

SAMPLE PREPARATION AND ANALYSIS

H. Sandström¹, S. Reeder², A. Bartha⁴, M. Birke³, F. Berge⁵, B. Davidsen⁵, A. Grimstvedt⁵, M-L. Hagel-Brunnström¹, W. Kantor³, E. Kallio¹, G. Klaver⁷, P. Lucivjansky⁶, D. Mackovych⁶, H. Mjartanova⁶, B. van Os⁷, P. Paslawski⁸, E. Popiolek⁸, U. Siewers³, Zs. Varga-Barna⁴, E. van Vilsteren⁷, and M. Ødegård⁵

¹Geological Survey of Finland, Espoo, Finland

²British Geological Survey, UK

³Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, Germany

⁴Geological Survey of Hungary, Budapest, Hungary

⁵Geological Survey of Norway, Trondheim, Norway

⁶Geological Survey of Slovak Republic, Slovak Republic

⁷Netherlands Institute of Applied Geosciences - National Geological Survey, Utrecht, The Netherlands

⁸Polish Geological Institute, Warszawa, Poland

⁹Service Géologique National, Orleans-Cedex, France

INTRODUCTION

Analytical Requirements

Regional, large-scale geochemical projects demand special requirements for chemical analysis:

- (i) the analytical methods used must be sufficiently sensitive to allow detection of a wide range of determinands in all of the sample media at background levels;
- (ii) the analytical precision must be good, preferably significantly better than natural geochemical variation;
- (iii) the analytical accuracy must also be good, preferably even better than that achieved in most national geochemical surveys; and
- (iv) all data and other records pertaining to the analysis and testing must be fully documented and traceable.

The reason for the last two points in particular is that the data are planned to be used extensively for environmental purposes, such as in the assessment of background concentrations of elements in different materials for setting up or updating national or European maximum contaminant levels (MCLs). The FOREGS geochemical project is also widely regarded as a pilot for the IUGS project 360 (Global Geochemical Baselines), the aims and methodological requirements of which are described by Plant *et al.* (1996). Accuracy of the European dataset is therefore essential since it may be used to 'normalise' other geochemical data at national and international scales worldwide. The methods used for this project are

also likely to become standard operating procedures (SOPs) for the global project, and hence should be reproducible in various laboratories throughout the world. Because of the stringent requirements regarding sensitivity and elemental coverage, the most sophisticated instrumental methods have to be utilised. This may restrict some skilled but poorly equipped laboratories from participating fully in the global project in the future.

Total element concentrations are most relevant for geochemical interpretation of data. For solid materials, this means that the silicate matrix either needs to be fully decomposed by mixed acid digestion before instrumental analysis, or a solid sampling technique such as X-ray fluorescence needs to be used. However, to address the needs of national and European level environmental authorities, information on leachable concentrations of the elements was also considered to be important. In environmental chemistry, a slightly unscientific and non-specific term, 'near total', is often used to describe the maximum concentration of an element that can be liberated from a material in its natural environment. An *aqua regia* leach or digestion is normally used for simulating this characteristic in the laboratory, although, unfortunately, almost every laboratory has its own standard operating procedure for carrying out *aqua regia* leaching. For this project, an *aqua regia* leach was adopted to determine the leachable concentrations of the elements in sediments and soils. Errors

introduced by a diversity of leaching procedures were avoided by having only one laboratory perform the extractions and analyses. The method used was validated against standard methods according to normal validation procedures in accredited laboratories.

Participating Laboratories and Analytical Techniques

Nine laboratories were involved in the project (Table 1). All solid samples collected by the 26 participating countries were shipped to the Geological Survey of the Slovak Republic (GSSR), which was in overall charge of sample preparation, sub-sampling, sample distribution to

the analytical laboratories and archiving of the excess sample material (see Section “Sample preparation”). In order to ensure data homogeneity and to avoid any bias between laboratories or analytical methods, each laboratory was nominated to take responsibility for carrying out analysis by a particular analytical technique or techniques on all samples of a certain type (Table 2). Some determinands were measured by more than one technique, e.g. a range of trace elements in soils and sediments were determined both by XRF and ICP-MS after mixed acid digestion. The actual data used were selected through careful consideration of a number of quality issues (see section “Analytical methods” for more details) and are listed in Table 2.

Table 1 Participating laboratories

Laboratory	Acronym
Bundesanstalt für Geowissenschaften und Rohstoffe, PF 510153, 30631 Hannover, Germany	BGR
British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK	BGS
Service Géologique National, BP 6009, 45060 Orleans-Cedex, France	BRGM
Geological Survey of Slovak Republic, Markušovská cesta 1, 05201 Spišská Nová Ves, Slovak Republic	GSSR
Geological Survey of Finland, Betonimiehenkuja 4, FIN-02150 Espoo, Finland	GTK
Geological Survey of Hungary, P.O.Box 106, H-1442 Budapest, Hungary	MAFI
Netherlands Institute of Applied Geoscience TNO-National Geological Survey, NITG, P.O.Box 80015, NL-3508 TA Utrecht, The Netherlands	NITG
Geological Survey of Norway, Leiv Eirikssons vei 39, N-7491 Trondheim, Norway	NGU
Polish Geological Institute, 4 Rakowiecka, 00-975, Warszawa, Poland	PGI

Table 2 Summary of analytical methods used for each sample media

Stream Waters		Humus	
Laboratory	Method	Laboratory	Method
BGR	ICP-QMS / ICP-AES	GSSR	Sample preparation
BGS	IC / DOC analyser	NITG	ICP-MS
BGS	DOC analyser	MAFI	Hg analyser
NGU	Hg analyser		
Top and Sub Soils		Stream and Floodplain Sediments	
Laboratory	Method	Laboratory	Method
GSSR	Sample Preparation	GSSR	Sample Preparation
NITG	Granulometry/TOC	GSSR	TOC
BGR	WD-XRF	BGS	XRF
GTK	ICP-MS	BRGM	ICP-MS
PGI	AR/ICP-AES	GTK/PGI	AR/ICP-AES
MAFI	Hg analyser	MAFI	Hg analyser

QUALITY ASSURANCE AND CONTROL

Sampling and sample preparation are the most critical processes contributing to the overall uncertainty budget. The methods and quality measures employed for sampling have been discussed earlier in this volume (see Chapter "Sampling"). The methods employed for sample preparation are described in section 3 of this chapter. A special homogeneity test protocol was established for the project to demonstrate the quality of the sample preparation. Approximately one percent of the prepared samples were split into four sub-samples, two pressed pellets prepared from each sub-sample, and each pellet analysed twice by XRF for ten major and minor elements in order to control the 'between-bottle' homogeneity and 'within-bottle' homogeneity.

Uncertainty in chemical analysis, although often significantly less than that associated with sampling and sample preparation, is nevertheless essential to understand and control. All of the participating laboratories listed in Table 1 were selected on the basis that they had established quality systems in place, they regularly participated in international proficiency testing schemes for the methods for which they were responsible, and their estimated analytical

uncertainty and sensitivity for all determinands was likely to be acceptable.

For the project, additional quality measures were used to provide extra assurance that the overall quality of data was to the high standards required. For all solid analyses, two reference materials (ISE 921 and ISE 982) were analysed at regular intervals (between 1 and 2%, depending on the method) to monitor long-term stability and to enable comparison of data from different methods and different laboratories. About 8% of the solid samples were also used for inter-laboratory comparison, *e.g.* about 50 soil samples were analysed by WD-XRF at BGS for comparison with the original BGR WD-XRF and GTK ICP-MS data.

In order to assess the precision of the chemical analysis relative to the variation due to sample preparation and sampling, duplicate samples and repeat measurements were taken. Approximately 5% of all sites were sampled in duplicate. The duplicate samples were prepared independently of each other and analysed randomly along with all other samples, with each duplicate sample also analysed in duplicate to allow estimation of sampling uncertainty by the ANOVA statistical interpretation method (Figure 1).

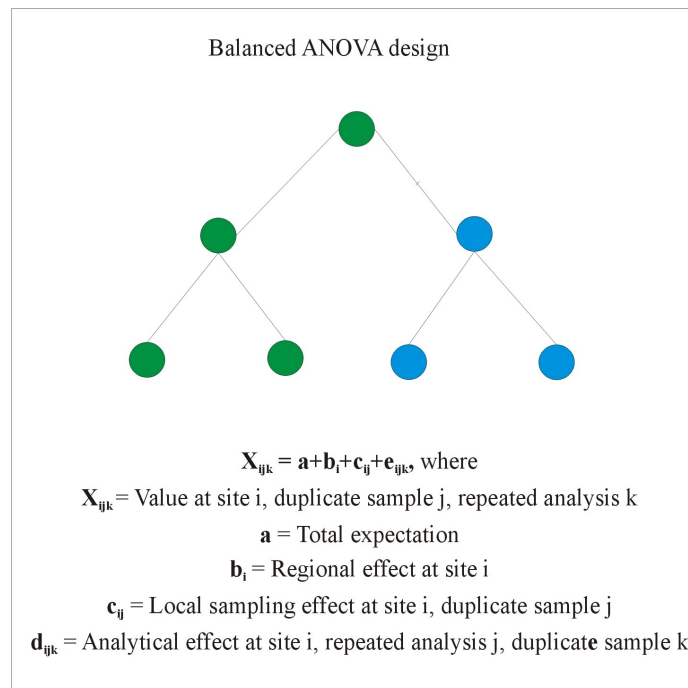


Figure 1. Quality control of sampling and analyses by replicates using ANOVA

SAMPLE PREPARATION

Stream Sediments

Stream sediment samples were wet sieved in the field. The <0.15 mm fraction was air dried and sent to the sample preparation laboratory at GSSR. In the laboratory, the samples were dried at 40°C , ground manually in a porcelain mortar and re-sieved to <0.15 mm.

The <0.15 mm fraction was split into two portions using a rotary divider and one of the portions was archived for further studies. The other portion was pulverized to a grain size <0.063 mm, homogenised and divided into bottles to be submitted to the analytical laboratories. The sample preparation procedure is illustrated in Figure 2.

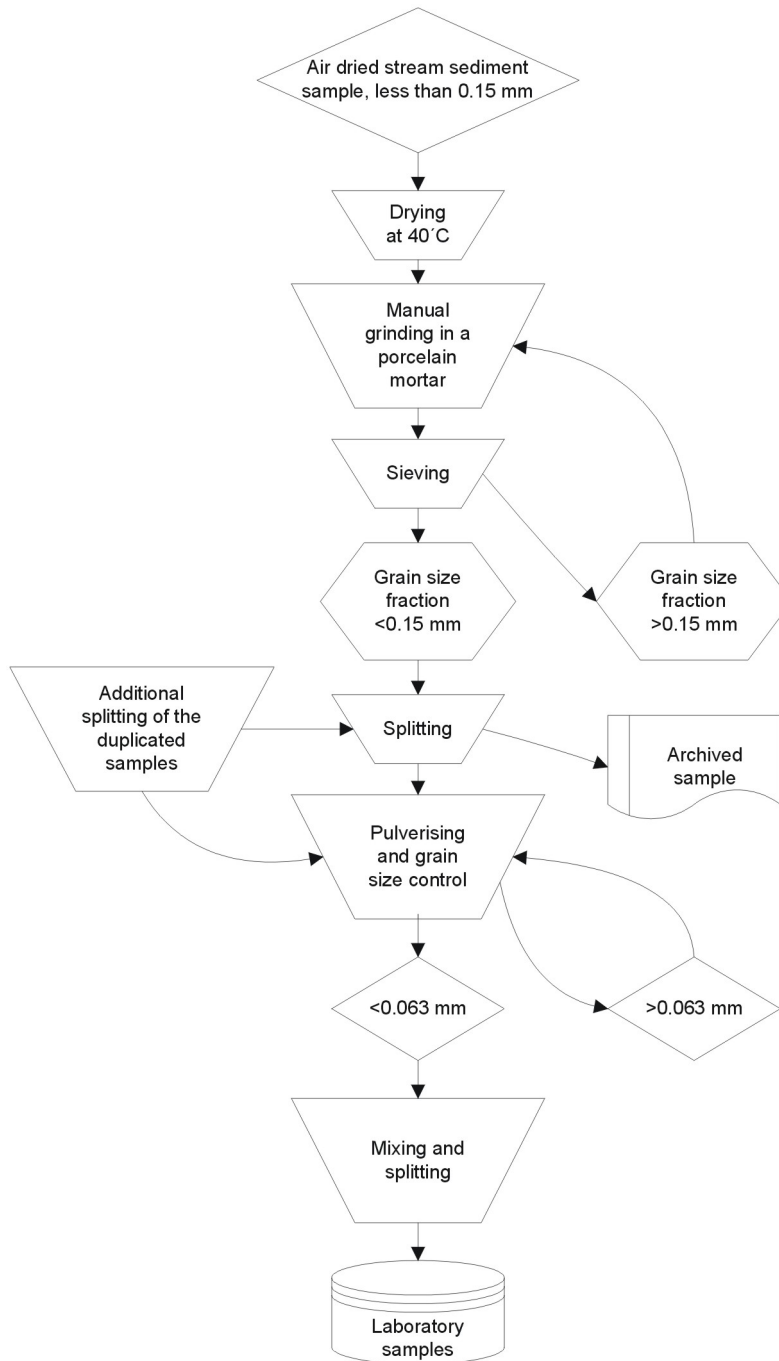


Figure 2 Sample pre-treatment procedure of stream sediment samples

Floodplain Sediments

Floodplain sediment samples were dried at 40°C, ground manually in a porcelain mortar, passed through a 2 mm sieve and split into two portions using a rotary divider, one of which was

archived for further studies. The other portion was pulverized in an agate planetary mill to a grain size <0.063 mm, homogenised and divided into bottles to be submitted to the analytical laboratories. The sample preparation procedure is illustrated in Figure 3.

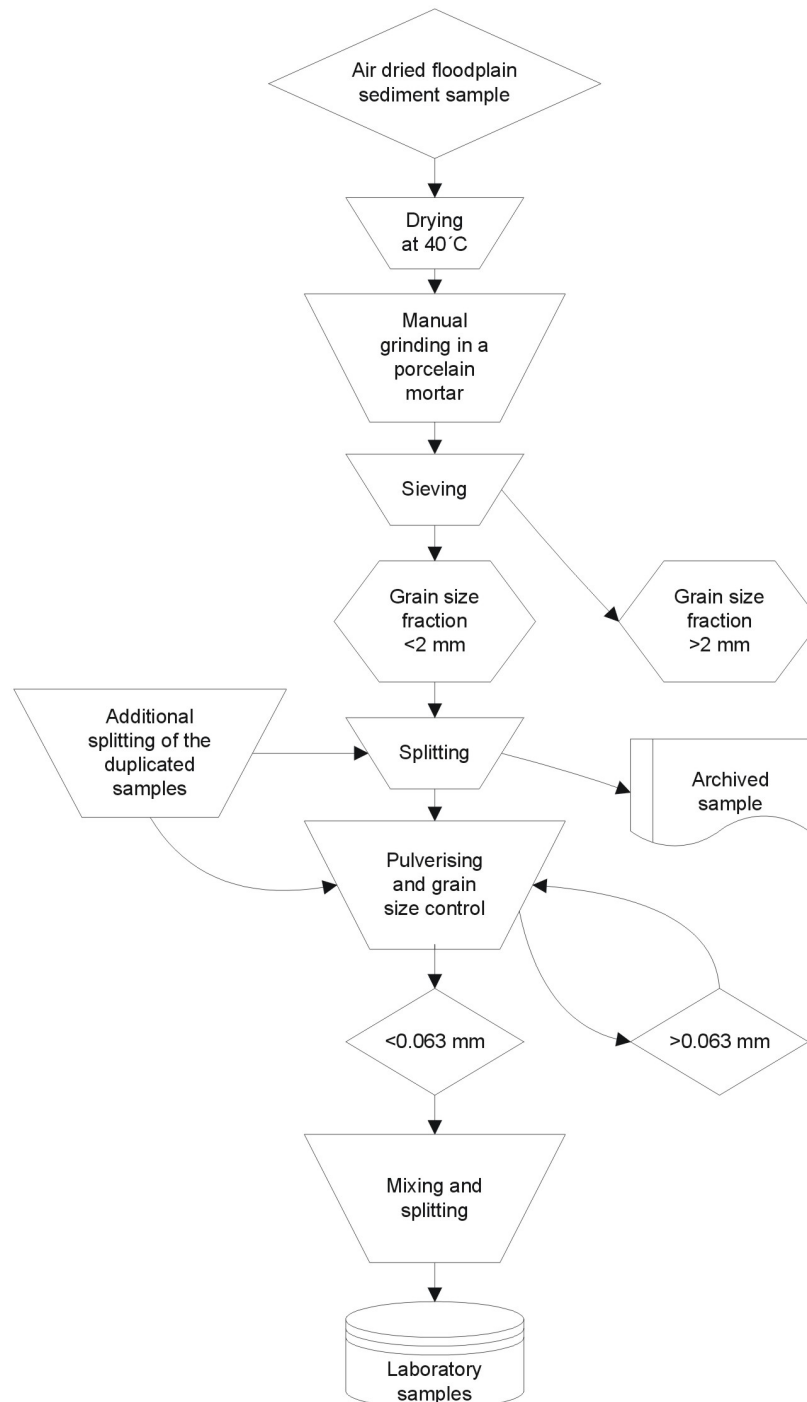


Figure 3. Sample pre-treatment procedure of flood plain sediments.

Soils

Soil samples were dried at 40°C, hammered to reduce agglomeration, disintegrated and homogenised in a porcelain mortar and passed through 2 mm sieve. Each sample was then split into three portions using a rotary divider, one of which was archived for further studies and the

second submitted for grain size analysis at NITG. The third portion was pulverized in a agate planetary mill to a grain size <0.063 mm, homogenised and divided into bottles to be submitted to the analytical laboratories. The sample preparation procedure is illustrated in Figure 4.

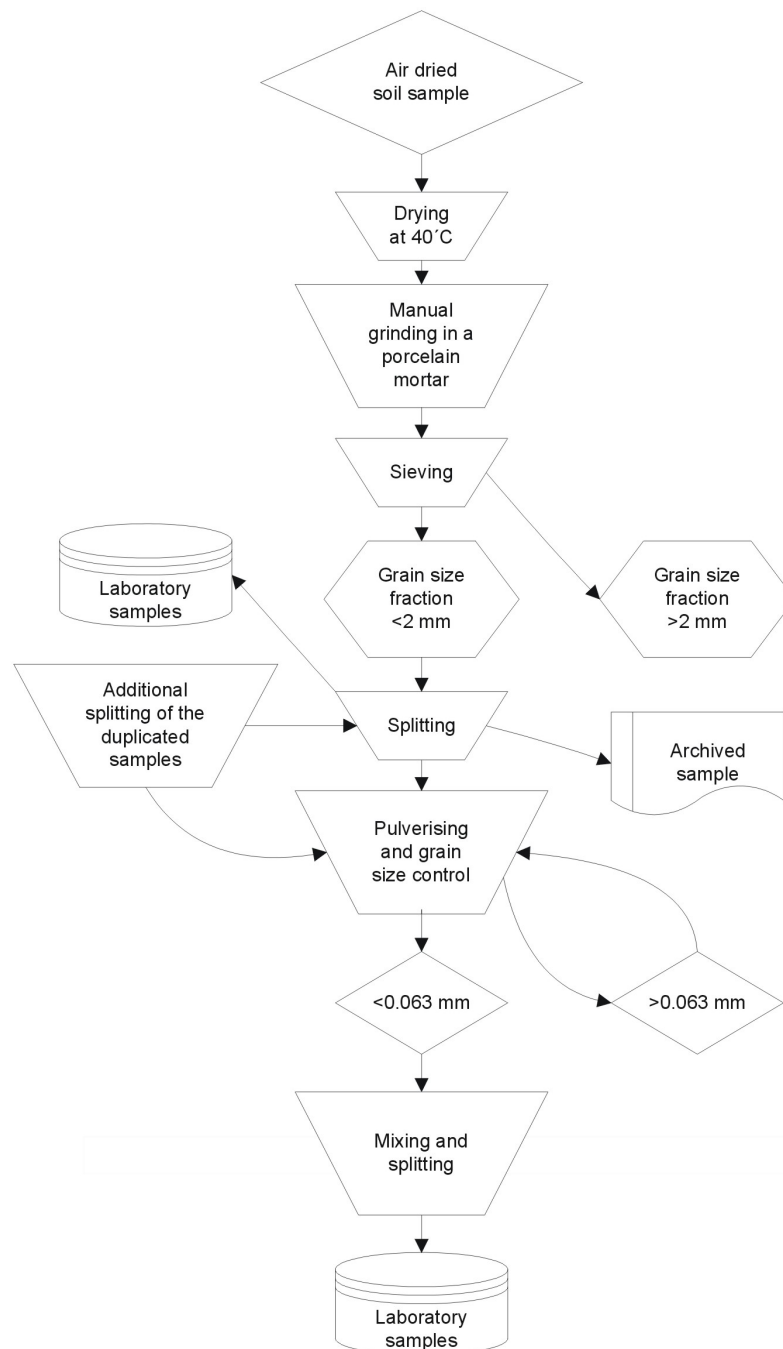


Figure 4. Pre-treatment procedure of soil samples.

Humus

The humus samples were initially air dried in the field and, once received by GSSR, were re-dried at ambient room temperature. After removing large roots and rock fragments, the samples were ground using an unglazed porcelain mortar and pestle and then sieved by hand through a 2 mm sieve. Each sample was then split into three

portions using a rotary divider, one of which was archived for further studies and the second submitted for ICP-MS analysis at NITG. The third portion was pulverized in an agate planetary mill to a grain size <0.063 mm, homogenised and submitted for mercury analysis at MAFI. The sample preparation procedure is illustrated in Figure 5.

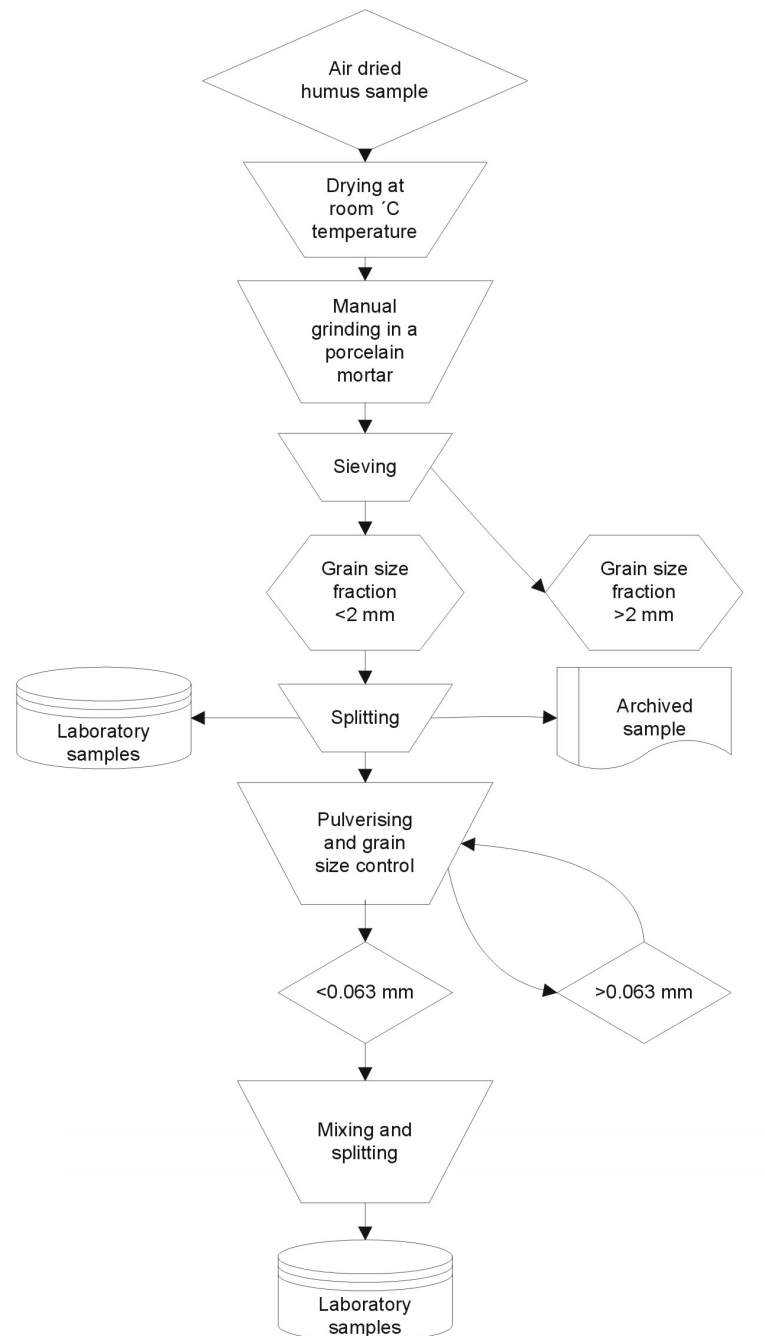


Figure 5. Pre-treatment procedure of humus samples.

ANALYTICAL METHODS

Stream Waters

Determination of anions

Anions were determined on stream water samples that were unfiltered and unpreserved but had been stored at between 1 and 8°C prior to analysis. The samples were analysed for major and trace anions, *i.e.* fluoride, chloride, nitrite, bromide, nitrate, orthophosphate and sulphate, by ion chromatography (IC). The determinations were made on a Dionex 4000i Ion Chromatograph using an AS14 analytical column with both conductivity and UV/visible absorbance detection. The method is accredited by the United Kingdom Accreditation Service (UKAS) according to the requirements of BS EN ISO 17025.

The samples were filtered to 0.45 µm before analysis. After chromatographic separation, all of the anions were measured using the conductivity detector. Nitrite, bromide and nitrate were also determined using the UV/visible absorption detector, and data for these anions were taken from this detector because of its better sensitivity.

For all anions, the accuracy of the method is better than ±10%, the bias is within ±3% and the precision at the 95% confidence interval is better than 5% at concentrations an order of magnitude above the limit of quantification. Limits of quantification (LoQ) for all anions are given in Table 3.

Determination of dissolved organic carbon

Dissolved organic carbon (DOC) was determined on stream water samples that were filtered to 0.45 µm on collection but were otherwise unpreserved. The samples were analysed using a Shimadzu TOC 5000 analyser with associated ASI 5000 auto-sampler. The method is accredited by the United Kingdom Accreditation Service according to the requirements of BS EN ISO 17025.

Samples were acidified and sparged prior to analysis to remove inorganic carbon. DOC was then determined by thermal combustion of the sample and the evolved CO₂ measured by non-dispersive infra-red (NDIR) detection.

The accuracy of the method is better than ±5%, the bias is within ±2%, and the precision at the 95% confidence interval is better than 6% at concentrations an order of magnitude above the limit of quantification, 0.5 mg l⁻¹.

Determination of major cations, metals and other inorganic elements

Stream water samples were filtered to less than 0.45 µm, acidified to 1% v/v with nitric acid and stored at less than 8°C. The samples were analysed by both inductively coupled plasma quadrupole mass spectrometry (ICP-QMS) and inductively coupled plasma atomic emission spectrometry (ICP-AES), using Perkin Elmer Sciex ELAN 5000A and Spectro Flame M instruments respectively, in accordance with the German norms DIN 38406-29 (ICP-MS) and DIN 38406-22 (ICP-AES).

The primary chemicals used to prepare the calibration and quality control standards and reagents were of analytical reagent grade. Multielement standard solutions for calibration were prepared from Claritas SPEX/Certiprep stock solutions. International certified reference materials (NIST 1640, NIST 1643d and SLSR-4) were included in every batch of 20 samples. Indium was used as an internal standard.

The accuracy of the methods for all determinands is better than ±10%, the bias is within ±3%, and the repeatability at the 95% confidence interval is better than 5% at concentrations an order of magnitude above the limit of quantification. Limits of quantification for all cations and trace metals are given in Table 3.

Determination of mercury

Stream water samples were filtered to less than 0.45 µm and preserved in the field using potassium dichromate dissolved in HNO₃. The samples were analysed for mercury by a cold vapour atomic absorption (CVAAS) technique using a CETAC M-6000A Hg Analyser. The method is accredited according to NS-EN ISO/IEC 17025.

The method is based on reduction of Hg ions in solution to atomic Hg vapour using stannous chloride (SnCl₂) as a reducing agent. The Hg/SnCl₂ emulsion is introduced into the top of a gas-liquid separator and is detected by CVAAS.

The accuracy of the method is estimated to be ±1-2%, without any systematic bias. Within batch precision at the 95% confidence interval is estimated to be about 1%, and long-term precision better than 8%. The limit of quantification is 0.01 µg l⁻¹.

Table 3. Summary of all elements and other determinands in the Atlas for each sample media, including the method and laboratory responsible for analysis and the limit of quantification.

Element	Soils		Sediments		Humus	Stream water	Element	Soils		Sediments		Humus	Stream water
	Total	<i>Aqua regia</i>	Total	<i>Aqua regia</i>				Total	<i>Aqua regia</i>				
Ag	0.01 ¹	-	-	-	-	0.002 ³	Sb	0.02 ¹	-	0.02 ¹	-	-	0.002 ³
Al / <i>Al</i> ₂ <i>O</i> ₃	0.05 ²	-	0.1 ²	-	-	0.1 ³	Sc	0.5 ¹	-	-	-	-	-
As	0.2 ¹	5 ¹	1 ¹	5 ¹	-	0.01 ³	Se	-	-	-	-	-	0.01
B	-	-	-	-	-	0.01 ³	<i>SiO</i> ₂	0.1 ²	-	0.1 ²	-	-	0.01 ⁴
Ba	5 ¹	1 ¹	3 ¹	1 ¹	1 ¹	0.005 ³	Sm	0.1 ¹	-	0.02 ¹	-	-	0.002 ³
Be	2 ¹	-	0.02 ¹	-	-	0.005 ³	Sn	2 ¹	-	1 ¹	-	-	-
Bi	0.5 ¹	-	-	-	-	0.002 ³	Sr	2 ¹	-	1 ¹	-	1 ¹	0.001 ⁴
Ca / <i>CaO</i>	0.01 ²	-	0.05 ²	-	-	0.001 ⁴	Ta	0.05 ¹	-	0.05 ¹	-	-	0.002 ³
Cd	0.01 ¹	-	0.02 ¹	-	0.1 ¹	0.002 ³	Tb	0.02 ¹	-	0.02 ¹	-	-	0.002 ³
Ce	0.15	-	0.02	-	-	0.002 ³	Te	0.02 ¹	-	-	-	-	0.005 ³
Co	3 ¹	1 ¹	2 ¹	1 ¹	0.1 ¹	0.005 ³	Th	0.1 ¹	-	1 ¹	-	-	0.002 ³
Cr	3 ¹	1 ¹	3 ¹	1 ¹	-	0.01 ³	Ti / <i>TiO</i> ₂	0.001 ²	-	0.005 ²	-	-	0.01 ³
Cs	0.5 ¹	-	4 ¹	-	-	0.002 ³	Tl	0.01 ¹	-	0.02 ¹	-	-	0.002 ³
Cu	0.01 ¹	1 ¹	1 ¹	1 ¹	0.3 ¹	0.005 ³	Tm	0.02 ¹	-	0.02 ¹	-	-	0.002 ³
Dy	0.1 ¹	-	0.02 ¹	-	-	0.002 ³	U	0.1 ¹	-	1 ¹	-	-	0.002 ³
Er	0.1 ¹	-	0.02 ¹	-	-	0.002 ³	V	0.5 ¹	1 ¹	2 ¹	1 ¹	-	0.05 ³
Eu	0.05 ¹	-	0.02 ¹	-	-	0.002	W	5 ¹	-	0.05 ¹	-	-	0.002 ³
Fe / <i>Fe</i> ₂ <i>O</i> ₃	0.01 ²	2 ¹	0.01 ²	2 ¹	-	1 ³	Y	3 ¹	-	0.02 ¹	-	-	0.002 ³
Ga	0.2 ¹	-	1 ¹	-	0.1 ¹	0.002 ³	Yb	0.05 ¹	-	0.02 ¹	-	-	0.002 ³
Gd	0.1 ¹	-	0.02 ¹	-	-	0.002 ³	Zn	3 ¹	1 ¹	1 ¹	1 ¹	1 ¹	0.01 ³
Ge	-	-	-	-	-	0.005 ³	Zr	3 ¹	-	1 ¹	-	-	0.002 ³
Hf	0.2 ¹	-	0.05 ¹	-	-	0.002 ³	EC	-	-	-	-	-	5
Hg	0.0001 ¹	-	0.0001 ¹	-	0.0001 ¹	-	HCO ₃ ⁻	-	-	-	-	-	-
Ho	0.02 ¹	-	0.02 ¹	-	-	0.002 ³	Br ⁻	-	-	-	-	-	0.01 ⁴
I	2 ¹	-	-	-	-	0.01 ³	Cl ⁻	-	-	-	-	-	0.1 ⁴
In	0.01 ¹	-	-	-	-	0.002 ³	F ⁻	-	-	-	-	-	0.05 ⁴
Li	-	-	0.05 ¹	-	-	0.005 ³	NO ₃ ⁻	-	-	-	-	-	0.04 ⁴
Lu	0.02 ¹	-	0.02 ¹	-	-	0.002 ³	SO ₄ ²⁻	-	-	-	-	-	0.3 ⁴
Mg / <i>MgO</i>	0.01 ²	-	0.1 ²	-	-	0.001 ⁴	DOC	-	-	-	-	-	3
Mn / <i>MnO</i>	0.001 ²	10 ¹	0.01 ²	10 ¹	-	0.05 ³	TOC	2	-	2	-	-	-
Mo	0.1 ¹	-	0.05 ¹	-	-	0.002 ³	Grainsize 0.002		-	-	-	Units: 1mg kg ⁻¹ , 2%, 3µg l ⁻¹ , 4mg l ⁻¹ , 5mS m ⁻¹	
Na / <i>Na</i> ₂ <i>O</i>	0.01 ²	-	0.2 ²	-	-	0.005 ⁴	Grainsize 0.06		-	-	-		
Nb	0.1 ¹	-	1 ¹	-	-	0.002 ³	Grainsize D50%		-	-	-		
Nd	0.15 ¹	-	0.02 ¹	-	-	0.005 ³	GrainsSortIndex		-	-	-		
Ni	2 ¹	2 ¹	1 ¹	2 ¹	0.3 ¹	0.005 ³							
<i>P</i> ₂ <i>O</i> ₅	0.001 ²	-	0.01 ²	-	-	-							
Pb	3 ¹	3 ¹	1 ¹	3 ¹	0.5 ¹	0.005 ³							
pH		-	-	-	-		ICP-MS	GSF	BGR	BRGM	NITG		
Pr	0.1 ¹	-	0.02 ¹	-	-	0.002 ³	ICP-AES	PIG	BGR				
Rb	2 ¹	-	1 ¹	-	0.2 ¹	0.002 ³	XRF	BGS	BGR				
S	-	50 ¹	-	50 ¹	-	-	IC	BGS			specific method		

Selection of stream water data

Data for the major cations (Ca, Mg, Na and K) and some of the more abundant trace metals (Sr, Mn and Al), as well as Si and total P, were taken from the ICP-AES dataset. All other trace metal data were obtained from the ICP-MS dataset. A range of trace metals were analysed by both ICP-AES and ICP-MS. The data were compared to ensure that there was good agreement between the two datasets, but the ICP-MS data were generally selected for publication because of the better sensitivity of this method. All cation and trace metal data determined by ICP techniques were considered to be of acceptable quality, with the exception of Ag. Contamination, probably arising from the poor quality of acid preservative used in some countries, was the likely cause of the poor quality Ag data.

Major anion data determined by IC, as well as the TOC data, were all considered to be of good quality. Because of the variable length of time between collection of samples and analysis in the laboratory, there is evidence that nitrite and phosphate, which are relatively unstable, may have been lost from solution. Data for nitrite and phosphate are therefore not considered to be acceptable for publication. The detection limits for bromide and phosphate were also not sufficiently sensitive for this study, and less than 10% of the samples contained concentrations of these anions above quantifiable levels.

Because of contamination caused by inappropriate sample bottles being used in some countries, the mercury data were, unfortunately, not accepted.

Data for major cations determined by ICP-AES and anions determined by IC were checked for accuracy by calculating an ionic charge balance and also by checking the ratio of conductivity to total dissolved solids (TDS). Unfortunately, the major anion in most waters was bicarbonate, which was determined by each country in the field. The quality of the bicarbonate data was highly variable, including errors in the analytical determination, errors in reporting units and some data were also not available. Nevertheless, a number of rules and additional checks were established and applied to the stream water dataset that enabled a thorough check on the overall quality of the analyses.

Further details of the full range of elements determined are given in Table 3.

Stream and Floodplain Sediments

Determination of TOC

Determination of the total carbon content of sediments was carried out by a pyrolysis technique with non-dispersive infrared detection using a Dohrmann-Rosemount DC-190 (USA) carbon analyser, with 183 boat sampling module and a Fuji model 3300 direct non-dispersive infrared gas detector. The method has been validated against EPA methods 415.1 and 9060, ISO 10694.

Well-mixed samples were treated with 50% HNO_3 and organic compounds were decomposed by pyrolysis in the presence of oxygen at a temperature of 800°C.

The uncertainty of the method is estimated to be $\pm 10\%$ and is mainly limited by sample heterogeneity.

Determination of mercury

Determination of total mercury was carried out using a cold vapour atomic absorption technique, involving preconcentration on a gold amalgam before detection with an Advanced Mercury Analyser (AMA-254, ALTEC) instrument.

The analysis was performed directly on solid samples without any sample preparation. Mercury is liberated from the sample during programmed temperature elevation to 850°C and amalgamated with gold to concentrate the determinand. Mercury vapour is then released from the amalgam by heating and detected using atomic absorption spectrometry.

The uncertainty of the analysis is typically better than $\pm 10\%$, or better than 5% in the case of higher concentrations. The limit of quantification of is $0.0001 \mu\text{g g}^{-1}$.

Total multielement determination by XRF

A range of elements were determined by wavelength dispersive x-ray fluorescence spectrometry (WD-XRFS) and energy dispersive polarised x-ray fluorescence spectrometry (ED(P)XRFS). The instruments used were Philips PW1480 and PW2400 WD-XRFs, with W and Rh anode x-ray tubes respectively, and a Spectro X-LAB 2000 ED-XRF with a Pd anode x-ray tube.

Samples were prepared by mixing with a binder then pressing into pressed powder pellets before analysis by both instrumental techniques. For the WD methods, secondary radiation is

collimated onto a diffraction crystal and its intensity at selected peak and background positions in the x-ray spectrum is measured using a detector mounted onto a goniometer. The net intensity, corrected for background, spectral interference and instrument drift, is calibrated against known synthetic standards and RMs. For the ED method, five different secondary/polarisation targets are used to give optimal coverage of 52 elements from Na to U; all elements are measured to improve the accuracy of the corrections on the analytes of interest. Rather than being diffracted, the whole of the emitted x-ray spectrum is detected simultaneously using a Si(Li) detector. The acquired spectrum is deconvoluted then evaluated using a calibration prepared by the instrument manufacturer. In general, data for lighter elements are taken from the WD instrument and data for the heavier elements from the ED instrument.

In practice, data for MgO, P₂O₅, K₂O, CaO, TiO₂, V, Cr, MnO, Cs, Ba, La and Ce were taken from the ED technique; data from the WD technique were used for all other elements. Further details of the full range of elements are given in Table 3.

The accuracy of the method for all determinands is better than $\pm 5\%$, and the repeatability at the 95% confidence interval is better than 5% at concentrations an order of magnitude above the limit of quantification. Limits of quantification for all determinands are given in Table 3.

Total multielement determination by ICP-MS

In addition to XRF analysis, a range of major and trace elements were also determined by quadrupole ICP-MS using a VG Elemental (UK) model PQ3 instrument equipped with a water cooled sample introduction system, a PlasmaScreen™ torch, a high efficiency interface device AutoRange Plus™, a simultaneous detector system and PlasmaLab ICP-MS Software Suite.

Prior to analysis, the sediment samples were decomposed by sintering with sodium peroxide (1 g sample and 3 g flux) at a temperature of 480°C. After cooling, the sinter was dissolved in 60 ml of deionised water and 20 ml of 50 % nitric acid. Rhodium was used as an internal standard.

At concentrations an order of magnitude above the limit of quantification, the uncertainty of the

method is between 5 and 10%, depending on the element. Limits of quantification are given in Table 3.

Acid leachable multielement determination by ICP-AES

In addition to the total concentrations of the elements, the acid leachable portion of selected elements were analysed after hot *aqua regia* leach by ICP-AES, using a J-Y 70 Plus Geoplasma ICP-AES instrument.

Samples were digested in *aqua regia* by weighing 1 g of sample in a polyethylene tube and adding 6 ml HCl and 2 ml HNO₃. The samples were left for 15 minutes at room temperature before heating in an aluminium block at 95°C for 60 minutes. After cooling, the samples were filtered and made up to 50 ml in a polyethylene flask.

Based on monitoring samples, the relative standard deviation of the measurements is typically between 3 and 7% for concentrations exceeding three times the limit of quantification of the particular element. Limits of quantification for all reported elements are given in Table 3.

Selection of stream and floodplain sediment data

A wide range of total multielement data determined by both ICP-MS and XRF methods were available. Data quality, including results of CRMs and ANOVA data for duplicate analyses, were assessed on an element-by-element basis. If only one of the two techniques was sufficiently sensitive to permit determination of a particular element at the background levels found in the samples, then this technique was automatically selected. If both techniques were sufficiently sensitive, the data from the technique with the best precision, based on the ANOVA duplicate analyses, were selected. The actual method used for each element is given in Table 3.

The quality of the ANOVA data for the ICP-AES analysis of the *aqua regia* solutions was also assessed. For a number of elements, the analytical variation exceeded that of the geochemical variation, and the data for these elements were not considered suitable for publication. Those elements with acceptable data quality are given in Table 3. *Aqua regia* data were also used for total S, for which no data were available by any other technique.

Soils

Determination of TOC

The total organic carbon content of soil samples was analysed using a LECO SC-DR144 instrument coupled to a Mettler AT 400 analytical balance.

The method is based on total combustion of the samples after removal of the carbonate phase by hydrochloric acid. After combustion in a 99.99 % oxygen flow at 1350°C, the evolved CO₂ is passed through a water and halogen trap and detected with an infrared detector. Analytical grade CaCO₃ was used to construct a four point linear calibration.

The limit of detection for total carbon is estimated to be 0.01 wt % and the uncertainty is estimated to be better than ±5%.

Determination of granulometry

Grain-size distributions between 0.1 and 2000 µm were measured by a Laser Particle Sizer (LPS) technique using a Malvern Mastersizer 2000 instrument (Malvern, UK) equipped with a Hydro 2000G sample dispersion accessory. The method is based on the correlation between the angles of light scattered from particles in a laser beam and the size distribution of these particles.

Samples were sieved to less than 2 mm, followed by removal of organic matter and shells by oxidising the sample with 10 ml 30% H₂O₂ and heating to 70°C. Carbonates and iron oxides are removed by adding 10% HCl and heating. A suspension of the sample in Na₄P₂O₇·10H₂O is measured with the Laser Particle Sizer instrument. Latex spheres with unique known grain sizes traceable to NIST (Malvern Quality Audit Standard QAS2002) were used to control the calibration of the Laser Particle Sizer.

The grain size distribution is expressed as the measured volume divided into 30 fractions, logarithmically spaced between 0.1 and 2000 µm. The software program is also able to calculate the different distribution classes (D (0.5), D (0.6), etc.).

Determination of mercury

Mercury in soils was determined by the method described above for sediments.

Total multielement determination by XRF

A range of elements was determined by wavelength dispersive x-ray fluorescence spectrometry (WD-XRFS) using Philips PW1480 and PW2400 WD-XRFS, with Cr and Rh anode x-ray tubes respectively.

Samples were prepared by milling to less than 40 µm particle size. Then 1000 mg per sample were mixed with 5.0 g lithium metaborate and 25 mg lithium bromide, and fused at 1200 °C for 20 minutes. Loss on ignition (LOI) was determined by heating to 1030 °C for 10 minutes. For samples with a LOI greater than 20%, 2.5 g lithium metaborate and 2.415 g lithium tetraborate were used. Pt95-Au5 crucibles and a commercial automatic fluxer (Herzog 12/1500) were used for the fusion.

The calibration was constructed using 130 certified reference materials and α corrections applied to correct for matrix interferences. In addition to the routine laboratory quality control protocol, LUFA-B (a German residual soil reference sample) was analysed regularly throughout the batches of samples presented for analysis.

Total multielement determination by ICP-MS

A range of rare earth elements (REE) and other trace metals were determined on soil samples using a Perkin Elmer Sciex Elan 5000 inductively coupled plasma mass spectrometer.

Two sample digestion methods were utilised for different elements in order to optimise the elemental recovery and detection limits. In the main method, 0.2 g of the soil sample was weighed into a Teflon dish and the organic material totally decomposed by evaporating the sample to dryness with 5 ml of 65% nitric acid, followed by the addition of 10 ml of 40% hydrofluoric and 4 ml of 70% perchloric acid and evaporated on a hot plate. The residue was dissolved in 20 ml of 8 mol l⁻¹ nitric acid and 1 ml of 30% hydrogen peroxide before filtration. The filtrate was saved and the filter paper ashed in a platinum crucible. The residue was still fused with 0.2 g of lithium metaborate and 0.02 g of sodium perborate followed by dissolution in 5 ml of 0.8 mol l⁻¹ nitric acid. The solutions were combined and made up to 100 ml in 1.8 mol l⁻¹ nitric acid. Measurement of these digests was carried out using a Perkin Elmer Sciex Elan 5000 inductively coupled plasma-mass spectrometer.

A simple cold dissolution method was applied for selected elements, viz: As, Cd, Cs, Cu, Mo, Ni, Pb and Sn. In this method, 0.1 g of the soil sample was weighed into a plastic test tube and 1.5 ml of nitric acid and 0.5 ml of hydrofluoric acid were added. The test tube was closed with a stopper, agitated and allowed to stand at room temperature for 48 h. Deionised water (8 ml) was then added and the solution allowed to stand for a further 48 h. The test tubes were then agitated and centrifuged and the digest extracted and filtered. The extract was diluted before analysis using a Perkin Elmer Sciex Elan 6000 inductively coupled plasma-mass spectrometer.

A reagent blank and two CRMs (Slovakian Residual Soil 982 and River Clay 981) were included as monitoring samples in every batch of 40 samples. In addition, CRMs were prepared within each batch of 80 samples for the main digestion method (syenite SY-2) and within each batch of 40 samples for the cold dissolution method (San Joaquin Soil NIST 2701).

At concentrations an order of magnitude above the limit of quantification, the uncertainty of the method is between 1 and 10%, depending on the element. Limits of quantification are given in Table 3.

Acid leachable multielement determination by ICP-AES

The acid leachable metal content of soils was determined by the same method described above for sediments.

Selection of soil data

A wide range of total multielement data determined by both ICP-MS and XRF methods were available. Data quality, including results of CRMs and ANOVA data for duplicate analyses, were assessed on an element-by-element basis. If only one of the two techniques was sufficiently sensitive to permit determination of a particular element at the background levels found in the samples, then this technique was automatically selected. If both techniques were sufficiently sensitive, the data from the technique with the best precision, based on the ANOVA duplicate analyses, were selected. The actual method used for each element is given in Table 3.

The quality of the ANOVA data for the ICP-AES analysis of the *aqua regia* solutions was also assessed. For a number of elements, the analytical variation exceeded that of the geochemical

variation, and the data for these elements were not considered suitable for publication. Those elements with acceptable data quality are given in Table 3. *Aqua regia* data were also used for total S, for which no data were available by any other technique.

Humus

Determination of mercury

Mercury in humus was determined by the method described above for sediments.

Total multielement determination by ICP-MS

Humic samples were analysed for total metal content by inductively coupled mass spectrometry. Two instruments were used: a Fisons Plasmaquad PQ2 ICPMS during the early stages of the project and latterly an Argilent 7500i ICPMS instrument. The calibration regime for both instruments was very similar.

Samples were extracted with nitric acid prior to analysis. Extraction with mild nitric acid was considered the most effective leach in environmental surveys to distinguish between metals, specifically Pb, Cd and Zn, derived from anthropogenic sources and metals derived from the natural background. The mild nitric acid attack used was expected to dissolve mainly the adsorbed, exchangeable and carbonate bound phases in the sample material.

Samples (400 mg) were placed in 50 ml polypropylene centrifuge tubes and 40 ml 4.5% sub-boiled HNO₃ was added. The tubes were placed in an ultrasonic bath for 90 minutes and then centrifuged at room temperature at 3000 rpm for 30 minutes prior to analysis.

The estimated relative standard deviation was better than 5% for most of the anthropogenic elements and always better than 10% for the elements reported. However, this estimate is valid only for a well-homogenised reference sample; the sampling uncertainty is significant for the humic samples.

Selection of humus data

The quality of the ANOVA data for Hg and the ICP-AES analysis of the *aqua regia* solutions was assessed. For a number of elements, the analytical variation exceeded that of the geochemical variation, and these elements were not considered

suitable for publication. Those elements with acceptable data quality are given in Table 3.

References

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