NGU Report 2011.043

The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils project (GEMAS) – Evaluation of quality control results of total C and S, total organic carbon (TOC), cation exchange capacity (CEC), XRF, pH, and particle size distribution (PSD) analysis

NGU
Norges geologiske undersøkelse
Geological Survey of Norway

Geological Survey of Norway
Postboks 6315 Sluppen
NO-7491 Trondheim, Norway
Tel.: 47 73 90 40 00
Telefax 47 73 92 16 20

REPORT

Report no.: 2011.043	ISSN 0800-3416	Grading: Open

Title:

The EuroGeoSurveys **GE**ochemical **M**apping of **A**gricultural and grazing land **S**oils project (GEMAS) - Evaluation of quality control results of total C and S, total organic carbon (TOC), cation exchange capacity (CEC), XRF, pH, and particle size distribution (PSD) analysis

Authors: Clemens Reimann, Alecos Demetriades, Ola A. Eggen, Peter Filzmoser and the EuroGeoSurveys Geochemistry Expert Group	Client: Eurometaux, EuroGeoSurveys
County: Europe	Commune:
Map-sheet name (M=1:250.000)	Map-sheet no. and -name (M=1:50.000)
Deposit name and grid-reference:	Number of pages: 90 Price (NOK): 115 Map enclosures:

Fieldwork carried out: 2008	Date of report: 05.06.2011	Project no.: 323500	Person responsible:

Summary:

Rigorous quality control (QC) is one of the keystones to the success of any regional geochemical mapping programme. For the EuroGeoSurveys (EGS) GEMAS (Geochemical mapping of agricultural and grazing land soils) project 2211 samples (including field duplicates) of agricultural soil (Ap, A_p-horizon, 0-20 cm) and 2118 samples (including field duplicates) from land under permanent grass cover ("grazing land" - Gr, topsoil 0-10 cm) were collected from a large part of Europe, centrally prepared (air dried, sieved to <2 mm, homogenised and split into sub-samples) and randomised prior to being sent out to contract laboratories. QC consisted of (1) collection of a field duplicate at a rate of 1 in 20 field samples, (2) preparation of two large project standards ("Ap" and "Gr") for insertion between the routine project samples, (3) preparation of an analytical replicate from each field duplicate and (4) randomisation of all samples prior to analysis.

Here QC-results covering analysis of total C and S (Leco), total organic carbon (TOC), cation exchange capacity (CEC), pH in a $CaCl_2$-extraction, total concentrations of 41 chemical elements by X-ray fluorescence (XRF) (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, SO_3, Cl, F, As, Ba, Bi, Ce, Co, Cr, Cs, Cu, Ga, Hf, La, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zn, Zr), loss on ignition (LOI), and particle size distribution (PSD) are reported. Precision, as well as the analytical results for the two project standards Ap and Gr are provided for all analysed parameters. Where applicable practical detection limits were calculated. Several quality issues were detected and needed to be corrected before the data files were released. QC-results for PSD revealed so serious quality issues that the data cannot be used for the project.

Keywords: quality control	accuracy	precision
ANOVA	XRF	CEC
TOC	C	S
pH	grain size distribution	

CONTENTS

1. INTRODUCTION

The introduction of rigorous error control procedures for regional geochemical programmes in the U.S.A., Canada and U.K. in the 1970s is seen as one of the significant milestones in the progress of exploration geochemistry (Miesch, 1964, 1967, 1973, 1976; Garrett, 1969, 1973, 1983; Howarth and Lowestein, 1971; Bølviken and Sinding-Larsen, 1973; Plant *et al.*, 1975; Thompson and Howarth, 1976, 1978, 1980; Howarth and Thompson, 1976; Garrett and Goss, 1978; Garrett *et al.*, 1980; Fletcher, 1981, 1986; Plant and Slater, 1986; Reimann, 1989, 2005; Thompson and Maguire, 1993; Brandvold and McLemore, 1998). The procedures used are based on (1) the collection of a field duplicate sample at every 20th sample site, (2) randomising all samples prior to submitting them for analyses, (3) the introduction of a control reference sample (project standard), unknown to, and unrecognisable by, the laboratory at a rate of one standard per ten to thirty samples, and (4) the insertion of analytical replicates or project samples at a rate of one in ten to twenty samples (*e.g.*, Plant, 1973; Plant *et al.*, 1975; Thompson and Howarth, 1978; Garrett *et al.*, 1980; Fletcher, 1981; Reimann, 1986, 1989; Reimann and Wurzer, 1986; Johnson, 2011). In combination, these procedures allow the detection and evaluation of most quality problems that can occur during sample analysis, and which may seriously affect the success of regional geochemical mapping projects.

Although analytical quality has increased tremendously over the last twenty to thirty years, and at the present time the majority of commercial laboratories are "accredited" for the analyses they carry out, there is still a need for independent and project related quality control (QC). This important requirement is often neglected and the erroneous results are then directly visible on the geochemical maps. For example, on the Ni map, presented by Rühling and Steinnes (1998) for Europe, country borders (Portugal, The Netherlands) rather than the true geochemical distribution patterns of the element are visible. In a way, the regional distribution, as displayed on the maps, is the "final" stage of the applied QC procedure in a regional geochemical mapping project (Reimann, 2005; Reimann *et al.*, 2008). "Noisy" maps are either caused by a too low sample density or, more often, by poor quality data, *i.e.*, insufficient quality control.

1.1 The GEMAS project

The administration of REACH (Registration, Evaluation and Authorisation of chemicals), the new European Chemicals Regulation adopted in December 2006 (EC, 2006a, 2009), and the pending EU Soil Protection Directive (Van Camp *et al.*, 2004; EC, 2006b), require additional knowledge about "soil quality" at the European scale. REACH specifies that industry must prove that it can produce and use its substances safely. Risks, due to the exposure to a substance during production and use at the local, regional and European scale, all need to be assessed. In contrast to human-made organic substances that do not occur naturally in the environment, all industries dealing with natural resources will face in the near future a number of specific questions:

- Most of their "products" occur also naturally – the natural background variation needs to be established, in addition to a methodology to differentiate the industrial impact from the natural geogenic background.

- What is the "bioavailability" of metals and other chemical elements in soil?
- What is the long-term fate of metals and other chemical elements added to soil?

Geological Surveys have been documenting the natural geochemical background of chemical elements in a variety of sample materials for more than 50 years. However, the existing exposure data at the national and regional scale are often not comparable at the European scale (different sampling strategies, different materials and equipment used for sampling and sample preparation, different sample preparation protocols, different analytical protocols, *etc.*), and are thus not able to provide a harmonised pan-European geochemical "background" variation. A reference network is, therefore, needed, where local data can be tied into continental (European) and, finally, global scale data (Darnley *et al.*, 1995). The EuroGeoSurveys Geochemical Atlas of Europe (FOREGS data set, Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006) has demonstrated that low-sample density geochemical mapping can provide the required information about the geochemical background in natural soil, stream water, stream and floodplain sediments. Harmonised geochemical data on agricultural soil do only exist for ten countries in north-eastern European (Reimann *et al.*, 2003), and data on grazing land soil are completely missing.

Food production and quality depend largely on the physical and chemical properties of agricultural and grazing land soil. It is widely neglected that on the continental scale the natural variability of chemical elements in soil spans several orders of magnitude (Reimann *et al.*, 2003, 2009; Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006; or refer to the soil geochemical maps of the Geochemical Atlas of Europe at: http://www.gtk.fi/publ/foregsatlas/). In agricultural sciences, the focus is on the major nutrients in soil, while trace elements and, especially contaminants (*e.g.*, metals), are widely neglected. In environmental sciences today, much of the political attention is focussed on "too high", toxic, element concentrations in soil. For a number of elements, maximum admissible concentrations have been defined for agricultural soil or sewage sludge used as fertiliser (EEC, 1996). By focussing on the rare toxic concentrations, it is not realised that often "too low", deficient element concentrations, will have a more severe influence on plant and animal productivity, and last but not least, human health. A sound documentation of element concentrations and their variation in agricultural and grazing land soil at the pan-European scale is, therefore, urgently needed, prior to taking political actions and before a monitoring network at a spatially extensive and, thus, very expensive scale is established. Such data, at the continental scale, are also desperately required in forensic chemistry. For example, regional differences can be used to trace the origin of food – refer to URL: http://www.trace.eu.org/.

The GEMAS project will deliver good quality and comparable exposure data of metals in agricultural and grazing land soil; soil properties known to influence the bioavailability and toxicity of metals (and other elements) will also be determined on soil at the European scale. Figures 1 and 2 show the sample coverage for agricultural soil (Ap-samples) and land under permanent grass cover (grazing land, Gr-samples).

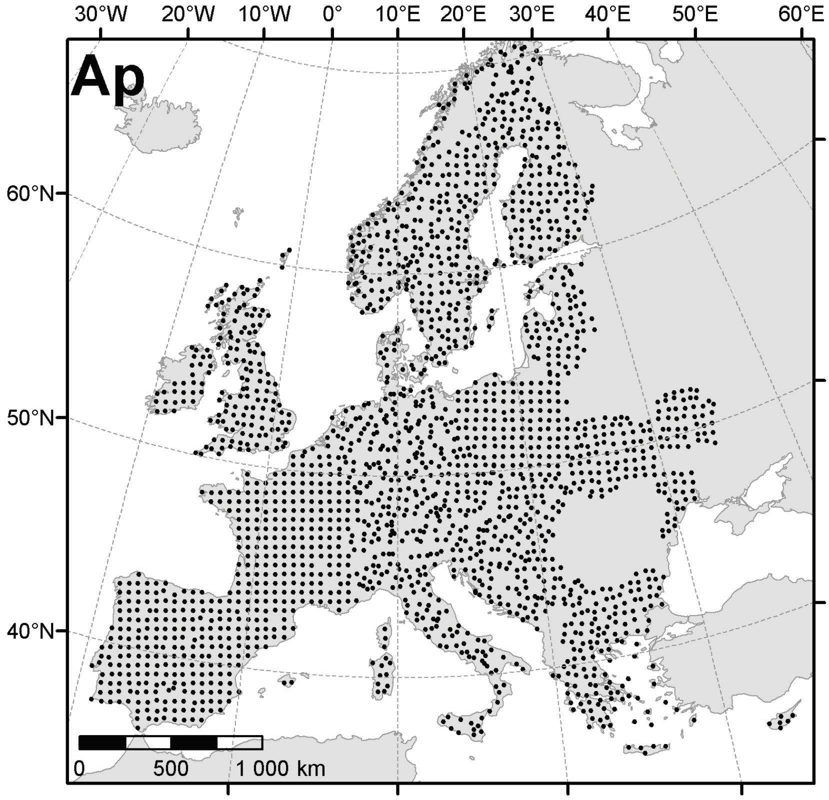


Figure 1. Sample locations for the agricultural soil (Ap-samples), EuroGeoSurveys GEMAS project.

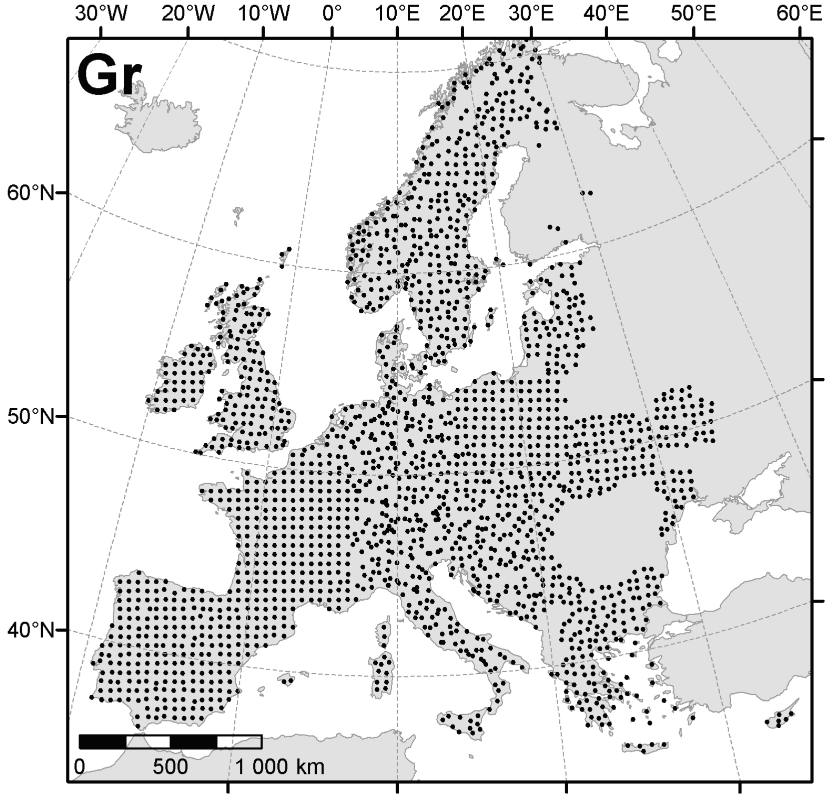


Figure 2. Sample locations for the grazing land soil (Gr-samples), EuroGeoSurveys GEMAS project.

It is often argued that local variation in soil types, agricultural practice and chemistry are far too high to allow for their geochemical mapping at the European scale. However, two recent projects of the European Geological Surveys have verified the opposite. The EuroGeoSurveys Geochemical Atlas of Europe (Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006) demonstrates that low-sample density geochemical mapping (1 sample site / 5000 km^2, *c.* 900 sample sites covering 4.500.000 km^2) at the European scale is possible for a variety of sample materials, including surface water, stream and floodplain sediments and soil (surface and subsurface). It has revealed important information about large-scale differences in the natural concentration, and variation, of chemical elements in the European surface environment. The Baltic Soil Survey (BSS - Reimann *et al.*, 2003) samples were collected at a density twice as high as that used for the Geochemical Atlas of Europe (1 site / 2500 km^2 , 1.800.000 km^2, *c.*750 sample sites in ten north-eastern European countries), and has revealed that even for agricultural soil there are discernible patterns, and its geochemical mapping at the European scale can and should be carried out.

An important part of the project is the establishment of a "soil sample archive" showing the status of European agricultural and grazing land soil in the year of collection (2008). Such an archive of samples at the European scale is invaluable in case of catastrophic events, natural or human disasters, or if industry has to proof "natural conditions" at a certain time in the future. Then these samples can be used to establish the European geochemical "datum" existing at the end of 2008, using state-of-the-art analytical techniques of that particular period, against which the new soil data can be compared.

Many Geological Surveys exist for more than 150 years, and they are one of the few European organisations that can undertake a project at this scale, and guarantee the long-term storage and availability of such a sample archive. The Geochemical Atlas of Europe project is an example (Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006).

To achieve the aforementioned aims, the quality of all analytical results presented today needs to be thoroughly documented. To claim that the data were produced in "accredited laboratories" is just not sufficient.

2. METHODS

The GEMAS project is carried out by the Geochemistry Expert Group of EuroGeoSurveys (EGS) in cooperation with Eurometaux and managed for EGS by the Geological Survey of Norway (NGU). Each member Geological Survey of EGS (except the Dutch Survey, TNO) agreed in late 2007/early 2008 to collect the samples needed for the GEMAS project in its country, according to a jointly agreed field procedure (EGS, 2008). In a couple of countries non-EGS organisations joined the project to facilitate mapping of all EU territory, including the new member States and the aspiring countries. Eurometaux agreed to fund part of the analytical work in exchange for access to the data as soon as these become available.

A field training course was organised in March 2008 in Berlin. At the field training course, each country was provided with a pack containing field equipment for the project that was purchased centrally for all participating countries (*e.g.*, RILSAN sample bags – free from contaminants, small cardboard cards for sample number, small zip-lock bags, strip-locks for the sample bags, scale bar for "surface" photographs, permanent ink markers). Following the field training course, a field manual for the project was published (EGS, 2008) and distributed to all participating organisations.

Sampling took place during the summer and autumn of 2008, with some very last samples arriving in early 2009. All samples were shipped to a central sample preparation facility at the Geological Survey of Slovakia (State Geological Institute of Dionyz Stur). The Geological Survey of Slovakia won a Europe-wide tender for sample preparation of the GEMAS samples. All soil samples were air dried, sieved to <2 mm using a nylon screen, homogenised and finally split into sub-samples. A total of 10 splits were prepared from each soil sample, 4 splits of 200 ml each for storage, 2 splits of 100 ml and 4 splits of 50 ml each for distribution to the laboratories carrying out the analytical work. The laboratory of the Geological Survey of Slovakia, which has the necessary equipment and a long experience in the preparation and certification of international reference materials, did also prepare the two project standards, Ap and Gr. Large amounts of the project standards are needed to monitor the quality of analytical results. These standard samples should not be recognisable by the receiving laboratory once spread among project samples.

After all GEMAS soil samples were received (no samples arrived from Albania, Belarus and Romania), NGU prepared a list of random numbers for each sample set, allowing for the insertion of one field duplicate, one analytical replicate of the field duplicate and the project standard per batch of 20 samples.

2.1 Analytical methods

2.1.1 Total C and S (NGU)

Both, total carbon and total sulphur were analysed at NGUs laboratory using a LECO SC-444 instrument. The principle of the method is that all carbon and sulphur in the sample are burned in an oxygen atmosphere to CO_2 and SO_2, respectively, which are then detected using an IR-cell. NGUs laboratory is accredited for these analyses.

2.1.2 Cation Exchange Capacity – CEC (Geological Survey of the Slovak Republic)

At a given pH value the cation exchange capacity (CEC) is the maximum quantity of total cations that a soil is capable of holding for exchange with the soil solution. It is measured in milliequivalent of hydrogen per 100 g (meq+/100 g), and for agricultural soils values between 10 and 30 meq/100 g are usually reported. CEC is used as a measure of fertility, nutrient retention capacity, and the capacity to protect groundwater from contamination. Clay, silt and humus have electrostatic surface charges that attract the ions in solution, and hold them. This holding capacity varies for the different clay types and clay-mixtures occurring in soil, and it is very dependent on the proportions of clay/silt/humus that are present in a particular soil. For example, humus rich soil will usually have a high CEC.

There exist a large variety of methods to measure CEC. Extraction with ammonium acetate and the silver-thiourea method are most widely used; for the GEMAS project, it was decided to use the latter. The method as such is described by Pleysier and Juo (1980), Searle (1984) and Sumner and Miller (1996).The laboratory of the Slovak Geological Survey is accredited for this method. A detailed method description is attached in the appendix (Appendix 7).

2.1.3 Total organic carbon - TOC (FUGRO, now KIWA)

Total Organic Carbon (TOC) was determined according to ISO standard 10694 "*Soil quality – determination of organic and total carbon after dry combustion*". The measurements were performed using a carbon/sulphur analyser (ELTRA Helios). The instrument is based on infrared spectroscopy.

To remove any inorganic carbon from the samples, one gram of sample was treated with hydrochloric acid (4 mol/L) in abundance. Care was taken to avoid spills of the reacting hydrochloric acid. The residence time was 4 hours at room temperature. The treated samples are then dried for 16 hours in an oven at a constant temperature of 70°C. After drying, 100 mg to 200 mg of the sample material are loaded into a 1350°C preheated furnace of the TOC-analyser. The exact weight of the sample is determined by the TOC-analyser. The organic carbon content is measured by an infrared cell.

2.1.4 pH_$CaCl_2$ (NGU)

The pH of the soil samples was measured in 0.01 M $CaCl_2$. A slurry of 16 g soil and 40 ml 0.1 M $CaCl_2$-solution was prepared. For very organic rich samples 10 g soil and 50 ml 0.1 M $CaCl_2$-solution were used. The samples were placed for 1 hour into an automatic shaker. Immediately after shaking, pH values of all prepared samples were measured within 2 hours using a pH-meter (Mettler Toledo Seven Easy pH-meter) equipped with a standard glass electrode. Calibrations, using standard buffer solutions, were carried out every 40 samples.

2.1.5 XRF and LOI (BGR)

The elements SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, SO_3, Cl, F, As, Ba, Bi, Ce, Co, Cr, Cs, Cu, Ga, Hf, La, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zn and Zr were determined by wavelength dispersive X-ray fluorescence spectrometry (WD-XRFS) using PANalytical PW2400 and AXIOS WD-XRFs, with Cr and Rh anode X-ray tubes, respectively.

The received splits of all samples were prepared for XRF analysis via milling to less than 63 µm particle size in a disk mill using agate vessels. Loss on ignition (LOI) was determined for all samples by slowly heating to 1030°C and keeping the samples at this temperature for 15 minutes in a muffle furnace.

Soil samples with a LOI <25% 1000 mg per sample were mixed with 5.0 g lithium metaborate and 25 mg lithium bromide in Pt95-Au5 crucibles, and fused at 1200°C for 20 minutes in a automatic fluxer (HAG 12-1500). For soil samples with a LOI >25%, 2.5 g lithium metaborate and 2.415 g lithium tetraborate were used. To correct for matrix and spectral interferences calibration curves were constructed using 130 certified reference materials.

XRF is the method of choice when total element concentrations in a sample are to be determined. However, very light elements (like Li, Be, B), or trace elements with very low concentrations (like Ag, Au, Se, Te) cannot be reliably determined by XRF.

2.1.6 Particle Size Distribution, grain size - PSD (FUGRO, now KIWA)

The determination of the particle size (grain size) distribution of soil (or sediment) samples according to ISO 11277 (1998) (Köhn pipette) is a very time consuming procedure and in practice impossible for very large sample sets. An alternative to the Köhn-pipette method is the sedigraph and comparability of the results to ISO 11277 has been demonstrated (Müller *et al.*, 2009). However, even this method is time consuming and not really suitable when thousands of samples need to be analysed. Usually laser based methods are thus used in such a case, and it was a laser based method that was offered by the contract laboratory (FUGRO, now KIWA). This method was accepted for the project "provided it delivers results that are comparable to ISO 11277 (1998)".

PSD was measured according to DIN-EN 725-5 (04/2007) / ISO 13320 (10/2009) by laser diffractometry. The samples were dispersed in a solution of 0.003 m $Na_4P_2O_7$ in water using an ultrasonic device.

Due to budget restrictions only the first 800 samples of each set of samples were analysed for PSD.

3. RESULTS

3.1 Randomised Samples

Samples are randomised for a variety of reasons. First of all randomisation of samples results in spreading analytical errors that are unavoidable during analysis (*e.g.*, slight time trends or breaks), evenly over all samples and, thus, the whole survey area. It decreases the chances that any time dependent errors in the laboratory, such as a slow drift from lower to higher reporting levels, can create its own "false" patterns on geochemical maps. It also allows to easily "hide" standards and replicates in a sample set submitted to the laboratory, since all samples are given new numbers. It is of interest to plot analytical results versus sample number if the samples are analysed in the exact sequence of the random numbers (the laboratory must be told not to randomise the samples again upon receiving them, because this is standard practice in many survey laboratories, though not necessarily in commercial laboratories). In such plots, a number of unwanted effects that can seriously disturb the analytical results of some samples become visible, *e.g.*, carry over or memory effects (high values following the analysis of a highly anomalous sample) – the samples should display random variation over the whole range. Such plots were prepared for all parameters. Figure 3 shows four examples from the agricultural soil (Ap) samples. The upper two diagrams (CEC and Cl) show clearly undesirable effects. For CEC there are many samples that exhibit unusually low results above sample number 4500; for Cl there occurs a break in the Cl-results at sample number 4500. If the samples were not randomised these effects would clearly lead to artificial patterns on the geochemical maps. For randomised samples a conscious decision needs to be taken whether precision (see below) is so seriously affected that all samples need to be re-analysed. The other two examples, the plots for Ba and Zn, show the expected random variation.

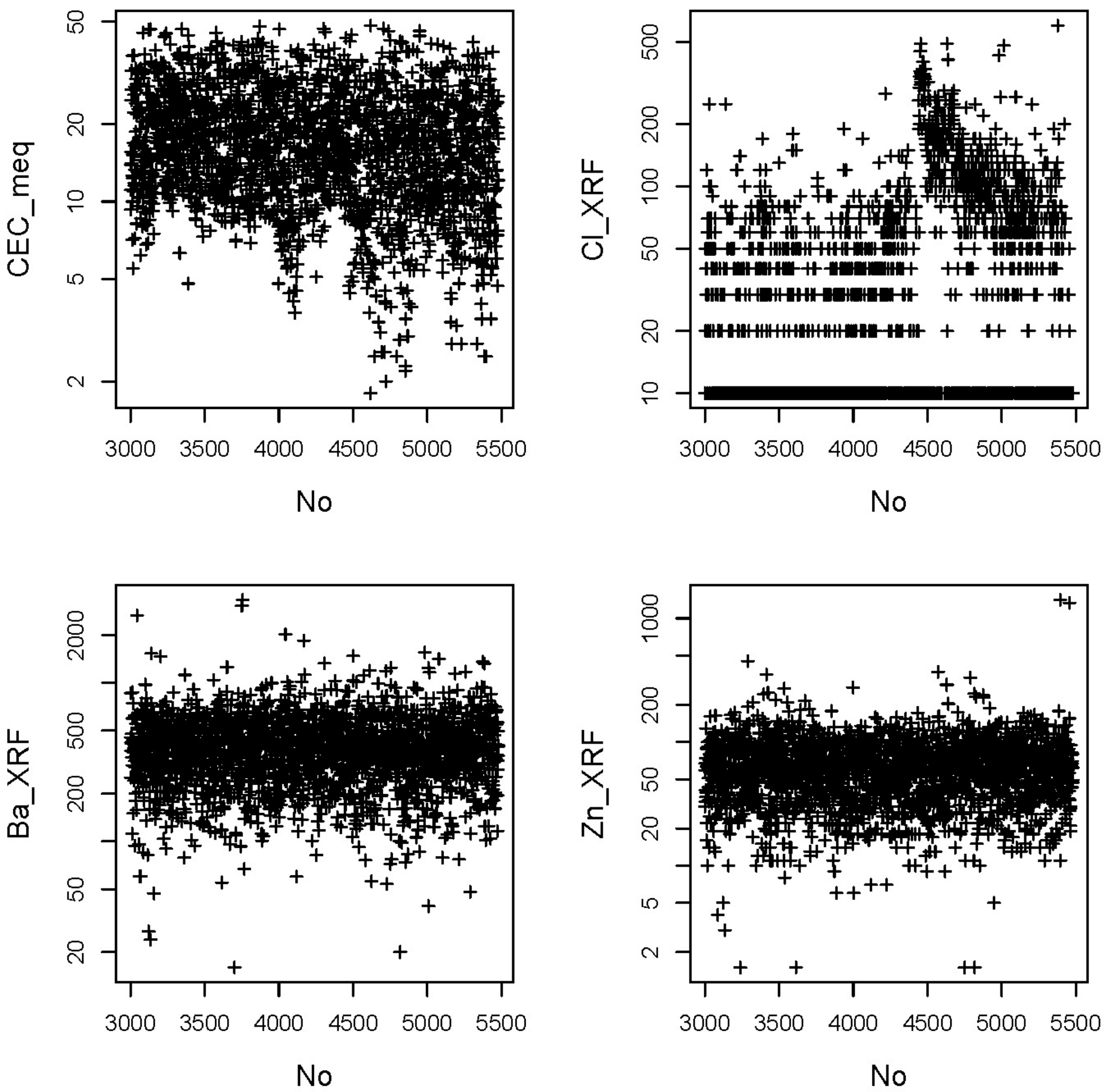


Figure 3. Sample number (sequence of analysis) plotted against analytical results for CEC, Cl, Ba and Zn. For Ba and Zn the plots indicate the expected random variation; for CEC and Cl, however, time dependent effects on the results are clearly indicated around sample number 4500 and above.

Randomisation of all samples requires that all project samples are received and prepared by the sample preparation laboratory before submitting them for analysis. Because this can take time, especially in large international cooperation projects, the temptation is strong not to randomise all samples, but rather submit a number of large batches, or even to start analyses by randomising the samples from a single country only. Based on the experience from several large geochemical mapping projects (Reimann *et al.*, 1998, 2003; Salminen *et al.*, 2005), the authors strongly advise to exercise patience until all samples are collected and prepared, and to randomise all project samples before sending them to the analytical laboratory. Getting a head start always caused problems with comparability of analytical batches later on, and subsequently a lot of extra work to validate the analytical results is required. For example, it would be almost impossible to correct for the effects seen in Figure 3, if results for different countries are at the front and end of the sample set.

3.2 Trueness, Accuracy, Repeatability – the project standard

The project standard is used to monitor accuracy. Accuracy is essentially the absence of bias. However, analytical results can be highly accurate without reflecting the "true" concentration value of a chemical element. To obtain an impression of "trueness" one or better several certified reference materials have to be analysed together with project samples. A disadvantage of using certified reference materials is that they are expensive and easy to detect by the laboratory. Furthermore, they may have been used to calibrate the method and will then not be able to deliver an objective impression of trueness for the project samples. For the GEMAS project about 20 different laboratories will analyse the two project standards Ap and Gr, and the results will be published in a separate report.

The project standards Ap and Gr also underwent a test for homogeneity according to ISO13528 (2005). All elements investigated passed the test for homogeneity (Dr. Pavol Lučivjanský, 2009; pers.com.).

The project standards Ap and Gr were inserted at an average rate of one in twenty at a random position in each batch of 20 samples before the soil samples were submitted to the laboratory. Project standard Ap was analysed 124 times, and standard Gr 118 times. Table 1 shows the analytical programme, the laboratories' detection limits and summarises the analytical results for the standard for all parameters. The average repeatability of all elements, calculated for the standard results, is also provided and can be used to obtain a first impression of precision (see below). Note that PSD is covered in an own chapter, because the results were found to be unacceptable for further use in the project.

Table 1. Analytical programme covered in this 2nd QC report and the laboratories' detection limits (DL), analytical results (mean, minimum (Min) and maximum (Max) concentration, standard deviation (StDev)) and coefficient of variation (CV %) for the project standards Ap and Gr. GRAV: gravimetric.

Parameter	***Method***	***DL***	***Unit***	***GEMAS Ap (N=124)***					***GEMAS Gr (N=118)***				
				Mean	***Min***	***Max***	***StDev***	***CV %***	***Mean***	***Min***	***Max***	***StDev***	***CV %***
C	LECO		wt%	2.7	2.3	3.9	0.164	6.2	1.1	0.97	1.3	0.060	5.5
S	LECO	0.01	wt%	0.014	<0.01	0.109	0.012	85	<0.01	<0.01	0.05	0.006	61
CEC	silver thiourea		meq/ 100 g	24	20	27	2.046	8.5	17	15	20	1.136	6.5
TOC	IR		wt%	1.2	1.1	1.5	0.089	7.2	1.1	0.9	1.4	0.097	9.1
pH_CaCl$_2$	pH-meter	0.1		7.3	7.2	7.5	0.056	0.8	5.9	5.8	6.1	0.050	0.8
SiO$_2$	XRF	0.1	wt%	56.8	56.5	57.1	0.143	0.3	72.9	72.3	73.4	0.187	0.3
TiO2	XRF	0.001	wt%	0.697	0.689	0.704	0.003	0.4	0.652	0.641	0.666	0.004	0.7
Al$_2$O$_3$	XRF	0.05	wt%	12.8	12.8	12.9	0.040	0.3	11.2	11.1	11.4	0.053	0.5
Fe$_2$O$_3$	XRF	0.01	wt%	5.25	5.21	5.31	0.019	0.4	3.86	3.81	3.93	0.021	0.6
MnO	XRF	0.001	wt%	0.098	0.094	0.102	0.001	1.4	0.080	0.077	0.084	0.002	1.9
MgO	XRF	0.01	wt%	2.37	2.34	2.41	0.015	0.6	0.968	0.950	0.990	0.010	1.0
CaO	XRF	0.005	wt%	5.57	5.47	5.66	0.048	0.9	0.482	0.464	0.526	0.012	2.5
Na$_2$O	XRF	0.01	wt%	1.03	0.99	1.09	0.013	1.3	1.20	1.17	1.23	0.013	1.1

Parameter	***Method***	***DL***	***Unit***	***GEMAS Ap (N=124)***					***GEMAS Gr (N=118)***				
				Mean	***Min***	***Max***	***StDev***	***CV %***	***Mean***	***Min***	***Max***	***StDev***	***CV %***
K_2O	XRF	0.005	wt%	2.30	2.23	2.37	0.025	1.1	2.16	2.09	2.21	0.022	1.0
P_2O_5	XRF	0.001	wt%	0.225	0.221	0.229	0.002	0.7	0.196	0.192	0.203	0.002	1.1
SO_3	XRF	0.01	wt%	0.082	0.070	0.120	0.006	7.7	0.006	0.005	0.030	0.003	51
Cl	XRF	0.002	wt%	0.004	<0.002	0.029	0.005	141	0.003	<0.002	0.011	0.002	86
F	XRF	0.05	wt%	0.057	<0.05	0.120	0.030	53	0.031	<0.05	0.090	0.015	48
LOI	GRAV	0.1	wt%	12.4	12.0	12.8	0.195	1.6	6.06	5.79	6.43	0.131	2.2
As	XRF	3	mg/kg	11	8	13	0.916	8.7	11	8	13	0.922	8.8
Ba	XRF	5	mg/kg	342	335	348	2.850	0.8	360	352	371	3.483	1.0
Bi	XRF	3	mg/kg	<3	<3	5	0.891	48	<3	<3	4	0.230	15
Ce	XRF	20	mg/kg	65	46	87	7.891	12	62	43	85	8.190	13
Co	XRF	3	mg/kg	14	9	18	1.801	13	11	8	15	1.405	13
Cr	XRF	4	mg/kg	111	105	131	3.072	2.8	97	89	107	3.287	3.4
Cs	XRF	3	mg/kg	8	6	11	0.901	11	6	<3	8	1.376	22
Cu	XRF	5	mg/kg	19	16	27	1.684	8.7	18	14	47	3.186	18
Ga	XRF	2	mg/kg	16	14	19	0.866	5.4	13	11	15	0.746	5.7
Hf	XRF	5	mg/kg	<5	<5	15	3.372	53	8	<5	16	3.779	47
La	XRF	20	mg/kg	24	<14	43	9.458	40	27	<14	44	7.513	28
Mo	XRF	2	mg/kg	<2	<2	6	0.515	48	<2	<2	9	1.032	80
Nb	XRF	2	mg/kg	14	13	17	0.908	6.3	13	10	15	0.836	6.4
Ni	XRF	3	mg/kg	52	49	62	1.536	3.0	38	35	43	1.583	4.2
Pb	XRF	3	mg/kg	21	17	25	1.710	8.3	19	14	29	2.218	12
Rb	XRF	2	mg/kg	99	87	108	3.986	4.0	86	76	92	3.812	4.4
Sb	XRF	5	mg/kg	<5	<5	9	1.099	39	<5	<5	7.0	1.138	48
Sc	XRF	2	mg/kg	13	10	15	1.007	8.0	9	8	10	0.753	8.3
Sn	XRF	4	mg/kg	<4	<4	9	0.778	37	<4	<4	21	2.849	89
Sr	XRF	2	mg/kg	148	145	151	1.631	1.1	90	88	92	0.769	0.9
Ta	XRF	5	mg/kg	<5	<5	7	0.512	20	<5	<5	5	0.594	36
Th	XRF	5	mg/kg	11	<3	15	2.308	22	12	8	16	1.617	14
U	XRF	3	mg/kg	3	<3	6	1.372	50	<3	<3	4	0.961	58
V	XRF	5	mg/kg	103	95	111	3.201	3.1	77	69	83	2.701	3.5
W	XRF	5	mg/kg	3	<3	7	0.992	36	<3	<3	5	0.888	45
Y	XRF	3	mg/kg	29	27	32	0.983	3.4	25	22	28	1.283	5.1
Zn	XRF	3	mg/kg	92	88	100	1.549	1.7	67	62	74	2.284	3.4
Zr	XRF	3	mg/kg	178	170	185	2.796	1.6	227	214	241	5.474	2.4

In addition, X-Charts were plotted for all elements, where element concentration is plotted against sample number (for an example from the Ap-standard see Fig. 4 – all plots are shown in Appendix 1 (Gr) and Appendix 2 (Ap). These plots allow the immediate detection of deviations in the analytical results for the standard samples: time trends, breaks between batches and outliers. Usually the mean and multiples of the standard deviation are shown in these X-Charts. Nevertheless, X-Charts are plotted, because one expects deviations, time trends, breaks in the data or data outliers, and it is thus questionable whether classical statistics are the best measure for central value and variation. Herein, instead of the mean, the median is plotted, and instead of plotting multiples of the standard deviation it was decided to plot limits for 10 and 20% precision, and to identify all samples that are beyond 30% precision by sample numbers. Furthermore, a loess regression line (see Reimann *et al.*, 2008) was added to facilitate the detection of time trends and/or breaks. In addition to a number of serious outliers (>+/- 30%), several time trends and/or breaks in the data were detected (see all plots in Appendix 1 and 2), and all had to be followed up before the data could be finally accepted. This resulted in several months delay until the final data could be released.

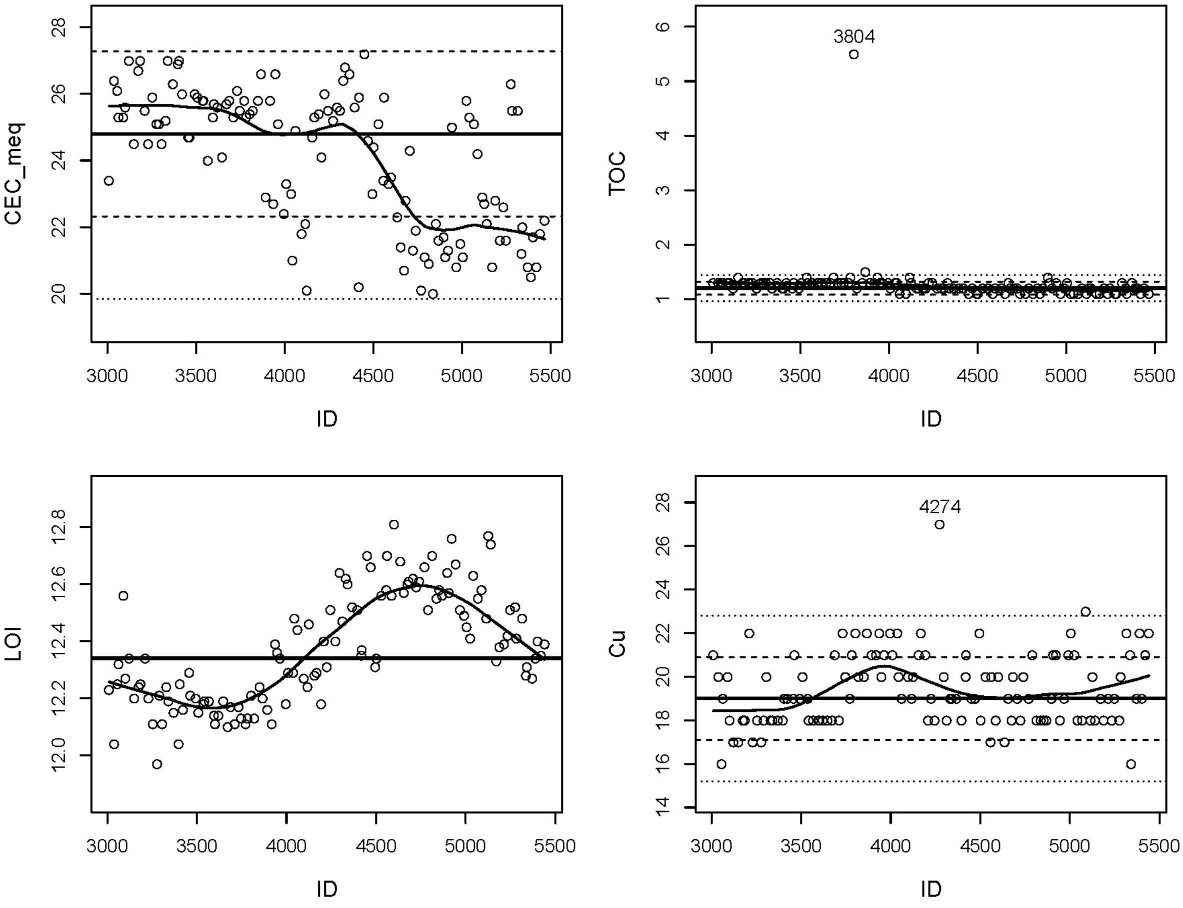


Figure 4. Example showing four selected X-Charts for the project standard Ap. Sample number (ID) is plotted against analytical result for the standard. The thick black line indicates the median value of all standard results, the dashed line is the limit for 10%, and the dotted line for 20% deviation from the median. Standard results that show a larger deviation than 30% from the median are indicated by sample number. The trend line is a loess regression line for the standard results and would help to identify time trends or breaks in the data. The charts for all elements are presented in Appendix 1 (Gr) and Appendix 2 (Ap).

3.3 Precision – the project duplicates

Precision is the closeness of agreement between independent test results obtained under stipulated conditions. It depends only on the distribution of random errors and does not relate to the "true" concentration value of a chemical element. Precision is normally expressed in terms of imprecision and estimated through the standard deviation of the test results. The precision is usually adjusted for the mean and expressed as the coefficient of variation (CV) in percent (see Massart *et al.*, 1988). A low standard deviation indicates a high precision. The values reported herein refer to repeatability conditions, where independent test results were obtained using the same method on identical test items (*i.e.*, samples) in the same laboratory using the same extraction and the same equipment over a short time span. Repeatability conditions involve the repeated execution of the entire method from the point at which the material reaches the laboratory, and not just repeat instrumental determinations on already prepared extracts. The latter, give impressive estimates of precision, but have no relevance to the precision achieved when real samples are analysed in the laboratory, since it does not take into account the natural inhomogeneity of the sample material, which is an important source of variability.

Precision is routinely estimated via the insertion of replicates of real project samples. For the GEMAS project an analytical replicate was prepared from each field duplicate and always inserted in position "20" (20, 40, 60...) for the field duplicate that was among the preceding 18 real samples (18 + 1 standard). Precision can then be calculated for each replicate pair at the different concentration ranges that the replicates cover, while the project standard can only provide an impression of precision for each chemical element at the concentration in the standard. For obtaining an overview it is, of course, desirable to calculate the overall precision for the project from these replicates. Thus, once all replicates were retrieved from the analytical results for each pair the squared difference was calculated. The sum of these values divided by the number of samples is a measure of variability. To obtain the standard deviation the square root of this variability measure is taken. The resulting estimate of precision, as shown in Table 2 as “Precision1”, corresponds to a CV value, because the standard deviation is divided by the overall mean of the samples. To obtain a rapid overview of "quality" of the analysis for the different elements, it can be advantageous to sort the table according to precision, and not alphabetically with respect to the elements.

This method of calculating "overall precision" does not take into account that precision will usually change with concentration (for an example see Fig. 2-5, p.32, in Fletcher, 1981, or Fig. 1-3 in Fauth *et al.*, 1985). Reimann and Wurzer (1986) introduced a method that can take care of this feature and express precision for different concentration ranges. It requires, however, a rather large number of replicates to be analysed, and the replicates to be well spread over the whole concentration range. Thus, quite different estimates of precision can be calculated for different concentration ranges. Precision is usually poor very near to the detection limit, and it becomes better with increasing concentrations until the analytical instrument’s optimal measuring range is reached, and decreases again towards high concentrations until the upper limit of detection is reached. The upper detection limit has usually no significance in regional geochemistry, but can become important when ore samples or strongly contaminated samples are analysed.

"Thompson and Howarth plots" (Thompson and Howarth, 1978) are a graphical way of representing the results of replicate-pair analyses. The mean of each replicate pair is plotted against the absolute difference between the two analyses. In these plots, lines can be drawn for any predefined precision level (*e.g.*, 10% and/or 20%) and percentile (*e.g.*, 90th or 99th), and the overall quality of the replicate analyses at different concentration ranges can be grasped at a glance. Pairs that deviate from the general trend should be identified. Batches where both, the project standard and the replicate pair, deviate will need to be re-analysed. Figure 5 shows an example of these plots. All plots for the Gr and the Ap samples are shown in Appendix 3 (Gr) and 4 (Ap), respectively.

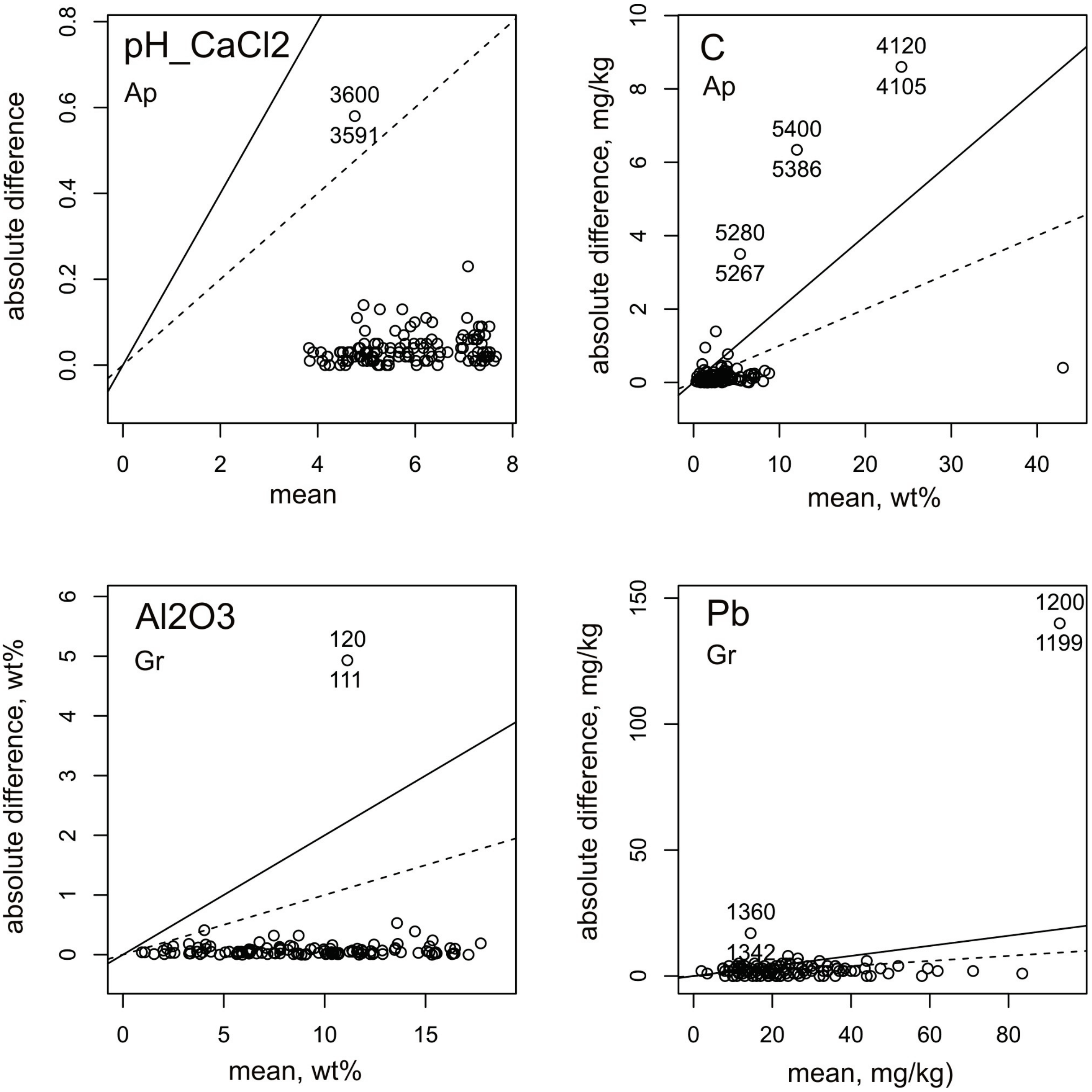


Figure 5. Four examples showing "Thompson and Howarth"-plots of replicate analyses. The mean of the replicate pairs is plotted along the x-axis, and the absolute difference of the two results along the y-axis. 10 % precision is indicated by the stippled line, and 20% precision by the continuous line. Pairs with poor precision can easily be identified and compared to the results from the project standard within the same batch of 20 samples. Plots for all elements are presented in Appendix 3 (Gr) and 4 (Ap).

As already visible in Tables 1 and 2, the plots indicate that there are a number of parameters where precision is rather poor. Results for these parameters may hold a certain information value, they will, however, not be used for mapping in the planned geochemical atlas. Single duplicate pairs with large deviations for parameters that showed otherwise a good precision were followed up by re-analyses of selected batches of samples, and such deviations could usually be sorted out before accepting the data for the final file.

3.3.1 Practical detection limit and precision equation

There exist a number of definitions for the "detection limit" in literature. In pure analytical chemistry the detection limit is the lowest quantity of a substance that can be distinguished from the absence of that substance (a *blank value*) within a stated confidence limit. This "theoretical" detection limit, which is valid when analysing a pure substance, is of little interest when analysing geological materials with a very complex matrix. Here the "practical" detection limit (Thompson and Howarth, 1978; Reimann and Wurzer, 1986) is in fact of relevance and is the value where the precision of duplicate analyses reaches ±100%. Nowadays, respectable commercial laboratories in the geosciences will quote such "practical detection limits", valid for the sample type for which the analytical services are requested, for their analytical packages, and not the often much lower and very impressive "theoretical" detection limits as provided, for example, by many instrument manufacturers.

Based on the results of replicate analyses, it is possible to estimate the "practical" detection limit, the detection limit valid for the GEMAS project samples, including extraction, and the precision equation for estimating precision at any concentration (Thompson and Howarth, 1978; Reimann and Wurzer, 1986; Demetriades and Karamanos, 2003; Demetriades, 2009, 2011). For this purpose it is necessary that the laboratory reports all instrument readings without any rounding or cut-off at the laboratories pre-determined detection limits, and even sub-zero measurements must be recorded and submitted. Reporting all values in this format was part of the commercial analytical contracts for the GEMAS project. However, for the XRF results this was not possible.

The modified Thompson and Howarth (1978) method includes the estimation of regression line coefficients by the "reduced major axis line" procedure (Demetriades and Karamanos, 2003; Demetriades, 2009, 2011), referred to as the "unique line of organic correlation" or "isogonic growth line" (Kermack and Haldane, 1950; Till, 1974). The optimum regression line coefficients are, therefore, extracted for the calculation of practical detection limit and precision equation at the 95% confidence level. The "practical detection limit" and precision equation were estimated for the GEMAS project agricultural and grazing land soil field duplicates and are provided in Table 2. "Precision 2" in Table 2 provides the overall precision of each determinand (element) at the point where the parabolic curve of precision versus concentration reaches the asymptote (or plateau) and stabilises. Precision 1, in contrast is the "classical" computation of precision adjusted for the mean and expressed as the coefficient of variation (CV) in percent (see, *e.g.*, Massard, 1988; Reimann *et al.*, 2008).

Table 2 also shows the detection limits, as provided by the laboratory, and the practical detection limits (PDLs), as estimated using the GEMAS replicate results by the modified method of Thompson and Howarth (1986 - Demetriades and Karamanos, 2003; Demetriades, 2009, 2011). The estimated practical detection limits are in many cases considerably lower than those quoted by the laboratory. The few exceptions are usually for elements where the project samples returned high values, because there were no replicate pairs close to the detection limit. In these cases, a reliable estimate of the practical detection limit is not possible.

Table 2. The laboratories "official" detection limits (LDL) and practical detection (PDL) limits calculated from the GEMAS project replicates using a modified version of Thompson and Howarth (1978). Precision (PREC) as calculated for the replicate results using two different methods (1: as described in Reimann et al., 2008; 2: as described by Demetriades and Karamanos, 2003; Demetriades, 2009, 2011). Precision in %, for method 2 at the 95% confidence level.

Parameter	***Method***	***Unit***	***LDL***	***Agricultural soil (Ap-samples)***			***Grazing land soil (Gr-samples)***		
				PDL	***PREC 1***	***PREC 2***	***PDL***	***PREC 1***	***PREC 2***
C	LECO	wt%	0.01	0.008	22	6	0.03	8	8
S	LECO	wt%	0.01	0.005	32	48	0.002	65	19
CEC	silver thiourea	meq/ 100 g	0.1	0.04	6	9	0.5	5	7
TOC	IR	wt%	0.1	0.3	22	9	0.003	10	11
pH_$CaCl_2$	pH-meter		0.1	0.1	1	3	0.1	1	3
SiO_2	XRF	wt%	0.1	0.01	1	0.4	0.1	1	1
TiO_2	XRF	wt%	0.001	0.005	1	2	0.003	2	1
Al_2O_3	XRF	wt%	0.05	0.04	1	1	0.02	4	1
Fe_2O_3	XRF	wt%	0.01	0.01	1	1	0.03	5	1
MnO	XRF	wt%	0.001	0.0001	2.2	2	0.0003	5	5
MgO	XRF	wt%	0.01	0.01	1	1	0.007	1	1
CaO	XRF	wt%	0.005	0.01	2	1	0.003	3	2
Na_2O	XRF	wt%	0.01	0.01	3	3	0.01	2	1
K_2O	XRF	wt%	0.005	0.001	2	2	0.01	3	1
P_2O_5	XRF	wt%	0.001	0.001	2	3	0.0006	6	3
SO_3	XRF	wt%	0.01	0.003	12	27	0.004	6	17
Cl	XRF	wt%	0.002	0.002	43	67*	0.001	70	233*
F	XRF	wt%	0.05	0.04	50	341*	0.03	49	372*
LOI	GRAV	wt%	0.01	0.04	7	1	0.06	3	2
As	XRF	mg/kg	3	0.4	15	21	0.4	30	17
Ba	XRF	mg/kg	5	2	3	1	2	2	3
Bi	XRF	mg/kg	3	2	31	576*	**	15	**
Ce	XRF	mg/kg	20	7	15	33	11	16	12
Co	XRF	mg/kg	3	1	16	27	0.2	13	31*
Cr	XRF	mg/kg	4	3	3	3	2	8	5
Cs	XRF	mg/kg	3	10	28	122*	1	27	59*
Cu	XRF	mg/kg	5	0.5	10	21	1	12	10
Ga	XRF	mg/kg	2	1	8	20	0.6	11	19
Hf	XRF	mg/kg	5	9	37	92	7	39	159*
La	XRF	mg/kg	20	64	27	120	12	32	73*
Mo	XRF	mg/kg	2	**	34	**	1	45	513*
Nb	XRF	mg/kg	2	0.2	8	15	0.2	8	15
Ni	XRF	mg/kg	3	1	4	5	2	12	5
Pb	XRF	mg/kg	3	0.3	98	13	2	38	12
Rb	XRF	mg/kg	2	0.2	4	6	0.4	3	4
Sb	XRF	mg/kg	5	**	18	**	**	38	**
Sc	XRF	mg/kg	2	1	10	33	0.6	11	17

Parameter	*Method*	*Unit*	*LDL*	*Agricultural soil (Ap-samples)*			*Grazing land soil (Gr-samples)*		
				PDL	*PREC 1*	*PREC 2*	*PDL*	*PREC 1*	*PREC 2*
Sn	XRF	mg/kg	4	2	45	577	4	63	153*
Sr	XRF	mg/kg	2	1	1	1	2	2	0.001
Ta	XRF	mg/kg	5	**	13	**	2	39	407*
Th	XRF	mg/kg	5	3	21	54	0.4	17	27
U	XRF	mg/kg	3	7	31	126	3	39	172*
V	XRF	mg/kg	5	2	3	5	1	5	9
W	XRF	mg/kg	5	**	22	**	2	47	300*
Y	XRF	mg/kg	3	2	4	1	0.7	4	12
Zn	XRF	mg/kg	3	1	2	2	0.2	5	4
Zr	XRF	mg/kg	3	1	3	4	4	3	2

*: too many values near DL to estimate reliable values

**: too few samples above detection to estimate PDL and Precision 2

LDL: Laboratories detection limit

PDL: practical detection limit

3.4 Analysis of variance (ANOVA)

In a comprehensive quality control programme, field duplicates are routinely collected at a number of randomly selected sites (usually 5-10%). These samples are used to estimate the variation introduced by sampling, and to answer the question of whether it is possible to obtain the same analytical results if undertaking the survey a second time at approximately the same sites. An estimate of the field variability is especially important in a monitoring programme, *i.e.*, when the sampling exercise is to be repeated after a number of years to detect any changes in time. It is noteworthy that in many European environmental monitoring programmes no indication of the sampling error or of the measurement uncertainty is provided. Without this information the data are not really suitable for monitoring or even mapping.

The precision of the field duplicates could be estimated in the same way as for the analytical replicates, and even Thompson and Howarth plots could be constructed. This will provide a good first estimate of the relative magnitude of the sampling error in relation to the analytical error. In a more formalised approach this can be done by carrying out an Analysis of Variance (ANOVA - *e.g.*, Scheffé, 1959, 1999). Principally, there exist two different designs for an ANOVA for a geochemical mapping project, balanced or unbalanced (Garrett, 1969, 1973, 1983; Miesch, 1976; Ramsey, 1998 - Fig. 6). In a "balanced" design, replicate analyses are made on both, the routine and field duplicates sample (Fig. 6a). In an "unbalanced" design, unequal numbers of analyses occur at each level of the design (Fig. 6b). In an unbalanced design, only one of the field duplicate pairs is split and analysed twice, substantially reducing the cost of analysis in a large project like GEMAS. For small projects a balanced design may be preferable to obtain sufficient replicate analyses. The results of the ANOVA provide estimates of the proportion of the total variability due to "nature" (geochemical variance), "sampling" (sampling or "at site" variance) and "analysis"(analytical error).

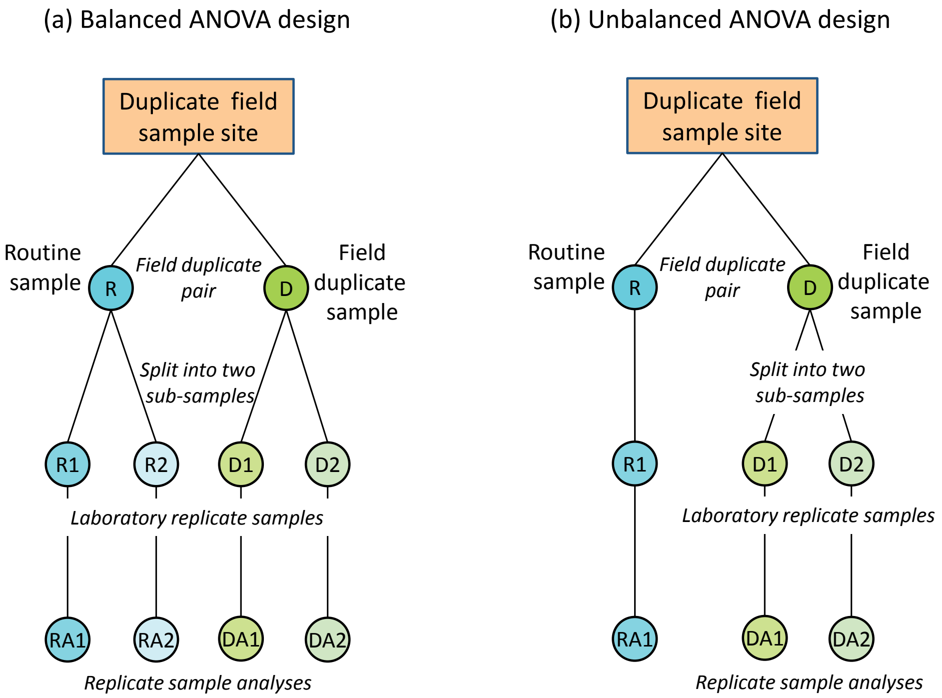


Figure 6. Balanced (left)and unbalanced (right) ANOVA design for the estimation of natural (geochemical), sampling (at site) and analytical variance. At every 20th sample site, or, in small countries with more than 10 but less than 20 sample sites, at one of the sample sites, a duplicate agricultural and grazing land soil sample was collected from the same plot of land, but different sub-sites. This field duplicate sample was used to prepare the analytical replicates.

An ANOVA is the final step of quality control for a regional geochemical mapping programme. Technical variability ("at site, sampling" and "analytical") should be considerably smaller than the regional variability for construction of a reliable geochemical map. According to Ramsey (1998) the suggested maximum of the technical variability should ideally not exceed 20% of total variance, of which the analytical variance could be expected to be up to 4%, and the sampling variance to be up to 16% of the total.

Table 3 shows the results of an unbalanced ANOVA for the GEMAS samples (A_p and Gr) and the distribution between "geochemical (natural)", "sampling (site)" and "analytical (analyt.)" variability. The median value for all samples is also provided.

Table 3. GEMAS Ap- and Gr-samples and results of an unbalanced ANOVA (%). All variables were log-transformed prior to the calculation. Left hand side in alphabetical according to element, and right hand side sorted according to increasing "geochemical (natural)" variation for an easy identification of "problematic" elements (less than 80% natural variation).

	Agricultural soil 0-20 cm (Ap)				***Grazing land soil 0-10 cm (Gr)***			
		VARIANCE, %				***VARIANCE, %***		
Parameter	***MEDIAN***	***nat.***	***site***	***analyt.***	***MEDIAN***	***nat.***	***site***	***analyt.***
C	2.21 wt%	97.7	1.1	1.2	3.3 wt%	98.4	0	1.6
S	0.02 wt%	80.1	0	19.9	0.02 wt%	87.1	3.7	9.2
CEC	16.4 meq/100 g	95.9	0	4.1	18.7 meq/100 g	96.5	1.5	2
TOC	1.75 wt%	93.5	0	6.5	2.7 wt%	97.2	0	2.8
pH_CaCl2	5,8	95.6	0	4.4	5.5	97.7	2.1	0.2
SiO2	67.2 wt%	99.7	0.1	0.2	64.8 wt%	99	0.9	0.1
TiO2	0.6 wt%	99.5	0.4	0.1	0.6 wt%	99.3	0.5	0.3
Al2O3	10.32 wt%	99.5	0.5	0.1	9.8 wt%	99.3	0.4	0.3
Fe2O3	3.49 wt%	99	1	0	3.43 wt%	98.7	0	1.2
MnO	0.08 wt%	98.9	1	0.1	0.07 wt%	98.2	1.3	0.5
MgO	0.91 wt%	99.4	0.5	0.1	0.86 wt%	99.3	0.5	0.2
CaO	1.19 wt%	99.3	0.7	0	1.07 wt%	98.9	1.1	0
Na2O	0.81 wt%	99.5	0.1	0.4	0.71 wt%	99.5	0.1	0.4
K2O	1.9 wt%	99.3	0.5	0.2	1.8 wt%	99.3	0.5	0.2
P2O5	0.18 wt%	98.3	1.6	0.2	0.18 wt%	97.7	0	2.3
SO3	0.01 wt%	96.4	0.9	2.8	0.01 wt%	96.3	2.8	0.9
Cl	0.003 wt%	69.4	9.3	21.3	<0.002 wt%	51.4	2.1	46.5
F	<0.05 wt%	38	0	62	<0.05 wt%	34.5	4.6	60.9
LOI	8.5 wt%	98.6	1.3	0.1	11.6 wt%	98.7	1.2	0.2
As	7 mg/kg	94.4	1.9	3.6	7 mg/kg	86	2.9	11.1
Ba	383 mg/kg	99.4	0.4	0.2	353 mg/kg	81.4	18.5	0.1
Bi	<3 mg/kg	20	18	62	<3 mg/kg	0	96.5	3.5

Sorted Ap		***sorted Gr***	
	%		***%***
Parameter	***natVar***	***Parameter***	***natVar***
Sb	0	Bi	0
Ta	0	Ta	0
Bi	20	Sb	12.6
W	37	F	34.5
F	38	Hf	38
Hf	45	W	41.5
Sn	45	Sn	49
La	62	Cl	51.4
Mo	62	Cs	58
Cs	66	U	65
U	66.5	Ce	72.2
Cl	69.4	La	73.5
Th	73.6	Mo	75.9
S	80.1	Sr	79.4
Pb	82	Ba	81.4
Ce	87	Th	83.8
Co	89.5	V	85.7
Sc	92	As	86
TOC	93.5	S	87.1
Ga	94	Pb	87.2
Cu	94	Y	87.4
Nb	94	Co	89.8

	Agricultural soil 0-20 cm (Ap)				***Grazing land soil 0-10 cm (Gr)***			
		VARIANCE, %				***VARIANCE, %***		
Parameter	***MEDIAN***	***nat.***	***site***	***analyt.***	***MEDIAN***	***nat.***	***site***	***analyt.***
Ce	58 mg/kg	87	0	13	56 mg/kg	72.2	11.6	16.2
Co	9 mg/kg	89.5	0	10.5	9 mg/kg	89.8	0.6	9.5
Cr	62 mg/kg	98	1	1	60 mg/kg	94.3	4.5	1.3
Cs	5 mg/kg	66	0	34	5 mg/kg	58	14.1	27.9
Cu	13 mg/kg	94	3	3	13 mg/kg	92.5	0	7.5
Ga	12 mg/kg	94	3	3	12 mg/kg	93.8	0	6.2
Hf	8 mg/kg	45	4.9	50	8 mg/kg	38	0	62
La	23 mg/kg	62	8	30	24 mg/kg	73.5	0	26.5
Mo	<2 mg/kg	62	0	38	<2 mg/kg	75.9	0	24.1
Nb	13 mg/kg	94	0	6	12 mg/kg	89.9	5.3	4.8
Ni	20 mg/kg	98	1	1	19 mg/kg	94.6	3.5	1.9
Pb	21 mg/kg	82	3	15	22 mg/kg	87.2	1.3	11.5
Rb	73 mg/kg	99.3	0.3	0.4	73 mg/kg	96.5	3.3	0.2
Sb	<5 mg/kg	0	0	100	<5 mg/kg	12.6	39.9	47.5
Sc	8 mg/kg	92	0	8	8 mg/kg	91.3	0	8.7
Sn	<4 mg/kg	45	0	55	<4 mg/kg	49	15.7	35.4
Sr	100 mg/kg	99.7	0.3	0.1	90 mg/kg	79.4	20.4	0.2
Ta	<5 mg/kg	0	0	100	<5 mg/kg	0	57.6	42.4
Th	9 mg/kg	73.6	5.7	20.8	11 mg/kg	83.8	0	16.2
U	<3 mg/kg	66.5	0	33.5	<3 mg/kg	65	2.7	32.2
V	68 mg/kg	97.2	2	0.8	67 mg/kg	85.7	12.6	1.7
W	<5 mg/kg	37	21	42	<5 mg/kg	41.5	11.1	47.4
Y	27 mg/kg	98.1	0.4	1.5	24 mg/kg	87.4	11.8	0.9
Zn	60 mg/kg	98.4	1.2	0.4	60 mg/kg	97.1	2.1	0.8
Zr	259 mg/kg	98.9	0	1.1	245 mg/kg	98.5	0	1.5

Sorted Ap		***sorted Gr***	
	%		***%***
Parameter	***natVar***	***Parameter***	***natVar***
As	94.4	Nb	89.9
pH_CaCl2	95.6	Sc	91.3
CEC	95.9	Cu	92.5
SO3	96.4	Ga	93.8
V	97.2	Cr	94.3
Ni	98	Ni	94.6
C	97.7	SO3	96.3
Y	98.1	CEC	96.5
P2O5	98.3	Rb	96.5
Cr	98	Zn	97.1
Zn	98.4	TOC	97.2
LOI	98.6	pH_CaCl2	97.7
MnO	98.9	P2O5	97.7
Zr	98.9	MnO	98.2
Fe2O3	99	C	98.4
CaO	99.3	Zr	98.5
K2O	99.3	Fe2O3	98.7
Rb	99.3	LOI	98.7
MgO	99.4	CaO	98.9
Ba	99.4	SiO2	99
TiO2	99.5	TiO2	99.3
Al2O3	99.5	Al2O3	99.3
Na2O	99.5	MgO	99.3
SiO2	99.7	K2O	99.3
Sr	99.7	Na2O	99.5

Table 3 demonstrates that for the majority of elements the data quality is good to excellent, and that the results can be reliably mapped. The most problematic elements in both data sets (Ap and Gr), where care is needed when mapping and using the results are Bi, Ta, Sb, W, F, Hf, Sn, Cl, Cs, U and Mo. The main problems occur often not at the "sampling (site)" but at the "analytical" level. This indicates that even for these elements it would be possible to overcome the problems by further improving their detection limits or by analysing all samples several times and using the median as the "analytical result". In general, these results can be taken as an indication of "good (reproducible) sampling". The "Ap" samples show often somewhat better results than the "Gr" samples. A possible explanation for this feature is that ploughed soils have been homogenised over many years, and the samples may also be more weathered and finer grained or just in general they are more homogeneous. In any case, it appears that agricultural soil is an especially suitable and easy sample material for continental scale geochemical mapping exercises.

4. COMPARISON OF XRF RESULTS WITH EARLIER RESULTS FROM AN AQUA REGIA EXTRACTION

Because for many elements, analysed here by XRF, the partial aqua regia extraction results have already been accepted, it is now possible to compare results from both methods in simple XY plots. Diagrams for all elements where such a plot could be drawn are shown in Appendix 5 and 6. It is also possible to calculate the “extractability” of the elements in an aqua regia extraction. Table 4 displays the extractability results. Extractability shows great variability, depending on element, from close to 100% (*e.g.*, Cu, Co, P) to less than 1% (*e.g.*, Hf, Zr, Na). Depending on the extractability of different elements in aqua regia one would expect to find always higher values for the XRF results (true total concentrations). A relatively good correlation between samples with “low” and “high” concentrations should still be expected between the two methods for many elements. The plots in Appendix 5 show that there are a number of elements where the correlation between aqua regia and XRF results is good (*e.g.*, As, Co, Cu, Fe, Mg, Ni, P, Pb, Zn), and other elements where very different maps must be expected when using aqua regia versus XRF results (*e.g.*, Ba, K, Na, Nb, Ti, Zr). Some outliers in the direction of too high XRF values can be expected due to mineralogical effects, while “too high” values in the aqua regia extraction should not occur. A few samples showed, however, too high values in the aqua regia results – these were all followed up via re-analysis of certain groups of samples and checking the sample locations on maps. In extreme cases, where deviations could not be explained, some single samples were removed from the XRF data set.

Table 4. Extractability of the elements analysed by XRF, delivering true total concentrations, in an aqua regia extraction. Right hand side in alphabetical order; left hand site: sorted according to increasing extractability.

Ap sample	***EXTR %***	***Gr sample***	***EXTR %***
Al	22	Al	22
As	81	As	85
Ba	17	Ba	19
Bi	10	Bi	12

Ap sample	***EXTR %***	***Gr sample***	***EXTR %***
Hf	1	Hf	1
Zr	1	Zr	1
Na	1	Na	1
W	3	Ti	3

Ap sample	***EXTR %***	***Gr sample***	***EXTR %***
Ca	61	Ca	66
Ce	53	Ce	52
Co	83	Co	82
Cr	34	Cr	34
Cs	23	Cs	21
Cu	115	Cu	118
Fe	72	Fe	73
Ga	32	Ga	32
Hf	1	Hf	1
K	8	K	8
La	69	La	63
Mg	55	Mg	56
Mn	80	Mn	81
Mo	41	Mo	40
Na	1	Na	1
Nb	4	Nb	5
Ni	79	Ni	79
P	83	P	83
Pb	77	Pb	83
Rb	21	Rb	20
Sb	9	Sb	13
Sc	29	Sc	28
Sn	33	Sn	42
Sr	19	Sr	21
Th	36	Th	26
Ti	3	Ti	3
U	38	U	52
V	40	V	41
W	3	W	4
Y	25	Y	28
Zn	74	Zn	75
Zr	1	Zr	1

Ap sample	***EXTR %***	***Gr sample***	***EXTR %***
Ti	3	W	4
Nb	4	Nb	5
K	8	K	8
Sb	9	Bi	12
Bi	10	Sb	13
Ba	17	Ba	19
Sr	19	Rb	20
Rb	21	Sr	21
Al	22	Cs	21
Cs	23	Al	22
Y	25	Th	26
Sc	29	Y	28
Ga	32	Sc	28
Sn	33	Ga	32
Cr	34	Cr	34
Th	36	Mo	40
U	38	V	41
V	40	Sn	42
Mo	41	Ce	52
Ce	53	U	52
Mg	55	Mg	56
Ca	61	La	63
La	69	Ca	66
Fe	72	Fe	73
Zn	74	Zn	75
Pb	77	Ni	79
Ni	79	Mn	81
Mn	80	Co	82
As	81	P	83
P	83	Pb	83
Co	83	As	85
Cu	115	Cu	118

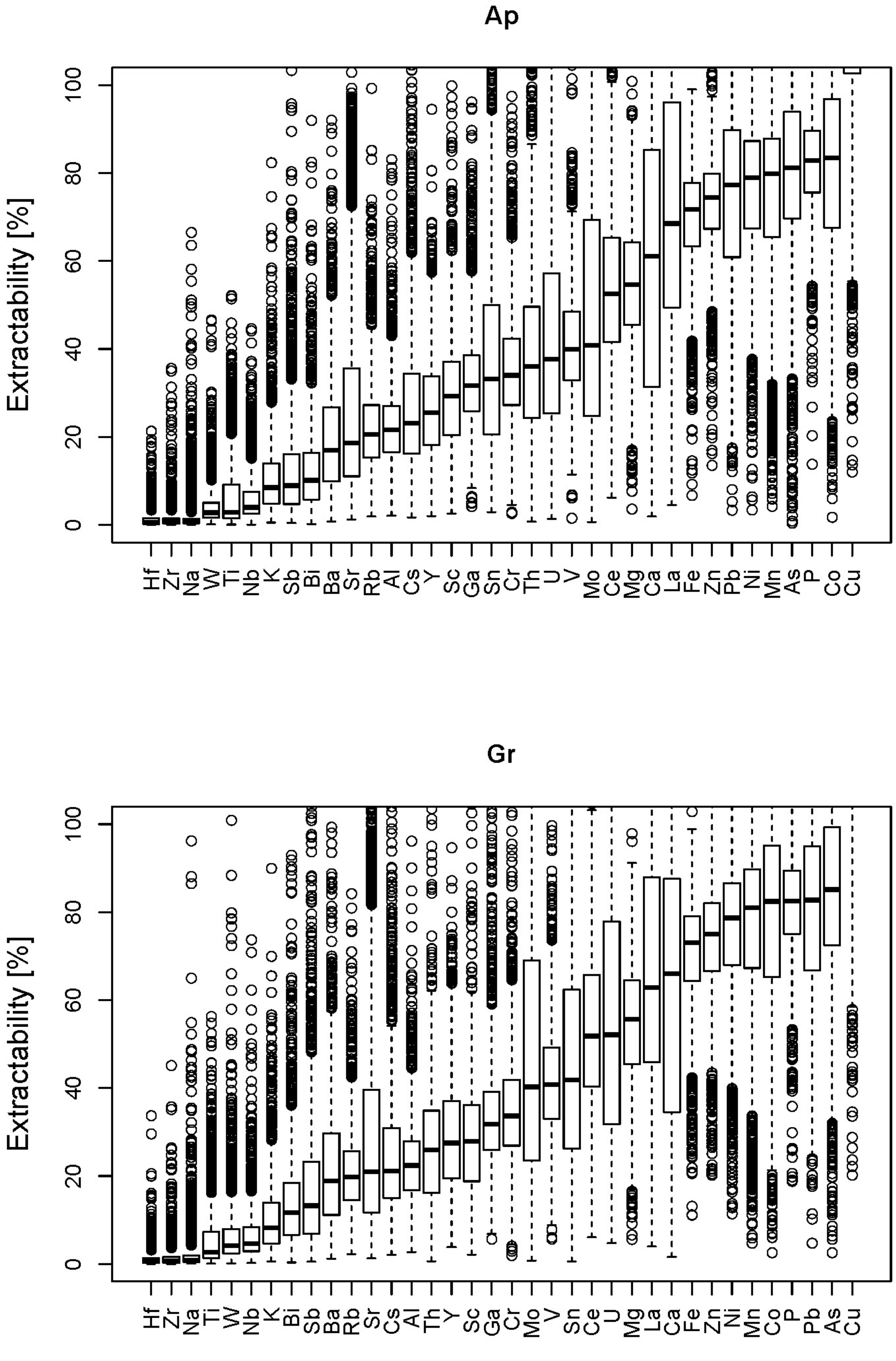


Figure 6. Boxplot comparison of "extractability" for those elements where results from both, XRF and aqua regia extraction exist. The boxplots are sorted according to the median from highest to lowest "extractability".

5. RESULTS – SOME FIRST MAPS

One additional quality criterion will be the appearance of the maps when the analytical results are plotted (Reimann *et al.*, 2008). Figure 7 shows a geochemical map for Si in agricultural soil, and Figure 8 the same map for Si in grazing land soil. The question to be asked is, "*do the maps contain any clear regional features or could they as easily represent random variability due to sampling and analytical errors, indicated by a lack of any significant regional trends*"? The maps show, however, clear regional scale features, the majority of anomalies are verified by several samples. The high values indicate the presence of quartz rich, and often quite coarse grained, soils. This is the final indication of the high quality of the GEMAS project analytical results. Information about data quality, or better suitability for mapping, can also be directly derived from the semivariogram, if kriging was used as the interpolation method (Reimann *et al.*, 2008).

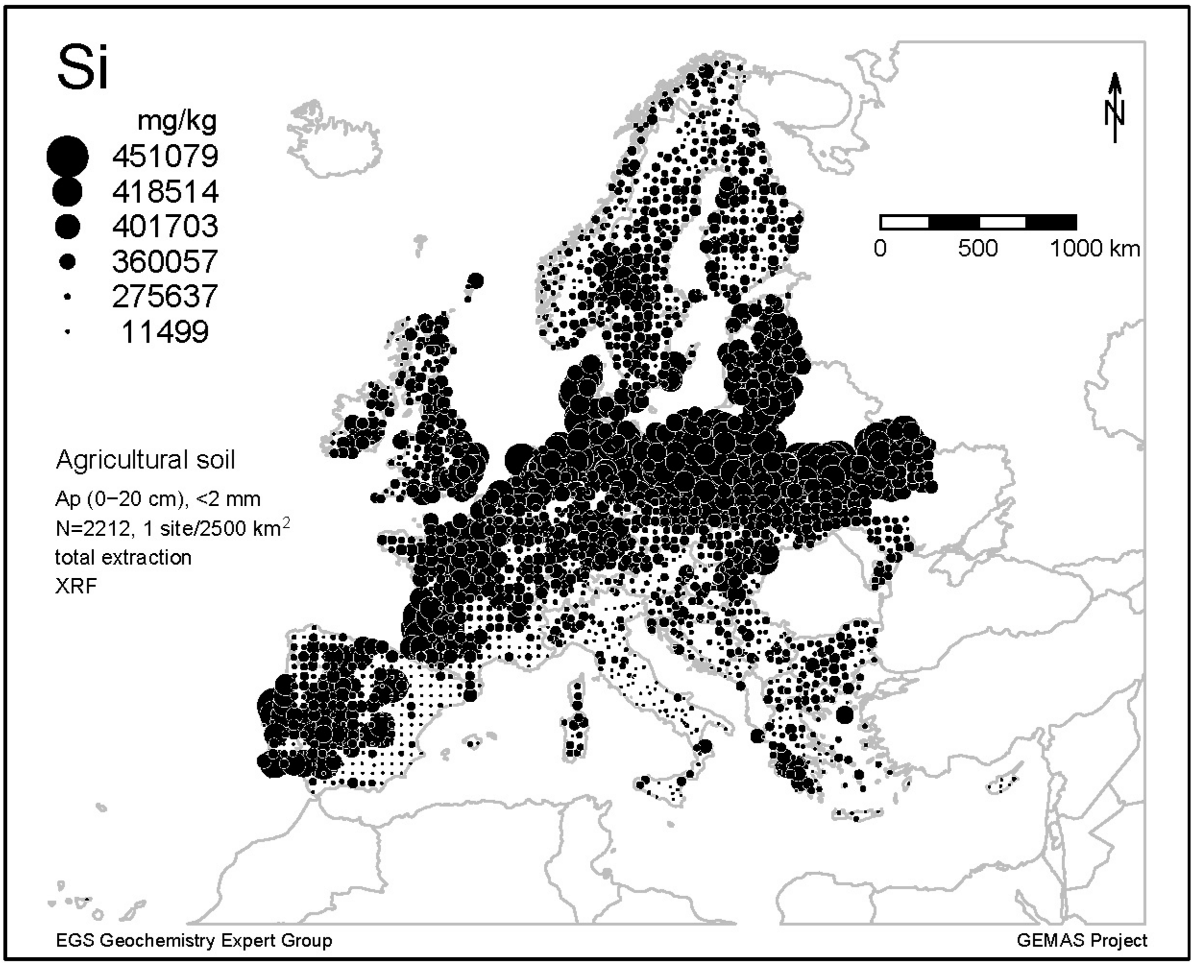


Figure 7. Growing dot map (for a description and discussion of the mapping technique see Reimann et al., 2008) for Si in agricultural soil of Europe (GEMAS Ap-samples).

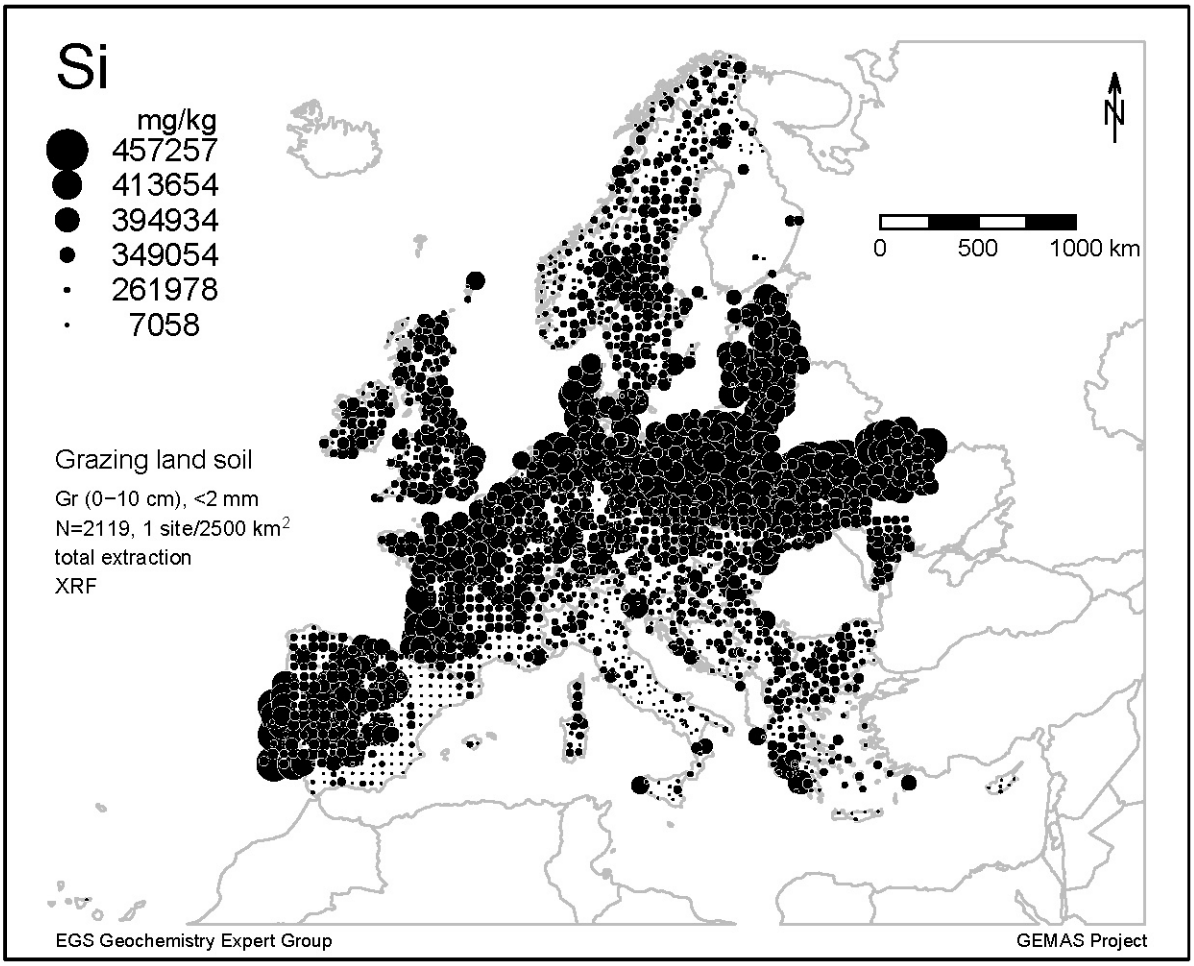


Figure 8. Growing dot map (for a description and discussion of the mapping technique see Reimann et al., 2008) for Si in grazing land soil of Europe (GEMAS Gr samples).

6. RESULTS THAT DID NOT PASS QC – PARTICLE SIZE DISTRIBUTION (PSD)

6.1 History

When results for the particle size distribution were received, and first statistical parameters were calculated for the clay (<2 µm), fine silt (2-20 µm) and sand (20-2000 µm) fraction, it turned out that the data showed unlikely results for the clay fraction. Based on experience with European soils, one should expect a value of about 20% for the clay fraction (Koen Oorts, pers. comm.) for agricultural soils. The PSD data received from FUGRO (now KIWA), however, returned a median of 0.7% clay for the first 800 Ap samples and 0.7% clay for the first 800 Gr-samples.

MIR spectra were measured for all GEMAS samples at CSIRO Land and Water in Adelaide, Australia. MIR-spectra can be used to predict a large variety of soil properties, including PSD, when proper models for the soils in question exist. Originally it was planned to use the 800 samples analysed by FUGRO (now KIWA) to build and validate a model for European soils and to then predict results for all samples. This is of course not possible with so clearly wrong data. However, CSIRO has proper models for Australian soils and these models were then used to predict the clay fraction for the GEMAS samples. Furthermore, the clay fraction in soil samples can be predicted when the effective CEC (i.e. CEC at pH of the soil) and TOC are known (Helling et al., 1964) and as such a second set of results that is independent of MIR predictions was obtained. These results are summarised in Table 5.

Table 5. GEMAS Particle Size Distribution (PSD): comparison of measured values as received from FUGRO (now KIWA) for the first 800 samples of each data set to predicted values for the same 800 samples each based on the Helling equation (Helling et al., 1964 – clay size fraction only) and the Australian soils MIR model of CSIRO.

Sample type	***Clay %***			***Fine silt %***		***Sand %***	
	FUGRO	***HELLING***	***MIR***	***FUGRO***	***MIR***	***FUGRO***	***MIR***
Ap	0.7	22	24.4	46.5	19.2	52.6	56.7
Gr	0.7	19.7	23.5	51	17.8	48	58.2

Both, the Helling equation and the MIR prediction returned quite well comparable values for the clay fraction in the expected range for European agricultural soils.

As a next step the results for the two standards were retrieved from the data set. To be able to compare directly to results from the European norm ISO 11277 (1998), some standard samples were also analysed in the laboratory of Erik Smolders (KUL - Division Soil and Water management, Belgium). Furthermore, the MIR predictions, based on the Australian soils model, were used as well as the results received from the Helling equation. Later on, the two standard samples were also analysed by Sedigraph and using the Köhn pipette method in the laboratory of BGR in Hannover, and by Laser (Coulter) in NGUs laboratory. Results show that large differences must be expected depending on method, and that the original results, as received from FUGRO (now KIWA), were definitely wrong (Table 6).

Table 6. PSD results using different methods for the GEMAS standards Ap and Gr.

	FUGRO (now KIWA), LASER (N=40)			***NGU-lab, Laser (N=5%)***		
Standard	***clay %***	***fine silt %***	***sand %***	***clay %***	***fine silt %***	***sand %***
Ap	1.1	35.6	63.2	15	45.7	39.3
Gr	0.6	26.3	73.1	8.2	28.7	63.2

	ISO 11277 (1998) Erik Smolders (N=2)			***BGR, Köhn pipette (N=5)***		
Standard	***clay %***	***fine silt %***	***sand %***	***clay %***	***fine silt %***	***sand %***
Ap	16.9	27.5	55.7	31.6	29.1	39.3
Gr	17.1	26.4	56.4	21.1	16.2	62.7

	Sedigraph, BGR (N=5)			***CSIRO, MIR-predicitions (N=40)***		
Standard	***clay %***	***fine silt %***	***sand %***	***clay %***	***fine silt %***	***sand %***
Ap	29	36	35	40.8	28.1	31.3
Gr	20.8	17.9	61.3	31.8	21.9	46.2

	Helling equation (N=40)
Standard	***clay %***
Ap	33.8
Gr	26.8

In discussions with the laboratory, it turned out that the wrong optical model was used to calculate the PSD results, and FUGRO (now KIWA) set out to recalculate all results once more. The final results for the last samples were received in April 2011 and are the base for the following QC results.

6.2 QC results for the recalculated PSD values

The last recalculated PSD results were received in April 2011. Standard and duplicate results were retrieved and the median for the 800 Ap and 800 Gr results was calculated.

Table 7 shows the results for the two standards Ap and Gr (N=40 each) as hidden among the first 800 samples. The median for the clay fraction for all samples is now 2.9% (Ap) and 1.9% (Gr) – still by far too low as is also clearly visible for the standards in Table 6. Furthermore, precision (expressed as coefficient of variation CV in Table 7) is very poor for the Ap standard and poor for the Gr standard. Table 8 shows precision as calculated for the duplicate pairs for the most important parameters. Based on the duplicates, precision appears somewhat better (clay fraction: 33% for the Ap samples and 15% for the Gr samples). For all samples, the median value for the clay fraction is now 1.6% for the agricultural soil (Ap) samples and 3% for the Grazing land soil (Gr) samples. This is still by far a too low value for European soils.

For the time being, and until an European soil model can be constructed for the MIR spectra, the only alternative is to use the results based on the Helling equation or the MIR results based on the Australian soil model for the project.

Table 7. Particle size distribution, corrected values for the project standards Ap and Gr (N=40 each). Analytical results (mean, minimum (Min) and maximum (Max) concentration) and coefficient of variation (CV %) for all grain size fractions reported (<X, X in µm; D25, 50 and 75; sort index (SI) and percentages of the clay, silt and sand fraction). For comparison, results received for the clay, sand and silt fraction from the MIR predictions, based on the Australian soil model, are also provided.

Parameter	***Agricultural soil (Ap)***					***Grazing land soil (Gr)***				
	Mean	***Min***	***Max***	***StDev***	***CV %***	***Mean***	***Min***	***Max***	***StDev***	***CV %***
<1.95	2.7	0.8	5.1	1.412	53	3.1	1.6	4.6	0.786	25
<9.48	26.9	17.1	34.4	4.744	18	21.1	12.2	30.2	4.747	22
<20.9	43.4	30.2	54.8	8.505	20	33.1	19.0	46.8	7.232	22
<68.33	66.0	45.5	82.1	12.430	19	52.0	30.7	70.4	9.430	18
<2000	100	100	100			100	100	100		
D25	9.2	6.7	15.4	2.412	26	14.4	7.2	40.1	6.411	45
D50	37.0	17.1	92.9	21.546	58	68.9	24.4	182	35.813	52
D75	381	48.5	1104	403.15	106	228	90.4	491	79.424	35
SI	5.4	2.4	11.6	3.278	60	4.1	3.1	5.4	0.555	14
clay%	2.6	0.8	5.1	1.418	54	3.1	1.6	4.6	0.788	25
silt%	59.8	39.7	76.5	12.745	21	45.6	26.8	62.1	8.537	19
sand%	37.6	21.8	57.3	12.020	32	51.3	33.3	71.6	9.304	18
MIR_clay%	40.7	36.0	43.0	1.457	4	32	28	37	2.100	7
MIR_finesilt%	27.8	23.0	31.0	1.527	5	22	12	25	2.265	11
MIR_sand%	31.4	28.0	38.0	2.394	8	46	40	54	3.020	7

Table 8. Precision as calculated using the duplicate results among the first 800 GEMAS Ap and Gr samples for the key PSD parameters.

Parameter	***Ap samples***	***Gr samples***
	Precision %	***Precision %***
D25	42	76
D50	108	109
D75	37	70
SI	21	25
clay	33	15
fine silt	10	17
sand	11	21
MIR_clay	10	17
MIR_fine silt	10	16
MIR_sand	6	9

It is actually known, that the laser method underestimates the clay (<2 µm) fraction substantially, and some authors have suggested that the <8 µm fraction should be used as a substitute for the clay fraction when the laser method is used (Konert and Vandenberghe, 1997). The overall median of the <9.48 µm fraction of the FUGRO (now KIWA) results corresponds quite well with the expected median for the standards according to the Köhn pipette method, however, the variation observed for the standards is still high (around 20%) and the results for all samples do not correlate well with the predicted clay content based on either the MIR spectra or the Helling equation.

All metal bioavailability work is based on results from the pipette method, which is also standard in soil sciences (but not any longer in geosciences), and thus data that are comparable to this method are needed. It is, however, unrealistic to analyse thousands or even hundreds of samples according to ISO 11277 (1998) within a realistic time and budget. Based on the results of the quality control procedures, the much too low results for the clay fraction, the high variability and the lack of any correlation with the ISO 11277 (1998) method-conform data for the clay fraction, the PSD results obtained by the laser method from FUGRO (now KIWA) must unfortunately be rejected from further use in the GEMAS project. At present an attempt is being made to build a European soil model for MIR predictions, based on a limited number of Sedigraph analyses at BRGs laboratory.

7. CONCLUSIONS

Results of quality control of the analytical results for C, S, CEC, TOC, pH_CaCl$_2$, LOI and major and trace elements by XRF (SiO$_2$, TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, MnO, MgO, CaO, Na$_2$O, K$_2$O, P$_2$O$_5$, SO$_3$, Cl, F, As, Ba, Bi, Ce, Co, Cr, Cs, Cu, Ga, Hf, La, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Sn, Sr, Ta, Th, U, V, W, Y, Zn and Zr) revealed a number of problems that needed to be resolved before the data could be accepted. For some parameters clear time trends or breaks in the concentration range were detected, most were within, however, the overall agreed precision bands. Nevertheless, such effects would lead to artefacts on the maps, if the samples had not been randomised. One such example concerns the CEC-results, Ap-samples, where a sudden break toward lower values was detected for the second half of the samples. No reason for this effect could be identified, and the results needed to be accepted as they stand. This was only possible because all samples had been randomised prior to submission to the laboratory. For randomised samples, such artefacts will result in an overall declining precision, but do not give any discernible patterns on the maps. For the laboratories, these plots clearly identify areas where quality improvements are needed.

Quality control of the particle size distribution results revealed so bad quality, both, before and after correction by the external laboratory (FUGRO, now KIWA), that the data had to be rejected from further use in the project. Judging by all results received so far, it is questionable that reliable PSD results, comparable to the the ISO 11277 (1998)-method, can be expected from a laser-based method. A prediction based on MIR spectra promises to be the considerably better solution for fast and easy PSD ISO 11277 (1998) comparable determinations for large data sets. This requires, however, that a MIR model is built and validated for European soils.

Trueness of the results can at present not be evaluated. This will need additional analyses of the GEMAS project standards by a number of external laboratories, and all results are expected and will be reported during 2011.

For a number of elements, the majority of the analytical results are very close to the method detection limits (*e.g.*, Sb, Bi, Ta, W, F, Hf, Sn and Cl), and it is here that most quality problems are observed. In all instances, where poor precision was observed this was due to very low concentrations of the measured elements/parameters in the samples. Even for such elements/parameters the high values (upper outliers) will usually be quite reliable. Nevertheless, there is definitely still room for improvements in analytical methodology (detection limits) for a number of interesting elements/parameters.

Results of the unbalanced ANOVA indicate that most elements/parameters covered in this report can be reliably mapped. Exceptions are the XRF results for Sb, Bi, Ta, W, F, Hf, Sn and Cl, where maps must be viewed with great care. However, due to the fact that all samples were randomised prior to analysis, multi-sample anomalies will still be reliable even for these elements. ANOVA also demonstrates that the main problems with technical variability occur at the analytical level. This indicates that the GEMAS sampling, as such, was of good quality and the samples large enough to be representative for the site. The main (and well known) problem with XRF analyses are the rather high detection limits of the method for many trace elements.

ACKNOWLEDGEMENTS

The GEMAS project is a cooperation project of the EuroGeoSurveys Geochemistry Expert Group with a number of outside organisations (*e.g.*, Alterra in The Netherlands, the Norwegian Forest and Landscape Institute, several Ministries of the Environment and University Departments of Geosciences in a number of European countries, CSIRO Land and Water in Adelaide, Australia).

All colleagues organising sampling in their countries, as well as the many field teams, are acknowledged for the work they have put into this project: *Austria:* Albert Schedl, Heinz Reitner, Edith Haslinger, Peter Filzmoser; *Belgium:* Walter De Vos; *Bosnia & Herzegovina*: Hazim Hrvatovic; Neven Miosic, Ferid Skopljak, Natalija Samardzic; *Bulgaria*: Valeri Trendavilov; *Croatia*: Josip Halamić, Ajka Šorša, Stjepan Husnjak; *Czech Republic*: Miloslav Duris; *Cyprus*: Zomenia Zomeni; *Denmark*: Vibeke Ernstsen; *Estonia*: Jaan Kivisilla, Walter

Petersell; *Finland*: Timo Tarvainen, Mikael Eklund; *France*: Ignace Salpeteur; *F.Y.R.O.M.*: Trajce Stafilov; *Germany*: Manfred Birke, Rainer Hoffmann, Jens Utermann, Beate Keilert, Lars Kaste, Michael Fuchs, Friedrich Krone; *Hellas*: Alecos Demetriades; *Hungary*: Gyozo Jordan, Ubul Fugedi, Laszlo Kuti; *Ireland*: Patrick O'Connor, Fionnuala Ni Mhairtin, Vincent Gallagher; *Italy*: Benedetto De Vivo, Annamaria Lima, Stefano Albanese, Enrico Dinelli, Domenico Cicchella, Paolo Valera; *Latvia*: Aivars Gilucis; *Lithuania*: Virgilija Gregorauskiene; *Luxembourg*: Robert Maquil; *Netherlands, The*: Gerben Mol; *Norway*: Clemens Reimann, Rolf Tore Ottesen, Tore Volden, Ola A. Eggen, Arnold Arnoldussen; *Poland*: Anna Pasieczna, Aleksandra Dusza, Paweł Kwecko; *Portugal*: Maria Joao Batista, Cátia Prazeres; *Serbia*: Aleksandra Gulan, Dragana Vidojević; *Slovakia*: Igor Slaninka, Peter Sefcik, Daniela Mackovych, Silvester Pramuka; *Slovenia*: Mateja Gosar; *Spain*: Juan Locutura, Alejandro Bel-lan; *Sweden*: Madelen Andersson, Kaj Lax; *Switzerland*: Peter Hayoz, Reto Giulio Meuli; *Ukraine*: Boris I. Malyuk, Volodymyr Klos; *United Kingdom*: Dee Flight, Andreas Scheib, Mick Strutt, Paul McDonnell.

All analytical results of the samples are provided to the country of origin immediately following the assessment of quality control results. The commodities organised in Eurometaux, financing parts of the project, are thanked for their input and continued interest in the project. Each commodity has immediate access to "its" element at the European scale.

All data (much more to come) will be published in an EGS Geochemical Atlas around 2012/2013, and until then they will be treated as confidential (non-available to project outsiders; no contribution – no data).

Very special thanks are due to Ilse Schoeters, who arranged the Expert Group’s contact with Eurometaux and made this all possible, and to Robert G. Garrett of the Geological Survey of Canada, who established the first contact between Ilse and the Geochemistry Expert Group’s chairman.

The analytical work was financed by the following organisations: Eurometaux, Cobalt Development Institute (CDI), European Copper Institute (ECI), Nickel Institute, Europe, European Precious Metals Federation (EPMF), International Antimony Association (i2a), International Manganese Institute (IMnI), International Molybdenum Association (IMoA), ITRI Ltd. (on behalf of the REACH Tin Metal Consortium), International Zinc Association (IZA), International Lead Association-Europe (ILA-Europe), European Borates Association (EBA), the (REACH) Vanadium Consortium (VC) and the (REACH) Selenium and Tellurium Consortium.

Finally, the directors of the European Geological Surveys and the additional participating organisations, are thanked for making sampling of almost all of Europe, in such a tight time schedule possible – quite a few budgets had to be accommodated on very short notice.

REFERENCES

Bølviken, B., Sinding-Larsen, R., 1973. Total error and other criteria in the interpretation of stream-sediment data. In: M.J. Jones (Editor), Geochemical Exploration 1972. Inst. Min. Metall., London, 285-295.

Brandvold, L.A., McLemore, V.T., 1998. A study of the analytical variation of sampling and analysis of stream-sediments from areas contaminated by mining and milling. J. Geochem. Explor. 64, 185-196.

Darnley, A., Björklund, A., Bølviken, B., Gustavson, N., Koval, P.V., Plant, J.A., Steenfelt, A., Tauchid, M., Xuejing, X., 1995. A global geochemical database for environmental and resource management. Recommendations for international geochemical mapping. Final report of IGCP-project 259, UNESCO Publishing, Paris, France, 122p.

De Vos, W., Tarvainen, T. (Chief-editors), Salminen, R., Reeder, S., De Vivo, B., Demetriades, A., Pirc, S., Batista, M. J., Marsina, K., Ottesen, R. T., O'Connor, P. J., Bidovec, M., Lima, A., Siewers, U., Smith, B., Taylor, H., Shaw, R., Salpeteur, I., Gregorauskiene, V., Halamic, J., Slaninka, I., Lax, K., Gravesen, P., Birke, M., Breward, N., Ander, E.L., Jordan, G., Duris, M., Klein, P., Locutura, J., Bel-lan, A., Pasieczna, A., Lis, J., Mazreku, A., Gilucis, A., Heitzmann, P., Klaver, G., Petersell, V., 2006. Geochemical Atlas of Europe, Part 2: Interpretation of Geochemical Maps, Additional Tables, Figures, Maps, and Related Publications. Geological Survey of Finland, Espoo, Finland, 690p. ISBN 951-690-956-6 [also available from: http://www.gtk.fi/publ/foregsatlas/].

Demetriades, A., 2009. Quality control procedures in applied geochemical surveys. Open File Report, Institute of Geology and Mineral Exploration, Athens, Hellas (in Greek with an English summary).

Demetriades, A., 2011. Understanding the quality of chemical data fron the urban environment – Part 2: Measurement uncertainty in the decision-making process. In: C.C. Johnson, A. Demetriades, J. Locutura, R.T. Ottesen (Editors), Mapping the chemical environment of urban areas. Wiley-Blackwell, Chichester, U.K., 77-98.

Demetriades, A., Karamanos, E., 2003. Quality assurance and quality control (QA/QC) for in-situ geochemical methods, estimation of measurement uncertainty and construction of probability risk assessment maps. Network Oriented Risk-assessment by In-situ Screening of Contaminated sites (NORISC), European Commission co-financed project, EVK4-CT-2000-00026. NORISC consortium report, Cologne, 20p.

DIN-EN 725-5, 2007. Advanced technical ceramics - Methods of test for ceramic powders - Part 5: Determination of the particle size distribution. DIN Deutsches Institut für Normung e.V., Berlin.

EC, 2006a. Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC. Official Journal of the European Union, Luxemburg, L 396/1-849 [http://ec.europa.eu/environment/chemicals/reach/reach_intro.htm].

EC, 2006b. Thematic Strategy for Soil Protection. Communication from the Commission to the Council, the European Parliament, the European Economic and Social Committee and the Committee of the Regions. Commission of the European Communities, Brussels, 22.9.2006, COM(2006)231 final, 12p. [http://eur-lex.europa.eu/smartapi/cgi/sga_doc?smartapi!celexplus!prod!DocNumber&lg=en&type_doc=COMfinal&an_doc=2006&nu_doc=231].

EC, 2009. Towards 2020: Making Chemicals Safer - The EU's contribution to the Strategic Approach to International Chemicals Management. Office for Official Publications of the European Communities, Luxemburg, 40p. [http://ec.europa.eu/environment/chemicals/reach/pdf/SAICM_09%20_en.pdf].

EEC, 1996. Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. Official Journal of the European Communities, Luxemburg, L181, 04/07/1986, 0006 – 0012 [http://europa.eu/legislation_summaries/agriculture/environment/l28088_en.htm] [http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31986L0278:EN:HTML].

EGS, 2008. EuroGeoSurveys Geochemistry Working Group. EuroGeoSurveys geochemical mapping of agricultural and grazing land in Europe (GEMAS) – Field manual. NGU report 2008.038, Norges geologiske undersøkelse,Trondheim, Norway, 46p.

Fauth, H., Hindel, R. Siewers, U., Zinner, J., 1985. Geochemischer Atlas Bundesrepublik Deutschland. Verteilung von Schwermetallen in Wässern und Bachsedimenten. Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover. Schweizerbart'sche Verlagsbuchandlung, Stuttgart, 79p.

Fletcher, W.K., 1981. Analytical methods in geochemical exploration. G.J.S. Govett (Editor), Handbook of Exploration Geochemistry, Vol., 1. Elsevier, Amsterdam, 25-46.

Fletcher, W.K., 1986. Analysis of soil samples. Chapter 4, In: W.K. Fletcher, S.J. Hoffman, M.B. Mehrtens, A.J. Sinclair & I. Thompson (Editors), Exploration geochemistry: Design and interpretation of soil surveys. Reviews in Economic Geology, Volume 3, Society of Economic Geologists, University of Texas, USA, 79-96.

Garrett, R.G., 1969. The determination of sampling and analytical errors in exploration geochemistry. Econ. Geol. 64, 568-574.

Garrett, R.G., 1973. The determination of sampling and analytical errors in exploration geochemistry - a reply. Econ. Geol. 68, 282-283.

Garrett, R.G., 1983. Sampling methodology. In: R.J. Howarth (Editor), Statistics and Data Analysis in Geochemical Prospecting, Vol. 2, Chapter 4. G.J.S. Govett (Editor), Handbook of Exploration Geochemistry. Elsevier, Amsterdam, 83-110.

Garrett, R.G., Goss, T.I., 1978. The statistical appraisal of survey effectiveness in regional geochemical surveys for Canada's uranium reconnaissance program. Math. Geol. 12, 443-458.

Garrett, R.G., Kane, V.G., Zeigler, R.K., 1980. The management and analysis of regional geochemical data. J. Geochem. Explor. 13, 115-152.

Helling C.S., Chesters G., Corey R.B., 1964. Contribution of organic matter and clay to soil cation-exchange capacity as affected by the pH of the saturating solution. Soil Science Society of America Proceedings 28, 517-520.

Howarth, R.J., Lowestein, P.L., 1971. Sampling variability of stream sediments in broad-scale regional geochemical reconnaissance. Trans. Inst. Min. Metall. 80, B363-372.

Howarth, R.J., Thompson, M., 1976. Duplicate analysis in geochemical practice, Part II. Analyst 101, 699-709.

ISO 11277, 1998. International Organisation for Standardisation. Soil quality - Determination of particle size distribution in mineral soil material - Method by sieving and sedimentation.

ISO/FDIS 13528, 2005. International Organisation for Standardisation. Statistical methods for use in proficiency testing by interlaboratory comparisons.

ISO 13320, 2009. International Organisation for Standardisation. Particle size analysis - Laser diffraction methods.

Johnson, C.C., 2011. Understanding the quality of chemical data fron the urban environment – Part 1: Quality control procedures. In: C.C. Johnson, A. Demetriades, J. Locutura, R.T. Ottesen (Editors), Mapping the chemical environment of urban areas. Wiley-Blackwell, Chichester, U.K., 61-76.

Kermack, K.A., Holdane, J.B.S., 1950. Organic correlation and allometry. Biometrika 37, 30-41.

Konert. M., Vandenberghe, J., 1997. Comparison of laser grain size analysis with pipette and sieve analysis: a solution for the underestimation of the clay fraction. Sedimentology 44, 523–535.

Massart, D.L., Vandeginste, B.G.M., Deming, S.N., Michotte, Y., Kaufmann, L., 1988. Chemometrics: A Textbook. Data Handling in Science and Technology – Volume 2. Elsevier, Amsterdam, The Netherlands, 488p.

Miesch, A.T, 1964. Effects of sampling and analytical error in geochemical prospecting. In: G.A. Parks (Editor), Computers in the Mineral Industry, Part 1. Stanford University Publ. Geol. Sci., 9 (1), 156-170.

Miesch, A.T., 1967. Theory of error in geochemical data. U.S. Geol. Surv., Prof. Paper 574-A, 17p.

Miesch, A.T., 1973. The determination of sampling and analytical errors in exploration geochemistry - a reply. Econ. Geol. 68, 281-282.

Miesch, A.T., 1976. Geochemical survey of Missouri: methods of sampling, laboratory analysis and statistical reduction of data. U.S. Geol. Surv. Prof. Paper 954-A, 39p.

Müller, H.-W., Dohrmann, R., Klosa, D., Rehder, S., Eckelmann, W., 2009. Comparison of two procedures for particle-size analysis: Köhn pipette and X-ray granulometry. J. Plant Nutr. Soil Sci. 172, 172-179.

Plant, J., 1973. A random numbering system for geochemical samples. Trans. Instn. Min. Metall. 82, B63-B66.

Plant, J., Slater, D., 1986. Regional geochemistry – potential developments. Trans. Instn. Min. Metall. 95, B63-B70.

Plant, J.A., Jeffery, K. Gill, E., Fage, C., 1975. The systematic determination of accuracy and precision in geochemical exploration data. J. Geochem. Explor. 4, 467-486.

Pleysier, J.L., Juo, A.S.R., 1980. A Single-Extraction Method Using Silver-Thiourea for Measuring Exchangeable Cations and Effective CEC in Soils With Variable Charges. Soil Science 129, 205-211.

Ramsey, M.H., 1998. Sampling as a source of measurement uncertainty: techniques for quantification and comparison with analytical sources. Journal of Analytical Atomic Spectrometry, 13, 97-104. Paper and program ROBCOOP4.EXE available from http://www.rsc.org/jaas (last access 25 May 2011).

Reimann, C., 1986. Externe Laborkontrolle für Geochemieprojekte - Notwendigkeit oder übertriebener Aufwand? Mitteilungen der Österreichischen Geologischen Gesellschaft 79, 175-191.

Reimann, C., 1989. Reliability of geochemical analyses: recent experiences. Trans. Instn. Min. Metal. 98, B123-B130.

Reimann, C., 2005. Sub-continental scale geochemical mapping: sampling, quality control and data analysis issues. Geochemistry, Exploration, Environment, Analysis 5, 311-323.

Reimann, C., Wurzer, F., 1986. Monitoring accuracy and precision - improvements by introducing robust and resistant statistics. Mikrochimica Acta 1986 II(1-6), 31-42.

Reimann, C., Äyräs, M., Chekushin, V.A., Bogatyrev, I., Boyd, R., Caritat, P. de, Dutter, R., Finne, T.E., Halleraker, J.H., Jæger, Ø., Kashulina, G., Niskavaara, H., Lehto, O., Pavlov, V., Räisänen, M. L., Strand, T., Volden, T., 1998. Environmental geochemical atlas of the central Barents Region. NGU-GTK-CKE special publication. Geological Survey of Norway, Trondheim, Norway, 745p., ISBN 82-7385-176-1.

Reimann, C., Siewers, U., Tarvainen, T., Bityukova, L., Eriksson, J., Gilucis, A., Gregorauskiene, V., Lukashev, V.K., Matinian, N.N., Pasieczna, A., 2003. Agricultural Soils in Northern Europe: A Geochemical Atlas. Geologisches Jahrbuch, Sonderhefte, Reihe D, Heft SD 5, Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, 279p, ISBN 3-510-95906-X.

Reimann, C., Filzmoser, P., Garrett, R.G., Dutter, R., 2008. Statistical Data Analysis Explained. Applied Environmental Statistics with R. Wiley, Chichester, 343p.

Reimann,C., Matschullat, J., Birke, M., Salminen, R., 2009. Arsenic distribution in the environment: the effects of scale. Appl. Geochem. 24, 1147-1167.

Rühling, Å., Steinnes, E., 1998. Atmospheric heavy metal deposition in Europe 1995 – 1998. Nordic Council of Ministers, Nord 1998, 15, 66 p.

Salminen, R. (Chief-editor), Batista, M.J., Bidovec, M. Demetriades, A., De Vivo. B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Å., Ottesen, R.-T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A., Tarvainen, T., 2005. Geochemical Atlas of Europe. Part 1 – Background Information, Methodology and Maps. Geological Survey of Finland, Espoo, Finland, 526p. ISBN 951-690-921-3 [also available at: http://www.gtk.fi/publ/foregsatlas/].

Scheffé, H., 1959. The analysis of variance. John Wiley and Sons Inc., New York, 477p. (reprinted 1999 by Wiley Interscience, New York).

Searle, P.L., 1984. The measurement of soil cation-exchange properties using the single extraction, silver thiourea method - an evaluation using a range of New-Zealand soils. Aust. J. Soil Res. 24(2), 193-200.

Sumner, M.E., Miller, W.P., 1996. Cation exchange capacity and exchange coefficients. p. 1201-1230. In Sparks D.L., ed. Methods of Soil Analysis, Part 3. Chemical Methods. Soil Science Society of America Book Series Number 5. American Society of Agronomy, Madison, WI.

Thompson, M., Howarth, R.J., 1976. Duplicate analysis in geochemical practice. Part 1. Theoretical approach and estimation of analytical reproducibility. Analyst 101, 690-698.

Thompson, M., Howarth, S.R., 1978. A new approach to the estimation of analytical precision. J. Geochem. Explor. 9, 23-30.

Thompson, M., Howarth, R.J., 1980. The frequency distribution of analytical error. Analyst 105, 1188-1195.

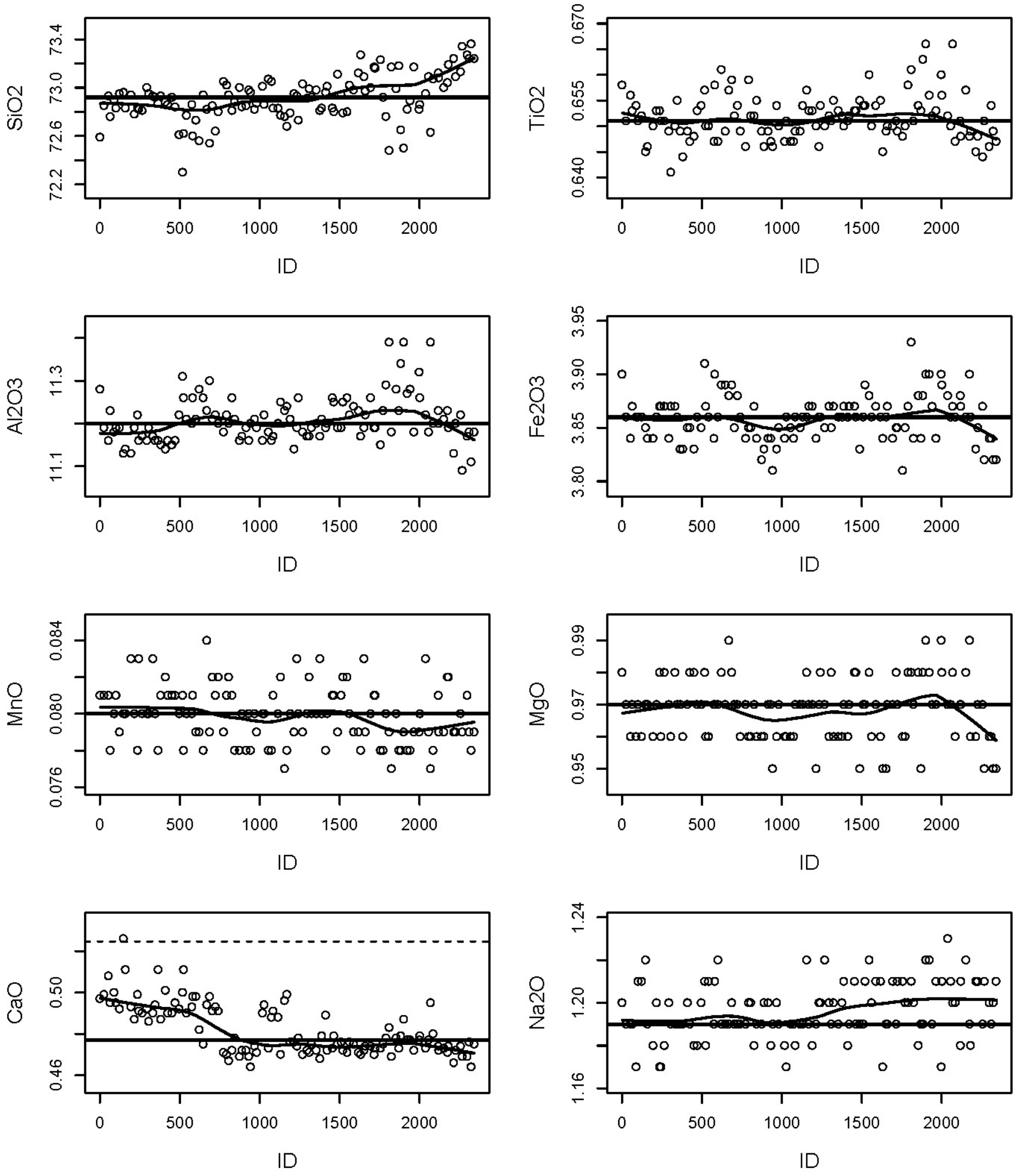
Thompson, M., Maguire, M., 1993. Estimating and using sampling precision in surveys of trace constituents of soils. Analyst 118, 1107-1110.

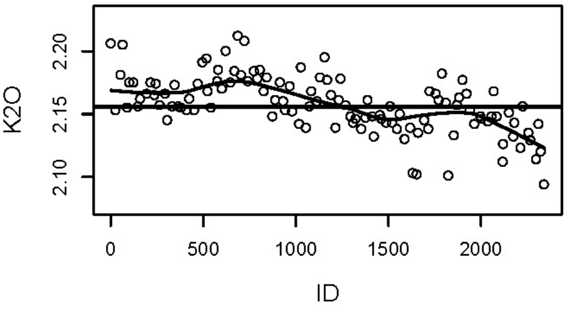
Till, R., 1974. Statistical methods for the earth scientist – an introduction. The Macmillan Press Ltd., London, 154p.

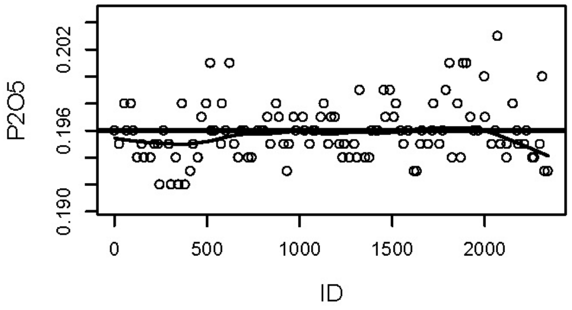
Van-Camp, L., Bujarrabal, B., Gentile, A.R., Jones, R.J.A., Montanarella, L., Olazabal, C., Selvaradjou, S-K., 2004. Reports of the Technical Working Groups established under the Thematic Strategy for Soil Protection, volumes 1 to 6. [Available at http://eusoils.jrc.ec.europa.eu/ESDB_Archive/eusoils_docs/doc.html#OtherReports].

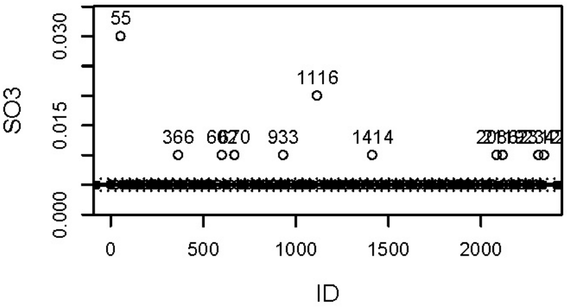
APPENDIX 1. X-Charts for the project standard Gr

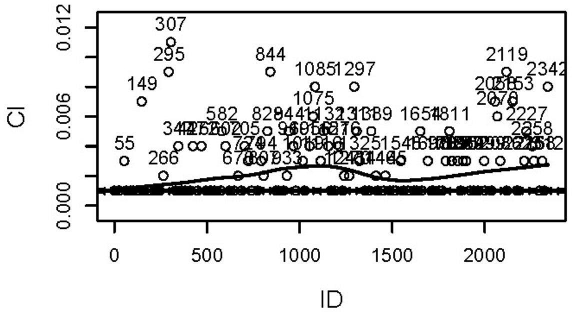
Sample number (ID) is plotted against analytical result for the standard. The thick black line indicates the median value of all standard results, and the dashed line is the limit for 10%, the dotted line for 20% deviation from the median. Standard results that show a larger deviation than 30% from the median are indicated by sample number. The trend line is a loess regression line for the standard results and would help to identify time trends or breaks in the data.

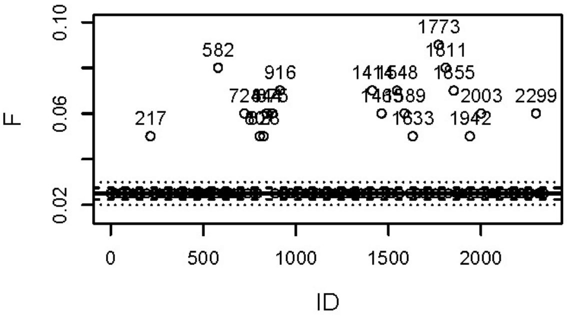

SiO2
72.2
72.6
73.0
73.4
TiO2
0.640
0.655
0.670
Al2O3
11.1
11.3
Fe2O3
3.80
3.85
3.90
3.95
MnO
0.076
0.080
0.084
MgO
0.95
0.97
0.99
CaO
0.46
0.50
Na2O
1.16
1.20
1.24
0
500
1000
1500
2000
ID

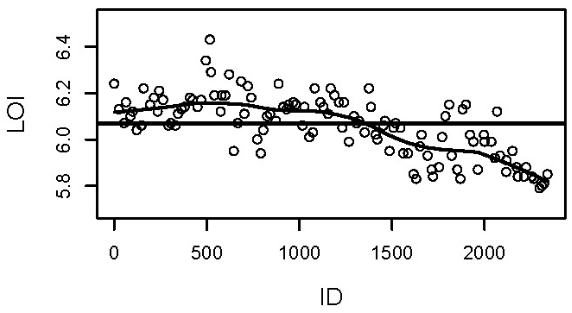

K2O
2.10
2.15
2.20
0
500
1000
1500
2000
ID

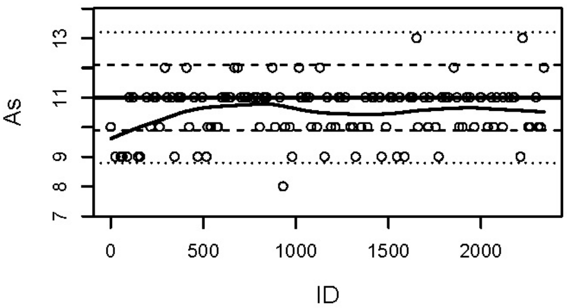

P2O5
0.190
0.196
0.202
0
500
1000
1500
2000
ID

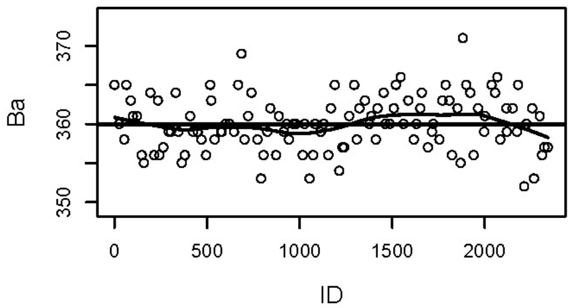

SO3
0.000
0.015
0.030
55
1116
366
670
933
1414
0
500
1000
1500
2000
ID

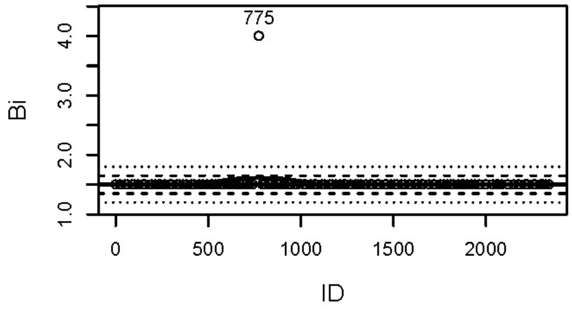

Cl
0.000
0.006
0.012
307
295
844
1085
1297
2119
149
2342
1075
582
1811
2227
2358
55
266
0
500
1000
1500
2000
ID

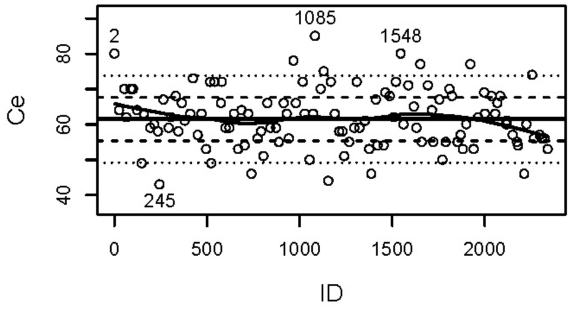

F
0.02
0.06
0.10
1773
582
1811
916
1414
1548
1855
2003
2299
217
1633
1942
0
500
1000
1500
2000
ID

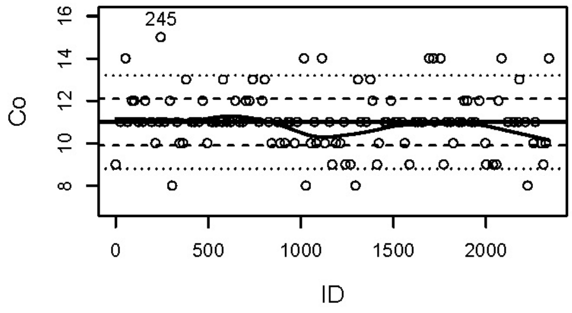

LOI
5.8
6.0
6.2
6.4
0
500
1000
1500
2000
ID

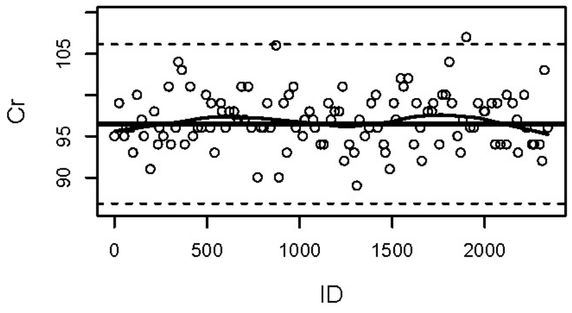

As
7
8
9
11
13
0
500
1000
1500
2000
ID

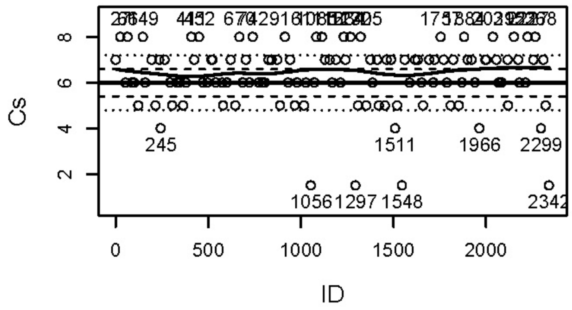

Ba
350
360
370
0
500
1000
1500
2000
ID

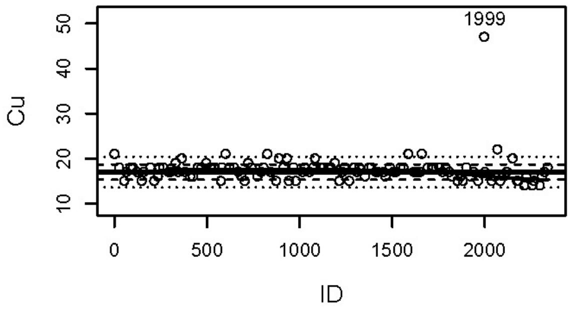

Bi
1.0
2.0
3.0
4.0
775
0
500
1000
1500
2000
ID

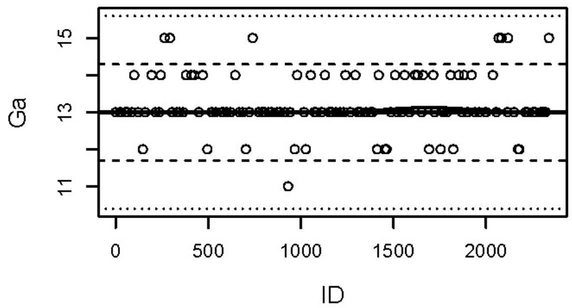

Ce
40
60
80
2
1085
1548
245
0
500
1000
1500
2000
ID

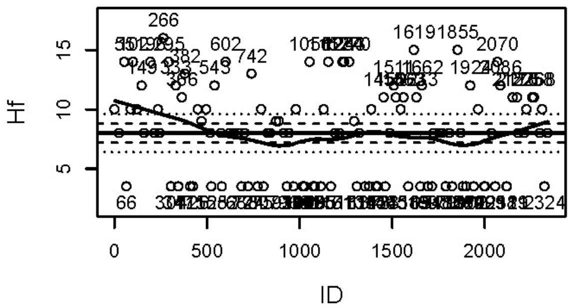

Co
8
10
12
14
16
245
0
500
1000
1500
2000
ID

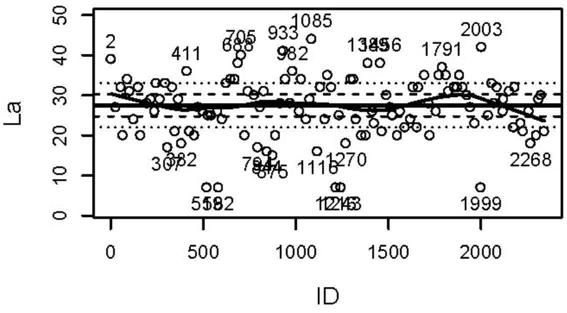

Cr
90
95
105
0
500
1000
1500
2000
ID

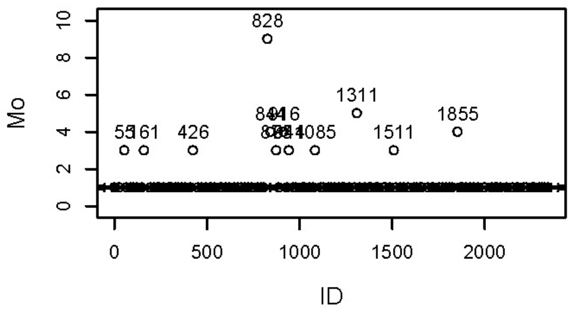

Cs
2
4
6
8
245
1511
1966
2299
1056
1297
1548
2342
0
500
1000
1500
2000
ID

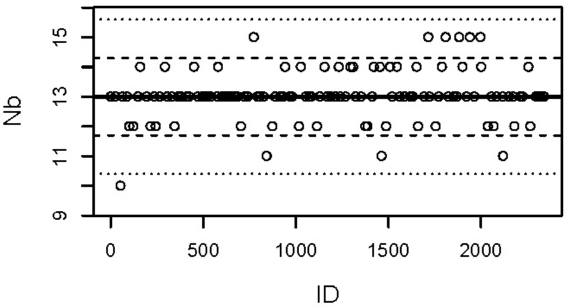

Cu
10
20
30
40
50
1999
0
500
1000
1500
2000
ID

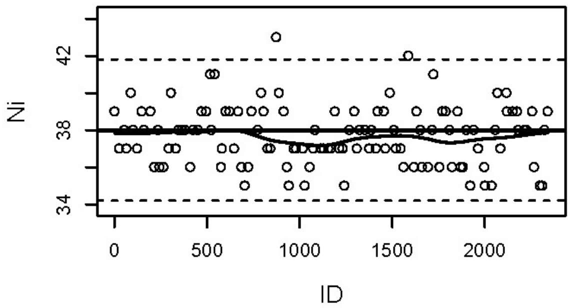

Ga
11
13
15
0
500
1000
1500
2000
ID

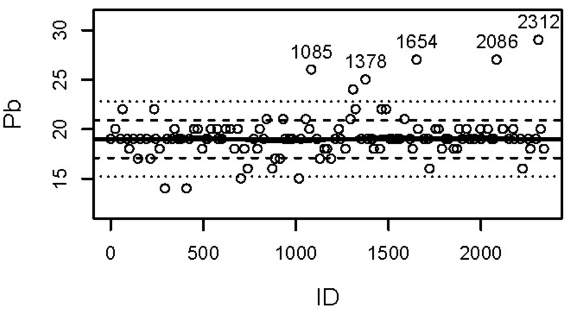

Hf
5
10
15
266
602
742
543
1619
1855
2070
1662
66
2324
0
500
1000
1500
2000
ID

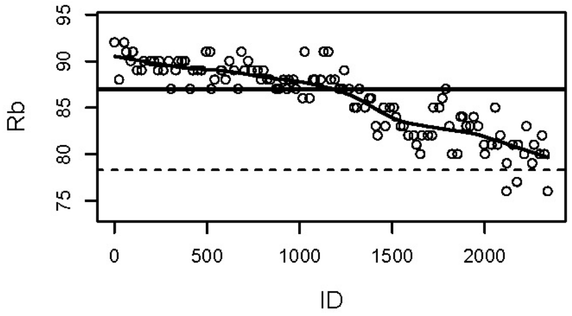

La
ID
0
10
20
30
40
50
500
1000
1500
2000
2
411
705
933
1085
982
1791
2003
307
382
794
875
1116
1270
558
582
1999
2268

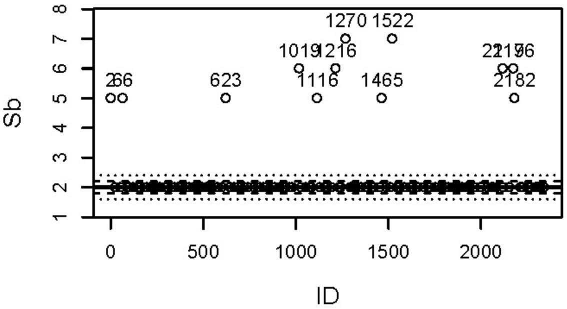

Mo
ID
0
2
4
6
8
10
500
1000
1500
2000
828
1311
1855
55
161
426
1085
1511

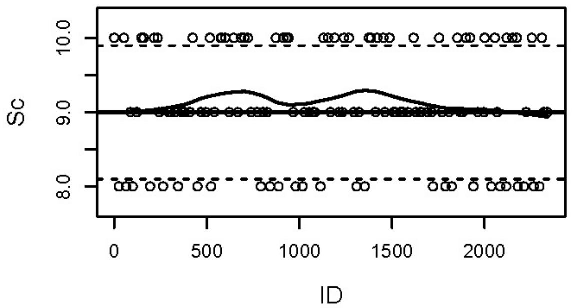

Nb
ID
9
11
13
15
0
500
1000
1500
2000

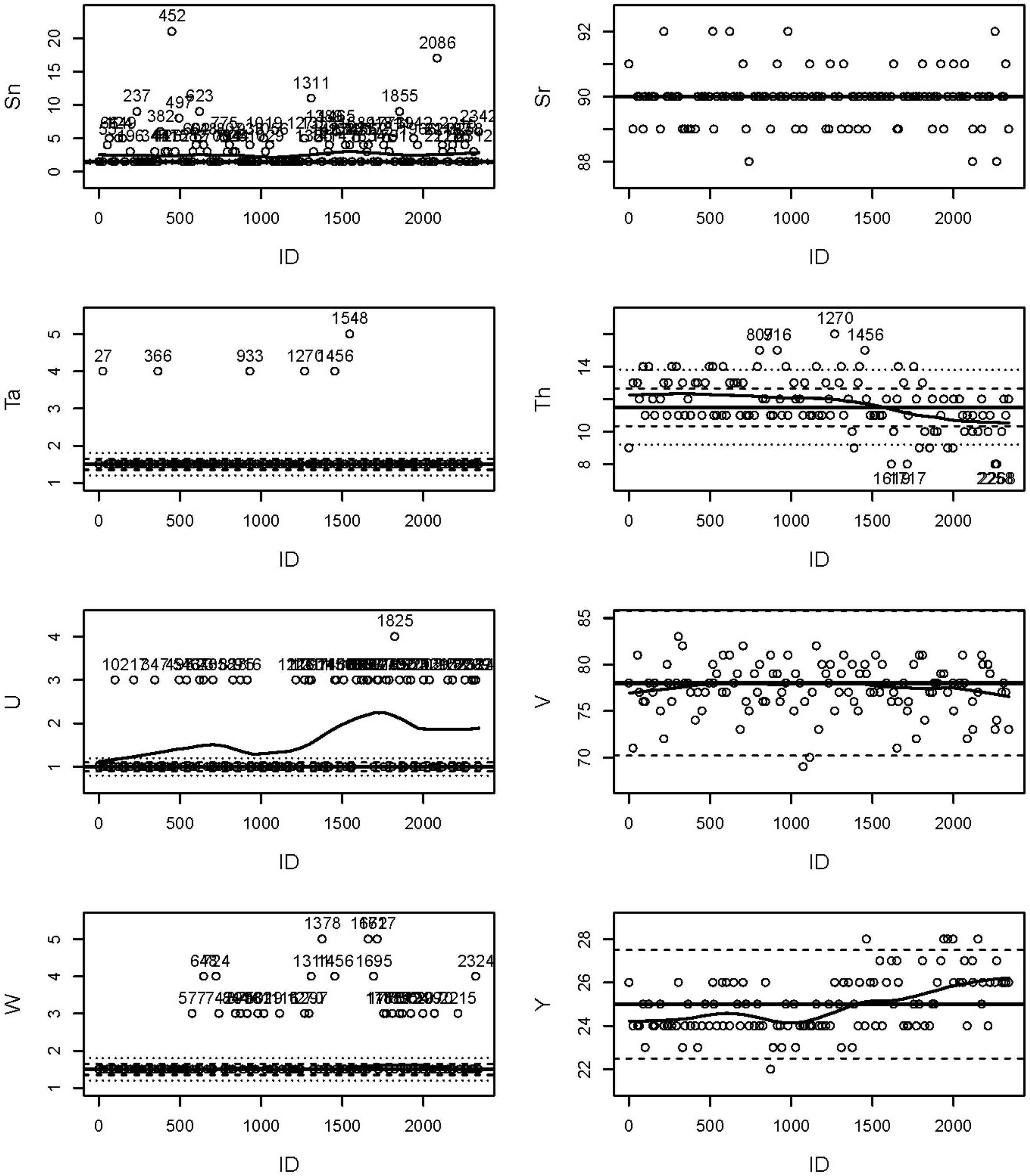

Ni
ID
34
38
42
0
500
1000
1500
2000

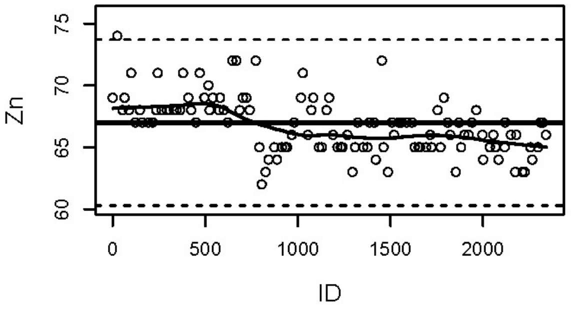

Pb
ID
15
20
25
30
0
500
1000
1500
2000
1085
1378
1654
2086
2312

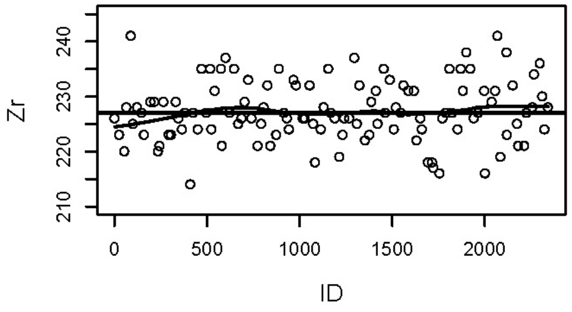

Rb
ID
75
80
85
90
95
0
500
1000
1500
2000

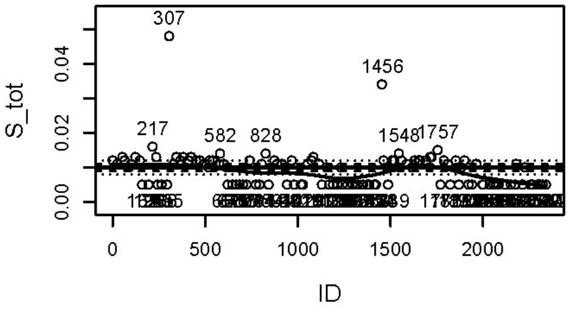

Sb
ID
1
2
3
4
5
6
7
8
0
500
1000
1500
2000
1270
1522
1019
1216
1116
1465
623
2182

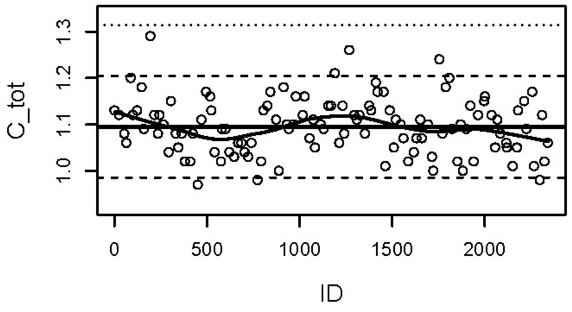

Sc
ID
8.0
9.0
10.0
0
500
1000
1500
2000

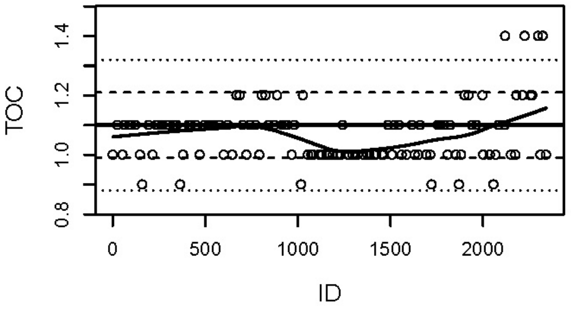

Sn
0
5
10
15
20
452
2086
1311
1855
237
623
497
382
2342
Sr
88
90
92
Ta
1
2
3
4
5
1548
27
366
933
1270
1456
Th
8
10
14
1270
807
916
1456
1617
1717
2258
U
1
2
3
4
1825
V
70
75
80
85
W
1
2
3
4
5
1378
1667
1627
648
724
1311
1456
1695
2324
577
1297
2215
Y
22
24
26
28
ID
0
500
1000
1500
2000

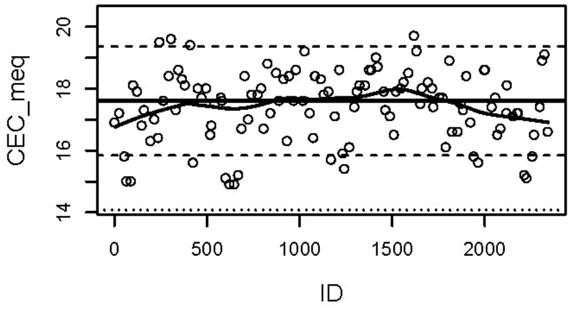

Zn
60
65
70
75
0
500
1000
1500
2000
ID

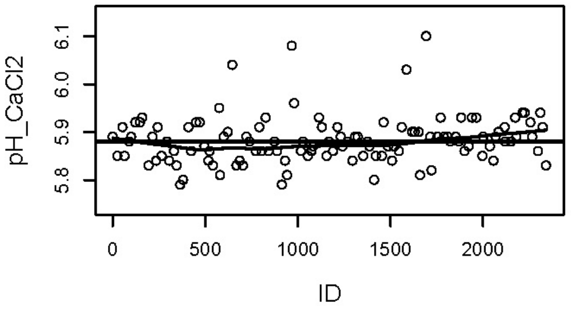

Zr
210
220
230
240
0
500
1000
1500
2000
ID


S_tot
0.00
0.02
0.04
307
217
582
828
1456
1548
1757
0
500
1000
1500
2000
ID


C_tot
1.0
1.1
1.2
1.3
0
500
1000
1500
2000
ID

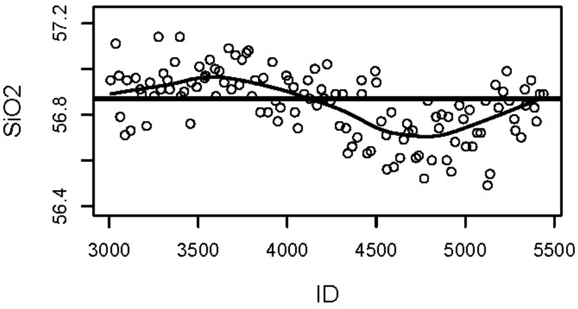

TOC
0.8
1.0
1.2
1.4
0
500
1000
1500
2000
ID


CEC_meq
14
16
18
20
0
500
1000
1500
2000
ID

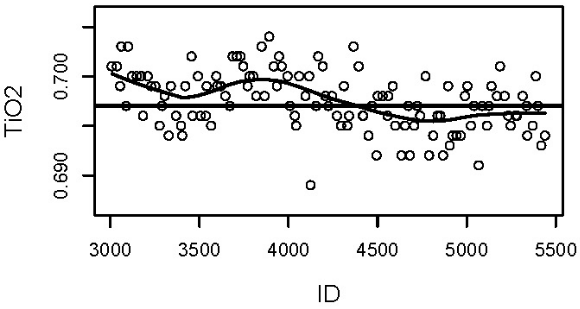

pH_CaCl2
5.8
5.9
6.0
6.1
0
500
1000
1500
2000
ID

APPENDIX 2. X-Charts for the project standard Ap

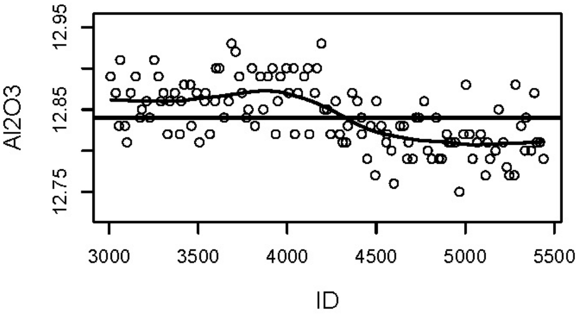
Sample number (ID) is plotted against analytical result for the standard. The thick black line indicates the median value of all standard results, the dashed line is the limit for 10%, and the dotted line for 20% deviation from the median. Standard results that show a larger deviation than 30% from the median are indicated by sample number. The trend line is a loess regression line for the standard results and would help to identify time trends or breaks in the data.



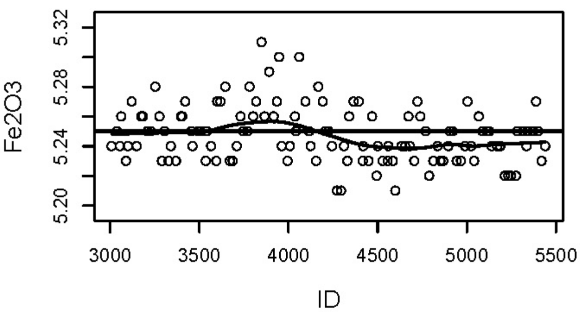
SiO2
56.4
56.8
57.2
3000
3500
4000
4500
5000
5500
ID



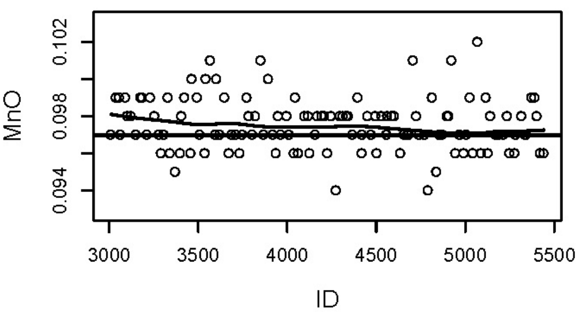
TiO2
0.690
0.700
3000
3500
4000
4500
5000
5500
ID



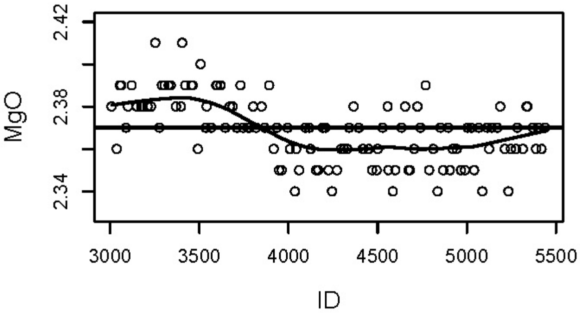
Al2O3
12.75
12.85
12.95
3000
3500
4000
4500
5000
5500
ID



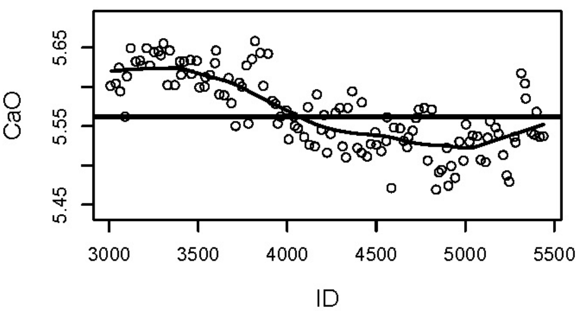
Fe2O3
5.20
5.24
5.28
5.32
3000
3500
4000
4500
5000
5500
ID



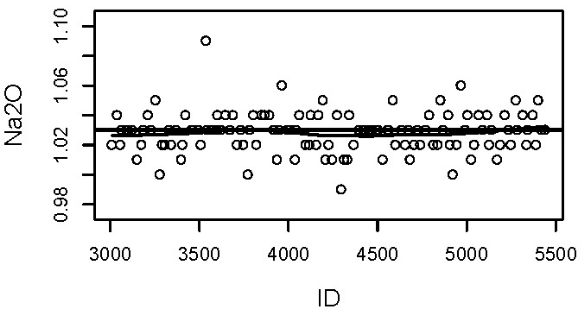
MnO
0.094
0.098
0.102
3000
3500
4000
4500
5000
5500
ID



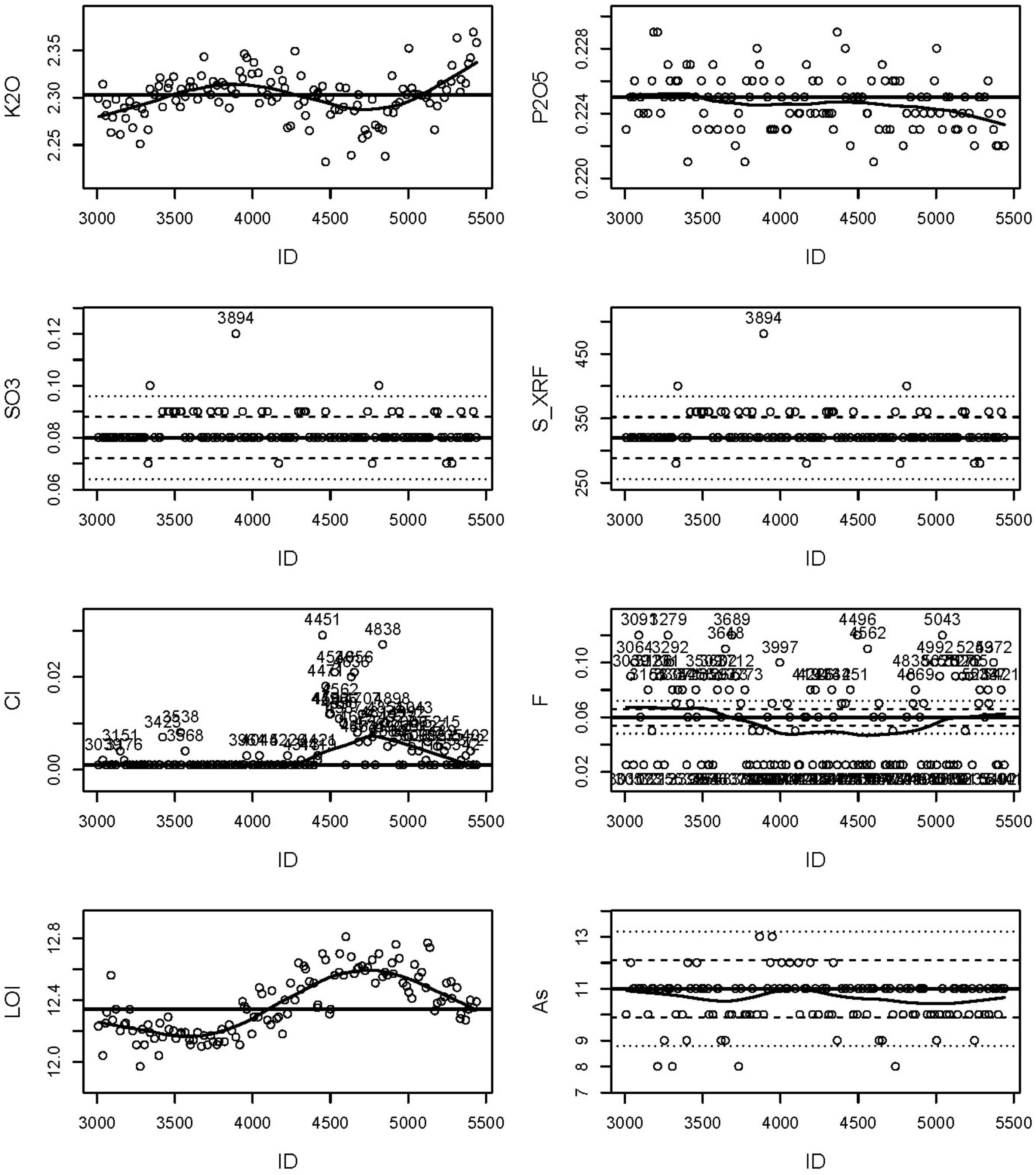
MgO
2.34
2.38
2.42
3000
3500
4000
4500
5000
5500
ID

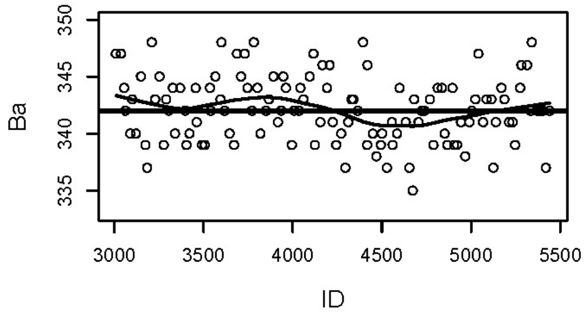


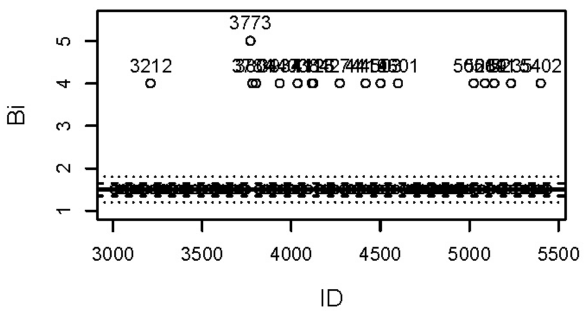
CaO
5.45
5.55
5.65
3000
3500
4000
4500
5000
5500
ID

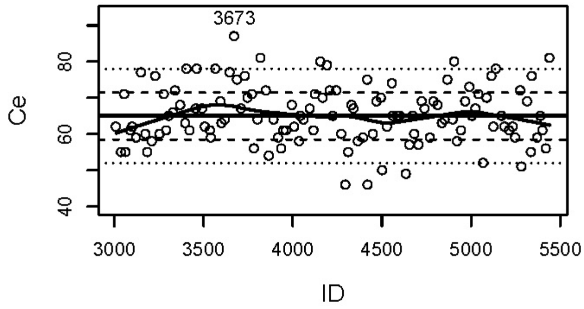


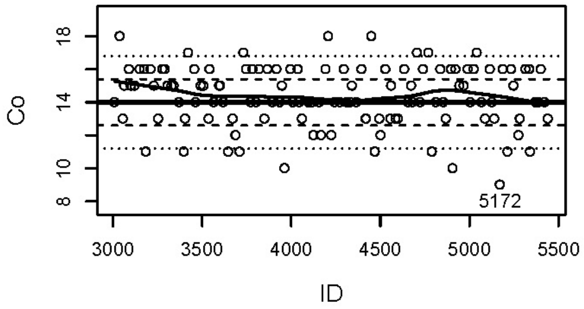
Na2O
0.98
1.02
1.06
1.10
3000
3500
4000
4500
5000
5500
ID

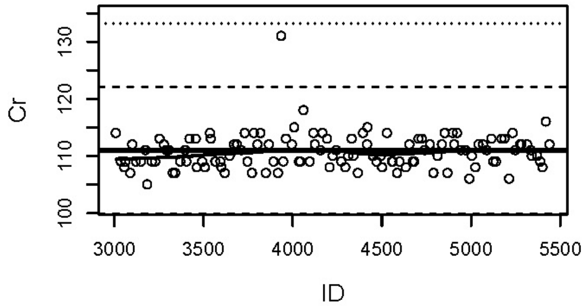

K2O
2.25
2.30
2.35
P2O5
0.220
0.224
0.228
SO3
0.06
0.08
0.10
0.12
3894
S_XRF
250
350
450
3894
Cl
0.00
0.02
4451
4838
3538
3423
3151
3968
F
0.02
0.06
0.10
3091
3279
3689
4496
5043
3064
3292
3648
4562
3997
4992
5372
LOI
12.0
12.4
12.8
As
7
8
9
10
11
12
13
3000
3500
4000
4500
5000
5500
ID

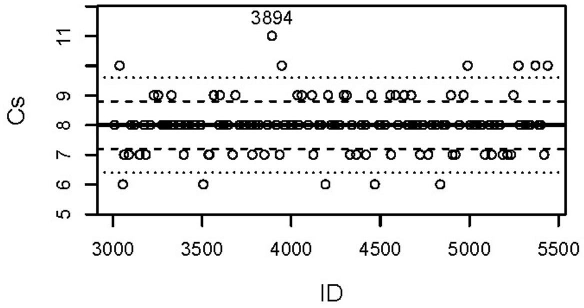

Ba
335
340
345
350
3000
3500
4000
4500
5000
5500
ID

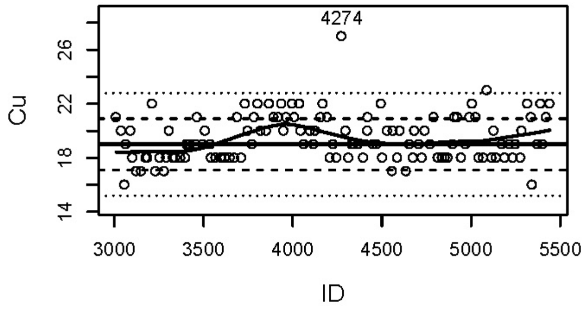

Bi
1
2
3
4
5
3773
3212
5402
3000
3500
4000
4500
5000
5500
ID

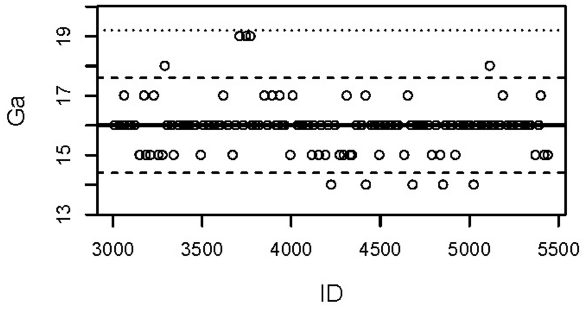

Ce
40
60
80
3673
3000
3500
4000
4500
5000
5500
ID

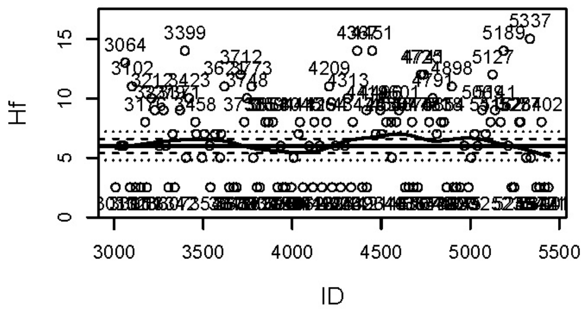

Co
8
10
14
18
5172
3000
3500
4000
4500
5000
5500
ID

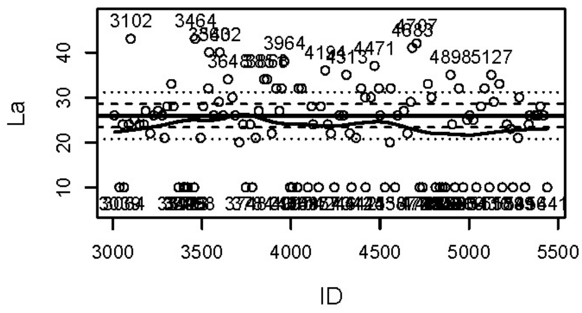

Cr
100
110
120
130
3000
3500
4000
4500
5000
5500
ID

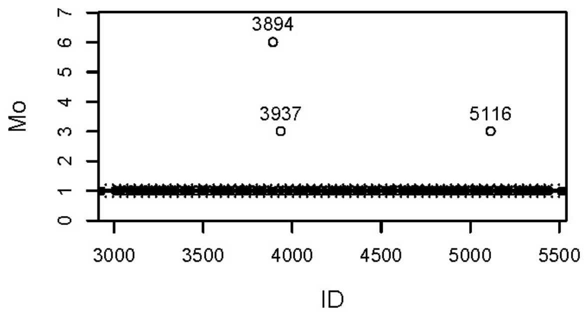

Cs
5
6
7
8
9
11
3894
3000
3500
4000
4500
5000
5500
ID

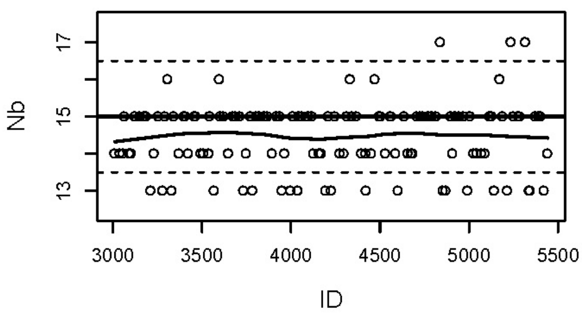

Cu
14
18
22
26
4274
3000
3500
4000
4500
5000
5500
ID

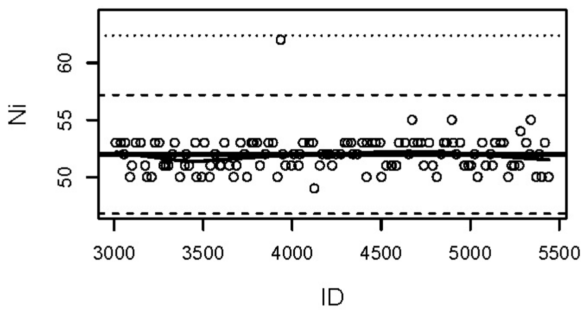

Ga
13
15
17
19
3000
3500
4000
4500
5000
5500
ID

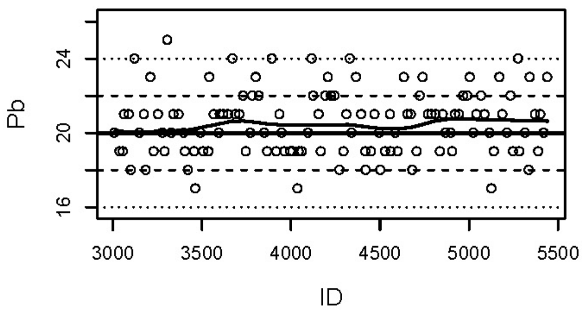

Hf
ID
0
5
10
15
3000
3500
4000
4500
5000
5500
3064
3399
3102
3712
3773
3423
3748
3458
4209
4313
4367
4751
4745
4898
4791
5189
5337
5127
5402

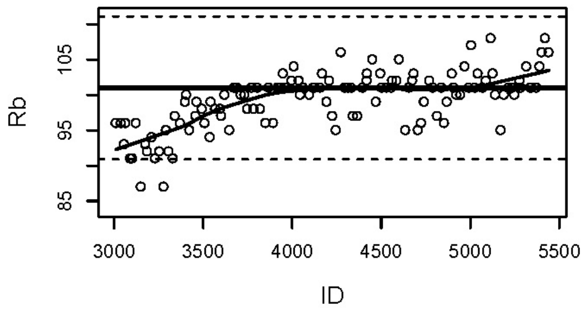

La
ID
10
20
30
40
3000
3500
4000
4500
5000
5500
3102
3464
3402
3964
4194
4313
4471
4707
4683
4898
5127

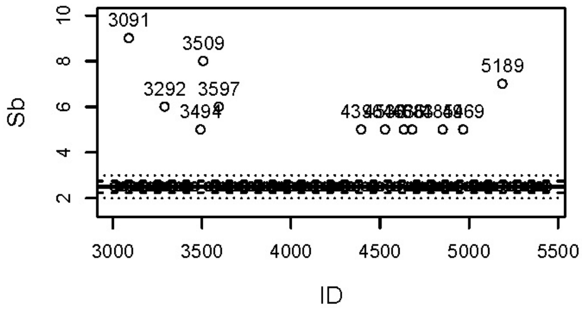

Mo
ID
0
1
2
3
4
5
6
7
3000
3500
4000
4500
5000
5500
3894
3937
5116

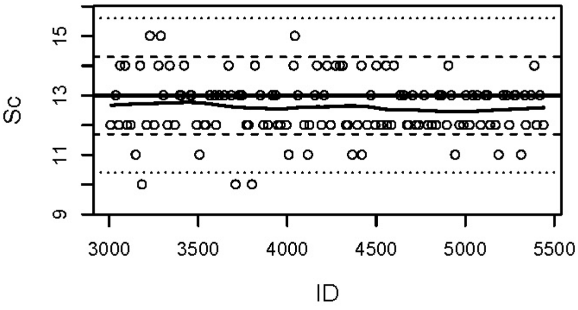

Nb
ID
13
15
17
3000
3500
4000
4500
5000
5500


Ni
ID
50
55
60
3000
3500
4000
4500
5000
5500

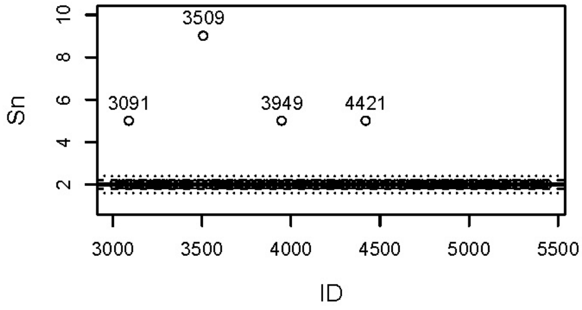

Pb
ID
16
20
24
3000
3500
4000
4500
5000
5500


Rb
ID
85
95
105
3000
3500
4000
4500
5000
5500

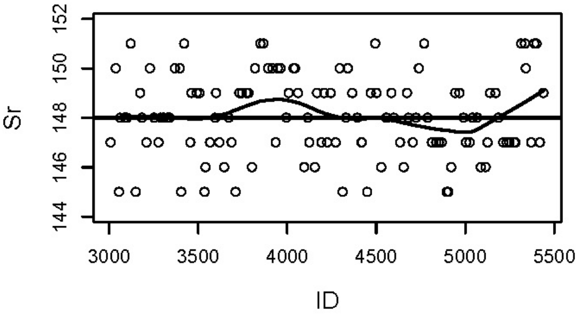

Sb
ID
2
4
6
8
10
3000
3500
4000
4500
5000
5500
3091
3509
3292
3597
3494
5189
4969



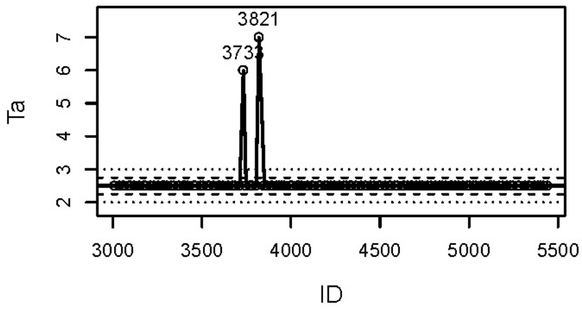
Sc
9
11
13
15
3000
3500
4000
4500
5000
5500
ID



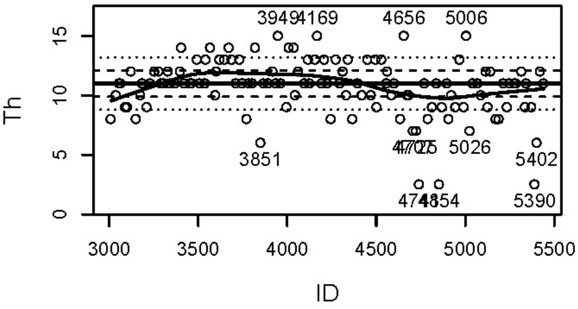
Sn
2
4
6
8
10
3509
3091
3949
4421
3000
3500
4000
4500
5000
5500
ID



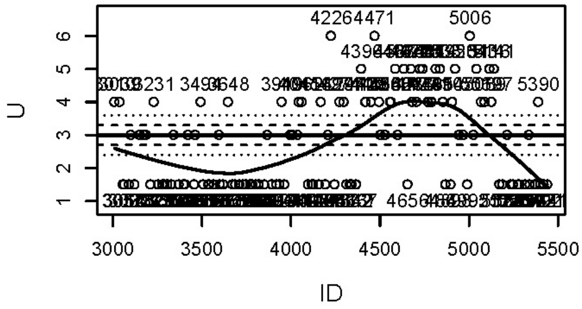
Sr
144
146
148
150
152
3000
3500
4000
4500
5000
5500
ID



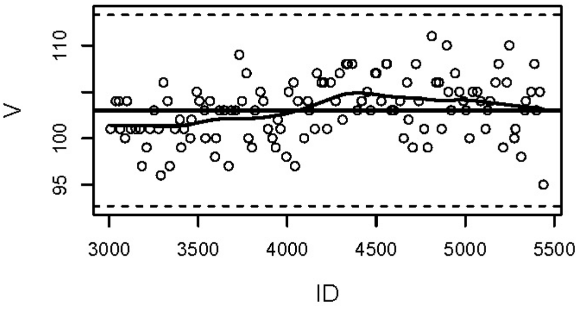
Ta
2
3
4
5
6
7
3821
3733
3000
3500
4000
4500
5000
5500
ID



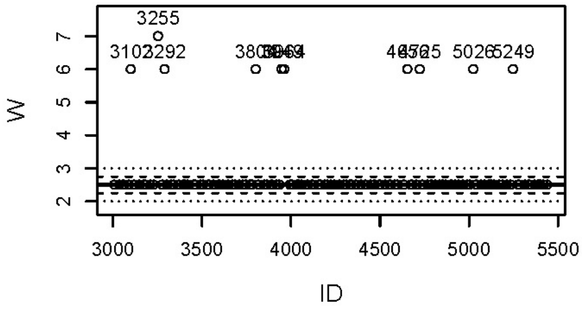
Th
0
5
10
15
3949
4169
4656
5006
3851
4725
5026
5402
4741
4854
5390
3000
3500
4000
4500
5000
5500
ID



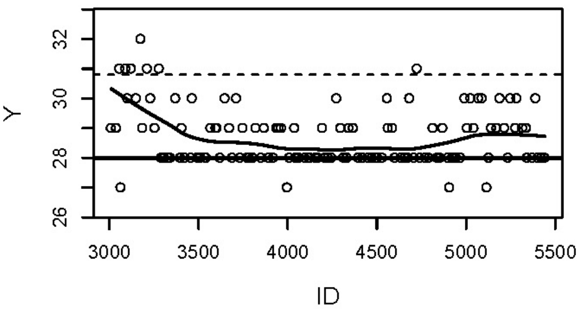
U
1
2
3
4
5
6
4226
4471
5006
3231
3494
3648
5390
4656
3000
3500
4000
4500
5000
5500
ID

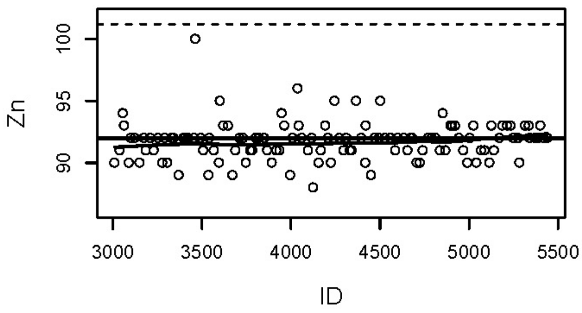


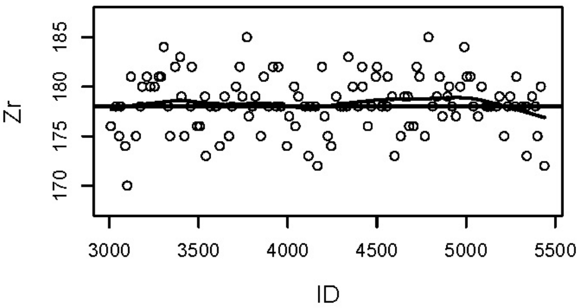
V
95
100
110
3000
3500
4000
4500
5000
5500
ID

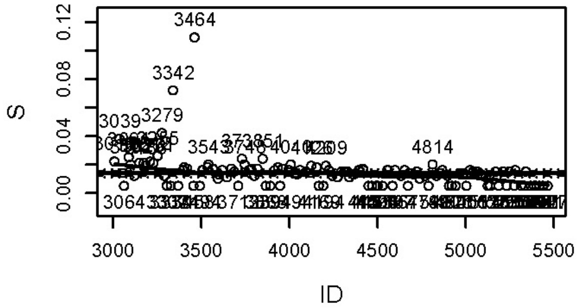


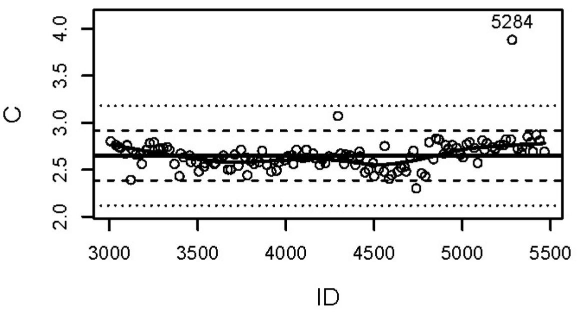
W
2
3
4
5
6
7
3255
3102
3292
5026
5249
3000
3500
4000
4500
5000
5500
ID

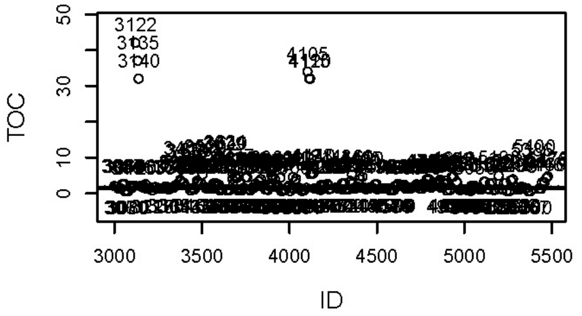

Y
26
28
30
32
3000
3500
4000
4500
5000
5500
ID

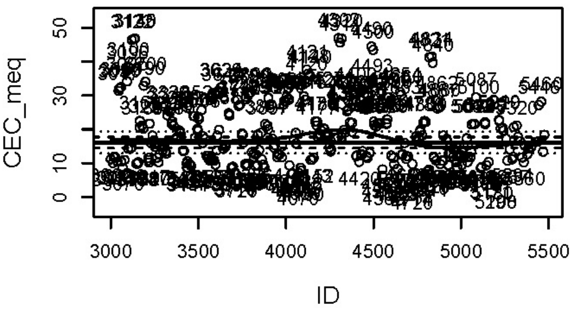

Zn
90
95
100
3000
3500
4000
4500
5000
5500
ID

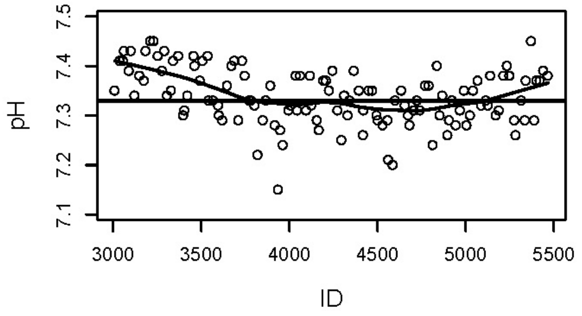

Zr
170
175
180
185
3000
3500
4000
4500
5000
5500
ID


S
0.00
0.04
0.08
0.12
3464
3342
3279
3039
3543
4814
3064
3000
3500
4000
4500
5000
5500
ID


C
2.0
2.5
3.0
3.5
4.0
5284
3000
3500
4000
4500
5000
5500
ID

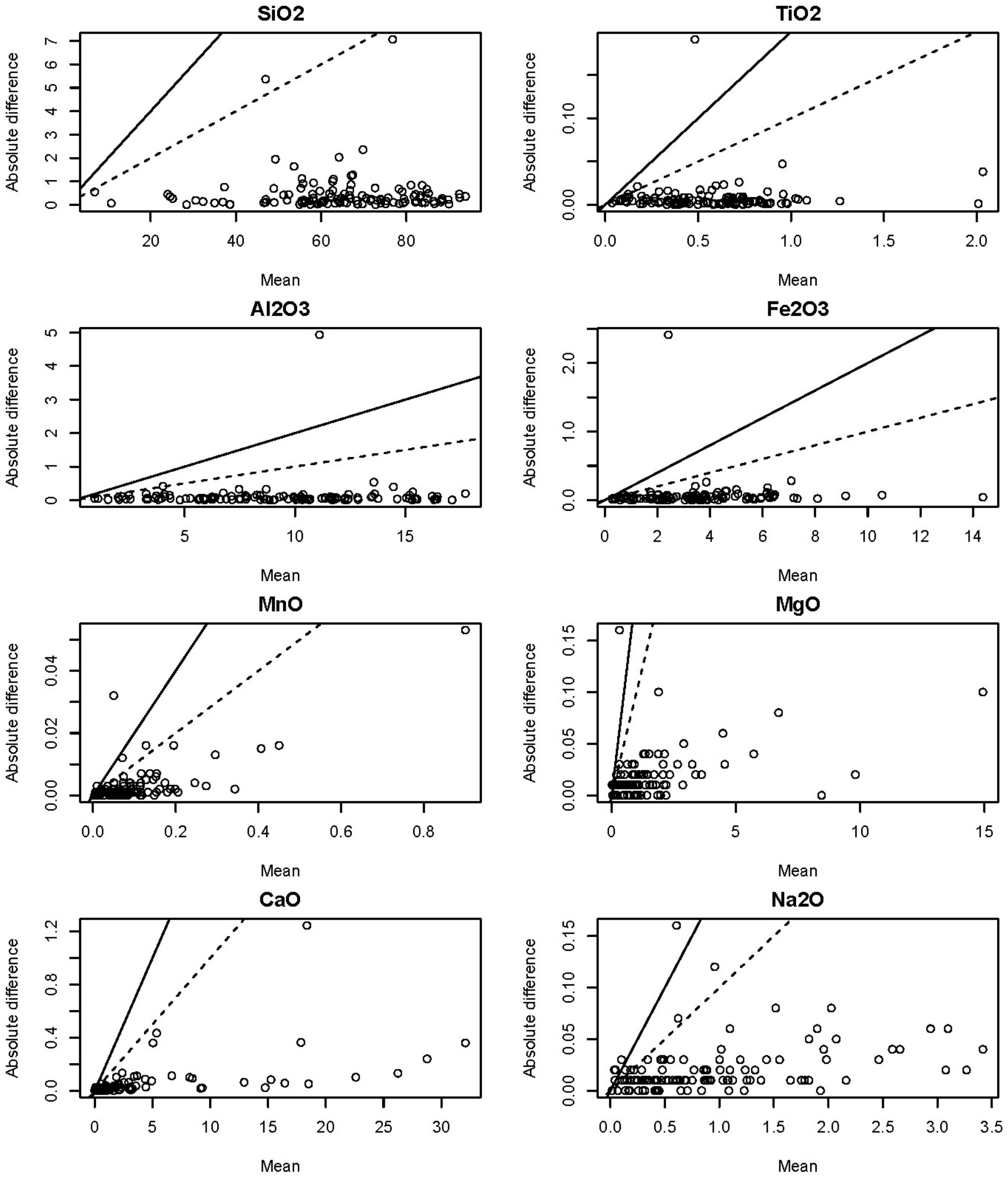

TOC
0
10
30
50
3122
3135
3140
4105
4120
5406
3000
3500
4000
4500
5000
5500
ID

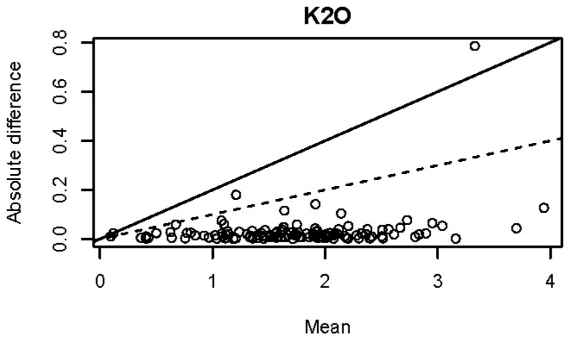

CEC_meq
0
10
30
50
4493
5087
5466
3000
3500
4000
4500
5000
5500
ID

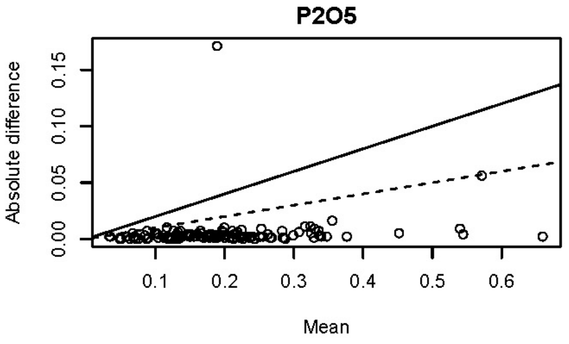

pH
7.1
7.2
7.3
7.4
7.5
3000
3500
4000
4500
5000
5500
ID

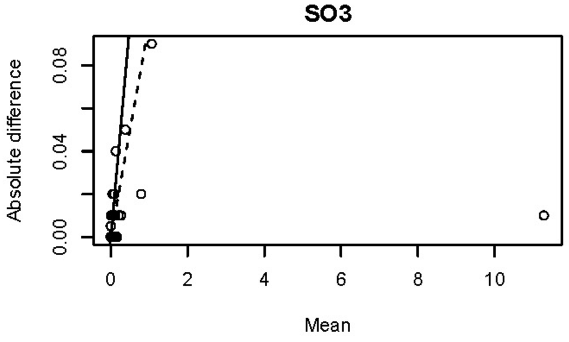
APPENDIX 3. "Thompson and Howarth"-plots of replicate analyses from the Gr samples

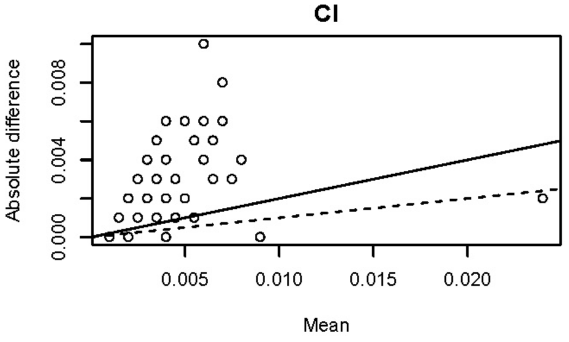
The mean of the replicate pairs is plotted along the x-axis, and the absolute difference of the two results along the y-axis. The limit for 10 % precision is indicated by the stippled line, and for 20% precision by the continuous line. On this plot, pairs with poor precision can easily be identified and compared to the results from the project standard within the same batch of 20 samples.

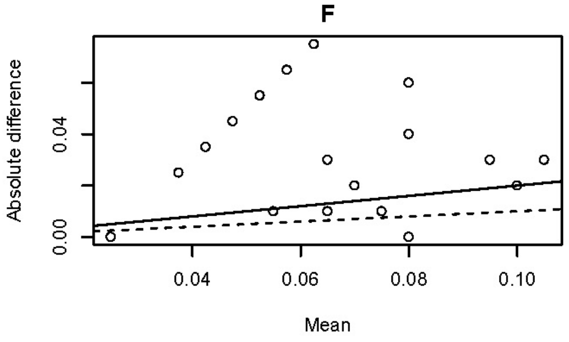

SiO2
Absolute difference
0 1 2 3 4 5 6 7
20 40 60 80
Mean
TiO2
Absolute difference
0.00 0.10
0.0 0.5 1.0 1.5 2.0
Mean
Al2O3
Absolute difference
0 1 2 3 4 5
5 10 15
Mean
Fe2O3
Absolute difference
0.0 1.0 2.0
0 2 4 6 8 10 12 14
Mean
MnO
Absolute difference
0.00 0.02 0.04
0.0 0.2 0.4 0.6 0.8
Mean
MgO
Absolute difference
0.00 0.05 0.10 0.15
0 5 10 15
Mean
CaO
Absolute difference
0.0 0.4 0.8 1.2
0 5 10 15 20 25 30
Mean
Na2O
Absolute difference
0.00 0.05 0.10 0.15
0.0 0.5 1.0 1.5 2.0 2.5 3.0 3.5
Mean

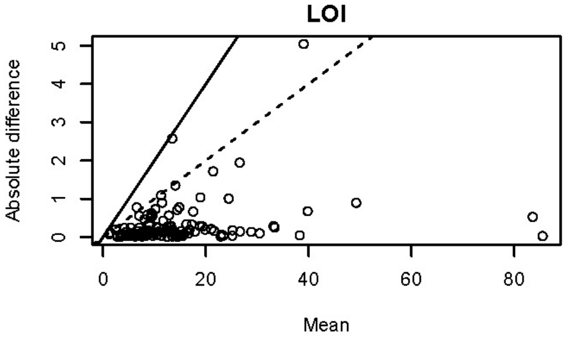

K2O
Absolute difference
0.0
0.2
0.4
0.6
0.8
0
1
2
3
4
Mean

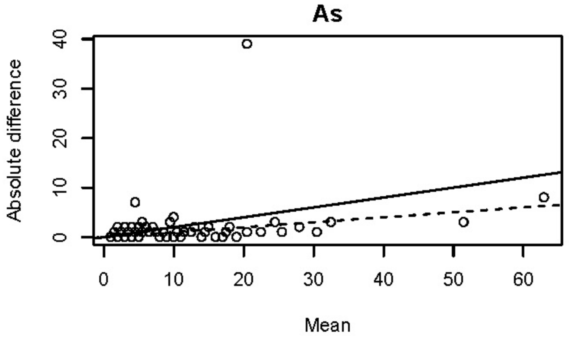

P2O5
Absolute difference
0.00
0.05
0.10
0.15
0.1
0.2
0.3
0.4
0.5
0.6
Mean

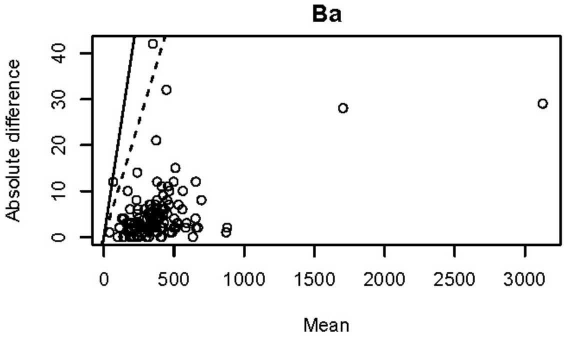

SO3
Absolute difference
0.00
0.04
0.08
0
2
4
6
8
10
Mean

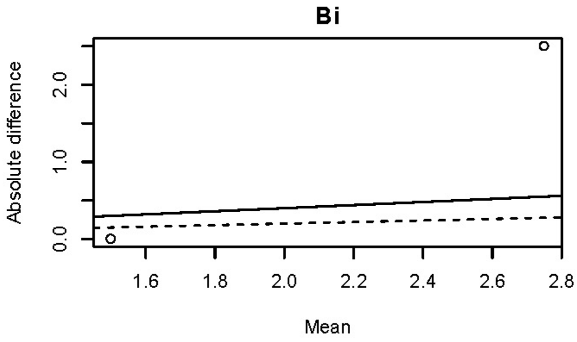

Cl
Absolute difference
0.000
0.004
0.008
0.005
0.010
0.015
0.020
Mean

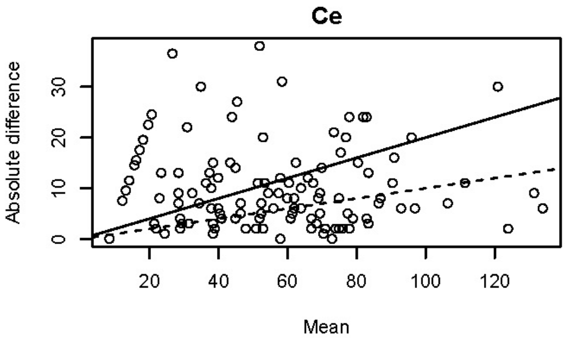

F
Absolute difference
0.00
0.04
0.04
0.06
0.08
0.10
Mean

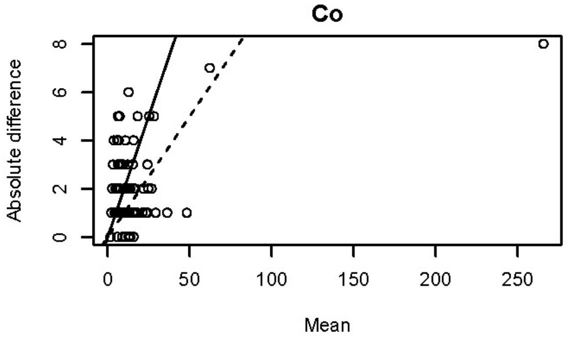

LOI
Absolute difference
0
1
2
3
4
5
0
20
40
60
80
Mean

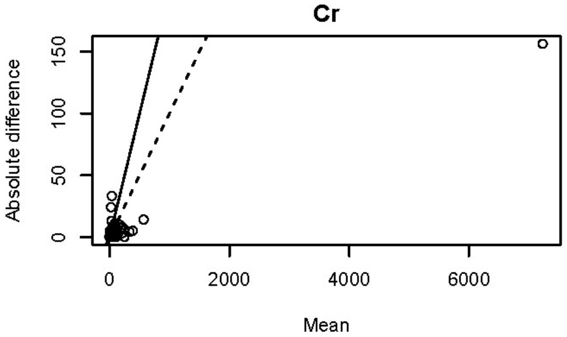

As
Absolute difference
0
10
20
30
40
0
10
20
30
40
50
60
Mean

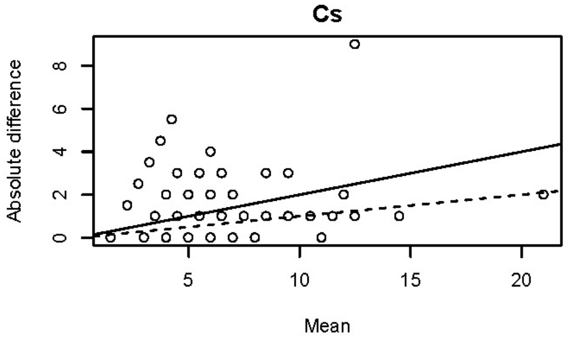

Ba
Absolute difference
0
10
20
30
40
0
500
1000
1500
2000
2500
3000
Mean

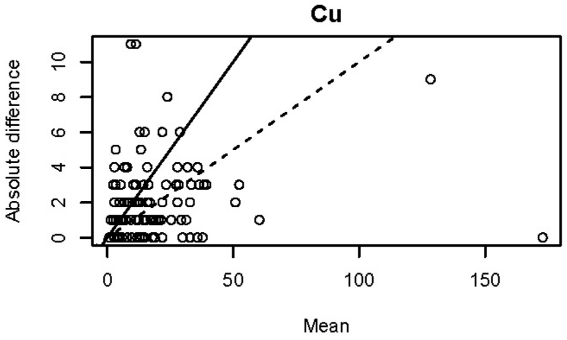

Bi

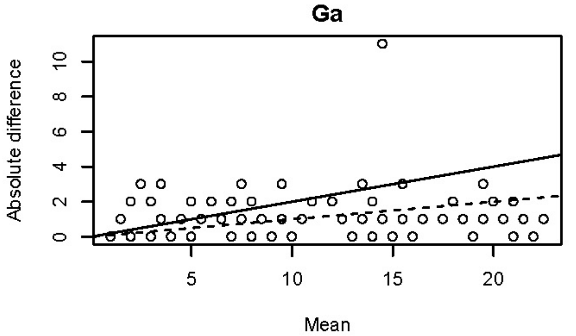

Ce

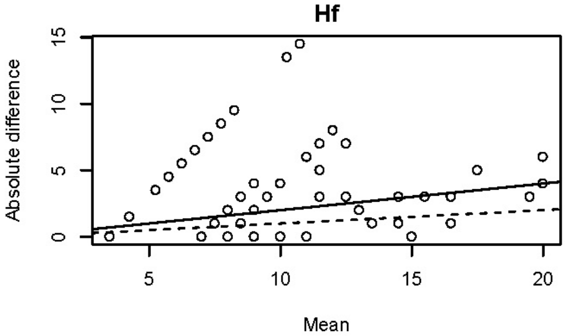

Co

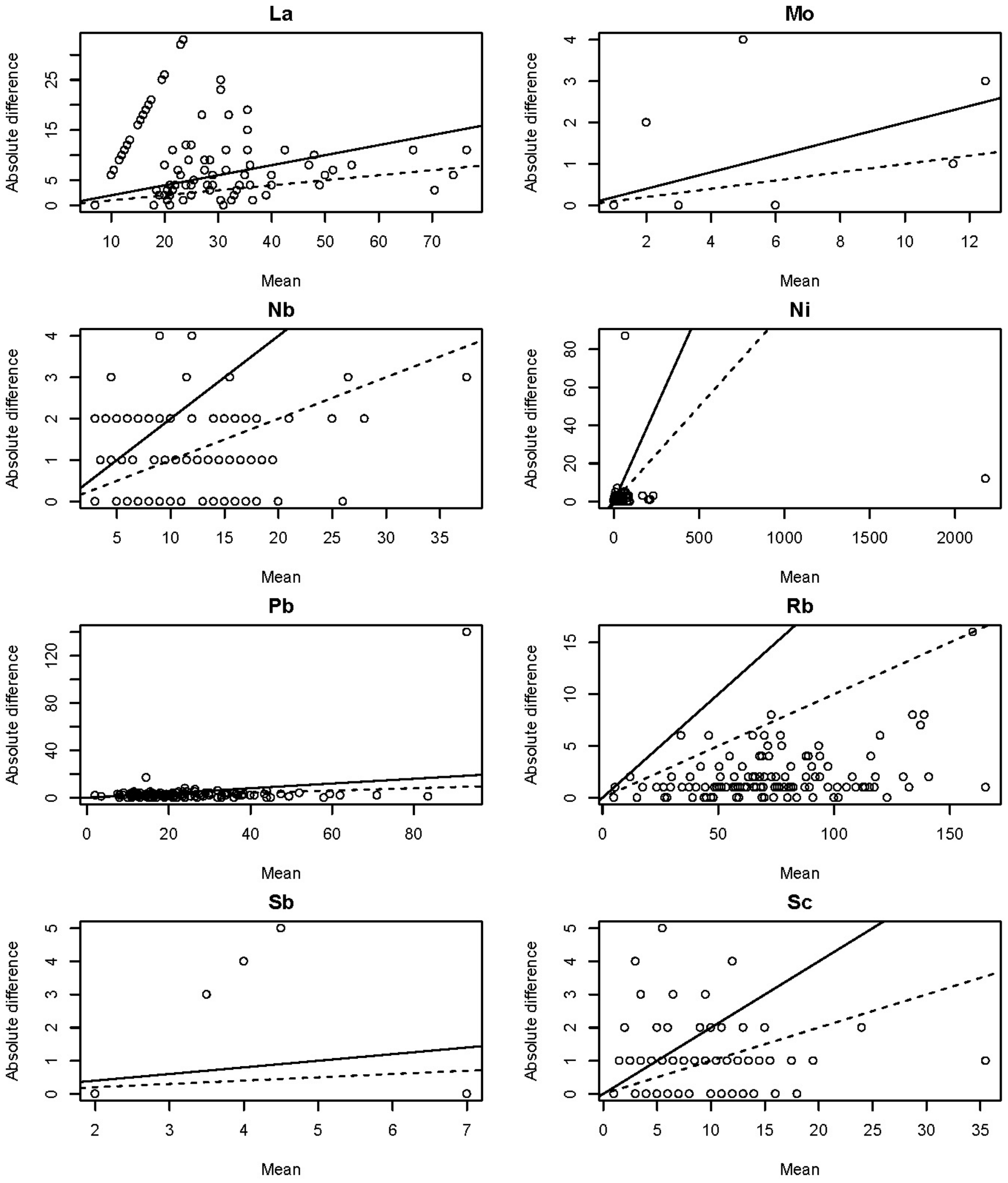

Cr

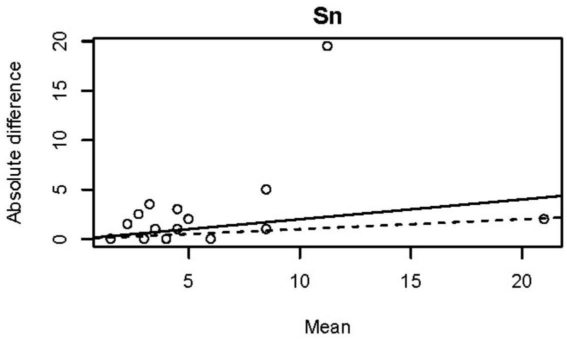

Cs

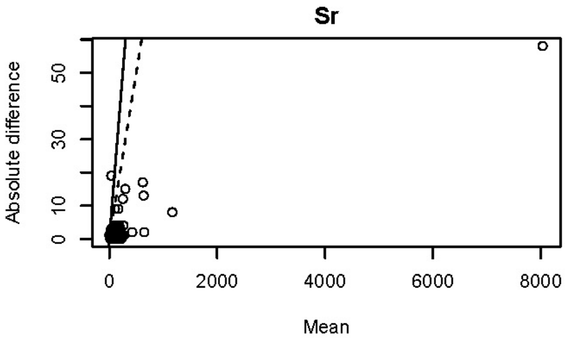

Cu

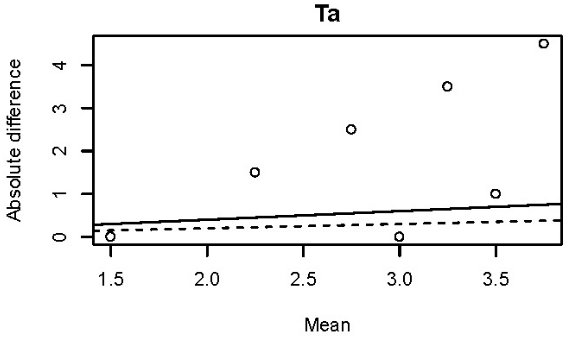

Ga

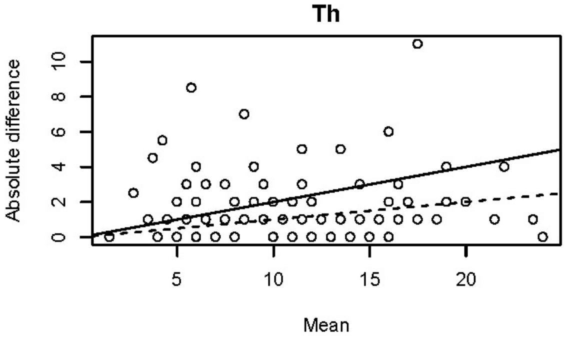

Hf

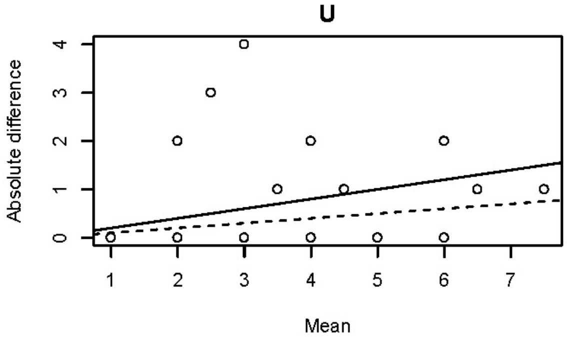

La
Absolute difference
0
5
15
25
10
20
30
40
50
60
70
Mean
Mo
Absolute difference
0
1
2
3
4
2
4
6
8
10
12
Mean
Nb
Absolute difference
0
1
2
3
4
5
10
15
20
25
30
35
Mean
Ni
Absolute difference
0
20
40
60
80
0
500
1000
1500
2000
Mean
Pb
Absolute difference
0
40
80
120
0
20
40
60
80
Mean
Rb
Absolute difference
0
5
10
15
0
50
100
150
Mean
Sb
Absolute difference
0
1
2
3
4
5
2
3
4
5
6
7
Mean
Sc
Absolute difference
0
1
2
3
4
5
0
5
10
15
20
25
30
35
Mean

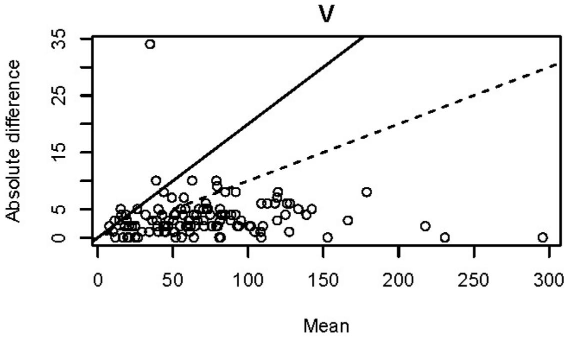

Sn
Absolute difference
0
5
10
15
20
5
10
15
20
Mean

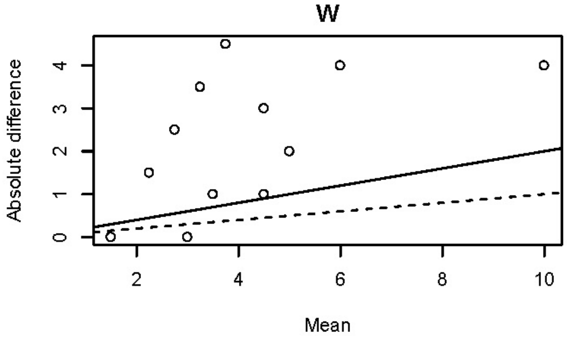

Sr
Absolute difference
0
10
30
50
0
2000
4000
6000
8000
Mean

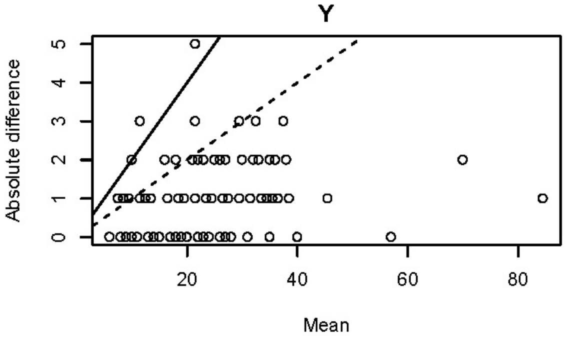

Ta
Absolute difference
0
1
2
3
4
1.5
2.0
2.5
3.0
3.5
Mean

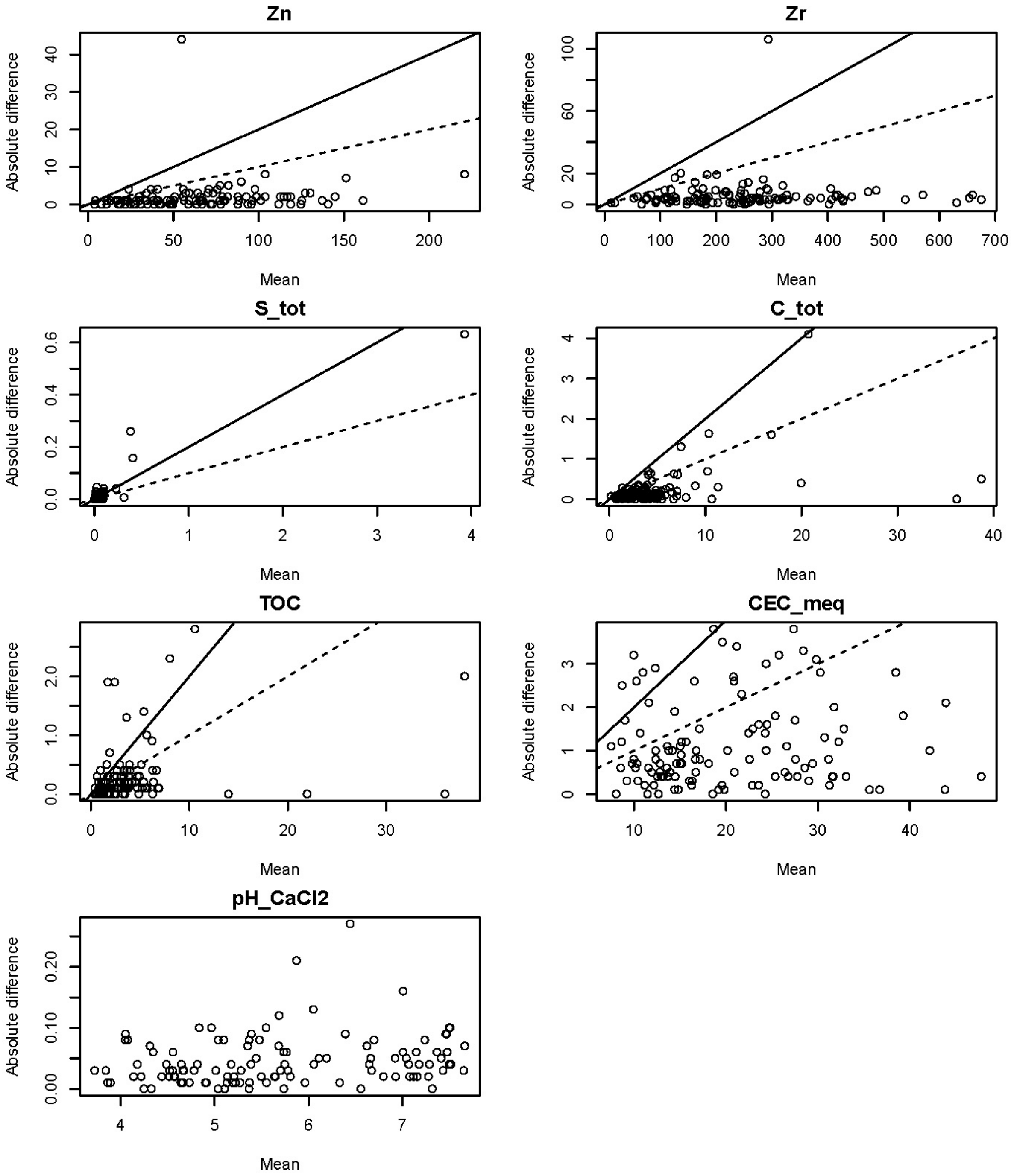

Th
Absolute difference
0
2
4
6
8
10
5
10
15
20
Mean


U
Absolute difference
0
1
2
3
4
1
2
3
4
5
6
7
Mean


V
Absolute difference
0
5
15
25
35
0
50
100
150
200
250
300
Mean

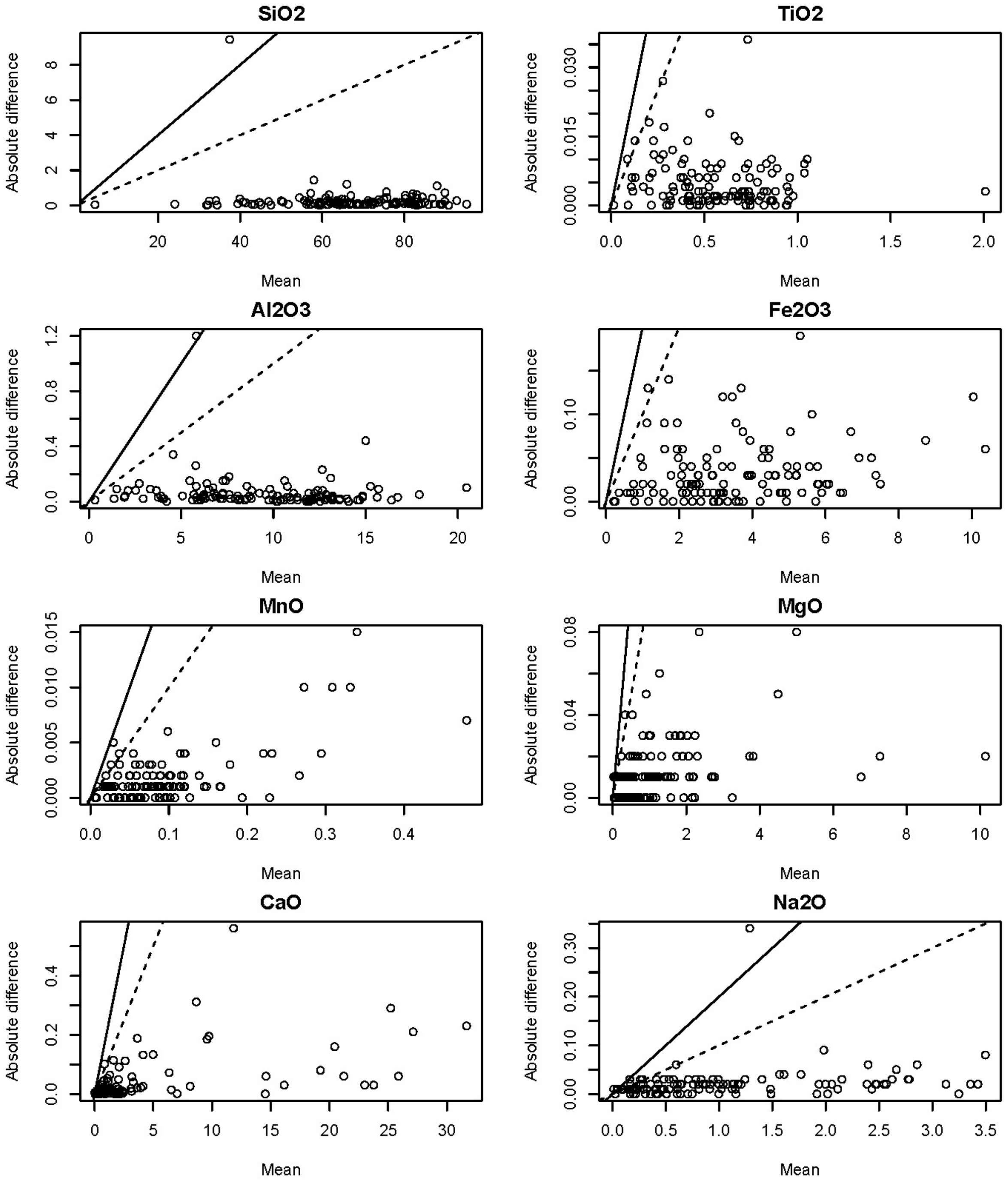

W
Absolute difference
0
1
2
3
4
2
4
6
8
10
Mean

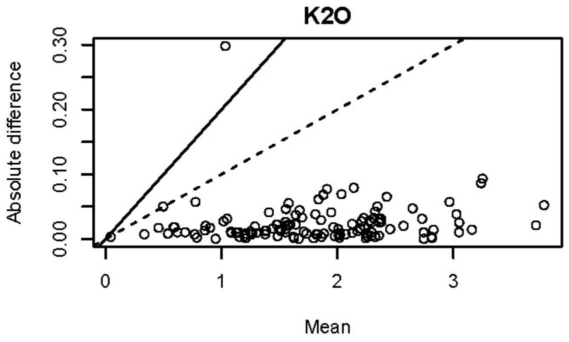

Y
Absolute difference
0
1
2
3
4
5
20
40
60
80
Mean

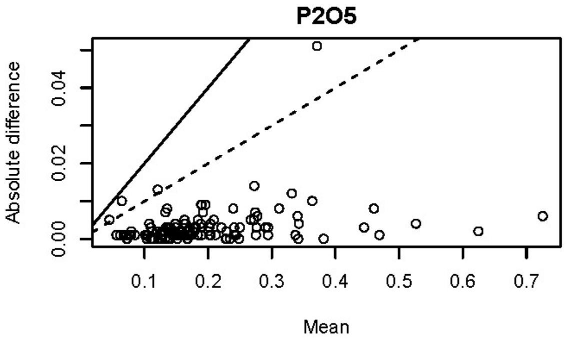

Zn
Absolute difference
0
10
20
30
40
0
50
100
150
200
Mean
Zr
Absolute difference
0
20
60
100
0
100
200
300
400
500
600
700
Mean
S_tot
Absolute difference
0.0
0.2
0.4
0.6
0
1
2
3
4
Mean
C_tot
Absolute difference
0
1
2
3
4
0
10
20
30
40
Mean
TOC
Absolute difference
0.0
1.0
2.0
0
10
20
30
Mean
CEC_meq
Absolute difference
0
1
2
3
10
20
30
40
Mean
pH_CaCl2
Absolute difference
0.00
0.10
0.20
4
5
6
7
Mean

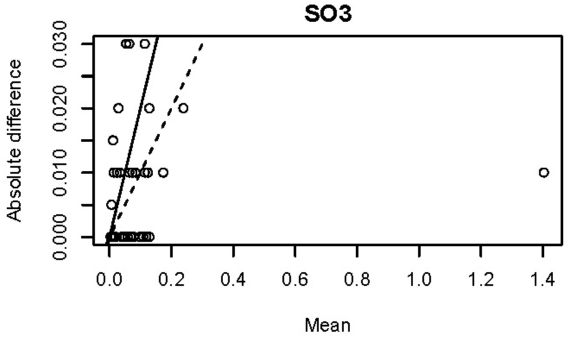
APPENDIX 4. "Thompson and Howarth"-plots of replicate analyses from the Ap samples

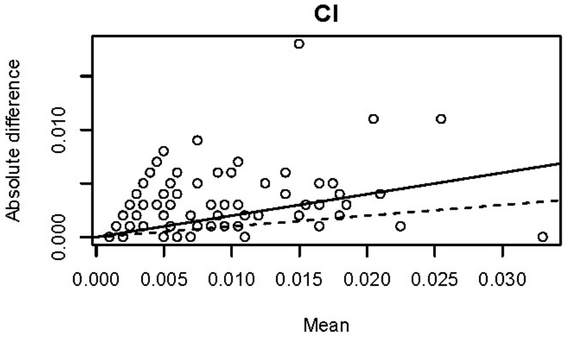
The mean of the replicate pairs is plotted along the x-axis, and the absolute difference of the two results along the y-axis. The limit for 10 % precision is indicated by the stippled line, and for 20% precision by the continuous line. On this plot, pairs with poor precision can easily be identified and compared to the results from the project standard within the same batch of 20 samples.

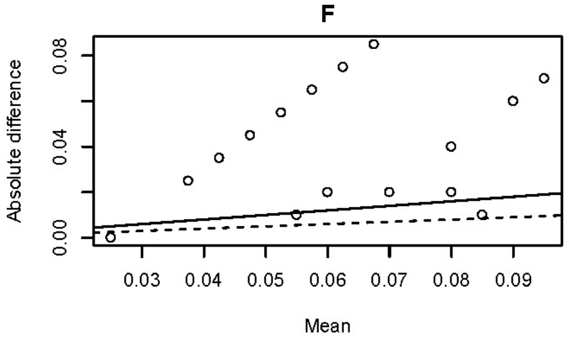

SiO2
Absolute difference
0
2
4
6
8
20
40
60
80
Mean
TiO2
Absolute difference
0.000
0.015
0.030
0.0
0.5
1.0
1.5
2.0
Mean
Al2O3
Absolute difference
0.0
0.4
0.8
1.2
0
5
10
15
20
Mean
Fe2O3
Absolute difference
0.00
0.10
0
2
4
6
8
10
Mean
MnO
Absolute difference
0.000
0.005
0.010
0.015
0.0
0.1
0.2
0.3
0.4
Mean
MgO
Absolute difference
0.00
0.04
0.08
0
2
4
6
8
10
Mean
CaO
Absolute difference
0.0
0.2
0.4
0
5
10
15
20
25
30
Mean
Na2O
Absolute difference
0.00
0.10
0.20
0.30
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Mean

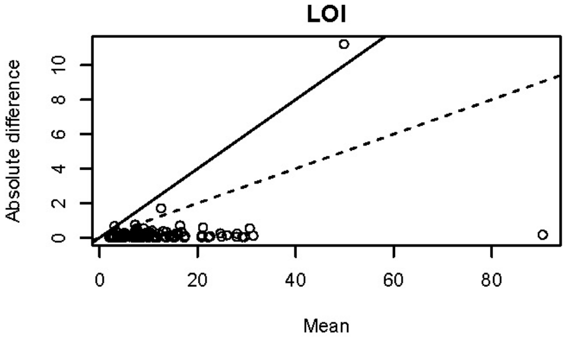

K2O
Absolute difference
0.00
0.10
0.20
0.30
0
1
2
3
Mean

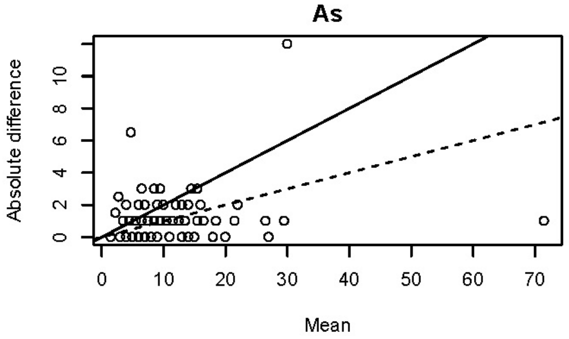

P2O5
Absolute difference
0.00
0.02
0.04
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Mean

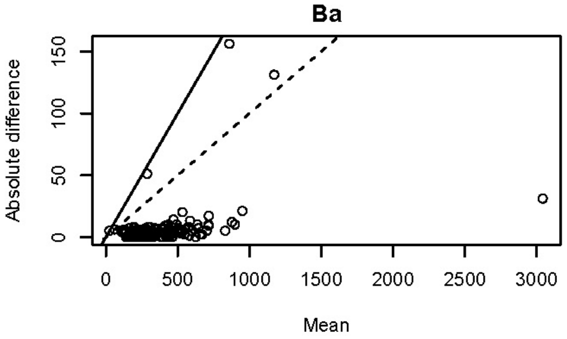

SO3
Absolute difference
0.000
0.010
0.020
0.030
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Mean

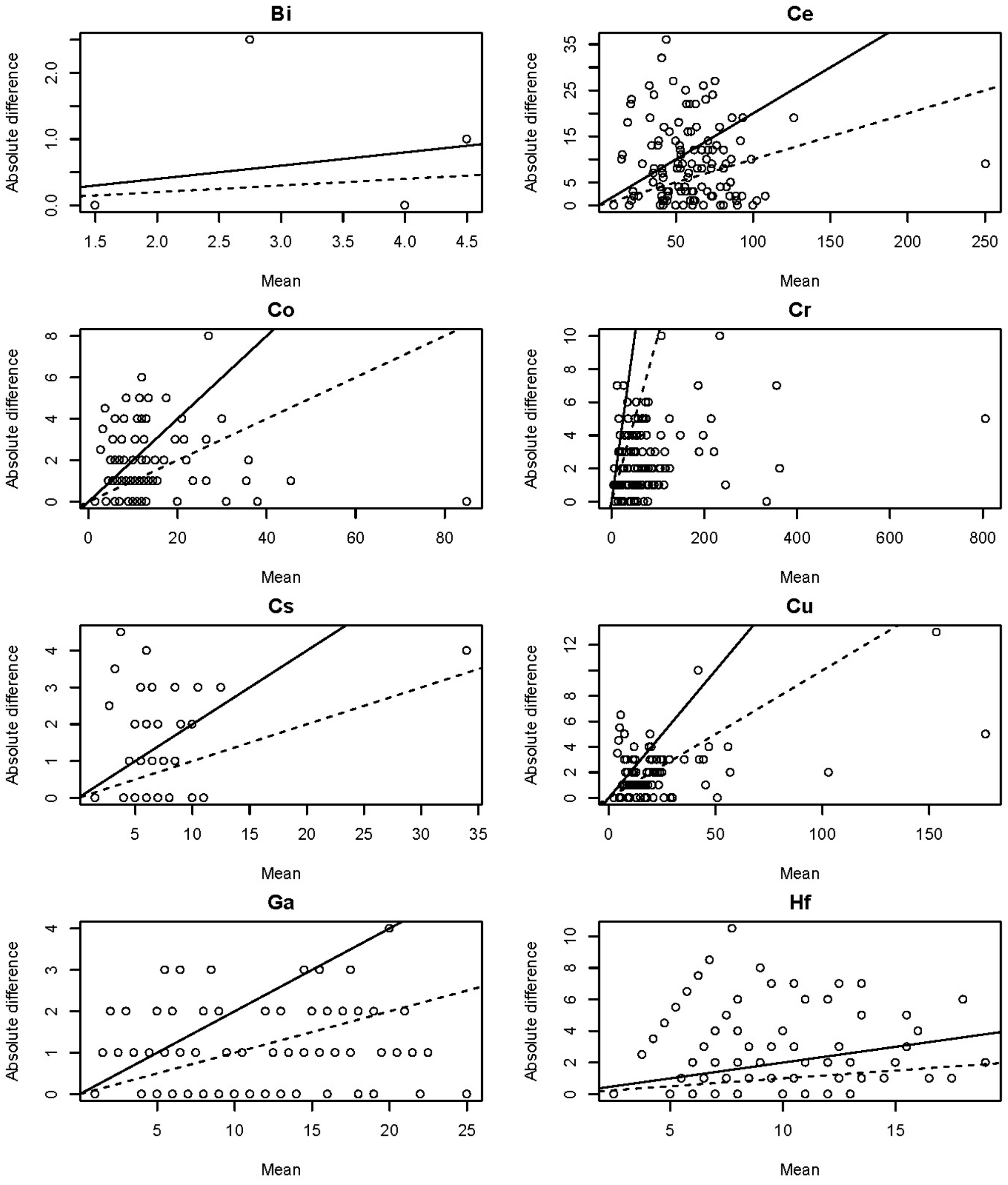

Cl
Absolute difference
0.000
0.010
0.000
0.005
0.010
0.015
0.020
0.025
0.030
Mean

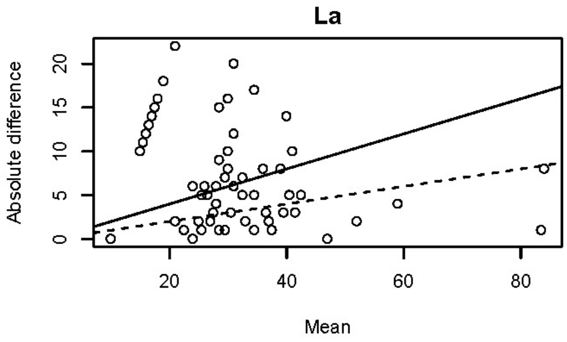

F
Absolute difference
0.00
0.04
0.08
0.03
0.04
0.05
0.06
0.07
0.08
0.09
Mean

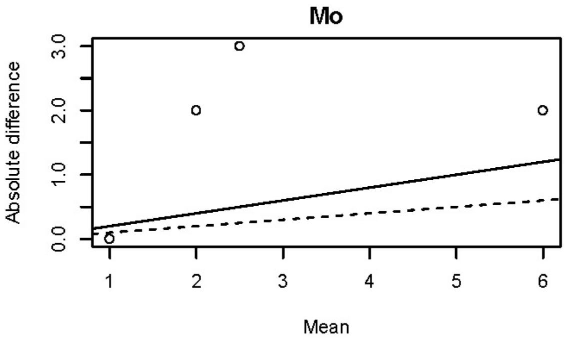

LOI
Absolute difference
0
2
4
6
8
10
0
20
40
60
80
Mean

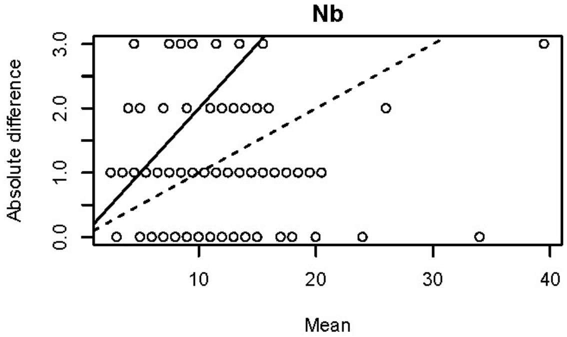

As
Absolute difference
0
2
4
6
8
10
0
10
20
30
40
50
60
70
Mean

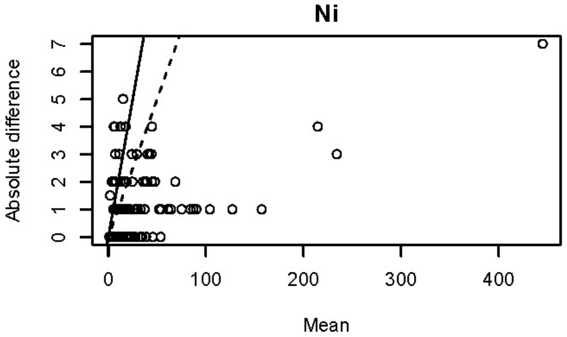

Ba
Absolute difference
0
50
100
150
0
500
1000
1500
2000
2500
3000
Mean

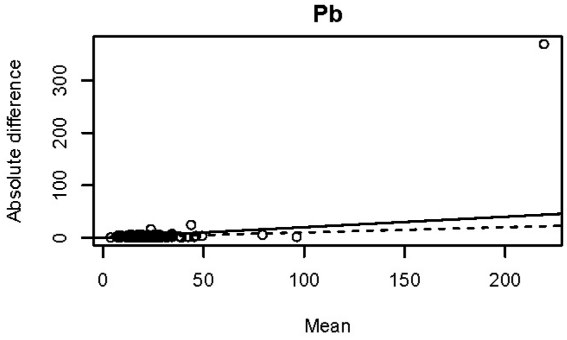

Bi
Absolute difference
0.0
1.0
2.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
Mean
Ce
Absolute difference
0
5
15
25
35
50
100
150
200
250
Mean
Co
Absolute difference
0
2
4
6
8
0
20
40
60
80
Mean
Cr
Absolute difference
0
2
4
6
8
10
0
200
400
600
800
Mean
Cs
Absolute difference
0
1
2
3
4
5
10
15
20
25
30
35
Mean
Cu
Absolute difference
0
2
4
6
8
12
0
50
100
150
Mean
Ga
Absolute difference
0
1
2
3
4
5
10
15
20
25
Mean
Hf
Absolute difference
0
2
4
6
8
10
5
10
15
Mean

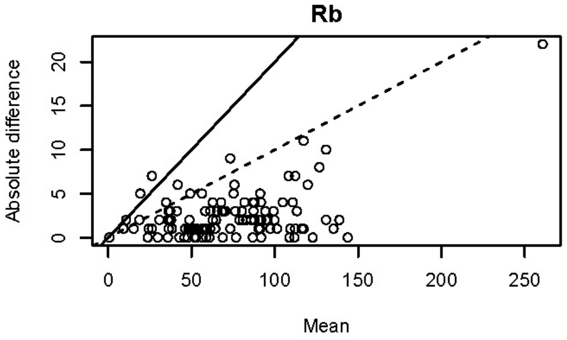

La
Absolute difference
0
5
10
15
20
20
40
60
80
Mean

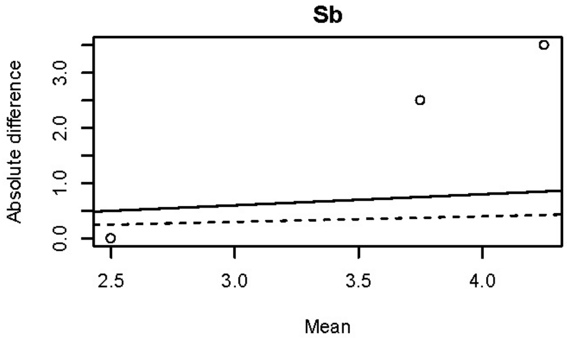

Mo
Absolute difference
0.0
1.0
2.0
3.0
1
2
3
4
5
6
Mean

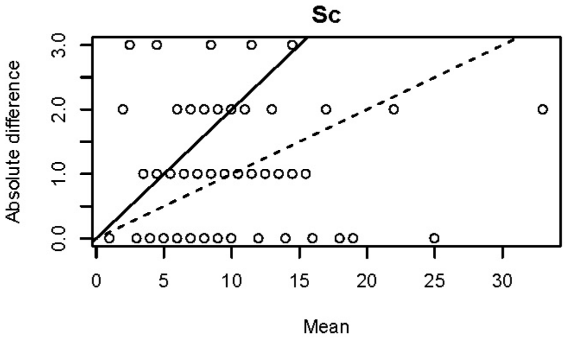

Nb
Absolute difference
0.0
1.0
2.0
3.0
10
20
30
40
Mean

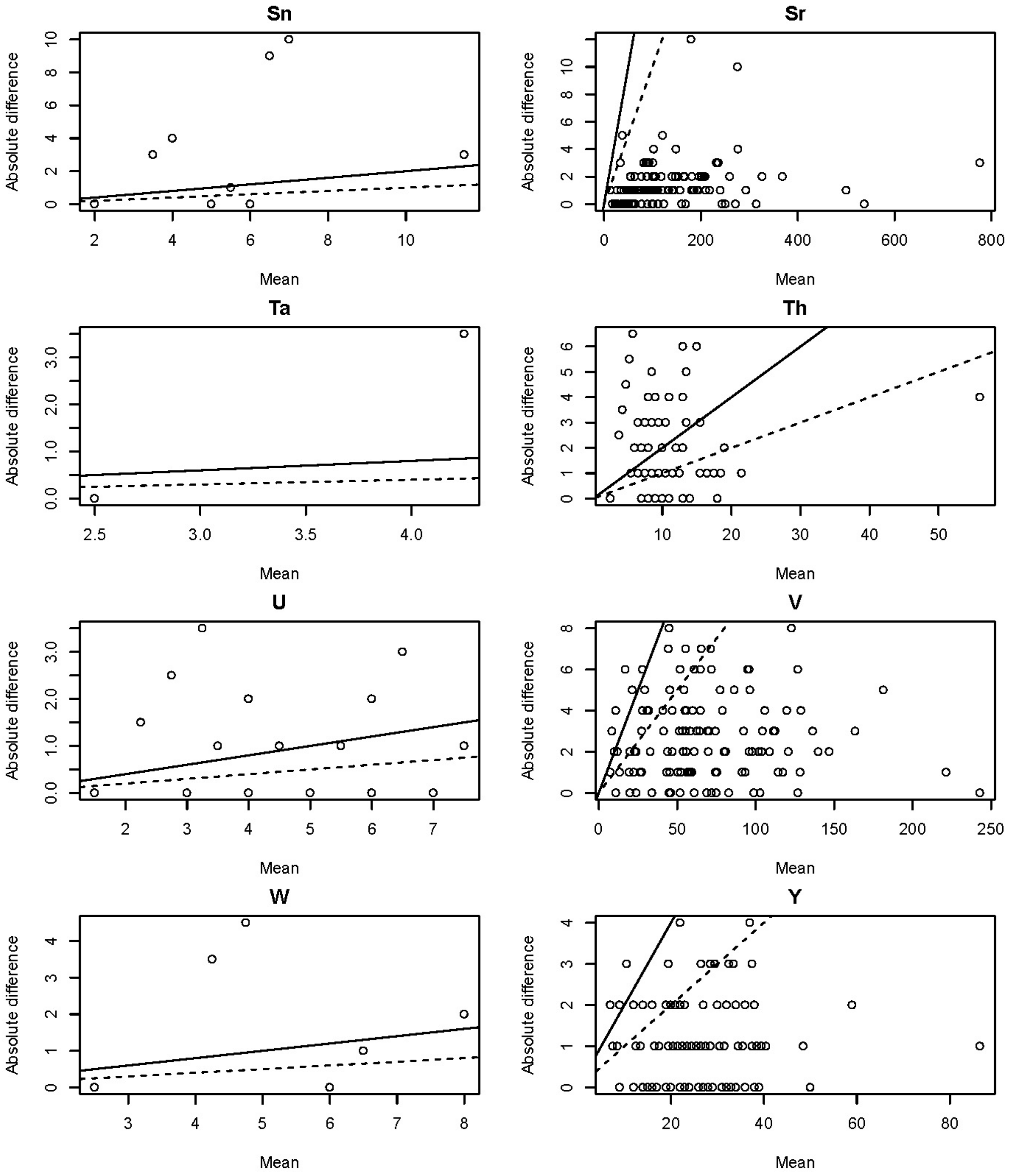

Ni
Absolute difference
0
1
2
3
4
5
6
7
0
100
200
300
400
Mean

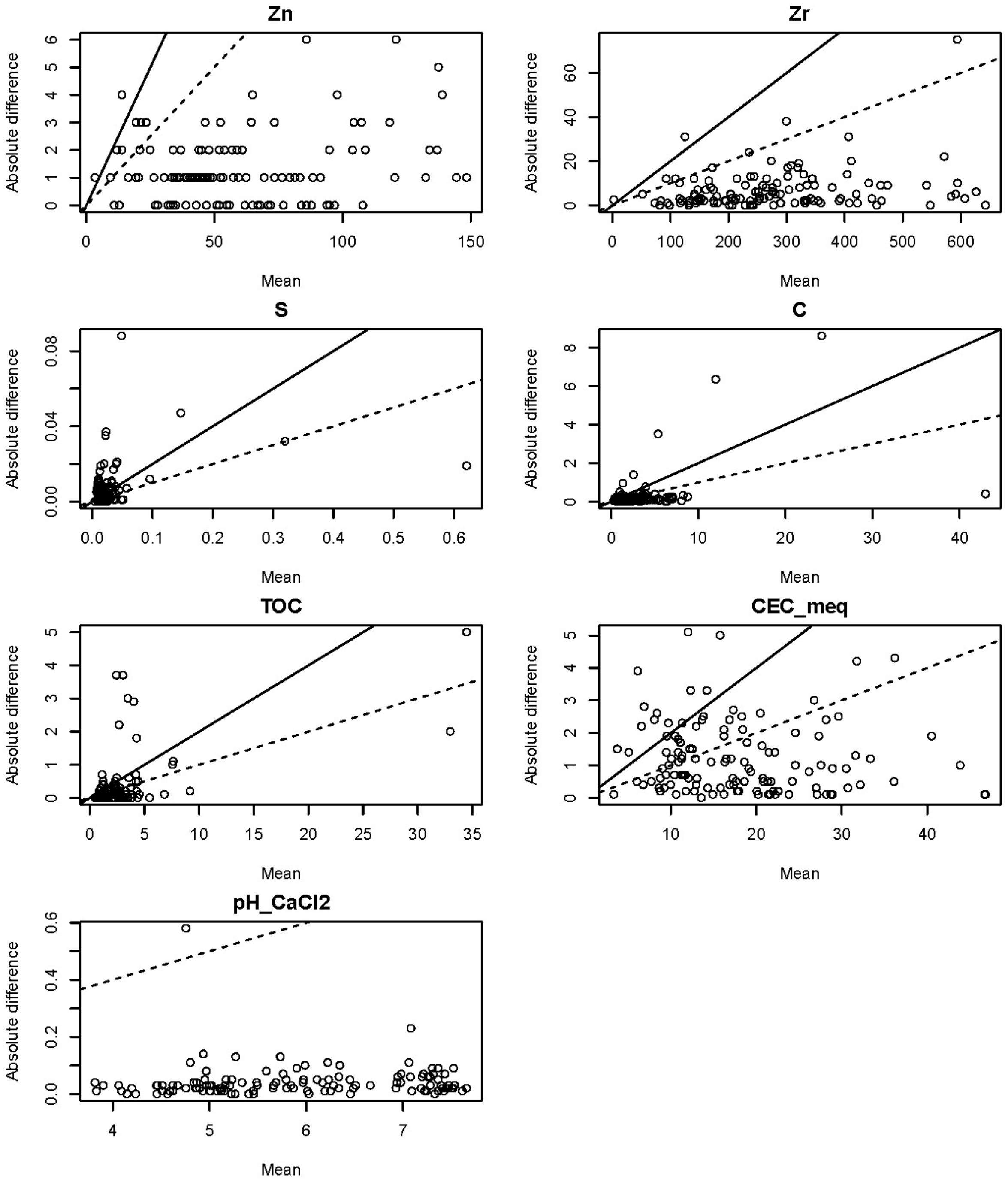

Pb
Absolute difference
0
100
200
300
0
50
100
150
200
Mean


Rb
Absolute difference
0
5
10
15
20
0
50
100
150
200
250
Mean


Sb
Absolute difference
0.0
1.0
2.0
3.0
2.5
3.0
3.5
4.0
Mean

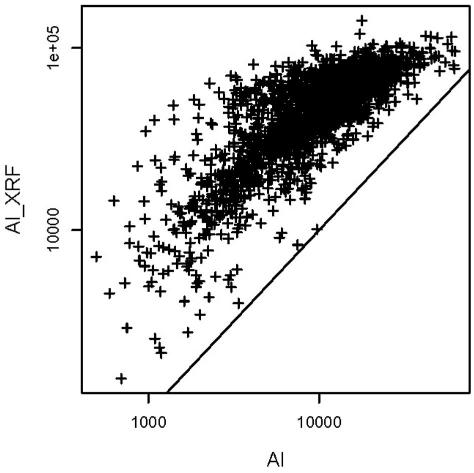

Sc
Absolute difference
0.0
1.0
2.0
3.0
0
5
10
15
20
25
30
Mean

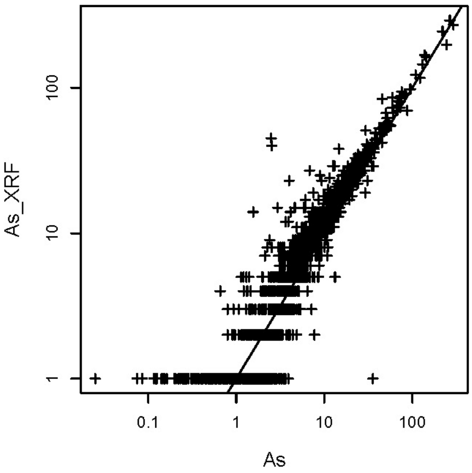

Sn
Absolute difference
0 2 4 6 8 10
2 4 6 8 10
Mean
Sr
Absolute difference
0 2 4 6 8 10
0 200 400 600 800
Mean
Ta
Absolute difference
0.0 1.0 2.0 3.0
2.5 3.0 3.5 4.0
Mean
Th
Absolute difference
0 1 2 3 4 5 6
10 20 30 40 50
Mean
U
Absolute difference
0.0 1.0 2.0 3.0
2 3 4 5 6 7
Mean
V
Absolute difference
0 2 4 6 8
0 50 100 150 200 250
Mean
W
Absolute difference
0 1 2 3 4
3 4 5 6 7 8
Mean
Y
Absolute difference
0 1 2 3 4
20 40 60 80
Mean

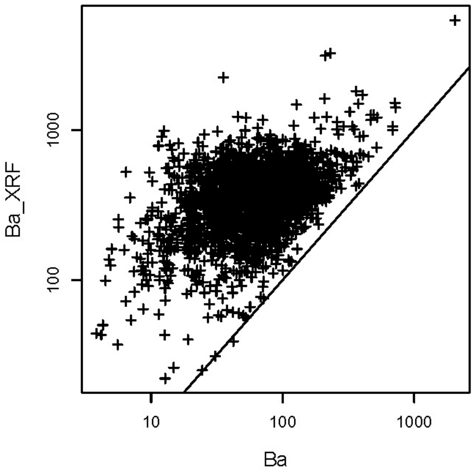

Zn
Zr
S
C
TOC
CEC_meq
pH_CaCl2
Absolute difference
Mean
0 1 2 3 4 5 6
0 50 100 150
0 20 40 60
0 100 200 300 400 500 600
0.00 0.04 0.08
0.0 0.1 0.2 0.3 0.4 0.5 0.6
0 2 4 6 8
0 10 20 30 40
0 1 2 3 4 5
0 5 10 15 20 25 30 35
0 1 2 3 4 5
10 20 30 40
0.0 0.2 0.4 0.6
4 5 6 7

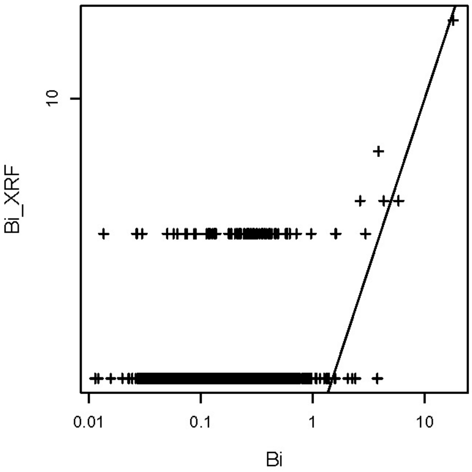
APPENDIX 5. XY-plots of XRF-results versus aqua regia results for the Gr samples

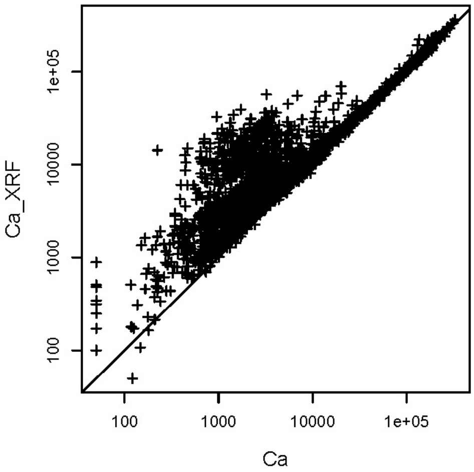
The 1:1 line is shown on all plots. Generally a higher analytical result for the XRF-analyses is to be expected.

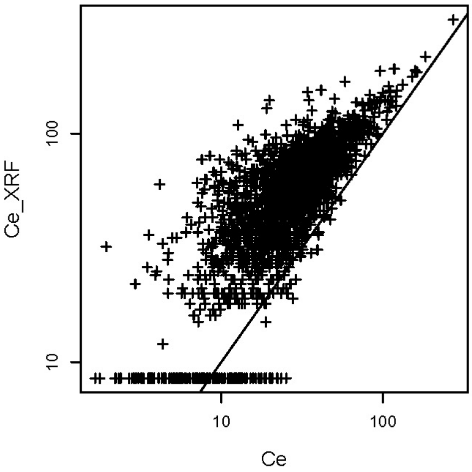

Al_XRF
1e+05
10000
1000
10000
Al

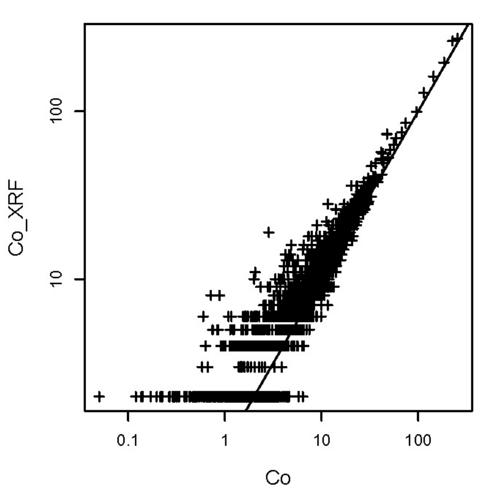

As_XRF
100
10
1
0.1
1
10
100
As

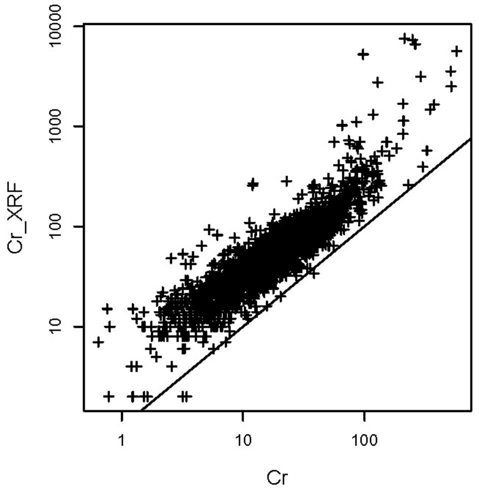

Ba_XRF
1000
100
10
100
1000
Ba

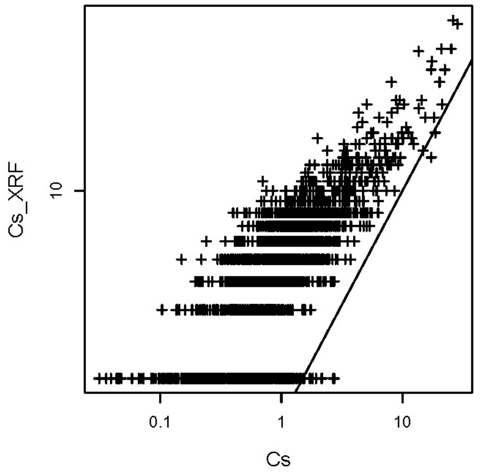

Bi_XRF
10
0.01
0.1
1
10
Bi

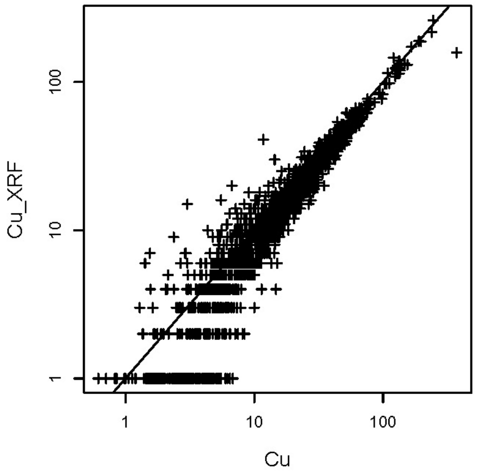

Ca_XRF
1e+05
10000
1000
100
100
1000
10000
1e+05
Ca

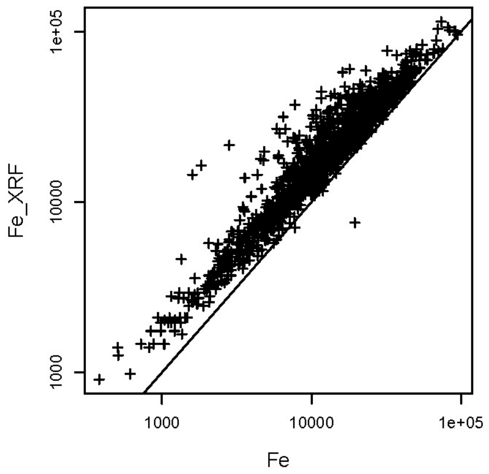

Ce_XRF
100
10
10
100
Ce

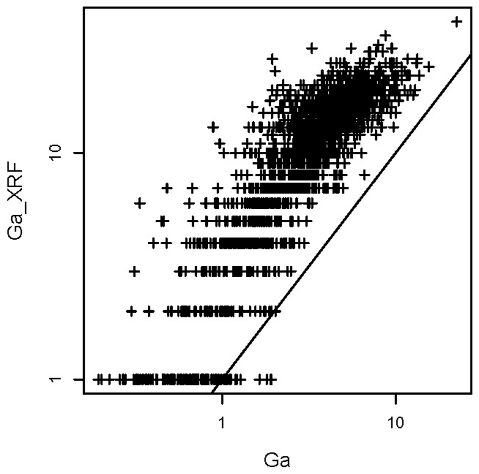

Co_XRF
100
10
0.1
1
10
100
Co

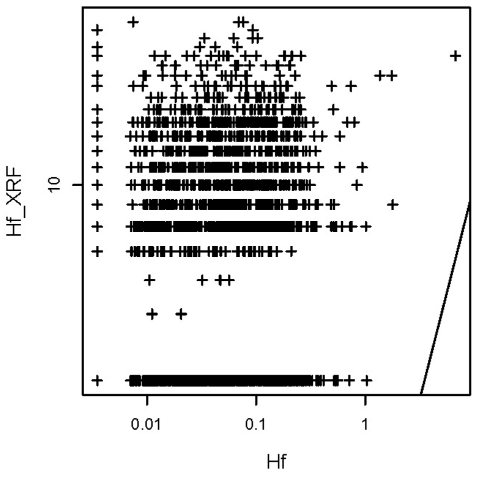

Cr_XRF
10000
1000
100
10
1
10
100
Cr

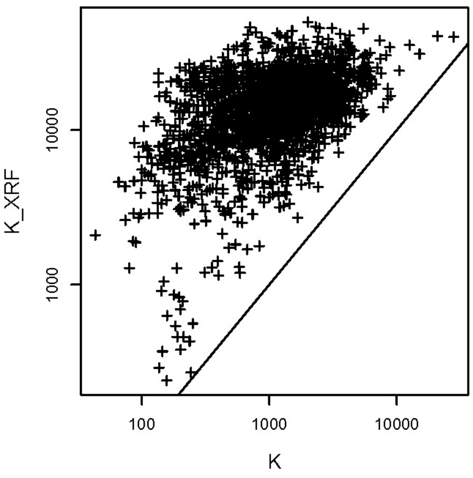

Cs_XRF
10
0.1
1
10
Cs

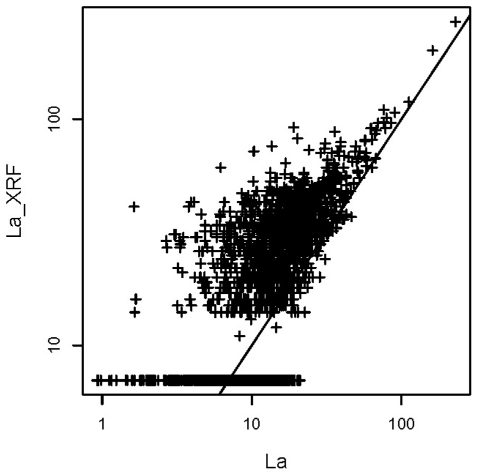

Cu_XRF
100
10
1
1
10
100
Cu

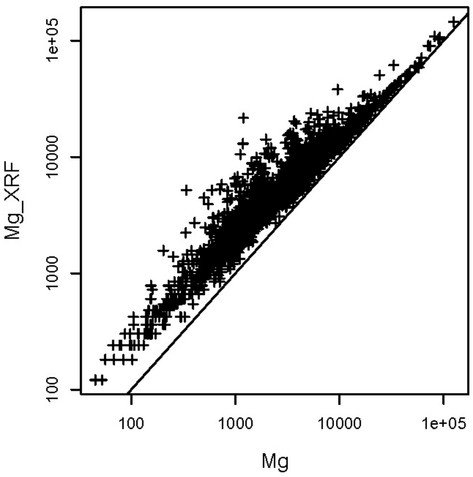

Fe_XRF
1e+05
10000
1000
1000
10000
1e+05
Fe

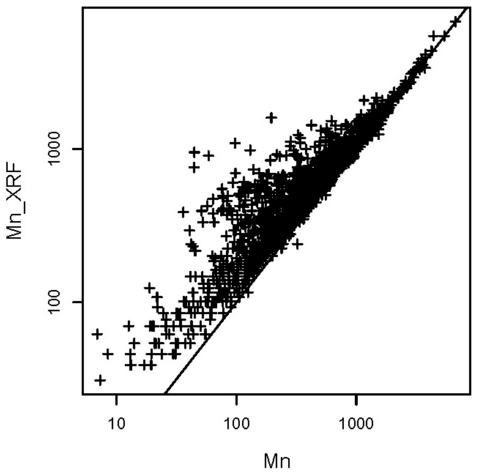

Ga_XRF
10
1
1
10
Ga

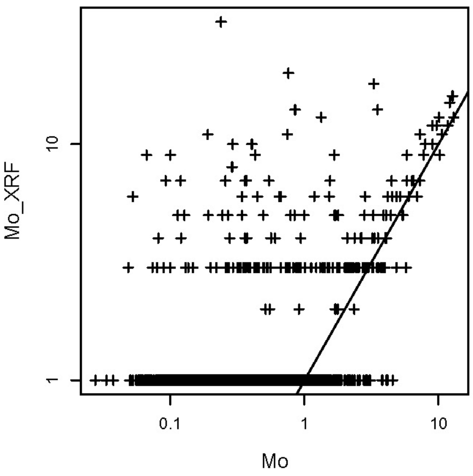

Hf_XRF
10
0.01
0.1
1
Hf

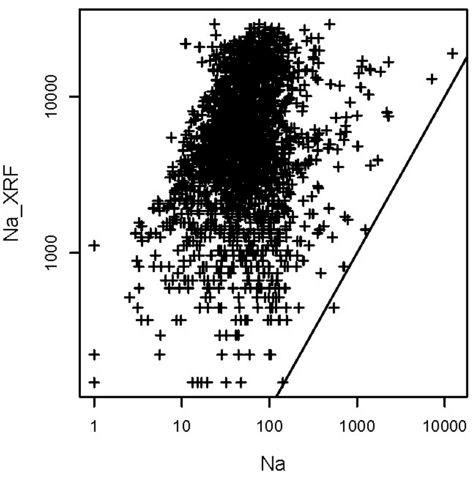

K_XRF
10000
1000
100
1000
10000
K

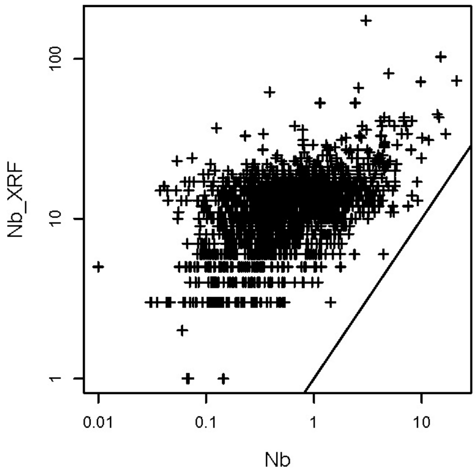

La_XRF
100
10
1
10
100
La

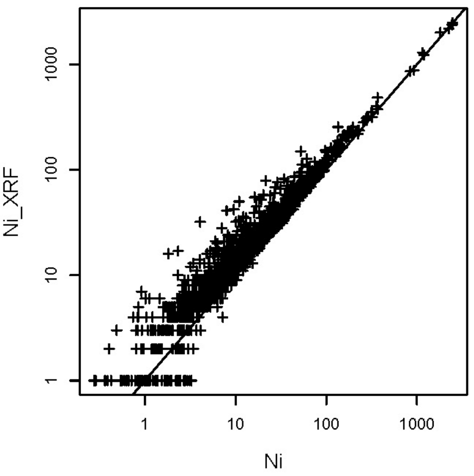

Mg_XRF
1e+05
10000
1000
100
100
1000
10000
1e+05
Mg

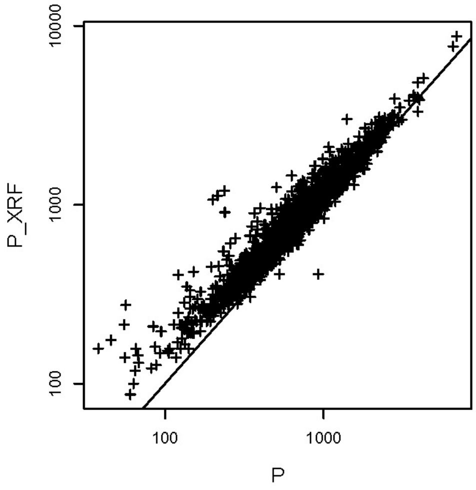

Mn_XRF
1000
100
10
100
1000
Mn

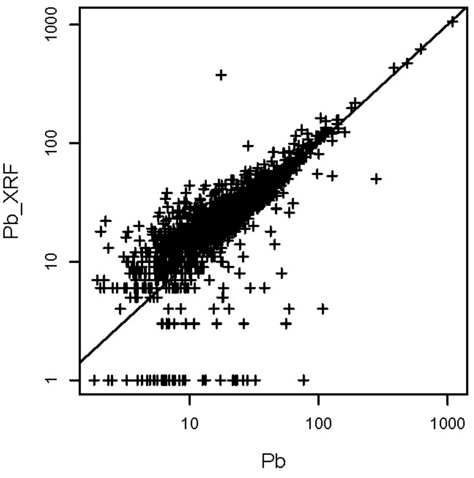

Mo_XRF
10
1
0.1
1
10
Mo

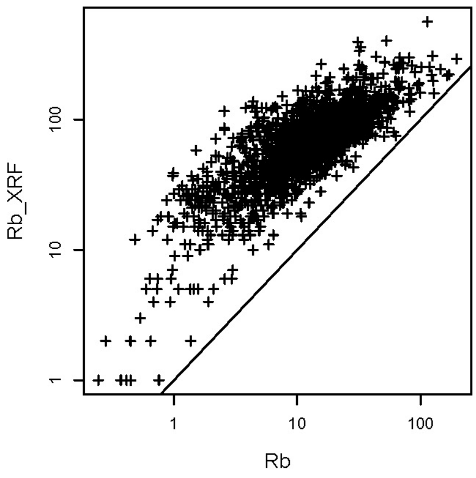

Na_XRF
10000
1000
1
10
100
1000
10000
Na

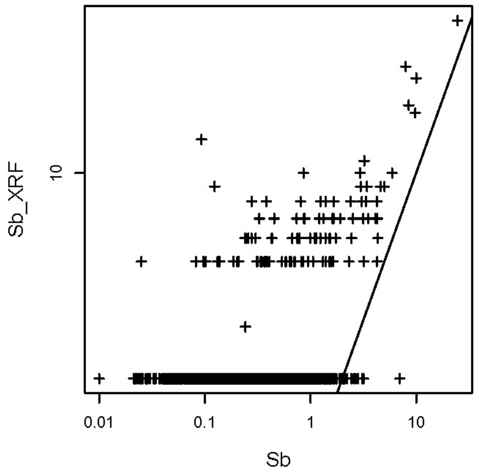

Nb_XRF
100
10
1
0.01
0.1
1
10
Nb

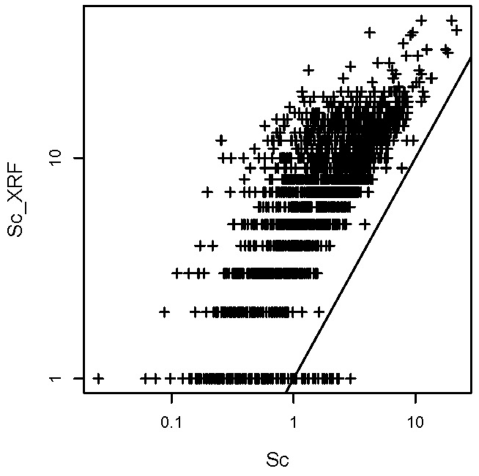

Ni_XRF
1000
100
10
1
1
10
100
1000
Ni

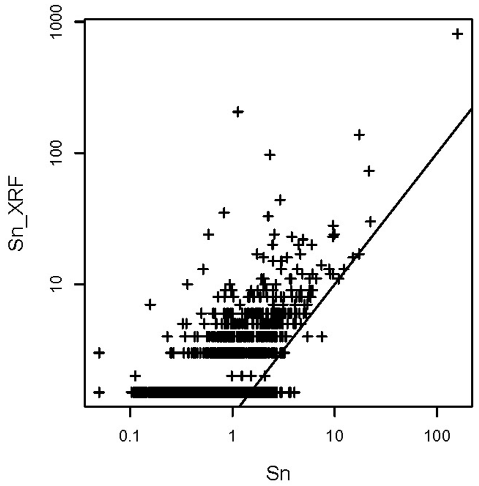

P_XRF
10000
1000
100
100
1000
P

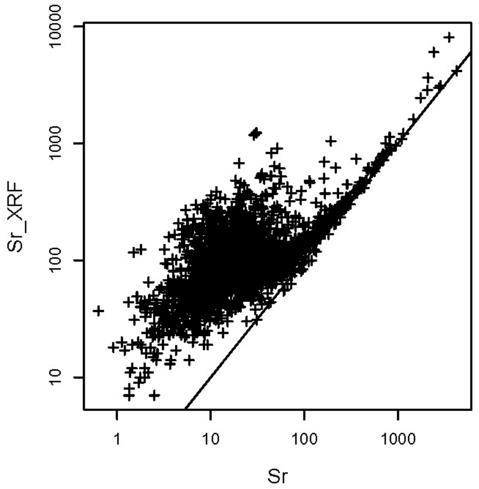

Pb_XRF
1000
100
10
1
10
100
1000
Pb

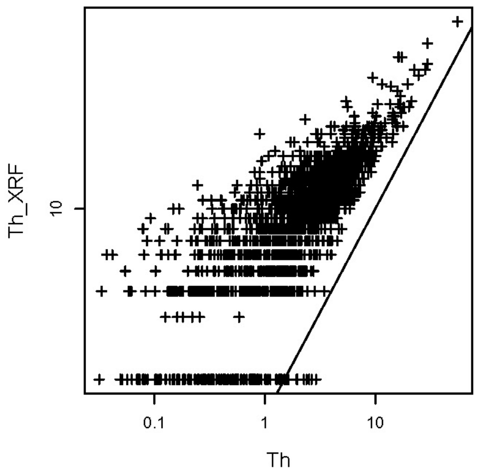

Rb_XRF
100
10
1
1
10
100
Rb

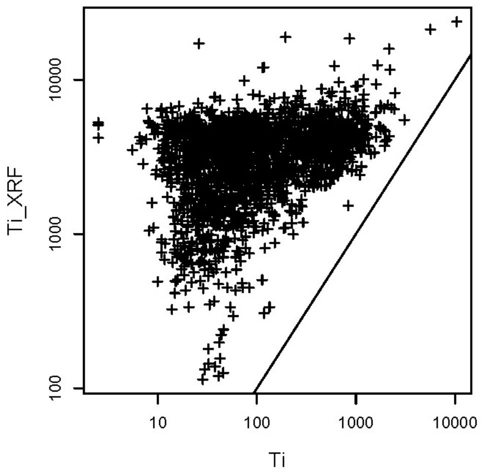

Sb_XRF
10
0.01
0.1
1
10
Sb

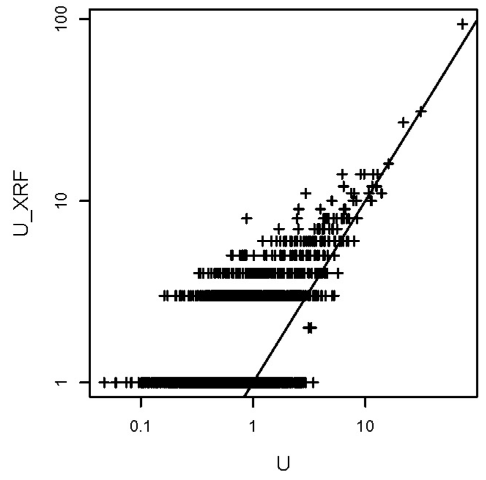

Sc_XRF
10
1
0.1
1
10
Sc

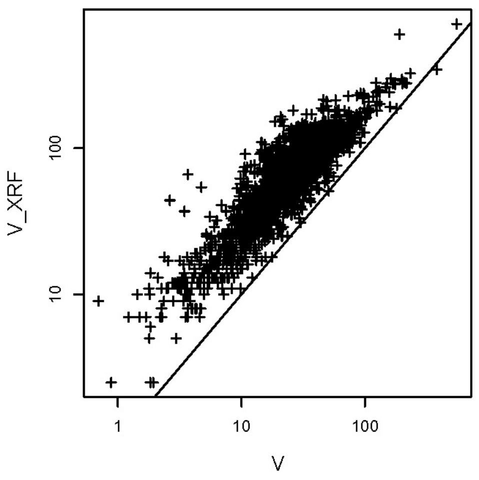

Sn_XRF
1000
100
10
0.1
1
10
100
Sn

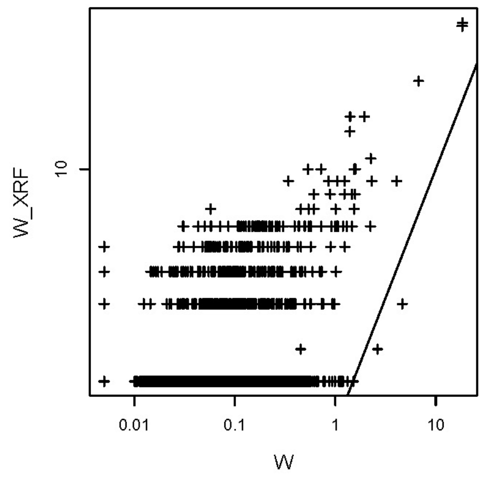

Sr_XRF
10000
1000
100
10
1
10
100
1000
Sr

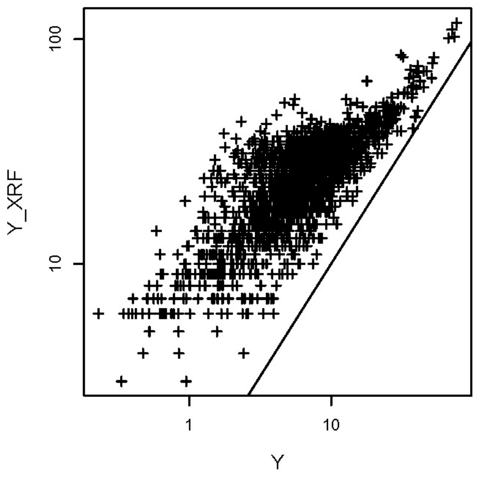

Th_XRF
10
0.1
1
10
Th

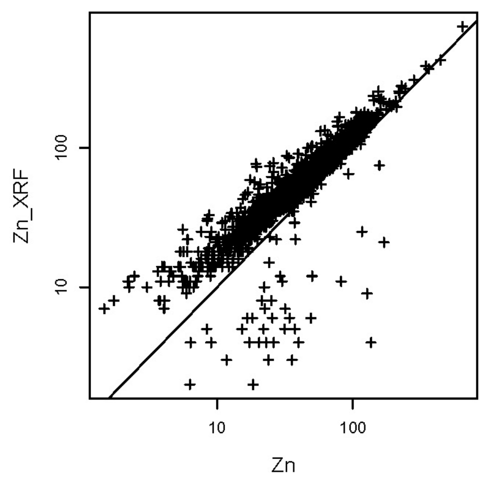

Ti_XRF
10000
1000
100
10
100
1000
10000
Ti

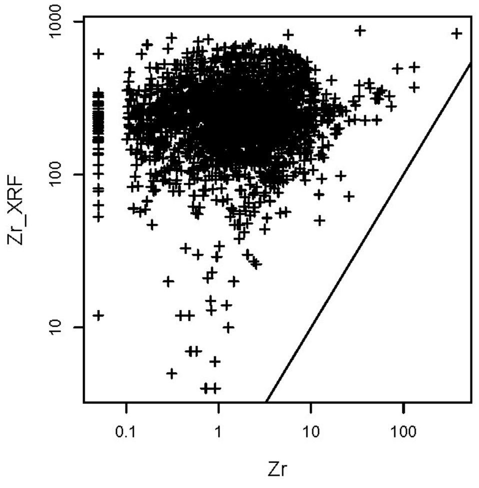

100
10
1
U_XRF
0.1
1
10
U


100
10
V_XRF
1
10
100
V


10
W_XRF
0.01
0.1
1
10
W

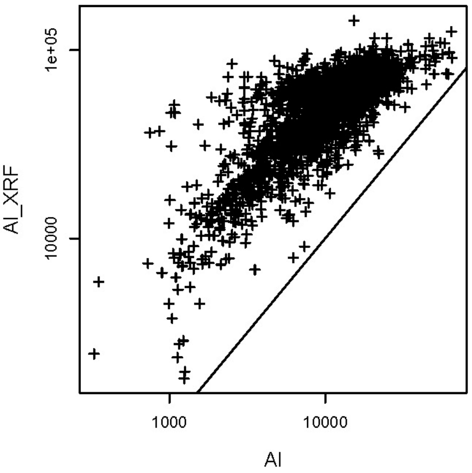

100
10
Y_XRF
1
10
Y

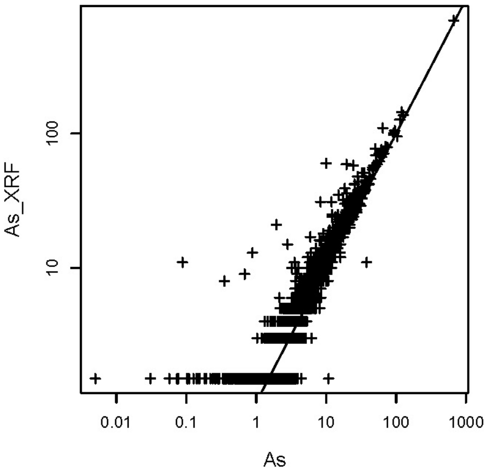

100
10
Zn_XRF
10
100
Zn

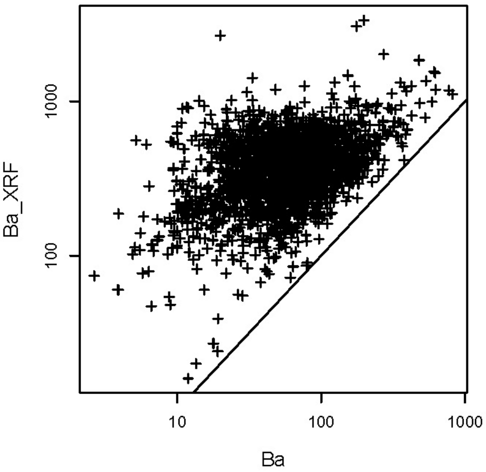

1000
100
10
Zr_XRF
0.1
1
10
100
Zr

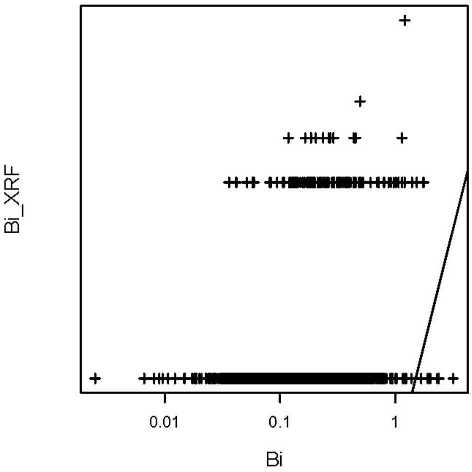
APPENDIX 6. XY-plots of XRF-results versus aqua regia results for the Ap samples

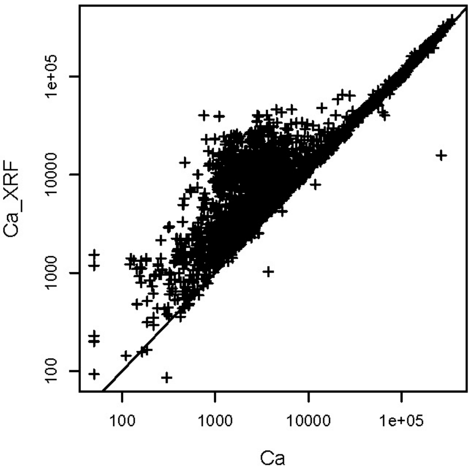
The 1:1 line is shown on all plots. Generally a higher analytical result for the XRF-analyses is to be expected.

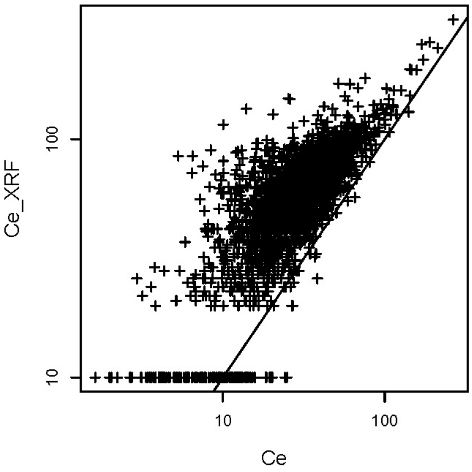

1e+05
10000
Al_XRF
1000
10000
Al

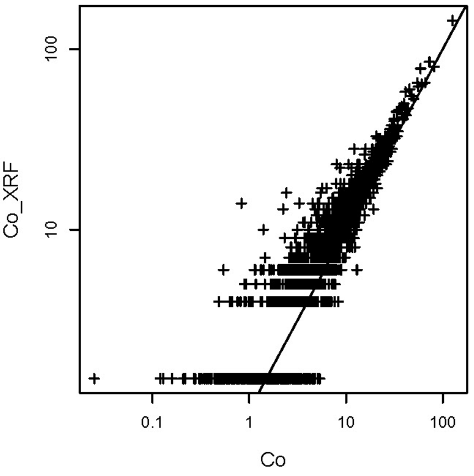

100
10
As_XRF
0.01
0.1
1
10
100
1000
As

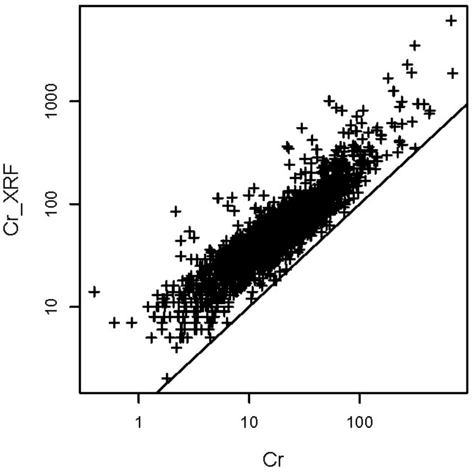

1000
100
Ba_XRF
10
100
1000
Ba

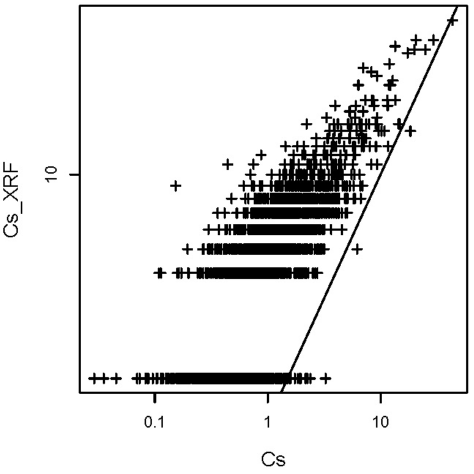

Bi_XRF
0.01
0.1
1
Bi

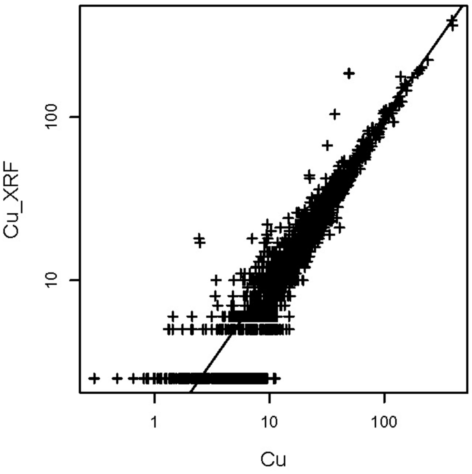

1e+05
10000
1000
100
Ca_XRF
100
1000
10000
1e+05
Ca

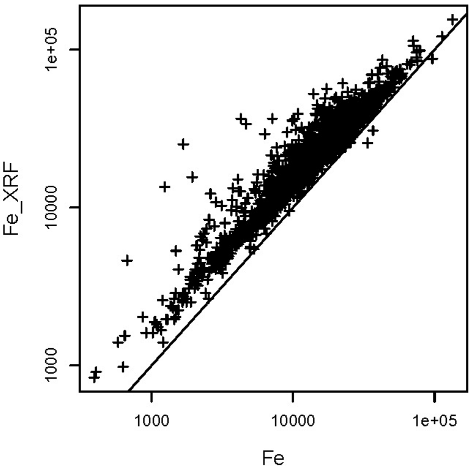

100
10
Ce_XRF
10
100
Ce

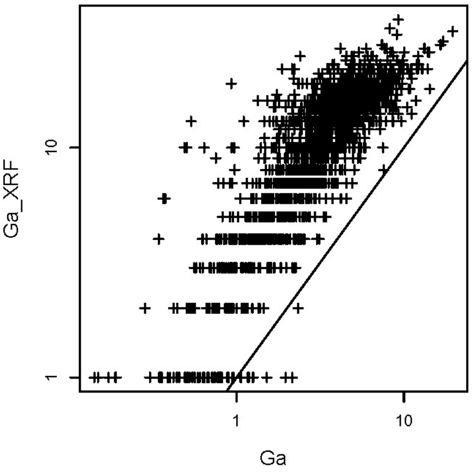

Co_XRF
100
10
0.1
1
10
100
Co

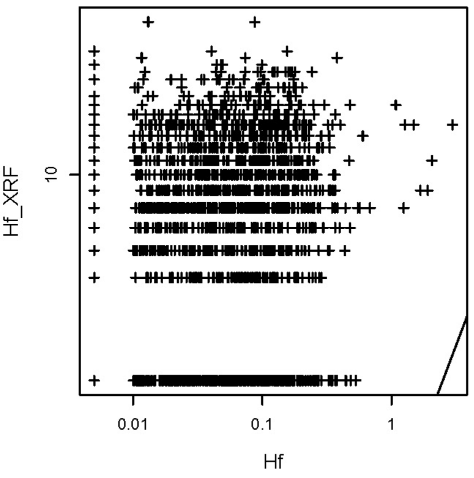

Cr_XRF
1000
100
10
1
10
100
Cr

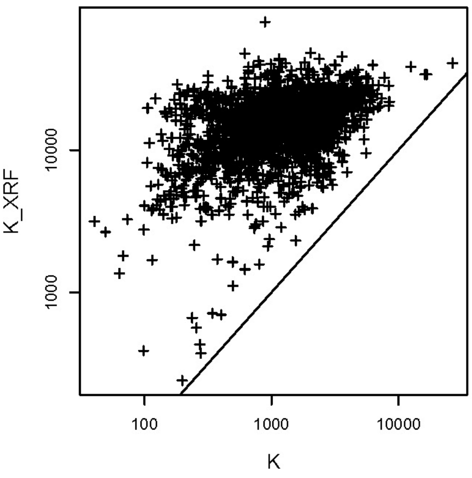

Cs_XRF
10
0.1
1
10
Cs

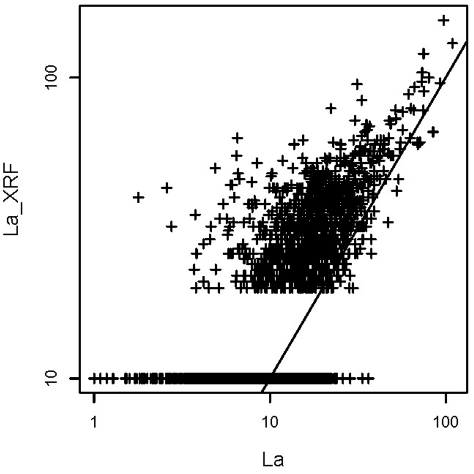

Cu_XRF
100
10
1
10
100
Cu

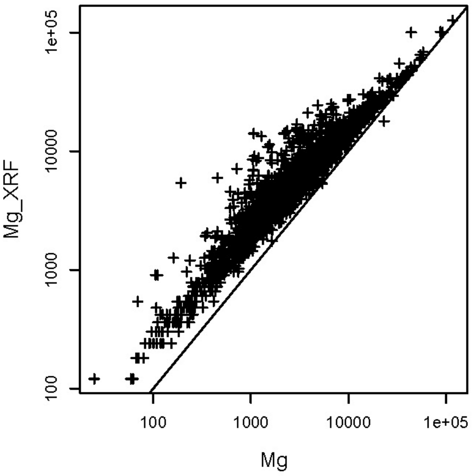

Fe_XRF
1e+05
10000
1000
1000
10000
1e+05
Fe

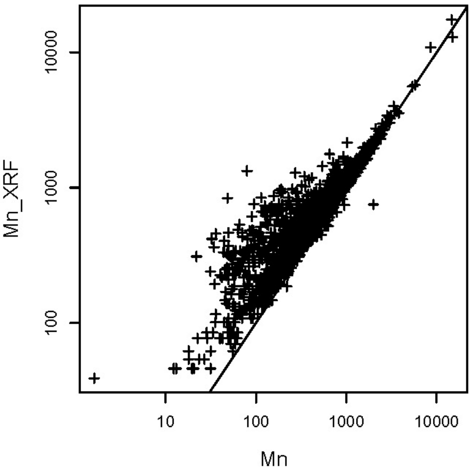

Ga_XRF
10
1
1
10
Ga

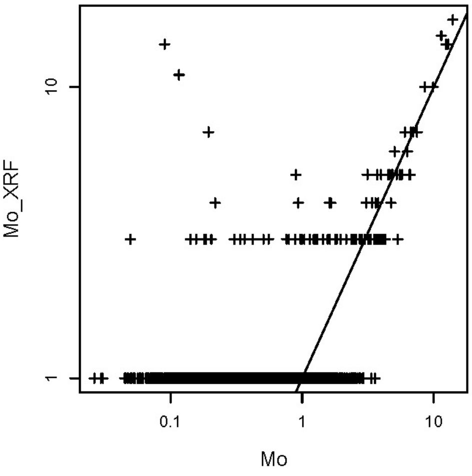

Hf_XRF
10
0.01
0.1
1
Hf

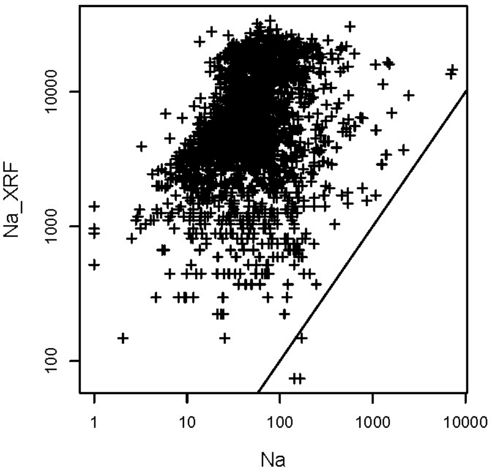

K_XRF
10000
1000
100
1000
10000
K

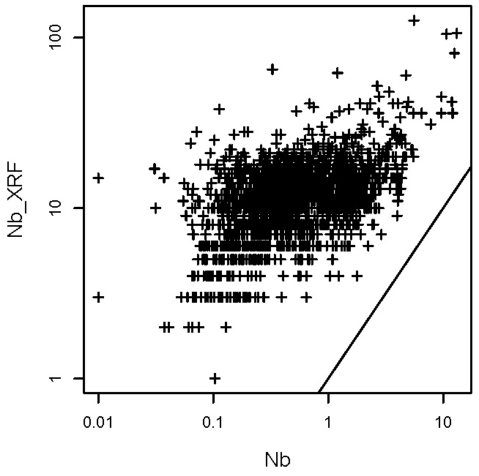

La_XRF
100
10
1
10
100
La

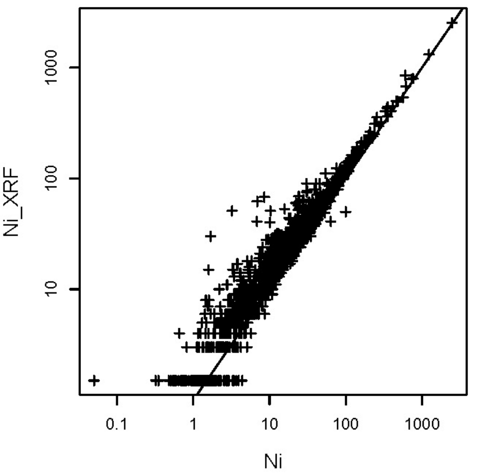

Mg_XRF
1e+05
10000
1000
100
100
1000
10000
1e+05
Mg

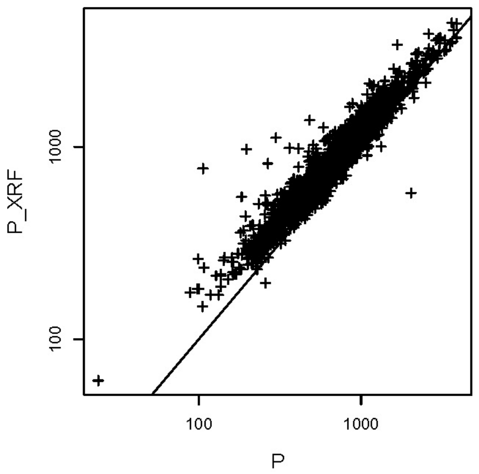

Mn_XRF
10000
1000
100
10
100
1000
10000
Mn

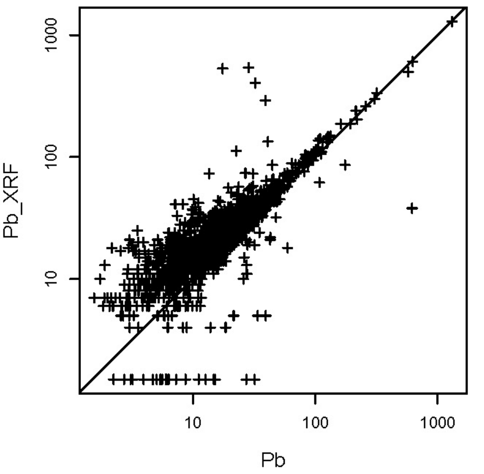

Mo_XRF
10
1
0.1
1
10
Mo

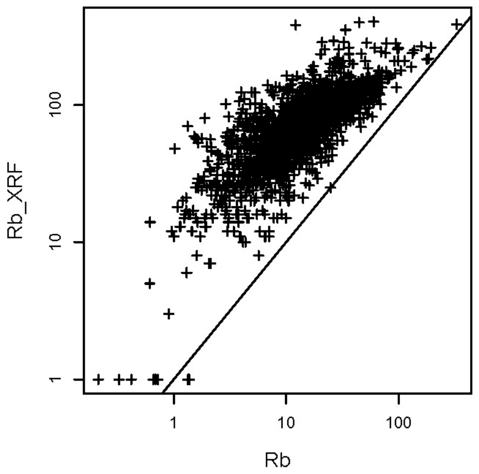

Na_XRF
10000
1000
100
1
10
100
1000
10000
Na

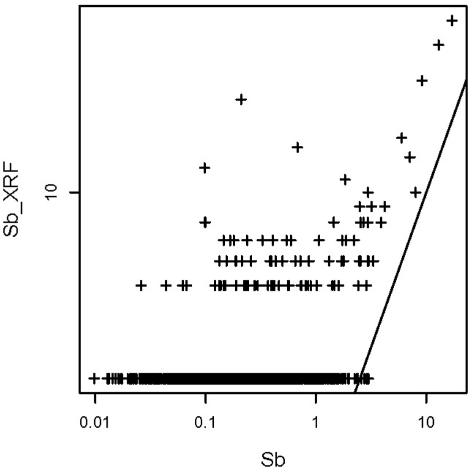

Nb_XRF
100
10
1
0.01
0.1
1
10
Nb

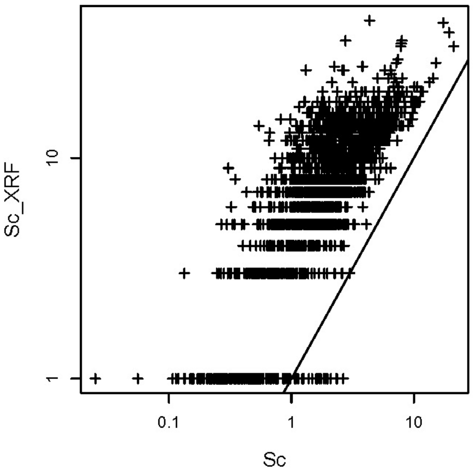

Ni_XRF
1000
100
10
0.1
1
10
100
1000
Ni

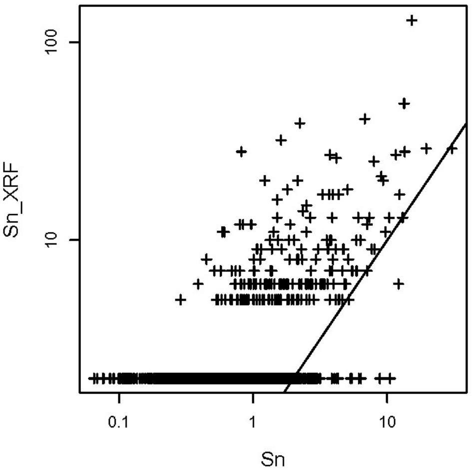

P_XRF
1000
100
100
1000
P

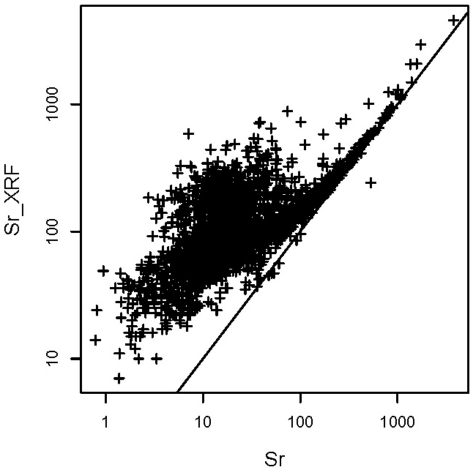

Pb_XRF
1000
100
10
10
100
1000
Pb

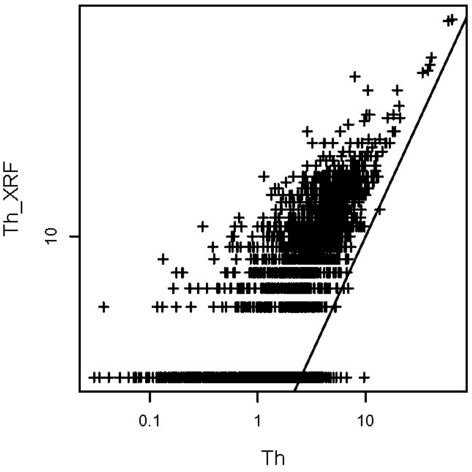

Rb_XRF
100
10
1
1
10
100
Rb

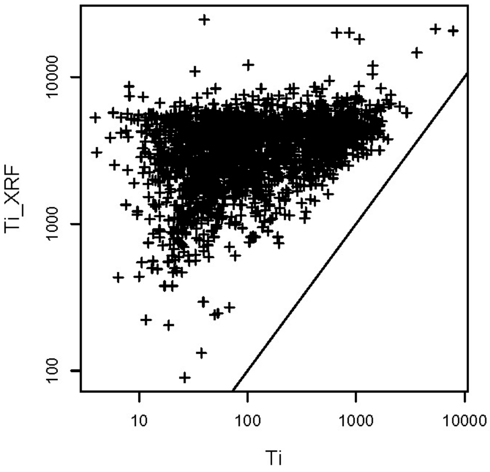

Sb_XRF
10
0.01
0.1
1
10
Sb

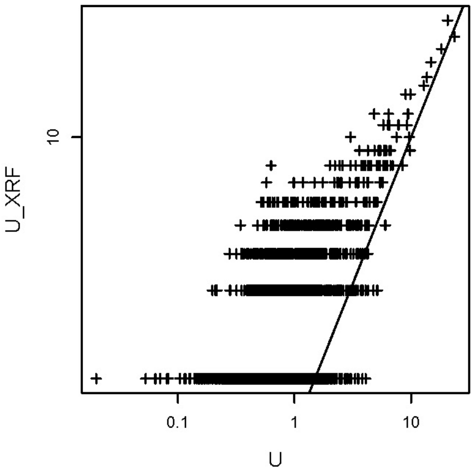

Sc_XRF
10
1
0.1
1
10
Sc

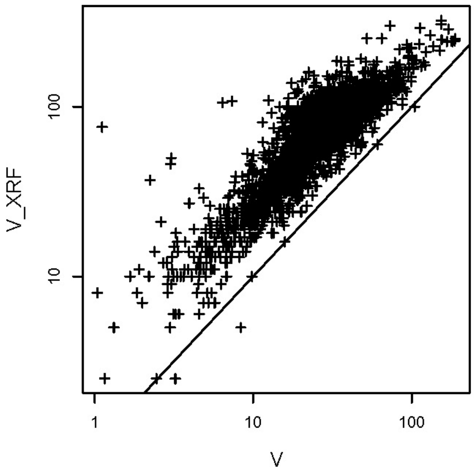

Sn_XRF
100
10
0.1
1
10
Sn

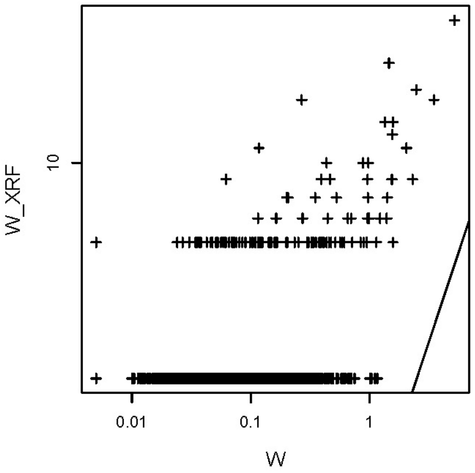

Sr_XRF
1000
100
10
1
10
100
1000
Sr

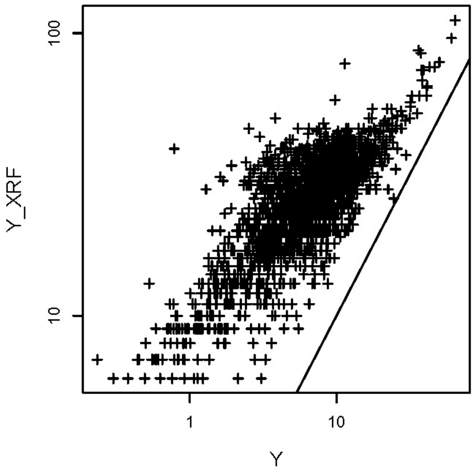

Th_XRF
10
0.1
1
10
Th

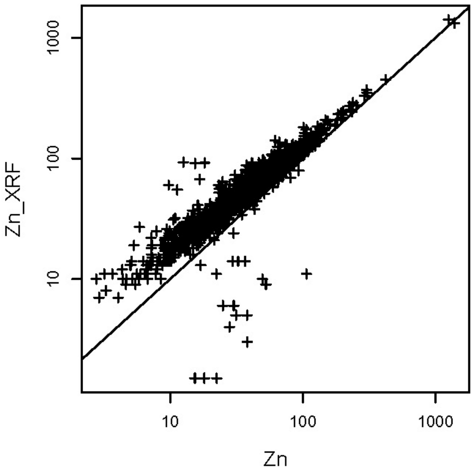

Ti_XRF
10000
1000
100
10
100
1000
10000
Ti

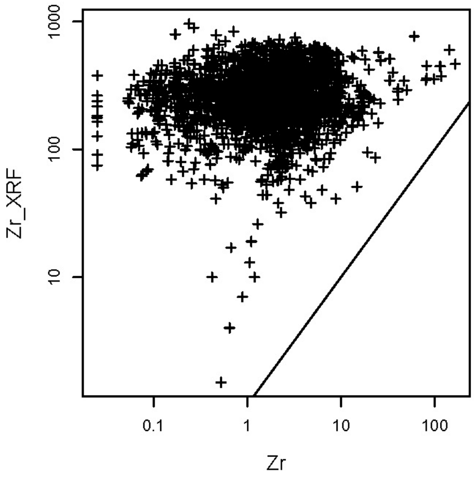

U_XRF
10
0.1
1
10
U


V_XRF
100
10
1
10
100
V


W_XRF
10
0.01
0.1
1
W


Y_XRF
100
10
1
10
Y


Zn_XRF
1000
100
10
10
100
1000
Zn


Zr_XRF
1000
100
10
0.1
1
10
100
Zr

APPENDIX 7. Detailed method description for CEC determination with the silver-thiourea method. ATTENTION: there are transposed digits in the “Calculation” formula on page 7 of the attached document: ”53940” is the correct factor for the calculation and not the stated “53490”.

Department of Sustainable Natural Resources

SOIL SURVEY STANDARD TEST METHOD

CATION EXCHANGE CAPACITY AND EXCHANGEABLE CATIONS BY SILVER THIOUREA

ABBREVIATED NAME	CEC
TEST NUMBER	C5
TEST METHOD TYPE	A
VERSION NUMBER	4

SCOPE

Cation Exchange Capacity (CEC) is a general indicator of soil storage capacity for available positively-charged plant nutrients such as calcium, magnesium, potassium and sodium. In some instances, this method appears to overestimate exchangeable magnesium in some saline and alkaline soils and can overestimate exchangeable potassium in some mica-rich soils.

PRINCIPLE

This method for the simultaneous measurement of CEC and exchangeable cations is based on the very high affinity of the silver-thiourea complex for occupying exchange sites on soil colloids. Residual silver is measured in a silver-thiourea extract by atomic absorption spectrometry to determine the total CEC. The displaced cations are also measured in the same extract by AAS.

SPECIAL APPARATUS

- Atomic absorption spectrophotometer with hollow cathode lamps to measure Ag, Na, K, Ca, Mg and Al.
- Diluter/Dispenser (Brand Diluette® Cat No 7046 54).

REAGENTS

General Reagents

(a) Glycol-Ethanol

Mix 100 mL ethylene glycol (ethanediol) with 36 mL deionised water and make to 1 L with ethanol.

(b) 0.01 M Ag-Thiourea

Dissolve 7.5 g thiourea in about 250 mL deionised water in a 1 L beaker. Dissolve 1.699 g $AgNO_3$ (AR) in 500 mL deionised water in a beaker. Slowly add the $AgNO_3$ solution to the Thiourea solution under vigorous stirring. Transfer the Ag-Th. to a 1 L volumetric flask and make to volume with deionised water. (See Note 1).

(c) Thiourea (0.75 g/L)

Dissolve 0.75 g of thiourea and dilute to 1 L with deionised water. Dilute 1:10 for preparation of silver standards and samples.

(d) Potassium (20 000 mg/L)

Dissolve 38.14 g of KCl (AR) and dilute to 1 L with deionised water.

(e) Potassium (2 000 mg/L)

Dissolve 3.81 g KCl (AR) and dilute to 1 L with deionised water.

(f) Sodium (15 000 mg/L)

Dissolve 38.13 g of NaCl (AR) and dilute to 1 L with deionised water.

(g) Sodium (1 500 mg/L)

Dissolve 3.81 g NaCl (A.R.) and dilute to 1 L with deionised water.

Standard Reference Solutions

Sodium 1 000 mg/L Std. Soln.

Dissolve 2.542 g of oven-dried sodium chloride (AR) in deionised water, transfer to a 1 L volumetric flask and make to volume with deionised water.

Potassium 1 000 mg/L Std. Soln.

Dissolve 1.907 g of oven-dried potassium chloride (AR) in deionised water, transfer to a 1 L volumetric flask and make to volume with deionised water.

Calcium 1 000 mg/L Std. Soln.

Disperse 2.497 g of oven-dried calcium carbonate (AR) in 50 mL deionised water. Add drop wise a minimum volume of HCl to effect complete solution of the $CaCO_3$. Transfer to a 1 L volumetric flask and make to volume with deionised water.

Magnesium 1 000 mg/L Std. Soln.

Dissolve 1 g of magnesium (AR) in a minimum quantity of 1 N HCl, transfer to a 1 L volumetric flask and make to volume with deionised water.

Aluminium 1 750 mg/L Std. Soln.

Dissolve 1.750 g of aluminium (AR) in minimum quantity of 1 N HCl (containing trace HNO_3), transfer to a 1 L volumetric flask and make to volume with deionised water.

Working Standard Solutions

Silver

Pipette 25 mL of 0.01M Ag-Thiourea reagent into a 200 mL volumetric flask and bulk to volume with 0.75 g/L Thiourea solution.

$$concentration\ Ag \equiv 134.8\ mg/L$$

Prepare a range of calibration standards using the Diluter/Dispenser and Table 1 (below) as a guide:

Table 1. Preparation of calibration solutions of silver

Standard No. →	1	2	3	4	5	6
Mls. 134.8 mg/LAg. Std. Soln.	0.05	0.10	0.20	0.30	0.40	0.50
Mls. 0.075 g/L Thiourea Soln.	4.95	4.90	4.80	4.70	4.60	4.50
Final Concentration of Ag (mg/L)	1.35	2.70	5.39	8.09	10.78	13.48

Sodium, Calcium and Magnesium

Transfer by pipette 20 mL of 1 000 mg/L Na, 25 mL of 1 000 mg/L Ca, and 2.5 mL of 1 000 mg/L Mg, into a 500 mL volumetric flask and make to volume with deionised water.

Concentrations:
Na ≡ 20 mg/L
Ca ≡ 50 mg/L
Mg ≡ 5 mg/L

Prepare a range of calibration standards using the diluter/dispenser and Table 2 as a guide.

Table 2. Preparation of calibration solutions of Na, Ca and Mg

Standard No. →		1	2	3	4	5	6
Mls. Na, Ca & Mg Working Standard		0.05	0.10	0.20	0.30	0.40	0.50
Mls. 2 000 mg/L Potassium Soln.		4.95	4.90	4.80	4.80	4.70	4.50
Final Concentration of ion (mg/L)	**Na**	0.20	0.40	0.80	1.20	1.60	2.00
	Ca	0.50	1.00	2.00	3.00	4.00	5.00
	Mg	0.05	0.10	0.20	0.30	0.40	0.50

Potassium

Pipette 10 mL of 1 000 mg/L potassium std. into a 500 mL volumetric flask and make to volume with deionised water.

$$concentration\ K \equiv 20\ mg/L$$

Prepare a range of calibration standards using the diluter/dispenser and Table 3 as a guide:

Table 3. Preparation of calibration solutions of potassium.

Standard No. →	1	2	3	4	5	6
Mls. 20 mg/L K std. Soln.	0.05	0.10	0.20	0.30	0.40	0.50
Mls. 1 500 mg/L Sodium Soln.	4.95	4.90	4.80	4.70	4.60	4.50
Final Concentration of K (mg/L)	0.20	0.40	0.80	1.20	1.60	2.00

Aluminium

Pipette 20 mL of 1 750 mg/L Aluminium Std. into a 250 mL volumetric flask and make to volume with deionised water.

$$concentration\ Al \equiv 140\ mg/L$$

Prepare a range of calibration standards using the diluter/dispenser and Table 4 as a guide:

Table 4. Preparation of calibration solutions of aluminium

Standard No. →	1	2	3	4	5	6
Mls. 140 mg/L Al Std. Soln.	0.05	0.10	0.20	0.30	0.40	0.50
Mls 2 000 mg/L Potassium Soln.	4.95	4.90	4.80	4.70	4.60	4.50
Final Concentration of Al (mg/L)	1.40	2.80	5.60	8.40	11.2	14.0

PROCEDURE

Removal of Soluble Salts

1. Weigh accurately 1 g of air-dry soil (<2 mm) into a small plastic shaking bottle.
2. Add about 15–20 mL of glycol-ethanol and shake for 1 hour at 15 rpm.
3. Filter through a Whatman No 42 filter paper, retaining as much of the soil as possible in the shaking bottle. Discard the filtrate.
4. Rinse the soil retained in the bottle with a further 15–20 mL of glycol-ethanol and pass through the filter paper. (See Note 2.)
5. Allow the soil to air-dry. Brush any soil particles adhering to the rim of the bottle into the filter paper and then return the filter paper and soil to the bottle.

Extraction for Cation Exchange Capacity and Exchangeable Cations

1. Add 50 mL of 0.01 M Ag-Thiourea and shake for 4 hours at 15 rpm.
2. Filter through a Whatman No 42 filter paper.
3. Retain the filtrate in a sealable glass container.

Measurement of Cation Exchange Capacity

1. Dilute the unknown sample by 100 with 0.75 g/L thiourea solution.
2. Set up the atomic absorption spectrophotometer to measure Ag according to the manufacturer's instructions. Measure the absorption of each of the standard solutions and diluted unknown samples.

Measurement of the Exchangeable Na, Ca, Mg, Al

1. Dilute the unknown sample by 10 with 2 000 mg/L potassium solution.
2. Set up the atomic absorption spectrophotometer to measure sodium according to the manufacturer's instructions. Measure the absorption of each of the standard solutions and diluted unknown samples.
3. Carry out the measurement of Ca, Mg and Al concentration in the same manner. A dilution ratio of 50 is suggested for calcium and magnesium, and a dilution ratio of 3 for aluminium.

Measurement of Exchangeable K

1. Dilute the unknown sample by 10 with 1 500 mg/L sodium solution.
2. Set up the atomic absorption spectrophotometer to measure potassium according to the manufacturer's instructions. Measure the absorption of the standard solutions and diluted unknown samples.

CALCULATIONS

Cation Exchange Capacity

From the working standards, draw a calibration curve of absorption versus Ag concentration. Read the Ag concentration of the unknown sample extract from the graph.

Calculate the Cation Exchange Capacity (CEC).

$$CEC = \frac{53\ 490 - (A\, x\, DF\ x\, 50\, mL)}{B\, x 1\ 078.8}$$

Where:

A = Ag concentration in diluted extract from graph (mg/L)
B = Oven-dry weight of sample (g)
DF = Dilution factor

Exchangeable Cations

From the working standards, draw a calibration curve of absorption versus cation concentration. Read the cation concentration of the unknown sample extract from the graph.

Calculate Exchangeable Cations.

$$Cation\,(mg/kg) = \frac{A\,x\,DF\,x\,50mL}{B}$$

Where:

A = Cation concentration in diluted extract from graph (mg/kg)
B = Oven-dry weight of sample (g)
DF = Dilution factor

$$Cation\,(me/100g) = \frac{Cation\,(mg/kg)}{E}$$

Where:

E = Equivalent weight of cation × 10

i.e.

Na = 229.9
K = 391.0
Ca = 200.4
Mg = 121.6
Al = 89.9

REPORTING THE RESULTS

Report CEC to one decimal place and exchangeable cations to one decimal place for meq/100 g or to the nearest whole number for mg/kg.

REFERENCES

Pleysier, JL & Juo, ASR 1980, A single-extraction method using silver-thiourea for measuring exchangeable cations and effective CEC in soils with variable charges. *Soil Science,* 129:4, 205-211.

Searle, PL 1984, The single-extraction silver thiourea method for measuring the cation exchange capacity of soil: Some preliminary comments. *New Zealand Soil News,* 32:4, 133-136.

NOTES

1. The volume of 0.01M Ag-Thiourea prepared should be adjusted according to the amount required for extraction and use in standard solutions.

2. The drying time is reduced if the final wash is done with water/ethanol mixture (36 mL deionised water/964 mL ethanol).

3. If the concentration in the samples is greater than that of the standards, carry out a further dilution with Na, Ca, Mg diluting solution by taking 25 mL of 0.01M Ag-Thiourea, 25 mL of 20 000 mg/L K and dilute to 250 mL with deionised water.

4. If the concentration in the samples is greater than that of the standards, carry out a further dilution with K diluting solution.

5. To prepare K diluting solution, take 25 mL of 0.01M Ag-Thiourea, 25 mL of 15 000 mg/L Na and dilute to 250 mL with deionised water.