Geochemistry: Methodology

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SAMPLE COLLECTION AND PREPARATION

Samples of soils and streams were collected over the whole of Northern Ireland in two campaigns. Stream sediment and water samples from western Northern Ireland were collected by British Geological Survey (BGS) between 1994 and 1996. Stream sampling over eastern counties was undertaken by the GSNI and the BGS under the Tellus survey in 2005 and 2006. Soil sampling of all of Northern Ireland was completed under the Tellus survey between 2004 and 2006.

The methods used for sample collection followed the protocols set out by the Geochemical Baselines Survey of the Environment (G-BASE), a long running programme of the British Geological Survey (Johnson, 2005). The methods 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) 259 for the preparation of internationally compatible regional geochemical maps. The methods for collecting stream sediment samples were originally recommended by Plant (1971) and Plant and Moore (1979), who also described the procedures on which the organisation of the sampling programme and sample preparation were based.

Stream sediments

2908 stream sediment samples were collected during the summers of 1994 to 1996 by the BGS and a further 2966 in 2005/6 by the Tellus survey (see supplementary map - drainage locations). Where possible, sites were situated on first or second-order streams. The combined surveys produced an average sampling density of one site per 2.4 km^2.

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. Samples were collected by pairs of samplers, usually university students. The sampling and data recording procedures were standardised before the main survey. Sampling teams were changed daily to reduce the possibility of sampling bias.

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 the fraction of sediment finer than 150 µm. 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 sieve and panning 2–3 kg of this sieved material using the method described by Leake and Aucott (1973).

In the 1994/6 survey, stream sediment samples were freeze-dried and then ground to <50 µm at a field laboratory. During the Tellus field campaign, 2005/6, samples were air-dried prior to dispatch in batches of 100 to an interim storage facility. Further air-drying was completed at the store to a level that would allow samples to be packaged for onward transport to the BGS analytical laboratory. On arrival at the laboratory 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. 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. Transposition of sample numbers and cross contamination of samples were prevented by preparing each sample individually.

Stream waters

Water samples were collected slightly upstream of the stream sediment site to avoid contamination by disturbed sediment or pore water, and great care was taken during the sampling procedure to avoid any other contamination. The methods used for collecting the samples were tested 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) 259 and 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).

Stream-water samples were collected from 2,846 sites during the 1994/6 survey and a further 3,063 sites by the Tellus survey in 2005/6 (see supplementary map - drainage locations). The combined surveys 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 but analytical methods differed. For the 1994/6 survey, two samples were collected in new 30 ml polystyrene bottles, one for multi-element analysis by ICP-AES and ICP-MS, and the other for determination of chloride and nitrate by Ion Chromatography. A third sample was taken in a polyethylene bottle for Total Organic Carbon (TOC). These samples were filtered through 0.45 µm cellulose filters; the containers were rinsed with filtered water from the site before collection of the actual sample. A fourth, unfiltered sample was collected in polythene bottles for the determination of pH and conductivity (30 ml), fluoride (30 ml), uranium (30 ml) and alkalinity (250 ml). All containers were rinsed with stream water prior to sample collection and particular care was taken with the pH and alkalinity samples to eliminate air bubbles and hence minimise degassing. For the later Tellus sampling, Nalgene™ bottles were preferred, but the procedures were similar.

On return to the field base each evening, pH was determined 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. Samples for ICP-AES and ICP-MS determination were acidified to 1 % v/v using ultrapure Aristar™-grade concentrated nitric acid.

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. All other samples were stored in cool, dark locations until dispatched to the laboratory, where they were stored at 4°C.

Soils

Soil samples were collected on a systematic basis from rural areas in most of the region, excluding only the major urban centres of Belfast and Bangor. Soils were also collected at a higher sampling density from the urban areas of Belfast, Bangor, Carrickfergus, Carryduff, Castlereagh, Greenisland, Holywood, Lisburn, Newtownabbey and Londonderry, although these urban results are not reported here.

In rural areas, samples were collected from alternate 1 km Irish national-grid squares. Site selection within each square was random, subject to the avoidance wherever possible of roads, tracks, railways, human habitation and other disturbed ground. At each site two composite samples of five auger flights were collected, each composite sample comprising 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 (see supplementary map - soil locations) and analysed, resulting in an average regional sampling density of 1 site per 2 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).

Photograph 4.7
Sediment sampling

Photograph 4.8
Soil sampling

The methods used for urban soils were similar except that (1) the sample density was higher, at four sites per square kilometre; (2) the sample sites corresponded closely to a predefined grid and did not avoid areas of human influence. In addition, extra samples requiring special treatment were taken for the determination of selected organic constituents (Smyth, 2009: especially Appendix 1).

At each soil sample site, information on the location, site and catchment geology, contamination, land use, and other features required for data interpretation were entered onto field cards. The sample location was also plotted on a field copy of the 1:50 000 Ordnance Survey of Northern Ireland (OSNI) map.

Observations from field cards were entered into a digital Access2000™ database after undergoing a field quality control process (Lister *et al*, 2005). This 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. Thus both a traditional paper archive of observations was maintained as well as the construction of a computerised database.

Soils were initially air-dried at the field-base prior to transport to the sample store where they were dried in a temperature controlled oven at 30°C for 2–3 days. At the end of each field campaign samples were checked against field sheets prior to packing for transport to the BGS laboratory for sample preparation. On arrival at the laboratory 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. Replicate samples were prepared by riffle splitting each of the duplicate samples. 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 laboratory on surface soils only. Sub-samples of milled soil were weighed and placed into tamper-evident plastic sample tubes. 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.

Prior to analysis, concealed certified reference materials and secondary reference materials were inserted into the sample batches. XRF analysis of the A samples was undertaken at the BGS; ICP analysis of A and S samples at SGS Laboratories, Toronto; and fire-assay of S samples at SGS Laboratories, Toronto.

Rocks

During the Tellus survey, 114 samples of fresh unaltered rock (approximately 15 kg) were collected randomly from outcrops across Northern Ireland. Samples were prepared at the BGS laboratory. Preparation began with a thorough washing of the sample to remove any rock dust 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 BGS analytical laboratory.

CHEMICAL ANALYSIS

As the 1994/6 and Tellus surveys were separated by a decade and involved analysis for a wide range of elements in several different sample media, several analytical methods and different laboratories were used.

Surface soil/ A sample

Samples from the 5–20 cm depth were analysed as follows:

1. BGS laboratory:
   a. XRF analysis for major oxides and trace elements on pressed powder pellets.
   b. 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.
   c. Loss on ignition (LOI): 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. LOI was calculated using the weight loss between the sample heated at 450°C and dried at 105°C.
2. SGS Laboratories (Toronto): *aqua regia* digestion of a 1 g sub-sample, followed by trace element analysis by ICP-OES and ICP-MS.

Deep soil/ S sample

Samples from the 35–50 cm depth were analysed as follows at SGS Laboratories:

1. *Aqua regia* digestion of a 1 g sub-sample, followed by trace element analysis by ICP-OES and ICP-MS.
2. Multi acid (HF-$HClO_4$-HCl-HNO_3) 'Near-total' digestion, followed by trace element analysis by ICP-OES and ICP-MS.
3. Lead fire assay of a 10 g sub-sample of milled material followed by Au, Pd and Pt analysis by ICP-MS.
4. Dilute hydrochloric acid digestion of a 1 g sub-sample followed by sulphate analysis by ICP-OES.

Stream sediments

1. BGS laboratory: XRF analysis for major oxides and trace elements on pressed powder pellets.
2. Acme Analytical Laboratories Ltd. (Vancouver): lead fire assay of a 10 g sub-sample of milled material followed by Au, Pd and Pt analysis by ICP-MS; boron analysis by ICP-MS.

Waters

1. ALcontrol Laboratories, Hoogvliet,Netherlands: anion and NPOC by Ion Chromatography.
2. GTK, Espoo, Finland: trace element analysis by ICP-AES and ICP-MS.

Photograph 4.9
Water sampling

Photograph 4.10
Rock sampling

Soils and stream sediments: trace element analysis by x-ray fluorescence spectrometry

Major and trace element determinations for stream sediment and soil samples were carried out by wavelength-dispersive X-ray fluorescence (XRF) spectrometry (Ingham and Vrebos, 1994) for both the 1994/6 and 2005/6 samples. The procedures were identical for both sample sets. Sample preparation and XRF analysis were completed at the BGS laboratory; advances in XRF analysis over the period between the two surveys facilitated a greater range of determinands and lower detection limits for the more recent Tellus samples.

1994/6 samples

The 1994/6 sediment samples were analysed by wavelength-dispersive X-ray Fluorescence (WD-XRF) using three different machines. A Philips PW1480 sequential spectrometer fitted with a tungsten-anode X-ray tube (3 kW 100 kV) was used for Ag, Cd, Sn, Sb, Cs, La and Ce. Two Philips PW2400 sequential spectrometers fitted with rhodium-anode X-ray tubes (3 kW 60 kV) were used for MgO, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3, V, Cr, Co and Ba as one suite and Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Pb, Bi, Th and U as another. The spectrometers were controlled using Philips X40 application software package, version 3.2 and 4.01 (PW1480) and version 3.9F and 4.02 (PW2400) running under DEC VMS operating system on a VAX4000 computer. For the later Tellus samples of 2005/6 the spectrometers used were a PANalytical Axios Advanced with 4 kW Rh tube and a Philips MagiX-PRO with 4 kW Rh tube.

Samples were prepared for analysis by grinding 12 g of sample and 3 g of Elvacite 2013 (n-butyl methacrylate copolymer, Dupont & Co) in an agate planetary ball mill (Fritsch P5) for 30 minutes. The mixture was then pressed at 25 t load into 40 mm diameter pellets using a Herzog (HTP-40) semi-automatic press.

The pellet was irradiated by X-rays, which induce 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). Calibrations were performed using the manufacturer's calibration algorithms and making corrections for matrix effects and spectral line overlap interferences. Up to two line-overlap interferences could be corrected for, using the X40 software.

Trace elements whose characteristic X-ray lines lie on the long-wavelength side of the Fe absorption edge (V, Cr, Co, Cs, Ba, La and Ce) are affected by absorption from major elements (Fe, Mn and Ti), and this absorption is not corrected for by this calibration method. Therefore, the results for these trace elements are not as accurate as those for other elements.

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 about 0.5 %, leading to uncorrected errors in most analytes.

For major element analysis, several RMs (e.g., GSD-7, GSS-1, LKSD-1, LKSD-4) were used for calibration 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 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 RMs.

2005/6 samples

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 (Tables 1, 2). Certified Reference Material (CRM) 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 RMs. 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).

The analytes determined and lower limits of detection (LLD) for both the 1994/6 and Tellus stream sediment samples are listed in Table 1 and Table 2. 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. LLDs were calculated from a matrix blank and the 'synthetic' Pro-Trace standards using Equation 1.

$$LLD=\frac{3}{m}\sqrt{\frac{Rb}{Tb}}$$

Where:

m = thousands of counts per second (kcps) per % of analyte

Rb = background count rate (kcps)

Tb = time on background (s)

Equation 1

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.

Tellus Data 2005/6			1994/6		
Analyte	LLD (%)	Method	Analyte	LLD (%)	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

Table 1

XRF analyses - majors.

Tellus Data 2005/6			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

Table 2

XRF analyses - trace elements.

Soils and stream sediments: gold and PGE by fire assay/ ICP-MS

Stream sediment and S soils were analysed by fire assay for gold, palladium and platinum. The 1994/6 stream sediment samples were analysed in early 2002 at Acme Analytical Laboratories Ltd. (Vancouver), who also analysed the Tellus stream sediments. SGS Laboratories analysed the Tellus S soils. For both sample types 10 g sub-samples of milled material were prepared and dispatched to the analytical contractors by the BGS laboratory. A standard lead fire assay process was completed on samples in both laboratories. Soil samples were fired for 60 minutes with a flux mixture containing lead oxide (litharge) in a gas furnace at 1050ºC ±100ºC. 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 Inductively Coupled Plasma-Mass Spectrometry (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 Perkin Elmer 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 3. 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.

Element	Soil Quoted Detection Limit (*ug*/kg)[3]	Sediment Quoted Detection Limit (*ug*/kg)[4]
Au	1.0 (2.0)[5]	1.0
Pt	0.5 (1.2)[5]	0.1
Pd	1.0 (1.1)[5]	0.5
[1]Rh	[2]na	0.05

1. semi-quantitative analysis.
2. not analysed
3. SGS Laboratories (Toronto).
4. Acme Laboratories (Vancouver).
5. Revised detection limit in brackets.

Table 3

Quoted and revised detection limits for Au, Pt, Pd (and Rh) by Fire Assay Analysis in soil and stream sediments.

Stream sediments: boron analysis by ICP-MS

Boron analyses of stream sediments, contemporaneous with the fire assay, were performed at Acme Analytical Laboratories Ltd. (Vancouver) as this element cannot be determined by XRF. 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 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 1994/6 samples was monitored using internal standard LIB-10. For Tellus samples quality control was monitored using internal standards C3, FA-100S and LIBF200.

Soils: aqua regia digest (HCl, HNO_3) and ICP-OES/ MS analysis

The *aqua regia* digest was performed on both the A, 'surface' and S 'deep' soil samples. The detection limits and analytical methodology is presented in Table 4. For each sample 1 ±0.005 g was weighed into a 50 mL centrifuge tube. 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.

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

Element	Detection limit (mg/kg)	Method	Element	Detection limit (mg/kg)	Method
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 4

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

Soils: near-total (HCl, HNO$_3$, HClO$_4$, HF) digest and ICP-OES/ MS analysis

The near-total digest (SGS method code ICM40B) was performed on the S soil samples only. Table 5 shows the detection limits and analytical methodology for the suite of elements.

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, with 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, and the dish 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.

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

Table 5

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

Soils: sulphate (SO$_4$) by hydrochloric acid (HCl) digest ICP-OES analysis

Sulphate analysis on a hydrochloric acid digest was performed on the S soil samples only (SGS method code CHAY50). The digest was:

1. 0.1 g of soil sample was weighed into a test tube.
2. 2 mL of distilled water was added.
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).

Stream waters

The stream water results from the 1994/6 and Tellus 2005/6 surveys, although produced more than a decade apart, integrate 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.

1994/6 water samples

Inductively coupled plasma atomic-emission spectrometry (ICP-AES)

ICP-AES was used to determine 14 elements in the 1994/6 samples. The instrument used was a Fisons Instruments ARL 3580, with mini torch. This size of torch uses less gas and power than a standard ICP torch but produces the same power density and comparable detection limits. The instrument incorporates two spectrometers, simultaneous and sequential, based on identical 1 m Paschen Runge concave grating systems. This study used the simultaneous spectrometer, which has 45 fixed channels. The light path from the torch to the spectrometers is partly enclosed in an argon-flushed tube to minimise the absorption of low-wavelength lines by the atmosphere. The image of the torch is positioned onto the photomultiplier tubes (PMTs) by moving the entrance slit to the spectrometer and determining the slit position which gives maximum peak intensity. In routine operation, samples were loaded in racks on an ARL Plasma Autosampler. The autosampler racks were constructed to hold the sample containers directly. Each rack holds up to 64 samples and the autosampler can hold up to three racks.

The elements determined, detection limits and units are listed in Table 6. The detection limits are based on five times the standard deviation of the blank and give a conservative value based on data merged from five years of operation. The ICP and autosampler are controlled using the manufacturer's PlasmaVision software, which incorporates 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), which allowed high-speed transmission of data for off-line data processing.

Element	Detection limit (µg/L)	Method	Element	Detection limit (µg/L)	Method
Al	14	ICP-AES	Mn	1	ICP-AES
B	11	ICP-AES	Na	12	ICP-AES
Ba	2	ICP-AES	P	61	ICP-AES
Ca	13	ICP-AES	Si	10	ICP-AES
Fe	4	ICP-AES	SO_4	64	ICP-AES
K	38	ICP-AES	Sr	1	ICP-AES
Mg	18	ICP-AES	Zn	7	ICP-AES

Table 6

ICP-AES: elements determined, detection limits and units for 1994/6 water analyses.

The spectrometer was calibrated by aspirating multi-element standard solutions and plotting emission intensity against concentration using the PlasmaVision software (Tait and Ault, 1992). They were prepared by serial dilution of stock standard solutions. The stock standard solutions for series B (trace elements) and D (Si) were prepared from single-element standard solutions, purchased from commercial suppliers. Series A (major elements) and C (anions) were prepared from the dissolution of pure solids, usually Specpure® metals and chemicals from Johnson Matthey Chemicals. Total sulphur is 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.

Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS was used to determine 23 trace elements in the 1994/6 water samples (Table 7). 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.

The ICP-MS instrument consists of an inductively coupled plasma, which provides a source of positively charged ions, and a quadrupole mass spectrometer, which detects these ions, linked by an interface. Liquid samples are pumped through a nebuliser, and the resulting sample aerosol and argon mixture passes 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 result in rapid desolvation, atomisation and ionisation of the sample aerosol.

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

Table 7

ICP-MS: elements determined, detection limits and units for 1994/6 water analyses.

The positively charged ions are extracted from the plasma into the vacuum system of the mass spectrometer. The ions pass through a sampling orifice of 1 mm diameter into a mechanically pumped vacuum system, where a supersonic jet forms. The central section of this jet is extracted through the skimmer orifice of 0.7 mm diameter and then focussed by a series of electrostatic ion lenses into the quadrupole mass analyser. DC and RF voltages are applied to opposite pairs of the four rods of the quadrupole. These voltages are varied such that only ions of a given mass:charge (m/z) ratio will have 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 has a relatively low resolving power (<400), it is sufficient to separate ion m/z from ion (m/z) +1 but not from a polyatomic ion with a very similar m/z.

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

Jarvis (1997) offers a simple description of the components of the instrumentation including the operational principles of quadrupole mass analyser. Montaser (1998) should be consulted for a comprehensive review of the technique and background theory. Detection limits (Table 8) were based on three standard deviations of a large number of 1 % nitric acid blanks inserted throughout all the analytical runs of 1994/6 waters. 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.

Element	Isotope	LOD based on blanks ug 1^{-1}
Li	7	0.2
Be	9	0.03
Al	27	2
V	51	0.2
Cr	52	0.4
Co	59	0.02
Ni	60	0.4
Cu	63	0.4
As	75	0.5
Rb	85	0.03
Y	89	0.01
Zr	90	0.02
Mo	98	0.03
Ag	109	0.1
Cd	114	0.01
Sn	120	0.04
Sb	121	0.05
Ba	137	0.1
La	139	0.01
Ce	140	0.01
Tl	205	0.01
Pb	208	0.04
Th	232	0.01
U	238	0.01

Table 8

Isotopes used and detection limits calculated from the blanks included with 1994/6 water samples.

Chloride and nitrate in 1994/6 waters by colorimetry

Chloride and nitrate (the latter as Total Oxidisable Nitrogen) were determined for each water sample using automated colorimetric techniques, a simple and reliable method requiring minimal sample preparation (filtration <0.45 µm). The system used was a Bran and Luebbe Analysing Technologies AutoAnalyser 3 continuous segmented flow system. The instrument was connected to a dedicated PC installed with AACE (AutoAnalyzer Control and Evaluation) software for interpretation and quantification of the results

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. 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.

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

Equation 2:

Chemical reaction for the quantification of chloride in stream water.

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 (NO2-) in the sample contributed to the final nitrate concentration, thus introducing a small positive bias to the 1994/6 nitrate measurements. The detection limits (Table 9) were 1.0 and 0.2 mg/L for Cl- and NO_3-, respectively.

Fluoride in 1994/6 waters 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 before measurement.

Non-purgeable organic carbon in stream waters (NPOC)

Analysis of non-purgeable organic carbon (NPOC) in a filtered water sample determines its dissolved organic carbon (DOC) content. The determination of NPOC was carried out 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, evolving carbon dioxide which 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 is accredited by UKAS.

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

Table 9

Anions and other parameters, detection limits for 1994/6 water samples.

2005/6 Tellus stream waters

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. Analysis for anions and NPOC was completed at ALcontrol Laboratories in Hoogvliet, The Netherlands. The ICP analysis was conducted at the laboratories of the Geological Survey of Finland (GTK) in Espoo.

Trace element analysis by ICP-AES

Analysis was undertaken on a Thermo Jarrel Ash IRIS Advantage AP-HR-DUO. The element suite, wavelengths and detection limits are shown in Table 10. 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.

Trace element analysis by ICP-MS

Analysis was undertaken on a PerkinElmer Sciex Elan 6000. The mass and detection limit for each element is shown in Table 11. For some elements (e.g., Cr) two masses were quantified in order to calculate known interferences and check for inter-element interferences.

Anion analysis

Anion analysis was conducted using a Metrohm 861 Compact Ion Chromatography System. Analytes and associated detection limits are shown in Table 12. Anions were analyzed in accordance with ISO 10304-1 (International Organization for Standardization, 1992).

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

Table 10

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

Element	Mass	Detection limit (ug/L)	Element	Mass	Detection limit (ug/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

Table 11

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

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.

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

Table 12

Anions and detection limits for Tellus water samples.

Analysis for non purgeable organic carbon (NPOC)

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.

QUALITY CONTROL

Similar sampling and analytical protocols were employed in the 1994/6 and Tellus surveys in order to minimise sampling and analytical errors and reduce the analytical uncertainty of the results. The methods of Plant *et al* (1975) were employed to monitor potential variance throughout the geochemical programme, 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.

Long-term analytical drift was monitored by analysing a series of standards representing the range of concentration for each element. The standards included several bulk stream sediment, stream water and soil samples collected over representative rock types in the area, termed Secondary Reference Materials (SRMs), in contrast to the accredited primary reference standards used for analytical calibration, or Certified Reference Materials (CRMs). For both 1994/6 and Tellus samples, two SRMs were analysed in every batch of 100 samples. Time-versus-concentration plots for each of these standard samples were used to identify shifts in the analytical data, and simple arithmetic factors were calculated to enable the data to be normalised for systematic drift. Details of the collection and use of the SRMs are given in Smyth (2009).

Although soil and stream sediment preparation and XRF analyses were undertaken at the BGS laboratory, separate facilities and staff 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* (2005).

Analysis of variance

Sampling and analytical precision were calculated using a procedure based on analysis of variance (ANOVA). At 180 sites, duplicate stream sediment samples were collected from sites a few metres away from the routine samples. The site numbers were chosen using random number tables. Each sample was dried and split into two portions, producing a total of four replicates from 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, to assess whether any sample pairs were consistently outlying. The pairs of samples were averaged, and routine and duplicate sample pairs were examined in a similar manner.

Plots of cumulative frequency versus concentration for each element were examined to assess the degree to which the distribution of the element conformed to the Gaussian distribution. ANOVA was not performed on those elements for which many values fell below or near the lower limit of detection (Ag, Bi, Cd, Sb).

A random nested model of ANOVA was selected because all the analyses were part of a single randomised data set (Snedecor and Cochran, 1989). The NESTED procedure from the SAS™ statistical software package was used to perform the ANOVA (SAS Institute Inc., 1989). Residual variance (representing *inter alia* inhomogeneities introduced in sample preparation and sub-sampling, and errors in chemical analysis), between-sample variance (representing within-site variability as well as any variability introduced by the process of sample collection) and between-site variance (representing the natural distribution of the elements in stream sediments) were calculated. Because the frequency distribution of most elements is multi-modal and none fit the Gaussian model perfectly, there is an unquantifiable overstatement of the between-site variance - a problem which is inherent in using ANOVA on geochemical data. The ANOVA results are given in Smyth (2009).

For stream waters, two sample numbers within every batch of 100 samples were reserved for the insertion of blank waters. These were made up from a stock supply of ultrapure de-ionised water and inserted in the field during sample collection. Blank waters were inserted into fluoride, chloride/nitrate and ICP-AES sample sets. Blank waters for ICP-AES and ICP-MS samples were acidified with 1 % v/v Aristar-grade concentrated nitric acid.

Following analysis of all suites of water samples, 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.

ICP-AES (1994/6 data)

Quality control in the ICP-AES analyses was maintained by means of drift-correction standards, in-house quality-control standards, and participation in the Aquacheck interlaboratory testing scheme. Drift-correction standards were measured before each sample run to validate the instrument calibration. The standards consisted of a blank and several multi-element solutions, covering all the elements determined. The software performs a two-point check on the calibration and alerts the user if the standard intensities are out of tolerance (typically ±20 %). The drift-correction standards were also measured throughout the run, typically after every 15 samples, to monitor instrument performance. 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 Quality-Control (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 determinant. When QC data were consistently outside these limits, data for the corresponding samples were rejected and the samples reanalysed.

ICP-MS (1994/6 data)

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, the samples were analysed neat, without any dilution or addition of internal standard, for stream waters with conductivities less than 2000 µS; this was applicable to most of the samples. Any samples with conductivities greater than 2000 µS were diluted with 1 % high purity nitric acid to reduce its conductivity to below this value.

A 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 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 and any anomalous results. As with the ICP-OES method, accuracy was monitored by regular participation in the Aquacheck inter-laboratory proficiency testing scheme for waters.

Colorimetry (1994/6 data)

Standards were run at the beginning of each analytical run. Each run contained 32 to 35 samples, depending on the determinant to be analysed. A quality-control check sample (independently analysed by ion chromatography) was included in each run.

Each run was examined to check that the drift between standards over the run and the difference between the QC check standard and its nominal value were less than 10 %. For nitrate determination, an additional check on the efficiency of the reduction column was carried out: if this was less than 90 %, the column was replaced and the samples re-analysed. Each analytical run was independently validated by a different analyst, using random checks on peak-height measurement, data transcription and sample dilutions.

Ionic balance

Ionic balances were calculated according to procedures described in Hem (1985), as a further test of the accuracy of the analytical determinations and to identify gross errors such as the accidental acidification of samples for anion analysis (e.g. excess nitrate). The charge balance was calculated as shown in Equation 3.

$$\text{Charge balance (\%)} = \frac{\text{(sum of cations - sum of anions)}}{\text{(sum of anions + sum of cations)}} \text{X100}$$

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

Equation 3
Charge balance calculation.

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). A plot of total dissolved solids against ionic balance shows the charge-balance error as a function of ionic strength and shows that the charge-balance error is higher at low ionic strengths, which is due mainly to the lower level of accuracy close to detection limit for anionic determinants. The application of modern analytical equipment and attainment of low detection limits for analyses dictates that the charge balance

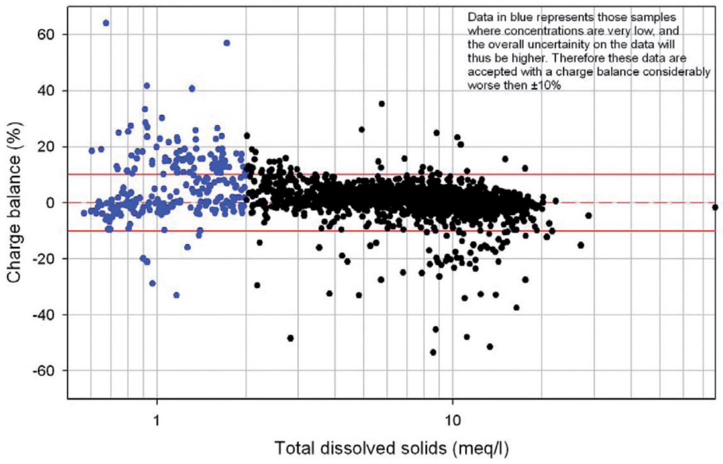

Figure 2
Total dissolved solids (meq/L) versus charge balance (%) for Tellus stream waters.

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 2). 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. Samples with a charge-balance error of greater than ±25 % were removed from the dataset used for the thematic studies.

INTEGRATION OF 1994/6 AND TELLUS SOIL, STREAM SEDIMENT AND WATER DATASETS

Soils

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). For the sediment and water data, changes in the range of analytes and improvements in detection limits were more problematical.

Stream sediments

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 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 1994/6 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.

Stream waters

The levelling of the 1994/6 and Tellus water datasets (Ander, 2009) 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 1994/6 and Tellus surveys. Changes and developments in analytical instrumentation were a major factor between the 1994/6 and Tellus sampling phases. The difference was most notable in the anions analysis (Table 13), with significant differences between the two surveys.

Analyte	1994/6 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

Table 13
ICP-AES: element suite, emission wavelengths and detection limits for Tellus water samples.

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 1994/6 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 1994/6 and Tellus quality controlled datasets were gridded as single merged datasets, resulting in a grid file dataset of combined 1994/6 and Tellus data. As, Cr and NO_3 could not be levelled across the temporal divide so separate grid files were produced for the 1994/6 and Tellus datasets of these analytes.

DATA AND IMAGE PROCESSING

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

Single-component images

The principal software for map production was ArcGIS™ v.9.2. A map template was designed which referenced a range of relevant vector and raster datasets. The design of the map template was based on the methods of the G-BASE program and 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 programme. 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 percentile classification scheme based on the G-BASE scheme was used (Figure 3). The GBASE 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 3). 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 the more detailed percentile classification suite was validated by the high correlation of anomalies to mapped bedrock and geological structure.

Statistics

A statistical summary for each determinand in the different sample media was produced. Statistics for the number of samples, minimum, maximum, range, arithmetic mean, median, and standard deviation are presented. Noninterpolated

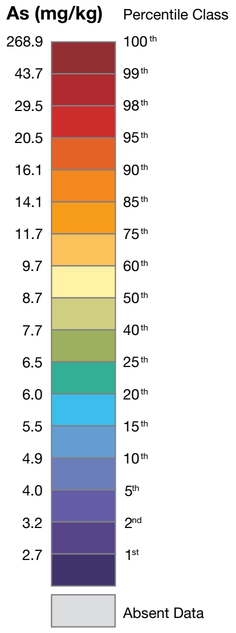

Figure 3
The Tellus percentile classification scheme.

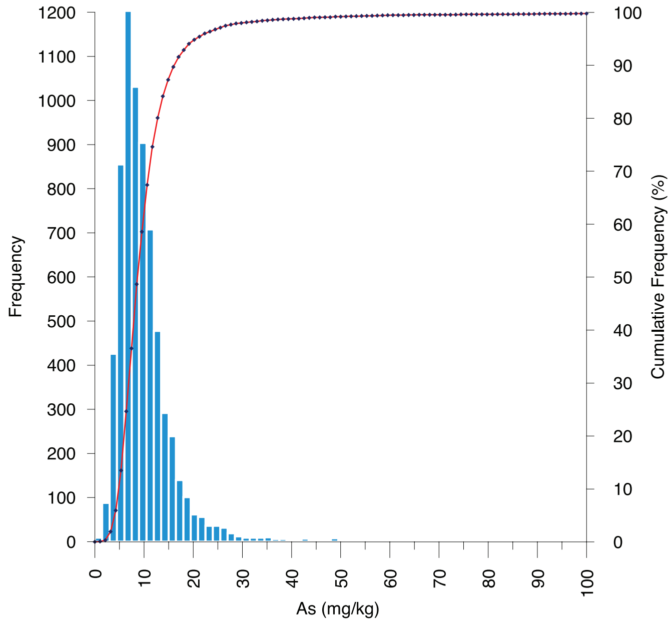

Figure 4
Histogram.

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.

Histogram

Histograms were plotted (Grapher™ v.6) for all quality controlled datasets. The class interval (Figure 4) 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.

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 bedrock geology polygon dataset. Due to the variety (>50) of different lithologies in Northern Ireland a simplified lithological classification scheme was developed which reduced the number of classes to eleven (Figure 5).

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 5).

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 a red-green-blue (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 14) is used to discriminate where elements are elevated in a particular area.

For example, where: Arsenic = Red, Copper = Green, Nickel = Blue

Red	Green	Blue	Colour	Interpretation
X			Red	Elevated As only
	X		Green	Elevated Cu only
		X	Blue	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

Table 14
Colour scheme for ternary images.
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.

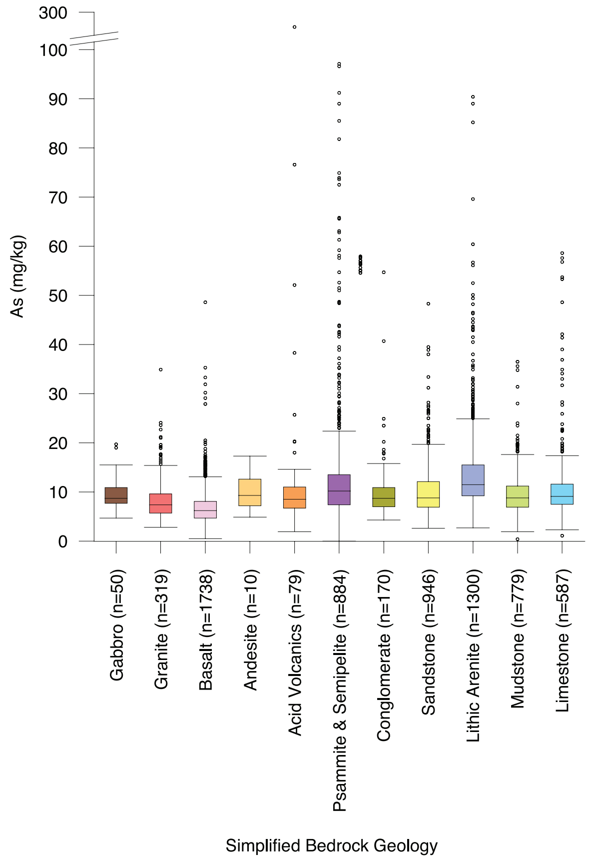

Figure 5
Box and whisker plot.

INTERPRETATION OF GEOCHEMICAL RESULTS

The aim of the G-BASE approach is to provide environmental baseline data on the surface environment. The distribution of each element is therefore described in relation to the major lithological, stratigraphical and structural subdivisions of the region, and the effects of metalliferous mineralisation and Quaternary processes are also discussed. This provides the background against which the influence of human activity can be assessed, and there are numerous examples in Northern Ireland of the local influence of industrial and other contaminative processes.

Stream sediments

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 that fewer samples are needed to represent a given area.

The interpretation of the results needs to 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 and particularly consider the following:

- 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 is the basis of the use of stream sediment sampling for mineral exploration, and similar observations may point to the existence of, for example, a small, hitherto unknown basic intrusion.
- In areas where bedrock is overlain by Quaternary deposits, this cover may have an influence on stream sediment geochemistry. In many parts of Britain, particularly in upland terrain, till may have little impact, probably because much of the finer material is locally derived. 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, giving high levels of a range of elements if clay minerals predominate in the fine fraction and low values of most elements if quartz is dominant and, in some circumstances, imposing the geochemical signature of source rocks which may differ from underlying bedrock.
- The processes by which stream sediment is derived from its parent rocks include chemical and physical weathering. 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 Mg, Ca, Mn, Fe and Sr are readily mobilised in surface and groundwaters. This leads to the concentration of minerals such as Fe-Ti oxides and zircon which are resistant to chemical weathering, and is reflected in high values of elements such as Ti and Zr. 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.

- 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: maximum concentrations of Fe_2O_3 and MnO in stream sediment samples from the present study are 57 % and 30 % 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.
- 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.

Soils

The geochemistry of soils is related to factors such as bedrock geology, superficial deposits, land use, climate and topography. The relative importance of each of these factors varies, both spatially and temporally. Material classified as 'soil' usually consists of variable proportions of: rock and mineral fragments in various states of weathering and alteration; clay minerals produced by the weathering process; other secondary minerals, notably the hydrous oxides of Fe, Mn and Al and some secondary carbonates; degraded organic matter ranging from plant debris to humins and including humic and fulvic acids; and living biota ranging in size from bacteria upwards. They also contain contaminants, from agriculture, mining, industry or other human activity.

Many soils are well stratified or vertically zoned in composition, as a result of leaching 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 and are transported downwards and redeposited by precipitation in the 'B' horizon (the process known as podzolisation). A full description of soil structure and composition may be found in texts such as FitzPatrick (1974), Hodgson (1976) and White (1979).

Thus 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 include: a lower rate of material transport, allowing more time for in-profile modification; a greater influence from site geology, as opposed to catchment geology; only partial water saturation (often with seasonal wetting and drying cycles), except for some bog soils; and often extensive anthropogenic modification in both agricultural and urban areas.

Because of the tendency of many trace elements, leached from the upper horizons, to concentrate in the Fe-oxide-rich 'B' horizon, this latter material is usually favoured for sampling as it therefore includes a natural pre-concentration stage. However, the sorption properties of the 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 gives rise to very localised high concentrations of these elements. In saturated peaty bog soils, acidic, anoxic reducing conditions prevail, and Fe, Al and even Si may be mobilised ('gleying'), transported and redeposited. Local chemical variations in such gleyed soils may be marked, with grey-green and yellow-red mottling evident.

In peaty soils, which form when conditions are such that 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 %) and 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 redeposited humic and Fe-oxide material, sometimes with an impermeable Fe oxide layer (iron pan). Such soils are common in upland Britain where rainfall is high and the bedrock quartzose and base-poor. On the steeper, more freely-drained slopes, the podzol profile is undeveloped, partly because of physical mixing by soil creep, and a 'brown earth' soil is produced. These soils tend to be coarser and more sandy than the peaty podzols, and consequently are relatively depleted in the clay-affinity elements such as Ga, and richer in such elements as Zr.

In contrast, soils developed over limestones tend to be very 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 humous 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, and the few surface streams present usually 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. In 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 common in urban areas and 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 higher horizons. Sampling a deeper horizon may avoid the effects of surface contamination, but not the 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.

Stream waters

There are several important controls on stream water geochemistry. The bedrock and superficial 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 superficial 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).

	Soils					Sediments					Waters	
	A-Shallow[2]		S-Deep			XRF		Fire Assay		ICP	ICP	
	XRF	ICP	Aqua	Near To.	Fire							
	2004/6					1994/6	2004/6	1994/6	2004/6		1994/6	2004/6
Ag	•	•	•	•		•	•				•	•
Al	•[1]	•[1]	•	•			•[1]				•	•
As	•	•	•	•		•	•					•
Au			•		•			•	•			•
B			•							•	•	•
Ba	•	•	•	•		•	•				•	•
Be			•	•								•
Bi	•	•	•	•		•	•					•
Br	•	•					•					•
Ca	•[1]	•[1]	•	•		•[1]	•[1]				•	•
Cd	•	•	•	•		•	•					•
Ce	•	•	•	•		•	•					
Cl	•	•					•					
Co	•	•	•	•		•	•					•
Cr	•	•	•	•		•	•					•
Cs	•	•	•	•		•	•					•
Cu	•	•	•	•		•	•					•
Fe	•[1]	•[1]	•	•		•[1]	•[1]				•	•
Ga	•	•	•	•		•	•					
Ge	•	•	•	•			•					
Hf	•	•	•	•			•					
I	•	•					•					
In	•	•	•	•			•					
K	•[1]	•[1]	•	•		•[1]	•[1]				•	•
La	•	•	•	•		•	•					•
Li				•								•
Lu				•								
Mg	•[1]	•[1]	•	•		•[1]	•[1]				•	•
Mn	•[1]	•[1]	•	•		•[1]	•[1]				•	•
Mo	•	•	•	•		•	•					•
Na	•[1]	•[1]	•				•[1]				•	•
Nb	•	•	•			•	•					
Nd	•	•					•					
Ni	•	•	•			•	•					•
P	•[1]	•[1]	•			•[1]	•[1]				•	•
Pb	•	•	•			•	•					•
Pd			•		•			•	•			•
Pt			•		•			•	•			•
Rb	•	•	•	•		•	•					•
Rh					•							•
S			•	•								•
Sb	•	•	•	•		•	•					•
Sc	•	•	•	•			•					
Se	•	•	•	•		•	•					•
Si	•[1]	•[1]									•	•
Sm	•	•					•					
Sn			•	•								•
SO$_3$	•	•					•					
SO$_4$											•	
Sn	•	•	•			•	•					
Sr	•	•	•	•		•	•				•	•
Tb				•								
Ta	•	•	•				•					
Te	•	•	•	•			•					
Th	•	•	•	•		•	•					•
Ti	•[1]	•[1]	•	•		•[1]	•[1]					•
Tl	•	•	•	•			•					•
U	•	•	•	•		•	•					•
V	•	•	•	•		•	•					•
W	•	•	•	•		•	•					•
Y	•	•	•	•		•	•					•
Yb	•	•	•	•			•					
Zn	•	•	•	•		•	•				•	•
Zr	•		•	•		•	•					•

[1] reported as wt % oxide

[2] A-Shallow soils analysed for pH and Loss on Ignition

Table 15
Tellus surveys, analytes and analytical methods.