NGU Report 2009.049

The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils project (GEMAS) - Evaluation of quality control results of aqua regia extraction analysis

NGU
Norges geologiske undersøkelse
Geological Survey of Norway

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

REPORT

Report no.: 2009.049	ISSN 0800-3416	Grading: Open

Title:
The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils project (GEMAS) - Evaluation of quality control results of aqua regia extraction 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: 94 Map enclosures:	Price (NOK): 132
Fieldwork carried out: 2008	Date of report: 22.10.2009	Project no.: 323500	Person responsible: Malin Andersson

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 53 chemical elements (Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, In, K, La, Li, Mg, Mn, Mo, Na, Nb, Ni, P, Pb, Pd, Pt, Rb, Re, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr), following an aqua regia extraction on a 15 g aliquot per sample of both sample materials, are reported. Practical detection limits and precision, as well as the analytical results for the two project standards Ap and Gr are provided for all 53 elements. All analyses were carried out within twenty days at ACME laboratories in Vancouver, Canada. No serious quality problems, other than a few occasional outliers for a number of elements (B, Ca, Cu, S and Sn) were detected, and the analytical results were accepted after investigating the reasons for these outliers.

Keywords: quality control	accuracy	precision
ANOVA	aqua regia extraction	

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 unrecognizable 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). In combination, these procedures allow the detection and evaluation of most quality problems that can occur during sampling, sample preparation and 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 maps. For example, in 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 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 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 dataset, 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 in 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).

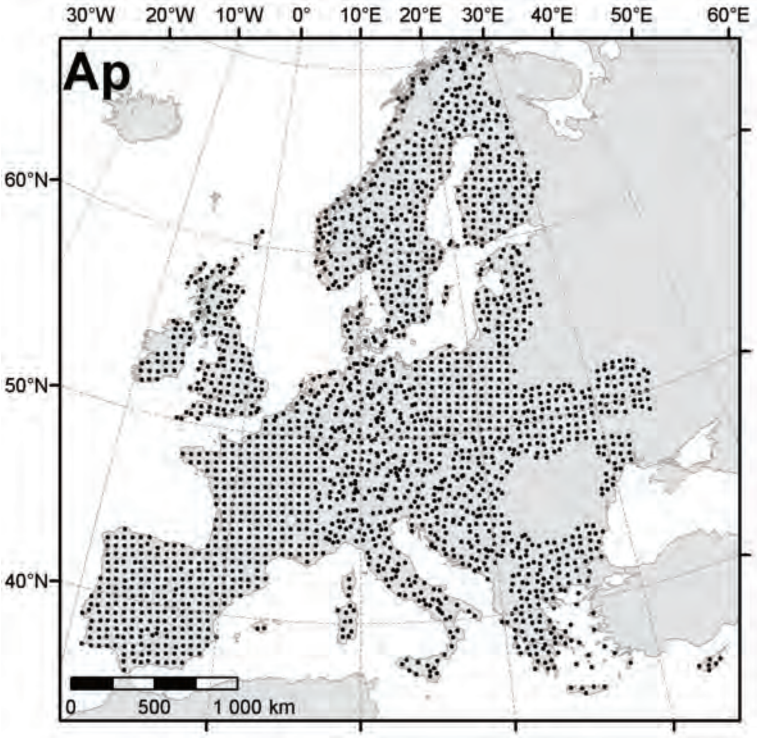

Figure 1. Sample locations for the agricultural soil (Ap-samples), EuroGeoSurveys GEMAS project.

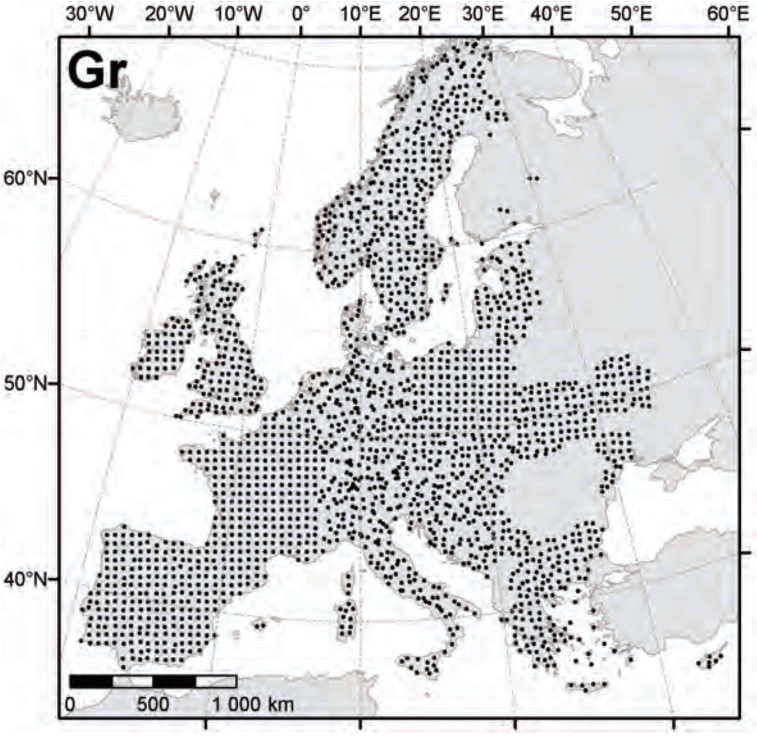

Figure 2. Sample locations for the grazing land soil (Gr-samples), EuroGeoSurveys GEMAS project.

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 demonstrated 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 to 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. 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, scalebar 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 State Geological Institute of Dionyz Stur, Slovakia. The State Geological Institute of Dionyz Stur, 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 State Geological Institute of Dionyz Stur, 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 method

All samples were shipped to ACME laboratories in Vancouver, Canada, which won the international tender for the analysis of the GEMAS samples using aqua regia extraction. At ACME labs the mineral soil samples underwent a modified aqua regia digestion prior to analysis. A weight of 15 g of the sieved mineral soil samples (<2 mm) were digested in 90 ml aqua regia and leached for one hour in a hot (95 ^{o}C) water bath. After cooling, the solution was made up to a final volume of 300 ml with 5% HCl. The sample weight to solution volume ratio is 1 g per 20 ml. The solutions were analysed using a Spectro Ciros Vision emission spectrometer (ICP-AES) and a Perkin Elmer Elan 6000/9000 inductively coupled plasma emission mass spectrometer (ICP-MS). In addition to the project standards and duplicate samples that were unknown to ACME , the laboratory inserted its own project standard and analytical replicates, and analytical results for these samples were reported separately. Finally, approximately 5000 samples were analysed by ACME labs for 53 chemical elements within a time span of 20 days from receiving the samples to final delivery of analytical results.

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, which 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. 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 Geological Survey laboratories, though not necessarily in commercial laboratories) it is of interest to plot analytical results versus sample number. 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 elements. Figure 3 shows four examples from the grazing land soil. No significant time trends, breaks, carry over or memory effects, or any other peculiarities related to location of the samples in the analytical sample batches could be detected.

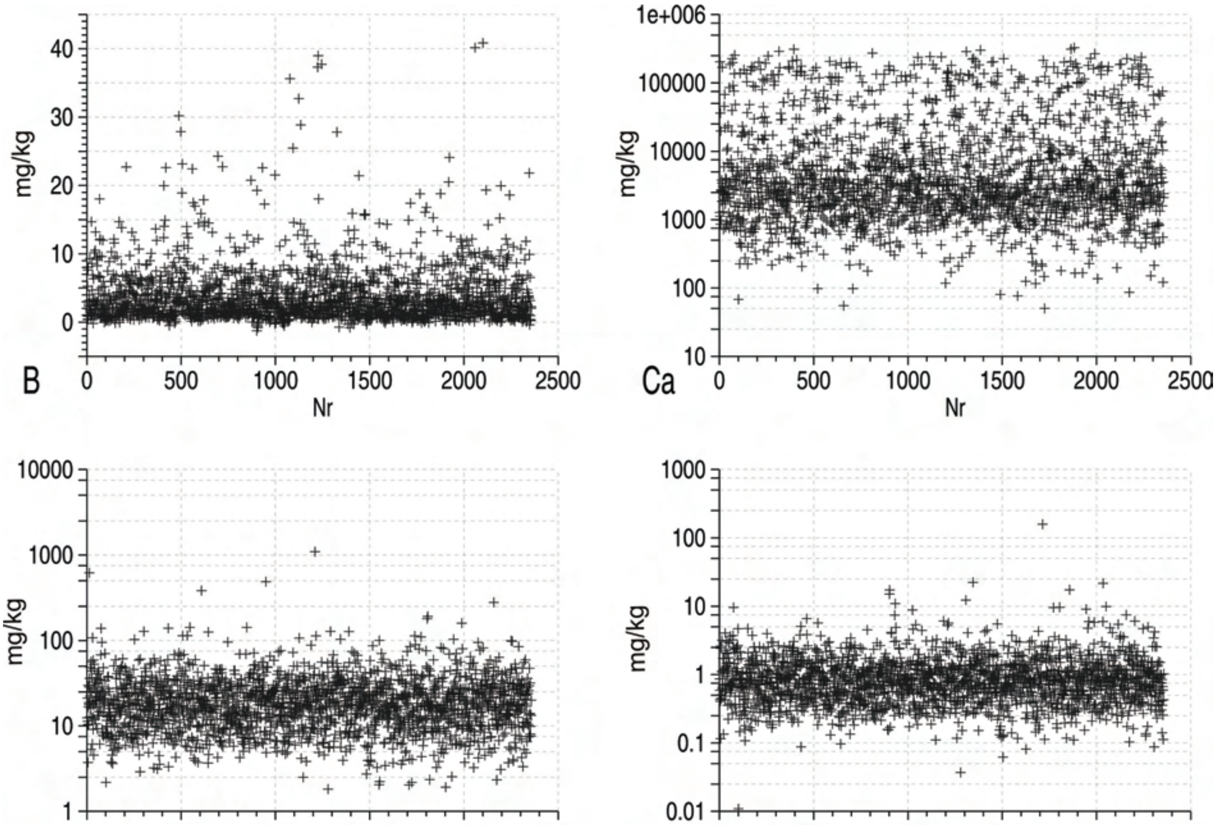

Figure 3. Sample number (sequence of analysis) plotted against analytical results for B, Ca, Pb and Sn. The plots indicate the expected random variation.

Randomisation of all samples requires that all project samples are received and prepared by the sample preparation laboratory first 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.

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. There exist only very few certified reference materials with values for an aqua regia extraction, and none for the analytical programme chosen for the GEMAS project. In addition, international reference materials are expensive and easy to detect by the laboratory. In the GEMAS project two standards from other continental scale mapping projects were inserted among the Ap-soil samples: 10 splits of an Australian soil standard (ORIS), and 10 splits of an American soil standard (SoNE-1). The GEMAS project standards, Ap and Gr, will in exchange be inserted in the Australian and North American projects when their continental samples are submitted for analysis. Furthermore, the standards Ap and Gr will be analysed in a number of laboratories of the European Geological Surveys. Comparing the results from different laboratories, it will in the end be possible to obtain a good impression of the "trueness" of the GEMAS project results in an aqua regia extraction.

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. In addition, the laboratory had inserted its own control reference material called DS7 (80 times among the A_p-samples, and 77 times among the Gr-samples). For the internal reference material DS7, ACME delivered its certificate of analysis for aqua regia digestion. Tables 1 and 2 give the analytical programme, ACME's official detection limits and a statistical summary of the results for the different standards used. 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). Original results for the ORIS (GeoScience Australia) and SoNE-1 (USGS) standards were provided for a near total 4-acid digestion (HF, $HClO_4$, HNO_3, HCl), which is considerably stronger than the aqua regia extraction used for the GEMAS project. These results allow judging the "extrability" of the elements in an aqua regia extraction, which varies strongly from much less than 10 % (e.g. Na, Ti) to almost 100% (e.g. As, Co), depending on the element and the form of binding in different minerals.

Table 1. Analytical programme and ACME laboratory detection limits (DL), analytical results (mean, minimum (MIN) and maximum (MAX) concentration) and coefficient of variation (CV-%) for the project standards Ap and Gr, as well as for the laboratory's internal reference material DS7 inserted in parallel. All analytical results in aqua regia extraction in mg/kg.

Element	DL	GEMAS Ap (n= 124)				DS7 (n=80)				GEMAS Gr (n= 118)				DS7 (n=77)			
		Mean	Min.	Max.	CV-%	**Mean**	Min.	Max.	CV-%	**Mean**	Min.	Max.	CV-%	**Mean**	Min.	Max.	CV-%
Ag	0.002	**0.054**	0.044	0.068	9	**0.777**	0.653	0.873	5	**0.030**	0.021	0.039	11	**0.782**	0.674	0.902	5
Al	100	**13080**	11481	15076	6	**10149**	8671	11053	4	**11372**	10236	12826	5	**10245**	9240	11144	4
As	0.1	**8.7**	7.6	9.7	5	**48.4**	44.1	53.9	4	**9.6**	8.5	11.2	5	**49.3**	45.3	54.7	4
Au	0.0002	**0.0017**	0.0004	0.0051	39	**0.0669**	0.0372	0.1260	18	**0.0017**	0.0006	0.0125	63	**0.0674**	0.0551	0.1513	20
B	1	**4.5**	2.7	7.0	19	**36.9**	30.6	42.1	7	**2.6**	0.7	**52.1**	179	**37.5**	31.9	45.3	7
Ba	0.5	**71**	63	84	5	**406**	376	459	4	**71**	61	86	6	**409**	365	455	5
Be	0.1	**0.65**	0.31	0.97	20	**1.57**	1.17	2.04	12	**0.64**	0.40	0.95	18	**1.60**	1.22	2.13	11
Bi	0.02	**0.36**	0.31	0.43	6	**4.42**	3.67	4.86	5	**0.32**	0.25	0.42	9	**4.53**	3.89	5.03	6
Ca	100	**37259**	34668	39947	3	**9167**	8342	9929	4	**2340**	1966	**4070**	9	**9137**	8402	10667	5
Cd	0.01	**0.22**	0.17	0.31	9	**6.13**	5.49	6.86	5	**0.20**	0.14	0.25	10	**6.31**	5.54	7.25	6
Ce	0.1	**28**	25	34	6	**34**	29	39	5	**27**	24	32	6	**34**	31	39	5
Co	0.1	**13**	11	15	5	**9**	8	11	5	**10**	9	12	5	**9**	8	10	4
Cr	0.5	**27**	24	31	7	**214**	191	256	7	**24**	21	27	5	**209**	182	259	7
Cs	0.02	**1.6**	1.1	1.9	9	**6.1**	5.6	6.7	4	**1.1**	0.8	1.2	8	**6.1**	5.4	6.7	4
Cu	0.01	**24**	21	26	5	**105**	95	116	4	**22**	18	33	9	**106**	92	119	6
Fe	100	**28407**	26157	30259	3	**23658**	22198	25181	2	**22186**	20901	23416	3	**23753**	22028	25076	3
Ga	0.1	**3.6**	3.2	4.2	6	**4.7**	4.3	5.2	4	**3.4**	3.0	4.0	6	**4.7**	4.2	5.2	5
Ge	0.1	**0.043**	< 0.1	0.109	57	**0.102**	0.030	0.171	30	**0.037**	< 0.1	0.103	65	**0.099**	0.006	0.195	35
Hf	0.02	**0.079**	0.055	0.116	15	**0.115**	0.087	0.148	10	**0.059**	0.034	0.094	19	**0.117**	0.076	0.154	12
Hg	0.005	**0.100**	0.075	0.129	9	**0.180**	0.142	0.208	7	**0.12**	0.10	0.15	7	**0.18**	0.16	0.20	5
In	0.02	**0.033**	0.019	0.047	16	**1.540**	1.315	1.711	5	**0.023**	< 0.02	0.035	23	**1.558**	1.341	1.775	7
K	100	**2364**	1935	2799	7	**4593**	4170	5382	5	**2110**	1855	2485	7	**4680**	4211	5463	6
La	0.5	**13**	11	16	7	**13**	11	16	7	**13**	11	16	7	**13**	11	15	7
Li	0.1	**22**	19	26	6	**29**	26	32	5	**15**	13	19	7	**29**	26	35	5
Mg	100	**9681**	9048	10401	3	**10172**	9571	10878	3	**3276**	2803	3808	6	**10249**	9349	10822	3
Mn	1	**684**	618	888	6	**612**	547	648	3	**566**	508	682	6	**617**	572	693	4
Mo	0.01	**0.70**	0.60	0.82	6	**20.37**	18.36	22.70	4	**0.79**	0.66	0.94	6	**20.04**	17.32	21.80	4
Na	10	**54**	42	66	9	**905**	711	1022	7	**34**	26	98	20	**908**	761	1094	8
Nb	0.02	**0.22**	0.16	0.30	11	**0.54**	0.40	0.79	14	**0.26**	0.17	0.41	12	**0.53**	0.35	0.77	17

Element	DL	GEMAS Ap (n= 124)				DS7 (n=80)				GEMAS Gr (n= 118)				DS7 (n=77)			
		Mean	Min.	Max.	CV-%	**Mean**	Min.	Max.	CV-%	**Mean**	Min.	Max.	CV-%	**Mean**	Min.	Max.	CV-%
Ni	0.1	**47**	42	51	4	**55**	49	60	5	**34**	31	39	5	**54**	48	59	4
P	10	**885**	740	1102	8	**750**	629	872	7	**775**	681	923	7	**749**	662	880	6
Pb	0.01	**18**	15	22	5	**66**	57	75	5	**16**	13	20	9	**66**	57	72	5
Pd	0.01	**0.0017**	< 0.01	0.0102	141	**0.0645**	0.0307	0.0955	21	**0.00028**	< 0.01	0.0086	784	**0.059**	0.029	0.098	21
Pt	0.002	**0.00089**	< 0.002	0.00382	85	**0.03527**	0.02891	0.04313	8	**0.00044**	< 0.002	0.0028	152	**0.035**	0.029	0.043	8
Rb	0.1	**17**	15	21	7	**36**	34	44	5	**14**	11	17	8	**37**	32	43	6
Re	0.001	**0.00013**	< 0.001	0.00126	492	**0.00358**	0.00096	0.00757	36	**0.00015**	< 0.001	0.0031	482	**0.0042**	0.0011	0.0074	32
S	200	**184**	116	288	14	**1816**	1651	1977	3	**119**	47	176	10	**1825**	1687	1943	3
Sb	0.02	**0.92**	0.59	1.21	13	**4.16**	1.90	5.79	21	**1.2**	0.9	1.6	11	**4.0**	2.8	6.5	21
Sc	0.1	**4.3**	3.8	4.8	5	**2.6**	2.2	3.1	7	**3.1**	2.7	3.6	6	**2.6**	2.1	3.0	7
Se	0.1	**0.57**	0.31	0.81	18	**3.34**	2.75	3.75	6	**0.35**	< 0.1	0.64	31	**3.37**	2.81	3.84	6
Sn	0.1	**0.89**	0.70	1.34	11	**5.13**	4.21	5.68	5	**1.5**	0.8	**13.1**	95	**5.2**	4.4	6.0	6
Sr	0.5	**82**	76	89	3	**71**	57	79	5	**20**	16	23	8	**71**	62	82	6
Ta	0.05	**0.0015**	< 0.05	0.0057	62	**0.0018**	< 0.05	0.0045	56	**0.00092**	< 0.05	**0.00440**	104	**0.00196**	< 0.05	0.00671	68
Te	0.02	**0.039**	< 0.02	0.114	47	**1.052**	0.853	1.276	7	**0.025**	< 0.02	0.064	58	**1.066**	0.896	1.272	7
Th	0.1	**4.7**	4.1	5.2	5	**4.1**	3.6	4.7	5	**3.9**	3.3	4.5	7	**4.1**	3.5	4.7	6
Ti	10	**32**	23	44	13	**1145**	988	1293	6	**47**	27	68	13	**1174**	987	1400	6
Tl	0.02	**0.14**	0.13	0.26	9	**4.01**	3.65	4.35	4	**0.14**	0.13	0.16	5	**4.03**	3.50	4.64	5
U	0.1	**0.80**	0.71	0.89	5	**4.72**	4.19	5.17	4	**0.49**	0.39	0.57	8	**4.78**	4.16	5.41	6
V	2	**24**	19	28	7	**79**	71	85	4	**22**	19	25	6	**79**	73	86	4
W	0.1	**0.061**	0.021	0.115	23	**2.980**	2.460	3.451	8	**0.051**	0.022	0.080	22	**2.995**	2.543	3.802	9
Y	0.01	**8.9**	7.9	9.9	4	**5.6**	4.5	6.4	7	**6.8**	5.6	7.8	6	**5.6**	4.5	6.9	8
Zn	0.1	**76**	69	84	4	**370**	347	403	3	**58**	51	67	5	**373**	344	418	4
Zr	0.1	**2.0**	1.7	2.3	6	**5.1**	4.5	5.7	6	**2.0**	1.3	2.6	13	**5.1**	4.2	6.2	7

Table 2. Analytical results for the standards ORIS (GeoScience Australia) and SoNE-1(USGS) in aqua regia and in a 4-acid extraction, and results for the laboratory standard DS7 in the two sample batches and, for comparison, the reference value for DS7 for aqua regia extraction. All analytical results in mg/kg.

Element	ORIS (n= 10)						SoNE-1 (n= 10)						DS7 (all aqua regia)		
	aqua regia				Total		aqua regia				Total		in Ap (n=80)	in Gr (n=77)	Ref.Val.
	ACME				USGS	extr.	ACME				USGS	extr.	ACME	ACME	ACME
	Mean	Min.	Max.	CV-%	Mean	%	Mean	Min.	Max.	CV-%	MEAN	%	Mean	Mean	Mean
Ag	0.022	0.019	0.025	11	<1		0.060	0.052	0.065	8	<1		0.777	0.782	0.890
Al	9996	9081	11129	6	40840	24	18737	16961	21536	8	59810	31	10149	10245	9590
As	5.9	5.4	6.5	6	6.4	92	9.6	8.9	10.4	5	11	87	48.4	49.3	48.2
Au	0.0260	0.0024	0.1309	168			0.0021	0.0018	0.0028	17			0.0669	0.0674	0.0700
B	2.0	1.2	4.1	47			5.4	3.5	6.8	20			36.9	37.5	39.0
Ba	91	81	105	8	352	26	235	221	258	5	740	32	406	409	370
Be	0.81	0.68	1.27	22	1.72	47	0.87	0.76	1.01	10	1.78	49	1.57	1.60	1.60
Bi	0.24	0.20	0.29	11	0.29	83	0.27	0.24	0.30	7	0.29	92	4.42	4.53	4.51
Ca	1127	1043	1330	9	1720	66	3777	3562	4043	4	6030	63	9167	9137	9300
Cd	0.10	0.06	0.13	28	0.15	64	0.46	0.38	0.51	9	0.43	107	6.13	6.31	6.38
Ce	43	39	46	6	65	66	47	42	52	7	73	64	34	34	36
Co	7	6	8	6	7.4	92	11	10	11	3	12	89	9	9	10
Cr	14	13	14	4	35	39	22	20	24	6	55	40	214	209	179
Cs	2.0	1.7	2.2	8	5.8	34	1.6	1.4	1.9	10	<5		6.1	6.1	6.4
Cu	11	10	13	7	13	88	19	17	20	5	22	87	105	106	109
Fe	15861	14939	16800	3	19200	83	21211	20541	22724	3	27775	76	23658	23753	23900
Ga	2.9	2.7	3.3	7	12	25	5.3	4.9	5.8	7	15	35	4.7	4.7	4.6
Ge	0.043	0.007	0.068	40			0.067	0.043	0.106	31			0.102	0.099	0.100
Hf	0.065	0.053	0.085	18			0.287	0.246	0.335	9			0.115	0.117	0.110
Hg	0.021	0.017	0.026	13	0.03	71	0.025	0.021	0.033	14	0.03	84	0.180	0.18	0.20
In	0.011	0.008	0.013	16	0.032	33	0.027	0.020	0.036	17			1.540	1.558	1.570
K	2126	1864	2482	9	14540	15	3004	2741	3487	7	18048	17	4593	4680	4400
La	22	18	26	10	33	68	24	22	28	7	36	67	13	13	12
Li	14	12	15	7	28	50	13	12	15	9	27	48	29	29	29
Mg	1609	1308	1949	12	2900	55	3505	3192	3989	7	6000	58	10172	10249	10500

Element	ORIS (n= 10)						SoNE-1 (n= 10)						DS7 (all aqua regia)		
	aqua regia				Total		aqua regia				Total		in Ap (n=80)	in Gr (n=77)	Ref.Val.
	ACME				USGS	extr.	ACME				USGS	extr.	ACME	ACME	ACME
	Mean	Min.	Max.	CV-%	Mean	%	Mean	Min.	Max.	CV-%	MEAN	%	Mean	Mean	Mean
Mn	459	434	501	4	469	98	538	508	560	3	601	90	612	617	627
Mo	0.84	0.80	0.90	5	0.95	88	0.74	0.63	0.80	6	1.2	61	20	20	21
Na	106	90	125	9	3500	3	49	44	54	7	7191	1	905	908	890
Nb	0.60	0.49	0.74	12	5.4	11	0.61	0.49	0.72	14	10	6	0.54	0.53	0.71
Ni	12	10	14	9	16	76	25	24	26	3	27	92	55	54	56
P	353	298	424	12	386	91	421	392	450	4	516	82	750	749	800
Pb	10	9	11	7	15	69	18	17	20	5	23	78	66	66	71
Pd	0.0005	< 0.01	0.0043	348			< 0.01	< 0.01	0.0070	227			0.064	0.059	0.058
Pt	0.00082	< 0.002	0.00280	128			0.00204	0.00138	0.00250	17			0.035	0.035	0.037
Rb	22	20	25	8	116	19	28	25	33	9	95	30	36	37	36
Re	0.00006	< 0.001	0.00155	1431			0.00033	< 0.001	0.00262	347			0.0036	0.0042	0.0040
S	167	154	180	4	200	84	159	137	175	7	299	53	1816	1825	1900
Sb	0.32	0.27	0.37	9	0.69	46	0.54	0.44	0.63	13	1.3	41	4.2	4.0	4.6
Sc	1.6	1.4	1.8	8	6.5	24	3.6	3.2	4.1	9	9	40	2.6	2.6	2.5
Se	0.27	0.08	0.54	47	<0.2		0.56	0.31	0.64	17	0.47	118	3.3	3.4	3.5
Sn	0.90	0.78	1.00	8	2.9	31	0.78	0.68	0.89	9	1.7	46	5.1	5.2	4.6
Sr	15	13	17	8	35	42	35	31	39	6	126	28	71	71	69
Ta	0.0008	0.0001	0.0023	92			0.0020	0.0010	0.0045	54			0.0018	0.0020	<0.05
Te	0.013	< 0.02	0.061	147	<0.1		0.030	0.009	0.052	43	<0.1		1.1	1.1	1.1
Th	5.8	5.2	6.6	8	11	53	6.5	5.9	7.3	7	11	59	4.1	4.1	4.4
Ti	59	36	77	22	1380	4	104	73	129	18	2600	4	1145	1174	1240
Tl	0.13	0.12	0.14	6	0.58	23	0.31	0.29	0.34	5	0.69	45	4.0	4.0	4.2
U	1.26	1.07	1.41	8	2.4	53	1.21	1.13	1.32	6	2.8	43	4.7	4.8	4.9
V	14	12	16	9	39	35	42	37	48	10	113	37	79	79	84
W	0.249	0.143	0.338	19	1.2	21	0.033	0.021	0.046	25	0.93	4	3.0	3.0	3.4
Y	5.4	4.7	6.0	6	11	49	12.4	10.7	14.0	7	20	62	5.6	5.6	5.2
Zn	39	35	43	5	51	77	65	59	70	5	81	80	370	373	411
Zr	2.4	1.8	2.9	15			11.7	10.1	12.9	9			5.1	5.1	5.4

In addition, X-Charts were plotted for all elements, where element concentration is plotted against sample number (for an example from the Gr-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. No serious time trends or breaks in the data were detected. However, for the grazing land soil (Gr samples) there occurred some single very serious outliers for a few elements (*e.g.*, B, Ca, Sn). These outliers cause the poor repeatability, visible for some elements when comparing the results of the other standards with those for the Gr standard in Table 1 (an indication that classical statistical methods provide the wrong estimators for this type of data, *i.e.*, a single outlier should not have such a major influence on the measure of overall repeatability as observed for B and Sn). In the end, these outliers were the only deviations from an overall excellent quality of the analytical results and needed discussion with the laboratory.

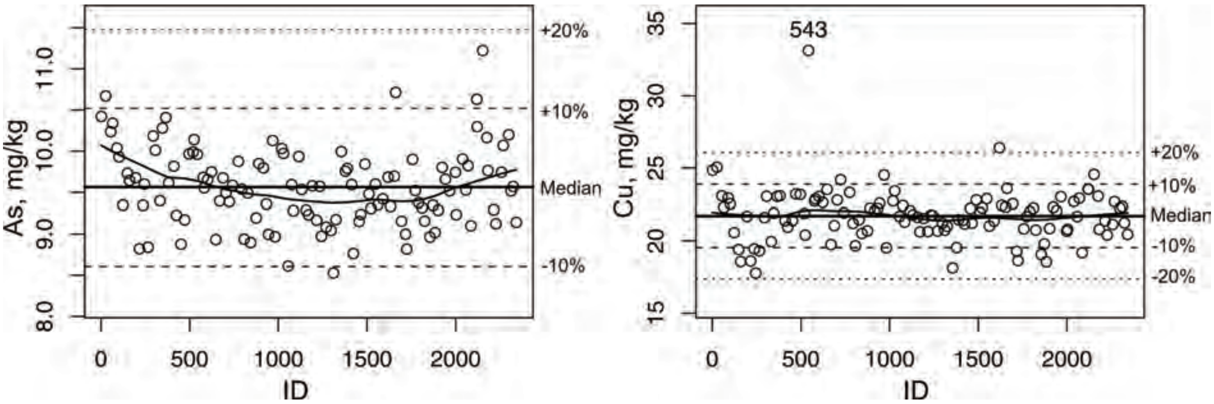

Figure 4. Example showing two selected X-Charts for the project standard Gr. Sample number (ID) is plotted against analytical result for the standard. The fat line indicates the median value of all standard results, the dashed line is the limit for 10%, the dotted line for 20% deviation from the median. 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. The charts for all elements are shown in Appendix 1 (Gr) and Appendix 2 (Ap).

The laboratory had also inserted its own reference material DS7 in between the Gr and Ap samples during analyses and these results can also be presented in the form of X-charts. These are presented in Appendix 3 (for Gr samples) and 4 (for Ap samples). These results reconfirm the impression gained from the project standards Gr and 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 the natural inhomogeneity of the sample material, which is an important source of variability, into account.

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, as received from ACME, 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 3, 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 instruments 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 5 (Gr) and 6 (Ap).

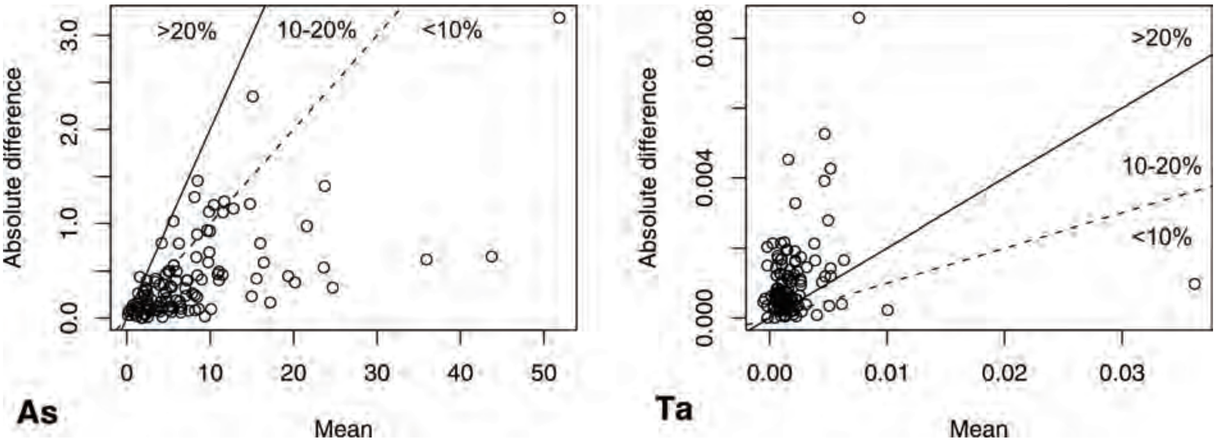

Figure 5. Example showing two "Thompson and Howarth"-plots of replicate analyses from the Gr samples. The mean of the replicate pairs is plotted along the x-axis, the absolute difference of the two results along the y-axis. 10 % precision is indicated by the stipulated line, 20% precision by the line. 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 5 (Gr) and 6 (Ap).

In general, no serious quality problems were detected and not a single batch was found where both, project standard and replicate pair, deviated at the same time, indicating a serious quality problem for the preceding 20 samples. However, exactly as for the standards, a few single pairs were observed, where one of the results was far off (for the GEMAS project a design was used where a third sample from almost the same location was in the same batch of 20 samples, so that it was possible to clearly recognise such "fliers" or "outliers"). This can result in a very poor overall precision figure – for an example see Pb for the grazing land soil in Table 3, the laboratory's own replicates show a poor "precision" of 74% compared, when all replicate pairs are taken into account to *c.* 10% as indicated by all other replicates and calculation methods. This deviation was again caused by one single extreme outlier (difference between replicates 250 mg/kg), which had a strong influence in one of the calculation methods. These single fliers occurred predominantly in the grazing land soil dataset and needed discussion and follow up with the laboratory. An important corollary from this work is that the processing of QC results by different methods and people, as carried out here, is advantageous for such a large international project, because differences in the produced results can provide valuable complementary information and pinpoint problems that may otherwise have been overlooked.

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 analyzing a pure substance, is of little interest when analyzing 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, the value where the precision of replicate analyses gets better than + 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, and the precision equation for estimating precision at any concentration (Thompson and Howarth, 1978; Reimann and Wurzer, 1986; Demetriades and Karamanos, 2003; Demetriades, 2009). 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 analytical contract with ACME.

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), 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 the ACME duplicate results (Table 3). "Precision 2" in Table 3 provides the overall precision of each 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 3 also shows the detection limits as provided by the laboratory, the practical detection limits as estimated using the GEMAS replicate results and as calculated using the ACME replicate analyses by the modified method of Thompson and Howarth (1986 - Demetriades and Karamanos, 2003; Demetriades, 2009). 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 (*e.g.*, Ca, Fe). In these cases, a reliable estimate of the practical detection limit is not possible.

Table 3. ACME laboratory "official" detection limit and practical detection limits calculated from the GEMAS project replicates using a modified version of Thompson and Howarth (1978). Precision 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, and Demetriades, 2009). ACME precision and practical detection limits are calculated on the analytical results of the laboratory's replicates. Detection limits in mg/kg, precision in %, for method 2 at the 95% confidence level.

Element	ACME	Agricultural soil (Ap-samples)						Grazing land soil (Gr-samples)					
		ACME	GEMAS replicates			ACME replicates		ACME	GEMAS replicates			ACME replicates	
		Practical	Practical	1	2	1	2	Practical	Practical	1	2	1	2
	DL	DL	DL	Precision	Precision	Precision	Precision	DL	DL	Precision	Precision	Precision	Precision
Ag	0.002	0.002	0.007	9	18	8	7	0.003	0.003	18	10	10	6
Al	100	104	4.0	6	8	3	5	33	10	6	8	3	5
As	0.1	0.065	0.005	8	10	4	6	0.17	0.014	6	12	14	5
Au	0.0002	0.002	0.0007	46	55	66	125	0.003	0.00009	61	76	102	89
B	1	0.31	0.76	23	14	18	24	0.5	0.3	27	30	24	17
Ba	0.5	0.88	1.3	7	8	5	8	0.2	0.8	6	8	11	6
Be	0.1	0.04	0.033	19	39	16	28	0.03	0.05	23	25	18	32
Bi	0.02	0.004	0.01	6	7	5	5	0.005	0.008	8	6	9	6
Ca	100	48	178	11	4	6	6	123	200	6	5	8	5
Cd	0.01	0.01	0.0086	8	9	9	8	0.01	0.0002	11	15	7	10.5
Ce	0.1	1.21	1.2	6	14	4	11	0.8	0.03	7	9	5	10
Co	0.1	0.013	0.085	6	8	4	6	0.04	0.1	18	8	5	8
Cr	0.5	0.45	0.019	6	8	5	5	0.06	0.25	11	14	4	6
Cs	0.02	0.014	0.011	7	9	4	8	0.06	0.02	8	10	5	14
Cu	0.01	0.02	0.27	5	4	4	6	0.1	0.1	5	10	3	6
Fe	100	121	163	3	5	3	5	45	330	4	9	2	5
Ga	0.1	0.026	0.065	5	6	4	8	0.03	0.005	6	8	4	9
Ge	0.1	0.64	0.019	52	58	47	98	0.02	0.05	49	85	52	84
Hf	0.02	0.006	0.01	12	9.5	14	16	0.007	0.008	18	20	12	12
Hg	0.005	0.003	0.002	13	15	13	15	0.003	0.003	26	14	17	13

Element	ACME	Agricultural soil (Ap-samples)						Grazing land soil (Gr-samples)					
		ACME	GEMAS replicates			ACME replicates		ACME	GEMAS replicates			ACME replicates	
		Practical	Practical	1	2	1	2	Practical	Practical	1	2	1	2
	DL	DL	DL	Precision	Precision	Precision	Precision	DL	DL	Precision	Precision	Precision	Precision
In	0.02	0.003	0.004	21	28	19	24	0.001	0.005	19	19	24	31
K	100	5.7	21	8	13	5	7	10	41	9	8	6	10
La	0.5	0.09	0.026	5	8.5	4	6	0.4	0.03	6	9	4	11
Li	0.1	0.04	0.28	6	8	4	6	0.08	0.2	7	8.5	4	6.5
Mg	100	3.1	64	5	6	3	6	11	3.4	4	7.5	3	6
Mn	1	14	2	6	7	8	10	7	1	7	7	6	9
Mo	0.01	0.01	0.018	9	17	7	7	0.004	0.01	10	15	9	12
Na	10	1.1	1.1	8	14	10	12	1.4	2	7	9	5	6
Nb	0.02	0.01	0.028	11	9	7	5	0.02	0.01	11	15	6	7
Ni	0.1	0.11	0.26	6	6.5	6	5	0.2	0.4	7	6	4	5
P	10	33	4.3	7	11	5	14	5	4	5	11	5	8
Pb	0.01	0.35	0.88	11	15	12	9	0.3	0.3	7	10	74	9
Pd	0.01	0.01	0.001	540	228	415	89	0.004	0.0005	1001	190	1247	52
Pt	0.002	0.0016	0.00007	131	89	76	95	0.002	0.0003	94	190	96	112
Rb	0.1	0.15	0.23	6	10	4	6	0.2	0.2	8	13	5	10
Re	0.001	0.0003	0.06	1079	100	1048	144	0.000007	0.0003	226	130	272	156
S	200	4	3.3	8	7	46	9	2	5	22	7	6	6.6
Sb	0.02	0.003	0.0002	12	18	7	8	0.008	0.02	14	17	9	6
Sc	0.1	0.0006	0.05	5	7.5	5	7	0.09	0.02	6	11	5	6
Se	0.1	0.04	0.1	19	17	18	25	0.02	0.08	18	22	17	32
Sn	0.1	0.01	0.0056	8	14	20	14	1.3	0.03	54	19	37	70
Sr	0.5	0.4	0.65	9	6	8	4	0.2	0.6	17	6	4	5
Ta	0.05	0.005	0.004	65	84	73	101	0.002	0.001	52	56	73	62
Te	0.02	0.01	0.021	53	24	60	95	0.01	0.02	60	28	50	44
Th	0.1	0.02	0.0008	5	9	5	6	0.02	0.03	7	13	4	7

Element	ACME	Agricultural soil (Ap-samples)						Grazing land soil (Gr-samples)					
		ACME	GEMAS replicates			ACME replicates		ACME	GEMAS replicates			ACME replicates	
		Practical	Practical	1	2	1	2	Practical	Practical	1	2	1	2
	DL	DL	DL	Precision	Precision	Precision	Precision	DL	DL	Precision	Precision	Precision	Precision
Ti	10	0.9	6.7	8	8	11	8	2.2	6.5	13	8	8	6
Tl	0.02	0.0005	0.00009	9	11	10	7	0.0001	0.01	7	20	5	9
U	0.1	0.04	0.015	5	5	5	11	0.008	0.03	6	4	6	7
V	2	0.09	0.07	8	10	5	6	0.3	0.1	5	10	4	6
W	0.1	0.01	0.0045	16	26	12	9	0.007	0.01	18	19	12	18
Y	0.01	0.04	0.053	4	9	3	6	0.08	0.1	6	5	4	8
Zn	0.1	0.26	1.0	4	5	5	8	0.4	3	6	18	6	6
Zr	0.1	0.02	0.07	12	8	8	9	0.08	0.1	12	9	6	6

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

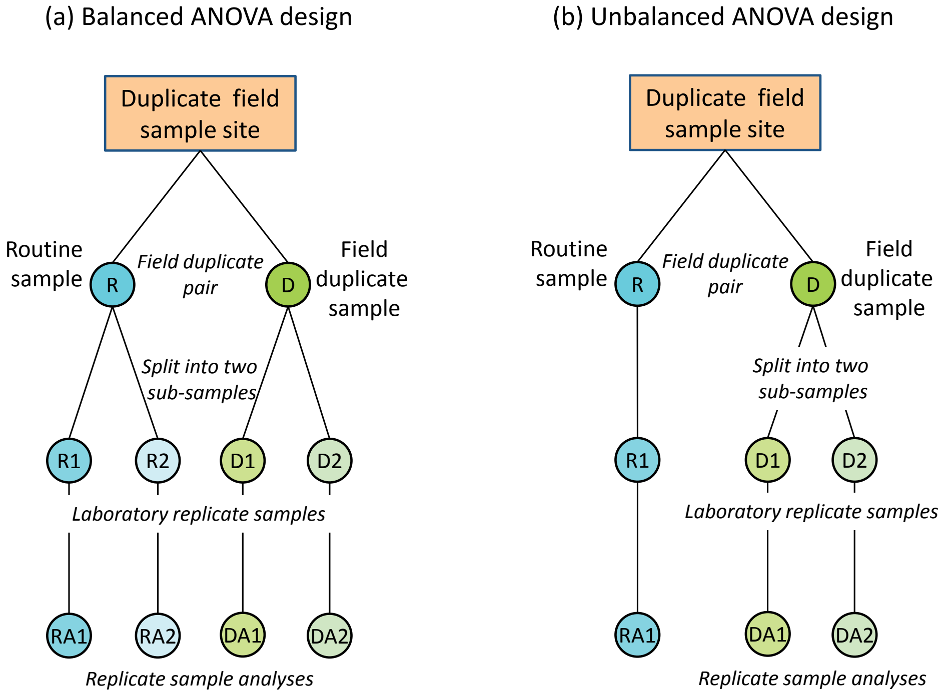

Figure 6. Balanced(left) and unbalanced (right) ANOVA design for the estimation of natural (geochemical), sampling(at site) and analytical variance. At every 20th sample site, or, in small countries with more than 10, but less than 20 sample sites, at one of the sample sites, a duplicate agricultural 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.

made on both, the routine and field duplicates sample (Fig. 6). In an "unbalanced" design unequal numbers of analyses occur at each level of the design (Fig. 6). 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).

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 4 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 (anal.)" variability. The median value for all samples is also provided.

Table 4 demonstrates that for the majority of elements the data quality is good to excellent, and that the results can be reliably mapped. Problematic elements in both datasets (A_p and Gr), where care is needed when mapping and using the results, are Re. Pd, Pt, Ta, Ge and Te. 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 analyzing all samples several times and using the median as the "analytical result". In general it can be taken as an indication of "good (reproducible) sampling". The "A_p" samples show often considerably better results than the "Gr" samples. A possible reason for this feature is that ploughed soils have been homogenised over many years and the samples may also be more weathered and finer grained (the latter assumption can be checked when the results of grain size analyses become available) 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.

Table 4: Overall median values for the GEMAS A_p- and Gr-samples and results of an unbalanced ANOVA. All variables were log-transformed prior to the calculation. Left hand alphabetical according to element, right hand site sorted according to increasing "geochemical (natural)" variation for an easy identification of "problematic" elements (less than 80% natural variation).

	Agricultural soils 0-20 cm (Ap samples)				Grazing land soils 0-10 cm (Gr samples)			
	MEDIAN	Variability - %			MEDIAN	Variability - %		
Element	**mg/kg**	**nat.**	**site**	**anal.**	**mg/kg**	**nat.**	**site**	**anal.**
Ag	0.038	97	0	3	0.039	93	4.4	2.2
Al	10926	99	0.8	0.7	10655	99	0.5	0.5
As	5.4	98	1.4	0.5	5.6	99	0.7	0.4
Au	0.00093	75	0	25	0.0010	60	0	40
B	2.4	87	0	13	2.6	77	11	13
Ba	61	99	0.8	0.4	63	99	0.8	0.4
Be	0.52	85	0	15	0.51	94	0	6.1
Bi	0.16	94	4.1	1.5	0.18	97	0	3.2
Ca	3029	99	0.9	0.2	3147	98	1.6	0.2
Cd	0.18	94	0	5.6	0.20	94	4.7	1.2
Ce	28	98	0.7	0.9	27	99	0.5	0.6
Co	7.4	99	0.7	0.3	7.2	99	0.3	0.3
Cr	20	99	0.4	0.7	20	99	0.7	0.4
Cs	1.1	99	0	0.9	1.1	99	0.5	0.7
Cu	14	99	0	1.5	15	98	1.2	0.4
Fe	17024	98	1.2	0.3	16888	99	0.7	0.2
Ga	3.4	99	0.6	0.8	3.4	98	1.1	0.5
Ge	<0.1	45	5.9	49	<0.1	37	21	42
Hf	0.048	92	0	8.1	0.045	94	0	6.1
Hg	0.030	93	0	6.7	0.035	96	1.3	3
In	0.018	75	0	25	0.018	86	0	14

Sorted according to increasing natural variability:							
Ap				Gr			
Element	**nat.**	**site**	**anal.**	**Element**	**nat.**	**site**	**anal.**
Re	22	0	78	Re	5	29	66
Pd	27	0	73	Pd	23	0	77
Ta	28	7	65	Ge	37	21	42
Ge	45	5.9	49	Pt	52	0	48
Pt	46	13.3	41	Au	60	0	40.1
Te	55	0.2	45	Ta	61	0	39
In	75	0	25	Te	67	0	33
Au	75	0	25	B	77	11	13
Se	84	6.1	10	Se	80	3.1	17
Be	85	0	15	In	86	0	14
B	87	0	13	Nb	89	10.3	0.7
Hf	92	0	8.1	Pb	92	7	0.6
Hg	93	0	6.7	S	93	2.1	4.7
W	93	0	6.7	Ag	93	4.4	2.2
Bi	94	4.1	1.5	Be	94	0	6.1
Cd	94	0	5.6	Hf	94	0	6.1
S	95	3	1.8	Cd	94	4.7	1.2
Sn	96	0	4.1	Hg	96	1.3	3
Ag	97	0	3	W	96	0	4.3
Pb	97	0	2.6	Sn	96	0.6	3.4
Sb	98	0	2.5	Zn	97	2.8	0.5

	Agricultural soils 0-20 cm (Ap samples)				Grazing land soils 0-10 cm (Gr samples)			
	MEDIAN	Variability - %			MEDIAN	Variability - %		
Element	mg/kg	nat.	site	anal.	mg/kg	nat.	site	anal.
K	1242	98	1.4	0.6	1121	99	0.7	0.5
La	14	99	0.5	0.9	14	99	0.4	0.5
Li	11	99	0.3	0.7	11	99	0.4	0.6
Mg	2839	99	0.5	0.2	2817	99	0.4	0.1
Mn	443	99	1	0.5	434	98	1.9	0.2
Mo	0.41	98	0	1.7	0.42	99	0.8	0.6
Na	48	98	0.9	0.8	49	98	0.7	1
Nb	0.48	99	0	1.2	0.52	89	10.3	0.7
Ni	15	99	0.6	0.2	14	100	0.3	0.2
P	650	98	0	2.2	641	98	0	1.7
Pb	16	97	0	2.6	18	92	7	0.6
Pd	<0.01	27	0	73	<0.01	23	0	77
Pt	<0.002	46	13.3	41	<0.002	52	0	48
Rb	14	99	0.6	0.7	14	99	0.9	0.6
Re	<0.001	22	0	78	<0.001	5	29	66
S	206	95	3	1.8	296	93	2.1	4.7
Sb	0.23	98	0	2.5	0.27	98	0.5	1.9
Sc	2.1	98	1.6	0.8	2.0	99	0	1.5
Se	0.35	84	6.1	10	0.40	80	3.1	17
Sn	0.72	96	0	4.1	0.81	96	0.6	3.4
Sr	18	99	1.2	0.3	18	99	1.2	0.2
Ta	<0.05	28	7	65	<0.05	61	0	39
Te	<0.02	55	0.2	45	0.020	67	0	33
Th	2.9	99	1	0.5	2.5	99	0.5	0.7
Ti	85	99	0.2	0.7	73	99	0.2	0.8

Sorted according to increasing natural variability:							
Ap				Gr			
Element	nat.	site	anal.	Element	nat.	site	anal.
Sc	98	1.6	0.8	Bi	97	0	3.2
Zr	98	0	2.3	Sb	98	0.5	1.9
P	98	0	2.2	Mn	98	1.9	0.2
Tl	98	0	2.2	V	98	0.4	1.6
K	98	1.4	0.6	Ca	98	1.6	0.2
V	98	0	2	Zr	98	0	1.8
Zn	98	1.4	0.6	Ga	98	1.1	0.5
As	98	1.4	0.5	P	98	0	1.7
Mo	98	0	1.7	Cu	98	1.2	0.4
Ce	98	0.7	0.9	Na	98	0.7	1
Fe	98	1.2	0.3	Rb	99	0.9	0.6
Na	98	0.9	0.8	Sc	99	0	1.5
Y	98	1.2	0.4	Sr	99	1.2	0.2
Cu	99	0	1.5	K	99	0.7	0.5
Mn	99	1	0.5	Mo	99	0.8	0.6
Sr	99	1.2	0.3	Ba	99	0.8	0.4
Th	99	1	0.5	Cs	99	0.5	0.7
Al	99	0.8	0.7	Th	99	0.5	0.7
La	99	0.5	0.9	As	99	0.7	0.4
Ga	99	0.6	0.8	Ce	99	0.5	0.6
Rb	99	0.6	0.7	Cr	99	0.7	0.4
Ba	99	0.8	0.4	Tl	99	0.4	0.7
Nb	99	0	1.2	U	99	0.6	0.5
Cr	99	0.4	0.7	Al	99	0.5	0.5
Ca	99	0.9	0.2	La	99	0.4	0.5

	Agricultural soils 0-20 cm (Ap samples)				Grazing land soils 0-10 cm (Gr samples)			
	MEDIAN	Variability - %			MEDIAN	Variability - %		
Element	mg/kg	nat.	site	anal.	mg/kg	nat.	site	anal.
Tl	0.12	98	0	2.2	0.11	99	0.4	0.7
U	0.77	99	0.4	0.6	0.74	99	0.6	0.5
V	25	98	0	2	26	98	0.4	1.6
W	<0.1	93	0	6.7	<0.1	96	0	4.3
Y	6.7	98	1.2	0.4	6.4	99	0.4	0.3
Zn	45	98	1.4	0.6	45	97	2.8	0.5
Zr	1.8	98	0	2.3	1.6	98	0	1.8

Sorted according to increasing natural variability:							
Ap				Gr			
Element	nat.	site	anal.	Element	nat.	site	anal.
Co	99	0.7	0.3	Li	99	0.4	0.6
Li	99	0.3	0.7	Ti	99	0.2	0.8
U	99	0.4	0.6	Fe	99	0.7	0.2
Cs	99	0	0.9	Y	99	0.4	0.3
Ti	99	0.2	0.7	Co	99	0.3	0.3
Ni	99	0.6	0.2	Mg	99	0.4	0.1
Mg	99	0.5	0.2	Ni	100	0.3	0.2

4. RESULTS – SOME FIRST EXAMPLES

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 Sr in agricultural soil, Fig. 8 the same map for Sr 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. This is the final indication of the high quality of the GEMAS project aqua regia 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).

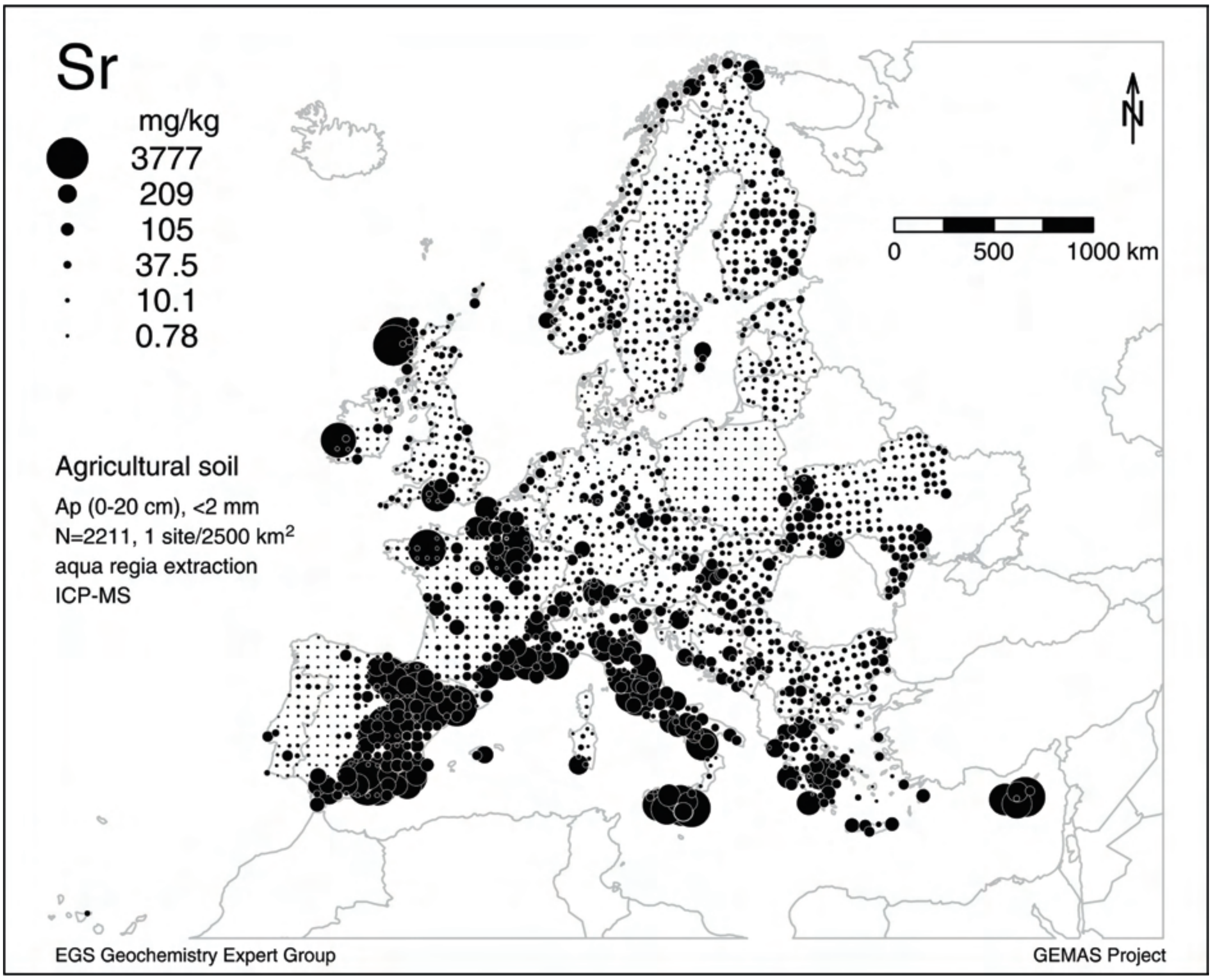

Figure 7. Growing dot map (for a description and discussion of the mapping technique see Reimann et al., 2008) for Sr in agricultural soils of Europe (GEMAS Ap-samples).

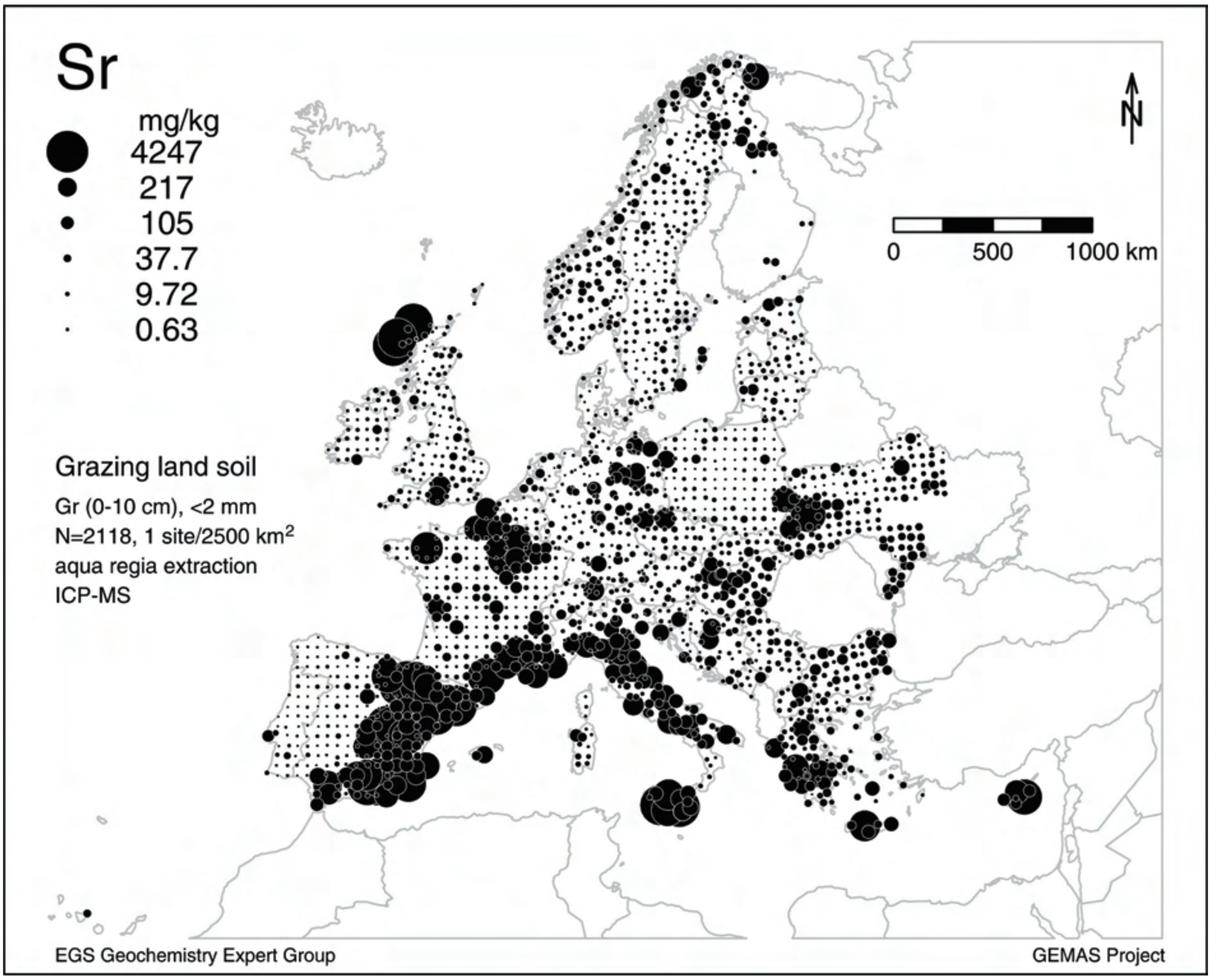

Figure 8. Growing dot map (for a description and discussion of the mapping technique see Reimann et al., 2008) for Sr in grazing land soil of Europe (GEMAS Gr samples).

5. RESULTS OF RE-ANALYSED SAMPLES

As detailed above, a number of unexplained outliers were observed for some of the standard samples and for some few duplicate pairs, but never within the same batch of 20 samples. In order to check these unexplained outliers, which occurred especially in the grazing land soil dataset, twenty-five samples were selected for re-analyses, covering the outliers as well as several surrounding samples. Original results were plotted against the new results in a series of XY-plots (Fig. 9 shows an example, all plots for the Gr-dataset are provided in Appendix 7). The outliers disappear without visible effects on neighbouring samples. For example, the four standard samples that showed some large discrepancies between the first and second determination, but for different elements, *i.e.*, Cu, Ca, Sn and B, do now fall exactly into the expected range for standard Gr. Otherwise, the repeatability of results is apparently quite good for the vast majority of elements. The same elements as indicated above as problematic show the largest deviations from the 1:1 line in these plots (see Appendix 7).

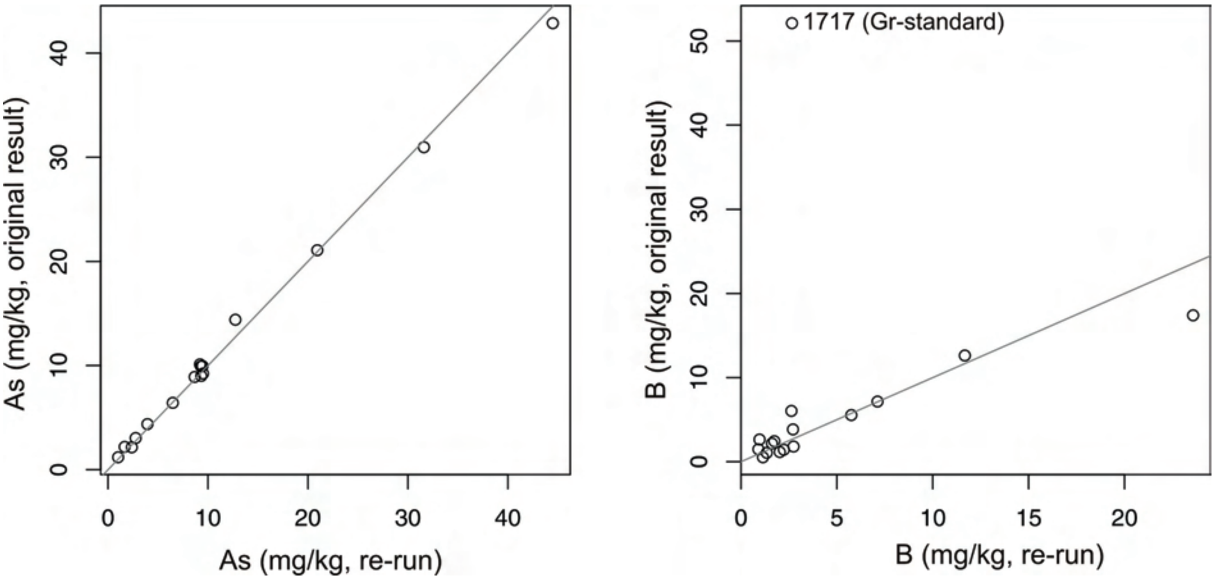

Figure 9. XY-plots for re-analyzed samples: X-axis result for the re-analyzed sample, Y-axis original result. The line indicates the expected 1:1 relation. Only the standard samples that caused ordering a re-analysis deviate seriously from the 1:1 line (see standard 1717 in the B-plot). All plots for the Gr-samples are shown in Appendix 7.

In terms of an explanation, for B it must be assumed that a wrong glass beaker (B-glass) was accidentally used during digestion for the one standard sample returning over 50 mg/kg B. For this project it had been agreed with the laboratory to use "old" glassware and when possible to avoid the use of B-glass in order to obtain the low detection limit required for B in an aqua regia extraction. For Ca it turned out that the sample with the highest Ca concentration of all samples was located in the immediate proximity to the standard sample and some cross-contamination must be assumed to be the source of the single high value. For Sn and Cu no good explanation for the outliers can be provided. However, in ICP-MS analyses Sn is one of the elements that can stick to the tube material used to feed the instrument. It is not necessarily removed during the washing procedure between the samples. The Sn can then be released from the tubes and cause unpredictable high Sn values at a later time (memory effect).

6. CONCLUSIONS

Results of quality control of the analytical results following an aqua regia extraction indicate an overall excellent quality. No serious time trends and no breaks in element concentration between batches were observed. Quality control using the hidden project QC-samples returns comparable results to QC carried out with the laboratories own control samples. Trueness can at present not be evaluated. This will need additional analyses of the GEMAS project standards by a number of external laboratories, results are expected within the coming year. For a number of elements the majority of the analytical results are very close to the detection limits (*e.g.*, Ge, Pt, Pd, Re, Ta, Te) and it is here that some quality problems are observed. In all instances where poor precision was observed this was due to very low concentrations. Nevertheless, there is definitely still room for improvements in analytical methodology (detection limits) for a number of interesting elements.

The main quality related issues detected were occasional, sometimes severe, outliers for single elements for the standard or one replicate analysis. However these outliers always occurred for single elements and single samples (never both standards included in many batches or standard and duplicate pairs in one and the same batch) and not as a systematic problem. Elements that showed such outliers include B, Ca, Cu, S and Sn. They must probably be seen as "system inherent" and unavoidable when using aqua regia extraction on a single sample. This problem could only be overcome by analysing (including extraction!) all samples in triplicate and using the median of the three determinations. Single outliers in the maps of these elements should thus be viewed with care. For example, for B some leaching from glassware in the laboratory (*e.g.*, when a new glass beaker was used) is the suspected culprit. The one Ca-outlier occurs in the immediate neighbourhood of a sample with an exceptionally high Ca-concentration and some cross-contamination or a carry-over effect may provide the explanation for the outlier. Results of the unbalanced ANOVA indicate that most elements can be reliably mapped. Exceptions are Pt, Pd, Re, Ta, Ge, and Te, 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. For some elements the detection limits in an aqua regia extraction are just still not low enough, which is often a question of price (it was, for example, originally planned to analyse all GEMAS samples for the PGEs with lower detection limits, however, the project funds were not sufficient).

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; *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.

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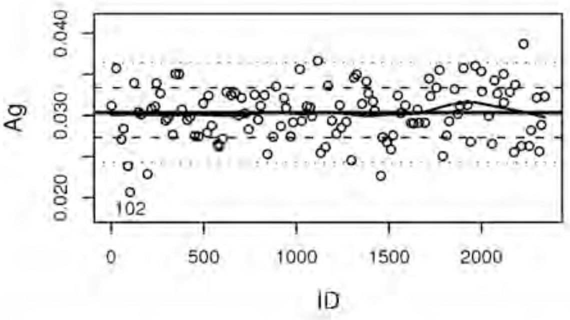
APPENDIX 1. X-Charts for the project standard Gr

All X-Charts for the project standard Gr. Sample number (ID) is plotted against analytical result for the standard. The fat line indicates the median value of all standard results, 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.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0.020
102
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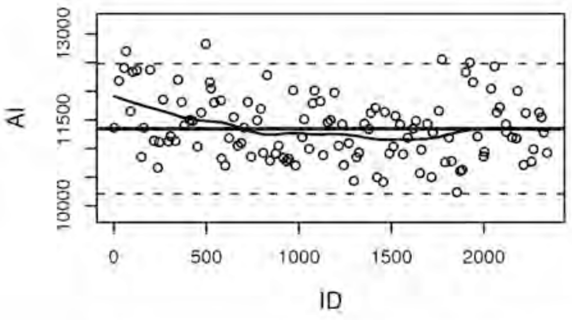
ID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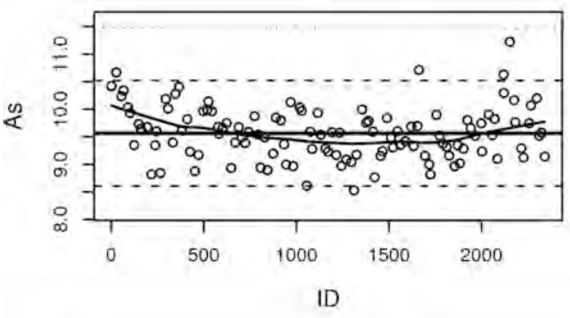
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8.0
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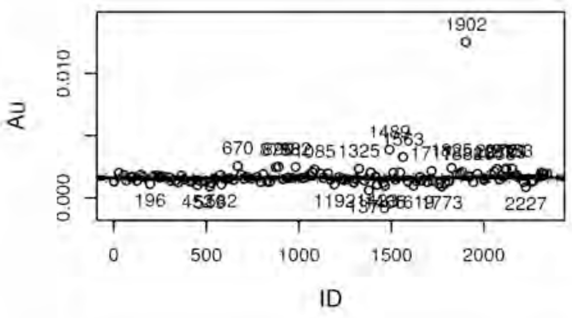
1000
1500
2000
ID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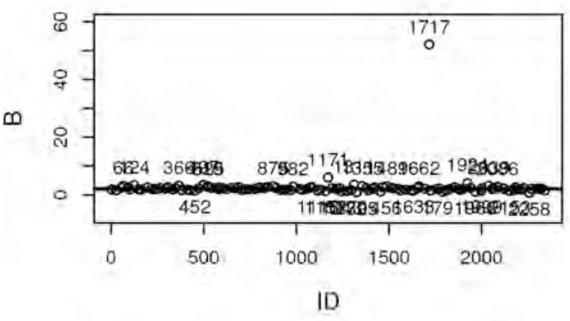
1489
1563
196
1192
1773
2227
0
500
1000
1500
2000
ID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452
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1000
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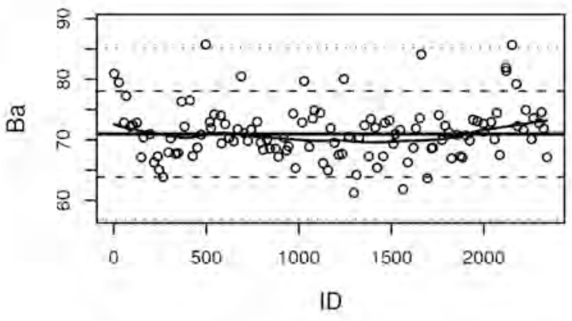
2000
ID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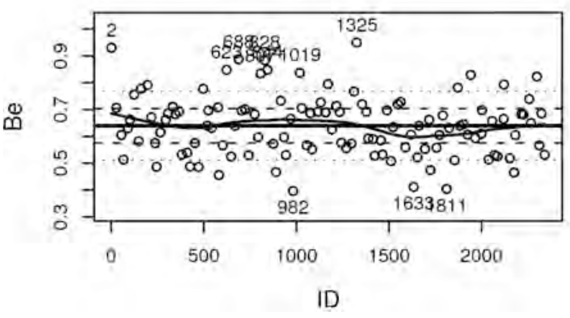
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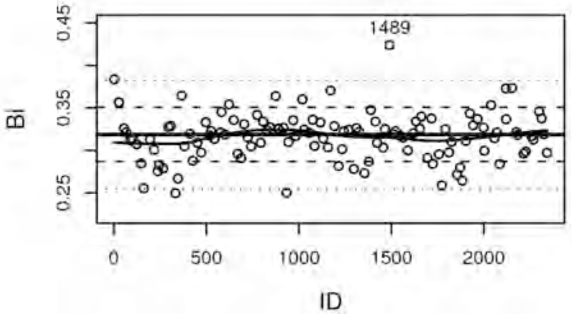
1811
0
500
1000
1500
2000
ID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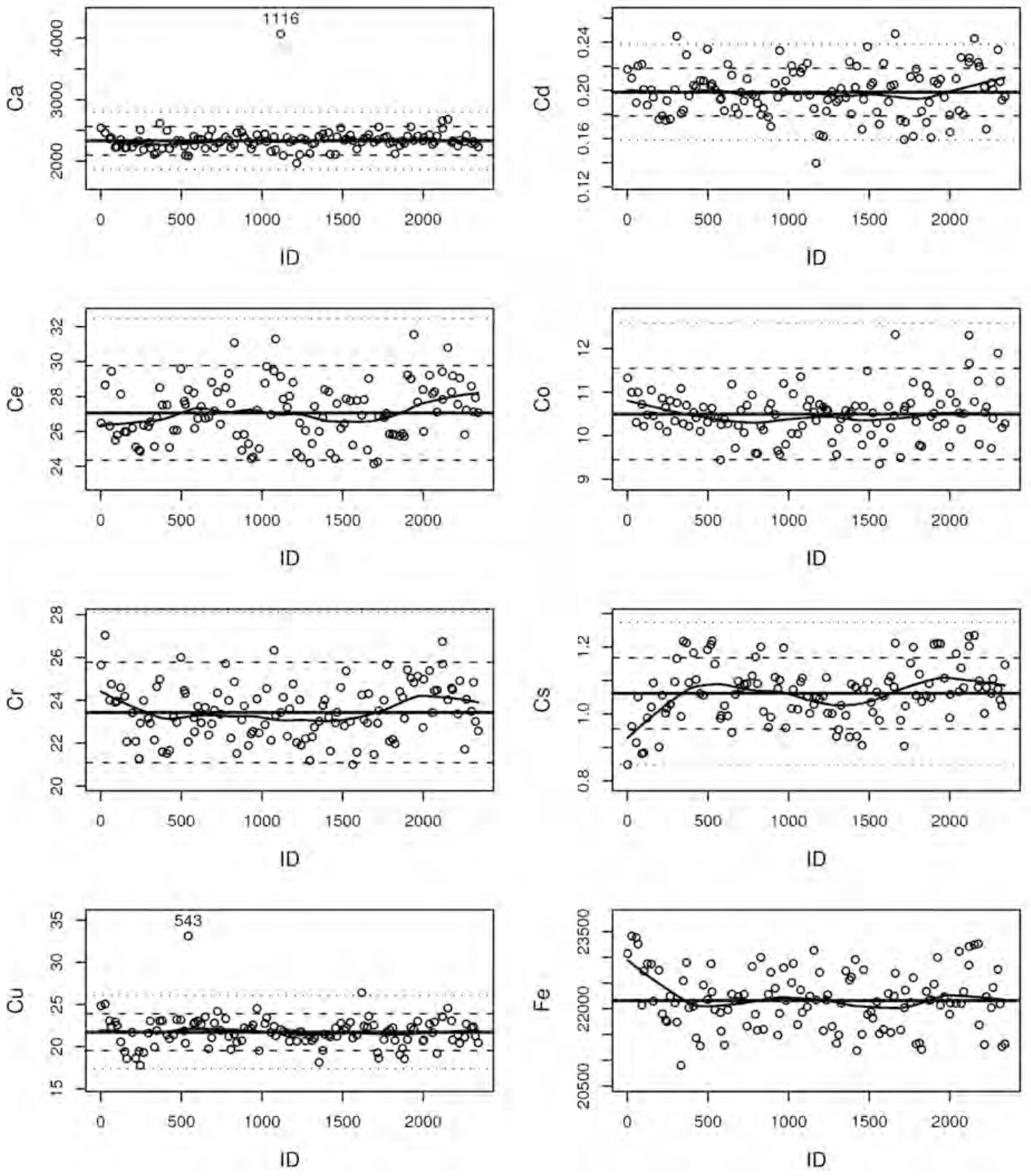
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9
10
11
12
Cr
20
22
24
26
28
Cs
0.8
1.0
1.2
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35
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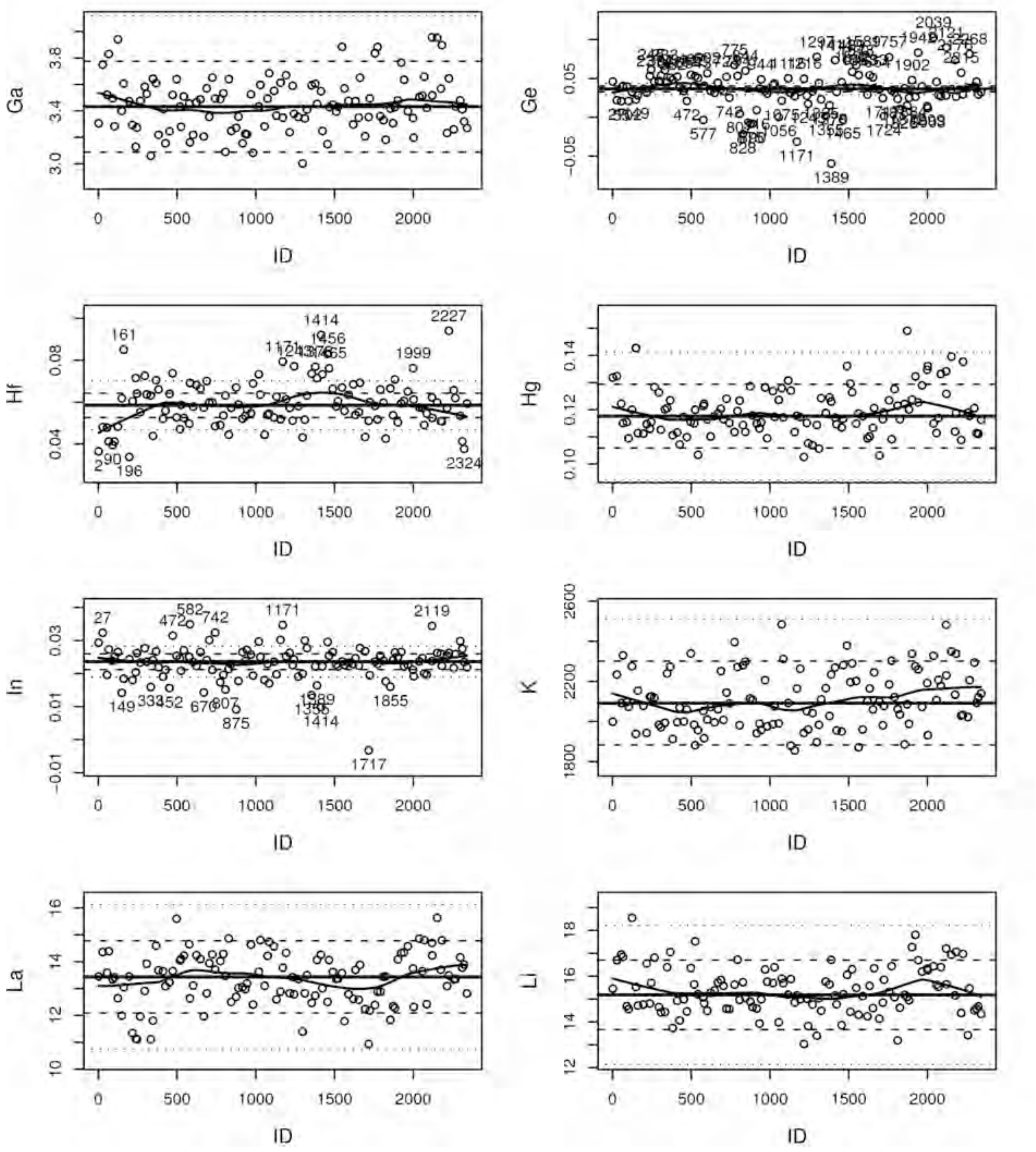
0
500
1000
1500
2000
ID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3.8
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0.05
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472
742
775
Hf
0.04
0.08
161
290
196
2
1414
1456
2227
1999
2324
Hg
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0.12
0.14
In
−0.01
0.01
0.03
27
472
582
742
1171
2119
149
333
352
676
807
875
1389
1356
1414
1855
1717
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La
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Li
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18
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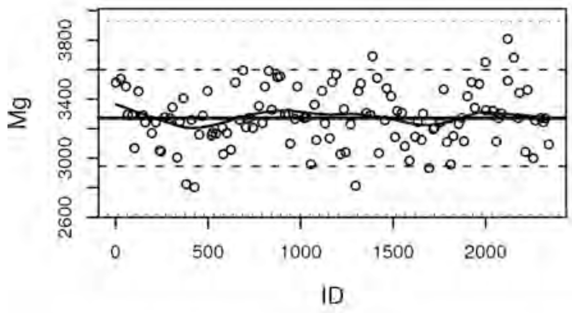
1000
1500
2000
ID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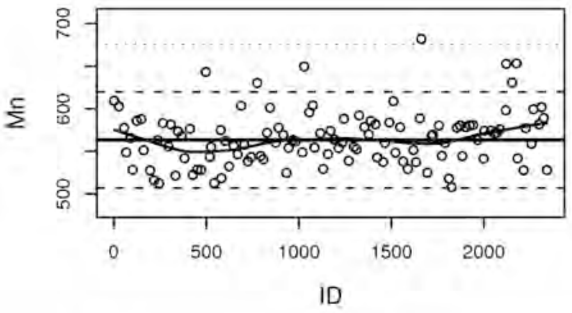
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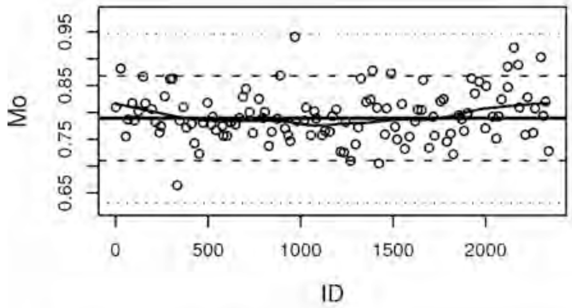
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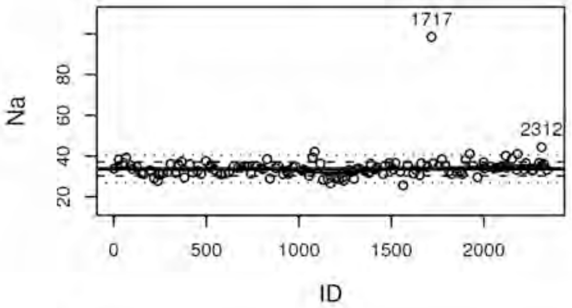
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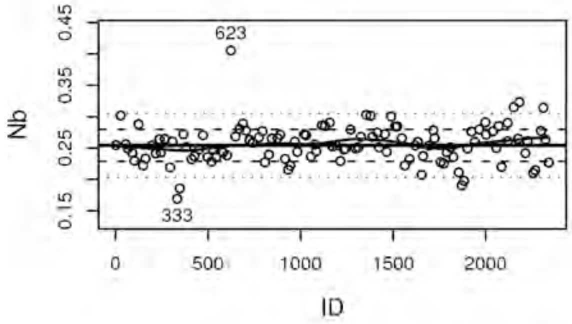
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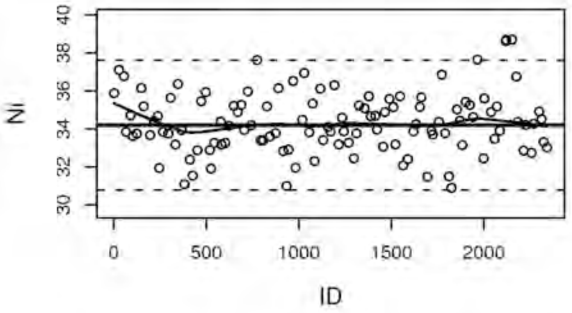
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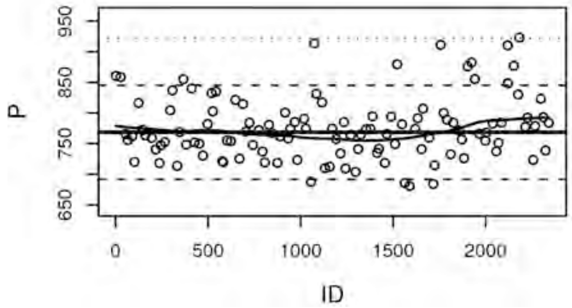
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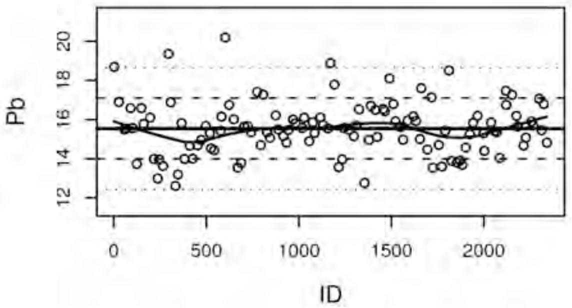
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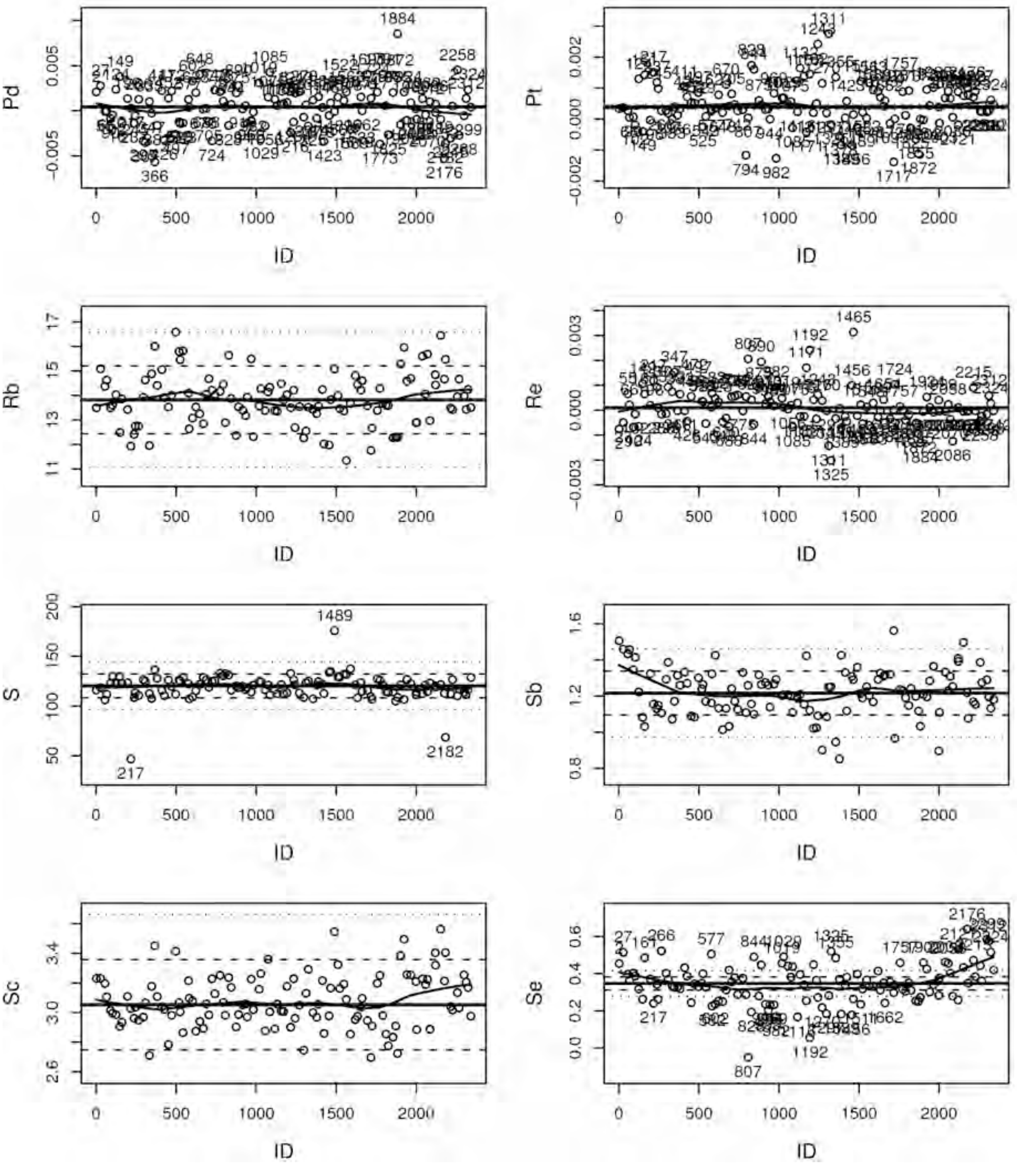
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S
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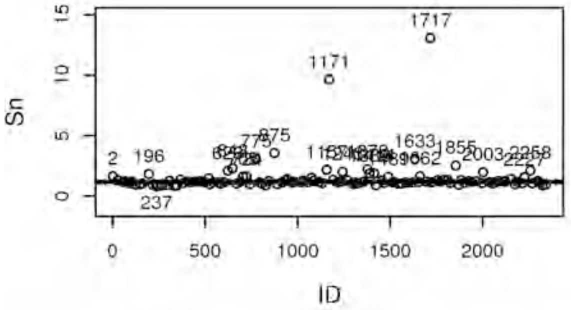
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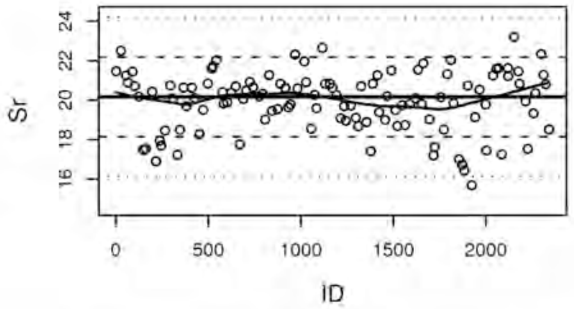
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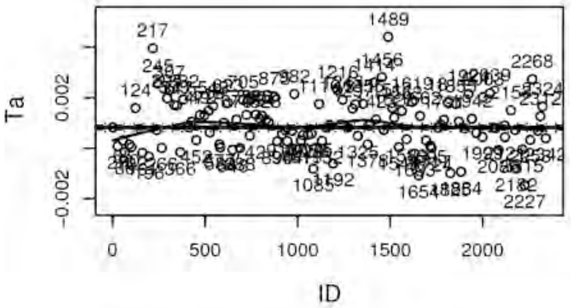
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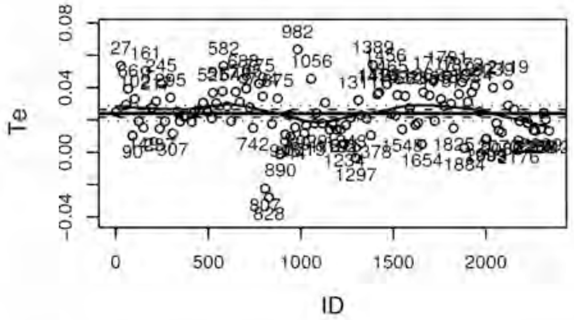
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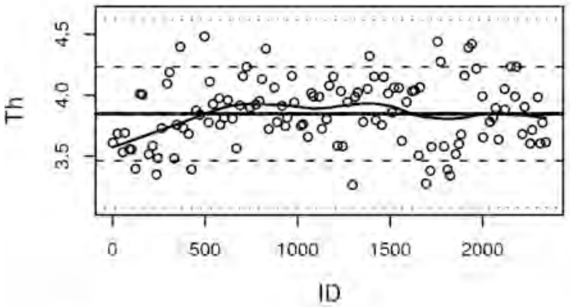
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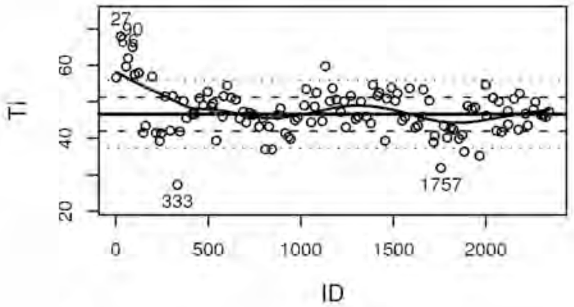
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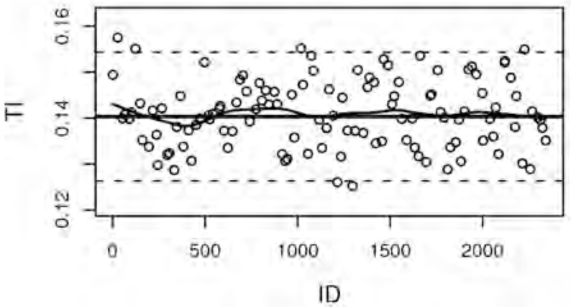
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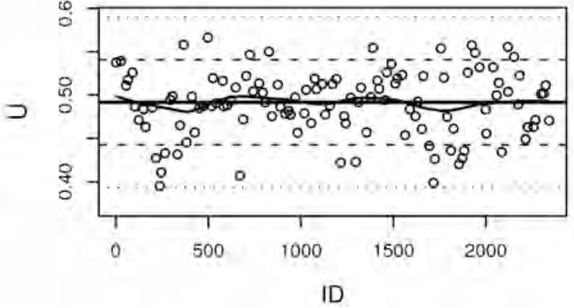
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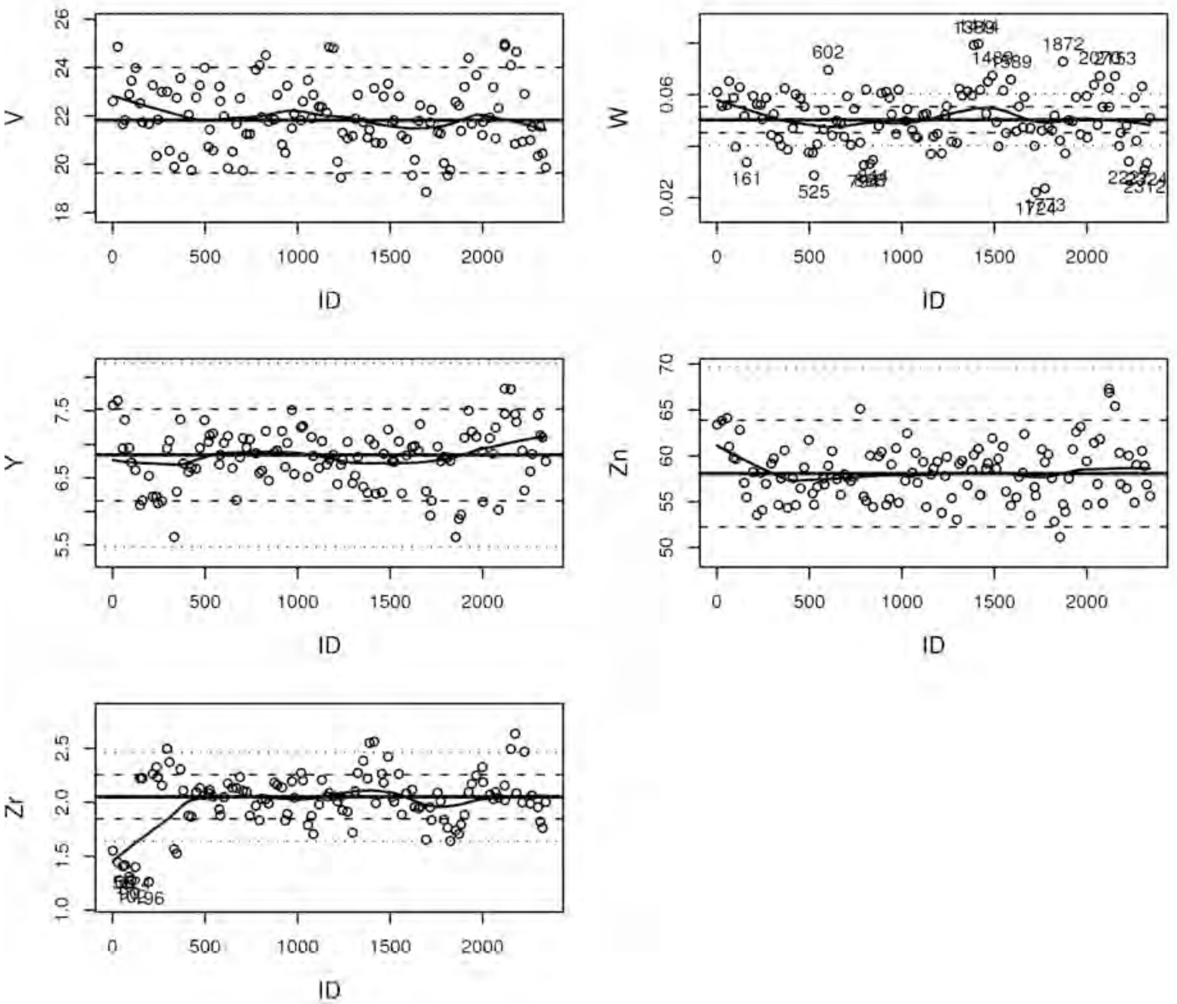
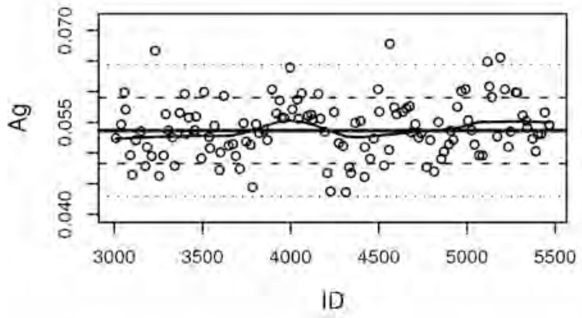
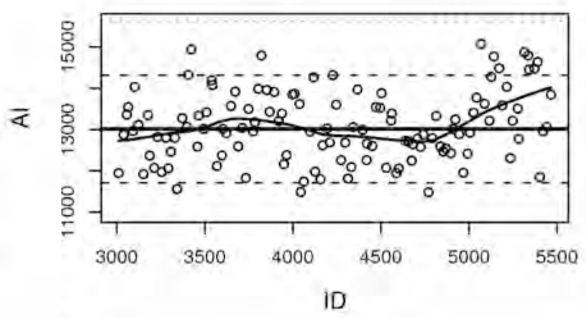
2000

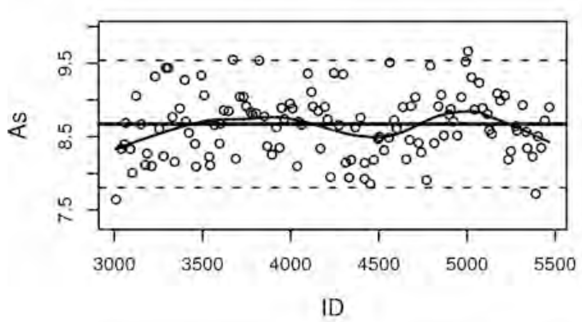

V
26
24
22
20
18
0
500
1000
1500
2000
ID
W
0.06
0.02
602
161
525
1872
1389
1489
1589
2070
2153
1724
1773
2312
ID
Y
7.5
6.5
5.5
ID
Zn
70
65
60
55
50
ID
Zr
2.5
2.0
1.5
1.0
96
ID

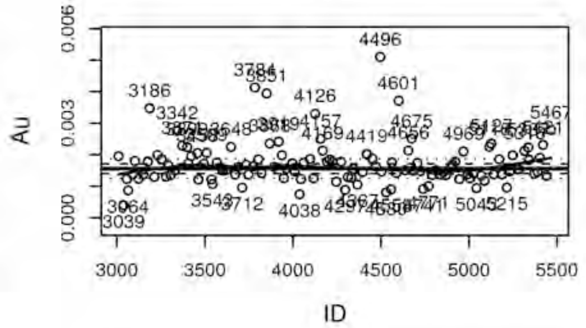
APPENDIX 2. X-Charts for the project standard Ap

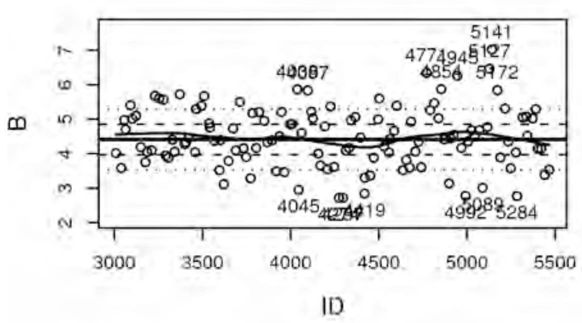
All X-Charts for the project standard Ap. Sample number (ID) is plotted against analytical result for the standard. The fat line indicates the median value of all standard results, the dashed line is the limit for 10%, the dotted line for 20% deviation from the median. Standard results that show a larger 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.

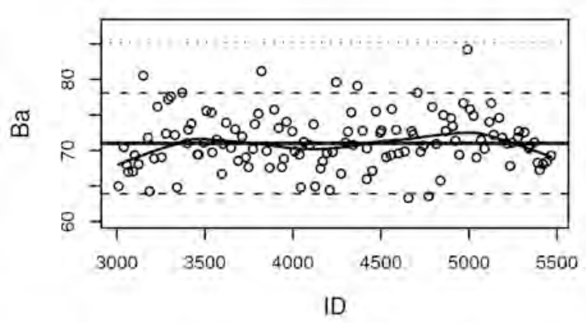

Ag
0.040
0.055
0.070
3000
3500
4000
4500
5000
5500
ID

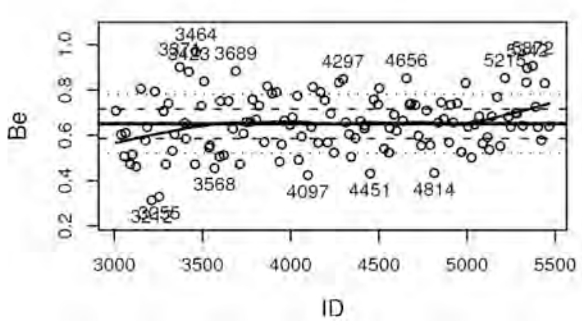

Al
11000
13000
15000
3000
3500
4000
4500
5000
5500
ID

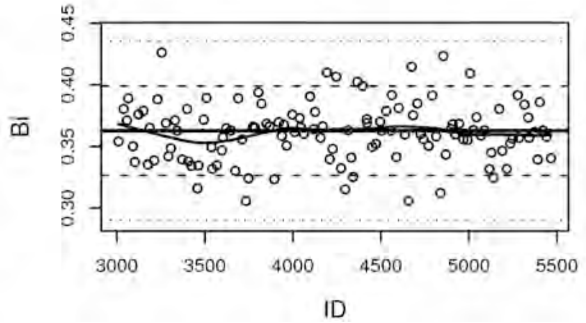

As
7.5
8.5
9.5
3000
3500
4000
4500
5000
5500
ID

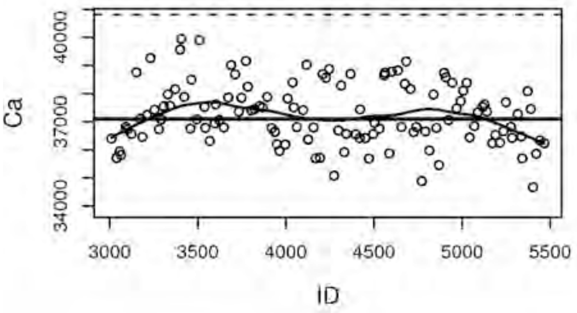

Au
0.000
0.003
0.006
4496
3784
3851
3186
4126
4601
3342
4675
5467
3064
3039
3543
3712
4038
5045
5215
3000
3500
4000
4500
5000
5500
ID

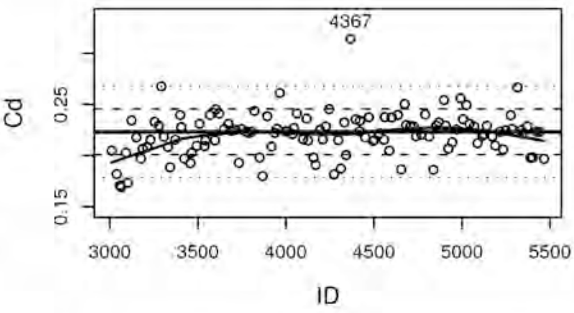

B
2
3
4
5
6
7
5141
5127
4856
5172
4045
4419
4992
5284
3000
3500
4000
4500
5000
5500
ID

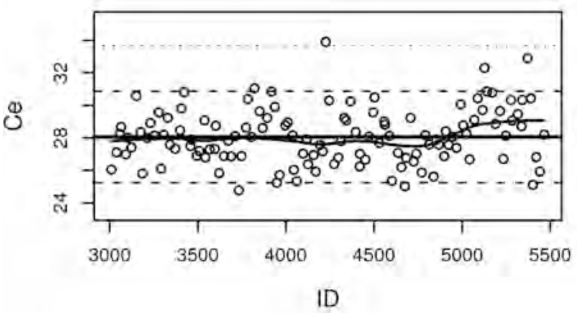

Ba
60
70
80
3000
3500
4000
4500
5000
5500
ID

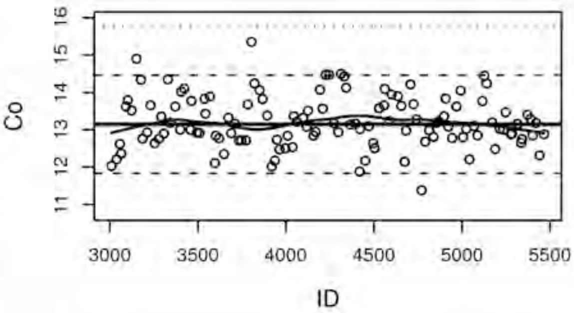

Be
0.2
0.4
0.6
0.8
1.0
3464
3423
3689
4297
4656
5215
3568
4097
4451
4814
3242
3000
3500
4000
4500
5000
5500
ID

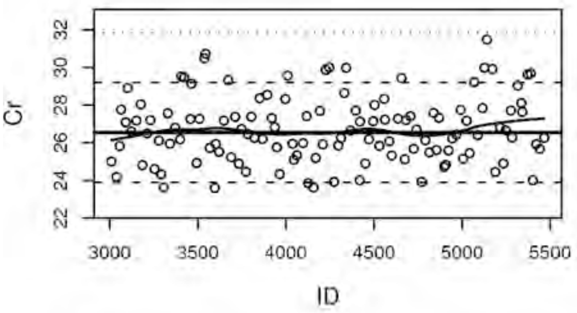

Bi
0.30
0.35
0.40
0.45
3000
3500
4000
4500
5000
5500
ID

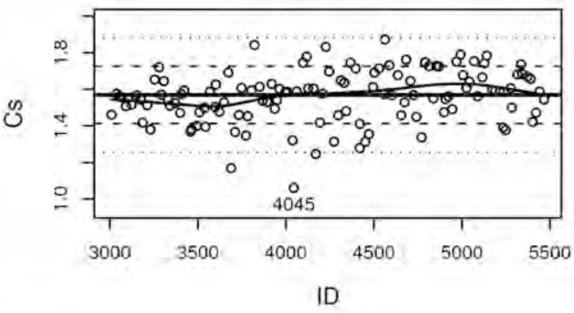

Ca
34000
37000
40000
3000
3500
4000
4500
5000
5500
ID

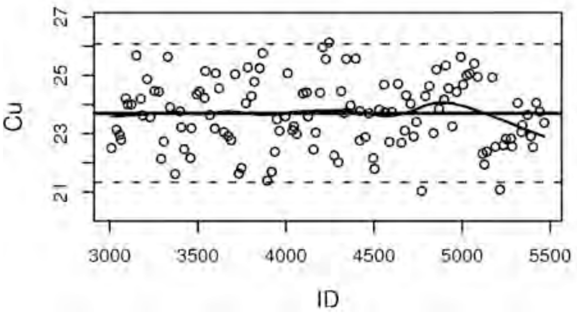

Cd
4367
0.15
0.25
3000
3500
4000
4500
5000
5500
ID

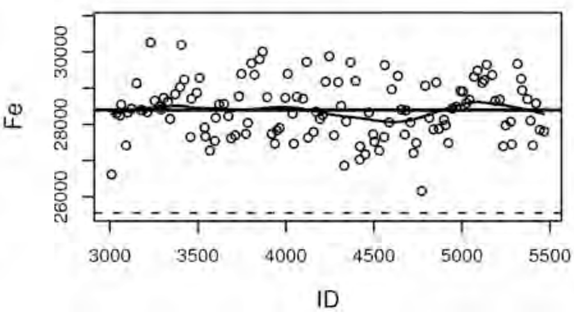

Ce
24
28
32
3000
3500
4000
4500
5000
5500
ID

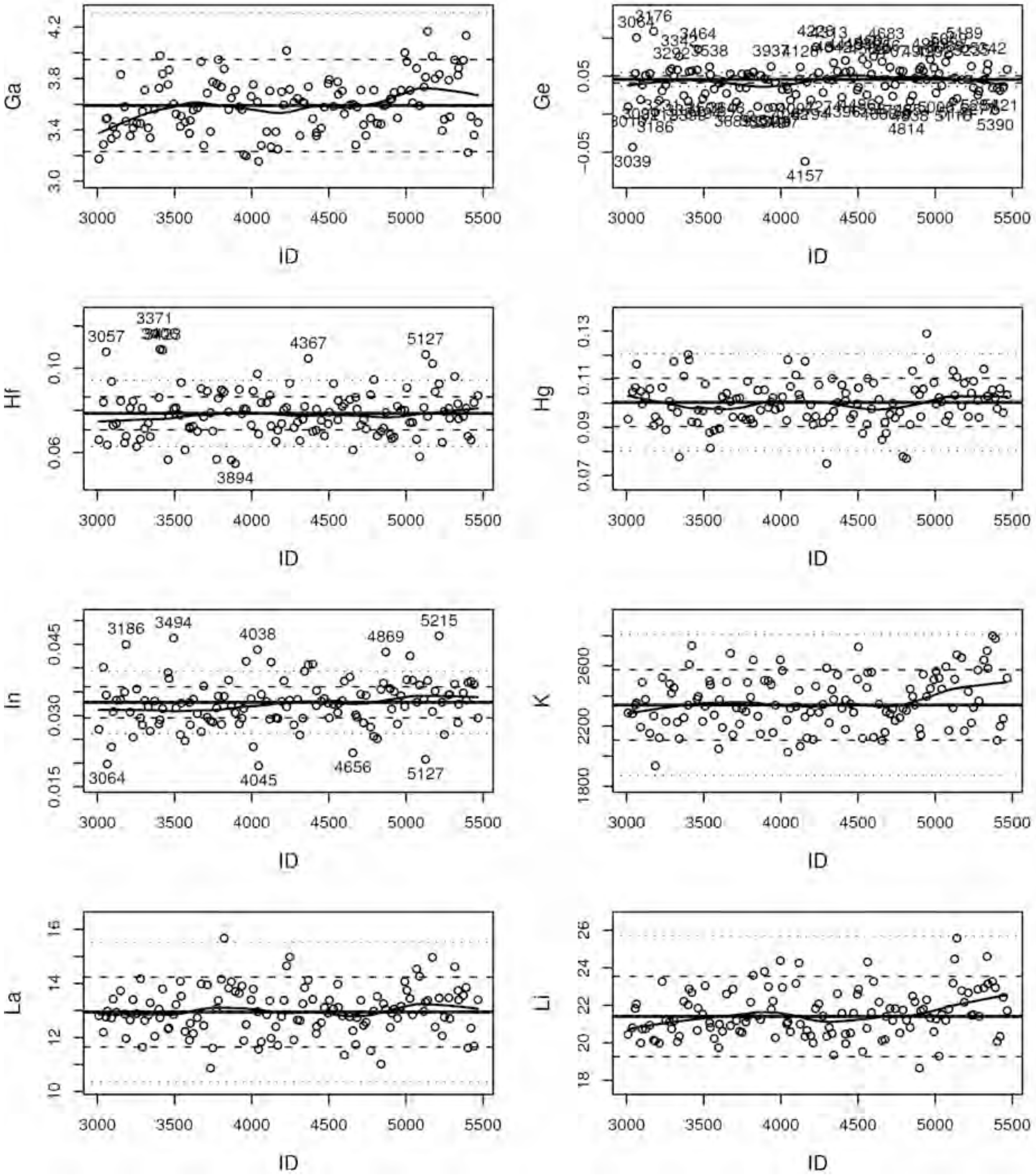

Co
11
12
13
14
15
16
3000
3500
4000
4500
5000
5500
ID

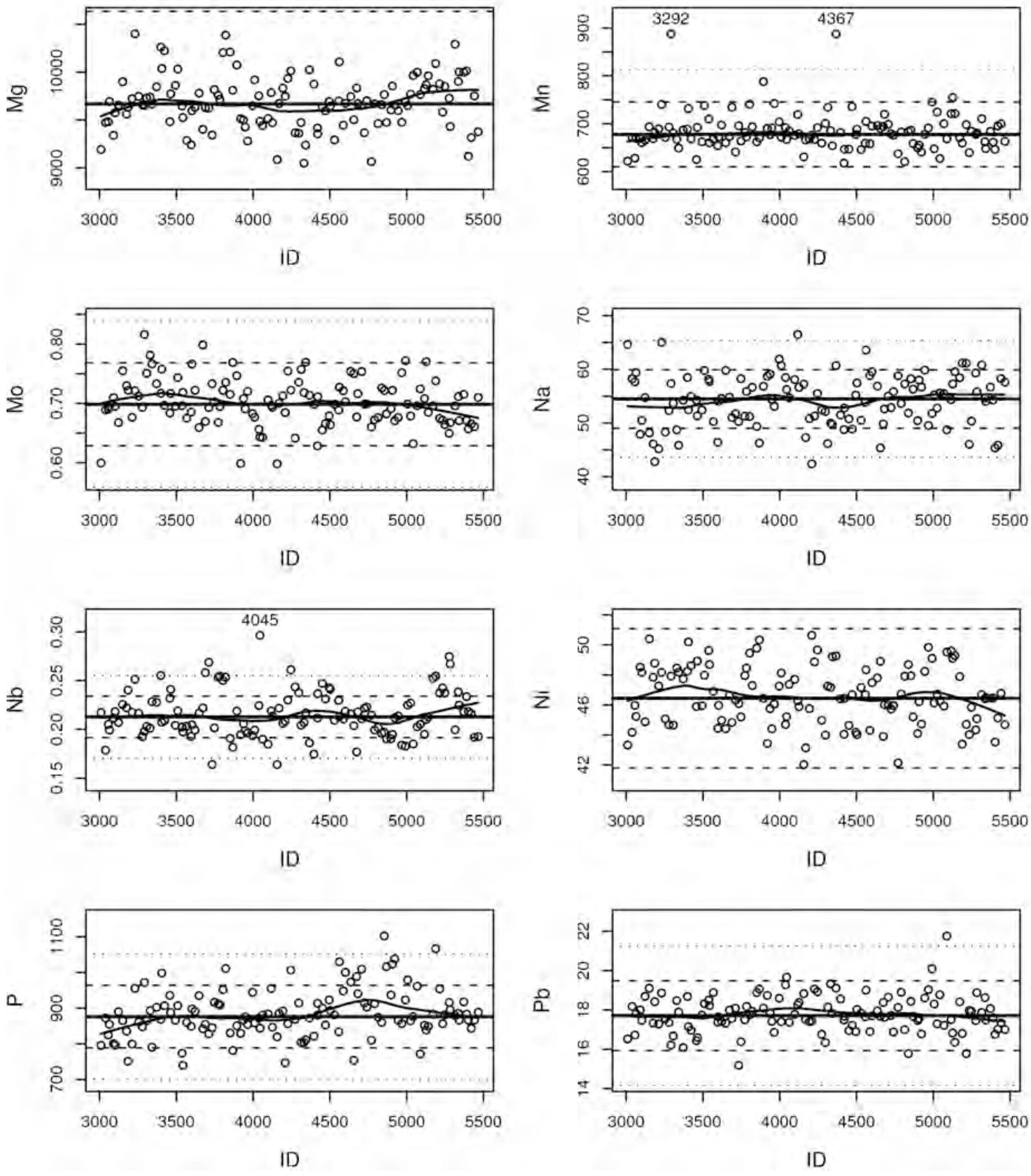

Cr
22
24
26
28
30
32
3000
3500
4000
4500
5000
5500
ID

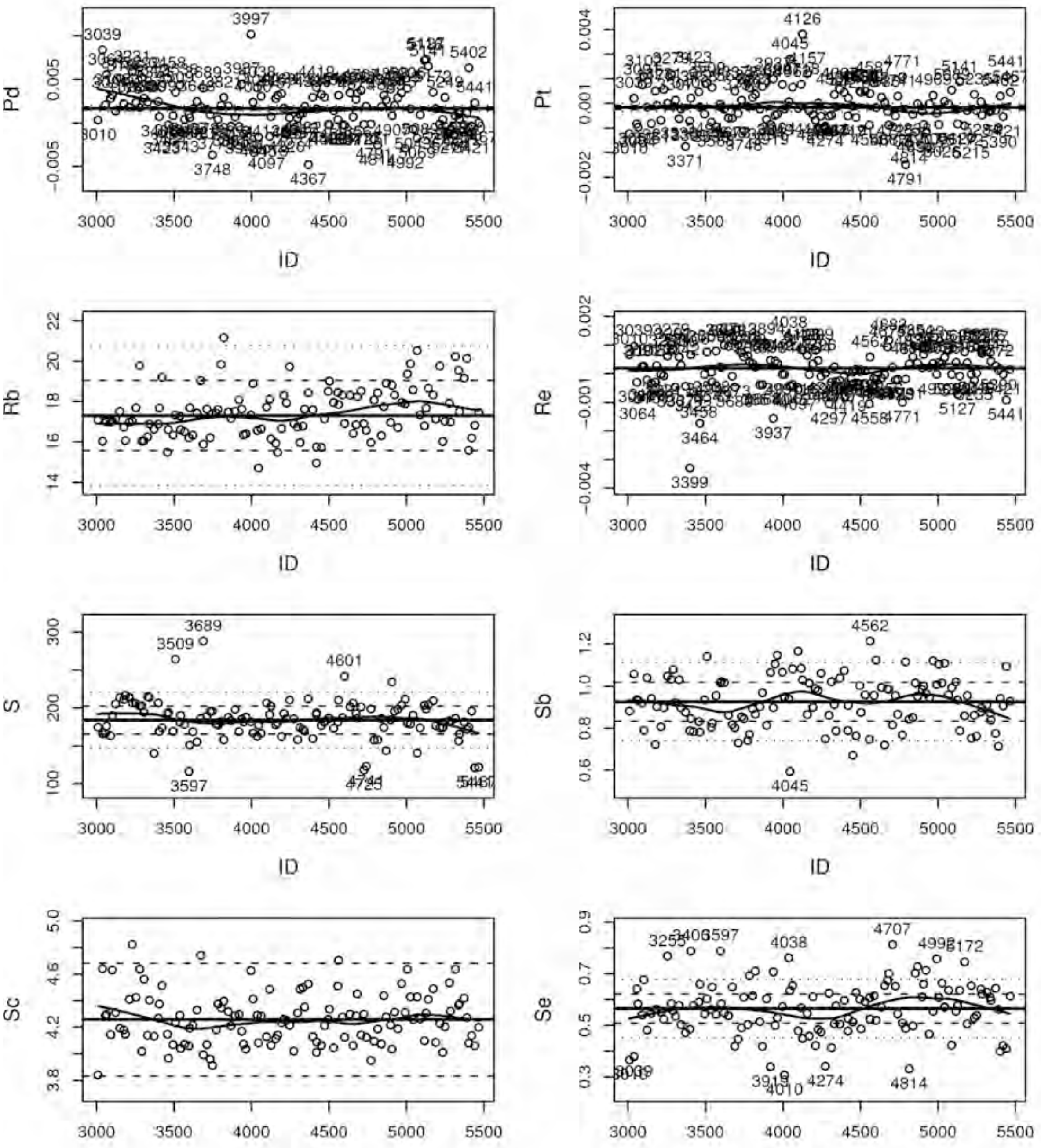

Cs
4045
1.0
1.4
1.8
3000
3500
4000
4500
5000
5500
ID

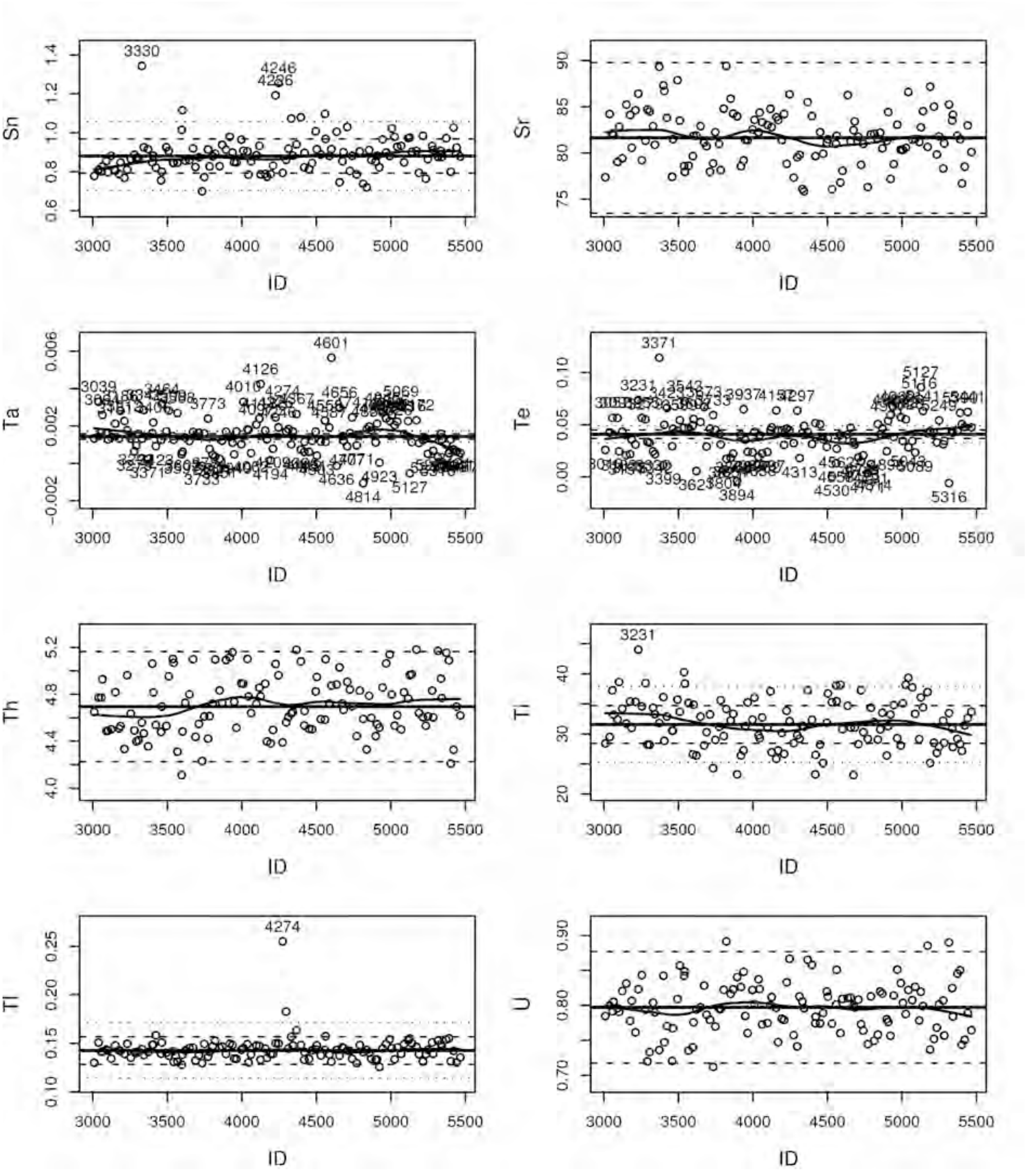

Cu
21
23
25
27
3000
3500
4000
4500
5000
5500
ID

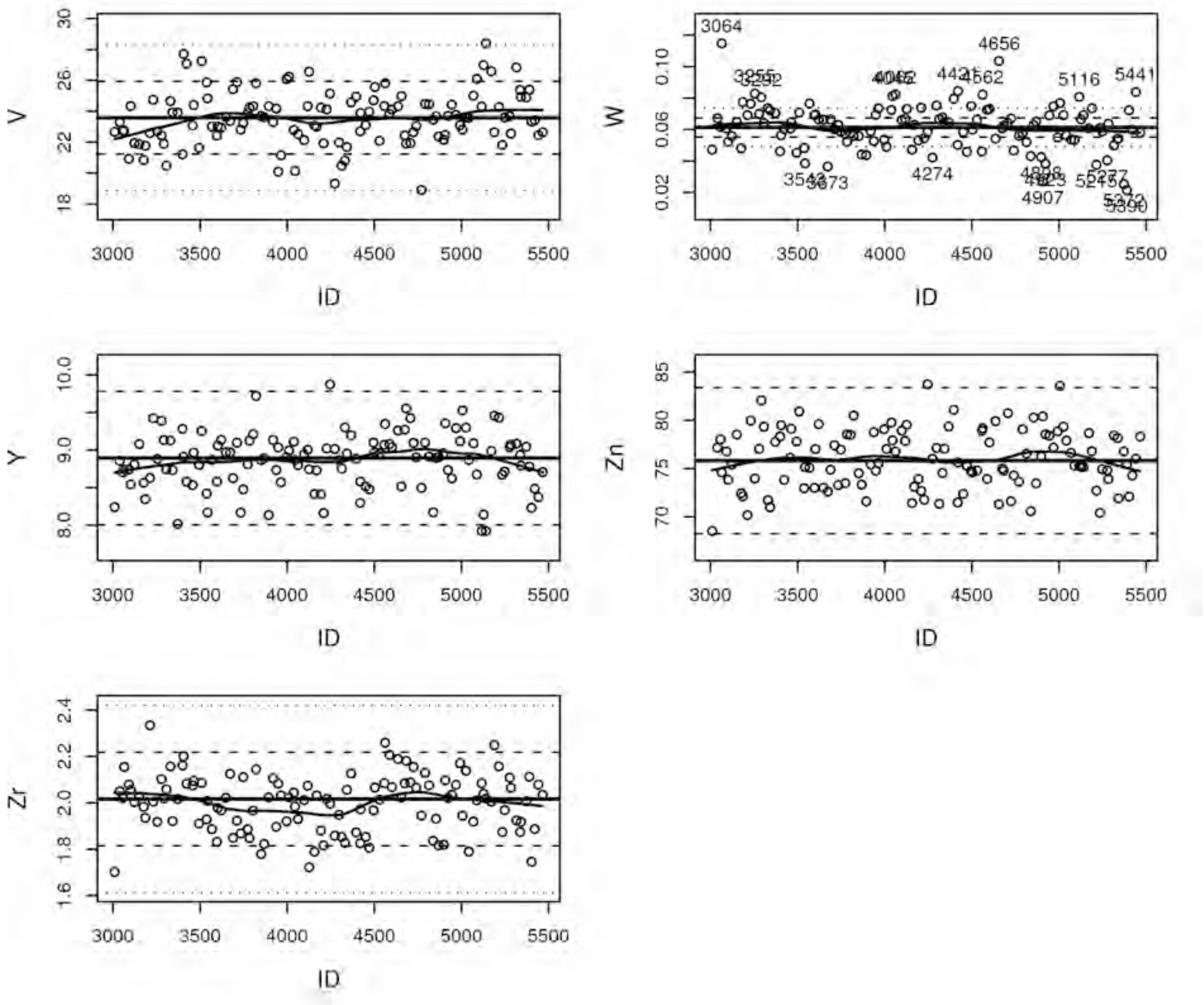

Fe
26000
28000
30000
3000
3500
4000
4500
5000
5500
ID


Ga
3.0
3.4
3.8
4.2
Ge
-0.05
0.05
3064
3176
3464
3538
3937
4126
4229
4683
5189
5342
3186
4814
5390
5421
3039
4157
Hf
0.06
0.10
3057
3371
4367
5127
3894
Hg
0.07
0.09
0.11
0.13
In
0.015
0.030
0.045
3186
3494
4038
4869
5215
3064
4045
4656
5127
K
1800
2200
2600
La
10
12
14
16
Li
18
20
22
24
26
3000
3500
4000
4500
5000
5500
ID


Mg
9000
10000
3000
3500
4000
4500
5000
5500
ID
Mn
600
700
800
900
3292
4367
ID
Mo
0.60
0.70
0.80
ID
Na
40
50
60
70
ID
Nb
0.15
0.20
0.25
0.30
4045
ID
Ni
42
46
50
ID
P
700
900
1100
ID
Pb
14
16
18
20
22
ID

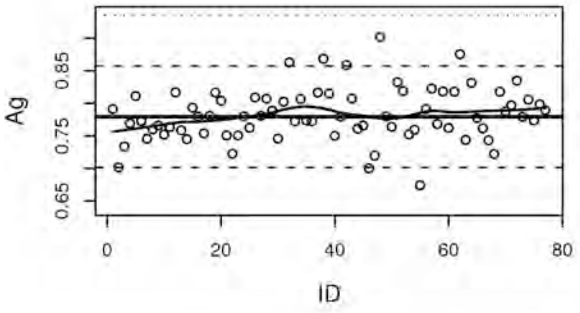

Pd
Pt
Rb
Re
S
Sb
Sc
Se
ID
3000
3500
4000
4500
5000
5500
-0.005
0.005
-0.002
0.001
0.004
14
16
18
20
22
-0.004
-0.001
0.002
100
200
300
0.6
0.8
1.0
1.2
3.8
4.2
4.6
5.0
0.3
0.5
0.7
0.9
3039
3997
3010
3748
4097
4367
5402
5441
4814
4992
4126
4045
4157
4771
5141
3371
4791
5215
5390
4038
3064
3458
3464
3399
3937
4297
4558
5127
3689
3509
4601
3597
4725
4562
4045
3255
3406
3597
4707
4998
5172
3919
4010
4274

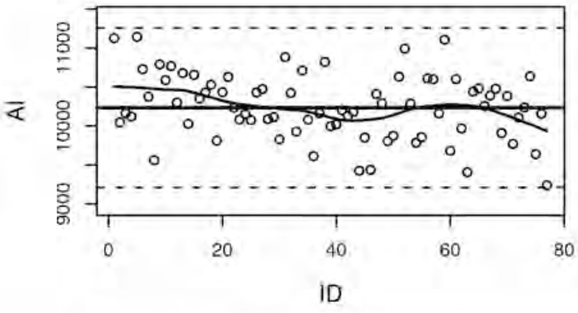

Sn
1.4
1.2
1.0
0.8
0.6
3330
4246
4236
Sr
90
85
80
75
Ta
0.006
0.002
-0.002
4601
4126
4010
4274
4656
5069
3039
3464
3773
3371
3733
4194
4636
4923
4814
5127
Te
0.10
0.05
0.00
3371
3231
3543
3937
4297
5127
5116
3399
3623
3894
4313
4530
5316
Th
5.2
4.8
4.4
4.0
Ti
40
30
20
3231
Tl
0.25
0.20
0.15
0.10
4274
U
0.90
0.80
0.70
3000
3500
4000
4500
5000
5500
ID

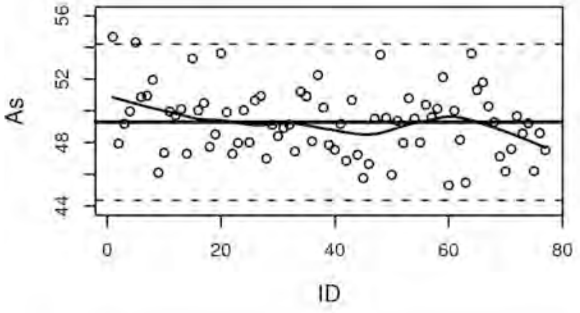

V
30
26
22
18
W
0.10
0.06
0.02
3064
3255
4656
4562
5116
5441
3543
3673
4274
4907
Y
10.0
9.0
8.0
Zn
85
80
75
70
Zr
2.4
2.2
2.0
1.8
1.6
3000
3500
4000
4500
5000
5500
ID

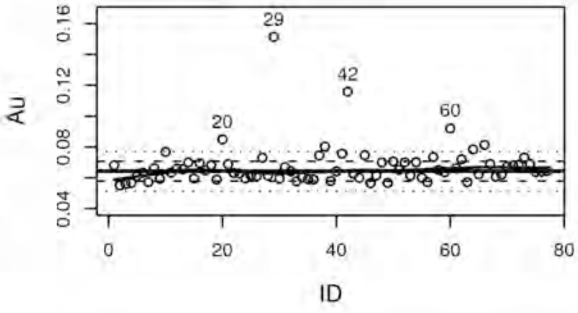
APPENDIX 3. X-Charts for laboratory standard DS7 as inserted between the Gr samples

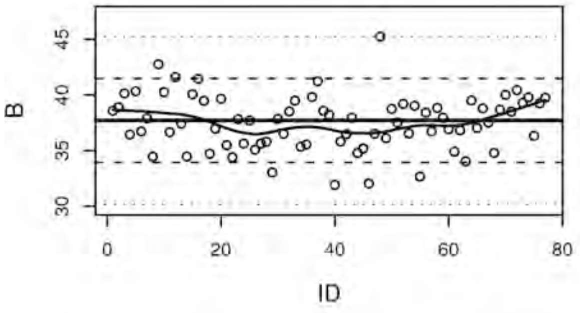
All X-Charts for the laboratory standard DS7 as inserted between the Gr samples. Sample number (ID) is plotted against analytical result for the standard. The fat line indicates the median value of all standard results, the dashed line is the limit for 10%, the dotted line for 20% deviation from the 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.

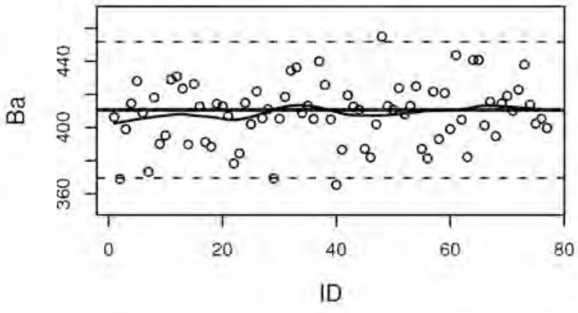

Ag
0.65
0.75
0.85
0
20
40
60
80
ID

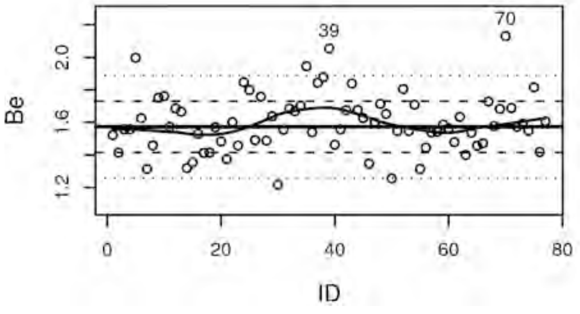

Al
9000
10000
11000
0
20
40
60
80
ID

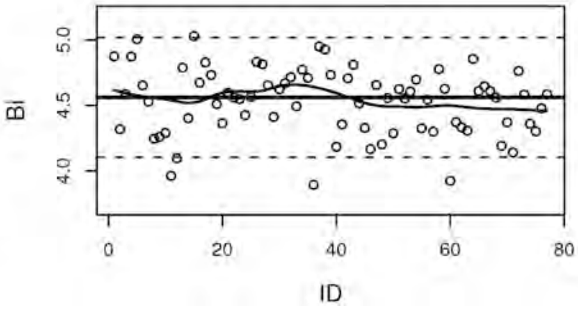

As
44
48
52
56
0
20
40
60
80
ID

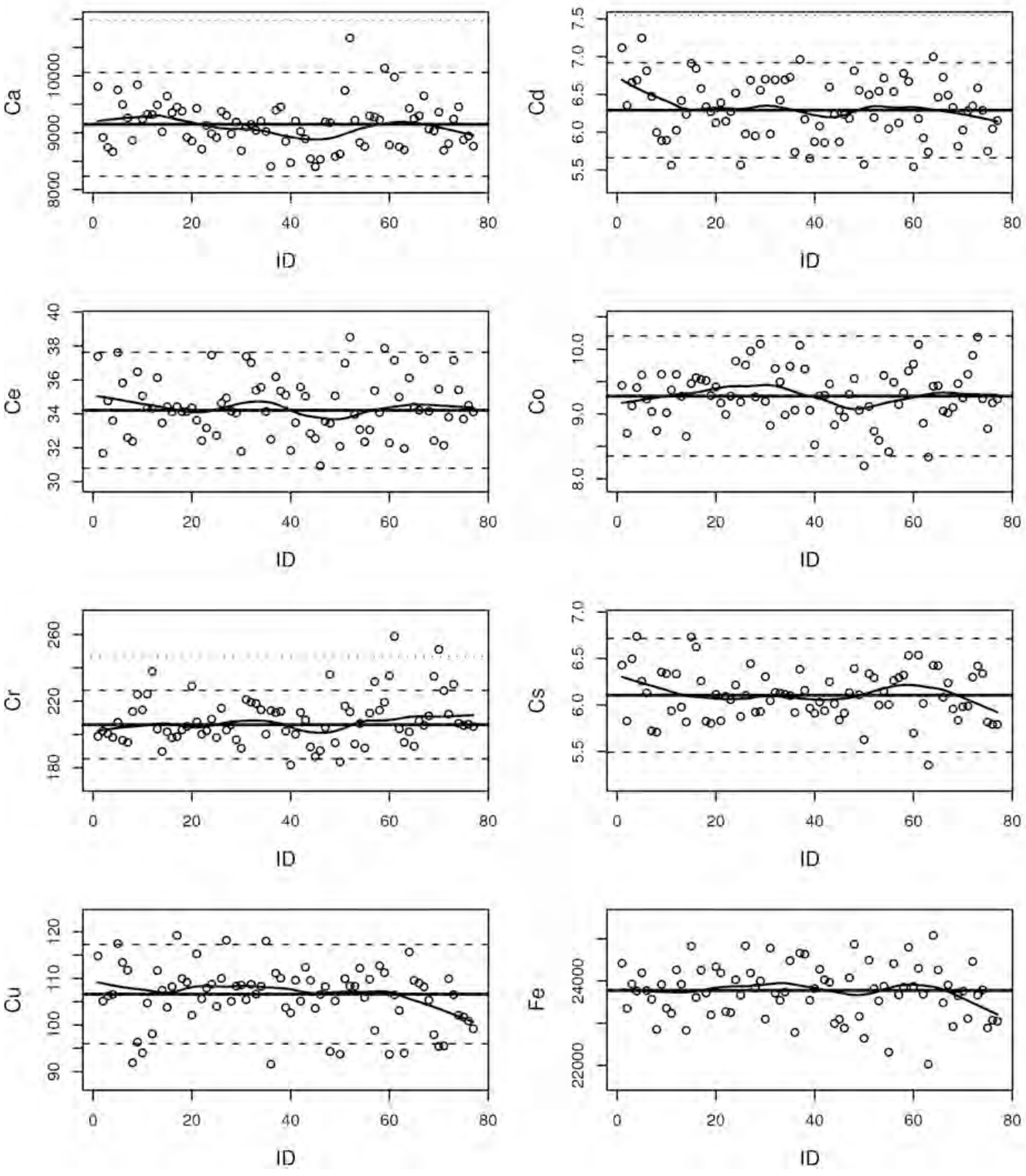

Au
0.04
0.08
0.12
0.16
29
42
20
60
0
20
40
60
80
ID

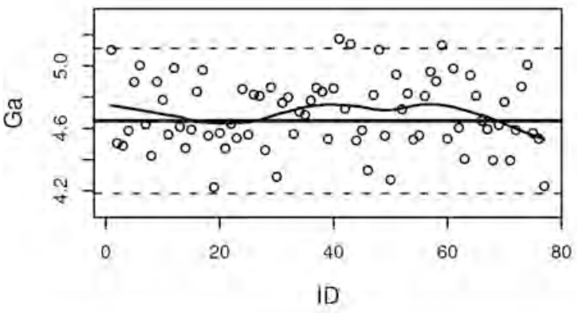

B
30
35
40
45
0
20
40
60
80
ID

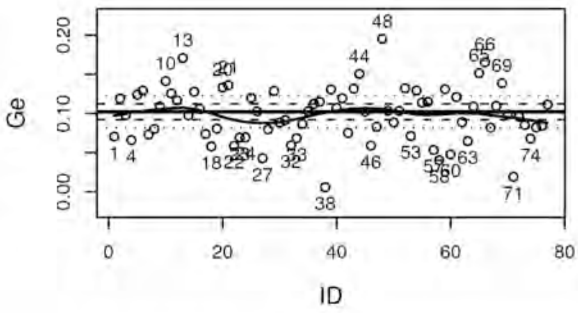

Ba
360
400
440
0
20
40
60
80
ID

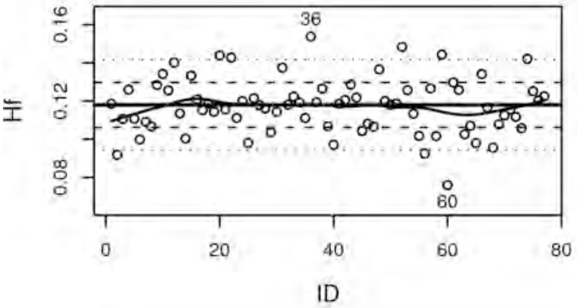

Be
1.2
1.6
2.0
39
70
0
20
40
60
80
ID

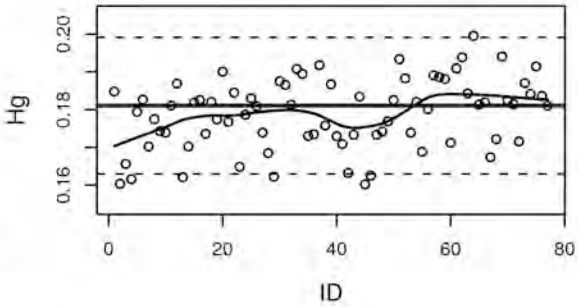

Bi
4.0
4.5
5.0
0
20
40
60
80
ID

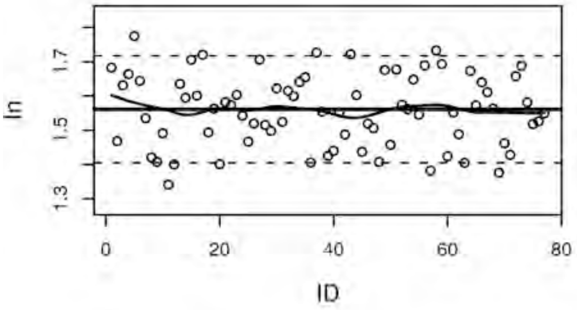

Ca
8000
9000
10000
Cd
5.5
6.0
6.5
7.0
7.5
Ce
30
32
34
36
38
40
Co
8.0
9.0
10.0
Cr
180
220
260
Cs
5.5
6.0
6.5
7.0
Cu
90
100
110
120
Fe
22000
24000
0
20
40
60
80
ID

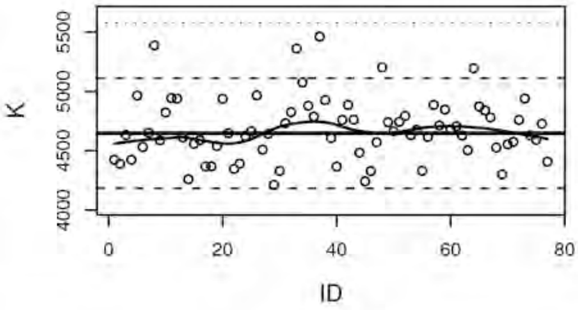

Ga
4.2
4.6
5.0
0
20
40
60
80
ID

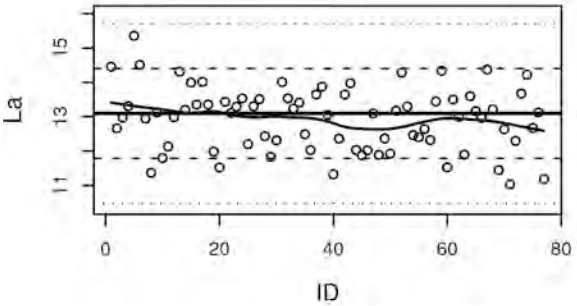

Ge
0.00
0.10
0.20
48
13
66
65
69
10
20
21
44
1
4
18
22
23
24
27
32
33
38
46
53
57
59
58
60
63
74
71
0
20
40
60
80
ID

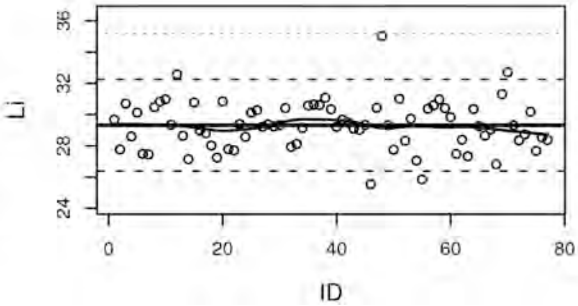

Hf
0.08
0.12
0.16
36
60
0
20
40
60
80
ID

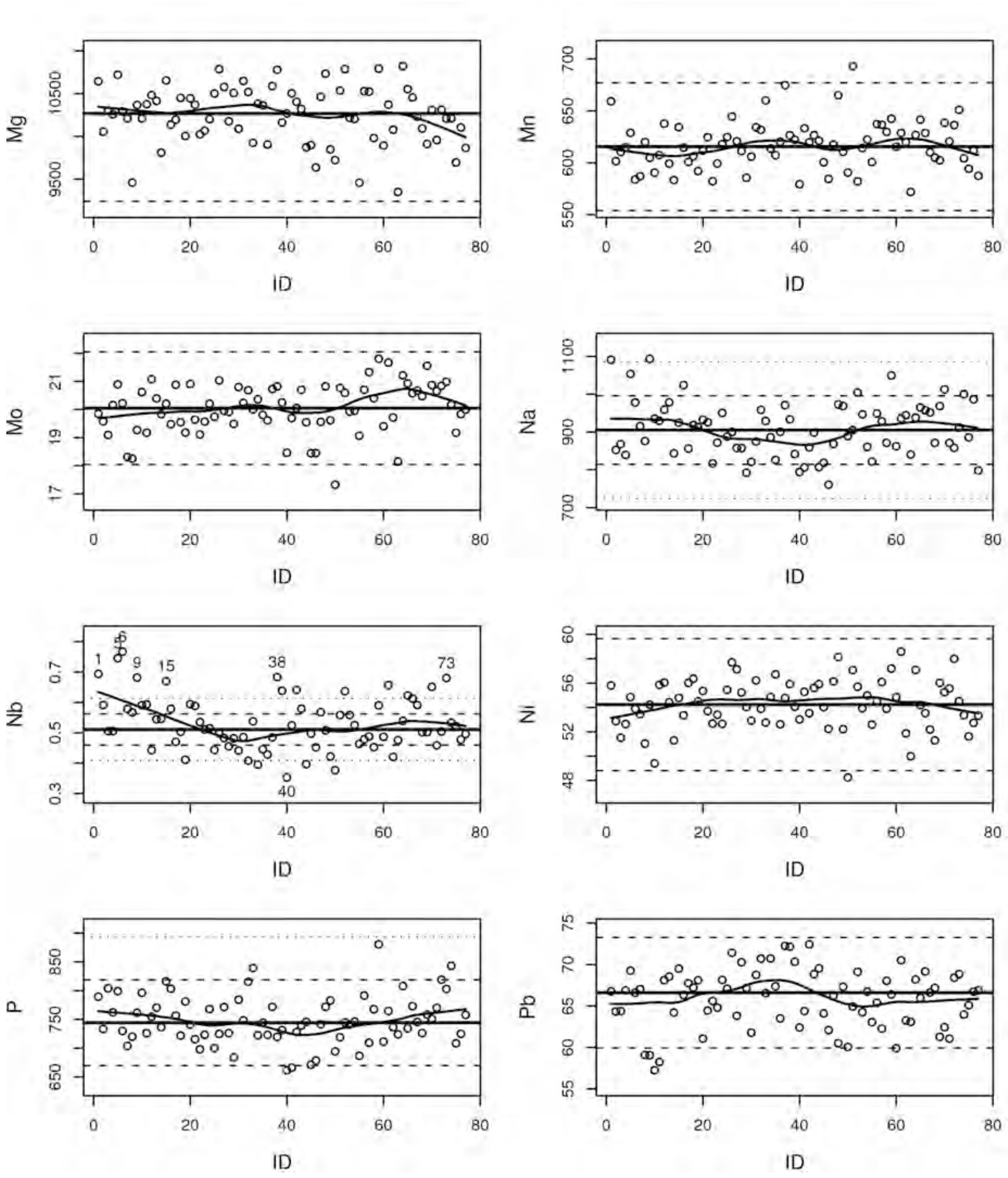

Hg
0.16
0.18
0.20
0
20
40
60
80
ID

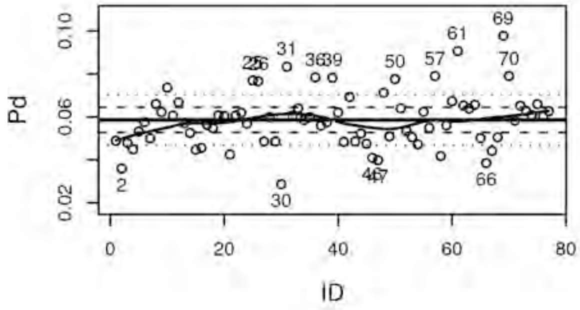

In
1.3
1.5
1.7
0
20
40
60
80
ID

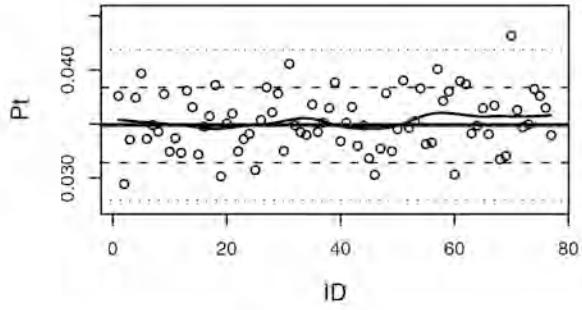

K
4000
4500
5000
5500
0
20
40
60
80
ID

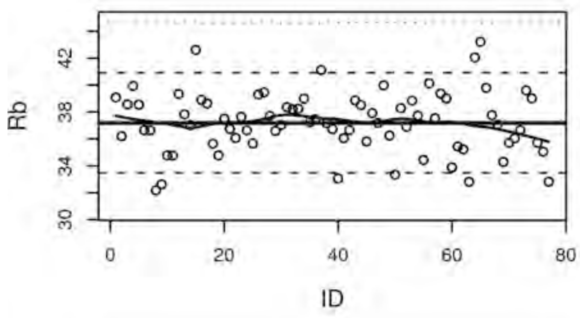

La
11
13
15
0
20
40
60
80
ID

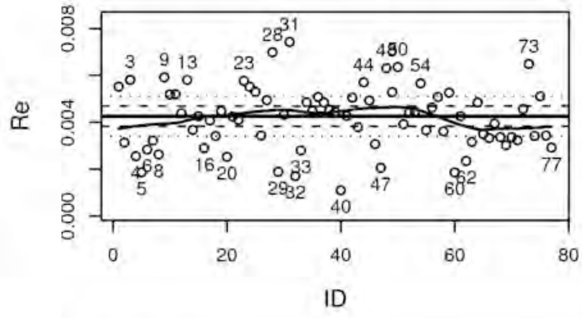

Li
24
28
32
36
0
20
40
60
80
ID

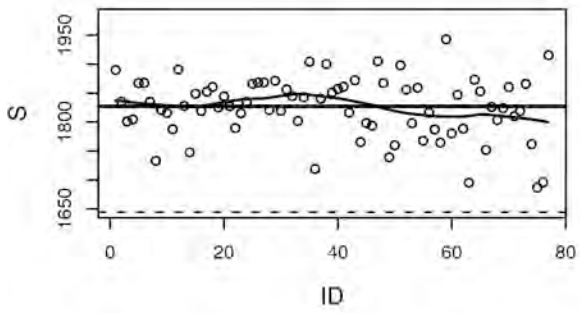

Mg
10500
9500
Mn
700
650
600
550
Mo
21
19
17
Na
1100
900
700
Nb
0.7
0.5
0.3
1
5
9
15
38
73
40
Ni
60
56
52
48
P
850
750
650
Pb
75
70
65
60
55
0
20
40
60
80
ID

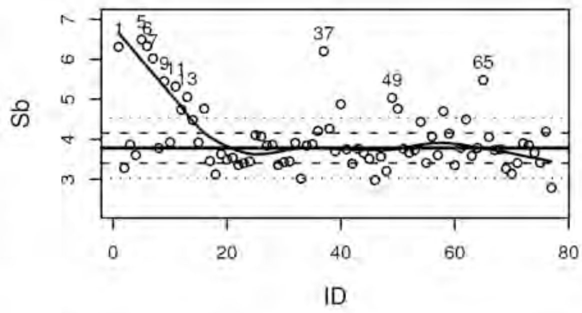

Pd
0.02
0.06
0.10
ID
0
20
40
60
80
69
61
31
25 26
36 39
50
57
70
2
30
46 47
66

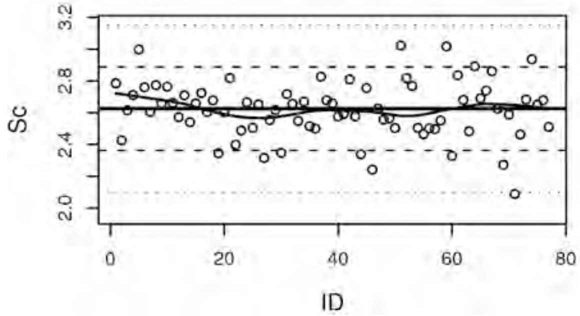

Pt
0.030
0.040
ID
0
20
40
60
80

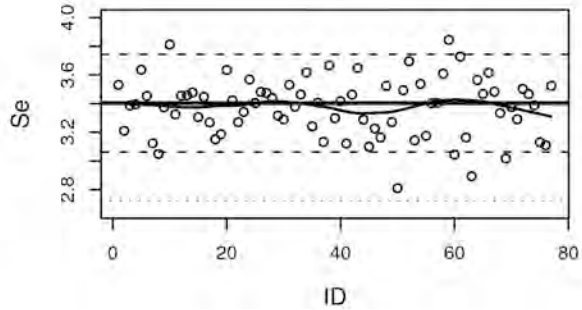

Rb
30
34
38
42
ID
0
20
40
60
80

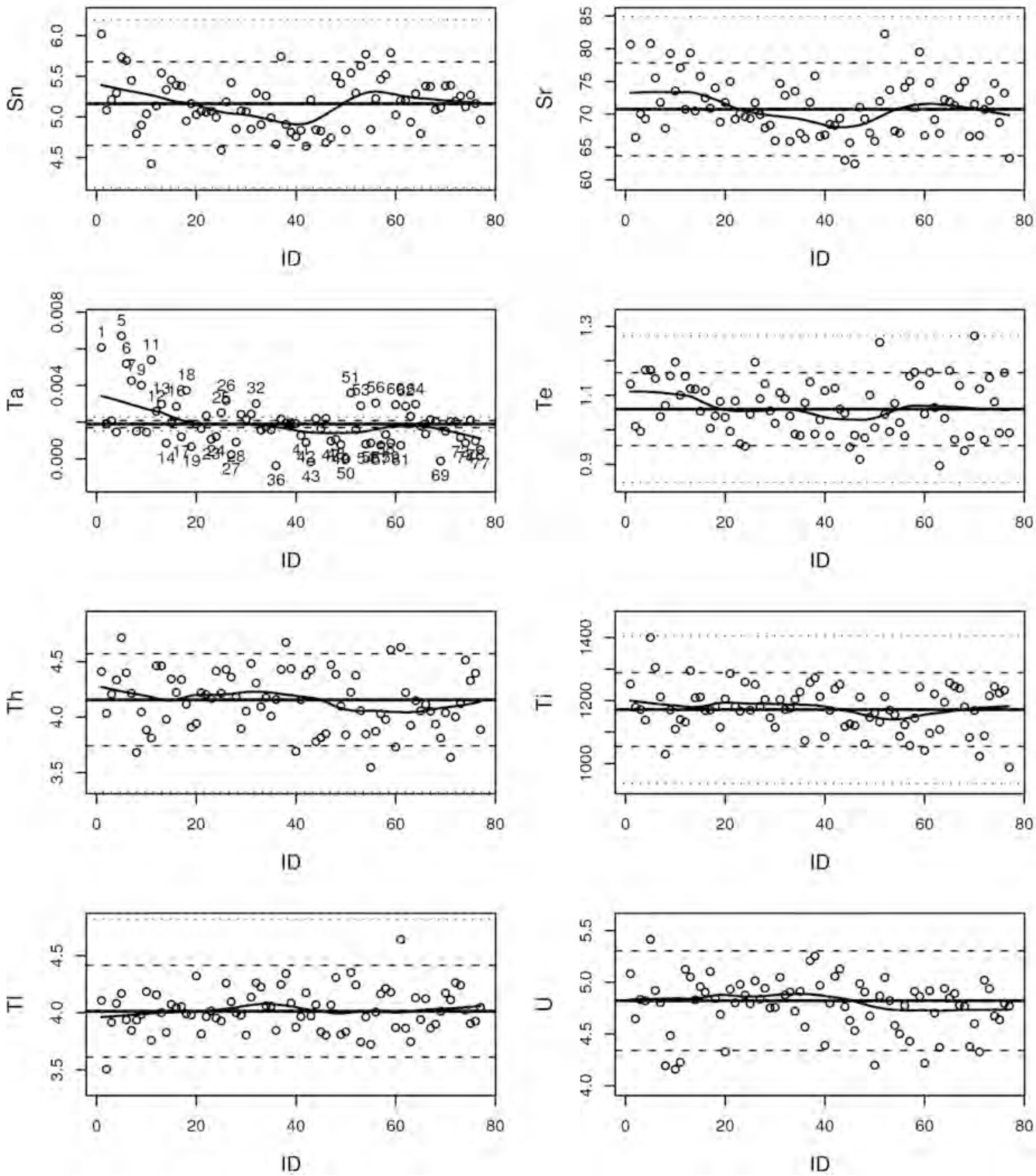

Re
0.000
0.004
0.008
ID
0
20
40
60
80
28 31
3
9
13
23
44
48 50
54
73
4
5
6
8
16
20
29
32
33
40
47
60
62
77

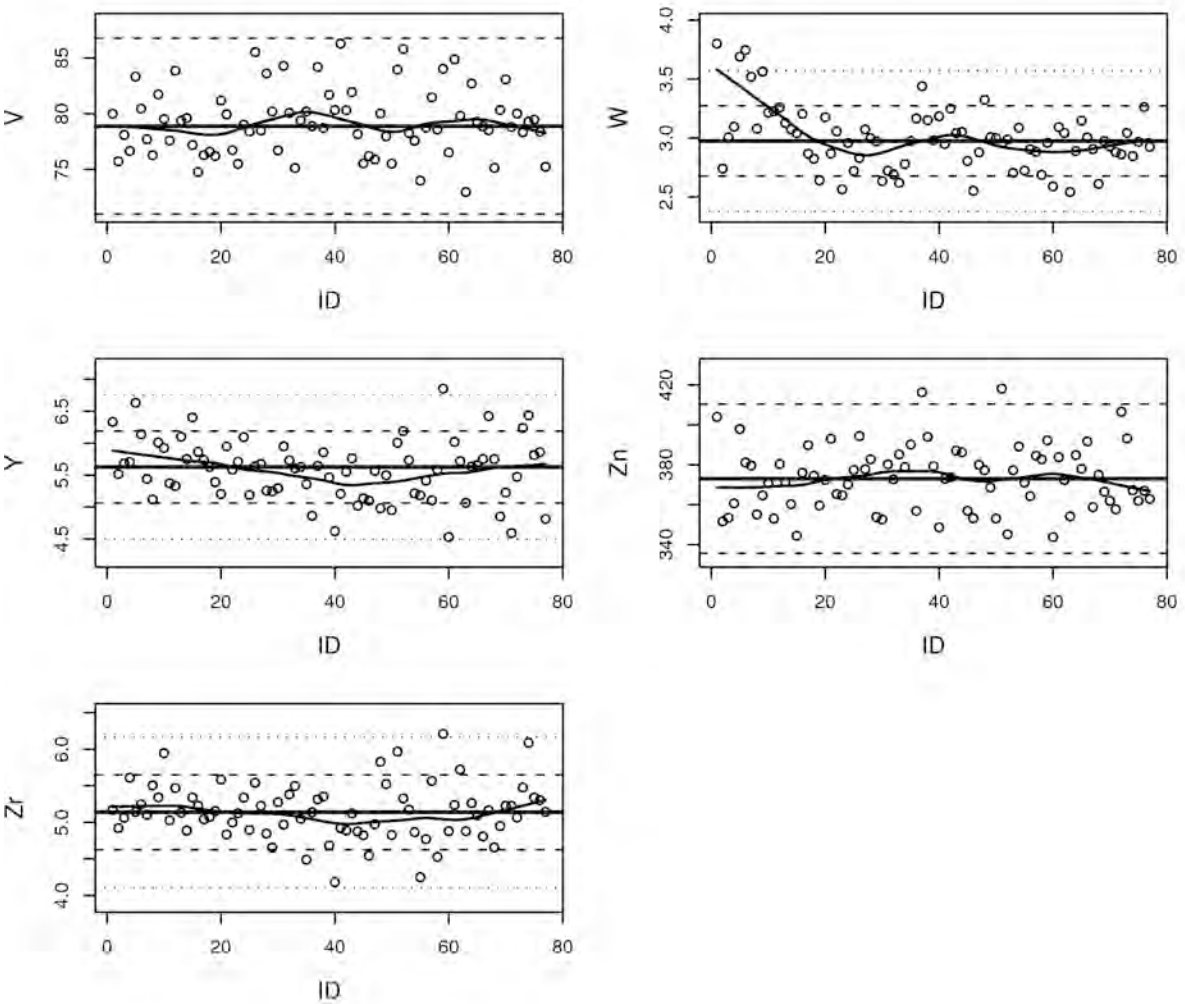

S
1650
1800
1950
ID
0
20
40
60
80


Sb
3
4
5
6
7
ID
0
20
40
60
80
1
5
6
7
9
11
13
37
49
65


Sc
2.0
2.4
2.8
3.2
ID
0
20
40
60
80

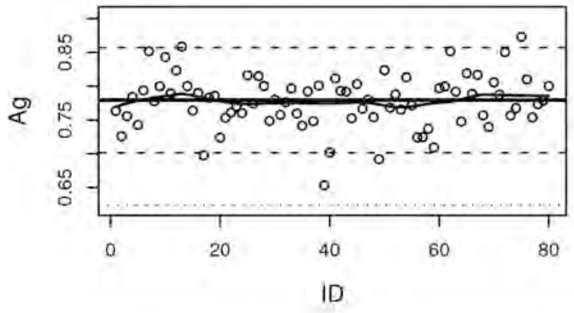

Se
2.8
3.2
3.6
4.0
ID
0
20
40
60
80

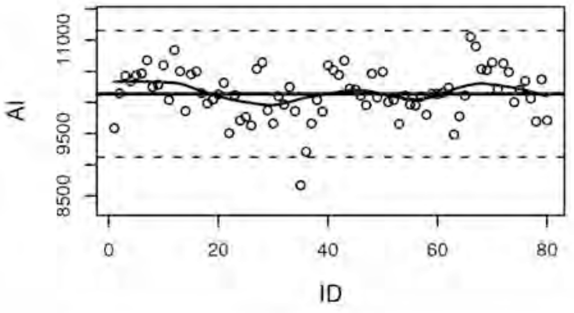

Sn
6.0
5.5
5.0
4.5
0
20
40
60
80
ID
Sr
85
80
75
70
65
60
0
20
40
60
80
ID
Ta
0.008
0.004
0.000
1
5
6
7
9
11
12
13
16
18
14
17
19
23
24
25
26
27
28
32
36
41
42
43
50
51
53
56
61
64
69
77
0
20
40
60
80
ID
Te
1.3
1.1
0.9
0
20
40
60
80
ID
Th
4.5
4.0
3.5
0
20
40
60
80
ID
Ti
1400
1200
1000
0
20
40
60
80
ID
Tl
4.5
4.0
3.5
0
20
40
60
80
ID
U
5.5
5.0
4.5
4.0
0
20
40
60
80
ID

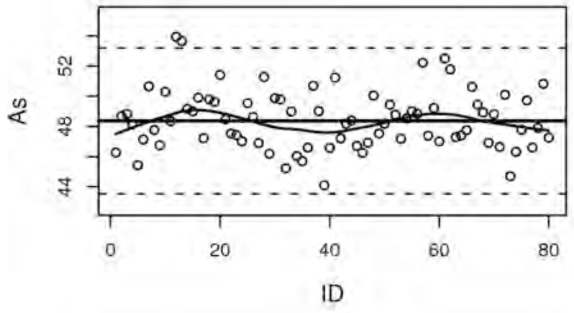

V
75
80
85
W
2.5
3.0
3.5
4.0
Y
4.5
5.5
6.5
Zn
340
380
420
Zr
4.0
5.0
6.0
0
20
40
60
80
ID

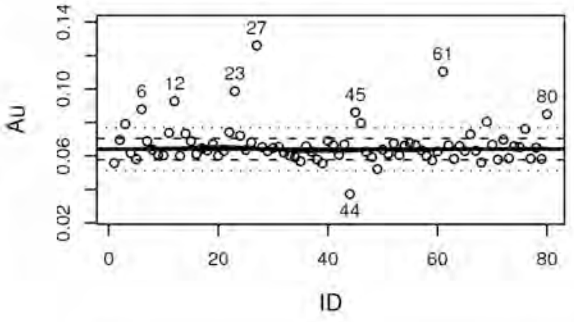
APPENDIX 4. X-Charts for laboratory standard DS7 as inserted between the Ap samples

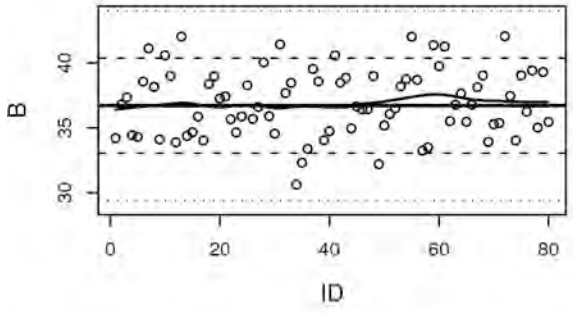
All X-Charts for the laboratory standard DS7 as inserted between the Ap samples. Sample number (ID) is plotted against analytical result for the standard. The fat line indicates the median value of all standard results, the dashed line is the limit for 10%, the dotted line for 20% deviation from the 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.

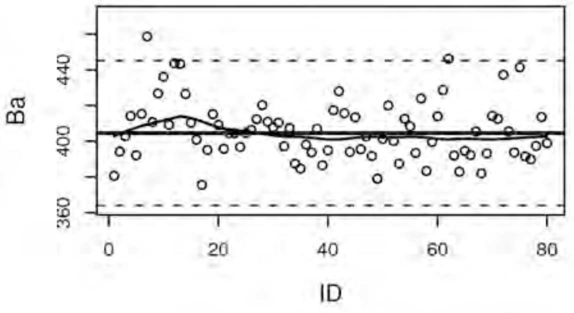

Ag
0.65
0.75
0.85
0
20
40
60
80
ID

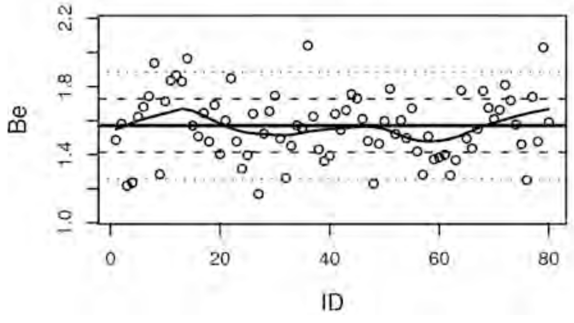

Al
8500
9500
11000
0
20
40
60
80
ID

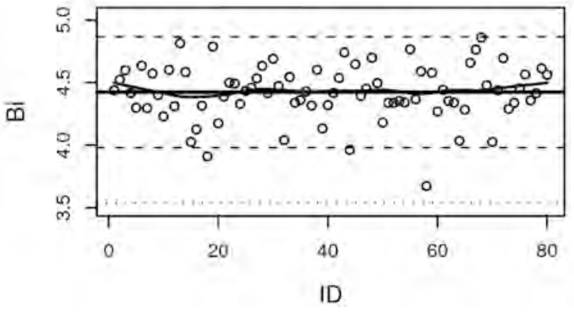

As
44
48
52
0
20
40
60
80
ID

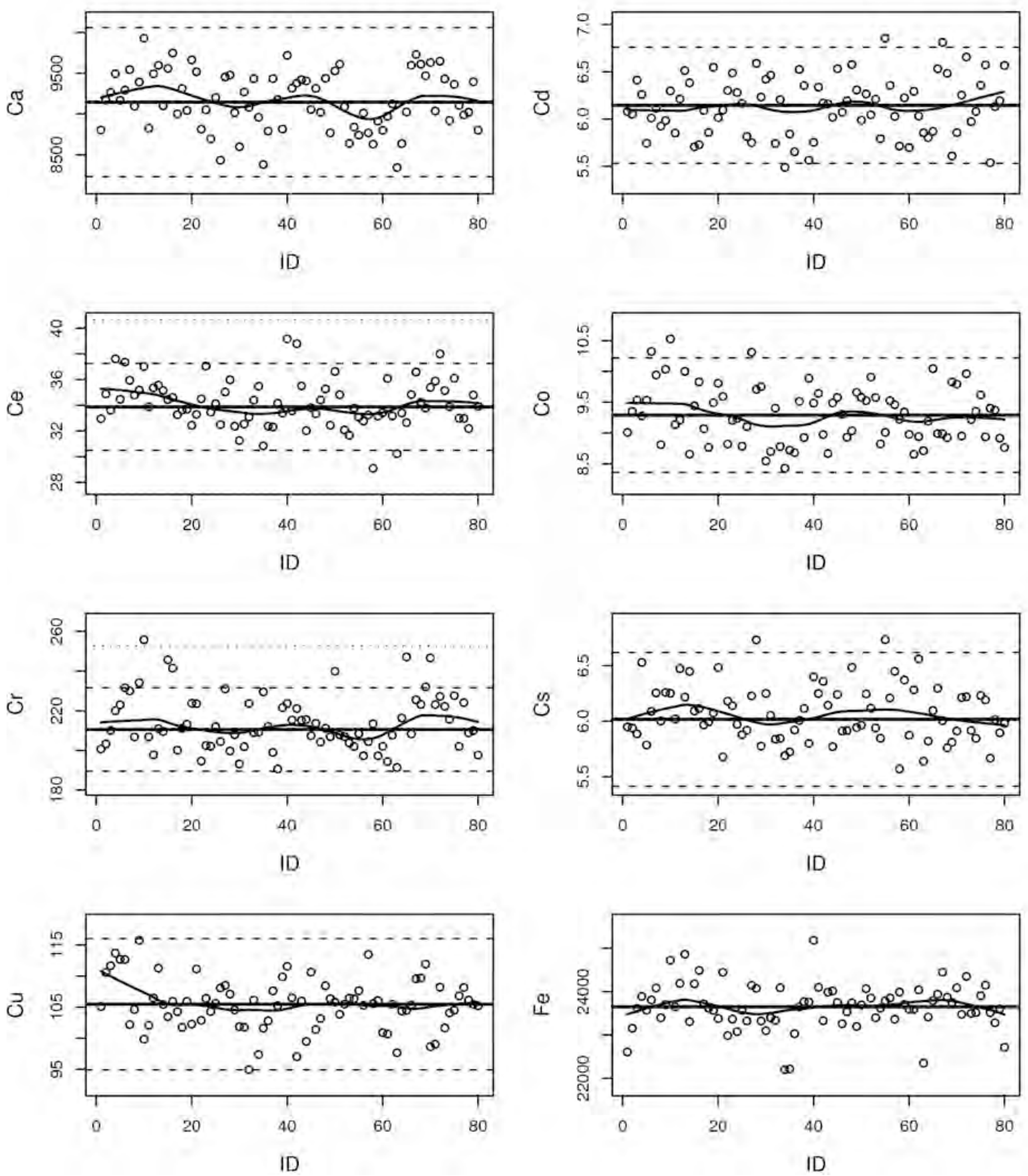

Au
0.02
0.06
0.10
0.14
27
61
23
12
6
45
80
44
0
20
40
60
80
ID

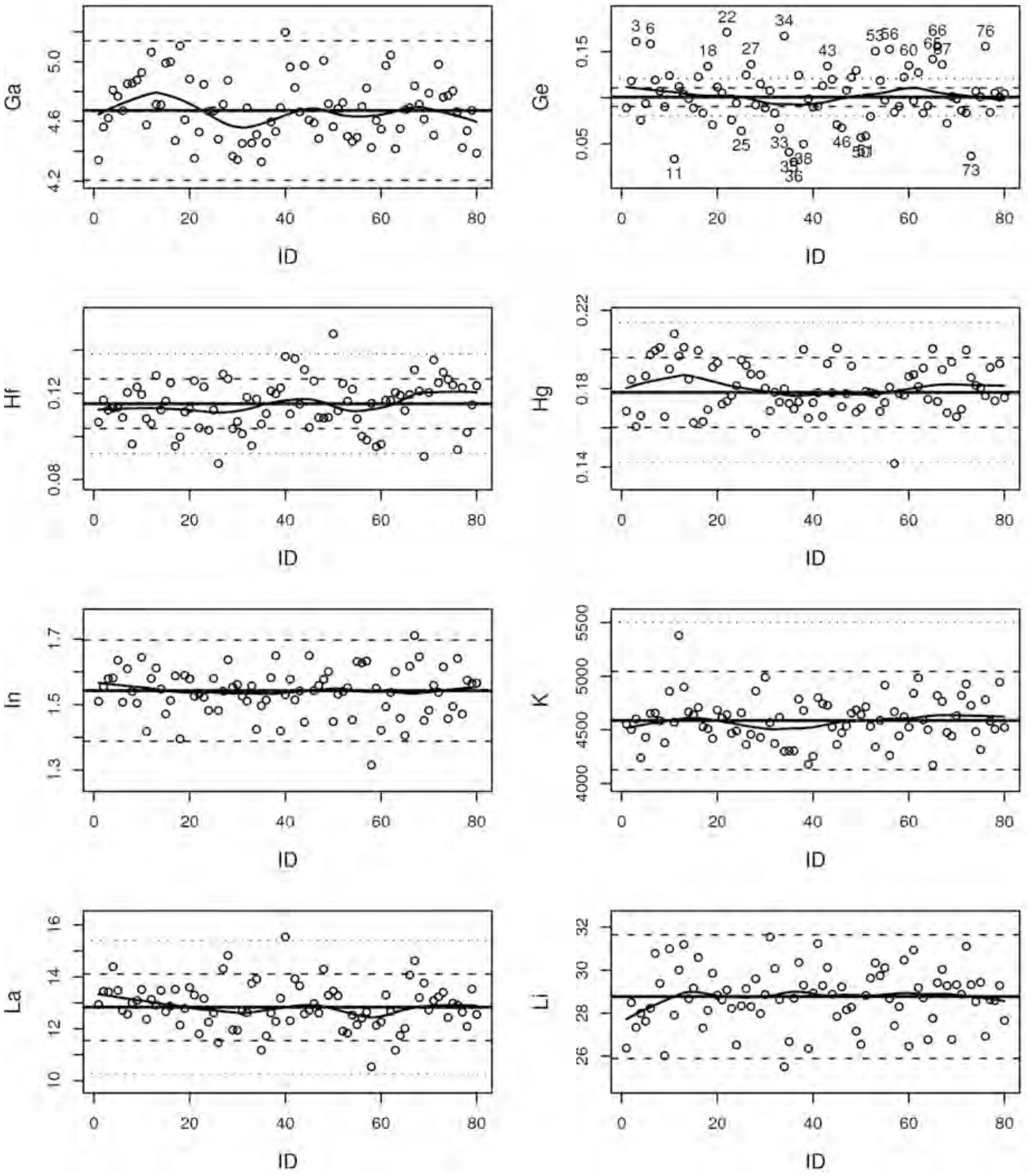

B
30
35
40
0
20
40
60
80
ID

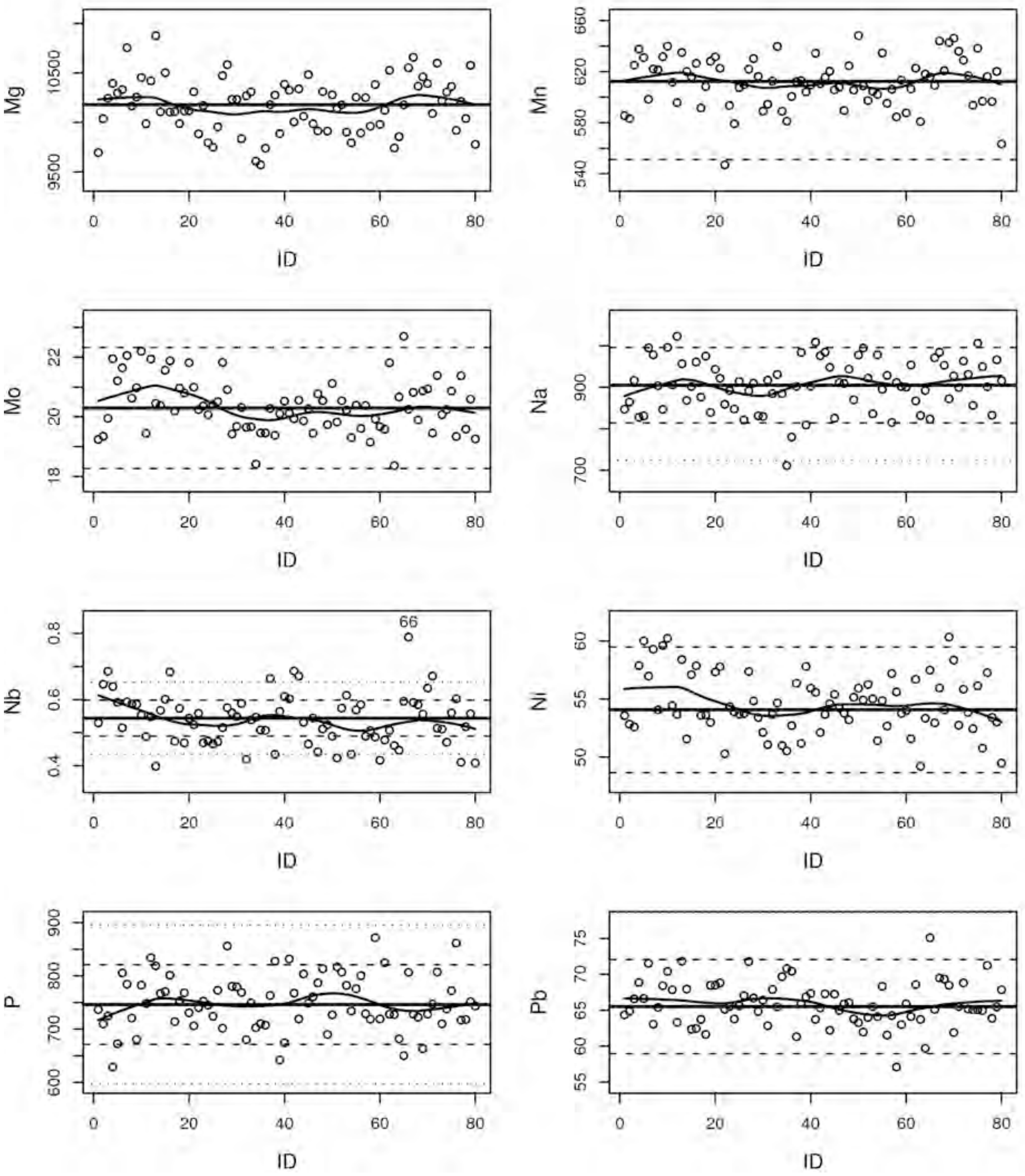

Ba
360
400
440
0
20
40
60
80
ID

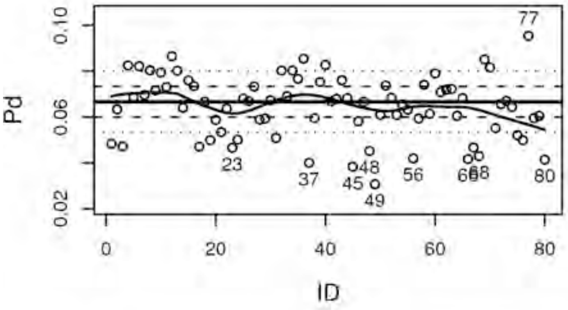

Be
1.0
1.4
1.8
2.2
0
20
40
60
80
ID

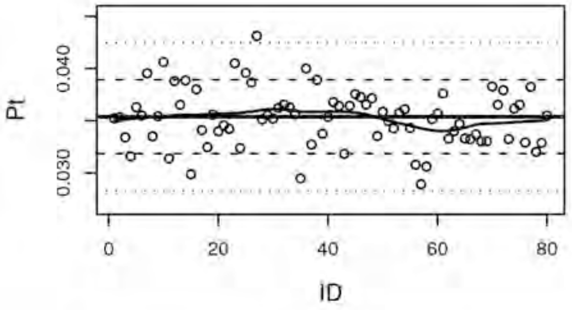

Bi
3.5
4.0
4.5
5.0
0
20
40
60
80
ID

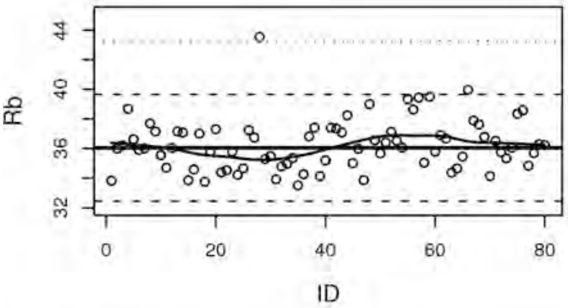

Ca
8500
9500
ID
0
20
40
60
80
Cd
5.5
6.0
6.5
7.0
ID
Ce
28
32
36
40
ID
Co
8.5
9.5
10.5
ID
Cr
180
220
260
ID
Cs
5.5
6.0
6.5
ID
Cu
95
105
115
ID
Fe
22000
24000
ID

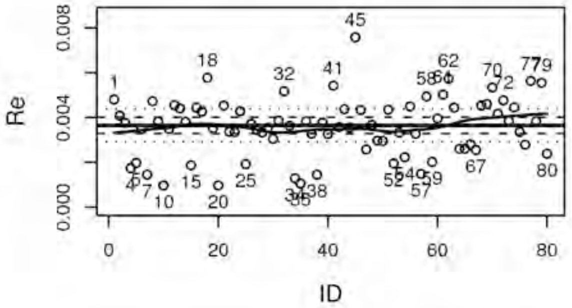

Ga
4.2
4.6
5.0
ID
0
20
40
60
80
Ge
0.05
0.15
3
6
22
34
18
27
53
56
66
76
43
60
65
67
11
25
33
46
50
51
38
37
36
73
Hf
0.08
0.12
Hg
0.14
0.18
0.22
In
1.3
1.5
1.7
K
4000
4500
5000
5500
La
10
12
14
16
Li
26
28
30
32

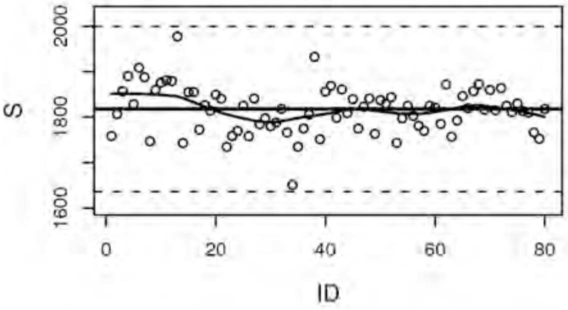

Mg
9500
10500
Mn
540
580
620
660
Mo
18
20
22
Na
700
900
Nb
0.4
0.6
0.8
66
Ni
50
55
60
P
600
700
800
900
Pb
55
60
65
70
75
0
20
40
60
80
ID

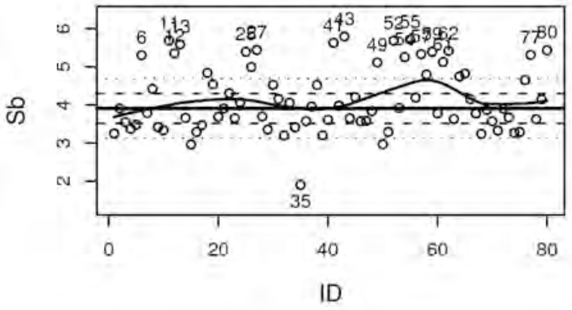

Pd
0.02
0.06
0.10
ID
0
20
40
60
80
77
23
37
45
48
49
56
66
68
80

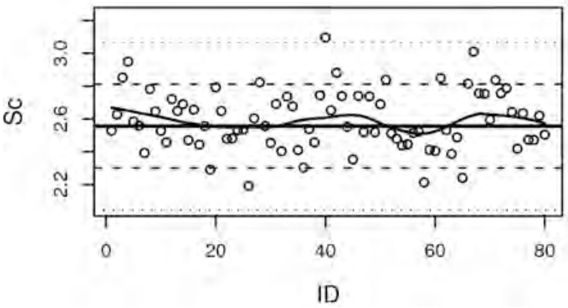

Pt
0.030
0.040
ID
0
20
40
60
80

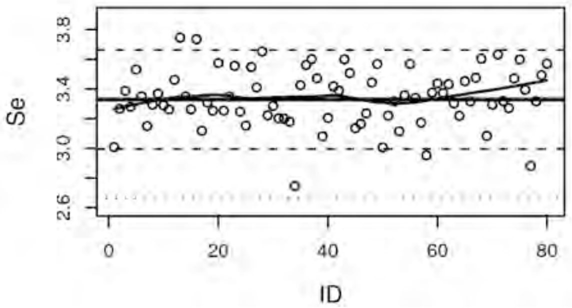

Rb
32
36
40
44
ID
0
20
40
60
80

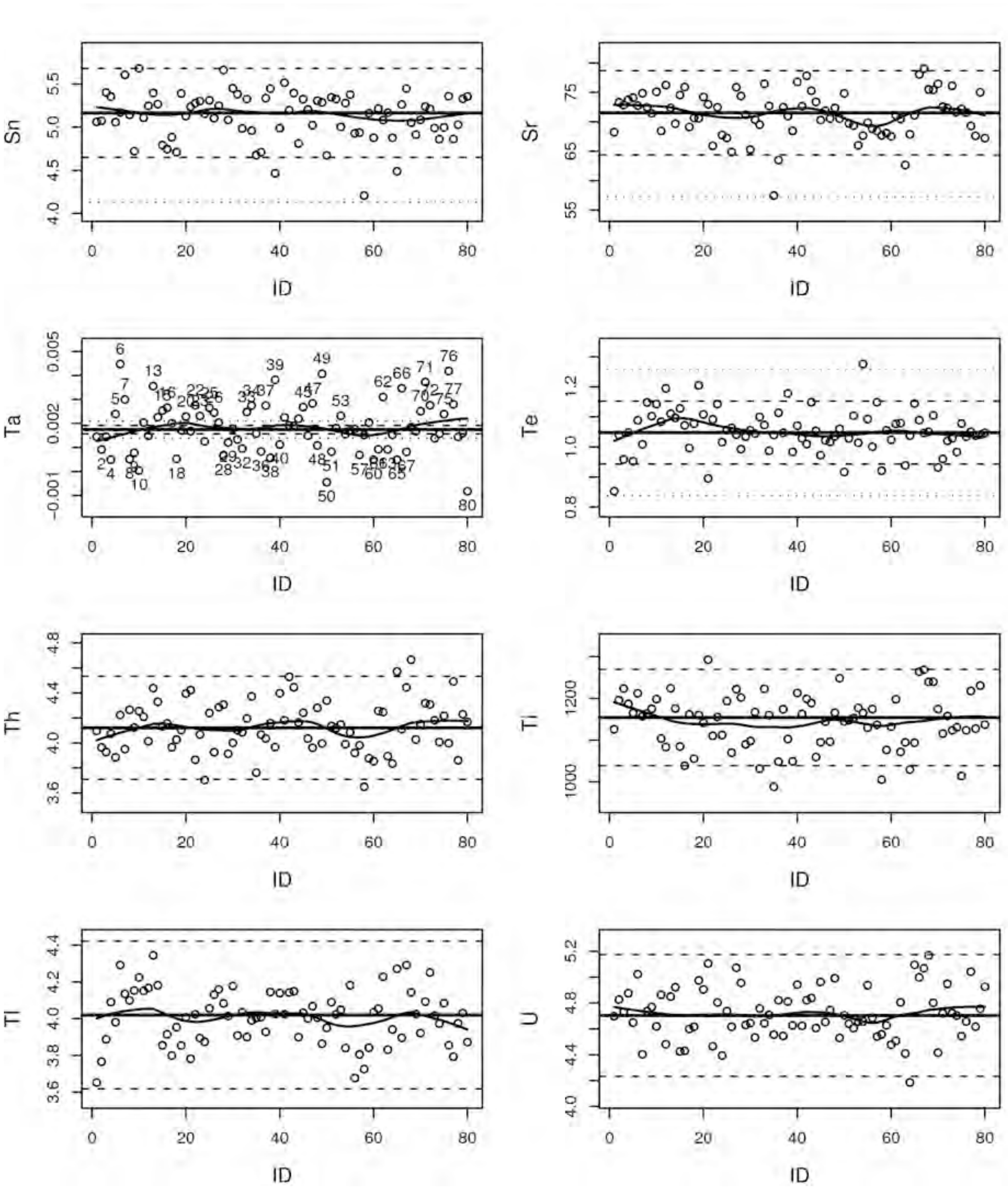

Re
0.000
0.004
0.008
ID
0
20
40
60
80
45
1
18
32
41
62
58
60
70
72
77
79
4
7
10
15
20
25
34
35
38
52
54
57
59
67
80

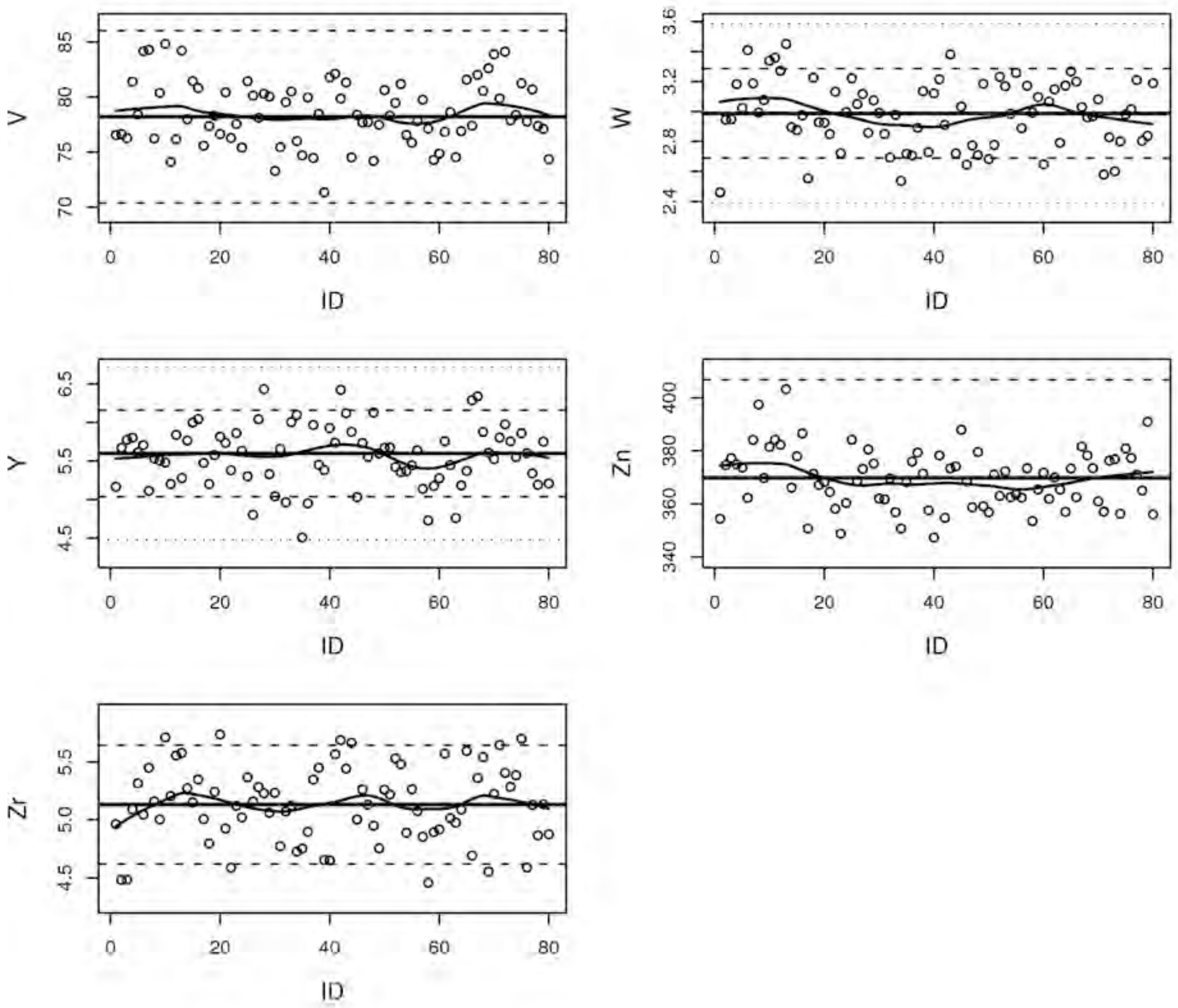

S
1600
1800
2000
ID
0
20
40
60
80


Sb
2
3
4
5
6
ID
0
20
40
60
80
6
11
12
13
26
27
41
43
49
52
55
54
57
59
62
77
80
35


Sc
2.2
2.6
3.0
ID
0
20
40
60
80

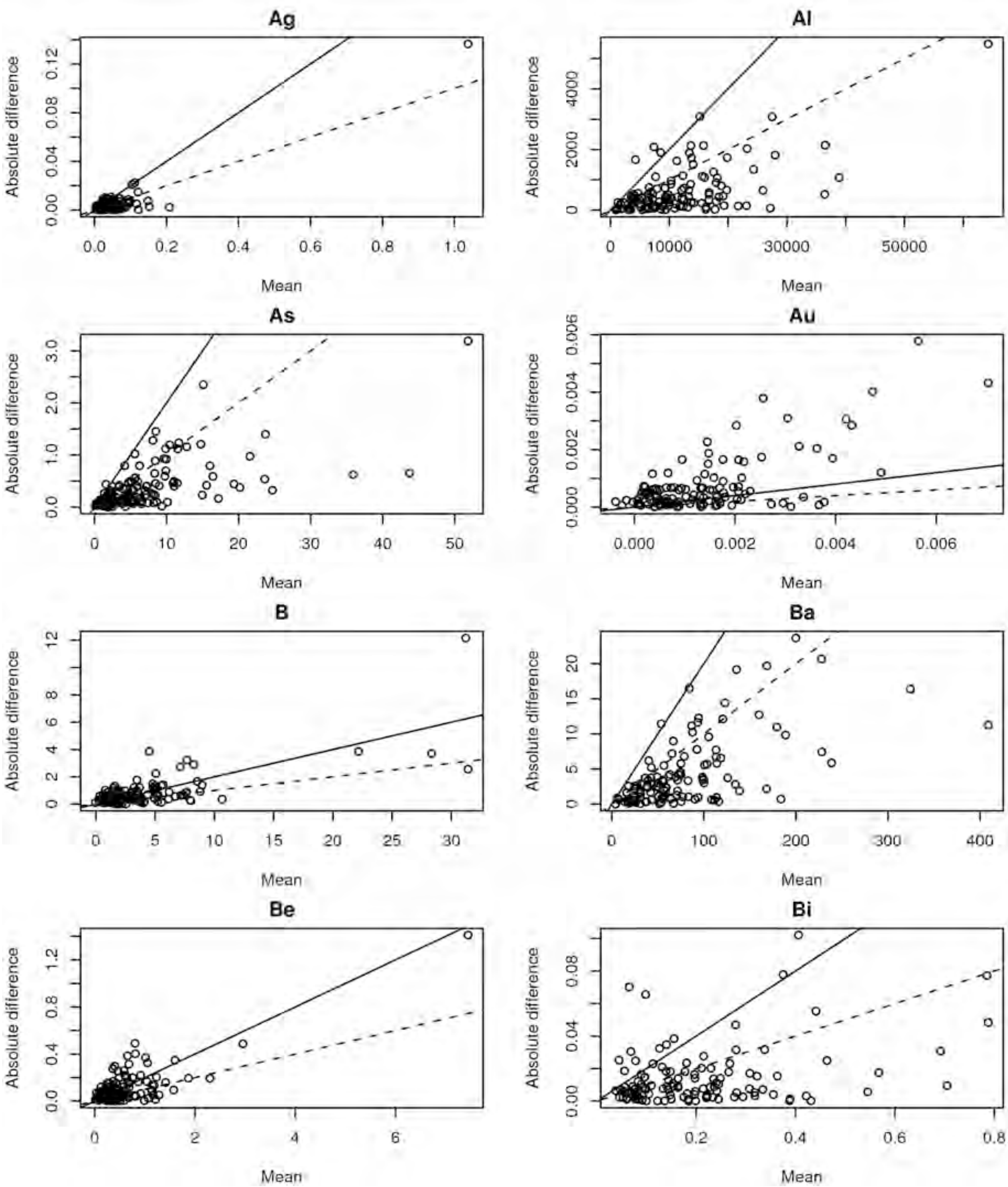

Se
2.6
3.0
3.4
3.8
ID
0
20
40
60
80

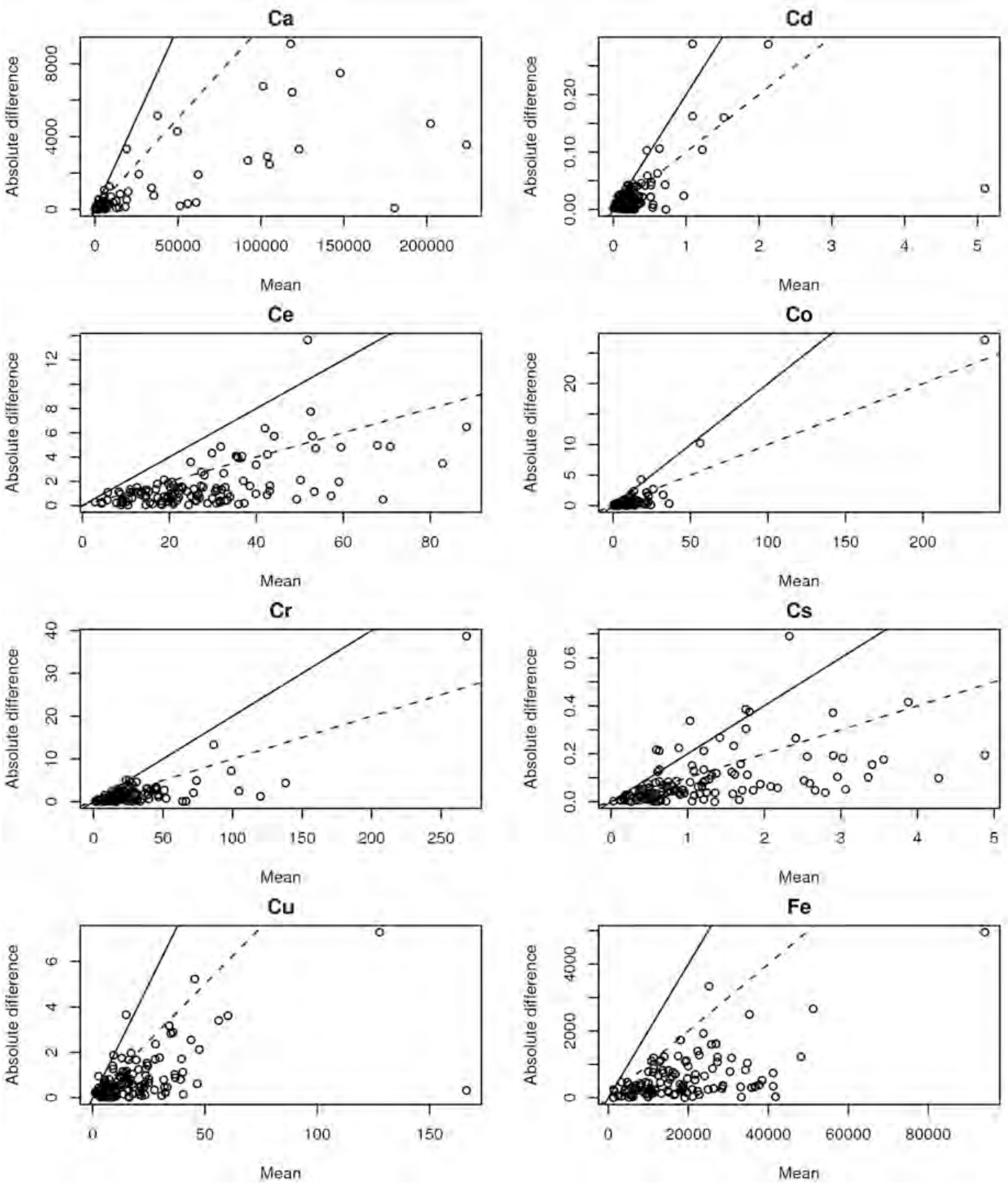

Sn
4.0
4.5
5.0
5.5
Sr
55
65
75
Ta
-0.001
0.002
0.005
6
13
39
49
76
7
5
16
15
22
25
20
26
33
34
37
45
47
53
62
66
71
70
72
77
75
2
4
8
10
18
28
29
32
36
38
40
48
51
50
57
60
63
65
67
80
Te
0.8
1.0
1.2
Th
3.6
4.0
4.4
4.8
Ti
1000
1200
Tl
3.6
3.8
4.0
4.2
4.4
U
4.0
4.4
4.8
5.2
0
20
40
60
80
ID

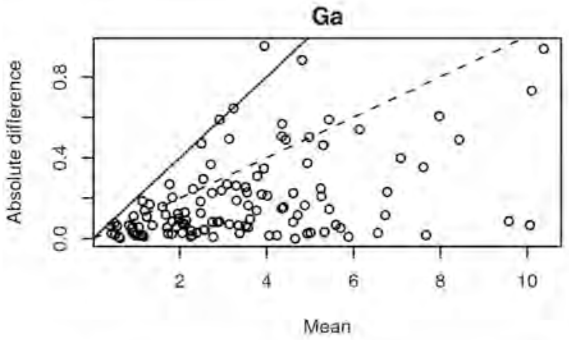

V
85
80
75
70
W
3.6
3.2
2.8
2.4
Y
6.5
5.5
4.5
Zn
400
380
360
340
Zr
5.5
5.0
4.5
0
20
40
60
80
ID

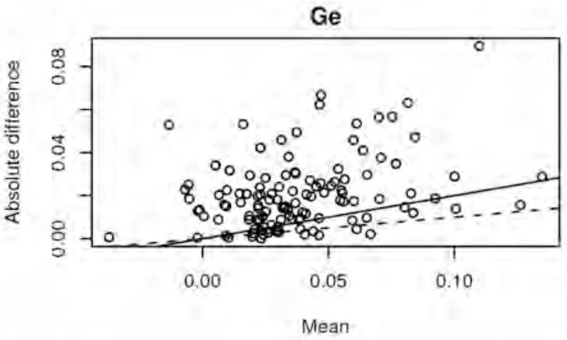
APPENDIX 5. "Thompson and Howarth"-plots of replicate analyses from the Gr samples

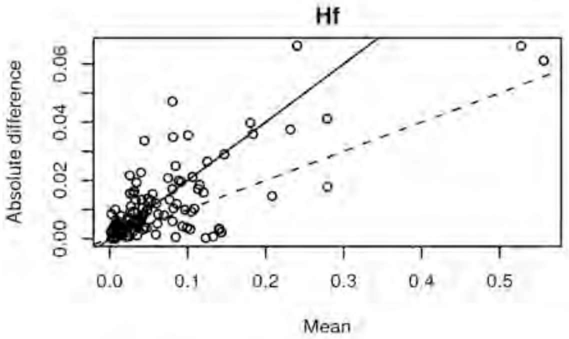
"Thompson and Howarth"-plots of replicate analyses from the Gr samples. The mean of the replicate pairs is plotted along the x-axis, the absolute difference of the two results along the y-axis. The limit for 10 % precision is indicated by the stipulated line, 20% precision by the line. In this plot pairs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

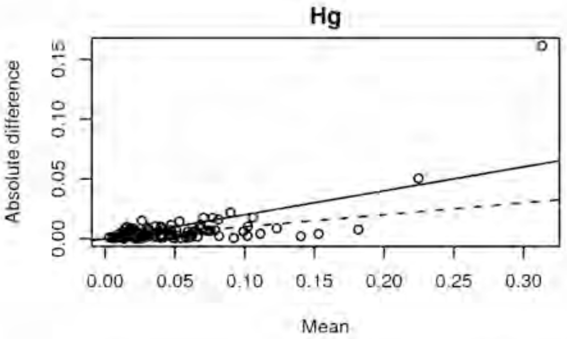

Ag
Al
As
Au
B
Ba
Be
Bi
Absolute difference
Mean
0.00
0.04
0.08
0.12
0.0
0.2
0.4
0.6
0.8
1.0
0
2000
4000
10000
30000
50000
1.0
2.0
3.0
10
20
30
40
50
0.000
0.002
0.004
0.006
2
4
6
8
12
5
15
25
100
200
300
400
0.4
0.8
1.2
0.08

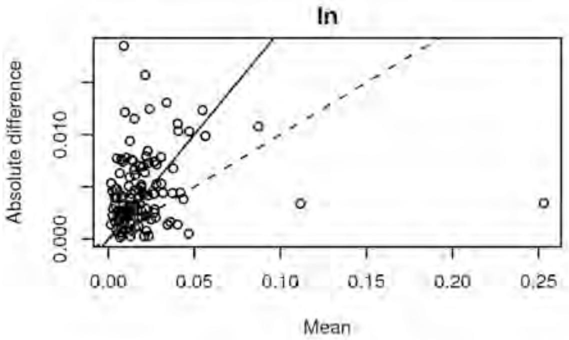

Ca
Absolute difference
0
4000
8000
0
50000
100000
150000
200000
Mean
Cd
Absolute difference
0.00
0.10
0.20
0
1
2
3
4
5
Mean
Ce
Absolute difference
0
2
4
6
8
12
0
20
40
60
80
Mean
Co
Absolute difference
0
5
10
20
0
50
100
150
200
Mean
Cr
Absolute difference
0
10
20
30
40
0
50
100
150
200
250
Mean
Cs
Absolute difference
0.0
0.2
0.4
0.6
0
1
2
3
4
5
Mean
Cu
Absolute difference
0
2
4
6
0
50
100
150
Mean
Fe
Absolute difference
0
2000
4000
0
20000
40000
60000
80000
Mean

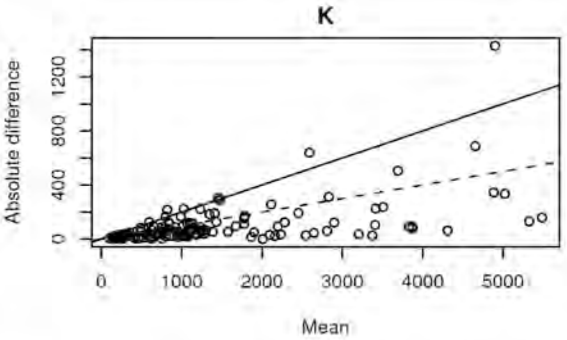

Ga
Absolute difference
0.0
0.4
0.8
2
4
6
8
10
Mean

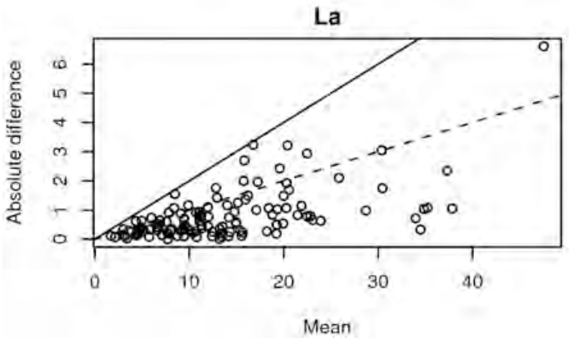

Ge
Absolute difference
0.00
0.04
0.08
0.00
0.05
0.10
Mean

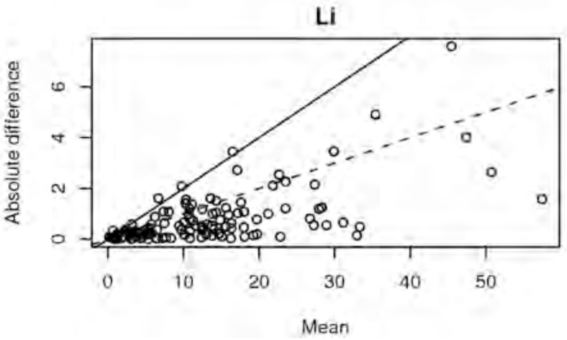

Hf
Absolute difference
0.00
0.02
0.04
0.06
0.0
0.1
0.2
0.3
0.4
0.5
Mean

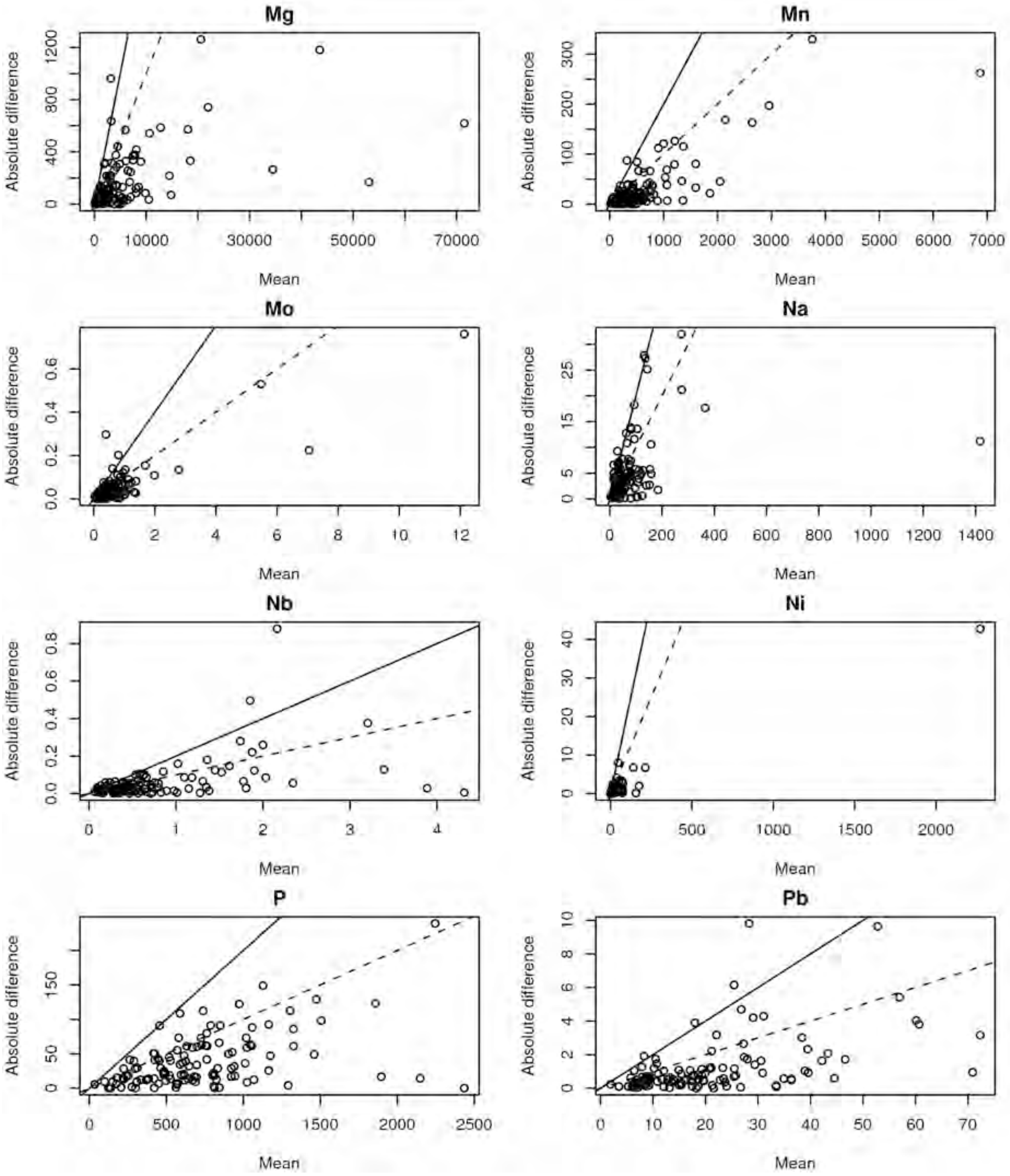

Hg
Absolute difference
0.00
0.05
0.10
0.15
0.00
0.05
0.10
0.15
0.20
0.25
0.30
Mean

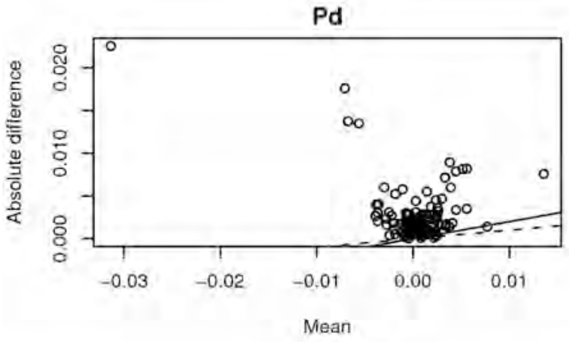

In
Absolute difference
0.000
0.010
0.00
0.05
0.10
0.15
0.20
0.25
Mean

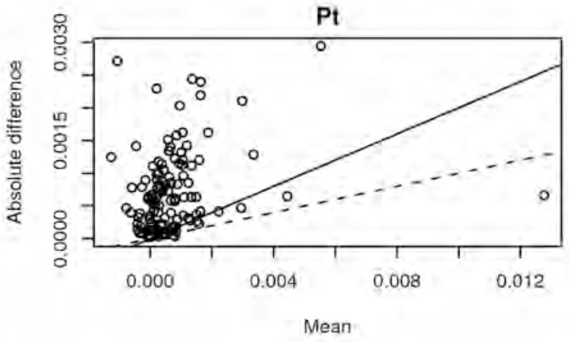

K
Absolute difference
0
400
800
1200
0
1000
2000
3000
4000
5000
Mean

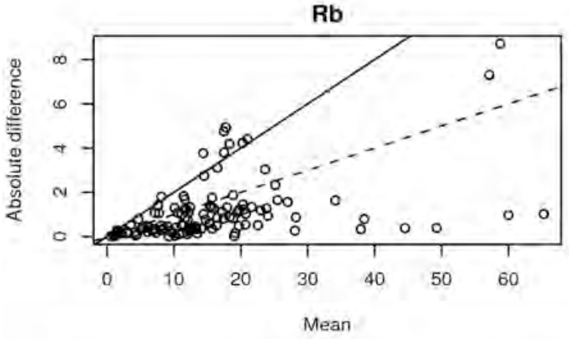

La
Absolute difference
0
1
2
3
4
5
6
0
10
20
30
40
Mean

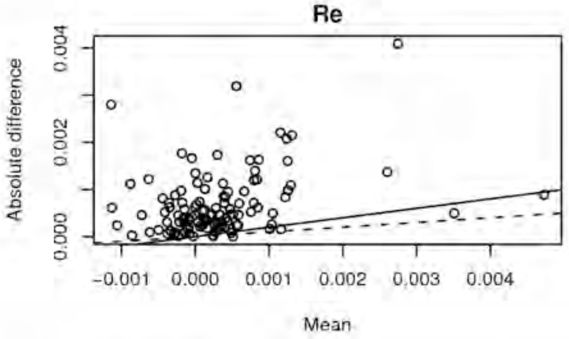

Li
Absolute difference
0
2
4
6
0
10
20
30
40
50
Mean

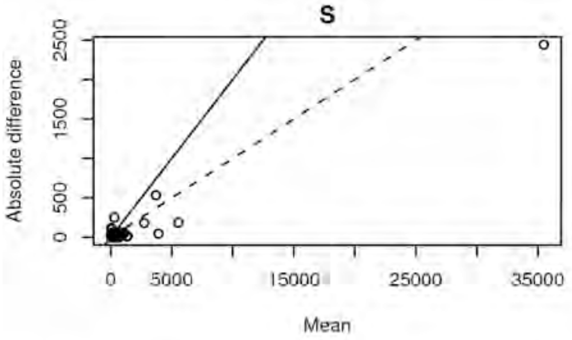

Mg
Absolute difference
0
400
800
1200
0
10000
30000
50000
70000
Mean
Mn
Absolute difference
0
100
200
300
0
1000
2000
3000
4000
5000
6000
7000
Mean
Mo
Absolute difference
0.0
0.2
0.4
0.6
0
2
4
6
8
10
12
Mean
Na
Absolute difference
0
5
15
25
0
200
400
600
800
1000
1200
1400
Mean
Nb
Absolute difference
0.0
0.2
0.4
0.6
0.8
0
1
2
3
4
Mean
Ni
Absolute difference
0
10
20
30
40
0
500
1000
1500
2000
Mean
P
Absolute difference
0
50
150
0
500
1000
1500
2000
2500
Mean
Pb
Absolute difference
0
2
4
6
8
10
0
10
20
30
40
50
60
70
Mean

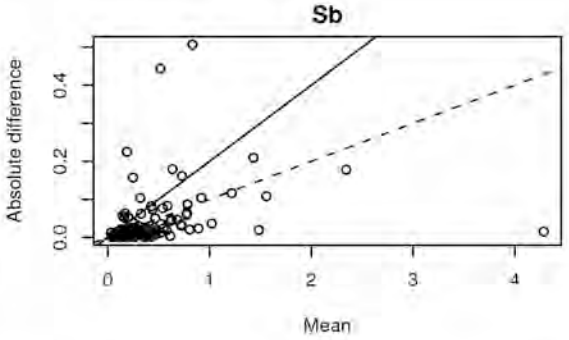

Pd
Absolute difference
0.000
0.010
0.020
-0.03
-0.02
-0.01
0.00
0.01
Mean

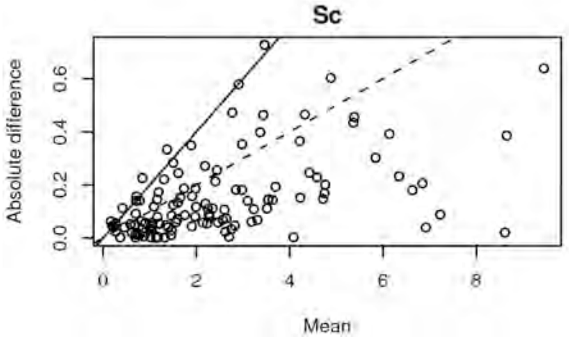

Pt
Absolute difference
0.0000
0.0015
0.0030
0.000
0.004
0.008
0.012
Mean

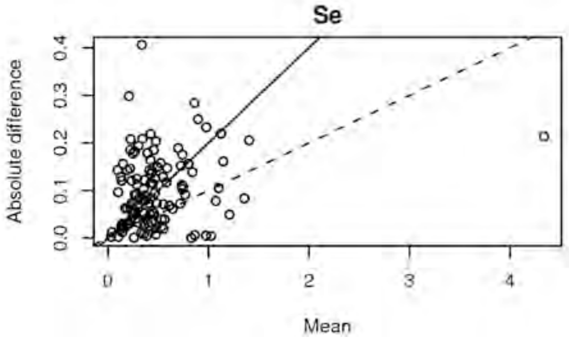

Rb
Absolute difference
0
2
4
6
8
0
10
20
30
40
50
60
Mean

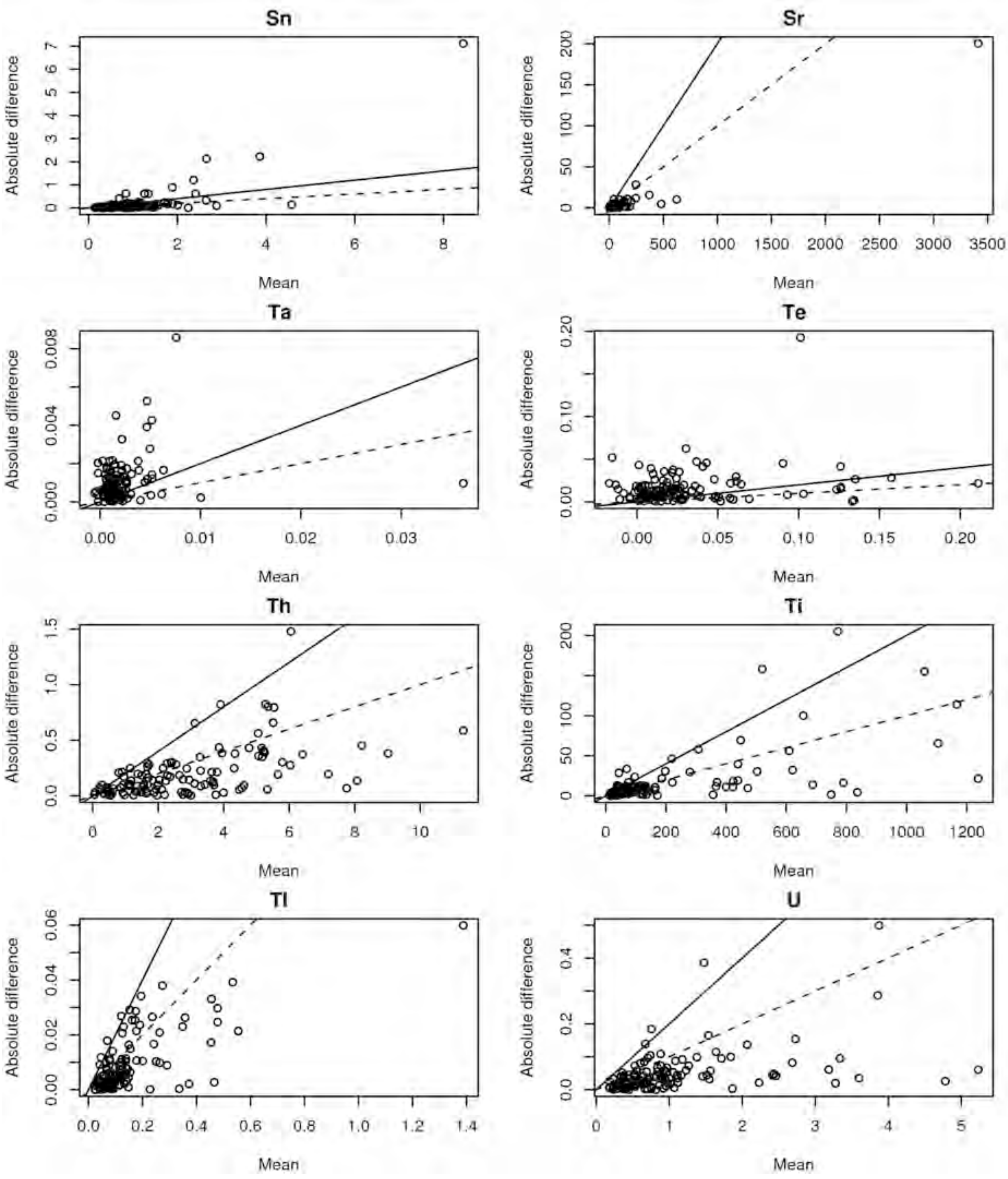

Re
Absolute difference
0.000
0.002
0.004
-0.001
0.000
0.001
0.002
0.003
0.004
Mean

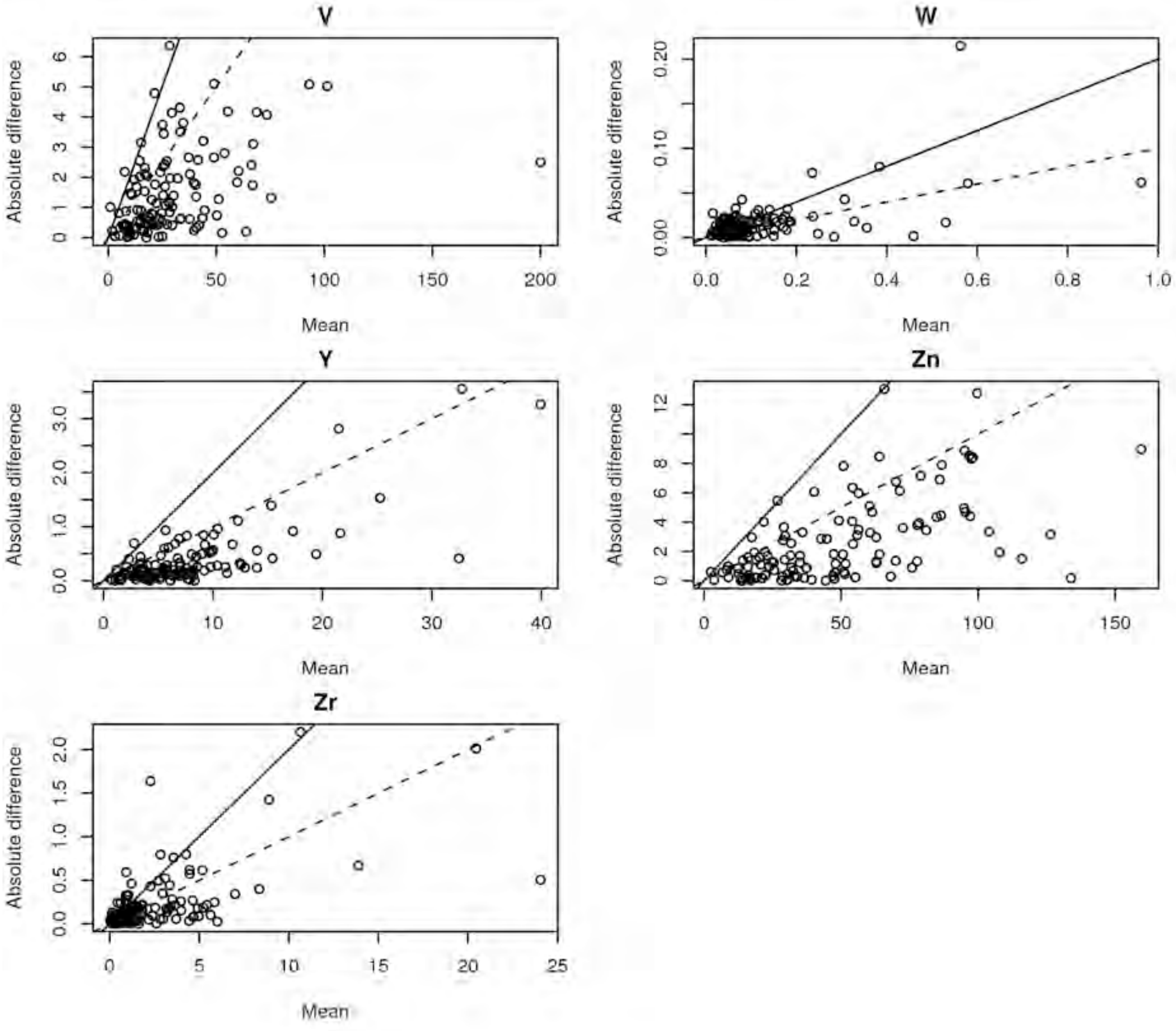

S
Absolute difference
0
500
1500
2500
0
5000
15000
25000
35000
Mean


Sb
Absolute difference
0.0
0.2
0.4
0
1
2
3
4
Mean


Sc
Absolute difference
0.0
0.2
0.4
0.6
0
2
4
6
8
Mean

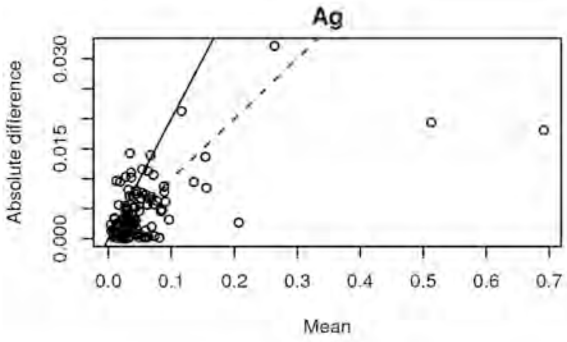

Se
Absolute difference
0.0
0.1
0.2
0.3
0.4
0
1
2
3
4
Mean

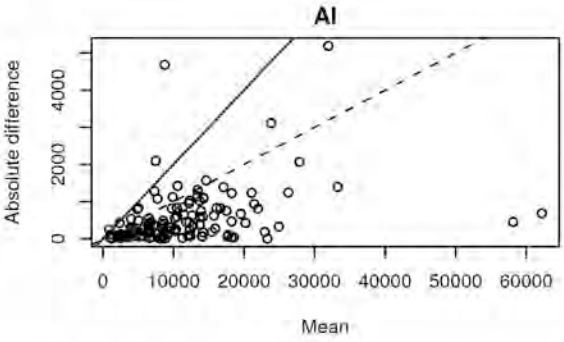

Sn
Absolute difference
0 1 2 3 4 5 6 7
0 2 4 6 8
Mean
Sr
Absolute difference
0 50 100 150 200
0 500 1000 1500 2000 2500 3000 3500
Mean
Ta
Absolute difference
0.000 0.004 0.008
0.00 0.01 0.02 0.03
Mean
Te
Absolute difference
0.00 0.10 0.20
0.00 0.05 0.10 0.15 0.20
Mean
Th
Absolute difference
0.0 0.5 1.0 1.5
0 2 4 6 8 10
Mean
Ti
Absolute difference
0 50 100 200
0 200 400 600 800 1000 1200
Mean
Tl
Absolute difference
0.00 0.02 0.04 0.06
0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4
Mean
U
Absolute difference
0.0 0.2 0.4
0 1 2 3 4 5
Mean

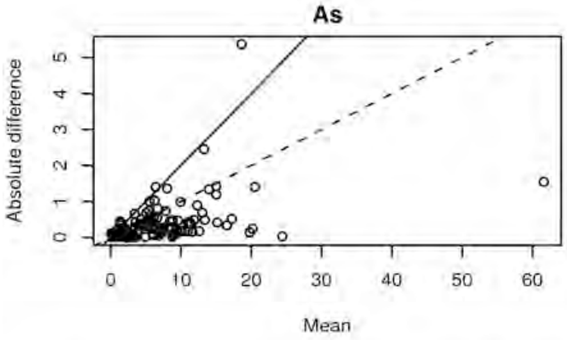

V
Absolute difference
0
1
2
3
4
5
6
0
50
100
150
200
Mean
W
Absolute difference
0.00
0.10
0.20
0.0
0.2
0.4
0.6
0.8
1.0
Mean
Y
Absolute difference
0.0
1.0
2.0
3.0
0
10
20
30
40
Mean
Zn
Absolute difference
0
2
4
6
8
12
0
50
100
150
Mean
Zr
Absolute difference
0.0
0.5
1.0
1.5
2.0
0
5
10
15
20
25
Mean

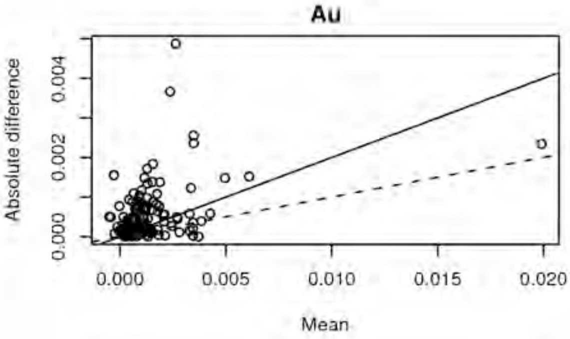
APPENDIX 6. "Thompson and Howarth"-plots of replicate analyses from the Ap samples

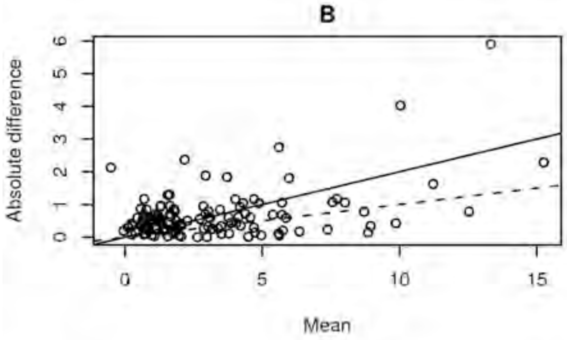
"Thompson and Howarth"-plots of replicate analyses from the Ap samples. The mean of the replicate pairs is plotted along the x-axis, the absolute difference of the two results along the y-axis. The limit for 10 % precision is indicated by the stipulated line, 20% precision by the line. In this plot pairs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

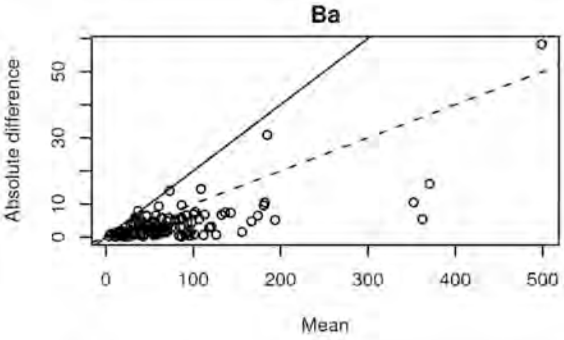

Ag

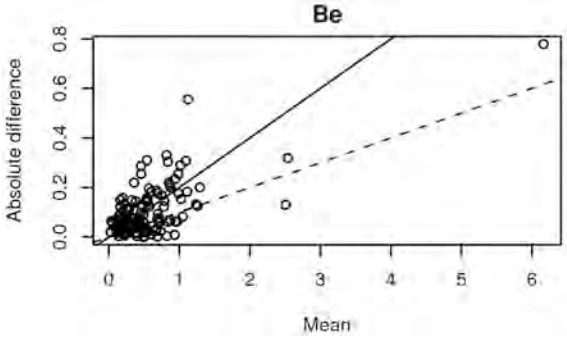

Al

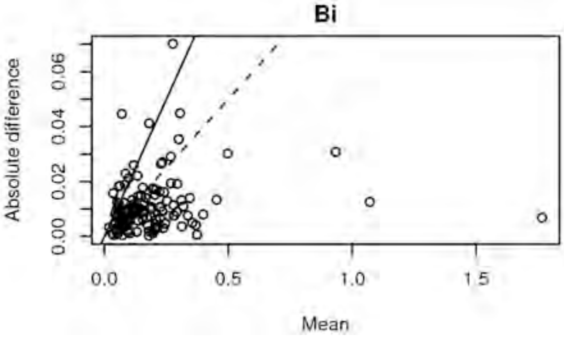

As

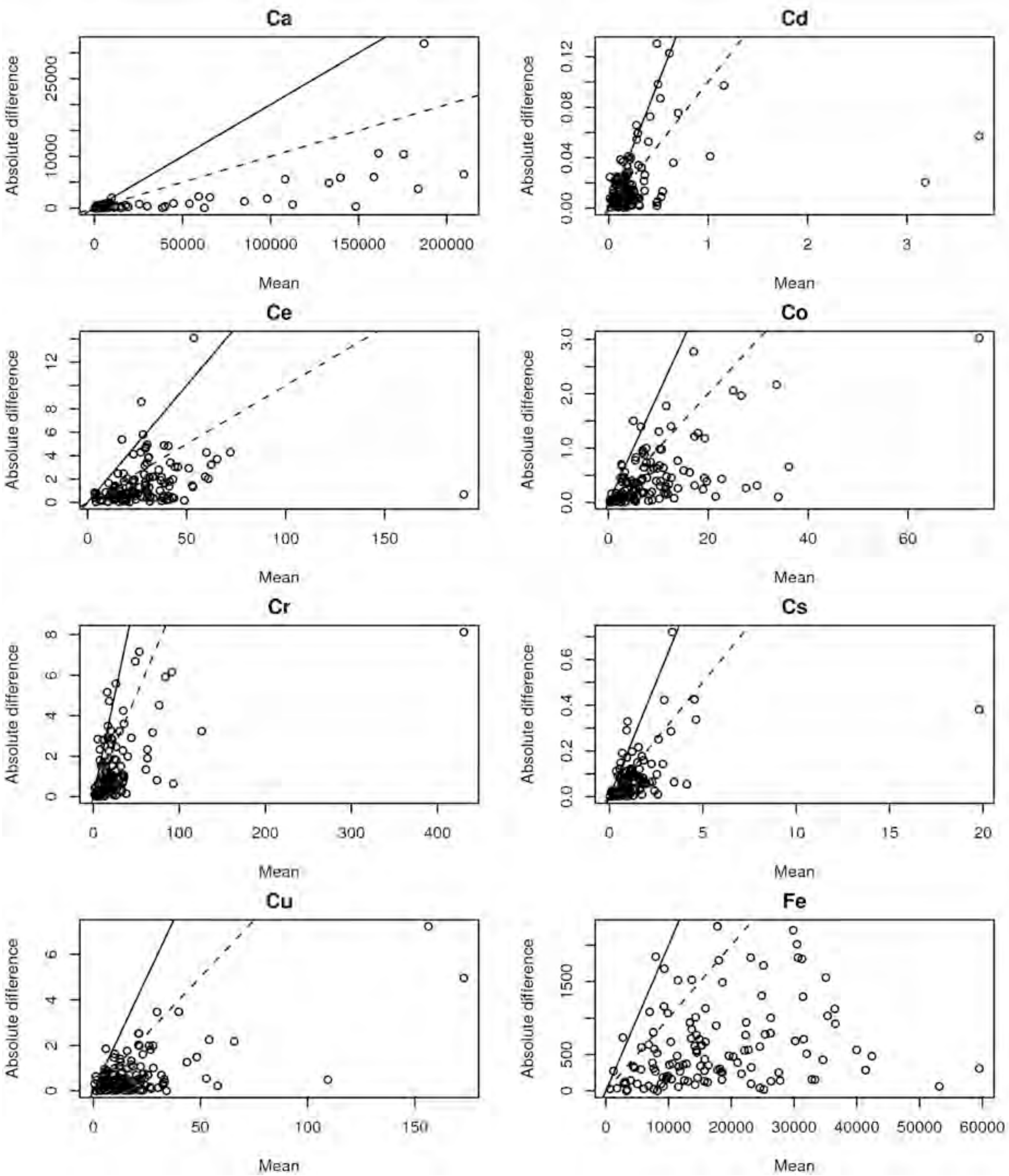

Au

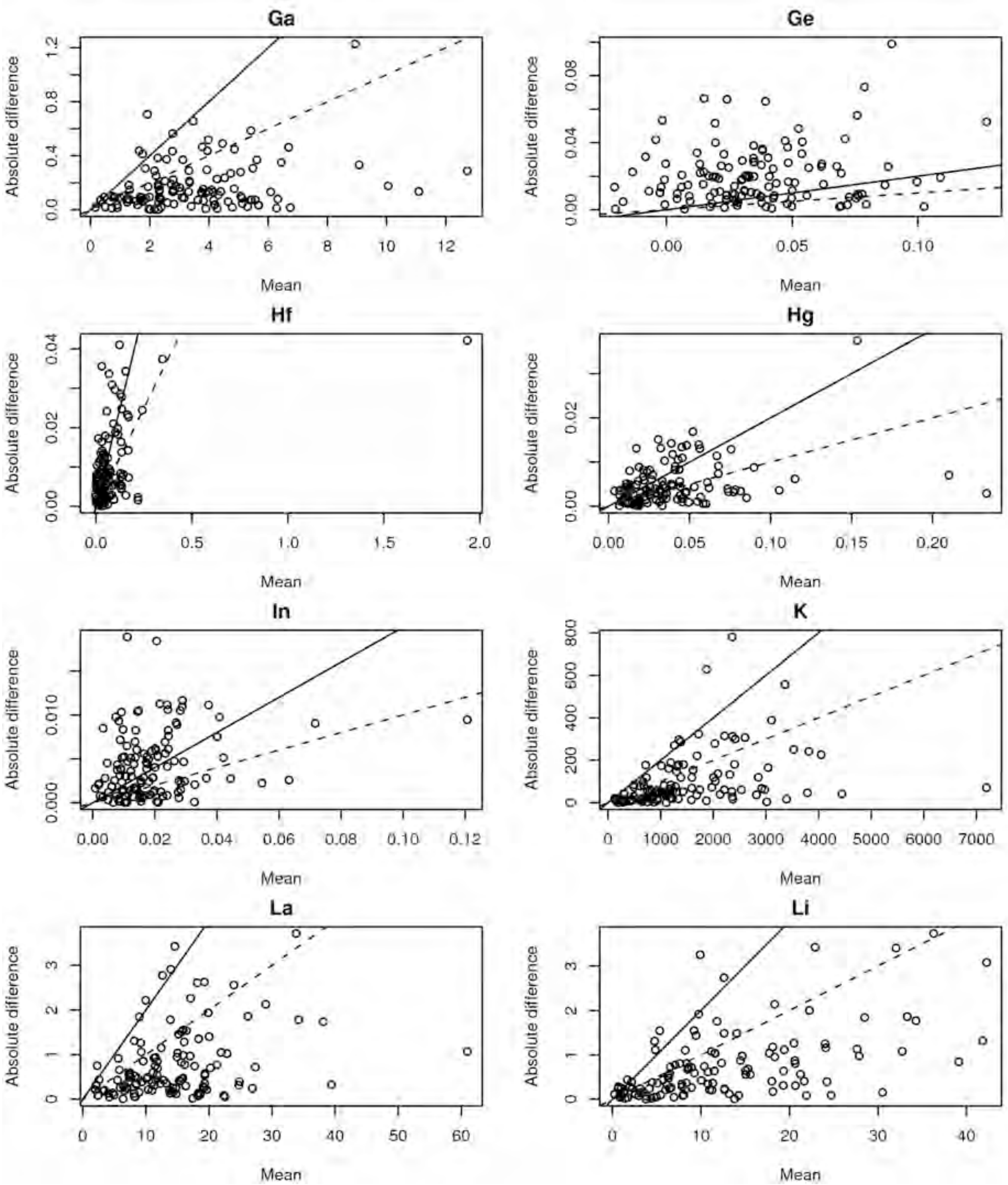

B

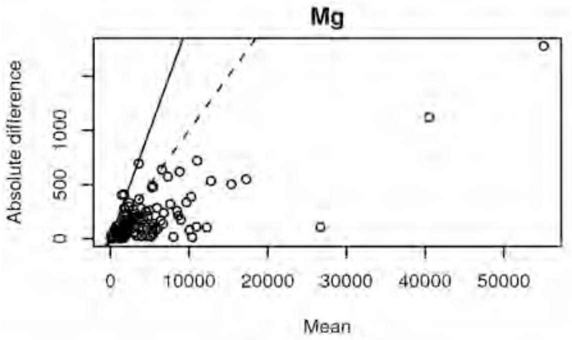

Ba

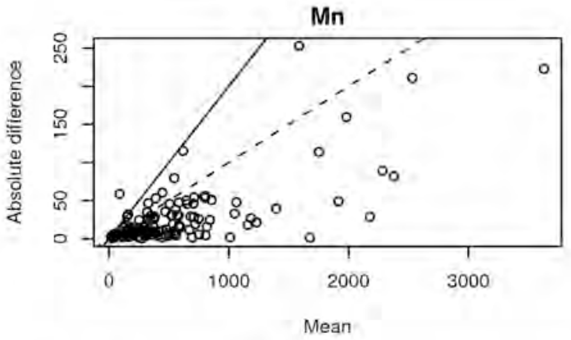

Be

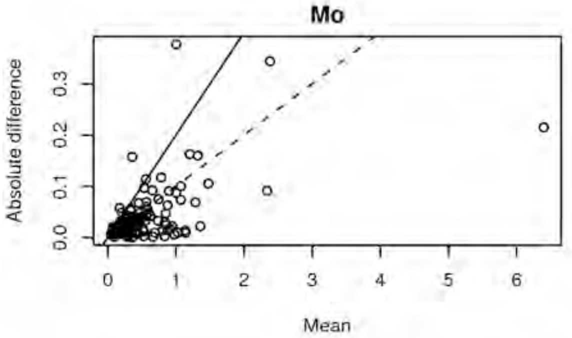

Bi

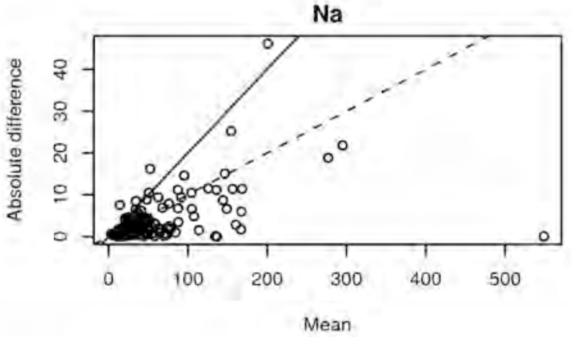

Ca
Absolute difference
0
10000
25000
Mean
0
50000
100000
150000
200000
Cd
Absolute difference
0.00
0.04
0.08
0.12
Mean
0
1
2
3
Ce
Absolute difference
0
2
4
6
8
12
Mean
0
50
100
150
Co
Absolute difference
0.0
1.0
2.0
3.0
Mean
0
20
40
60
Cr
Absolute difference
0
2
4
6
8
Mean
0
100
200
300
400
Cs
Absolute difference
0.0
0.2
0.4
0.6
Mean
0
5
10
15
20
Cu
Absolute difference
0
2
4
6
Mean
0
50
100
150
Fe
Absolute difference
0
500
1500
Mean
0
10000
20000
30000
40000
50000
60000

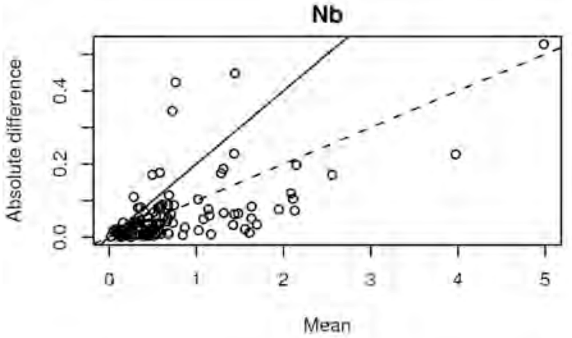

Ga
Absolute difference
0.0
0.4
0.8
1.2
0
2
4
6
8
10
12
Mean
Ge
Absolute difference
0.00
0.04
0.08
0.00
0.05
0.10
Mean
Hf
Absolute difference
0.00
0.02
0.04
0.0
0.5
1.0
1.5
2.0
Mean
Hg
Absolute difference
0.00
0.02
0.00
0.05
0.10
0.15
0.20
Mean
In
Absolute difference
0.000
0.010
0.00
0.02
0.04
0.06
0.08
0.10
0.12
Mean
K
Absolute difference
0
200
400
600
800
0
1000
2000
3000
4000
5000
6000
7000
Mean
La
Absolute difference
0
1
2
3
0
10
20
30
40
50
60
Mean
Li
Absolute difference
0
1
2
3
0
10
20
30
40
Mean

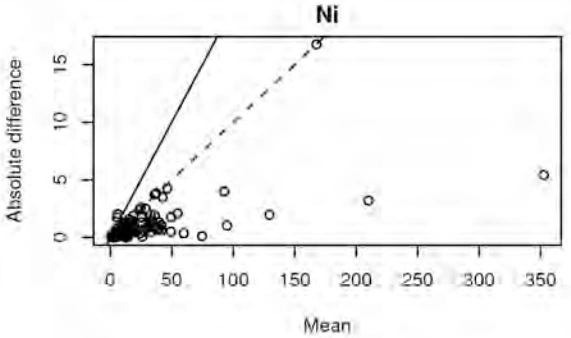

Mg

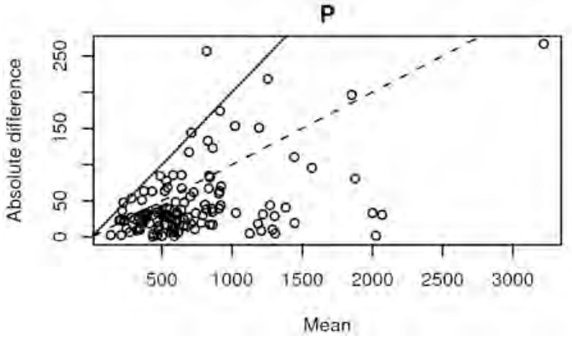

Mn

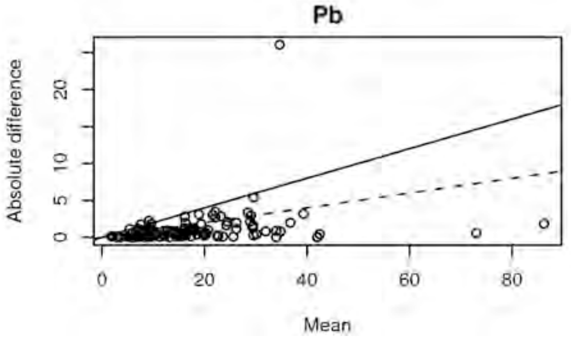

Mo

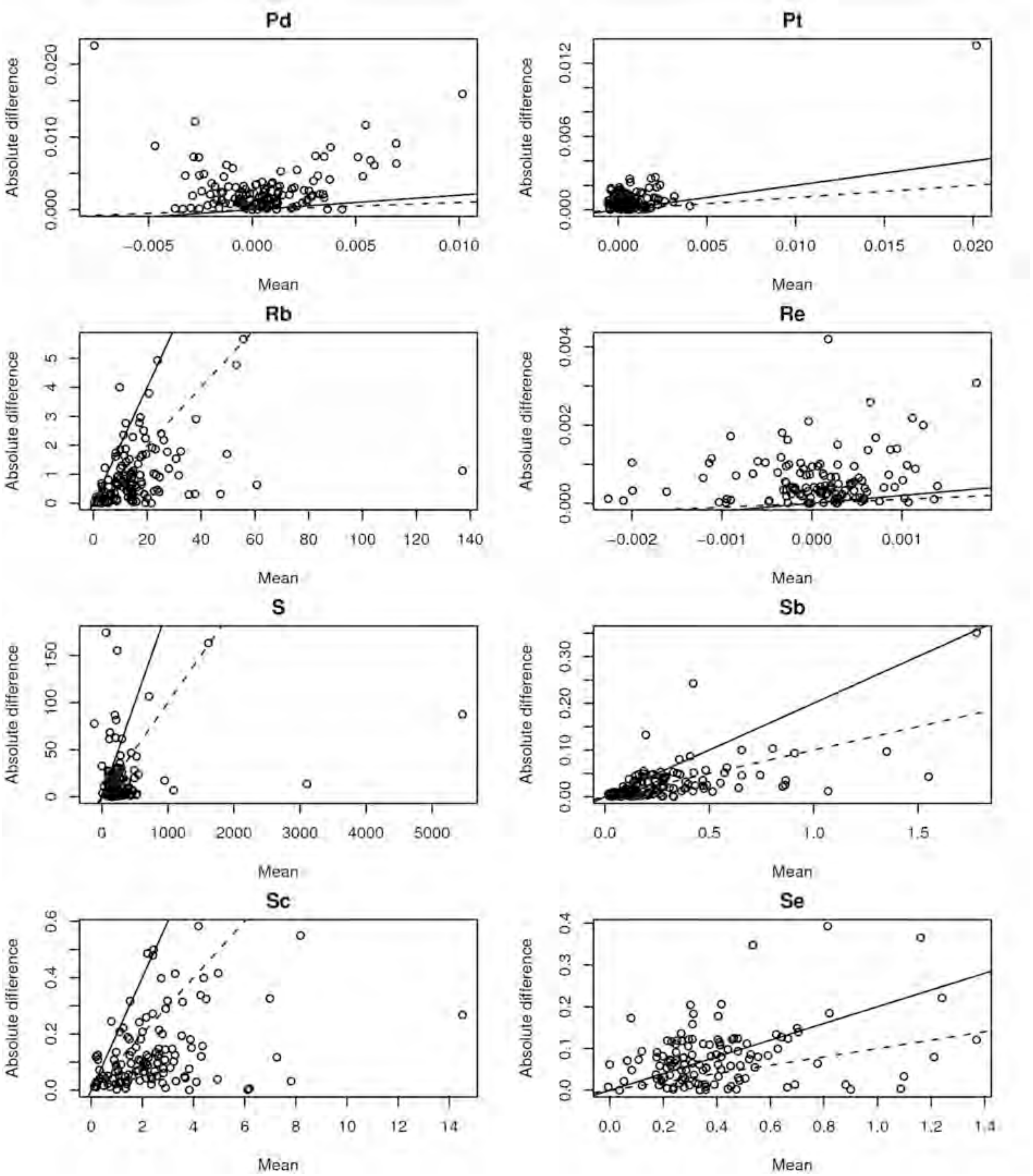

Na

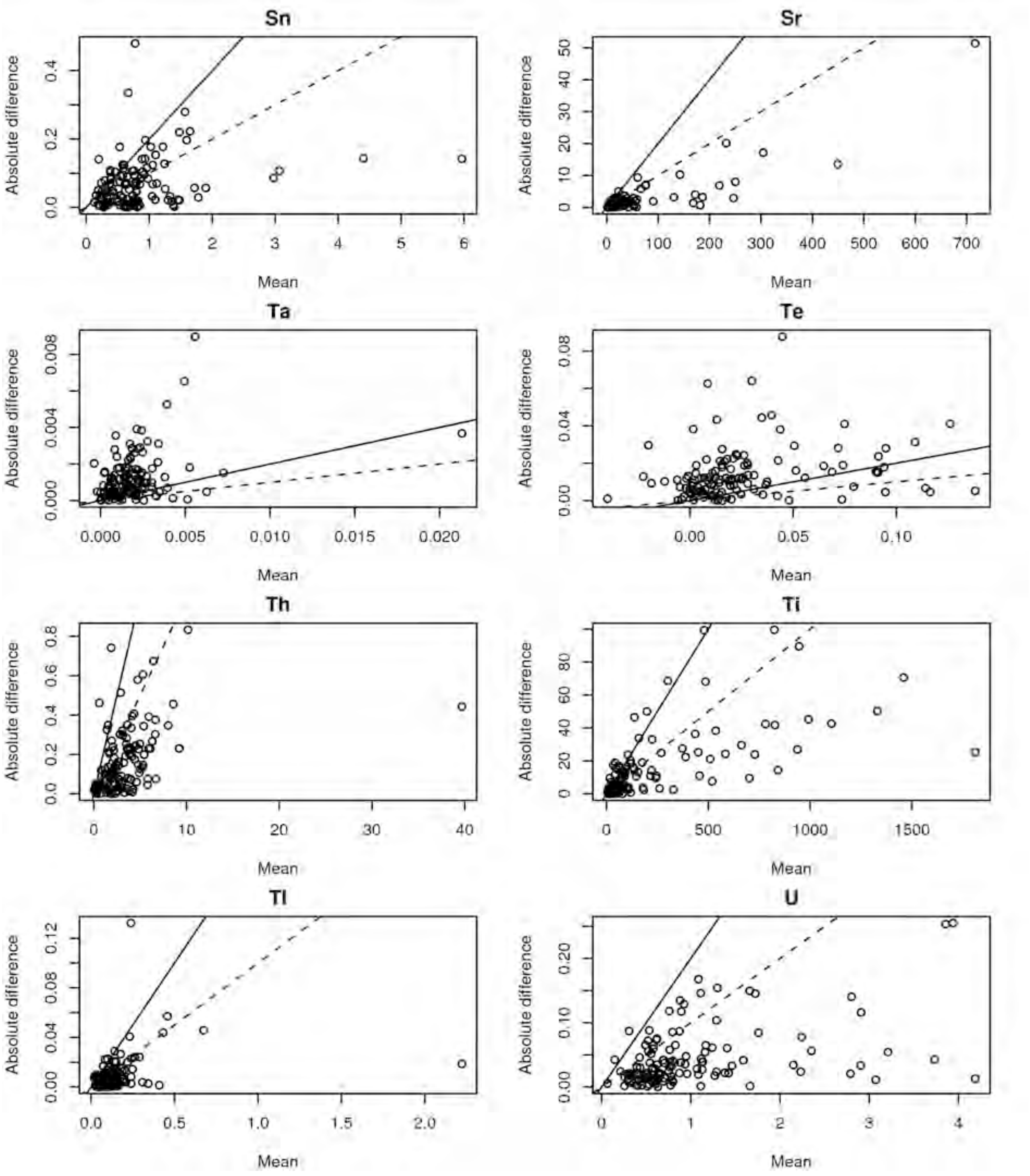

Nb

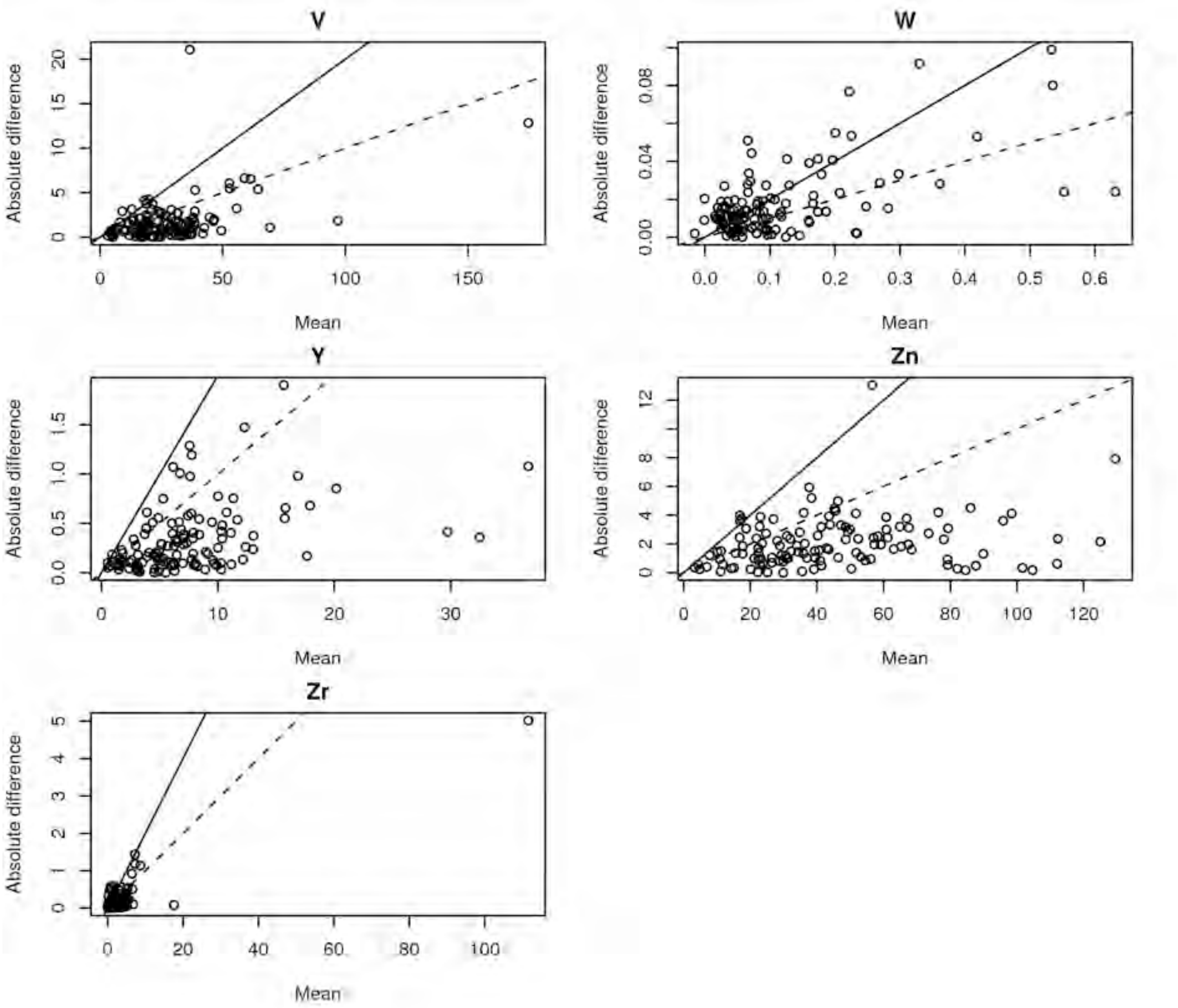

Ni


P


Pb

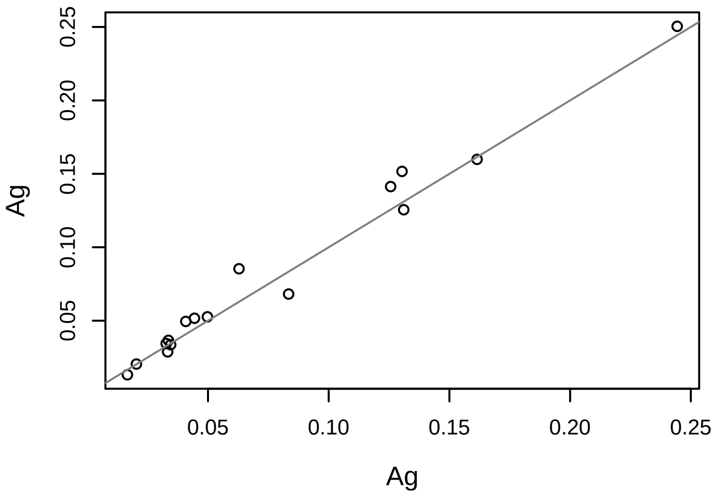

Pd
Absolute difference
0.000
0.010
0.020
−0.005
0.000
0.005
0.010
Mean
Pt
Absolute difference
0.000
0.006
0.012
0.000
0.005
0.010
0.015
0.020
Mean
Rb
Absolute difference
0
1
2
3
4
5
0
20
40
60
80
100
120
140
Mean
Re
Absolute difference
0.000
0.002
0.004
−0.002
−0.001
0.000
0.001
Mean
S
Absolute difference
0
50
100
150
0
1000
2000
3000
4000
5000
Mean
Sb
Absolute difference
0.00
0.10
0.20
0.30
0.0
0.5
1.0
1.5
Mean
Sc
Absolute difference
0.0
0.2
0.4
0.6
0
2
4
6
8
10
12
14
Mean
Se
Absolute difference
0.0
0.1
0.2
0.3
0.4
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Mean

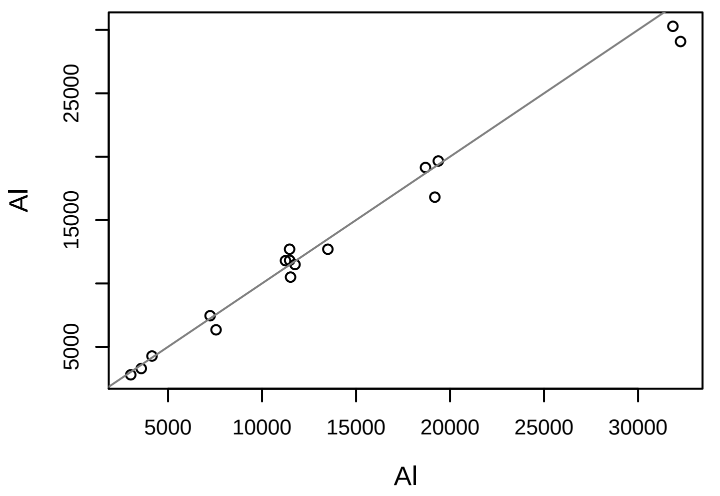

Sn
Absolute difference
0.0
0.2
0.4
0
1
2
3
4
5
6
Mean
Sr
Absolute difference
0
10
20
30
40
50
0
100
200
300
400
500
600
700
Mean
Ta
Absolute difference
0.000
0.004
0.008
0.000
0.005
0.010
0.015
0.020
Mean
Te
Absolute difference
0.00
0.04
0.08
0.00
0.05
0.10
Mean
Th
Absolute difference
0.0
0.2
0.4
0.6
0.8
0
10
20
30
40
Mean
Ti
Absolute difference
0
20
40
60
80
0
500
1000
1500
Mean
Tl
Absolute difference
0.00
0.04
0.08
0.12
0.0
0.5
1.0
1.5
2.0
Mean
U
Absolute difference
0.00
0.10
0.20
0
1
2
3
4
Mean

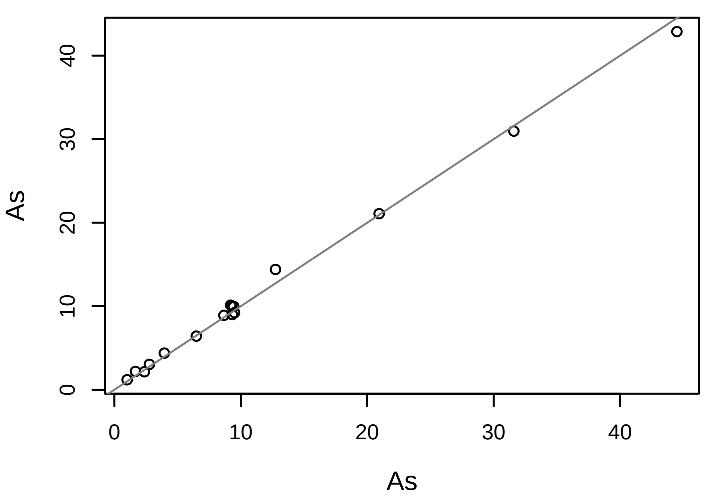

V
Absolute difference
0
5
10
15
20
Mean
0
50
100
150
W
Absolute difference
0.00
0.04
0.08
Mean
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Y
Absolute difference
0.0
0.5
1.0
1.5
Mean
0
10
20
30
Zn
Absolute difference
0
2
4
6
8
12
Mean
0
20
40
60
80
100
120
Zr
Absolute difference
0
1
2
3
4
5
Mean
0
20
40
60
80
100

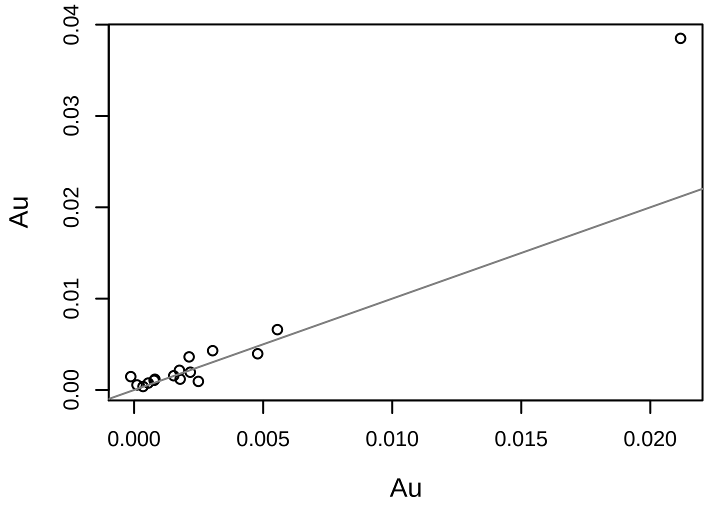
APPENDIX 7. XY-plots for re-analyzed samples

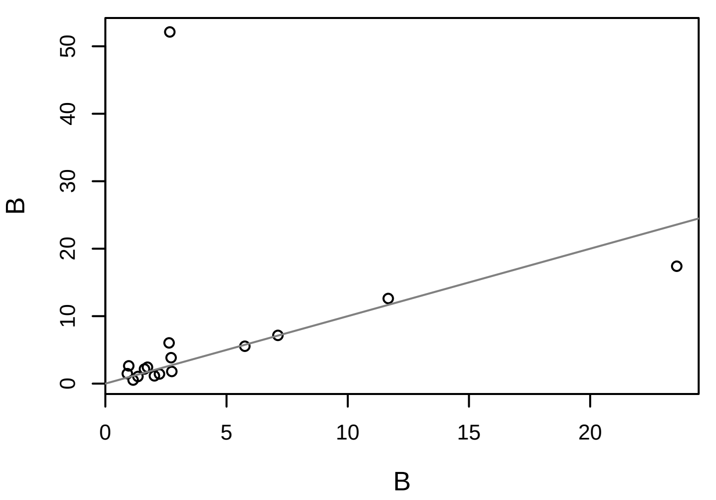
XY-plots for re-analyzed samples: X-axis result for the re-analyzed sample, Y-axis original result. The line indicates the expected 1:1 relation. Only the standard samples that caused ordering a re-analysis deviate seriously from the 1:1 line.

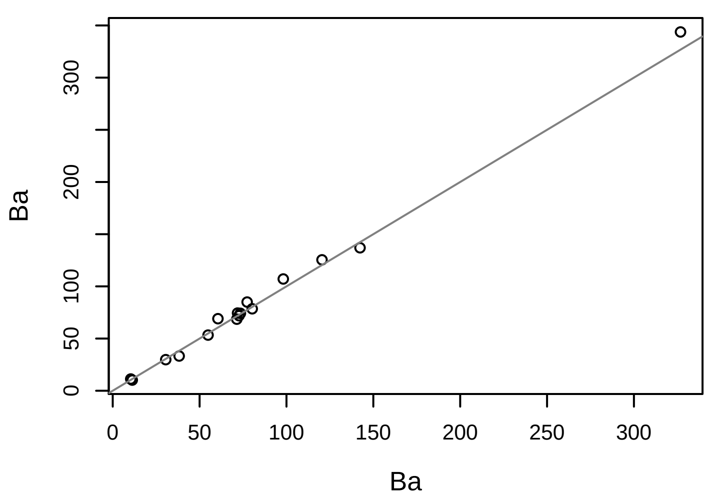

Ag
0.05
0.10
0.15
0.20
0.25
0.05
0.10
0.15
0.20
0.25
Ag

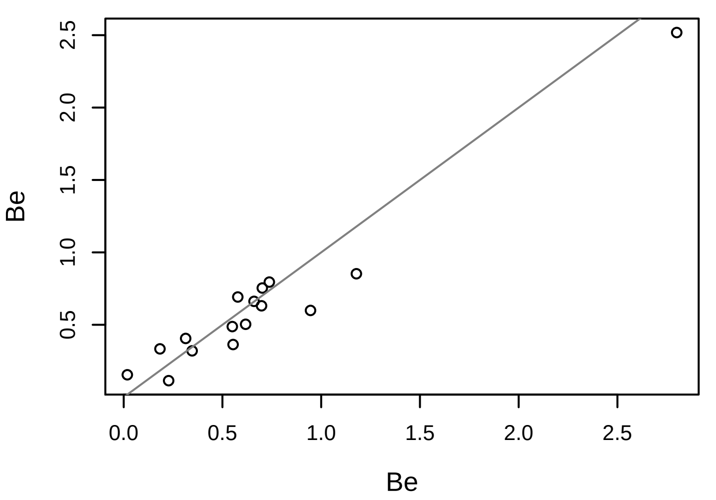

Al
5000
15000
25000
5000
10000
15000
20000
25000
30000
Al

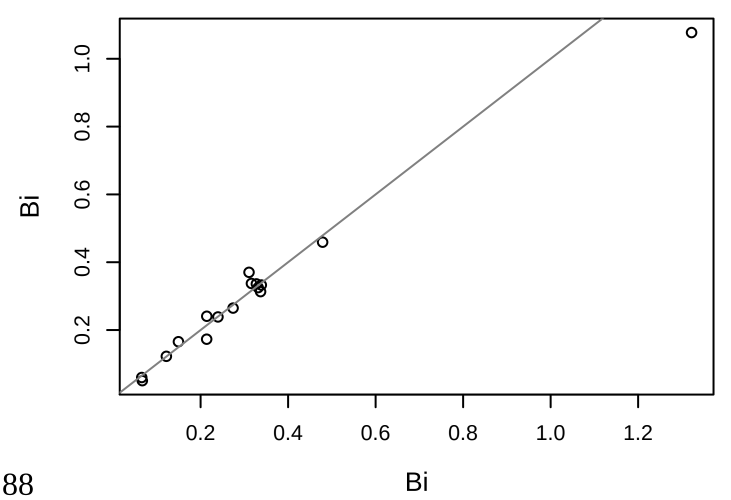

As
0
10
20
30
40
0
10
20
30
40
As

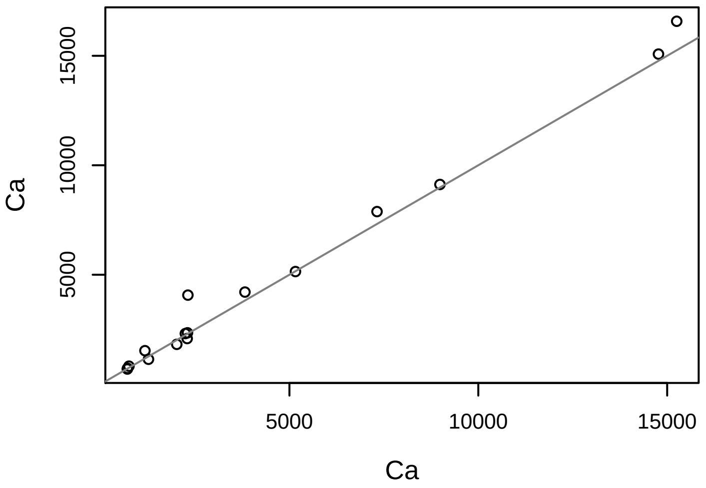

Au
0.00
0.01
0.02
0.03
0.04
0.000
0.005
0.010
0.015
0.020
Au

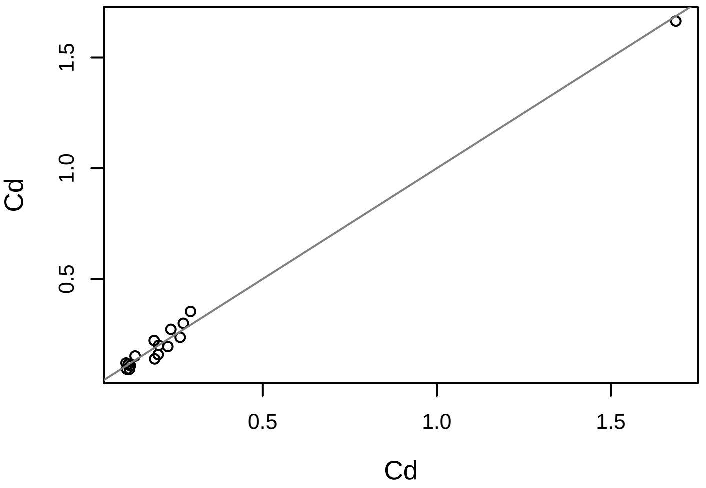

B
0
10
20
30
40
50
0
5
10
15
20
B

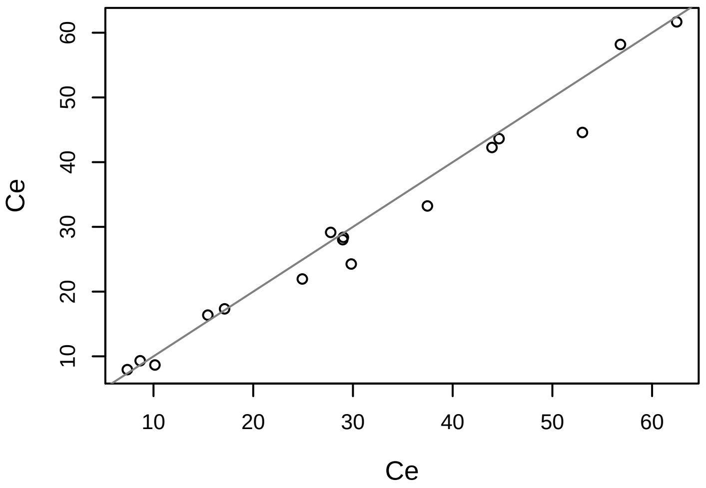

Ba
0
50
100
200
300
0
50
100
150
200
250
300
Ba

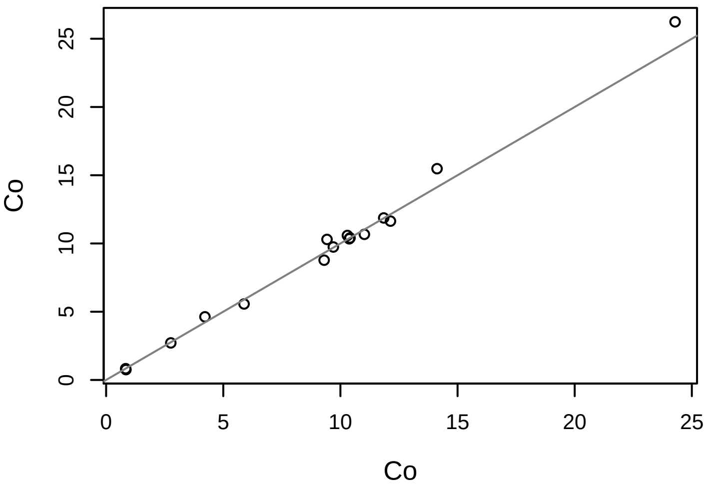

Be
0.5
1.0
1.5
2.0
2.5
0.0
0.5
1.0
1.5
2.0
2.5
Be

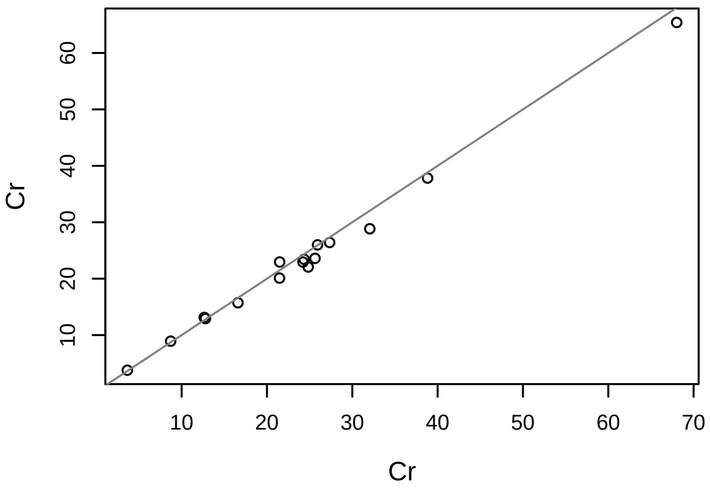

Bi
0.2
0.4
0.6
0.8
1.0
0.2
0.4
0.6
0.8
1.0
1.2
Bi

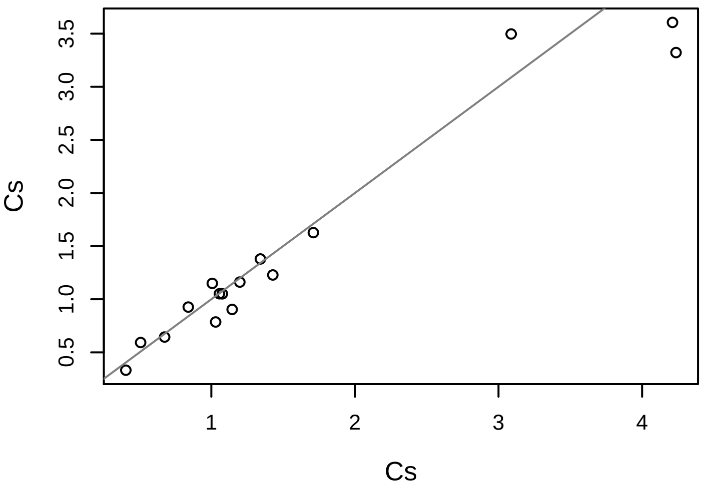

Ca
5000
10000
15000
5000
10000
15000
Ca


Cd
0.5
1.0
1.5
0.5
1.0
1.5
Cd


Ce
10
20
30
40
50
60
10
20
30
40
50
60
Ce


Co
0
5
10
15
20
25
0
5
10
15
20
25
Co


Cr
10
20
30
40
50
60
10
20
30
40
50
60
70
Cr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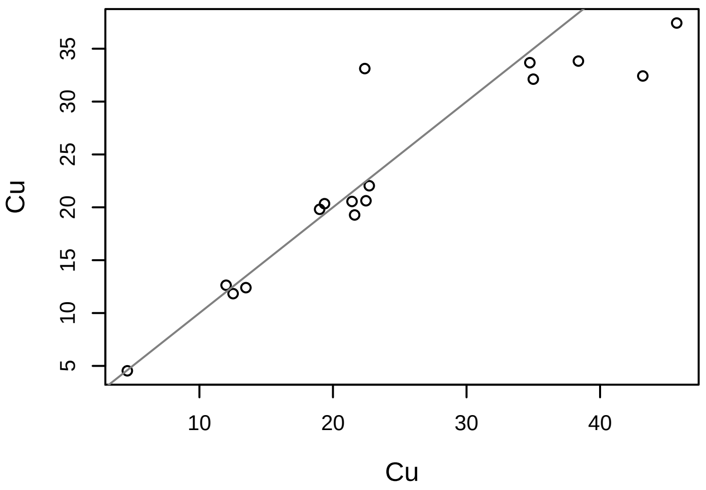
4
Cs


Cu
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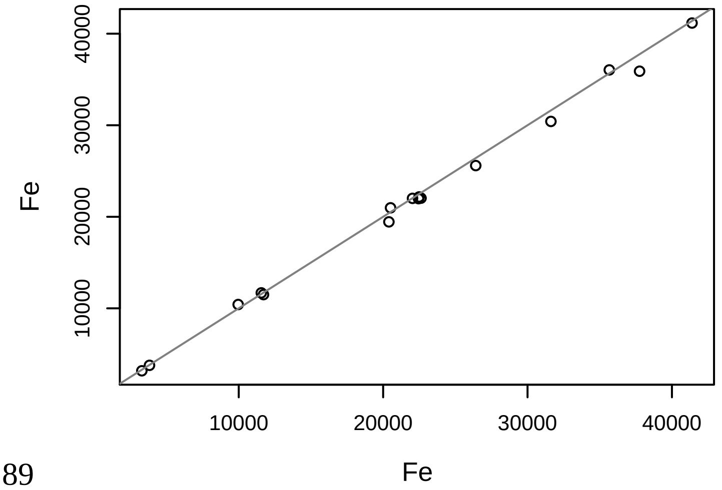
Cu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10000
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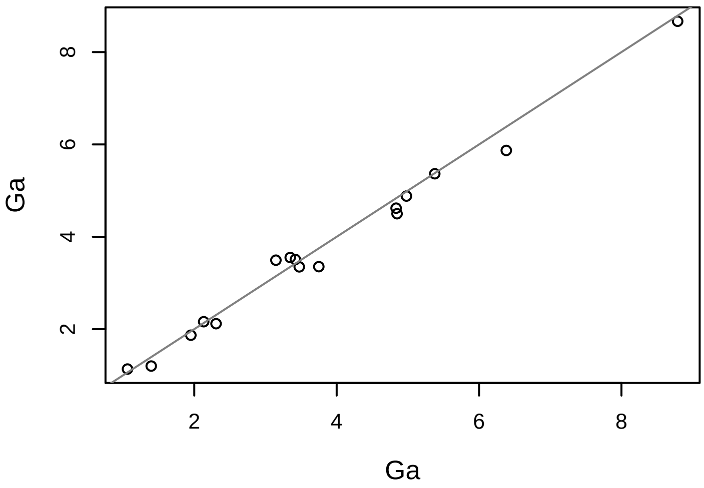
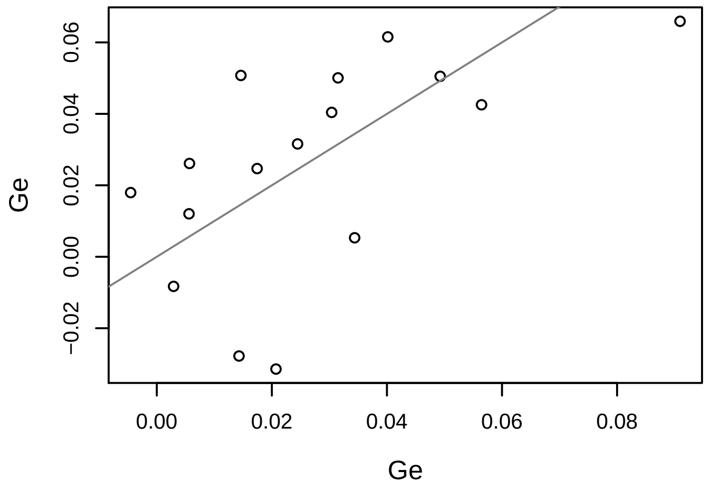
40000
10000
20000
30000
40000
Fe


Ga
Ga
2
4
6
8
2
4
6
8


Ge
Ge
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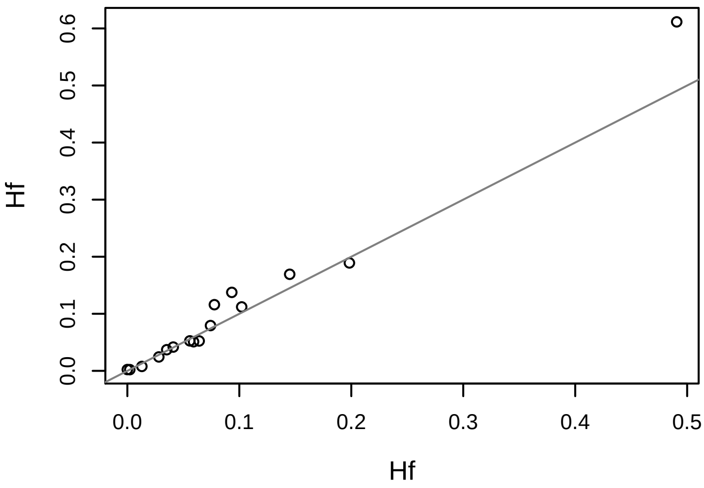
0.00
0.02
0.04
0.06
0.00
0.02
0.04
0.06
0.08


Hf
Hf
0.0
0.1
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0.6
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0.1
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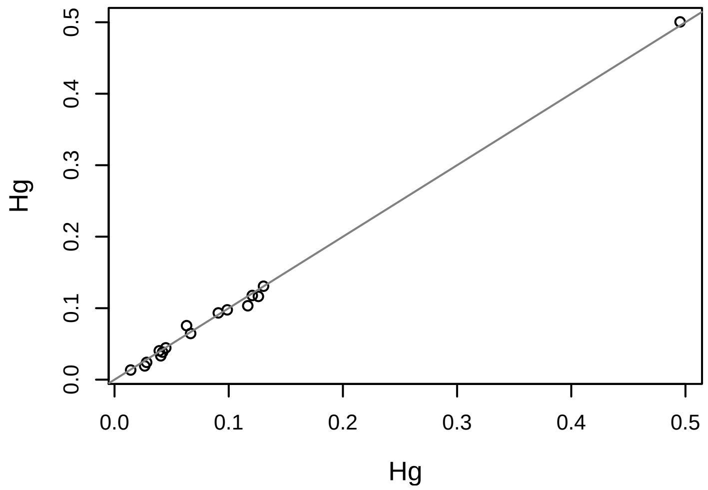
0.3
0.4
0.5


Hg
Hg
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0.5
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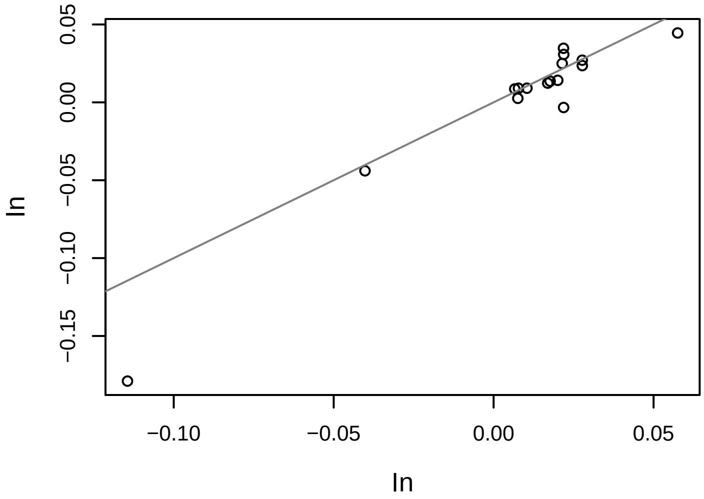
0.4
0.5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In
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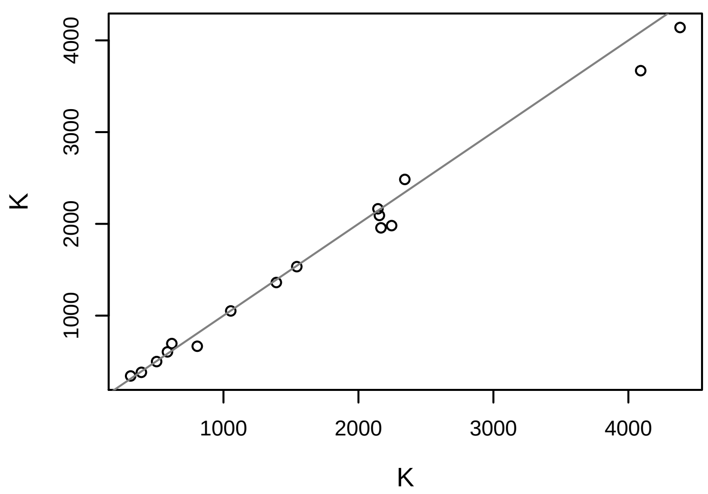
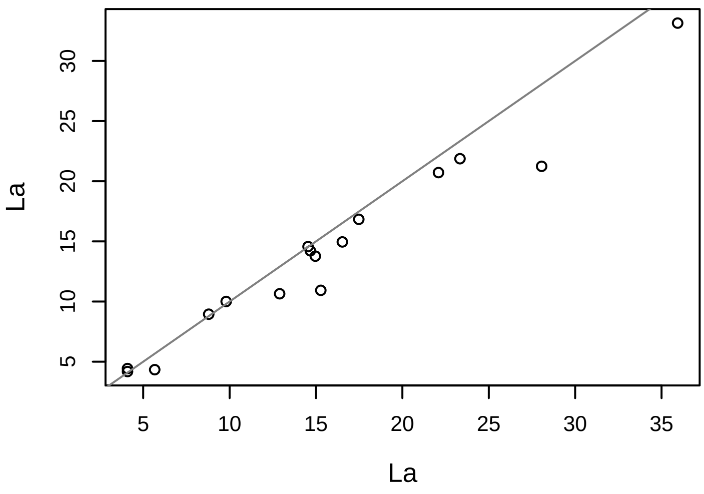
−0.10
−0.05
0.00
0.05
−0.10
−0.05
0.00
0.05


K
K
1000
2000
3000
4000
1000
2000
3000
4000


La
La
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20
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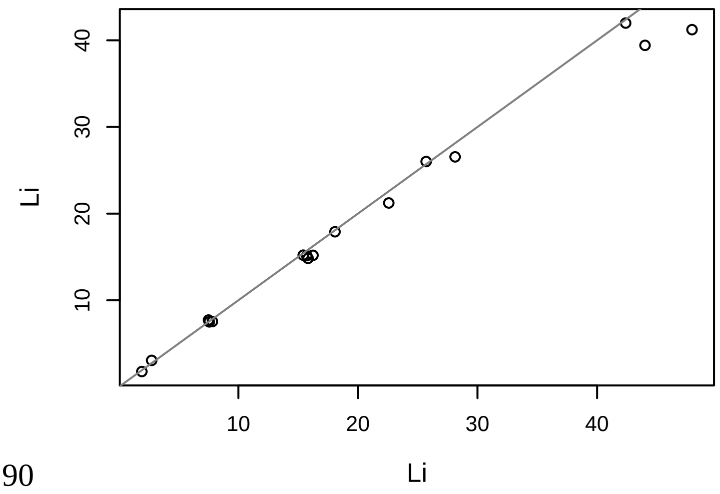
Li
Li
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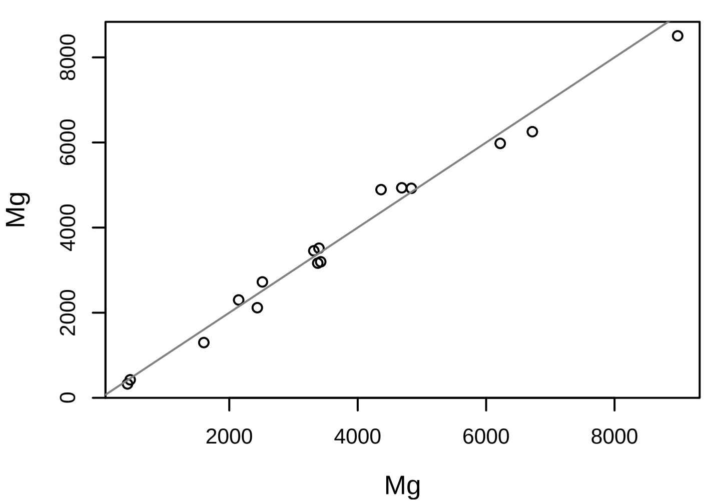
40
10
20
30
40


Mg
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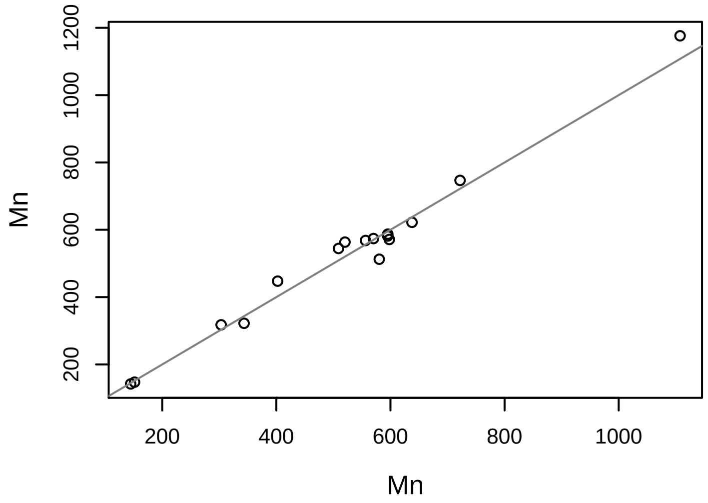
2000
4000
6000
8000
Mg
2000
4000
6000
8000


Mn
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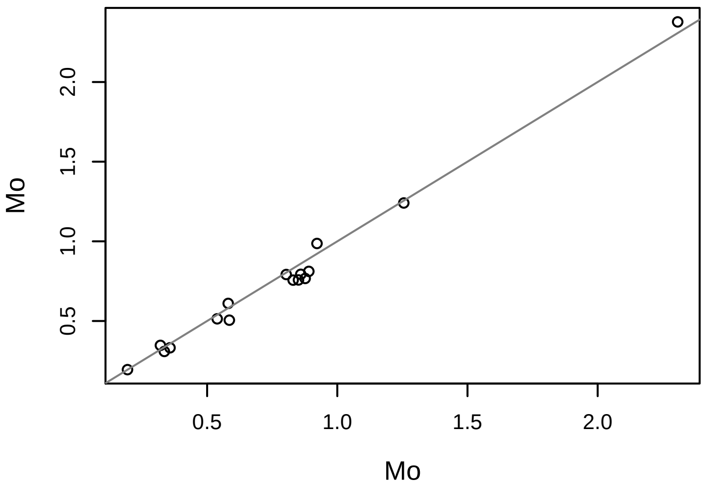
400
600
800
1000
1200
Mn
200
400
600
800
1000


Mo
0.5
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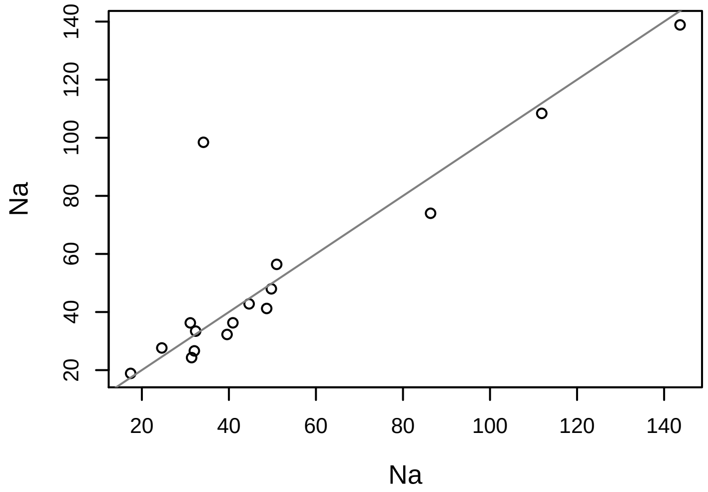
1.5
2.0
Mo
0.5
1.0
1.5
2.0


Na
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80
100
120
140
Na
20
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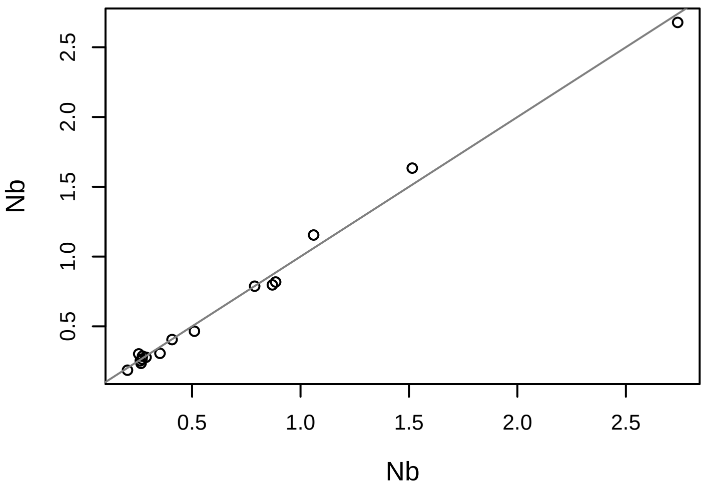
80
100
120
140


Nb
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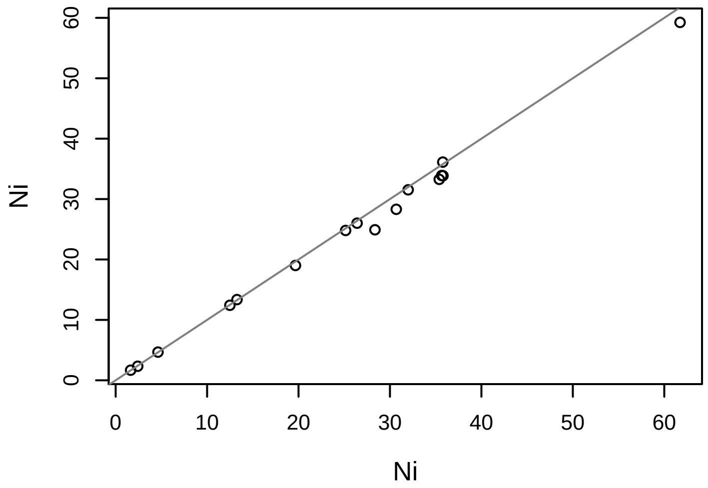
1.5
2.0
2.5
Nb
0.5
1.0
1.5
2.0
2.5


Ni
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Ni
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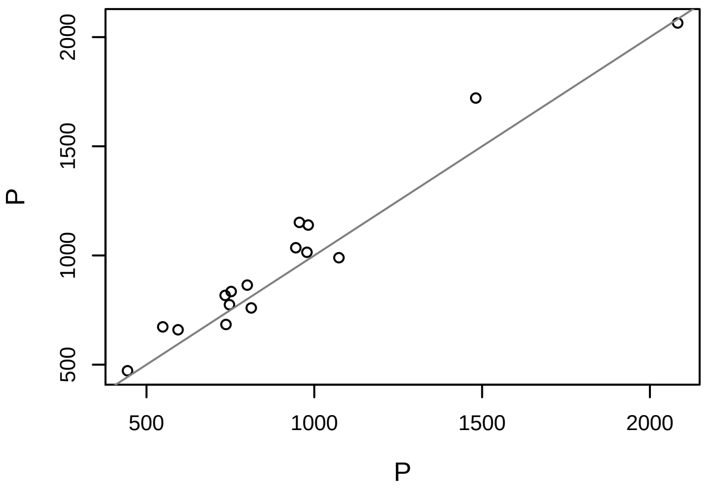
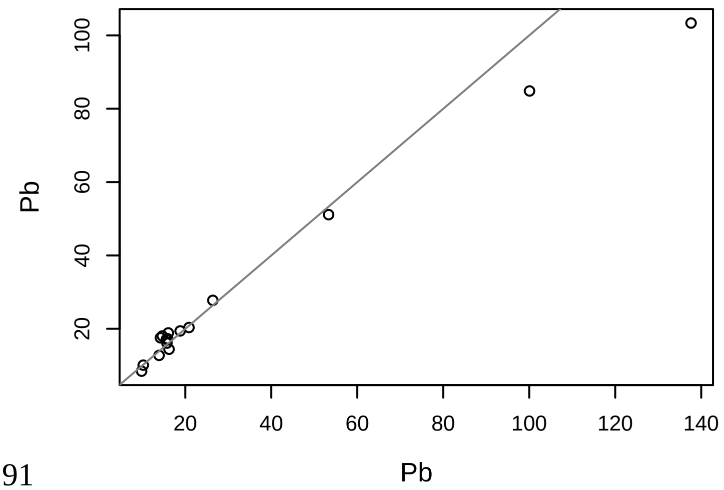
40
50
60


P
500
1000
1500
2000
P
500
1000
1500
2000


Pb
20
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100
Pb
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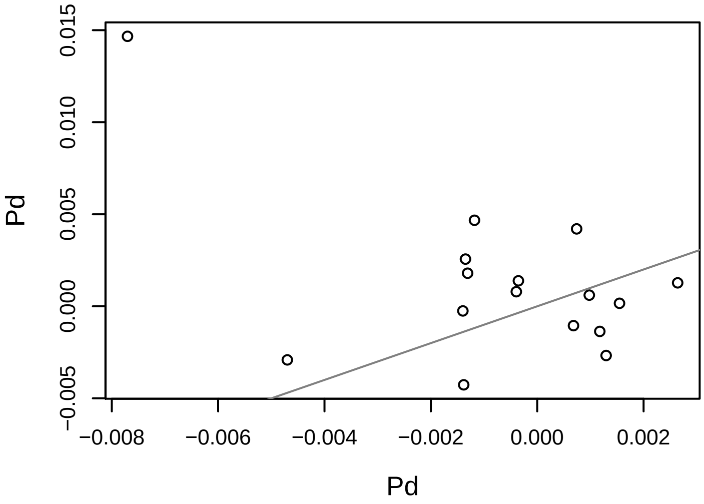
80
100
120
140


Pd
Pd
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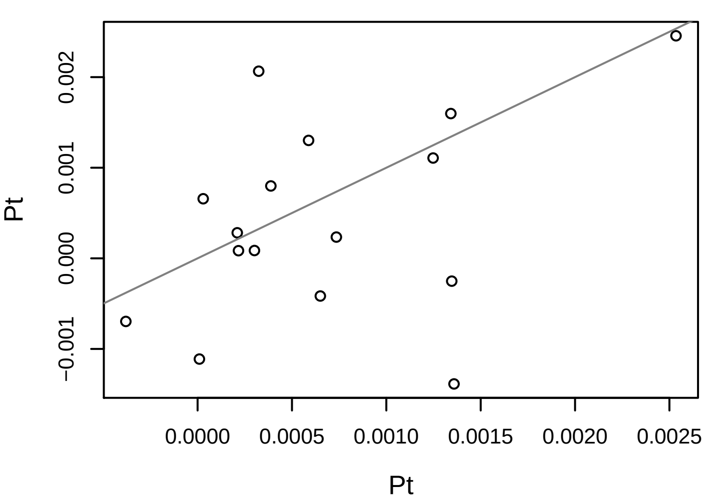
0.000
0.005
0.010
0.015
−0.008
−0.006
−0.004
−0.002
0.000
0.002


Pt
Pt
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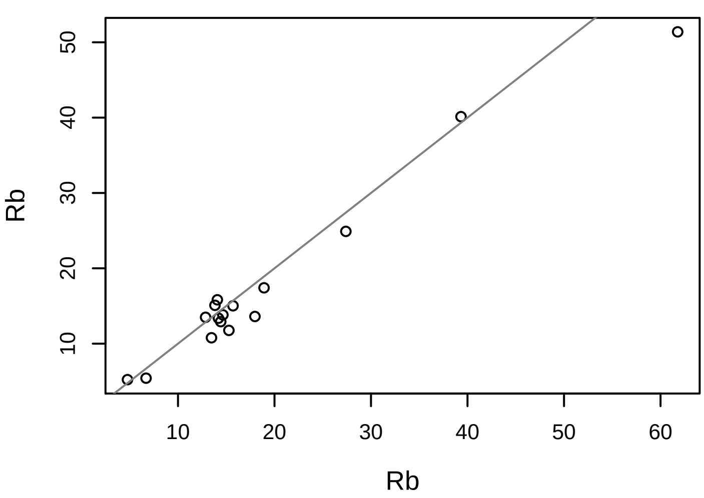
0.000
0.001
0.002
0.0000
0.0005
0.0010
0.0015
0.0020
0.0025


Rb
Rb
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50
10
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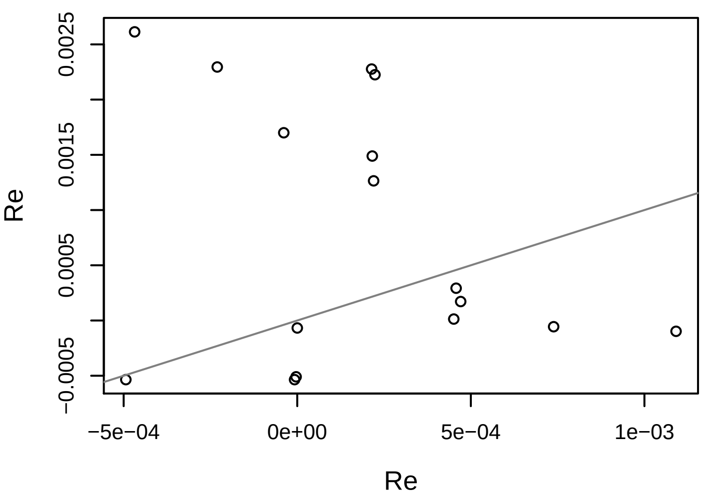
Re
Re
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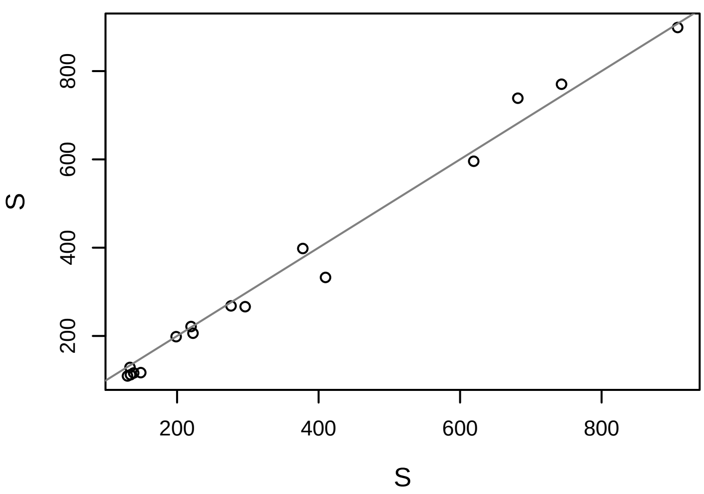
0.0005
0.0015
0.0025
−5e−04
0e+00
5e−04
1e−03


S
S
200
400
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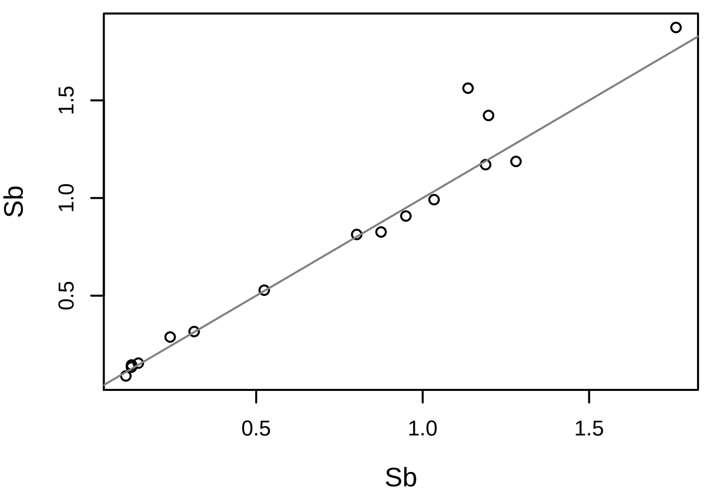
800
200
400
600
800


Sb
Sb
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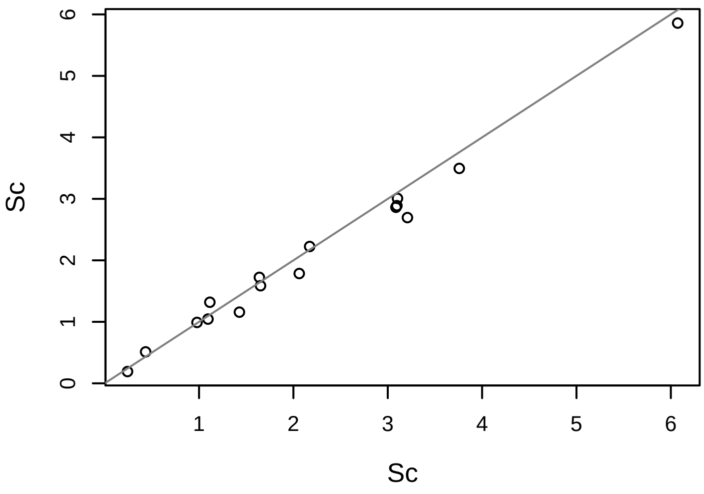
1.5
0.5
1.0
1.5


Sc
Sc
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3
4
5
6
1
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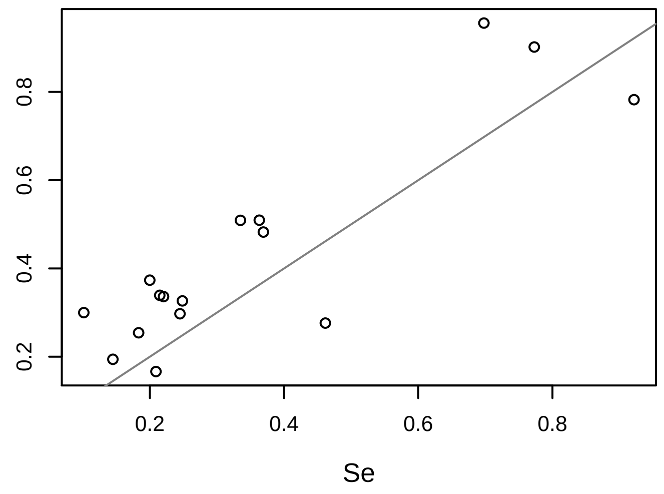
3
4
5
6


Se
Se
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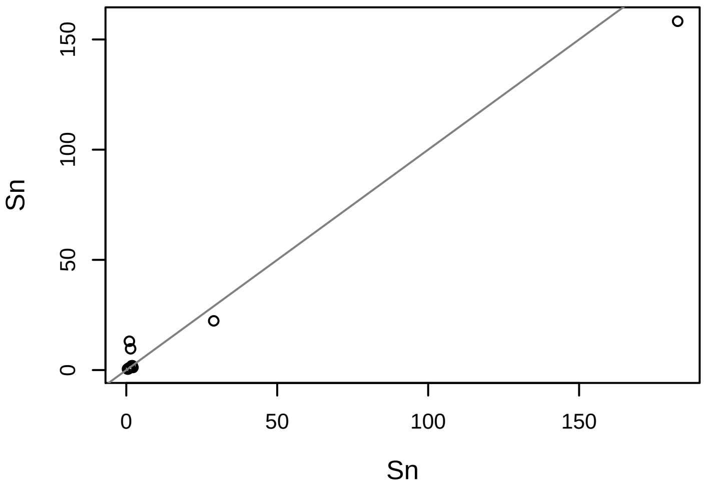
0.4
0.6
0.8
0.2
0.4
0.6
0.8


Sn
Sn
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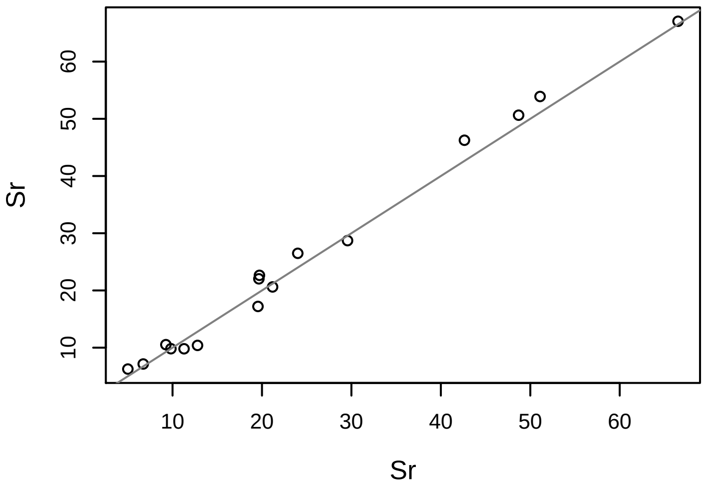
100
150


Sr
Sr
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40
50
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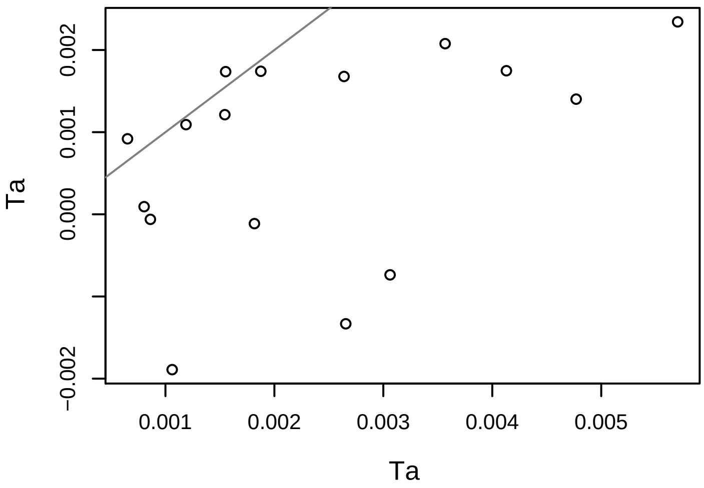
Ta
Ta
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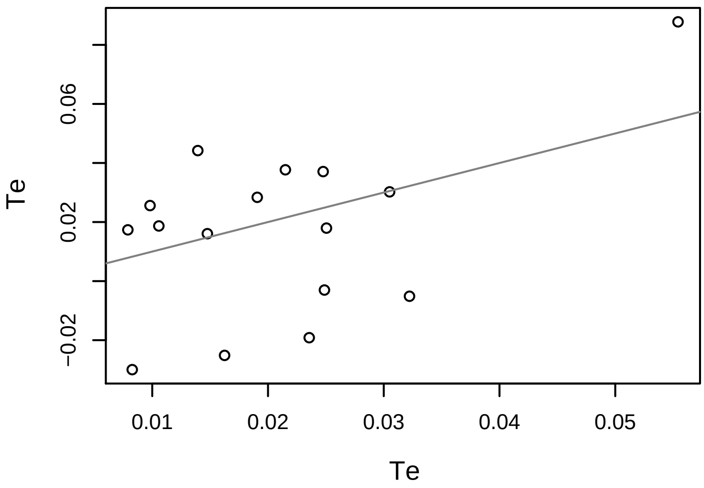
0.002
0.003
0.004
0.005
−0.002
0.000
0.001
0.002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Te
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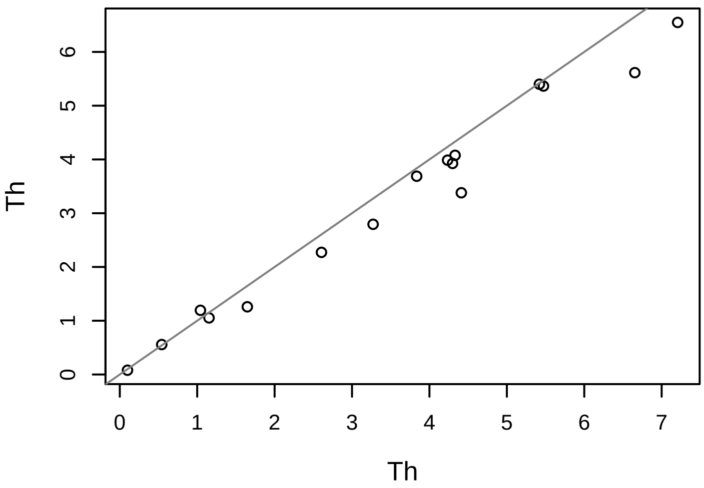
0.02
0.03
0.04
0.05
−0.02
0.02
0.06


Th
Th
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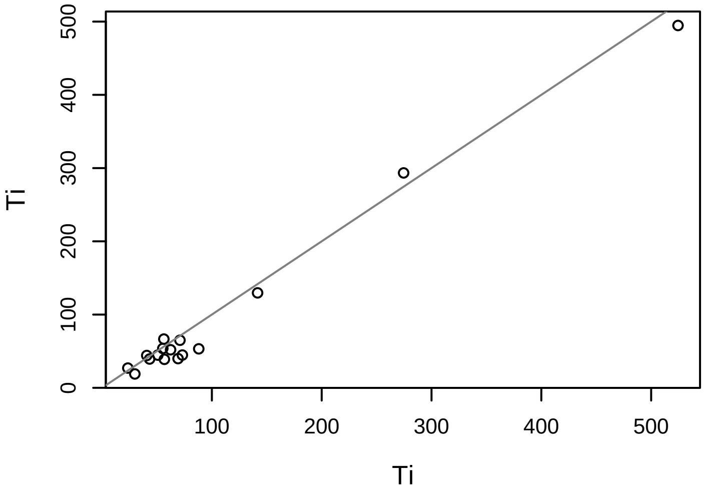
6
7


Ti
Ti
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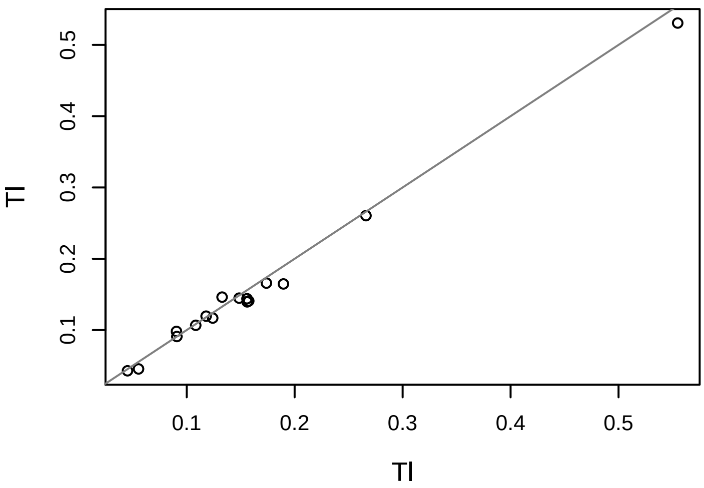
300
400
500


Tl
Tl
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0.2
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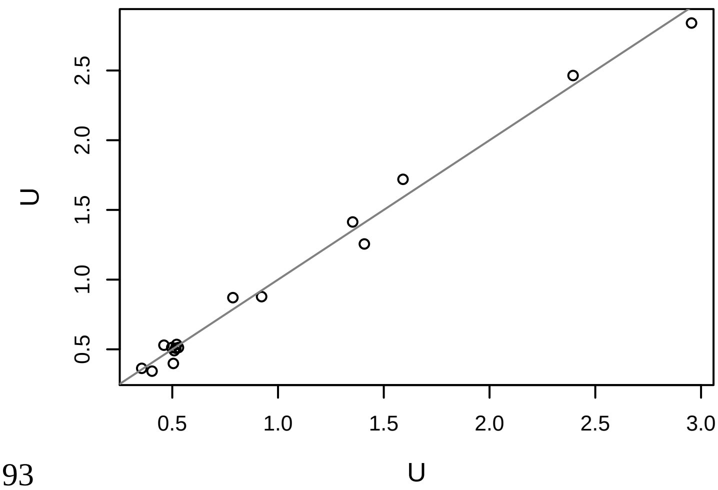
0.4
0.5


U
U
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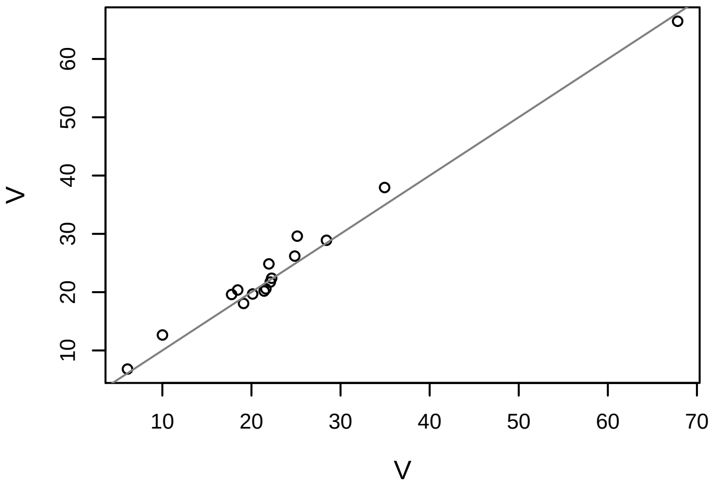
2.5
3.0


V
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V
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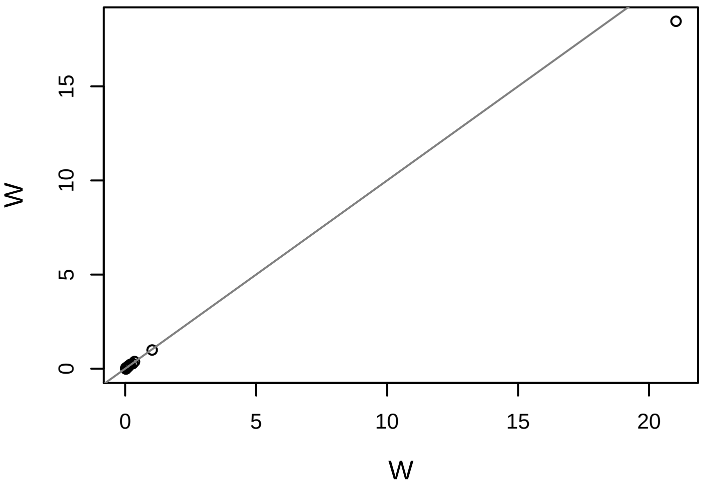
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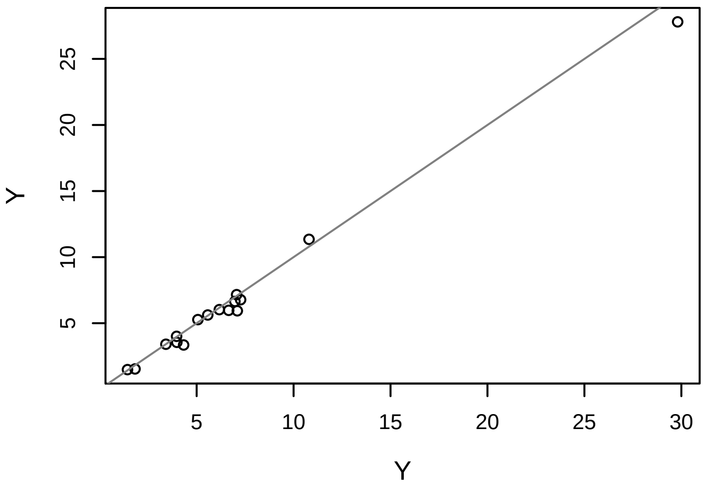
W
0
5
10
15


Y
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Y
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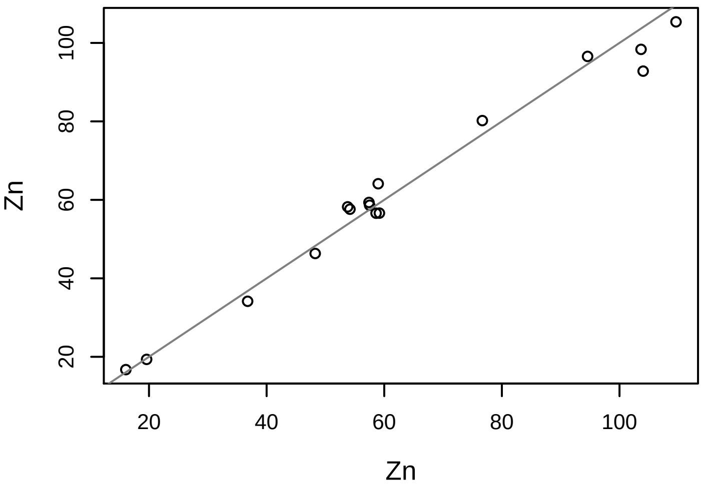
Zn
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Zn
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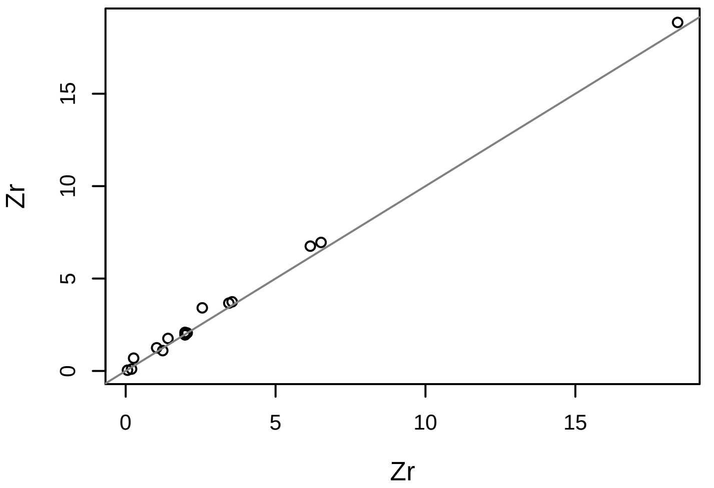
80
100


Zr
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Zr
0
5
10
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