASE field batches. However, they were used in the calibration of the ICP instrumentation and within-lab quality control monitoring.

- Secondary reference waters

  Two different secondary reference waters (SRW) were inserted into each Tellus field batch at a rate of two blind samples per batch, an additional, unconcealed SRW was also inserted. The use of SRW permitted an investigation of analytical drift and enabled micro-levelling between sample batches where necessary. Secondary reference waters were not inserted into the G-BASE sample batches.

In order to provide an assessment of temporal variability between the two surveys a group of water samples were collected in a north-south zone which overlapped the eastern margin of the G-BASE stream sampling area and the western margin of the Tellus sampling area. Analysis of these samples indicated similar values for a range of determinands. The boundary between the two survey areas coincided with the limits of several river catchments, in part minimising the effect of the two different surveys. All G-BASE and Tellus quality controlled datasets were gridded as single merged datasets, resulting in a grid file dataset of combined G-BASE and Tellus data. Separate grid files were produced for G-BASE and Tellus stream water As, Cr and NO_3 due to the inability to level these datasets across the temporal divide.

11.5 IONIC BALANCE

As a further test of the accuracy of the analytical determinations ionic balances were calculated according to procedures described in Hem (1985). The charge balance was calculated as shown in Equation 3.

Equation 3: Charge balance calculation.

$$\text{Charge balance (\%)} = \frac{(\text{sum of cations - sum of anions})}{(\text{sum of anions} + \text{sum of cations})} \text{ x} 100$$

Where 'cations' represents Ca, Mg, Na and K. 'Anions' represents HCO_3, SO_4, Cl, NO_3, all converted to milli-equivalents per litre.

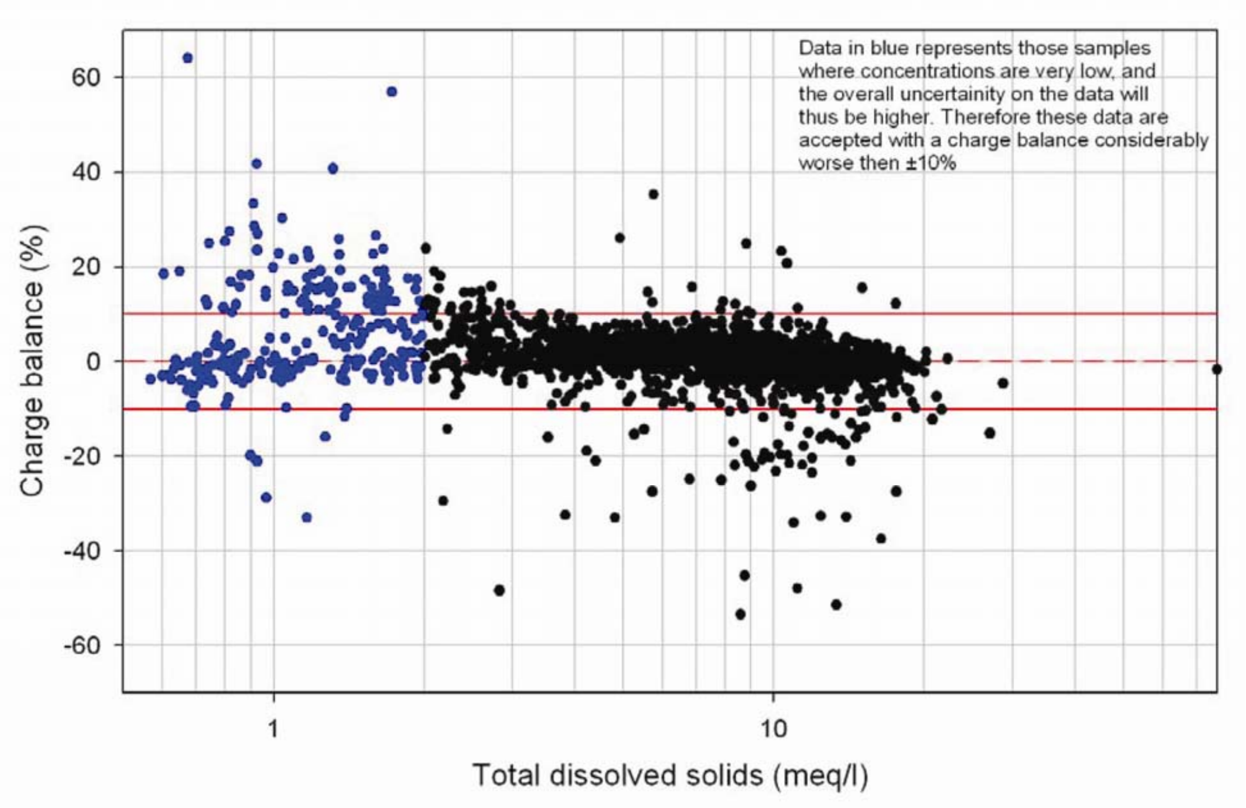


Figure 20: Total dissolved solids (meq/L) versus charge balance (%) for Tellus stream waters.

Charge balance is based on the principal of electro-neutrality of water and the observation that the eight major ions comprise >95% of the total dissolved ions in most natural stream waters (Appelo and Postma, 1994).

The application of modern analytical equipment and attainment of low detection limits for analyses dictates that the charge balance error should be less than ±5 %. For the purposes of regional geochemical studies a nominal charge balance error of ±10 % was within accepted limits (Figure 20). Charge balance errors were accepted irrespective of their value where the total of cations or anions was <1 meq/L. At values below this threshold the variance of data may be accounted for by analytical error near the detection limit.

11.5.1 Analysis of variance

Sampling and analytical precision were calculated using a procedure based on analysis of variance (ANOVA). In each stream sediment, stream water and soil field batch a duplicate sample was collected a few metres away from a routine sample, representing approximately one site in 94 samples. Each duplicate sample was dried and split into two portions, producing a total of four samples for each "site" for chemical analysis. As a check against mis-labelling or other error the analyses of the two portions were plotted against each other for selected elements of differing chemical properties. This was to assess if any sample pairs were consistently outlying.

A random nested model of ANOVA was used because all the analyses were part of a single randomised data set (Snedecor and Cochran, 1989). An Excel™ macro was written to perform the analysis (Johnson, 2002). The following parameters were calculated for each ANOVA test;

- Natural geochemical variance/ between-site variance

  Representing the variance in the dataset attributable to the natural distribution of each determinand in the survey area. Related to large-scale variation caused by changes in bedrock lithology, drift and soil type. Anthropogenic influences/ contamination can also contribute to this variance.

- Site variance/ between-sample variance

  Representing the small-scale or within-site variability, as well as any variability introduced by the process of sample collection and to a lesser extent sample preparation. Related to the characteristics of each site and variation in chemistry at distances from 5m (sediments, waters) to 20m (soils). Site characteristics such as slope and site inhomogeneity may contribute to this variance. Ideally this variance should be <16% (Ramsey et al, 1992).

- Intra-sample variance/ residual variance

  Representing the within sample inhomogeneities. Variance potentially introduced in sample preparation and sub-sampling. Includes errors in chemical analysis and artefacts of the sampling methodology, e.g., sampling by depth and not soil horizon. The natural characteristics of element distribution and mode of occurrence contribute to this variance, e.g., the "nugget effect". Ideally this variance should be <4% (Ramsey et al, 1992).

Table 30: Percentage of variance in stream sediment samples.

Element	Natural Geochemical Variance	Site Variance	Intra-sample Variance
As	72.4	-5.0	32.6
B[1]	96.2	-1.5	5.3
Ba	98.1	1.8	0.1
Ca	94.3	4.7	1.0
Cd	58.0	11.1	30.9
Cr	97.9	1.9	0.2
Cu	96.9	2.6	0.4
K	98.3	1.5	0.2
Mg	97.4	1.8	0.8
Mo	68.6	3.5	27.9
Ni	97.4	2.5	0.1
P	92.2	7.2	0.6
Pb	89.8	9.5	0.7
Sb	59.2	15.6	25.2
Se	9.2	6.6	84.2
Sn	24.9	1.6	73.5
U	74.6	0.2	25.2
Zn	91.7	8.1	0.2
Au[2]	48.5	-2.8	54.3
Pd[2]	35.5	-27.0	91.5
Pt[2]	54.6	-18.9	64.3

[1] *Boron analysed by Na_2O_2 fusion/ ICP-MS.* [2] *Au, Pd, Pt analysed by fire assay/ ICP-MS*

Due to the fact that the frequency distribution of most elements is multi-modal with outliers and none fit the Gaussian model perfectly, there is an unquantifiable overstatement of the natural geochemical variance/ between-site variance, a problem which is inherent in using an ANOVA statistical process on geochemical data. Statistical F-tests have not been quoted because the data do not satisfy this and other assumptions required for formal analysis of variance (Eisenhart, 1947). The percentage of variance attributable to natural geochemical variance, site variance and sample variance are given in Table 30 (sediments), Table 31 (waters) and Table 32 (soils). These provide a general indication of the appropriateness of the sampling and analytical methodology and indicate which element data is more reliable.

Table 31: Percentage of variance in stream water samples.

Element	Natural Geochemical Variance	Site Variance	Intra-sample Variance
ICP-AES/ ICP-MS Analyses			
Al	93.0	4.0	3.0
As	95.7	-0.7	5.0
B	92.1	-1.6	9.5
Ba	97.7	0.0	2.3
Br	96.9	-1.1	4.2
Ca	100.0	0.0	0.0
Co	92.2	5.4	2.4
Cr	66.7	11.1	22.2
Cu	95.4	2.0	2.6
Fe	97.7	2.0	0.3
Ho	97.3	-0.3	3.0
K	99.4	-0.1	0.7
La	91.0	0.8	8.2
Li	97.3	-0.3	3.0
Mg	100.0	0.0	0.0
Mn	86.1	12.2	1.7
Mo	99.6	-0.1	0.5
Na	99.9	-0.1	0.2
Ni	97.2	-0.2	3.0
P	98.8	-0.1	1.3
Pb	94.1	3.0	2.9
Rb	99.7	0.1	0.2
Sb	98.6	0.4	1.0
Si	99.9	0.0	0.1
SO_4	99.9	0.0	0.1
Sr	99.8	0.0	0.2
Ti	86.3	8.1	5.6
U	99.5	0.0	0.5
V	97.4	1.0	1.6
Y	99.4	0.2	0.4
Zn	84.8	7.8	7.4
Zr	90.9	0.1	9.0
Ion Chromatography Analyses			
Br	64.1	13.3	22.6
Cl	99.8	0.0	0.2
F	97.1	0.4	2.5
NO_3	93.0	3.1	3.9
P	78.9	-7.2	28.3
SO_4	99.9	0.0	0.1
TIC/TOC Analysis			
NPOC	96.9	-0.8	3.9

ANOVA analysis for Al, As, B, Ba, Br, Ca, Fe, K, La, Li, Mg, Mn, Mo, Na, Rb, Sb, Si, SO_4, Sr, Ti, U, Y, and Zn is based on 34 sites. For Co, P (ICP), Zr, Cl, F and SO_4 (IC) 33 sites were used. For Cu and V 32 sites. For Ho, Ni, Pb, and NO3 31 sites. For Br (30 sites), NPOC (28 sites) and P by IC 17 sites.

The low site variance and intra-sample variance values for the water dataset (Table 31) reflect the homogeneous distribution of trace elements in water. High intra-sample variances for As, B, Br, Cr, La, P, Ti, Zn and Zr suggest a range of potential factors affecting the concentration of these elements, the majority are post-collection and may include;

1. Element state- whether dissolved or bound.
2. Replicate preparation- potential anthropogenic contamination.
3. Storage reactions- interaction of the water sample with sample bottle material. In the case of unacidified samples, bacterial processes in the sample prior to analysis may also contribute to variance.
4. Analytical variance- possibly related to interference with other elements, high concentrations of these elements in the sample, or analytical variability near the detection limit.

Table 32: Percentage of variance in soil samples.

Element	Natural Geochemical Variance	Site Variance	Intra-sample Variance
CaO	96.9	2.1	1.0
Fe_2O_3	98.1	1.5	0.4
K_2O	99.4	0.6	0.0
MgO	96.8	2.5	0.7
MnO	95.7	3.6	0.7
Na_2O	91.4	7.5	1.1
P_2O_5	92.1	7.6	0.3
As	94.5	4.4	1.1
Cd	74.6	5.5	19.9
Cr	97.8	2.1	0.1
Cu	93.5	6.2	0.3
Mo	78.1	21.9	0.0
Ni	98.2	1.6	0.2
Pb	84.7	11.8	3.5
Sb	65.6	4.6	29.8
Se	86.2	7.5	6.3
Sn	65.5	25.7	8.8
U	90.6	2.8	6.6
Zn	96.6	3.2	0.2
pH[1]	93.0	6.3	0.7
LOI	96.7	2.7	0.6
Au[2]	41.2	-9.2	68.0
Pd[2]	51.2	7.0	41.8
Pt[2]	17.3	4.7	78.0

[1] *calculated on the anti-log of pH* [2] *25 to 50 cm depth sample, fire assay analysis.*

The ANOVA results for soils (Table 32) show high intra-sample variance (>4%) for Cd, Mo, Sb, Se, Sn, and U. Sample heterogeneity as well as sample preparation and analysis can contribute to this variance. In addition, where a significant proportion of the values for an analyte occur near the detection limit the variability of data near the detection limit can contribute to the observed variance. Single sample pairs with significant variance can also reduce the statistical validity of the ANOVA analysis. One possibility is that the source and mode of occurrence of elements influences the observed variance. In the example of Cd, Mo, Sb, Se, Sn, and U, these mineralisation related elements may occur as discrete grains in Northern Ireland soils, particularly in mineralised areas such as the Sperrins and South Armagh. The occurrence of U in mineral grain lattices may also contribute to the elevated intra-sample variance for this element. Very high intra-sample variance values (c.>30%) are present for Au, Pd and Pt. This may reflect the primary occurrence of Au and Pt as discrete grains, known as the "nugget effect", and to a lesser extent Pd. Alternatively, a high proportion of values near the detection limit and other factors (as outlined above) may account for the observed variances. The very high sample variance for these elements impacts on the interpretation of anomalies, only spatially extensive anomalies should be considered in any interpretation and single site anomalies viewed with caution.

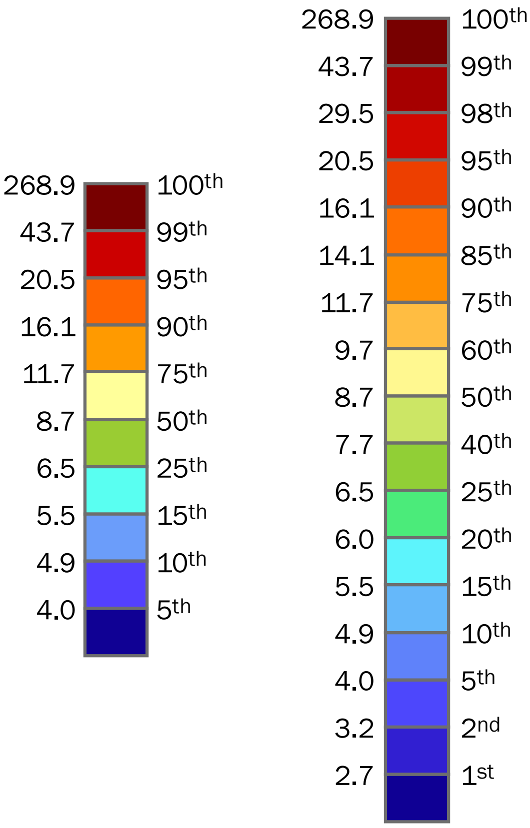
12 Data and Image Processing

The geochemical and field observational data were entered into an ORACLE™ database maintained on the GSNI server. The data was also entered onto the British Geological Survey Geochemistry Database, held in an ORACLE™ relational database management system.

12.1 SINGLE-COMPONENT IMAGES

The principal software for map production was ArcGIS™ v.9.2 developed by Environmental Systems Research Institute, Inc. (ESRI). A map template was designed which referenced a range of vector and raster datasets resident on the GSNI server. These datasets represented cartographic, geological and topographic information. Geographic vector datasets included geology and drift, soil type, drainage, and river catchments. Raster datasets included a digital elevation model and raster versions of Ordnance Survey of Northern Ireland (OSNI) map publications. The design of the map template was based on the methods of the G-BASE program, the same colour gradient and statistical techniques were used to represent the geochemical dataset. The geochemistry database is held locally on the GSNI server with direct linkage to the database files from ArcGIS™.

Regional datasets were imported into ArcGIS™ and grids were produced using the Spatial Analyst extension. The parameters of gridding were those routinely used for producing interpolated images in the G-BASE program. Inverse Distance Weighting (IDW) was used as the interpolation method with a grid cell size of 250 m, a fixed search radius of 1500 m and power value of 2. The IDW method assigns a higher weighting to measured values closer to the predicted location than distal values, i.e., measured values closer to the predicted location have a greater influence on the predicted value than measured locations further away. ArcGIS™ grids were stored locally on the GSNI server.



(a.) G-BASE (b.) Tellus

Figure 21: Examples of (a) G-BASE and; (b) Tellus percentile classification schemes.

A percentile classification scheme based on the G-BASE scheme was used (Figure 21). The G-BASE percentile scheme routinely plots the 5th, 10th, 15th, 25th, 50th, 75th, 90th, 95th and 99th percentiles using a gradational colour scheme from dark blue through blue to green, yellow, orange, red and dark red. A similar colour scheme was used for the Tellus geochemistry images. A standard percentile suite of 1st, 2nd, 5th, 10th, 15th, 20th, 25th, 40th, 50th, 60th, 75th, 85th, 90th, 95th, 98th and 99th percentiles were used for Tellus maps (Figure 22). Additional percentiles to those normally used on G-BASE maps facilitated a more detailed presentation of low, intermediate and high concentration distribution. The implementation of a larger percentile classification suite was validated by the high correlation of anomalies to mapped bedrock and geological structure.

Urban geochemical datasets were also imported into ArcGIS™ where individual sample values were presented as coloured dot maps (Figure 23) using a similar colour ramp as the regional data presentation. The diameter of the coloured dots was varied on a scale, with smallest diameter corresponding to the lowest class interval and largest diameter corresponding to the maximum class interval. A percentile classification was used to assign class intervals. Urban datasets were not presented as grids due to the high spatial variability of urban geochemistry.

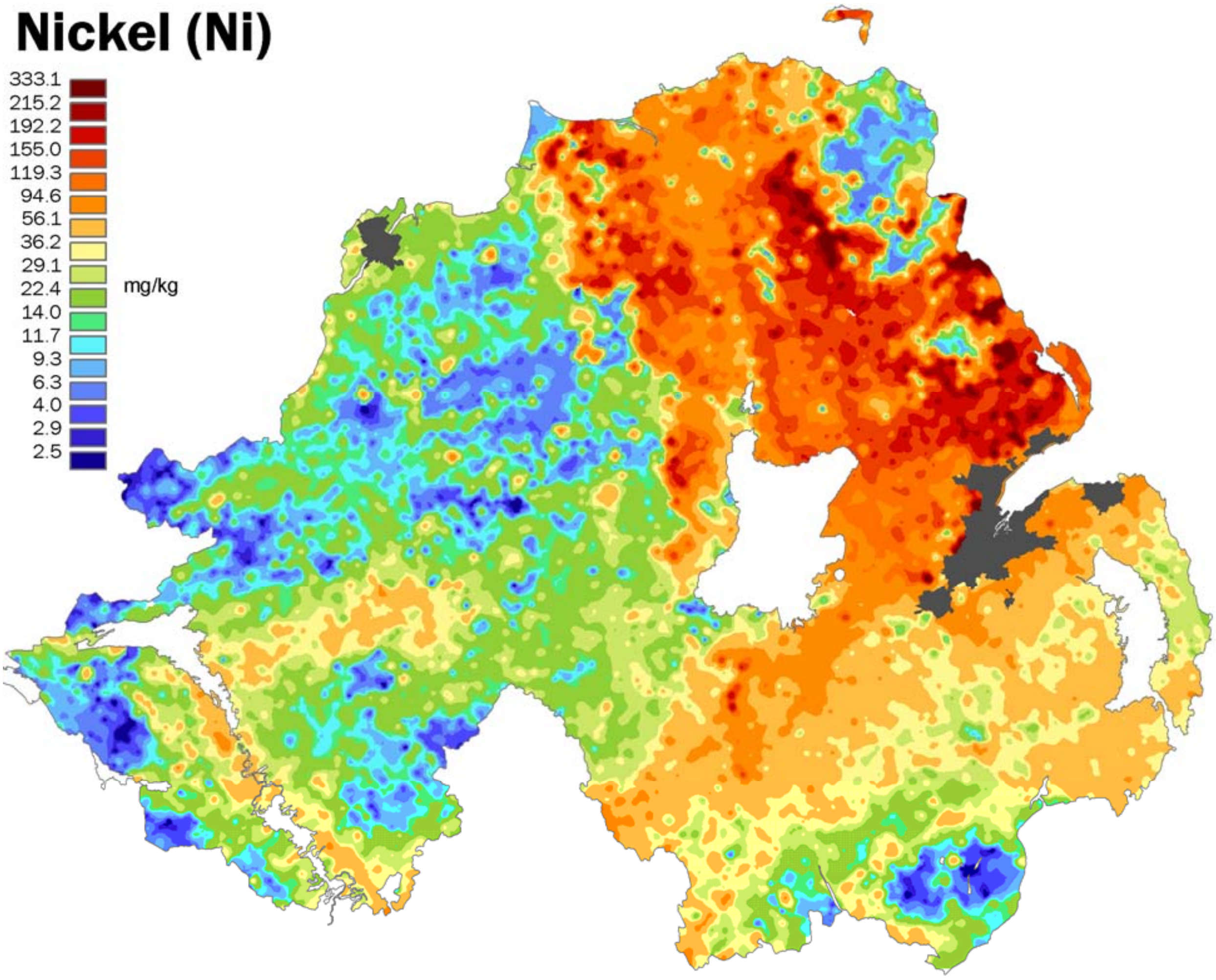


Figure 22: Example of a Tellus percentile classified map, nickel (mg/kg) surface soil (XRF).

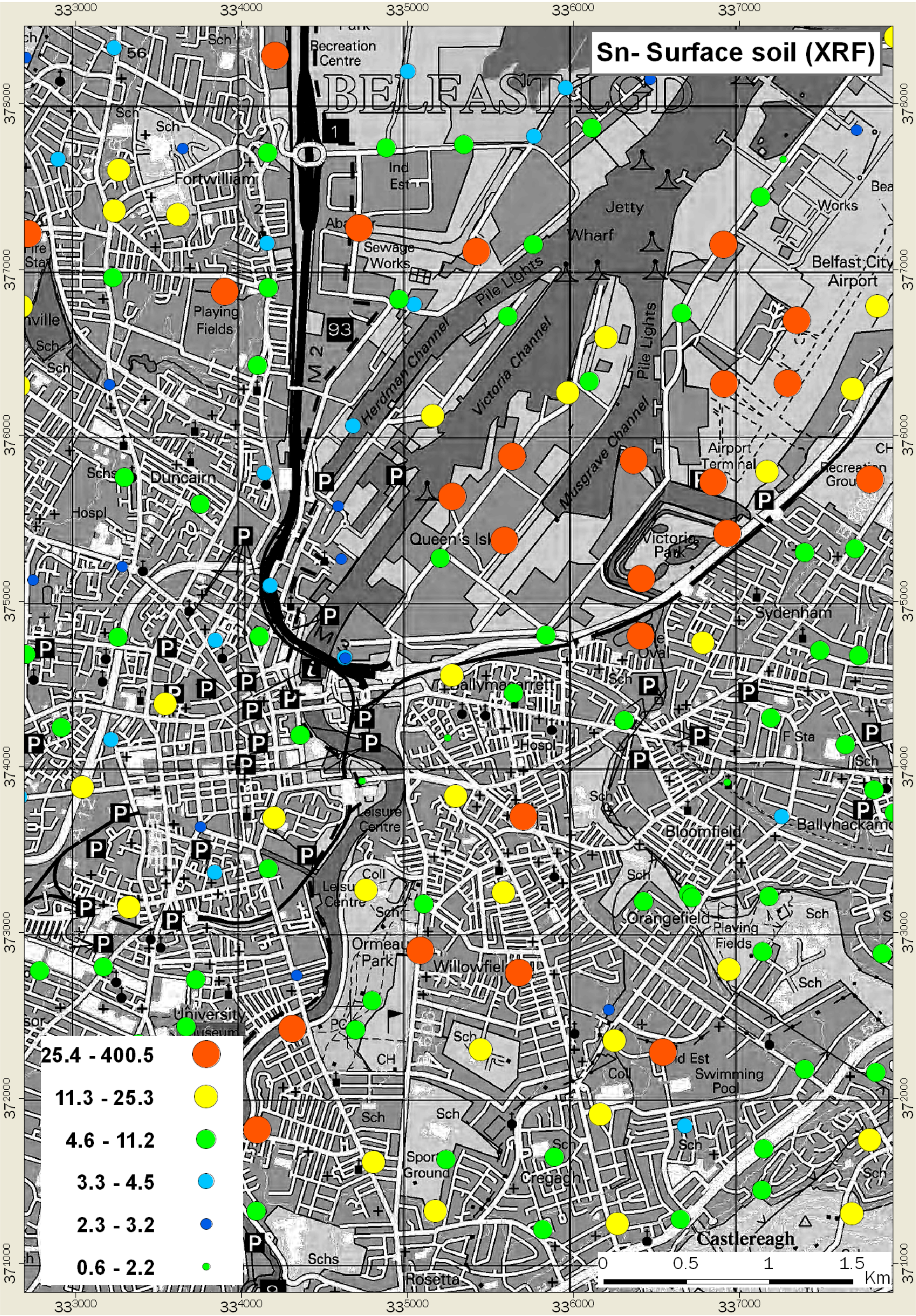


Figure 23: Example map of Sn (mg/kg) in surface soils of Belfast (XRF).

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12.2 STATISTICAL INFORMATION

A statistical summary for each determinand in the different sample media was produced. These summaries are presented in the Tellus atlas. Statistics for the number of samples, minimum, maximum, range, arithmetic mean, median, and standard deviation are presented. Non-interpolated quality controlled datasets were used for statistical purposes. Statistics were generated in Microsoft Excel™ software. Where a statistical parameter produced a value below the detection limit the parameter is recorded as less than the applicable detection limit, i.e., < “DL”.

12.2.1 Histogram

Histograms were plotted (Grapher™ v.6) for all quality controlled datasets. The class interval (Figure 24) was chosen using an arbitrary system based on a value between one-quarter and one-half of the standard deviation. A cumulative frequency plot for each dataset was included with the histogram.

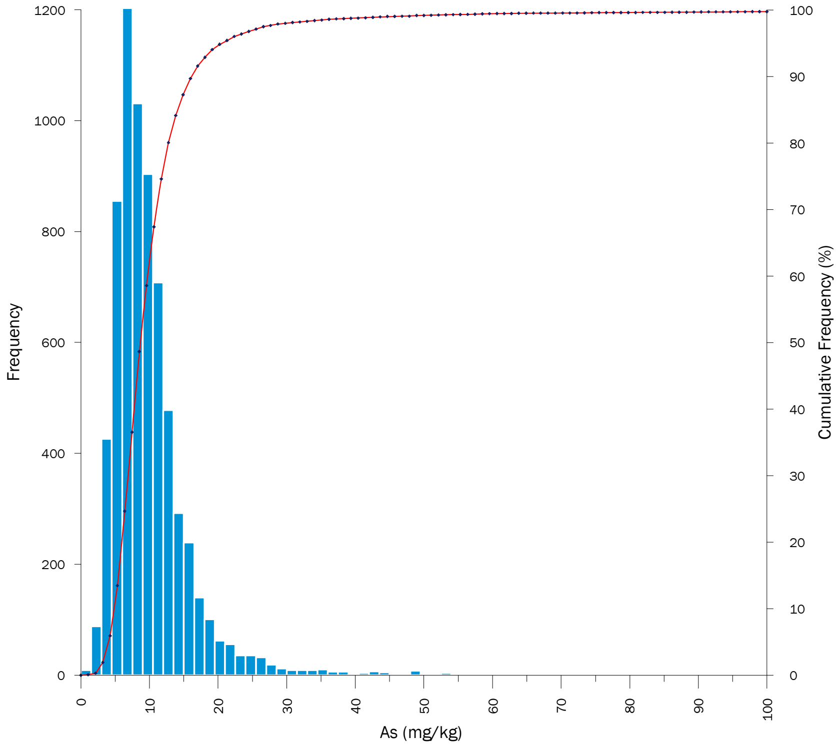

Figure 24: Example histogram for arsenic (mg/kg) in surface soil (XRF).

12.2.2 Box and whiskers plot

Every sample site for both soil and stream datasets was given a bedrock classification according to the 1:250 000 scale mapped geology. A GIS spatial join procedure was employed in ArcGIS™ v.9.2 to classify each sample site using a solid geology polygon dataset. Due to the variety (>50) of different lithologies in Northern Ireland a simplified lithological classification scheme was developed (Table 33). This reduced the number of classes to eleven (Figure 25).

Table 33: Simplified lithological scheme, number of sites classified and constituent lithologies.

Simplified Lithology	Sample Site Classification		Constituent Lithologies
	Soil	Stream	
Gabbro	50	37	Gabbro, diorite
Granite	319	296	Granite, granodiorite, felsite, granite dykes, granophyre, quartz feldspar porphyry, tonalite
Basalt	1738	1394	Basalt, metamorphosed basaltic rock, metamorphosed lava & tuff, interbasaltic bauxitic clay, dolerite
Andesite	10	9	Andesite
Acid Volcanics	79	76	Rhyolite, rhyodacite, agglomerate, lava or extrusive igneous rock (undifferentiated)
Psammite and semipelite	884	889	All psammite layers, Killeter Quartzite, metamorphosed lava & tuff (Dalradian)
Conglomerate	170	184	All conglomerates and psephite
Sandstone	946	924	All sandstone units, breccia and sandstone interbedded
Lithic arenite	1300	1015	Lithic arenites of the Southern Uplands-Down-Longford Terrane
Mudstone	779	602	All mudstone units, argillaceous layers, silty mudstone
Limestone	587	448	Limestone, argillaceous limestone, limestone & argillaceous rocks interbedded, mudmound reef limestone, limestone & mudstone interbedded, chalk & sandstone, dolomitic limestone

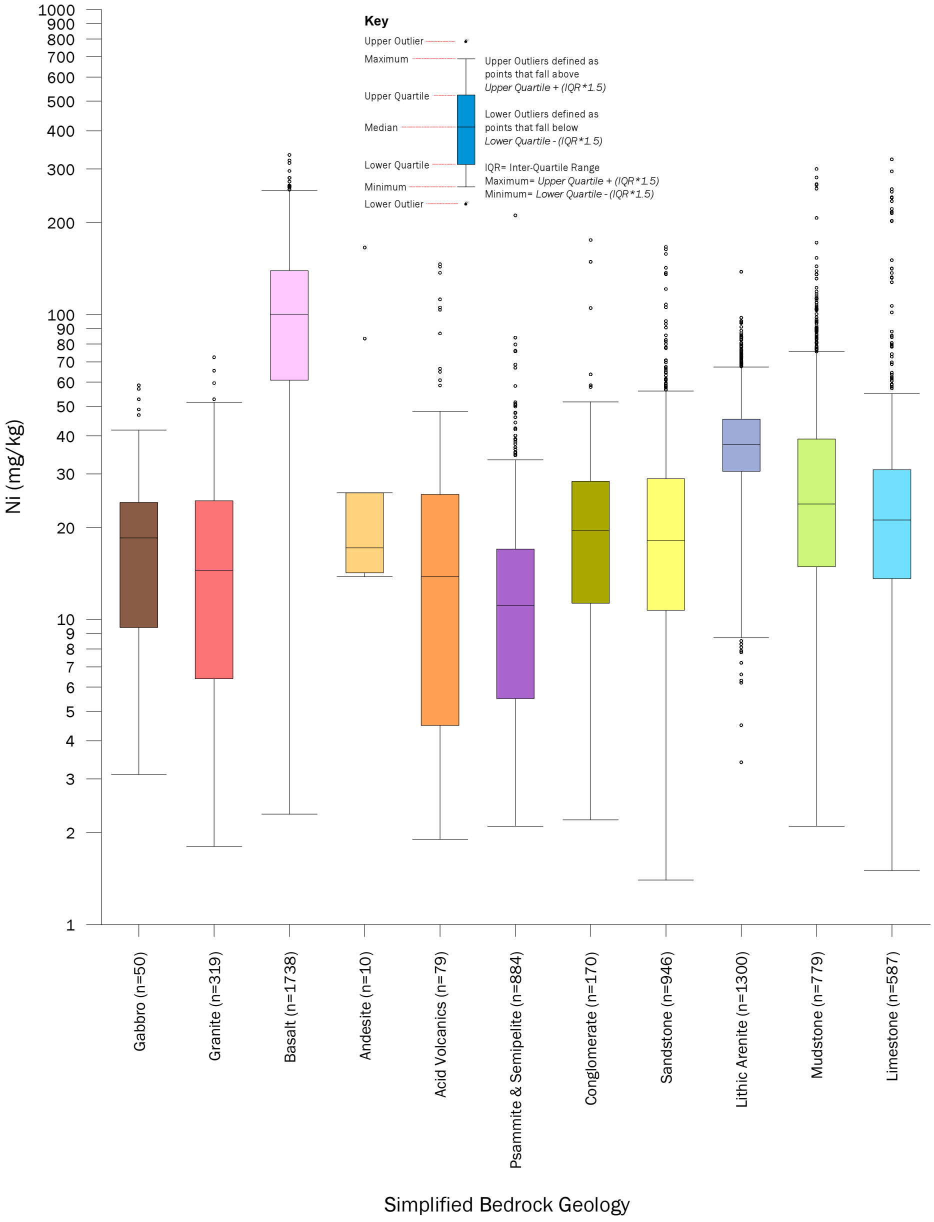

Figure 25: Example of box and whisker plot, classified using simplified bedrock geology.

The geochemical datasets with appended sample site geology were exported from ArcGIS™ in the dBase file format. These were subsequently imported into Grapher™ v.6 (Golden Software) where they were presented as box and whisker plots (Figure 25). It was decided to retain the gabbro, andesite and acid volcanic classifications despite a low number of sample sites due to the distinctive nature and chemistry of these lithologies. The parameters for each box and whisker plot are shown in Figure 26.

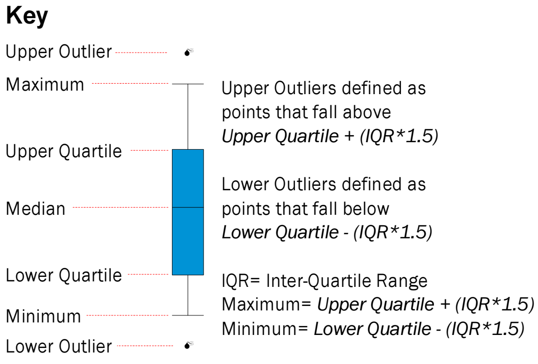

Figure 26: Box and whisker parameters calculated for stream and soil datasets.

Estimated crustal values for each element are presented in Table 34, together with whole-rock values for basalt, granite, shale and limestone. The values should be used as a guide only.

Table 34: Estimated concentrations of elements in bedrock lithologies.

Element	Continental Crust	Upper	Basalt	Granite	Shale	Limestone
Source	*(2)*	*(4)*	*(3,2)*	*(3,2,1)*	*(3,1)*	*(3,1)*
Ag	0.07	0.05	0.1	0.04	0.05	<0.1
As	1.8	1.5	2	1.5	15	1
Ba	425	550	250	600	700	100
Bi	0.17	0.13	0.15	0.1	0.18	
CaO	5.8	4.2	9.4	2.2	3.1	42.3
Cd	0.2	0.1	0.2	0.1	0.3	0.04
Ce	60	64	35	80	50	10
Co	25	10	50	1	20	4
Cr	100	35	200	4	100	10
Cu	55	25	100	10	50	4
Fe_2O_3	8.0	5	12.2	3.9	6.7	0.5
Ga	15	17	12	18	20	4
K_2O	2.5	3.4	1	4	3.2	0.3
La	30	30	10	50	20	6
MgO	3.9	2.2	7.5	0.3	2.5	7.8
MnO	0.12	0.08	0.28	0.06	0.11	0.14
Mo	1.5	1.5	1	2	3	0.4
Nb	20	25	20	20	20	0.3
Ni	75	20	150	1	70	12
P_2O_5	0.24	0.17	0.32	0.17	0.17	0.09
Pb	12	20	5	20	20	8
Rb	90	112	30	150	140	5
Sb	0.2	0.2	0.2	0.2	1	0.2
Se	0.05	0.05	0.05	0.05	0.6	0.08
Sn	2	3	1	3	4	<1
Sr	375	350	465	285	300	500
Th	9.6	10.7	2.2	17	12	2
TiO_2	1	0.5	1.5	0.4	0.8	0.07
U	2.7	2.8	0.6	4.8	4	2
V	135	60	250	20	130	15
Y	33	22	25	40	25	15
Zn	70	71	100	40	100	25
Zr	165	190	150	180	160	20

Values in mg/kg, except those for CaO, Fe_2O_3, K_2O, MgO, MnO, P_2O_5 and TiO_2, which are in percent. Sources of the data: (1) Turekian and Wedepohl (1961); (2) Taylor (1964); (3) Levinson (1974); (4) Taylor and McLennan (1985) (except P2O5, from Weaver and Tarney (1984), and Sn, estimated from 1, 2 and 3).

13 Interpretation of Geochemical Results

The principal aim of the geochemical survey was to provide environmental baseline data for the surface environment of Northern Ireland. The distribution of each element was interpreted in relation to the major lithological, stratigraphical and structural subdivisions of Northern Ireland geology. The effects of metalliferous mineralisation and Quaternary processes were also considered. This provides an environmental background against which the influence of human activity can be assessed both now and in the future. Urban geochemical datasets were integrated with 1:10 000 scale OSNI urban mapping as a means of defining source-anomaly relationships. Other data resources such as historical land-use were used to interpret the geochemical data such that the correlation of urban geochemistry to temporal patterns of changing land-use could be investigated.

13.1 STREAM SEDIMENT SAMPLES

The geochemical images show the concentrations of the chemical elements (expressed as oxides for the major elements) in the <150 µm fractions of stream sediment. The chemical compositions of the samples give an indication of the composition of the bedrock (subject to the caveats set out below), and have the advantage over rock and soil samples in that fewer samples are needed to represent a given area.

The geological bedrock (Figure 27) is the single most important control on the geochemical baseline. However, the interpretation of the results should take into account the ways in which the chemical composition of the fine fraction of a stream sediment sample may differ from the typical composition of the bedrock in the source area.

1. Bedrock variability

   A very small area of a compositionally contrasting rock type may have a detectable influence on the trace and major-element content of stream sediment downstream. This 'geochemical signature' is the basis for the use of stream sediment sampling in mineral exploration, and similar observations may point to the existence of, for example, a small, hitherto unknown basic intrusion.

2. Influence of Quaternary deposits

   In areas where bedrock is overlain by Quaternary deposits, this drift cover will influence stream sediment geochemistry. Where bedrock is covered by exotic glacial, glaciofluvial or lacustrine deposits, or by well-sorted sediments (e.g. glaciofluvial or aeolian sands), these deposits may have a greater influence on stream sediment geochemistry than bedrock. Potentially yielding high levels of a range of elements if clay minerals predominate in the fine fraction and low values for many elements if quartz is dominant. In some circumstances Quaternary deposits may impose the geochemical signature of their source rocks which may differ from underlying bedrock. The geochemistry of transported drift deposits may be used as a tool in prospecting for mineral deposits located within the area of glacial influence.

3. Properties of physical and chemical weathering

   The processes by which a stream sediment is derived from its parent rocks include both physical and chemical weathering. Physical weathering involves the breakdown of rocks into their constituent mineral grains and the further comminution of those grains. The relative concentrations of the constituent minerals are likely to be modified by glaciofluvial processes and by modern alluvial processes. Minerals such as quartz, garnet and baryte, which tend to survive as large grains, will be selectively removed by sieving during sample collection. Primary rock-forming minerals such as feldspars and ferromagnesian silicates may be replaced by low-temperature minerals such as clays and chlorites, and certain elements such as Ca, Fe, Mg, Mn and Sr are readily mobilised in surface waters and groundwaters. This leads to an increase in the relative abundance of resistate minerals such as Fe-Ti oxides and zircon. This is reflected in high values for elements such as Ti and Zr.

4. Sorption by Fe-Mn hydrous oxides

   In streams with high pH and Eh, dissolved Fe and Mn from reducing ground, soil or interstitial pore-water sources are precipitated as hydrous oxides, sometimes in considerable abundance. The maximum concentrations of Fe_2O_3 and MnO in stream sediment samples from the present study are 50.8% and 9.23% respectively. These precipitates are present partly as colloidal particles and partly as coatings to particles of all sizes. These hydrous oxides are capable of sorbing a wide range of trace elements, particularly As, Mo and Ba and the elements of the first-row transition series. Under favourable conditions, recently precipitated hydrous oxides can produce very high concentrations of these elements in the fine fraction of the sediment thereby reducing the correlation of stream sediment geochemistry with bedrock geochemistry.

5. Anthropogenic sources of elements

Stream sediment may contain material unrelated to the bedrock upstream, derived from anthropogenic contamination of the stream or its catchment. The latter includes pollution from mining, agriculture (e.g. phosphate fertilisers, which commonly contain U as well as P_2O_5), industry, sewage treatment, domestic sources, and material deposited beside roads. Figures 28 and 29 give an overview of land use throughout the area.

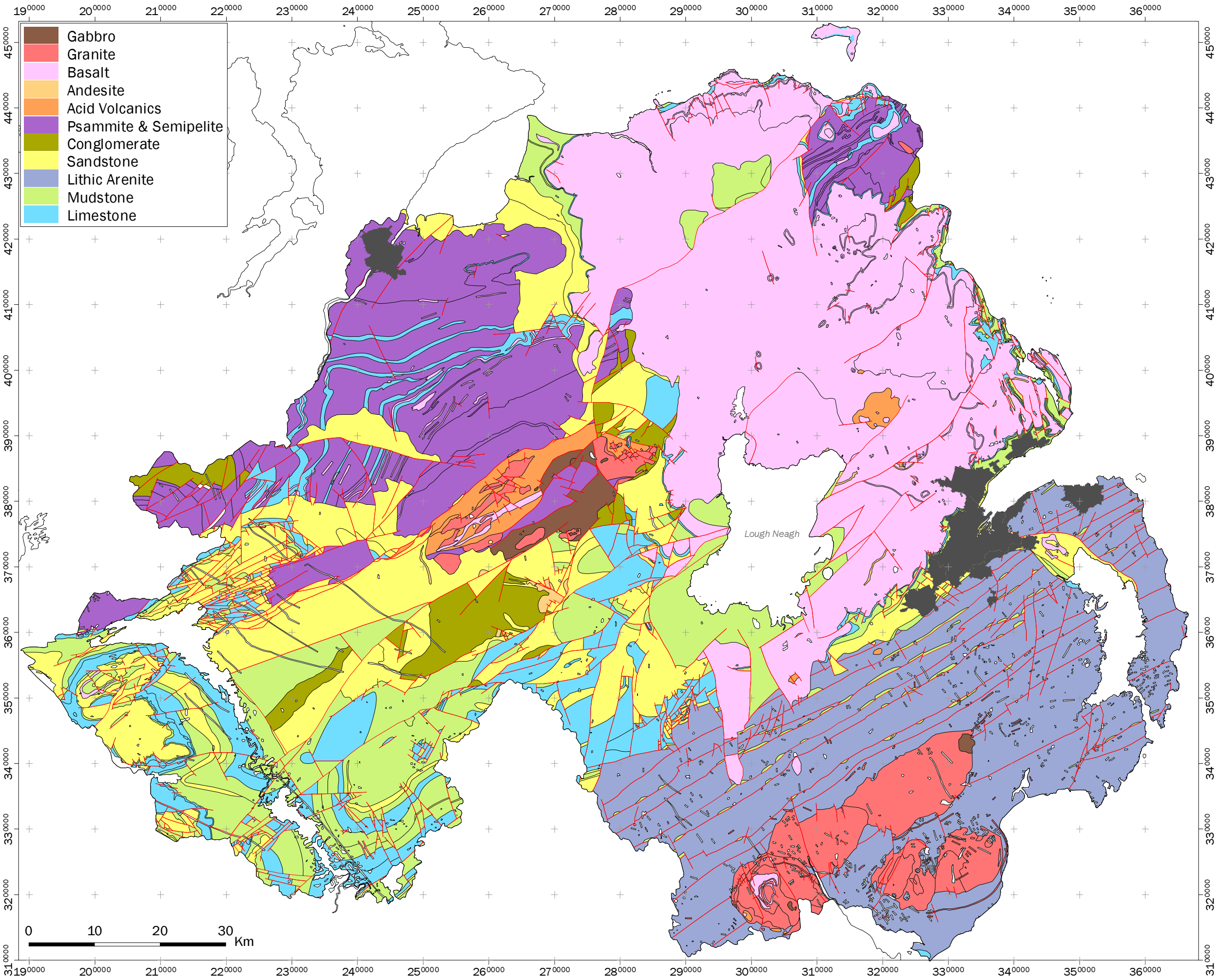

Figure 27: Simplified geological map of Northern Ireland.

13.2 SOIL SAMPLES

The geochemistry of soils is related to factors such as bedrock geology (Figure 27), drift cover (Figure 28), land use (Figure 29) and topography (Figures 29 and 30). The use of GIS software enabled these spatial datasets to be integrated into the interpretation of the geochemical data. The relative importance of each of these factors varies, both spatially and temporally. Material classified as 'soil' usually consists of variable proportions of;

- Rock/ mineral fragments - rock and mineral fragments in various states of weathering and alteration.
- Clay minerals - produced by the weathering of rock and mineral fragments.

- Secondary minerals - notably the hydrous oxides of Al, Fe, and Mn and secondary carbonates.
- Organic matter - organic matter in various stages of decomposition, ranging from plant debris to humins and including humic and fulvic acids.
- Living organisms - ranging in size from bacteria upwards.
- Air/ water - present within pore spaces and within primary mineral grains and secondary weathering products.
- Contaminants - historical and modern day contaminants sourced from industry, agriculture, mining and other anthropogenic sources.

Many soils are well stratified or vertically zoned in composition, as a result of leaching by percolating rainwater and depositional processes within the soil profile. In many soils in temperate climatic zones on non-carbonate bedrock, minerals and organic material are leached from the upper 'A' horizons of a soil profile and are transported downwards and re-deposited by precipitation in the 'B' horizon (the process known as podzolisation). A full description of soil structure and composition may be found in textbooks such as Fitzpatrick (1974), Hodgson (1976), White (1979), Bridges (1997) and Puri (2002). A comparison of soil geochemistry with stream sediment geochemistry may be expected to show both similarities and differences, although similar types of minerals and chemical compounds may be present. The more important physical differences between soil and stream sites include;

- Rates of transport - a lower rate of material transport in soil, allowing more time for in-profile modification.
- Influence of geology - a greater influence from site geology for soils and catchment geology for stream sites. Sediment geochemistry reflects the average composition for the area upstream of the sample site and is therefore representative of a larger area. Soil composition may indicate localised conditions in the immediate sample environment.
- Water saturation - only partial water saturation of soils in comparison to stream sites, often with seasonal wetting and drying cycles. Except for some bog soils and peat substrates which may be permanently waterlogged.
- Anthropogenic modification - soils may have undergone extensive anthropogenic modification and management in both agricultural and urban areas.

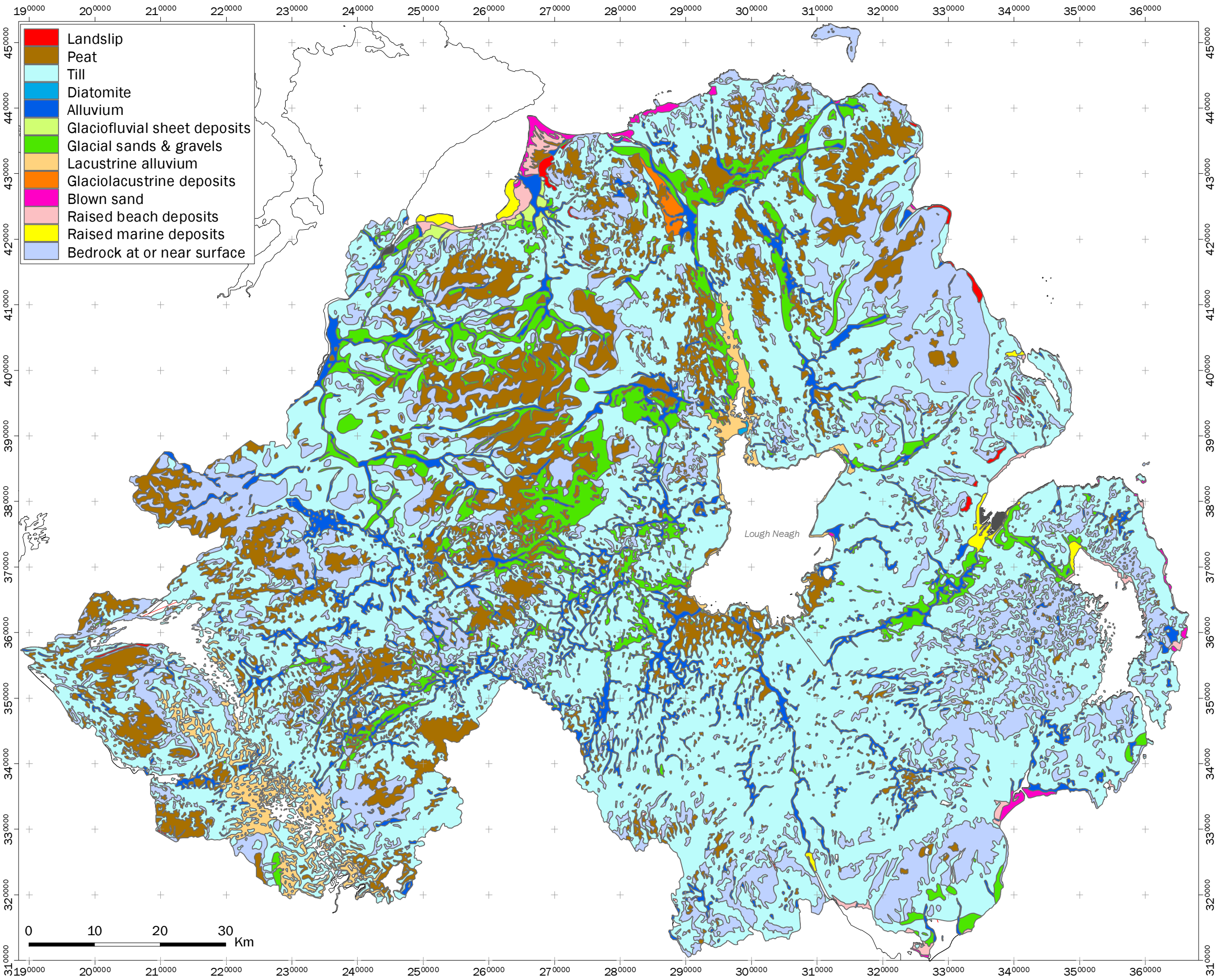

Figure 28: Superficial deposits map of Northern Ireland.

Samples from the Fe-oxide-rich 'B' horizon are usually favoured for geochemical sampling due to the natural pre-concentration of trace elements in this horizon as a consequence of downward leaching. However, the sorption properties of secondary oxides in soils are not always the same as their equivalents in stream sediments. Consistently high concentrations of Mn oxides and associated trace metals such as Co are rare in most soils, though the formation of oxide nodules may give rise to very localised high concentrations of these elements. In saturated peaty bog soils, acidic, anoxic reducing conditions prevail, and Al, Fe and even Si may be mobilised ('gleying'), transported and re-deposited. Local chemical variations in such gleyed soils may be marked, with grey-green and yellow-red mottling evident.

In peaty soils, which form in conditions where the rate of accumulation of plant debris exceeds the rate of decay, the organic-matter content in the upper layers of the soil may be very high (>90%). The humic and fulvic acids produced by the humification process play a major part in leaching within the soil column, such that the mineral 'A' horizon below the peat layer may consist only of quartz sand while the 'B' horizon contains abundant re-deposited humic and Fe-oxide material. An impermeable Fe-oxide layer (iron pan) may also be present. Soils of this nature are common in upland areas of Northern Ireland where rainfall is high. Extensive areas of relatively undisturbed peat soils can be found on the high ground of the Sperrins, Mournes and Antrim plateau.

In contrast, soils developed over limestones tend to be thin, alkaline, well-drained 'rendzinas', in which the carbonates and other soluble minerals have been leached, leaving only a thin residual mineral soil below an organic humus horizon. Resistate minerals tend to become concentrated in these well-drained soils, giving rise to elevated levels of such elements as La and Y. The high pH of these soils directly affects the natural flora and also controls the type of cultivation practised, as do the acidic, base-poor peat soils, giving a direct link between bedrock geochemistry and land use. Highly permeable limestone bedrock also gives rise to sub-surface drainage flow, e.g., Marble Arch Caves, and the few surface streams present may dry up in the summer as the water table falls. Soils in intensively farmed agricultural areas are further modified by physical disturbance (e.g. ploughing) and chemical modification (liming, fertilisers, pesticides) which may affect both the major nutrient elements such as Ca, K and P and supplement trace elements such as Zn.

13.2.1 Urban areas

In many urban areas with a history of industrial activity, contamination by heavy metals and other wastes may be severe, especially in the upper part of the soil profile. 'Made ground', often incorporating solid industrial wastes such as slags, mine spoil, ashes and ceramics, is very common in urban areas. This may give rise to some soils which are unusually metal-rich throughout their profiles, in contrast to soils in areas that are less disturbed where contamination may be confined to the upper horizons. Sampling the deeper 'B' horizon may avoid the effects of surface contamination, but not in contaminated 'made ground' profiles. Since both similar and different geochemical processes operate in stream sediments and soils, data for the two sample types were processed and plotted separately.

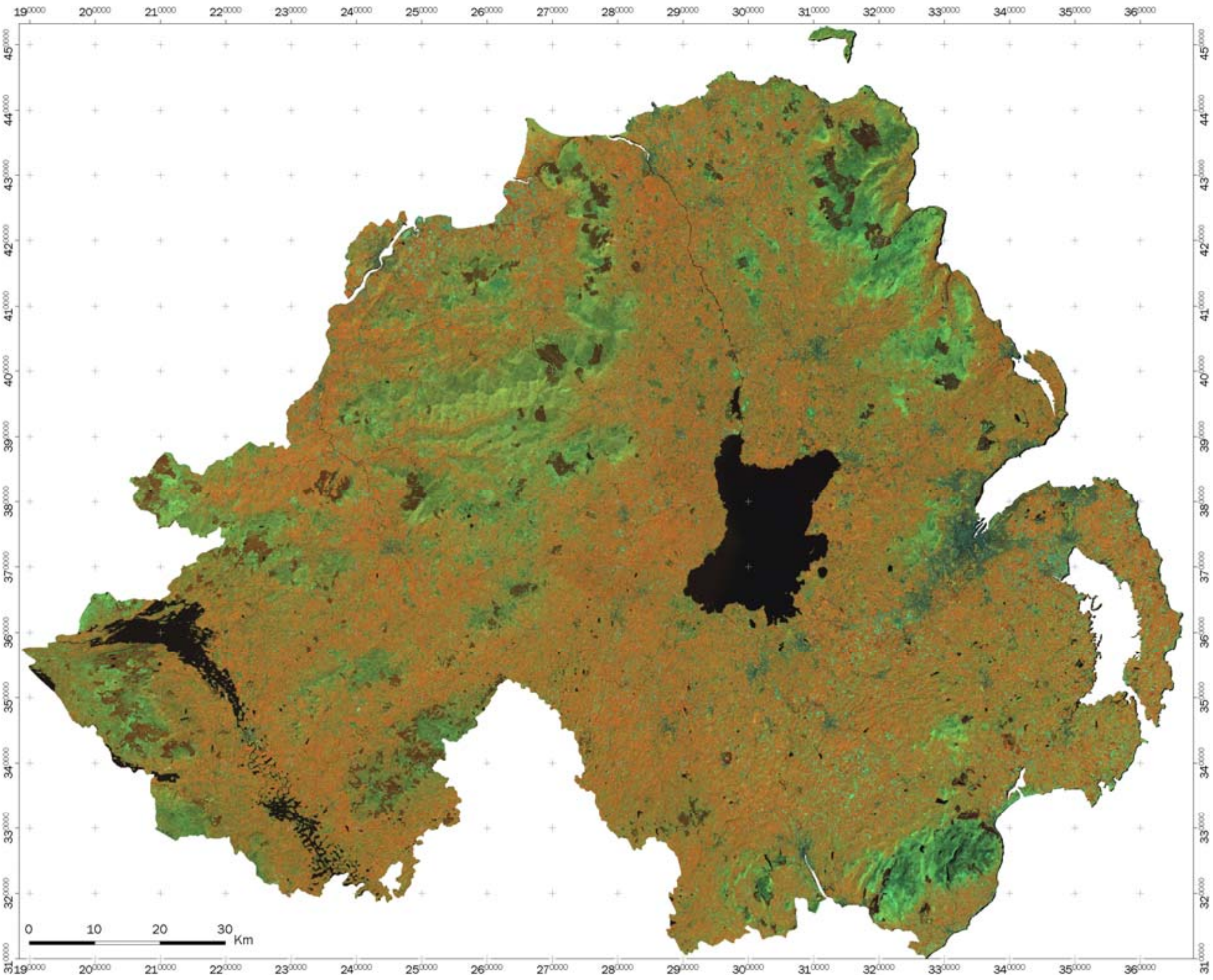

Figure 29: Landsat mosaic (Bands 4, 5, 7) of Northern Ireland.

13.3 WATER SAMPLES

There are several important controls on stream water geochemistry. The solid and drift geology of the area covered by this survey shows wide variety, both in chemical composition (often one of the principal determinants of stream-water chemistry) and in physical properties. Groundwater flow, residence time, topography, climate and land use are all controls on stream-water chemistry.

The chemistry of stream water at a sampling location is dependent on biological and hydrological processes as well as chemical processes. The water in streams is a mixture of waters that have passed through different environments. This mixing takes place in the unsaturated and saturated zones, in the riparian zone and within the stream channel. The relative proportions of these components are dependent on catchment properties such as topography and the characteristics of the bedrock. For example, soil and rock permeability and hydraulic connectivity determine the importance of groundwater in contributing to stream flow. Present and antecedent weather conditions also influence the proportions of these components, and thereby stream-flow discharge and current catchment hydrological status. Once water has reached the stream channel, in-stream processes can have a significant influence in modifying stream-water chemistry, particularly of the less mobile elements.

Factors controlling the chemical composition of stream water include:

- Atmospheric deposition and rain-water composition.
- Bedrock composition and soil type, long-term weathering and leaching processes.
- Occurrence of drift deposits, type and composition.
- Processes controlling the chemistry of soil solution.
- The influence of terrestrial flora and fauna.
- Mineral weathering, groundwater composition and residency time.
- Catchment hydrology and extent.
- Anthropogenic influences in the terrestrial, marine and atmospheric environment.
- In-stream processes, e.g., precipitation, mobilisation.

More comprehensive descriptions of the processes controlling the composition of natural water are given by Drever (1997), Stumm and Morgan (1981) and Stumm (1994).

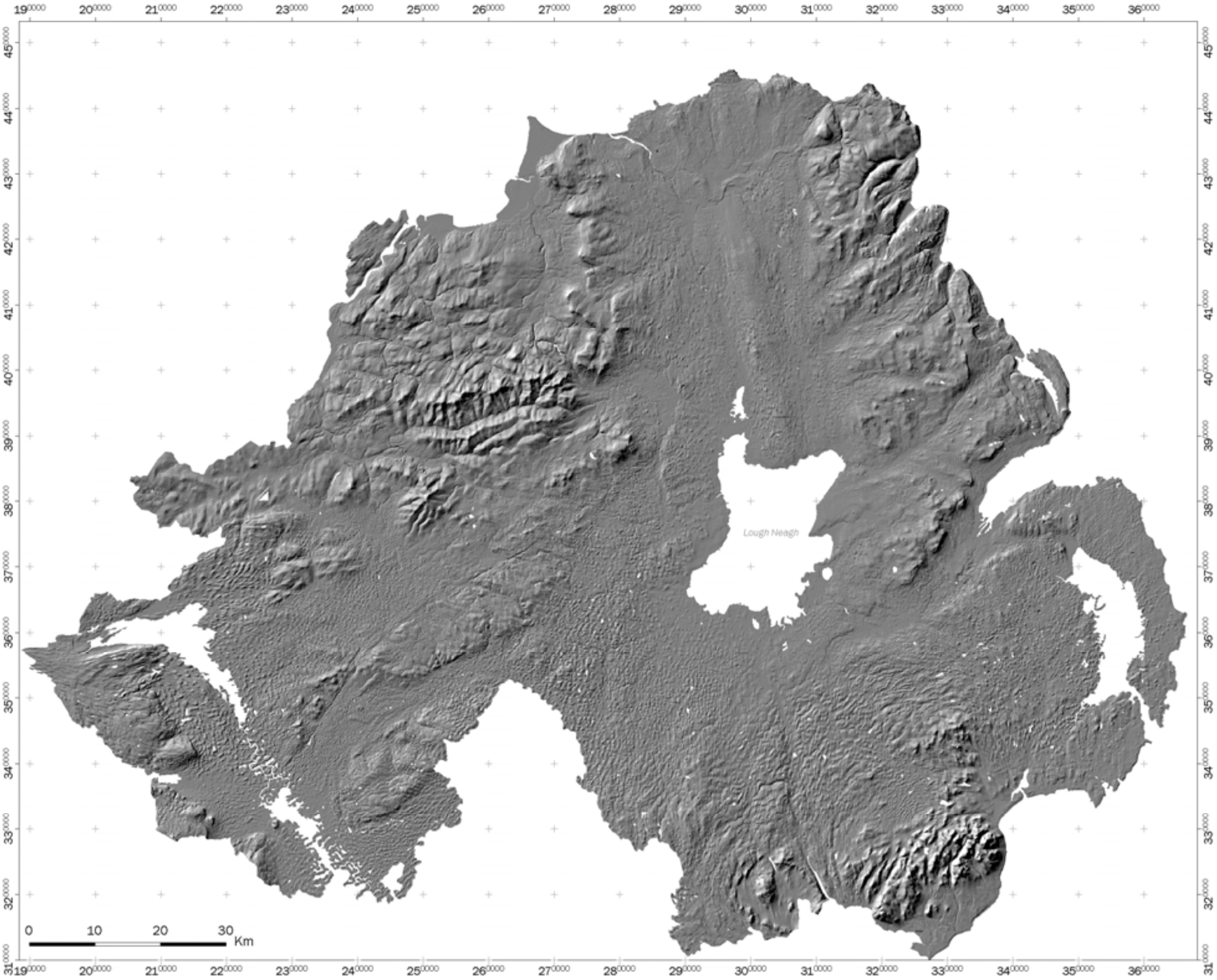

Figure 30: Digital elevation model (DEM) of Northern Ireland.

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14 Ternary Images

ArcGIS™ was used to produce ternary images using the interpolated grid data files. Each grid was assigned to one of the primary colours (red, green, blue) with a gradation of intensity from lowest to highest value. The monochrome images were combined to produce an RGB composite image. The combination of different intensities for the different bands facilitates the definition and delineation of anomalous zones for any combination of three determinands.

A colour scheme (Table 35) is used to discriminate where elements are elevated in a particular area, e.g.,

For example, where;

Arsenic = Red Copper = Green Nickel = Blue

Table 35: Colour scheme for Ternary images.

Red	Green	Blue	Colour	[1]Interpretation
X				Elevated As only
	X			Elevated Cu only
		X		Elevated Ni only
X	X		Yellow	Elevated As + Cu
X		X	Magenta	Elevated As + Ni
	X	X	Cyan	Elevated Cu + Ni
X	X	X	White	Elevated As + Cu + Ni

[1] *Where arsenic = red, copper = green, and nickel = blue. Note: black in a ternary image corresponds to localities where the lowest intensity and hence concentration is present for each of the three parameters. White corresponds to an area of highest intensity/ highest concentration for each of the three parameters. Table 35. Simplified colour scheme for ternary images for the example As (red), Cu (green), Ni (blue).*

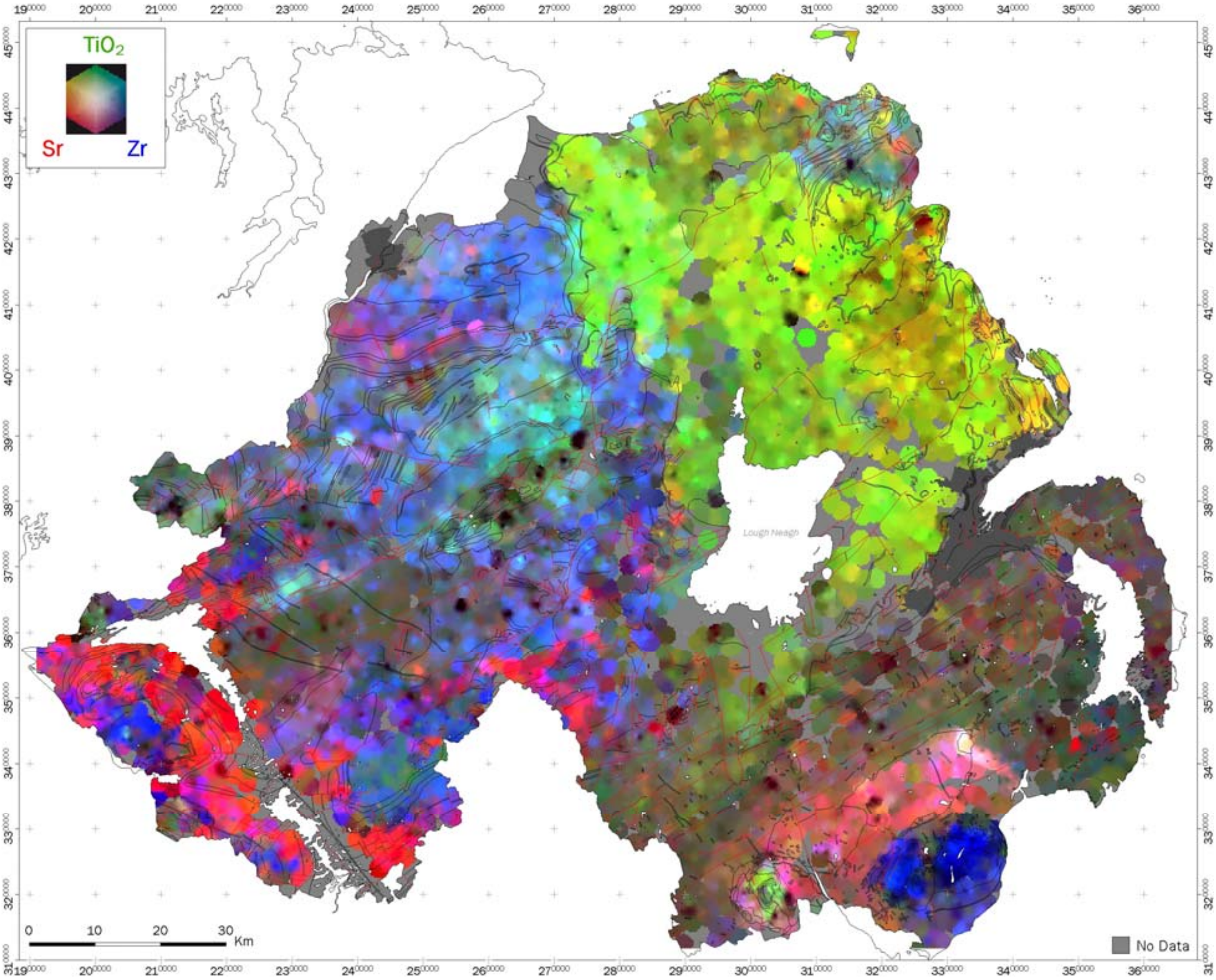

Figure 31: Ternary image of Sr-Ti-Zr in regional stream sediments.

14.1 TERNARY IMAGE OF Sr-Ti-Zr IN REGIONAL STREAM SEDIMENTS

The red band of this image (Figure 31) represents strontium (Sr), the green band titanium (Ti) and the blue band zirconium (Zr). When combined in a ternary image these elements provide a useful indication of variability in sediment sources and depositional environments due to the markedly different geochemical characteristics of the three elements. Stream sediments overlying the Tertiary-age basalt lithology of Co. Antrim have a dominance of Ti relative to Sr and Zr. This corresponds with the naturally high concentration of Ti in basic igneous lithologies and sediments derived from such lithologies. Towards the coastal area of Co. Antrim the Sr concentration of sediment increases. This corresponds to an area with bedrock at/ near surface. It is speculated that elevated Sr in this area may indicate increased feldspar content in stream sediments in proximity to bedrock sources.

In the western part of Northern Ireland zirconium predominates in sediments overlying psammites and semi-pelites, reflecting a source of Zr in minerals such as zircon and sphene. In the Mourne Mountains Complex elevated Zr in stream sediment reflects the natural abundance of this element in zircon and sphene hosted by the granitic lithology. Strontium concentrations are generally elevated in the south-west part of sampled area, indicative of locations with carbonate lithologies, e.g., Ballyshannon Limestone Formation. Sediments on the Newry Igneous Complex also contain elevated Sr concentration reflecting the elevated Sr concentration of the underlying granodiorite source. Sediments on the Shanmullagh Sandstone Formation and on the shale and lithic arenite of the Southern Uplands-Down-Longford Terrane have low concentration for all three elements, reflecting a low natural abundance of these elements in sandstone and shale. The only conspicuous locality of elevated Sr, Ti and Zr in stream sediments occurs at the ultramafic-intermediate complex at Slievegarran on the north-east side of the Newry Igneous Complex. At this location biotite pyroxenite and meladolerite may provide a geogenic source for these elements.

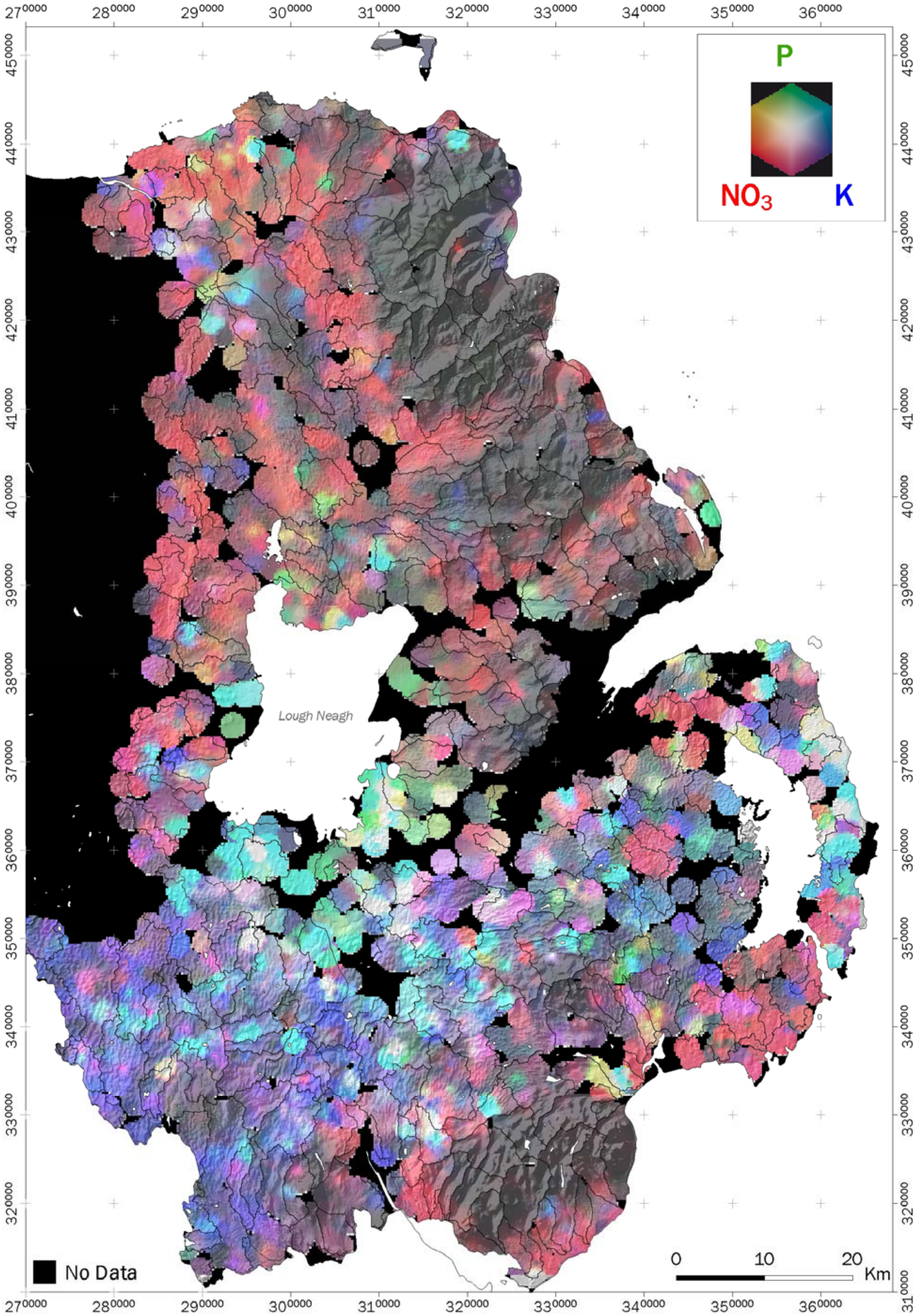

Figure 32: Ternary image of NO_3-P-K in Tellus regional stream waters.

Topography reproduced from the Ordnance Survey of Northern Ireland's data with the permission of the Controller of Her Majesty's Stationery Office. © Crown copyright and database rights DMOU205.

14.2 TERNARY IMAGE OF NO_3-P-K IN REGIONAL STREAM WATERS

Nitrate is displayed as the red band, phosphorus as the green band and potassium as the blue band in this image (Figure 32). The NO_3 dataset is derived by ion chromatography analysis, the K and P datasets by ICP-AES analysis. Only the eastern part of Northern Ireland is displayed, corresponding to the Tellus samples collected in the summer of 2005. The image is draped on a high-resolution digital elevation model (DEM) to aid interpretation. Stream water catchments are also plotted to highlight the variation of stream water chemistry in different catchments. The image highlights the underlying geological control and the dominant effect of land-use on stream water chemistry.

Stream waters in Co. Antrim have spatially extensive elevated NO_3 concentration. Sporadic localities with elevated K and P are present, set against a dominant background of elevated NO_3. Abundant localities with elevated concentration for any combination of the three determinands are present on the shale and lithic arenite of the Southern Upland-Down-Longford Terrane. A regional background of elevated K predominates suggesting a geogenic source of potassium from feldspars present in the lithic arenite and shale bedrock. Elevated NO_3 concentrations are present to the north of Warrenpoint, on the Mourne Plain and in the vicinity of Downpatrick. The distribution of NO_3 suggests the influence of land-use on stream water chemistry and a possible correlation with farming practices. This is corroborated by low concentrations for all three determinands in streams flowing on upland areas. Indeed, the existence of very low values for all three determinands in upland terrain allows speculation that land-use and not geology is the control on the distribution of NO_3, P and K in stream water.

It is speculated that absence of sustained farming practice coupled with low rates of artificial and slurry fertiliser application in these upland areas may account for the low values of stream water nitrate. Of note is the dominance of phosphorus in streams on the southern and eastern margins of Lough Neagh. The source of the phosphorus is undetermined, but may correspond to land-use and farming practices. The ternary image suggests that a potential source of phosphorus to Lough Neagh is present on the southern and eastern margins of Lough Neagh. This may contribute to the eutrophication of Lough Neagh.

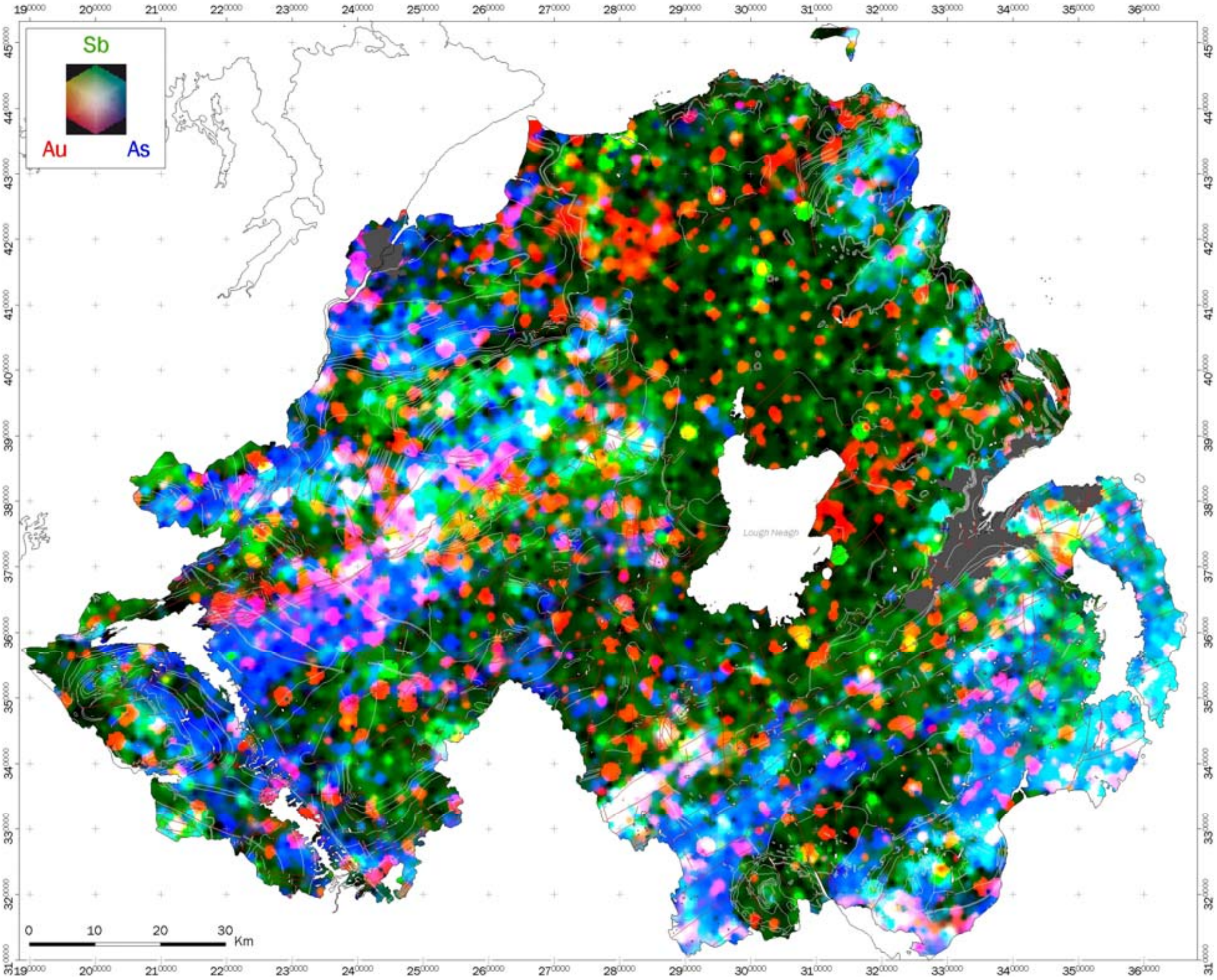

Figure 33: Ternary image of Au-Sb-As in regional soil.

14.3 TERNARY IMAGE OF Au-Sb-As IN REGIONAL SOIL

This image (Figure 33) displays gold (Au) as the red band, antimony (Sb) as the green band and arsenic (As) as the blue band. Both the Sb and As datasets represent XRF analyses of surface soil (5 to 20cm depth) samples. The Au dataset is derived by fire assay of deep soil (35 to 50 cm depth) samples. The image therefore combines surface soil and deep soil geochemical characteristics. Although not convention, the integration of different sample types in this instance facilitates an interpretation of the underlying geological controls on soil geochemistry.

The image is primarily intended to assess the potential prospectivity for gold mineralisation occurrences in Northern Ireland. The image utilises the spatial distribution of the commodity of interest, i.e., gold, as well as the distribution of commonly associated elements, i.e., pathfinders, in this instance arsenic and antimony. Localities with elevated Au, As and Sb are shown as white coloured areas on the image. Areas with elevated concentration for a single element plot as either red, green or blue colouration. Where two of the three elements are anomalous magenta or yellow colouration predominates. Whilst localities with elevated concentration for all three elements (i.e., white colouration) are of most interest, those areas represented by magenta or yellow colouration are also of potential interest. There are localities with elevated concentration of all three elements in the general region of Omagh, with anomalies in the vicinity of the known gold deposits at Cavanacaw and Curraghinalt. Sporadic anomalies occur across the Sperrins area, with notable anomalies near Castlederg, south of Newtownstewart, north-east of Omagh and near Carnanelly mountain. Anomalies also occur near Slieve Gallion, on lithologies belonging to the Tyrone Igneous Complex. North-west of Carnlough (Antrim coast) a small anomaly is present in soils on Upper Basalt Formation near Knockore. To the south, another anomaly occurs on identical lithology near Capanagh Wood.

Extensive anomalies are present in the vicinity of Keady (South Armagh) and in the general area of the Holywood Hills (north-west of Newtownards). In the Keady area historical base-metal mine workings and occurrences of gold mineralisation corroborate the presence of anomalous gold, antimony and arsenic concentrations in soil. In the case of the Holywood hills there were no known gold occurrences that would account for the observed anomalies at the time of publication of this work. An anomaly north-east of Rostrevor may be related to the intrusion of the Mourne Granite Complex and/or hydrothermal activity associated with this complex. Anomalies to the south-east of Downpatrick also suggest potential prospectivity at several localities in this area.

15 Concluding Remarks

The Tellus geochemical programme provides an exemplary baseline geochemical dataset for the environment of Northern Ireland. The adoption of and adherence to the G-BASE protocols of the British Geological Survey has facilitated the production of a dataset that complements and merges with existing geochemical datasets for England, Scotland and Wales. The comprehensive analysis of samples using a range of techniques and methods will enable detailed research to be conducted on sources of trace elements and their mobility in the surficial environment. Specific highlights of the geochemical programme include:

15.1 FIELD & LABORATORY PROCEDURES

Despite the completion of the drainage sampling programme over two discrete periods of time the application of systematic sampling techniques and analytical methodologies combined with the implementation of quality control procedures during both sampling phases has facilitated the merging of these two datasets.

15.2 NEW DATABASES & MAPS

The Tellus project has produced a baseline dataset for the environment of Northern Ireland. This dataset comprises trace element data for soils in both the rural and urban environments and stream waters and sediments for the rural environment. These analytes have been presented as maps suitable for use by professional geologists as well as the general public.

15.3 NATURAL VS. ANTHROPOGENIC ANOMALIES

The interpretation of geochemical anomalies and integration of Tellus geophysical data has enabled geochemical anomalies to be correlated to bedrock geology and structure as well as localities of known and potential mineralisation. Integration of the geochemical datasets with land-use and topographic data has revealed the presence of anthropogenic influences on the environment, e.g., Sn anomalies near urbanised areas. Despite the presence of mixed natural and anthropogenic signatures in some localities the multi-element nature of the dataset has enabled anthropogenic anomalies to be identified from the natural geochemical signature.

15.4 END-USERS

Products (datasets, maps, reports, interpretation) of the geochemistry programme will assist a range of public and private sector individuals and organisations to complete tasks relevant to the application and development of national and European Union legislation, the description and understanding of the bedrock and surficial environment, the discovery of new sites of mineralisation and the impact of human activities on the environment.

Appendix 1

URBAN ORGANIC SAMPLING PROCEDURES DEVISED BY DR. RORY DOHERTY, QUEEN'S UNIVERSITY, BELFAST

Anti-contamination

Samplers will make every effort to reduce the possibility of contamination of the sample or cross-contamination between samples.

Samplers will wear two pairs of sterile gloves. The upper pair will be discarded after each site and replaced with a new pair before commencing the next.

All tools for collecting and handling the organic sample (auger, stainless steel trowel) will be cleaned after each site, using a brush, pressure-sprayer (hand-pumped), and paper towels. The sample should be handled as little as possible and touched only with these tools. Prior to sampling at each site, 'an initial auger sample shall be collected and discarded to 'clean' the auger flight' (G-BASE Manual, Johnson 2005).

The organic sample at each site will be a composite sample mixed from five sub-samples extracted from the five holes into a disposable tub, mixed with the trowel and then transferred to the receptacle with the trowel. The mixing tub will be discarded after each site.

Sampling location and pattern

Samples locations will be recorded and numbered as per the G-BASE Manual.

The sampling pattern at each site will be the normal G-BASE pattern of five holes at the centre and corners of a 20 m square.

Organic samples will be collected from the same auger holes as the inorganic samples at the usual depth of the inorganic A sample (20 cm). Samplers will collect samples for the A samples at the usual five holes, taking approx 150 mL more sample than usual from each hole for the organic sample. The organic component will be temporarily collected at each site in a disposable tub. The inorganic A sample component will be bagged into the usual Kraft paper bags.

If the ground is stony, it may be necessary to sample from more than the usual five holes. Extra holes should be within 1m of the central hole.

To prevent contamination, a separate auger will be used to collect the inorganic S samples from the same holes. These will be collected and bagged in Kraft™ paper bags in the G-BASE way.

After collecting material from all five holes, the organic A sample will be mixed in the disposable tub with a stainless steel trowel. After mixing, the organic sample will be deposited into the glass receptacle provided by the contractor, using the s/s trowel, filling the receptacle to the top, and sealing it. Extraneous material (rubbish and stones) should be discarded. The sample will be numbered in a sequence to be agreed.

Duplicate samples will be taken on a similar pattern from a square adjacent to the original square, as prescribed in the G-BASE manual (Johnson, 2005).

Temporary storage

Immediately after sampling, the organic sample receptacles will be placed in cool boxes proved by the Contractor. The optimum temperature for storage and transit is 4ºC (according to BS 10175 and ISO10381-1) and samples should be kept in the dark. The Contractor may provide additional instructions. The samples should not be frozen.

Dispatch

The cool boxes of samples will be collected by the Contractor at the end of each day, Monday to Thursday inclusive, for shipment to the laboratory. Samples will not be collected on Fridays or Saturdays as there would be a possibility of the samples not remaining cooled until Monday. On Fridays and Saturdays, therefore, the sampling teams will store the samples until Monday in the Carrickfergus core-store refrigerator.

The team leader will provide lists of samples with the containers and will obtain a timed receipt from the courier for each batch.

Appendix 2

FORMATIONS/ LITHOLOGIES SAMPLED FOR THE LITHOGEOCHEMICAL PROGRAM

Igneous lithologies

The following formations/ lithologies were sampled;

Tyrone Plutonic Group

Tyrone Volcanic Group- Rhyolite

Tyrone Volcanic Group- Lava & Extrusive Rock

Tyrone Volcanic Group- Copney Pillow Lava

Tyrone Volcanic Group- Tonalite

Newry Granodiorite, Mourne Granite

Lower Basalt Formation

Upper Basalt Formation

Sedimentary lithologies

The following formations/ lithologies were sampled;

Gilnahirk Group

Gala Group

Hawick Group

Shanmullagh Sandstone Formation

Ballyshannon Limestone Formation

Bundoran Shale Formation

Mullaghmore Sandstone Formation

Sherwood Sandstone Group

Mercia Mudstone Group

Waterloo Mudstone Formation

Ulster White Limestone Formation

Metamorphic lithologies

The following formations/ lithologies were sampled;

Claudy Formation

Dart Formation

Glenelly Formation

Mullaghcarn Formation

Appendix 3

SOIL RANDOM NUMBER LIST 1

Random Number List 1 (Soil)

Atlas Name	**Area Code**	**Sample Number Range**
Northern Ireland	**55**	**to**

NOT COLLECTED IN THE FIELD: SAMPLES 10, 11, 22, 30, 68, 75, 78, 86

SAMPLE NUMBERS 10, 11 AND 75 ARE BLANK FOR XRF

	A	S					A	S					A	S					A	S			
1						26						51						76			DUP A		
2						27						52						77					
3						28						53						78	SUB-SAMP				
4						29						54						79					
5						30	Dermot S4					55						80					
6						31						56						81			DUP B		
7						32						57						82					
8						33						58						83					
9						34						59						84					
10	TILL 1/ TDB-1					35						60						85					
11	CURR (SGS only)					36						61						86	SUB-SAMP				
12						37						62						87					
13						38						63						88					
14						39						64						89					
15						40						65						90					
16						41						66						91					
17						42						67						92					
18						43						68	STANDARD					93					
19						44						69						94					
20						45						70						95					
21						46						71						96					
22	STANDARD					47						72						97					
23						48						73						98					
24						49						74						99					
25						50						75	TILL 2 / WPR-1					100					

SAMPLE NUMBERS 10, 11 AND 75 ARE BLANK FOR XRF

Standard 22		To Carrickfergus	
Standard 68		To Keyworth	

Summary

Dup Sample	Sub-Sample		Standards		Unused Numbers
76	**86**		**68**	**22**	
81	**78**		Dermot's SRM **30**		For sample numbers 10 and 75, CRM **TILL1** and CRM **TILL 2** respectively are used for “**A**” sample aqua regia analysis (SGS), and for “**S**” sample “Near-total”, aqua regia and SO4 analysis (SGS). For #10 and #75 the CRM TDB-1 and WPR-1 respectively are used for the PGE lead fire assay. XRF ARE BLANK

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