Worldwide Interlaboratory Comparison on the Determination of Trace Elements in Fish Sample IAEA-MESL-ILC-TE-BIOTA-2021

IAEA

International Atomic Energy Agency

WORLDWIDE INTERLABORATORY COMPARISON ON THE DETERMINATION OF TRACE ELEMENTS IN FISH SAMPLE IAEA-MESL-ILC-TE-BIOTA-2021

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INTERNATIONAL ATOMIC ENERGY AGENCY
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FOREWORD

The protection of the marine environment is a high priority worldwide. The identification of environmental pollution is based on monitoring campaigns that periodically assess the quality of seawater, marine sediments and biota samples. The reliability and comparability of analytical results produced in this context are crucial for the management of the marine environment in general, for example in taking decisions and meaningful actions related to remediation policies.

The IAEA provides support to Member States in the field of data quality and quality assurance by organizing interlaboratory comparisons and producing marine certified reference materials (biota and sediments), characterized for trace elements and the methyl mercury mass fractions.

Interlaboratory comparisons involve the comparison of participants' respective results to an assigned value, which is usually derived as a consensus value from the overall population of obtained results. Their design enables participating laboratories to monitor and demonstrate their measurement performance and analytical competence and, at the same time, allows them to identify existing gaps and problem areas where further improvement is needed.

This publication summarizes the results of the IAEA-MESL-2021-01-ILC-TE-BIOTA interlaboratory comparison on the determination of trace elements and methylmercury in fish sample organized in 2021.

The IAEA is grateful to the Government of Monaco for the support provided to its Marine Environment Laboratories as well as to the participants and laboratories taking part in this intercomparison exercise. The IAEA officers responsible for this publication were S. Azemard and E. Vasileva of the IAEA Marine Environment Laboratories.

CONTENTS

1 INTRODUCTION

1.1 BACKGROUND

The Marine Environmental Studies Laboratory (MESL) of the IAEA Marine Environment Laboratories (NAML) has the programmatic responsibility to provide assistance to Member States laboratories in maintaining and improving the reliability of analytical measurement results, both for trace elements and organic contaminants. This is accomplished through the provision of reference materials of marine origin, validated analytical procedures, training on the implementation of internal quality control, and through the evaluation of measurement performance via the organized worldwide and regional interlaboratory comparisons.

The results from the interlaboratory comparisons (ILCs) or proficiency tests (PTs) are of crucial importance for the participating laboratories as they provide clear information on their measurement capabilities.

1.2 OBJECTIVES

These exercises are designed to evaluate the measurement performance and analytical capabilities of participating laboratories, but also to identify existing gaps and problem areas where further development is still needed. Regular participation of laboratories in ILCs provides objective evidence of analytical performance for accreditation purposes.

1.3 SCOPE OF THE INTERLABORATORY COMPARISON

The present ILC was designed to evaluate the measurement performance of trace elements and methyl mercury (MeHg) in fish. In November 2020, invitation letters were sent to 307 laboratories from 87 Member States, which previously participated, or expressed interest in the participation to the IAEA ILCs. Positive responses with intent to participate were received from 123 laboratories in 59 Member States.

At the beginning of April 2021 each laboratory received one bottle of the test sample, accompanied by an information sheet and instructions on the use of the NAML online reporting system. Participants were requested to determine as many elements as possible from the following list: As, Cd, Co, Cr, Cu, Fe, Hg, MeHg, Mn, Ni, Pb, Se and Zn, using the analytical procedures routinely applied in their laboratories. The deadline for reporting reuslts was set at the end of October 2021.

Participating laboratories were requested to report their results for the ILC sample accompanied with standard and expanded uncertainties, description and results of internal quality control samples (e.g certified reference materials CRMs or other reference materials (RMs)), analyte recovery, detection and quantification limits (DL and QL respectively), digestion and instrumental technique used.

In addition, participating laboratories were requested to answer some questions on their analytical procedure, calibration, recovery correction, uncertainties estimation, moisture determination, validation of analytical method, CRM or RM used, quality procedures and accreditation.

In total, 78 laboratories from 48 Member States reported results back to the MESL. Despite several deadline extensions, about 40% of laboratories coud not report results mainly due to COVID related restrictions (i.e., work from home, lack of personel). Draft evaluation reports summarising performance results of each participating laboratory were available through the online platform from the beginning of November 2021.

The data submitted by the laboratories, together with the technical and statistical evaluations of the results for the requested trace elements, are included in this report. All results were treated confidentially, and each laboratory was identified with a unique confidential code number.

1.4 STRUCTURE

This publication is structured in five sections, section 1 being the introduction. Section 2 describes the test sample and the procedure applied for the calculation of assigned values. The individual performances assessment with z and Zeta-scores is explained in section 3 and obtained results are reviewed in section 4. Section 5 provides some conclusions on results obtained in this ILC.

2 DESCRIPTION OF ILC TEST MATERIAL

IAEA-MESL-2021-01-ILC-TE-BIOTA is a fish flesh homogenate sample from the North Sea. The raw test sample was freeze-dried, ground to powder, sieved at 250μm, then mechanically homogenized, and packed in sealed plastic containers.

Homogeneity test was performed at the MESL following the ISO/Guide 35:2017 standard guidelines [1], using preliminary validated analytical methods.

The assigned values were determined according to the requirements of the ISO/IEC 17043:2010 standard [2]. The assigned values were calculated as a robust means (ISO 13528:2015 [3]) from the results reported by the participants in this ILC and the results obtained at the MESL with preliminary validated analytical methods.

The assigned value has a direct impact on conclusions about the 'measurement capability' of the participating laboratories, and therefore, the most metrologically credible value should be sought. In this ILC, the assigned values were derived from participants results. Despite the use of robust statistics that helped dealing with a non-normal distribution (i.e., outliers) a preliminary review of the dataset was performed to ensure technical validity of results used in the calculation of consensus values.

RMs and CRMs play a critical role in assessing accuracy and comparability of results and are part of quality control strategies. Participating laboratories were requested to report results for their internal quality control sample (i.e., RMs or CRMs). All data reported without an internal quality control result were not retained for the calculation of assigned values (140 values rejected).

In addition, for Co, Cr and Pb with mass fraction close to the typical quantification limits of most of the instrumental techniques used in this exercise, it was decided to evaluate the quantification limits reported by participating laboratories. The mass fraction obtained for Co, Cr and Pb internally by MESL were used to set a first estimation of the mass fraction. Then Co, Cr and Pb values reported either with no estimation of quantification limit or with quantification limits not compatible with estimated MESL mass fractions were not included for the calculation of assigned values.

Therefore, 150 out of 657 reported measurement results were excluded, before applying the robust statistics calculations.

Expanded uncertainties (U) associated with the assigned values were estimated according to the ISO Guide 35:2017 [1], using Eq. (1).

$$U = k \times \sqrt{u_{char}^2 + u_{stab}^2 + u_{ho}^2} \tag{1}$$

where:

k: is the coverage factor; k=2, representing 95% level of confidence.

u_{hom} is the standard uncertainty, due to between units inhomogeneity, evaluated by analysis of variance (ANOVA) [1]

u_{stab} is the standard uncertainty, due to stability of the sample. Based on previous experience with similar sample matrices u_{stab} component was considered to have negligible contribution and was set at 0%.

u_{char} is the uncertainty of characterization, estimated according to the recommendations of the ISO Guide 35:2017 [1] using Eq. (2).

$$u_{char} = 1.25 \times \frac{s^*}{\sqrt{n}} \tag{2}$$

Where: s^* is the robust standard deviation and n is the number of measurement results.

All assigned values and expanded uncertainties obtained in this study are presented in Table 1. For Cr the expanded uncertainty was beyond 20% due to a lack of agreement between reported results. Therefore, the assigned value is given for information only and Cr will not be considered further in this ILC test sample.

TABLE 1. ASSIGNED VALUES AND UNCERTAINTY FOR THE ILC TEST SAMPLE

Element	Unit	Assigned value	Expanded uncertainty ($k=2$)
As	mg kg^{-1}	4.5	0.3
Cd	mg kg^{-1}	0.72	0.04
Co	mg kg^{-1}	0.059	0.007
*Cr**	*mg kg^{-1}*	*0.6*	*0.2*
Cu	mg kg^{-1}	3.9	0.2
Fe	mg kg^{-1}	140	15
Hg	mg kg^{-1}	0.122	0.005
MeHg	mg kg^{-1} as Hg	0.095	0.009
Mn	mg kg^{-1}	6.1	0.1
Ni	mg kg^{-1}	0.62	0.1
Pb	mg kg^{-1}	0.054	0.008
Se	mg kg^{-1}	3.0	0.3
Zn	mg kg^{-1}	102	8

Information value only

3   EVALUATION OF ANALYTICAL PERFORMANCE

The individual laboratory performance was expressed in terms of *z*-scores and Zeta-scores, in accordance with ISO/IEC 17043:2010 [2].

The determination of target standard deviation σ$_p$, for the proficiency assessment was based on the outcome of previous ILCs organized by the MESL for the same population of laboratories and similar sample matrices and was fixed to 12.5% of the assigned values. The appropriateness of this level of tolerated variability of results was confirmed by calculation of the robust standard deviation of the participant's results and the uncertainty of the assigned values for the respective measurands.

The *z*-score, which is calculated following the Eq. (3), defines the difference between the mean value provided by the laboratory and the assigned value, expressed in the units of the target standard deviation (σ$_p$).

$$z = \frac{x_{lab} - x_{ass}}{\sigma_p} \tag{3}$$

The Zeta-score, which is calculated following the Eq. (4), demonstrates the agreement of the results reported by participating laboratories with the assigned value within the respective uncertainties. The denominator in the Eq. (4) is calculated from the combined uncertainty of the assigned value and the combined uncertainty reported by the respective participant ($k=1$).

$$\text{Zeta} = \frac{x_{lab} - x_{ass}}{\sqrt{u_{x_{lab}}^2 + u_{x_{ass}}^2}} \tag{4}$$

where:

x_{lab} is the result reported by the participating laboratory (expressed as the mean of multiple determinations)

x_{ass} is the assigned value

σ_p is the target standard deviation

u_{xlab} is the combined uncertainty (k=1) reported by the participating laboratory

u_{ref} is the combined uncertainty (k=1) of the assigned value

As results were not all reported with associated combined and expanded uncertainties, the following measures were taken:

- If no uncertainties were reported at all, no Zeta-scores were calculated;
- If only expanded uncertainties were reported together with a coverage factor, combined uncertainties were calculated (by dividing expanded uncertainty by respective coverage factor) before the calculation of Zeta-score;
- Uncertainties reported as relative values were recalculated as absolute value before calculation of Zeta-score.

The interpretation of a laboratory's performance was evaluated according to the following internationally accepted limits [2]:

$$|\,z \text{ or Zeta}\,| \leq 2 \qquad \text{Satisfactory}$$
$$2 < |\,z \text{ or Zeta}\,| < 3 \qquad \text{Questionable}$$
$$|\,z \text{ or Zeta}\,| \geq 3 \qquad \text{Unsatisfactory}$$

4   RESULTS AND DISCUSSION

Seventy-eight sets of data for 13 elements were submitted by participating laboratories, comprising 641 numerical analytical results. Sixteen results were reported as less than the quantification limit.

Graphical representations of reported results, Kernel density plots [4] , z and Zeta-scores as well as short summary of statistical evaluation of the results are provided in the Appendix. Figures 1 and 3 summarize the overall performance as defined by z-score, by analyte and by participating laboratory respectively. Figure 2 and 4 summarizes the overall performance as defined by Zeta-scores by trace element and by participating laboratory respectively.

Table 2 and Table 3 show the overall performance as defined by *z*-score and Zeta-scores respectively by trace element. Table 4 shows the evaluation of the reported DL and QL versus the assigned mass fractions for trace elements in the test biota sample for results reported as less than quantification limits.

None of the participating laboratories reported the full list of 13 possible analytes. Seventy-five percent of the participating laboratories reported the obtained mass fractions results for Cd, Cu, Fe and Zn. With the exception of MeHg, all analytes were determined by at least half of the participating laboratories.

When compared with a previous ILC organized with a biota of marine origin [5] it can be observed that fewer participating laboratories reported results for Pb (58% versus 74%). This is not surprising since the concentration of Pb in the current ILC sample is more than 10 times lower to that of the sample in the previous ILC, and close or below typical quantification limits of some instrumental techniques used in this exercise (i.e., optical emission or atomic absorption). This might indicate the absence of developed method for low level of Pb in fish in some participant laboratories. Some of the participating laboratories are dealing with food analysis, and therefore use method validated for the determination of analytes at food safety regulatory levels which can be much greater than environmental concentrations. In the case of Pb in seafood, the maximum limit in EU regulation is about 20 times higher than in the ILC sample.

While 73% of participating laboratories did report results for total Hg, only 25% of them did perform the speciation of mercury in the ILC sample. This shows an increased measurement capability compared to the previous ILC organized in fish sample [5] (17%). The implementation of the Minamata convention [6], especially the article 19, should lead to increasing number of laboratories involved in the monitoring of mercury, including mercury species. The ongoing assistance provided to Member States involved in the implementation of Minamata convention should be continued.
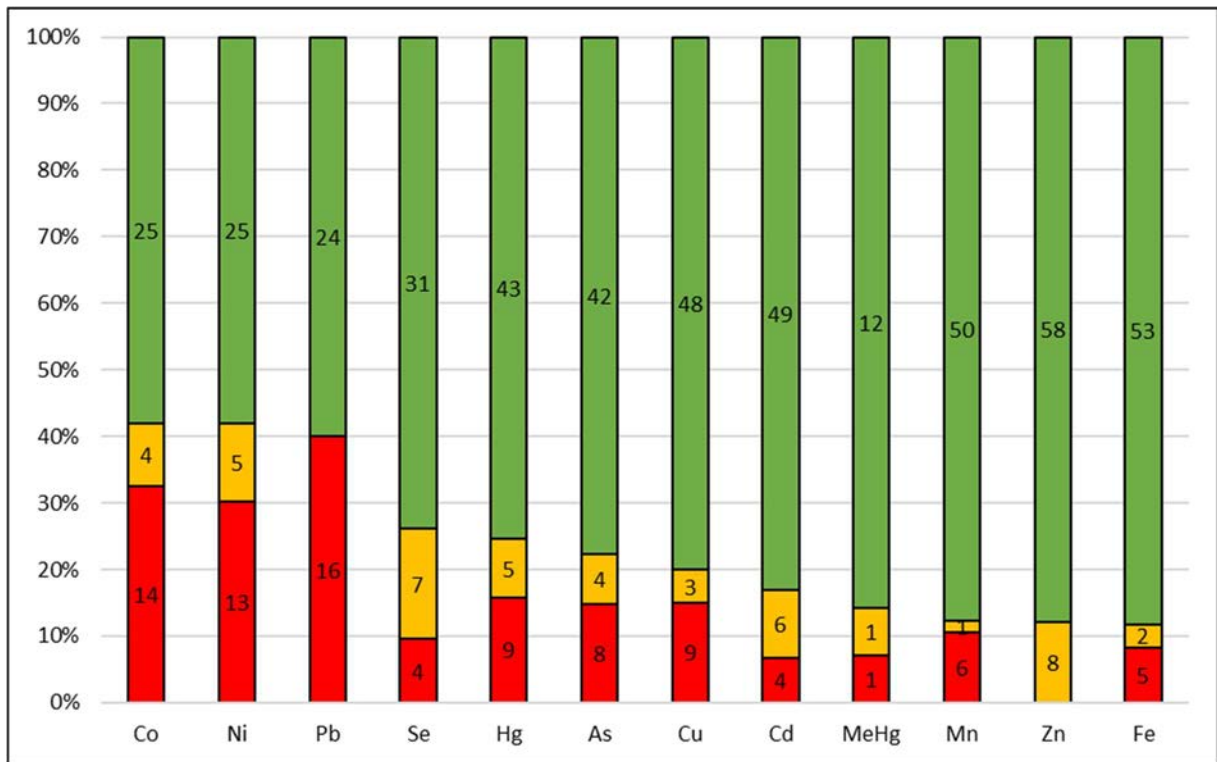
FIG. 1. z-scores calculated from the results reported by the participating laboratories for each trace element. Numbers provided in the bars are for participating laboratories.
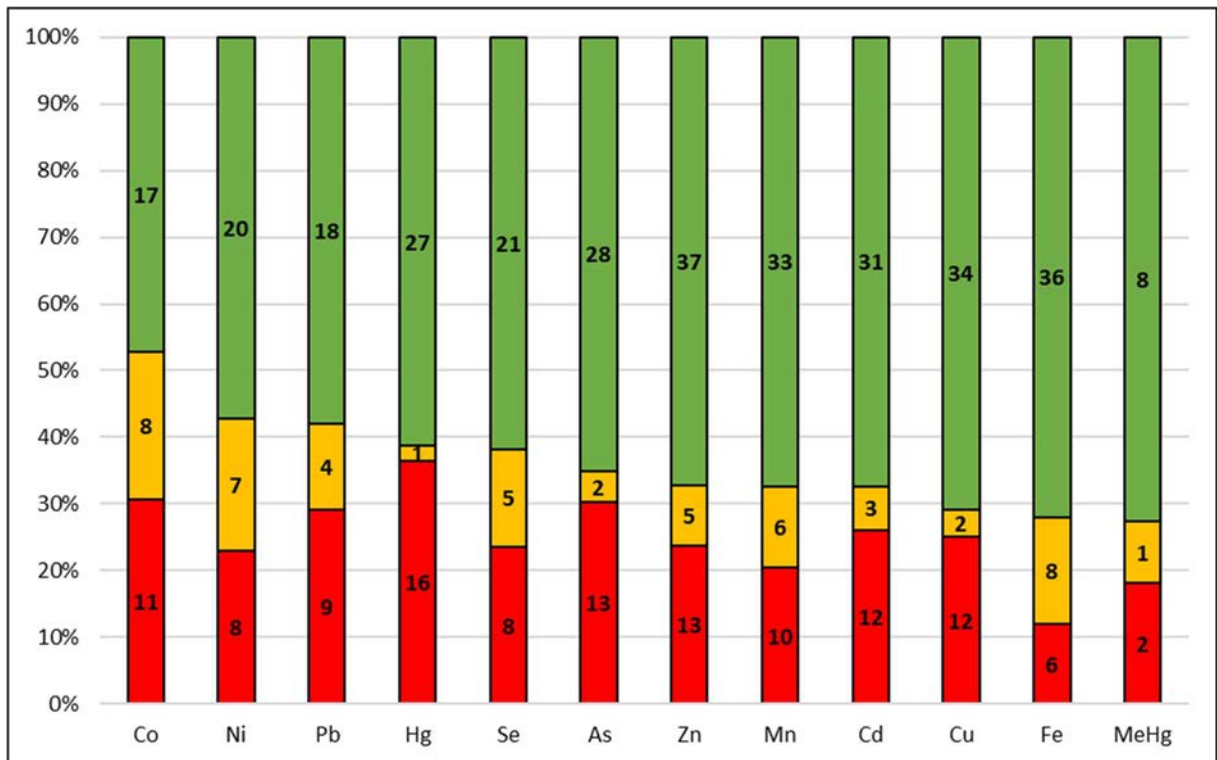
FIG. 2. Zeta-scores calculated from the results reported by the participating laboratories for each trace element. Numbers provided in the bars are for participating laboratories.

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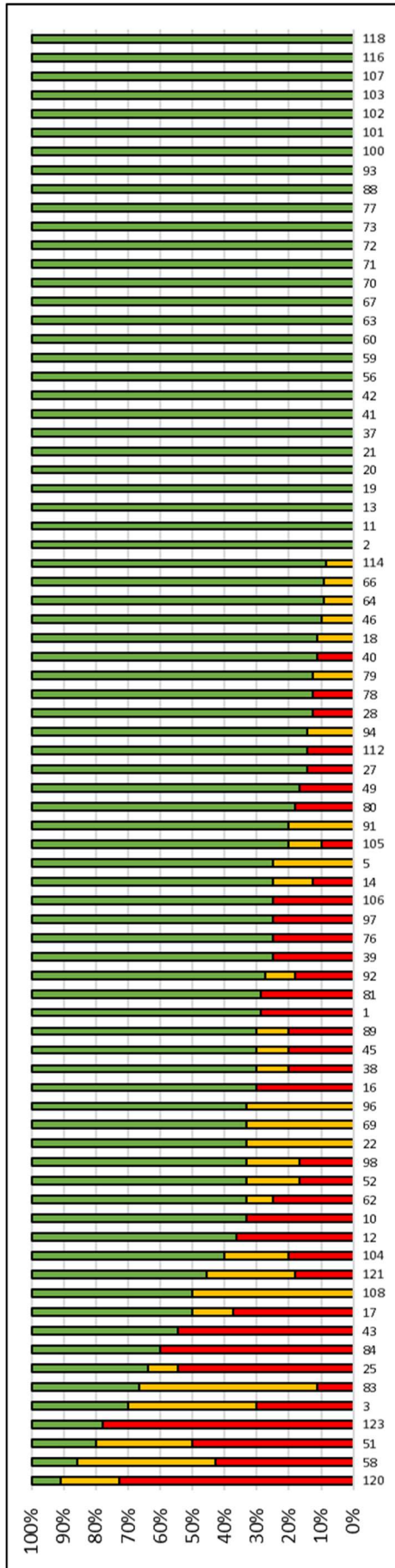
FIG. 3. z-scores calculated from the results reported by the participating laboratories per laboratory.

$|z| \geq 3$, $2< |z| <3$, $|z| \leq 2$
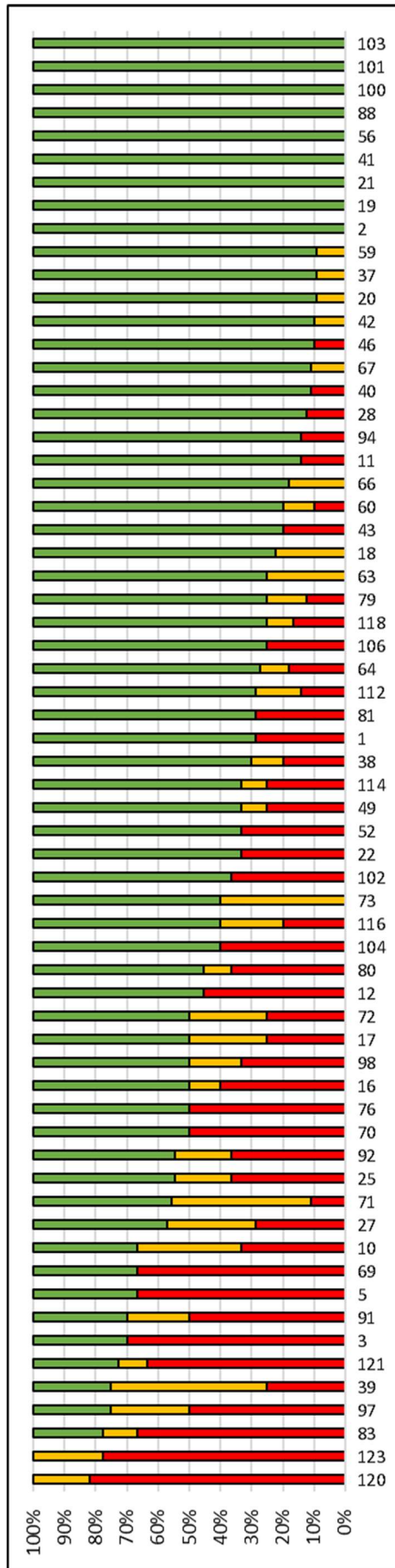
FIG. 4. Zeta-scores calculated from the results reported by the participating laboratories for each trace per laboratory.

$|Zeta| \geq 3$, $2< |Zeta| <3$, $|Zeta| \leq 2$

TABLE 2. OVERALL ASSESSMENT OF LABORATORIES PERFORMANCE (z-SCORE) BY TRACE ELEMENT*

Lab. Code	As	Cd	Co	Cu	Fe	Hg	MeHg	Mn	Ni	Pb	Se	Zn
1	-3.08	1.24		-0.41	-0.67	6920		-0.77				1.44
2						-0.70						
3	2.42	-2.57	13.38	2.21	0.63	2.40		1.61	12.82	10.37		1.39
5		-2.43		-0.79		-1.18						-1.68
10		0.58				-0.83				201.88		
11	0.24		-1.05		-0.34	1.38	0.53				-0.39	0.24
12	0.37	-0.22	4.43	5.32	-0.95	0.02		-1.85	8.34	-0.84	3.55	-0.10
13	0.09	0.69		0.02		0.15			-0.06	-1.43	-0.64	-0.62
14	-1.24	2.33		-3.75	0.40	-0.20		-0.16			-0.80	-0.25
16	0.36	0.83	-7.10	0.63		0.07		1.24	9.38	4.05	1.50	-0.05
17		1.06		0.94	-0.80	7.48		-0.96	3.17	61.48		2.98
18	-0.47	0.04		0.55	-1.22	-0.11		-0.33	2.23		-0.68	0.21
19	-0.83		0.54		-0.08			-0.39			0.58	-0.08
20	0.49	0.65	-1.47	-0.52	-0.97	-0.29		-0.26	-1.65	-0.80	-0.79	-0.36
21		0.72		0.12	-0.06	-0.04						
22	-0.30										-2.19	0.05
25	0.62	-0.22	3.93	1.09	6.23	53.20		4.63	49.68	109.53	-2.60	-0.97
27	-1.88		7.53	0.22	-1.03	1.11		-1.03				-0.91
28	-7.10	1.79		0.35	-1.16	-1.51		-1.86	1.13			0.67
37	-0.55	0.70	-1.49	-0.75	-0.25	-0.09		-0.16	-1.51	-0.44	-0.27	-0.16
38	-4.90	2.00	-0.72	-0.16	0.39	-1.09		-0.60	4.20	0.59		0.18
39				3.74	-1.12			0.94				-0.32
40	-0.83	0.59	3.98	-0.64		0.15	1.09	0.70			-0.18	0.97
41						-0.68	0.67					
42	1.13	0.67	0.68	0.48	-0.55	0.24		0.39	0.99		0.36	-0.08
43	-0.41	7.78	3.39	16.21	3.09	-0.13		0.48	37.03	70.02	0.81	0.99

* | z | ≥ 3,   2< | z | <3

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TABLE 2. OVERALL ASSESSMENT OF LABORATORIES PERFORMANCE (z-SCORE) BY TRACE ELEMENT (cont.)*

Lab. Code	As	Cd	Co	Cu	Fe	Hg	MeHg	Mn	Ni	Pb	Se	Zn
45	-3.28	-0.84	3.84	0.36	-0.53	-0.02		-0.92	-2.97	0.69		0.18
46	0.92	0.68	-1.57	-0.69	-0.79			-0.59	0.24	0.01	2.95	-0.43
49	0.95	1.37	-0.63	-0.21	-0.38			1.57	1.12	-1.43	0.98	0.63
51	-2.50	-2.20	-6.28	-5.71	-1.87	6855.39	7739.37	-5.03	6.93	22.57	-2.76	-1.29
52	5.99				-0.34	2.27		-0.22			0.89	0.00
56						-0.02						
58	3.32	-1.70		7.18	2.18	7948.94					2.67	2.55
59	-0.96	-0.47	1.63	0.12	0.03	-1.01		0.95	-1.38	-0.94	-0.05	-0.18
60	0.03	-0.06		-0.68	1.39	-1.77		0.38	0.80	-1.90	-0.01	-0.29
62	0.56	0.07	2.31	-0.23	4.13	0.13	-0.36	0.04	3.70	5.06	-0.83	-1.78
63	-0.08	-0.55	-1.30	0.14	-0.24	0.24	1.57	0.12	-0.34	0.76	-1.07	0.10
64	0.77	1.23	0.50	0.42	0.68	-2.05		0.89	-0.57	-0.79	1.46	0.62
66	0.83	0.58	-1.42	-0.50	-0.32	0.37		0.34	-2.37	-0.28	0.28	0.03
67	0.27	0.60	-0.41	-0.40	-1.02			0.35	-0.77	1.19		0.50
69				0.19	-1.79							-2.43
70						-1.13	-0.31					
71		-0.33	1.27	0.08	-1.35			-0.53	-1.55	-1.38	-1.52	-0.57
72				-1.50	-1.28	0.09						-0.85
73	0.30	0.16			-0.19			0.70				0.67
76		-2.00	-0.77	-3.34	-0.14		-0.42	-3.35	-0.86			1.37
77						0.13	1.18					
78	-0.40	-1.00	-0.99	-0.72	-0.29			-0.79	-4.57			-0.67
79	0.60	0.97	2.71	0.27				0.40		0.25	0.64	0.38
80	0.95	0.83	6.73	0.12	0.26	-0.33		1.01	1.45	10.52	-0.45	1.04
81	-4.48	0.53		-0.69	0.40	7205.11		-1.23				0.31
83	-0.78	-2.66		-2.67	-2.72	-2.16		-0.59	-1.93		-3.07	-2.19

* $|z| \geq 3$ (red), $2 < |z| < 3$ (orange)

TABLE 2. OVERALL ASSESSMENT OF LABORATORIES PERFORMANCE (z-SCORE) BY TRACE ELEMENT (cont.)*

Lab. Code	As	Cd	Co	Cu	Fe	Hg	MeHg	Mn	Ni	Pb	Se	Zn
84		-0.03		-4.50	31.31	10.71						-0.42
88	0.71	0.20	-0.81	-0.38	0.84		-0.02	1.04	-0.99	0.30	0.05	-0.24
89	-0.70	75.33	-2.58	-0.67		-0.09		-0.51	0.04	1.38	26.80	-0.80
91	-1.03	-0.83	-1.13	-0.96	-0.95			0.05	-1.01	-1.19	-2.18	-2.99
92	2.58	0.49	3.80	0.44	-0.84	-1.62		0.11	1.88	5.43	-0.92	0.13
93			-0.68		1.96							
94		-0.71		-0.71	0.61			-0.87	0.13		-0.57	-2.56
96	-1.35	-0.94				-2.49				-0.59		0.00
97			6.92	2.19	1.11			1.10				
98	-0.71							-3.14			-0.05	-0.57
100						-0.33						0.50
101	1.14	0.89		0.59	1.19	-0.61		0.69				0.34
102	1.24	-1.65	-0.55	-0.17	0.25	-0.81		0.96	-0.88	-1.03	0.52	
103			1.81		-0.34			0.41				-1.28
104	-0.77	-0.88		1.09	0.40				3.27			2.85
105	-0.42	-1.01	-1.90	-0.23	-1.69			-0.49	2.84	12.59	-0.09	0.01
106	-1.20	-0.04				-0.79				3.41		-1.34
107		-0.92		-0.81	-0.51	-0.52		-0.23		-0.79	0.59	
108						1.09	-2.47					
112	0.24	-1.41		-0.25	-0.32	-0.46		0.11		25.58	0.33	0.42
114	-0.36	-0.70	-0.14	-0.02	0.82	1.01	-1.56	2.68	0.00	1.04		1.10
116	0.18	0.00	-1.22	1.96	-1.49	0.45	-0.10	-0.71	-1.12			0.59
118		0.77	-1.99	-0.82	-1.03	-0.13	-1.26	-0.17	-0.20	-0.40	0.91	1.31
120	-5.91	-7.87	-7.32	-1.76	-4.54	-5.64		-5.40	-7.31	-5.02	-2.97	-2.45
121	-2.94	-0.54	-2.44	-1.35	-1.07	-0.63		0.13	-2.99	4.30	-4.80	-1.40
123		12.44	241.94	4.90	1.03	-7.93		41.73	5.37	490.27		-0.98

* $|z| \geq 3$, $2 < |z| < 3$

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TABLE 3. OVERALL ASSESSMENT OF LABORATORIES PERFORMANCE (ZETA-SCORE) BY TRACE ELEMENT*

Lab. Code	As	Cd	Co	Cu	Fe	Hg	MeHg	Mn	Ni	Pb	Se	Zn
1	-3.41	0.67		-0.44	-0.73	5.26		-1.01				0.99
2						-0.70						
3	0.70	-11.55	3.16	6.17	1.38	4.05		0.91	14.77	3.13		3.74
5		-6.06		-1.54		-0.52				45.02		-4.87
10		2.33										
11	0.60		-1.77		-0.67		1.05				-0.79	0.53
12	1.37	-0.99	8.10	24.08	-1.92	3.23		-6.19	12.52	-1.27	7.38	-0.29
13						0.11						
14												
16	0.96	3.68	-3.89	0.39	-0.93	0.05		4.65	3.53	1.17	2.84	-0.15
17		1.13		1.02	-2.22	4.72		-1.27	2.44	8.80		2.61
18	-0.89	0.06		0.99	-0.13	-0.18		-0.63	2.23		-1.15	0.39
19	-1.39		0.66					-0.54			0.84	-0.14
20	0.71	0.94	-0.30	-0.86	-1.43	-0.48		-0.41	-2.06	-0.15	-1.18	-0.55
21		1.45		0.22	-0.10	-0.06						
22	-0.47										-3.39	0.05
25	0.59	-0.67	1.36	0.99	3.94	11.58		7.90	5.12	2.11	-2.69	-1.14
27	-4.82		1.84	0.87	-2.39	5.31		-1.15				-2.62
28	-23.82	1.95		0.39	-1.32	-1.51		-1.97	0.78			0.99
37	-1.37	1.97	-2.73	-1.52	-0.27	-0.28		-0.41	-1.77	-0.60	-0.55	-0.39
38	-12.58	2.04	-0.87	-0.17	0.40	-1.99		-1.02	3.55	0.37		0.22
39			4.22	5.01	-2.54			2.19				-0.97
40	-1.39	0.83		-1.12	-0.77	0.18	0.63	1.15			-0.23	0.98
41						-1.23	0.96					
42	2.45	1.55	0.90	0.97		0.00		0.78	0.78		0.60	-0.13
43			0.00		3.22			0.02			0.02	1.45

* |Zeta| ≥ 3, 2< |Zeta| <3

TABLE 3. OVERALL ASSESSMENT OF LABORATORIES PERFORMANCE (ZETA-SCORE) BY TRACE ELEMENT (cont.)*

Lab. Code	As	Cd	Co	Cu	Fe	Hg	MeHg	Mn	Ni	Pb	Se	Zn
45												
46	1.84	1.06	-1.90	-0.74	-1.70			-1.14	0.29	0.01	5.46	-1.02
49	2.51	1.59	-0.05	-0.71	-0.89	1393.16	1223.20	5.62	0.78	-0.10	1.85	2.00
51												
52	18.67				-0.67	3.36		-0.39			1.85	0.00
56						-0.01						
58												
59	-0.84	-0.54	2.81	0.08	0.03	-0.66		0.64	-1.58	-0.91	-0.03	-0.16
60	0.05	-0.12		-1.40	1.96	-4.35		0.66	0.90	-2.35	-0.01	-0.58
62												
63	-0.25	-1.97	-2.08	0.49	-0.51	0.66	2.77	0.42	-0.45	1.14	-2.35	0.27
64	0.53	5.52	0.71	1.00	1.57	-1.17		2.28	-0.19	-0.43	3.60	1.98
66	1.26	1.06	-2.34	-0.90	-0.40	0.76		0.74	-2.92	-0.40	0.35	0.03
67	0.97	2.38	-0.56	-1.69	-1.84			0.94	-0.75	0.81		1.18
69				0.15	-3.21	-5.37						-6.70
70							-0.58					
71		-1.20	2.02	0.27	-2.55			-1.43	-2.06	-2.09	-3.53	-1.52
72				-5.98	-1.21	0.24						-2.55
73	0.76	0.43			-0.41			2.47				2.08
76		-4.99	-0.14	-14.55	-0.34		-0.03	-12.64	-1.04			4.37
77												
78												
79	3.28	1.08	11.55	0.48	0.46	-0.60		2.46	1.63	11.09	-1.01	3.02
80	1.40	3.31	2.56	0.97				1.02		0.10	0.55	0.85
81	-6.67	0.31		-0.76	0.39	5.26		-1.70				0.24
83	-1.76	-8.46		-8.76	-5.44	-5.90		-1.28	-2.74		-6.57	-4.93

* | Zeta | ≥ 3, 2< | Zeta | <3

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TABLE 3. OVERALL ASSESSMENT OF LABORATORIES PERFORMANCE (ZETA-SCORE) BY TRACE ELEMENT (cont.)*

Lab. Code	As	Cd	Co	Cu	Fe	Hg	MeHg	Mn	Ni	Pb	Se	Zn
84												
88	1.19	0.30	-1.13	-0.66	0.98		-0.02	1.39	-0.91	0.19	0.08	-0.40
89												
91	-3.10	-3.22	-2.07	-4.36	-2.12			0.13	-1.49	-0.99	-4.93	-8.52
92	8.55	1.17	5.27	0.77	-1.73	-6.32		0.28	2.81	4.10	-2.21	0.37
93												
94		-0.88		-0.52	0.67			-1.49	0.13		-0.80	-5.29
96	-3.14											
97			7.34	4.79	2.03			2.07				
98	-1.60							-8.46			-0.08	-1.70
100						-0.77						
101		0.87		0.56	1.15	-0.73		0.82			1.31	0.84
102	4.27	-7.41	-1.00	-0.82	0.58	-4.70		3.37	-1.25	-1.33		1.08
103	0.94	-0.57	1.26		-0.46			1.14				-1.92
104				3.81	0.87				0.84			9.08
105												
106	-1.04	-0.11				-1.07						
107												
108										3.59		
112		-5.74		-0.68	-0.61	-1.57		0.36	0.00			1.23
114	0.52	-1.76	-0.25	-0.05	0.85	3.93	-3.42	3.99		2.24	0.53	2.52
116	-1.06	0.00	-2.57	7.42	-3.41	1.89	-0.21	-2.46	-1.66	0.48		1.86
118	0.45	1.64	-3.18	-2.32	-1.44	-0.15	-1.26	-0.28	-0.22	-0.37	0.99	3.33
120	-9.18	-35.26	-14.83	-2.72	-8.70	-4.73		-10.92	-10.67	-5.29	-2.13	-5.89
121	-7.25	-0.91	-5.08	-6.50	-2.39	-1.03		0.42	-4.64	3.24	-9.89	-4.34
123		12.42	19.75	21.92	2.38	-3.00		32.62	6.46	48.37		-3.07

* | Zeta | ≥ 3, 2< | Zeta | <3

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TABLE 4. EVALUATION OF THE REPORTED DL AND QL VERSUS THE ASSIGNED
MASS FRACTIONS FOR TRACE ELEMENTS

Lab code	Analyte	Reported DL (mg kg^{-1})	Reported QL (mg kg^{-1})	Assigned Value (mg kg^{-1})	Evaluation
1	Pb	0.2	0.5	0.054	C
28	Pb	1.65	5	0.054	C
39	Cd	1.5	5	0.72	C
39	Ni	2	6	0.62	C
39	Pb	2	6	0.054	C
42	Pb	0.05	0.15	0.054	C
72	Mn	2.2	7.3	6.1	C
81	Pb	0.2	0.5	0.054	C
89	Fe	0.8		140	NC
98	Cd	4	12	0.72	C
98	Co	1	3	0.059	C
98	Hg	2	6	0.122	C
98	Ni	1	3	0.62	C
98	Pb	1	3	0.054	C

*C: Consistent (Reported DL and QL > Assigned values) NC: Not Consistent (Reported DL and QL > Assigned values)

4.1 z-SCORES

The z-scores compare the participating laboratories deviation from the assigned value with the target standard deviation σ_p for proficiency assessment. σ_p was set up by the ILC organizer to 12.5 %, so the maximum acceptable deviation ($|z| \leq 2$) was 25% of the assigned value.

As indicated in section 2, z-scores could only be calculated for 12 out of 13 analytes reported as no assigned value was derived for Cr. As a result, out of the 78 datasets received from participating laboratories totaling 641 numerical results, 595 z-scores were calculated. From these 595 calculated z-scores, 77% were considered to be satisfactory with $|z| < 2$, and 15% were considered to be unsatisfactory with $|z| > 3$.

Among the 78 participating laboratories, 27 (36% of participants) achieved satisfactory z- scores $|z| \leq 2$ for all their reported values. On the other hand, 9 participating laboratories (12% of participants) had more than half of their results considered as unsatisfactory ($|z| \geq 3$). The overall results were similar to the results observed in our previous ILC organized in 2017 with the same sample matrix [5].

As shown in Figure 1 the proportion of acceptable results per analytes was 58% or better for all evaluated trace elements. Co, Ni, and Pb appeared to be the analytes reported with the highest proportion of unsatisfactory z-scores. This indicates that the accurate determination of those elements in the ILC test sample was challenging, probably due to their low mass fraction. Indeed, as seen in Figure 5, a large proportion of unsatisfactory z-scores observed were positive

(showing over estimation), for analytes in the ng g^{-1} concentration range. A possible reason for positive bias, especially for analytes with low concentration could be contamination during sample preparation or instrumental analysis. Participating laboratories receiving *z*-scores greater to 3 are encouraged to look for possible source of contamination in their laboratory (water, acid, sample containers, cleaning procedure...). The estimation of the quantification limits of method using procedural blanks could also be beneficial in case of results showing overestimation of the results.

The use of non-validated analytical procedure can also be a reason for unsatisfactory results. This view is underpinned from the results provided by laboratories using or not CRMs to validate their analytical method. Indeed, 27% of results reported by participating laboratories not using CRMs were evaluated as unsatisfactory. In comparison, laboratories which use CRMs in their procedures, had less than half (12%) of unsatisfactory reported results.

Participating laboratories with results assessed as questionable and/or unsatisfactory with *z* - scores are encouraged to carefully check laboratory procedures and working instructions applied. It should be noted that few results received extremely high z-scores (>100) probably due to erroneous units or calculation errors.
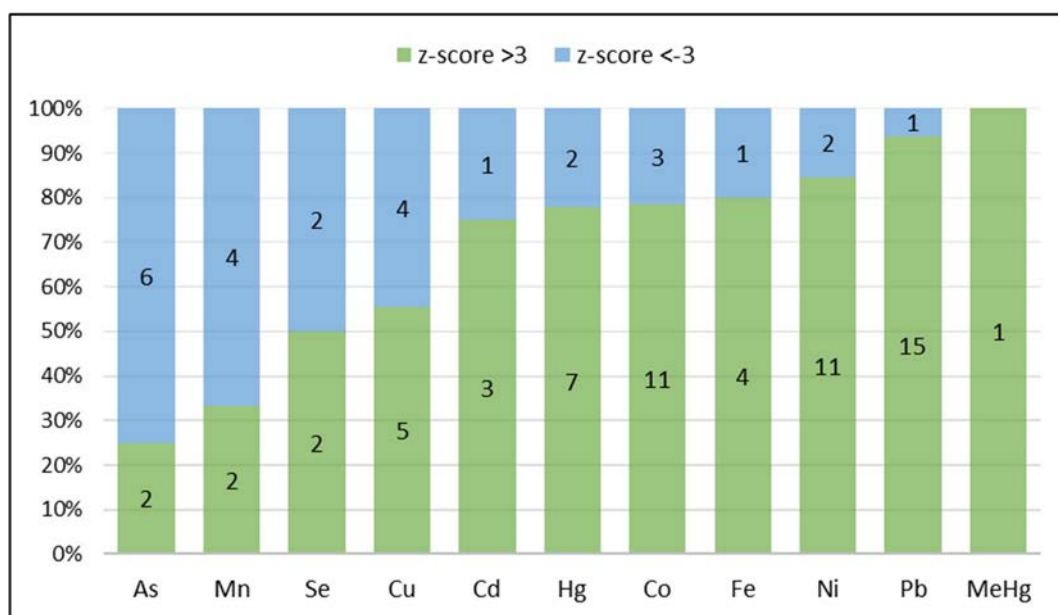
FIG. 5. Distribution of z-scores.

4.2   ZETA-SCORES

The Zeta-score shows the agreement of laboratory result with the assigned value considering the respective uncertainties. The denominator in Eq. (4) includes combined uncertainties of the assigned value and the reported values by the participating laboratories.

Seventeen participating laboratories in the ILC (22%) did not report uncertainties with their reported values and Zeta-scores could therefore not be calculated. The proportion of participating laboratories not providing uncertainties as part of their results is comparable to a previous ILC [5].

As it can be seen on Figures 1 to 4, the comparison of measurement performances evaluated with z-score and Zeta-score clearly indicate that the number of unsatisfactory Zeta-scores is higher than the number of unsatisfactory z-scores (15% of calculated z-scores and 25% of calculated Zeta-scores). Nine participating laboratories (11% of all participating laboratories) reported values which were evaluated as 100% satisfactory with both $\left|z\right|$ and $\left|\text{Zeta}\right| \leq 2$.

About half (46%) of values rated as unsatisfactory based on Zeta-scores were also rated as unsatisfactory using z - scores evaluation. An unsatisfactory Zeta-score can be explained as for z-score by an inaccurate result and participating laboratories reporting values receiving $\left|z\right|$ and $\left|\text{Zeta}\right| > 3$ are encouraged to review their analytical procedures, as already mentioned in 4.1.

As Zeta-scores include the estimation of uncertainties, values receiving $\left|\text{Zeta}\right| > 3$ while $\left|z\right| < 3$ could indicate an underestimation of uncertainties. Indeed the 42 values receiving satisfactory z-scores and unsatisfactory Zeta-scores were all reported with uncertainties less than 5%. Out of these, about 30% were reported with standard uncertainty estimated from the standard deviation of replicate determination. In general, laboratories should keep in mind that uncertainties based on the precision of measurement results (standard deviation) are frequently underestimated. In many cases, they just reflect variations coming from the measurement step and usually do not include the contribution of uncertainty coming from other major contributors like recovery, procedural blank, moisture content etc.

4.3   ANALYTICAL METHODS

Table 5 is showing the wide range of analytical methods applied by participating laboratories in this ILC along abbreviations used in this report.

Table 6 shows the distribution of values reported by different techniques as well as the number of participating laboratories being equipped with each instrumentation. Analytical methods used by participating laboratories in this ILC can be divided to three groups: nondestructive techniques (neutron activation (NAA), X-ray Fluorescence spectrometry (XRF)); plasma spectrometric methods (inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES)) and atomic absorption spectrometry methods. The most used instrumental method was ICP-MS, which accounted for 57% of reported values and was used by 47% of the participating laboratories.

Table 5: INSTRUMENTAL TECHNIQUES USED IN IAEA-MESL-ILC-TE-BIOTA-2021 AND THEIR ABBREVIATIONS

Method abbreviation	Instrumental Techniques description
AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectrometry
CV	Cold Vapour
ET	Electro Thermal atomisation
F	Flame atomisation
GC	Gaz Chromatography
HPLC	High Performance Liquid Chromatography
Hyd	Hydride Generation
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
NAA	Neutron Activation (or Instrumental neutron activation)
Volt	Voltammetry
XRF	X-ray Fluorescence Spectrometry

TABLE 6. DISTRIBUTION OF THE INSTRUMENTAL METHODS APPLIED IN THE ILC

Instrumental Method	% of Reported values	Number of participating laboratories
ICP-MS	56.6%	37
F-AAS	8.3%	17
ET-AAS	7.0%	11
ICP-OES	6.7%	10
XRF	5.4%	6
NAA	5.1%	7
Solid-AAS	3.2%	18
CV-AAS	2.7%	17
Not reported	1.9%	1
CV-AFS	1.4%	9
Hyd-AAS	1.3%	6
GC-AFS	0.6%	4
Volt	0.5%	1
HPLC-ICPMS	0.3%	2
Hyd-AFS	0.3%	1
CV-ICP-MS	0.2%	1
GC ECD	0.2%	1

The share of *z*-scores in each category (satisfactory, questionable, or unsatisfactory) for values reported using most common analytical methods are presented in Figure 6, along with the number of values. Highest proportion of values rated as unsatisfactory ($|z| > 3$) are obtained by participating laboratories using ET-AAS and XRF.
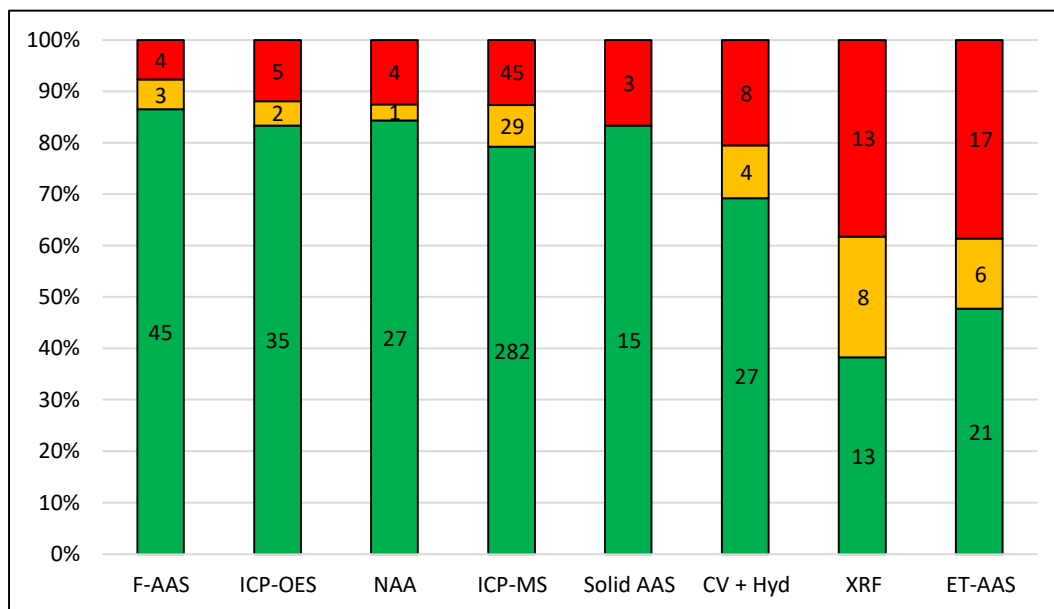
FIG 6: z-scores per instrumental methodologies ($|z| \geq 3$, $2 < |z| < 3$, $|z| \leq 2$)

Some methodologies (CV, Hyd, Solid AAS, HPLC, GC) are specific to some analytes (As, Hg and MeHg) explaining why they represent less than 5% of total reported values (Table 6). The percentage of values reported per different techniques along the share of unsatisfactory *z*-scores for those analytes are shown in Tables 7 to 9.

ICP-MS is the most used analytical technique by participating laboratories measuring arsenic in the ILC sample. All values obtained by ICP-MS, ICP-OES and NAA were assessed as satisfactory. On the other hand, some of the values obtained with analytical methodology based on hydride generation were not satisfactory and most of them were lower than assigned value. This could be linked to the incomplete digestion of arseno-betaine, which is needed to get accurate results when hydride techniques are applied.

For mercury, the use of solid mercury analyzers is the most popular technique followed by CV - AAS. As already observed in previous ILCs, values reported using solid mercury analyzers are all assessed as satisfactory, confirming that this technique is an adequate methodology to be applied for mercury determination in samples with low concentration. The absence of a sample preparation step is a major benefit, especially at trace level to avoid potential contamination.

The speciation of mercury was performed mainly with chromatographic methods often involving some derivatization steps. With the exception of one value reported with an

erroneous unit, all applied methodologies produced satisfactory results. Two participating laboratories measured MeHg using non-specific instrumentation, but specific extraction of organic mercury combined with a solid mercury analyzer.

TABLE 6. INSTRUMENTAL METHODS APPLIED FOR DETERMINATION OF As MASS FRACTIONS IN THE ILC

Instrumental Method	% of reported values	% of $|z|>3$
ICP-MS	61%	0%
Neutron Activation	11%	0%
Graphite Furnace AAS	7%	50%
Hydride AAS	7%	75%
XRF	7%	50%
ICP-OES	4%	0%
Hydride AFS	2%	100%

TABLE 7. INSTRUMENTAL METHODS APPLIED FOR DETERMINATION OF Hg MASS FRACTIONS IN THE ILC

Instrumental Method	% of reported values	% of $|z|>3$
Hg Solid-AAS	32%	0%
Cold Vapor AAS	30%	12%
ICP-MS	19%	9%
Cold Vapor AFS	11%	0%
Hydride AAS	4%	0%
Cold Vapor ICP-MS	2%	0%
Not reported	2%	0%
XRF	2%	100%

TABLE 8. INSTRUMENTAL METHODS APPLIED FOR DETERMINATION OF MeHg MASS FRACTIONS IN THE ILC

Instrumental Method	% of reported values	% of $|z|>3$
GC-CV-AFS	64%	11%
HPLC-ICPMS	14%	0%
Hg Solid-AAS (organic Hg)	14%	0%
GC-ECD	7%	0%

4.4 QUESTIONNAIRE AND OTHER VALIDATION PARAMETERS

As explained in 1.3, participating laboratories were requested to complete a questionnaire in addition to submitting results. Only 85% of participating laboratories actually returned filled questionnaires and most of them did not answer all requested questions. Participating laboratories that did not complete the questionnaire are encouraged to do so in future exercises as responses are helpful in the interpretation of results.

Only 4 participating laboratories declared to being accredited to ISO/IEC 17025:2017 [7], and only one laboratory stated that the determination of trace elements in biota samples was on their scope of accreditation.

Thirteen participants reported having a quality system in place, but not all of them provided analytical results from the analysis of CRMs, and only some of them declared using validated methods. A quality system describing internal quality control procedures (i.e., control charts, use of CRMs, validation reports...) is helpful to assure the quality of results produced by a laboratory. Participating laboratories are encouraged to include the regular use of internal quality control in their quality system.

Thirteen participating laboratories (17%) did not report results for CRM analyzed as part of their internal quality control as requested in the reporting form. This was already observed in previous ILC [5]. It could be due to the lack of appropriate CRM availability in the participating laboratories. The regular use of a CRM as part of the internal quality control process is one way to ensure the quality of results produced in a laboratory as recommended under ISO/IEC 17025:2017 [7]. Participating laboratories not analyzing CRMs on a regular basis with their test samples are therefore encouraged to do so. An important principle for the selection of appropriate reference materials by laboratories is the principle of matrix and concentration range matching. CRMs used in this interlaboratory comparison were generally appropriately selected. Most of laboratories used biota of a marine origin (i.e., IAEA 407 Fish and IAEA 436-A Tuna fish from IAEA, DORM-4 fish protein from NRCC), when analyzing the trace elements in the ILC fish sample.

As mentioned in 1.3, analyte recovery was part of the reporting form for each analyte, 42 participating laboratories reported recovery values, calculated using CRM results. Only 5 participating laboratories declared performing recovery corrections of their results. About 90% of values reported as not corrected for recovery obtained satisfactory scores, meaning participating laboratories have correctly estimated that their recoveries were fit for purpose. Indeed, most of the reported recoveries were in the range of $100 \pm 25\%$.

The fish sample used as a test sample in the present ILC was freeze-dried as part of its preparation procedure. At the time of bottling, the moisture content of the material was around 6%. Depending on local storage conditions and humidity levels, the ILC sample might absorb

moisture from the environment. Consequently, users were advised to determined moisture content of the test sample. As the moisture is an operationally dependent parameter [8] detailed procedure on moisture content determination in the test sample was provided in the accompanying letter. Nineteen participating laboratories (25%) reported results that were corrected for moisture. Of these, 7 reported the use of the recommended protocol (85°C). Inadequate determination of moisture can be a source of bias, especially for biological matrices where moisture content is often more than 5% of the tissue analyzed. The moisture content reported by the participating laboratories were in the range of 3 to 9%.

ILC participating laboratories were requested to report the detection and quantification limits of their analytical procedures used in this ILC. These method parameters are an element of method validation and are especially important for the determination of analytes at sub ng g^{-1} level such as Pb, Cd and Hg. Indeed, looking at calculated z-scores for Cd, Co, Ni, Pb and Hg, the participating laboratories that did not evaluate their detection and quantification limits adequately received higher numbers of unsatisfactory results (38% instead of 19%).

About 80% of results were reported with the associated detection limit of the applied analytical procedure, and 75% with detection and quantification limits. In general, quantification limits were correctly estimated when compared with reported values. Ten laboratories reported values lower than their declared quantification limit for at least one analyte. As shown in Table 4 most of non numerical results (i.e., reported as <QL or DL) were correctly evaluated (i.e., assigned values < reported quantification limit). One exception was observed for laboratory 89, which reported unrealistic detection limit.

5   CONCLUSIONS

The current ILC attracted a significant number of participants from 48 members states demonstrating worldwide interest of laboratories for the external evaluation of their analytical performances.

About 80% of reported values were assessed as satisfactory based on z-scores. This is in accordance with results from previously organized ILCs and could be considered as satisfactory. However, for some analytes (i.e., Co, Pb, Ni, Cd, Hg) present at low to ultra-low concentration levels (below ng g^{-1}), some laboratories likely faced contamination problems.

Only 65% of reported values were assessed as satisfactory using Zeta-scores, showing that an additional effort is needed from some participating laboratories for the evaluation of combined uncertainties associated with measurement results. There is still almost 20% of participating laboratories that did not report measurement results with their respective associated uncertainties.

Participating laboratories are encouraged to carefully investigate the cause of any unsatisfactory scores (i.e., |z| or |Zeta| > 3) and put in place the necessary corrective actions to prevent reoccurrence of the problem. This is a requirement for accreditation to ISO/IEC 17025:2017 [7].

Some participating laboratories still need to improve their quality assurance and/or quality control procedures, to implement regular analysis of CRMs and the use of quality control charts in their daily laboratory practice. This process provides continuous feedback to the analyst and is an essential tool for data quality monitoring and for assuring the production of reliable results.

A full catalogue of available IAEA reference materials is published regularly and can be consulted on the IAEA website: http://www.iaea.org/programmes/aqcs.

The implementation of the Minamata convention [8], especially article 19, should lead to increasing number of laboratories involved in the monitoring of mercury, including mercury species. There are many participating laboratories performing Hg measurement (73%) and most of the results produced are assessed as satisfactory (73%), which is encouraging. The proportion of participating laboratories performing mercury speciation is still low (18% of participating laboratories), but reported values are almost all assessed as satisfactory. The ongoing assistance provided to Member States involved in the implementation of Minamata convention should be continued.

Participating laboratories reporting total mercury are encouraged to look at existing methodologies for mercury speciation that could be implemented with their existing instrumentation. Indeed, some non-chromatographic methods combining specific extraction and solid mercury analyzer showed to be adequate in this ILC.

As a post action of their participation in this ILC, participating laboratories are encouraged to contact the organizers to get more information on the above discussed points if necessary.

APPENDIX: PERFORMANCE EVALUATION BY ELEMENT

Evaluation of Reported data for As

Kernel density Plot
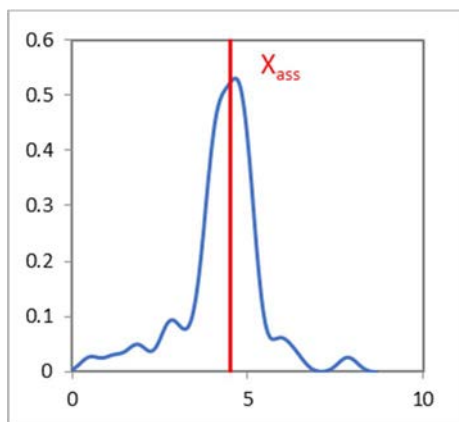
Summary of results:

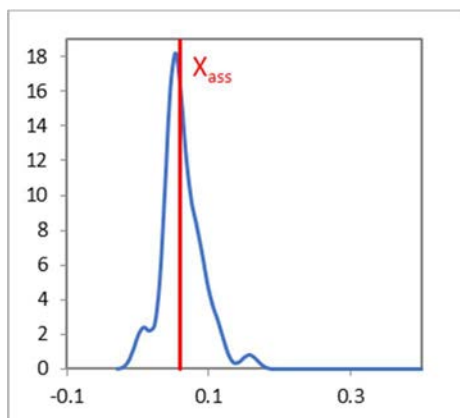|	Satisfactory	Questionable	Unsatisfactory
z-score	78%	7%	15%
Zeta-score	65%	5%	30%

X_{ass}:	4.5 mg kg^{-1}
U_{ass} (k=2):	0.3 mg kg^{-1}
$2\sigma_p$:	1.1 mg kg^{-1}
Number of results:	54
Number of method:	7

Reported results and expanded uncertainties:

—— X_{ass} ; $\overline{X}_{lab} \pm U_{lab}$; ---- $X_{ass} \pm 2\sigma_p$; ---- $X_{ass} \pm U_{ass}$(k=2)
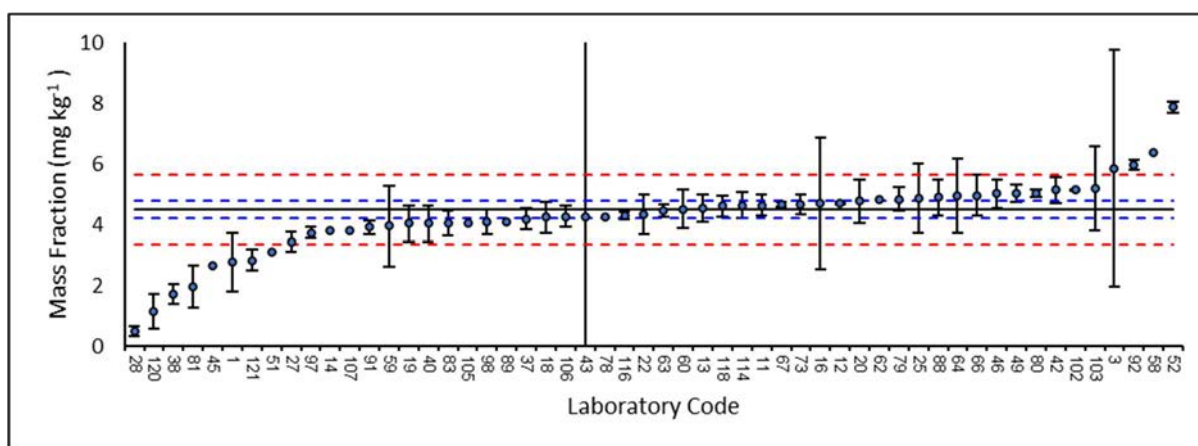
Performance evaluation: ▪ z-score ▪ Zeta-score
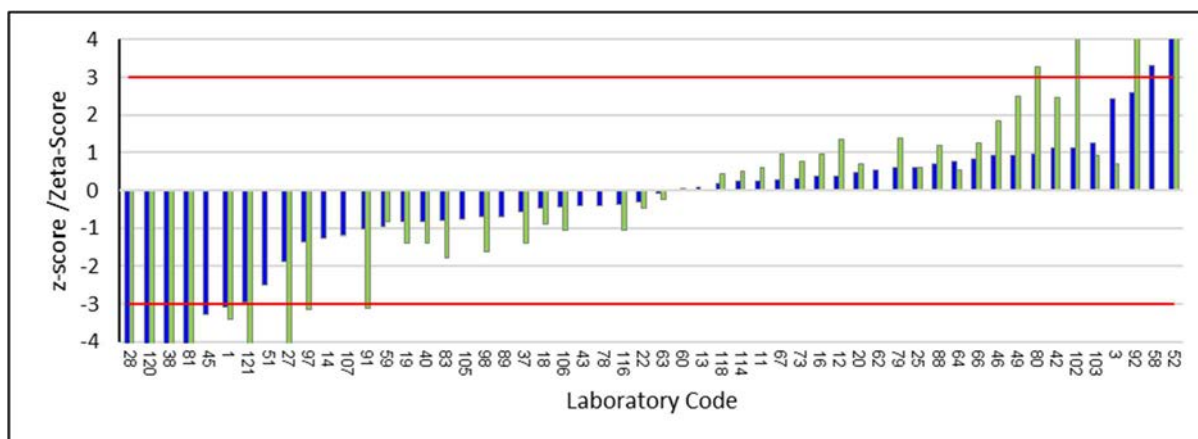
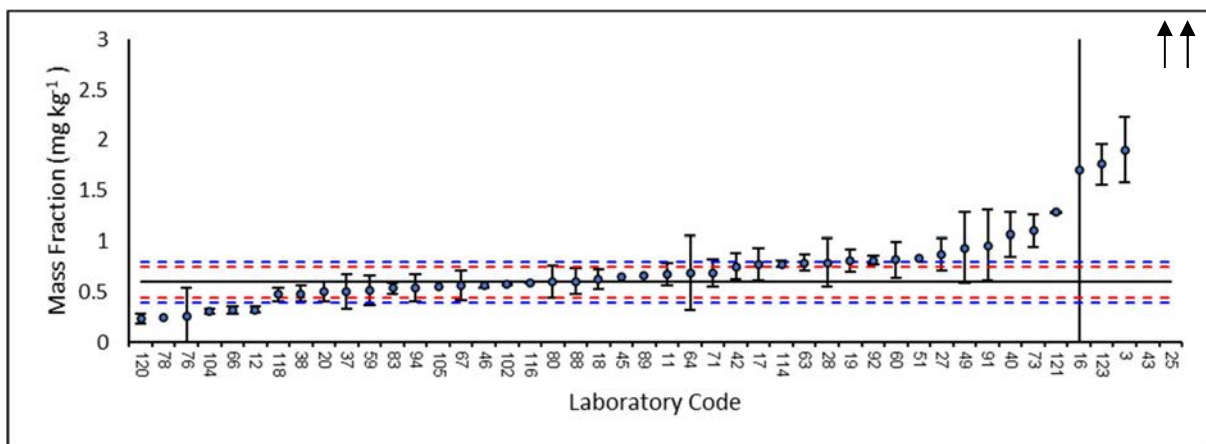# Evaluation of Reported data for Cd

Kernel density Plot
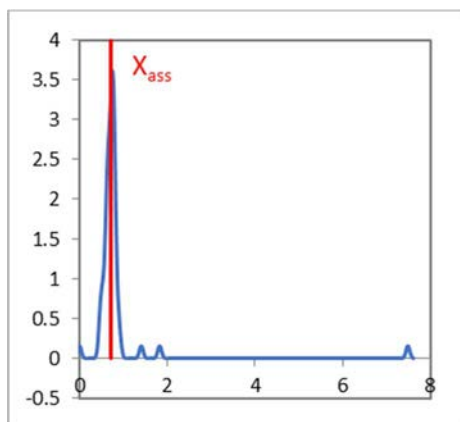
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	83%	10%	7%
Zeta-score	67%	7%	26%

X_{ass}:	0.72 mg kg^{-1}
U_{ass} (k=2):	0.04 mg kg^{-1}
$2\sigma_p$:	0.18 mg kg^{-1}
Number of results:	59
Number of method:	7

Reported results and expanded uncertainties:

—— X_{ass} ; $\overline{X}_{lab} \pm U_{lab}$; ---- $X_{ass} \pm 2\sigma_p$; ---- $X_{ass} \pm U_{ass}$(k=2)
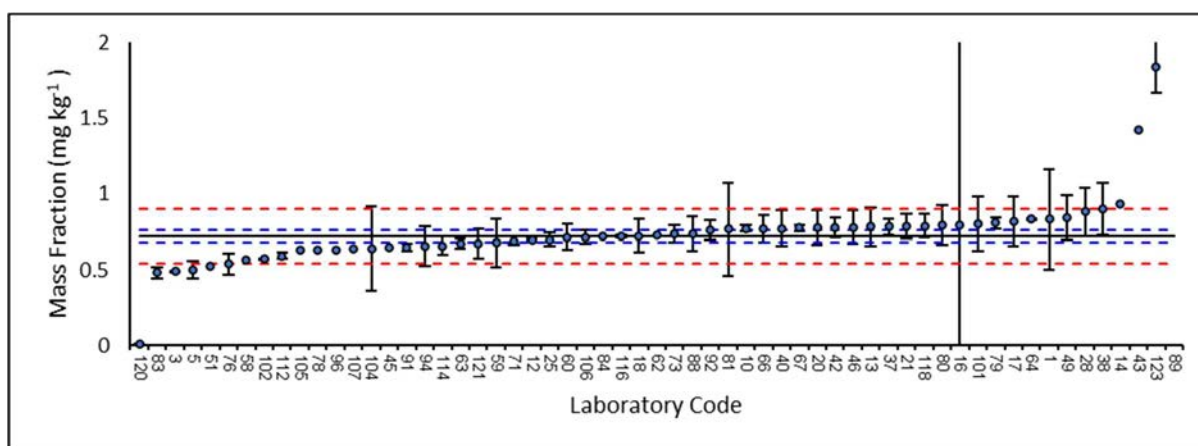
Performance evaluation: ■ z-score ■ Zeta-score
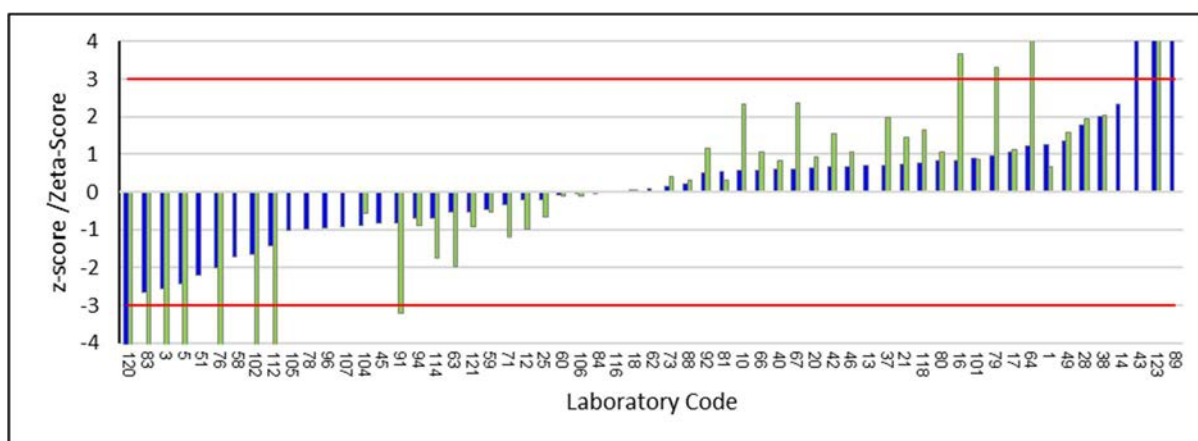
Evaluation of Reported data for Co

Kernel density Plot

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	58%	9%	33%
Zeta-score	47%	27%	31%

X_{ass}:	0.059 mg kg^{-1}
U_{ass} (k=2) :	0.007 mg kg^{-1}
$2\sigma_p$:	0.015 mg kg^{-1}
Number of results:	43
Number of method:	4

Reported results and expanded uncertainties:

—— X_{ass} ; $\overline{X}_{lab} \pm U_{lab}$; ---- $X_{ass} \pm 2\sigma_p$; ---- $X_{ass} \pm U_{ass}$(k=2)
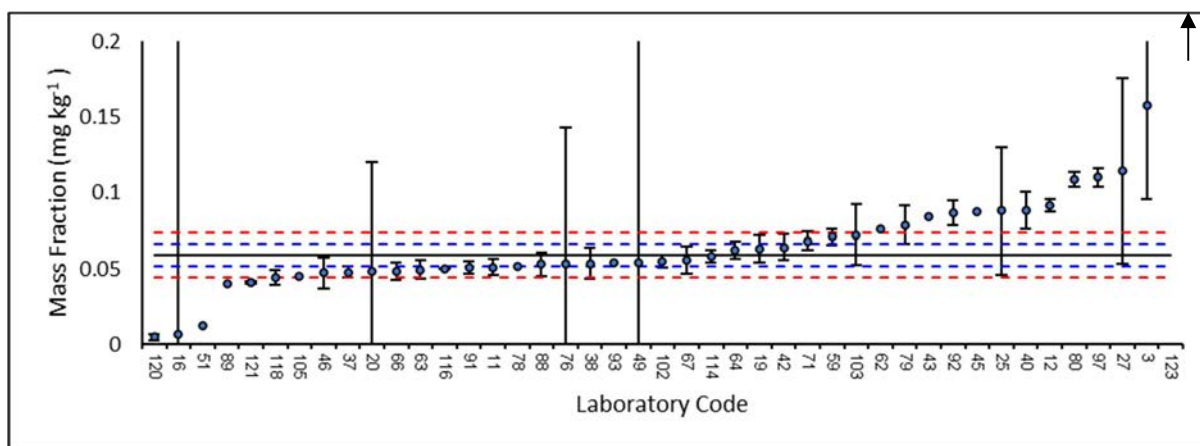
Performance evaluation: ▬ z-score ▬ Zeta-score
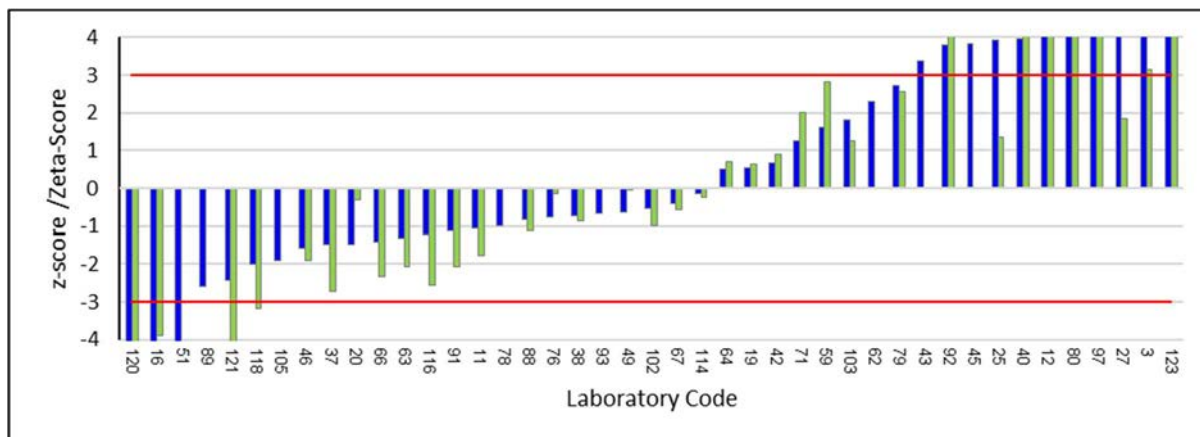
Evaluation of Reported data for Cr

Kernel density Plot
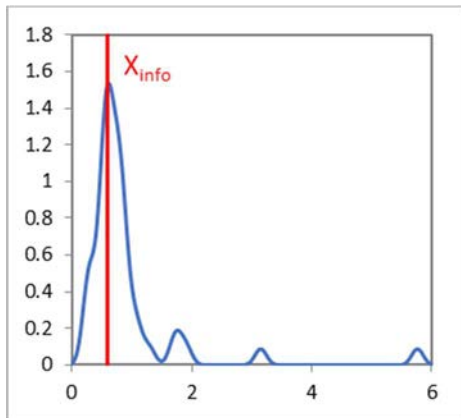
Summary of results:

X_{info}:	0.6 mg kg^{-1}
U_{info} (k=2) :	0.2 mg kg^{-1}
$2\sigma_p$:	0.15 mg kg^{-1}
Number of results:	36
Number of method:	6

Reported results and expanded uncertainties:

—X_{ass} ; $\overline{\underline{\Phi}}X_{lab} \pm U_{lab}$; ---- $X_{ass} \pm 2\sigma_p$; ---- $X_{ass} \pm U_{ass}$(k=2)

Evaluation of Reported data for Cu

Kernel density Plot
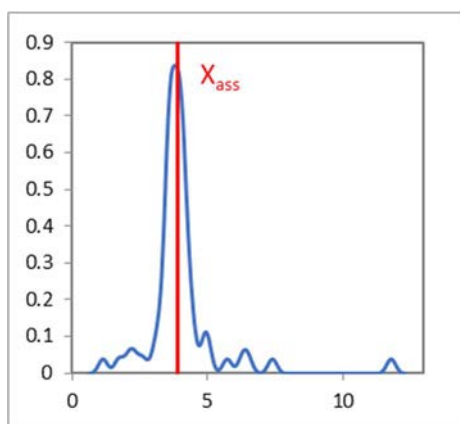
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	80%	5%	15%
Zeta-score	71%	4%	25%

Summary of results:

X_{ass}:	3.9 mg kg^{-1}
U_{ass} (k=2) :	0.2 mg kg^{-1}
$2\sigma_p$:	1 mg kg^{-1}
Number of results:	60
Number of method:	6

Reported results and expanded uncertainties:

—— X_{info} ; $X_{lab} \pm U_{lab}$; ---- $X_{info} \pm 2\sigma_p$; ---- $X_{info} \pm U_{info}$(k=2)
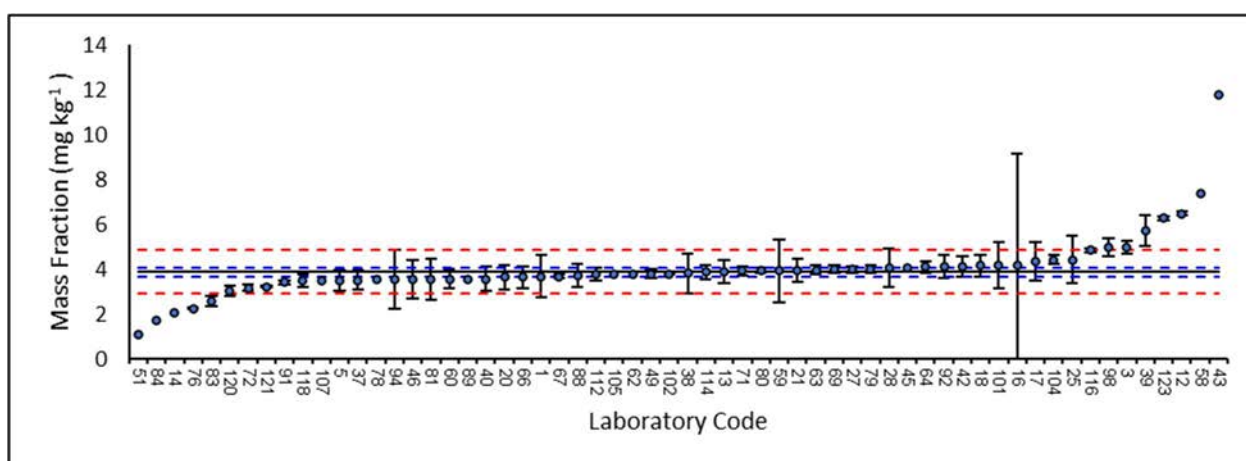
Performance evaluation: ■ z-score ■ Zeta-score
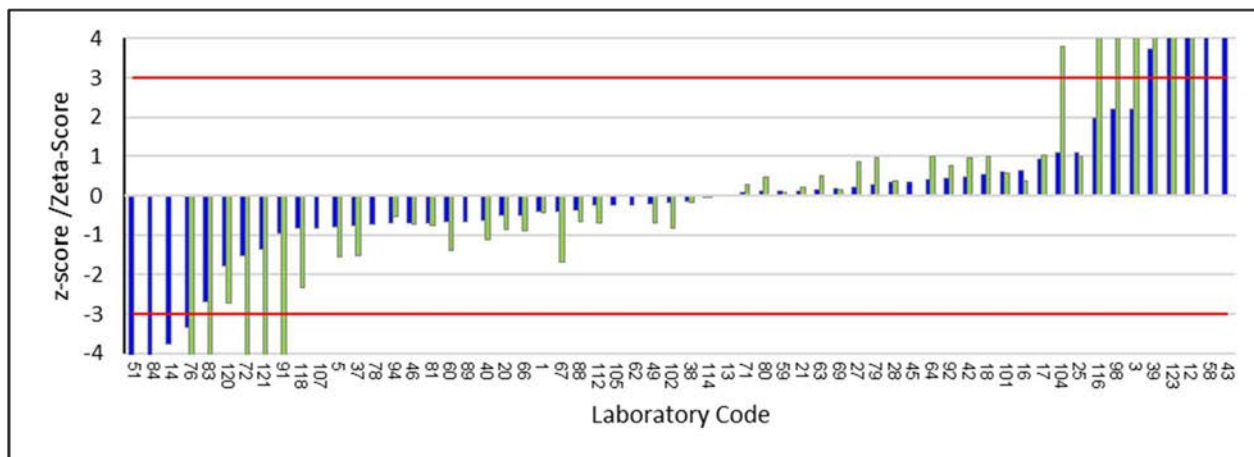
Evaluation of Reported data for Fe
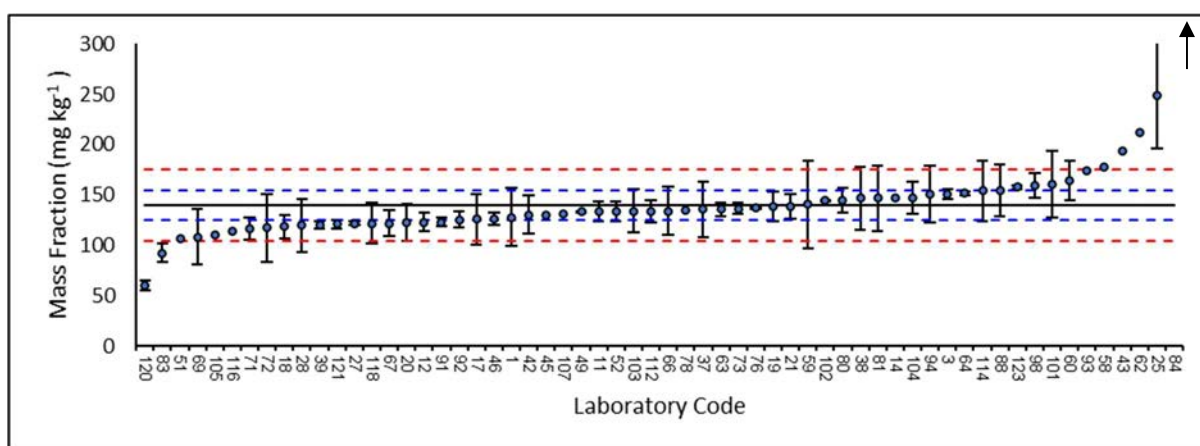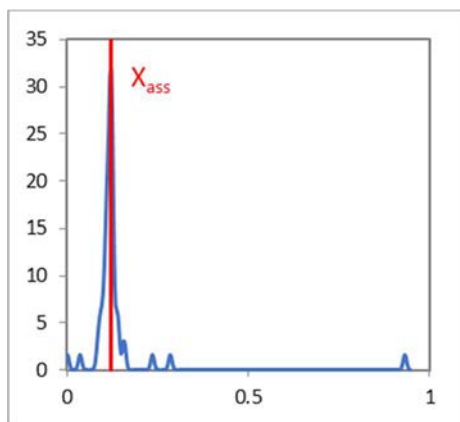
Kernel density Plot
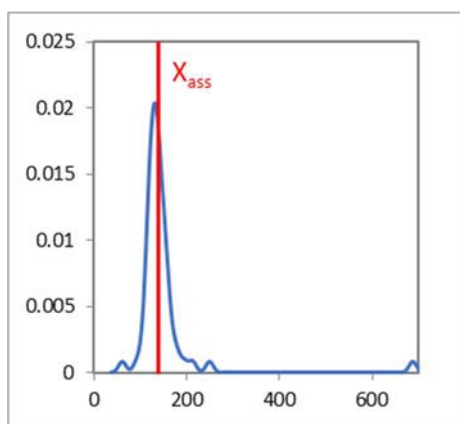
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	88%	3%	8%
Zeta-score	72%	16%	12%

Summary of results:

X_{ass}:	140 mg kg^{-1}
U_{ass} ($k=2$) :	15 mg kg^{-1}
$2\sigma_p$:	35 mg kg^{-1}
Number of results:	53
Number of method:	5

Reported results and expanded uncertainties:

—— X_{info} ; $X_{lab} \pm U_{lab}$; ---- $X_{info} \pm 2\sigma_p$; ---- $X_{info} \pm U_{info}(k=2)$

Performance evaluation: ■ z-score ■ Zeta-score
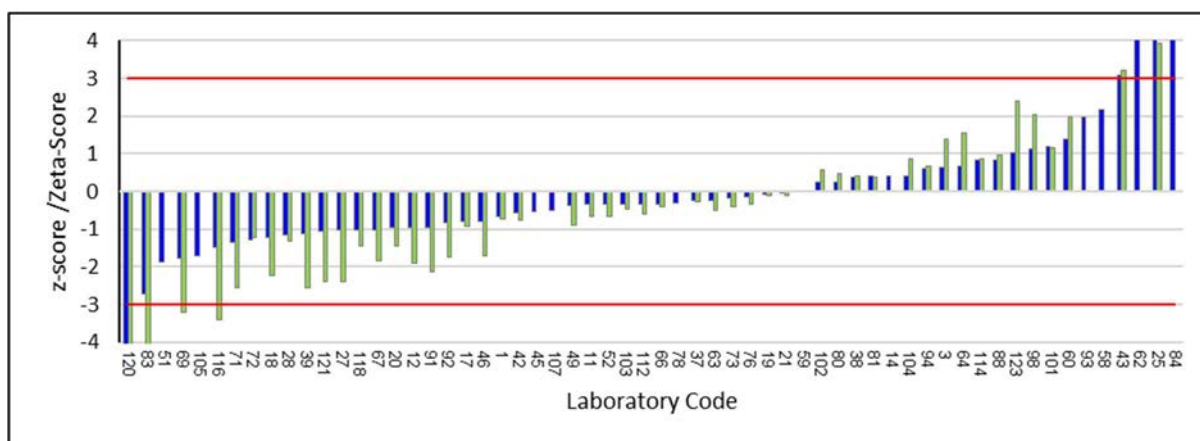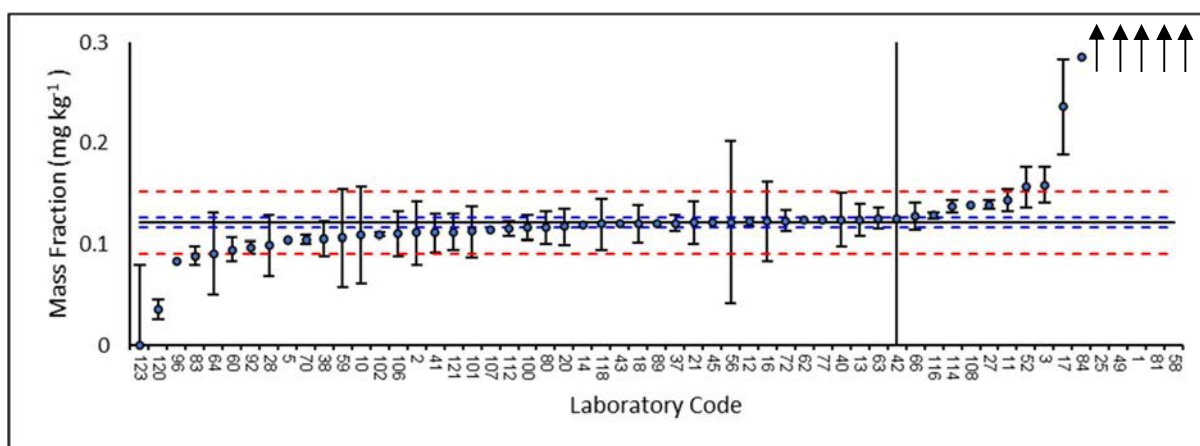
Evaluation of Reported data for Hg

Kernel density Plot

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	75%	9%	16%
Zeta-score	72%	16%	12%

X_{ass}:	0.122 mg kg^{-1}
U_{ass} (k=2) :	0.005 mg kg^{-1}
$2\sigma_p$:	0.030 mg kg^{-1}
Number of results:	57
Number of method:	8

Reported results and expanded uncertainties:

—— X_{ass} ; ⊤⊕⊥ $X_{lab} \pm U_{lab}$; ---- $X_{ass} \pm 2\sigma_p$; ---- $X_{ass} \pm U_{ass}$(k=2)
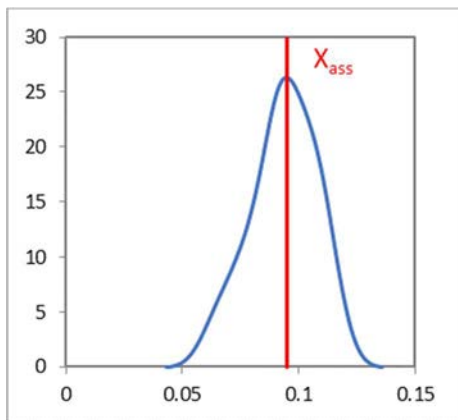

Performance evaluation: ■ z-score ■ Zeta-score
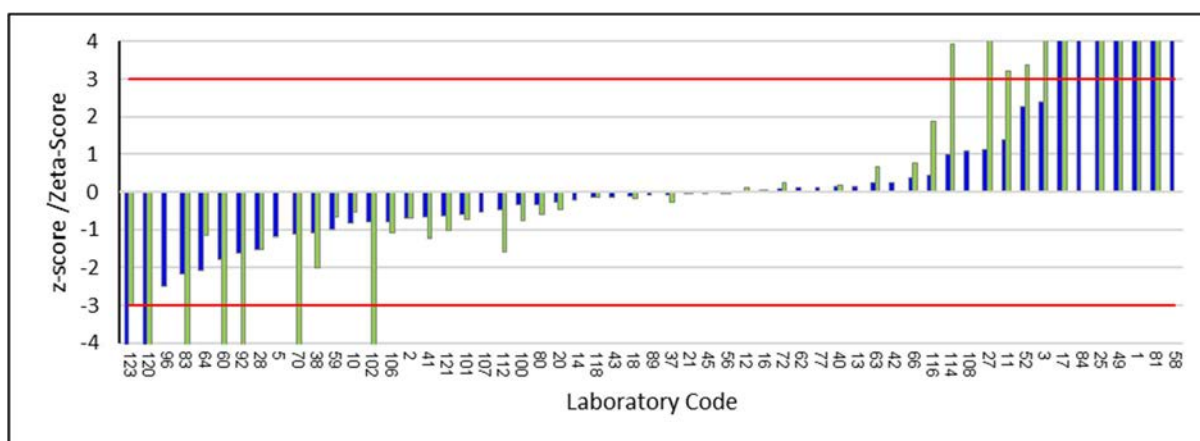
Evaluation of Reported data for MeHg
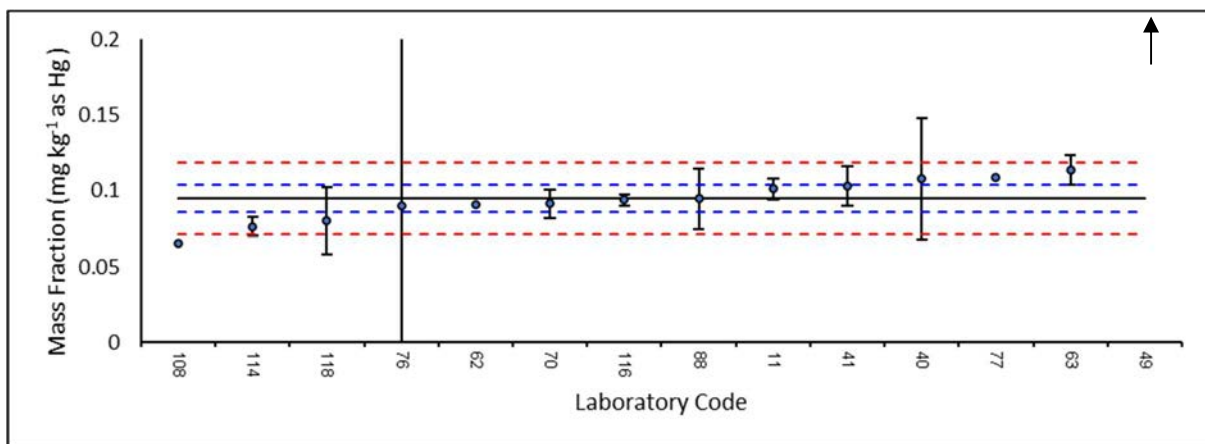
Kernel density Plot

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	86%	7%	7%
Zeta-score	73%	9%	18%

X_{ass}:	0.095 mg kg^{-1} as Hg
U_{ass} (k=2) :	0.009 mg kg^{-1} as Hg
$2\sigma_p$:	0.024 mg kg^{-1} as Hg
Number of results:	14
Number of method:	4

Reported results and expanded uncertainties:

$$\text{—} X_{ass} ; \quad \Phi X_{lab} \pm U_{lab}; \quad \text{----} X_{ass} \pm 2\sigma_p ; \quad \text{----} X_{ass} \pm U_{ass}(k=2)$$

Performance evaluation: ■ z-score ■ Zeta-score
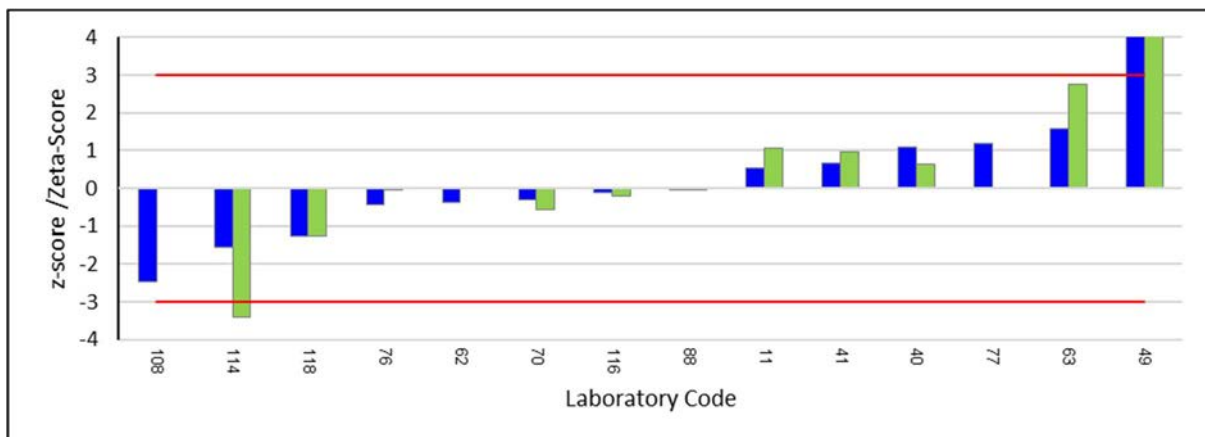
Evaluation of Reported data for Mn

Kernel density Plot

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	88%	2%	11%
Zeta-score	67%	12%	20%

X_{ass}:	6.1 mg kg^{-1}
U_{ass} (k=2) :	0.4 mg kg^{-1}
$2\sigma_p$:	1.5 mg kg^{-1}
Number of results:	57
Number of method:	6

Reported results and expanded uncertainties:

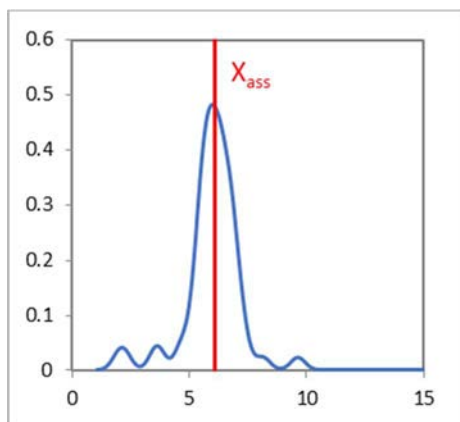—— X_{ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{ass} \pm 2\sigma_p$; ---- $X_{ass} \pm U_{ass}$(k=2)

Performance evaluation: ■ z-score ■ Zeta-score

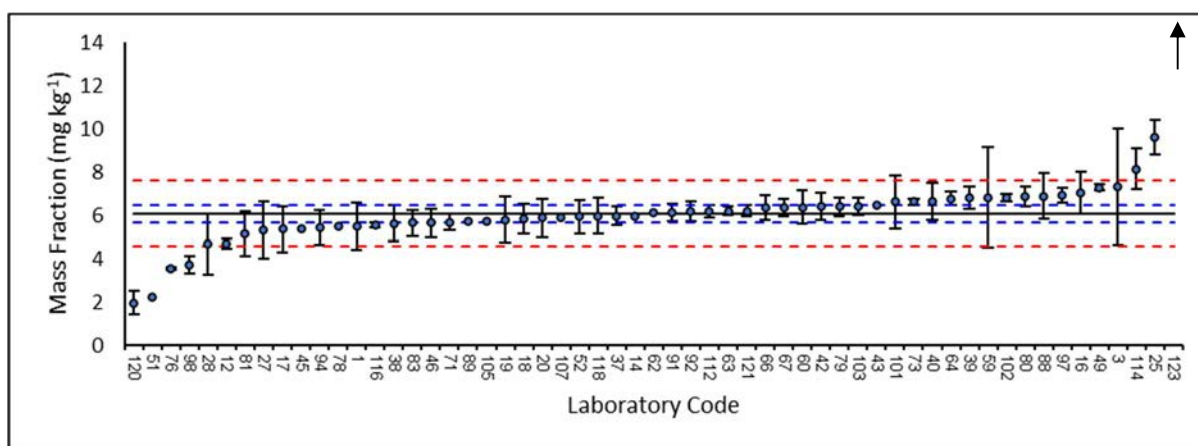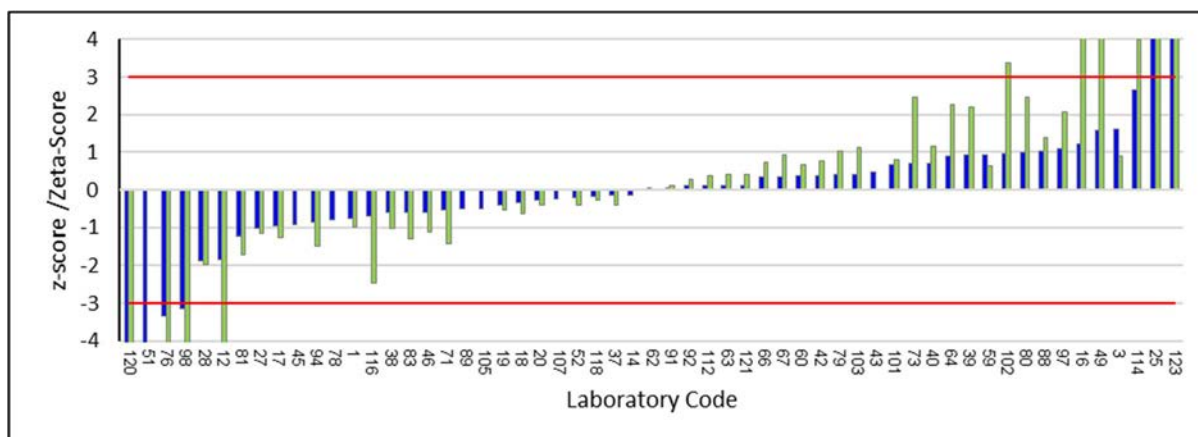# Evaluation of Reported data for Ni

Kernel density Plot

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	58%	12%	30%
Zeta-score	57%	20%	23%

X_{ass}:	0.62 mg kg^{-1}
U_{ass} (k=2) :	0.10 mg kg^{-1}
$2\sigma_p$:	0.16 mg kg^{-1}
Number of results:	43
Number of method:	5

Reported results and expanded uncertainties:

—— X_{ass} ;　$X_{lab} \pm U_{lab}$; ---- $X_{ass} \pm 2\sigma_p$; ---- $X_{ass} \pm U_{ass}(k=2)$
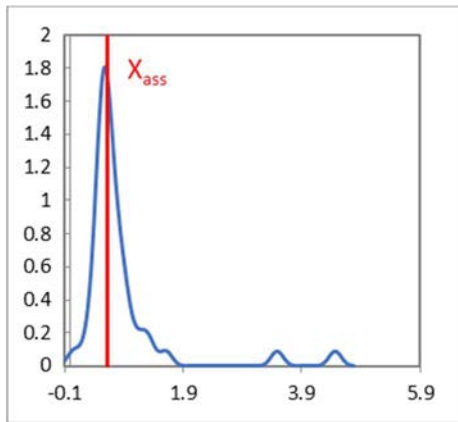

Performance evaluation: ■ z-score ■ Zeta-score
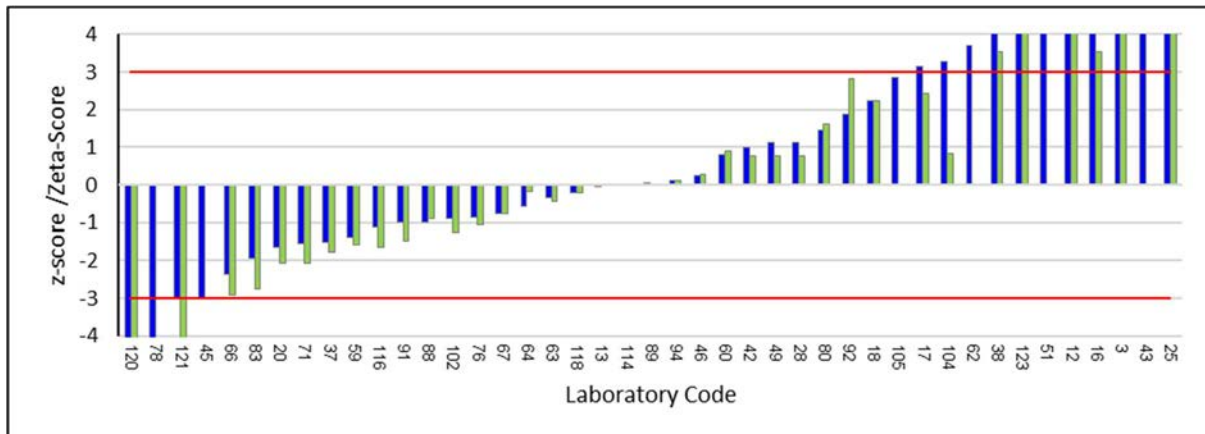
Evaluation of Reported data for Pb

Kernel density Plot
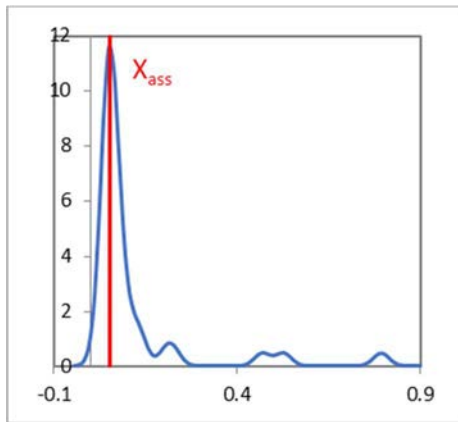
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	60%	0%	40%
Zeta-score	58%	13%	29%

X_{ass}:	0.054 mg kg^{-1} as Hg
U_{ass} (*k*=2) :	0.008 mg kg^{-1} as Hg
$2\sigma_p$:	0.013 mg kg^{-1} as Hg
Number of results:	40
Number of method:	4

Reported results and expanded uncertainties:

—— X_{ass} ; $\overline{\underline{\bullet}}X_{lab} \pm U_{lab}$; ---- $X_{ass} \pm 2\sigma_p$; ---- $X_{ass} \pm U_{ass}$(*k*=2)

Performance evaluation: ■ *z*-score ■ Zeta-score
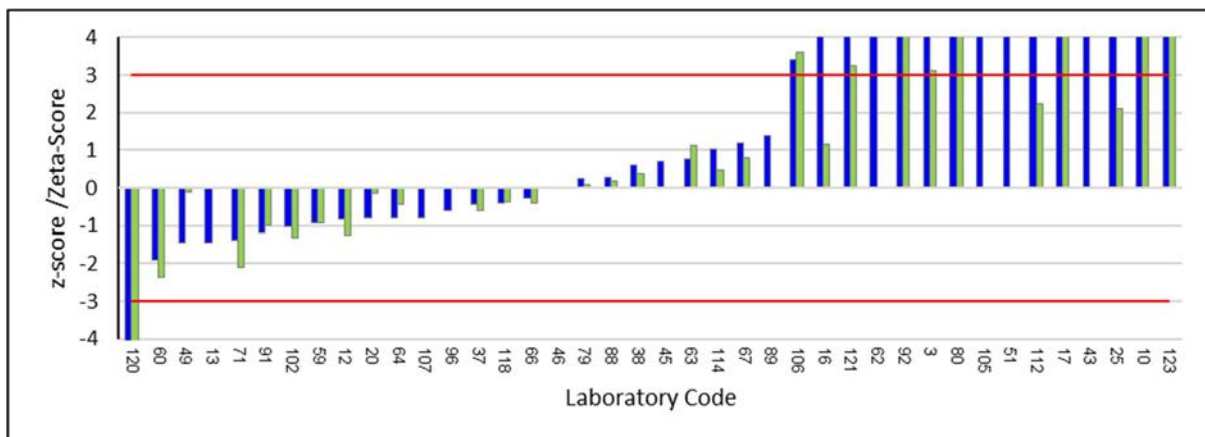
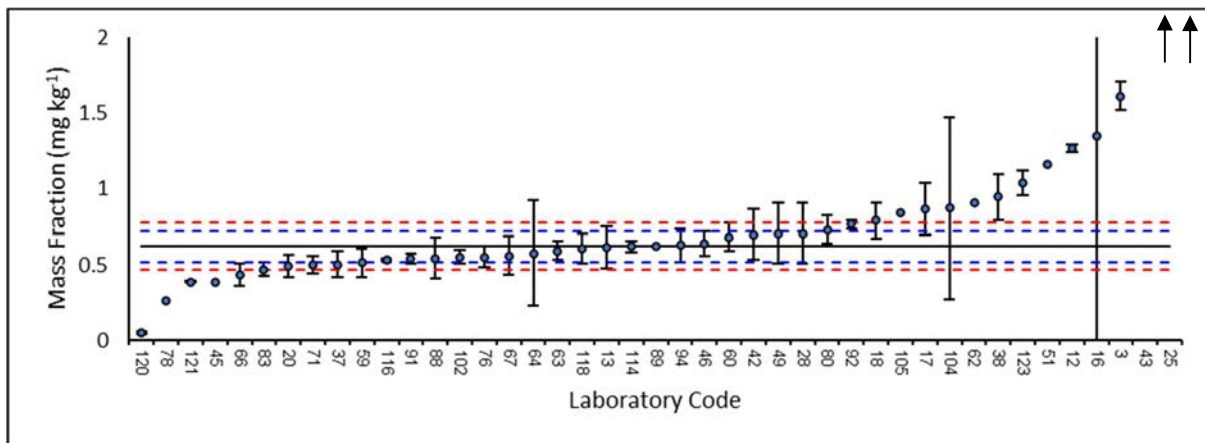# Evaluation of Reported data for Se

Kernel density Plot
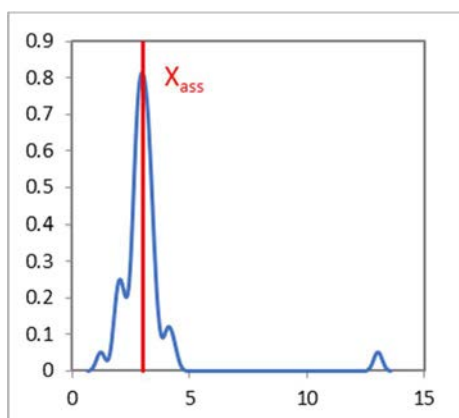
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	74%	17%	10%
Zeta-score	62%	15%	24%

X_{ass}:	3.0 mg kg^{-1}
U_{ass} (k=2) :	0.3 mg kg^{-1}
$2\sigma_p$:	0.8 mg kg^{-1}
Number of results:	42
Number of method:	6

Reported results and expanded uncertainties:

— X_{ass} ; ⊕ $X_{lab} \pm U_{lab}$; ---- $X_{ass} \pm 2\sigma_p$; ---- $X_{ass} \pm U_{ass}$(k=2)
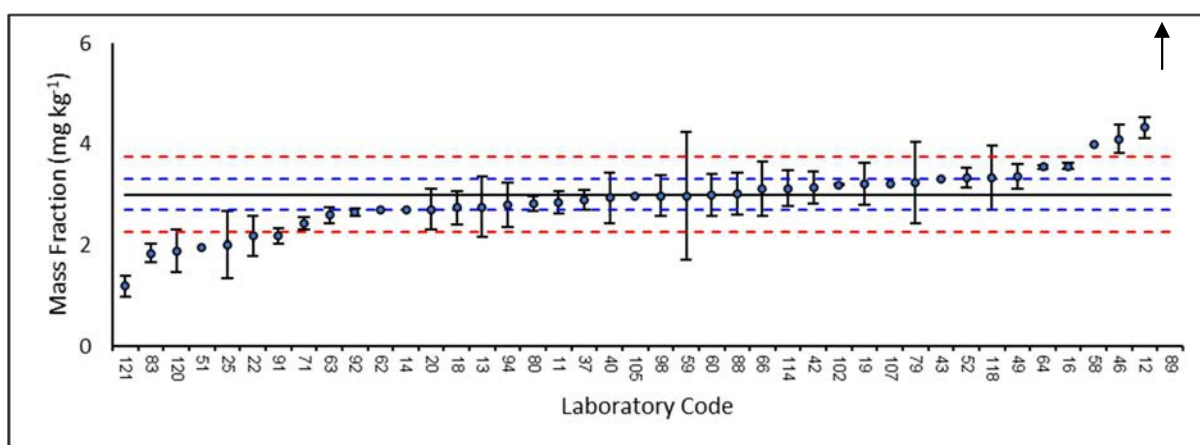
Performance evaluation: ■ z-score ■ Zeta-score
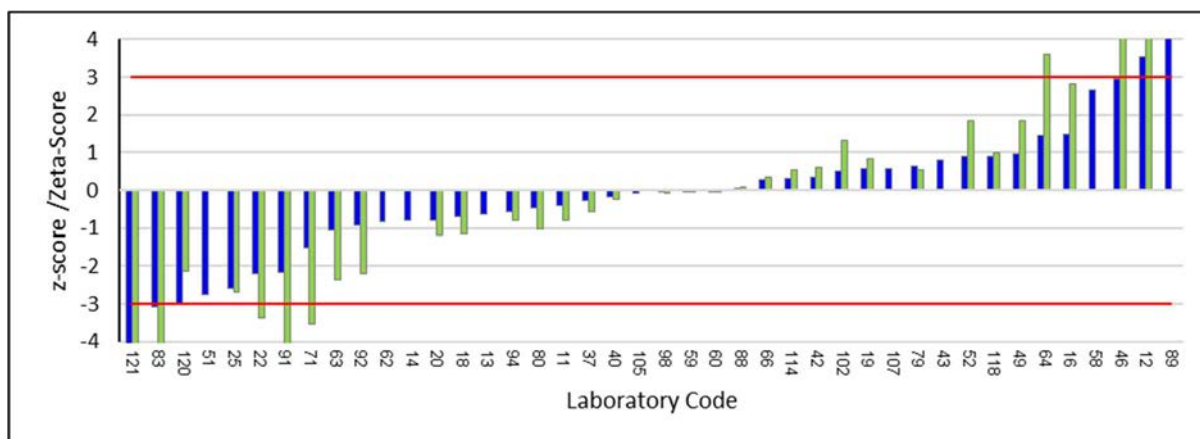
Evaluation of Reported data for Zn
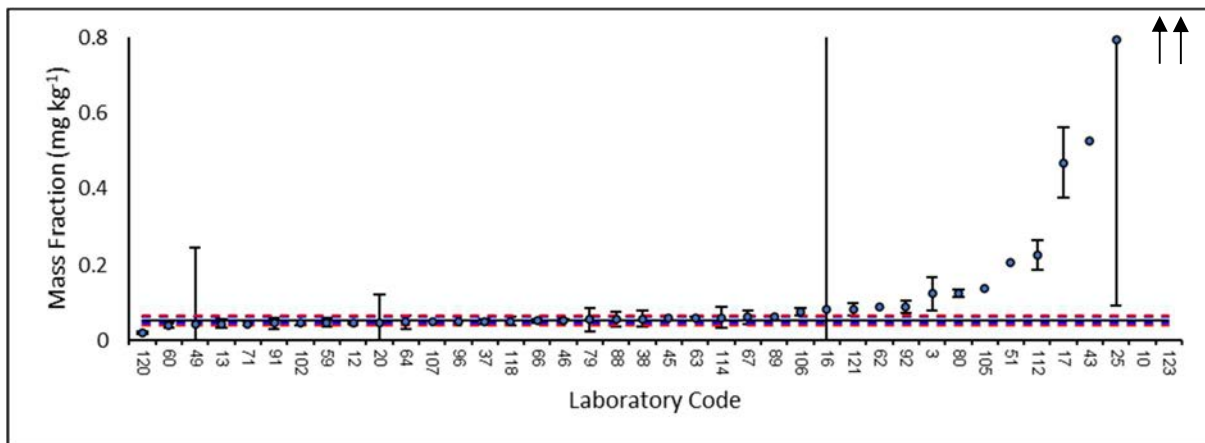
Kernel density Plot

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	88%	12%	0%
Zeta-score	67%	9%	24%

X_{ass}:	102 mg kg^{-1}
U_{ass} (k=2) :	8 mg kg^{-1}
$2\sigma_p$:	25 mg kg^{-1}
Number of results:	66
Number of method:	5

Reported results and expanded uncertainties:

—— X_{ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{ass} \pm 2\sigma_p$; ---- $X_{ass} \pm U_{ass}$(k=2)

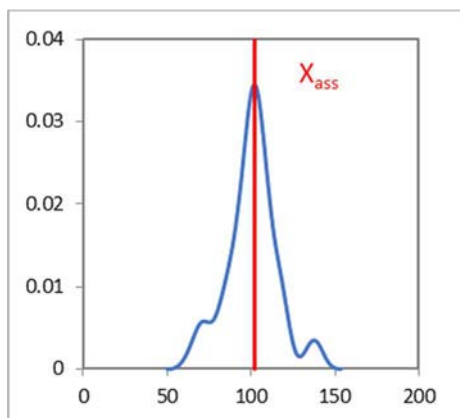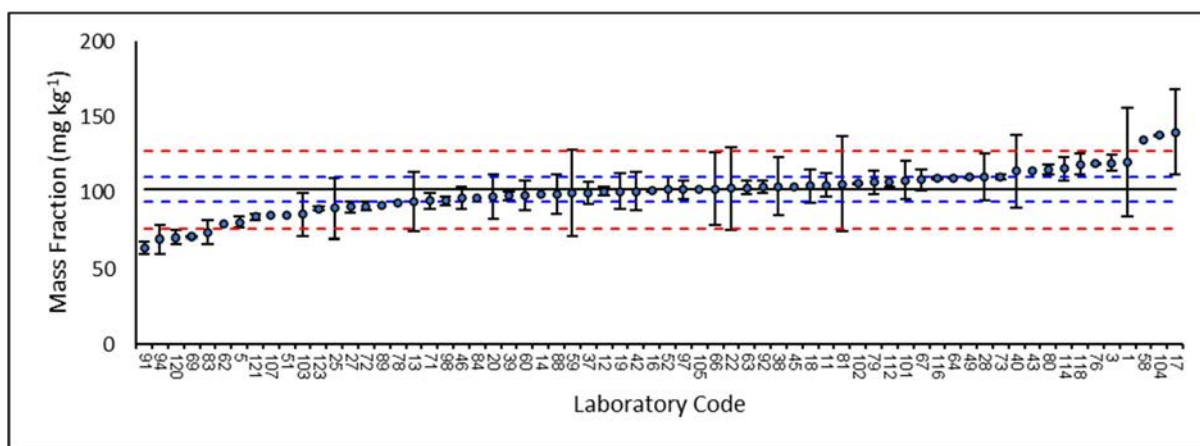Performance evaluation: ■ z-score ■ Zeta-score
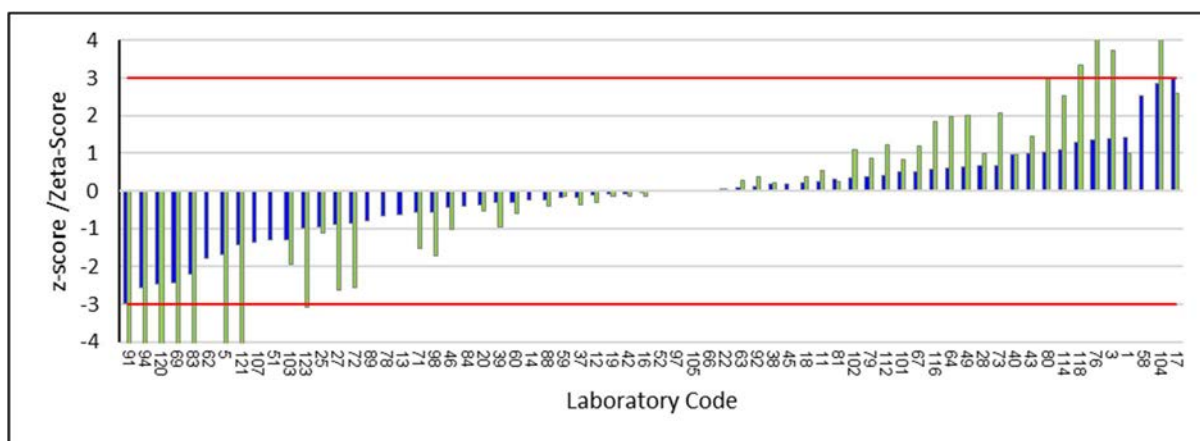
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