WAGENINGEN EVALUATING PROGRAMMES FOR ANALYTICAL LABORATORIES

PROF. TESTING
RvA R 002

International Manure and Refuse Sample Exchange Program

marsep

Quarterly Report 2019.2 April - June

WAGENINGEN
UNIVERSITY & RESEARCH

Introduction

Dear WEPAL-participants,

Herewith we present to you the second report of 2019 for MARSEP.

A new version of the participant’s website was launched at the end of June, that has a more logical structure, making the reports better accesible. Unfortunately, there had been some problems with this new release, just at the time on which most of you had to report results. Fortunately, it only affected the access to former reports and had no effect on the data entry site. But it could have made participants, who were facing some problems during reporting, slightly insecure. So a number of participants contacted us and we hope we have solved the problems quickly and in a satisfactory manner. Of course we apologize for this disturbance.

As announced, we added a few new determinands on request of new MARSEP participants who had been participating in another proficiency test, that stopped its services. We did not receive results for all new determinands. We were glad to receive results for dry weight, Residu on Ignition (ROI) and Chemical Oxygen Demand (COD) and mineral oil. Not only the new participants reported these determinands, but we have also received results from the regular MARSEP participants. Although we did not receive enough results to apply the NDA statistics, this result is hopeful and an example for the other participants.

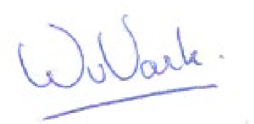
Recently a few articles have been published about the metrological tracebility of consensus values obtained from proficiency tests. As a result of these publications our statement about the tracebility of the assigned values has been modified. Please have a look at page 9 of the general information.

In the last four years, we introduced several new features on the participants’ website and in the reports, in an attempt to give you a better view on the performance of your laboratory. We hope these new features are useful. At this moment, we would like to have your opinion about the services of WEPAL, the PT programmes andthe reports, but we also want to make an inventory of your needs, wishes and suggestions. We are going to organise a small survey in September for this purpose. We really hope you will take some time to complete that survey and help us to improve our proficiency testing programmes.

As always, we would like to mention that access to the participants’ website is restricted. If any problems may occur with username or password, please contact our administration (info.wepal@wur.nl).

Please feel free to send us your ideas or remarks on the programmes. This could lead us to further improvements (info.wepal@wur.nl). We are always looking forward to hearing from you,

Yours sincerely,



Winnie van Vark
Manager WEPAL

Calculated with Matlab NDA version: WepalNDAstat_V19_2
Figures version: WepalQuasi_figures_V19_1

Calculated 05-07-2019 (10:20)
Approved by Winnie van Vark, manager WEPAL

Important Information

The results of the July - September period will be processed in the first week of October 2019. Participants are kindly requested to take care that the results of this series are submitted **before the first of October 2019.** All results, which are received later, will not be reported.

The 2019.4 samples will be mailed at the beginning of September 2019.

Content

General Information

Accreditation

The Wageningen Evaluating Programmes for Analytical Laboratories organisation is accredited for the organisation of Inter laboratory Studies by the Dutch Accreditation Council RvA since April 26, 2000. The accreditation is based on the ISO/IEC-requirements (General requirements for proficiency testing, ISO/IEC 17043:2010). The scope of accreditation can be found on the website of RvA. The accreditation covers the quality system of the organisation as well as the determinand groups printed in bold in the first column in table 1. Within these determinand groups only the determinands printed in bold in the second column meet the criteria for accreditation. These criteria are based on information about the homogeneity and stability of the samples. This information is available when sufficient participants have reported results for a determinand in the past 3 years.

Table 1 *Scope of the WEPAL programs.*

IPE **Determinand Group**	**Determinand**
Inorganic Chemical Composition ***(Nutrients, major and trace elements)***	Ag, **As**, **B**, **Ba**, Be, Bi, **Br, Ca**, **Cd**, **Cl**, **Co**, **Cr**, **Cs**, **Cu**, F, **Fe**, Ga, **Hg**, I, **K**, **Li**, **Mg**, **Mn**, **Mo**, **N - Kjeldahl**, N - NH_4, **N - NO_3**, **Na**, **Ni**, **P**, **Pb**, Pd, Pt, **Rb**, Rh, **S**, **Sb**, **Se**, Sn, SO_4, **Sr**, Ti, **V**, **Zn**
Real totals ***(Elementary analyses, Elements including in silicates)***	**Al**, **C - elementary**, **N - elementary**, Si
Acid extractable inorganic composition (So-called totals) ***(Elements excluding in silicates)***	**Al**, Si
Other determinations ***(Stable isotope ratios)***	**delta ^{13}C, delta ^{15}N**
Nutritional values	ADF-ash-free, Crude fibre**,** NDF-ash-containing, NDF-ash-free, Polysaccharides (starch), **Total ash**, Total Disaccharides, Total fat, Total monosaccharides

ISE **Group**	**Determinand**
Real totals (inorganic composition) ***(Major and trace elements)***	Ag, **Al**, **As**, B, **Ba**, Be, Bi, **Br**, **C - elementary**, **Ca**, **Cd**, **Ce**, **Co**, **Cr**, **Cs**, **Cu**, F, **Fe**, **Ga**, Ge, **Hg**, I, **K**, **La**, Li, **Mg**, **Mn**, **Mo**, **N - elementary**, **Na**, **Nb**, **Nd**, **Ni**, **P**, **Pb**, Pd, Pt, **Rb**, Rh, **S**, **Sb**, **Sc**, Se, **Si**, **Sn**, **Sr**, Te, **Th**, **Ti**, Tl, **U**, **V**, **W**, **Y**, **Zn**, **Zr**
Acid extractable (So-called totals) ***(Major and trace elements)***	Ag, **Al**, **As**, B, **Ba**, **Be**, Bi, Br, **Ca**, **Cd**, Ce, **Co**, **Cr**, **Cu**, F, **Fe**, Ga, **Hg**, I, **K**, La, Li, **Mg**, **Mn**, **Mo**, **N**, Na, Nb, Nd, **Ni**, **P**, **Pb**, Pt, Rb, **S**, **Sb**, Sc, Se, Si, **Sn**, Sr, Te, Th, Ti, Tl, U, **V**, Y, **Zn**, Zr
Aqua Regia (ISO 11466) ***(Major and trace elements)***	Ag, **Al**, **As**, **B**, **Ba**, **Be**, Bi, Br, **Ca**, **Cd**, Ce, **Co**, **Cr**, **Cu**, F, **Fe**, Ga, **Hg**, I, **K**, La, Li, **Mg**, **Mn**, **Mo**, **Na**, Nd, **Ni**, **P**, **Pb**, Pt, Rb, **S**, **Sb**, Sc, **Se**, Si, **Sn**, **Sr**, Te, Th, **Ti**, **Tl**, U, **V**, Y, **Zn**, Zr
Extraction with boiling 2M HNO_3 ***(Available trace metals)***	**Cd**, **Co**, **Cr**, **Cu**, **Hg**, **Mo**, **Ni**, **Pb**, Tl, **Zn**
Extraction with 0.1M $NaNO_3$ ***(Available trace metals)***	**Cd, Cu, Ni,** Pb**, Zn**
Extraction with 0.01M $CaCl_2$ 1:10 ***(Available nutrients)***	Al, B, Cd, CN, Co, Cr, Cu, Fe, K, Mg, Mn, **N - NH_4**, **N - NO_3**, N total soluble, Na, Ni, P, Pb, SO_4, Zn
Soil characteristics ***(Particle size distribution, pH, Inorg. and org. C, Conductivity)***	**C - org others (W&B a.o.)**, **EC-SC (ISO 11265)**, **Fraction < 16 µm**, **Fraction < 2 µm**, **Fraction < 63 µm**, **Fraction > 63 µm**, **Org.matter (L.O.I.)**, **pH - $CaCl_2$**, **pH - H_2O**, **pH - KCl**, **TC=Total C (org.+inorg.)**, **TIC=Tot.Inorg C($CaCO_3$)**, **TOC=Total Org. C,** Active Lime (as $CaCO_3$)

ISE **Group**	**Determinand**
Other determinations ***(Moisture content, CN detn., stable isotope ratios, additional extractions)***	**B - Hot water**, CN - Free, CN - Total, delta ^{13}C, delta ^{15}N, K - HCl, Mg - NaCl, **Moisture-content**
Fluoride (Swiss standard procedure**)**	F - Total
Digestion with conc. HNO_3 + conc. HCl + H_2O_2 (UNEP-UN/EC 91075A)	Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, S, Sb, Se, Si, Sn, Sr, Tl, V, Zn
Pot. CEC using 1M NH_4-acetate at pH=7	Al, **Ca**, **CEC**, **K**, **Mg**, **Na**
Pot. CEC using 1M or 0.1M $BaCl_2$-TEA at pH=8.1 (ISO 13536 OR BZE)	Al, Ca, CEC, K, Mg, Na
Pot. CEC using 1M NH_4Cl (BZE)	Al, Ca, CEC, Fe, H, K, Mg, Mn, Na
Act. CEC using 0.01M $BaCl_2$ (ISO 11260)	Al, Ca, CEC, Fe, H, K, Mg, Mn, Na
Act. CEC using 0.1M $BaCl_2$ (UNEP-UN/EC 91065A)	Al, Ca, CEC, Fe, H, K, Mg, Mn, Na
Act. CEC using cobaltihexamine (AFNOR NFX 31 130)	Al, **Ca, CEC**, Fe, H, **K, Mg**, Mn, **Na**
Mehlich-3 ***(Major and trace elements)***	**Al**, As, **B**, **Ca**, Cd, Cr, **Cu**, **Fe**, **K**, **Mg**, **Mn**, **Na**, **P**, Pb, **Zn**
Extraction with Ca-lactate (VDLUFA)	K, P
Extraction with double-Lactate (VDLUFA)	K, P
Water soluble 1:10 (w/v) (EN-12457-4)	Br, Cl, F, N - NO_3
Extraction with 0.01M $CaCl_2$ + 0.005M DTPA 1:10 (w/v) ***(Micro nutrients)***	**Cu, Fe, Mn, Zn**
Extraction with 1M KCl 1:10 (w/v)	**N - NH_4, N - NO_3**
Phosphorus and related analysis	Al - Ox, Fe - Ox, P - Ox, P - AL, P - Bray, **P - Olsen**, Pw
Extraction with 1M HCl (Polish standard)	B, Cu, Fe, Mn, Zn
Water soluble 1:10 (w/v) (NL VPR C85-06)	Br, Cl, F, SO_4
UK Soil Methods	**K - NH_4NO_3 (1/5), Mg - NH_4NO_3 (1/5), P – $NaHCO_3$ (1/20), pH - H_2O (2/5)**

SETOC **Group**	**Determinand**
Polycyclic aromatic hydrocarbons	**acenaphtene**, acenaphtylene, **anthracene**, **benz(a)anthracene**, **benzo(a)pyrene**, **benzo(b)fluoranthene**, **benzo(ghi)perylene**, **benzo(k)fluoranthene**, **chrysene**, **dibenz(ah)anthracene**, **fluoranthene**, **fluorene**, **indeno(1,2,3-cd)pyrene**, naphtalene, **phenanthrene**, **pyrene**, **EPA∑PAH(16)**
Polychlorobiphenyls	**PCB 028**, PCB 031, **PCB 052**, PCB 077, PCB 081, **PCB 101**, PCB 105, PCB 114, **PCB 118**, PCB 123, PCB 126, PCB 128, PCB 138, PCB 149, **PCB 153**, PCB 156, PCB 157, PCB 167, PCB 169, **PCB 180**, PCB 189, **∑PCB(7)**
Organochlorine pesticides	1,2,3 trichlorobenzene, 1,2,3,4 tetrachlorobenzene, 1,2,3,5 tetrachlorobenzene, 1,2,4 trichlorobenzene, 1,2,4,5 tetrachlorobenzene, 1,3,5 trichlorobenzene, aldrin, alpha-endosulfan, alpha-HCH, beta-endosulfan, beta-HCH, chlordane, cis-chlordane, delta-HCH, dieldrin, endosulfan, endosulfan sulfate, endrin, gamma-HCH, heptachlor, heptachlor epoxide, **hexachlorobenzene**, hexachlorobutadiene, isodrin, o,p`-DDD, o,p`-DDE, o,p`-DDT, p,p`-DDD, **p,p`-DDE**, p,p`-DDT,

SETOC **Group**	**Determinand**
	pentachlorobenzene, pentachlorophenol, Sum tetrachlorobenzenes, Sum trichlorobenzenes, telodrin, toxaphene, trans-chlordane
Other parameters ***(CN fractions, Org. and inorg. C, Halogeneted hydrocarbons, Mineral oil)***	AOX, CN - Free, **CN - Total**, EOX, Inorganic carbon, **Mineral oil, GC**, Mineral oil, IR, **Organic carbon**, Particles < 2 µm, Particles < 63 µm, Particles > 63 µm
Metals (aqua regia) ***(Major and trace elements)***	**As**, **Ba**, **Cd**, **Co**, **Cr**, **Cu**, **Hg**, **Mo**, **Ni**, **Pb**, **Zn**
Dibenzo-P Dioxin	1,2,3,4,6,7,8 Cl_7DD, 1,2,3,4,7,8 Cl_6DD, 1,2,3,6,7,8 Cl_6DD, 1,2,3,7,8 Cl_5DD, 1,2,3,7,8,9 Cl_6DD, 2,3,7,8 Cl_4DD, Cl_8DD
Dibenzofuran	1,2,3,4,6,7,8 Cl_7DF, 1,2,3,4,7,8 Cl_6DF, 1,2,3,4,7,8,9 Cl_7DF, 1,2,3,6,7,8 Cl_6DF, 1,2,3,7,8 Cl_5DF, 1,2,3,7,8,9 Cl_6DF, 2,3,4,6,7,8 Cl_6DF, 2,3,4,7,8 Cl_5DF, 2,3,7,8 Cl_4DF, Cl_8DF
Brominated Flame Retarders	BDE 028, BDE 047, BDE 066, BDE 085, BDE 099, BDE 100, BDE 153, BDE 154, BDE 183, BDE 209
Experimental	DEHP, Tributyl Tin (TBT)

MARSEP **Group**	**Determinand**
Real totals	Al, As, B, Ba, Be, Bi, Br, C, Ca, Cd, Co, Cr, Cu, F, Fe, Ga, Hg, I, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, Tl, V, Zn
Acid extractable (So-called totals) ***(Major and trace elements)***	Ag, **Al**, **As**, **B**, **Ba**, Be, Bi, C, **Ca**, **Cd**, Cl, **Co**, **Cr**, **Cu**, F, **Fe**, Ga, **Hg**, I, **K**, Li, **Mg**, **Mn**, **Mo**, **N**, N - NH4, N - NO3, **Na**, **Ni**, **P**, **Pb**, **S**, S - SO_4, Sb, Se, Si, Sn, Sr, Ti, Tl, **V, Zn**
Other determinations ***(Halogenated hydrocarbons, LOI)***	AOX, **loss-on-ignition**

BIMEP **Group**	**Determinand**
General Analysis ***(Proximate analysis)***	**ash, calorific value, moisture**, **Volatile Matter**
Elementary Analysis	**Carbon (C), Cl, Hydrogen (H), Nitrogen (N),** Oxygen (O)**, S**
Water Soluble Elements	Cl, K, Na
Major Elements	Al, Ca, Fe, K, Mg, Na, P, Si
Minor Elements	As, Ba, Be, Cd, Co, Cr, Cu, F, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Te, Ti, Tl, V, Zn

Subcontracting

Some aspects of the proficiency testing scheme may from time to time be subcontracted. When subcontracting occurs it is placed with a competent subcontractor. WEPAL is responsible to the scheme participants for the subcontractor's work.

The analysis for the homogeneity tests of the samples used in this proficiency test are carried out by a subcontractor.

Confidentiality of results

The confidentiality of the results is extremely important in the Wepal programs. The participants may opt for a code name that indicates their laboratory, or one that ensures their anonymity. In the reports, only the code names will be mentioned.

When an accrediting body or a regulatory authority requires the proficiency test results to be provided by WEPAL the participants shall be notified and asked for permission.

Participants are not allowed to report information published in this report other then their own data. For example it is not allowed to produce publications from data produced by other laboratories published in this report.

Complaints and or remarks
The reports of WEPAL are assembled with the utmost care. Please contact us on info.wepal@wur.nl if you feel that the reports are not at a satisfactory standard, if you encountered errors in your results or if you want to appeal against the evaluation of your performance. Also feel free to contact us if you have any other complaints, remarks and or suggestions.

Homogeneity and stability of the distributed samples

Homogeneity tests

WEPAL has developed special equipment for the production of representative subsamples (Houba, 1993) from a bulk material. The proper functioning of this equipment is tested by a homogeneity test in the final subsamples. To perform this test, samples are collected at regular intervals during the preparation of the samples. The collected samples, with a minimum of 10, are analysed in duplicate measurements under repeatability conditions. A selection of critical determinands is chosen for the tests. The results of the homogeneity tests are published in the annual reports.
All samples used in this round of the proficiency test have passed the homogeneity test.

Check of results

Before distribution of the periodic reports to the participants, a final check is made based on the results found by the participants. This check is made for all reported determinands. The variations between laboratories and concentrations are compared with the patterns as found in the previous 5 years. The expected pattern is a high CV at a low concentration and a gradually decreasing CV at higher concentrations till a more or less constant level of CV-values is reached (Houba et al., 1986). Significant deviations from this expected pattern are mentioned in the periodic reports.

All data of this period are compared with the general patterns as published in the latest year report. No deviating values were found.

Stability of the distributed samples

The dry testmaterials have been shown to be stable over a number of years when stored at room temperature. Yearly the results of the samples included in the proficiency tests are compared with historical data to monitor stability.

The quarterly report

In order to evaluate the accuracy and precision of the analytical procedures used, five proficiency testing programs have been established. At this moment the WEPAL Exchange Programs comprises approximately 600 laboratories in many countries. The participating laboratories receive four air-dried samples every three months and analyse the samples according to their own procedures. The results of the determinations are collected and processed at Wageningen University and published every three months. The participating laboratories are informed of the results in the third week of the next three-month period. Each participant can compare his results with those of all the other members of the exchange program. WEPAL will not comment on results unless asked to do so.

Reporting of data

The analysed components must be reported in oven dry (105 ˚C) material. For this purpose the moisture content has to be determined separately and the analytical results have to be recalculated. To get reproducible results of these moisture contents we recommend you to dry the material during at least 3 hours at 105 ˚C and let cool down in a desiccator before weighing.

Statistics

Normal Distribution Approximation (NDA)

Interlaboratory studies like those of WEPAL-QUASIMEME frequently give rise to datasets that have complex distributions including excessive tailing and multiple modes. Consequently, sophisticated statistical methods are required to obtain meaningful assessments. A methodology is needed that does not rely on arbitrary outlier removal or subjective manual interpretations. The model that is chosen calculates population characteristics (mean and standard deviation) from experimental datasets as described by Cofino et al. (2000) and Molenaar, Cofino and Torfs (2018).
The statistical principles of the model used to assess the data are outlined in two steps. Firstly, the full model is described, thereafter a description is given of the way the model is implemented for the assessment of the data in WEPAL and Quasimeme.

We assume that we have a set of probability density functions $q_i, i = 1, \dots, N$. We set ourselves to establish the "average" probability density function $\bar{q}$, or in other words, the probability density function $\bar{q}$ that best describes the set. It is insightful to make at this point an analogy with the calculation the arithmetic mean, of a set of data $a_i, i = 1, \dots, N$. The average $\bar{a}$ can be defined as the point that minimises the sum of the squared Euclidean distances $d(\bar{a}, a_i)$ to the given data. This can be accomplished by equating the first derivative of $\sum_{i=1}^{N} d^2(\bar{a}, a_i) = \sum_{i=1}^{N} (\bar{a} - a_i)^2$ with respect to $\bar{a}$ to zero. One readily finds the well known expression $\bar{a} = \frac{1}{N} \sum_{i=1}^{N} a_i$
In a similar manner we construct the average probability density function $\bar{q}$ of the set of probability density functions $q_i, i = 1, \dots, N$. We define a measure $d(p, q)$ for the distance between two probability density functions p and q. In literature, many different distance measures are described. In the Cofino model, we use a distance based on the Bhattacharyya coefficient $S_B(p, q) = \int_{\Omega} \sqrt{pq}$, namely $d(p, q) = \sqrt{2(1 - S(p, q)^2)}$. We obtain $\bar{q}$ by minimising the sum of the square distances from each probability density function q_i to $\bar{q}$, thus by equating the first derivative of $\sum_{i=1}^{n} d(\bar{q}, q_i)^2$ with respect to $\bar{q}$ to zero. The calculation itself is extensive and not given here. The mean and standard deviation of the population are calculated using the first and second moments of the probability density function $\bar{q}$. The variance obtained from the second moment comprises both a within-laboratory and between-laboratory component.

In WEPAL and Quasimeme, laboratories report single data, there is no information about the underlying probability function. To cope with this problem a specific implementation of the model is used: the so-called Normal Distribution Approximation (NDA). The NDA approach is parametrised to reproduce the population characteristics of truly normal distributions, and is a robust method to evaluate interlaboratory studies.
The NDA approach has been devised using a set of normal distributions $q_i = N(\mu_i, \sigma), i = 1, \dots, N$. We assume thus that all normal distributions have the same standard deviation σ. The expected values μ_i are also taken to be normally distributed: $\mu_i = N(\bar{\mu}, S)$. It appears that the mean $\bar{\mu}$ and the standard deviation S of the normal distribution describing the population can be exactly reproduced when $\sigma = 0.78 * S$. In the NDA method, the standard deviation S is calculated directly from the total variance, no distinction between within-laboratory and between-laboratory components is made.

In practice we have N laboratories each reportin a single value. This gives rise to a dataset $x_i, i = 1, \dots, N.$ is used. We calculate the population standard deviation from this dataset using the robust estimate *S=1.4826*MAD* (MAD: median of absolute standard deviations). The normal distributions associated with the data x_i are estimated by $q_i = N(x_i, 0.78S) = N(x_i, 1.16 * MAD)$. We calculate the average probability density function $\overline{q}$ of the set of normal distributions qi as described above. The mean and standard deviation of the interlaboratory study are obtained using the first and second moments of the average probability density function $\overline{q}$.

The NDA-mean (assigned value)

The NDA mean is obtained from the main mode of the data using the Cofino Model, and is centered around the highest density of values. Unless otherwise stated, the NDA mean is based on this consensus value of *all* data. Although *all* data are included in the assessment, those values that lie some distance from the NDA mean contribute less to the mean than values which occur at or near the mean.
With the NDA model mean and standard deviation are calculated using all reported data when at least 8 results are left after removal of reported 'lower than' (<) and 0 (= zero) values. No outliers are removed.

Traceability of the assigned value

The aim of this proficiency testing scheme is to establish comparability among laboratories. "Real life" samples are collected, processed and distributed so that the true concentrations of measurands are not known. Assigned values are based on consensus values, obtained from the results of the participants using their routine methods. WEPAL is confident that the assigned values have an acceptable degree of traceability based on the following considerations:

1. The large majority of participants in the programmes have an extensive experience with the analyses and are accredited, implying the use of validated methods, certified reference materials and internal quality control procedures in well equipped, maintained and managed laboratories.
2. The programmes have an international participation, participants use standards that may differ according to country and/or methods that are based on different measurement principles;
3. The data submitted by laboratories are analysed with robust statistics that associates a weighing factor to each individual result. The probability distributions of the raw and analysed data are graphically depicted and carefully examined. Consensus is assumed and an assigned value is established when the probability function of the weighed dataset (in terms of the model the mean pdf of the population of pdfs submitted by the laboratories) is near normal.
4. The fact that consensus is achieved with data from experienced laboratories working with well-developed quality systems that employ a variety of methods is interpreted as evidence that possible biases arising from laboratories and/or methods is averaged out so that the consensus represents a reliable, traceable value. See Thompson (2016, 2018).

Uncertainty of the assigned value

According to ISO 13528: 2015 (Cor. 2016-10), the uncertainty in the assigned value is calculated as:

$$\mathbf{u_x = 1.25 * s / \sqrt{N}}$$

s = robust standard deviation
N = number of results

Depending on the NDA standard deviation calculated and the number of determinations observed, the uncertainty in the assigned value may influence the evaluation of the results (calculated Z-scores). Therefore, the uncertainty is included in the Total Error which is used to evaluate the results from the participating laboratories.

Median and MAD

For each determinand a median value and a median of absolute deviations (MAD) are calculated using all reported data except the reported '<' values. Deviating results like stragglers and outliers are not removed. The median is the middle observation of the sorted observations. In the case of an even number of observations it is the mean of the two middle observations. Using the median instead of mean, extreme data have less influence. MAD is the median of the absolute values of the observations minus their median.

The Z′-score assesment

In this proficiency test the robust standard deviation is used as standard deviation for proficiency assessment. A Z′-score is calculated for each determinand which is given an assigned value:

$$z_i{}' = \frac{(x_i - x_{pt})}{\text{Total Error}}$$

in which:

x_i = the reported value by laboratory i
x_{pt} = the mean of all values calculated with the NDA model

From 2019 onwards, the uncertainty of the assigned value is taken into consideration when calculating the Z-scores. :

$$\text{Total Error} = \sqrt{u_X^2 + s^2}$$

In this formula, $\boldsymbol{u_x}$ represents the uncertainty of the assigned value as given above and s is the robust standard deviation calculated with the NDA method and used as the standard deviation for proficiency assessment.

Evaluation of results

For the evaluation of results the absolute value of the Z′-score is used.
Questionable results 2 < | $z_i{}'$ | < 3 are marked as stragglers (*).
Deviating results with | $z_i{}'$| > 3 are marked as outliers (**).

Results reported as 'smaller than' (< or LCV's (left censored values)) are also evaluated. It is not possible to calculate a Z′-score for LCV's. A simple quality criterion is used:

NDA-mean - 2* Total Error < LCV < NDA-mean + 6* Total Error : LCV consistent with assigned value.

LCV < NDA-mean - 2* Total Error : inconsistent with assigned value, i.e. LCV reported would have been questionable or unsatisfactory, when reported as a numerical value.

LCV > NDA-mean + 6* Total Error : inconsistent with assigned value, i.e. LCV reported by laboratory much higher than numerical values reported by other laboratories.

LCV key: C – Consistent
I – Inconsistent

Rounding of results

Rounding interval is set to have at least three significant digits for the results. This is based on the value of the mean. If no mean value is available (less than 8 results) the median is used. In cases where between laboratory variation is small (based on the standard deviation) an extra digit is shown. For the statistical results (mean, standard deviation, median and MAD) one extra digit is shown.
Note that larger results are also rounded (e.g. 1809 may be rounded as 1810).

Materials Analysed

Table 2 *Materials analysed in this period.*

Sample	Sample ID	Type	Origin
1	286	sewage sludge	Netherlands
2	262	Compost	Switzerland
3	263	Compost	Switzerland
4	273	Sewage Sludge	United Kingdom

Method Indicating Code (MIC)

In order to evaluate the analytical results for each reported element a Method Indicating Code (MIC) is used. Details of the analytical procedures used by the individual participants are indicated by a number of characters, added at the end of each row with results. With these MIC codes you can easily compare the results obtained by your laboratory with th results from other laboratories using the same results.

References and related literature

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Used abbrevations and symbols

Table 3 *Used abbreviations and symbols*

Where	Abbreviation	Explanation
General information	NDA	Normal Distribution Assumption
General information	u_x	uncertainty
General information, Summary	LCV	left censored values (<)
General information, Results	CV	coëfficient of variation
Summary Statistics	NOBS	number of observations
Results	MIC	method indicating code
Results	MAD	median absolute deviation
Results	Sd	standard deviation
Results, Z-scores	<	value smaller than
Results, Z-scores	C	consistent with assigned value
Results, Z-scores	I	inconsistent with assigned value
Results, Z-scores	*	straggler
Results, Z-scores	**	outlier
Results, Z-scores	-	no result was submitted
Results statistical values	-	not calculated
Z-scores	#	less than 8 values, no mean and Sd calculated

(Template vs 2019.2)

Acid extractable
(So-called totals)
Analysis MARSEP 2019.2

Acid extractable (So-called totals) Summary Statistics

Sample/ Determinand	Assigned Value	Units	NDA st.dev	NDA rel. st.dev (%)	Nobs numerical	Nobs LCV	Median	MAD	Model Mean	Uncer-tainty
286										
Ag		*µg/kg*			*3*	*0*	*2720*	*81*		
Al	16.9	g/kg	0.9	5.5	13	0	17.0	0.6	16.90	0.32
As	5.56	mg/kg	0.85	15.3	13	0	5.46	0.60	5.558	0.294
B	20.9	mg/kg	3.2	15.2	8	0	21.8	2.3	20.87	1.40
Ba	370	mg/kg	22	6.0	8	0	365	15	369.6	9.8
Be		*µg/kg*			*4*	*0*	*156*	*65*		
C		*g/kg*			*3*	*0*	*284*	*7*		
Ca	55.1	g/kg	2.2	3.9	24	0	55.3	1.4	55.07	0.55
Cd	1.03	mg/kg	0.08	7.4	24	0	1.02	0.06	1.027	0.019
Cl		*mg/kg*			*2*	*0*	*2549*	*641*		
Co	5.24	mg/kg	0.50	9.6	22	0	5.29	0.35	5.237	0.134
Cr	49.8	mg/kg	4.8	9.5	24	0	50.1	3.4	49.79	1.21
Cu	341	mg/kg	23	6.7	26	0	339	16	341.4	5.6
Fe	48.2	g/kg	1.6	3.3	20	0	47.8	1.2	48.23	0.45
Hg	708	µg/kg	94	13.3	20	0	693	68	707.9	26.4
K	2.56	g/kg	0.58	22.8	24	0	2.59	0.41	2.561	0.149
Li		*mg/kg*			*2*	*0*	*6.03*	*0.63*		
Mg	8.75	g/kg	0.52	6.0	25	0	8.81	0.37	8.748	0.131
Mn	485	mg/kg	23	4.7	17	0	484	15	485.5	6.9
Mo	10.8	mg/kg	0.5	4.2	21	0	10.8	0.3	10.82	0.12
N	37.8	g/kg	1.3	3.5	21	0	38.0	0.9	37.85	0.36
N - NH4 (as N)		*mg/kg*			*2*	*0*	*20078*	*17107*		
N - NO3 (as N)		*mg/kg*			*1*	*0*	*10.1*			
Na	0.620	g/kg	0.051	8.2	12	0	0.632	0.035	0.6196	0.0183
Ni	31.3	mg/kg	2.3	7.5	24	0	31.1	1.6	31.29	0.60
P	37.8	g/kg	2.5	6.7	27	0	37.8	1.8	37.76	0.61
Pb	51.2	mg/kg	4.7	9.1	23	0	50.9	3.3	51.22	1.21
S	10105	mg/kg	673	6.7	11	0	9960	480	10105.0	253.5
S - SO4 (as S)		*mg/kg*			*2*	*0*	*7604*	*3802*		
Sb		*µg/kg*			*7*	*0*	*3148*	*252*		
Se		*µg/kg*			*5*	*0*	*2456*	*262*		
Si		*g/kg*			*1*	*0*	*1.21*			
Sn		*mg/kg*			*5*	*0*	*22.8*	*1.2*		
Sr		*mg/kg*			*1*	*0*	*233*			
Ti		*mg/kg*			*2*	*0*	*611*	*78*		
Tl		*µg/kg*			*2*	*0*	*148*	*21*		
U		*mg/kg*			*1*	*0*	*1.40*			
V	15.4	mg/kg	0.9	5.8	10	0	15.4	0.6	15.40	0.35
Zn	886	mg/kg	49	5.5	26	0	890	34	885.6	12.0

Acid extractable (So-called totals) Summary Statistics

Sample/ Determinand	Assigned Value	Units	NDA st.dev	NDA rel. st.dev (%)	Nobs numerical	Nobs LCV	Median	MAD	Model Mean	Uncer-tainty
262										
Ag		*µg/kg*			*1*	*0*	*66.4*			
Al	11.4	g/kg	2.4	21.5	10	0	11.7	1.7	11.37	0.96
As	7.00	mg/kg	0.40	5.7	10	0	7.09	0.27	7.004	0.157
B	16.2	mg/kg	3.0	18.7	8	0	16.7	2.1	16.20	1.34
Ba		*mg/kg*			*5*	*0*	*98.0*	*15.4*		
Be		*µg/kg*			*3*	*0*	*480*	*10*		
C		*g/kg*			*3*	*0*	*175*	*6*		
Ca	46.9	g/kg	2.0	4.3	22	0	47.0	1.3	46.86	0.54
Cd	0.371	mg/kg	0.025	6.8	21	0	0.373	0.017	0.3712	0.0069
Co	5.81	mg/kg	0.44	7.6	19	0	5.80	0.29	5.806	0.126
Cr	81.2	mg/kg	17.5	21.5	21	0	84.7	11.7	81.16	4.76
Cu	43.2	mg/kg	2.1	5.0	23	0	43.0	1.5	43.15	0.56
Fe	15.1	g/kg	1.2	7.8	17	0	15.0	0.8	15.15	0.36
Hg	103	µg/kg	17	16.1	17	0	103	12	103.2	5.0
K	11.3	g/kg	1.5	13.5	23	0	11.0	1.1	11.28	0.40
Li		*mg/kg*			*2*	*0*	*16.3*	*0.1*		
Mg	7.60	g/kg	0.38	4.9	23	0	7.59	0.25	7.598	0.098
Mn	620	mg/kg	25	4.1	15	0	620	18	620.0	8.2
Mo	3.57	mg/kg	0.40	11.3	18	0	3.54	0.29	3.572	0.119
N	13.4	g/kg	0.6	4.7	19	0	13.4	0.4	13.38	0.18
Na	0.486	g/kg	0.056	11.6	11	0	0.491	0.041	0.4855	0.0212
Ni	27.5	mg/kg	1.6	6.0	21	0	27.6	1.1	27.52	0.45
P	3.21	g/kg	0.19	5.9	24	0	3.23	0.13	3.208	0.048
Pb	39.8	mg/kg	3.7	9.2	20	0	39.7	2.4	39.81	1.02
S	1936	mg/kg	91	4.7	10	0	1942	71	1935.6	35.8
S - SO4 (as S)		*mg/kg*			*1*	*0*	*1833*			
Sb		*µg/kg*			*4*	*0*	*770*	*69*		
Se		*µg/kg*			*5*	*0*	*380*	*163*		
Si		*g/kg*			*1*	*0*	*0.390*			
Sn		*mg/kg*			*3*	*0*	*3.10*	*0.41*		
Sr		*mg/kg*			*1*	*0*	*102*			
Ti		*mg/kg*			*2*	*0*	*301*	*31*		
Tl		*µg/kg*			*0*	*1*				
U		*mg/kg*			*1*	*0*	*0.681*			
V		*mg/kg*			*7*	*0*	*26.0*	*3.5*		
Zn	136	mg/kg	4	3.3	23	0	135	3	136.1	1.2

Acid extractable (So-called totals) Summary Statistics

Sample/ Determinand	Assigned Value	Units	NDA st.dev	NDA rel. st.dev (%)	Nobs numerical	Nobs LCV	Median	MAD	Model Mean	Uncer-tainty
263										
Ag		*µg/kg*			*1*	*0*	*64.5*			
Al	14.5	g/kg	3.0	20.7	10	0	14.8	1.9	14.51	1.19
As	8.66	mg/kg	0.19	2.2	10	0	8.72	0.14	8.663	0.076
B	18.6	mg/kg	6.1	32.7	8	0	18.9	4.2	18.58	2.68
Ba		*mg/kg*			*5*	*0*	*93.0*	*9.8*		
Be		*µg/kg*			*3*	*0*	*600*	*40*		
C		*g/kg*			*3*	*0*	*138*	*4*		
Ca	49.5	g/kg	1.9	3.8	22	0	49.4	1.3	49.45	0.50
Cd	0.395	mg/kg	0.025	6.3	21	0	0.392	0.018	0.3949	0.0068
Co	7.18	mg/kg	0.52	7.3	19	0	7.20	0.36	7.181	0.150
Cr	73.0	mg/kg	7.2	9.9	21	0	72.8	5.0	72.98	1.97
Cu	44.9	mg/kg	2.0	4.5	23	0	44.7	1.4	44.88	0.53
Fe	17.3	g/kg	0.8	4.6	17	0	17.5	0.5	17.29	0.24
Hg	88.3	µg/kg	7.7	8.7	17	0	90.8	5.6	88.26	2.33
K	8.36	g/kg	1.11	13.3	23	0	8.43	0.73	8.360	0.289
Li		*mg/kg*			*2*	*0*	*18.8*	*1.2*		
Mg	8.42	g/kg	0.54	6.4	23	0	8.50	0.37	8.422	0.141
Mn	699	mg/kg	17	2.4	15	0	700	12	699.2	5.5
Mo	2.86	mg/kg	0.34	12.0	18	0	2.88	0.25	2.858	0.101
N	9.94	g/kg	0.58	5.9	19	0	9.97	0.43	9.941	0.167
Na	0.625	g/kg	0.089	14.2	11	0	0.623	0.063	0.6254	0.0335
Ni	32.2	mg/kg	1.4	4.3	21	0	32.3	0.9	32.20	0.38
P	2.38	g/kg	0.15	6.4	24	0	2.38	0.11	2.378	0.039
Pb	34.5	mg/kg	2.2	6.3	20	0	34.6	1.5	34.53	0.61
S	1496	mg/kg	107	7.1	10	0	1503	86	1496.3	42.1
S - SO4 (as S)		*mg/kg*			*1*	*0*	*1419*			
Sb		*µg/kg*			*4*	*0*	*755*	*61*		
Se		*µg/kg*			*5*	*0*	*380*	*140*		
Si		*g/kg*			*1*	*0*	*0.331*			
Sn		*mg/kg*			*3*	*0*	*3.20*	*0.78*		
Sr		*mg/kg*			*1*	*0*	*114*			
Ti		*mg/kg*			*2*	*0*	*503*	*83*		
Tl		*µg/kg*			*0*	*1*				
U		*mg/kg*			*1*	*0*	*0.822*			
V		*mg/kg*			*7*	*0*	*34.8*	*4.4*		
Zn	136	mg/kg	5	3.5	23	0	137	3	135.9	1.2

Acid extractable (So-called totals) Summary Statistics

Sample/ Determinand	Assigned Value	Units	NDA st.dev	NDA rel. st.dev (%)	Nobs numerical	Nobs LCV	Median	MAD	Model Mean	Uncer-tainty
273										
Ag		*µg/kg*			*3*	*0*	*7817*	*182*		
Al	46.8	g/kg	3.7	7.9	13	0	47.6	2.5	46.80	1.28
As	12.7	mg/kg	0.9	7.0	13	0	12.8	0.6	12.67	0.31
B	21.3	mg/kg	1.1	5.0	8	0	21.1	0.8	21.30	0.47
Ba	517	mg/kg	34	6.6	8	0	514	23	517.2	15.0
Be		*µg/kg*			*4*	*0*	*2426*	*177*		
C		*g/kg*			*3*	*0*	*277*	*4*		
Ca	31.7	g/kg	1.5	4.8	24	0	31.6	1.0	31.68	0.39
Cd	1.51	mg/kg	0.12	7.9	24	0	1.49	0.09	1.506	0.030
Cl		*mg/kg*			*2*	*0*	*1850*	*460*		
Co	108	mg/kg	8	7.1	22	0	108	5	107.6	2.0
Cr	138	mg/kg	12	8.9	24	0	138	8	137.7	3.1
Cu	327	mg/kg	23	7.0	26	0	326	16	327.5	5.6
Fe	21.8	g/kg	0.7	3.0	20	0	21.8	0.5	21.85	0.18
Hg	2911	µg/kg	168	5.8	20	0	2889	118	2911.5	47.0
K	3.17	g/kg	0.83	26.0	23	0	3.39	0.52	3.172	0.215
Li		*mg/kg*			*2*	*0*	*17.7*	*1.1*		
Mg	5.52	g/kg	0.43	7.7	25	0	5.50	0.31	5.524	0.107
Mn	557	mg/kg	32	5.8	17	0	564	23	557.2	9.8
Mo	9.06	mg/kg	0.38	4.1	21	0	9.13	0.25	9.061	0.102
N	34.5	g/kg	0.7	2.1	21	0	34.5	0.5	34.53	0.20
N - NH4 (as N)		*mg/kg*			*2*	*0*	*17782*	*15572*		
N - NO3 (as N)		*mg/kg*			*1*	*0*	*19.7*			
Na	1.91	g/kg	0.11	5.6	12	0	1.92	0.07	1.906	0.039
Ni	134	mg/kg	6	4.8	24	0	136	4	134.4	1.6
P	27.7	g/kg	1.5	5.5	27	0	27.7	1.1	27.73	0.37
Pb	220	mg/kg	12	5.5	23	0	220	8	220.4	3.1
S	10276	mg/kg	687	6.7	11	0	10000	514	10275.6	259.0
S - SO4 (as S)		*mg/kg*			*2*	*0*	*9762*	*1573*		
Sb		*µg/kg*			*7*	*0*	*9129*	*1170*		
Se		*µg/kg*			*5*	*0*	*2538*	*549*		
Si		*g/kg*			*1*	*0*	*0.494*			
Sn		*mg/kg*			*5*	*0*	*43.4*	*0.6*		
Sr		*mg/kg*			*1*	*0*	*166*			
Ti		*mg/kg*			*2*	*0*	*211*	*29*		
Tl		*µg/kg*			*2*	*0*	*166*	*18*		
U		*mg/kg*			*1*	*0*	*3.20*			
V	26.8	mg/kg	4.6	17.2	10	0	26.2	3.3	26.80	1.82
Zn	708	mg/kg	32	4.5	26	0	710	21	707.8	7.9

Acid extractable (So-called totals) Data and Statistics

Sample	286	262	263	273	MIC
Ca (g/kg)					
LAB A	55.8	50.2	51.3	33.3	HO|AR|IA
LAB B	59.6 *	47.6	51.9	33.9	
LAB C	57.1	50.0	51.2	31.8	
LAB D	53.9	47.0	49.5	31.6	MC|NP|IA
LAB E	55.7	48.4	49.9	27.5 *	MC|AS|ZA
LAB F	52.0	41.0 *	46.0	29.0	HC|AR|IM
LAB G	55.0	47.3	48.8	31.3	MC|AR|AB
LAB H	57.5	45.9	49.1	31.1	MC|NA|IM
LAB I	55.5	-	-	32.8	HO|AR|IM
LAB J	55.3	47.0	49.9	32.3	AO|EO|AA
LAB K	58.3	47.4	49.7	32.3	MC|AR|IA
LAB L	51.1	43.6	48.3	30.7	MC|AR|IA
LAB M	54.8	43.7	45.6	31.0	
LAB N	55.3	50.2	47.6	38.2 **	
LAB O	52.5	42.9	49.1	30.2	MC|NA|IA
LAB P	48.8 *	46.4	48.3	31.9	AO|EO|AA
LAB Q	55.6	43.3	48.0	30.9	
LAB R	55.9	49.7	50.3	32.7	MC|AR|IA
LAB S	55.7	46.4	47.9	31.6	HO|EO|IA
LAB T	56.7	55.3 **	54.4 *	34.7	HO|AR|IA
LAB U	54.8	47.0	52.3	32.6	MC|EO|IM
LAB V	52.3	-	-	27.4 *	-|AR|IM
LAB W	52.0	46.0	52.0	1.40 **	MC|NA|IA

================= Statistical Results =================

	286	262	263	273
NDA mean	55.07	46.86	49.45	31.68
NDA st dev	2.15	2.01	1.89	1.51
Coeff Var (%)	3.9	4.3	3.8	4.8
N	24	22	22	24
Median	55.30	47.00	49.42	31.60
MAD	1.40	1.26	1.27	1.04
Total Error	2.22	2.08	1.95	1.56

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Sample	286	262	263	273	MIC
Cd (mg/kg)					
LAB A	1.08	0.360	0.390	1.59	HO|AR|IA
LAB B	1.00	0.373	0.373	1.50	
LAB D	1.06	0.366	0.382	1.49	
LAB E	1.01	0.446 *	0.397	1.62	
LAB F	1.00	0.370	0.400	1.50	HC|AR|IM
LAB H	0.853 *	0.344	0.358	1.39	MC|AR|IM
LAB I	1.07	0.366	0.383	1.61	MC|NA|IM
LAB J	0.986	-	-	1.48	HO|AR|IM
LAB K	0.800 *	0.360	0.390	1.48	AO|EO|AA
LAB L	1.07	0.341	0.392	1.48	MC|AR|IM
LAB O	0.981	0.405	0.295 **	1.60	MC|AR|IM
LAB P	1.07	0.375	0.410	1.58	
LAB R	1.05	0.400	0.420	1.40	
LAB S	1.09	0.420	0.420	1.59	MC|NA|IA
LAB T	1.03	0.379	0.376	1.54	MC|AR|IM
LAB U	1.40 **	0.454 **	0.441	1.46	AO|EO|AA
LAB V	1.02	0.375	0.366	1.48	
LAB W	0.953	0.370	0.400	1.19 *	MC|AR|IM
LAB X	1.19 *	0.355	0.417	1.37	HO|EO|IA
LAB Y	1.01	0.390	0.410	1.64	HO|AR|IA
LAB Z	0.920	0.330	0.390	1.49	MC|EO|IM
LAB AB	0.476 **	-	-	0.934 **	MC|AR|IA
LAB AC	1.00	-	-	1.50	-|AR|IM
LAB AG	1.10	0.440 *	0.480 **	1.40	MC|NA|IA

================= Summary Statistics ================

	286	262	263	273
NDA mean	1.027	0.3712	0.3949	1.506
NDA st dev	0.076	0.0253	0.0250	0.119
Coeff Var (%)	7.4	6.8	6.3	7.9
N	24	21	21	24

(cont.)

Sample	286		262		263		273		MIC
Cd (mg/kg) (cont.)									
	=================		Statistical Results		=================				
NDA mean	1.027		0.3712		0.3949		1.506		
NDA st dev	0.076		0.0253		0.0250		0.119		
Coeff Var (%)	7.4		6.8		6.3		7.9		
N	24		21		21		24		
Median	1.015		0.3730		0.3920		1.492		
MAD	0.055		0.0170		0.0180		0.090		
Total Error	0.078		0.0262		0.0259		0.123		
N (g/kg)									
LAB A	37.7		12.6		9.50		34.2		HO|KJ| T
LAB B	38.0		12.9		9.47		34.8		
LAB C	36.8		12.5		10.0		34.1		
LAB E	38.2		13.2		10.1		34.6		
LAB F	37.2		13.3		9.86		34.2		HO|KJ| T
LAB G	38.8		13.8		10.4		34.9		HC|KJ| T
LAB H	36.5		-		-		33.2		HO|KJ|SV
LAB J	38.2		14.2		10.1		35.0		-| -|CN
LAB K	37.1		13.7		9.50		33.9		HC|KJ| T
LAB L	38.9		13.7		10.4		35.3		
LAB M	35.0	*	13.0		9.10		31.0	**	
LAB N	37.1		14.1		10.1		33.4		-| -|CN
LAB O	38.8		14.2		10.7		35.5		HC|KJ| T
LAB P	39.9		13.3		9.50		35.3		HO|KJ| T
LAB Q	38.0		13.4		9.85		34.4		
LAB R	38.1		13.4		9.91		34.5		
LAB T	39.7		13.8		10.4		35.9		-| -|CN
LAB V	35.9		12.7		9.40		34.0		-|EO| T
LAB X	44.1	**	15.1	*	10.8		38.9	**	HO|AR|IA
LAB Y	36.1		12.9		9.97		34.5		MC|EO|IM
LAB Z	39.0		-		-		37.4	**	HC|KJ|SV
	=================		Statistical Results		=================				
NDA mean	37.85		13.38		9.941		34.53		
NDA st dev	1.33		0.63		0.584		0.73		
Coeff Var (%)	3.5		4.7		5.9		2.1		
N	21		19		19		21		
Median	38.01		13.40		9.970		34.50		
MAD	0.91		0.44		0.430		0.50		
Total Error	1.38		0.66		0.608		0.76		
P (g/kg)									
LAB B	44.2	*	3.26		2.22		27.3		HO|AR|IA
LAB C	39.8		3.58		2.47		29.2		
LAB D	42.9		3.20		2.50		30.7		
LAB E	34.5		3.14		2.36		26.0		
LAB F	37.7		3.10		2.40		28.0		MC|NP|IA
LAB G	35.0		3.00		2.09		27.4		MC|AS|ZA
LAB H	40.0		3.50		2.40		28.0		HC|AR|IM
LAB I	34.8		3.23		2.24		26.2		MC|AR|IM
LAB J	39.2		3.12		2.33		27.7		MC|NA|IM
LAB K	37.8		-		-		27.3		HO|NS|SV
LAB L	38.8		3.31		2.51		28.7		AO|EO|SV
LAB M	37.7		3.42		2.45		29.2		MC|AR|IA
LAB N	36.2		3.30		2.33		26.5		MC|AR|IA
LAB O	38.8		3.43		2.52		30.2		
LAB P	37.0		3.40		2.80	*	29.3		
LAB Q	29.5	**	2.88		2.21		27.0		MC|NA|IA
LAB R	40.3		3.69	*	2.55		29.0		HO|NS|SV
LAB S	35.4		3.08		2.38		27.8		AO|EO|SV
	=================		Summary Statistics		================				
NDA mean	37.76		3.208		2.378		27.73		
NDA st dev	2.52		0.189		0.153		1.52		
Coeff Var (%)	6.7		5.9		6.4		5.5		
N	27		24		24		27		

Acid extractable (So-called totals) Data and Statistics

Sample	286		262		263		273		MIC
P (g/kg) (cont.)									
LAB	36.1		3.23		2.34		25.2		
LAB	38.9		3.05		2.31		27.7		
LAB	38.0		3.00		2.27		27.1		MC|AR|IA
LAB	35.3		3.23		2.49		25.6		HO|EO|IA
LAB	39.5		3.15		2.38		29.1		HO|AR|IA
LAB	36.4		3.23		2.49		27.5		MC|EO|IM
LAB	38.4		-		-		26.7		HO|EO|SV
LAB	40.5		-		-		30.1		HC|KJ|SV
LAB	36.0		3.10		2.20		27.0		MC|NA|IA
	=================		Statistical Results		=================				
NDA mean	37.76		3.208		2.378		27.73		
NDA st dev	2.52		0.189		0.153		1.52		
Coeff Var (%)	6.7		5.9		6.4		5.5		
N	27		24		24		27		
Median	37.76		3.230		2.380		27.65		
MAD	1.76		0.130		0.110		1.05		
Total Error	2.59		0.195		0.158		1.57		

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Sample	286		262		263		273		MIC
Zn (mg/kg)									
LAB A	909		138		138		726		HO|AR|IA
LAB B	961		135		124	*	717		
LAB C	1010	*	132		133		784	*	
LAB D	813		132		134		665		
LAB E	919		135		137		704		MC|NP|IA
LAB F	886		126	*	139		730		MC|AS|ZA
LAB G	900		140		280	**	660		HC|AR|IM
LAB H	849		137		132		701		MC|AR|IM
LAB I	896		135		138		700		MC|NA|IM
LAB J	942		-		-		741		HO|AR|IM
LAB K	839		134		133		668		AO|EO|AA
LAB L	880		134		138		738		MC|AR|IM
LAB M	810		140		132		663		MC|AR|IA
LAB N	875		132		129		688		
LAB O	936		141		140		722		
LAB P	838		132		133		673		MC|NA|IA
LAB Q	928		143		138		724		MC|AR|IM
LAB R	732	**	137		137		714		AO|EO|AA
LAB S	892		142		137		706		
LAB T	911		132		135		723		MC|AR|IA
LAB U	836		132		138		647		HO|EO|IA
LAB V	895		140		141		724		HO|AR|IA
LAB W	864		140		144		721		MC|EO|IM
LAB X	887		-		-		580	**	MC|AR|IA
LAB Y	861		-		-		665		-|AR|IM
LAB Z	1100	**	140		130		760		MC|NA|IA
	=================		Statistical Results		=================				
NDA mean	885.6		136.1		135.9		707.8		
NDA st dev	49.1		4.5		4.8		32.1		
Coeff Var (%)	5.5		3.3		3.5		4.5		
N	26		23		23		26		
Median	889.6		135.0		137.0		710.0		
MAD	34.1		3.0		3.4		20.9		
Total Error	50.5		4.6		4.9		33.0		

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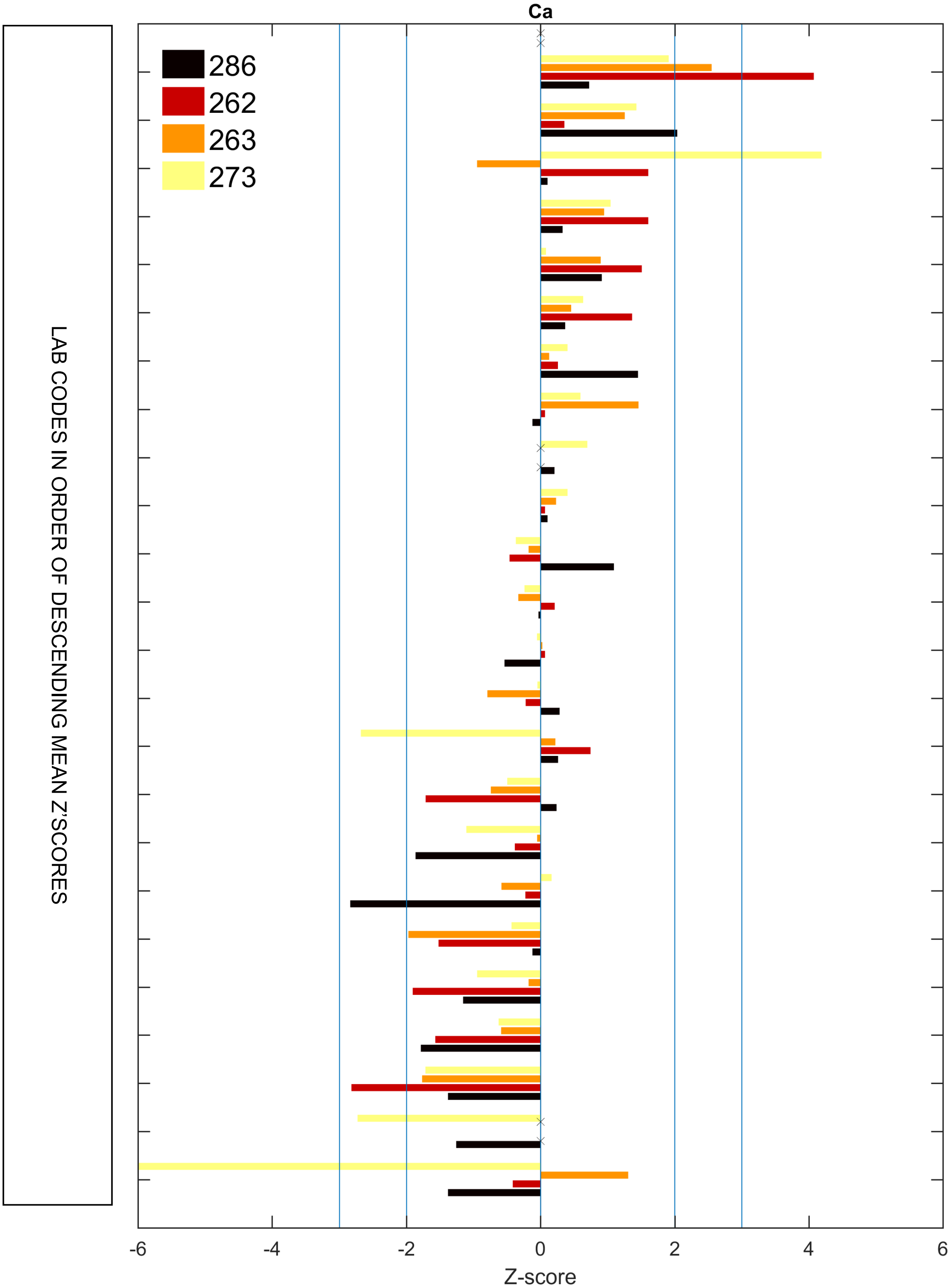
Method group Acid extractable (So-called totals)

Code	System used for digestion/extraction
-	not applicable (i.c.o. elemental analysers)
BB	Berghoff bomb
AO	Dry ashing open system
AC	Dry ashing closed system
MO	Microwave open system
MC	Microwave closed system
HO	Heating system open (i.e. plate or block)
HC	Heating system closed (i.e. plate or block)
S	Shaking (extraction)
Z	Other (specify)

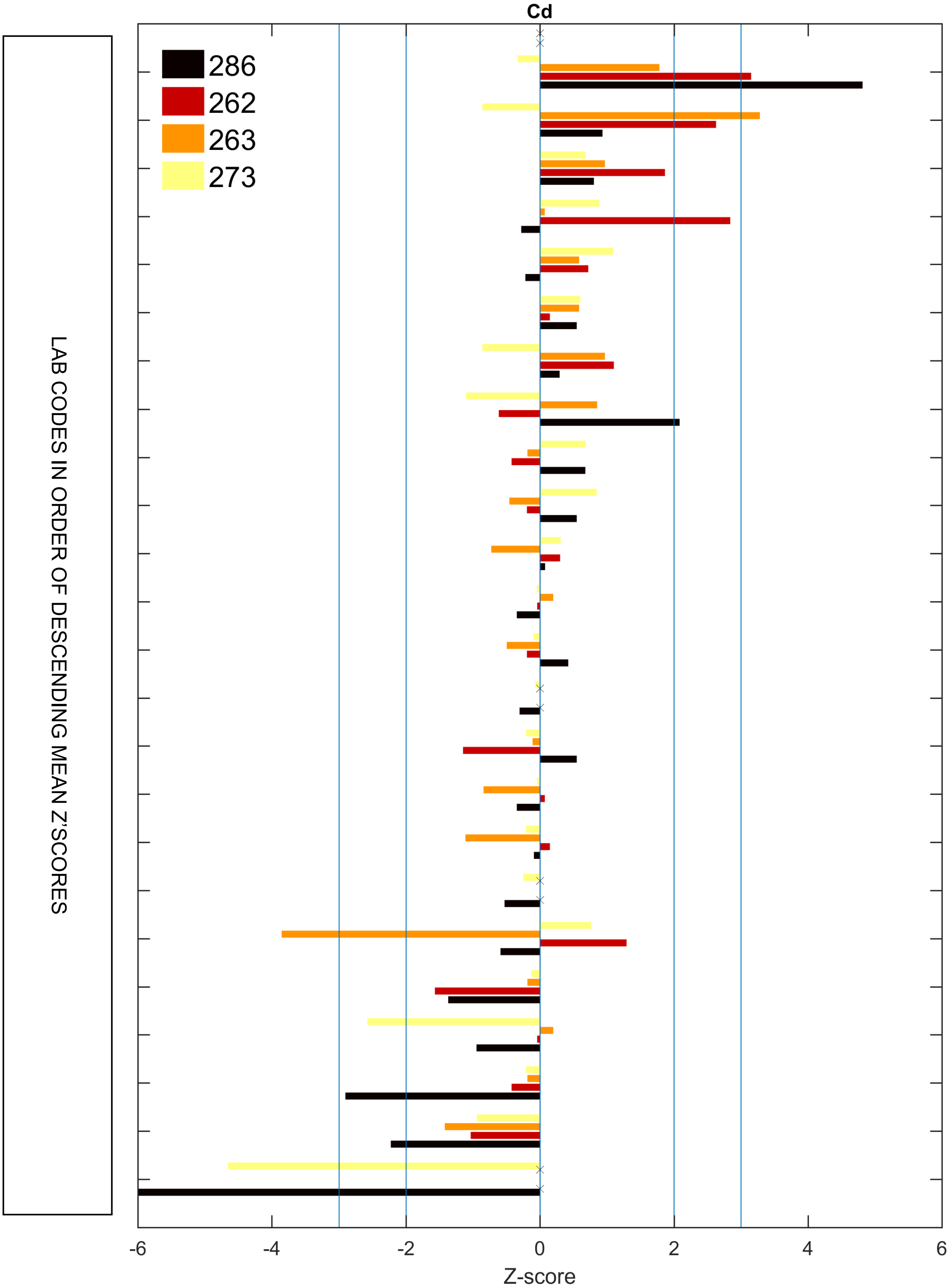
Code	Digestion/extraction for MARSEP Acid Extractable
-	no acids/chemicals used
AR	Aqua Regia (HNO3/HCl (1:3))
AS	HNO3/HCl (3:1) (reverse Aqua Regia)
NA	HNO3
NS	HNO3/H2SO4
NP	HNO3/H2O2
KJ	H2SO4 (+K2SO4) (Kjeldahl)
EW	Extraction with water
EO	Extraction with acid(s)
Z	Other (specify)

Code	Detection MARSEP Acid Extractable
AA	AAS Flame without preconcentration air/acetylene
AB	AAS Flame without preconcentration N2O/acetylene
BA	AAS-ETA (graphite furnace)
FE	AES Flame Emission
IA	ICP-AES
IM	ICP-MS
HA	Hydride Technique
HC	Cold Vapour Technique
CI	Ion Chromatography
CN	C/N elemental analyser
HG	Hg analyser (i.e. AMA254, DMA80)
SV	Spectrophotometry (visible)
ED	Direct Voltammetry
T	Titrimetry
WG	Gravimetry
Z	Other (specify)

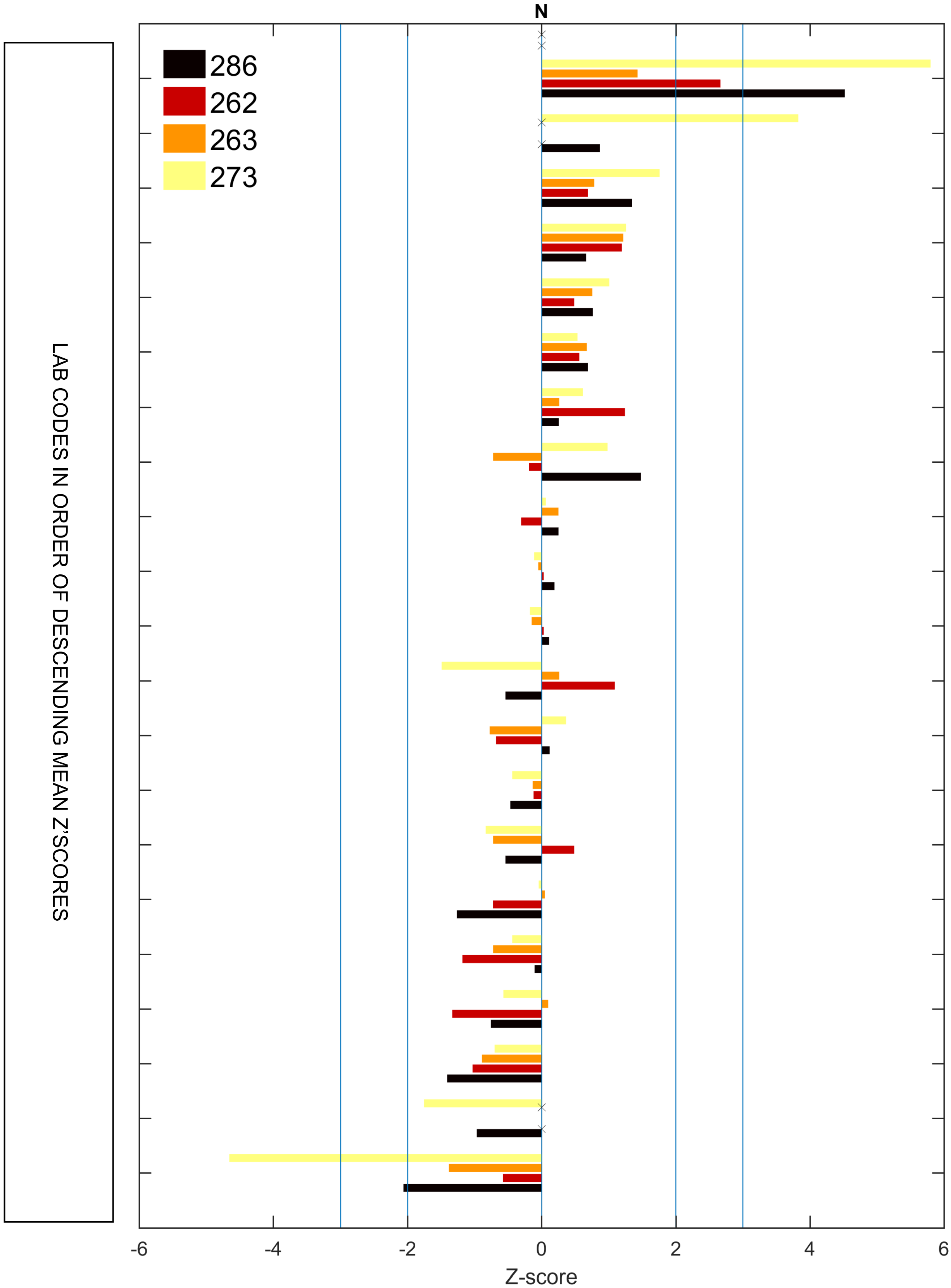
Acid extractable (So-called totals) Combined Zscores



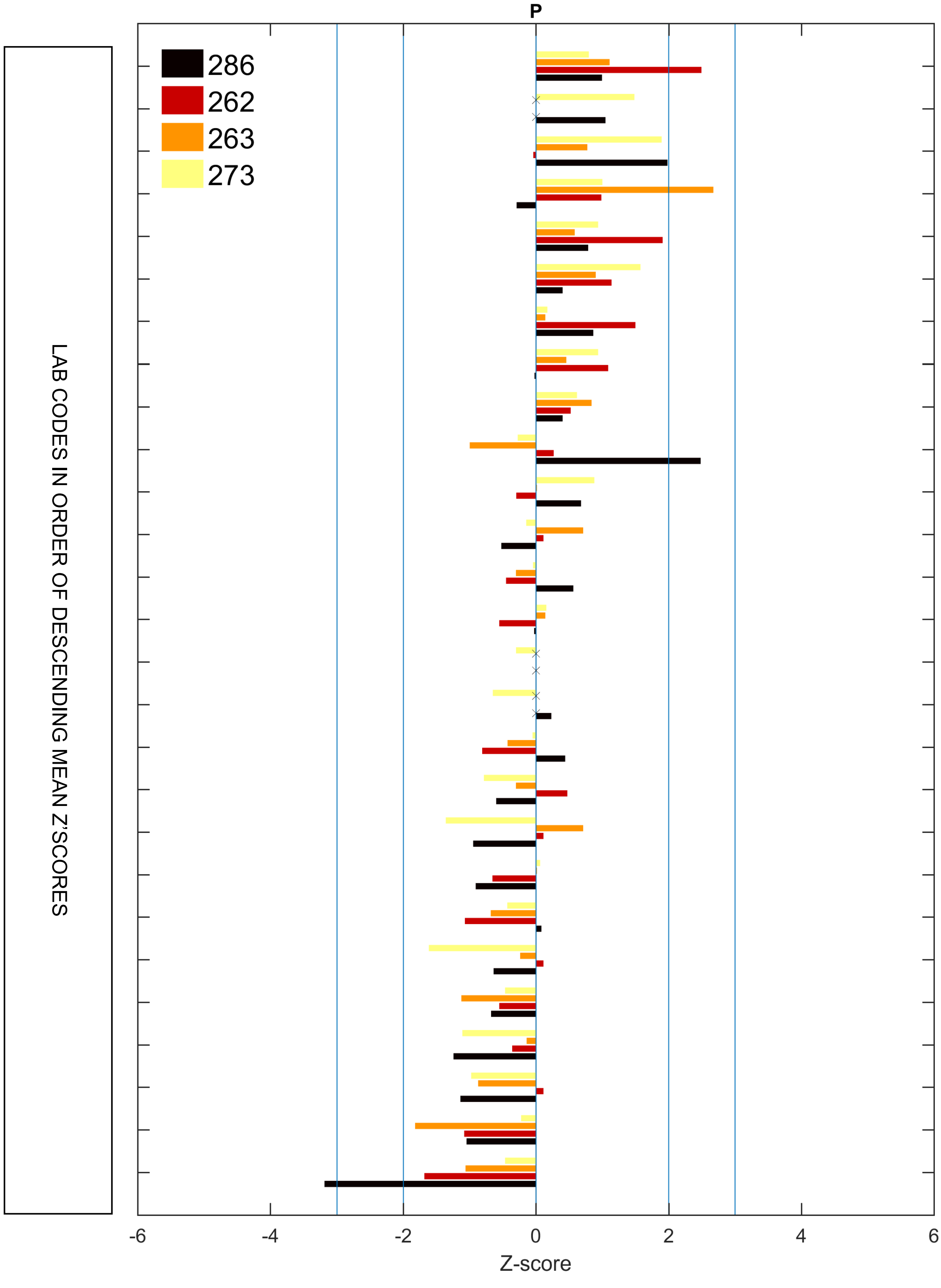
Acid extractable (So-called totals) Combined Zscores



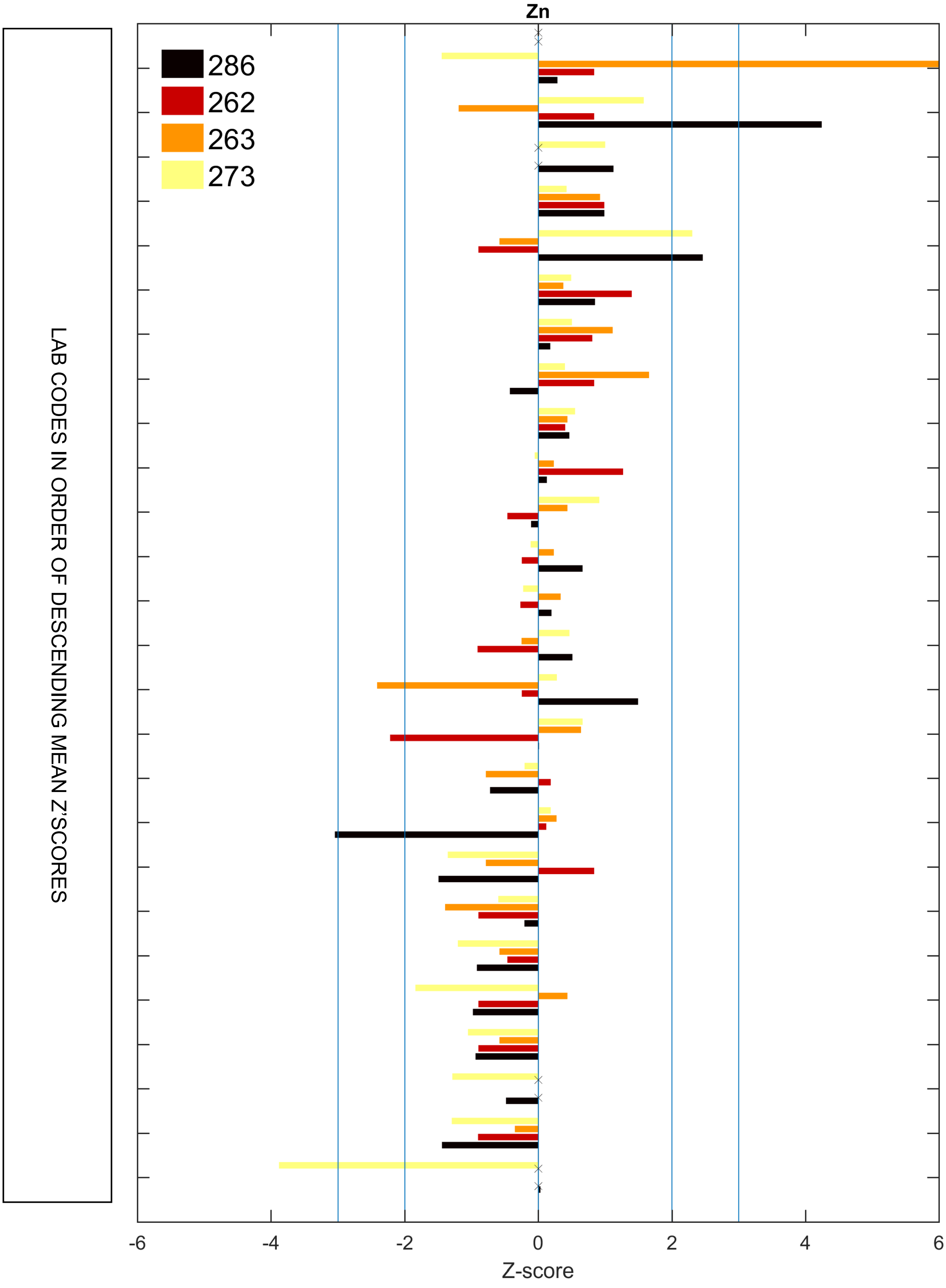
Acid extractable (So-called totals) Combined Zscores



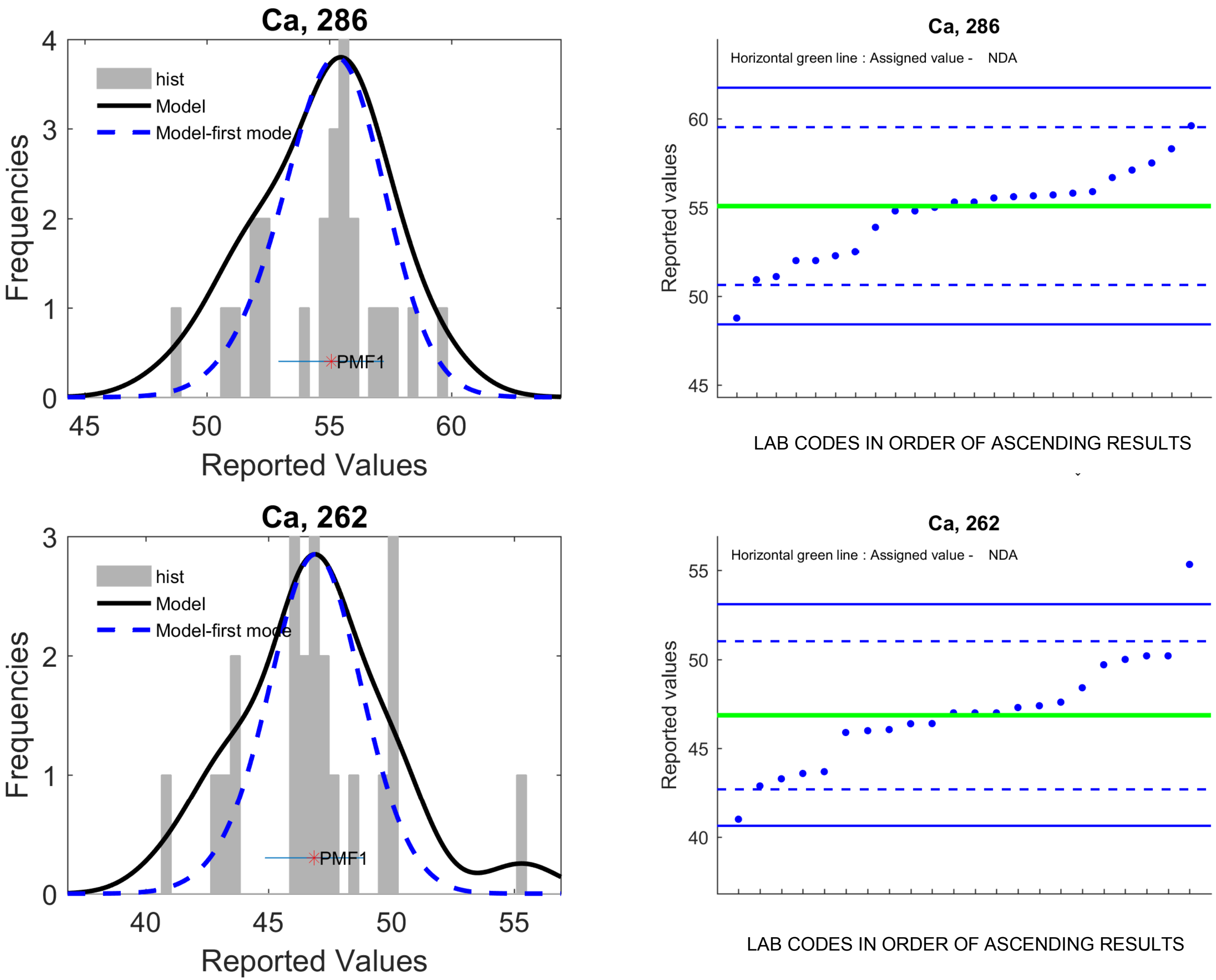
Acid extractable (So-called totals) Combined Zscores



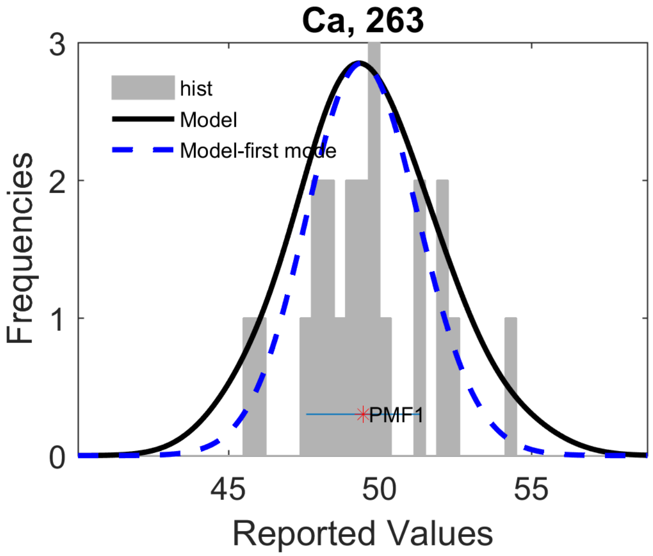
Acid extractable (So-called totals) Combined Zscores

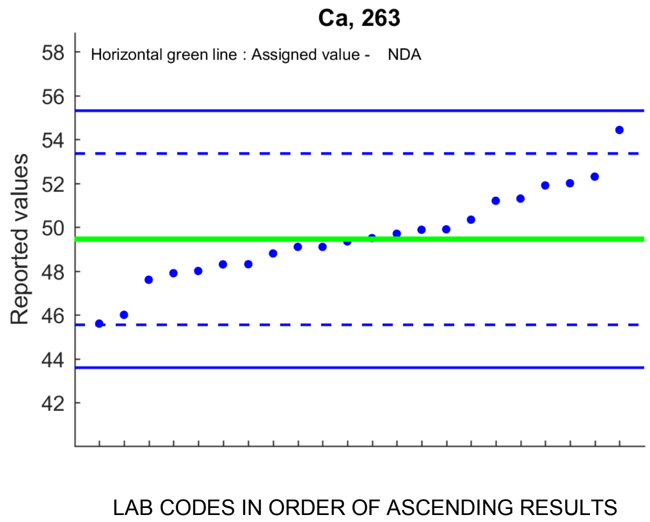


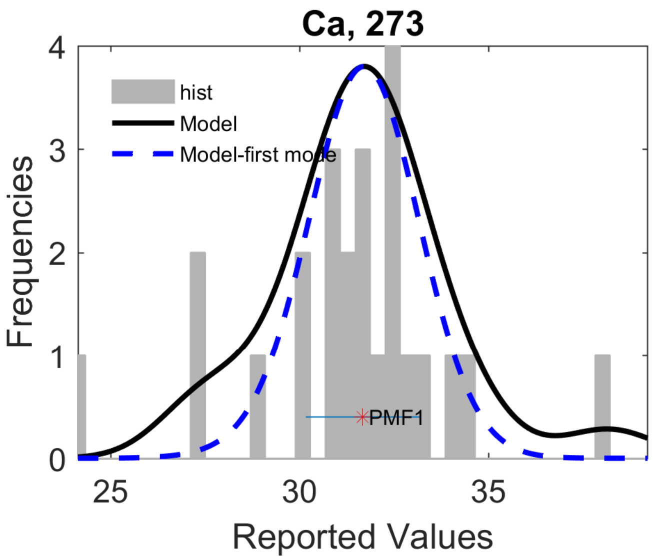
Acid extractable (So-called totals) Histogram+PDFs and Ranked overview

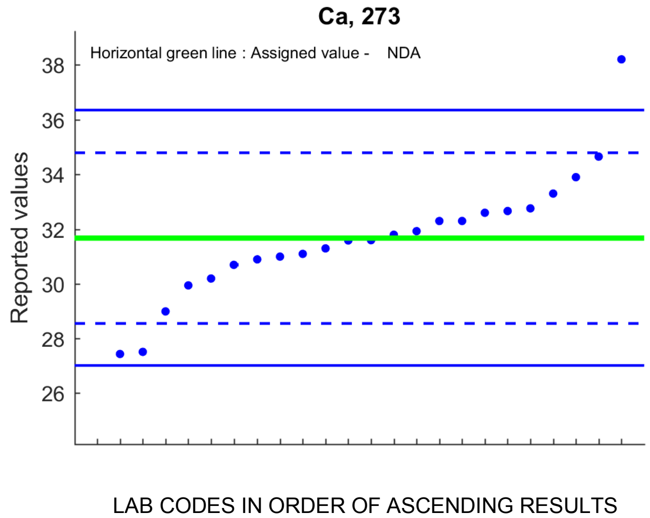


Acid extractable (So-called totals) Histogram+PDFs and Ranked overview

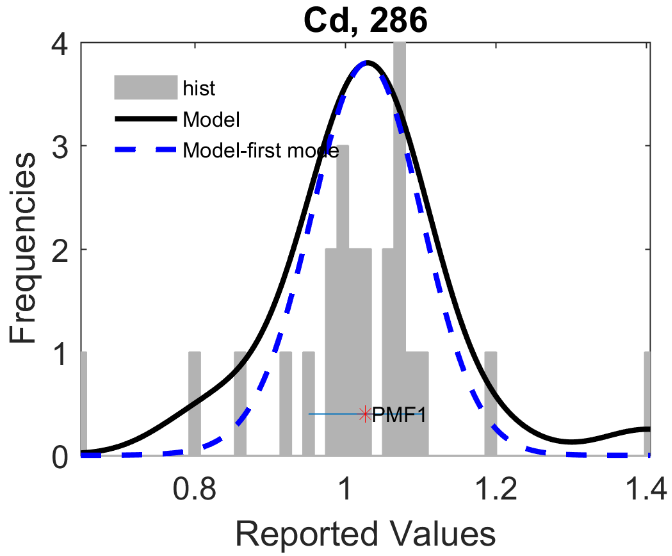


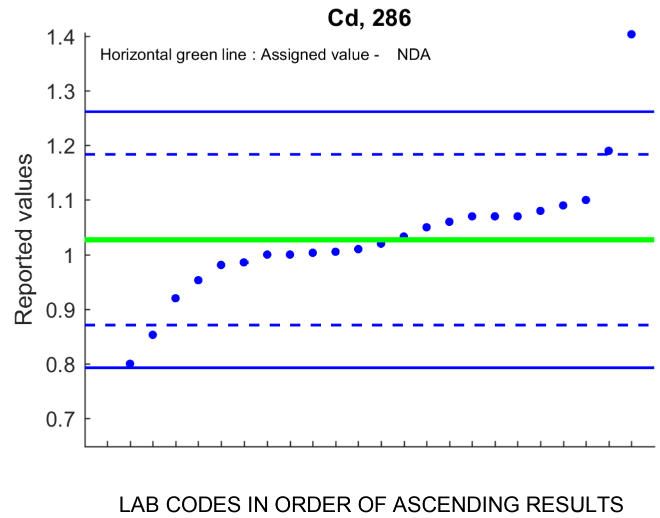


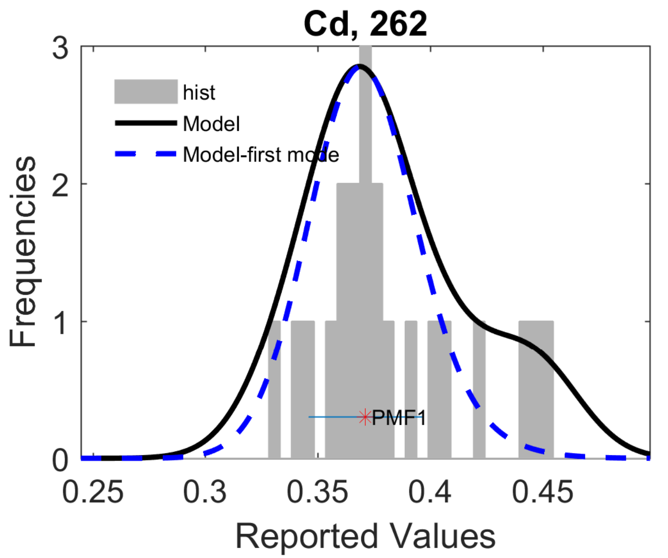


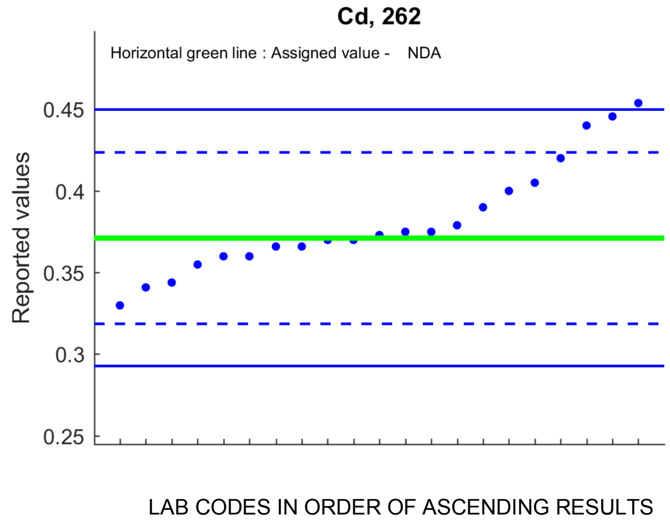


Acid extractable (So-called totals) Histogram+PDFs and Ranked overview

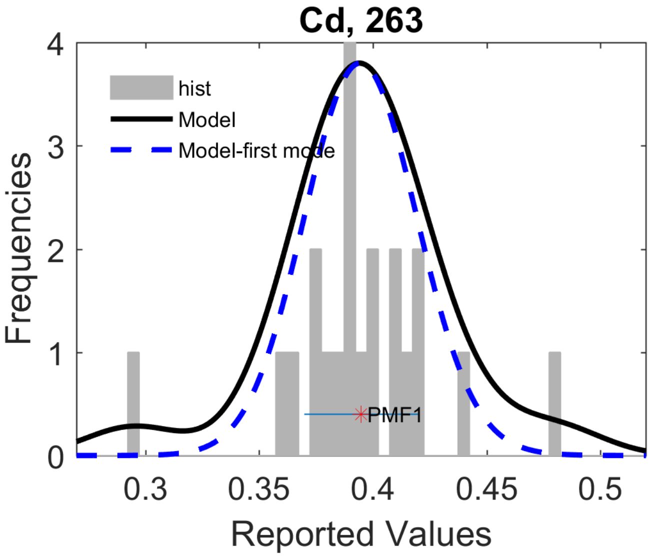


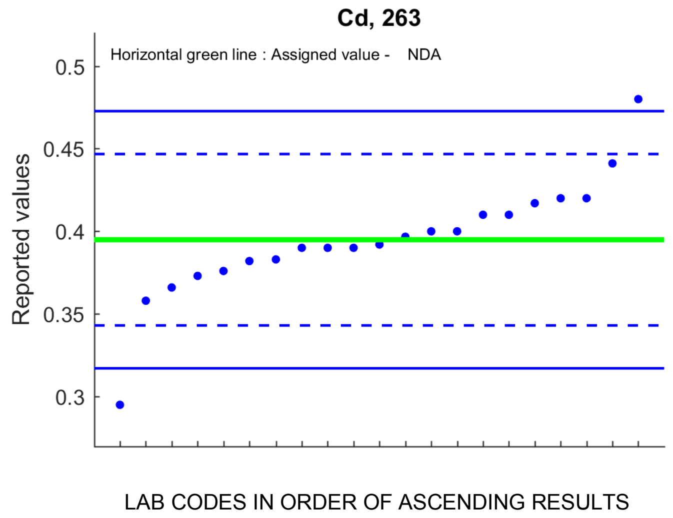


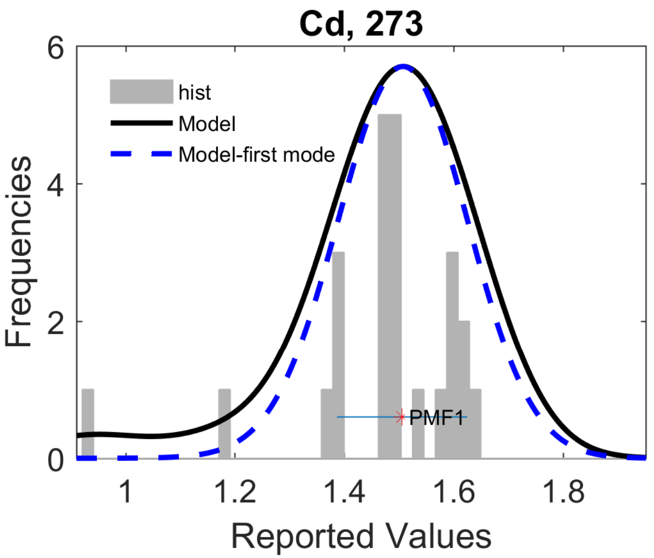


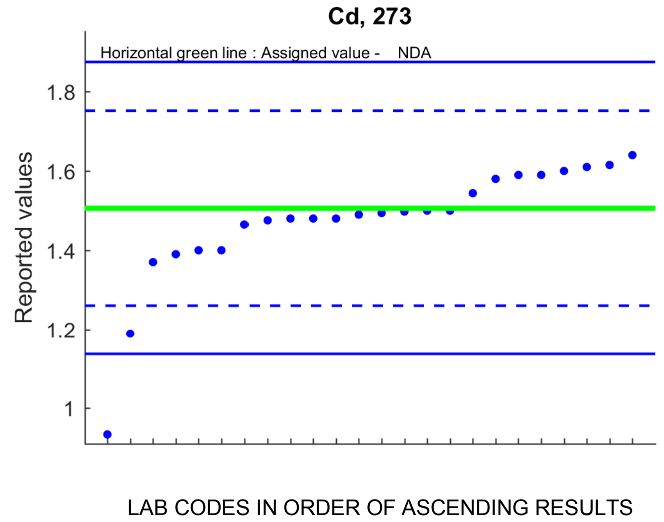


Acid extractable (So-called totals) Histogram+PDFs and Ranked overview

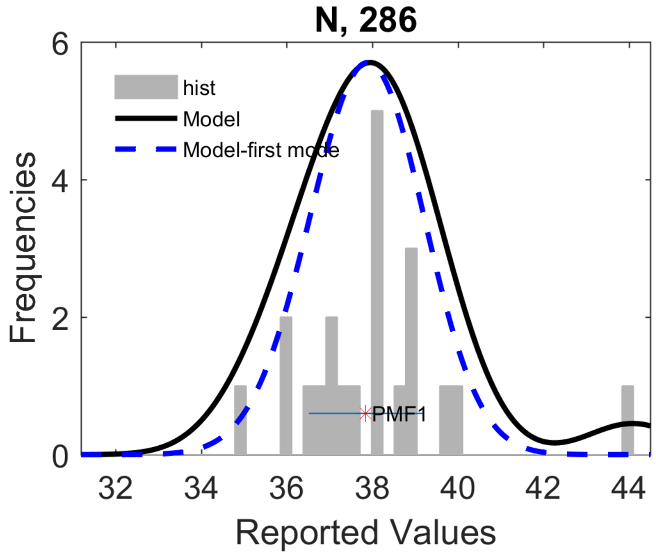


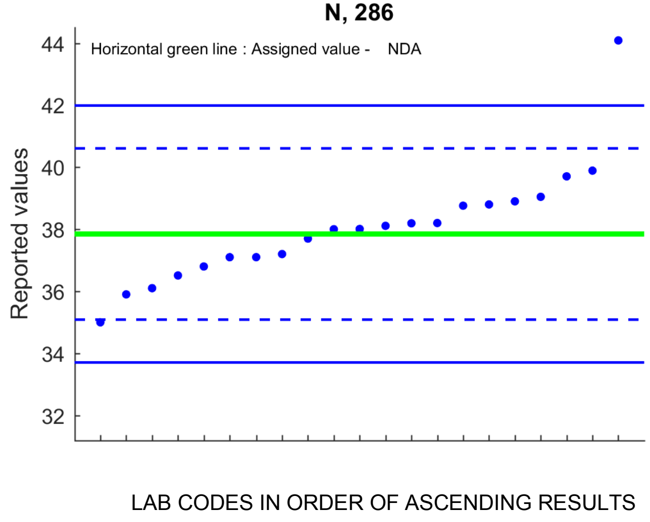


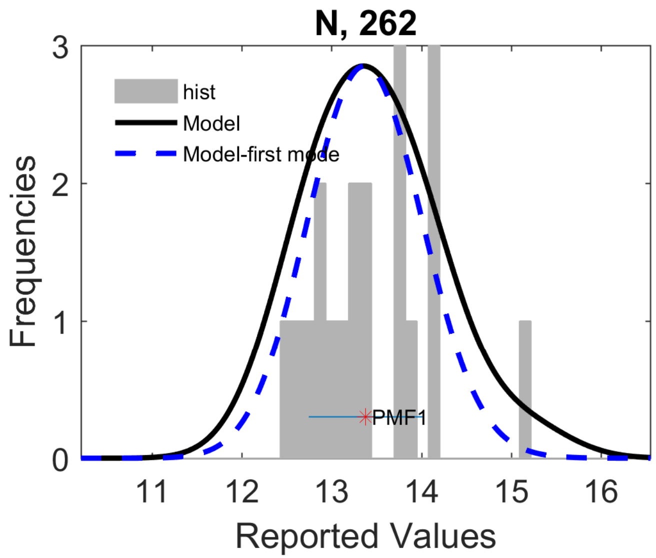


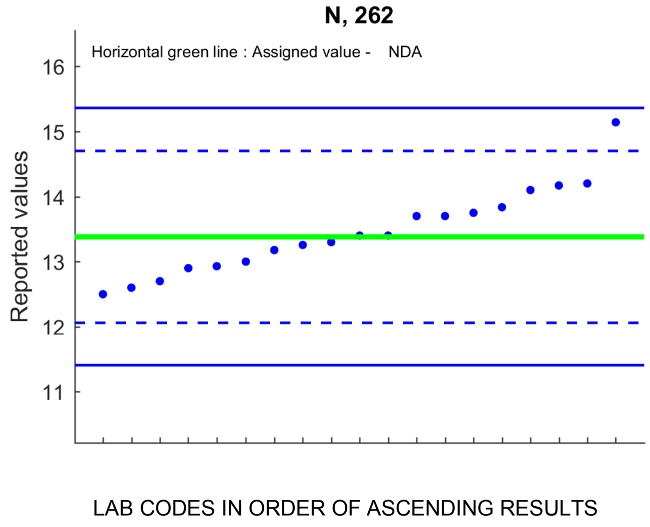


Acid extractable (So-called totals) Histogram+PDFs and Ranked overview

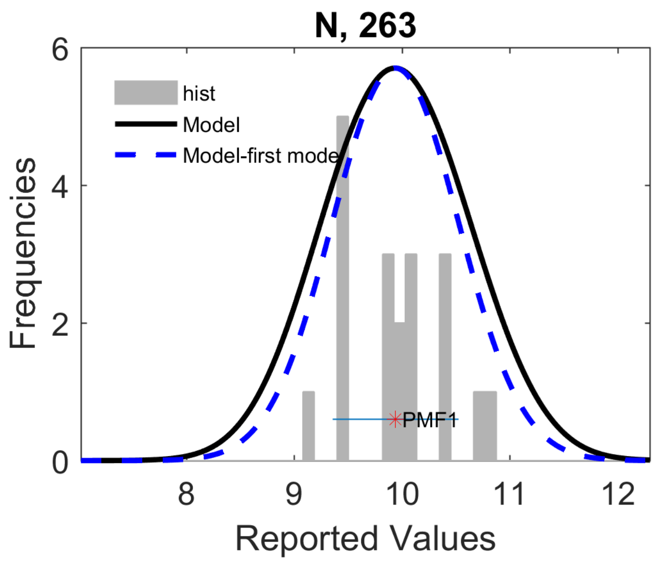


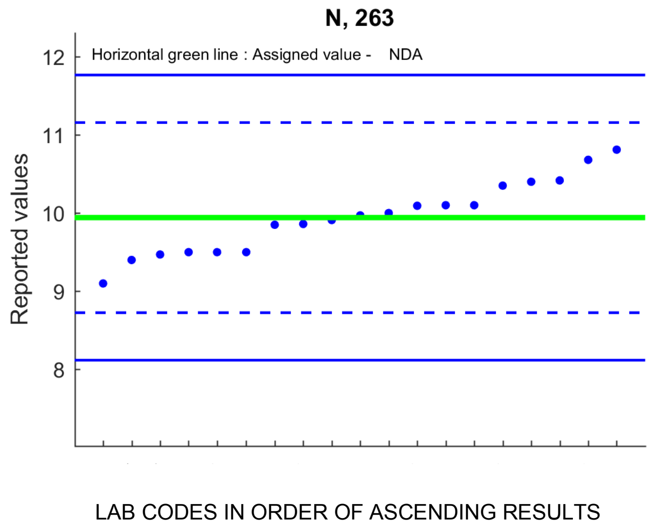


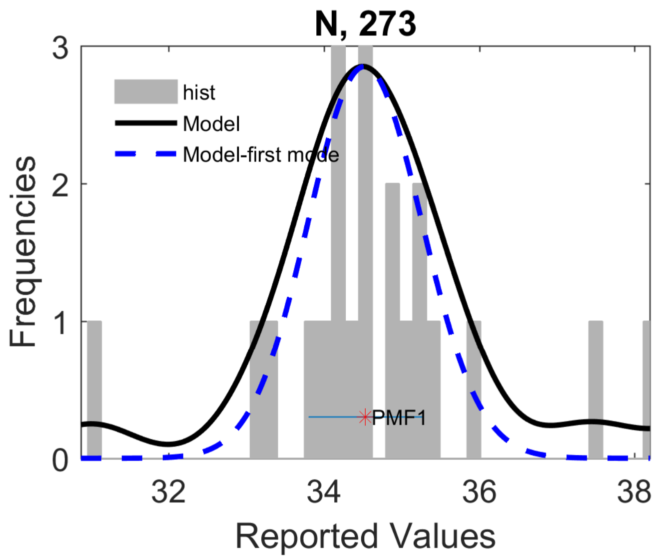


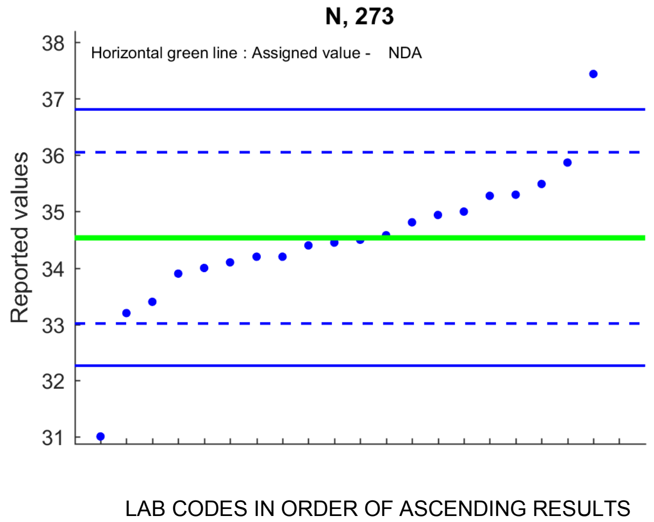


Acid extractable (So-called totals) Histogram+PDFs and Ranked overview

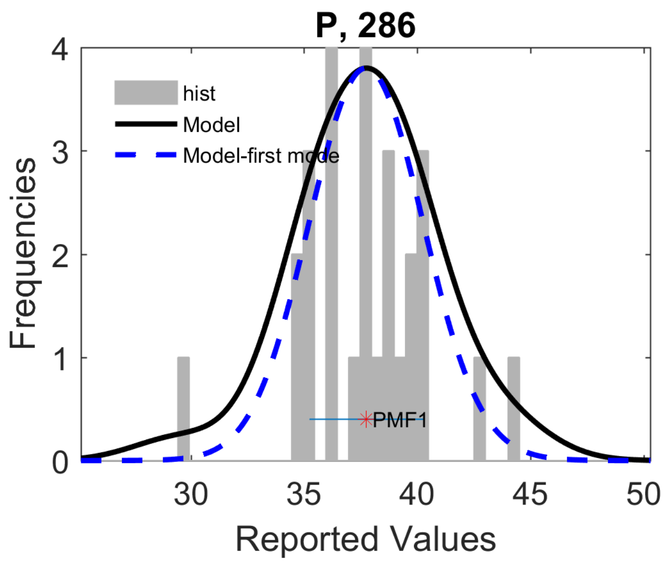


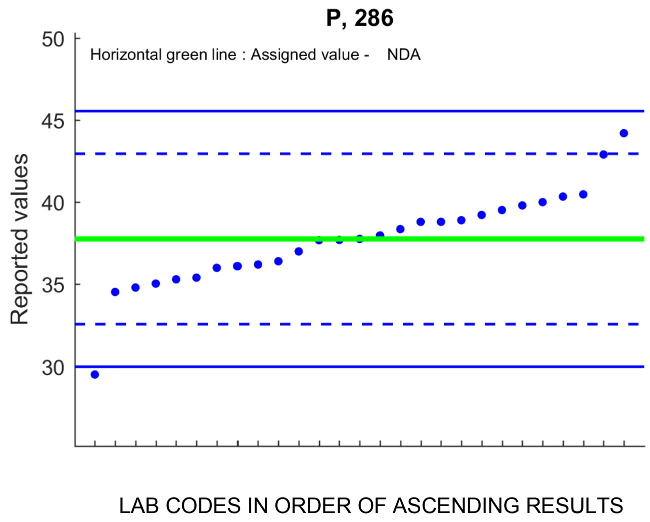


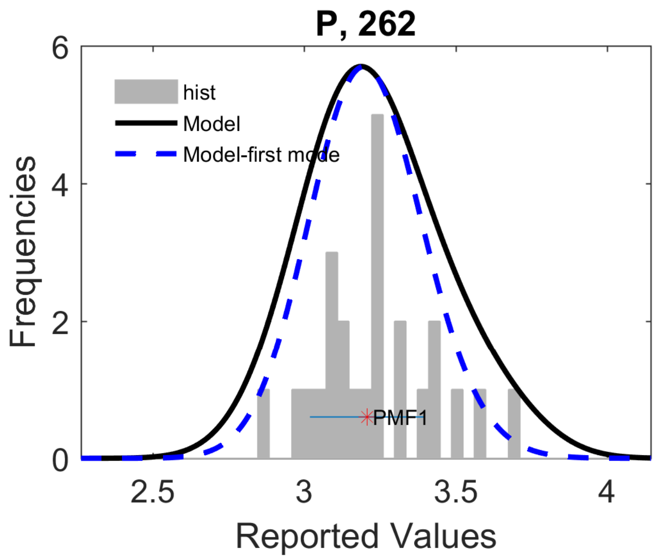


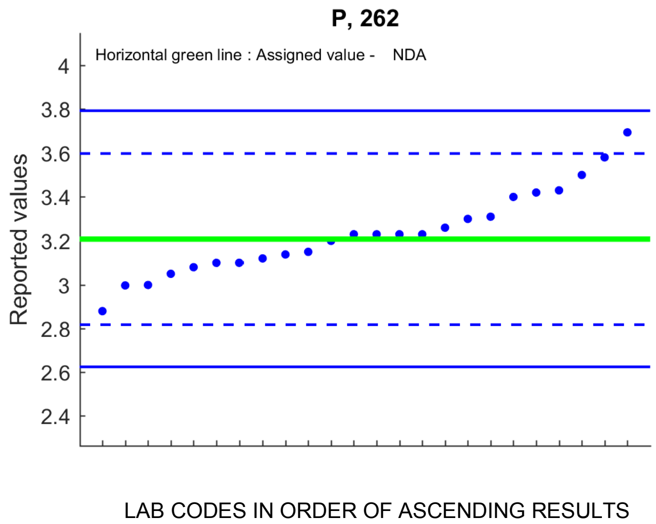


Acid extractable (So-called totals) Histogram+PDFs and Ranked overview

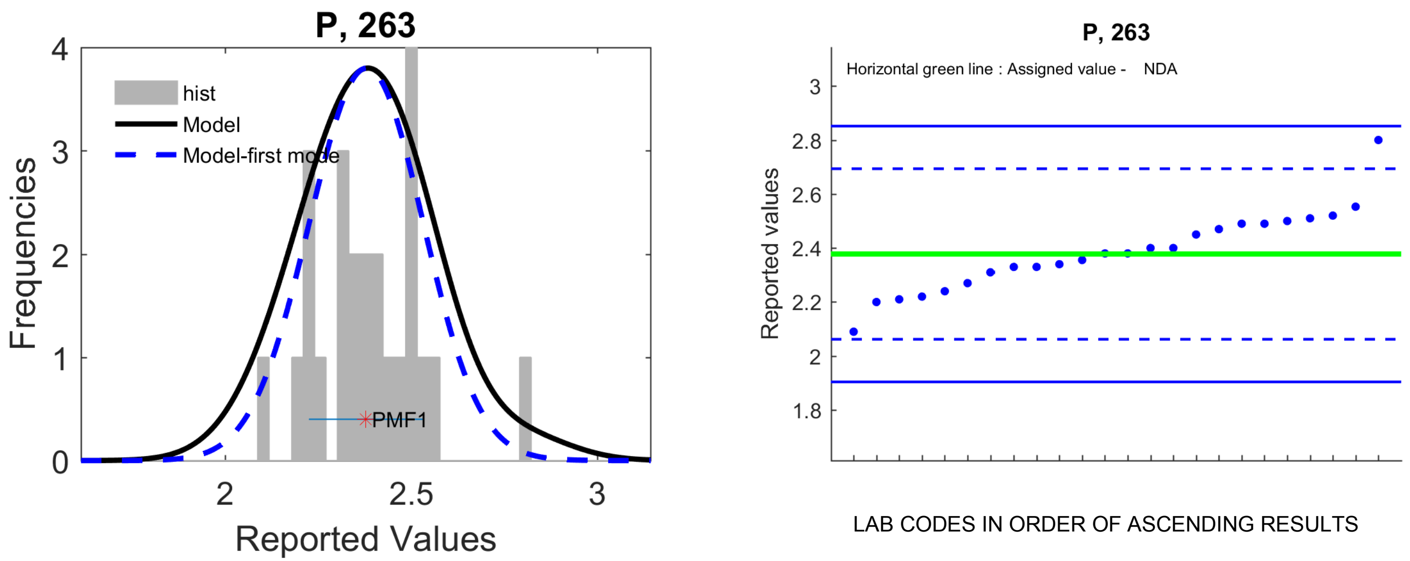


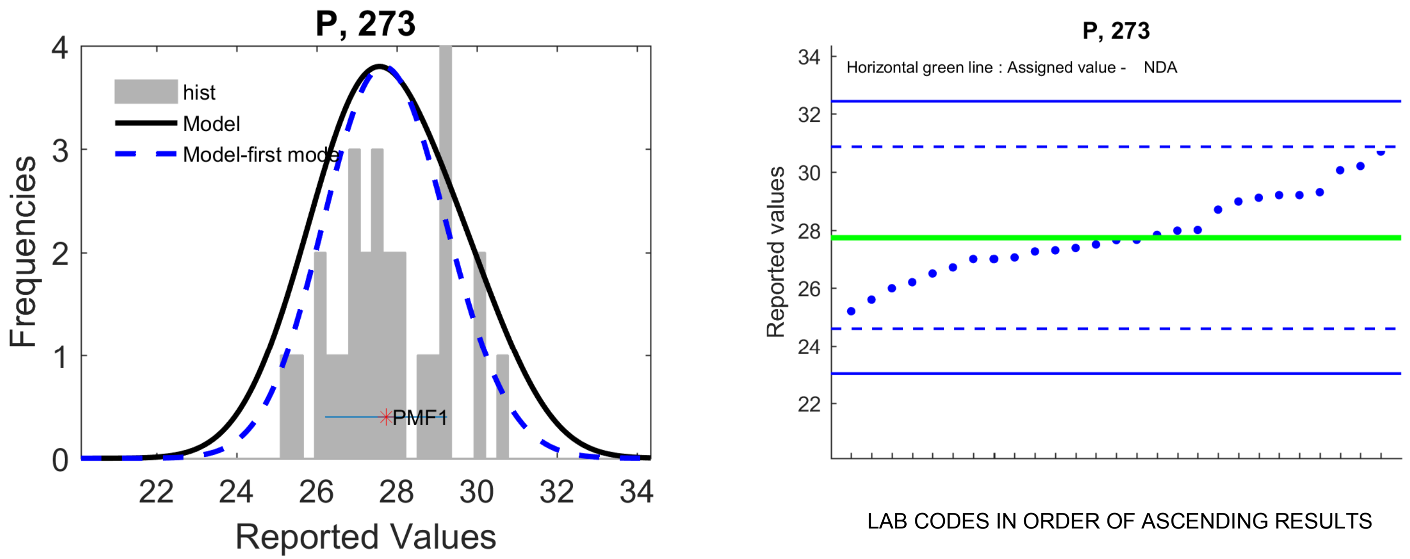




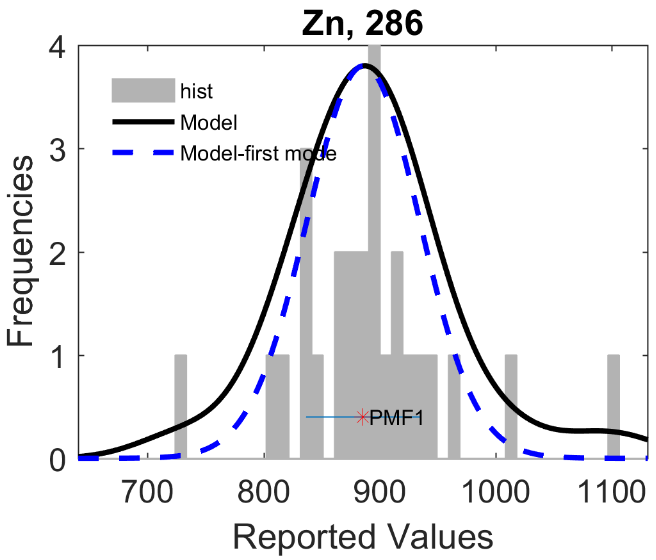


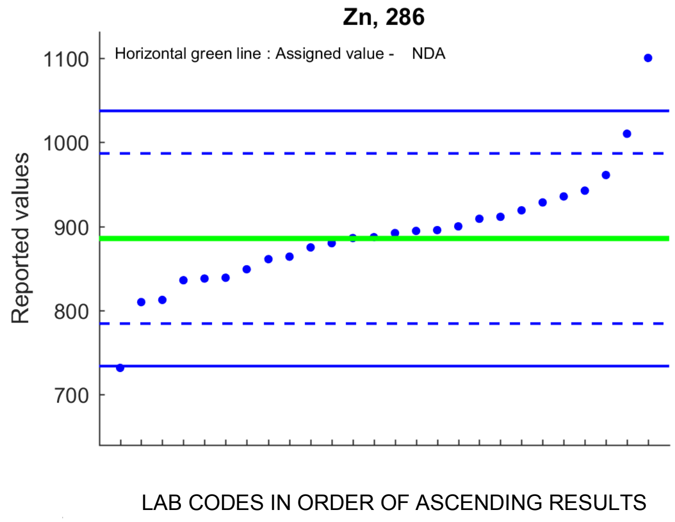
Acid extractable (So-called totals) Histogram+PDFs and Ranked overview

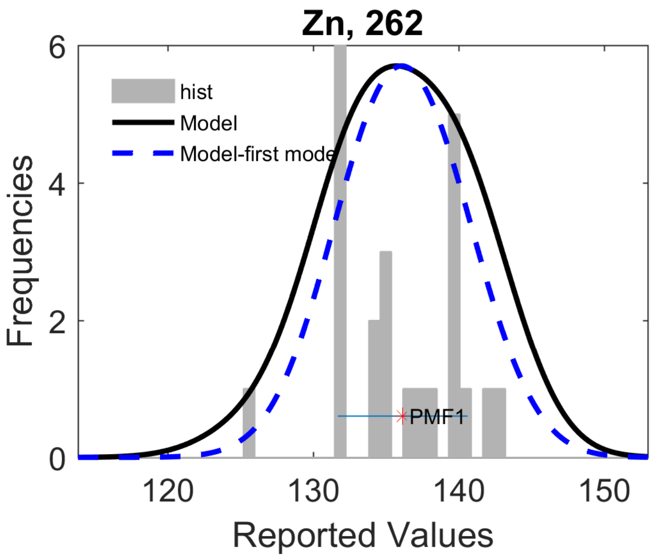


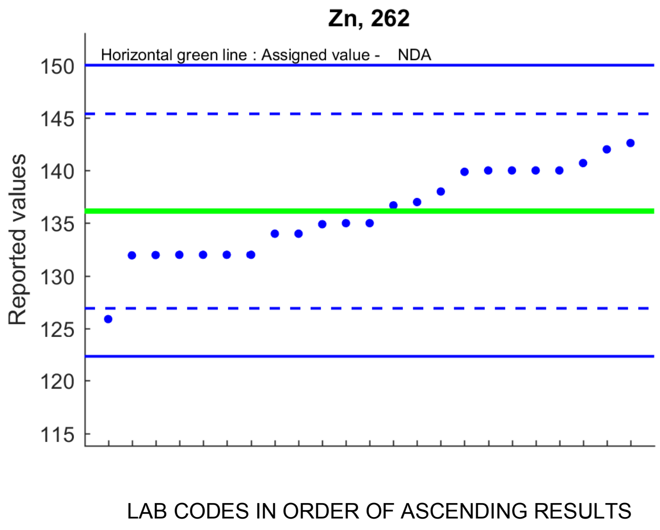


Acid extractable (So-called totals) Histogram+PDFs and Ranked overview

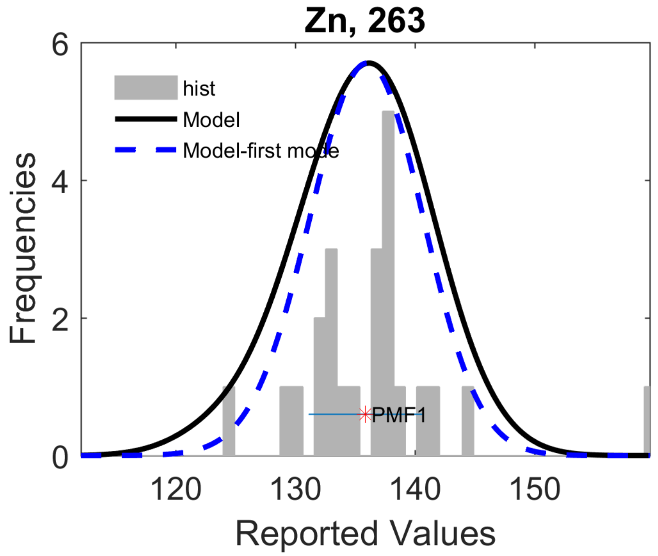


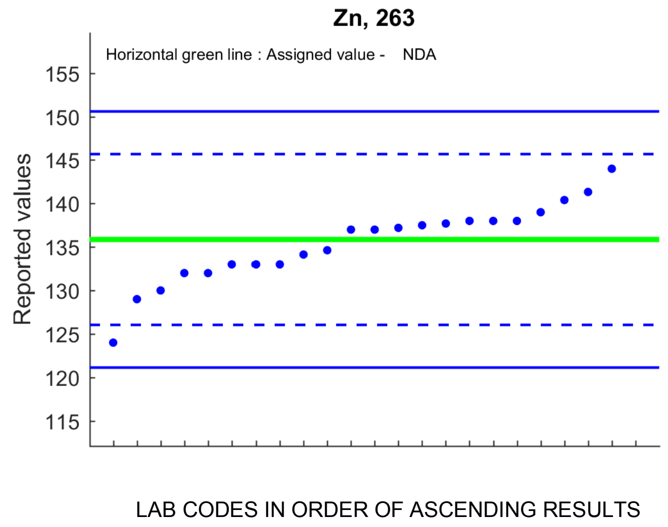


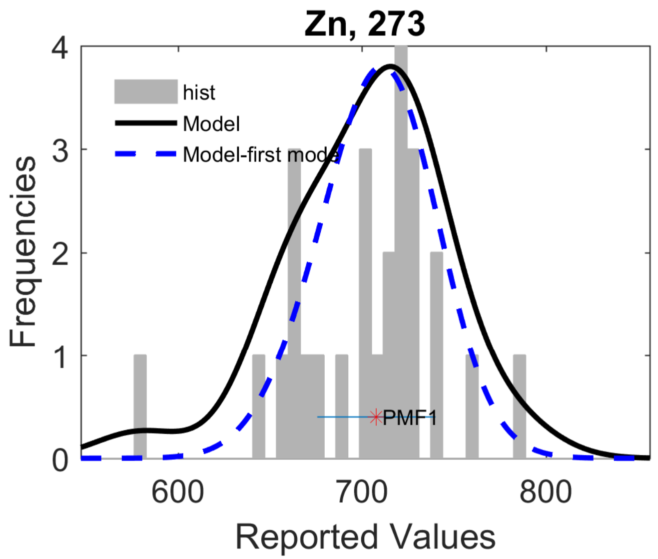


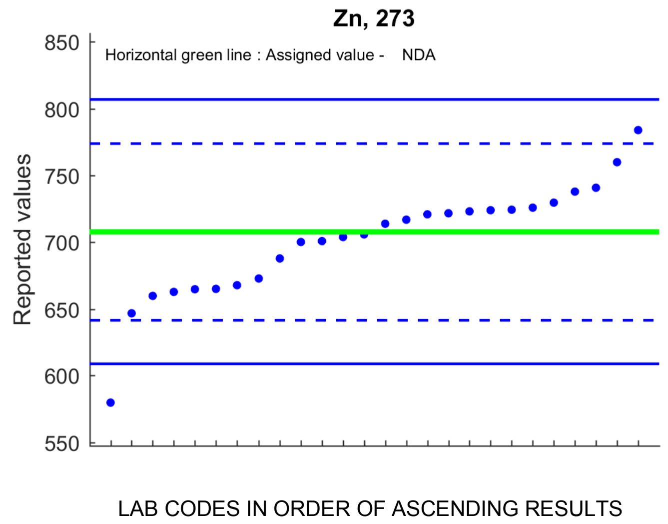


Acid extractable (So-called totals) Histogram+PDFs and Ranked overview









Other determinations
Analysis MARSEP 2019.2

Other determinations Summary Statistics

Sample/ Determinand	Assigned Value	Units	NDA st.dev	NDA rel. st.dev (%)	Nobs numerical	Nobs LCV	Median	MAD	Model Mean	Uncer-tainty
286										
AOX		*mg/kg*			*4*	*0*	*191*	*6*		
loss-on-ignition	52.9	%	0.8	1.6	20	0	52.9	0.6	52.90	0.24
residu-on-ignition		*%*			*6*	*0*	*47.0*	*0.0*		
COD		*g/kg*			*3*	*0*	*639*	*116*		
mineral oil		*g/kg*			*2*	*0*	*7.59*	*0.13*		
dry weight		*%*			*5*	*0*	*92.9*	*0.1*		

Sample/ Determinand	Assigned Value	Units	NDA st.dev	NDA rel. st.dev (%)	Nobs numerical	Nobs LCV	Median	MAD	Model Mean	Uncer-tainty
262										
AOX		*mg/kg*			*4*	*0*	*48.1*	*2.6*		
loss-on-ignition	28.5	%	0.7	2.4	19	0	28.5	0.5	28.51	0.20
residu-on-ignition		*%*			*3*	*0*	*71.0*	*0.2*		
COD		*g/kg*			*1*	*0*	*233*			
dry weight		*%*			*2*	*0*	*96.8*	*0.5*		

Sample/ Determinand	Assigned Value	Units	NDA st.dev	NDA rel. st.dev (%)	Nobs numerical	Nobs LCV	Median	MAD	Model Mean	Uncer-tainty
263										
AOX		*mg/kg*			*4*	*0*	*59.0*	*2.4*		
loss-on-ignition	24.0	%	0.6	2.6	19	0	24.0	0.4	23.95	0.18
residu-on-ignition		*%*			*3*	*0*	*75.9*	*0.1*		
COD		*g/kg*			*1*	*0*	*291*			
dry weight		*%*			*2*	*0*	*97.2*	*0.4*		

Sample/ Determinand	Assigned Value	Units	NDA st.dev	NDA rel. st.dev (%)	Nobs numerical	Nobs LCV	Median	MAD	Model Mean	Uncer-tainty
273										
AOX		*mg/kg*			*4*	*0*	*372*	*5*		
loss-on-ignition	52.4	%	0.7	1.3	20	0	52.4	0.5	52.43	0.19
residu-on-ignition		*%*			*6*	*0*	*47.6*	*0.2*		
COD		*g/kg*			*3*	*0*	*950*	*468*		
mineral oil		*g/kg*			*2*	*0*	*12.8*	*0.4*		
dry weight		*%*			*5*	*0*	*92.9*	*0.4*		

Other determinations MIC List

Sample	286		262		263	273		MIC
loss-on-ignition (%)								
LAB A	53.0		28.2		24.0	52.3		
LAB B	54.3		30.4	*	24.0	52.3		
LAB C	52.2		28.1		23.9	52.6		
LAB D	52.8		28.2		25.0	52.4		DT|WG
LAB E	53.0		29.0		25.0	53.0		
LAB F	53.9		28.9		24.4	52.7		DS|WG
LAB G	52.4		28.9		23.7	51.8		DT|WG
LAB H	52.3		28.0		23.4	52.3		DT|WG
LAB I	52.9		29.1		24.0	52.3		DT|WG
LAB J	53.2		28.0		23.5	52.7		DT|WG
LAB K	54.0		29.3		24.1	53.4		
LAB L	52.7		27.9		23.0	52.8		
LAB M	53.4		28.2		23.9	52.9		DT|WG
LAB N	54.5		33.5	**	25.1	33.2	**	ZA|WG
LAB O	51.0	*	28.5		22.9	51.4		
LAB P	52.0		28.1		23.7	51.3		DT|WG
LAB Q	52.7		29.0		24.5	51.8		DT|WG
LAB R	52.1		28.1		22.9	51.8		DT|WG
LAB T	54.2		29.4		24.4	53.6		DT|WG
LAB V	52.5		-		-	52.4		

	=================	Statistical Results	=================	
NDA mean	52.90	28.51	23.95	52.43
NDA st dev	0.85	0.70	0.63	0.68
Coeff Var (%)	1.6	2.4	2.6	1.3
N	20	19	19	20
Median	52.87	28.50	23.99	52.37
MAD	0.57	0.50	0.41	0.49
Total Error	0.88	0.73	0.66	0.71

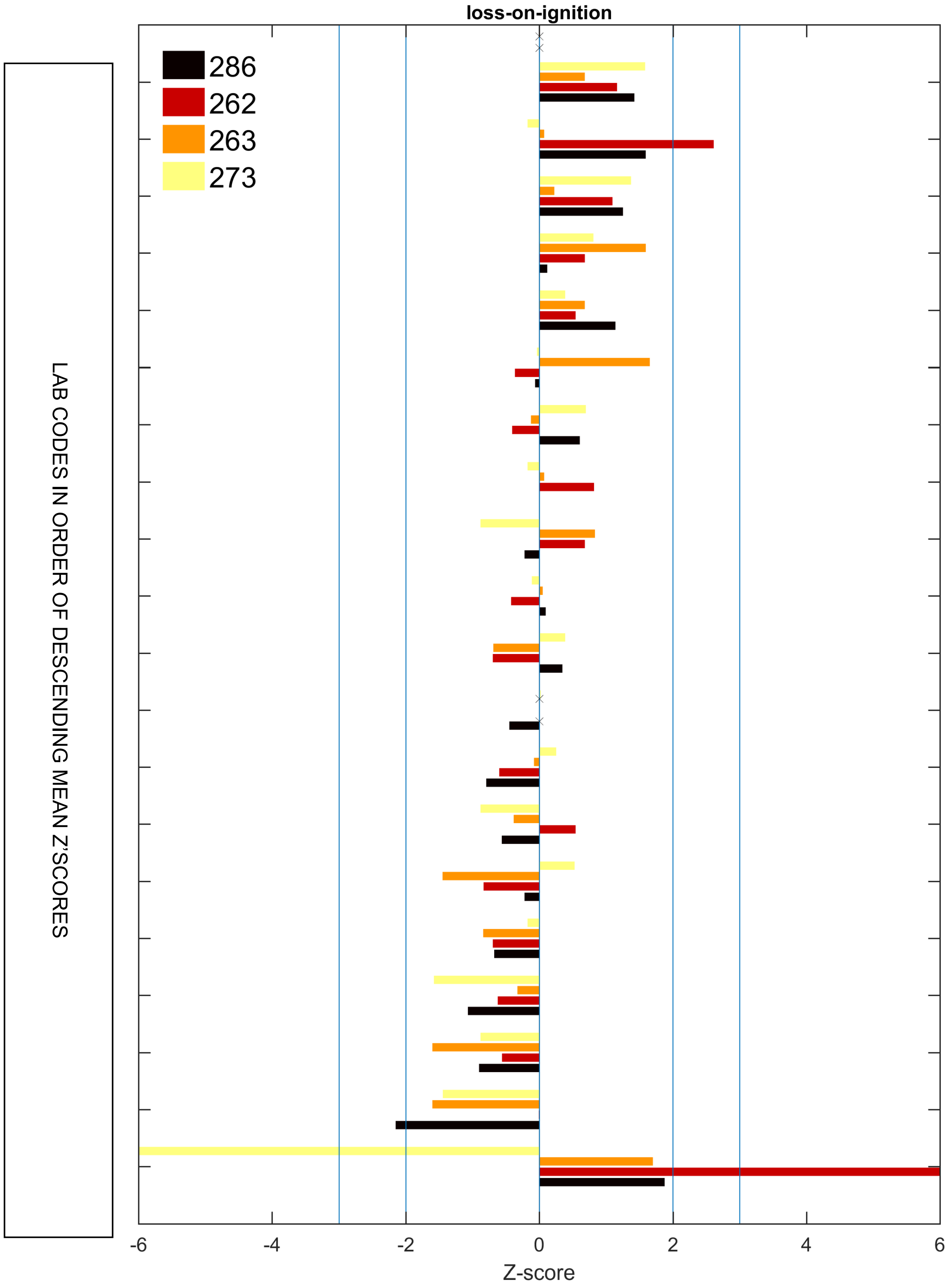
===

Method group Other determinations

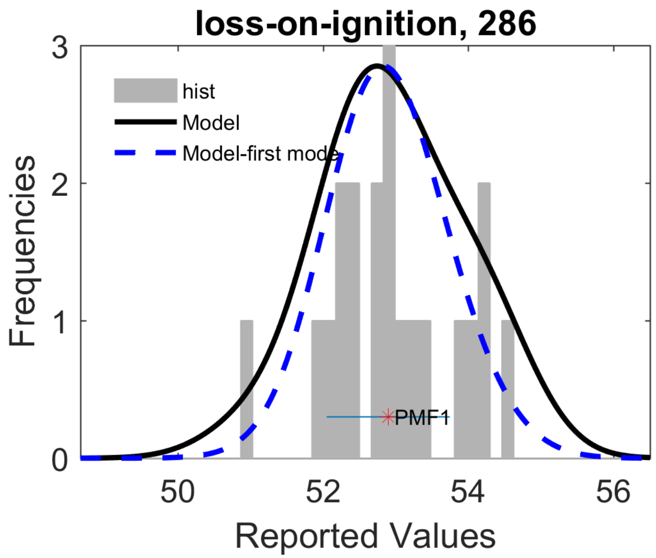
Code	Digestion/Extraction MARSEP Other Determinations
EA	Method exactly according to DIN 38414 S18
DS	Dry combustion temperature 500 degr.C
DT	Dry combustion temperature 550 degr.C
Z	Other (specify)

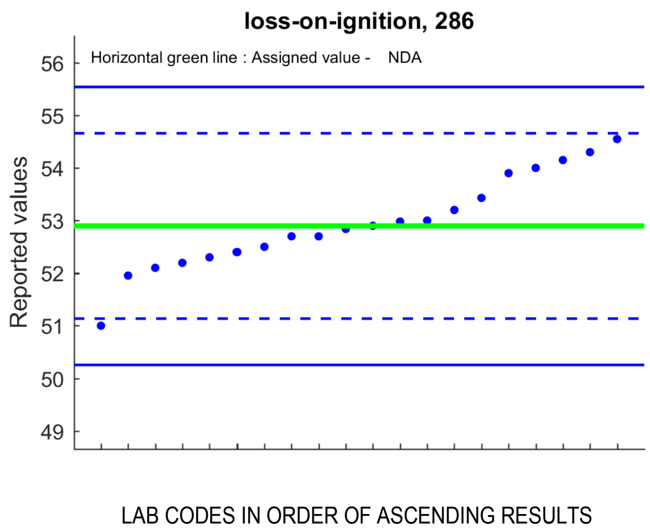
Code	Detection Other Determinations
T	Titrimetry/ coulometry
WG	Gravimetry
Z	Other (specify)

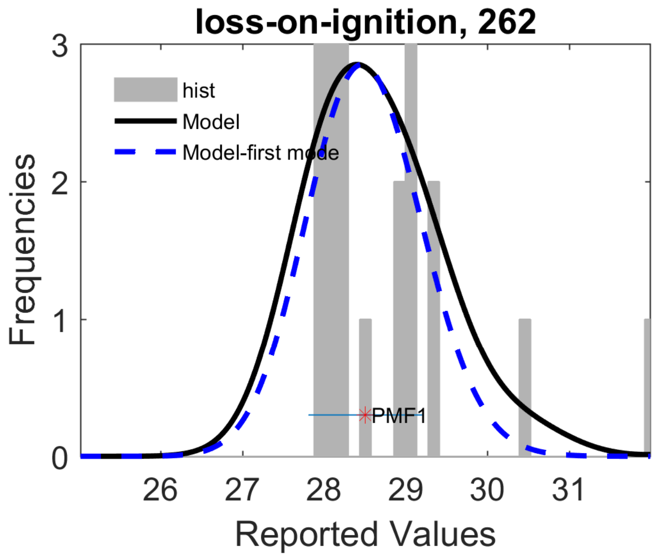
Other determinations Combined Zscores

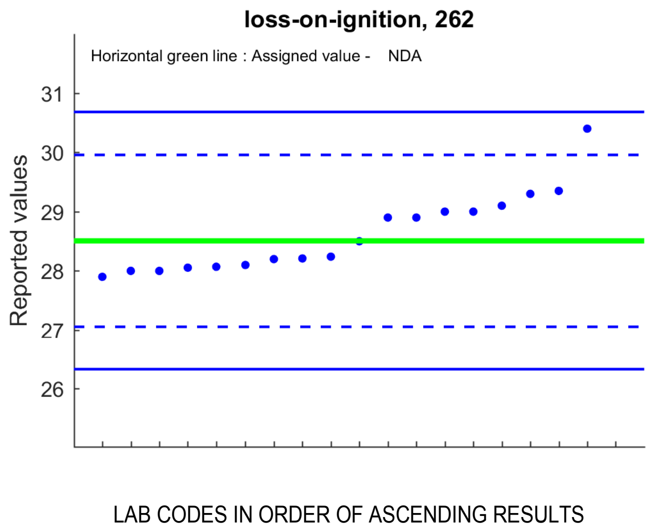


Other determinations Histogram+PDFs and Ranked overview

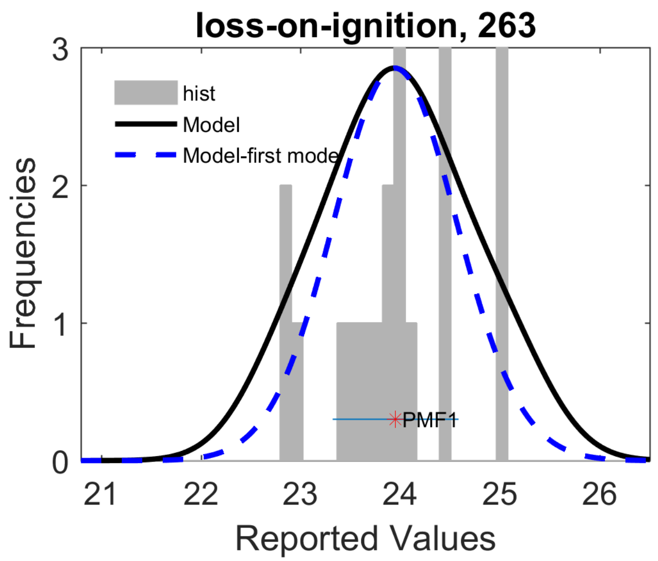


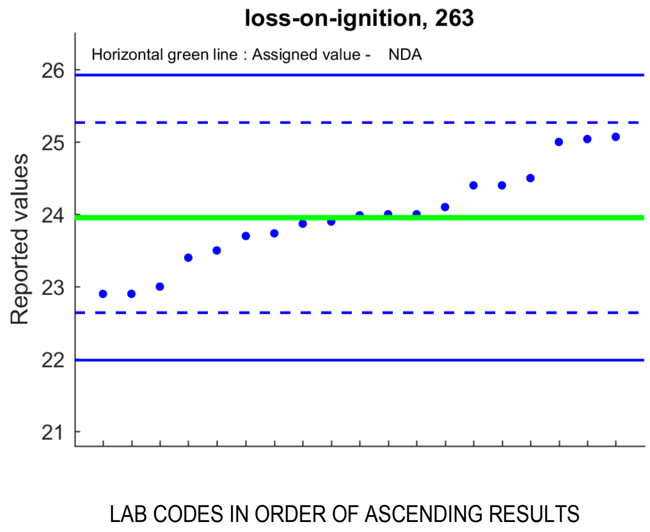


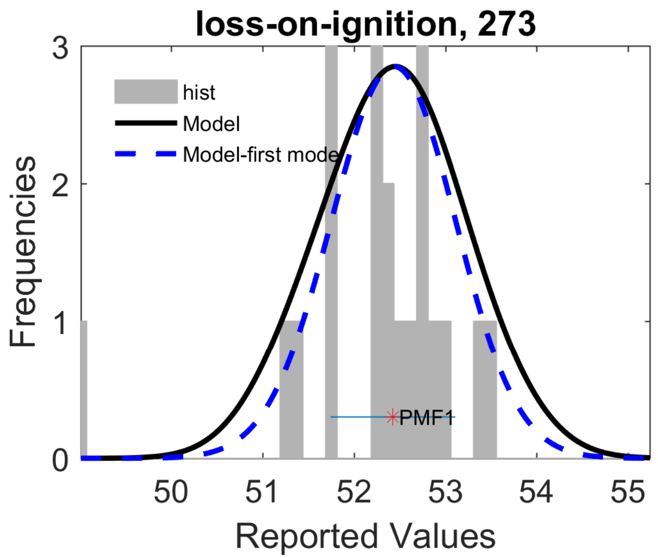


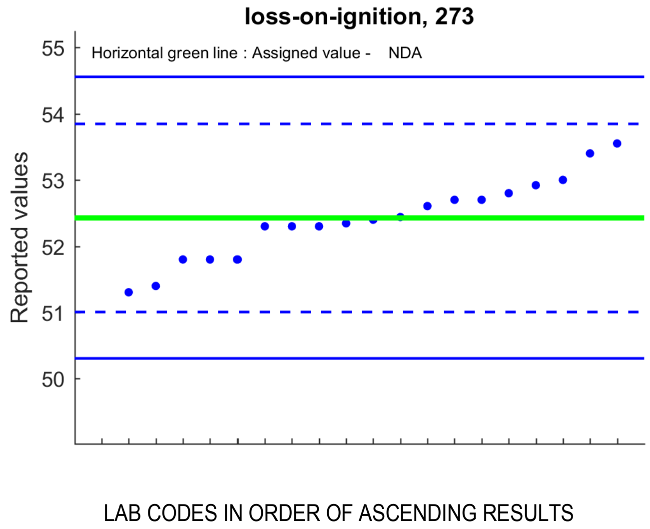


Other determinations Histogram+PDFs and Ranked overview









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