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The Eurogeosurveys geochemical mapping of agricultural and grazing land soils (GEMAS) - Third quality control report

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The EuroGeoSurveys geochemical mapping of agricultural and grazing land soils project (GEMAS) - Evaluation of quality control results of particle size estimation by MIR prediction, Pb-isotope and MMI®-extraction analysis and results of the GEMAS ring test for the standards Ap and Gr

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REPORT

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The Eurogeosurveys **GE**ochemical **M**apping of **A**gricultural and grazing land **S**oils project (GEMAS) - Evaluation of quality control results of particle size estimation by MIR prediction, Pb-isotope and MMI®-extraction analysis and results of the GEMAS ring test for the standards Ap and Gr

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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 Pb isotope ratios, 55 chemical elements (Ag, Al, As, Au, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hg, In, K, La, Li, Mg, Mn, Mo, Nb, Nd, Ni, P, Pb, Pd, Pr, Rb, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, U, V, W, Y, Yb, Zn and Zr) following an MMI® extraction, and prediction of particle size distribution based on MIR spectra are reported. Precision, as well as the analytical and statistical results for the standards are provided for all analysed parameters. Where applicable practical detection limits were calculated. Several quality issues were detected and needed to be corrected before the data files were released. Almost all results could be accepted for further use in the project.

Results of a ring test with the two GEMAS project standards Ap and Gr demonstrate that for the majority of elements the GEMAS results are rather close to their respective reference or assigned values. The observed bias for all elements (aqua regia extraction as well as total concentrations) is provided in this report.

Keywords: quality control	accuracy	precision
ANOVA	MMI	Pb-isotopes
grain size	clay	

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 20^{th} sample site, (2) randomising all samples prior to submitting them for analyses, (3) the introduction of a control reference sample (project standard), unknown to, and unrecognisable by, the laboratory at a rate of one standard per ten to thirty samples, and (4) the insertion of analytical replicates or project samples at a rate of one in ten to twenty samples (*e.g.*, Plant, 1973; Plant *et al.*, 1975; Thompson and Howarth, 1978; Garrett *et al.*, 1980; Fletcher, 1981; Reimann, 1986, 1989; Reimann and Wurzer, 1986; Johnson, 2011). In combination, these procedures allow the detection and evaluation of most quality problems that can occur during sample analysis, and which may seriously affect the success of regional geochemical mapping projects.

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

Only in the last few years it is possible to routinely analyse many samples for a variety of isotope ratios reliably and fast on a high resolution (sector field) inductively coupled plasma mass spectrometer (HR-ICP-MS) or a multi-collector ICP-MS. Although the lead isotope ratios are often used in environmental sciences to establish contamination (for a recent review see Komarek *et al.*, 2008), their regional distribution at the Earth surface has never been established so far. For this reason the Geological Survey of Norway decided to sponsor the measurement of the lead isotope ratios in a HNO_3 extraction for the GEMAS Ap samples. The GEMAS project samples would provide a unique opportunity to measure other isotope systems, and to document their background variation at the continental scale, but unfortunately no other survey laboratory was willing to bear the cost involved. Note that Sr-isotopes in the Gr samples are presently determined at a university laboratory.

Aqua regia extractable and total element concentrations, as determined by XRF, are the backbone of the GEMAS project (see Reimann *et al.*, 2009a, 2011, 2012). An aqua regia extraction is still a very strong extraction and will not provide a realistic impression of the bioavailable part of the total element pool in a soil sample. Many weak extractions have been suggested to determine the bioavailable element concentrations in soil samples. Most are quite element specific, they work only well for one or a small group of elements. A general problem with weak extractions is the stability and comparability of the analytical results over time. The project management was very happy when a commercial laboratory, SGS in Toronto, offered to analyse free of charge the GEMAS samples using their weak extraction method, called MMI® (mobile metal ions), which was especially developed for multi-element

analysis. This provides the unique opportunity to map for the first time element concentrations in a weak extraction at the continental scale.

Particle size determination by laser diffraction carried out by FUGRO (now KIWA) was the only method that delivered results of unacceptable quality to the GEMAS project (see Reimann *et al.*, 2011). The amount of the clay fraction in soil samples is, however, of importance in risk assessment for quite a few elements. Fortunately, mid-infrared spectra (MIR) were reported for all elements. The clay, silt and sand fractions of a soil sample can be quite reliably predicted, based on the MIR spectra if a suitable model for the soils at hand exists. To build-up such a model for European agricultural soils, the particle size distribution of more than 100 selected GEMAS soil samples was determined at the Bundesanstalt für Geowissenschaften und Rohstoffe (BGR) laboratory using the time consuming and costly classical methods. These results were then used to build-up a model for the prediction of the clay, silt and sand fraction in the GEMAS samples by CSIRO Land and Water in Australia (Janik *et al.*, 2011).

1.1 The GEMAS project

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

- Most of their "products" occur also naturally – the natural background variation needs to be established, in addition to a methodology to differentiate the industrial impact from the natural geogenic background.
- What is the "bioavailability" of metals and other chemical elements in soil?
- What is the long-term fate of metals and other chemical elements added to soil?

Geological Surveys have been documenting the natural geochemical background of chemical elements in a variety of sample materials for more than 50 years. However, the existing exposure data at the national and regional scale are often not comparable at the European scale (different sampling strategies, different materials and equipment used for sampling and sample preparation, different sample preparation protocols, different analytical protocols, *etc.*), and are thus not able to provide a harmonised pan-European geochemical "background" variation. A reference network is, therefore, needed, where local data can be tied into continental (European) and, finally, global scale data (Darnley *et al.*, 1995). The EuroGeoSurveys Geochemical Atlas of Europe (FOREGS data set, Salminen *et al.*, 2005; De Vos, Tarvainen *et al.*, 2006) has demonstrated that low-sample density geochemical mapping can provide the required information about the geochemical background in natural soil, stream water, stream and floodplain sediments. Harmonised geochemical data on agricultural soil do only exist for ten countries in north-eastern Europe (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, 2009b; 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).

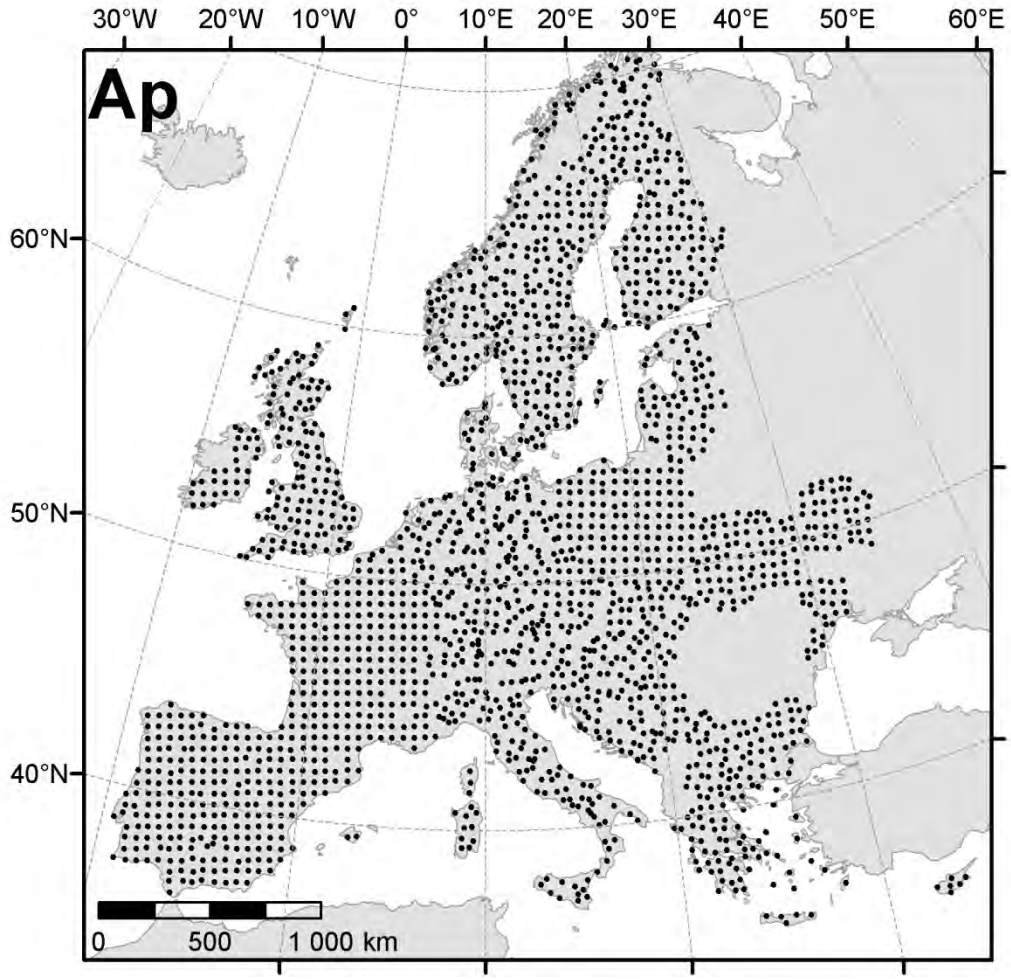

Figure 1. Sample locations for the agricultural soil (Ap-samples), EuroGeoSurveys GEMAS project.

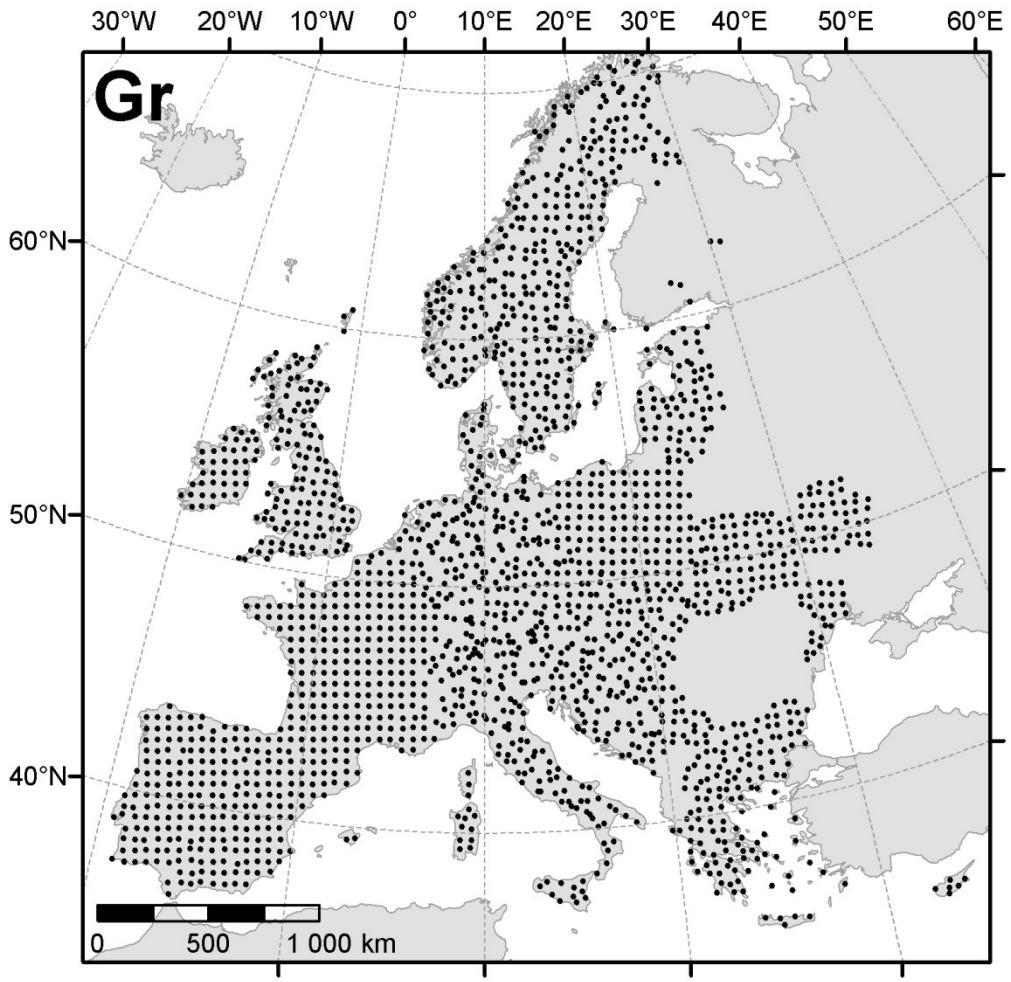

Figure 2. Sample locations for the grazing land soil (Gr-samples), EuroGeoSurveys GEMAS project.

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

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

Many Geological Surveys exist for more than 150 years, and they are one of the few European organisations that can undertake a project at this scale, and 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, and the Italian Survey) agreed in late 2007/early 2008 to collect the samples needed for the GEMAS project in its country, according to a jointly agreed field procedure (EGS, 2008). In a couple of countries non-EGS organisations joined the project to facilitate mapping of all EU territory, including the new member States and the aspiring countries. The Netherlands were covered by Alterra, and Italy by a group of University professors. Eurometaux agreed to fund part of the analytical work in exchange for access to the data as soon as these become available.

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

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

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

2.1 Analytical methods

2.1.1 Lead isotope ratios (NGU)

All Pb isotope ratio measurements were carried out on a high resolution sector field inductively coupled plasma mass spectrometer (HR-ICP-MS; ELEMENT 1, Finnigan MAT, Bremen, Germany). A soil sample weight of 0.5 g was carefully stirred with 8 ml 7N HNO_3 in

PTFE vessels on a Vortex Genie shaker before the samples were extracted under nitrogen pressure at 250°C in an ultraclave (Milestone). During heating, the pressure increases from the start pressure of 50 bar to approximately 120 bar. After cooling, the acid extracts were filtered through Watman folded filters. All samples were diluted to Pb concentrations below 100 µg/L and a HNO_3-concentration of 5% (v/v) prior to HR-ICP-MS analysis. The common lead isotope standard NIST SRM 981 was used to correct for instrumental mass discrimination. The instrumental uncertainty in each measurement was between 0.003 and 0.0002 on the ratio. The certified reference material Mess-3 (NRC, National Research Council Canada) was prepared in the same way as the samples and used as a day-to-day control standard of both the HR-ICP-MS analysis and the digestion. From these data, the reproducibility of the Pb isotope ratio was estimated at 0.11% for $^{208}Pb/^{207}Pb$ and 0.10% for $^{206}Pb/^{207}Pb$.

2.1.2 MMI® extraction (SGS, Toronto)

Extracts were prepared using standard MMI® protocol; 50 g of sample was mixed with 50 mL of MMI-M solution and shaken for thirty minutes. They were allowed to stand overnight before centrifuging for ten minutes at 8500 rpm, using a Sorvall Evolution RC (Thermo Elemental Corporation). Extracts were analysed, using a NexION 300D ICP-MS fitted with a Universal Reaction Cell (Perkin Elmer Corporation), by measuring against calibration standards prepared in MMI matrix solution. Chromium, V and Se were measured in Dynamic Reaction Cell mode using ammonia reaction gas to remove matrix interferences. Sulphur was measured by ICP-OES (Optima 4300DV, Perkin Elmer Corporation) using matrix matched standards. Laboratory internal quality control (QC) criteria included randomised duplicate analysis every thirteen samples, plus blank and reference materials inserted after every 46 analyses. The acceptance criteria were based on a limiting repeatability of 20%, and a detection limit of 2.5 x the reporting limit for each analyte.

2.1.3 Grain size: clay, silt and sand via MIR prediction (CSIRO)

The results for the particle size distribution, as analysed by laser diffractometry by KIWA (former FUGRO), did not pass quality control (see 2nd GEMAS QC report: Reimann *et al.*, 2011). It was, thus, necessary to find an alternative method to obtain at least reliable results for the clay size fraction. Mid-infrared spectroscopy (MIR) spectra were recorded for all GEMAS samples at CSIRO Land and Water in Adelaide, Australia. Multivariate regression models based on MIR spectra can be used to predict a large variety of soil properties, including clay, silt and sand concentrations, when accurate and robust models for the soils in question exist. At the time when the 2nd QC report was prepared there existed no model based on European soils.

In the meantime, a model to predict the content of clay, silt and sand based on MIR spectra and particle size reference data of the European soils from the GEMAS project was constructed (Janik *et al.*, 2011 – Appendix 3) . The predicted results for clay, silt and sand using the European soils model were used for QC in this report. Details of the models are presented in a separate CSIRO report (Janik *et al.*, 2011 – Appendix 3) which also summarises the lab-internal QC results. From the statistical measures of coefficient of variation (R^2) and the residual predictive deviation (RPD = standard deviation/root mean square error), the authors concluded that the predictions of the clay fraction are of good quality, while sand and silt are only of indicator quality. This report provides an independent estimation of the quality, based on the hidden GEMAS QC samples in the data set, unknown to CSIRO. *Note that the predictions of clay, silt and sand by MIR is based on three different models and that the results are independent from one another*. They should, thus, not be expected to sum up to 100% as they would do in a usual particle size determination. This is also the reason that only the predictions for the clay size fraction are used in the presentations of the final GEMAS project 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 reduces 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 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 parameters. Figure 3 shows four examples from the agricultural soil (Ap) samples. All plots showed the expected random variation.

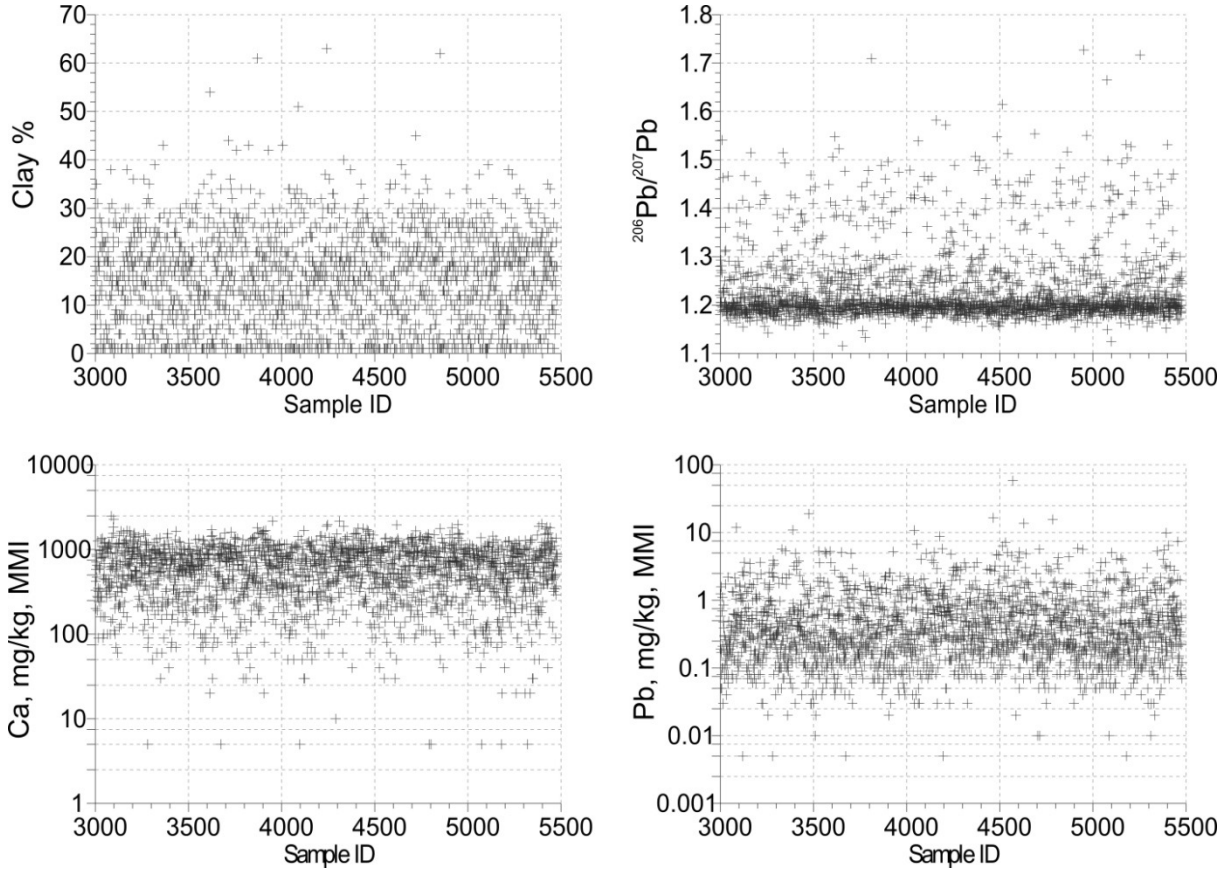

Figure 3. Sample number (sequence of analysis) of the Ap samples plotted against MIR-predicted clay content and analytical results for lead isotope ($^{206}Pb/^{207}Pb$) ratios and analytical results from the MMI® extraction.

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. A disadvantage of using certified reference materials is that they are expensive and easy to detect by the laboratory. Furthermore, they may have been used to calibrate the method and will then not be able to deliver an objective impression of trueness for the project samples. For the GEMAS project about 20 different laboratories analysed the two project standards Ap and Gr using a variety of analytical techniques and the results are published in a separate report (see Appendix 2). Trueness is thus established via the bias observed for the project standards (Chapter 6 in this report).

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

For lead isotope determinations and the prediction of clay, silt and sand, based on the MIR spectra, 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. Due to a misunderstanding, the GEMAS Ap samples for the MMI® extraction were delivered to the laboratory without the standard samples inserted; the samples reached the lab with only two international project standards, MRIS2 (4x) and SoNE-1 (5x), inserted. The laboratory inserted its own internal standards MMI16 (35x) and MMI18 (32x) and X-charts could only be prepared for these internal laboratory standards (not shown here but discussed with the laboratory).

Table 1. Statistical results (mean, minimum (Min) and maximum (Max) concentration, standard deviation (StDev) and coefficient of variation (CV %)) for the MIR-predicted results of the clay, silt and sand fraction and for the lead isotope ratios as analysed by HR-ICP-MS for the project standards Ap and Gr.

Parameter	***Method***	***Unit***	***GEMAS Ap (N=124)***					***GEMAS Gr (N=118)***				
			Min	***Mean***	***Max***	***StDev***	***CV%***	***Min***	***Mean***	***Max***	***StDev***	***CV%***
sand	MIR	%	20	26	45	3.36	13	31	41	78	5.75	14
silt	MIR	%	29	49	56	4.27	9	19	34	60	4.42	13
clay	MIR	%	22	28	32	1.16	4	1	21	25	3.25	15
$^{207}Pb/^{208}Pb$	HR-ICP-MS		0.401	0.403	0.406	0.00064	0.16	not determined				
$^{208}Pb^{206}Pb$	HR-ICP-MS		2.042	2.064	2.074	0.00483	0.23					
$^{206}Pb^{207}Pb$	HR-ICP-MS		1.195	1.201	1.221	0.00248	0.21					

Table 1 summarises the analytical results for the GEMAS standards Ap and Gr for clay, sand and silt fractions, and the results for the Ap standard only for the lead isotopes. For MIR predictions and the lead isotope ratios, average repeatability of all elements, calculated for the standard results, is also provided and can be used to obtain a first impression of precision at the concentration in the standards (see above).

Table 2A and B summarise the results of the two SGS MMI® in-house standards MMI16 and MMI18, which were analysed routinely within the GEMAS Ap samples, and their reference values are also provided for comparison.

Table 2A. Analytical programme covered by the MMI® extraction and the laboratory detection limits (LDL), reference values of the in-house standard MMI16, and statistical results (mean, minimum (Min) and maximum (Max) concentration, standard deviation (StDev) and coefficient of variation (CV %)) for the SGS in-house standard MMI16 routinely analysed with the GEMAS Ap samples. Notation: NA – not available.

Element	***LDL***	***MMI16 Reference values***	***GEMAS MMI16 (N=35) RESULTS***				
			Min	***Mean***	***Max***	***StDev***	***CV***
	mg/kg	***mg/kg***	***mg/kg***	***mg/kg***	***mg/kg***	***mg/kg***	***%***
Ag	0.001	0.0180	0.0150	0.0189	0.0240	0.0017	9
Al	1	41.8	31.0	42.4	54.0	4.56	11
As	0.01	0.0130	<0.01	0.0149	0.0200	0.0056	38
Au	0.0001	0.0260	0.0202	0.0269	0.0370	0.0021	8
Ba	0.01	0.0580	0.0600	0.0694	0.0900	0.0054	8
Bi	0.001	NA	All values below DL				
Ca	10	212	180	233	280	19.5	8
Cd	0.001	0.0040	0.0040	0.0045	0.0050	0.0005	11
Ce	0.005	0.0165	0.0110	0.0168	0.0260	0.0025	15
Co	0.005	0.0540	0.0420	0.0578	0.0710	0.0067	12
Cr	0.001	0.0500	0.0340	0.0475	0.0860	0.0070	15
Cs	0.0005	0.0110	0.0101	0.0116	0.0140	0.0010	8
Cu	0.01	0.6240	0.4900	0.6629	0.8900	0.0757	11
Dy	0.001	0.0023	<0.001	0.0023	0.0030	0.0005	22
Er	0.0005	0.0009	<0.0005	0.0009	0.0012	0.0002	18
Eu	0.0005	0.0010	<0.0005	0.0010	0.0015	0.0002	18
Fe	1	2.50	<0.001	2.67	4.00	0.5078	19
Ga	0.001	0.0004	All values below DL				
Gd	0.001	0.0040	0.0030	0.0041	0.0060	0.0006	14
Hg	0.001	0.0160	0.0090	0.0176	0.0270	0.0032	18
In	0.0005	NA	All values below DL				
K	0.1	39.0	33.0	38.6	50.0	2.68	7
La	0.001	0.0040	0.0020	0.0040	0.0060	0.0007	17
Li	0.005	0.0020	All values below DL				
Mg	1	30.0	26.0	34.9	44.0	4.30	12
Mn	0.01	0.0900	0.0400	0.1214	0.2400	0.0274	23
Mo	0.005	0.0450	0.0330	0.0489	0.0760	0.0076	16
Nb	0.0005	NA	All values below DL				
Nd	0.001	0.0145	0.0100	0.0148	0.0210	0.0020	14
Ni	0.005	0.2310	0.1520	0.2357	0.3740	0.0369	16

Element	*LDL*	*MMI16 Reference values*		*GEMAS MMI16 (N=35) RESULTS*				
				Min	*Mean*	*Max*	*StDev*	*CV*
	mg/kg	*mg/kg*		*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*%*
P	0.1	0.2000		<0.1	0.2529	0.4000	0.0710	28
Pb	0.01	0.0880		0.0500	0.0934	0.1400	0.0188	20
Pd	0.001	0.0240		0.0190	0.0247	0.0310	0.0022	9
Pr	0.001	0.0020		<0.001	0.0025	0.0040	0.0006	23
Pt	0.001	NA		All values below DL				
Rb	0.005	0.2970		0.2850	0.3242	0.4160	0.0210	6
S	0.5	37.0		29.8	37.3	45.0	2.50	7
Sb	0.001	0.0005		<0.001	0.0005	0.0020	0.0001	15
Sc	0.005	0.0070		<0.005	0.0090	0.0150	0.0018	20
Se	0.01	0.0000		0.0050	0.0106	0.0200	0.0047	44
Sm	0.001	0.0040		0.0030	0.0045	0.0060	0.0007	16
Sn	0.001	NA		All values below DL				
Sr	0.01	0.4650		0.4300	0.5006	0.6200	0.0366	7
Ta	0.001	NA		All values below DL				
Tb	0.001	0.0005		All values below DL				
Te	0.01	NA		All values below DL				
Th	0.0005	0.0210		0.0140	0.0203	0.0290	0.0024	12
Ti	0.003	0.0090		<0.003	0.0042	0.0110	0.0020	47
Tl	0.0005	NA		All values below DL				
U	0.001	0.0450		0.0350	0.0477	0.0620	0.0059	12
V	0.001	0.0900		0.0400	0.0772	0.1250	0.0232	30
W	0.001	NA		All values below DL				
Y	0.005	0.0090		0.0060	0.0095	0.0130	0.0015	15
Yb	0.001	0.0007		All values below DL				
Zn	0.02	0.2330		0.2000	0.2829	0.6100	0.0441	16
Zr	0.005	0.0140		<0.005	0.0164	0.0230	0.0023	14

Table 2B. Analytical programme covered by the MMI® extraction and the laboratory detection limits (LDL), reference values of the in-house standard MMI18, and statistical results (mean, minimum (Min) and maximum (Max) concentration, standard deviation (StDev) and coefficient of variation (CV %)) for the SGS in-house standard MMI18 routinely analysed with the GEMAS Ap samples. Notation: NA – not available.

Element	***LDL***	***MMI18 Reference values***	***GEMAS MMI18 (N=32) RESULTS***				
			Min	***Mean***	***Max***	***StDev***	***CV***
	mg/kg	***mg/kg***	***mg/kg***	***mg/kg***	***mg/kg***	***mg/kg***	***%***
Ag	0.001	0.0213	0.0240	0.0282	0.0340	0.0021	7
Al	1	28.1	20.0	28.7	39.0	2.72	9
As	0.01	0.0123	<0.01	0.0131	0.0200	0.0045	34
Au	0.0001	0.0079	0.0090	0.0104	0.0130	0.0006	6
Ba	0.01	0.1602	0.1300	0.1616	0.2200	0.0152	9
Bi	0.001	NA	All values below DL				
Ca	10	169	190	213	250	14.1	7
Cd	0.001	0.0747	0.0890	0.1006	0.1160	0.0050	5
Ce	0.005	0.0214	0.0200	0.0262	0.0380	0.0031	12
Co	0.005	0.0673	0.0620	0.0834	0.1070	0.0085	10
Cr	0.001	0.0305	0.0210	0.0318	0.0510	0.0051	16
Cs	0.0005	NA	0.0059	0.0067	0.0077	0.0004	6
Cu	0.01	0.7732	0.7400	0.9316	1.26	0.0954	10
Dy	0.001	0.0037	<0.001	0.0034	0.0050	0.0008	24
Er	0.0005	0.0016	<0.0005	0.0014	0.0020	0.0002	16
Eu	0.0005	0.0012	<0.0005	0.0012	0.0016	0.0002	18
Fe	1	2.86	<1	3.81	5.00	0.5830	15
Ga	0.001	NA	All values below DL				
Gd	0.001	0.0059	0.0040	0.0056	0.0080	0.0009	16
Hg	0.001	NA	0.0040	0.0075	0.0420	0.0025	34
In	0.0005	NA	All values below DL				
K	0.1	NA	26.0	30.3	36.0	1.87	6
La	0.001	0.0065	0.0060	0.0077	0.0120	0.0010	13
Li	0.005	NA	All values below DL				
Mg	1	86.5	88.0	103	121	6.59	6
Mn	0.01	NA	0.4100	0.6942	0.9100	0.0762	11
Mo	0.005	0.0328	0.0260	0.0351	0.0490	0.0043	12
Nb	0.0005	0.0001	All values below DL				
Nd	0.001	0.0176	0.0140	0.0203	0.0290	0.0030	15
Ni	0.005	0.5068	0.4540	0.5695	0.7610	0.0514	9
P	0.1	NA	0.4000	0.7290	1.0000	0.1420	20
Pb	0.01	0.3003	0.2200	0.3252	0.4400	0.0531	16
Pd	0.001	0.0129	0.0130	0.0164	0.0210	0.0014	8
Pr	0.001	0.0034	<0.001	0.0036	0.0050	0.0008	22
Pt	0.001	0.0060	0.0050	0.0068	0.0090	0.0007	11
Rb	0.005	0.1565	0.1510	0.1693	0.1930	0.0087	5
S	0.5	50.0	46.0	54.5	68.0	3.90	7

Element	LDL	MMI18 Reference values	GEMAS MMI18 (N=32) RESULTS				
			Min	Mean	Max	StDev	CV
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	%
Sb	0.001	0.0002	<0.001	<0.001	0.0020	0.0001	17
Sc	0.005	0.0033	<0.005	<0.005	0.0120	0.0017	40
Se	0.01	NA	<0.01	<0.01	0.0200	0.0036	48
Sm	0.001	0.0052	0.0040	0.0054	0.0070	0.0008	15
Sn	0.001	0.0002	All values below DL				
Sr	0.01	1.07	1.11	1.24	1.43	0.0695	6
Ta	0.001	NA	All values below DL				
Tb	0.001	0.0008	All values below DL				
Te	0.01	NA	All values below DL				
Th	0.0005	0.0200	0.0150	0.0200	0.0260	0.0023	12
Ti	0.003	0.0063	<0.003	0.0083	0.0250	0.0041	49
Tl	0.0005	0.0002	All values below DL				
U	0.001	0.0271	0.0180	0.0267	0.0390	0.0038	14
V	0.001	0.0800	0.0270	0.0627	0.1230	0.0225	36
W	0.001	0.0002	All values below DL				
Y	0.005	0.0203	0.0025	0.0215	0.0300	0.0037	17
Yb	0.001	0.0009	<0.001	<0.001	0.0010	0.0002	32
Zn	0.02	0.6618	0.7700	0.9016	1.12	0.0601	7
Zr	0.005	0.0266	0.0220	0.0302	0.0400	0.0035	12

Table 3 shows the statistical results for the two international project standards SoNE-1 and MRIS2. MRIS2 has also been analysed in the Australian National Geochemical Survey Programme (NGSA – Caritat and Cooper, 2011) in an MMI® extraction and thus values for comparison are provided, otherwise these data are given here as reference for future projects.

Table 3. Median values for the two international project standards SoNE-1 and MRIS2 in the MMI® extraction. For MRIS2, results are also provided from the national geochemical survey of Australia (NGSA – Caritat and Cooper, 2011).

Element	LDL	GEMAS PROJECT RESULTS		NGSA PROJECT RESULTS	Element	LDL	GEMAS PROJECT RESULTS		NGSA PROJECT RESULTS
		MEDIAN		MEDIAN			MEDIAN		MEDIAN
		SoNE-1	MRIS2	MRIS2			SoNE-1	MRIS2	MRIS2
		(N=4)	(N=5)	(N=16)			(N=4)	(N=5)	(N=16)
	mg/kg	mg/kg	mg/kg	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg
Ag	0.001	0.04250	0.00200	0.00700	Nd	0.001	0.4050	0.3660	0.5395
Al	1	81.5	55.0	16.0	Ni	0.005	2.70	4.38	3.75
As	0.01	0.0200	0.0200	0.0100	P	0.1	3.30	6.00	3.40
Au	0.0001	0.0007	0.0004	0.0003	Pb	0.01	0.2750	0.0300	0.0200
Ba	0.01	15.1	2.58	1.20	Pd	0.001	<0.001	<0.001	<0.001
Bi	0.001	<0.001	<0.001	<0.001	Pr	0.001	0.0800	0.0770	0.1160
Ca	10	1175	590	500	Pt	0.001	<0.001	<0.001	<0.001
Cd	0.001	0.1795	0.0160	0.0180	Rb	0.005	0.2675	0.2750	0.0784
Ce	0.005	0.2745	0.4750	0.6125	S	0.5	35.3	35.6	N/A

Element	*LDL*	*GEMAS PROJECT RESULTS*		*NGSA PROJECT RESULTS*
		MEDIAN		*MEDIAN*
		SoNE-1	*MRIS2*	*MRIS2*
		(N=4)	*(N=5)*	*(N=16)*
	mg/kg	*mg/kg*	*mg/kg*	*mg/kg*
Co	0.005	1.080	1.490	0.286
Cr	0.001	0.1330	0.4400	0.0575
Cs	0.0005	0.0020	0.0016	0.0047
Cu	0.01	2.01	2.61	0.8600
Dy	0.001	0.1025	0.0860	0.1115
Er	0.0005	0.0643	0.0613	0.0630
Eu	0.0005	0.0246	0.0193	0.0263
Fe	1	19.0	101	27.0
Ga	0.001	0.0020	0.0020	0.0330
Gd	0.001	0.1180	0.0940	0.1315
Hg	0.001	<0.001	<0.001	<0.001
In	0.0005	<0.0005	<0.0005	N/A
K	0.1	211	153	48.5
La	0.001	0.1990	0.1930	0.2690
Li	0.005	0.0915	0.0140	0.0095
Mg	1	250	264	248
Mn	0.01	52.9	101	22.3
Mo	0.005	0.0160	0.0220	<0.005
Nb	0.0005	0.0009	0.0009	<0.0005

Element	*LDL*	*GEMAS PROJECT RESULTS*		*NGSA PROJECT RESULTS*
		MEDIAN		*MEDIAN*
		SoNE-1	*MRIS2*	*MRIS2*
		(N=4)	*(N=5)*	*(N=16)*
	mg/kg	*mg/kg*	*mg/kg*	*mg/kg*
Sb	0.001	0.0055	0.0010	<0.001
Sc	0.005	0.0255	0.0640	0.0200
Se	0.01	0.0200	<0.01	0.0095
Sm	0.001	0.0985	0.0870	0.1220
Sn	0.001	<0.001	<0.001	<0.001
Sr	0.01	6.96	3.18	2.37
Ta	0.001	<0.001	<0.001	<0.001
Tb	0.001	0.0160	0.0140	0.0210
Te	0.01	<0.01	<0.01	<0.01
Th	0.0005	0.1043	0.1100	0.1355
Ti	0.003	0.0415	0.0610	0.0265
Tl	0.0005	0.0014	<0.0005	<0.0005
U	0.001	0.3075	0.6550	0.5115
V	0.001	0.0345	0.0650	0.0155
W	0.001	<0.001	0.0010	<0.001
Y	0.005	0.4775	0.5620	0.6455
Yb	0.001	0.0575	0.0570	0.0490
Zn	0.02	0.7000	0.6900	1.0350
Zr	0.005	0.1335	0.0740	0.0440

In addition, X-Charts were plotted for clay, silt, sand and the lead isotope results, where element concentration is plotted against sample number. For the MMI® results, these plots were prepared based on the laboratories in-house standards. 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. Some serious outliers (>+/-30%) needed to be followed up and resulted in the reanalysis of some samples. They were usually caused by a sample mix-up within an analytical batch.

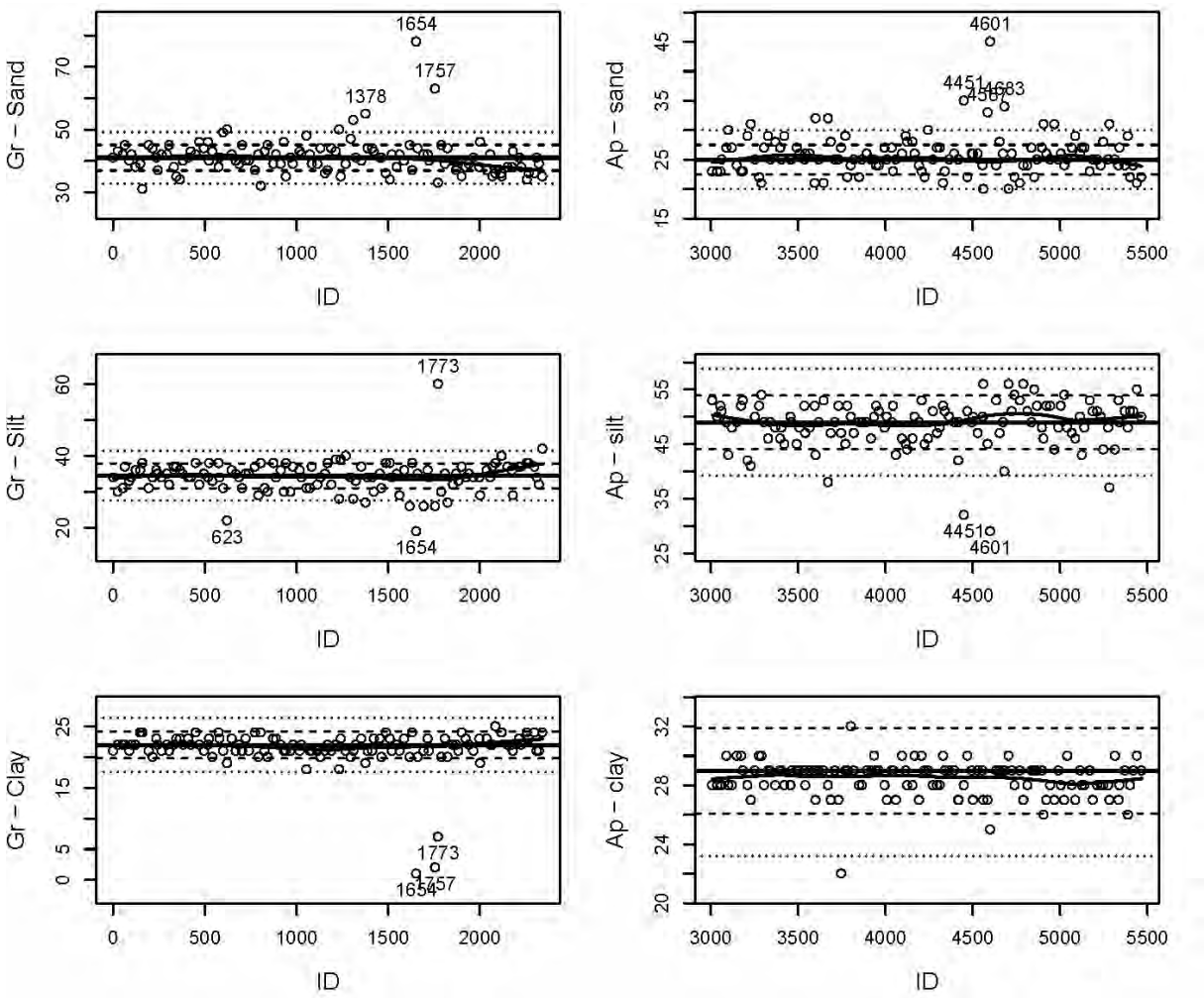

Figure 4A. X-Charts for the project standards Ap and Gr, for the prediction of the sand, silt and clay fraction. Sample number (ID) is plotted against analytical result for the standard. The thick black line indicates the median value of all standard results, the dashed line is the limit for 10%, and the dotted line for 20% deviation from the median. Standard results that show a larger deviation than 30% from the median are indicated by sample number. The trend line is a loess regression line for the standard results and would help to identify time trends or breaks in the data.

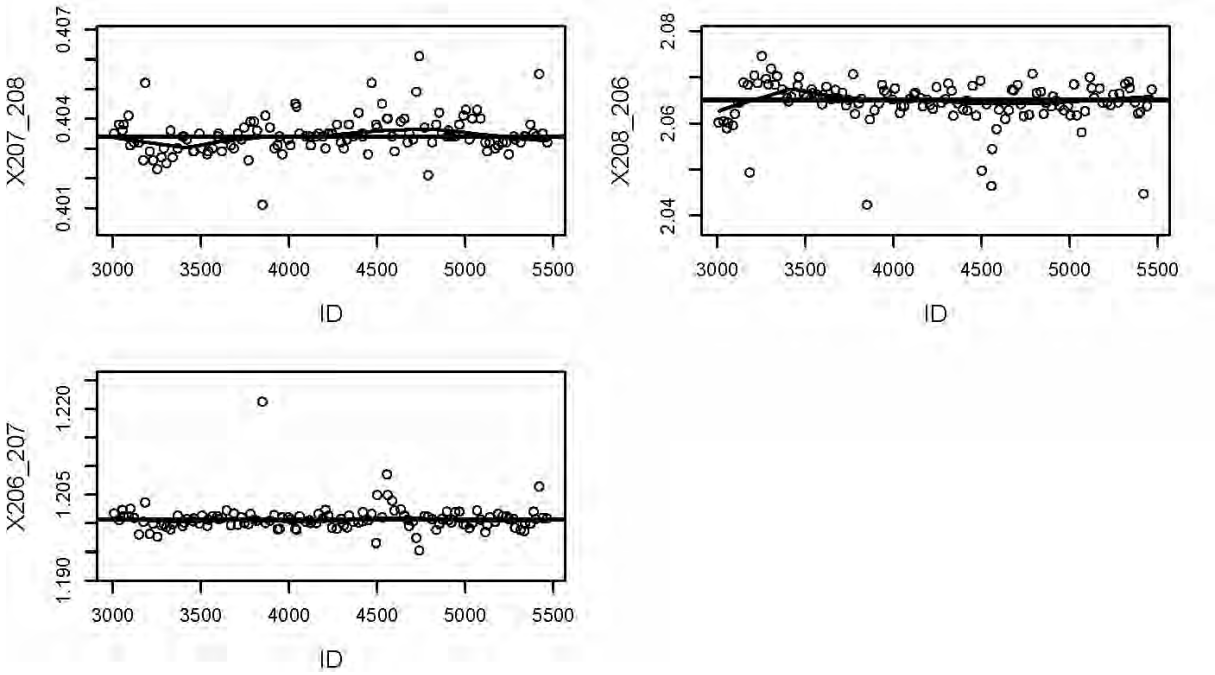

Figure 4B. X-Charts for the project standard Ap for the determination of Pb-isotope ratios by HR-ICP-MS. Sample number (ID) is plotted against analytical result for the standard. The thick black line indicates the median value of all standard results, no dashed or dotted lines are shown here because precision is much better than 10%. The trend line is a loess regression line for the standard results.

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 per cent (see Massart *et al.*, 1988). A low standard deviation indicates a high precision. The values reported herein refer to repeatability conditions, where independent test results were obtained using the same method on identical test items (*i.e.*, samples) in the same laboratory using the same extraction and the same equipment over a short time span. Repeatability conditions involve the repeated execution of the entire method from the point at which the material reaches the laboratory, and not just repeat instrumental determinations on already prepared extracts. The latter, give impressive estimates of precision, but have no relevance to the precision achieved when real samples are analysed in the laboratory, since it does not take into account the natural inhomogeneity of the sample material, which is an important source of variability.

Precision is routinely estimated by the insertion of replicates of real project samples. For the GEMAS project an analytical replicate was prepared from each field duplicate and always inserted in position "20" (20, 40, 60...) for the field duplicate that was among the preceding 18 real samples (18 + 1 standard). Precision can then be calculated for each replicate pair at the different concentration ranges that the replicates cover, while the project standard can only provide an impression of precision for each chemical element at the concentration in the standard. For obtaining an overview it is, of course, desirable to calculate the overall precision for the project from these replicates. Thus, once all replicates were retrieved from the analytical results for each pair the squared difference was calculated. The sum of these values divided by the number of samples is a measure of variability. To obtain the standard deviation

the square root of this variability measure is taken. The resulting estimate of precision, as shown in Table 4 as “Precision1”, corresponds to a CV value, because the standard deviation is divided by the overall mean of the samples. To obtain a rapid overview of "quality" of the analysis for the different elements, it can be advantageous to sort the table according to precision, and not alphabetically with respect to the elements.

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

"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.*, 90^{th} or 99^{th}), 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 5A shows these plots for the predicted particle size fractions, and Figure 5B for the Pb isotope ratios. All plots for the elements analysed in the MMI® extraction for the Ap samples are shown in Appendix 1.

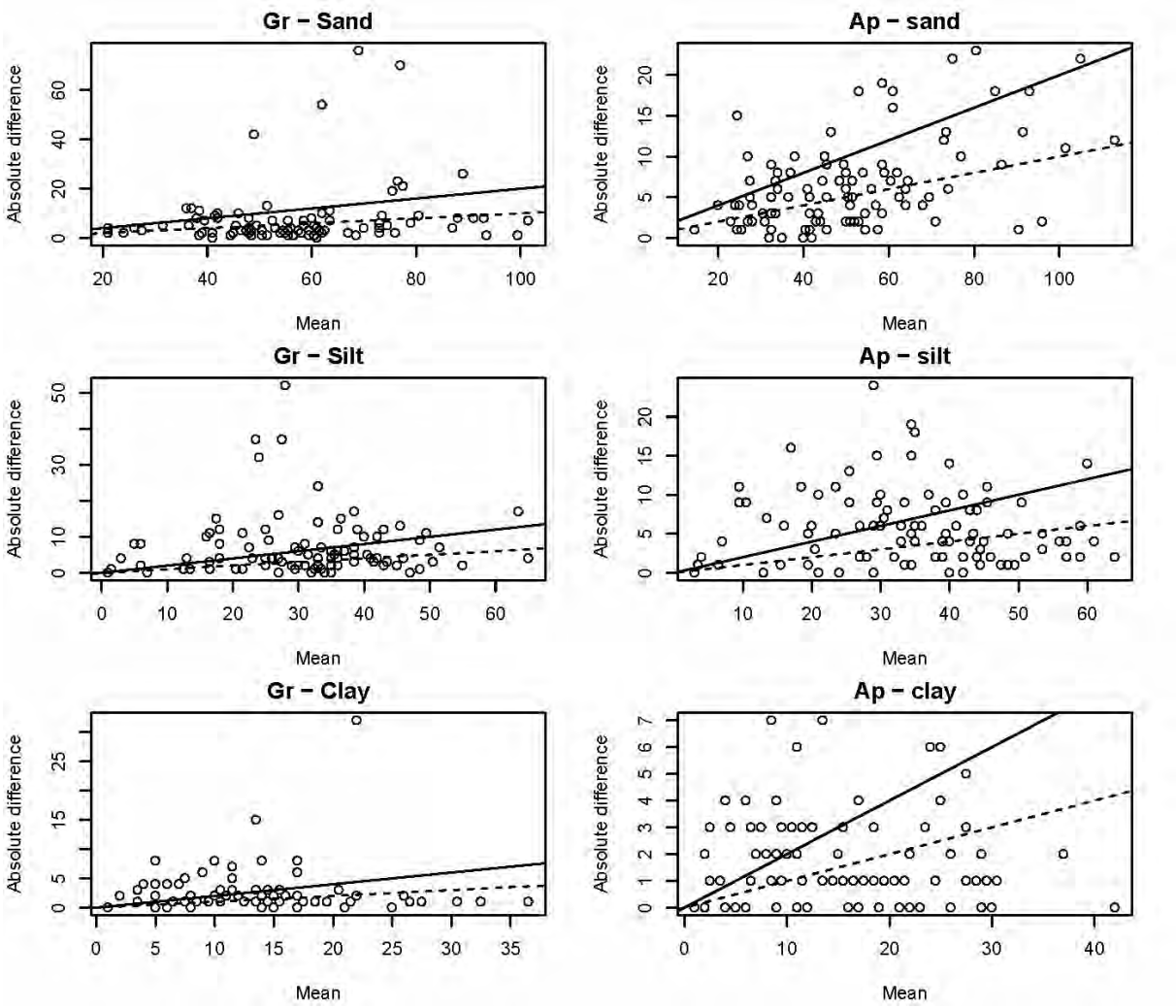

Figure 5A. "Thompson and Howarth"-plots of replicate predictions of the clay, sand and silt fractions based on the measured MIR spectra. The mean of the replicate pairs is plotted along the x-axis, the absolute difference of the two results along the y-axis. 10 % precision is indicated by the stippled line, 20% precision by the continuous line. Pairs with poor precision can easily be identified and compared to the results from the project standard within the same batch of 20 samples.

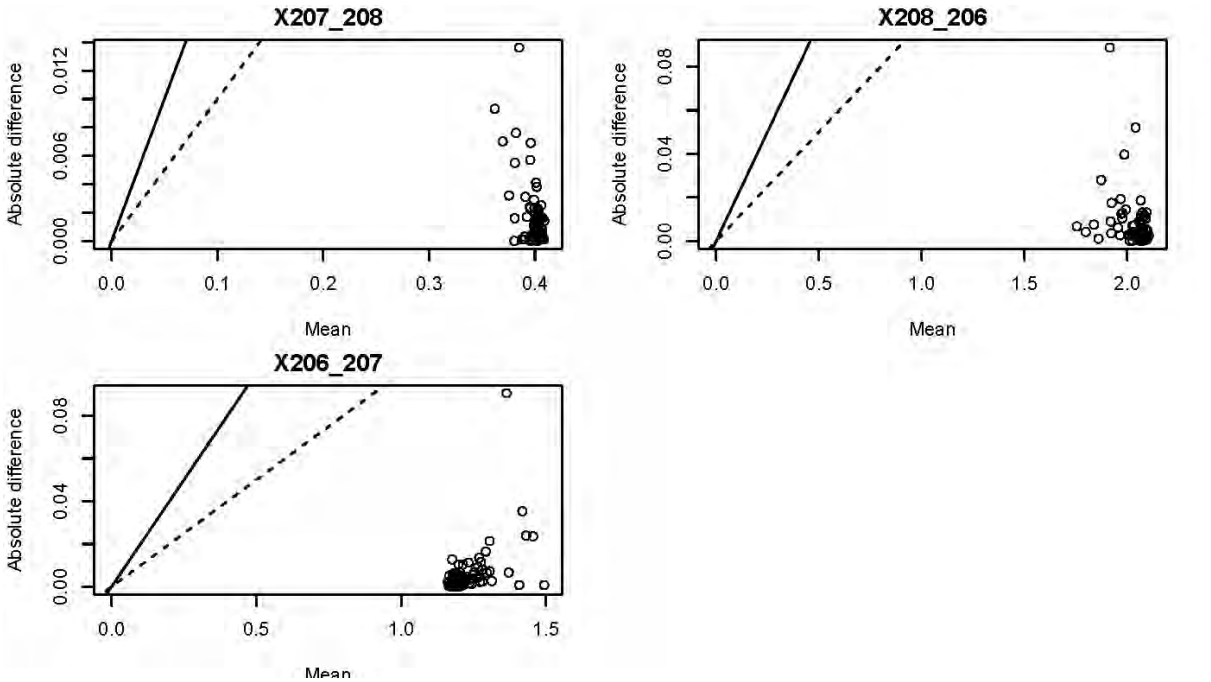

Figure 5B. "Thompson and Howarth"-plots of replicate analyses of the Pb-isotopes by HR-ICP-MS. The mean of the replicate pairs is plotted along the x-axis, the absolute difference of the two results along the y-axis. 10 % precision is indicated by the stippled line, 20% precision by the continuous line. Pairs with poor precision can easily be identified by plotting to the left and above the precision lines in the plot. The plots here highlight the excellent precision of the Pb isotope ratio determinations.

As already visible in Tables 1 and 4, the plots indicate that there exist a number of parameters where precision is rather poor. Results for these parameters may hold a certain information value, they will, however, not be used for mapping in the planned geochemical atlas. Single duplicate pairs with large deviations for parameters that showed otherwise a good precision were followed up by re-analyses of selected batches of samples or some single samples, and such deviations could usually be sorted out before accepting the data for the final file.

3.3.1 Practical detection limit and precision equation

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

Based on the results of replicate analyses, it is possible to estimate the "practical" detection limit, the detection limit valid for the GEMAS project samples, including extraction, and the precision equation for estimating precision at any concentration (Thompson and Howarth, 1978; Reimann and Wurzer, 1986; Demetriades and Karamanos, 2003; Demetriades, 2009, 2011). For this purpose it is necessary that the laboratory reports all instrument readings without any rounding or cut-off at the laboratories pre-determined

detection limits, and even sub-zero measurements must be recorded and submitted. Reporting all values in this format was part of the analytical contracts for the GEMAS project (*e.g.*, aqua regia extraction). However, for the MMI® results this was not possible, and the results are limited by the laboratory detection limit. In this case, the practical detection limit verifies the laboratory detection limit, and it also shows the possibility for an even lower detection limit for most elements, if the laboratory provided the results without rounding at their respective limits (Table 4).

The modified Thompson and Howarth (1978) method includes the estimation of regression line coefficients by the "reduced major axis line" procedure (Demetriades and Karamanos, 2003; Demetriades, 2009, 2011), referred to as the "unique line of organic correlation" or "isogonic growth line" (Kermack and Haldane, 1950; Till, 1974). The optimum regression line coefficients are, therefore, extracted for the calculation of practical detection limit and precision equation at the 95% confidence level. The "practical detection limit" and precision equation were estimated for the GEMAS project agricultural soil field duplicates and are tabulated in Table 4. "Precision 2" in Table 4 provides the overall precision of each determinand (element) at the point where the parabolic curve of precision versus concentration reaches the asymptote (or plateau) and stabilises. Precision 1, in contrast is the "classical" computation of precision adjusted for the mean and expressed as the coefficient of variation (CV) in per cent (see, *e.g.*, Massard, 1988; Reimann *et al.*, 2008).

Table 4 also shows the detection limits, as provided by the laboratory, and the practical detection limits (PDLs), as estimated using the GEMAS replicate results by the modified method of Thompson and Howarth (1986 - Demetriades and Karamanos, 2003; Demetriades, 2009, 2011). In addition, precision and the practical detection limit was estimated on the analytical replicates of GEMAS samples, which were analysed independently by the SGS laboratory, as part of its internal control. The estimated practical detection limits are in many cases considerably lower than those quoted by the laboratory. The few exceptions are usually for elements (*e.g.*, Fe, K, Mg) where the project samples returned high values, because there were no replicate pairs close to the detection limit.

Table 4. The laboratories MMI® "official" detection limits and practical detection limits calculated from the GEMAS project field duplicate-replicate samples, and SGS replicated analysis of GEMAS samples, using a modified version of Thompson and Howarth (1978). Precision (PREC) as calculated for the replicate results using two different methods (1: as described in Reimann et al., 2008; 2: as described by Demetriades and Karamanos, 2003; Demetriades, 2009, 2011). Precision in %, for method 2 at the 95% confidence level.

Element	***Unit***	***LDL***	***GEMAS Ap samples***					
			GEMAS Field duplicates			***SGS Analytical replicates***		
			PDL	***PREC 1***	***PREC 2***	***PDL***	***PREC 1***	***PREC 2***
Ag	mg/kg	0.001	0.00007	13	9	0.0007	7	4
Al	mg/kg	1	0.459	12	10	0.462	9	5
As	mg/kg	0.01	0.011	18	51	0.003	16	23
Au	mg/kg	0.0001	0.00002	20	28	0.00002	21	23
Ba	mg/kg	0.01	0.033	17	5	0.009	9	8
Bi	mg/kg	0.001	*	33	*	*	10	*
Ca	mg/kg	10	6.56	8	5	4.68	4	5
Cd	mg/kg	0.001	0.00001	7	8	0.0004	5	7
Ce	mg/kg	0.005	0.005	46	8	0.007	10	5
Co	mg/kg	0.005	0.023	16	22	0.020	15	23
Cr	mg/kg	0.001	0.002	18	11	0.004	9	7
Cs	mg/kg	0.0005	0.000003	24	9	0.00003	10	4
Cu	mg/kg	0.01	0.015	18	7	0.005	5	6

Element	*Unit*	*LDL*	*GEMAS Ap samples*					
			GEMAS Field duplicates			*SGS Analytical replicates*		
			PDL	*PREC 1*	*PREC 2*	*PDL*	*PREC 1*	*PREC 2*
Dy	mg/kg	0.001	0.001	62	8	0.001	9	5
Er	mg/kg	0.0005	0.0007	63	9	0.0005	8	6
Eu	mg/kg	0.0005	0.00001	39	10	0.00029	9	5
Fe	mg/kg	1	9.16	18	9	1.16	6	5
Ga	mg/kg	0.001	0.00007	22	27	0.00005	16	14
Gd	mg/kg	0.001	0.0008	51	6	0.0019	8	6
Hg	mg/kg	0.001	*	28	*	0.0007	64	55
In	mg/kg	0.0005	*	7	*	*	9	*
K	mg/kg	0.1	0.220	5	6	0.548	3	5
La	mg/kg	0.001	0.003	54	10	0.003	9	5
Li	mg/kg	0.005	0.0002	11	8	0.00005	14	8
Mg	mg/kg	1	1.14	5	4	0.502	6	4
Mn	mg/kg	0.01	0.582	11	14	0.368	8	10
Mo	mg/kg	0.005	0.0003	8	13	0.0002	8	7
Nb	mg/kg	0.0005	0.0002	29	24	0.00002	13	12
Nd	mg/kg	0.001	0.0004	49	9	0.0065	9	4
Ni	mg/kg	0.005	0.005	9	7	0.021	7	9
P	mg/kg	0.1	0.01	27	10	0.09	9	5
Pb	mg/kg	0.01	0.015	11	5	0.0005	8	9
Pd	mg/kg	0.001	*	*	*	*	*	*
Pr	mg/kg	0.001	0.001	49	10	0.001	9	5
Pt	mg/kg	0.001	*	*	*	*	*	*
Rb	mg/kg	0.005	0.001	7	9	0.0002	5	5
S	mg/kg	0.5	0.768	11	7	0.669	5	4
Sb	mg/kg	0.001	0.001	15	28	*	13	*
Sc	mg/kg	0.005	0.001	25	20	0.001	7	4
Se	mg/kg	0.01	0.144	27	106	0.024	25	74
Sm	mg/kg	0.001	0.00003	50	8	0.0013	9	5
Sn	mg/kg	0.001	*	49	*	0.0002	21	27
Sr	mg/kg	0.01	0.003	7	7	0.016	6	6
Ta	mg/kg	0.001	*	0	*	*	*	*
Tb	mg/kg	0.001	0.0004	55	13	0.0002	9	8
Te	mg/kg	0.01	*	*	*	*	*	*
Th	mg/kg	0.0005	0.0001	16	8	0.0009	6	4
Ti	mg/kg	0.003	0.006	35	23	0.002	26	10
Tl	mg/kg	0.0005	0.00008	10	24	0.00003	9	13
U	mg/kg	0.001	0.004	9	10	0.0001	6	6
V	mg/kg	0.001	0.001	51	23	0.001	12	10
W	mg/kg	0.001	*	25	*	0.00013	26	18
Y	mg/kg	0.005	0.005	63	8	0.001	10	8
Yb	mg/kg	0.001	0.0001	55	10	0.0008	15	6
Zn	mg/kg	0.02	0.013	14	12	0.009	7	7
Zr	mg/kg	0.005	0.001	15	12	0.001	7	4

*: too many values near DL to estimate reliable values

LDL: Laboratory detection limit

PDL: Practical detection limit, but is limited by the LDL, since concentration values below detection limit were not reported

PREC 2: Overall Precision is estimated where the precision versus concentration curve reaches a plateau

The new grain size data based on the MIR spectra, predicted using a European soil model, based on particle size analyses performed at the BGR laboratory according to the DIN/ISO methods, are by far better than the original data set received from laser diffraction (Reimann *et al.*, 2011). There is also an overall improvement in the precision, estimated by the two different methods (Table 5), again in comparison to the previous results (Reimann *et al.*, 2011). The calculated practical detection limit on the MIR method replicate results, using the European soil model, is quite good, suggesting that the sensitivity of this particular method is fit-for-purpose with respect to the GEMAS project.

Table 5. Practical detection (PDL) limits for sand, silt and clay 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; Demetriades, 2009, 2011). Precision in % for method 2 at the 95% confidence level.

Agricultural soil samples (N=104 pairs)				***Grazing land soil samples (N=93 pairs)***			
Parameter	***PDL %***	***PREC 1 %***	***PREC 2 %***	***Parameter***	***PDL %***	***PREC 1 %***	***PREC 2 %***
Sand	0.421	12	24	Sand	9.529	18	29
Silt	1.334	15	31	Silt	0.064	25	34
Clay	0.670	11	17	Clay	0.498	26	26

3.4 Analysis of variance (ANOVA)

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

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

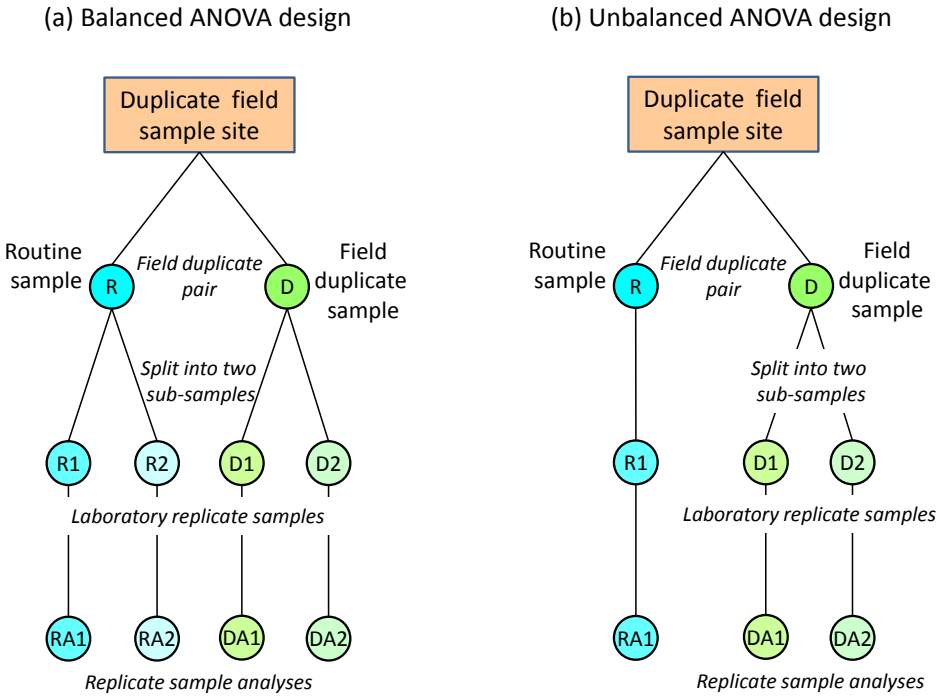

Figure 6. Balanced (left)and unbalanced (right) ANOVA design for the estimation of natural (geochemical), sampling (at site) and analytical variance. At every 20th sample site, or, in small countries with more than 10, but less than 20 sample sites, at one of the sample sites, a duplicate agricultural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

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

Table 6 shows the results of an unbalanced ANOVA for the MMI® analysis of the GEMAS Ap-samples and the distribution between "geochemical (natural)", "sampling (site)" and "analytical (anal.)" variability. The median value for all samples is also provided.

Table 6. Results of an unbalanced ANOVA (%) for the MMI® extraction, GEMAS Ap-samples. All variables were log-transformed prior to the calculation. Left hand side ANOVA results in alphabetical order according to element, and right hand side sorted according to increasing "geochemical (natural)" variation for an easy identification of "problematic" elements (less than 80% natural variation). Notation: natural (geochemical); site (sampling); analytical.

Element	***GEMAS Ap samples***				***Element***	***SORTED natVar***
	Median	***natural***	***site***	***analytical***		
	mg/kg	***%***	***%***	***%***		***%***
Ag	0.014	97.4	0.0	2.6	Pd	*
Al	61	97.4	0.0	2.6	Pt	*
As	0.02	92.5	2.2	5.2	Te	8.2
Au	0.0003	94.2	0.0	5.8	Se	75.4
Ba	1.09	96.5	0.0	3.5	Hg	87.5
Bi	0.0005	96.8	0.0	3.2	K	90.7

Element	*GEMAS Ap samples*					*Element*	*SORTED natVar*
	Median	*natural*	*site*	*analytical*			
	mg/kg	*%*	*%*	*%*			*%*
Ca	595	96.3	3.2	0.6		In	92.3
Cd	0.054	97.6	1.4	1.0		As	92.5
Ce	0.135	93.9	1.6	4.4		Pb	92.9
Co	0.1815	95.7	3.2	1.1		Th	93.1
Cr	0.065	97.0	0.0	3.0		Sc	93.2
Cs	0.0007	96.3	1.1	2.6		Eu	93.3
Cu	1.34	94.0	4.7	1.3		Sn	93.4
Dy	0.035	95.5	0.0	4.5		Tl	93.6
Er	0.0202	96.6	1.0	2.4		Sm	93.7
Eu	0.0075	93.3	2.2	4.5		Ce	93.9
Fe	31	97.7	0.6	1.8		Tb	93.9
Ga	0.002	94.3	0.0	5.7		Cu	94.0
Gd	0.036	94.2	0.0	5.8		Au	94.2
Hg	0.0005	87.5	5.2	7.4		Gd	94.2
In	0.00025	92.3	0.0	7.7		Ga	94.3
K	64.2	90.7	8.9	0.4		S	94.4
La	0.049	96.9	0.0	3.1		Sb	94.6
Li	0.0025	97.0	0.6	2.5		Nd	95.0
Mg	52	97.1	2.5	0.4		Mn	95.1
Mn	19.6	95.1	3.9	1.0		Mo	95.2
Mo	0.015	95.2	0.0	4.8		Ti	95.2
Nb	0.0009	96.5	0.0	3.5		Rb	95.4
Nd	0.1015	95.0	1.3	3.7		Dy	95.5
Ni	0.652	98.3	1.2	0.5		Y	95.6
P	4	98.3	0.7	1.0		Co	95.7
Pb	0.32	92.9	3.6	3.5		V	96.1
Pd	0.0005	*	*	*		Ca	96.3
Pr	0.02	96.3	2.2	1.5		Cs	96.3
Pt	0.0005	*	*	*		Pr	96.3
Rb	0.069	95.4	4.0	0.6		Ba	96.5
S	24.2	94.4	0.0	5.6		Nb	96.5
Sb	0.002	94.6	2.9	2.5		Er	96.6
Sc	0.016	93.2	3.0	3.8		Bi	96.8
Se	0.01	75.4	6.6	18.1		La	96.9
Sm	0.029	93.7	2.3	4.1		Yb	96.9
Sn	0.0005	93.4	0.0	6.6		Cr	97.0
Sr	1.67	97.6	1.7	0.7		Li	97.0
Ta	0.0005	99.3	0.7	0.0		W	97.0
Tb	0.005	93.9	0.0	6.1		Mg	97.1
Te	0.005	8.2	54.8	37.0		Zn	97.1
Th	0.0221	93.1	0.4	6.5		Ag	97.4
Ti	0.038	95.2	0.0	4.8		Al	97.4
Tl	0.0006	93.6	5.3	1.1		Zr	97.4

Element	GEMAS Ap samples					Element	SORTED natVar
	Median	natural	site	analytical			
	mg/kg	%	%	%			%
U	0.084	98.5	1.1	0.4		Cd	97.6
V	0.027	96.1	0.1	3.8		Sr	97.6
W	0.001	97.0	0.5	2.6		Fe	97.7
Y	0.1835	95.6	0.0	4.4		Ni	98.3
Yb	0.016	96.9	2.1	1.0		P	98.3
Zn	0.76	97.1	1.9	1.0		U	98.5
Zr	0.051	97.4	0.0	2.6		Ta	99.3

*: Too many values near DL

Table 6 demonstrates that for the majority of elements the data quality is good to excellent, and that the results can be reliably mapped. The most problematic elements in the MMI® Ap data set, where care is needed when mapping and using the results are Pd, Pt, Te and Se. Surprisingly for quite a few elements Ramsey's 4% limit at the analytical level (Ramsey, 1998) is exceeded: As, Au, Ce, Dy, Eu, Ga, Gd, Hg, In, Mo, S, Se, Sm, Sn, Tb, Te, Th, Ti and Y; the results, however, are saved because of the very small sampling variance. The ANOVA results indicate that even for these elements it would be possible to overcome the problems by further improving their detection limits or by analysing all samples several times and using the median as the "analytical result".

Table 7 shows the unbalanced ANOVA results for the MIR based prediction of the particle size: sand, silt and clay. For the Ap samples all three are within acceptable limits, though the prediction of the clay fraction is clearly better. For the Gr samples the quality of the prediction of the silt fraction is poor and for the sand fraction the 20% level of the technical variance is almost reached. Again the prediction of the clay fraction is clearly better. When assessing all the results of QC (standards, precision and ANOVA), the only size fraction that is really fit for the purposes of the GEMAS project is the clay fraction of both Ap and Gr samples, which is also the conclusion reached by Janik *et al.* (2011).

Table 7. Unbalanced ANOVA results based on the GEMAS Ap- and Gr-field duplicates and replicate samples for sand, silt and clay determined by the MIR method. All variables were log-transformed prior to the calculation. Notation: natural (geochemical); site (sampling); analytical.

GEMAS Ap samples (N=104)					GEMAS Gr samples (N=93)				
Parameter	Overall median %	Variance %			Parameter	Overall median %	Variance %		
		natural	site	analytical			natural	site	analytical
Sand	48	89.0	3.7	7.4	Sand	56	80.4	0	19.6
Silt	36	84.4	3.6	12.0	Silt	32.5	69.7	0	30.3
Clay	13.5	91.3	3.1	5.6	Clay	12	90.8	0	9.2

For the Pb isotopes the unbalanced ANOVA (Table 8) indicates again that the data quality is good and that the results can be used to provide reliable maps at the European scale.

Table 8. Unbalanced ANOVA results based on the GEMAS Ap-replicate samples for the determination of Pb-isotope ratios by HR-ICP-MS. Notation: natural (geochemical); site (sampling); analytical.

Ratio	***GEMAS Ap samples***			
	Median	***natural***	***site***	***analytical***
		%	***%***	***%***
$^{206}Pb/^{207}Pb$	1.202	92.6	5.9	1.4
$^{207}Pb/^{208}Pb$	0.403	85.4	10.1	4.5
$^{208}Pb/^{206}Pb$	2.067	93	5.1	1.9

In general, the ANOVA results can be taken as an indication of "good (reproducible) sampling". In conclusion, it appears that agricultural soil, as for the aqua regia extraction and XRF, is an especially suitable and easy sample material for continental scale geochemical mapping exercises (Reimann *et al.*, 2009b, 2011).

4. EXTRACTION POWER OF MMI® METHOD

The extractability of elements in an aqua regia extraction with respect to XRF results (true total concentrations) was discussed in the second GEMAS project QC report (Reimann *et al.*, 2011). The MMI® method is a partial method, and used up to now in only one continental wide project, the Australian National Geochemical Survey (Caritat *et al.*, 2011). Hence, it is important to evaluate its “extraction power” in the GEMAS project with respect to both aqua regia and XRF results.

Table 9 displays the calculated MMI®-extractability (MMI®/other method *100) results in comparison to the total element concentrations (XRF) and to the aqua regia extraction in per cent. MMI® extractability shows great variability, depending on the element, varying from 30 to 37% (*e.g.*, Cd, Au, Ag) to less than <1% (*e.g.*, Sb, Th, Sc, P, Al) with respect to aqua regia extractions, and 5.6 to 10.3% (*e.g.*, U, Ca, Cu) to less than <1% (*e.g.*, Sb, Th, Sc, P) with respect to XRF total results. Note that “extractability” was calculated here based on the median results for the compared methods and not sample per sample. It is quite apparent from the extractability values that the MMI® method is a very weak extraction for all elements, determined on the GEMAS Ap samples, and leaches only the weakly adsorbed elements from soil. Hence, it should be a good method for the assessment of element bioavailability, but also in mineral exploration for the location of concealed mineralisation.

Table 9. Extractability of the elements analysed by the MMI® method in relation to aqua regia extraction (near total), and XRF (true total concentrations). Left hand side in alphabetical order according to element names; right hand side sorted according to decreasing extractability of the MMI® method.

Element	GEMAS Ap-samples				
	MMI Q50	Aqua regia extraction		XRF determinations	
		Aqua regia Q50	% Extract.	XRF Q50	% Extract.
	mg/kg	mg/kg		mg/kg	
Ag	0.014	0.038	36.8	-	-
Al	62	10,993	0.564	55,069	0.113
As	0.02	5.48	0.365	7.00	0.286
Au	0.0003	0.0009	33.3	-	-
Ba	1.09	62	1.76	384	0.284
Bi	<0.001	0.17	-	1.50	-
Ca	600	3,034	19.8	8,494	7.06
Cd	0.054	0.18	30.0	-	-
Ce	0.135	28.4	0.475	58.0	0.233
Co	0.182	7.5	2.43	9.00	2.02
Cr	0.065	20	0.325	62.0	0.105
Cs	0.0007	1.1	0.064	5.00	0.014
Cu	1.34	14.5	9.24	13.0	10.3
Fe	31	17,200	0.180	24,550	0.126
Ga	0.002	3.43	0.058	12.0	0.017
Hg	<0.001	0.03	-	-	-
In	<0.0005	0.018	-	-	-
K	64.2	1,250	5.14	15,819	0.406
La	0.049	14.3	0.343	23.0	0.213
Li	0.0025	11.4	-	-	-
Mg	52	2,860	1.82	5,488	0.948
Mn	19.65	445	4.42	604	3.253
Mo	0.015	0.42	3.57	1.00	1.500
Nb	0.0009	0.48	0.188	13.0	0.007
Ni	0.652	14.7	4.44	20.0	3.26
P	4.1	653	0.628	786	0.522
Pb	0.32	15.8	2.03	21.0	1.52
Pd	<0.001	<0.001	-	-	-
Pt	<0.001	<0.001	-	-	-
Rb	0.069	14.3	0.483	73.0	0.095
S	24.2	207	11.7	-	-
Sb	0.002	0.234	0.855	2.50	0.080
Sc	0.016	2.15	0.744	8.00	0.200

Sorted GEMAS Ap samples according to % Extractability of the MMI® method results			
Element	Aqua regia	Element	XRF
	% Extract.		% Extract.
Ag	37	Cu	10.3
Au	33	Ca	7.06
Cd	30	U	5.60
Ca	20	Ni	3.26
S	12	Mn	3.25
U	11	Co	2.02
Sr	9.3	Sr	1.66
Cu	9.2	Pb	1.52
K	5.1	Mo	1.50
Ni	4.4	Zn	1.26
Mn	4.4	Mg	0.948
Mo	3.6	Y	0.681
Zr	2.8	P	0.522
Se	2.8	K	0.406
Y	2.8	As	0.286
Co	2.4	Ba	0.284
Pb	2.0	Th	0.246
Mg	1.8	Ce	0.233
Ba	1.8	La	0.213
Zn	1.7	Sc	0.200
W	1.4	Fe	0.126
Sb	0.85	Al	0.113
Th	0.76	Cr	0.105
Sc	0.74	Rb	0.095
P	0.63	Sb	0.080
Al	0.56	W	0.040
Tl	0.50	V	0.040
Rb	0.48	Zr	0.020
Ce	0.48	Ga	0.017
As	0.36	Cs	0.014
La	0.34	Nb	0.007
Cr	0.33	Ti	0.001
Nb	0.19		

Element	GEMAS Ap-samples				
	MMI Q50	Aqua regia extraction		XRF determinations	
		Aqua regia Q50	% Extract.	XRF Q50	% Extract.
	mg/kg	mg/kg		mg/kg	
Se	0.01	0.354	2.82	-	-
Sn	<0.001	0.723	-	2.00	-
Sr	1.675	18.1	9.25	101	1.66
Ta	<0.001	<0.005	-	2.50	-
Te	<0.01	<0.02	-	-	-
Th	0.0221	2.89	0.765	9.00	0.246
Ti	0.038	86	0.044	3,621	0.001
Tl	0.0006	0.12	0.500	-	-
U	0.084	0.77	10.9	1.50	5.60
V	0.027	25.4	0.106	68.0	0.040
W	0.001	0.073	1.37	2.50	0.040
Y	0.184	6.69	2.75	27.0	0.681
Zn	0.76	45	1.69	60.5	1.26
Zr	0.051	1.79	2.85	259	0.020

Sorted GEMAS Ap samples according to % Extractability of the MMI® method results				
Element	Aqua regia		Element	XRF
	% Extract.			% Extract.
Fe	0.18			
V	0.11			
Cs	0.064			
Ga	0.058			
Ti	0.044			

5. RESULTS – SOME FIRST MAPS

One additional quality criterion for a data set will be the appearance of the maps when the analytical results are plotted (Reimann *et al.*, 2008). Figure 7 shows a map of the clay size fraction in European agricultural soils (Ap), Figure 8 a map for the $^{206}Pb/^{207}Pb$-ratio and Figure 9 a map for Cs as determined in an MMI® extraction of the Ap samples. The question to be asked is, "*do the maps contain any clear regional features or could they as easily represent random variability due to a too low sample density or sampling and analytical errors, indicated by a lack of any significant regional trends*"? All three maps show, however, clear regional scale features. This is the final indication of the high quality of the GEMAS project analytical results, which has been achieved by applying strict independent quality control procedures. Information about data quality, or better suitability for mapping, can also be directly derived from the semi-variogram analysis, if kriging is used as the interpolation method (Reimann *et al.*, 2008).

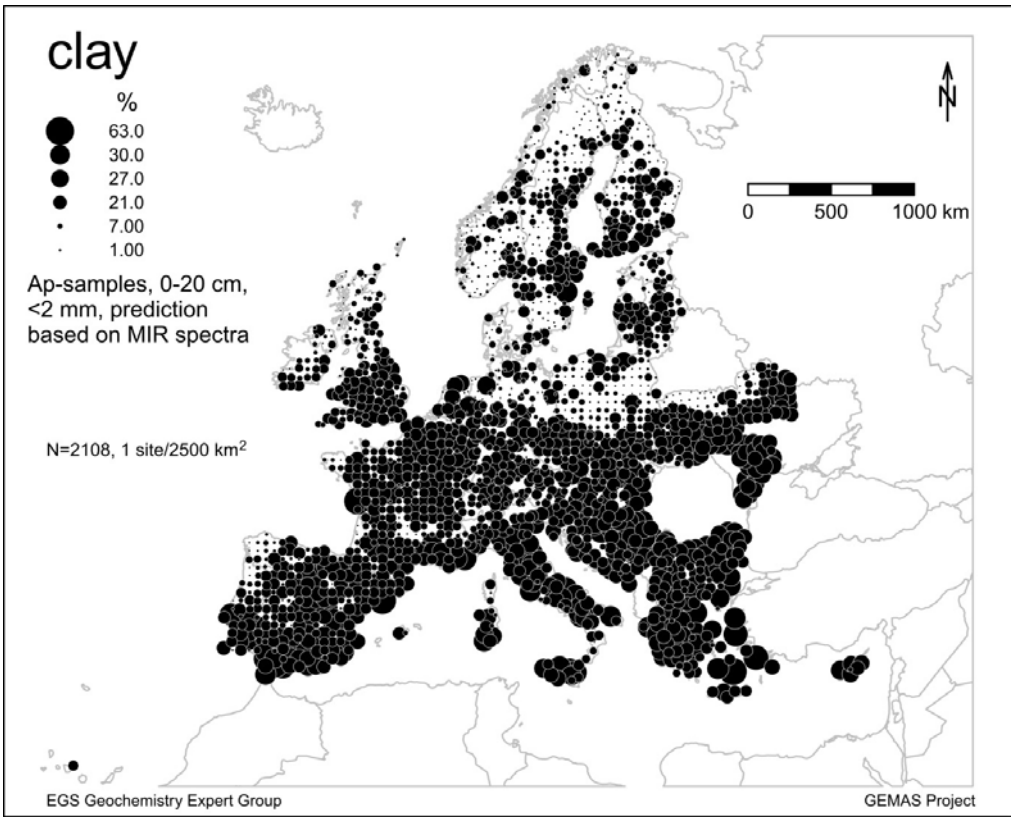

Figure 7. Growing dot map (for a description and discussion of the mapping technique see Reimann et al., 2008) for "% clay" in agricultural soil of Europe (GEMAS Ap-samples).

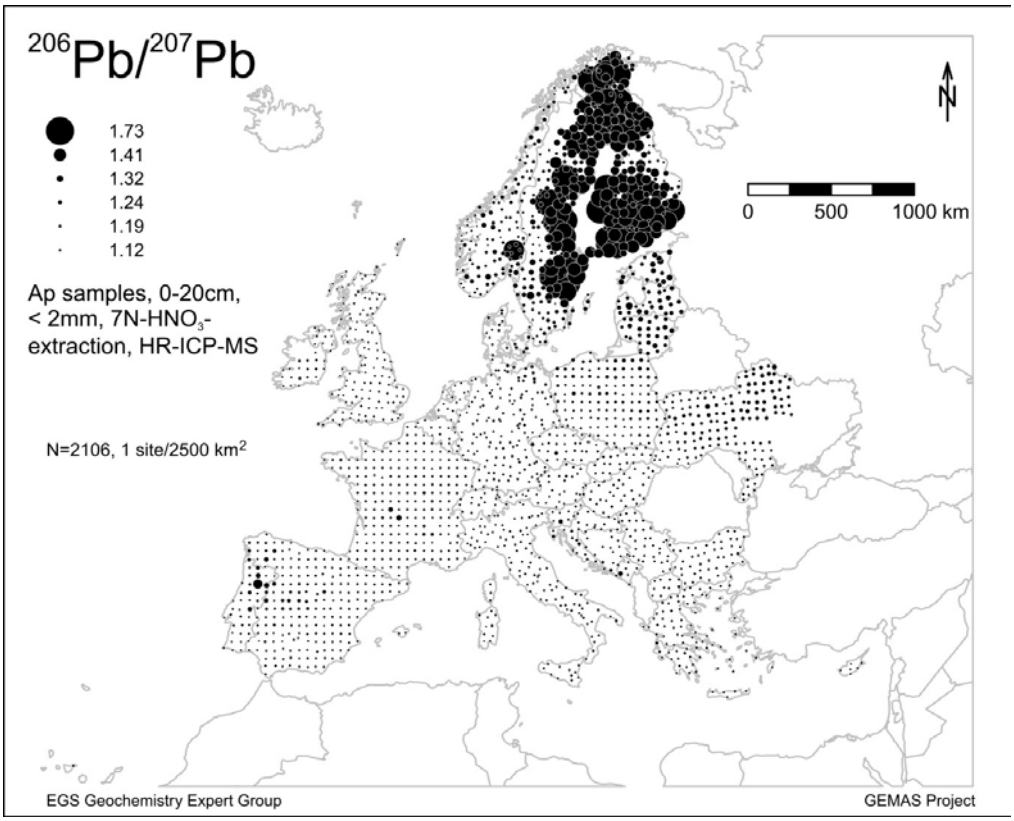

Figure 8. Growing dot map (for a description and discussion of the mapping technique see Reimann et al., 2008) of the $^{206}Pb/^{207}Pb$ ratio in agricultural soils of Europe (GEMAS Ap-samples).

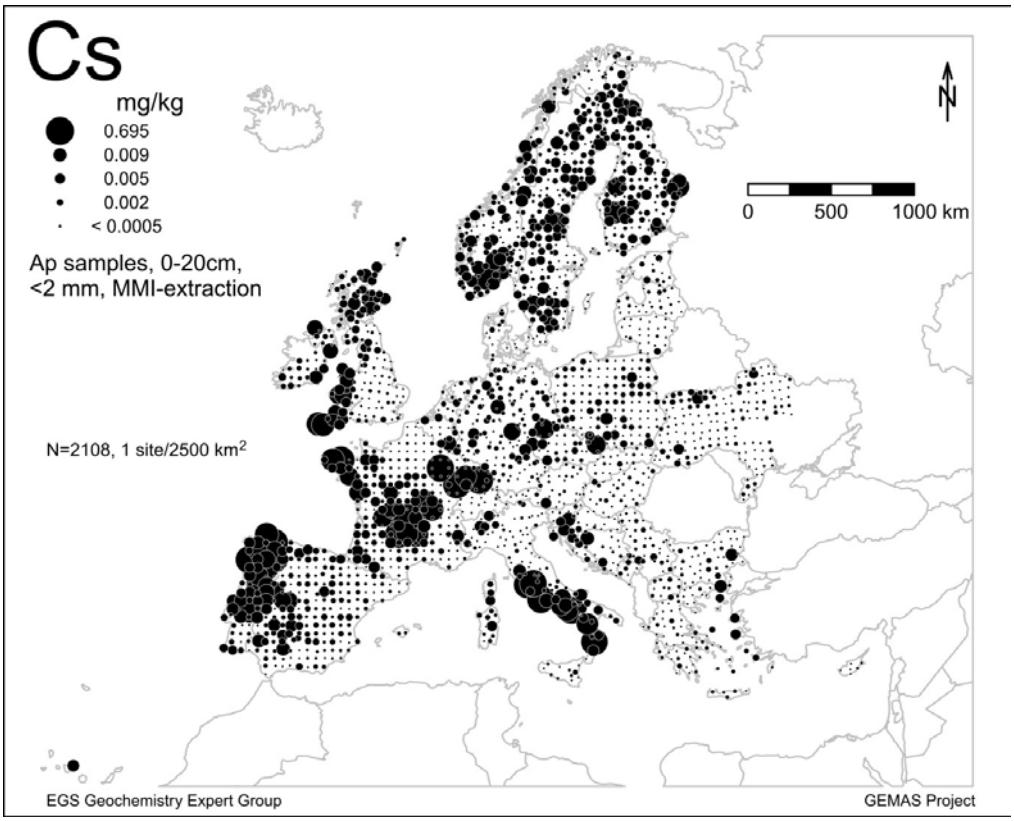

Figure 9. Growing dot map (for a description and discussion of the mapping technique see Reimann et al., 2008) of Cs following a MMI®-extraction in agricultural soils of Europe (GEMAS Ap-samples).

6. TRUENESS OF GEMAS ANALYTICAL RESULTS – THE RING TEST

The chosen procedures for QC within the GEMAS project as documented in Reimann *et al*. (2009a, 2011) and this report here guarantee that the data are fit-for-purpose (in case of the GEMAS project for the plotting of reliable geochemical maps, depicting processes determining the distribution of measured elements/parameters at the European scale), they can, however, not provide information about the "*trueness*" of analytical results. Analytical results can be highly accurate without reflecting the 'true' concentration value of a chemical element. In a geochemical mapping project, high accuracy is of primary importance to reflect regional scale differences and needs as such more attention than the "*trueness*" of analytical results; whether the data reflect the '*true*' concentrations of an investigated element is in this connection a secondary consideration. However, when wishing to compare the data to results from other investigations, trueness, or better the documentation of the deviation of project results from the "*true*" values, the bias, becomes suddenly very important. '*Bias*' is the difference between an analytical result and an accepted reference value (Reimann et al., 2008; Bièvre et al., 2011; Demetriades, 2011; Johnson, 2011).

The trueness of the analytical results can be judged directly if certified reference materials were hidden between the real project samples, unrecognisable by the laboratory. However, certified reference materials:

(1) Are expensive and valuable because the available amount is limited, and it is unrealistic to insert (hide) a certified reference material several times among the real project samples weighing usually 50 – 100 g (or more) each.
(2) May look different than the project samples in terms of colour and/or texture and are then easily recognisable as "special" for the laboratory.

(3) Are often not certified for the same sequence of parameters/elements that are reported by the project.
(4) May have a different matrix than the project samples, and
(5) May have been used to calibrate the analytical instruments.

Thus, for the GEMAS project a different approach was chosen. Two large project standards, Ap and Gr, were produced. These standards were hidden more than 100 times in each of the two sample sets (Ap and Gr), and analysed together with the real project samples.

To estimate the bias of the GEMAS project results, the two project standards were sent out to 21 laboratories/institutions in16 countries to carry out a proficiency test (Kriete, 2011). A proficiency test is originally designed to check the analytical performance of the participating laboratories. A laboratory can pass such a test or fail – for certain elements, or even a whole analytical technique. If a sufficient number of laboratories have participated in such a proficiency test, it is also possible to establish the analysed samples as reference materials – with reference values including their uncertainty. For the participating laboratories, their performance and whether they "passed of failed" is of greatest interest. For the GEMAS project the most important result was, however, to obtain reference values for the two standards (Ap and Gr), and to document the bias of the methods chosen for the project in relation to these reference values. The performance of the laboratories was the main result of an internal report to all laboratories, attached here as *Appendix2*.

In total, 21 institutions or laboratories from 16 countries agreed to participate in the GEMAS ring test and submitted analytical data (Table 10). The samples AP and GR were distributed to the participants in April 2010. The final deadline for submitting results was July 2011 in order to include as many data sets as possible. Several institutions provided data from different laboratories or sections applying different analytical methods. Since these were treated at different laboratories in total 36 data sets were available (Table 10). The data for the project standards, as obtained during the routine analytical work for the GEMAS project, were taken from the QC-reports (Reimann *et al*., 2009a, 2011) and treated as a "normal" laboratory contribution.

For the assessment, the consensus value of all participants was established as '*assigned value*' or '*reference value*'. This '*assigned value*' is regarded as the best estimate of the "*true value*". According to the recommendation of ISO 13528 robust statistics were applied for the estimation of consensus values. Table 11 shows the established reference values in comparison to the results received in the GEMAS project. Results demonstrate that for the majority of elements the GEMAS results are rather close to the reference value. It is clear that the aqua regia method for the GEMAS project is a weak variant of the many existing varieties of aqua regia extractions. The elements Ti, Ga, K, Na, Cs show a bias of over -40%.

Table 10. Participating laboratories in the ring test of the GEMAS project for the Ap and Gr standards.

Country	***Institution***	***No. Data Sets***	***Analytical Methods***
Germany	Federal Institute for Geoscience and Natural Resources	7*	FB-XRF; ICP-MS, ICP-OES PP-XRF
	TU Freiberg	4	FB-XRF; ICP-MS, ICP-OES PP-XRF
	Biolab	1	ICP-OES
Austria	Geological Survey of Austria	1	PP-XRF
Australia	Geoscience Australia, Canberra	1	XRF, ICP-MS
Canada	ACME Analytical Laboratories	1*	ICP-MS
United Kingdom	British Geological Survey	3	PP/FB-XRF, ICP-MS
Czech Republic	Czech Geological Survey	3	AAS, wet chemistry, ICP-MS, PP-XRF
Switzerland	University Lausanne	1	FB/PP XRF
Slovakia	Geological Survey of the	2	ICP-OES, AAS

Country	*Institution*	*No. Data Sets*	*Analytical Methods*
	Slovak Republic		
Poland	Polish Geological Institute	3	PP-XRF, ICP-OES, ICP-MS
Portugal	National Laboratory of Energy and Geology	2	XRF, ICP-OES, AAS
F.Y.R.O.M.	Cyril and Methodius University Skopje	1	ICP-OES, AAS
Italy	University of Bologna	1	PP-XRF
Norway	Geological Survey of Norway (NGU)	1	FB/PP XRF, ICP-OES
Spain	Geological Survey of Spain (IGME)	2	XRF, ICP-MS
Sweden	Geological Survey of Sweden (SGU)	1	ICP-MS
United States	US Geological Survey	1	ICP-OES,-/MS, AAS

*: this laboratory delivered also the analytical results used for the GEMAS project

Table 11. Results of the ring test of the Ap and Gr standards showing the assigned values, the mean value of the GEMAS QC data and the relative bias. N=number of laboratories contributing to this parameter (if N<5 no assigned value provided – see Table 12), only parameters/analytes that are reported in the GEMAS project are provided, for further elements and more details on the statistics behind this table see ring test report as delivered to the participating laboratories (Appendix 2).

	GEMAS Ap standard					*GEMAS Gr standard*			
	Assigned value	*N*	*GEMAS QC data*	*Relative bias*		*Assigned value*	*N*	*GEMAS QC data*	*Relative bias*
TOTAL	***wt%***		***wt%***	***%***		***wt%***		***wt%***	***%***
SiO_2	56.7	14	56.8	0.2		72.7	14	72.9	0.3
TiO_2	0.693	18	0.697	0.6		0.651	18	0.652	0.2
Al_2O_3	12.9	18	12.8	-0.8		11.4	18	11.2	-1.8
Fe_2O_3	5.3	18	5.25	-0.9		4.01	18	3.86	-3.7
MnO	0.097	19	0.098	1.0		0.081	18	0.08	-1.2
CaO	5.72	18	5.57	-2.6		0.511	18	0.482	-5.7
MgO	2.34	17	2.37	1.3		0.969	17	0.968	-0.1
Na_2O	1.05	16	1.03	-1.9		1.23	17	1.2	-2.4
K_2O	2.44	17	2.3	-5.7		2.27	17	2.16	-4.8
P_2O_5	0.225	15	0.225	0.0		0.198	17	0.196	-1.0
LOI	12.2	14	12.4	1.6		5.78	14	6.06	4.8
TOTAL	***mg/kg***	***N***	***mg/kg***	***%***		***mg/kg***	***N***	***mg/kg***	***%***
As	10	20	11	8.5		11	20	11	2.7
Ba	346	25	342	-1.1		372	25	360	-3.2
Bi	0.36		<3			0.30		<3	
C			2700					1100	
Ce	63	18	65	3.8		60	17	62	3.1
Co	14	23	14	-2.4		11	23	11	-2.5
Cr	100	25	111	11		84	25	97	15
Cs	8.2	12	8	-2.9		5.8	11	6	3.0
Cu	25	24	19	-23		22	24	18	-19

	GEMAS Ap standard					*GEMAS Gr standard*			
	Assigned value	***N***	***GEMAS QC data***	***Relative bias***		***Assigned value***	***N***	***GEMAS QC data***	***Relative bias***
Ga	16	16	16	-0.7		14	16	13	-5.0
Hf	4.4	9	<5			5.9	10	8	+26
La	32	16	24	-25		30	15	27	-10
Mo	0.97		<2			1.05		<2	
Nb	13	18	14	3.7		12	18	13	4.2
Ni	52	25	52	-0.3		39	25	38	-2.6
Pb	22	23	21	-4.3		20	23	19	-3.9
Rb	110	20	99	-10		91	20	86	-5.4
S	331	9	140	-68		265	9	<100	
Sb	1.9	9	<5			2.3	9	<5	
Sc	13	16	13	-0.2		10	16	9	-13
Sn	3.4	11	<4			3.7	11	<4	
Sr	149	23	148	-0.5		91	23	90	-1.4
Ta	1.1	5	<5			0.95	5	<5	
Th	10	17	11	9.2		9.4	17	12	27.7
U	2.8	13	3	6.6		2.4	13	<3	
V	104	25	103	-1.0		80	25	77	-3.5
W	1.9	7	3	47		1.5	7	<3	
Y	23	20	29	25		21	20	25	19
Zn	91	25	92	1.2		69	24	67	-2.6
Zr	175	19	178	1.9		224	19	227	1.5
Aqua regia	***mg/kg***	***N***	***mg/kg***	***%***		***mg/kg***	***N***	***mg/kg***	***%***
Ag			0.054					0.030	
Al	1847	10	1307	29		1688	10	1138	33
As	9.6	13	8.7	-9.6		10	13	9.6	-7.0
Au			0.0017					0.0017	
Ba	77	11	71	-7.9		82	11	71	-14
B			4.5					2.6	
Be	0.91	7	0.65	-28		0.92	7	0.64	-30
Bi	0.33	6	0.36	7.9		0.28	5	0.32	15
Ca	38094	10	37307	2.1		2687	10	2359	12
Cd	0.21	7	0.22	4.9		0.18	7	0.2	13
Ce	35	6	28	-20		39	6	27	-32
Co	12	12	13	11		10	12	10	-0.6
Cr	35	12	27	-23		31	12	24	-23
Cs	2.7	5	1.6	-41		2.0	5	1.1	-46
Cu	24	13	24	1.3		22	13	22	-0.2
Fe	30214	10	28396	6.0		24339	10	22171	8.9
Ga	8.0	6	3.6	-55		7.6	6	3.4	-55
Ge			0.043					0.037	
Hf			0.079					0.059	
Hg			0.10					0.12	

	GEMAS Ap standard					*GEMAS Gr standard*			
	Assigned value	***N***	***GEMAS QC data***	***Relative bias***		***Assigned value***	***N***	***GEMAS QC data***	***Relative bias***
In			0.033					0.023	
K	3976	8	2357	41		3553	8	2100	41
La	16	7	13	-17		18	7	13	-30
Li	26	9	22	-16		21	9	15	-28
Mg	10613	11	9708	8.5		4046	11	3256	20
Mn	689	11	682	1.1		604	11	565	6.4
Mo	0.77	5	0.7	-8.8		0.88	5	0.79	-10
Na	119	7	52	56		67	6	37	44
Nb			0.22					0.26	
Ni	44	13	47	5.9		36	13	34	-6.1
P	851	7	886	-4.1		781	7	772	1.1
Pb	17	12	18	5.1		15	12	16	6.3
Pd			0.0017					0.0003	
Pt			0.0009					0.0004	
Rb	30	5	17	-42		28	5	14	-49
Re			0.00013					0.00015	
S			184					119	
Sb	1.0	7	0.92	-9.2		1.4	7	1.2	-16
Sc	5.1	7	4.3	-15		4.0	7	3.1	-23
Se			0.57					0.35	
Sn			0.89					1.5	
Sr	81	11	82	0.9		22	11	20	-7.7
Ta			0.0015					0.00092	
Te			0.039					0.025	
Th	4.8	5	4.7	-1.7		4.5	5	3.9	-14
Ti	90	6	30	67		120	6	48	60
Tl	0.19	5	0.14	-26		0.19	5	0.14	-26
U	0.91	5	0.8	-12		0.73	5	0.49	-33
V	37	10	24	-35		34	10	22	-35
W			0.061					0.051	
Y	9.8	6	8.9	-9.1		7.9	6	6.8	-14
Zn	86	13	76	-12		68	13	58	-14
Zr			2.0					2.0	

Table 12 shows the results of the ring test for parameters/elements where no assigned reference value is provided due to the small number of participating laboratories. However, even this small number of determinations gives an indication of the ”trueness” of GEMAS Ap and Gr standard results.

Table 12. Results of the ring test of the Ap and Gr standards showing the determined values from different laboratories, and the mean of the GEMAS QC data. For more details refer to Appendix 2.

Parameter	***Unit***	***GEMAS Ap QC data***	***LAB1***	***LAB2***	***LAB3***	***LAB4***	***LAB5***	***GEMAS Gr QC data***	***LAB1***	***LAB2***	***LAB3***	***LAB4***
CEC	meq/100g	24						17				
total C	wt%	2.7						1.1				
pH_$CaCl_2$		7.3	7.3					5.9	5.9			
TOC	wt%	1.2	1.2	1.4				1.1	1.1	1		
Aqua regia extraction								**Aqua regia extraction**				
Ag	mg/kg	0.054	0.054	0.053	0.063	0.063		0.03	0.03	0.037	0.041	0.046
Au	mg/kg	0.0017	0.0015					0.0017	0.0017	0.0022		
B	mg/kg	4.5	4.5					2.6	2.6			
Ge	mg/kg	0.043						0.037				
Hf	mg/kg	0.079	0.079	0.077	0.082			0.059	0.059	0.013		
Hg	mg/kg	0.1	0.1	0.13	0.11	0.13		0.12	0.12	0.14	0.13	0.19
In	mg/kg	0.033						0.023				
Nb	mg/kg	0.22	0.22	0.29	0.21	0.2		0.26	0.26	0.42	0.4	0.37
Pd	mg/kg	0.0017						0.00028				
Pt	mg/kg	0.00089						0.00044				
Re	mg/kg	0.00013						0.00015				
S	mg/kg	184	116	186	242	248		119	119	155	153	163
Se	mg/kg	0.57	0.57	1.09	0.4	0.39		0.35	0.35	0.26	0.28	
Sn	mg/kg	0.89	0.89	1.2				1.5	1.5	1.9		
Ta	mg/kg	0.0015	0.001					0.00092	0.002			
Te	mg/kg	0.039	0.039	0.043				0.025	0.025	0.035		
W	mg/kg	0.061	0.043					0.051	0.058			
Zr	mg/kg	2	2	1.64	1.63	1.53	2.2	2	2	1.09	0.43	3.24

7. CONCLUSIONS

Results of quality control for (a) prediction of the particle size distribution (clay, silt and sand fraction) based on the MIR spectra for GEMAS Ap and Gr samples, (b) analysis of Pb-isotope ratios of the GEMAS Ap samples by HR-ICP-MS following a 7N HNO_3-extraction and (c) the determination of 55 chemical elements (Ag, Al, As, Au, Ba, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hg, In, K, La, Li, Mg, Mn, Mo, Nb, Nd, Ni, P, Pb, Pd, Pr, Rb, S, Sb, Sc, Se, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, U, V, W, Y, Yb, Zn and Zr) following a weak MMI®-extraction of the Ap samples are presented.

Quality control of the particle size distribution results (prediction of clay, silt and sand fraction via MIR spectra based on a European soils model), demonstrate that the clay size fraction can be well predicted and used for mapping, while the estimation of the silt and sand fractions are at present of indicator quality only. A further improvement of the European soils model would be desirable and, if accomplished, MIR has clearly the potential to provide a very easy and cheap method to obtain reliable particle size information on European soils.

Quality control for the Pb-isotope analysis demonstrates that these results are of good quality and can be used to map the lead isotopic landscape of the continent. Although Pb-

isotopes are much used in environmental sciences to speculate on contamination (Komarek *et al.*, 2008), the lead isotopic background has never been established at the European scale. The maps show that the continental-scale isotopic background needs to be established before reaching far-fetched conclusions about the sources of an element in the environment. The results suggest that it would be highly interesting and that it is actually possible to establish the continental-scale systematics of some other isotope systems (like Cu, Fe, Hg...). Such data are, for example, of great importance for forensic studies.

Quality control of the results from the MMI®-extraction show for the majority of elements a surprisingly high quality given a weak extraction. There are, however, problems with a number of elements that their detection limits are not low enough. Most problematic are Bi, In, Pd, Pt, Ta, Te, followed by Hg, Se and W. The other 46 elements all show acceptable and usable results.

Results of the ring test with the two GEMAS standards Ap and Gr demonstrate that for the majority of elements the GEMAS results are rather close to their respective reference or assigned values. It is also clear that the aqua regia method chosen for the GEMAS project is a weak variant of the many existing varieties of aqua regia extractions. The elements Ti, Ga, K, Na, Cs show a bias of over -40%, while most metals come close to the assigned "true" value in an aqua regia extraction.

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

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REFERENCES

Bièvre, de P., Dybkær, R., Fajgelj, A., Hibbert, B., 2011. Metrological traceability of measurement results in chemistry: Concepts and implementation. IUPAC Technical Report, 83(10), 1873-1935.

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

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

Caritat, P. de, Cooper, M., 2011. National Geochemical Survey of Australia: Data Quality Assessment. Geoscience Australia, Record 2011/21 (2 Volumes), 478pp.

Caritat, P. de, Cooper, M., Jaireth, S., Bastrakov, E., 2011. National Geochemical Survey of Australia: Preliminary implications for energy and mineral explorations. Geoscience, Australia, Record 2011/29, 84p.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

ISO 11277: 05.98 Soil quality - Determination of particle size distribution in mineral soil material - Method by sieving and sedimentation.

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

Janik, L., McLaughlin, M.J., Forrester, S., 2011. Predicting particle size distribution in soils of the GEMAS sampling program using infrared spectroscopy and partial least squares regression. CSIRO Commercial-in-confidence report. 22p. – provided as Appendix 3 in this report.

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

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

Komárek, M., Ettler, V., Chrastný, V., Mihaljevič, M., 2008. Lead isotopes in environmental studies: A review. Environ. Internat. 34, 562-577.

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

Kriete, C., 2011. Report on the GEMAS project proficiency test: Laboratory Assessment. Federal Institute for Geosciences and Natural Resources, Hannover, Germany. Internal Report, 57p. Provided as Appendix 3 in this report.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Reimann, C., Demetriades, A., Eggen, O.A., Filzmoser, P., 2009a.The EuroGeoSurveys Geochemical Mapping of Agricultural and Grazing Land Soils Project (GEMAS) – Evaluation of Quality Control Results of Aqua Regia Extraction Analysis. Norges Geologiske Undersøkelse Report, 2009.049, 94 pp. Available online at http://www.ngu.no/upload/Publikasjoner/Rapporter/2009/2009_049.pdf - last accessed on 26 October 2011.

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

Reimann, C., Demetriades, A., Eggen, O. A., Filzmoser, P., EuroGeoSurveys Geochemistry Expert Group, 2011. The EuroGeoSurveys Geochemical mapping of agricultural and grazing land soils project (GEMAS) – Evaluation of quality control results of total C and S, total organic carbon (TOC), cation exchange capacity (CEC), XRF, pH, and particle size distribution (PSD) analyses. NGU Report 2011.043, 90p.

Reimann, C., Caritat, P. de, GEMAS Project Team, NGSA Project Team, 2012. New soil composition data for Europe and Australia: Demonstrating comparability, identifying continental-scale processes and learning lessons for global geochemical mapping. Sci. Total Environ. 416, 239-252.

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

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

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

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

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

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

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

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

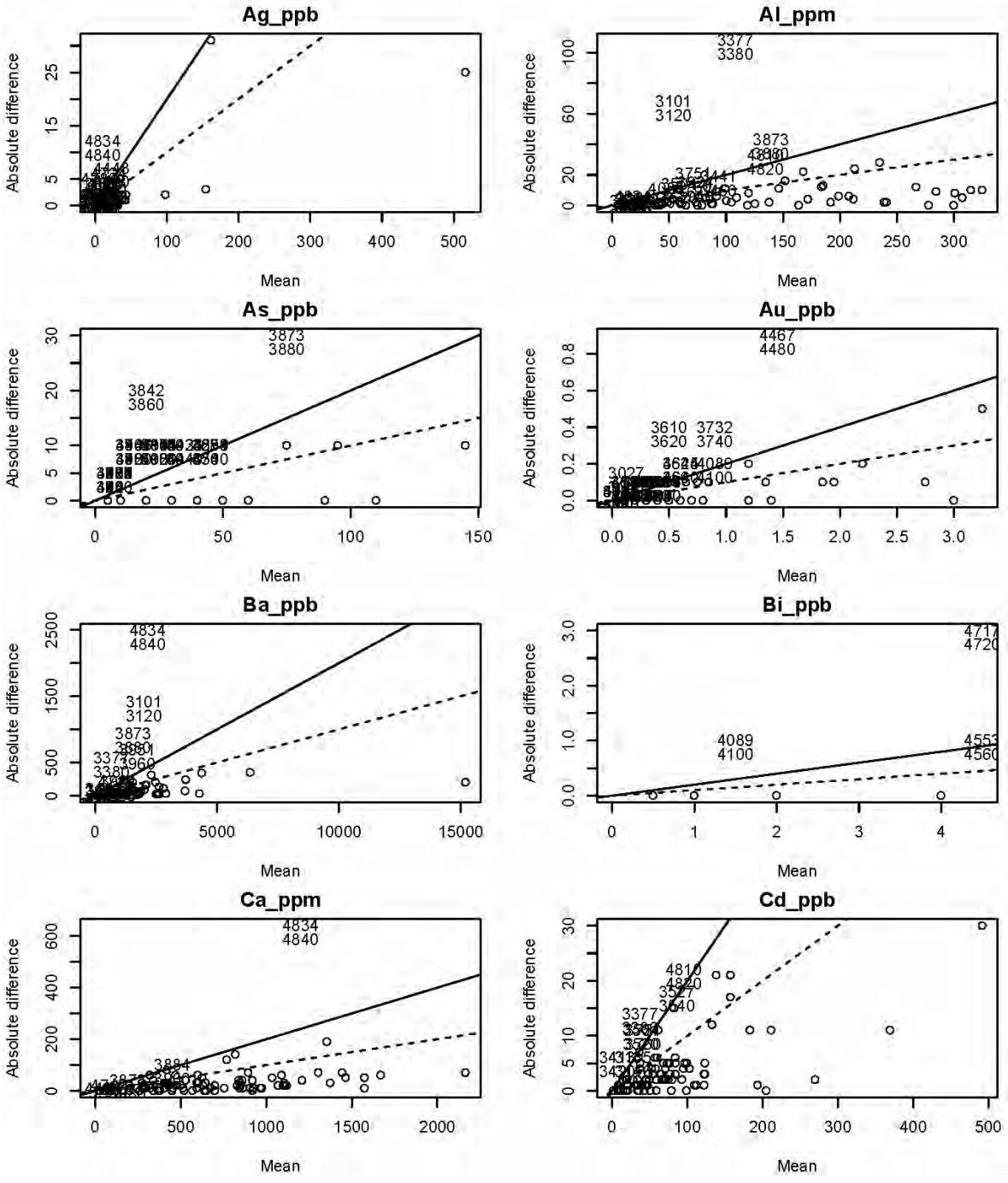
Thompson, M., Maguire, M., 1993. Estimating and using sampling precision in surveys of trace constituents of soils. Analyst 118, 1107-1110.

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

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

APPENDIX 1. ***"Thompson and Howarth"-plots of MMI® 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 stippled line, 20% precision by the continuous line. On this plot, pairs with poor precision can easily be identified and compared to the results from the project standard within the same batch of 20 samples.


Ag_ppb
Absolute difference
Mean
4834
4840
Al_ppm
3377
3380
3101
3120
3873
4820
As_ppb
3873
3880
3842
3860
Au_ppb
4467
4480
3610 3732
3620 3740
Ba_ppb
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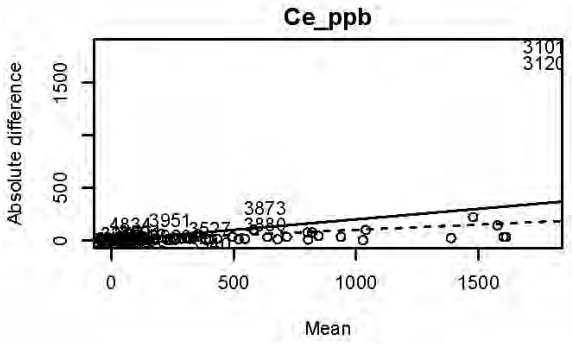
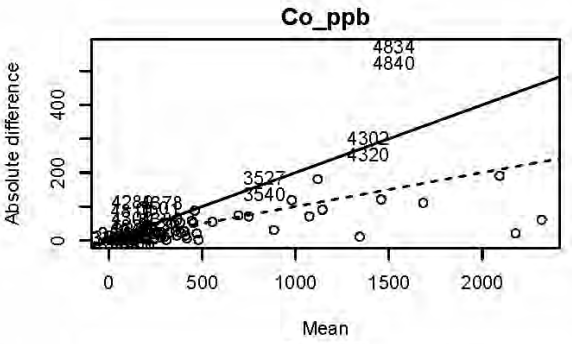
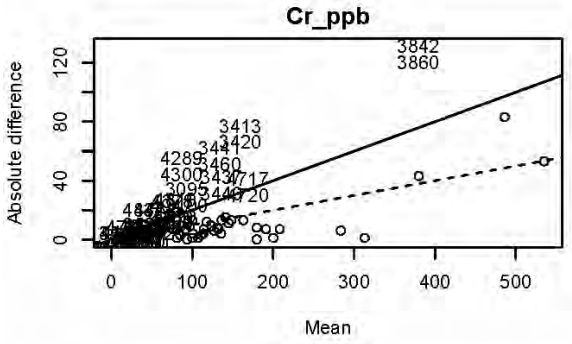
4100
Ca_ppm
4834
4840
Cd_ppb
4810


Ce_ppb
Absolute difference
Mean
3101
3120
3873
3880
3951


Co_ppb
Absolute difference
Mean
4834
4840
4302
4320
3527
3540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Absolute difference
Mean
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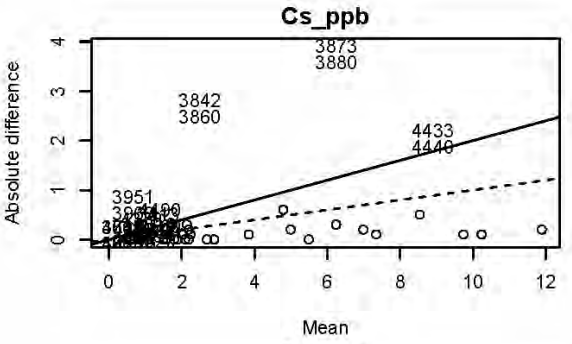
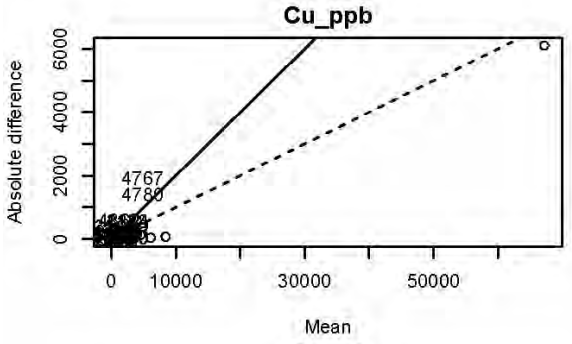
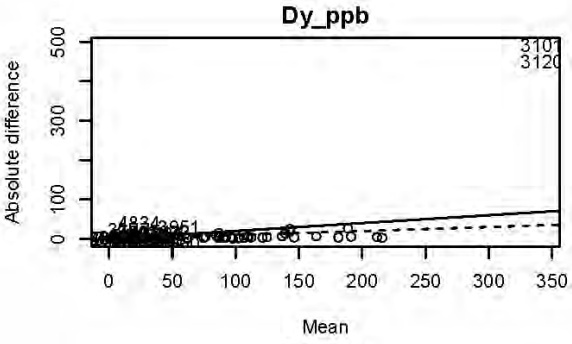
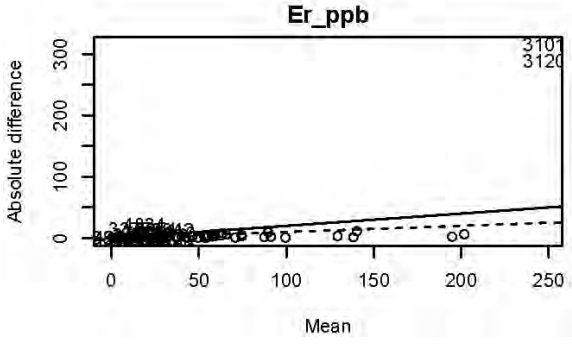
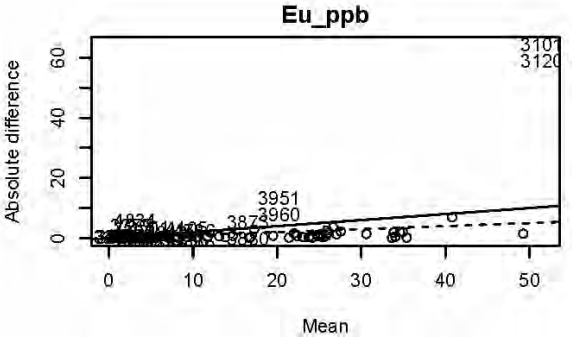
3860
3413
3420
4289
3460
4300
3717
4720

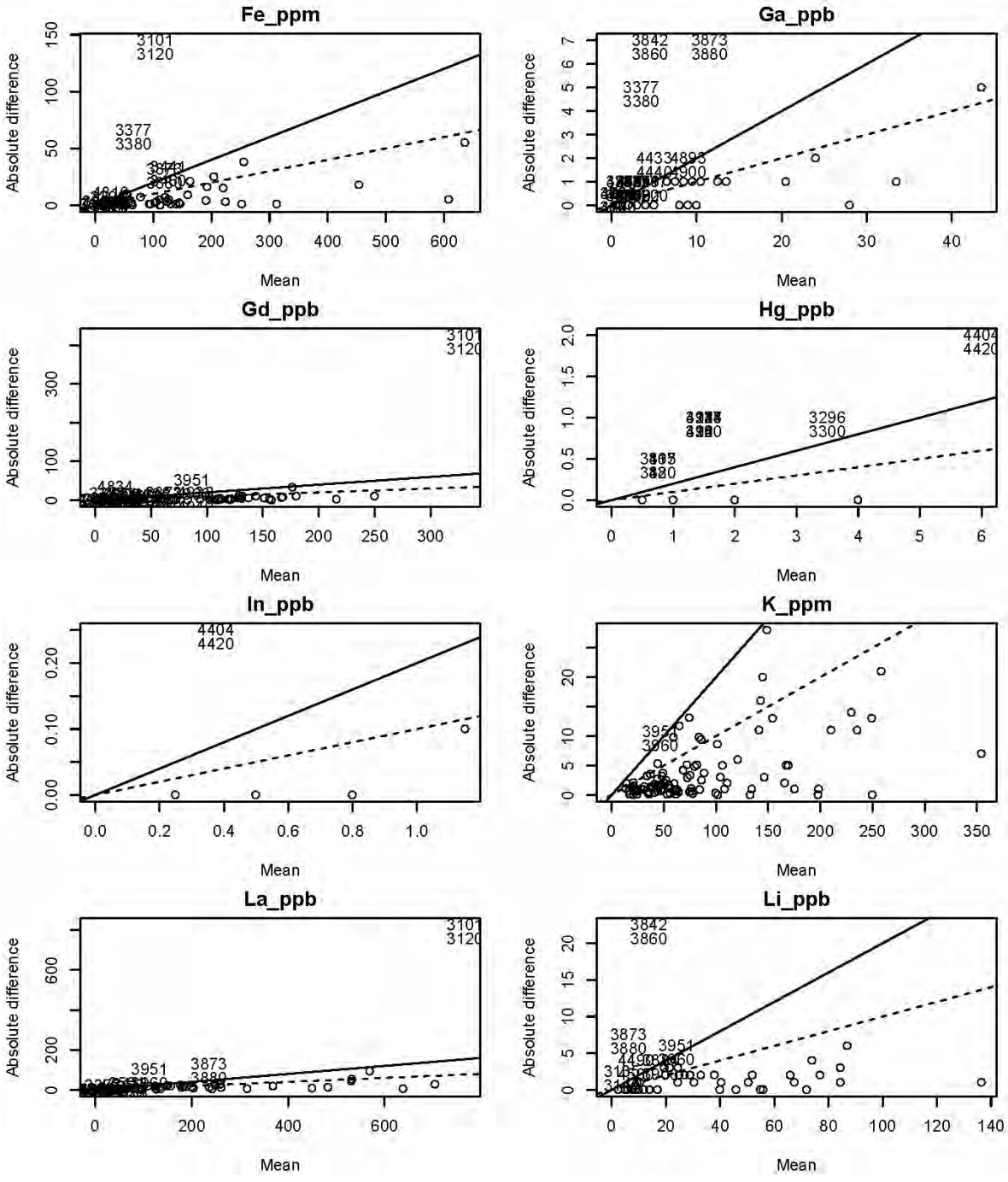

Cs_ppb
Absolute difference
Mean
3873
3880
3842
3860
4433
4440
3951


Cu_ppb
Absolute difference
Mean
4767
4780


Dy_ppb
Absolute difference
Mean
3101
3120


Er_ppb
Absolute difference
Mean
3101
3120


Eu_ppb
Absolute difference
Mean
3101
3120
3951
3960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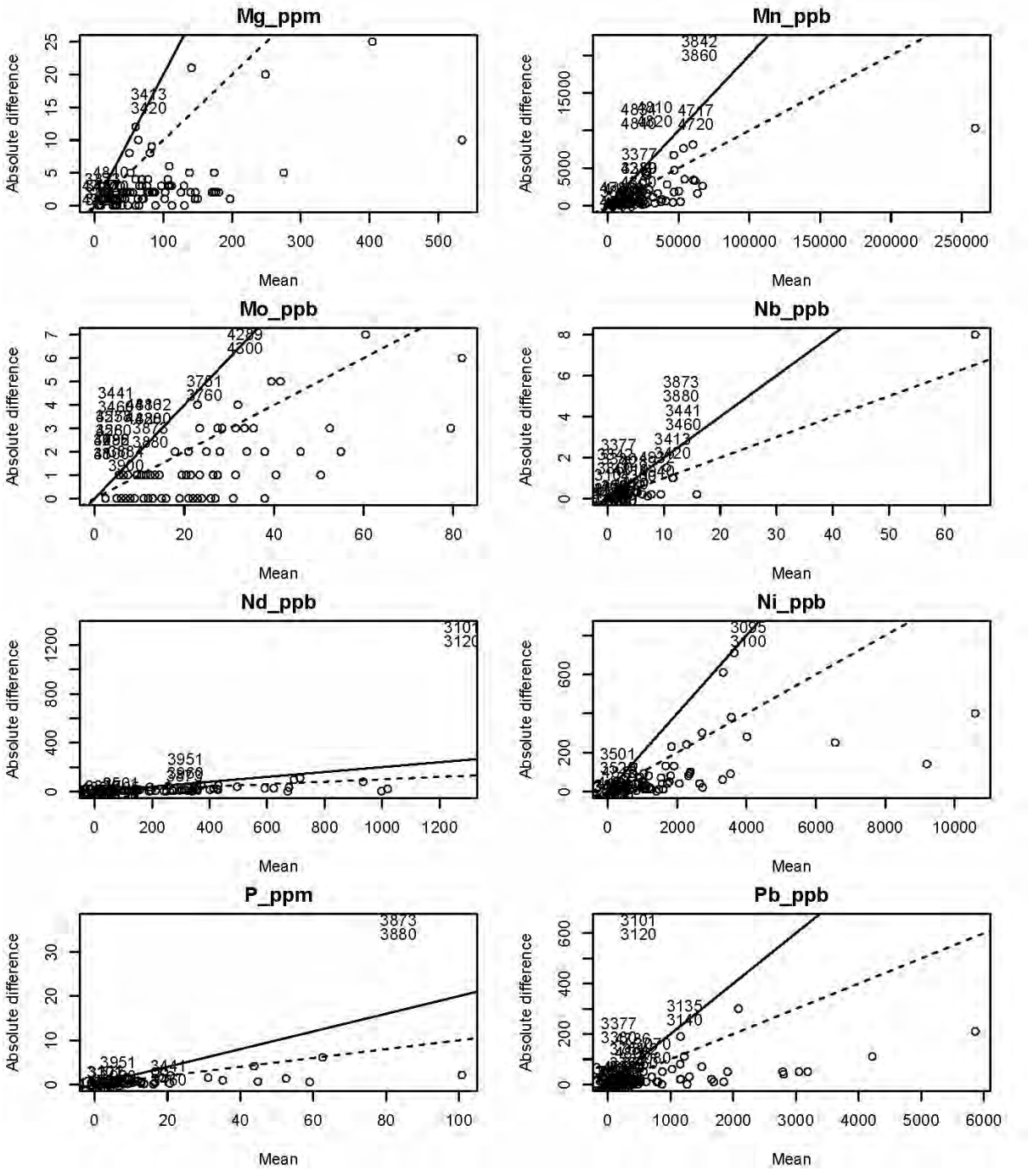
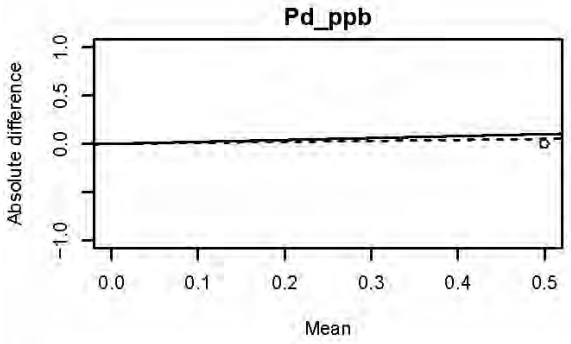
Absolute difference
Mean
3101
3120
3377
3380
Ga_ppb
Absolute difference
Mean
3842
3860
3873
3880
3377
3380
Gd_ppb
Absolute difference
Mean
3101
3120
3951
Hg_ppb
Absolute difference
Mean
4404
4420
3296
3300
In_ppb
Absolute difference
Mean
4404
4420
K_ppm
Absolute difference
Mean
3960
La_ppb
Absolute difference
Mean
3101
3120
3951
3873
3880
Li_ppb
Absolute difference
Mean
3842
3860
3873
3880
3951


Mg_ppm
Absolute difference
Mean
Mn_ppb
Absolute difference
Mean
Mo_ppb
Absolute difference
Mean
Nb_ppb
Absolute difference
Mean
Nd_ppb
Absolute difference
Mean
Ni_ppb
Absolute difference
Mean
P_ppm
Absolute difference
Mean
Pb_ppb
Absolute difference
Mean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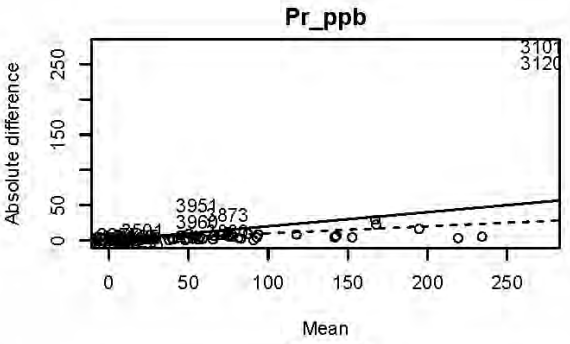
Absolute difference
Mean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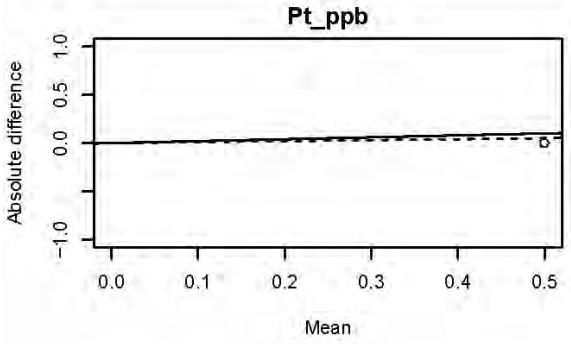
Absolute difference
Mean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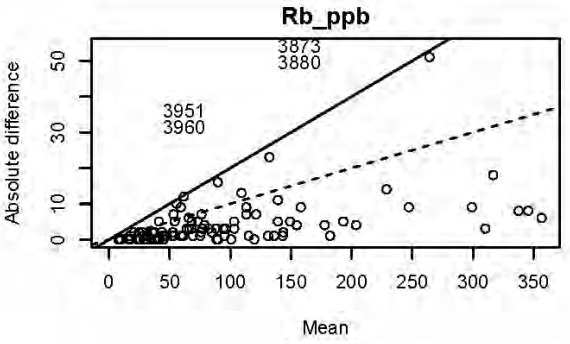
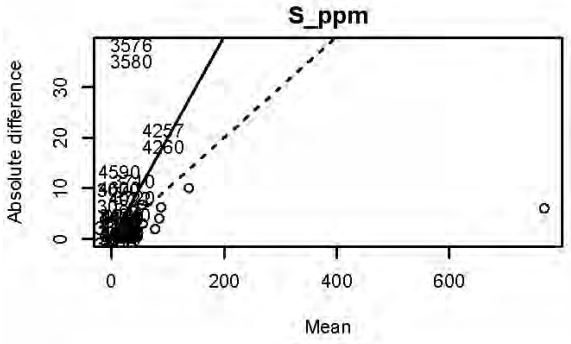
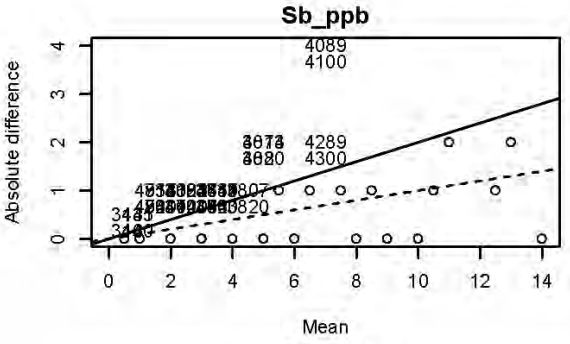
Absolute difference
Mean


Rb_ppb
Absolute difference
Mean


S_ppm
Absolute difference
Mean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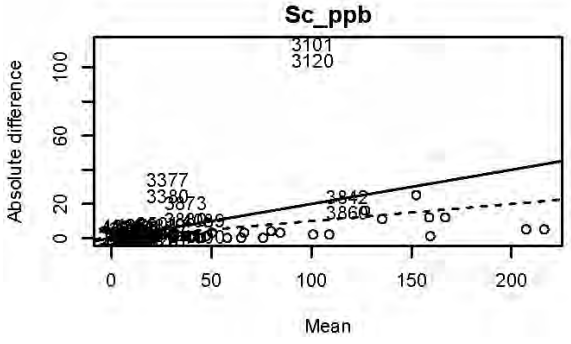
Mean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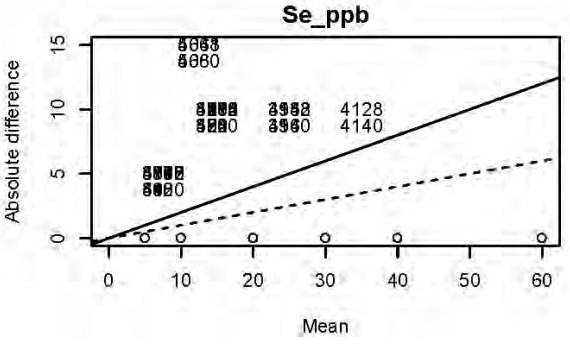
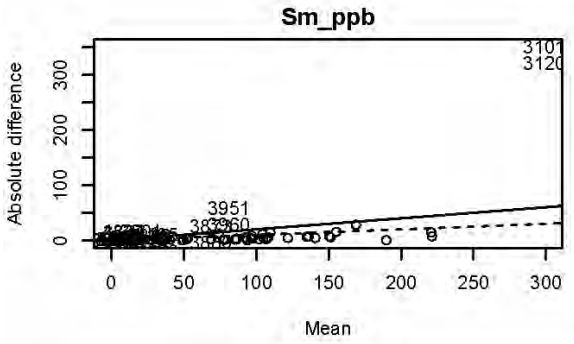
Absolute difference
Mean


Se_ppb
Absolute difference
Mean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Absolute difference
Mean
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3120
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200
300
0
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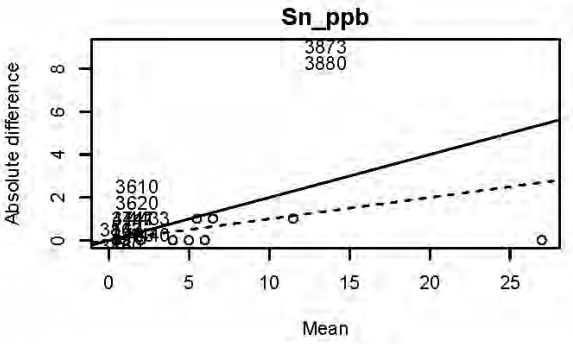
100
150
200
250
300


Sn_ppb
Absolute difference
Mean
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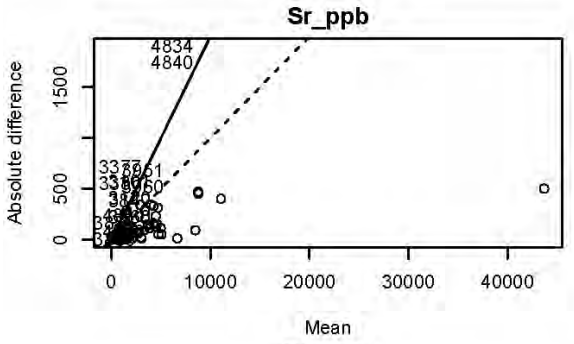
10
15
20
25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Mean
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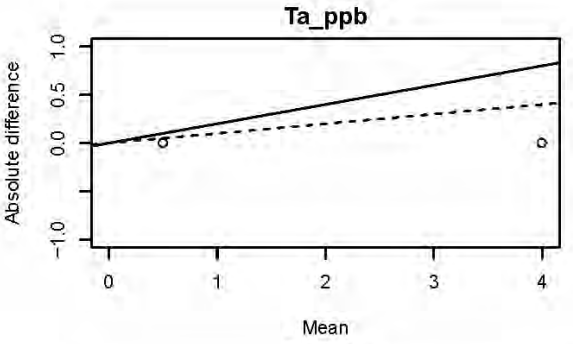
30000
40000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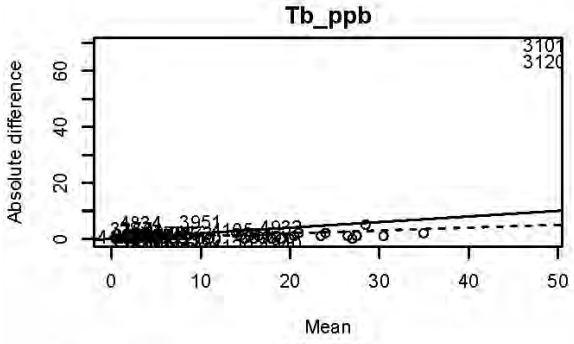
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Absolute difference
Mean
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3120
3951
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20
40
60
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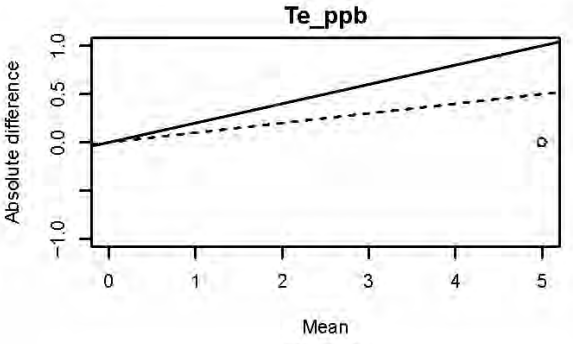
10
20
30
40
50


Te_ppb
Absolute difference
Mean
−1.0
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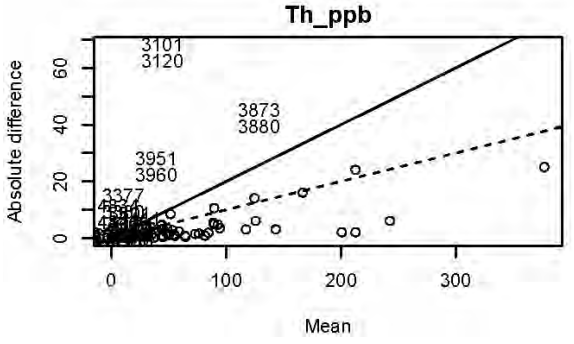
0.5
1.0
0
1
2
3
4
5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Mean
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3120
3873
3880
3951
3960
3377
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20
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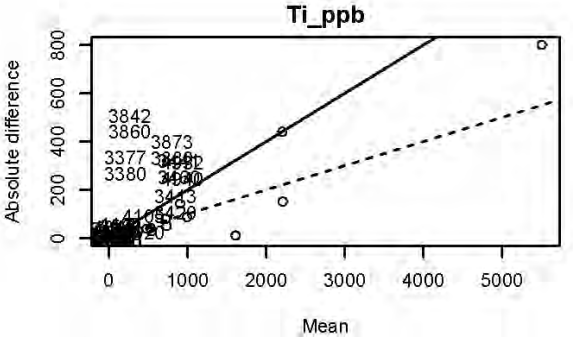
60
0
100
200
300


Ti_ppb
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Mean
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3873
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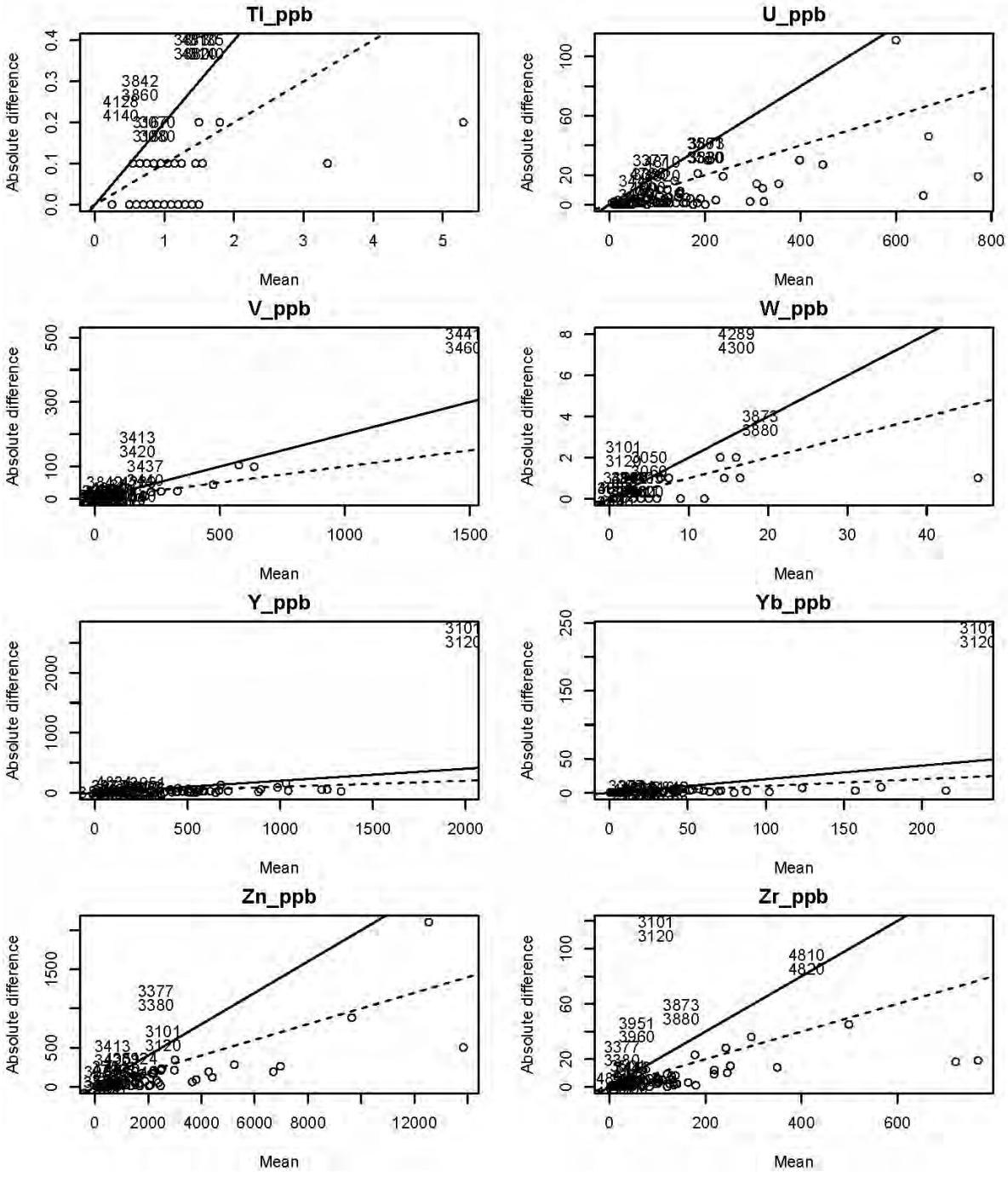
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Mean
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U_ppb
Absolute difference
Mean
V_ppb
Absolute difference
Mean
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3420
3437
W_ppb
Absolute difference
Mean
4289
4300
3873
3880
3101
Y_ppb
Absolute difference
Mean
3101
3120
Yb_ppb
Absolute difference
Mean
3101
3120
Zn_ppb
Absolute difference
Mean
3377
3380
3101
3120
3413
Zr_ppb
Absolute difference
Mean
3101
3120
4810
4820
3873
3880
3951
3960
3377

APPENDIX 2. ***Results of the GEMAS ring test as supplied to the participating laboratories*****.**

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Report on the GEMAS project proficiency test:

Laboratory assessment

Cornelia Kriete, Federal Institute for Geosciences and Natural Resources, Germany

The main aim of the GEMAS project was to produce harmonized data for European agricultural and grazing land soils. Quality control (QC) is one of the keystones to the success of such European scale mapping project.

The QC consisted of (1) collection of a field duplicate at a rate of one in twenty field samples, (2) preparation of two large project standards (Ap and Gr) for insertion between true samples, (3) preparation of an analytical duplicate from each field duplicate and (4) randomization of all samples prior to analysis. In combination, these procedures allow the detection and evaluation of most quality problems that can occur during sampling, sample preparation and analysis.

The project standards Ap and Gr were used to monitor precision. They were inserted at an average rate of one in twenty at a random position in each batch of 20 samples before soil samples were submitted to the laboratory. GEMAS project standard Ap was analysed 124 times, and standard Gr 118 times.

In the context of the GEMAS project a proficiency test based on the project standards was carried out to check the comparability of individual national laboratory data with the data used for mapping.

Samples

For quality assurance purposes two samples were prepared by the Geoanalytical Laboratories of the State Geological Institute of Dionyz Stur (SGUDS) in Slovakia. The sample AP represents an agricultural soil sample, while the sample GR stems from grazing land.

The material was sampled, dried, sieved to a particle size of < 2mm and homogenized, as described in the report of Mackových and Lučivjanský (2009). The homogeneity was tested by SGUDS laboratory according to ISO 13528, using XRF analyses with pressed pellets preparation.

Homogeneity could be approved for both samples for 23 main and trace elements analysed at the 5g test portion size level

Both samples were used as quality control samples and analysed continuously together with the regular soil samples by the BGR XRF-laboratory (total contents) and ACME (aqua regia extracts).

The results are reported by Reimann et al 2009 and 2011.

The data from these reports were also treated as (special) participants in the proficiency test.

The samples AP and GR were distributed to the participants in April 2010, final deadline for submitting the results was end of July 2011.

There was no prescribed set of analytes requested, instead the participants were asked to provide data according to their laboratory capabilities, but preferably total element and aqua regia extractable concentrations.

Furthermore no analytical methods were prescribed (with the exception of AR-extraction).

Laboratories

At a whole 21 institutions or laboratories from 16 countries agreed to participate and submitted their analytical data. Several institutions provided data from different laboratories or sections applying different analytical methods. Since they were treated at different laboratories all in all there were 36 data sets available.

Additionally some laboratories also digested powdered samples for comparison purposes. The results will be published later.

The participating countries / laboratories and the analytical techniques applied are listed in table 1

Table 1 Participating laboratories

Lab/Country	single Laboratory	main Analytical method(s)
ACME	ACME – QC Report	only AR: ICP-MS
Australia	Australia (subcontractor: commercial lab)	XRF (main) ICP-MS (traces) AR: ICP-MS
Austria	Austria	PP-XRF
Germany - BGR	BGR 1 BGR 2 BGR 4 BGR 5 BK BGR 7 BK BGR 9 BGR 10 – QC-Report	FB-XRF ICP-MS ICP-OES ICP-MS ICP-OES PP-XRF FB-XRF
UK: Brit. Geol. Surv.	BGS UK 1 BGS UK 2 BGS UK 3	PP/FB-XRF FB-XRF ICP-MS
Czech Republic	Czech 1 Czech 2 Czech 3	AAS (+divers) ICP-MS PP-XRF
Germany - Biolab	Biolab	AR: ICP-OES
Germany - TU Freiberg	Freiberg 1 Freiberg 2 Freiberg 3 Freiberg 6	ICP-MS FB-XRF PP-XRF ICP-OES
Fyrom	Fyrom	ICP-OES / AAS
Italy	Italy	PP-XRF
NGU	NGU	FB/PP XRF and ICP-OES (AR)
Poland	Poland 1 Poland 2 Poland 3	PP-XRF ICP-OES ICP-MS
Portugal	Portugal 1 Portugal 2	XRF ICP-OES / AAS
Switzerland	Switzerland	FB/PP XRF
Slovakia	Slovakia 1 Slovakia 2	ICP-OES AAS
Spain	Spain 1 Spain 2	XRF ICP-MS
Sweden	Sweden	ICP-MS
USGS	USGS	ICP-OES / -MS, AAS

The contributions of some laboratories are not considered in this PT report, because there were too few data sets for evaluation:

D Fugro Consult	Fugro – QC - Report	TOC
NGU	NGU 2	TC, pH
Switzerland	NABO	PAK
UK	Univ. East Anglia	Sr Isotopes

Data Screening

No special instructions were given to the participants concerning sample treatment, analytes, number of replicates and data format. Since not all labs used the provided data sheets or changed them, at first all data had to be converted into a consistent form, i.e. into oxide form for major components (in %m/m) and element form for traces (in mg/kg).
Data for AR extractable concentrations were treated as separate analytes, named with an "AR" added to the element abbreviation.
Data were checked for implausible results and concerning labs were asked to check their submission.

The laboratories submitted varying number of repetitions (between 1 and 10), frequently 3 - 5. For the assessment the lab mean values were used.
Data from QC- reports (BGR 10, ACME for AR) represent the means of more repetitions, but were treated as a "normal" laboratory.
Data sets close to detection/quantification limit, i.e. with more than 20% "less than values" were completely rejected and not assessed. In a few cases with occasional (< 20% of repetitions) "less than values" those were rejected and the resulting very small shift in lab mean was accepted.
Though all in all 36 data sets were available this does not imply, that there are the same number for all analytes. In maximum there are data from 25 laboratories per analyte. In contrast there are several analytes with very few data. Those data sets with less than 5 results were not further evaluated for statistical reasons (the data for Ag(AR) were excluded for chemical reasons).
Therefore the data for pH, TC or TOC, PAK e.g. are not considered here.
In some cases the comparability of extraction procedures was difficult to assess, so NGU used a special acid digestion procedure setting HCl aside. The results being comparable to usual AR extracts they were treated as such. Additional data for other extraction methods were not considered further.

After all data for 95 analytes could be evaluated for both samples (59 total contents, 35 AR extractable contents and LOI).

Statistical Treatment

The prepared data sets were imported to the validated software package ProLab+ (quodata GmbH, Dresden) especially designed for proficiency test evaluation.
For the assessment the consensus value of all participants was used as assigned value.
This approach was chosen because

- data from QC reports were not available for all analytes to be evaluated (Ag, Be, Bi, Cd,Dy, Er, Eu, Gd, Ge, Hf, Hg, Ho, La, Li, Lu, Mo, Nd, Pr, Sb, Se, Sm, Sn, Ta, Tb, Tl, Tm, U, W, Yb, all total contents)

- consensus values are independent from potential method bias, while QC-Report data are derived from only one analytical technique

According to the recommendation of ISO 13528 robust statistics were applied for the estimation of consensus values. For the robust mean (as assigned value) the Hampel estimator (Huber 1981) was chosen and the Q-method (Uhlig 1997) for the robust standard deviation (sd).

For assessment of individual laboratory results commonly the z-scores are used:

$$\text{z-score} = \frac{x(\text{lab}) - x(\text{assigned})}{sd(\text{assigned})}$$

Since these z-scores prefer slightly those labs with results too low, the modified z_U-scores were used instead, which lead to a more 'fair' assessment (Uhlig and Henschel 1997) especially for large standard deviations.

Preliminary computations revealed, that the robust standard deviations (or coefficients of variations rsp.) exceed 50% for several analytes, thus tolerance limits would be more than ±100%, implying, that even negative concentrations would be accepted.
To avoid such unrealistically large tolerance intervals, upper limits were established for the assigned standard deviations:

main components -	15%
traces down to app. 5 mg/kg -	25%
traces below app 5 mg/kg -	30%

These limits had to be applied for 27 analytes (AP) and 31 analytes (GR), in total 36% of all analytes.

The resulting z_U-score have to be interpreted as follows:

$\lvert z_U \rvert < 2$	result satisfying, acceptable
$\lvert z_U \rvert > 2$	result questionable, not acceptable

Results

In table 2 the results of the statistical evaluation are listed:

- robust mean = assigned value
- number of contributing lab means
- robust standard deviation, reproducibility (variability between lab means)
- assigned standard deviation, used for z_U-score calculation

The (mean) repeatability standard deviation is not given, because it is irrelevant due to the high variability of laboratory repetitions (1 to >> 100 for QC-Reports)

Table 2 Ring test parameters

	AP				GR			
Analyte	robust mean	n	robust sd (reprod.)	sd assignd	robust mean	n	robust sd (reprod.)	sd assignd
	% m/m		% m/m	% m/m	% m/m		% m/m	% m/m
SIO2	56,722	14	0,878	0,878	72,677	14	1,212	1,212
TIO2	0,693	18	0,031	0,031	0,651	18	0,053	0,053
TIO2AR	0,015	6	0,003	0,002	0,020	6	0,006	0,003
AL2O3	12,925	18	0,338	0,338	11,401	18	0,438	0,438
AL2O3AR	3,486	10	0,979	0,523	3,191	10	1,104	0,479
FE2O3	5,300	18	0,239	0,239	4,013	18	0,262	0,262
FE2O3AR	4,318	10	0,508	0,508	3,482	10	0,449	0,449
MNO	0,097	19	0,006	0,006	0,081	18	0,003	0,003
MNOAR	0,089	11	0,007	0,007	0,078	11	0,008	0,008
CAO	5,717	18	0,218	0,218	0,511	18	0,041	0,041
CAOAR	5,327	10	0,730	0,730	0,376	10	0,072	0,056
MGO	2,343	17	0,103	0,103	0,969	17	0,085	0,085
MGOAR	1,760	11	0,285	0,264	0,671	11	0,152	0,101
NA2O	1,053	16	0,109	0,109	1,231	17	0,085	0,085
NA2OAR	0,016	7	0,013	0,002	0,009	6	0,010	0,001
K2O	2,440	17	0,126	0,126	2,270	17	0,106	0,106
K2OAR	0,479	8	0,211	0,072	0,428	8	0,212	0,064
P2O5	0,225	15	0,012	0,012	0,198	17	0,016	0,016
P2O5AR	0,195	7	0,022	0,022	0,179	7	0,011	0,011
LOI	12,180	14	0,594	0,594	5,778	14	0,697	0,697
	mg/kg		mg/kg	mg/kg	mg/kg		mg/kg	mg/kg
AG	0,183	6	0,233	0,055	0,225	6	0,336	0,067
AS	10,136	20	1,298	1,298	10,709	20	2,106	2,106
ASAR	9,628	13	1,536	1,536	10,319	13	1,050	1,050
BA	345,907	25	28,330	28,330	371,766	25	34,991	34,991
BAAR	77,121	11	14,102	14,102	82,163	11	16,299	16,299
BE	2,079	9	0,720	0,624	1,891	9	0,553	0,553
BEAR	0,907	7	0,344	0,272	0,919	7	0,237	0,237
BI	0,355	5	0,080	0,080	0,297	5	0,090	0,089
BIAR	0,334	6	0,057	0,057	0,278	5	0,045	0,045
CD	0,211	7	0,027	0,027	0,195	7	0,056	0,056
CDAR	0,210	7	0,041	0,041	0,177	7	0,058	0,053
CE	62,617	18	7,240	7,240	60,116	17	7,215	7,215
CEAR	35,216	6	7,293	7,293	39,479	6	13,622	9,870
CO	14,350	23	2,709	2,709	11,281	23	2,238	2,238
COAR	11,738	12	2,083	2,083	10,059	12	1,974	1,974
CR	99,920	25	17,231	17,231	84,437	25	19,754	19,754
CRAR	34,966	12	8,072	8,072	31,319	12	8,602	7,830
CS	8,238	12	1,282	1,282	5,824	11	2,095	1,456
CSAR	2,727	5	1,542	0,818	2,027	5	1,272	0,608
CU	24,541	24	5,536	5,536	22,186	24	4,902	4,902
CUAR	23,690	13	2,048	2,048	22,054	13	2,403	2,403
DY	3,488	8	1,200	1,046	3,064	8	1,039	0,919
ER	1,840	8	0,908	0,552	1,638	8	0,835	0,491
EU	1,123	8	0,217	0,217	1,013	8	0,175	0,175
GA	16,118	16	1,166	1,166	13,690	16	0,887	0,887
GAAR	7,986	6	2,448	1,996	7,621	6	4,372	1,905
GD	4,502	8	0,728	0,728	4,052	8	0,718	0,718

Table 2 cont.	AP				GR			
Analyte	robust mean	n	robust sd (reprod.)	sd assignd	robust mean	n	robust sd (reprod.)	sd assignd
	mg/kg		mg/kg	mg/kg	mg/kg		mg/kg	mg/kg
GE	1,046	6	0,794	0,314	1,070	6	1,038	0,321
HF	4,366	9	2,017	1,310	5,871	10	1,343	1,343
HG	0,125	6	0,010	0,010	0,149	6	0,038	0,038
HO	0,653	8	0,251	0,196	0,582	8	0,251	0,174
LA	32,199	16	3,236	3,236	29,933	15	5,582	5,582
LAAR	15,658	7	2,026	2,026	18,469	7	5,565	4,617
LI	45,118	9	12,513	11,279	36,536	9	9,389	9,134
LIAR	26,327	9	5,757	5,757	20,699	9	5,692	5,175
LU	0,242	8	0,149	0,072	0,221	8	0,130	0,066
MO	0,966	10	0,387	0,290	1,052	10	0,264	0,264
MOAR	0,767	5	0,198	0,198	0,879	5	0,094	0,094
NB	13,496	18	1,981	1,981	12,475	18	1,818	1,818
ND	28,809	13	3,489	3,489	26,759	13	3,268	3,268
NI	52,155	25	4,070	4,070	39,024	25	4,170	4,170
NIAR	44,402	13	6,339	6,339	36,202	13	4,953	4,953
PB	21,948	23	1,968	1,968	19,772	23	1,962	1,962
PBAR	17,127	12	2,355	2,355	15,056	12	1,972	1,972
PR	7,219	8	0,707	0,707	6,785	8	1,131	1,131
RB	110,376	20	8,516	8,516	90,932	20	6,695	6,695
RBAR	29,546	5	12,864	7,386	27,552	5	16,257	6,888
S	330,965	9	200,613	82,741	265,389	9	148,579	66,347
SB	1,898	9	0,255	0,255	2,248	9	0,413	0,413
SBAR	1,013	7	0,465	0,304	1,436	7	0,431	0,431
SC	13,024	16	3,527	3,256	10,295	16	3,003	2,574
SCAR	5,089	7	1,043	1,043	4,020	7	1,462	1,005
SE	0,500	7	0,252	0,150	0,270	7	0,148	0,081
SM	5,488	8	0,598	0,598	4,997	9	0,880	0,880
SN	3,393	11	1,259	1,018	3,665	11	1,089	1,089
SR	148,704	23	8,188	8,188	91,261	23	4,619	4,619
SRAR	81,267	11	7,769	7,769	21,658	11	2,849	2,849
TA	1,132	5	0,308	0,308	0,945	5	0,266	0,266
TB	0,673	7	0,128	0,128	0,590	7	0,132	0,132
TH	10,074	17	1,564	1,564	9,395	17	1,925	1,925
THAR	4,782	5	0,572	0,572	4,515	5	0,922	0,922
TL	0,567	7	0,108	0,108	0,522	7	0,086	0,086
TLAR	0,188	5	0,021	0,021	0,189	5	0,036	0,036
TM	0,237	7	0,147	0,071	0,211	7	0,144	0,063
U	2,837	13	0,861	0,851	2,349	13	0,621	0,621
UAR	0,908	5	0,155	0,155	0,728	5	0,236	0,218
V	103,999	25	9,351	9,351	79,763	25	9,648	9,648
VAR	37,021	10	7,937	7,937	33,841	10	11,149	8,460
W	1,926	7	0,863	0,578	1,540	7	0,918	0,462
Y	23,217	20	5,930	5,804	20,959	20	6,213	5,240
YAR	9,792	6	1,093	1,093	7,888	6	1,775	1,775
YB	1,842	10	1,100	0,553	1,671	10	1,221	0,501
ZN	90,909	25	9,159	9,159	68,788	24	9,477	9,477
ZNAR	85,925	13	11,218	11,218	67,810	13	7,825	7,825
ZR	174,747	19	18,830	18,830	223,574	19	25,680	25,680

The individual assessment (z_U-scores) for each laboratory is distributed separately and treated confidently. In this report lab codes are used.

Table 3 provides an overview on the laboratory performances, also illustrated in Fig. 1

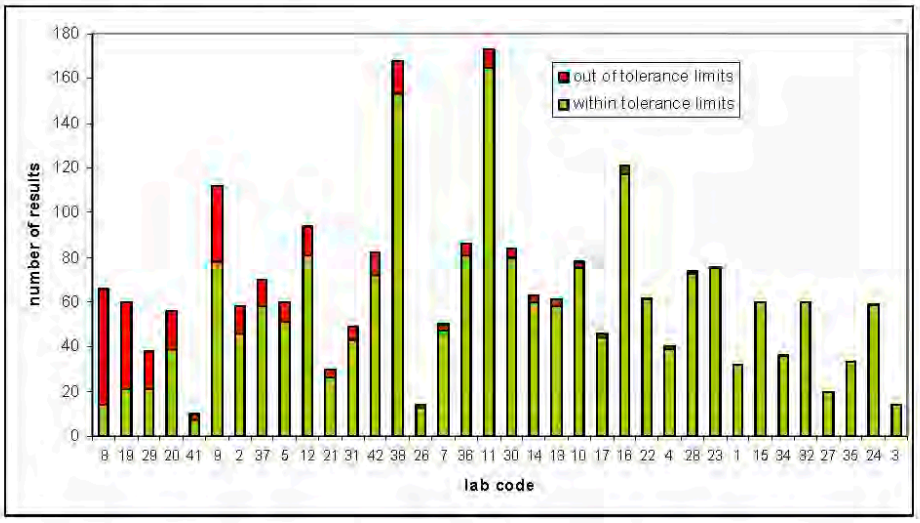
For eight laboratories 100% of their results are within the z_U-score limits ± 2.

In contrast, seven laboratories achieved less than 80 % satisfying result. This percentage is commonly used as a threshold for passing a proficiency test.

Table 3 Lab performances

Lab Code	number of results	within tolerance limit	not within tolerance	percentage
8	66	14	52	21%
19	60	21	39	35%
29	38	21	17	55%
20	56	39	17	70%
41	10	7	3	70%
9	112	78	34	70%
2	58	46	12	79%
37	70	58	12	83%
5	60	51	9	85%
12	94	81	13	86%
21	30	26	4	87%
31	49	43	6	88%
42	82	72	10	88%
38	168	153	15	91%
26	14	13	1	93%
7	50	47	3	94%
36	86	81	5	94%
11	173	165	8	95%
30	84	80	4	95%
14	63	60	3	95%
13	61	58	3	95%
10	78	75	3	96%
17	46	44	2	96%
16	121	117	4	97%
22	62	61	1	98%
4	40	39	1	98%
28	74	73	1	99%
23	76	75	1	99%
1	32	32	0	100%
15	60	60	0	100%
34	36	36	0	100%
32	60	60	0	100%
27	20	20	0	100%
35	33	33	0	100%
24	59	59	0	100%
3	14	14	0	100%
total	**2295**	**2012**	**283**	**87,7%**

Fig 1 Laboratory performance



Charts with the individual laboratory results for each analyte can be found in the attachment.

Literature

Huber, P.J. (1981) Robust Statistics, John Wiley

Mackových and Lučivjanský (2009) Preparation of GEMAS Project Standards and Homogeneity Test. Report Geological Institute of Dionyz Stur, Geoanalytical Laboratories, Slovak Republik

Reimann, C., Demetriades, A., Eggen, O.A., Filzmoser, P and EuroGeoSurvey expert group. (2009) The EuroGeoSurvey GEochemical Mapping of Agricultural and grazing land Solis project – Evaluation of quality control results of aqua regia extraction analyis

Reimann, C., Demetriades, A., Eggen, O.A., Filzmoser, P and EuroGeoSurvey expert group. (2011) The EuroGeoSurvey GEochemical Mapping of Agricultural and grazing land Solis project – Evaluation of quality control results of total C and S, total organic carbon (TOC), cation exchange capacity (CEC), XRF, pH and particle size distribution (PSD) analyis

Uhlig, S. (1997) Robust estimation of variance components in the 1-way random effect model with maximum breakdown point. Industrial statistics. Ed. Kitsos and Edler. Physica Heidelberg

Uhlig, S. and Henschel, P. (1997) Limits of Tolerance and z-scores in ring tests. Fres. J. Anal. Chem. 358, 671-766

Report on the GEMAS project proficiency test:

Laboratory assessment

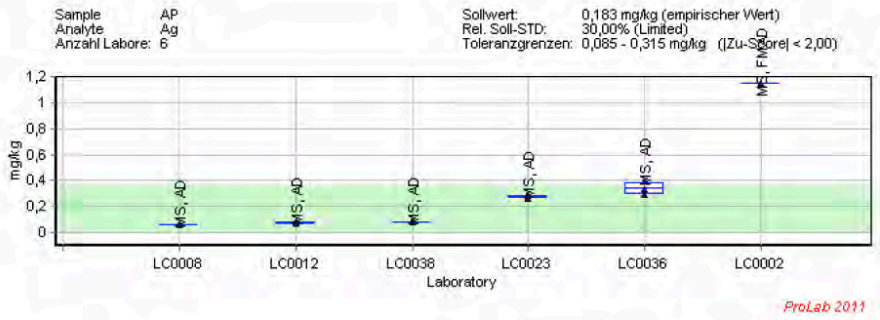
Attachment:

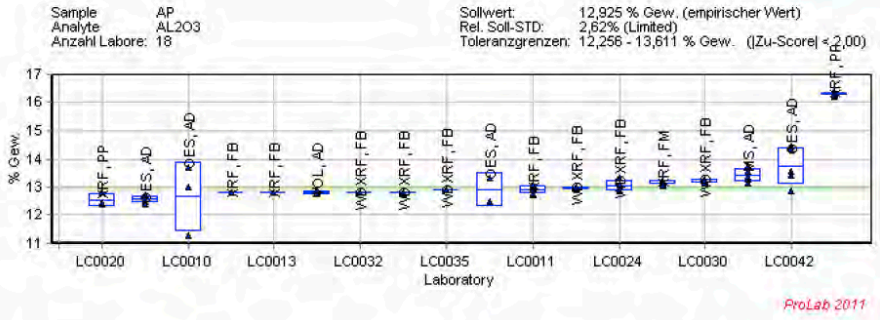
Bar Charts with individual analytical results

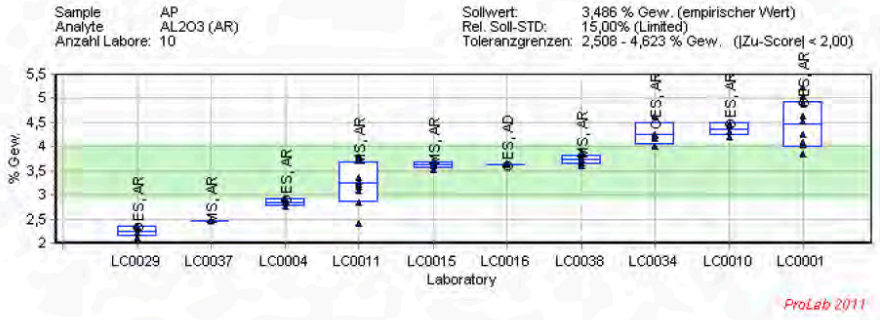
Explanations

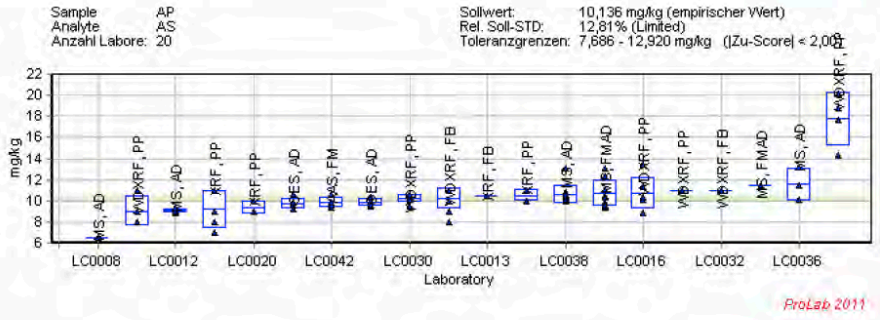
The green band in the charts marks the confidence interval for the robust mean

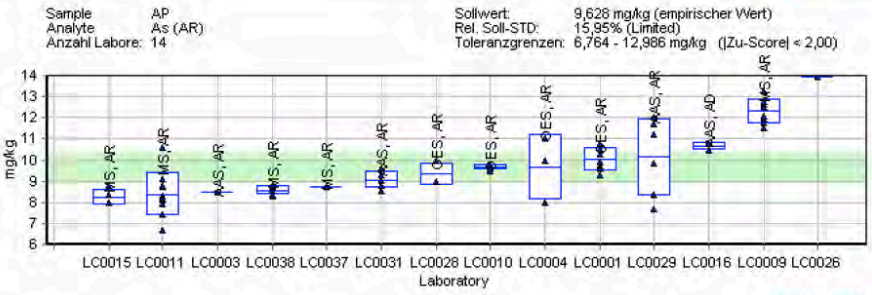
Anzahl Labore	number of laboratories
Sollwert	assigned value (robust mean)
Rel. Soll-STD	relative assigned standard deviation
Toleranzgrenzen	limit of tolerance (within $\|z_{\square}\|<2$)

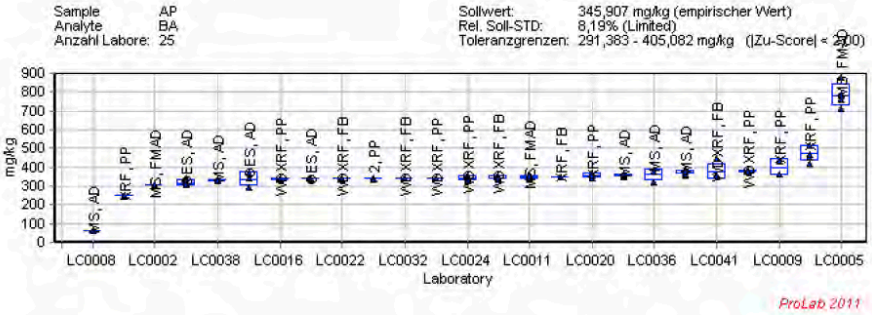

Sample AP
Analyte Ag
Anzahl Labore: 6
Sollwert: 0,183 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,085 - 0,315 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008
LC0012
LC0038
LC0023
LC0036
LC0002
ProLab 2011

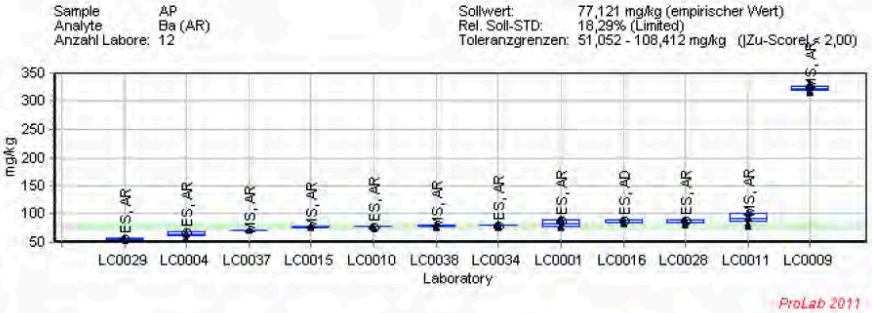

Sample AP
Analyte AL2O3
Anzahl Labore: 18
Sollwert: 12,925 % Gew. (empirischer Wert)
Rel. Soll-STD: 2,62% (Limited)
Toleranzgrenzen: 12,256 - 13,611 % Gew. (|Zu-Score| < 2,00)
% Gew.
Laboratory
LC0020
LC0010
LC0013
LC0032
LC0035
LC0011
LC0024
LC0030
LC0042
ProLab 2011

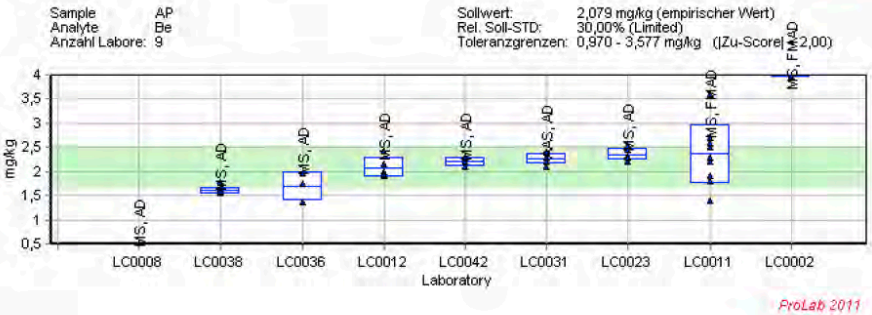

Sample AP
Analyte AL2O3 (AR)
Anzahl Labore: 10
Sollwert: 3,486 % Gew. (empirischer Wert)
Rel. Soll-STD: 15,00% (Limited)
Toleranzgrenzen: 2,508 - 4,623 % Gew. (|Zu-Score| < 2,00)
% Gew.
Laboratory
LC0029
LC0037
LC0004
LC0011
LC0015
LC0016
LC0038
LC0034
LC0010
LC0001
ProLab 2011

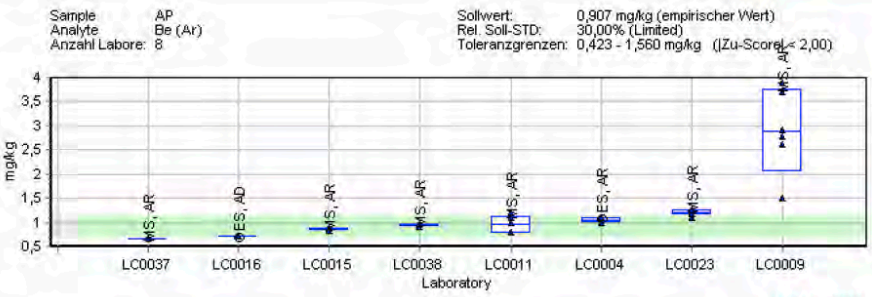

Sample AP
Analyte AS
Anzahl Labore: 20
Sollwert: 10,136 mg/kg (empirischer Wert)
Rel. Soll-STD: 12,81% (Limited)
Toleranzgrenzen: 7,686 - 12,920 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008
LC0012
LC0020
LC0042
LC0030
LC0013
LC0038
LC0016
LC0032
LC0036
ProLab 2011

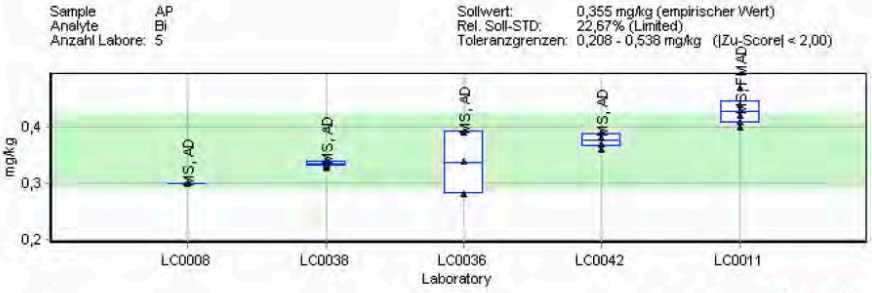

Sample AP
Analyte As (AR)
Anzahl Labore: 14
Sollwert: 9,628 mg/kg (empirischer Wert)
Rel. Soll-STD: 15,95% (Limited)
Toleranzgrenzen: 6,764 - 12,986 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0015 LC0011 LC0003 LC0038 LC0037 LC0031 LC0028 LC0010 LC0004 LC0001 LC0029 LC0016 LC0009 LC0026
Laboratory
ProLab 2011

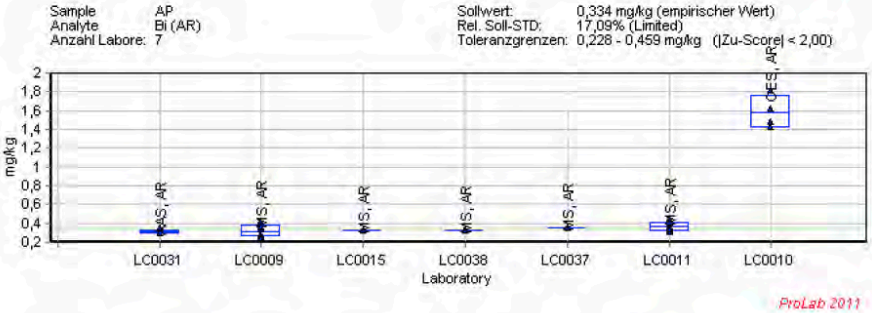

Sample AP
Analyte BA
Anzahl Labore: 25
Sollwert: 345,907 mg/kg (empirischer Wert)
Rel. Soll-STD: 8,19% (Limited)
Toleranzgrenzen: 291,383 - 405,082 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008 LC0002 LC0038 LC0016 LC0022 LC0032 LC0024 LC0011 LC0020 LC0036 LC0041 LC0009 LC0005
Laboratory
ProLab 2011

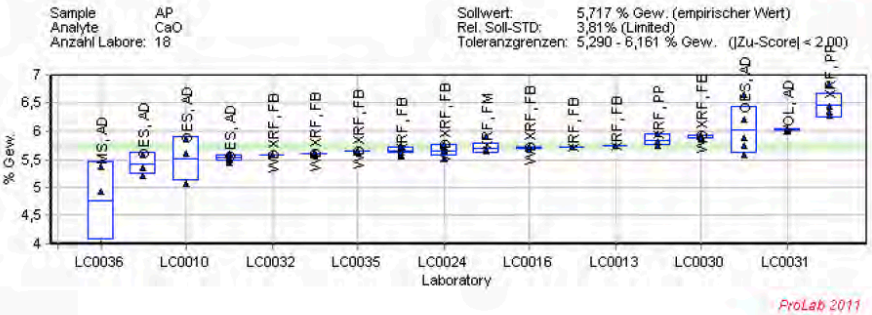

Sample AP
Analyte Ba (AR)
Anzahl Labore: 12
Sollwert: 77,121 mg/kg (empirischer Wert)
Rel. Soll-STD: 18,29% (Limited)
Toleranzgrenzen: 51,052 - 108,412 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0029 LC0004 LC0037 LC0015 LC0010 LC0038 LC0034 LC0001 LC0016 LC0028 LC0011 LC0009
Laboratory
ProLab 2011

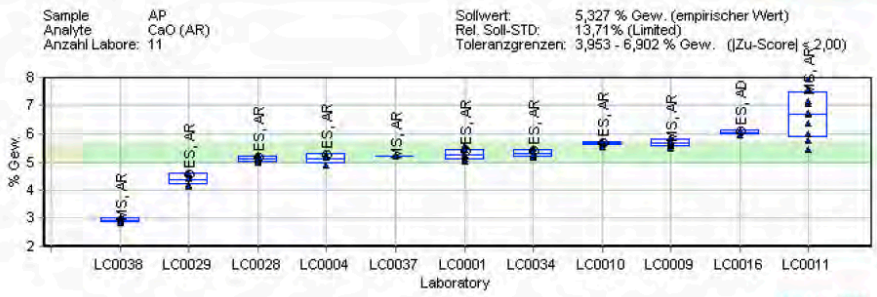

Sample AP
Analyte Be
Anzahl Labore: 9
Sollwert: 2,079 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,970 - 3,577 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008 LC0038 LC0036 LC0012 LC0042 LC0031 LC0023 LC0011 LC0002
Laboratory
ProLab 2011

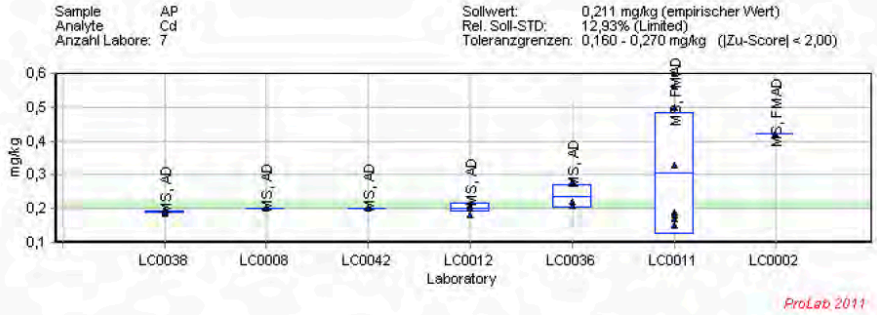

Sample AP
Analyte Be (Ar)
Anzahl Labore: 8
Sollwert: 0,907 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,423 - 1,560 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0037
LC0016
LC0015
LC0038
LC0011
LC0004
LC0023
LC0009
ProLab 2011

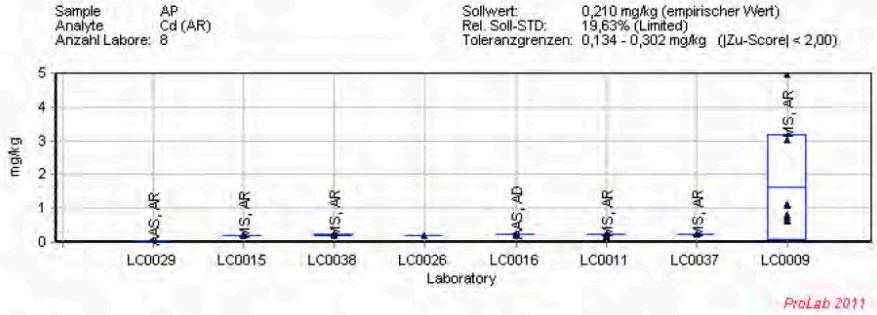

Sample AP
Analyte Bi
Anzahl Labore: 5
Sollwert: 0,355 mg/kg (empirischer Wert)
Rel. Soll-STD: 22,67% (Limited)
Toleranzgrenzen: 0,208 - 0,538 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008
LC0038
LC0036
LC0042
LC0011
ProLab 2011

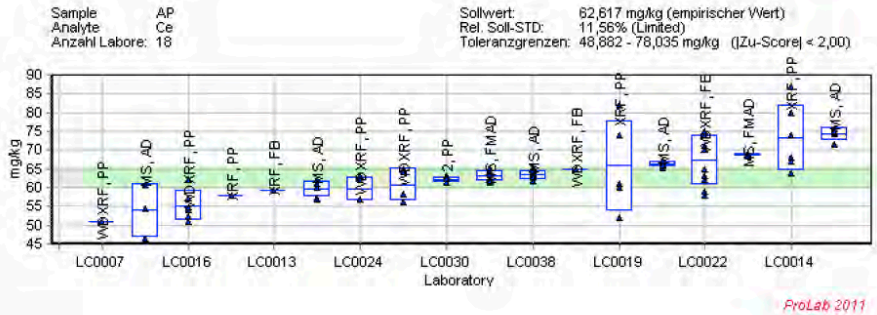

Sample AP
Analyte Bi (AR)
Anzahl Labore: 7
Sollwert: 0,334 mg/kg (empirischer Wert)
Rel. Soll-STD: 17,09% (Limited)
Toleranzgrenzen: 0,228 - 0,459 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0031
LC0009
LC0015
LC0038
LC0037
LC0011
LC0010
ProLab 2011

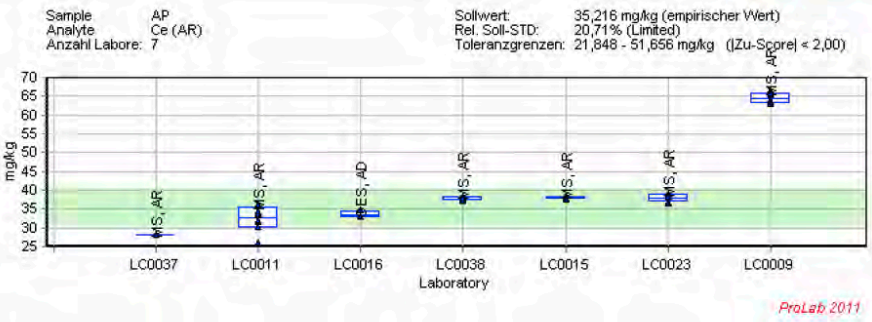

Sample AP
Analyte CaO
Anzahl Labore: 18
Sollwert: 5,717 % Gew. (empirischer Wert)
Rel. Soll-STD: 3,81% (Limited)
Toleranzgrenzen: 5,290 - 6,161 % Gew. (|Zu-Score| < 2,00)
% Gew.
Laboratory
LC0036
LC0010
LC0032
LC0035
LC0024
LC0016
LC0013
LC0030
LC0031
ProLab 2011

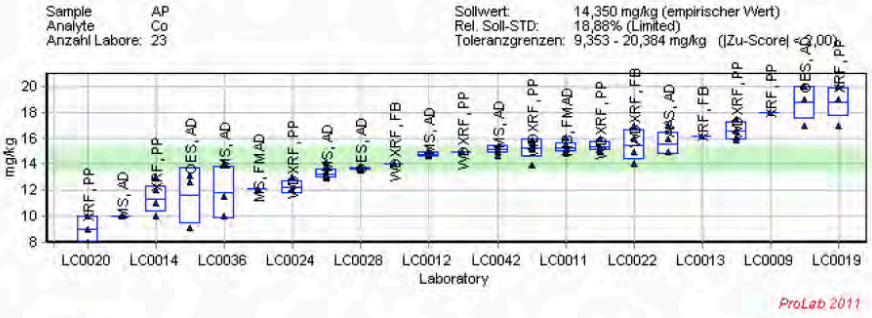

Sample AP
Analyte CaO (AR)
Anzahl Labore: 11
Sollwert: 5,327 % Gew. (empirischer Wert)
Rel. Soll-STD: 13,71% (Limited)
Toleranzgrenzen: 3,953 - 6,902 % Gew. (|Zu-Score| < 2,00)
% Gew.
LC0038 LC0029 LC0028 LC0004 LC0037 LC0001 LC0034 LC0010 LC0009 LC0016 LC0011
Laboratory
ProLab 2011

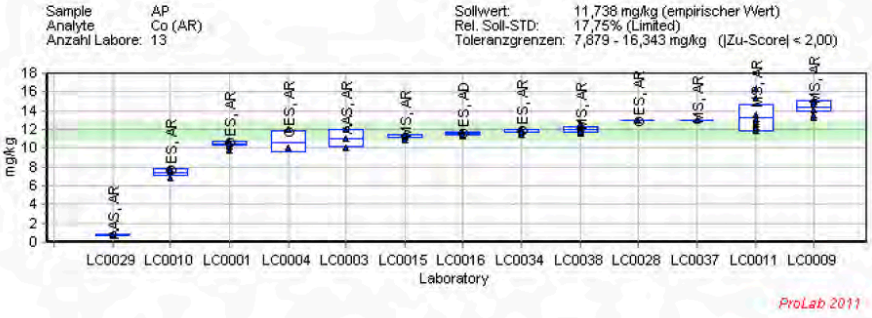

Sample AP
Analyte Cd
Anzahl Labore: 7
Sollwert: 0,211 mg/kg (empirischer Wert)
Rel. Soll-STD: 12,93% (Limited)
Toleranzgrenzen: 0,160 - 0,270 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0038 LC0008 LC0042 LC0012 LC0036 LC0011 LC0002
Laboratory
ProLab 2011

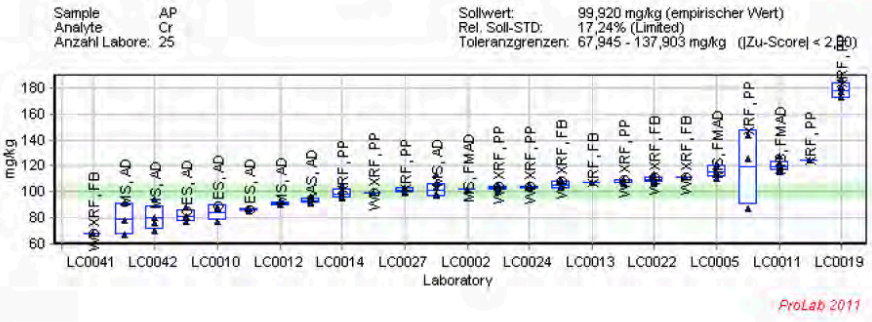

Sample AP
Analyte Cd (AR)
Anzahl Labore: 8
Sollwert: 0,210 mg/kg (empirischer Wert)
Rel. Soll-STD: 19,63% (Limited)
Toleranzgrenzen: 0,134 - 0,302 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0029 LC0015 LC0038 LC0026 LC0016 LC0011 LC0037 LC0009
Laboratory
ProLab 2011

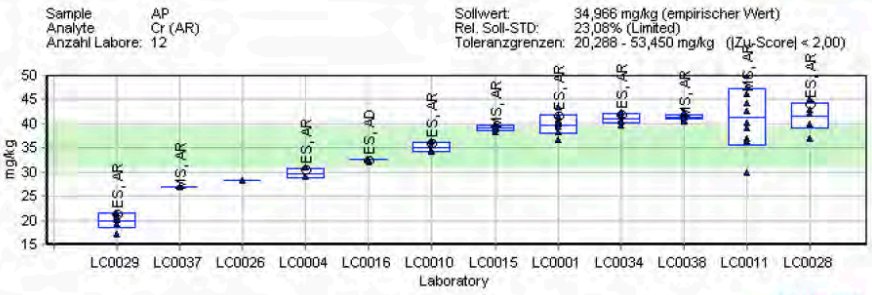

Sample AP
Analyte Ce
Anzahl Labore: 18
Sollwert: 62,617 mg/kg (empirischer Wert)
Rel. Soll-STD: 11,56% (Limited)
Toleranzgrenzen: 48,882 - 78,035 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0007 LC0016 LC0013 LC0024 LC0030 LC0038 LC0019 LC0022 LC0014
Laboratory
ProLab 2011

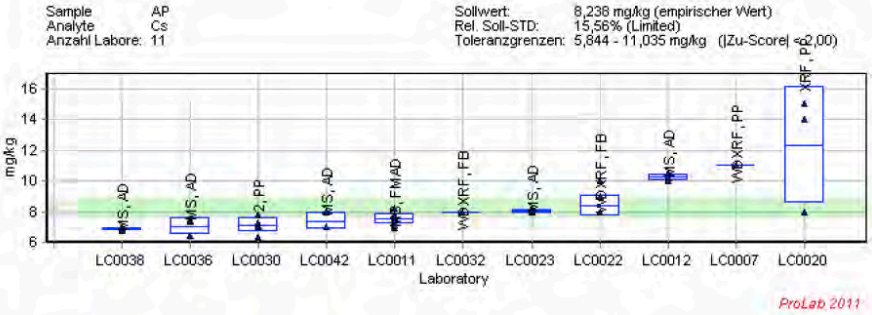

Sample AP
Analyte Ce (AR)
Anzahl Labore: 7
Sollwert: 35,216 mg/kg (empirischer Wert)
Rel. Soll-STD: 20,71% (Limited)
Toleranzgrenzen: 21,848 - 51,656 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0037 LC0011 LC0016 LC0038 LC0015 LC0023 LC0009
ProLab 2011

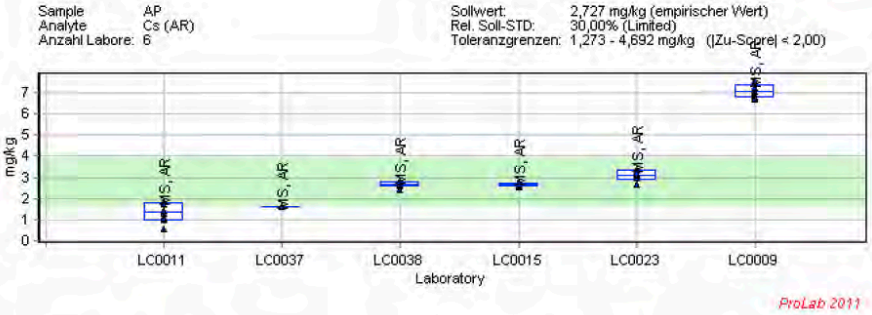

Sample AP
Analyte Co
Anzahl Labore: 23
Sollwert: 14,350 mg/kg (empirischer Wert)
Rel. Soll-STD: 18,88% (Limited)
Toleranzgrenzen: 9,353 - 20,384 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0020 LC0014 LC0036 LC0024 LC0028 LC0012 LC0042 LC0011 LC0022 LC0013 LC0009 LC0019
ProLab 2011

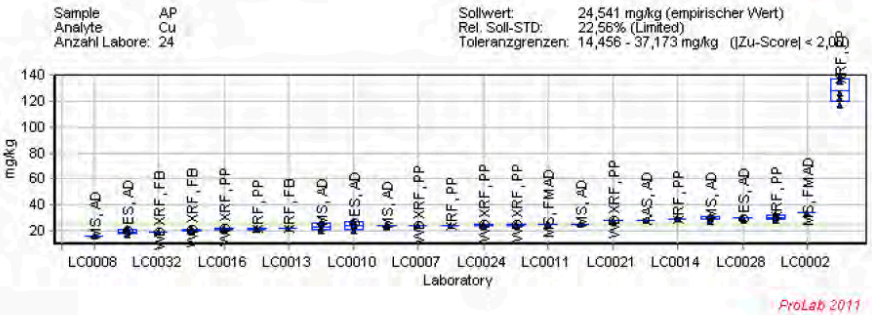

Sample AP
Analyte Co (AR)
Anzahl Labore: 13
Sollwert: 11,738 mg/kg (empirischer Wert)
Rel. Soll-STD: 17,75% (Limited)
Toleranzgrenzen: 7,879 - 16,343 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0029 LC0010 LC0001 LC0004 LC0003 LC0015 LC0016 LC0034 LC0038 LC0028 LC0037 LC0011 LC0009
ProLab 2011

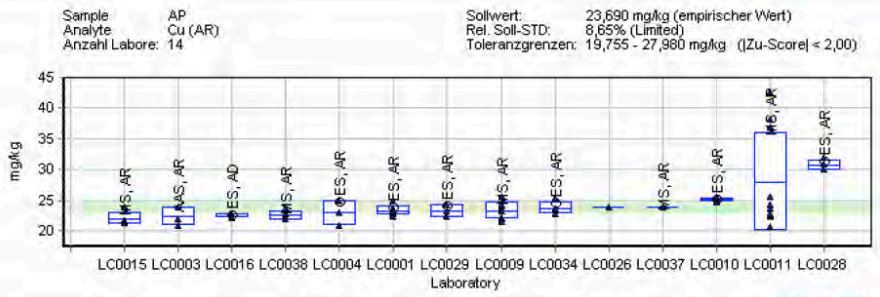

Sample AP
Analyte Cr
Anzahl Labore: 25
Sollwert: 99,920 mg/kg (empirischer Wert)
Rel. Soll-STD: 17,24% (Limited)
Toleranzgrenzen: 67,945 - 137,903 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0041 LC0042 LC0010 LC0012 LC0014 LC0027 LC0002 LC0024 LC0013 LC0022 LC0005 LC0011 LC0019
ProLab 2011

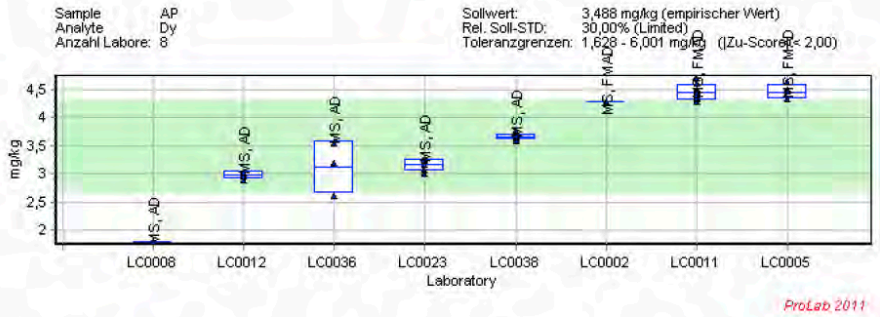

Sample AP
Analyte Cr (AR)
Anzahl Labore: 12
Sollwert: 34,966 mg/kg (empirischer Wert)
Rel. Soll-STD: 23,08% (Limited)
Toleranzgrenzen: 20,288 - 53,450 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0029 LC0037 LC0026 LC0004 LC0016 LC0010 LC0015 LC0001 LC0034 LC0038 LC0011 LC0028
ProLab 2011

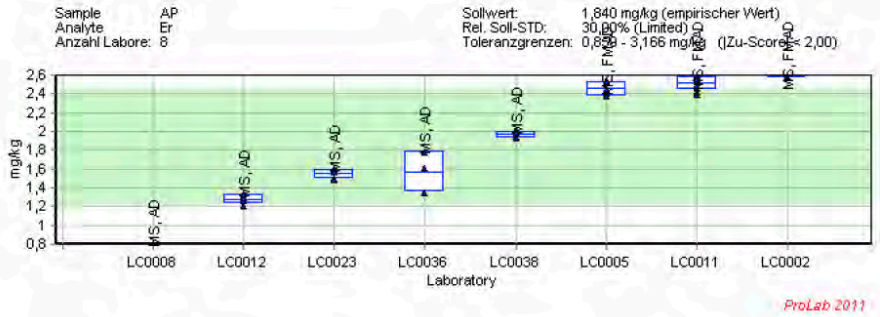

Sample AP
Analyte Cs
Anzahl Labore: 11
Sollwert: 8,238 mg/kg (empirischer Wert)
Rel. Soll-STD: 15,56% (Limited)
Toleranzgrenzen: 5,844 - 11,035 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0038 LC0036 LC0030 LC0042 LC0011 LC0032 LC0023 LC0022 LC0012 LC0007 LC0020
ProLab 2011

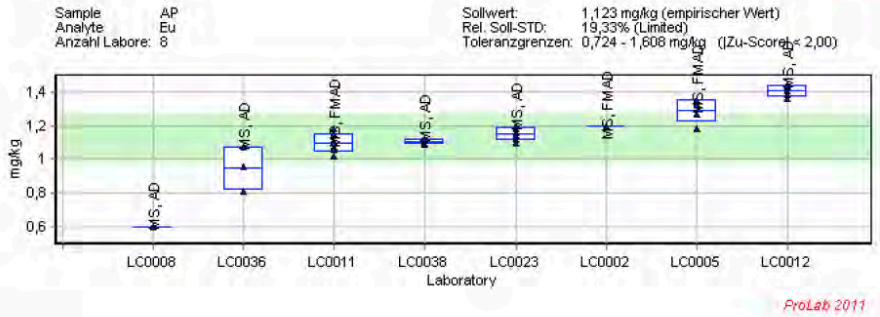

Sample AP
Analyte Cs (AR)
Anzahl Labore: 6
Sollwert: 2,727 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 1,273 - 4,692 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0011 LC0037 LC0038 LC0015 LC0023 LC0009
ProLab 2011

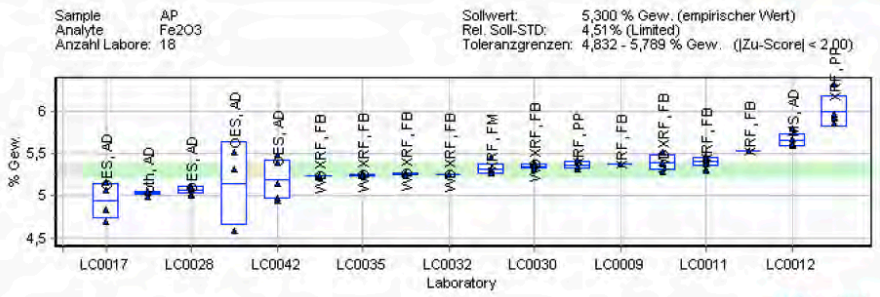

Sample AP
Analyte Cu
Anzahl Labore: 24
Sollwert: 24,541 mg/kg (empirischer Wert)
Rel. Soll-STD: 22,56% (Limited)
Toleranzgrenzen: 14,456 - 37,173 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0032 LC0016 LC0013 LC0010 LC0007 LC0024 LC0011 LC0021 LC0014 LC0028 LC0002
ProLab 2011

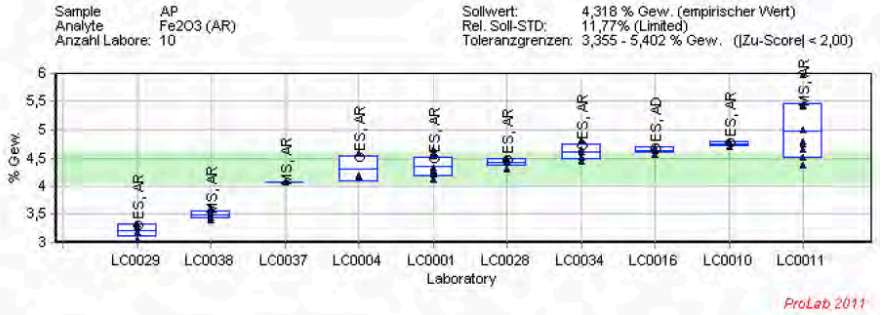

Sample AP
Analyte Cu (AR)
Anzahl Labore: 14
Sollwert: 23,690 mg/kg (empirischer Wert)
Rel. Soll-STD: 8,65% (Limited)
Toleranzgrenzen: 19,755 - 27,980 mg/kg (|Zu-Score| < 2,00)
mg/kg
45
40
35
30
25
20
MS, AR
AAS, AR
OES, AD
MS, AR
OES, AR
OES, AR
OES, AR
MS, AR
OES, AR
MS, AR
OES, AR
MS, AR
OES, AR
LC0015 LC0003 LC0016 LC0038 LC0004 LC0001 LC0029 LC0009 LC0034 LC0026 LC0037 LC0010 LC0011 LC0028
Laboratory
ProLab 2011

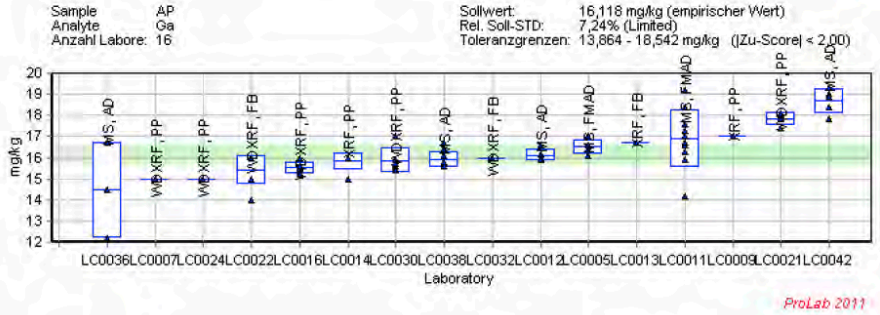

Sample AP
Analyte Dy
Anzahl Labore: 8
Sollwert: 3,488 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 1,628 - 6,001 mg/kg (|Zu-Score| < 2,00)
mg/kg
4,5
4
3,5
3
2,5
2
MS, AD
MS, AD
MS, AD
MS, AD
MS, AD
MS, FMAD
MS, FMAD
MS, FMAD
LC0008 LC0012 LC0036 LC0023 LC0038 LC0002 LC0011 LC0005
Laboratory
ProLab 2011

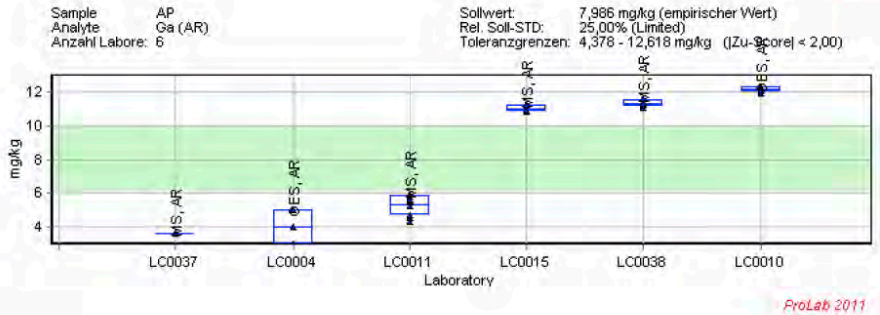

Sample AP
Analyte Er
Anzahl Labore: 8
Sollwert: 1,840 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,859 - 3,166 mg/kg (|Zu-Score| < 2,00)
mg/kg
2,6
2,4
2,2
2
1,8
1,6
1,4
1,2
1
0,8
MS, AD
MS, AD
MS, AD
MS, AD
MS, AD
MS, FMAD
MS, FMAD
MS, FMAD
LC0008 LC0012 LC0023 LC0036 LC0038 LC0005 LC0011 LC0002
Laboratory
ProLab 2011

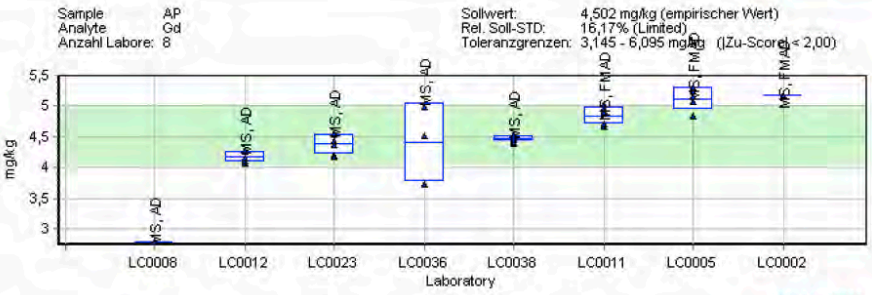

Sample AP
Analyte Eu
Anzahl Labore: 8
Sollwert: 1,123 mg/kg (empirischer Wert)
Rel. Soll-STD: 19,33% (Limited)
Toleranzgrenzen: 0,724 - 1,608 mg/kg (|Zu-Score| < 2,00)
mg/kg
1,4
1,2
1
0,8
0,6
MS, AD
MS, AD
MS, FMAD
MS, AD
MS, AD
MS, FMAD
MS, FMAD
MS, AD
LC0008 LC0036 LC0011 LC0038 LC0023 LC0002 LC0005 LC0012
Laboratory
ProLab 2011

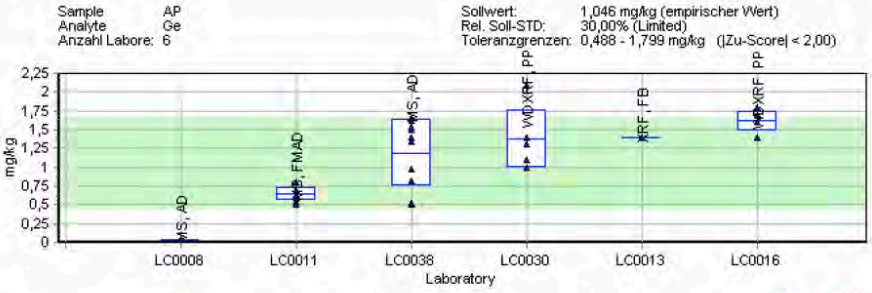

Sample AP
Analyte Fe2O3
Anzahl Labore: 18
Sollwert: 5,300 % Gew. (empirischer Wert)
Rel. Soll-STD: 4,51% (Limited)
Toleranzgrenzen: 4,832 - 5,789 % Gew. (|Zu-Score| < 2,00)
% Gew.
LC0017 LC0028 LC0042 LC0035 LC0032 LC0030 LC0009 LC0011 LC0012
Laboratory
ProLab 2011

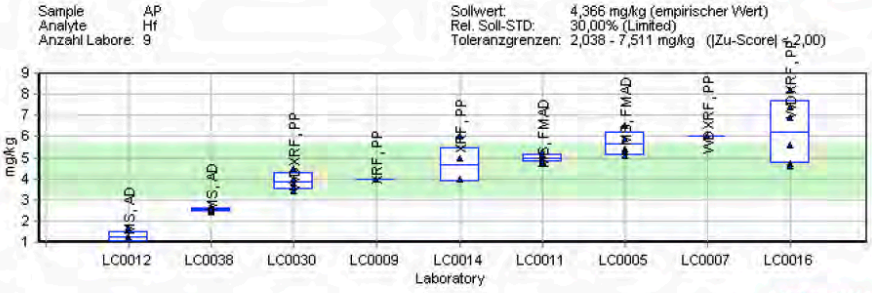

Sample AP
Analyte Fe2O3 (AR)
Anzahl Labore: 10
Sollwert: 4,318 % Gew. (empirischer Wert)
Rel. Soll-STD: 11,77% (Limited)
Toleranzgrenzen: 3,355 - 5,402 % Gew. (|Zu-Score| < 2,00)
% Gew.
LC0029 LC0038 LC0037 LC0004 LC0001 LC0028 LC0034 LC0016 LC0010 LC0011
Laboratory
ProLab 2011

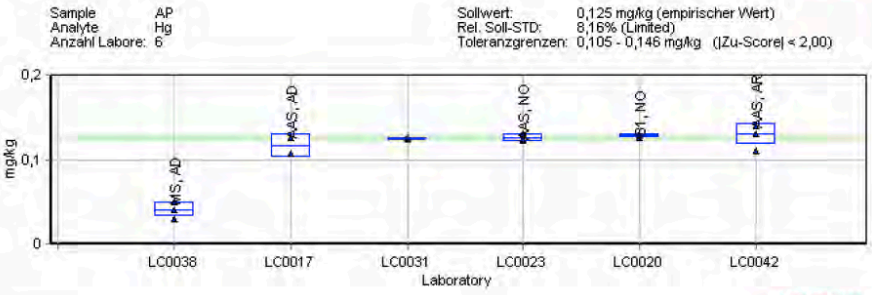

Sample AP
Analyte Ga
Anzahl Labore: 16
Sollwert: 16,118 mg/kg (empirischer Wert)
Rel. Soll-STD: 7,24% (Limited)
Toleranzgrenzen: 13,864 - 18,542 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0036 LC0007 LC0024 LC0022 LC0016 LC0014 LC0030 LC0038 LC0032 LC0012 LC0005 LC0013 LC0011 LC0009 LC0021 LC0042
Laboratory
ProLab 2011

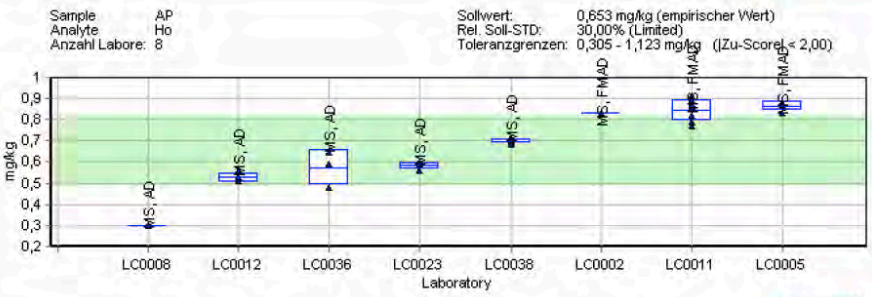

Sample AP
Analyte Ga (AR)
Anzahl Labore: 6
Sollwert: 7,986 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 4,378 - 12,618 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0037 LC0004 LC0011 LC0015 LC0038 LC0010
Laboratory
ProLab 2011

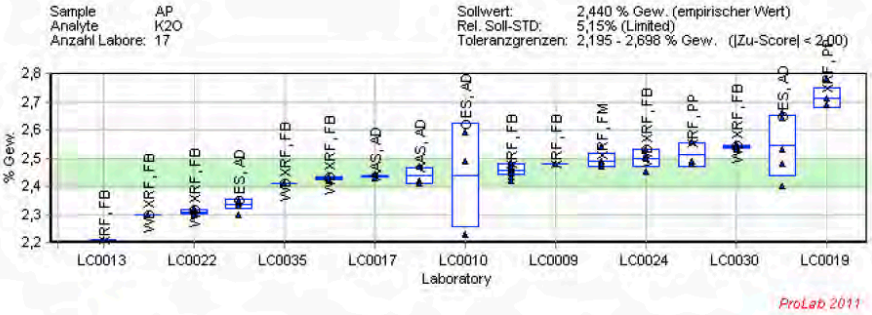

Sample AP
Analyte Gd
Anzahl Labore: 8
Sollwert: 4,502 mg/kg (empirischer Wert)
Rel. Soll-STD: 16,17% (Limited)
Toleranzgrenzen: 3,145 - 6,095 mg/kg (|Zu-Score| < 2,00)
mg/kg
5,5
5
4,5
4
3,5
3
MS; AD
MS; FMAD
LC0008
LC0012
LC0023
LC0036
LC0038
LC0011
LC0005
LC0002
Laboratory
ProLab 2011

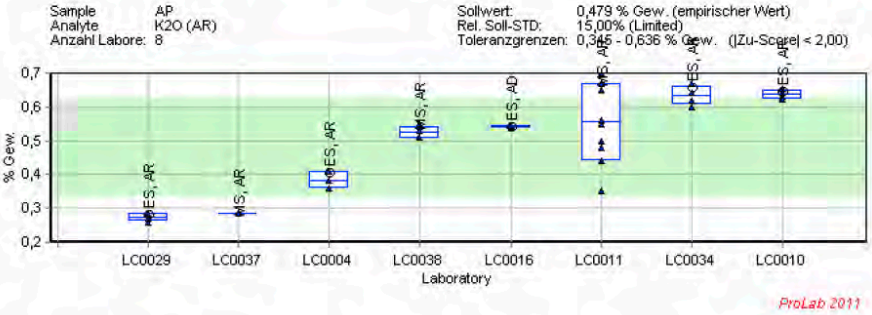

Sample AP
Analyte Ge
Anzahl Labore: 6
Sollwert: 1,046 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,488 - 1,799 mg/kg (|Zu-Score| < 2,00)
mg/kg
2,25
2
1,75
1,5
1,25
1
0,75
0,5
0,25
0
MS; AD
MS; FMAD
VWD; XRF, PP
XRF, FB
LC0008
LC0011
LC0038
LC0030
LC0013
LC0016
Laboratory
ProLab 2011

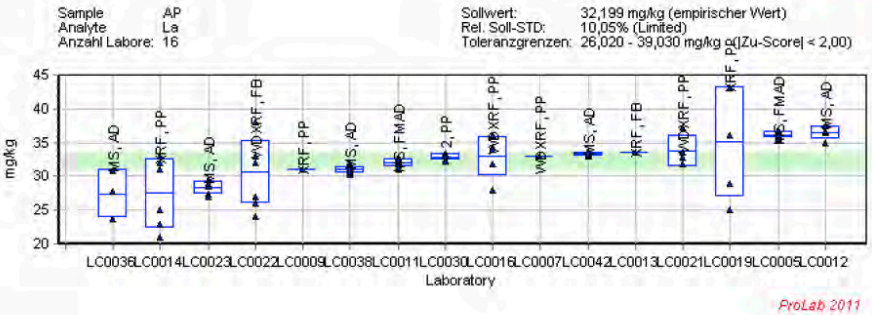

Sample AP
Analyte Hf
Anzahl Labore: 9
Sollwert: 4,366 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 2,038 - 7,511 mg/kg (|Zu-Score| < 2,00)
mg/kg
9
8
7
6
5
4
3
2
1
MS; AD
MS; FMAD
VWD; XRF, PP
XRF, PP
LC0012
LC0038
LC0030
LC0009
LC0014
LC0011
LC0005
LC0007
LC0016
Laboratory
ProLab 2011

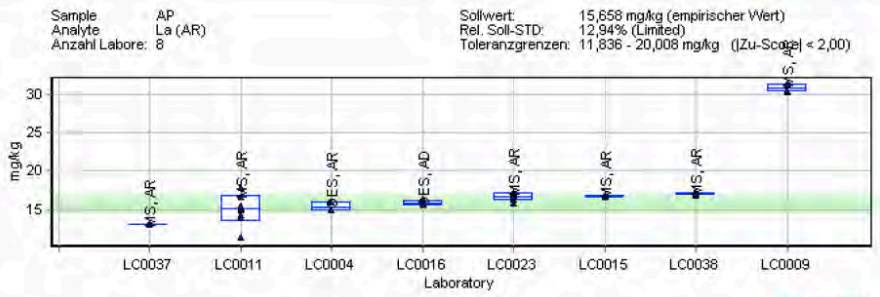

Sample AP
Analyte Hg
Anzahl Labore: 6
Sollwert: 0,125 mg/kg (empirischer Wert)
Rel. Soll-STD: 8,16% (Limited)
Toleranzgrenzen: 0,105 - 0,146 mg/kg (|Zu-Score| < 2,00)
mg/kg
0,2
0,1
0
MS; AD
AAS; AD
AAS; NO
B1; NO
AAS; AR
LC0038
LC0017
LC0031
LC0023
LC0020
LC0042
Laboratory
ProLab 2011

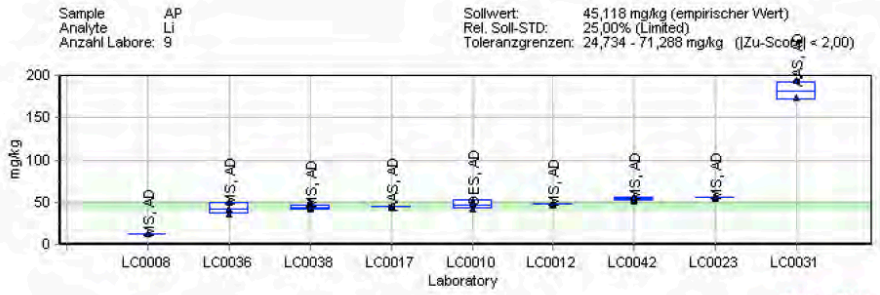

Sample AP
Analyte Ho
Anzahl Labore: 8
Sollwert: 0,653 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,305 - 1,123 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008 LC0012 LC0036 LC0023 LC0038 LC0002 LC0011 LC0005
Laboratory
ProLab 2011

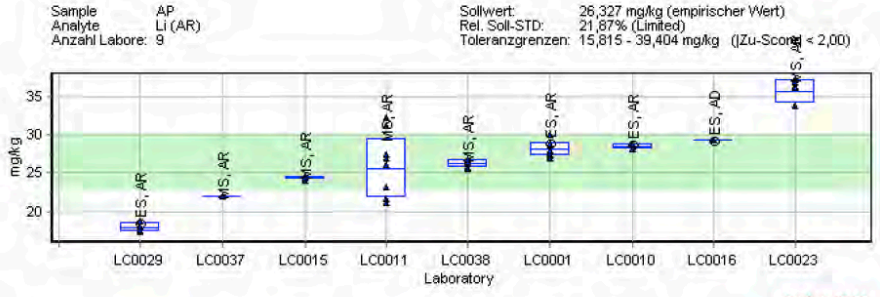

Sample AP
Analyte K2O
Anzahl Labore: 17
Sollwert: 2,440 % Gew. (empirischer Wert)
Rel. Soll-STD: 5,15% (Limited)
Toleranzgrenzen: 2,195 - 2,698 % Gew. (|Zu-Score| < 2,00)
% Gew.
LC0013 LC0022 LC0035 LC0017 LC0010 LC0009 LC0024 LC0030 LC0019
Laboratory
ProLab 2011

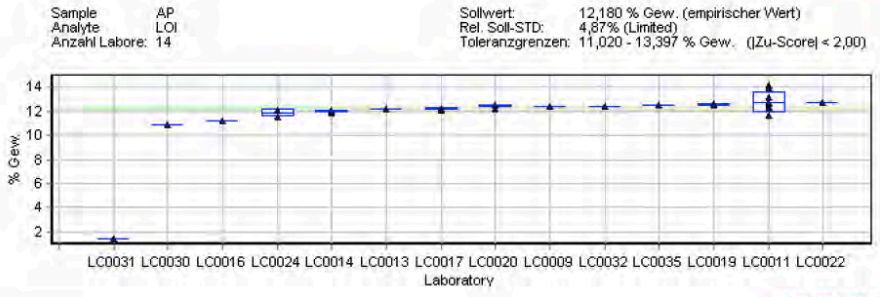

Sample AP
Analyte K2O (AR)
Anzahl Labore: 8
Sollwert: 0,479 % Gew. (empirischer Wert)
Rel. Soll-STD: 15,00% (Limited)
Toleranzgrenzen: 0,345 - 0,636 % Gew. (|Zu-Score| < 2,00)
% Gew.
LC0029 LC0037 LC0004 LC0038 LC0016 LC0011 LC0034 LC0010
Laboratory
ProLab 2011

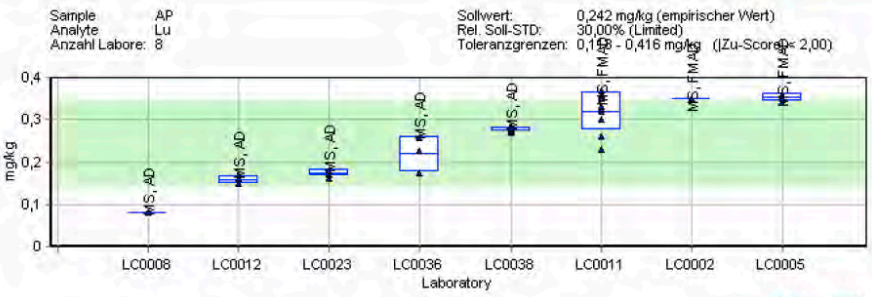

Sample AP
Analyte La
Anzahl Labore: 16
Sollwert: 32,199 mg/kg (empirischer Wert)
Rel. Soll-STD: 10,05% (Limited)
Toleranzgrenzen: 26,020 - 39,030 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0036 LC0014 LC0023 LC0022 LC0009 LC0038 LC0011 LC0030 LC0016 LC0007 LC0042 LC0013 LC0021 LC0019 LC0005 LC0012
Laboratory
ProLab 2011

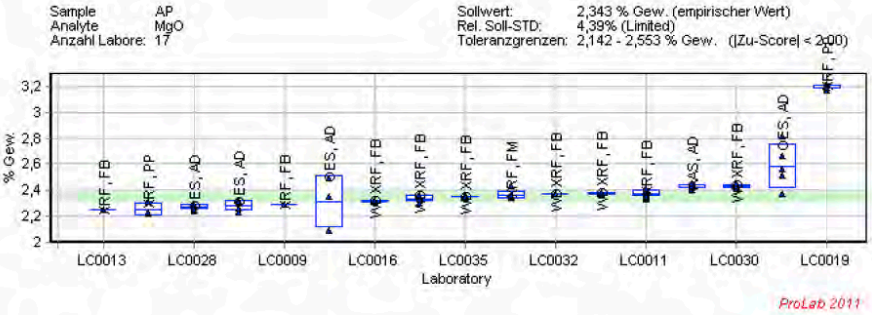

Sample AP
Analyte La (AR)
Anzahl Labore: 8
Sollwert: 15,658 mg/kg (empirischer Wert)
Rel. Soll-STD: 12,94% (Limited)
Toleranzgrenzen: 11,836 - 20,008 mg/kg (|Zu-Score| < 2,00)
mg/kg
30
25
20
15
ICP-MS, AR
ICP-OES, AR
ICP-OES, AD
LC0037 LC0011 LC0004 LC0016 LC0023 LC0015 LC0038 LC0009
Laboratory
ProLab 2011

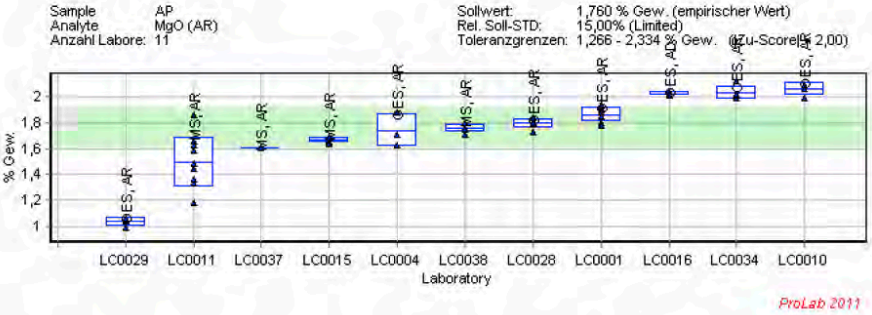

Sample AP
Analyte Li
Anzahl Labore: 9
Sollwert: 45,118 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 24,734 - 71,288 mg/kg (|Zu-Score| < 2,00)
mg/kg
200
150
100
50
0
ICP-MS, AD
ICP-OES, AD
LC0008 LC0036 LC0038 LC0017 LC0010 LC0012 LC0042 LC0023 LC0031
Laboratory
ProLab 2011

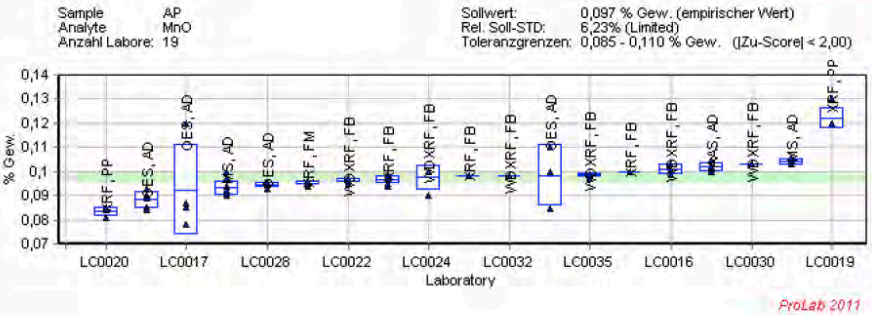

Sample AP
Analyte Li (AR)
Anzahl Labore: 9
Sollwert: 26,327 mg/kg (empirischer Wert)
Rel. Soll-STD: 21,87% (Limited)
Toleranzgrenzen: 15,815 - 39,404 mg/kg (|Zu-Score| < 2,00)
mg/kg
35
30
25
20
ICP-OES, AR
ICP-MS, AR
ICP-OES, AD
LC0029 LC0037 LC0015 LC0011 LC0038 LC0001 LC0010 LC0016 LC0023
Laboratory
ProLab 2011

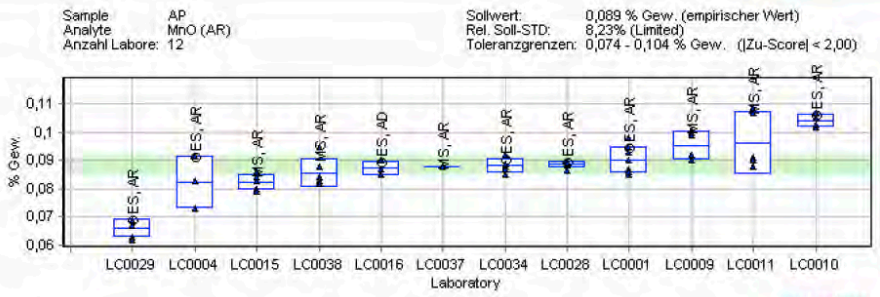

Sample AP
Analyte LOI
Anzahl Labore: 14
Sollwert: 12,180 % Gew. (empirischer Wert)
Rel. Soll-STD: 4,87% (Limited)
Toleranzgrenzen: 11,020 - 13,397 % Gew. (|Zu-Score| < 2,00)
% Gew.
14
12
10
8
6
4
2
LC0031 LC0030 LC0016 LC0024 LC0014 LC0013 LC0017 LC0020 LC0009 LC0032 LC0035 LC0019 LC0011 LC0022
Laboratory
ProLab 2011

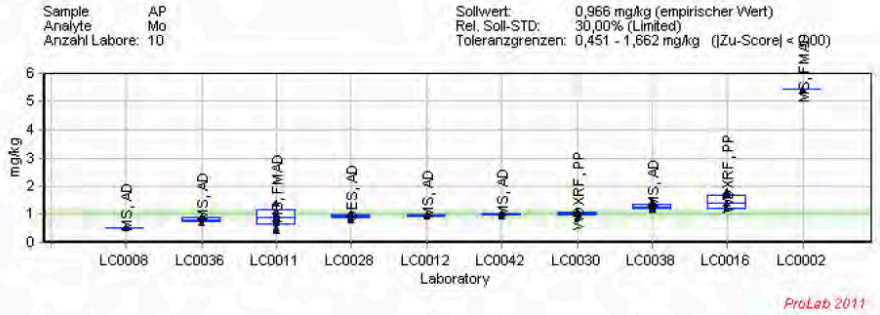

Sample AP
Analyte Lu
Anzahl Labore: 8
Sollwert: 0,242 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,169 - 0,416 mg/kg (|Zu-Score| < 2,00)
mg/kg
0,4
0,3
0,2
0,1
0
MS, AD
MS, FM
LC0008
LC0012
LC0023
LC0036
LC0038
LC0011
LC0002
LC0005
Laboratory
ProLab 2011

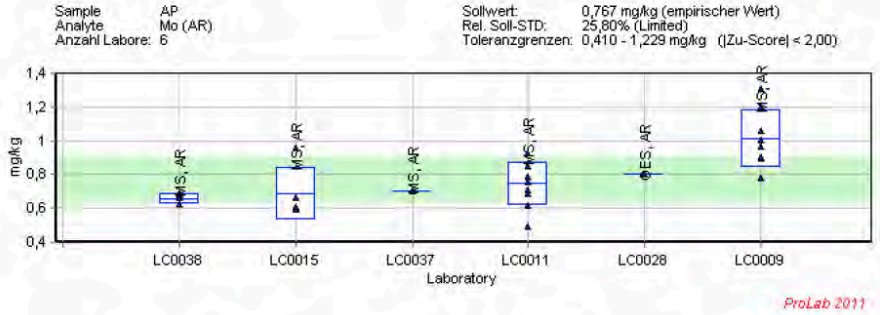

Sample AP
Analyte MgO
Anzahl Labore: 17
Sollwert: 2,343 % Gew. (empirischer Wert)
Rel. Soll-STD: 4,39% (Limited)
Toleranzgrenzen: 2,142 - 2,553 % Gew. (|Zu-Score| < 2,00)
% Gew.
3,2
3
2,8
2,6
2,4
2,2
2
XRF, FB
XRF, PP
OES, AD
XRF, FM
AAS, AD
LC0013
LC0028
LC0009
LC0016
LC0035
LC0032
LC0011
LC0030
LC0019
Laboratory
ProLab 2011

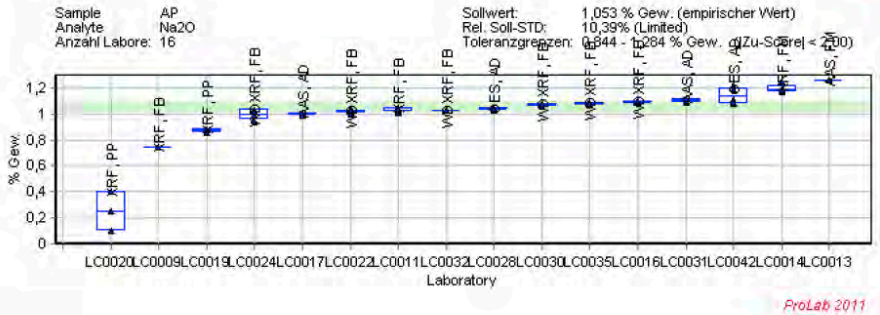

Sample AP
Analyte MgO (AR)
Anzahl Labore: 11
Sollwert: 1,760 % Gew. (empirischer Wert)
Rel. Soll-STD: 15,00% (Limited)
Toleranzgrenzen: 1,266 - 2,334 % Gew. (|Zu-Score| < 2,00)
% Gew.
2
1,8
1,6
1,4
1,2
1
OES, AR
MS, AR
LC0029
LC0011
LC0037
LC0015
LC0004
LC0038
LC0028
LC0001
LC0016
LC0034
LC0010
Laboratory
ProLab 2011

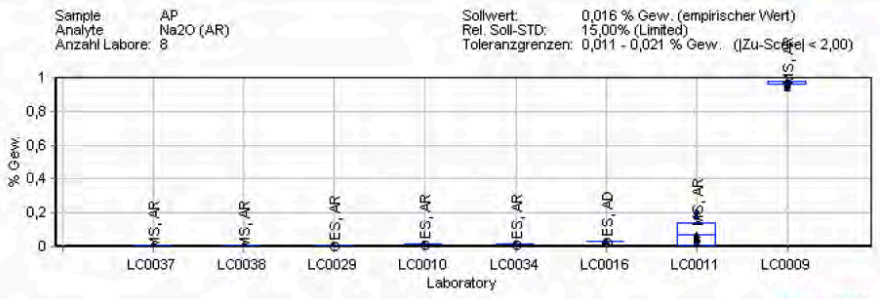

Sample AP
Analyte MnO
Anzahl Labore: 19
Sollwert: 0,097 % Gew. (empirischer Wert)
Rel. Soll-STD: 6,23% (Limited)
Toleranzgrenzen: 0,085 - 0,110 % Gew. (|Zu-Score| < 2,00)
% Gew.
0,14
0,13
0,12
0,11
0,1
0,09
0,08
0,07
XRF, PP
OES, AD
XRF, FB
XRF, FM
LC0020
LC0017
LC0028
LC0022
LC0024
LC0032
LC0035
LC0016
LC0030
LC0019
Laboratory
ProLab 2011

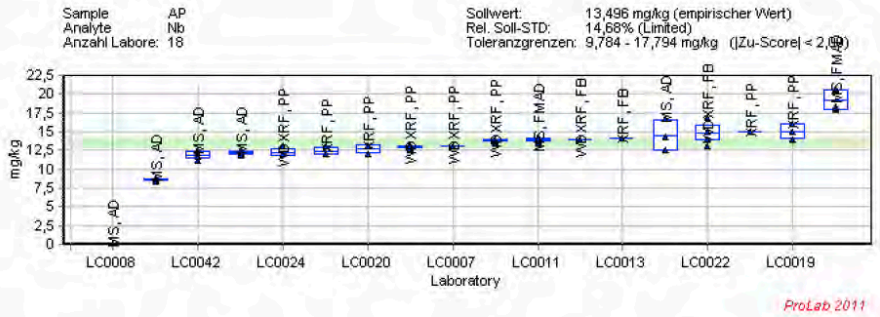

Sample AP
Analyte MnO (AR)
Anzahl Labore: 12
Sollwert: 0,089 % Gew. (empirischer Wert)
Rel. Soll-STD: 8,23% (Limited)
Toleranzgrenzen: 0,074 - 0,104 % Gew. (|Zu-Score| < 2,00)
% Gew.
0,11
0,1
0,09
0,08
0,07
0,06
ES, AR
LC0029 LC0004 LC0015 LC0038 LC0016 LC0037 LC0034 LC0028 LC0001 LC0009 LC0011 LC0010
Laboratory
ProLab 2011

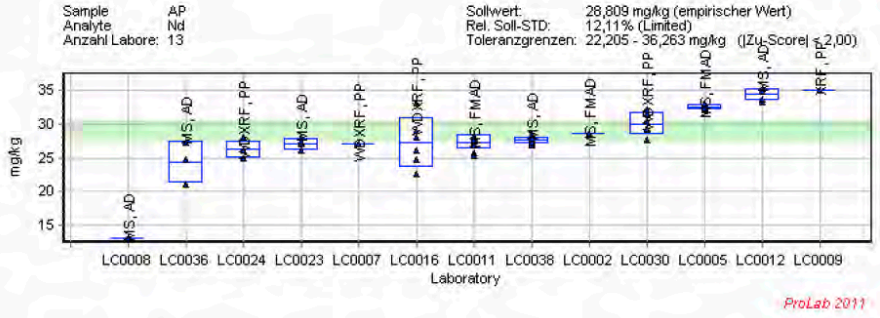

Sample AP
Analyte Mo
Anzahl Labore: 10
Sollwert: 0,966 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,451 - 1,662 mg/kg (|Zu-Score| < 2,00)
mg/kg
6
5
4
3
2
1
0
MS, AD
LC0008 LC0036 LC0011 LC0028 LC0012 LC0042 LC0030 LC0038 LC0016 LC0002
Laboratory
ProLab 2011

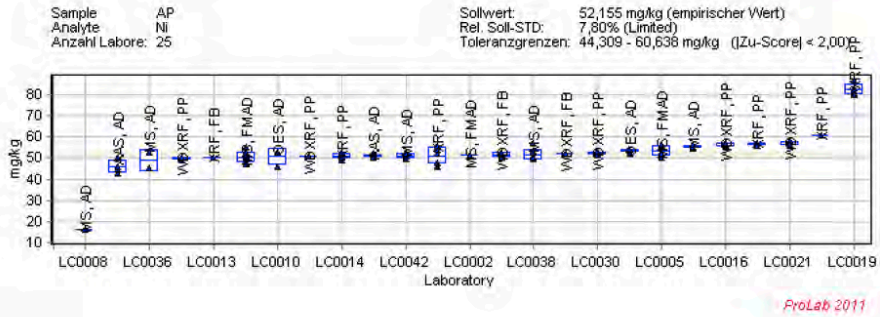

Sample AP
Analyte Mo (AR)
Anzahl Labore: 6
Sollwert: 0,767 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,80% (Limited)
Toleranzgrenzen: 0,410 - 1,229 mg/kg (|Zu-Score| < 2,00)
mg/kg
1,4
1,2
1
0,8
0,6
0,4
MS, AR
LC0038 LC0015 LC0037 LC0011 LC0028 LC0009
Laboratory
ProLab 2011

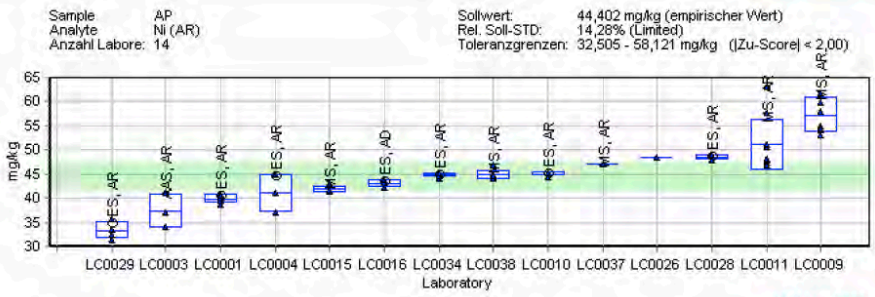

Sample AP
Analyte Na2O
Anzahl Labore: 16
Sollwert: 1,053 % Gew. (empirischer Wert)
Rel. Soll-STD: 10,39% (Limited)
% Gew.
1,2
1
0,8
0,6
0,4
0,2
0
XRF, PP
XRF, FB
AAS, AD
ES, AD
LC0020 LC0009 LC0019 LC0024 LC0017 LC0022 LC0011 LC0032 LC0028 LC0030 LC0035 LC0016 LC0031 LC0042 LC0014 LC0013
Laboratory
ProLab 2011

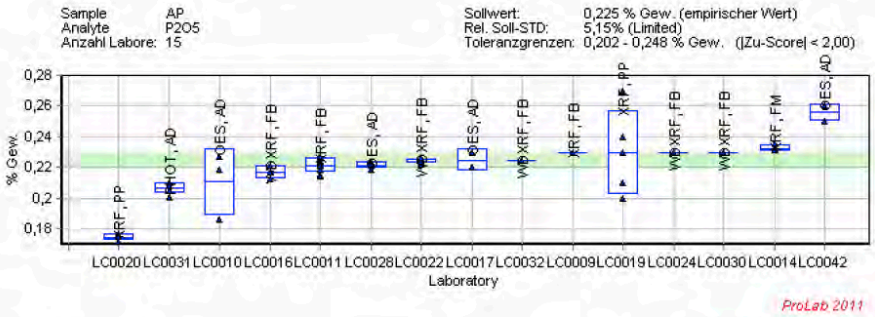

Sample AP
Analyte Na2O (AR)
Anzahl Labore: 8
Sollwert: 0,016 % Gew. (empirischer Wert)
Rel. Soll-STD: 15,00% (Limited)
Toleranzgrenzen: 0,011 - 0,021 % Gew. (|Zu-Score| < 2,00)
% Gew.
Laboratory
LC0037 LC0038 LC0029 LC0010 LC0034 LC0016 LC0011 LC0009
ProLab 2011

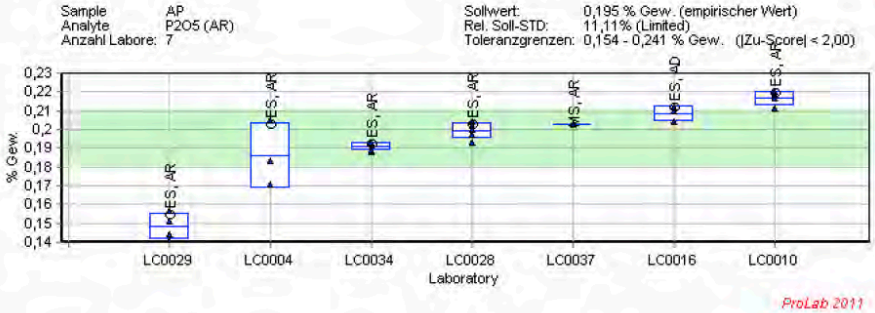

Sample AP
Analyte Nb
Anzahl Labore: 18
Sollwert: 13,496 mg/kg (empirischer Wert)
Rel. Soll-STD: 14,68% (Limited)
Toleranzgrenzen: 9,784 - 17,794 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0042 LC0024 LC0020 LC0007 LC0011 LC0013 LC0022 LC0019
ProLab 2011

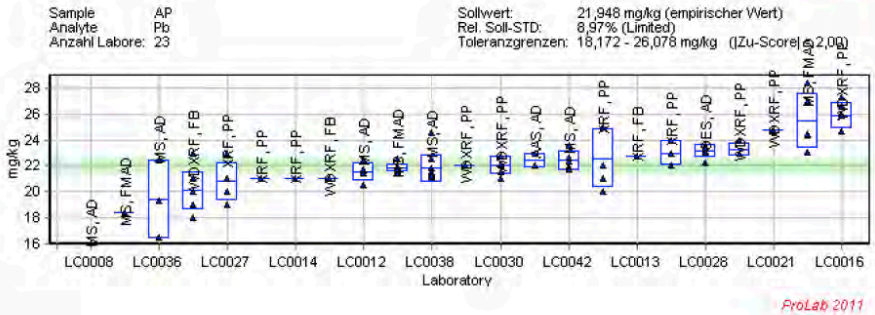

Sample AP
Analyte Nd
Anzahl Labore: 13
Sollwert: 28,809 mg/kg (empirischer Wert)
Rel. Soll-STD: 12,11% (Limited)
Toleranzgrenzen: 22,205 - 36,263 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0036 LC0024 LC0023 LC0007 LC0016 LC0011 LC0038 LC0002 LC0030 LC0005 LC0012 LC0009
ProLab 2011

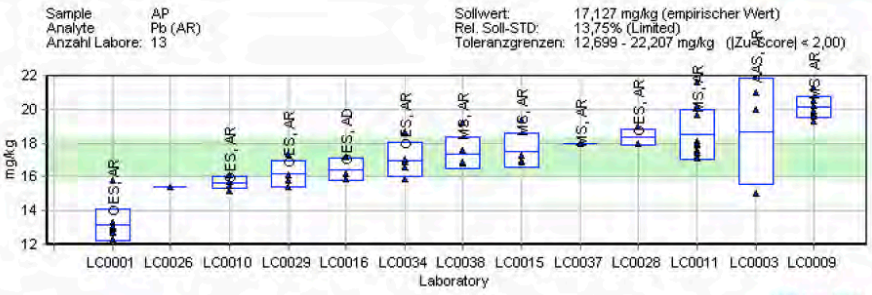

Sample AP
Analyte Ni
Anzahl Labore: 25
Sollwert: 52,155 mg/kg (empirischer Wert)
Rel. Soll-STD: 7,80% (Limited)
Toleranzgrenzen: 44,309 - 60,638 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0036 LC0013 LC0010 LC0014 LC0042 LC0002 LC0038 LC0030 LC0005 LC0016 LC0021 LC0019
ProLab 2011

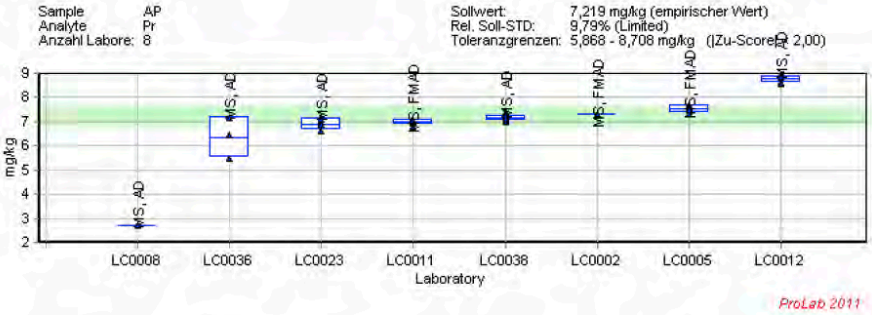

Sample AP
Analyte Ni (AR)
Anzahl Labore: 14
Sollwert: 44,402 mg/kg (empirischer Wert)
Rel. Soll-STD: 14,28% (Limited)
Toleranzgrenzen: 32,505 - 58,121 mg/kg (|Zu-Score| < 2,00)
mg/kg
65
60
55
50
45
40
35
30
OES, AR
AAS, AR
OES, AR
OES, AR
MS, AR
OES, AD
OES, AR
MS, AR
OES, AR
MS, AR
OES, AR
MS, AR
MS, AR
LC0029 LC0003 LC0001 LC0004 LC0015 LC0016 LC0034 LC0038 LC0010 LC0037 LC0026 LC0028 LC0011 LC0009
Laboratory
ProLab 2011

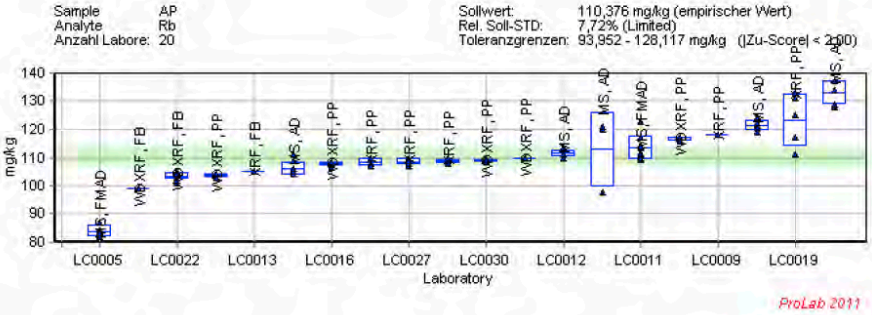

Sample AP
Analyte P2O5
Anzahl Labore: 15
Sollwert: 0,225 % Gew. (empirischer Wert)
Rel. Soll-STD: 5,15% (Limited)
Toleranzgrenzen: 0,202 - 0,248 % Gew. (|Zu-Score| < 2,00)
% Gew.
0,28
0,26
0,24
0,22
0,2
0,18
XRF, PP
PHOT, AD
OES, AD
WD-XRF, FB
XRF, FB
OES, AD
WD-XRF, FB
OES, AD
WD-XRF, FB
XRF, FB
XRF, PP
WD-XRF, FB
WD-XRF, FB
XRF, FM
OES, AD
LC0020 LC0031 LC0010 LC0016 LC0011 LC0028 LC0022 LC0017 LC0032 LC0009 LC0019 LC0024 LC0030 LC0014 LC0042
Laboratory
ProLab 2011

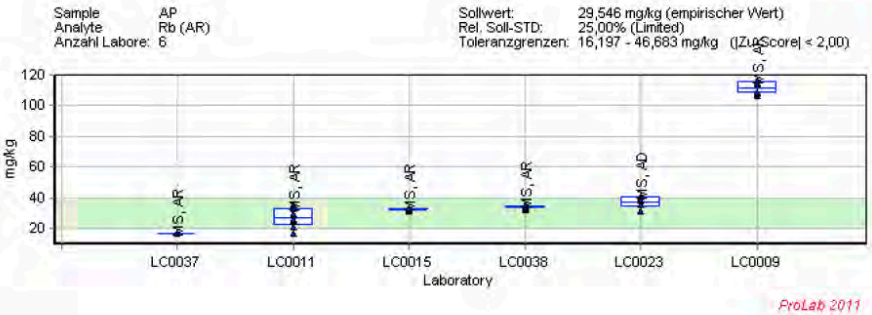

Sample AP
Analyte P2O5 (AR)
Anzahl Labore: 7
Sollwert: 0,195 % Gew. (empirischer Wert)
Rel. Soll-STD: 11,11% (Limited)
Toleranzgrenzen: 0,154 - 0,241 % Gew. (|Zu-Score| < 2,00)
% Gew.
0,23
0,22
0,21
0,2
0,19
0,18
0,17
0,16
0,15
0,14
OES, AR
OES, AR
OES, AR
OES, AR
MS, AR
OES, AD
OES, AR
LC0029 LC0004 LC0034 LC0028 LC0037 LC0016 LC0010
Laboratory
ProLab 2011

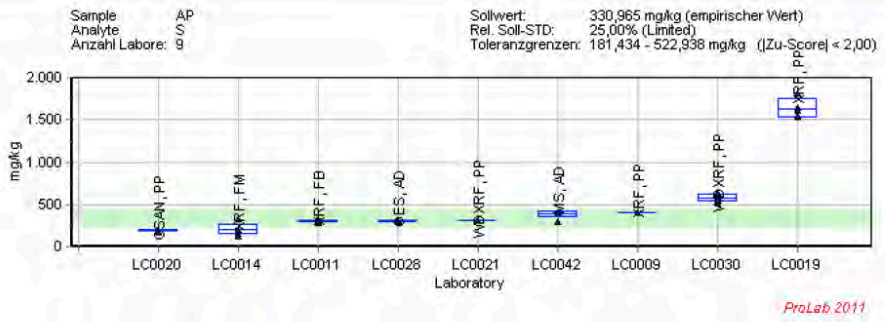

Sample AP
Analyte Pb
Anzahl Labore: 23
Sollwert: 21,948 mg/kg (empirischer Wert)
Rel. Soll-STD: 8,97% (Limited)
Toleranzgrenzen: 18,172 - 26,078 mg/kg (|Zu-Score| < 2,00)
mg/kg
28
26
24
22
20
18
16
MS, AD
MP, FM AD
MS, AD
WD-XRF, FB
XRF, PP
XRF, PP
XRF, PP
WD-XRF, FB
MS, AD
MP, FM AD
MS, AD
WD-XRF, PP
WD-XRF, PP
AAS, AD
MS, AD
XRF, PP
XRF, FB
XRF, PP
OES, AD
WD-XRF, PP
WD-XRF, PP
MP, FM AD
XRF, PP
LC0008 LC0036 LC0027 LC0014 LC0012 LC0038 LC0030 LC0042 LC0013 LC0028 LC0021 LC0016
Laboratory
ProLab 2011

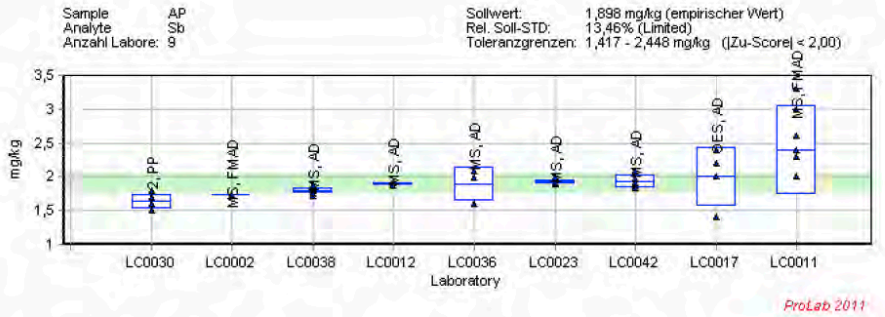

Sample AP
Analyte Pb (AR)
Anzahl Labore: 13
Sollwert: 17,127 mg/kg (empirischer Wert)
Rel. Soll-STD: 13,75% (Limited)
Toleranzgrenzen: 12,699 - 22,207 mg/kg (|Zu-Score| ≤ 2,00)
mg/kg
Laboratory
LC0001 LC0026 LC0010 LC0029 LC0016 LC0034 LC0038 LC0015 LC0037 LC0028 LC0011 LC0003 LC0009
ProLab 2011

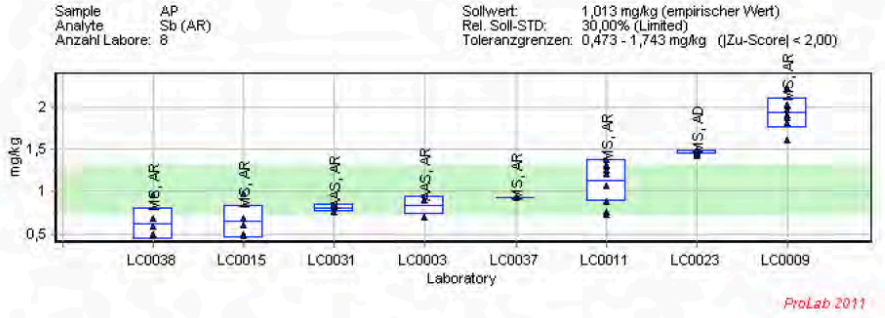

Sample AP
Analyte Pr
Anzahl Labore: 8
Sollwert: 7,219 mg/kg (empirischer Wert)
Rel. Soll-STD: 9,79% (Limited)
Toleranzgrenzen: 5,868 - 8,708 mg/kg (|Zu-Score| ≤ 2,00)
mg/kg
Laboratory
LC0008 LC0036 LC0023 LC0011 LC0038 LC0002 LC0005 LC0012
ProLab 2011

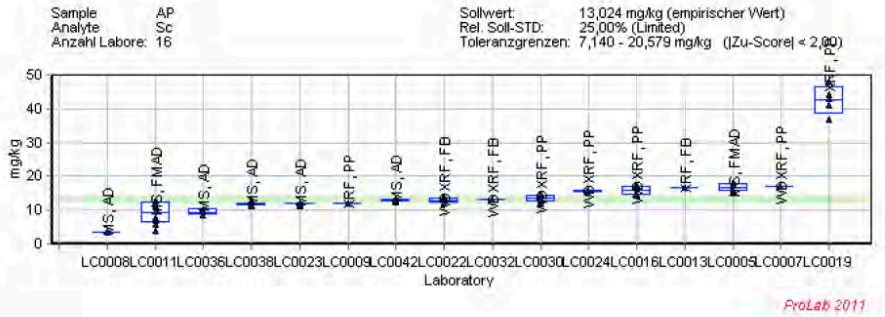

Sample AP
Analyte Rb
Anzahl Labore: 20
Sollwert: 110,376 mg/kg (empirischer Wert)
Rel. Soll-STD: 7,72% (Limited)
Toleranzgrenzen: 93,952 - 128,117 mg/kg (|Zu-Score| ≤ 2,00)
mg/kg
Laboratory
LC0005 LC0022 LC0013 LC0016 LC0027 LC0030 LC0012 LC0011 LC0009 LC0019
ProLab 2011

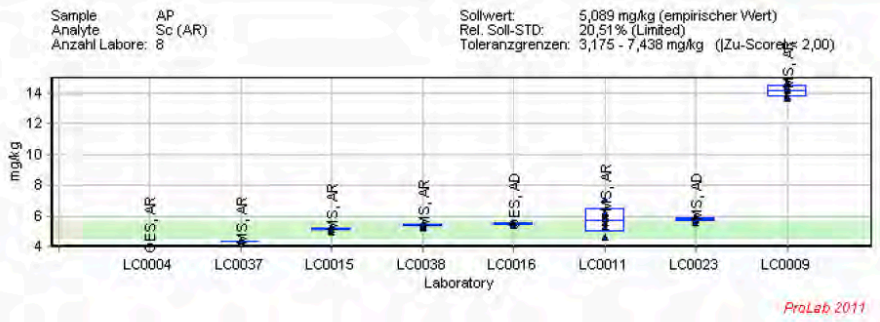

Sample AP
Analyte Rb (AR)
Anzahl Labore: 6
Sollwert: 29,546 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 16,197 - 46,683 mg/kg (|Zu-Score| ≤ 2,00)
mg/kg
Laboratory
LC0037 LC0011 LC0015 LC0038 LC0023 LC0009
ProLab 2011

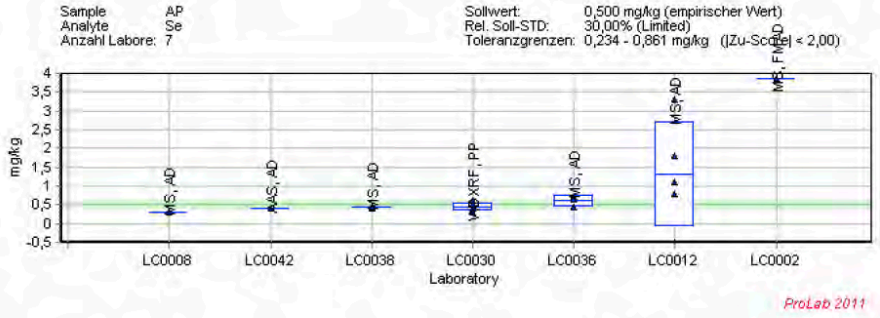

Sample AP
Analyte S
Anzahl Labore: 9
Sollwert: 330,965 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 181,434 - 522,938 mg/kg (|Zu-Score| < 2,00)
mg/kg
2.000
1.500
1.000
500
0
LC0020 LC0014 LC0011 LC0028 LC0021 LC0042 LC0009 LC0030 LC0019
Laboratory
ProLab 2011

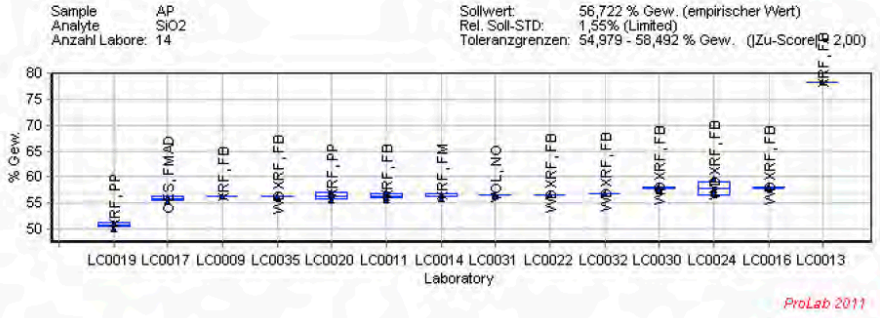

Sample AP
Analyte Sb
Anzahl Labore: 9
Sollwert: 1,898 mg/kg (empirischer Wert)
Rel. Soll-STD: 13,46% (Limited)
Toleranzgrenzen: 1,417 - 2,448 mg/kg (|Zu-Score| < 2,00)
mg/kg
3,5
3
2,5
2
1,5
1
LC0030 LC0002 LC0038 LC0012 LC0036 LC0023 LC0042 LC0017 LC0011
Laboratory
ProLab 2011

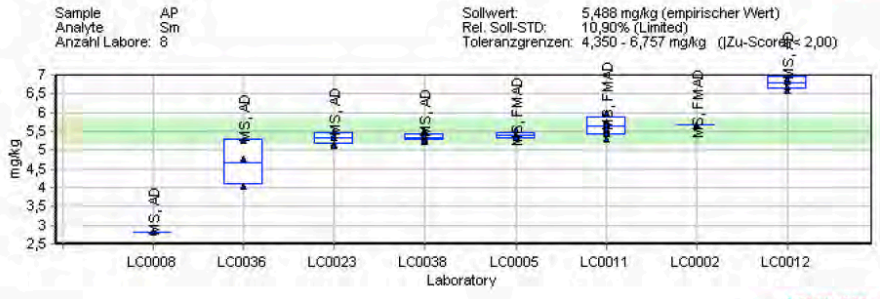

Sample AP
Analyte Sb (AR)
Anzahl Labore: 8
Sollwert: 1,013 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,473 - 1,743 mg/kg (|Zu-Score| < 2,00)
mg/kg
2
1,5
1
0,5
LC0038 LC0015 LC0031 LC0003 LC0037 LC0011 LC0023 LC0009
Laboratory
ProLab 2011

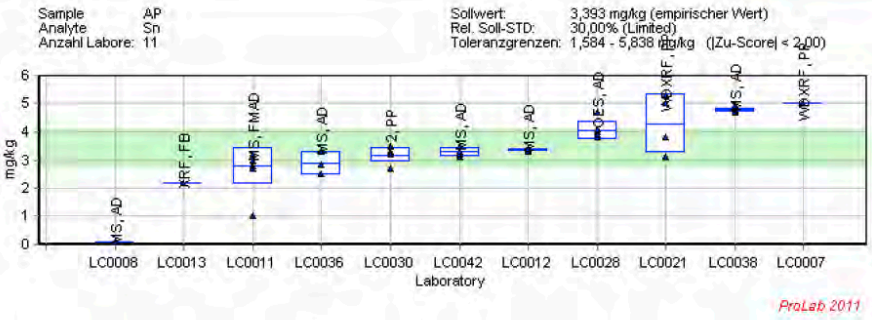

Sample AP
Analyte Sc
Anzahl Labore: 16
Sollwert: 13,024 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 7,140 - 20,579 mg/kg (|Zu-Score| < 2,00)
mg/kg
50
40
30
20
10
0
LC0008 LC0011 LC0036 LC0038 LC0023 LC0009 LC0042 LC0022 LC0032 LC0030 LC0024 LC0016 LC0013 LC0005 LC0007 LC0019
Laboratory
ProLab 2011

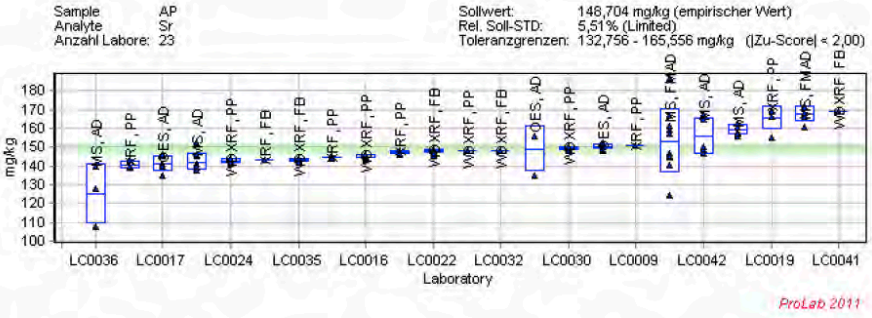

Sample AP
Analyte Sc (AR)
Anzahl Labore: 8
Sollwert: 5,089 mg/kg (empirischer Wert)
Rel. Soll-STD: 20,51% (Limited)
Toleranzgrenzen: 3,175 - 7,438 mg/kg (|Zu-Score| < 2,00)
mg/kg
14
12
10
8
6
4
ES, AR
MS, AR
MS, AR
MS, AR
ES, AD
MS, AR
MS, AD
AS, AR
LC0004
LC0037
LC0015
LC0038
LC0016
LC0011
LC0023
LC0009
Laboratory
ProLab 2011

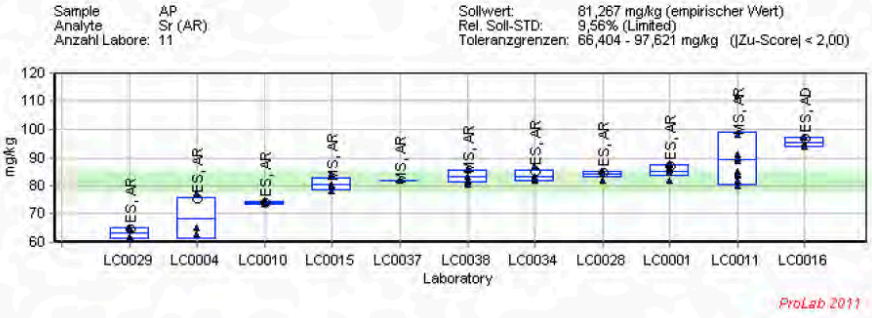

Sample AP
Analyte Se
Anzahl Labore: 7
Sollwert: 0,500 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,234 - 0,861 mg/kg (|Zu-Score| < 2,00)
mg/kg
4
3,5
3
2,5
2
1,5
1
0,5
0
-0,5
MS, AD
AAS, AD
MS, AD
XRF, PP
MS, AD
MS, AD
MS, FM AD
LC0008
LC0042
LC0038
LC0030
LC0036
LC0012
LC0002
Laboratory
ProLab 2011

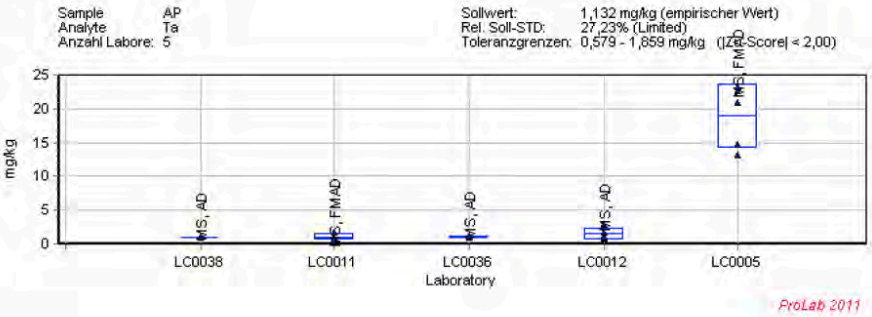

Sample AP
Analyte SiO2
Anzahl Labore: 14
Sollwert: 56,722 % Gew. (empirischer Wert)
Rel. Soll-STD: 1,55% (Limited)
Toleranzgrenzen: 54,979 - 58,492 % Gew. (|Zu-Score| < 2,00)
% Gew.
80
75
70
65
60
55
50
XRF, PP
OES, FMAD
XRF, FB
WD-XRF, FB
XRF, PP
XRF, FB
XRF, FM
VOL, NO
WD-XRF, FB
WD-XRF, FB
WD-XRF, FB
WD-XRF, FB
WD-XRF, FB
XRF, FB
LC0019 LC0017 LC0009 LC0035 LC0020 LC0011 LC0014 LC0031 LC0022 LC0032 LC0030 LC0024 LC0016 LC0013
Laboratory
ProLab 2011

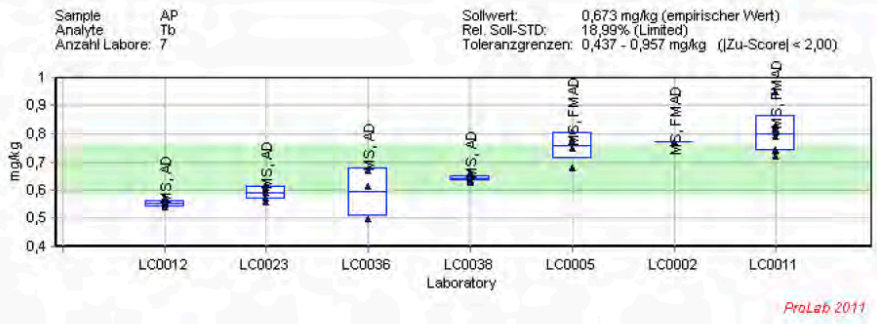

Sample AP
Analyte Sm
Anzahl Labore: 8
Sollwert: 5,488 mg/kg (empirischer Wert)
Rel. Soll-STD: 10,90% (Limited)
Toleranzgrenzen: 4,350 - 6,757 mg/kg (|Zu-Score| < 2,00)
mg/kg
7
6,5
6
5,5
5
4,5
4
3,5
3
2,5
MS, AD
MS, AD
MS, AD
MS, AD
MS, FMAD
MS, FMAD
MS, FMAD
MS, AR
LC0008
LC0036
LC0023
LC0038
LC0005
LC0011
LC0002
LC0012
Laboratory
ProLab 2011

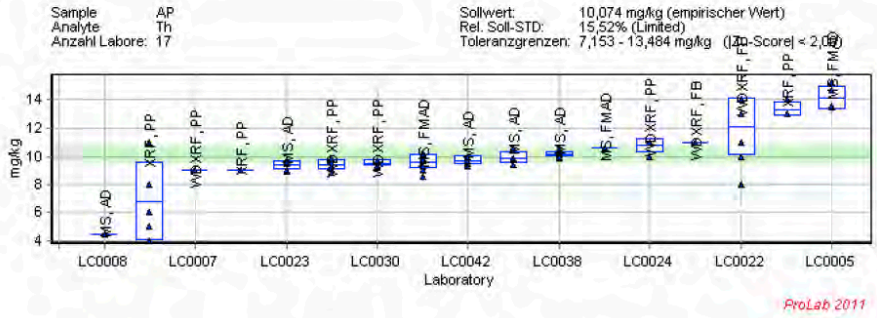

Sample AP
Analyte Sn
Anzahl Labore: 11
Sollwert: 3,393 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 1,584 - 5,838 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008 LC0013 LC0011 LC0036 LC0030 LC0042 LC0012 LC0028 LC0021 LC0038 LC0007
Laboratory
ProLab 2011

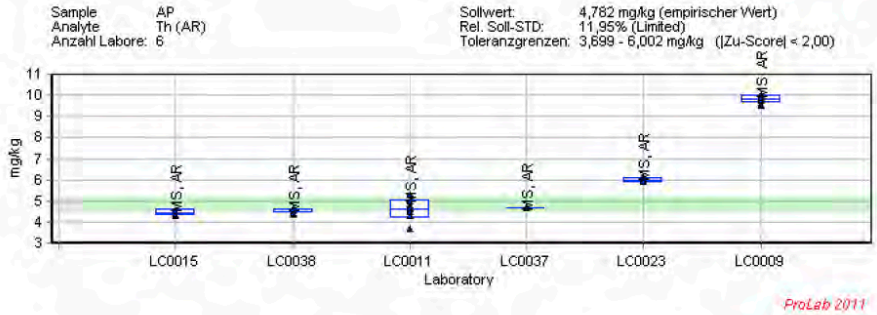

Sample AP
Analyte Sr
Anzahl Labore: 23
Sollwert: 148,704 mg/kg (empirischer Wert)
Rel. Soll-STD: 5,51% (Limited)
Toleranzgrenzen: 132,756 - 165,556 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0036 LC0017 LC0024 LC0035 LC0016 LC0022 LC0032 LC0030 LC0009 LC0042 LC0019 LC0041
Laboratory
ProLab 2011

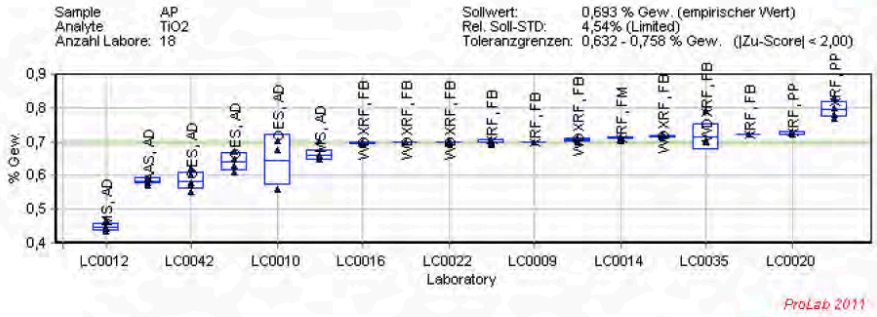

Sample AP
Analyte Sr (AR)
Anzahl Labore: 11
Sollwert: 81,267 mg/kg (empirischer Wert)
Rel. Soll-STD: 9,56% (Limited)
Toleranzgrenzen: 66,404 - 97,621 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0029 LC0004 LC0010 LC0015 LC0037 LC0038 LC0034 LC0028 LC0001 LC0011 LC0016
Laboratory
ProLab 2011

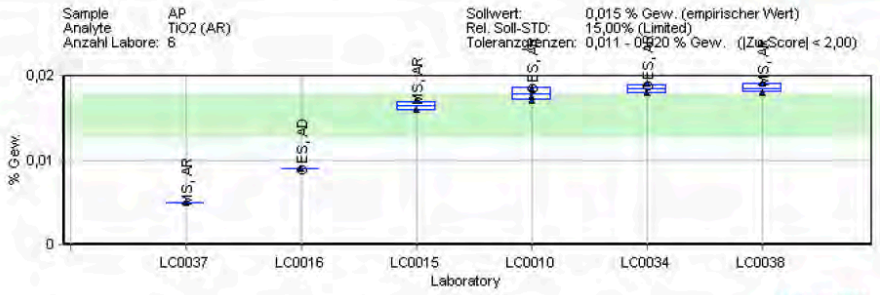

Sample AP
Analyte Ta
Anzahl Labore: 5
Sollwert: 1,132 mg/kg (empirischer Wert)
Rel. Soll-STD: 27,23% (Limited)
Toleranzgrenzen: 0,579 - 1,859 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0038 LC0011 LC0036 LC0012 LC0005
Laboratory
ProLab 2011

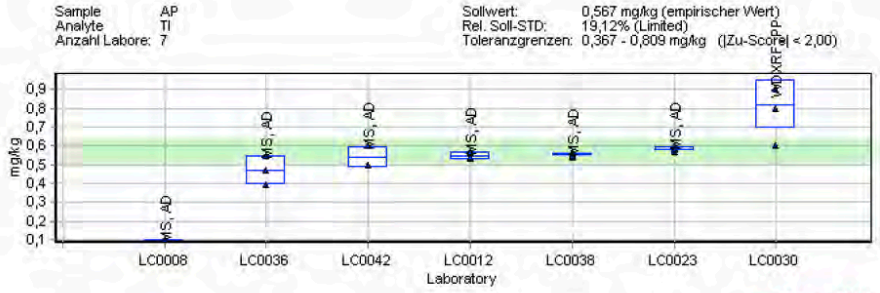

Sample AP
Analyte Tb
Anzahl Labore: 7
Sollwert: 0,673 mg/kg (empirischer Wert)
Rel. Soll-STD: 18,99% (Limited)
Toleranzgrenzen: 0,437 - 0,957 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0012
LC0023
LC0036
LC0038
LC0005
LC0002
LC0011
Laboratory
ProLab 2011

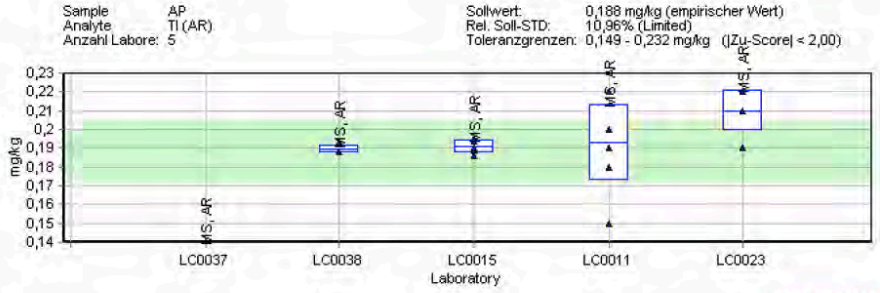

Sample AP
Analyte Th
Anzahl Labore: 17
Sollwert: 10,074 mg/kg (empirischer Wert)
Rel. Soll-STD: 15,52% (Limited)
Toleranzgrenzen: 7,153 - 13,484 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008
LC0007
LC0023
LC0030
LC0042
LC0038
LC0024
LC0022
LC0005
Laboratory
ProLab 2011

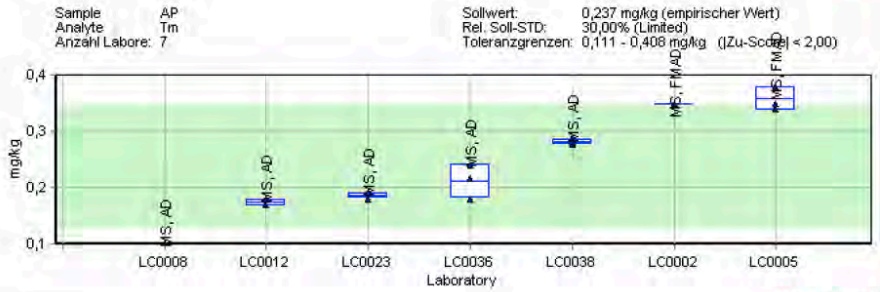

Sample AP
Analyte Th (AR)
Anzahl Labore: 6
Sollwert: 4,782 mg/kg (empirischer Wert)
Rel. Soll-STD: 11,95% (Limited)
Toleranzgrenzen: 3,699 - 6,002 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0015
LC0038
LC0011
LC0037
LC0023
LC0009
Laboratory
ProLab 2011

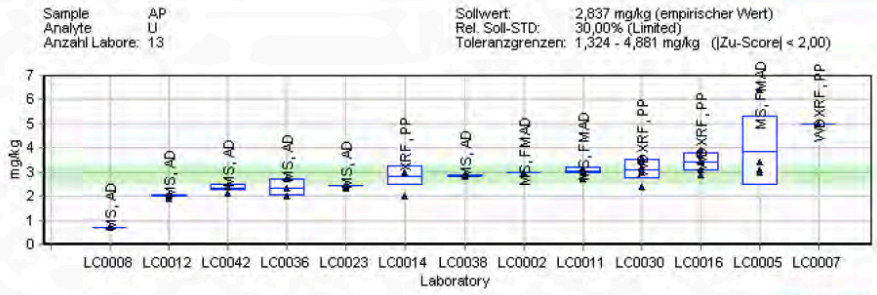

Sample AP
Analyte TiO2
Anzahl Labore: 18
Sollwert: 0,693 % Gew. (empirischer Wert)
Rel. Soll-STD: 4,54% (Limited)
Toleranzgrenzen: 0,632 - 0,758 % Gew. (|Zu-Score| < 2,00)
% Gew.
LC0012
LC0042
LC0010
LC0016
LC0022
LC0009
LC0014
LC0035
LC0020
Laboratory
ProLab 2011

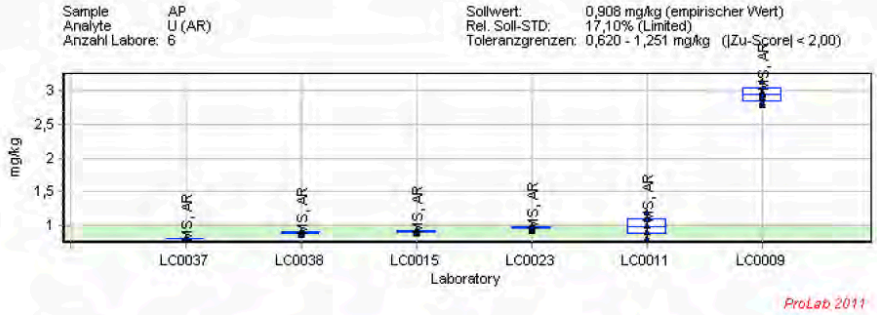

Sample AP
Analyte TiO2 (AR)
Anzahl Labore: 6
Sollwert: 0,015 % Gew. (empirischer Wert)
Rel. Soll-STD: 15,00% (Limited)
Toleranzgrenzen: 0,011 - 0,020 % Gew. (|Zu-Score| < 2,00)
% Gew.
0,02
0,01
0
MS, AR
ES, AD
MS, AR
ES, AR
ES, AD
MS, AR
LC0037
LC0016
LC0015
LC0010
LC0034
LC0038
Laboratory
ProLab 2011

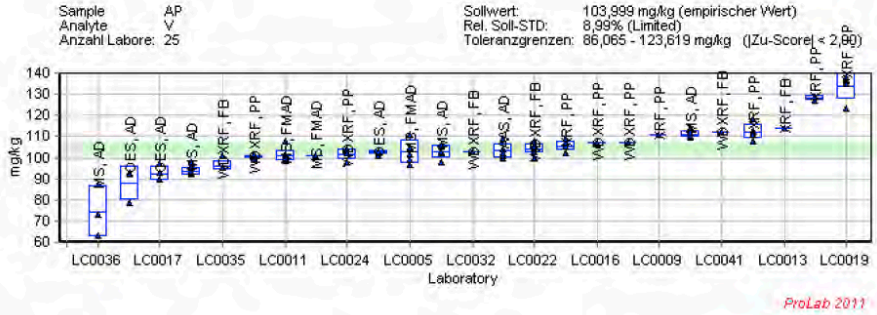

Sample AP
Analyte Tl
Anzahl Labore: 7
Sollwert: 0,567 mg/kg (empirischer Wert)
Rel. Soll-STD: 19,12% (Limited)
Toleranzgrenzen: 0,367 - 0,809 mg/kg (|Zu-Score| < 2,00)
mg/kg
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
MS, AD
MS, AD
MS, AD
MS, AD
MS, AD
MD, XRF
LC0008
LC0036
LC0042
LC0012
LC0038
LC0023
LC0030
Laboratory
ProLab 2011

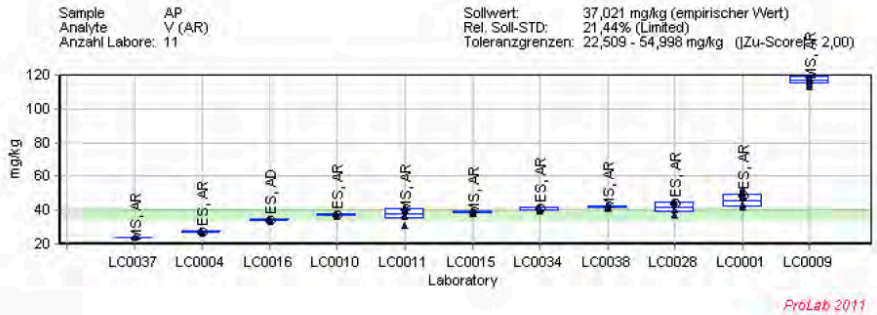

Sample AP
Analyte Tl (AR)
Anzahl Labore: 5
Sollwert: 0,188 mg/kg (empirischer Wert)
Rel. Soll-STD: 10,96% (Limited)
Toleranzgrenzen: 0,149 - 0,232 mg/kg (|Zu-Score| < 2,00)
mg/kg
0,23
0,22
0,21
0,2
0,19
0,18
0,17
0,16
0,15
0,14
MS, AR
MS, AR
MS, AR
MS, AR
MS, AR
LC0037
LC0038
LC0015
LC0011
LC0023
Laboratory
ProLab 2011

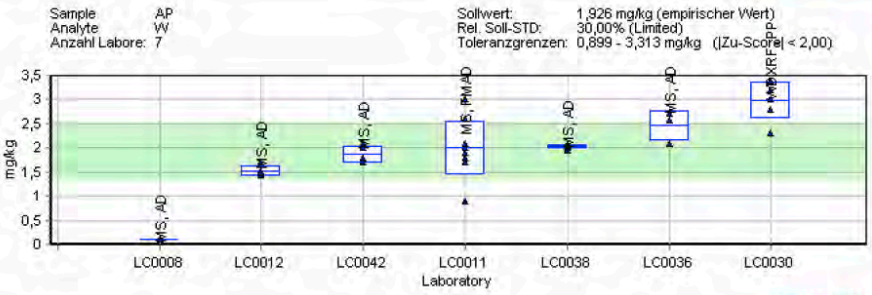

Sample AP
Analyte Tm
Anzahl Labore: 7
Sollwert: 0,237 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,111 - 0,408 mg/kg (|Zu-Score| < 2,00)
mg/kg
0,4
0,3
0,2
0,1
MS, AD
MS, AD
MS, AD
MS, AD
MS, AD
MS, FM, AD
MS, FM, AD
LC0008
LC0012
LC0023
LC0036
LC0038
LC0002
LC0005
Laboratory
ProLab 2011

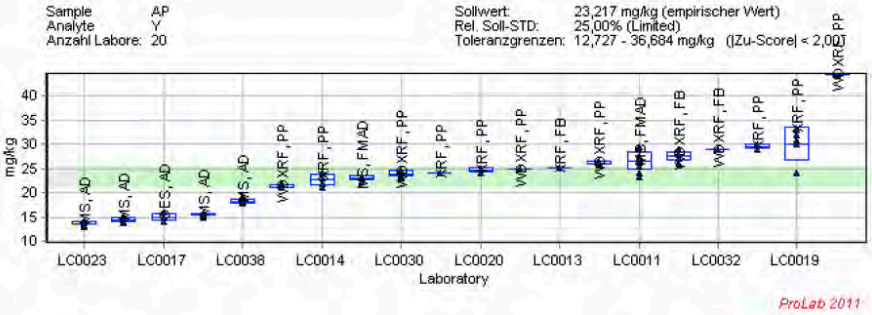

Sample AP
Analyte U
Anzahl Labore: 13
Sollwert: 2,837 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 1,324 - 4,881 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008 LC0012 LC0042 LC0036 LC0023 LC0014 LC0038 LC0002 LC0011 LC0030 LC0016 LC0005 LC0007
Laboratory
ProLab 2011

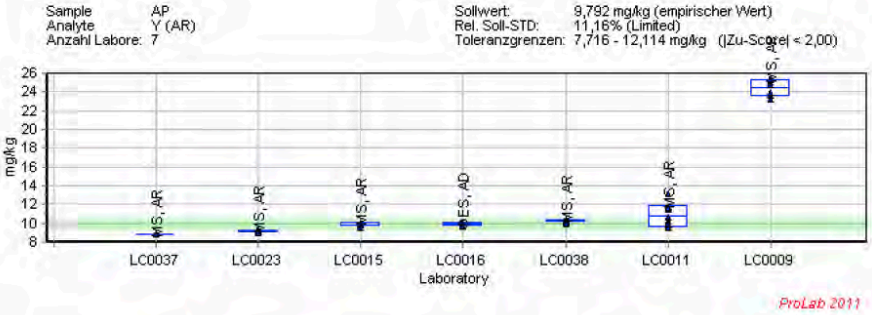

Sample AP
Analyte U (AR)
Anzahl Labore: 6
Sollwert: 0,908 mg/kg (empirischer Wert)
Rel. Soll-STD: 17,10% (Limited)
Toleranzgrenzen: 0,620 - 1,251 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0037 LC0038 LC0015 LC0023 LC0011 LC0009
Laboratory
ProLab 2011

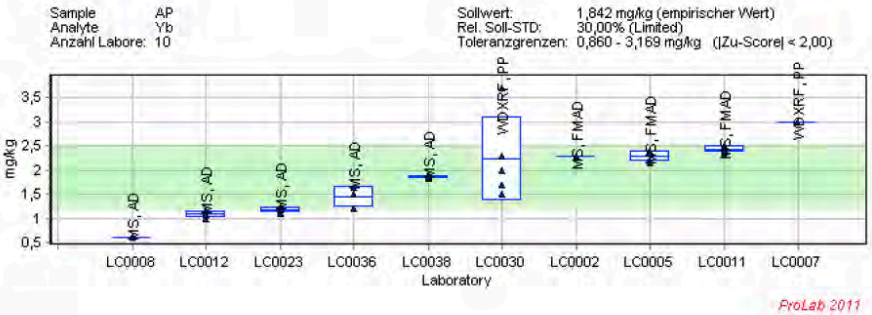

Sample AP
Analyte V
Anzahl Labore: 25
Sollwert: 103,999 mg/kg (empirischer Wert)
Rel. Soll-STD: 8,99% (Limited)
Toleranzgrenzen: 86,065 - 123,619 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0036 LC0017 LC0035 LC0011 LC0024 LC0005 LC0032 LC0022 LC0016 LC0009 LC0041 LC0013 LC0019
Laboratory
ProLab 2011

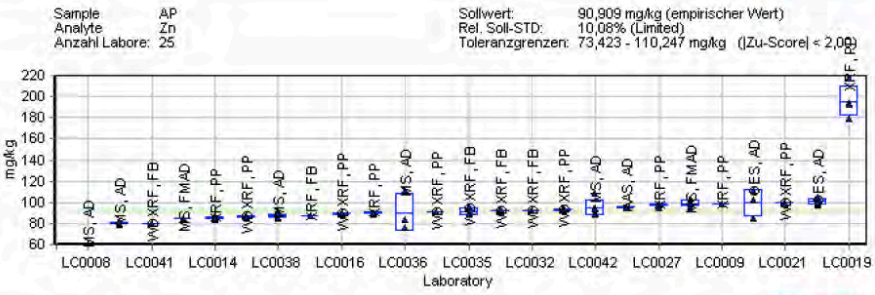

Sample AP
Analyte V (AR)
Anzahl Labore: 11
Sollwert: 37,021 mg/kg (empirischer Wert)
Rel. Soll-STD: 21,44% (Limited)
Toleranzgrenzen: 22,509 - 54,998 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0037 LC0004 LC0016 LC0010 LC0011 LC0015 LC0034 LC0038 LC0028 LC0001 LC0009
Laboratory
ProLab 2011

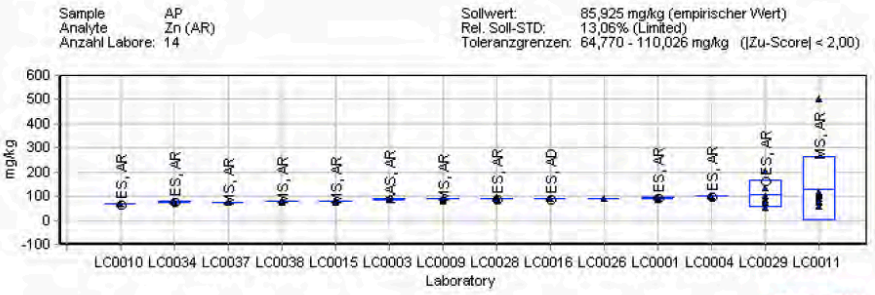

Sample AP
Analyte W
Anzahl Labore: 7
Sollwert: 1,926 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,899 - 3,313 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008
LC0012
LC0042
LC0011
LC0038
LC0036
LC0030
ProLab 2011

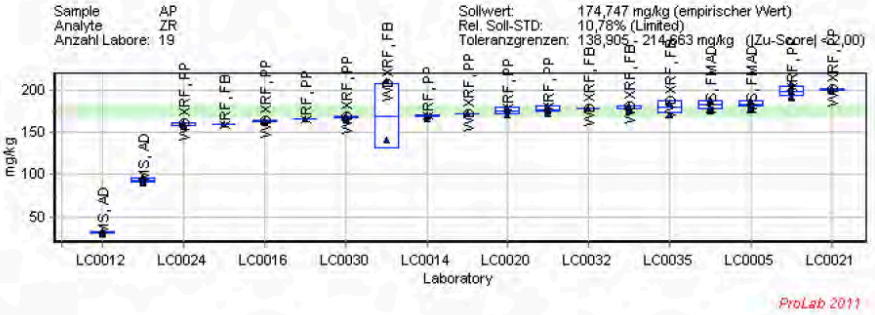

Sample AP
Analyte Y
Anzahl Labore: 20
Sollwert: 23,217 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 12,727 - 36,684 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0023
LC0017
LC0038
LC0014
LC0030
LC0020
LC0013
LC0011
LC0032
LC0019
ProLab 2011

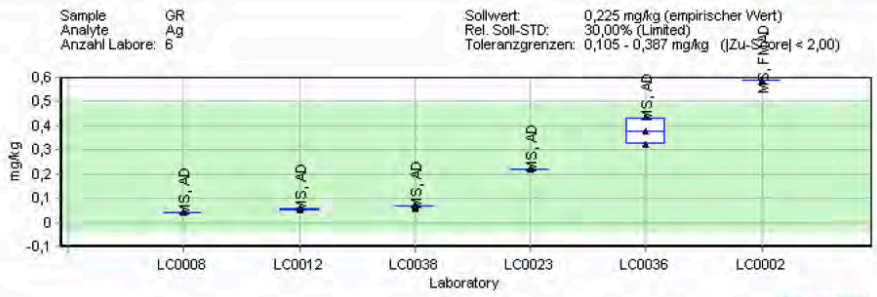

Sample AP
Analyte Y (AR)
Anzahl Labore: 7
Sollwert: 9,792 mg/kg (empirischer Wert)
Rel. Soll-STD: 11,16% (Limited)
Toleranzgrenzen: 7,716 - 12,114 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0037
LC0023
LC0015
LC0016
LC0038
LC0011
LC0009
ProLab 2011

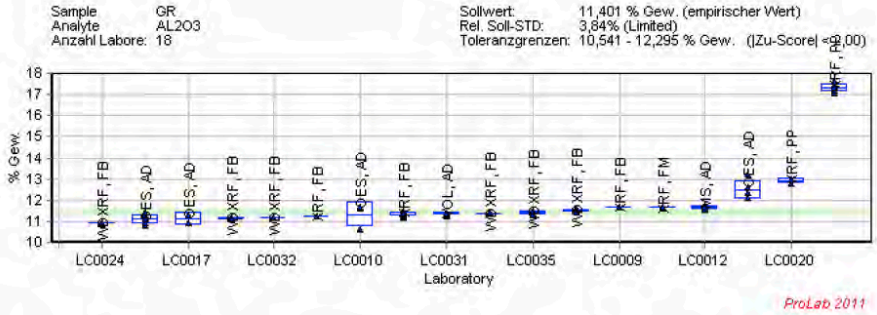

Sample AP
Analyte Yb
Anzahl Labore: 10
Sollwert: 1,842 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,860 - 3,169 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008
LC0012
LC0023
LC0036
LC0038
LC0030
LC0002
LC0005
LC0011
LC0007
ProLab 2011

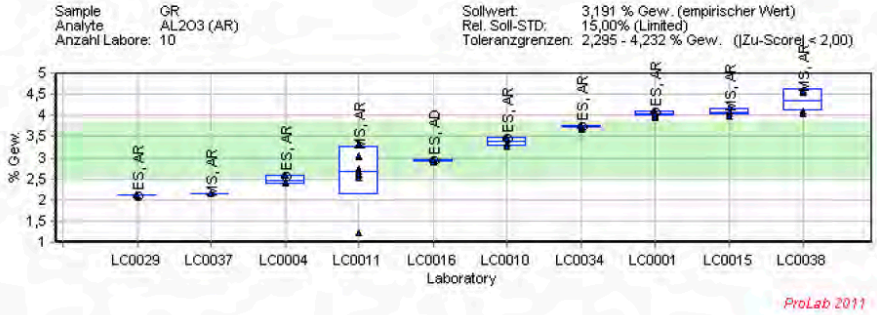

Sample AP
Analyte Zn
Anzahl Labore: 25
Sollwert: 90,909 mg/kg (empirischer Wert)
Rel. Soll-STD: 10,08% (Limited)
Toleranzgrenzen: 73,423 - 110,247 mg/kg (|Zu-Score| < 2,00)
mg/kg
220
200
180
160
140
120
100
80
60
MS, AD
MS, AD
WD XRF, FB
MS, FMAD
RF, PP
WD XRF, PP
MS, AD
RF, FB
WD XRF, PP
RF, PP
MS, AD
WD XRF, PP
WD XRF, FB
WD XRF, FB
WD XRF, FB
WD XRF, PP
MS, AD
AAS, AD
RF, PP
MS, FMAD
RF, PP
ES, AD
WD XRF, PP
ES, AD
LC0008 LC0041 LC0014 LC0038 LC0016 LC0036 LC0035 LC0032 LC0042 LC0027 LC0009 LC0021 LC0019
Laboratory
ProLab 2011

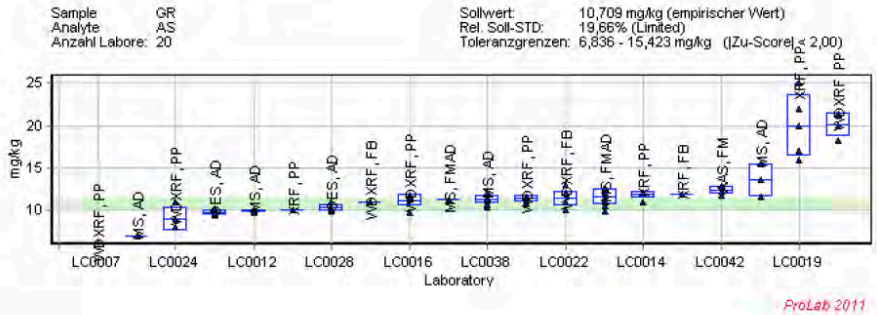

Sample AP
Analyte Zn (AR)
Anzahl Labore: 14
Sollwert: 85,925 mg/kg (empirischer Wert)
Rel. Soll-STD: 13,06% (Limited)
Toleranzgrenzen: 64,770 - 110,026 mg/kg (|Zu-Score| < 2,00)
mg/kg
600
500
400
300
200
100
0
-100
ES, AR
ES, AR
MS, AR
MS, AR
MS, AR
AAS, AR
MS, AR
ES, AR
ES, AD
ES, AR
ES, AR
ES, AR
MS, AR
LC0010 LC0034 LC0037 LC0038 LC0015 LC0003 LC0009 LC0028 LC0016 LC0026 LC0001 LC0004 LC0029 LC0011
Laboratory
ProLab 2011

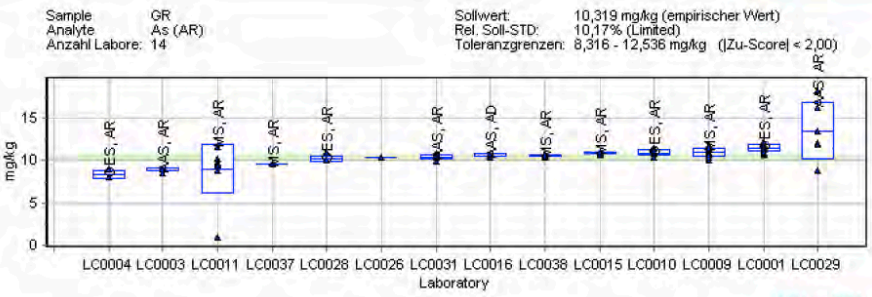

Sample AP
Analyte ZR
Anzahl Labore: 19
Sollwert: 174,747 mg/kg (empirischer Wert)
Rel. Soll-STD: 10,78% (Limited)
Toleranzgrenzen: 138,905 - 214,663 mg/kg (|Zu-Score| < 2,00)
mg/kg
200
150
100
50
MS, AD
MS, AD
WD XRF, FP
XRF, FB
WD XRF, PP
XRF, PP
WD XRF, PP
WD XRF, FB
XRF, PP
WD XRF, PP
XRF, PP
XRF, PP
WD XRF, FB
WD XRF, FB
WD XRF, FB
MS, FMAD
MS, FMAD
XRF, PP
WD XRF, FP
LC0012 LC0024 LC0016 LC0030 LC0014 LC0020 LC0032 LC0035 LC0005 LC0021
Laboratory
ProLab 2011

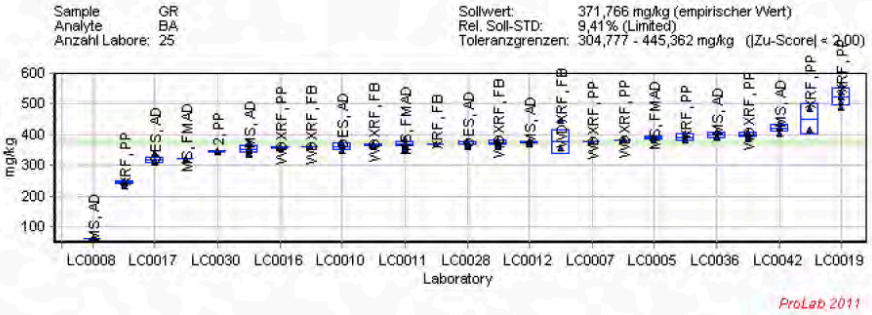

Sample GR
Analyte Ag
Anzahl Labore: 6
Sollwert: 0,225 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,105 - 0,387 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008
LC0012
LC0038
LC0023
LC0036
LC0002
ProLab 2011

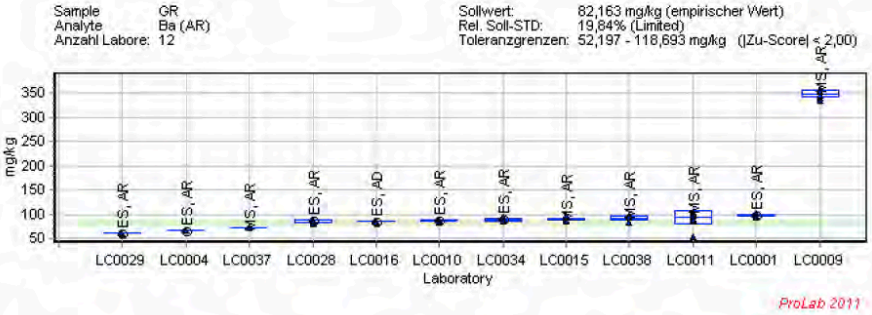

Sample GR
Analyte AL2O3
Anzahl Labore: 18
Sollwert: 11,401 % Gew. (empirischer Wert)
Rel. Soll-STD: 3,84% (Limited)
Toleranzgrenzen: 10,541 - 12,295 % Gew. (|Zu-Score| < 2,00)
% Gew.
Laboratory
LC0024
LC0017
LC0032
LC0010
LC0031
LC0035
LC0009
LC0012
LC0020
ProLab 2011

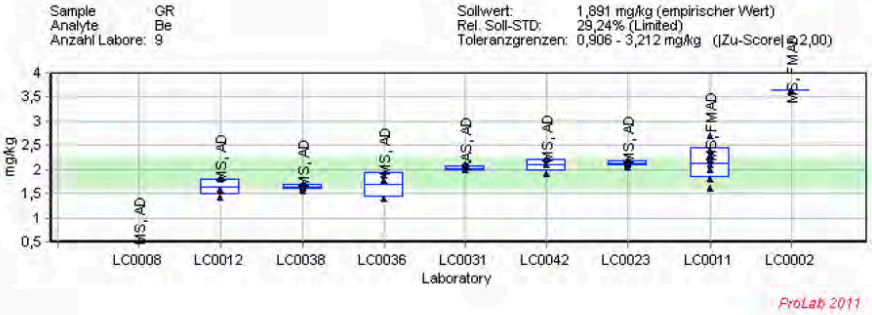

Sample GR
Analyte AL2O3 (AR)
Anzahl Labore: 10
Sollwert: 3,191 % Gew. (empirischer Wert)
Rel. Soll-STD: 15,00% (Limited)
Toleranzgrenzen: 2,295 - 4,232 % Gew. (|Zu-Score| < 2,00)
% Gew.
Laboratory
LC0029
LC0037
LC0004
LC0011
LC0016
LC0010
LC0034
LC0001
LC0015
LC0038
ProLab 2011

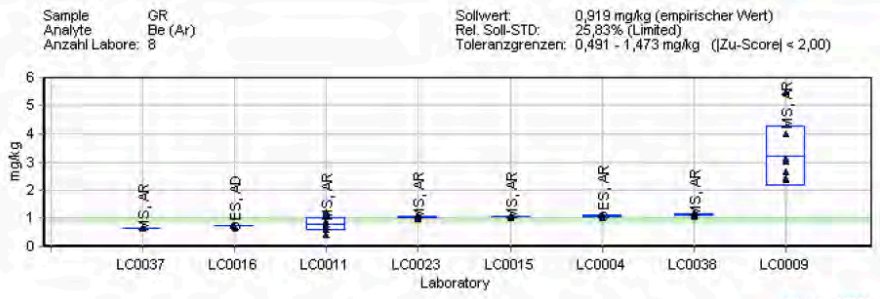

Sample GR
Analyte AS
Anzahl Labore: 20
Sollwert: 10,709 mg/kg (empirischer Wert)
Rel. Soll-STD: 19,66% (Limited)
Toleranzgrenzen: 6,836 - 15,423 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0007
LC0024
LC0012
LC0028
LC0016
LC0038
LC0022
LC0014
LC0042
LC0019
ProLab 2011

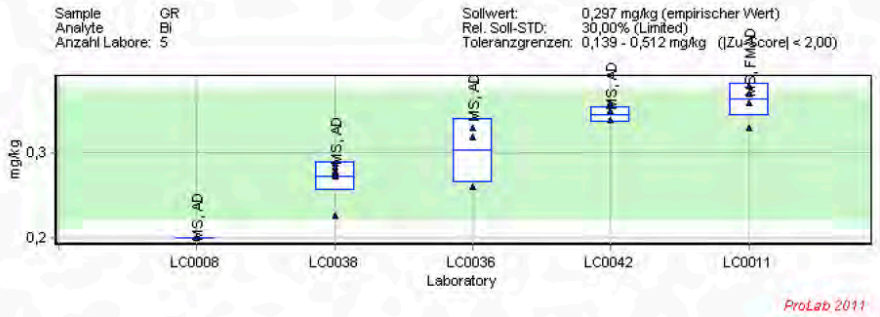

Sample GR
Analyte As (AR)
Anzahl Labore: 14
Sollwert: 10,319 mg/kg (empirischer Wert)
Rel. Soll-STD: 10,17% (Limited)
Toleranzgrenzen: 8,316 - 12,536 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0004 LC0003 LC0011 LC0037 LC0028 LC0026 LC0031 LC0016 LC0038 LC0015 LC0010 LC0009 LC0001 LC0029
ProLab 2011

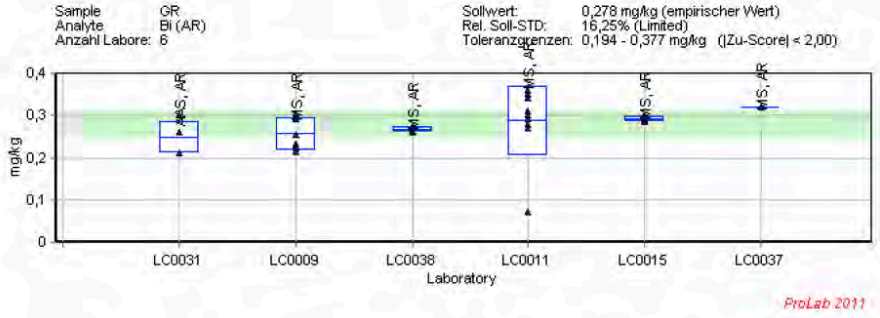

Sample GR
Analyte BA
Anzahl Labore: 25
Sollwert: 371,766 mg/kg (empirischer Wert)
Rel. Soll-STD: 9,41% (Limited)
Toleranzgrenzen: 304,777 - 445,362 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0017 LC0030 LC0016 LC0010 LC0011 LC0028 LC0012 LC0007 LC0005 LC0036 LC0042 LC0019
ProLab 2011

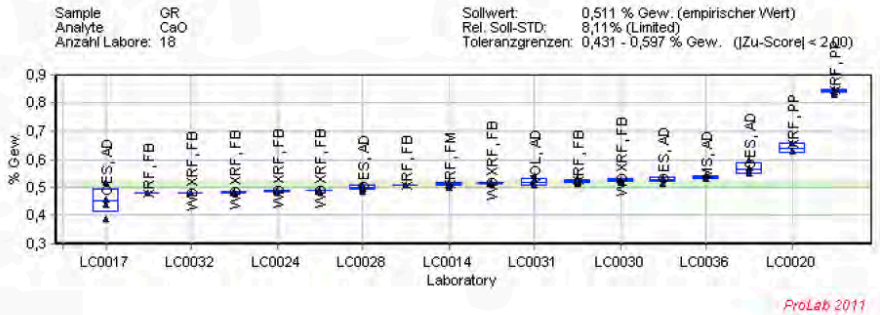

Sample GR
Analyte Ba (AR)
Anzahl Labore: 12
Sollwert: 82,163 mg/kg (empirischer Wert)
Rel. Soll-STD: 19,84% (Limited)
Toleranzgrenzen: 52,197 - 118,693 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0029 LC0004 LC0037 LC0028 LC0016 LC0010 LC0034 LC0015 LC0038 LC0011 LC0001 LC0009
ProLab 2011

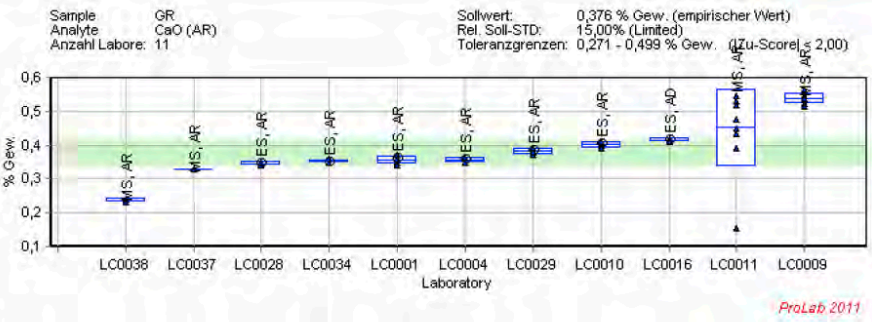

Sample GR
Analyte Be
Anzahl Labore: 9
Sollwert: 1,891 mg/kg (empirischer Wert)
Rel. Soll-STD: 29,24% (Limited)
Toleranzgrenzen: 0,906 - 3,212 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0012 LC0038 LC0036 LC0031 LC0042 LC0023 LC0011 LC0002
ProLab 2011

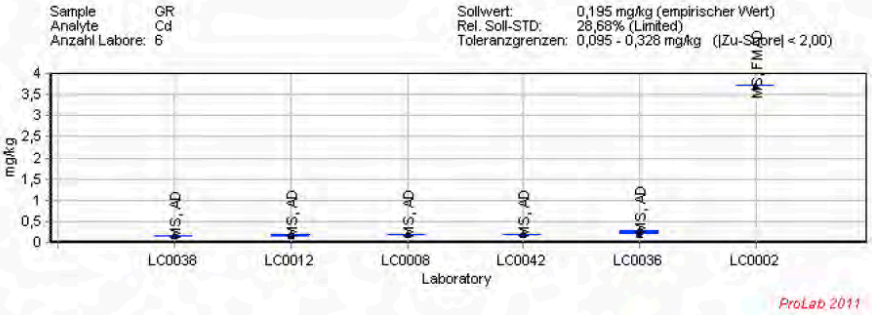

Sample GR
Analyte Be (Ar)
Anzahl Labore: 8
Sollwert: 0,919 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,83% (Limited)
Toleranzgrenzen: 0,491 - 1,473 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0037 LC0016 LC0011 LC0023 LC0015 LC0004 LC0038 LC0009
Laboratory
ProLab 2011


Sample GR
Analyte Bi
Anzahl Labore: 5
Sollwert: 0,297 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,139 - 0,512 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008 LC0038 LC0036 LC0042 LC0011
Laboratory
ProLab 2011

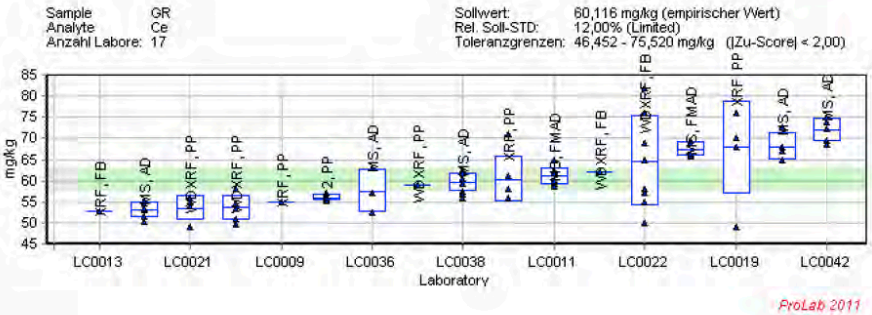

Sample GR
Analyte Bi (AR)
Anzahl Labore: 6
Sollwert: 0,278 mg/kg (empirischer Wert)
Rel. Soll-STD: 16,25% (Limited)
Toleranzgrenzen: 0,194 - 0,377 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0031 LC0009 LC0038 LC0011 LC0015 LC0037
Laboratory
ProLab 2011

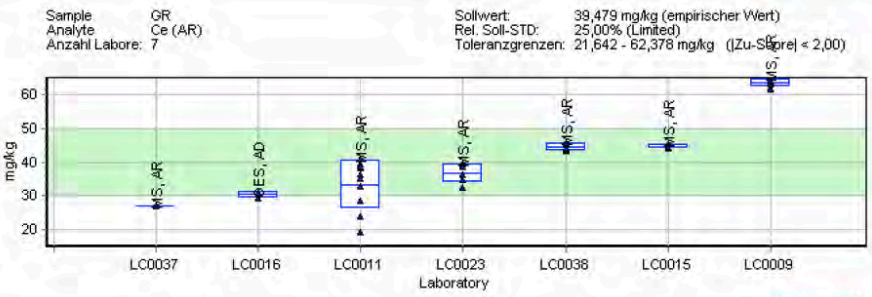

Sample GR
Analyte CaO
Anzahl Labore: 18
Sollwert: 0,511 % Gew. (empirischer Wert)
Rel. Soll-STD: 8,11% (Limited)
Toleranzgrenzen: 0,431 - 0,597 % Gew. (|Zu-Score| < 2,00)
% Gew.
LC0017 LC0032 LC0024 LC0028 LC0014 LC0031 LC0030 LC0036 LC0020
Laboratory
ProLab 2011

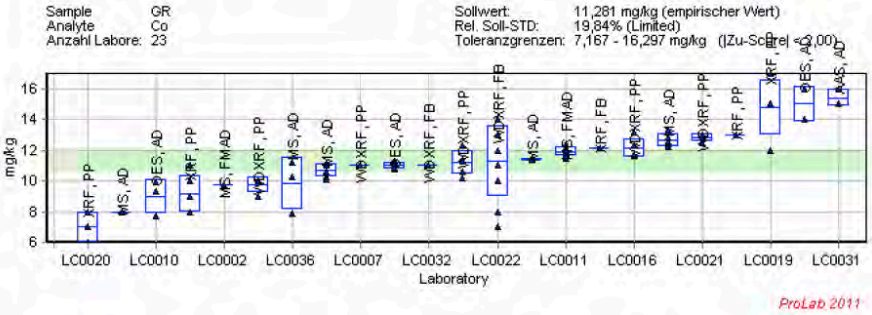

Sample GR
Analyte CaO (AR)
Anzahl Labore: 11
Sollwert: 0,376 % Gew. (empirischer Wert)
Rel. Soll-STD: 15,00% (Limited)
Toleranzgrenzen: 0,271 - 0,499 % Gew. (|Zu-Score| < 2,00)
% Gew.
0,6
0,5
0,4
0,3
0,2
0,1
MS, AR
ES, AR
ES, AD
LC0038
LC0037
LC0028
LC0034
LC0001
LC0004
LC0029
LC0010
LC0016
LC0011
LC0009
Laboratory
ProLab 2011

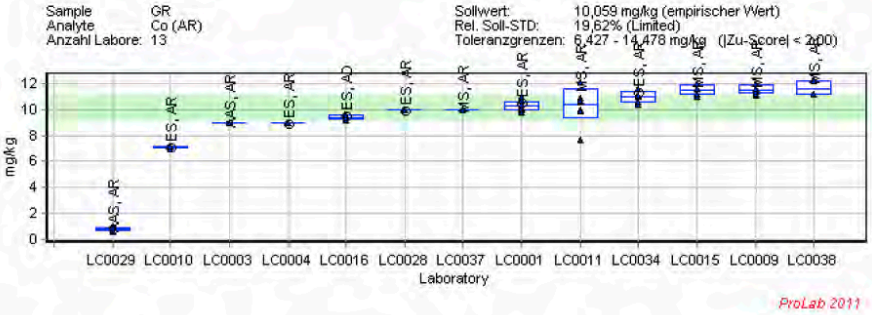

Sample GR
Analyte Cd
Anzahl Labore: 6
Sollwert: 0,195 mg/kg (empirischer Wert)
Rel. Soll-STD: 28,68% (Limited)
Toleranzgrenzen: 0,095 - 0,328 mg/kg (|Zu-Score| < 2,00)
mg/kg
4
3,5
3
2,5
2
1,5
1
0,5
0
MS, AD
MS, FMAD
LC0038
LC0012
LC0008
LC0042
LC0036
LC0002
Laboratory
ProLab 2011

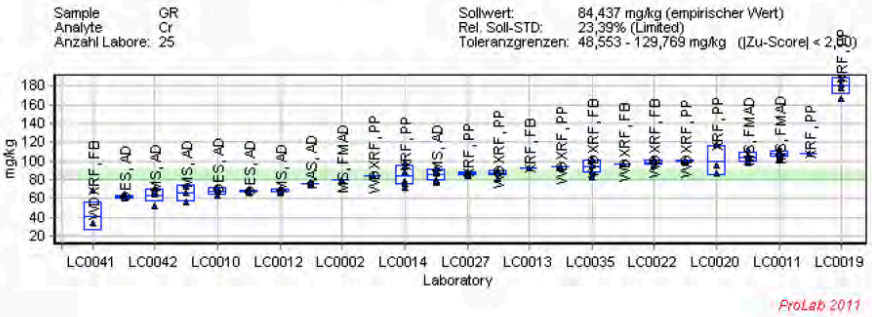

Sample GR
Analyte Cd (AR)
Anzahl Labore: 8
Sollwert: 0,177 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,083 - 0,305 mg/kg (|Zu-Score| < 2,00)
mg/kg
2
1,5
1
0,5
0
AAS, AR
MS, AR
MS, AD
LC0029
LC0026
LC0038
LC0015
LC0037
LC0011
LC0016
LC0009
Laboratory
ProLab 2011

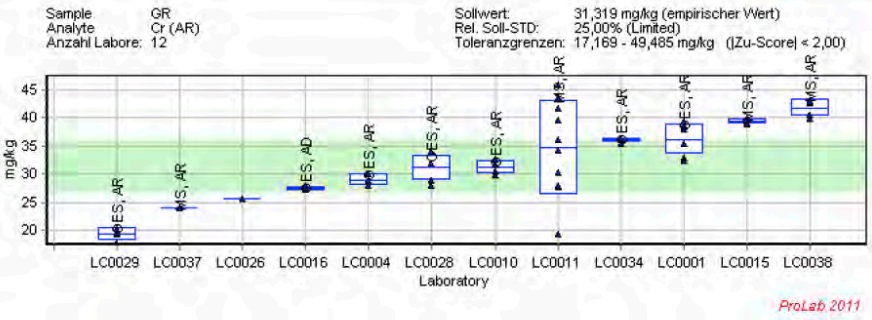

Sample GR
Analyte Ce
Anzahl Labore: 17
Sollwert: 60,116 mg/kg (empirischer Wert)
Rel. Soll-STD: 12,00% (Limited)
Toleranzgrenzen: 46,452 - 75,520 mg/kg (|Zu-Score| < 2,00)
mg/kg
85
80
75
70
65
60
55
50
45
XRF, FB
MS, AD
WD-XRF, PP
XRF, PP
MS, FMAD
LC0013
LC0021
LC0009
LC0036
LC0038
LC0011
LC0022
LC0019
LC0042
Laboratory
ProLab 2011

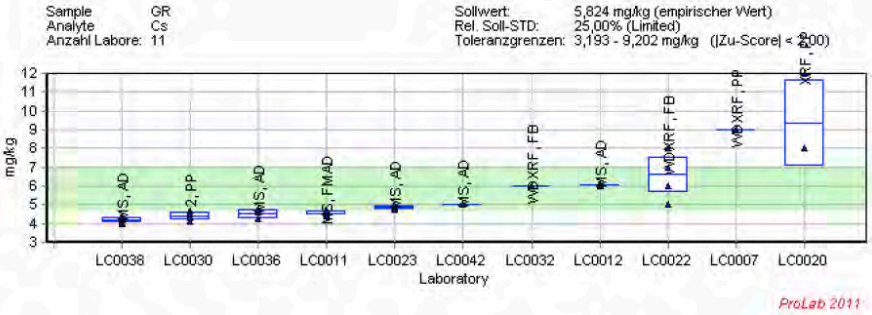

Sample GR
Analyte Ce (AR)
Anzahl Labore: 7
Sollwert: 39,479 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 21,642 - 62,378 mg/kg (|Zu-Score| ≤ 2,00)
mg/kg
Laboratory
LC0037 LC0016 LC0011 LC0023 LC0038 LC0015 LC0009
ProLab 2011

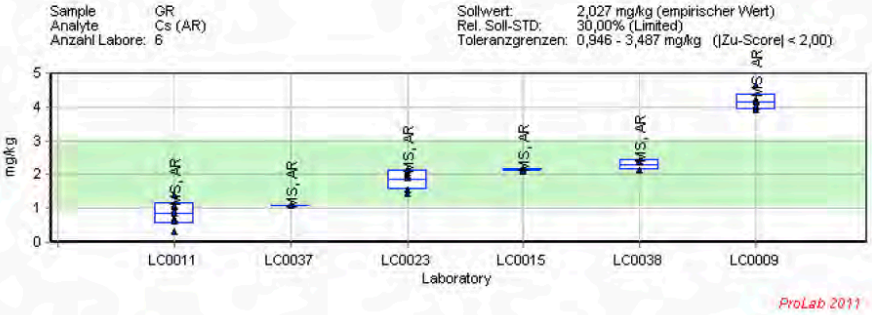

Sample GR
Analyte Co
Anzahl Labore: 23
Sollwert: 11,281 mg/kg (empirischer Wert)
Rel. Soll-STD: 19,84% (Limited)
Toleranzgrenzen: 7,167 - 16,297 mg/kg (|Zu-Score| ≤ 2,00)
mg/kg
Laboratory
LC0020 LC0010 LC0002 LC0036 LC0007 LC0032 LC0022 LC0011 LC0016 LC0021 LC0019 LC0031
ProLab 2011

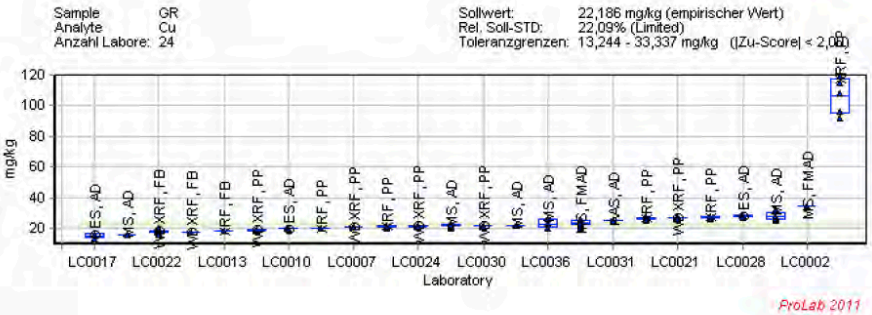

Sample GR
Analyte Co (AR)
Anzahl Labore: 13
Sollwert: 10,059 mg/kg (empirischer Wert)
Rel. Soll-STD: 19,62% (Limited)
Toleranzgrenzen: 6,427 - 14,478 mg/kg (|Zu-Score| ≤ 2,00)
mg/kg
Laboratory
LC0029 LC0010 LC0003 LC0004 LC0016 LC0028 LC0037 LC0001 LC0011 LC0034 LC0015 LC0009 LC0038
ProLab 2011

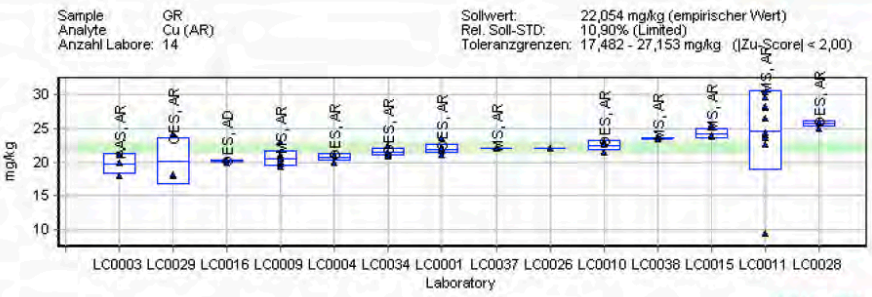

Sample GR
Analyte Cr
Anzahl Labore: 25
Sollwert: 84,437 mg/kg (empirischer Wert)
Rel. Soll-STD: 23,39% (Limited)
Toleranzgrenzen: 48,553 - 129,769 mg/kg (|Zu-Score| ≤ 2,00)
mg/kg
Laboratory
LC0041 LC0042 LC0010 LC0012 LC0002 LC0014 LC0027 LC0013 LC0035 LC0022 LC0020 LC0011 LC0019
ProLab 2011

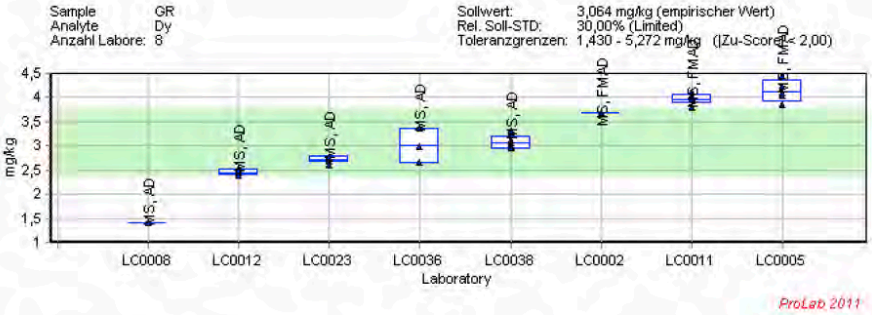

Sample GR
Analyte Cr (AR)
Anzahl Labore: 12
Sollwert: 31,319 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 17,169 - 49,485 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0029 LC0037 LC0026 LC0016 LC0004 LC0028 LC0010 LC0011 LC0034 LC0001 LC0015 LC0038
ProLab 2011

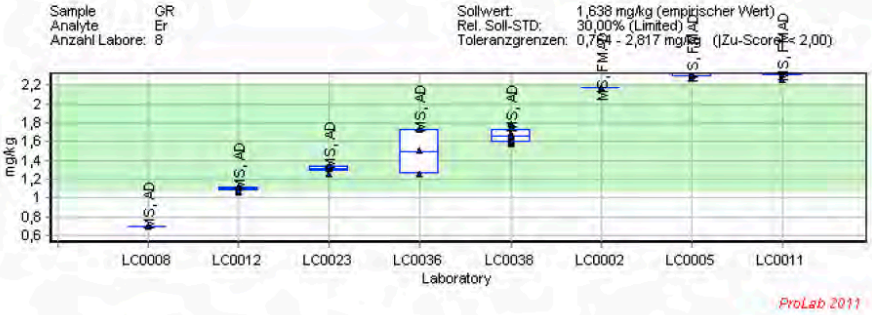

Sample GR
Analyte Cs
Anzahl Labore: 11
Sollwert: 5,824 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 3,193 - 9,202 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0038 LC0030 LC0036 LC0011 LC0023 LC0042 LC0032 LC0012 LC0022 LC0007 LC0020
ProLab 2011

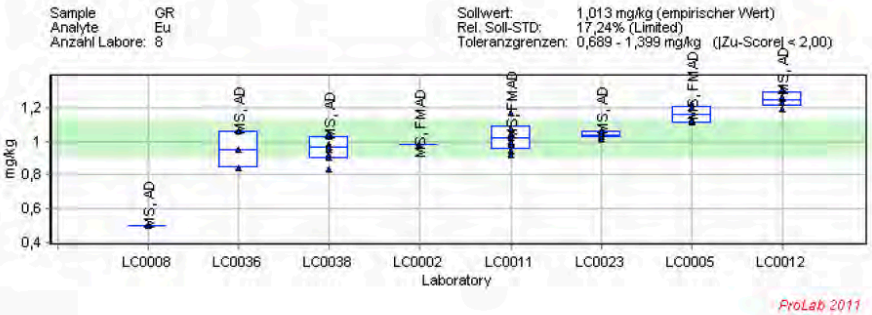

Sample GR
Analyte Cs (AR)
Anzahl Labore: 6
Sollwert: 2,027 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,946 - 3,487 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0011 LC0037 LC0023 LC0015 LC0038 LC0009
ProLab 2011

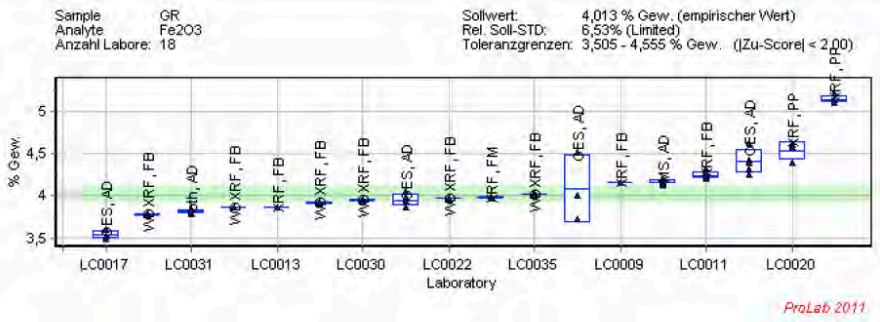

Sample GR
Analyte Cu
Anzahl Labore: 24
Sollwert: 22,186 mg/kg (empirischer Wert)
Rel. Soll-STD: 22,09% (Limited)
Toleranzgrenzen: 13,244 - 33,337 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0017 LC0022 LC0013 LC0010 LC0007 LC0024 LC0030 LC0036 LC0031 LC0021 LC0028 LC0002
ProLab 2011

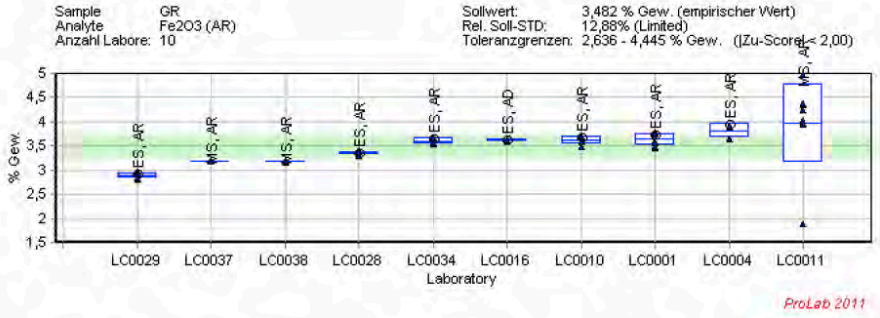

Sample GR
Analyte Cu (AR)
Anzahl Labore: 14
Sollwert: 22,054 mg/kg (empirischer Wert)
Rel. Soll-STD: 10,90% (Limited)
Toleranzgrenzen: 17,482 - 27,153 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0003 LC0029 LC0016 LC0009 LC0004 LC0034 LC0001 LC0037 LC0026 LC0010 LC0038 LC0015 LC0011 LC0028
ProLab 2011

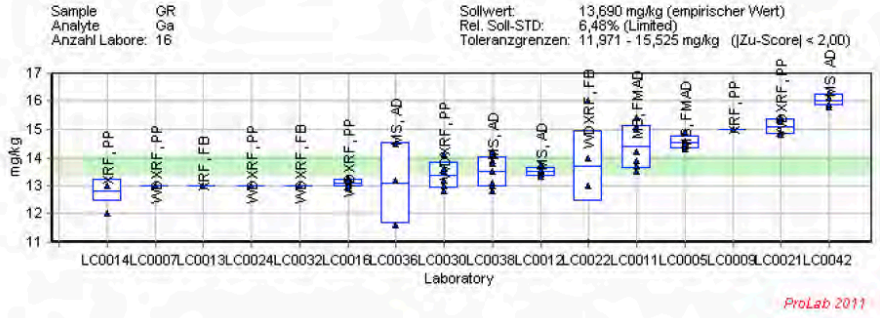

Sample GR
Analyte Dy
Anzahl Labore: 8
Sollwert: 3,064 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 1,430 - 5,272 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0012 LC0023 LC0036 LC0038 LC0002 LC0011 LC0005
ProLab 2011

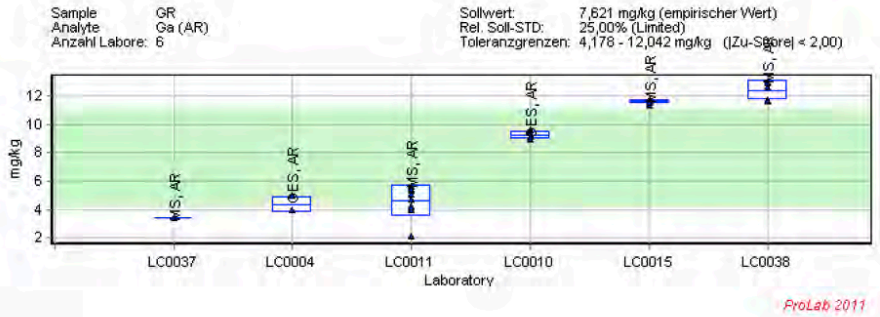

Sample GR
Analyte Er
Anzahl Labore: 8
Sollwert: 1,638 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,764 - 2,817 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0012 LC0023 LC0036 LC0038 LC0002 LC0005 LC0011
ProLab 2011

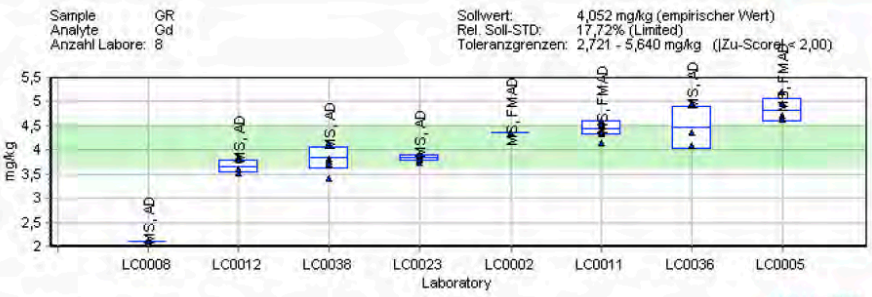

Sample GR
Analyte Eu
Anzahl Labore: 8
Sollwert: 1,013 mg/kg (empirischer Wert)
Rel. Soll-STD: 17,24% (Limited)
Toleranzgrenzen: 0,689 - 1,399 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0036 LC0038 LC0002 LC0011 LC0023 LC0005 LC0012
ProLab 2011

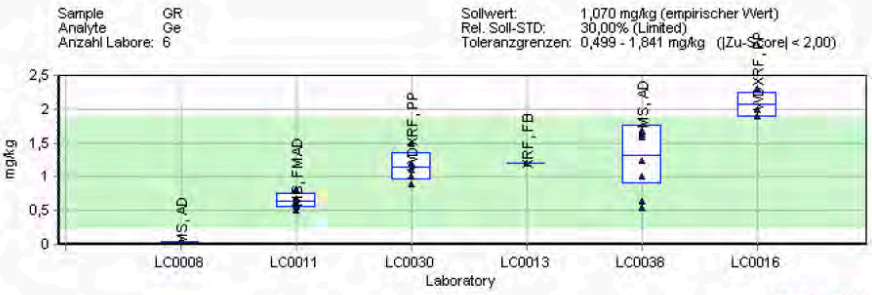

Sample GR
Analyte Fe2O3
Anzahl Labore: 18
Sollwert: 4,013 % Gew. (empirischer Wert)
Rel. Soll-STD: 6,53% (Limited)
Toleranzgrenzen: 3,505 - 4,555 % Gew. (|Zu-Score| < 2,00)
% Gew.
Laboratory
LC0017 LC0031 LC0013 LC0030 LC0022 LC0035 LC0009 LC0011 LC0020
ProLab 2011

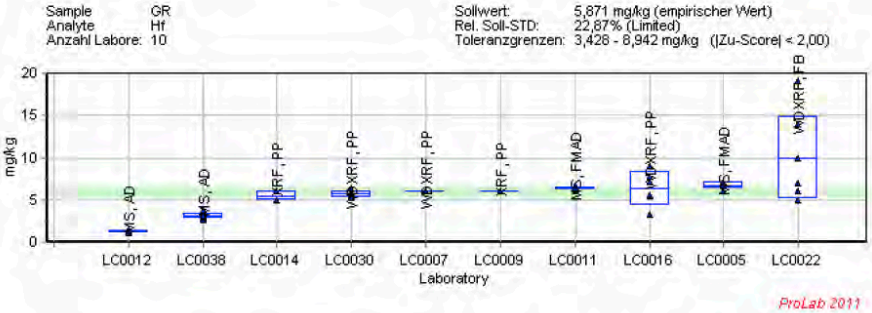

Sample GR
Analyte Fe2O3 (AR)
Anzahl Labore: 10
Sollwert: 3,482 % Gew. (empirischer Wert)
Rel. Soll-STD: 12,88% (Limited)
Toleranzgrenzen: 2,636 - 4,445 % Gew. (|Zu-Score| < 2,00)
% Gew.
Laboratory
LC0029 LC0037 LC0038 LC0028 LC0034 LC0016 LC0010 LC0001 LC0004 LC0011
ProLab 2011

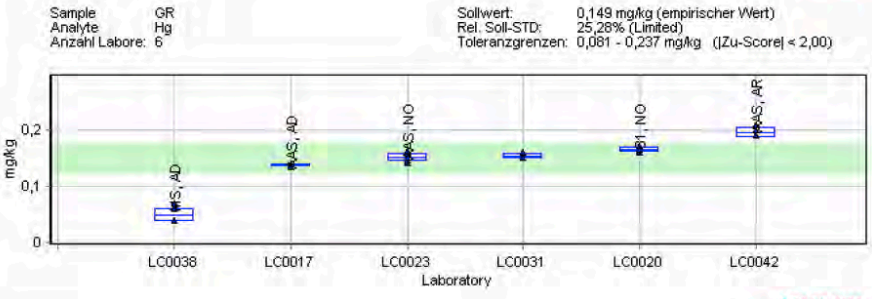

Sample GR
Analyte Ga
Anzahl Labore: 16
Sollwert: 13,690 mg/kg (empirischer Wert)
Rel. Soll-STD: 6,48% (Limited)
Toleranzgrenzen: 11,971 - 15,525 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0014 LC0007 LC0013 LC0024 LC0032 LC0016 LC0036 LC0030 LC0038 LC0012 LC0022 LC0011 LC0005 LC0009 LC0021 LC0042
ProLab 2011

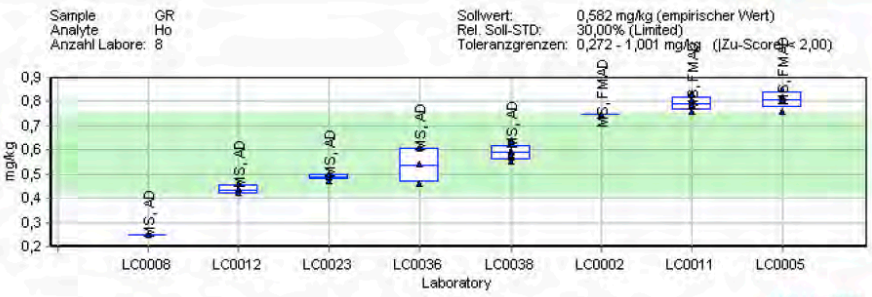

Sample GR
Analyte Ga (AR)
Anzahl Labore: 6
Sollwert: 7,621 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 4,178 - 12,042 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0037 LC0004 LC0011 LC0010 LC0015 LC0038
ProLab 2011

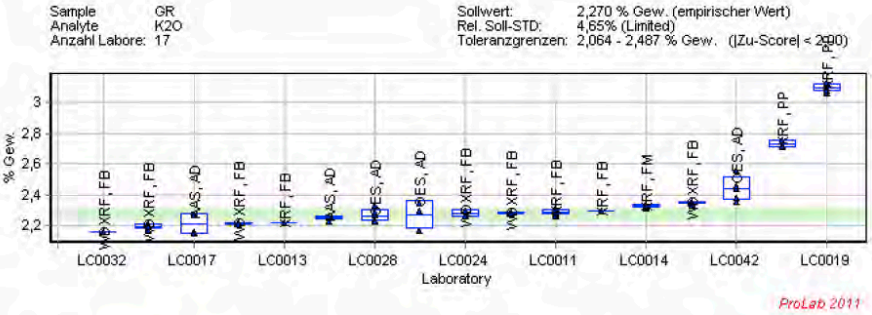

Sample GR
Analyte Gd
Anzahl Labore: 8
Sollwert: 4,052 mg/kg (empirischer Wert)
Rel. Soll-STD: 17,72% (Limited)
Toleranzgrenzen: 2,721 - 5,640 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008
LC0012
LC0038
LC0023
LC0002
LC0011
LC0036
LC0005
ProLab 2011

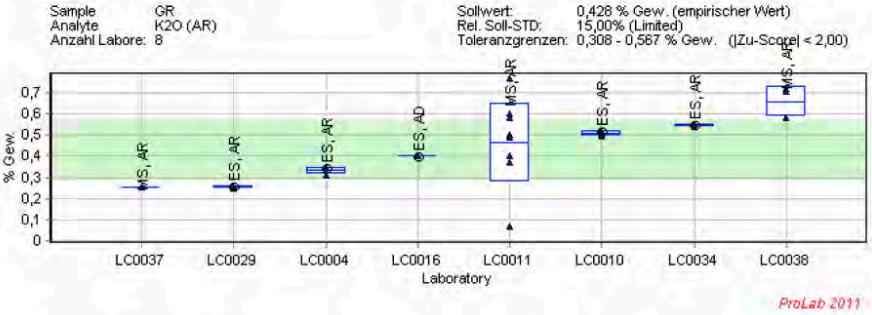

Sample GR
Analyte Ge
Anzahl Labore: 6
Sollwert: 1,070 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,499 - 1,841 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008
LC0011
LC0030
LC0013
LC0038
LC0016
ProLab 2011

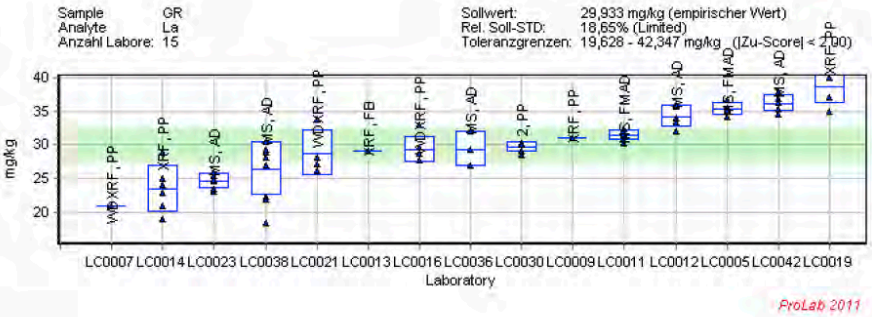

Sample GR
Analyte Hf
Anzahl Labore: 10
Sollwert: 5,871 mg/kg (empirischer Wert)
Rel. Soll-STD: 22,87% (Limited)
Toleranzgrenzen: 3,428 - 8,942 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0012
LC0038
LC0014
LC0030
LC0007
LC0009
LC0011
LC0016
LC0005
LC0022
ProLab 2011

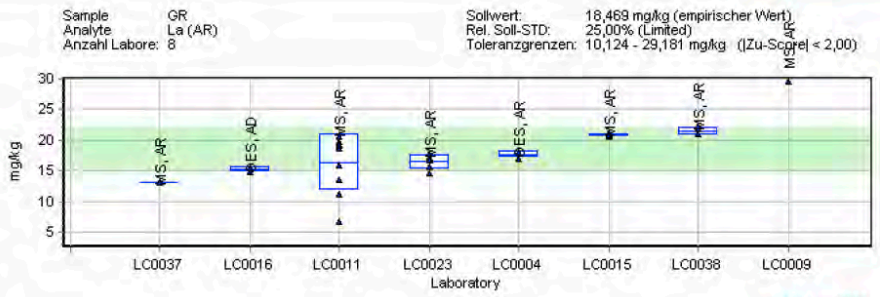

Sample GR
Analyte Hg
Anzahl Labore: 6
Sollwert: 0,149 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,28% (Limited)
Toleranzgrenzen: 0,081 - 0,237 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0038
LC0017
LC0023
LC0031
LC0020
LC0042
ProLab 2011

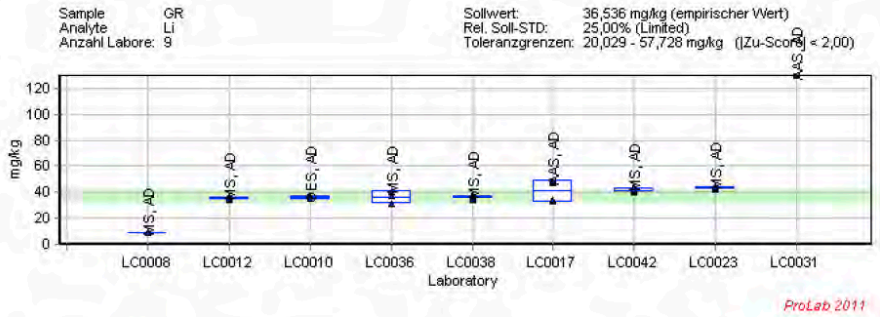

Sample GR
Analyte Ho
Anzahl Labore: 8
Sollwert: 0,582 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,272 - 1,001 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008 LC0012 LC0023 LC0036 LC0038 LC0002 LC0011 LC0005
Laboratory
ProLab 2011

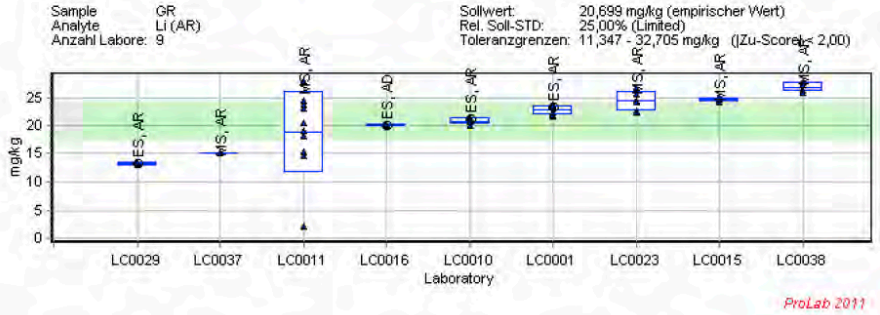

Sample GR
Analyte K2O
Anzahl Labore: 17
Sollwert: 2,270 % Gew. (empirischer Wert)
Rel. Soll-STD: 4,65% (Limited)
Toleranzgrenzen: 2,064 - 2,487 % Gew. (|Zu-Score| < 2,00)
% Gew.
LC0032 LC0017 LC0013 LC0028 LC0024 LC0011 LC0014 LC0042 LC0019
Laboratory
ProLab 2011

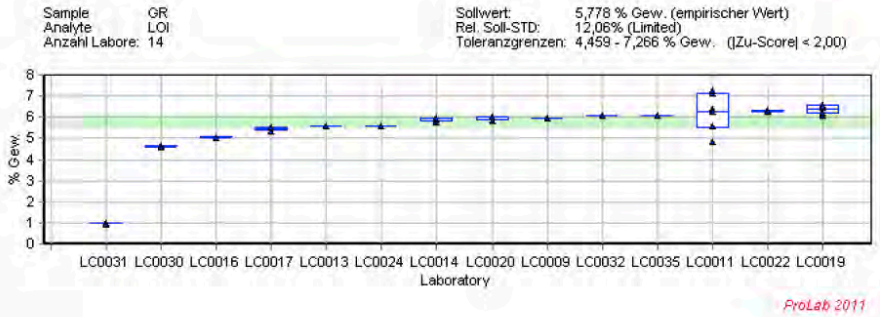

Sample GR
Analyte K2O (AR)
Anzahl Labore: 8
Sollwert: 0,428 % Gew. (empirischer Wert)
Rel. Soll-STD: 15,00% (Limited)
Toleranzgrenzen: 0,308 - 0,567 % Gew. (|Zu-Score| < 2,00)
% Gew.
LC0037 LC0029 LC0004 LC0016 LC0011 LC0010 LC0034 LC0038
Laboratory
ProLab 2011

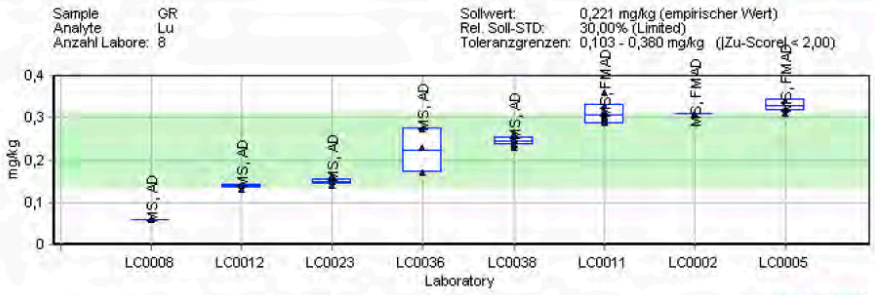

Sample GR
Analyte La
Anzahl Labore: 15
Sollwert: 29,933 mg/kg (empirischer Wert)
Rel. Soll-STD: 18,65% (Limited)
Toleranzgrenzen: 19,628 - 42,347 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0007 LC0014 LC0023 LC0038 LC0021 LC0013 LC0016 LC0036 LC0030 LC0009 LC0011 LC0012 LC0005 LC0042 LC0019
Laboratory
ProLab 2011

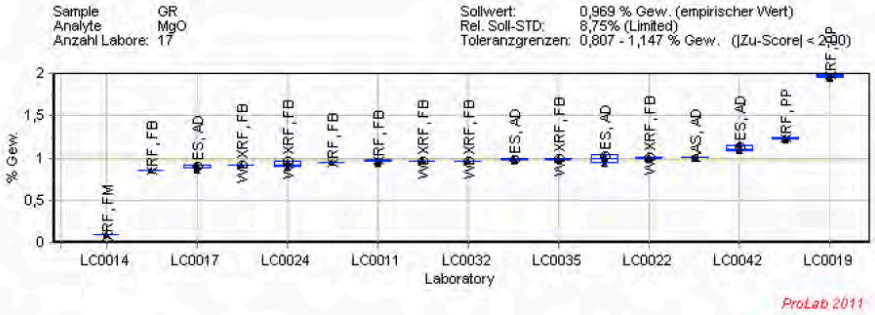

Sample GR
Analyte La (AR)
Anzahl Labore: 8
Sollwert: 18,469 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 10,124 - 29,181 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0037 LC0016 LC0011 LC0023 LC0004 LC0015 LC0038 LC0009
Laboratory
ProLab 2011

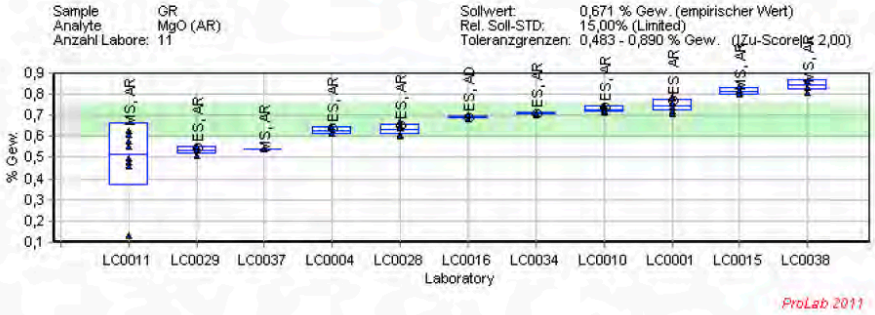

Sample GR
Analyte Li
Anzahl Labore: 9
Sollwert: 36,536 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 20,029 - 57,728 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008 LC0012 LC0010 LC0036 LC0038 LC0017 LC0042 LC0023 LC0031
Laboratory
ProLab 2011

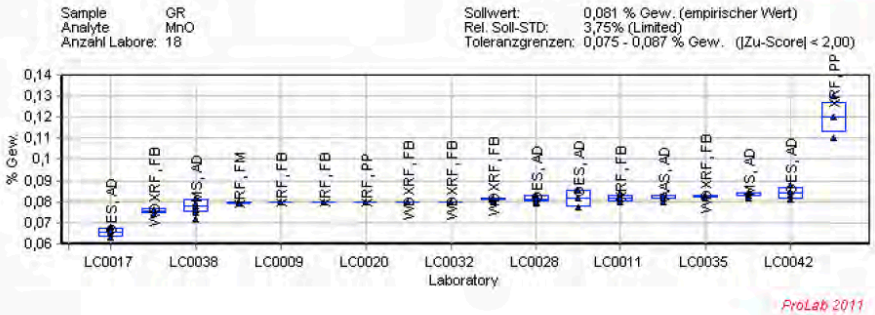

Sample GR
Analyte Li (AR)
Anzahl Labore: 9
Sollwert: 20,699 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 11,347 - 32,705 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0029 LC0037 LC0011 LC0016 LC0010 LC0001 LC0023 LC0015 LC0038
Laboratory
ProLab 2011

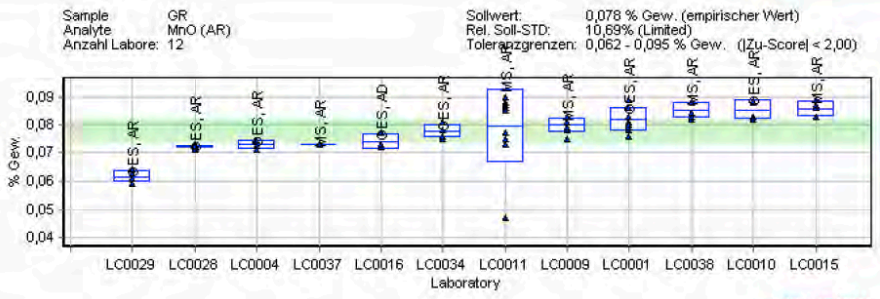

Sample GR
Analyte LOI
Anzahl Labore: 14
Sollwert: 5,778 % Gew. (empirischer Wert)
Rel. Soll-STD: 12,06% (Limited)
Toleranzgrenzen: 4,459 - 7,266 % Gew. (|Zu-Score| < 2,00)
% Gew.
LC0031 LC0030 LC0016 LC0017 LC0013 LC0024 LC0014 LC0020 LC0009 LC0032 LC0035 LC0011 LC0022 LC0019
Laboratory
ProLab 2011

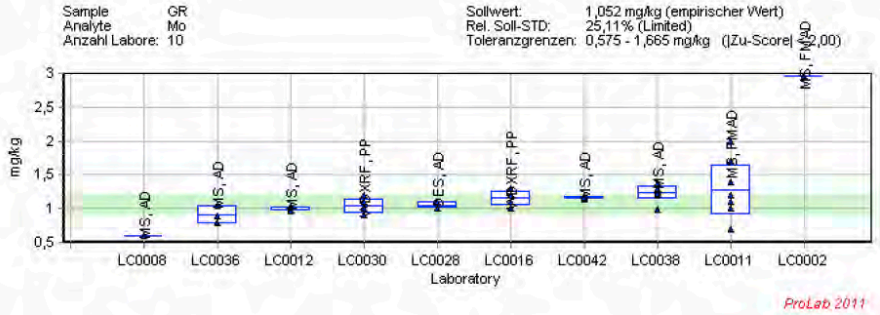

Sample GR
Analyte Lu
Anzahl Labore: 8
Sollwert: 0,221 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,103 - 0,360 mg/kg (|Zu-Score| < 2,00)
mg/kg
0,4
0,3
0,2
0,1
0
MS, AD
MS, FM AD
MS, FM AD
MS, FM AD
LC0008
LC0012
LC0023
LC0036
LC0038
LC0011
LC0002
LC0005
Laboratory
ProLab 2011

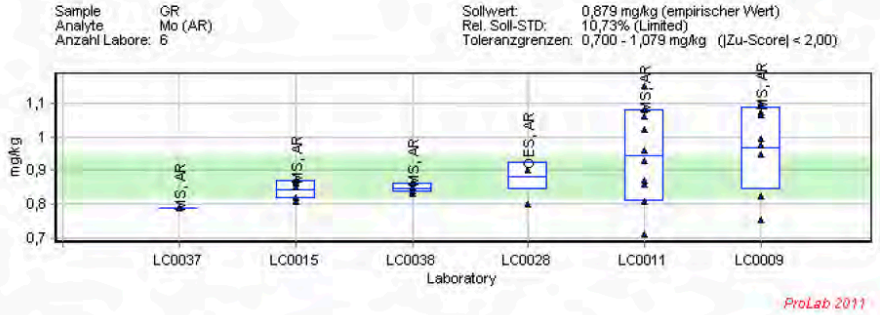

Sample GR
Analyte MgO
Anzahl Labore: 17
Sollwert: 0,969 % Gew. (empirischer Wert)
Rel. Soll-STD: 8,75% (Limited)
Toleranzgrenzen: 0,807 - 1,147 % Gew. (|Zu-Score| < 2,00)
% Gew.
2
1,5
1
0,5
0
XRF, FM
XRF, FB
ES, AD
WD-XRF, FB
WD-XRF, FB
XRF, FB
XRF, FB
WD-XRF, FB
WD-XRF, FB
ES, AD
WD-XRF, FB
ES, AD
WD-XRF, FB
AAS, AD
ES, AD
XRF, PP
XRF, PP
LC0014
LC0017
LC0024
LC0011
LC0032
LC0035
LC0022
LC0042
LC0019
Laboratory
ProLab 2011

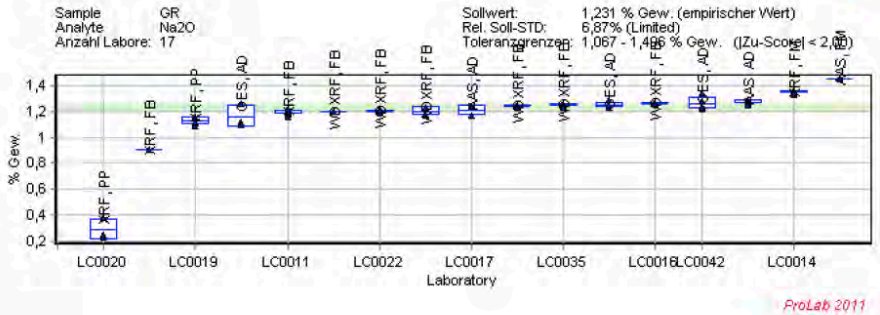

Sample GR
Analyte MgO (AR)
Anzahl Labore: 11
Sollwert: 0,671 % Gew. (empirischer Wert)
Rel. Soll-STD: 15,00% (Limited)
Toleranzgrenzen: 0,483 - 0,890 % Gew. (|Zu-Score| < 2,00)
% Gew.
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
MS, AR
ES, AR
MS, AR
ES, AR
ES, AR
ES, AD
ES, AR
ES, AR
ES, AR
MS, AR
MS, AR
LC0011
LC0029
LC0037
LC0004
LC0028
LC0016
LC0034
LC0010
LC0001
LC0015
LC0038
Laboratory
ProLab 2011

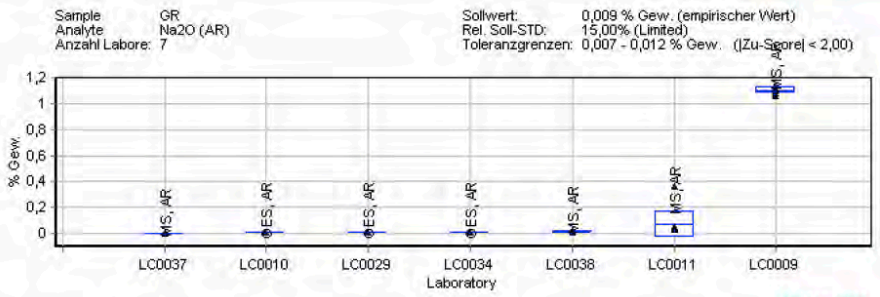

Sample GR
Analyte MnO
Anzahl Labore: 18
Sollwert: 0,081 % Gew. (empirischer Wert)
Rel. Soll-STD: 3,75% (Limited)
Toleranzgrenzen: 0,075 - 0,087 % Gew. (|Zu-Score| < 2,00)
% Gew.
0,14
0,13
0,12
0,11
0,1
0,09
0,08
0,07
0,06
ES, AD
WD-XRF, FB
MS, AD
XRF, FM
XRF, FB
XRF, FB
XRF, PP
WD-XRF, FB
WD-XRF, FB
WD-XRF, FB
ES, AD
ES, AD
XRF, FB
AAS, AD
WD-XRF, FB
MS, AD
ES, AD
XRF, PP
LC0017
LC0038
LC0009
LC0020
LC0032
LC0028
LC0011
LC0035
LC0042
Laboratory
ProLab 2011

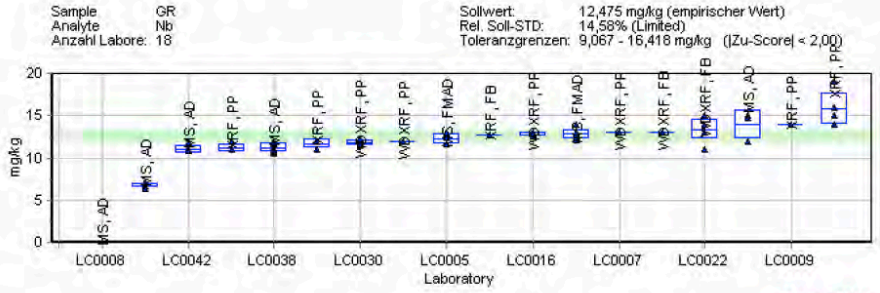

Sample GR
Analyte MnO (AR)
Anzahl Labore: 12
Sollwert: 0,078 % Gew. (empirischer Wert)
Rel. Soll-STD: 10,69% (Limited)
Toleranzgrenzen: 0,062 - 0,095 % Gew. (|Zu-Score| < 2,00)
% Gew.
0,09
0,08
0,07
0,06
0,05
0,04
ES, AR
MS, AR
OES, AD
LC0029 LC0028 LC0004 LC0037 LC0016 LC0034 LC0011 LC0009 LC0001 LC0038 LC0010 LC0015
Laboratory
ProLab 2011

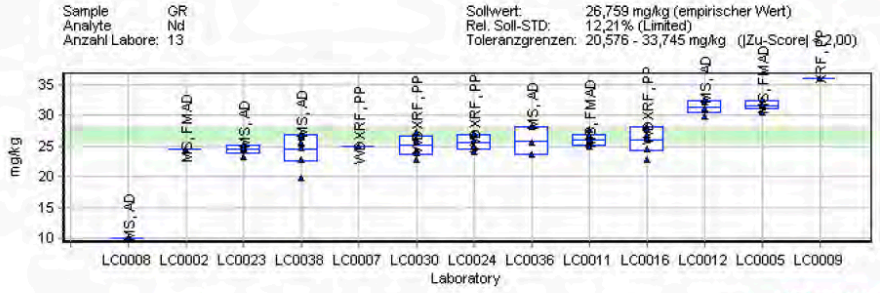

Sample GR
Analyte Mo
Anzahl Labore: 10
Sollwert: 1,052 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,11% (Limited)
Toleranzgrenzen: 0,575 - 1,665 mg/kg (|Zu-Score| < 2,00)
mg/kg
3
2,5
2
1,5
1
0,5
MS, AD
XRF, PP
OES, AD
MS, FM, AD
LC0008 LC0036 LC0012 LC0030 LC0028 LC0016 LC0042 LC0038 LC0011 LC0002
Laboratory
ProLab 2011

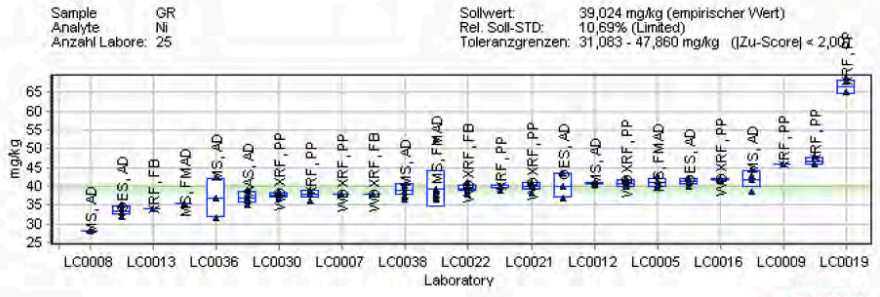

Sample GR
Analyte Mo (AR)
Anzahl Labore: 6
Sollwert: 0,879 mg/kg (empirischer Wert)
Rel. Soll-STD: 10,73% (Limited)
Toleranzgrenzen: 0,700 - 1,079 mg/kg (|Zu-Score| < 2,00)
mg/kg
1,1
1
0,9
0,8
0,7
MS, AR
OES, AR
LC0037 LC0015 LC0038 LC0028 LC0011 LC0009
Laboratory
ProLab 2011

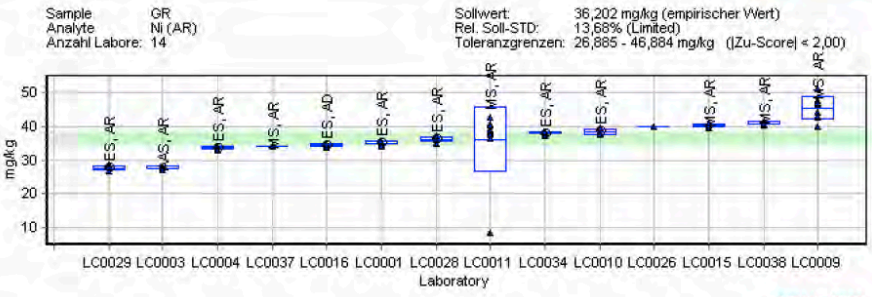

Sample GR
Analyte Na2O
Anzahl Labore: 17
Sollwert: 1,231 % Gew. (empirischer Wert)
Rel. Soll-STD: 6,87% (Limited)
Toleranzgrenzen: 1,067 - 1,396 % Gew. (|Zu-Score| < 2,00)
% Gew.
1,4
1,2
1
0,8
0,6
0,4
0,2
XRF, PP
XRF, FB
OES, AD
AAS, AD
LC0020 LC0019 LC0011 LC0022 LC0017 LC0035 LC0018 LC0042 LC0014
Laboratory
ProLab 2011

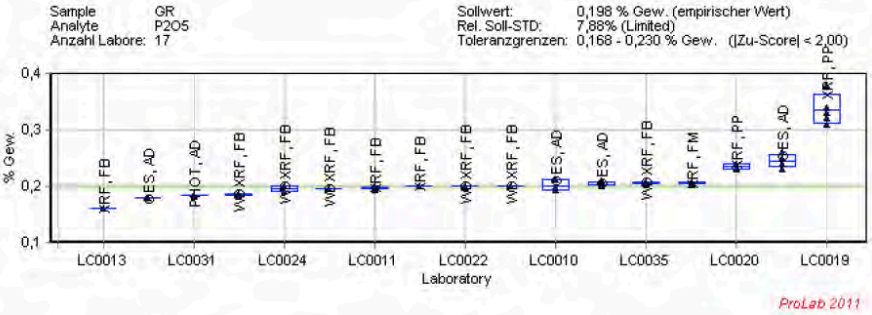

Sample GR
Analyte Na2O (AR)
Anzahl Labore: 7
Sollwert: 0,009 % Gew. (empirischer Wert)
Rel. Soll-STD: 15,00% (Limited)
Toleranzgrenzen: 0,007 - 0,012 % Gew. (|Zu-Score| < 2,00)
% Gew.
LC0037 LC0010 LC0029 LC0034 LC0038 LC0011 LC0009
Laboratory
ProLab 2011

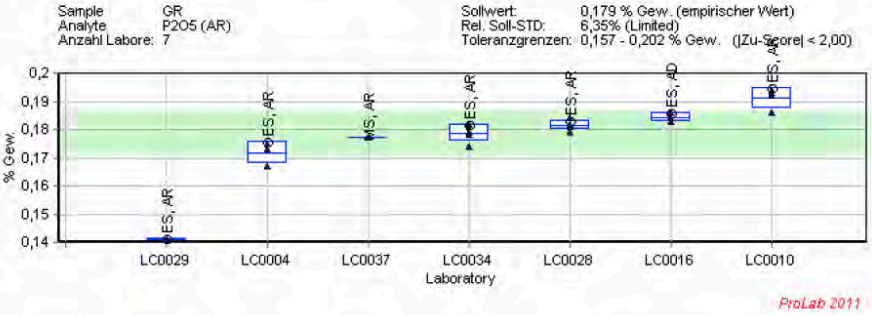

Sample GR
Analyte Nb
Anzahl Labore: 18
Sollwert: 12,475 mg/kg (empirischer Wert)
Rel. Soll-STD: 14,58% (Limited)
Toleranzgrenzen: 9,067 - 16,418 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008 LC0042 LC0038 LC0030 LC0005 LC0016 LC0007 LC0022 LC0009
Laboratory
ProLab 2011

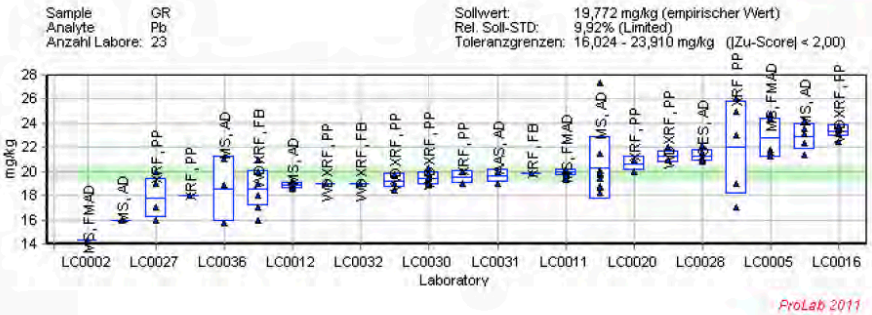

Sample GR
Analyte Nd
Anzahl Labore: 13
Sollwert: 26,759 mg/kg (empirischer Wert)
Rel. Soll-STD: 12,21% (Limited)
Toleranzgrenzen: 20,576 - 33,745 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008 LC0002 LC0023 LC0038 LC0007 LC0030 LC0024 LC0036 LC0011 LC0016 LC0012 LC0005 LC0009
Laboratory
ProLab 2011

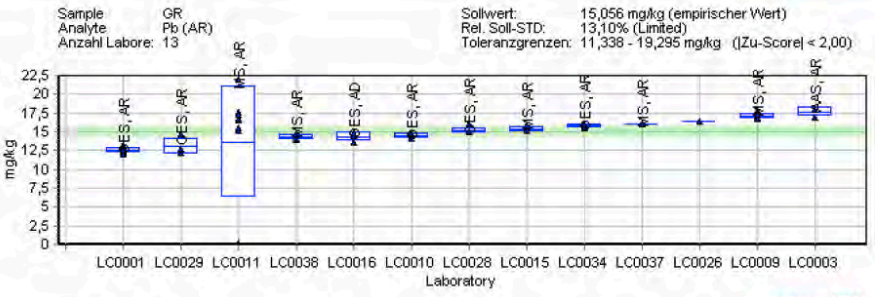

Sample GR
Analyte Ni
Anzahl Labore: 25
Sollwert: 39,024 mg/kg (empirischer Wert)
Rel. Soll-STD: 10,69% (Limited)
Toleranzgrenzen: 31,083 - 47,860 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008 LC0013 LC0036 LC0030 LC0007 LC0038 LC0022 LC0021 LC0012 LC0005 LC0016 LC0009 LC0019
Laboratory
ProLab 2011

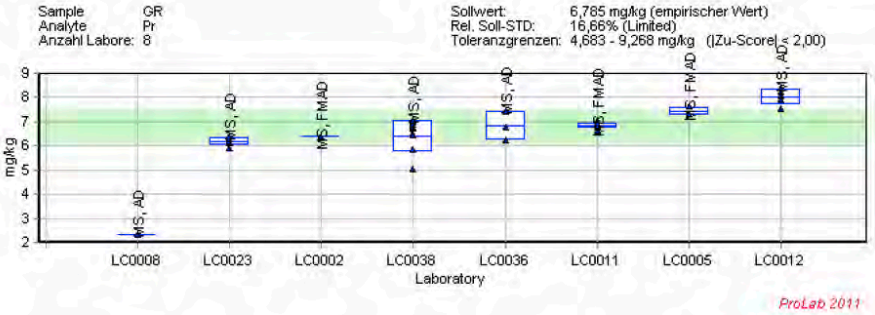

Sample GR
Analyte Ni (AR)
Anzahl Labore: 14
Sollwert: 36,202 mg/kg (empirischer Wert)
Rel. Soll-STD: 13,68% (Limited)
Toleranzgrenzen: 26,885 - 46,884 mg/kg (|Zu-Score| ≤ 2,00)
mg/kg
50
40
30
20
10
ES, AR
AAS, AR
ES, AR
MS, AR
ES, AD
ES, AR
ES, AR
MS, AR
ES, AR
ES, AR
MS, AR
MS, AR
MS, AR
LC0029 LC0003 LC0004 LC0037 LC0016 LC0001 LC0028 LC0011 LC0034 LC0010 LC0026 LC0015 LC0038 LC0009
Laboratory
ProLab 2011

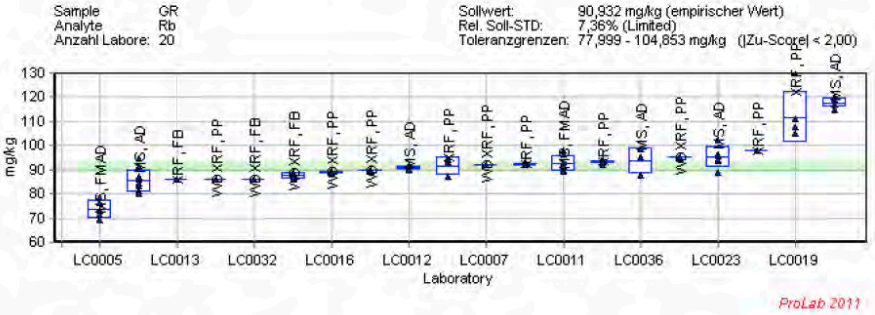

Sample GR
Analyte P2O5
Anzahl Labore: 17
Sollwert: 0,198 % Gew. (empirischer Wert)
Rel. Soll-STD: 7,88% (Limited)
Toleranzgrenzen: 0,168 - 0,230 % Gew. (|Zu-Score| ≤ 2,00)
% Gew.
0,4
0,3
0,2
0,1
XRF, FB
ES, AD
PHOT, AD
WD-XRF, FB
WD-XRF, FB
WD-XRF, FB
XRF, FB
XRF, FB
WD-XRF, FB
WD-XRF, FB
ES, AD
ES, AD
WD-XRF, FB
XRF, FM
XRF, PP
ES, AD
XRF, PP
LC0013 LC0031 LC0024 LC0011 LC0022 LC0010 LC0035 LC0020 LC0019
Laboratory
ProLab 2011

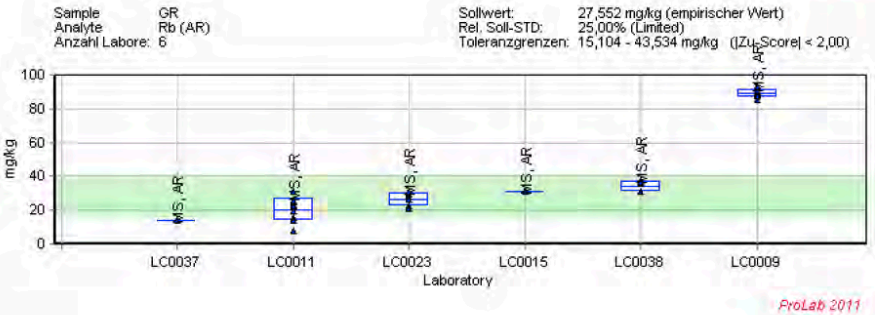

Sample GR
Analyte P2O5 (AR)
Anzahl Labore: 7
Sollwert: 0,179 % Gew. (empirischer Wert)
Rel. Soll-STD: 6,35% (Limited)
Toleranzgrenzen: 0,157 - 0,202 % Gew. (|Zu-Score| ≤ 2,00)
% Gew.
0,2
0,19
0,18
0,17
0,16
0,15
0,14
ES, AR
ES, AR
MS, AR
ES, AR
ES, AR
ES, AD
ES, AR
LC0029 LC0004 LC0037 LC0034 LC0028 LC0016 LC0010
Laboratory
ProLab 2011

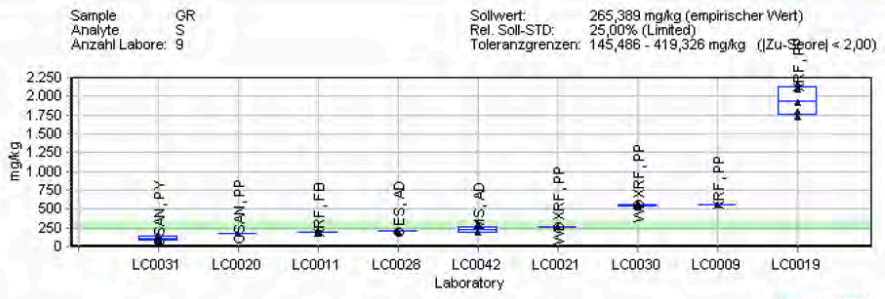

Sample GR
Analyte Pb
Anzahl Labore: 23
Sollwert: 19,772 mg/kg (empirischer Wert)
Rel. Soll-STD: 9,92% (Limited)
Toleranzgrenzen: 16,024 - 23,910 mg/kg (|Zu-Score| ≤ 2,00)
mg/kg
28
26
24
22
20
18
16
14
MS, FMAD
MS, AD
XRF, PP
XRF, PP
MS, AD
WD-XRF, FB
MS, AD
WD-XRF, PP
WD-XRF, FB
WD-XRF, PP
WD-XRF, PP
XRF, PP
AAS, AD
XRF, FB
MS, FMAD
MS, AD
XRF, PP
WD-XRF, PP
ES, AD
XRF, PP
MS, FMAD
MS, AD
WD-XRF, FP
LC0002 LC0027 LC0036 LC0012 LC0032 LC0030 LC0031 LC0011 LC0020 LC0028 LC0005 LC0016
Laboratory
ProLab 2011

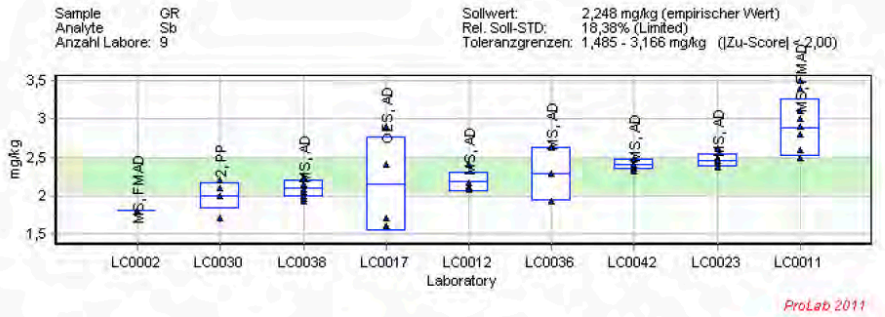

Sample GR
Analyte Pb (AR)
Anzahl Labore: 13
Sollwert: 15,056 mg/kg (empirischer Wert)
Rel. Soll-STD: 13,10% (Limited)
Toleranzgrenzen: 11,338 - 19,295 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0001 LC0029 LC0011 LC0038 LC0016 LC0010 LC0028 LC0015 LC0034 LC0037 LC0026 LC0009 LC0003
ProLab 2011

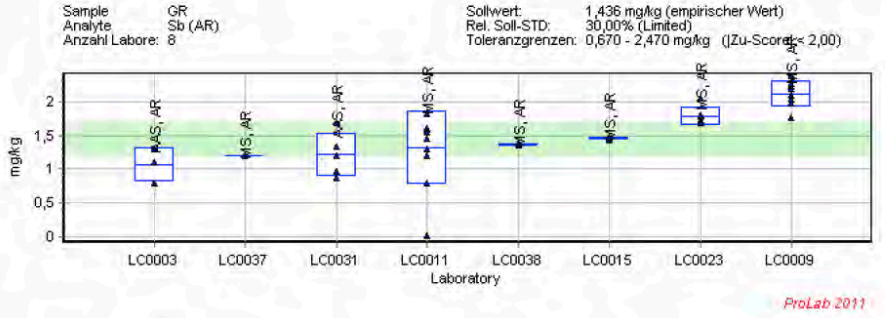

Sample GR
Analyte Pr
Anzahl Labore: 8
Sollwert: 6,785 mg/kg (empirischer Wert)
Rel. Soll-STD: 16,66% (Limited)
Toleranzgrenzen: 4,683 - 9,268 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0023 LC0002 LC0038 LC0036 LC0011 LC0005 LC0012
ProLab 2011

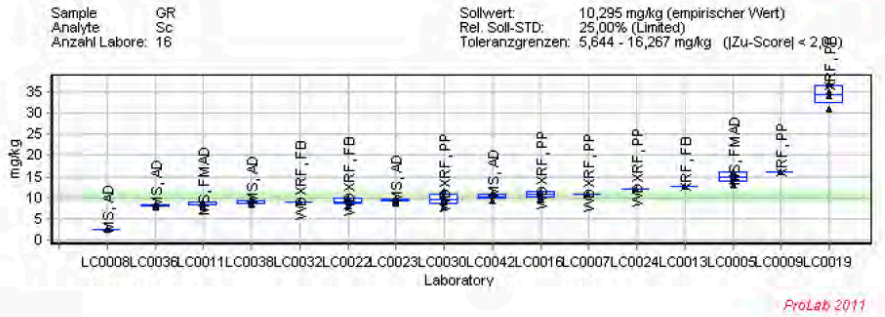

Sample GR
Analyte Rb
Anzahl Labore: 20
Sollwert: 90,932 mg/kg (empirischer Wert)
Rel. Soll-STD: 7,36% (Limited)
Toleranzgrenzen: 77,999 - 104,853 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0005 LC0013 LC0032 LC0016 LC0012 LC0007 LC0011 LC0036 LC0023 LC0019
ProLab 2011

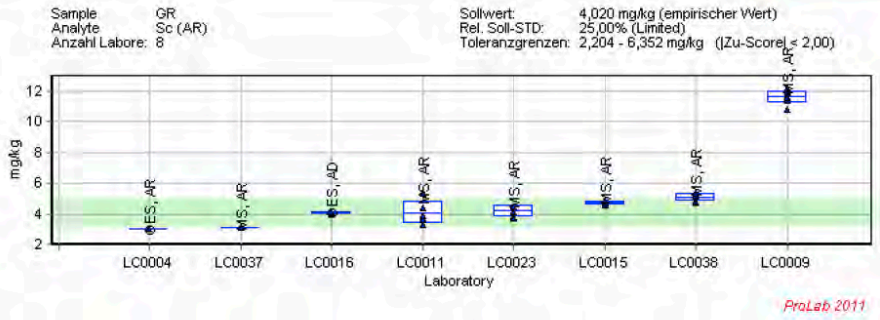

Sample GR
Analyte Rb (AR)
Anzahl Labore: 6
Sollwert: 27,552 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 15,104 - 43,534 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0037 LC0011 LC0023 LC0015 LC0038 LC0009
ProLab 2011

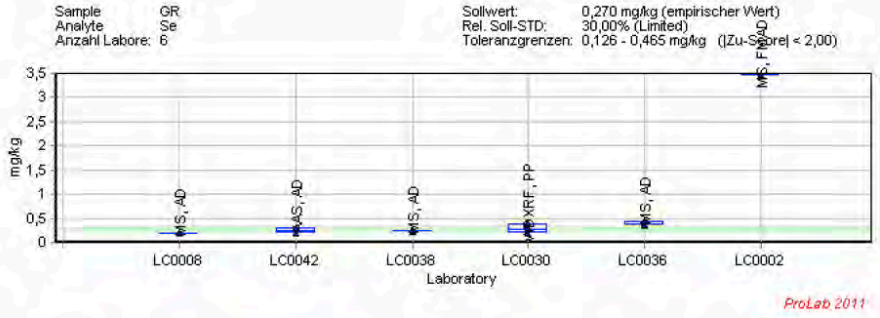

Sample GR
Analyte S
Anzahl Labore: 9
Sollwert: 265,389 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 145,486 - 419,326 mg/kg (|Zu-Score| < 2,00)
mg/kg
2.250
2.000
1.750
1.500
1.250
1.000
750
500
250
0
OSAN, PY
OSAN, PP
XRF, FB
OES, AD
MS, AD
WD-XRF, PP
WD-XRF, PP
XRF, PP
XRF, FB
LC0031
LC0020
LC0011
LC0028
LC0042
LC0021
LC0030
LC0009
LC0019
Laboratory
ProLab 2011

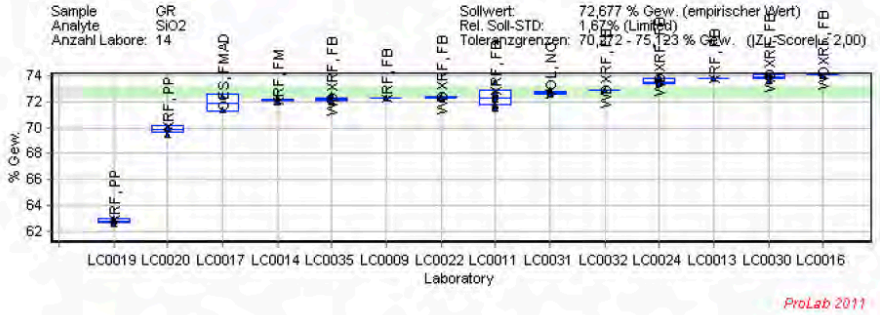

Sample GR
Analyte Sb
Anzahl Labore: 9
Sollwert: 2,248 mg/kg (empirischer Wert)
Rel. Soll-STD: 18,38% (Limited)
Toleranzgrenzen: 1,485 - 3,166 mg/kg (|Zu-Score| < 2,00)
mg/kg
3,5
3
2,5
2
1,5
MS, FMAD
XRF, PP
MS, AD
OES, AD
MS, AD
MS, AD
MS, AD
MS, FMAD
LC0002
LC0030
LC0038
LC0017
LC0012
LC0036
LC0042
LC0023
LC0011
Laboratory
ProLab 2011

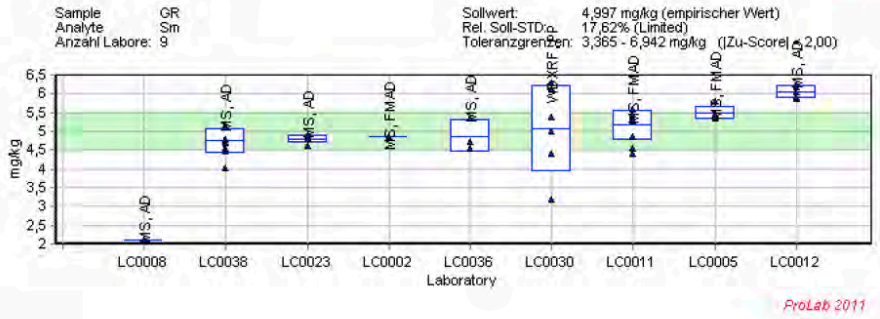

Sample GR
Analyte Sb (AR)
Anzahl Labore: 8
Sollwert: 1,436 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,670 - 2,470 mg/kg (|Zu-Score| < 2,00)
mg/kg
2
1,5
1
0,5
0
AAS, AR
MS, AR
AAS, AR
MS, AR
MS, AR
MS, AR
MS, AR
MS, AR
LC0003
LC0037
LC0031
LC0011
LC0038
LC0015
LC0023
LC0009
Laboratory
ProLab 2011

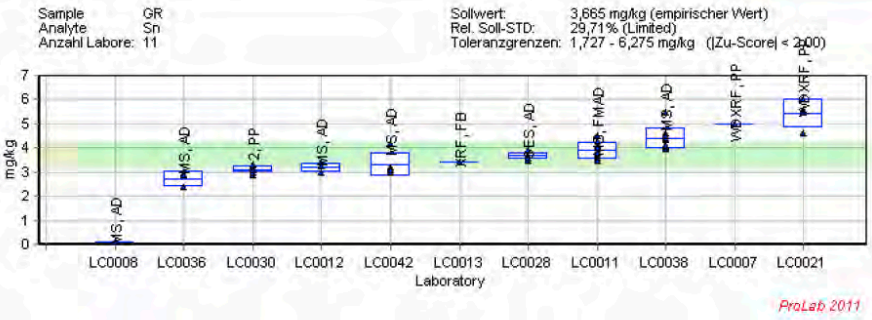

Sample GR
Analyte Sc
Anzahl Labore: 16
Sollwert: 10,295 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 5,644 - 16,267 mg/kg (|Zu-Score| < 2,00)
mg/kg
35
30
25
20
15
10
5
0
MS, AD
MS, AD
MS, FMAD
MS, AD
WD-XRF, FB
WD-XRF, FB
MS, AD
WD-XRF, PP
MS, AD
WD-XRF, PP
WD-XRF, PP
WD-XRF, PP
XRF, FB
MS, FMAD
XRF, PP
LC0008
LC0036
LC0011
LC0038
LC0032
LC0022
LC0023
LC0030
LC0042
LC0016
LC0007
LC0024
LC0013
LC0005
LC0009
LC0019
Laboratory
ProLab 2011

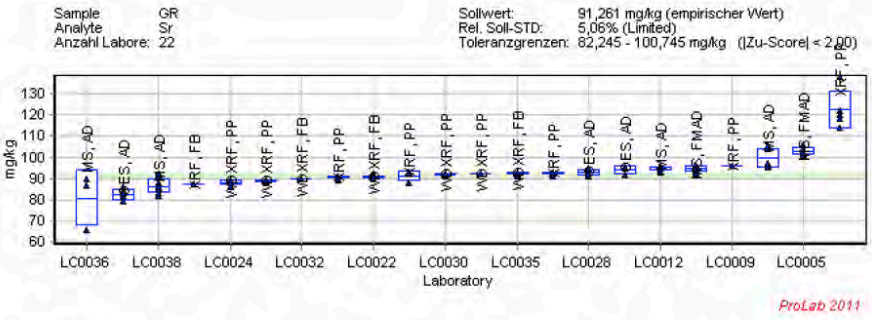

Sample GR
Analyte Sc (AR)
Anzahl Labore: 8
Sollwert: 4,020 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 2,204 - 6,352 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0004 LC0037 LC0016 LC0011 LC0023 LC0015 LC0038 LC0009
ProLab 2011

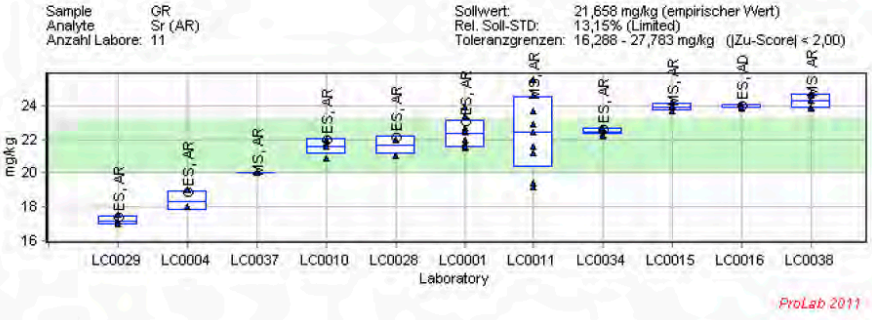

Sample GR
Analyte Se
Anzahl Labore: 6
Sollwert: 0,270 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,126 - 0,465 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0042 LC0038 LC0030 LC0036 LC0002
ProLab 2011

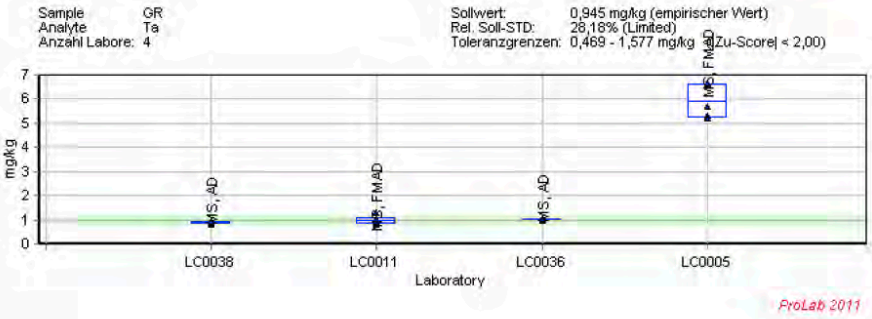

Sample GR
Analyte SiO2
Anzahl Labore: 14
Sollwert: 72,677 % Gew. (empirischer Wert)
Rel. Soll-STD: 1,67% (Limited)
Toleranzgrenzen: 70,422 - 75,123 % Gew. (|Zu-Score| < 2,00)
% Gew.
Laboratory
LC0019 LC0020 LC0017 LC0014 LC0035 LC0009 LC0022 LC0011 LC0031 LC0032 LC0024 LC0013 LC0030 LC0016
ProLab 2011

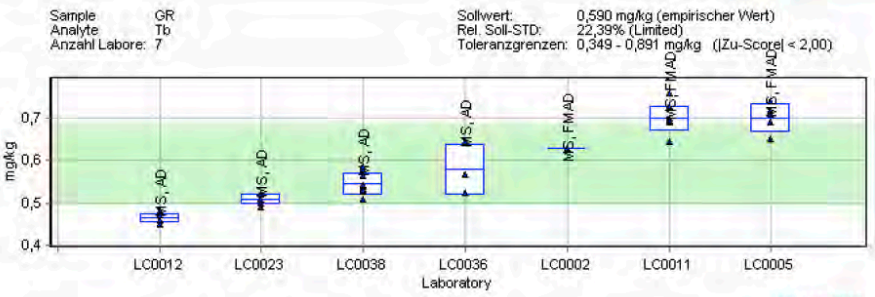

Sample GR
Analyte Sm
Anzahl Labore: 9
Sollwert: 4,997 mg/kg (empirischer Wert)
Rel. Soll-STD: 17,62% (Limited)
Toleranzgrenzen: 3,365 - 6,942 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0038 LC0023 LC0002 LC0036 LC0030 LC0011 LC0005 LC0012
ProLab 2011

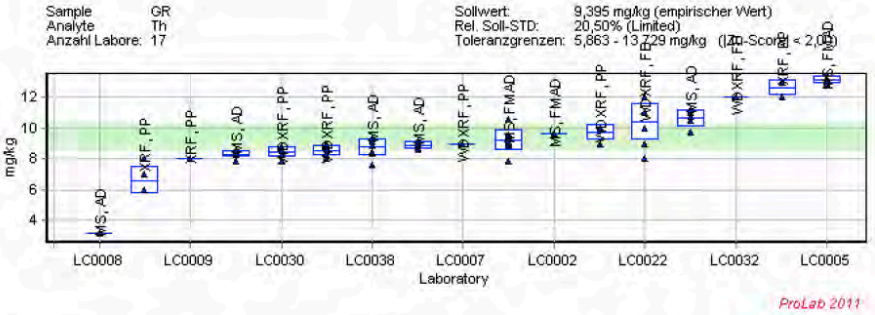

Sample GR
Analyte Sn
Anzahl Labore: 11
Sollwert: 3,665 mg/kg (empirischer Wert)
Rel. Soll-STD: 29,71% (Limited)
Toleranzgrenzen: 1,727 - 6,275 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008 LC0036 LC0030 LC0012 LC0042 LC0013 LC0028 LC0011 LC0038 LC0007 LC0021
Laboratory
ProLab 2011

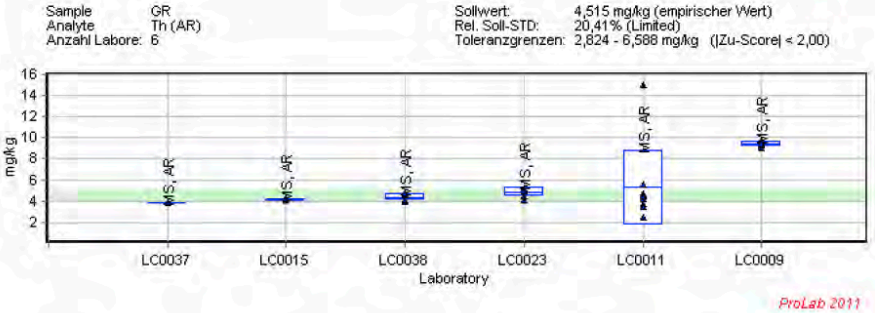

Sample GR
Analyte Sr
Anzahl Labore: 22
Sollwert: 91,261 mg/kg (empirischer Wert)
Rel. Soll-STD: 5,06% (Limited)
Toleranzgrenzen: 82,245 - 100,745 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0036 LC0038 LC0024 LC0032 LC0022 LC0030 LC0035 LC0028 LC0012 LC0009 LC0005
Laboratory
ProLab 2011

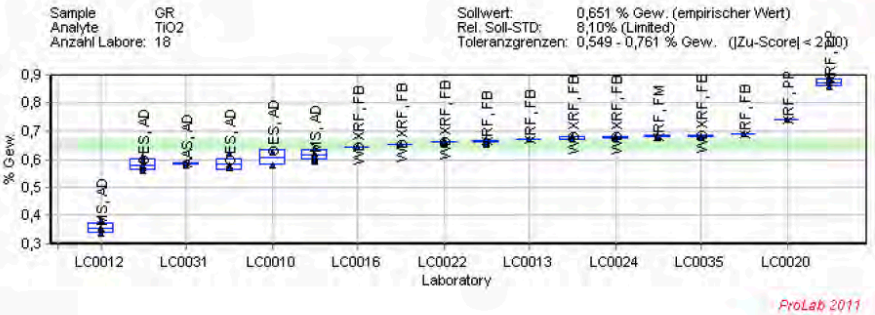

Sample GR
Analyte Sr (AR)
Anzahl Labore: 11
Sollwert: 21,658 mg/kg (empirischer Wert)
Rel. Soll-STD: 13,15% (Limited)
Toleranzgrenzen: 16,288 - 27,783 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0029 LC0004 LC0037 LC0010 LC0028 LC0001 LC0011 LC0034 LC0015 LC0016 LC0038
Laboratory
ProLab 2011

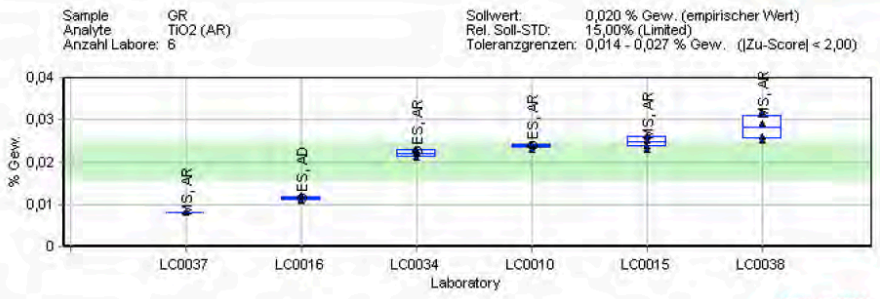

Sample GR
Analyte Ta
Anzahl Labore: 4
Sollwert: 0,945 mg/kg (empirischer Wert)
Rel. Soll-STD: 28,18% (Limited)
Toleranzgrenzen: 0,469 - 1,577 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0038 LC0011 LC0036 LC0005
Laboratory
ProLab 2011

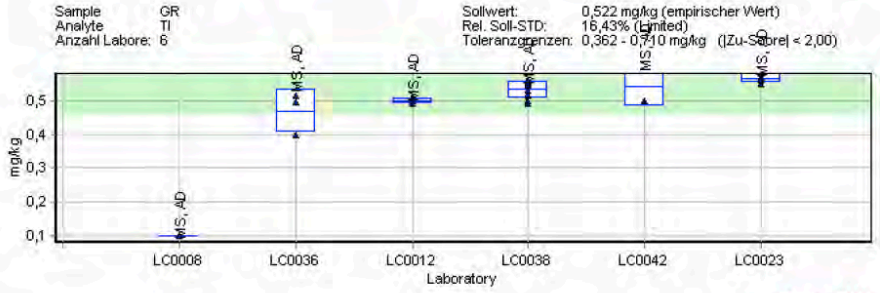

Sample GR
Analyte Tb
Anzahl Labore: 7
Sollwert: 0,590 mg/kg (empirischer Wert)
Rel. Soll-STD: 22,39% (Limited)
Toleranzgrenzen: 0,349 - 0,891 mg/kg (|Zu-Score| < 2,00)
mg/kg
0,4
0,5
0,6
0,7
MS, AD
MS, FM AD
LC0012
LC0023
LC0038
LC0036
LC0002
LC0011
LC0005
Laboratory
ProLab 2011

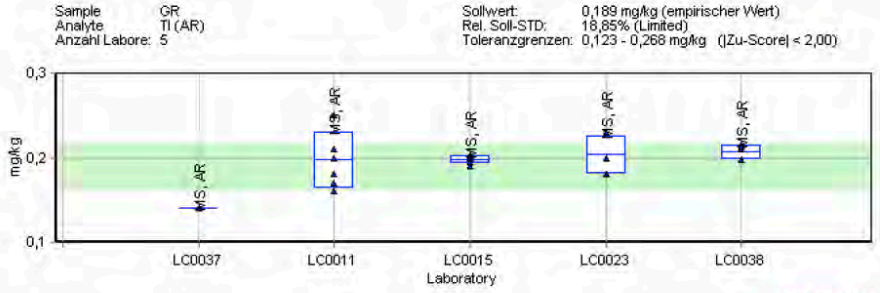

Sample GR
Analyte Th
Anzahl Labore: 17
Sollwert: 9,395 mg/kg (empirischer Wert)
Rel. Soll-STD: 20,50% (Limited)
Toleranzgrenzen: 5,863 - 13,729 mg/kg (|Zu-Score| < 2,00)
mg/kg
4
6
8
10
12
MS, AD
WD XRF, PP
XRF, PP
MS, FM AD
WD XRF, FB
MS, AR
LC0008
LC0009
LC0030
LC0038
LC0007
LC0002
LC0022
LC0032
LC0005
Laboratory
ProLab 2011

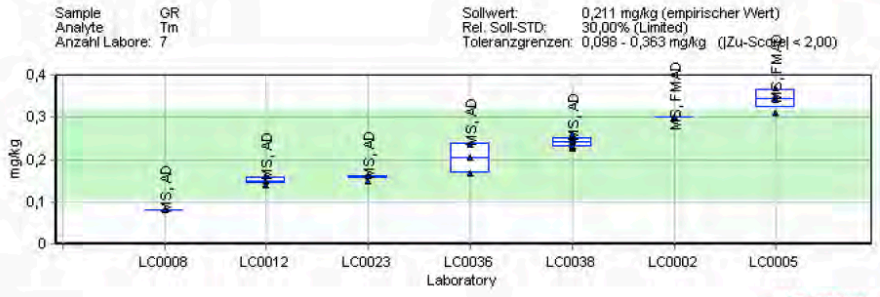

Sample GR
Analyte Th (AR)
Anzahl Labore: 6
Sollwert: 4,515 mg/kg (empirischer Wert)
Rel. Soll-STD: 20,41% (Limited)
Toleranzgrenzen: 2,824 - 6,588 mg/kg (|Zu-Score| < 2,00)
mg/kg
2
4
6
8
10
12
14
16
MS, AR
LC0037
LC0015
LC0038
LC0023
LC0011
LC0009
Laboratory
ProLab 2011

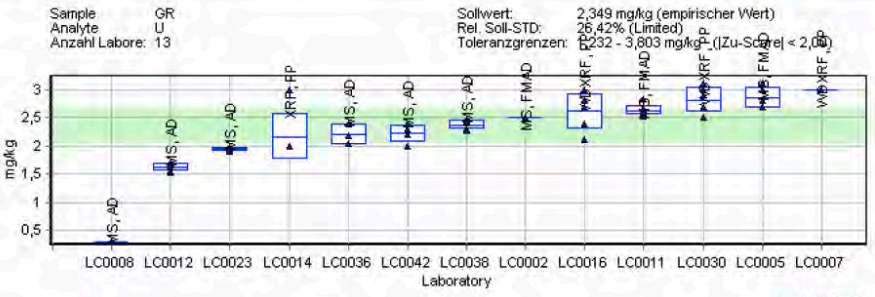

Sample GR
Analyte TiO2
Anzahl Labore: 18
Sollwert: 0,651 % Gew. (empirischer Wert)
Rel. Soll-STD: 8,10% (Limited)
Toleranzgrenzen: 0,549 - 0,761 % Gew. (|Zu-Score| < 2,00)
% Gew.
0,3
0,4
0,5
0,6
0,7
0,8
0,9
MS, AD
ES, AD
AAS, AD
WD XRF, FB
XRF, FB
XRF, FM
XRF, PP
LC0012
LC0031
LC0010
LC0016
LC0022
LC0013
LC0024
LC0035
LC0020
Laboratory
ProLab 2011

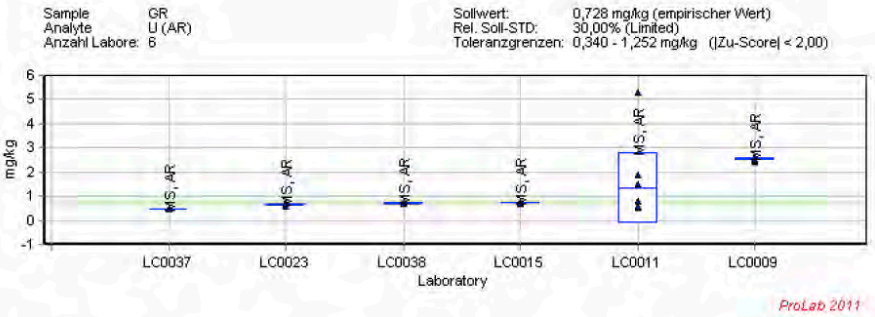

Sample GR
Analyte TiO2 (AR)
Anzahl Labore: 6
Sollwert: 0,020 % Gew. (empirischer Wert)
Rel. Soll-STD: 15,00% (Limited)
Toleranzgrenzen: 0,014 - 0,027 % Gew. (|Zu-Score| < 2,00)
% Gew.
0,04
0,03
0,02
0,01
0
MS, AR
ES, AD
ES, AR
ES, AR
MS, AR
MS, AR
LC0037
LC0016
LC0034
LC0010
LC0015
LC0038
Laboratory
ProLab 2011

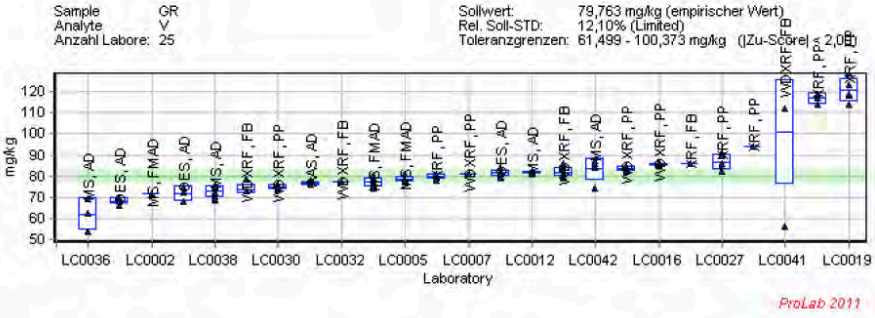

Sample GR
Analyte Tl
Anzahl Labore: 6
Sollwert: 0,522 mg/kg (empirischer Wert)
Rel. Soll-STD: 16,43% (Limited)
Toleranzgrenzen: 0,362 - 0,710 mg/kg (|Zu-Score| < 2,00)
mg/kg
0,5
0,4
0,3
0,2
0,1
MS, AD
MS, AD
MS, AR
MS, AR
MS, AD
MS, AD
LC0008
LC0036
LC0012
LC0038
LC0042
LC0023
Laboratory
ProLab 2011

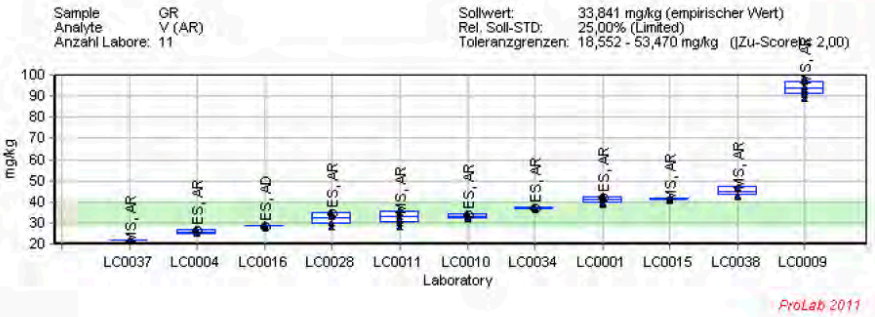

Sample GR
Analyte Tl (AR)
Anzahl Labore: 5
Sollwert: 0,189 mg/kg (empirischer Wert)
Rel. Soll-STD: 18,85% (Limited)
Toleranzgrenzen: 0,123 - 0,268 mg/kg (|Zu-Score| < 2,00)
mg/kg
0,3
0,2
0,1
MS, AR
MS, AR
MS, AR
MS, AR
MS, AR
LC0037
LC0011
LC0015
LC0023
LC0038
Laboratory
ProLab 2011

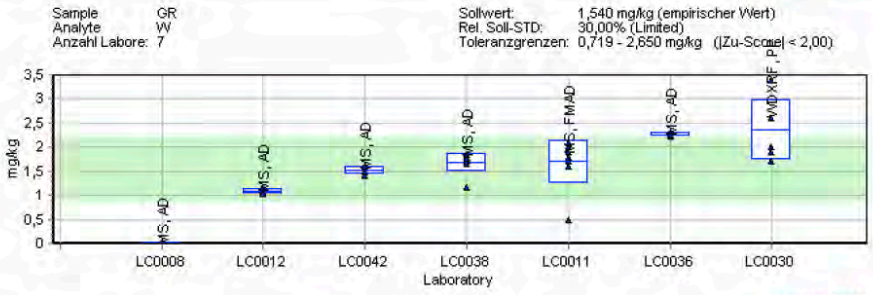

Sample GR
Analyte Tm
Anzahl Labore: 7
Sollwert: 0,211 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,098 - 0,363 mg/kg (|Zu-Score| < 2,00)
mg/kg
0,4
0,3
0,2
0,1
0
MS, AD
MS, AD
MS, AD
MS, AD
MS, AD
ME, FM AD
ME, FM AD
LC0008
LC0012
LC0023
LC0036
LC0038
LC0002
LC0005
Laboratory
ProLab 2011

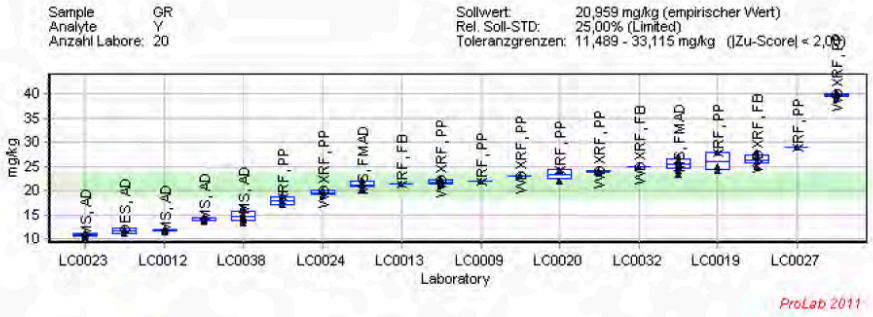

Sample GR
Analyte U
Anzahl Labore: 13
Sollwert: 2,349 mg/kg (empirischer Wert)
Rel. Soll-STD: 26,42% (Limited)
Toleranzgrenzen: 1,232 - 3,803 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0012 LC0023 LC0014 LC0036 LC0042 LC0038 LC0002 LC0016 LC0011 LC0030 LC0005 LC0007
ProLab 2011

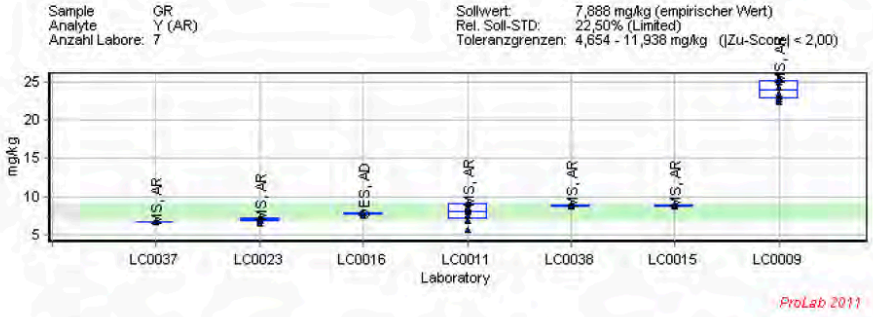

Sample GR
Analyte U (AR)
Anzahl Labore: 6
Sollwert: 0,728 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,340 - 1,252 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0037 LC0023 LC0038 LC0015 LC0011 LC0009
ProLab 2011

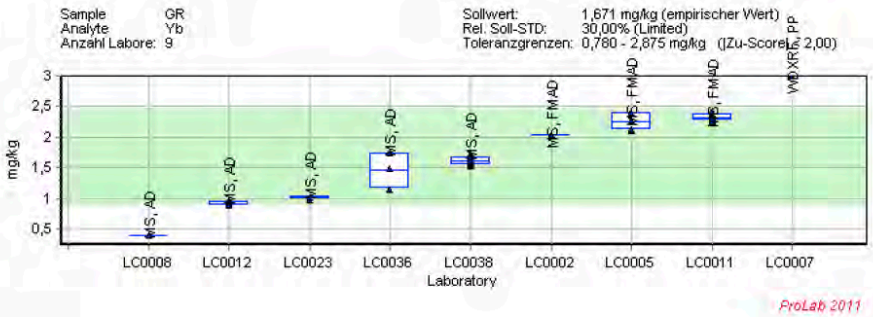

Sample GR
Analyte V
Anzahl Labore: 25
Sollwert: 79,763 mg/kg (empirischer Wert)
Rel. Soll-STD: 12,10% (Limited)
Toleranzgrenzen: 61,499 - 100,373 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0036 LC0002 LC0038 LC0030 LC0032 LC0005 LC0007 LC0012 LC0042 LC0016 LC0027 LC0041 LC0019
ProLab 2011

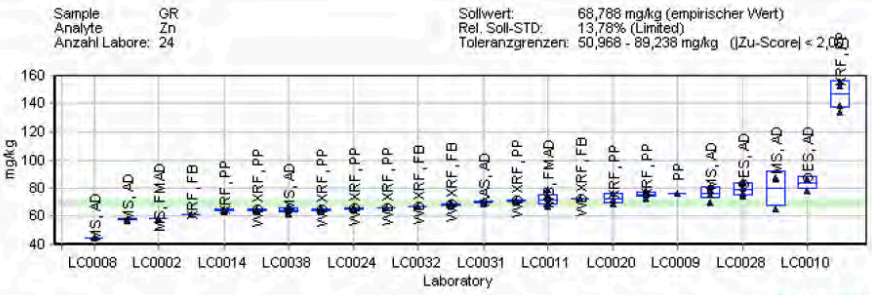

Sample GR
Analyte V (AR)
Anzahl Labore: 11
Sollwert: 33,841 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 18,552 - 53,470 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0037 LC0004 LC0016 LC0028 LC0011 LC0010 LC0034 LC0001 LC0015 LC0038 LC0009
ProLab 2011

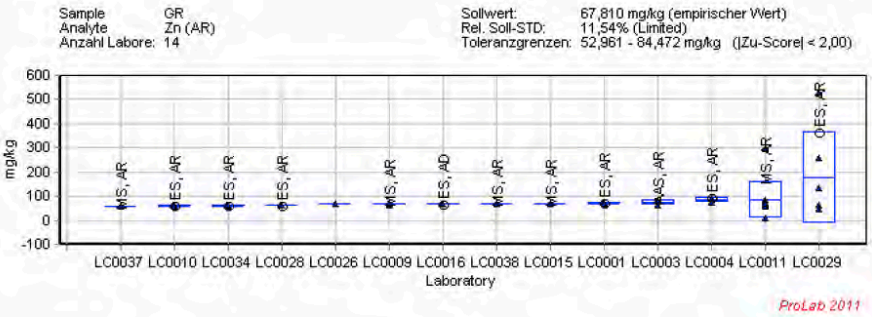

Sample GR
Analyte W
Anzahl Labore: 7
Sollwert: 1,540 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,719 - 2,650 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008
LC0012
LC0042
LC0038
LC0011
LC0036
LC0030
Laboratory
ProLab 2011

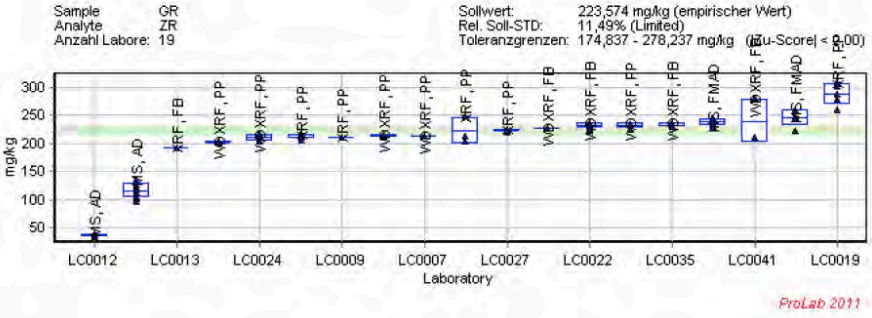

Sample GR
Analyte Y
Anzahl Labore: 20
Sollwert: 20,959 mg/kg (empirischer Wert)
Rel. Soll-STD: 25,00% (Limited)
Toleranzgrenzen: 11,489 - 33,115 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0023
LC0012
LC0038
LC0024
LC0013
LC0009
LC0020
LC0032
LC0019
LC0027
Laboratory
ProLab 2011


Sample GR
Analyte Y (AR)
Anzahl Labore: 7
Sollwert: 7,888 mg/kg (empirischer Wert)
Rel. Soll-STD: 22,50% (Limited)
Toleranzgrenzen: 4,654 - 11,938 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0037
LC0023
LC0016
LC0011
LC0038
LC0015
LC0009
Laboratory
ProLab 2011


Sample GR
Analyte Yb
Anzahl Labore: 9
Sollwert: 1,671 mg/kg (empirischer Wert)
Rel. Soll-STD: 30,00% (Limited)
Toleranzgrenzen: 0,780 - 2,875 mg/kg (|Zu-Score| < 2,00)
mg/kg
LC0008
LC0012
LC0023
LC0036
LC0038
LC0002
LC0005
LC0011
LC0007
Laboratory
ProLab 2011


Sample GR
Analyte Zn
Anzahl Labore: 24
Sollwert: 68,788 mg/kg (empirischer Wert)
Rel. Soll-STD: 13,78% (Limited)
Toleranzgrenzen: 50,968 - 89,238 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0008 LC0002 LC0014 LC0038 LC0024 LC0032 LC0031 LC0011 LC0020 LC0009 LC0028 LC0010
ProLab 2011


Sample GR
Analyte Zn (AR)
Anzahl Labore: 14
Sollwert: 67,810 mg/kg (empirischer Wert)
Rel. Soll-STD: 11,54% (Limited)
Toleranzgrenzen: 52,961 - 84,472 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0037 LC0010 LC0034 LC0028 LC0026 LC0009 LC0016 LC0038 LC0015 LC0001 LC0003 LC0004 LC0011 LC0029
ProLab 2011


Sample GR
Analyte ZR
Anzahl Labore: 19
Sollwert: 223,574 mg/kg (empirischer Wert)
Rel. Soll-STD: 11,49% (Limited)
Toleranzgrenzen: 174,837 - 278,237 mg/kg (|Zu-Score| < 2,00)
mg/kg
Laboratory
LC0012 LC0013 LC0024 LC0009 LC0007 LC0027 LC0022 LC0035 LC0041 LC0019
ProLab 2011

APPENDIX 3. ***Predicting particle size distribution in soils of the GEMAS sampling programme using infrared spectroscopy and partial least squares regression***

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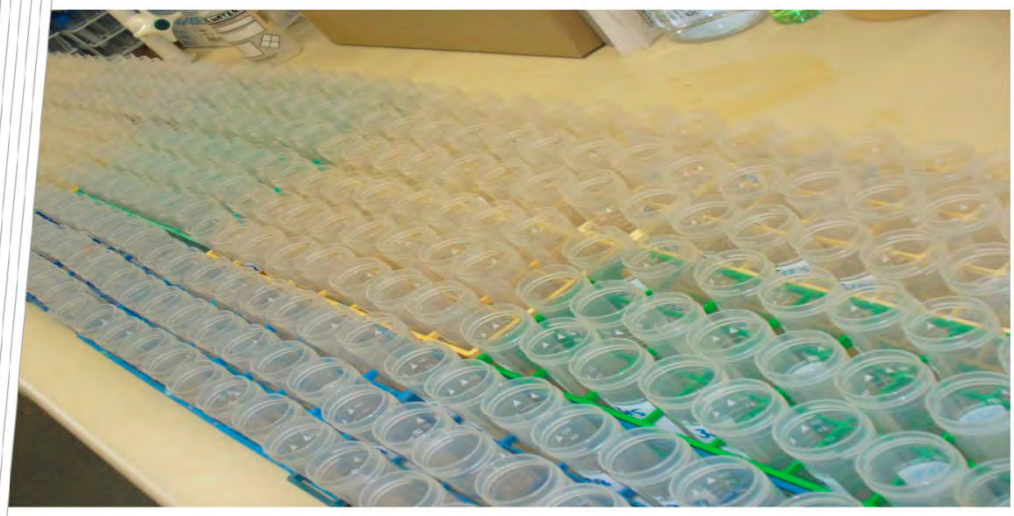
Les Janik, Michael J. McLaughlin, Sean Forrester
CSIRO Land and Water, Adelaide, Australia

Particle size analysis of GEMAS Soils



www.csiro.au

Les Janik, Michael J McLaughlin and Sean Forrester

Draft final report: 15th October 2011

Predicting particle size distribution in soils of the GEMAS sampling program using infrared spectroscopy and partial least-squares regression

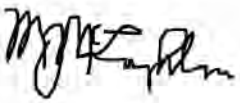
Commercial-in-confidence

Copyright and Disclaimer

Statement of Authentication

We, the undersigned, declare that the objectives laid down in the protocol were achieved and that the data generated are valid. The report fully and accurately reflects the procedures used and the raw data generated in the studies contained in this report.

Signature of authorised individuals:



Name: Dr. Michael J McLaughlin

Date: 15th October 2011

EXECUTIVE SUMMARY

- The aim of this project was to use mid-infrared (MIR) spectroscopic analysis to develop a calibration model to predict the particle size distribution values in the soils of the GEMAS soil sampling program.
- Experimental particle size analysis data were obtained for 147 samples chosen from the GEMAS sample set using the Sedigraph method.
- Principal component analysis of the spectra of the 147 samples chosen for particle size analysis indicated that they were a reasonable representation of the whole GEMAS sample set, except perhaps for the highly organic soils and very low carbonate soils.
- MIR spectra from the 147 samples with known particle size analysis were used to develop calibrations of sand, silt and clay percentages in the samples with portions of the spectral signature. Initially, a composite model was developed using spectral and laboratory determined particle size data for all three fractions simultaneously (sand, silt and clay) and calibrations using this model were found to be only poor to indicator quality.
- Individual models were then developed for each size fraction - sand, silt and clay - and calibrations were found to be slightly better with R^2 values for sand - 0.68, silt – 0.65 and clay – 0.73.
- Final validation of the model was carried out with the 147 samples being split into two sets; the first 100 for calibration and the remaining 47 for validation ("test" set). The models were found to predict with "indicator" accuracy the sand, silt and clay% values in the validation soils, similar to that of the calibration model.
- Compared to other published work on the prediction of particle size fractions with MIR spectroscopy and PLS regression (R^2 values often found to be >0.90), the errors in this regression in these analyses were higher than expected. This may be related to carbonate being included in one or more of the particle size fractions as determined by laboratory analysis.

- The optimised PLS model was applied to the full prediction in the 4313 soils of the GEMAS soil sampling program. Samples with high prediction "deviation" were omitted from prediction.

TABLE OF CONTENTS

1 PROJECT BACKGROUND

Predictions of soil particle size have been investigated using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, where soil properties important in partitioning mechanisms can be rapidly predicted without the need for costly chemical analysis procedures (Janik and Skjemstad 1995).. Mid-infrared diffuse reflectance (DRIFT) spectroscopic characterization of soils was pioneered by CSIRO in Australia in the 1990's (Nguyen *et al.* 1991) and, since the availability of PC-based chemometric applications, DRIFT with partial least squares (PLS) regression has become popular for prediction of soil properties important in agricultural systems (Janik and Skjemstad 1995; Janik et al. 1998; Bertrand et al. 2002; Forrester et al. 2003; Reeves III et al. 2005; Rossel et al. 2006; Janik et al. 2007; Ludwig et al. 2008; Terhoeven-Urselmans et al. 2008). In these studies and applications, soil chemical and physical properties have been modelled and predicted from infrared spectra of soils which have been combined into regression models with laboratory derived reference data. When robust PLS regression models are derived this allows for the prediction of chemical and physical properties of unknown soils with accuracy comparable to the original laboratory methods.

The basis of the DRIFT PLS method assumes that there is a known correlation between the soil spectral intensity signature and soil component composition and chemistry. In this method a dried sample of soil is placed under an incident beam of infrared radiation (IR) and the reflected radiation is determined as a spectrum. The absorption of radiation of various frequencies is then correlated with the properties of interest in the soil (Figure 1).

Figure 1. Basis of soil analysis using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy.

Samples used for DRIFT analysis require minimal treatment and only a few grams of powdered, air-dry soil are required. MIR spectroscopy relies on molecular vibration

frequencies of the relatively "light" (high frequency) C-H, N-H and O-H bonds as well as the "heavier" (lower frequency) C-O, N-O, C-C, Al-O, Fe-O and Si-O bonds (4,000-400 cm^{-1} or 2,500-25,000 nm), and in the NIR the weaker overtones and combinations of the C-H, N-H and O-H bonds in the NIR (12,500-4,000 cm^{-1} or 800-2,500 nm). In soils the observed spectral absorbances are due mostly to the readily identifiable fundamental MIR frequencies of major soil components such as sand, clay minerals, carbonates, quartz, organic matter, iron oxides and water in various chemical and physical environments. Major soil properties such as soil texture, mineralogy, cation-exchange capacity, organic matter, and in this present case particle size analysis, can thus be predicted using MIR methodology provided that there are well-defined correlations between the soil properties and soil composition (Janik et al. 1998).

2 PROJECT AIM

The aim of this project was to use mid-infrared spectroscopy and partial least-squares (PLS) regression analysis of soils to develop a calibration model to predict the sand, silt and clay contents in the soils of the GEMAS soil sampling program.

3 MATERIALS AND METHODS

3.1 SOILS

A total of 4813 soils were sent to CSIRO by Eurometaux for this study. A total of 147 soils were selected for IR analysis to be used in the development of calibration and validation models. Soils were oven dried at 40°C for 12 h and cooled in a desiccator prior to MIR analysis. The soil pH data in 0.01 M calcium chloride ($CaCl_2$) and particle size data (*Sedigraph* method) were provided to CSIRO by Eurometaux (EU). For each soil, clay was defined as the <2 µm fraction, sand (total) as the 63-2000 µm fraction and silt determined by difference between 100 and clay-plus-sand.

3.2 MIR ANALYSIS, MODEL DEVELOPMENT AND VALIDATION

3.2.1 MIR Spectra

DRIFT spectra were obtained for <2 mm soil samples in a *Pike* diffuse reflectance auto-sampler on a Perkin-Elmer *Spectrum-One* instrument in the range 7800-500 cm^{-1} and at a resolution of 8 cm^{-1}. From these spectra, there were two subset of soil selected to validate the PLS model calibration (n=100 for calibration and n=47 for model validation).

3.2.2 Regression Analysis Method

Multivariate analysis was carried out using PLS regression and full "leave-one-out" cross-validation. PLS models were built from the DRIFT spectra (X-predictor variables) and

experimental sand% (Y-dependent variables) values. Two forms of PLS regression were tested; PLS-1 where each particle size analysis (PSA) component is determined independently from the others and separate PLS model vectors are derived for each component, and PLS-2 where the three PSA components were modeled together deriving PLS vectors common to the three components.

Prior to PLS regression, the DRIFT spectra were baseline corrected using the Unscrambler software. PLS models were cross-validated against the experimental sand% values. During cross-validation, optimum frequencies were selected from the full spectral range until a maximum R^2 was obtained.

The PLS regression statistics were reported in terms of the coefficient of determination (R^2), root mean square of error (RMSE), standard deviation (SD) and ratio of prediction to deviation (RPD = SD/RMSE). In the case of infrared regression predictions, RPD values <1.5 are considered poor, 1.5-2.0 suggests indicator quality, 2.0-3.0 suggest good quality, and >3.0 are analytical quality. Models that explain most of the variance and lie close to the 1:1 relationship between predicted and observed are preferred.

A further test of prediction potential was carried out using a calibration model built from experimental sand, silt and clay % values on 100 soils and applied to predict sand% values for a further 47 independent "test" soils (validation soils). Outlier samples were removed from the regression and validation. First an optimised PLS model was derived from the PSA values for 147 soils to determine the best infrared frequencies to use for model development. A new model was then built from PSA values for the 100 calibration soils using only these frequencies as PLS inputs and applied to the independent test set for validation of the model.

The final prediction of PSA values in the remaining 4313 soils used the optimised PLS regression model. In addition to the PSA value predictions, a further parameter "deviation" was calculated for each sample as an error indicator. This "deviation" parameter is defined by the Unscrambler™ software as "a function of the global model error, the sample leverage, and the spectrum residual X-variance". A large deviation indicates that the sample spectrum used for prediction is not similar to the samples used to make the calibration model and is a prediction outlier. A small PLS "deviation" indicates a good fit with the model. That being said, a large "deviation" value does not mean that the predicted value is in error but that it is uncertain. In this report, "deviation" values can be empirically classed as follows:

- <20 Excellent fit of sample with model
- 20-30 Good fit
- 30-40 Marginal fit
- >40 Poor fit

4 RESULTS AND DISCUSSION

4.1 SPECTRA

Data variability can be easily depicted from infrared spectra by using principal components analysis (PCA) score versus score plots. In these plots, illustrated in Figure 2 for the GEMAS soil set, the scores are projected along the PC axes representing the most important soil components e.g. soil organic matter, carbonate, clay or quartz.

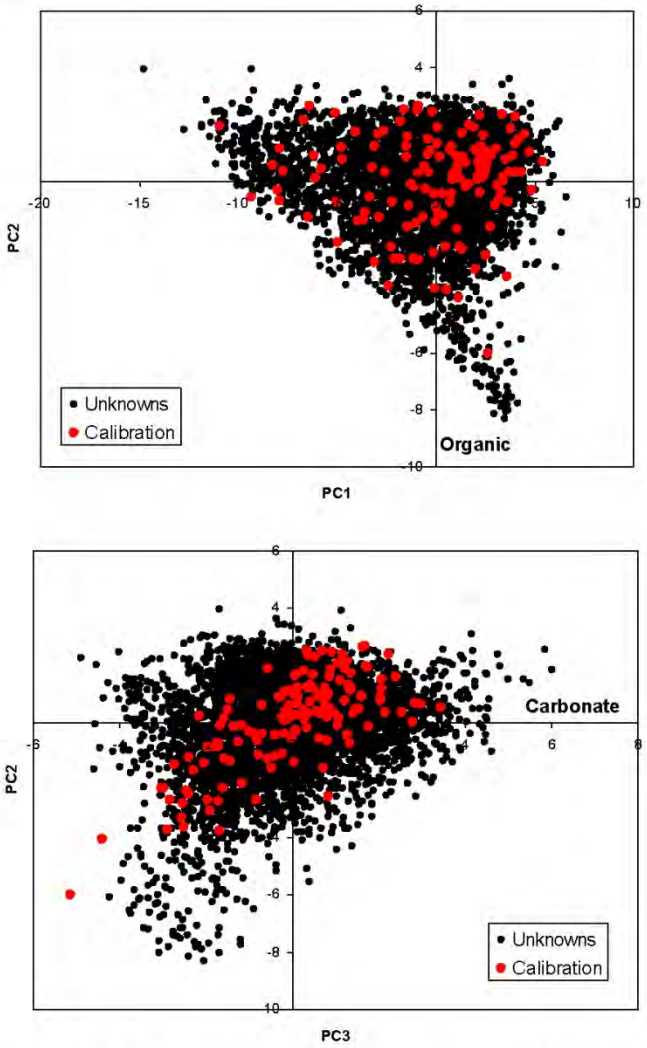


Figure 2. Plots of principal components scores projected along the first three PC axes. The PCA model scores for the calibration samples (●) are overlayed onto the unknown sample (●) scores. The dominant soil chemistry due to carbonate and organic matter are shown along PC axis 2 and 3 respectively.

While the score plots derived from the DRIFT spectra show that the calibration samples generally cover the unknowns there are areas within the unknowns that are not covered by the PSA calibration samples, particularly for the organic soils and to some extent the low carbonate soils.

4.2 PSA DATA

Before carrying out the PLS calibration modelling, the relationships between sand, silt and clay contents were examined to see if there were any inherent correlations between *Sedigraph* data for sand, silt and clay in soils from Europe. Figure 3 depicts plots of silt and clay versus sand, and also clay versus silt.

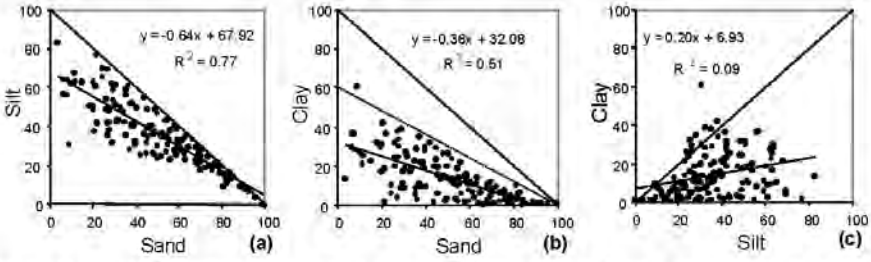


Figure 3. Plots depicting correlation between Sedigraph data for (a) silt and sand, (b) clay and sand, and (c) clay and silt. Plots show the data points, the regression line and the 1:1 slope. The dotted line in (a) represents the 60% line.

A moderate inverse regression (R^2 = 0.77) was shown in Figure 3a for silt versus sand, although there was considerable divergence at high silt (low sand) values. The inverse regression between clay and sand was weaker, with an R^2 of only 0.51. Furthermore, it appeared that for many of the samples with <20% clay, there was almost no correlation with sand. There was also no significant correlation between clay and silt data.

These relationships raise the question of what is the basis for the PSA, i.e. which are the soil components mostly associated with sand, silt and clay data. In general, high sand samples are thought to contain mostly sand-sized quartz particles, very little clay, and usually low soil organic matter because of the low surface area. In contrast, the high clay samples are usually characterised by clay minerals (mostly as kaolinite, illite and smectite), soil organic matter in the form of plant and soil biota debris, and water due to the high surface area. Silt soil components are expected to behave somewhat as a combination of sand and clay but can be compositionally highly variable.

In an attempt to understand some of the anomalies present in the PSA data, the role of soil organic carbon in the form of soil organic matter, and soil inorganic carbon as carbonate minerals was examined. The first effect of soil carbon is as a diluent of the soil mineral components supposedly contributing to the measured sand, silt and clay fractions. The

amount of soil carbon can be quite large in some soils, illustrated in Figure 4 by the carbon distributions (as a percentage of total soil mass) in the calibration soils. In general both total organic carbon (TOC) and carbonate are removed from the soil during ignition (measured as LOI). Up to 20-30% of the soil mass is thus lost during ignition (Figure 4d) plus some water bound by soil organic matter and water of hydration in carbonate and other soil minerals. This means that there will inevitably be significant errors in the reference PSA data unless steps have been taken to normalise the soil mass contributing to the PSA data or removing the TOC and carbonate prior to PSA analysis.

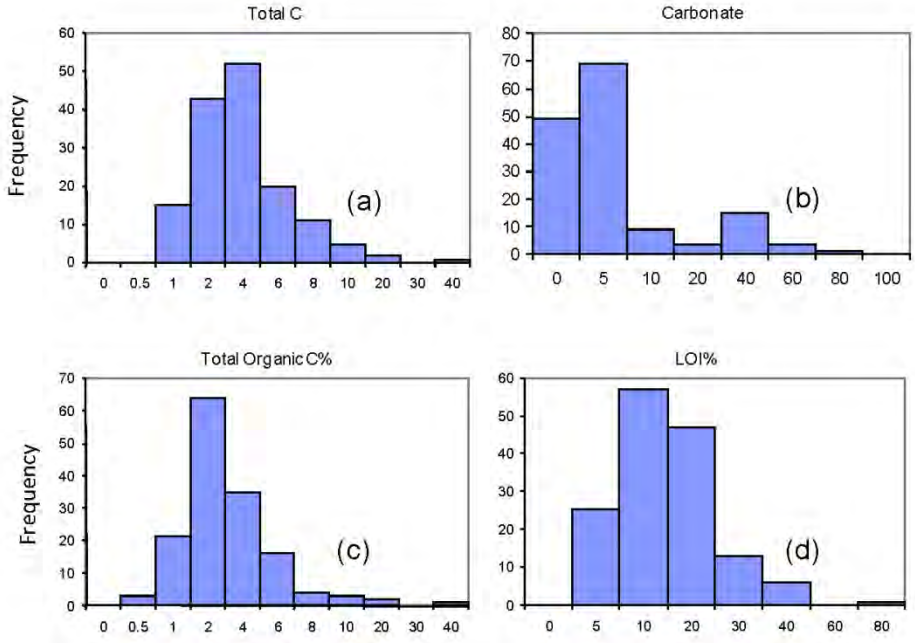


Figure 4. Frequency histograms of carbon in the calibration soils represented as (a) total carbon (TC), (b) carbonate, (c) total organic carbon (TOC), and (d) loss on ignition (LOI).

The role of inorganic carbon, as carbonate minerals, is difficult to deal with. It is not removed by chemical oxidation such as peroxide and may be randomly or systematically distributed throughout the PSA fractions. If the carbonate is more heavily represented in one of the PSA fractions then it may be difficult to determine which fraction it is in, and how much. If it is randomly distributed throughout all PSA fractions then this may present additional errors in the laboratory PSA determinations. In this present analysis, it is strongly suspected that the soil carbonate may contribute to some of the PSA fractions leading to increased apparent prediction errors.

4.3 PREDICTION

4.3.1 PLS-2 regression

A plot of the spectral standard deviation (SD) and the first two PLS loading weights used for the best calibration in the combined modelling of sand, silt and clay can be found in Figure 5. These loading weights are common to all three components. A total of 14 PCs were used to model the PSA data and while this may seem excessive, it was felt that there were sufficient samples in the set to support this number of PCs.

Loading weights 1 and 2, shown in Figure 5, accounted for 56 and 14% of the total spectral variance respectively in the analysis of all three components – sand, silt and clay. The spectral correlations were due to clay (negatively in Wt-1 mostly smectite near 3620 cm^{-1} and 1630cm^{-1}, and positive in Wt2 as kaolinite near 3695, 800 and 700 cm^{-1}). Strong negative peaks were observed near 2000-1800 cm^{-1} attributed to quartz. A positive peak due to 2520 cm^{-1} was assigned to calcite (carbonate). It is therefore apparent that, besides quartz sand and clay minerals, carbonate is implicated in the PLS regression model.

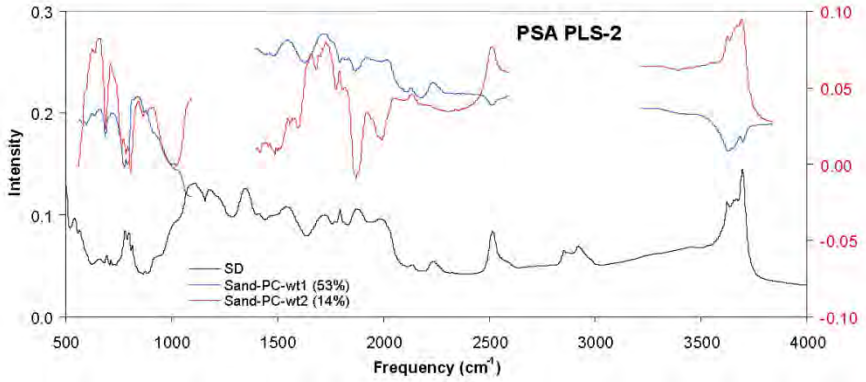


Figure 5. Plots of spectral standard deviations (SD) and the PLS loading weights for the first two factors; weight-1 (—) and weight-2 (—), used to model sand, silt and clay % values from DRIFT spectra.

PLS-2 cross-validation, using the full spectral range, highlighted a number of outliers – samples #975, 1118, 3870, 3966, 4915 and 5095 – which were removed prior to further modelling. The resulting regressions, illustrated in Figure 6, gave R^2 values for sand, silt and clay of 0.61, 0.53 and 0.66 respectively for 14 PLS PCs, and RMSECV values of 14.1, 11.5 and 6.3% respectively. During model training, irrelevant DRIFT frequencies were removed resulting in the optimised model. The optimized PLS cross-validation regression resulted in "indicator" accuracy model for sand and clay, with RPD values of 1.6 and 1.8, and "poor" quality for silt with a RPD = 1.4.

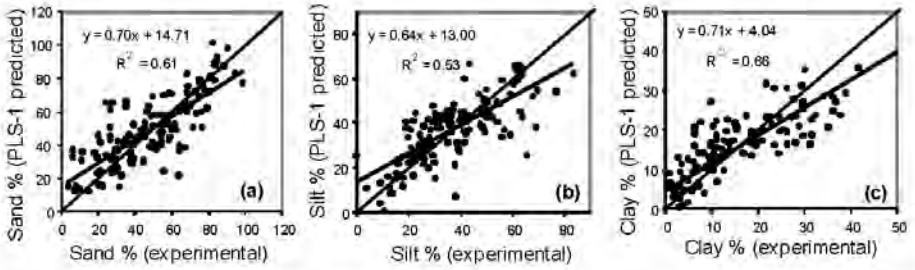


Figure 6. Plot of PLS (DRIFT data) cross-validation PSA values versus experimental PSA values for (a) sand, (b) silt and (c) clay.

A useful property of PLS-2 regression is that any inherent relationship between the predicted data is maintained, i.e. that the sum of predicted sand silt and clay is still equal to 100%, and the cross-correlations between sand, silt and clay is close to that of the laboratory data. The sum of predicted values for sand, silt and clay were found to sum to 100% for all samples in the cross-validation model. Considering the fact that the quality of the cross-validation predictions were only of "indicator" quality, but that the sum of sand, silt and clay values were still 100%, it may be that the reason for the seemingly low accuracy is that the PLS "interprets" the soil components giving rise to particular PSA data are different to the components relating to the laboratory method. It may be, in fact, that there are non-systematic soil components included with the sand, silt and clay fractions. It was difficult to determine what were the key compositional parameters in the soil that relate to PSA analyses from purely the laboratory data, since there was no information provided as to how soil composition related to PSA data.

It could be that the infrared PLS method may actually be accurate for a different interpretation of PSA than the laboratory method as used in this present study. Sand and clay components are clearly depicted by the loading weights but these may not necessarily be the only key soil parameters associated directly with the laboratory PSA data, leading to difficulties with the PLS modelling.

Figure 7 confirms that the infrared cross-validation data maintained the inherent relationships between sand, silt and clay in the reference laboratory data as illustrated in Figure 3.

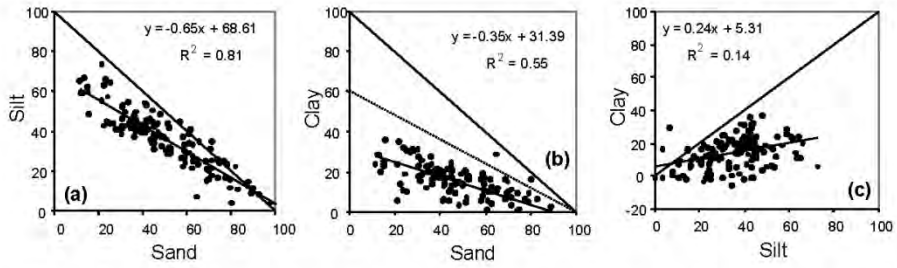


Figure 7. Plots depicting correlation between PLS cross-validation data for (a) silt and sand, (b) clay and sand, and (c) clay and silt. Plots show the data points, the regression line and the 1:1 slope. The dotted line in (a) represent the 60% line.

4.3.2 PLS-1 regression

4.3.2.1 Sand

4.3.2.1.1 Cross-validation

As mentioned earlier, the PLS-1 and PLS-2 methods differ in that, in PLS-1 only a single component is modelled at a time and each component has its own specific set of PLS vectors, whereas in PLS-2 a number of components are modelled together with a common set of PLS vectors. In this section of the work, sand, silt and clay will be predicted separately with PLS-1.

A plot of the spectral SD and the first two PLS loading weights used for the best calibration for sand can be found in Figure 8. Loading weights 1 and 2 accounted for 53 and 14% of the total spectral variance respectively. The spectral correlations were due to clay (negatively, mostly smectite near 3620 cm^{-1} and 1630cm^{-1}) and soil organic matter (positively, 2850 and 2920 cm^{-1}). A strong negative feature was observed near 1100 cm^{-1} (usually attributed to the peak inversion "*Restrahlen*" effect of silicate minerals with DRIFT spectroscopy) but could not be unambiguously assigned to quartz.

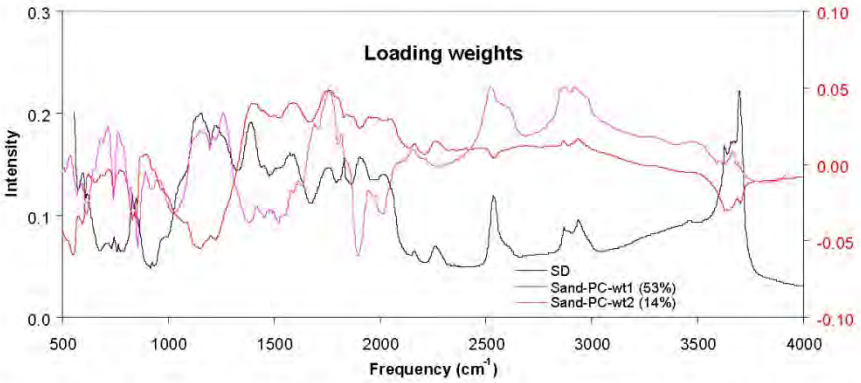


Figure 8. Plots of spectral standard deviations (SD) and the PLS coefficients for the first three factors used to model sand% values from full-range DRIFT spectra.

Although there were peaks in loading weight-1 near 1100-1200 cm^{-1} and 1850 cm^{-1}, the lack of strong, positive quartz signatures near 2000-1800 cm^{-1} in the second factor weight were puzzling since quartz is usually a major contributor to the sand fraction in PSA predictions using MIR. In fact, the second PLS loading weight was really surprising since now we can see strong *negative* quartz signatures at 2000-1800 cm^{-1}, in contrast to the expected positive quartz peak in the loading weights for other soils. We can also see that, for the GEMAS soils, a strong carbonate signature (peak near 2520 cm^{-1}) contributes positively to sand%. This strongly suggests carbonates were contributing to the sand fraction as determined in the laboratory.

PLS cross-validation, using the full spectral range, resulted in a regression R^2 = 0.55 (7-PCs). Further PLS-1 modelling was then performed on a reduced, optimized range of spectral data after omitting the relatively non-important spectral frequencies. The optimized PLS cross-validation regression resulted in an "indicator" accuracy model with an RPD = 1.7, R^2 = 0.68 and RMSECV = 13.1% (Figure 9a). A summary of the regression results can be found in Table 1. It is also apparent from Figure 9b that there is a very strong correlation between cross-validation values derived from the PLS-2 versus PLS-1 models, apart from some scatter in the regression values, consistent with the sum of PLS-1 cross-validation sand, silt and clay data generally close to 100%, with 85% of the samples giving sums of sand, silt and clay within the range 90-110%.

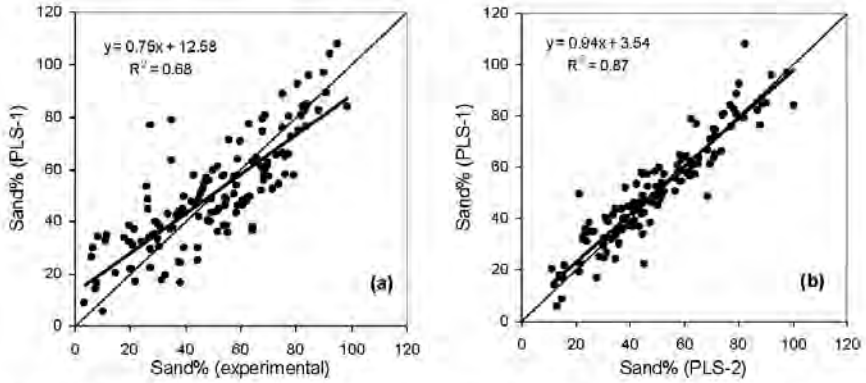


Figure 9. Plot of PLS (DRIFT data) cross-validation (a) sand % values versus experimental values, and (b) PLS1 versus PLS-2 values.

4.3.2.1.2 Validation of the PLS model with the "test" set

While the prediction model errors can be initially assessed by using cross-validation, a better test is to use a separate validation "test" set to validate the model.

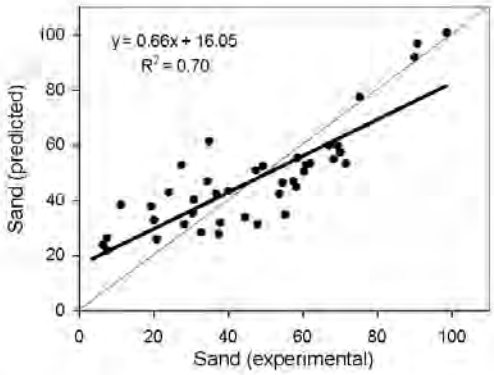


Figure 10. Regression plot of the predicted sand% versus experimental values in the validation "test" samples (n = 47). X-axis and Y-axis are in % units. The solid line is the model regression and dotted line is the 1:1 line.

Validation of the PLS model in this case used a calibration made from the first 100 soil samples (minus outlier or omitted samples) to predict sand values in the remaining 47 independent "test" soils (minus outliers to give 41 samples). The regression plot of predicted sand values versus experimental values is illustrated in Figure 10. The achieved RPD confirmed "indicator" accuracy for the predicted sand% values as for the original cross-validation (RPD = 1.8, R^2 = 0.70 and RMSE = 12.7%, see Table 1).

4.3.2.1.3 Prediction of sand for the unknown soils

The PLS model developed in 4.3.2.1.1 and 4.3.2.1.2 was applied to the prediction of sand% values for all unknown soils of the GEMAS sampling program. In order to get some idea of the confidence in the predictions, threshold values for prediction "deviation" were set to filter any suspect predicted values, particularly values <0 or >100% for sand%.

Although actual prediction errors could not be determined (since the samples were true unknowns), an indication of the expected confidence could be determined from the outputs of the prediction routine in the Unscrambler software. A total of 46 samples indicated deviation values >40. Predictions for these samples were rejected as they were considered to be too unreliable[1]. Of these, 9 samples; #89, 171, 902, 1230, 1253, 1279, 1358, 3364 and 4851, had prediction deviations >60, with 7 of these samples having negative sand% predictions. Three other samples; #4721, 4242 and 1477, also predicted negative values, having deviation values between about 45-52, and another two, #2140 and 3526, also with >45% deviations, resulted in >145% sand%. Unfortunately there were many sand% predictions within the deviation range >40 whose predicted values were within 0 and 100% but with no other indication other than deviation that could be used to assess their accuracy and hence

[1] Predicted values can be provided although considered to be unreliable

were rejected. Even with this restriction in place, 415 samples registered predicted values >100%, and 123 of these >120%.

Histogram plots of the prediction and error distributions in the calibration and unknown sets are depicted in Figure 11a-c. The distribution of predicted sand% values (Figure 11b) was found to be similar to that of the calibration+validation set (Figure 11a), in that the greatest population was in the 40-80% group, although there were now a significant population >100%. The most dominant error of 20-30 units (Figure 10c) occurred for 2313 samples, with a further 1920 samples with deviation of 10-20 units and 650 samples with deviation >30. This suggests that even though the calibration was classed as "indicator", according to the RPD, the fit of the PLS model to most of the spectra in the unknown sample set was considered to be good.

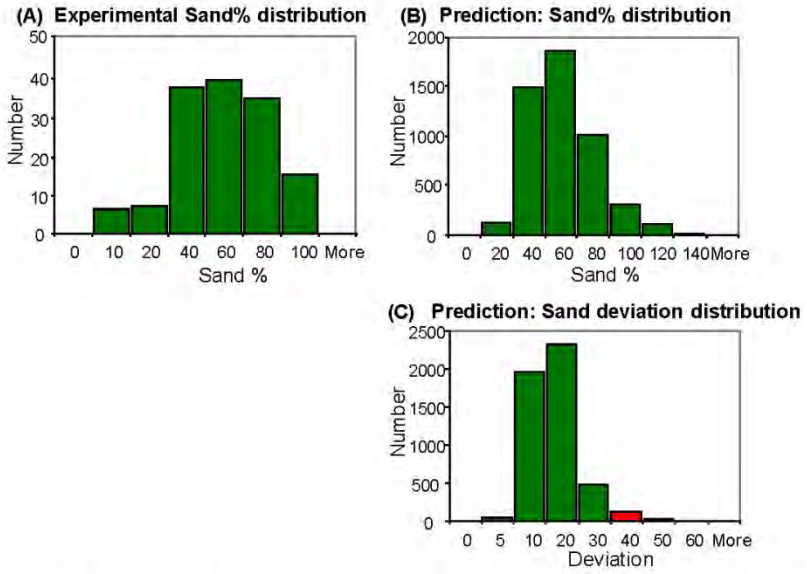


Figure 11. Histograms of experimental sand% values (A), predicted sand% values (B) and prediction deviations for sand% (C).

4.3.2.1.4 Conclusions (Sand)

The DRIFT PLS model for sand% was found to cross-validate with "indicator" accuracy, with an RPD = 1.7 and R^2 = 0.68. This relatively poor performance of the PLS model for prediction, compared to some data sets from other sources, may have been due to a combination of factors. The presence of carbonate interference may be one cause, as shown to be the case in previous work (CSIRO, unpublished). Another reason may be due to the high proportion of silt in many of these samples, thus impacting on the interference of silt spectral components on the apparent soil chemistry attributed to the sand fraction. The most

puzzling observation however was that quartz MIR peaks were not positively related to sand content as measured by the laboratory.

While most of the sand% prediction for the unknown soils were within the 0-40 PLS "deviation" parameter values, indicating a good fit of the unknown spectra, a significant number of samples were far greater, resulting in negative predicted values. There were also a significant number of >100% predicted values due to the low accuracy of the model.

A more thorough statistical assessment of the soil composition and laboratory methods responsible for the PLS calibration model may therefore be warranted before a further investment in trying to optimize the PLS modelling. The results suggested that spectra of the majority of the soils in the unknown set of samples could be fitted quite well by the PLS models.

4.3.2.2 Silt

4.3.2.2.1 Cross-validation regression

A plot of the PLS coefficients from the first three PCs (PLS factors) used for the optimum calibration can be found in Figure 12. The first two PCs accounted for 60% and 33% respectively of the total spectral variance for a model using 10 PLS factors for a minimum Y residual. The spectral correlations were due to clay (mostly smectite near 3620 cm^{-1} and 1630cm^{-1} and kaolinite near 3695 cm^{-1}) and quartz (1860 cm^{-1}).

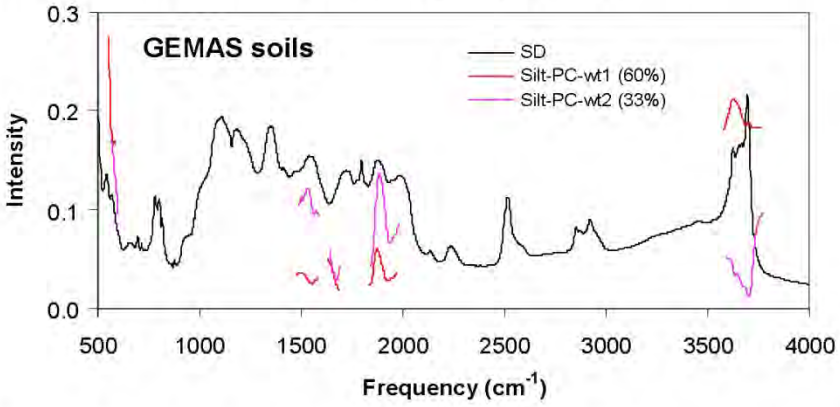


Figure 12. Plots of spectral standard deviations (SD) and the PLS loading weights for the first two PCs used to model silt%.

The PLS cross-validation model for silt resulted in a "indicator" accuracy model with an R^2 = 0.65, RMSECV = 9.7% and RPD = 1.7, (Figure 13). A summary of the results of regressions can be found in Table 1.

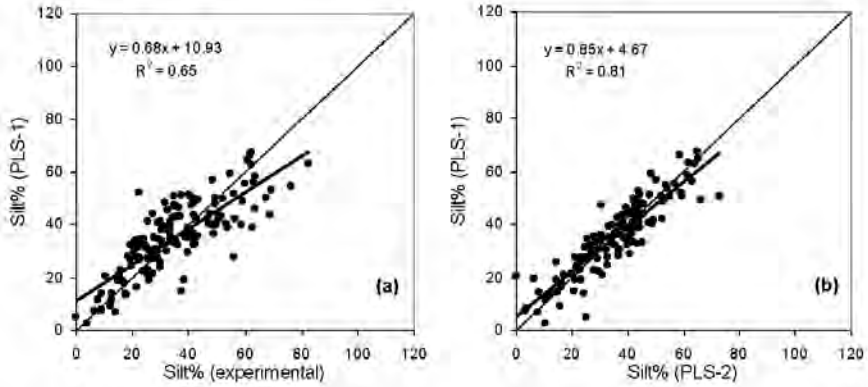


Figure 13. Plot of PLS (DRIFT data) predicted silt% values versus experimental silt% values. The solid line is the model regression, the dotted line is the 1:1 line.

It is apparent from Figure 13b that there is a very strong correlation between cross-validation values derived from the PLS-2 versus PLS-1 models, apart from some scatter in the regression values. This is consistent with the sum of PLS-1 cross-validation sand, silt and clay data generally being close to 85% of the samples giving sums of sand, silt and clay within 90-110%.

4.3.2.2.2 Validation of the PLS model with the "test" set

The prediction ability of the PLS model to accurately determine silt% in soils was further tested using a calibration set of 100 soil samples to predict silt% values in the remaining 47 independent test soils (minus excluded outliers). The regression plot of predicted silt% values versus experimental values is depicted in Figure 14. The achieved RPD confirmed "poor" to "indicator" accuracy for the predicted silt% values (R^2 = 0.62, RMSE = 10.3% and RPD = 1.6, see Table 1) similar to that for the original cross-validation.

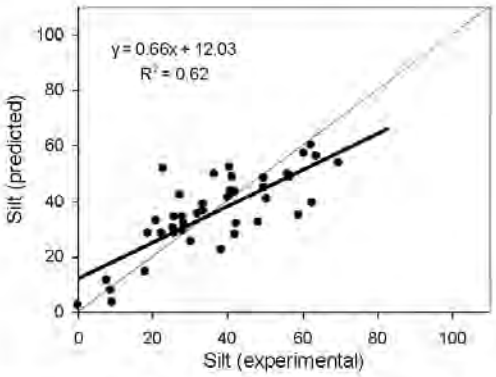


Figure 14. Regression plot of the prediction of silt% versus experimental values in the validation "test" samples (n = 46). X-axis and Y-axis are in % units. Solid line is the PLS-1 model regression and dotted line is the 1:1 line.

4.3.2.2.3 Prediction of silt for the unknown soils

The PLS-1 model was applied to the prediction of silt% values for all unknown soils of the GEMAS sampling program. The distribution of predicted silt% values (Figure 15b) was found to be very similar to that of the calibration+validation set (Figure 15a), with a slightly higher proportion of silt% samples at 0-2% silt content.

Although actual prediction errors could not be determined, since the samples are true unknowns, an indication of the expected errors could be, however, determined from the outputs of the prediction routine in the Unscrambler software. A histogram plot of the error distribution is depicted in Figure 15c. The most dominant error of 10-20 units occurred for 2646 samples, with a further 1117 samples with deviation of 20-30 units and only 118 samples with deviation >30. This suggests that even though the calibration was classed as "indicator", according to the RPD, the prediction error was reasonable.

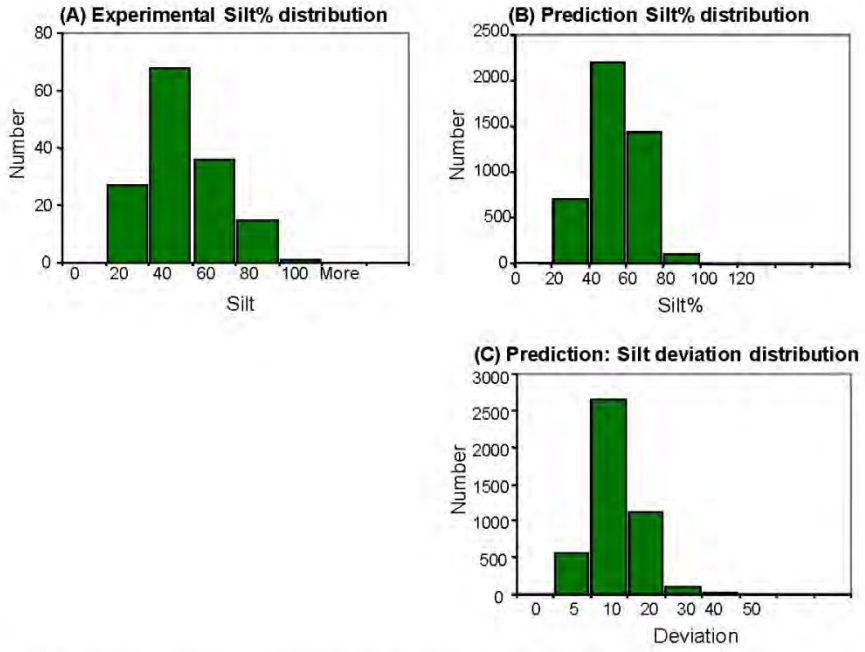


Figure 15. Histograms of experimental silt% values (A), predicted silt% values (B) and prediction deviations for silt% (C).

4.3.2.2.4 Conclusions (silt)

In this study, the PLS model for silt% was found to cross-validate with "indicator" accuracy. The results suggested that spectra of the majority of the soils in the unknown set of samples could be fitted well by the PLS models implying that the prediction errors for the unknowns was similar to that of the calibration set.

4.3.2.3 Clay

4.3.2.3.1 Cross-validation regression

A plot of the PLS coefficients from the first three PCs (PLS factors) used for the optimum calibration can be found in Figure 16. The first two loading weights (PC1 = 61 and PC2 = 13) for a model using 12 PLS factors. The spectral correlations were due to clay (mostly smectite near 3620 cm^{-1} and 1630cm^{-1}) and soil organic matter (negative 2850, 2920, 1720 and 1400 cm^{-1}). The negative correlation with SOM was somewhat unexpected since high SOM is usually thought to be associated with high clay.

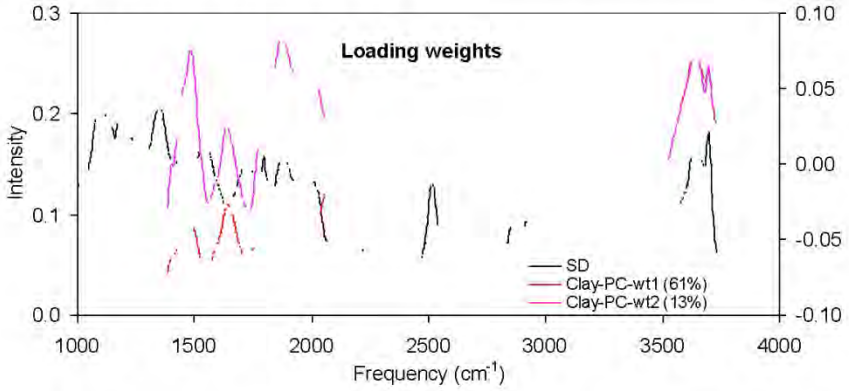


Figure 16. Plots of spectral standard deviations (SD) and the PLS loading weights for the first two PCs used to model clay%.

The PLS cross-validation model for clay, using only spectral DRIFT data, resulted in a "indicator" to "good" accuracy model with a RPD = 2.0, R^2 = 0.73 and RMSECV = 5.8% (Figure 12). A summary of the results of regressions can be found in Table 1.

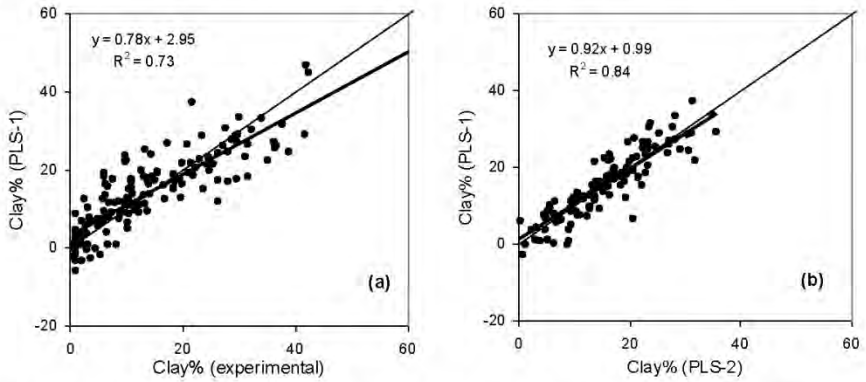


Figure 16. Plot of PLS (DRIFT data) predicted clay% values versus experimental clay% values. The solid line is the model regression, the dotted line is the 1:1 line.

Table 1. Results for the modelling of sand, silt and clay% regression from the DRIFT spectra. Statistics are described by coefficient of determination (R^2), root mean square of error (RMSE), standard deviation (SD) and ratio of prediction to deviation (RPD). Statistics are also shown for prediction of the 46 sample test set and the full set of unknown samples from the composite PLS model†. For cross-validation RMSE = RMSECV.

	Sand% PLS (DRIFT model)	Sand% PLS (DRIFT Test model)	Sand% predictions
Min	3.5	3.5	6.5
Max	98.9	98.9	132.5
N	138	41	*4905
R^2	0.68	0.70	
RMSE	13.1	12.7	
SD	22.7	22.7	20.1
RPD	1.7	1.8	

	Silt% PLS DRIFT model)	Silt% PLS (DRIFT Test model)	Silt% predictions
Min	0.1	0.1	0.0
Max	83.0	83.0	88.2
N	139	43	*4927
R^2	0.65	0.62	
RMSE	9.7	10.3	
SD	16.6	16.3	14.1
RPD	1.7	1.6	

	Clay% PLS (DRIFT model)	Clay% PLS (DRIFT Test model)	Clay% predictions
Min	0.6	1.0	0.0
Max	60.8	36.7	65.0
N	145	46	*4951
R^2	0.73	0.70	
RMSE	5.8	6.0	
SD	11.7	11.0	8.4
RPD	2.0	1.8	

†Min, Max, SD, and RMSECV are in % units. [1] Predicted values can be provided although considered to be unreliable.

4.3.2.3.2 Validation of the PLS model with the "test" set

The prediction ability of the PLS model to accurately determine clay% in soils was further tested using a calibration set of 100 soil samples to predict clay% values in the remaining 47 independent test soils. The regression plot of predicted clay% values versus experimental values is depicted in Figure 17. The achieved RPD confirmed "indicator" accuracy for the predicted clay% values (RPD = 1.8, R^2 = 0.70 and RMSE = 6.9%, see Table 1) similar to that for the original cross-validation.

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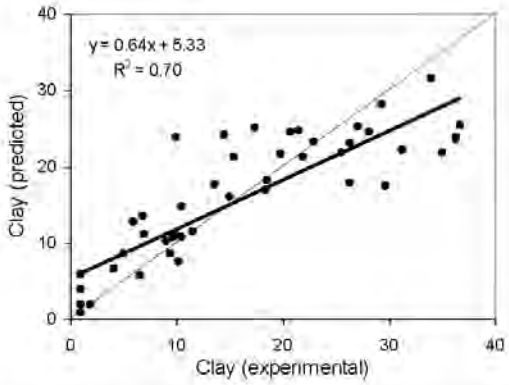

Figure 17. Regression plot of the prediction of clay% versus experimental values in the validation "test" samples (n = 46). X-axis and Y-axis are in % units. Solid line is the model regression and dotted line is the 1:1 line.

4.3.2.3.3 Prediction of clay for the unknown soils

The PLS model was applied to the prediction of clay% values for all unknown soils of the GEMAS sampling program. The distribution of predicted clay% values (Figure 18b) was found to be very similar to that of the calibration+validation set (Figure 18a), with a slightly higher proportion of clay% samples at 0-2% clay content.

Although actual prediction errors could not be determined, since the samples were true unknowns, an indication of the expected errors could be, however, determined from the outputs of the prediction routine in the Unscrambler software. A Histogram plot of the error distribution is depicted in Figure 18c. The most dominant error of 2-5 units occurred for 2662 samples, with a further 2016 samples with deviation of 5-10 units and only 263 samples with deviation >10. This suggests that even though the calibration was classed as "indicator", according to the RPD, the prediction error was suggested as low.

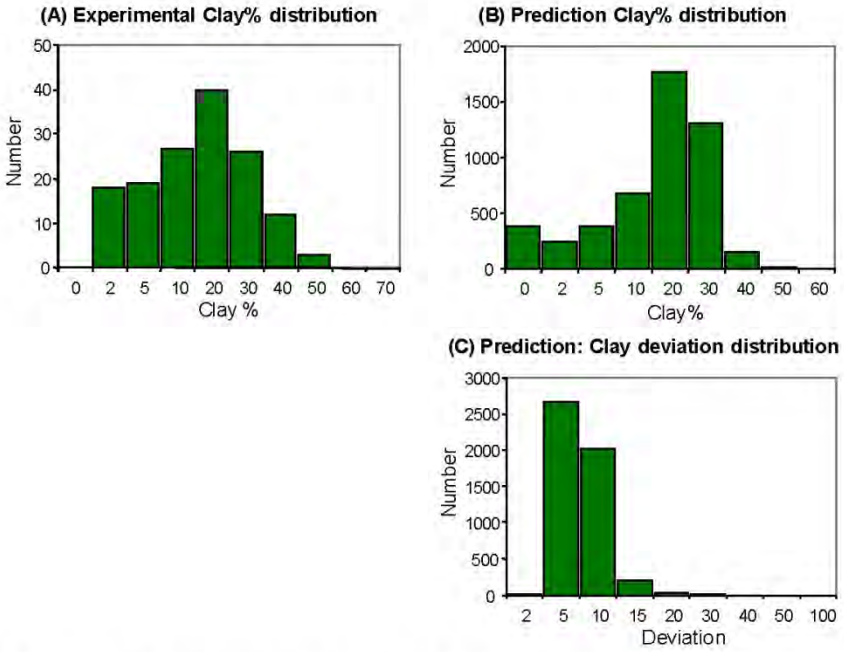

Figure 18. Histograms of experimental clay% values (A), predicted clay% values (B) and prediction deviations for clay% (C).

4.3.2.3.4 Conclusions (Clay)

In this study, the PLS model for clay% was found to cross-validate with "indicator" accuracy. This poor performance of the PLS model for prediction was likely due to a combination of dilution of the true soil fraction by carbonate and organic matter, and of possible cementing of small clay-sized particles into larger aggregates by calcrete. The results suggested that spectra of the majority of the soils in the unknown set of samples could be fitted well by the PLS models implying that the prediction errors for the unknowns was similar to that of the calibration set.

5 CONCLUSIONS

PSA data regression models by mid-infrared DRIFT spectroscopy and partial least squares regression (PLS-1), while only rated as "indicator" quality, were used to predict sand, silt and clay fractions in the GEMAS sampling programs. This method of analysis can be useful for the very rapid prediction of unknown samples. The distributions of PSA fractions in the predicted unknowns were found to be similar to those of the calibration samples, and the prediction error "deviations" considered to be generally acceptable. The PLS model accuracies were found to be lower than for some other comparative studies and it has been concluded that part of the modelling error was due to the presence of carbonate particles

distributed within some, or all, the PSA fractions. Further work may be required to resolve the issue of carbonate impact on PSA analysis.

6 REFERENCES

Bertrand I, Janik LJ, Holloway RE, Armstrong RD, McLaughlin MJ. (2002). The rapid assessment of concentrations and solid phase associations of macro- and micronutrients in alkaline soils by mid-infrared diffuse reflectance spectroscopy. *Australian Journal of Soil Research*, **40**, 1339-1356.

Forrester S, Janik L, Beech A, McLaughlin M. (2003). Recent developments in routine soil analysis by mid-infrared: rapid and cost-effective laboratory analysis. In 'Tools for Nutrient and Pollutant Management: Applications to agriculture and environmental quality'. Palmerston, New Zealand. (Ed. LD Currie and JA Hanly) (Fertilizer and Lime Research Centre, Massey University: New Zealand).

Janik LJ, Skjemstad JO. (1995). Characterization and analysis of soils using midinfrared partial least-squares .2. Correlations with some laboratory data. *Australian Journal of Soil Research*, **33**, 637-650.

Janik LJ, Merry RH, Skjemstad JO. (1998). Can mid infrared diffuse reflectance analysis replace soil extractions? *Australian Journal of Experimental Agriculture*, **38**, 681-696.

Janik LJ, Merry RH, Forrester ST, Lanyon DM, Rawson A. (2007). Rapid prediction of soil water retention using mid infrared spectroscopy. *Soil Science Society of America Journal*, **71**, 507-514.

Janik LJ, Skjemstad JO, Shepherd KD, Spouncer LR. (2007). The prediction of soil carbon fractions using mid-infrared-partial least square analysis. *Australian Journal of Soil Research*, **45**, 73-81.

Ludwig B, Nitschke R, Terhoeven-Urselmans T, Michel K, Flessa H. (2008). Use of mid-onfrared spectroscopy in the diffuse reflectance mode for the proediction of the composition of organic matter in soil and litter. *Journal of Plant Nutrition and Soil Science*, **171**, 384-391.

McBride MB. (1989). Reactions controlling heavy metal solubility in soil. *Advances in Soil Science*, **10**, 1-56.

McLaughlin, M. J. (2001). Ageing of metals in soils changes bioavailability. Fact Sheet on Environmental Risk Assessment 4, 1-6. September 2001. Ontario, Canada, International Council on Metals and the Environment.

Nguyen TT, Janik LJ, Raupach M. (1991). Diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy in soil studies. *Australian Journal of Soil Research*, **29**, 49-67.

Ozanne PG, Shaw TC. (1967). Phosphate sorption by soils as a measure of the phosphate requirement for pasture growth. *Australian Journal of Agricultural Research*, **18**, 601-612.

Reeves III JB, Francis BA, Hamilton SK. (2005). Specular reflection and diffuse reflectance spectroscopy of soils. *Applied Spectroscopy*, **59,** 39-46.

Rossel RAV, Walvoort DJJ, McBratney AB, Janik LJ, Skjemstad JO. (2006). Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. *Geoderma*, **131,** 59-75.

Sauve S, Hendershot W, Allen HE. (2000). Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. *Environmental Science and Technnology*, **34,** 1125-1131.

Terhoeven-Urselmans T, Bruns C, Schmilewski G, Ludwig B. (2008). Quality assessment of growing media with near-infrared spectroscopy: Chemical characteristics and plant assays. *European Journal of Horticultural Science*, **73,** 28-36.