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IAEA Analytical Quality in Nuclear Applications Series No. 74

Interlaboratory Comparison on the Determination of Trace Elements and Methyl Mercury in Sediment Sample IAEA-158A

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INTERLABORATORY COMPARISON ON THE DETERMINATION OF TRACE ELEMENTS AND METHYL MERCURY IN SEDIMENT SAMPLE IAEA-158A

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The Agency's Statute was approved on 23 October 1956 by the Conference on the Statute of the IAEA held at United Nations Headquarters, New York; it entered into force on 29 July 1957. The Headquarters of the Agency are situated in Vienna. Its principal objective is "to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world''.

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IAEA Analytical Quality in Nuclear Applications Series No. 74

INTERLABORATORY COMPARISON ON THE DETERMINATION OF TRACE ELEMENTS AND METHYL MERCURY IN SEDIMENT SAMPLE IAEA-158A

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2024

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FOREWORD

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 when taking decisions and meaningful actions in relation 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) which are characterized for trace elements and the methylmercury mass fractions.

To ensure compliance with the international standard ISO/IEC 17034:2016, certified reference materials produced by the IAEA are characterized with the participation of analytical laboratories with demonstrated measurement competence. This is ensured by regularly organizing targeted interlaboratory comparisons involving these laboratories. 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.

This publication summarizes the results of the interlaboratory comparison on the determination of trace elements and methylmercury in a sediment sample organized in 2022.

The IAEA is grateful to the Government of Monaco for its support and wishes to thank the participants and laboratories involved in this comparison exercise. The IAEA officer responsible for this publication was S. Azemard of the Marine Environment Laboratories.

CONTENTS

1 INTRODUCTION

1.1 BACKGROUND

The Marine Environmental Studies Laboratory (MESL) of the International Atomic Energy Agency's 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 certified reference materials (CRM's) of marine origin, validated analytical procedures, training on the implementation of internal quality control, and through the evaluation of measurement performance via interlaboratory comparisons (ILC).

The production process of CRM's followed by MESL implies to perform a characterization exercise with laboratories with demonstrated analytical capabilities so called "experts". The demonstration of competence of collaborating laboratories is a way to ensure compliance with ISO/IEC 17034:2016 [1]. The results of ILC or Proficiency Tests (PT) provide clear information on measurement capabilities of the participating laboratories.

1.2 OBJECTIVE

The ILC presented in this report was designed to evaluate the measurement performance and analytical capabilities of laboratories already identified as "experts", new identified as potential 'experts" based on worldwide ILC's organized by MESL and laboratories that have analytical capabilities for rare earth elements (REE's). REEs are considered as emerging contaminants and are often used as tracers in geological and hydrothermal systems, but only very few marine sediments CRM's have been certified for REEs. The characterization of REEs in a candidate CRM's implies to develop a network of laboratories with demonstrated capabilities in the determination of REEs.

1.3 SCOPE

The present ILC study was designed to evaluate the measurement performance of selected laboratories for trace and rare earth elements and methyl mercury (MeHg) in sediment. The scope of this publication is to describe obtained results of mentioned ILC.

1.4 STRUCTURE

This publication is structured in five sections, section 1 being the introduction. Section 2 describes the test sample. The individual performance 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 STUDY SET UP

In February 2022, invitation letters were sent to 43 laboratories from 24 Member States, which previously participated in the IAEA characterization exercises or have been selected as potential collaborators. Positive responses with intent to participate were received from 24 laboratories in 17 Member States.

In April 2022 each laboratory received one bottle of the test sample, accompanied by an information sheet. Participants were requested to determine as many elements as possible from the following list: Ag, Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Cs, Dy, Er, Eu, Fe, Gd, Hg, Hf, Ho, K, La, Li, Lu, MeHg, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, Rb, Sb, Se, Sc, Sm, Sn, Sr, Ta, Tb, Th, Ti, Tm, U, V, Y, Yb and Zn) using the analytical procedures routinely applied in their laboratories. The deadline for reporting results was set at the end of June 2022.

Participating laboratories were requested to report their results for the ILC sample together with standard and expanded uncertainties, description and results of internal quality control samples (e.g CRMs or other reference materials (RMs)), analyte recovery, detection and quantification limits, 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, 16 laboratories from 12 Member States, reported results back to MESL. 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.

3 DESCRIPTION OF ILC TEST MATERIAL

The ILC test sample (IAEA-158A) is an estuarine sediment sample from the North Sea, which was characterized in a separate exercise. All details on sample preparation, homogeneity, stability, and assignment of values can be found in the certification report [2].

The assigned values used in this report to evaluate the reported results are presented in Table 1. The assigned value has a direct impact on the conclusions about the 'measurement capability' of the participating laboratories, and therefore, the most metrologically credible value should be sought. Therefore, the IAEA-158A certified values determined according to the requirements of the ISO/IEC 17034:2016 [1] and ISO/IEC guide 35:2017 [3] for Al, As, Ba, Ca, Cd, Ce, Co, Cr, Eu, Fe, K, La, Li, Mg, Mn, Na, Nd, Ni, Pb, Rb, Sm, Sr, U, V, Y, Yb have been used as assigned values in this ILC. For other analytes, mass fractions provided as information in the certificate of IAEA-158A were considered sufficiently credible if arising from at least 5 results and with associated expanded uncertainty being less than 20%. As a result, for Dy, Ho, Lu, MeHg, Sc, Ta, Tb, Th and Ti information values of IAEA-158A are considered as assigned values for this exercise. Results reported by the participating laboratories for other analytes (i.e. Ag, Cs, Cu, Er, Gd, Hg, Hf, Pr, Sb, Se, Sn and Tm) will not be further discussed in this report.

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

Element	Assigned value[1] (mg kg^{-1})	U (k=2)[2] (mg kg^{-1})
Al	52.2×10^3	2.4×10^3
As	12.0	1.0
Ba	1.031×10^3	0.083×10^3
Ca	65.3×10^3	2.8×10^3
Cd	0.361	0.043
Ce	54.1	5.6
Co	9.19	0.90
Cr	77.0	8.2
Dy	*3.35*	*0.41*
Eu	1.098	0.085
Fe	26.6×10^3	1.2×10^3
Ho	*0.692*	*0.074*
K	20.5×10^3	1.5×10^3
La	28.5	3.1
Li	33.5	3.3
Lu	*0.307*	*0.026*
MeHg[3]	*1.80×10^{-3}*	*0.26×10^{-3}*
Mg	10.86×10^3	0.58×10^3
Mn	367	19
Na	23.91×10^3	0.88×10^3
Nd	25.1	2.6
Ni	31.1	2.1
Pb	41.0	5.2
Rb	87.4	7.2
Sc	*8.20*	*0.84*
Sm	4.64	0.52
Sr	478	54
Ta	*0.984*	*0.14*
Tb	*0.633*	*0.061*
Th	*8.39*	*0.64*
Ti	*3.29×10^3*	*0.59×10^3*
U	2.40	0.33
V	74.1	5.2
Y	17.1	1.1
Yb	2.02	0.24
Zn	141	18

Analyte in italic are information values.

[1] The value is the mean of the means of sets of data, each set being obtained by a different laboratory. The information values are reported on dry mass basis and are traceable to the SI.

[2] The uncertainty is expressed as an expanded uncertainty with a coverage factor k=2, corresponding to a level of confidence of about 95%, estimated in accordance with the JCGM 100:2008 [4], and ISO/IEC Guide 35:2017 [3].

[3]as Hg.

4 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 [5].

The determination of target standard deviation σ_p, for the proficiency assessment was based on the outcome of previous ILCs organized by MESL for the same population of laboratories and similar sample matrices and was set as 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 as shown in Eq. (1), defines the difference between the mean value provided by the laboratory and the reference value, expressed in the units of the target standard deviation.

$$z = \frac{x_{lab} - x_{ass}}{\sigma_p} \qquad (1)$$

where:

x_{lab} is the result reported by the participating laboratory

x_{ass} is the assigned value

σ_p is the target standard deviation

The Zeta-score, which is calculated as shown in Eq. (2), demonstrates the agreement of the results reported by participating laboratories with the reference value within the respective uncertainties. The denominator in the Eq. (2) is calculated from the combined uncertainty of the assigned value and the combined uncertainty reported by the respective participant (*k*=1).

$$\text{Zeta} = \frac{x_{lab} - x_{ass}}{\sqrt{u_{x_{lab}}^2 + u_{x_{ass}}^2}} \qquad (2)$$

where:

x_{lab} is the result reported by the participating laboratory

x_{ass} is the assigned value

u_{xlab} is the combined uncertainty reported by the participating laboratory

u_{xass} is the combined uncertainty of the assigned value.

The interpretation of a laboratory's performance was evaluated according to the following internationally accepted limits [5]:

	$\lvert z \text{ or Zeta} \rvert \leq 2$	Satisfactory
	$2 < \lvert z \text{ or Zeta} \rvert < 3$	Questionable
	$\lvert z \text{ or Zeta} \rvert \geq 3$	Unsatisfactory

5 RESULTS AND DISCUSSION

Sixteen sets of data for 49 analytes were submitted by participating laboratories, comprising 312 numerical results. As explained above, *z*-scores and Zeta-scores were only calculated for 36 analytes (258 numerical results). Eight participating laboratories reported results for both trace element and REEs, 4 only for trace elements and 4 only for mercury and MeHg.

The reported results (mean ± expanded uncertainty) per analyte are shown in the Appendix using a scatter plot along assigned value, assigned expanded uncertainty and 2 times standard deviation. In addition, the reported results have been displayed using Pomplot [6]. The PomPlot graphical method displays the relative deviation of individual results (x_{lab}) from the assigned value (x_{ass}) on the horizontal axis and relative uncertainties on the vertical axis. Distances (D) and uncertainties (u) are calculated as described in Eq. (5) and Eq. (6) and are expressed as a multiple of median absolute deviation (MAD) calculated with Eq. (7).

$$D_i = x_{lab,i} - x_{ass}, \quad (i=1,\ldots n) \tag{5}$$

$$u = \sqrt{u_{xlab}^2 + u_{xass}^2} \tag{6}$$

$$\text{MAD} = \text{Median}\,|D_i|, \quad (i = 1, \ldots n) \tag{7}$$

Where:

n is the number of reported values per analyte

x_{lab} is the result reported by the participating laboratory

x_{ass} is the assigned value

u_{xlab} is the combined uncertainty reported by the participating laboratory

u_{xass} is the combined uncertainty of the assigned value.

As shown in Figure 1, the points on the right and left side of the graph correspond to biased results, results reported with small uncertainties are shown on the top of the graph, while points at the bottom of the graph represent results reported with large uncertainties. The assigned value (named Ref value in the graphs) and the value(s) from the organizer are also shown on graphs presented in the Appendix for comparison purpose.

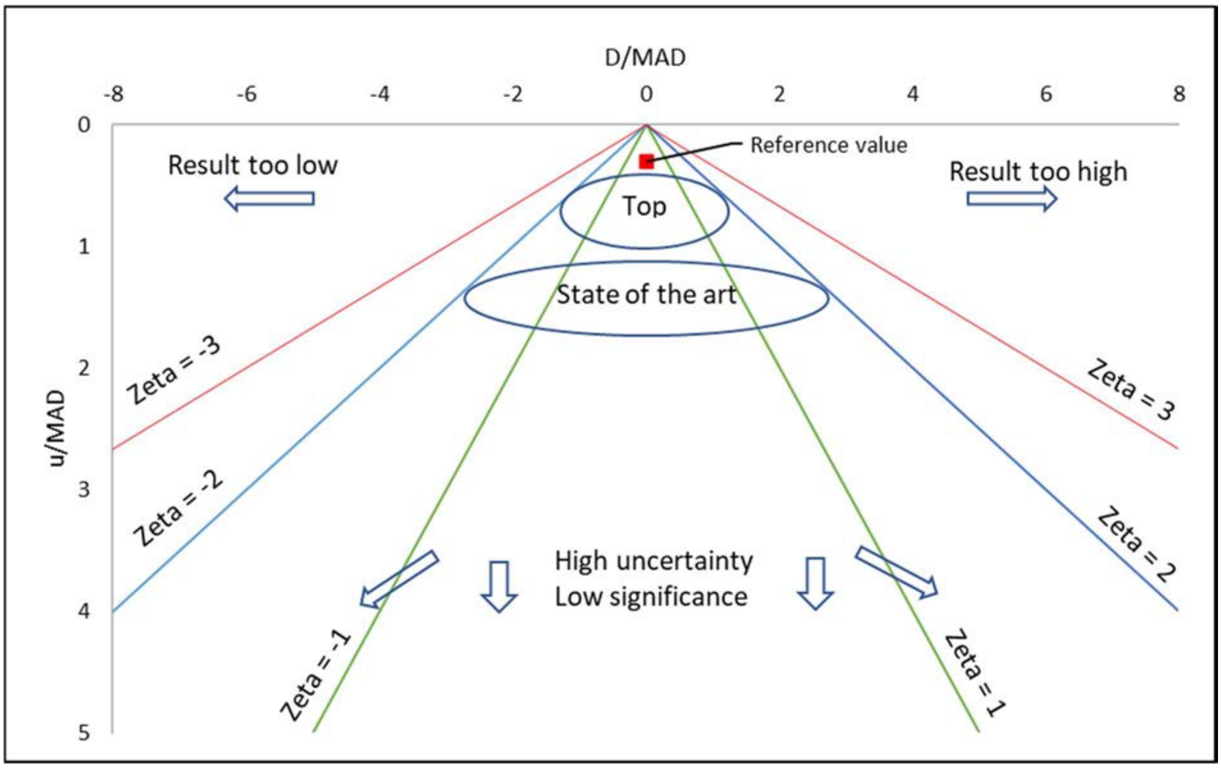
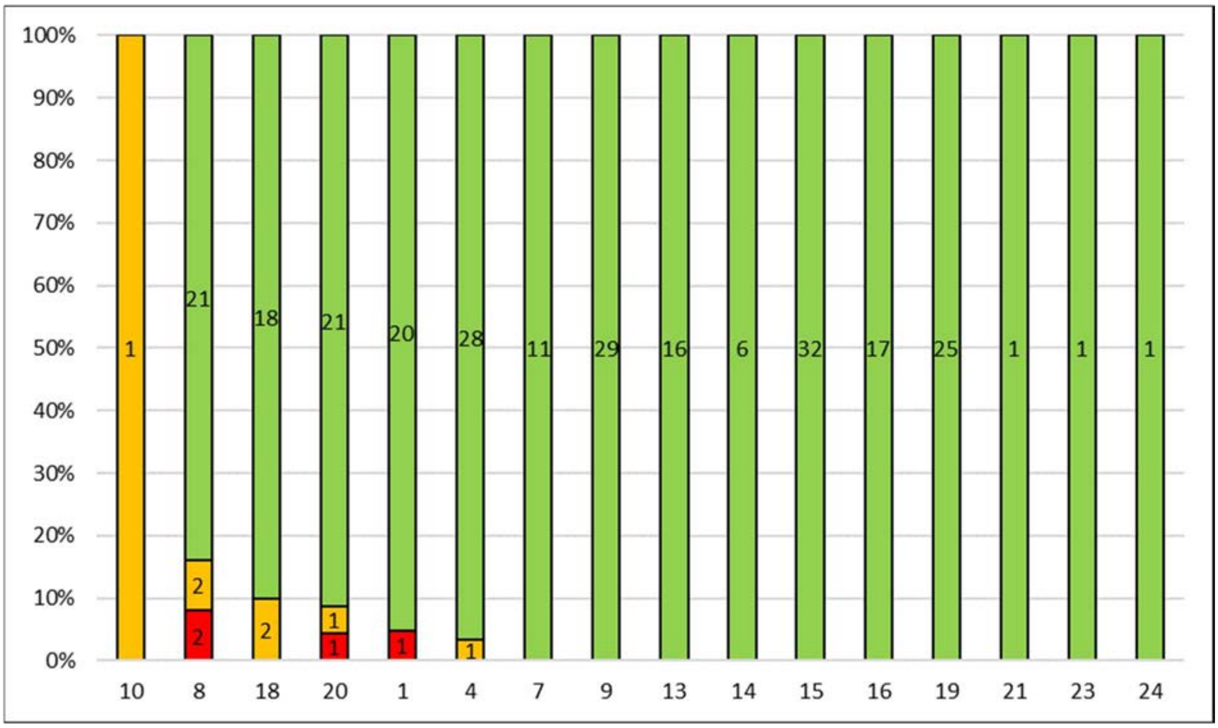


FIG. 1. Interpretation of a PomPlot (adapted from [6]).

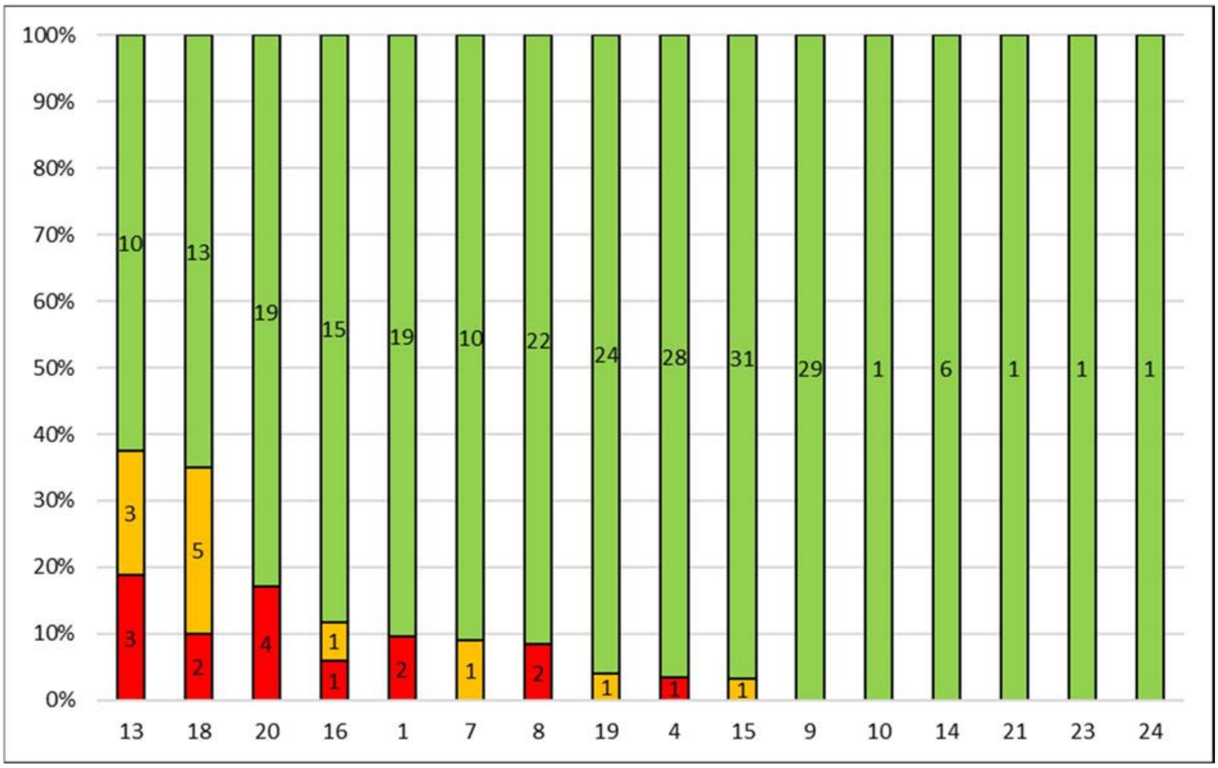
Figures 2 and 4 summarize the overall performance as defined by *z*-scores, by participating laboratories and by analyte respectively. Figure 3 and 5 summarize the overall performance as defined by Zeta-scores by participating laboratories and by analytes respectively.

Table 2 and Table 3 show the overall performance as defined by *z*-scores and Zeta-scores respectively by trace element.



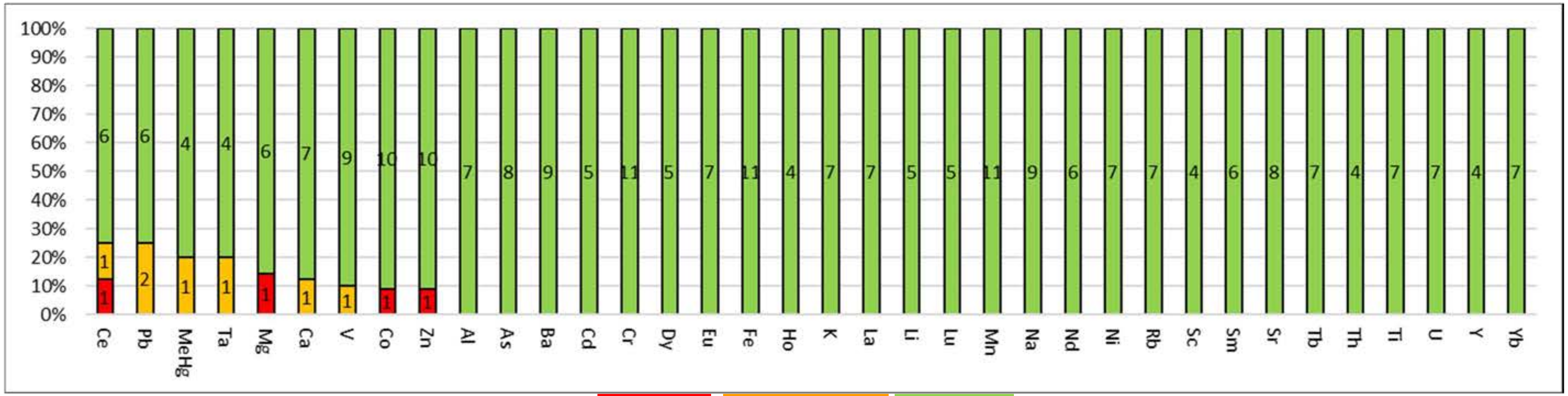
|z| ≥ 3, 2< |z| <3, |z| ≤ 2

FIG. 2. z-scores calculated from the results reported by the participating laboratories per laboratory. Numbers provided in the bars are the number of analytes reported.



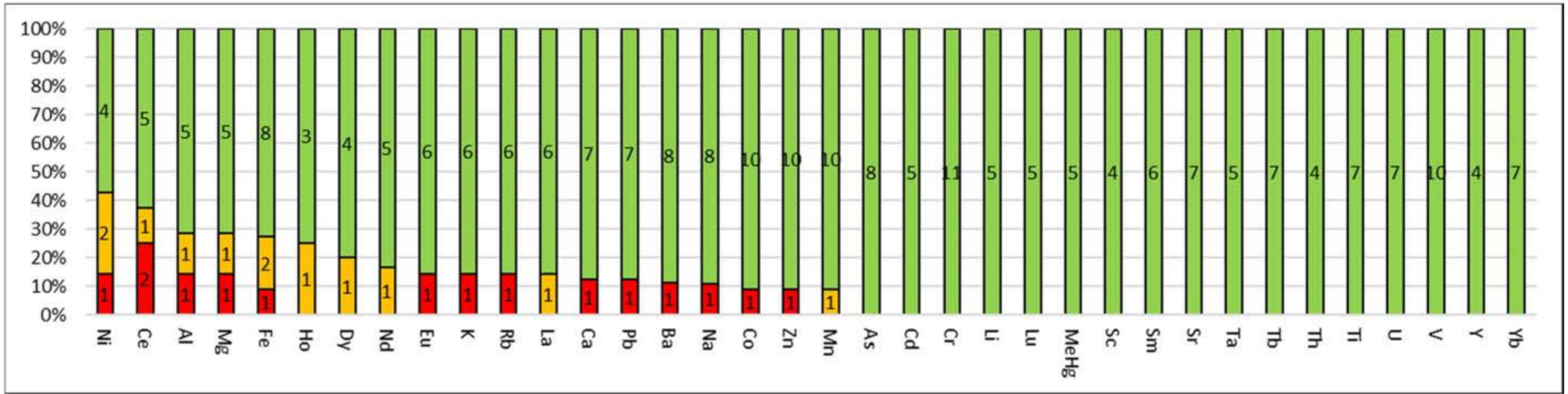
|Zeta| ≥ 3, 2 < |Zeta| < 3, |Zeta| ≤ 2

FIG. 3. Zeta-scores calculated from the results reported by the participating laboratories per laboratory. Numbers provided in the bars are the number of analytes reported.



|Zeta| ≥ 3, 2 < |Zeta| < 3, |Zeta| ≤ 2

FIG. 4. z-scores calculated from the results reported by the participating laboratories for each analyte. Numbers provided in the bars are the number of participating laboratories reporting results.



|Zeta| ≥ 3, 2 < |Zeta| < 3, |Zeta| ≤ 2

FIG. 5. Zeta-scores calculated from the results reported by the participating laboratories for each analyte. Numbers provided in the bars arethe number of participating laboratories reporting results..

TABLE 2. OVERALL ASSESSMENT OF LABORATORIES PERFORMANCE (*Z*-SCORE) BY TRACE ELEMENT (|Z|>3, 2< | Z | <3)

	Laboratory Codes															
Analyte	1	4	7	8	9	10	13	14	15	16	18	19	20	21	23	24
Al		-0.1		-0.2			-1.3		0.1	-0.3	-0.6	-0.1				
As	-0.4	-0.1	0.2	-0.1	0.4				-0.3			-0.3	0.1			
Ba	-1.5	0.1		-0.5	-0.3		0.0		0.1	0.1		0.2	0.5			
Ca	-0.3			-2.8	0.0		-0.4		-0.3	0.1		-0.2	0.6			
Cd			0.5		0.4			-1.2			-0.2	-0.1				
Ce	0.2	0.5		3.1	-0.4				0.3		2.5	-1.4	1.3			
Co	-0.6	-0.5	0.4	5.4	0.2		-0.3		0.2	0.3	-0.2	0.2	0.7			
Cr	-0.2	0.1	0.7	1.5	0.5		-0.7	-1.4	-0.2	-0.1	-0.1	-0.9				
Dy		-1.3		-0.1	0.4				-0.3		1.7					
Eu	-0.5	-1.8		0.6	-0.1				0.0		0.9		-0.1			
Fe	-0.6	-0.2		0.7	0.0		-0.6	-0.4	0.3	-0.6	-0.4	0.3	0.7			
Ho					0.0				-0.8		1.4	-0.5				
K				-0.3	-0.3		-1.8		-0.1	-0.1		0.7	1.0			
La	0.0	0.0		0.2	-1.0				0.2		1.8		0.7			
Li			0.2						-0.9	0.2	0.3	0.9				
Lu		0.0			-0.1				-0.1		0.3		0.4			
MeHg						2.0			-0.1					-0.9	0.8	-0.9
Mg		0.2			-0.7		-0.8		0.3	-0.2		-0.3	10.5			
Mn		-0.2	1.1	-0.4	0.1		-0.1	-0.7	-0.2	-0.2	-0.1	0.6	0.1			
Na	-0.1	0.0		0.2	-0.4		-0.8		-0.2	0.9		0.4	-0.4			
Nd	0.3	0.1			-0.8				-0.2		1.9		1.3			
Ni			0.0		0.1		0.7		-0.8	1.0	-0.2	0.3				
Pb		2.8	-0.1		0.5			-0.1	-0.1	-0.4	2.4	0.2				
Rb	-0.7	0.0		0.5			-0.6		-0.2			0.4	-1.1			
Sc	-0.6	-0.5		0.3									0.6			
Sm	-0.1	-0.6		-0.2	-0.7				0.0				1.1			

TABLE 3. OVERALL ASSESSMENT OF LABORATORIES PERFORMANCE (*Z*-SCORE) BY TRACE ELEMENT (|Z|>3, 2< |Z| <3) cont.

	Laboratory Codes															
Analyte	1	4	7	8	9	10	13	14	15	16	18	19	20	21	23	24
Sr	-0.6	-0.1		-1.1	-0.4		0.0		-0.1	0.1		0.4				
Ta	-1.1	-0.8		2.1								0.1	0.5			
Tb	-0.9	-0.7		1.3	0.0				0.6		0.9		-1.2			
Th	-0.3	-0.3		0.2									0.3			
Ti		1.0		0.3	0.3		-1.0		0.6	0.0		-0.4				
U	-0.6	-0.1	-0.4	1.4	-0.1				0.3			-0.7				
V		0.4	0.5	-0.1	0.5		-0.5		0.4	-0.1	0.6	-0.2	2.3			
Y		0.4			0.3				-0.3			-0.1				
Yb	-0.4	0.1		0.5	-0.2				0.1		0.5		0.8			
Zn	6.5	0.4	-1.1		0.0		0.2	-0.6	-0.1	-0.6	0.1	0.1	0.0			

TABLE 4. OVERALL ASSESSMENT OF LABORATORIES PERFORMANCE (ZETA-SCORE) BY TRACE ELEMENT (|ZETA|>3, 2< |ZETA| <3)

	Laboratory Codes															
Analyte	1	4	7	8	9	10	13	14	15	16	18	19	20	21	23	24
Al		-0.3		-0.4			-4.8		0.2	-1.6	-2.9	-0.4				
As	-0.9	-0.1	0.1	-0.1	1.0				-0.6			-0.5	0.0			
Ba	-3.6	0.1		-0.4	-0.8		0.0		0.3	0.3		0.4	1.5			
Ca	-0.9			-12.8	0.2		-1.4		-0.9	0.3		-0.8	1.8			
Cd			0.4		0.8			-1.4			-0.4	-0.1				
Ce	0.4	0.8		1.3	-0.8				0.6		3.7	-2.7	3.1			
Co	-1.2	-0.9	0.5	5.2	0.5		-0.4		0.4	0.7	-0.4	0.5	1.7			
Cr	-0.5	0.2	0.9	0.8	1.0		-1.2	-1.3	-0.3	-0.3	-0.1	-1.9				
Dy		-1.1		0.0	0.6				-0.6		2.5					
Eu	-1.1	-4.1		0.4	-0.1				0.1		1.6		-0.2			
Fe	-1.7	-0.5		1.1	0.1		-2.1	-1.8	0.6	-2.7	-2.0	0.8	3.9			

TABLE 5. OVERALL ASSESSMENT OF LABORATORIES PERFORMANCE (ZETA-SCORE) BY TRACE ELEMENT (|ZETA|>3, 2< | ZETA | <3) cont.

	Laboratory Codes															
Analyte	1	4	7	8	9	10	13	14	15	16	18	19	20	21	23	24
Ho					0.0				-1.7		2.1	-0.8				
K				-0.8	-1.1		-5.5		-0.2	-0.2		1.9	0.6			
La	0.1	-0.1		0.3	-1.9				0.4		2.8		1.6			
Li			0.0						-1.7	0.4	0.5	1.6				
Lu		0.0			-0.3				-0.1		0.6		1.0			
MeHg						1.4			-0.1					-1.5	0.5	-1.4
Mg		0.3			-1.1		-2.7		0.6	-0.9		-1.0	6.3			
Mn		-0.4	3.0	-0.8	0.3		-0.2	-1.7	-0.7	-1.2	-0.2	1.6	0.5			
Na	-0.4	0.1		0.3	-1.6		-3.5		-0.6	1.9		1.5	-1.8			
Nd	0.5	0.2			-1.5				-0.4		3.0		1.8			
Ni			0.0		0.3		2.2		-2.0	3.6	-0.3	0.6				
Pb		1.9	-0.2		0.9			-0.1	-0.2	-0.8	3.3	0.3				
Rb	-1.6	-0.1		0.6			-1.6		-0.5			0.9	-3.1			
Sc	-1.1	-1.0		0.3									1.4			
Sm	-0.2	-1.1		-0.2	-1.3				0.0				0.4			
Sr	-1.2	-0.2			-0.8		0.0		-0.1	0.3		0.7				
Ta	-1.7	-0.5		0.4								0.1	0.8			
Tb	-1.9	-1.0		0.3	-0.1				1.4		1.5		-0.7			
Th	-0.6	-0.6		0.3									1.0			
Ti		1.1		0.3	0.5		-1.3		0.7	0.0		-0.5				
U	-0.9	-0.1	-0.1	0.9	-0.1				0.4			-1.0				
V		0.8	0.3	-0.2	1.3		-0.9		1.1	-0.4	1.1	-0.4	2.0			
Y		0.8			0.6				-0.8			-0.1				
Yb	-0.7	0.1		0.4	-0.4				0.2		0.7		1.6			
Zn	11.0	0.6	-1.1		0.0		0.3	-1.1	-0.1	-1.2	0.1	0.1	-0.1			

5.1 *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 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 were only calculated for 36 analytes. As a result, out of the 16 datasets received from participating laboratories, 258 *z*-scores were calculated. From these 258 calculated *z*-scores, 95.7% were satisfactory with $|z| \leq 2$, and 1.6% were considered to be unsatisfactory with $|z| > 3$. Among the 16 participating laboratories, 10 (62.5% of participating laboratories) achieved satisfactory *z*- scores $|z| \leq 2$ for all their reported values.

Participating laboratories with results assessed as questionable and/or unsatisfactory are encouraged to carefully check laboratory procedures and applied working instructions.

5.2 ZETA-SCORES

The Zeta-score shows the agreement of the laboratory result with the reference value considering the respective uncertainties. The denominator in Eq. (2) includes the combined uncertainties of the reference values and the reported values by the participating laboratories.

As it can be seen on Figures 1 to 5, the comparison of measurement performances evaluated with *z*-score and Zeta-score indicates that the number of unsatisfactory Zeta-scores is slightly higher than the number of unsatisfactory *z*-score (1.6% of calculated *z*-scores and 6% of calculated Zeta-scores). Only 6 participating laboratories (37.5% of participating laboratories) reported values which were evaluated as 100% satisfactory with both $|z|$ and $|\text{Zeta}| \leq 2$, out of which 3 are participating laboratories reporting only MeHg.

Zeta-scores include the estimation of uncertainties, so values receiving $|\text{Zeta}| > 3$ while $|z| < 3$ could indicate an underestimation of uncertainties. In Figure 5, absolute Zeta-scores are plotted against expanded uncertainties of results reported by participants. Almost 40% of the results receiving questionable or unsatisfactory Zeta-scores have been reported with expended uncertainties lower than 5%, many being estimated as standard deviation of replicate analyses. In general, laboratories should keep in mind that uncertainties based only on the precision of measurement results (measurement 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 such as recovery, procedural blank, moisture content *etc*.

On the other hand (as shown in Figure 5), some results were reported with high uncertainties (i.e., above 40%) which does not appear consistent with the uncertainties reported for the same analytes measured by the same instrumental techniques.

Participating laboratories reporting values receiving $|z|$ and $|\text{Zeta}| > 3$ are encouraged to review their analytical procedures, as already mentioned in 4.1. Indeed 3 out of 4 reported results receiving an unsatisfactory z-score ($|z| > 3$) also received an unsatisfactory Zeta-score.

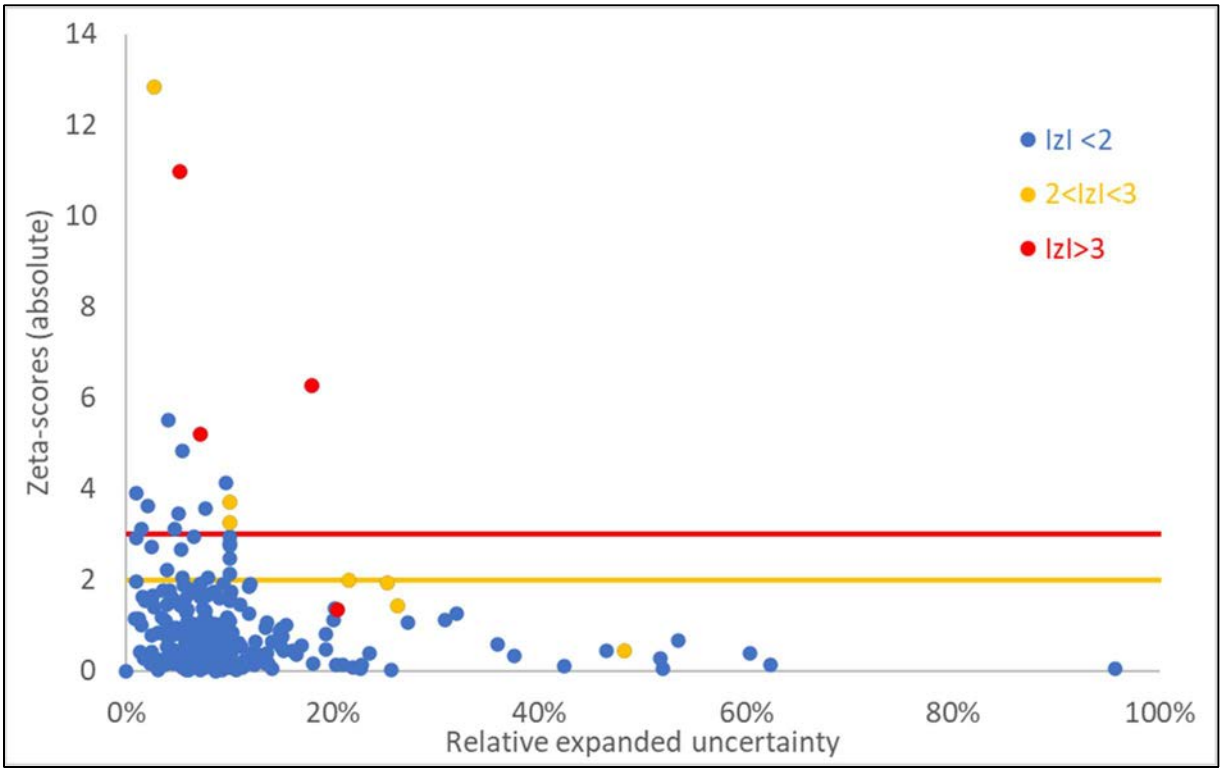


FIG. 6. Zeta-scores versus reported expanded uncertainties.

5.3 ANALYTICAL METHODS

Table 4 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 analysis, X-ray fluorescence spectroscopy); plasma spectrometric methods (inductively coupled plasma mass spectrometry and inductively coupled plasma optical emission spectrometry) and atomic absorption spectroscopy methods. The most used instrumental methods were inductively coupled plasma mass spectrometry and neutron activation, which accounted for almost 75% of reported values and were used by 69% of the participating laboratories. This is a slightly different picture than for previous ILC's on the same matrix where typically neutron activation did not represent more than 10% of the reported results. This is related to the fact that a large part of the analytical laboratories determining REEs are using neutron activation.

TABLE 4. DISTRIBUTION OF THE INSTRUMENTAL METHODS APPLIED IN THE ILC

Instrumental Method	Reported values	Number of laboratories
Inductively coupled plasma mass spectrometry	42.2%	7
Neutron activation analysis	37.2%	4
Inductively coupled plasma optical emission spectrometry	15.9%	4
Flame atomic absorption spectroscopy	1.9%	1
Gas chromatography atomic fluorescence spectrometry	1.6%	4
X-ray fluorescence spectroscopy	0.8%	1
Graphite furnace atomic absorption spectroscopy	0.4%	1

5.4 REVIEW OF QUESTIONNAIRES

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]. All participating laboratories reported results for a CRM along their results of the ILC sample for at least part of the reported results.

It should be noted that CRM's used by the participating laboratories are generally characterized for only part of the analytes of this exercise. As a result, 3 participating laboratories declared as not having applied fully validated methodologies to perform the measurements of the ILC sample. This underlines the importance of this exercise to help participating laboratories validate their methods for a wide range of analytes including trace elements, methylmercury and REEs.

All participating laboratories have quality control procedure in place, but only 75% of them have a quality system. Only 2 participating laboratories declare to be accredited for the determination of trace elements in marine sediments.

ILC participating laboratories were requested to report the detection limit of their analytical procedures used in this ILC. All results were reported with the associated detection and quantification limit of the applied analytical procedure.

All information reported by participating laboratories underlay their proper application of the quality control procedure and traceability concept.

6 CONCLUSIONS

The current ILC was designed to evaluate the analytical capabilities of selected laboratories. The obtained results in the ILC demonstrate the measurement capabilities of invited laboratories with very few exceptions.

More than 95% of reported values were assessed as satisfactory based on *z*-scores which demonstrates the accuracy of results produced by the selected laboratories. On the other hand, some results were not considered as satisfactory based on Zeta-scores (6%), indicating a tendency of under-estimating uncertainties associated with the reported results.

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].

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: REPORTED RESULTS BY ELEMENTS

A.1. EVALUATION OF REPORTED DATA FOR Al

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	71%	14%	14%

X_{Ass}:	52.2 g kg^{-1}
U_{Ass} (k=2):	2.4 g kg^{-1}
$2\sigma_p$:	13.1 mg kg^{-1}
Number of results:	7
Number of method:	3

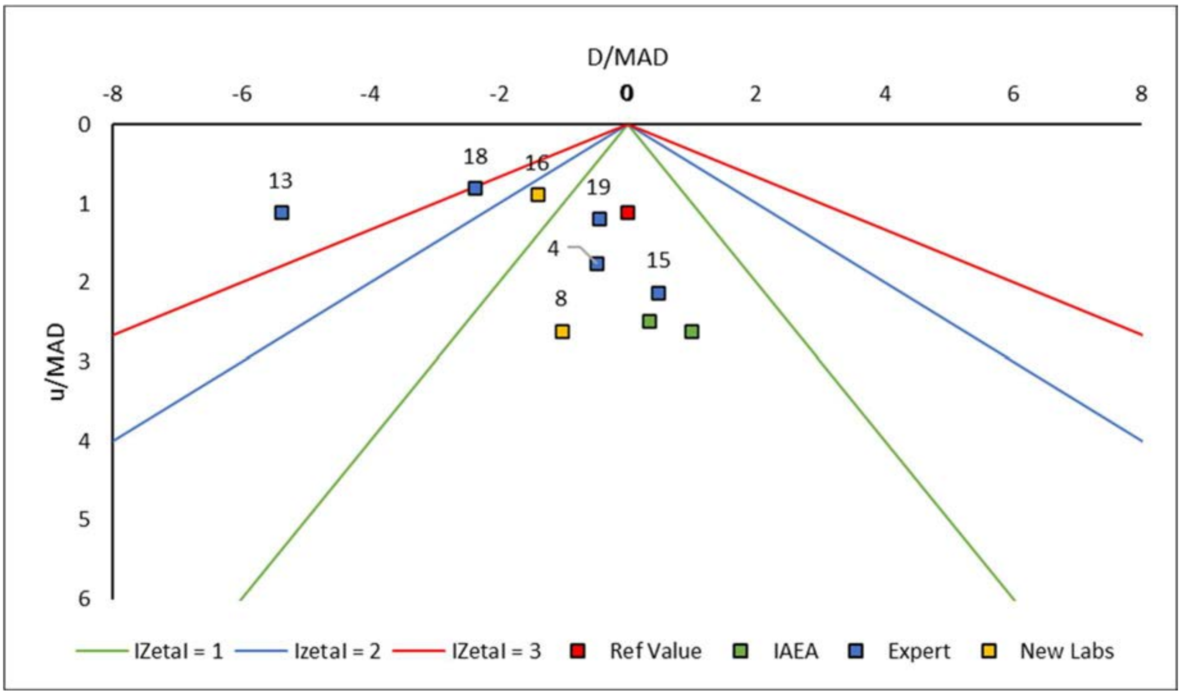
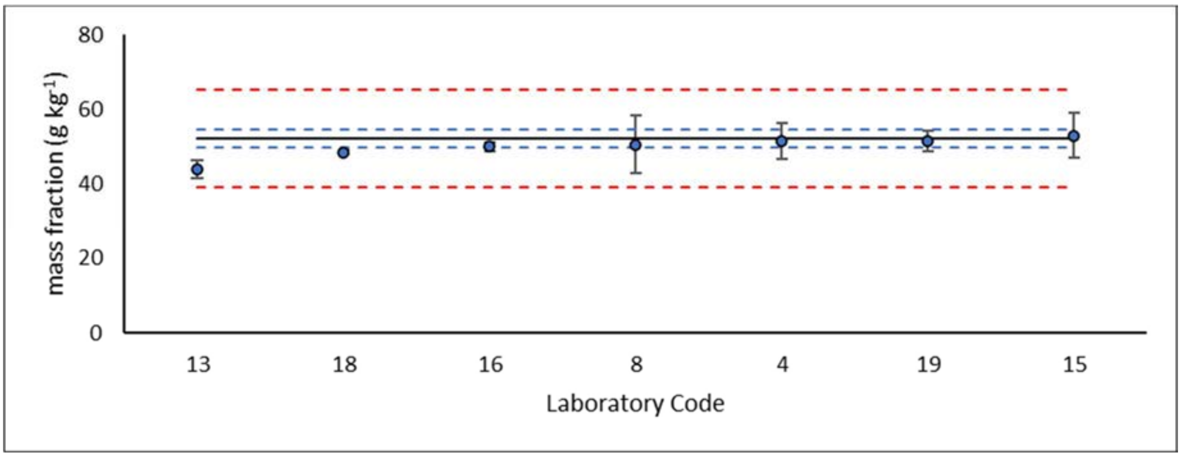


FIG. 7. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 8. Reported results and expanded uncertainties.

A.2. EVALUATION OF REPORTED DATA FOR As

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	12.0 mg kg^{-1}
U_{Ass} (k=2):	1.0 mg kg^{-1}
$2\sigma_p$:	3.0 mg kg^{-1}
Number of results:	8
Number of method:	2

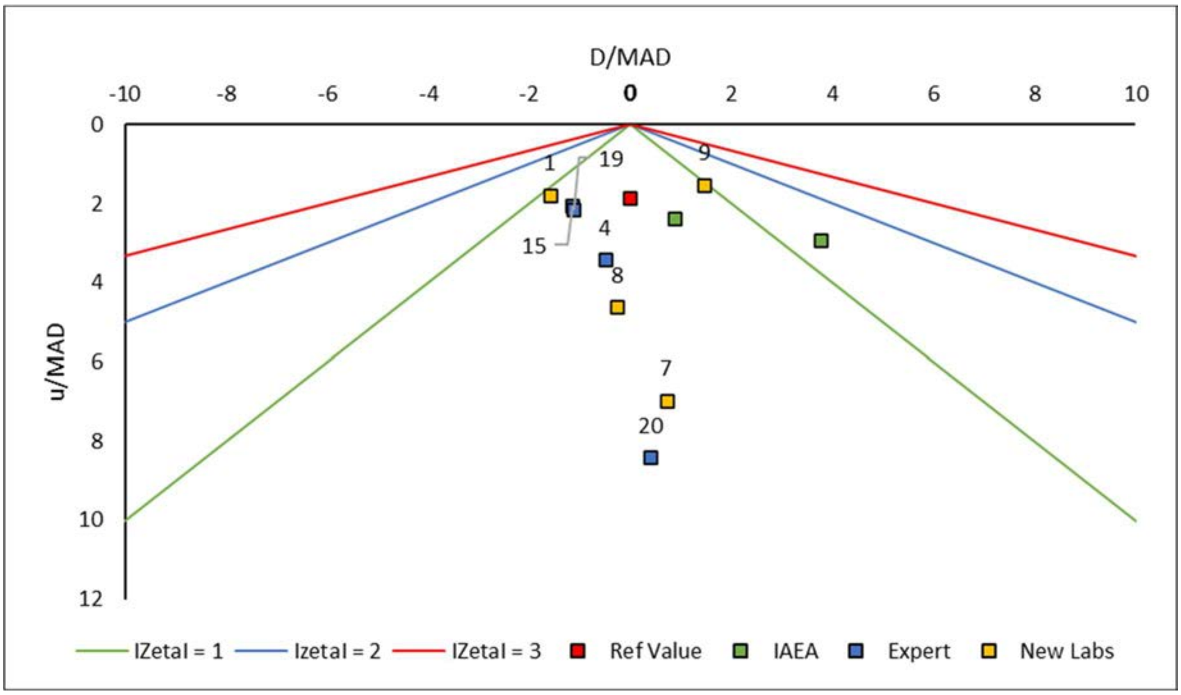
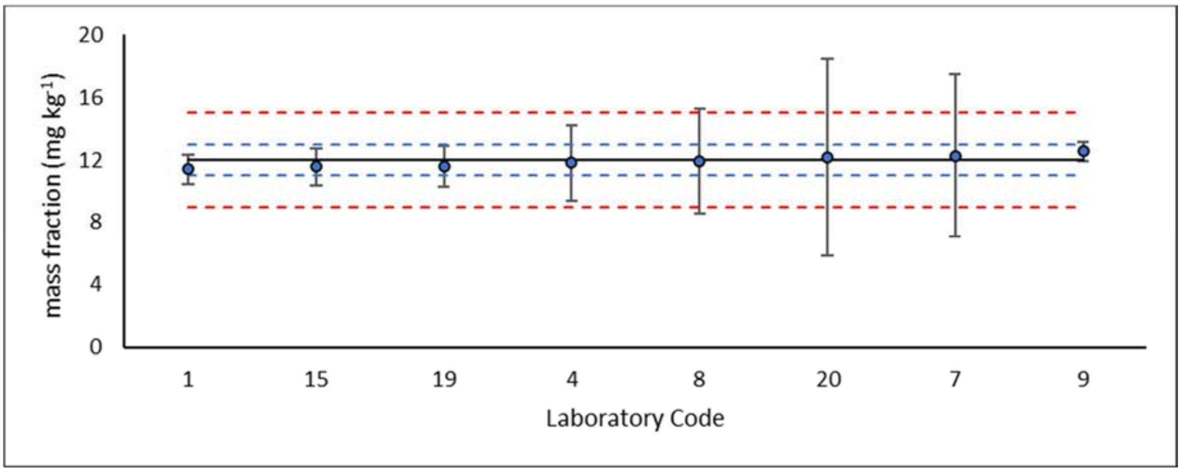


FIG. 9. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 10. Reported results and expanded uncertainties.

A.3. EVALUATION OF REPORTED DATA FOR Ba

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	89%	0%	11%

X_{Ass}:	1031 mg kg^{-1}
U_{Ass} (k=2):	83 mg kg^{-1}
$2\sigma_p$:	258 mg kg^{-1}
Number of results:	9
Number of method:	3

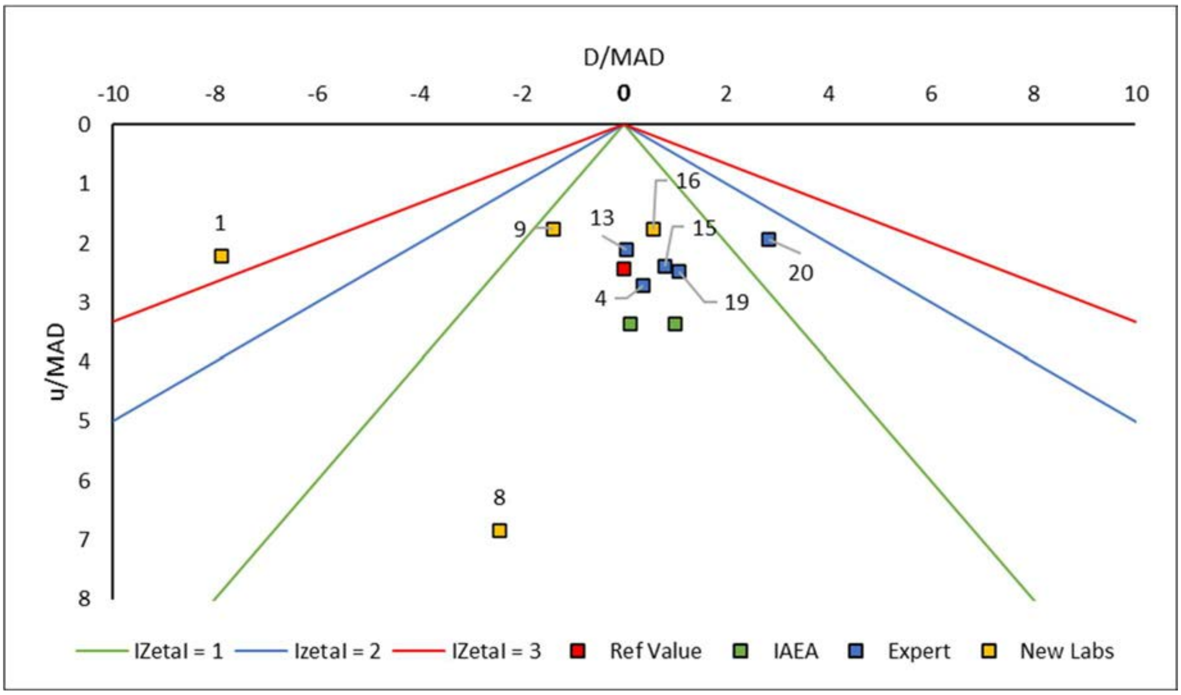
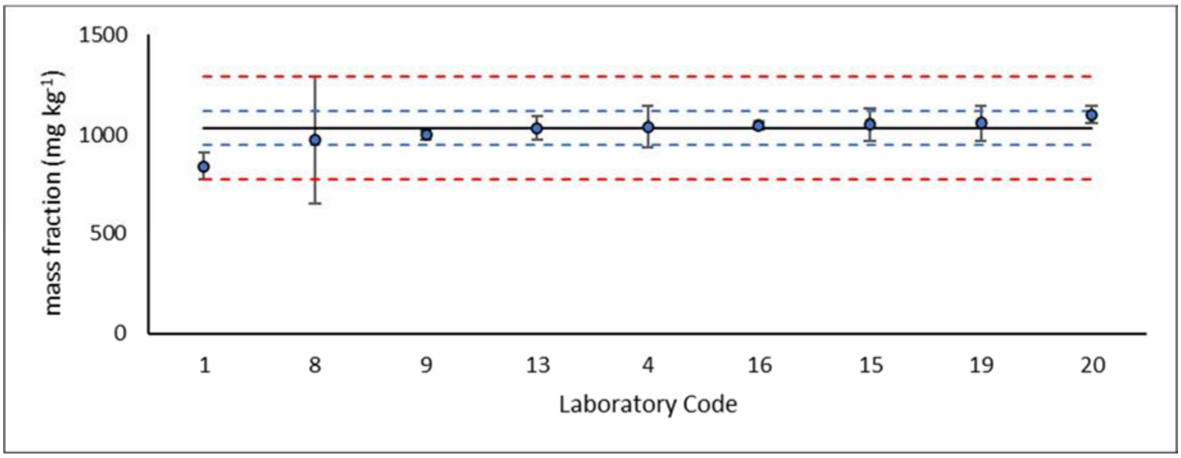


FIG. 11. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 12. Reported results and expanded uncertainties.

A.4. EVALUATION OF REPORTED DATA FOR Ca

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	88%	13%	0%
Zeta-score	88%	13%	0%

X_{Ass}:	65.3 g kg^{-1}
U_{Ass} (k=2):	2.8 g kg^{-1}
$2\sigma_p$:	16.3 g kg^{-1}
Number of results:	8
Number of method:	3

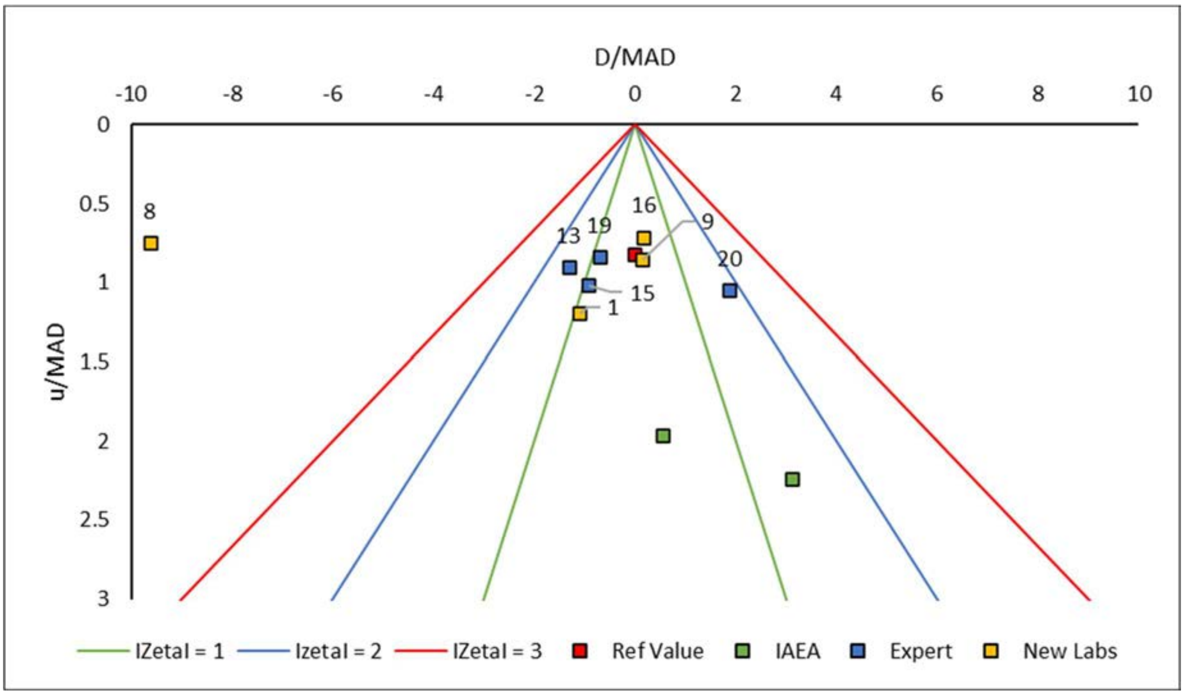
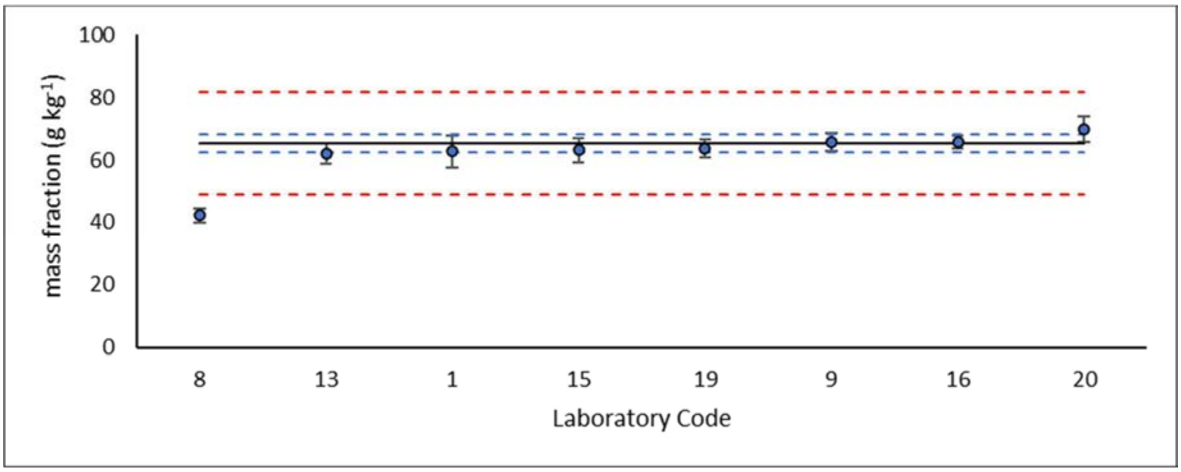


FIG. 13. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 14. Reported results and expanded uncertainties.

A.5. EVALUATION OF REPORTED DATA FOR Cd

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	0.361 mg kg^{-1}
U_{Ass} (k=2):	0.043 mg kg^{-1}
$2\sigma_p$:	0.090 mg kg^{-1}
Number of results:	5
Number of method:	2

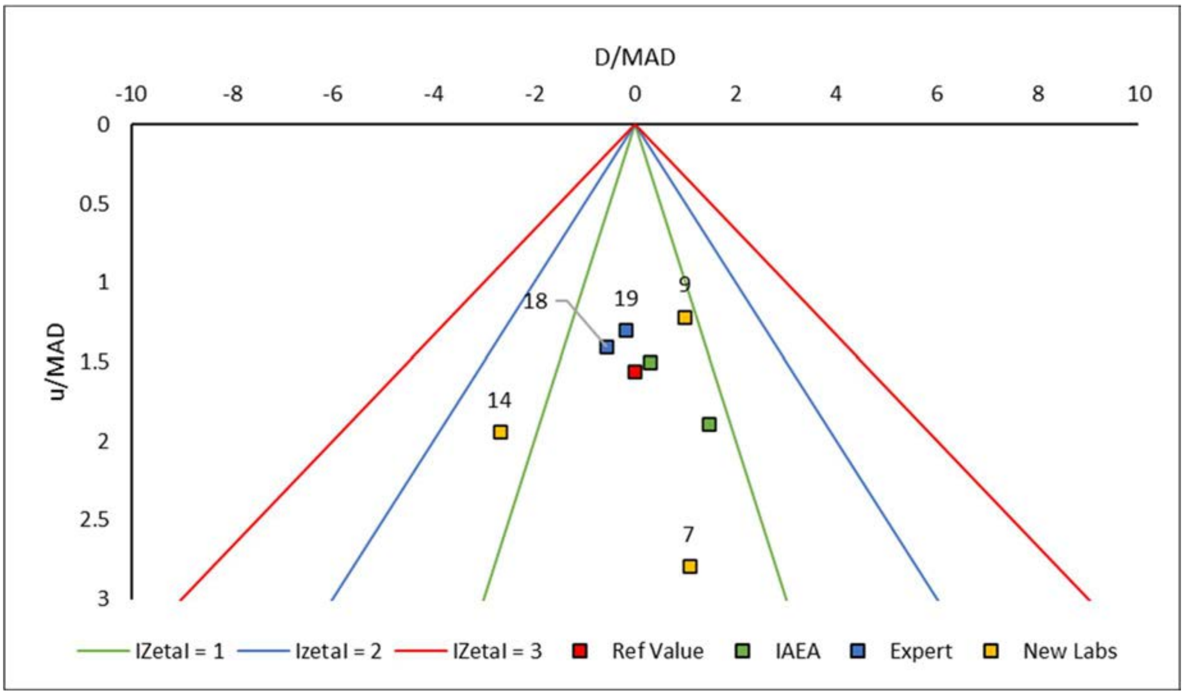
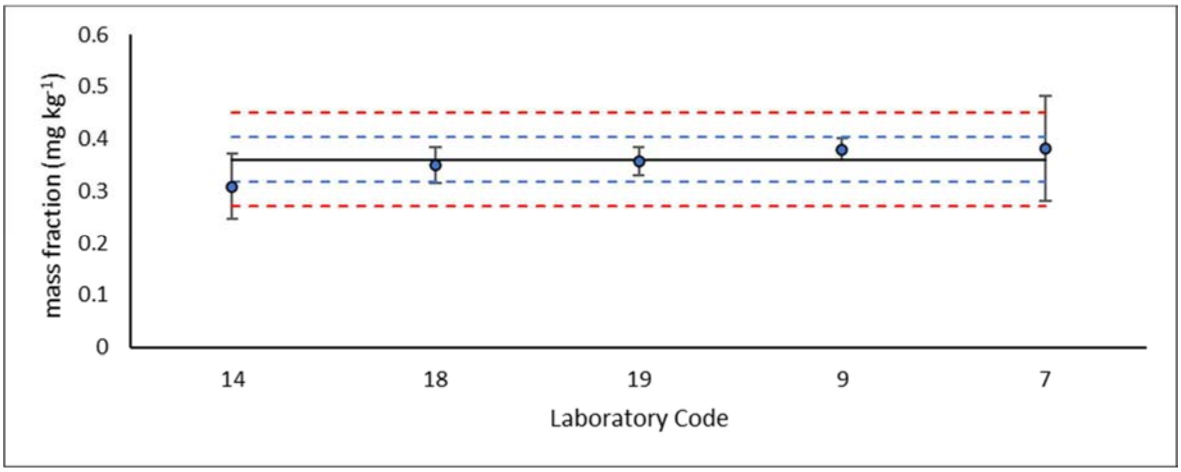


FIG. 15. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 16. Reported results and expanded uncertainties.

A.6. EVALUATION OF REPORTED DATA FOR Ce

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	75%	13%	13%
Zeta-score	63%	13%	25%

X_{Ass}:	54.1 mg kg^{-1}
U_{Ass} (k=2):	5.6 mg kg^{-1}
$2\sigma_p$:	13.5 mg kg^{-1}
Number of results:	8
Number of method:	2

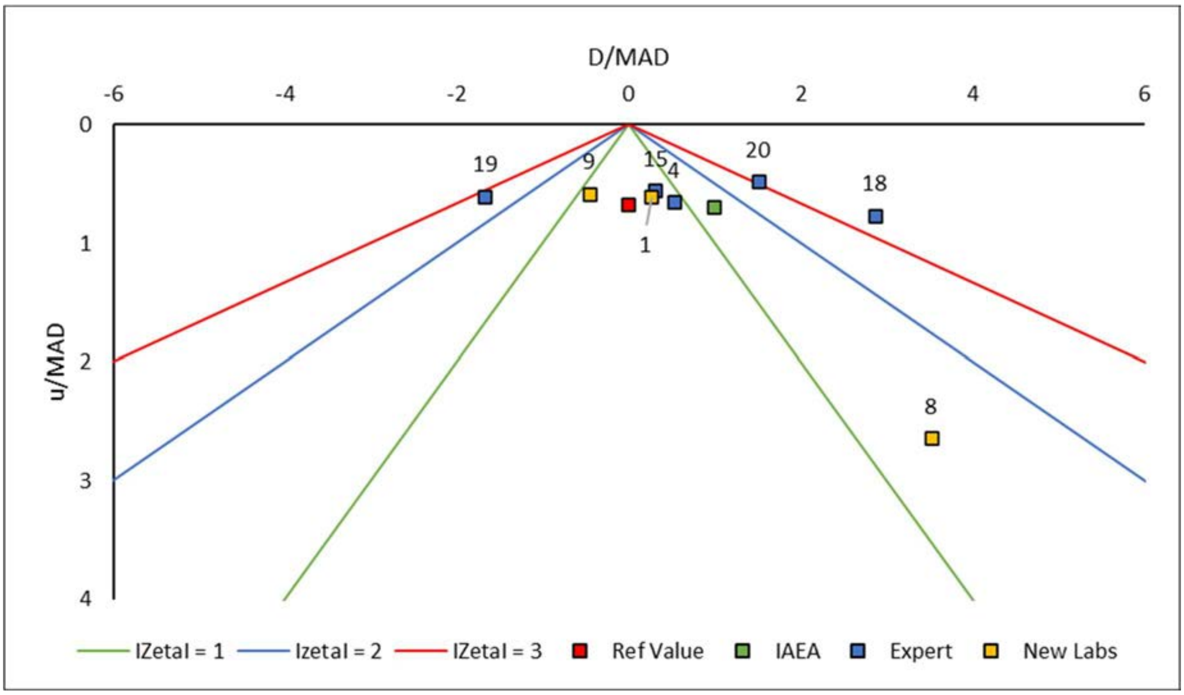
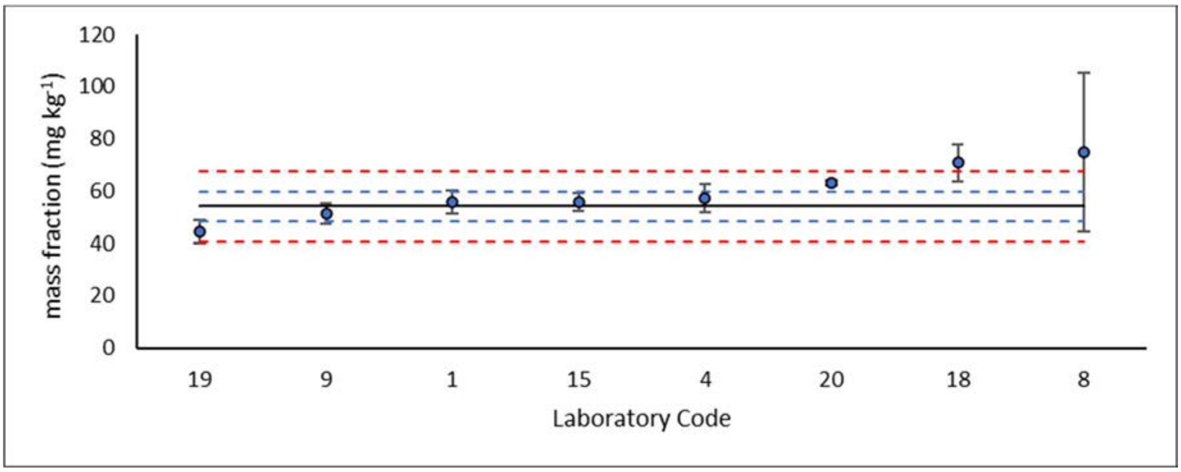


FIG. 17. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 18. Reported results and expanded uncertainties.

A.7. EVALUATION OF REPORTED DATA FOR Co

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	91%	0%	9%
Zeta-score	91%	0%	9%

X_{Ass}:	9.19 mg kg^{-1}
U_{Ass} (k=2):	0.90 mg kg^{-1}
$2\sigma_p$:	2.30 mg kg^{-1}
Number of results:	11
Number of method:	3

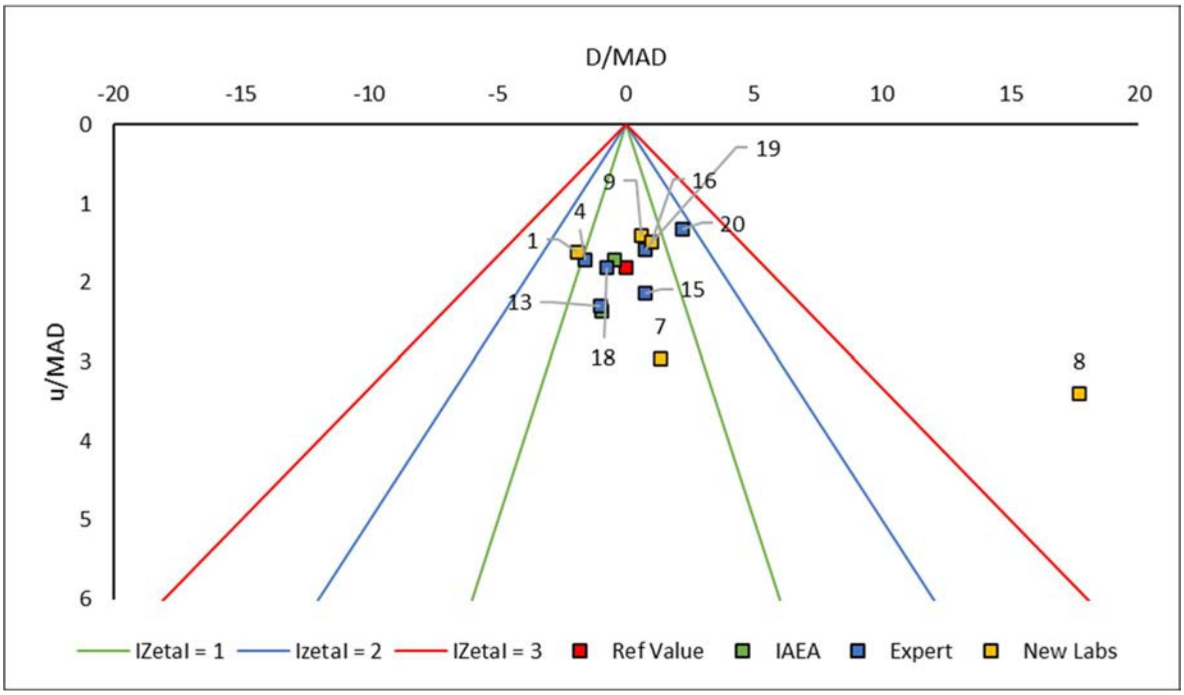
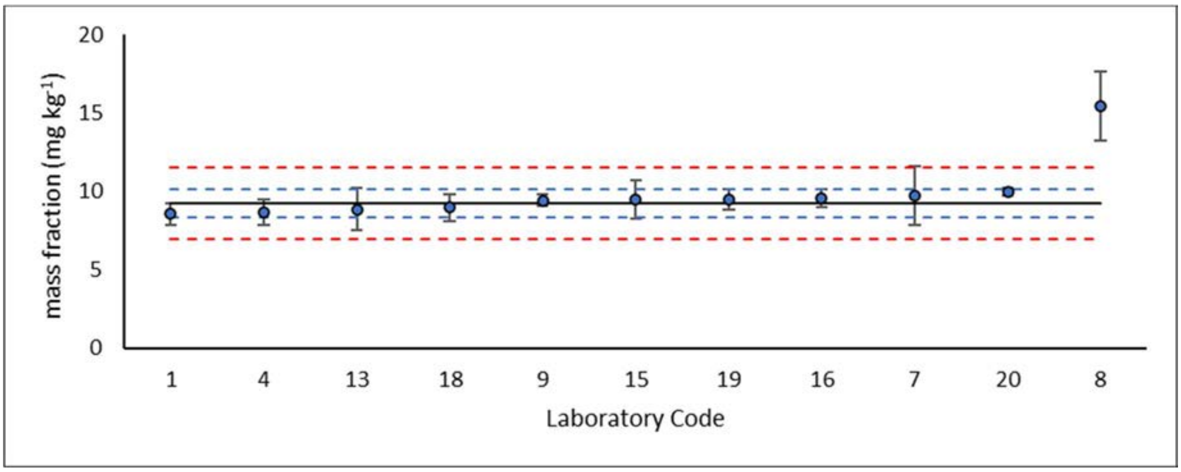


FIG. 19. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 20. Reported results and expanded uncertainties.

A.8. EVALUATION OF REPORTED DATA FOR Cr

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	77.0 mg kg^{-1}
U_{Ass} (k=2):	8.2 mg kg^{-1}
$2\sigma_p$:	19.3 mg kg^{-1}
Number of results:	11
Number of method:	4

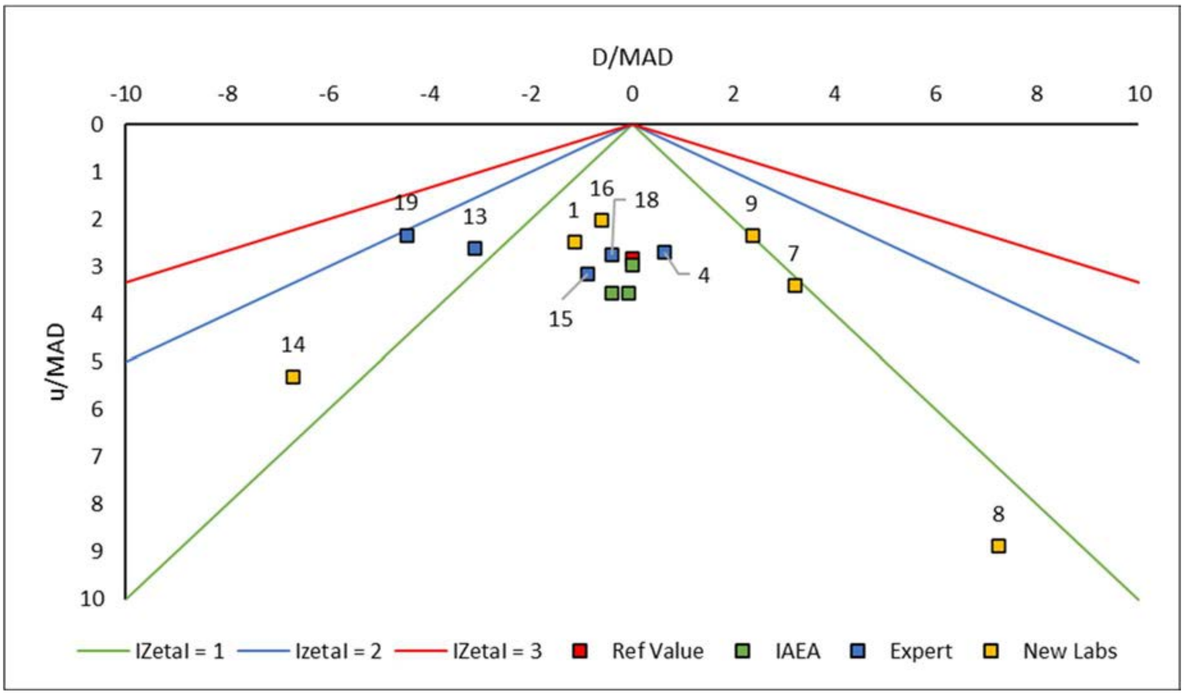
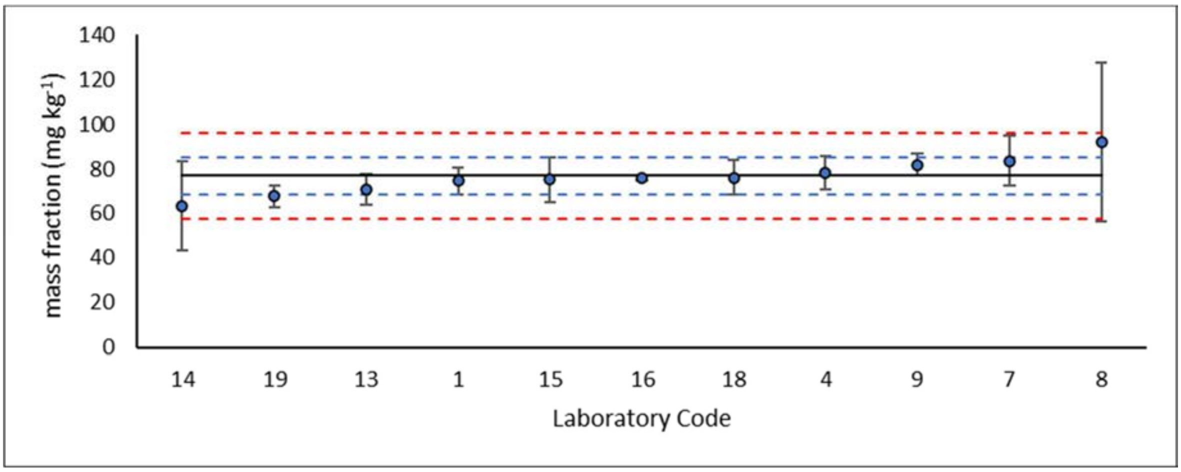


FIG. 21. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 22. Reported results and expanded uncertainties.

A.9. EVALUATION OF REPORTED DATA FOR Dy

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	3.35 mg kg^{-1}
U_{Ass} (k=2):	0.41 mg kg^{-1}
$2\sigma_p$:	0.84 mg kg^{-1}
Number of results:	5
Number of method:	2

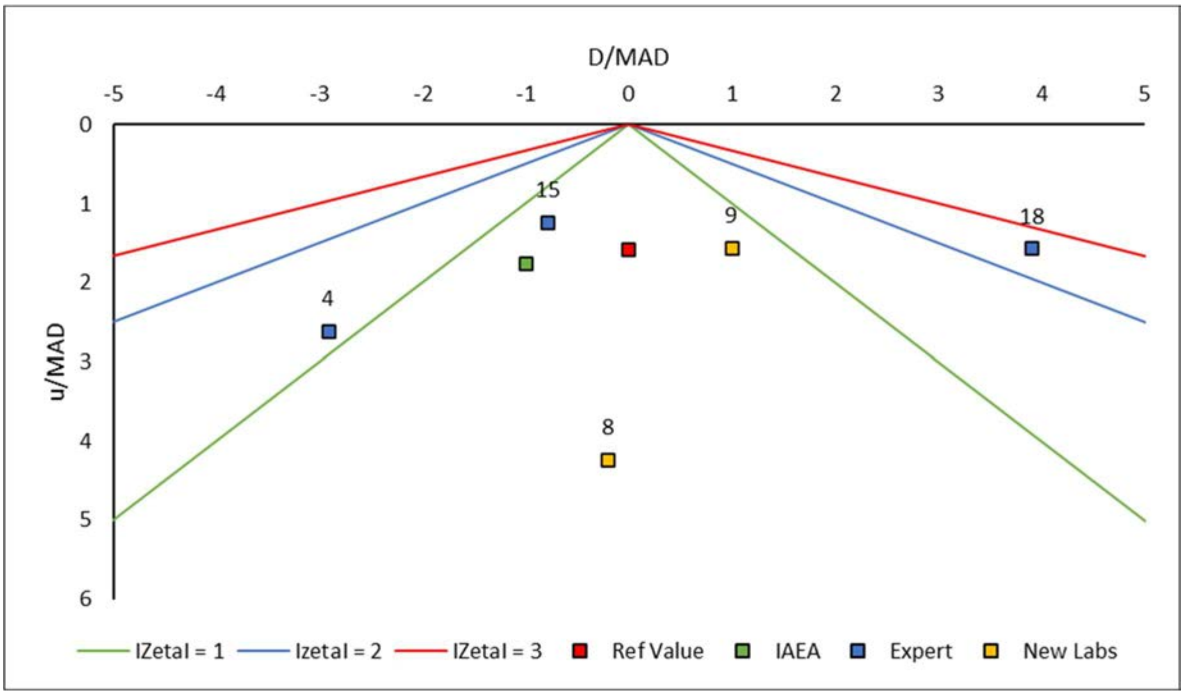
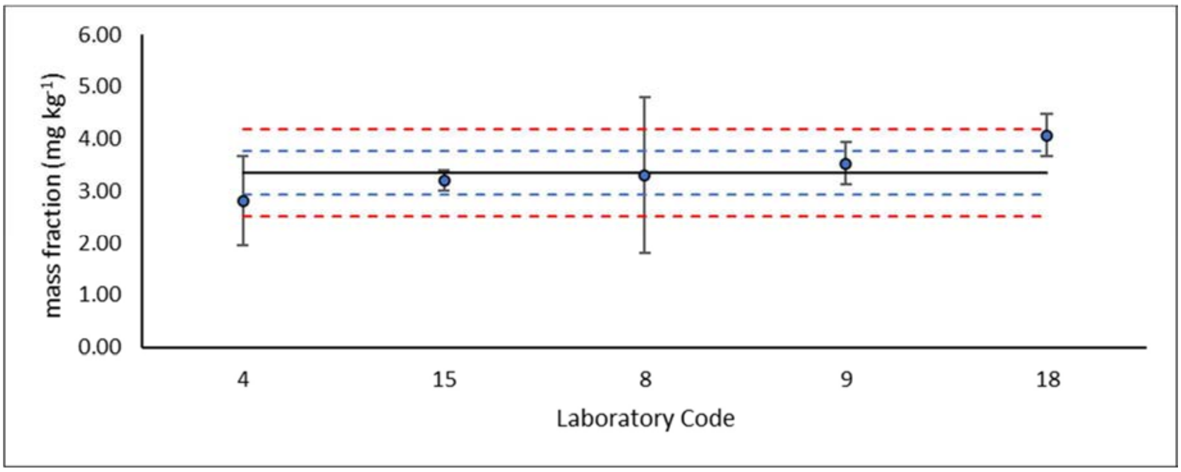


FIG. 23. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 24. Reported results and expanded uncertainties.

A.10. EVALUATION OF REPORTED DATA FOR Eu

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	86%	0%	14%

X_{Ass}:	1.098 mg kg^{-1}
U_{Ass} (k=2):	0.085 mg kg^{-1}
$2\sigma_p$:	0.275 mg kg^{-1}
Number of results:	7
Number of method:	2

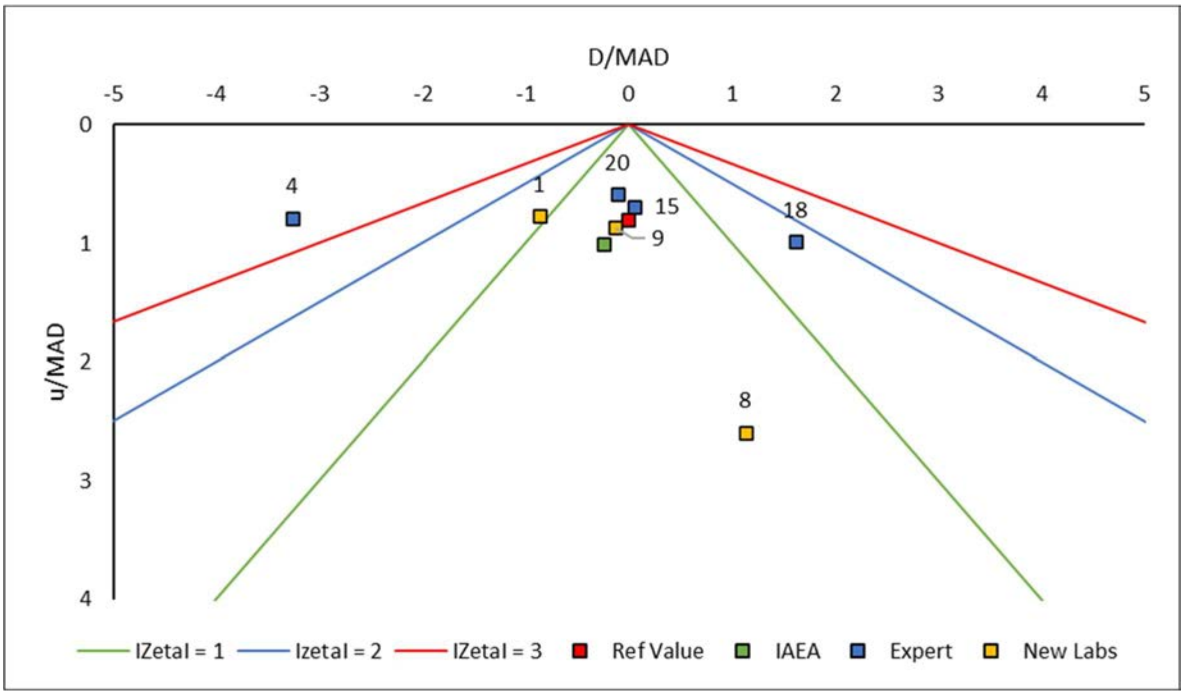
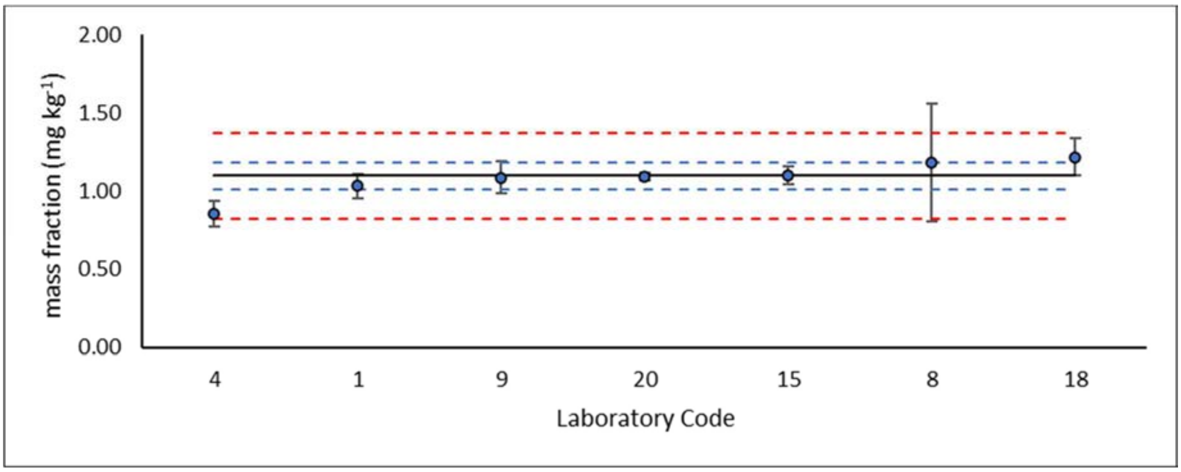


FIG. 25. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 26. Reported results and expanded uncertainties.

A.11. EVALUATION OF REPORTED DATA FOR Fe

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	73%	18%	9%

X_{Ass}:	26.6 g kg^{-1}
U_{Ass} (k=2):	1.2 g kg^{-1}
$2\sigma_p$:	6.7 g kg^{-1}
Number of results:	11
Number of method:	4

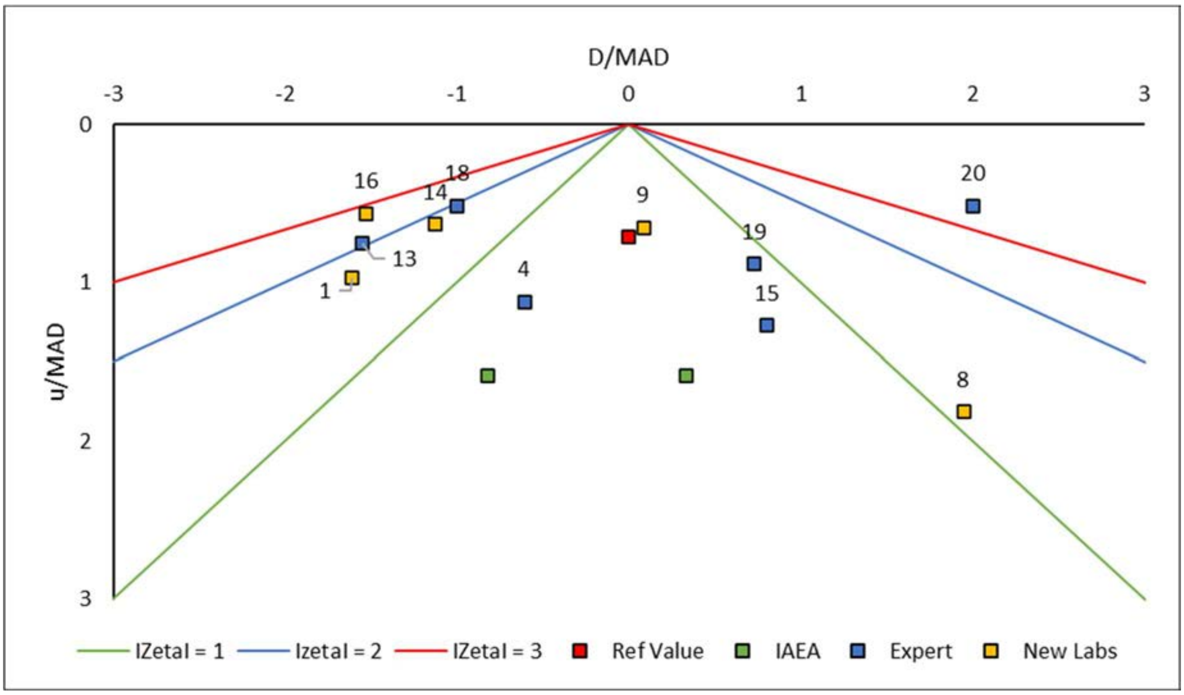
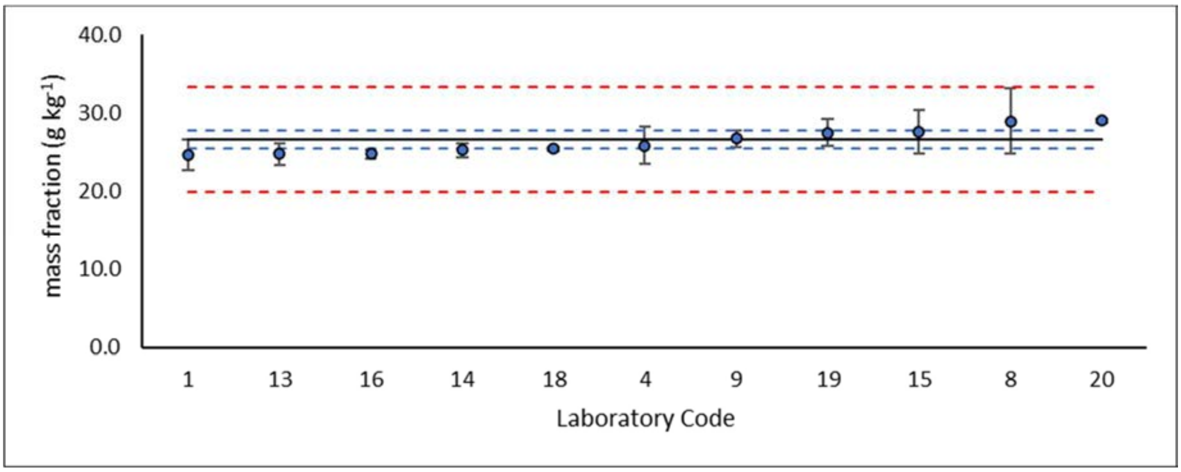


FIG. 27. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 28. Reported results and expanded uncertainties.

A.12. EVALUATION OF REPORTED DATA FOR Ho

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	75%	25%	0%

X_{Ass}:	0.692 mg kg^{-1}
U_{Ass} (k=2):	0.074 mg kg^{-1}
$2\sigma_p$:	0.173 mg kg^{-1}
Number of results:	4
Number of method:	1

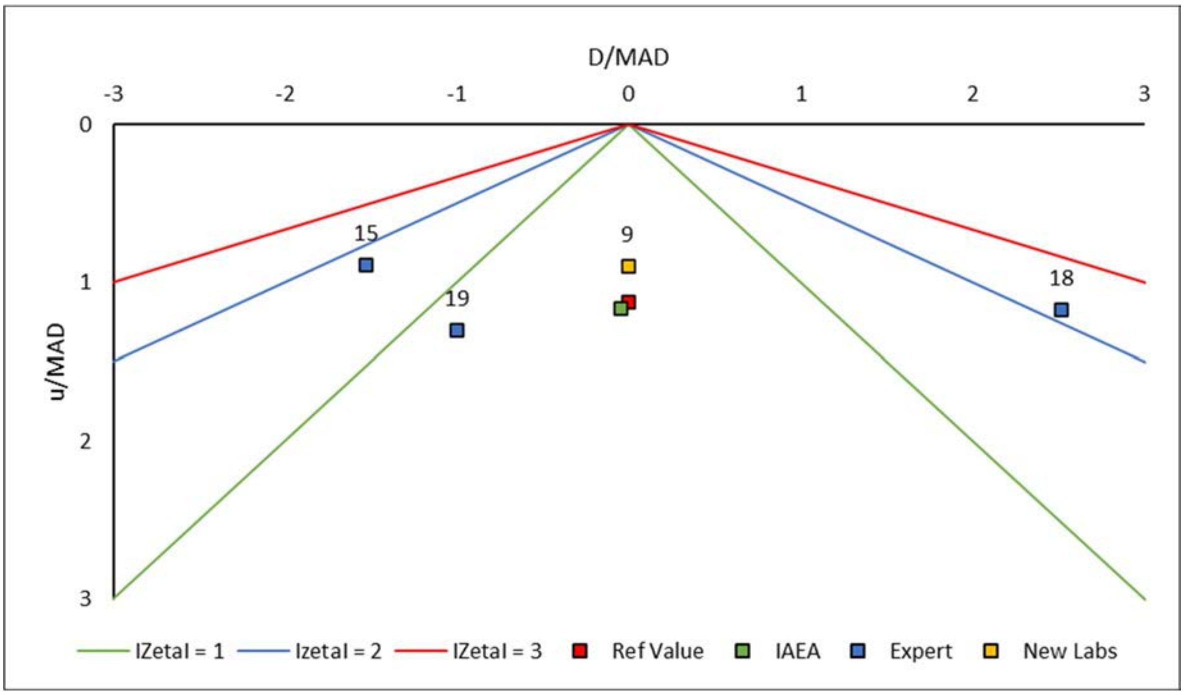
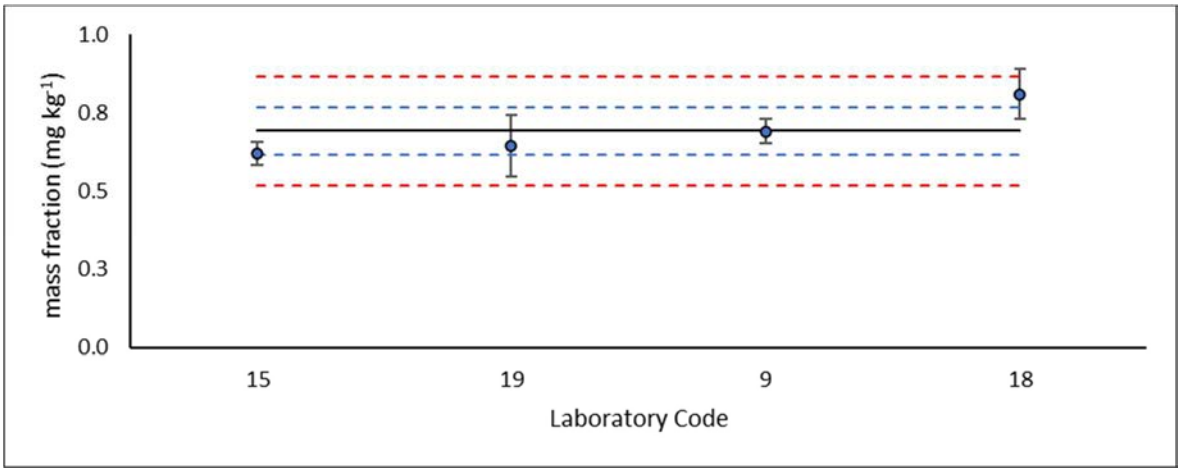


FIG. 29. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 30. Reported results and expanded uncertainties.

A.13. EVALUATION OF REPORTED DATA FOR K

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	86%	0%	14%

X_{Ass}:	20.5 g kg^{-1}
U_{Ass} (k=2):	1.5 g kg^{-1}
$2\sigma_p$:	5.1 g kg^{-1}
Number of results:	7
Number of method:	3

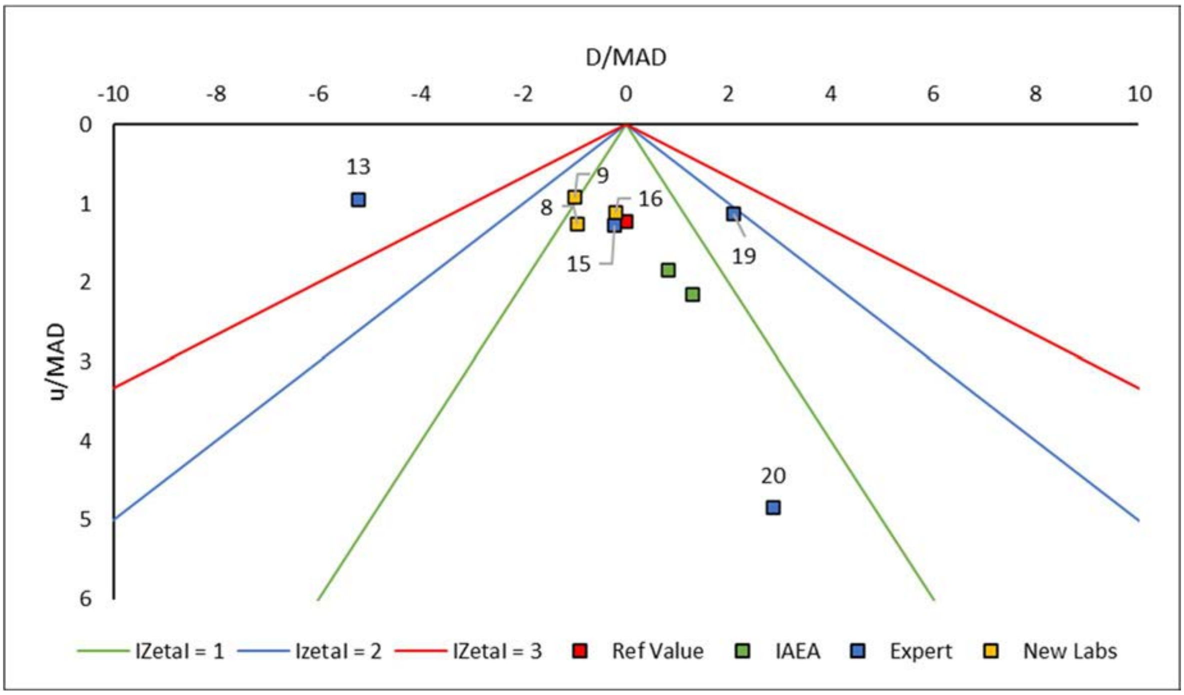
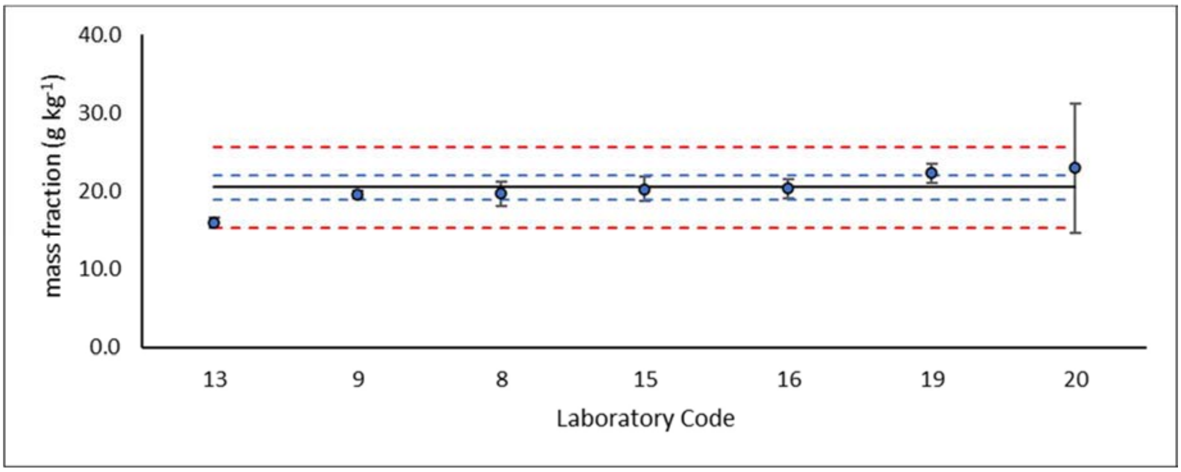


FIG. 31. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 32. Reported results and expanded uncertainties.

A.14. EVALUATION OF REPORTED DATA FOR La

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	86%	14%	0%

X_{Ass}:	28.5 mg kg^{-1}
U_{Ass} (k=2):	3.1 mg kg^{-1}
$2\sigma_p$:	7.1 mg kg^{-1}
Number of results:	7
Number of method:	2

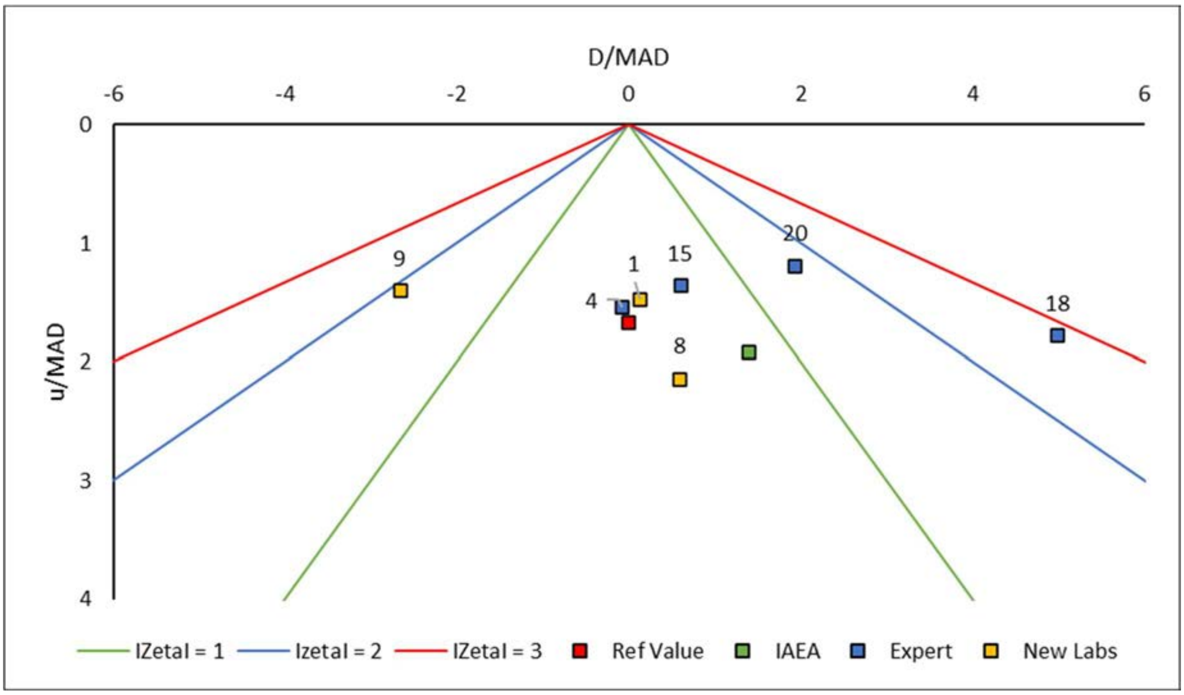
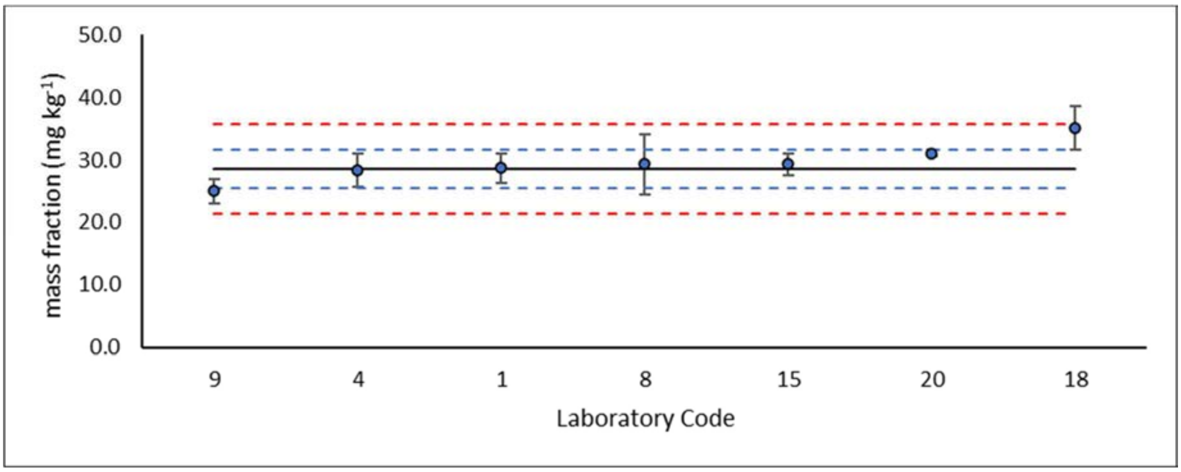


FIG. 33. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 34. Reported results and expanded uncertainties.

A.15. EVALUATION OF REPORTED DATA FOR Li

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	33.5 mg kg^{-1}
U_{Ass} (k=2):	3.3 mg kg^{-1}
$2\sigma_p$:	8.4 mg kg^{-1}
Number of results:	5
Number of method:	2

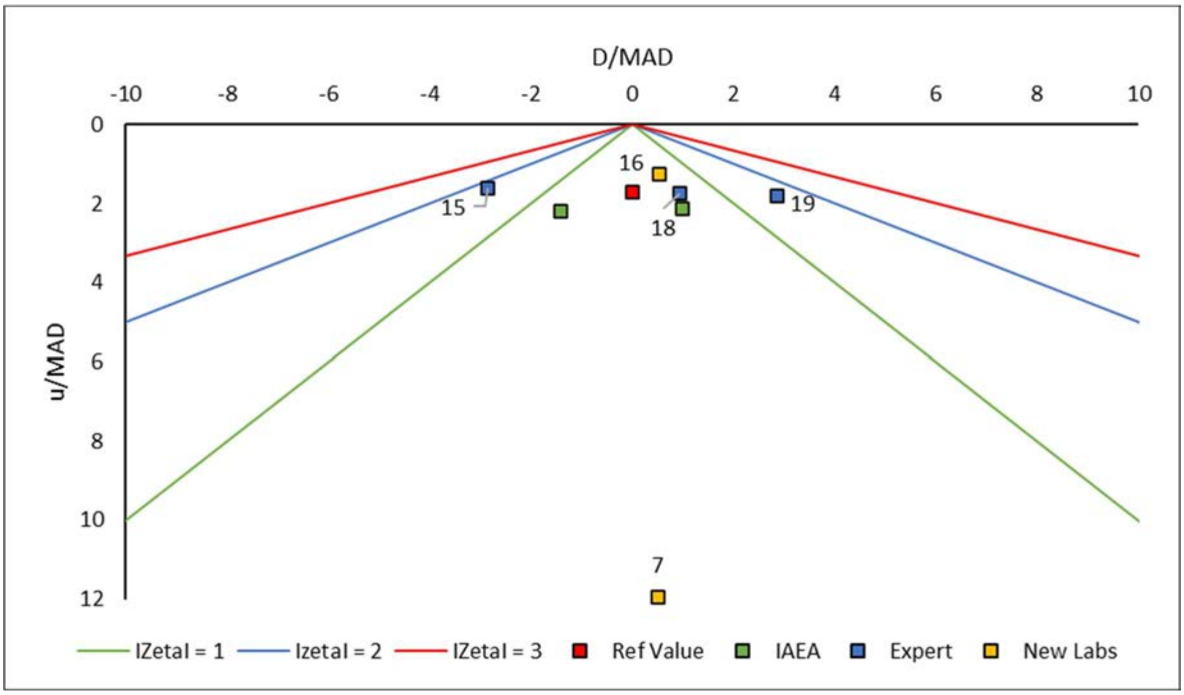
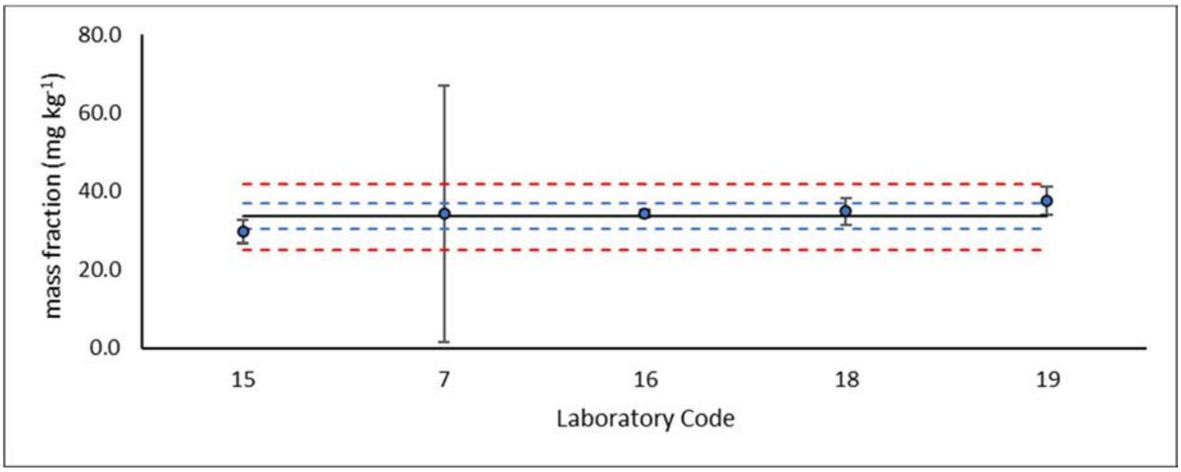


FIG. 35. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 36. Reported results and expanded uncertainties.

A.16. EVALUATION OF REPORTED DATA FOR Lu

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	0.307 mg kg^{-1}
U_{Ass} (k=2):	0.026 mg kg^{-1}
$2\sigma_p$:	0.077 mg kg^{-1}
Number of results:	5
Number of method:	2

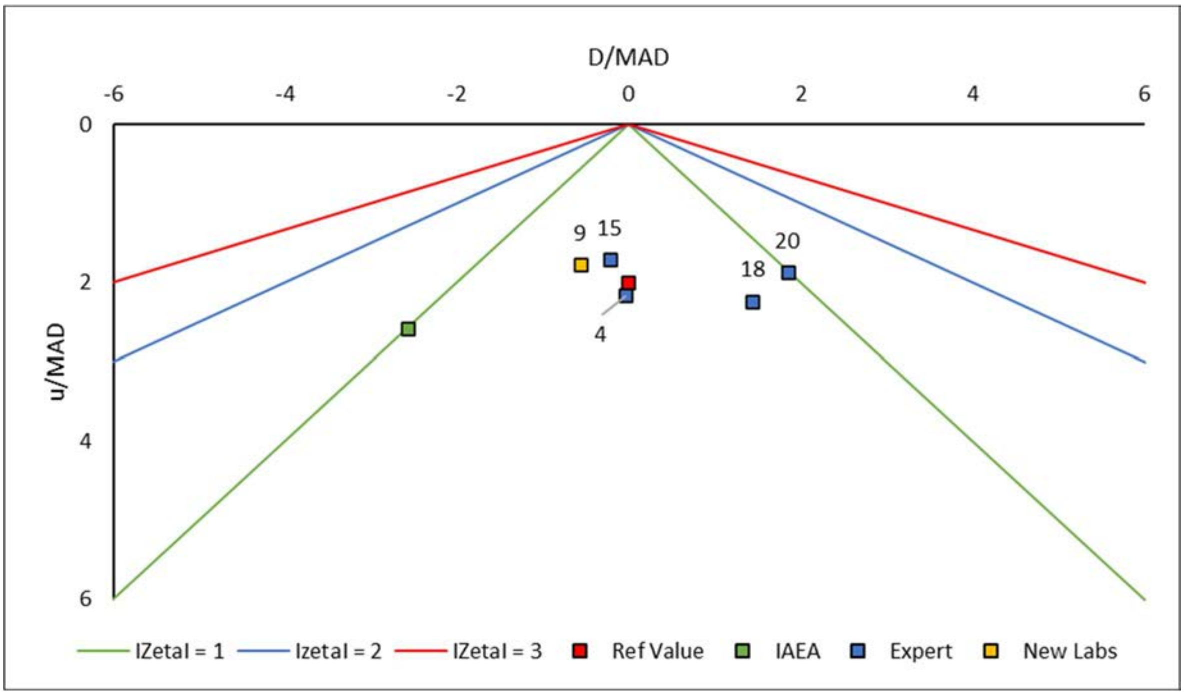
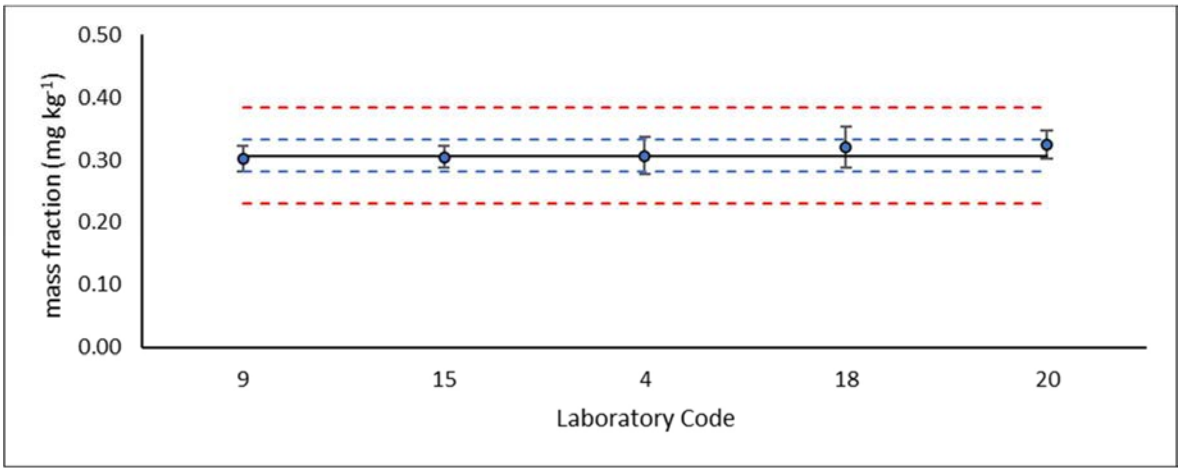


FIG. 37. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 38. Reported results and expanded uncertainties.

A.17. EVALUATION OF REPORTED DATA FOR MeHg

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	80%	20%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	1.80 µg kg^{-1} as Hg
U_{Ass} (k=2):	0.26 µg kg^{-1} as Hg
$2\sigma_P$:	0.45 µg kg^{-1} as Hg
Number of results:	5
Number of method:	2

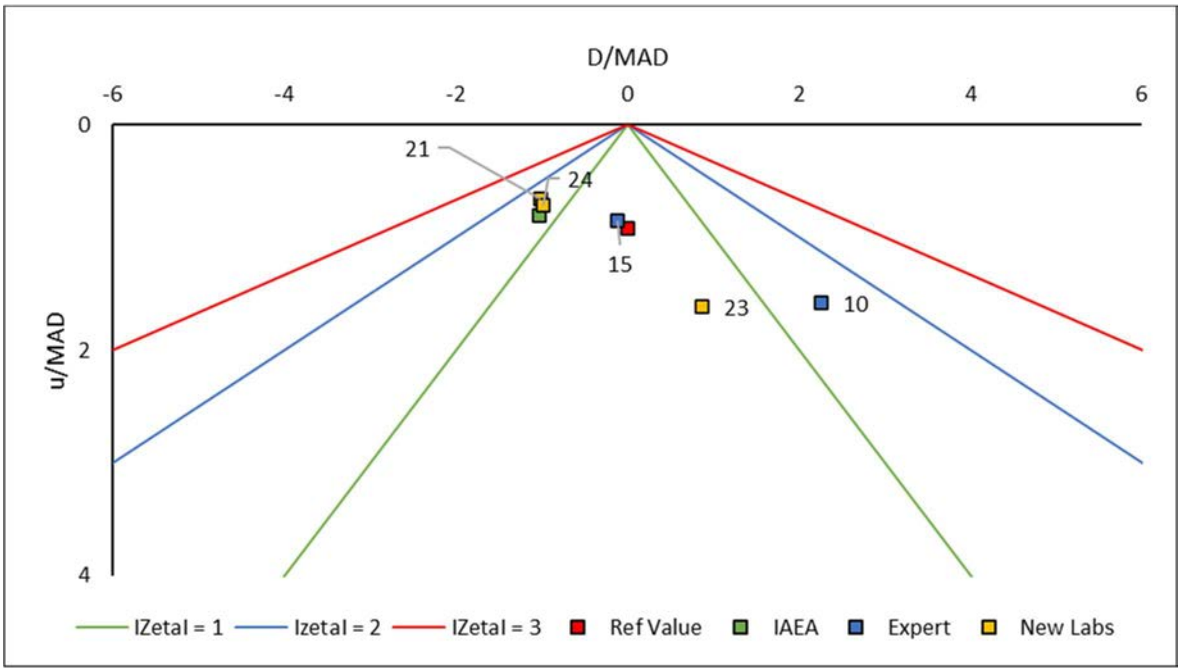
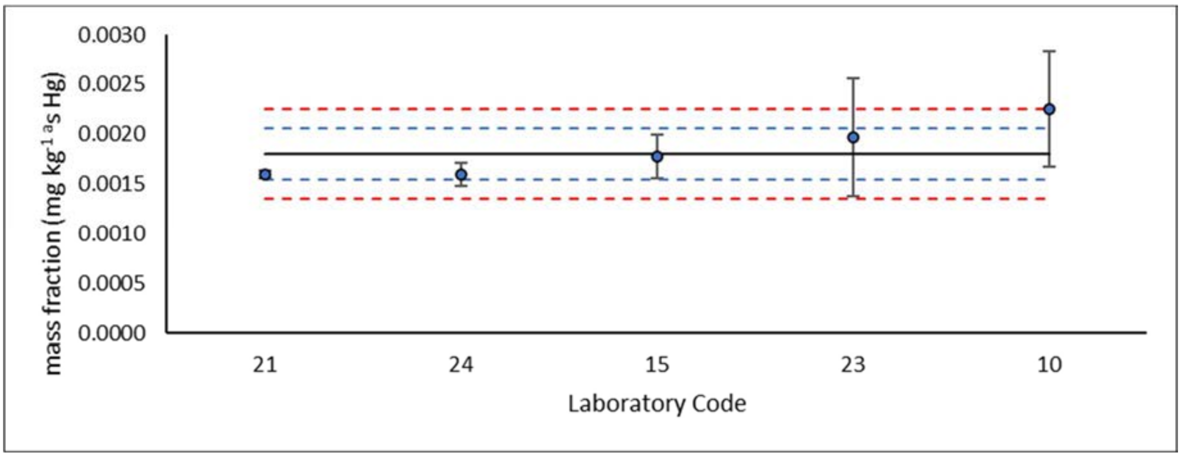


FIG. 39. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 40. Reported results and expanded uncertainties.

A.18. EVALUATION OF REPORTED DATA FOR Mg

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	86%	0%	14%
Zeta-score	72%	14%	14%

X_{Ass}:	10.86 g kg^{-1}
U_{Ass} (k=2):	0.58 g kg^{-1}
$2\sigma_p$:	2.72 g kg^{-1}
Number of results:	7
Number of method:	3

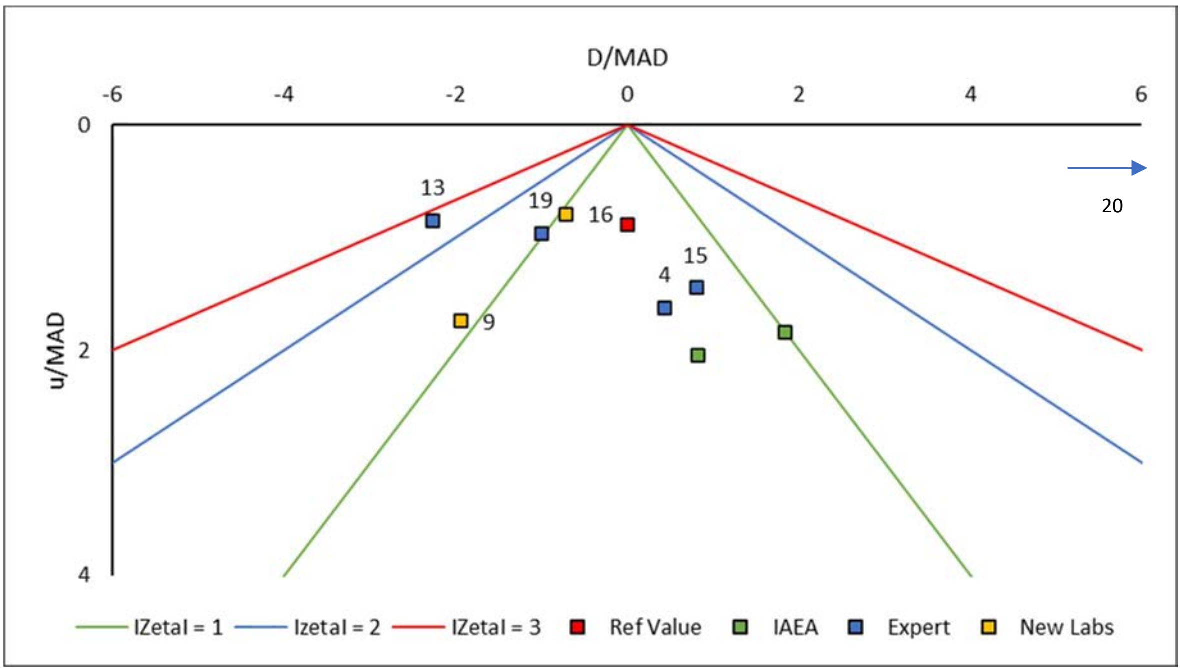
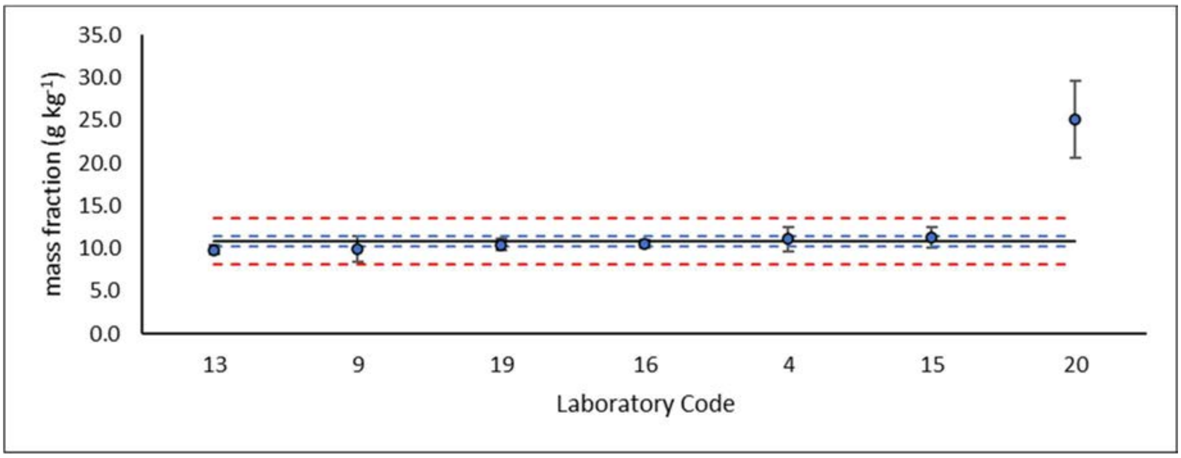


FIG. 41. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 42. Reported results and expanded uncertainties.

A.19. EVALUATION OF REPORTED DATA FOR Mn

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	91%	9%	0%

X_{Ass}:	367 mg kg^{-1}
U_{Ass} (k=2):	19 mg kg^{-1}
$2\sigma_p$:	91.8 mg kg^{-1}
Number of results:	11
Number of method:	4

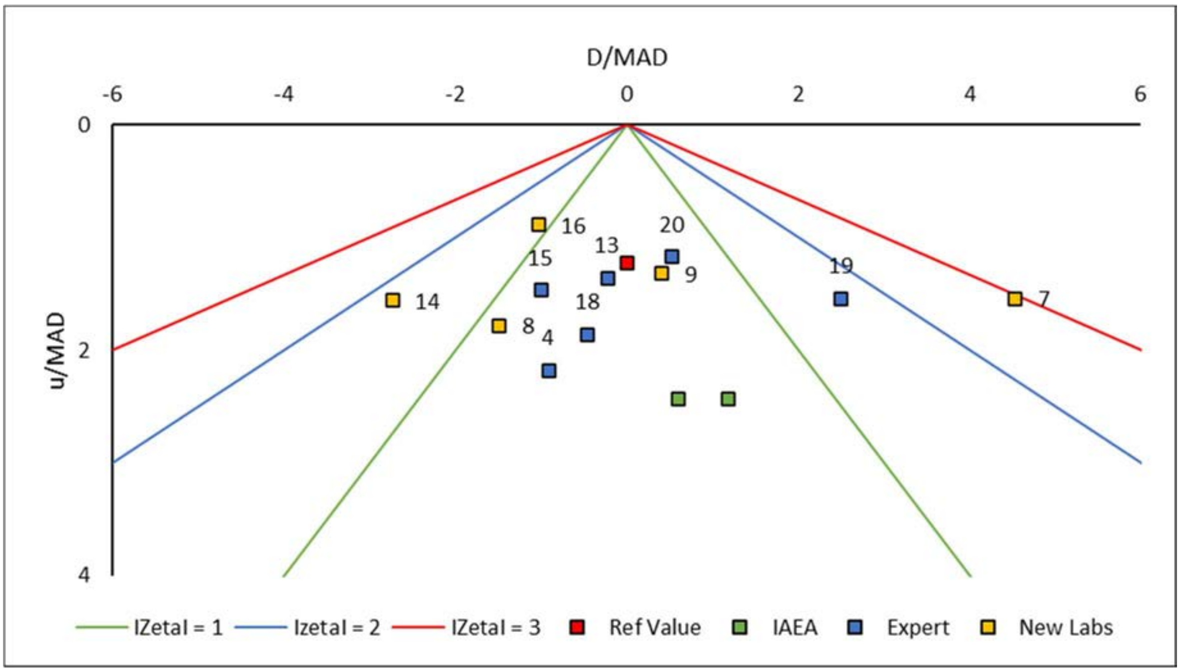
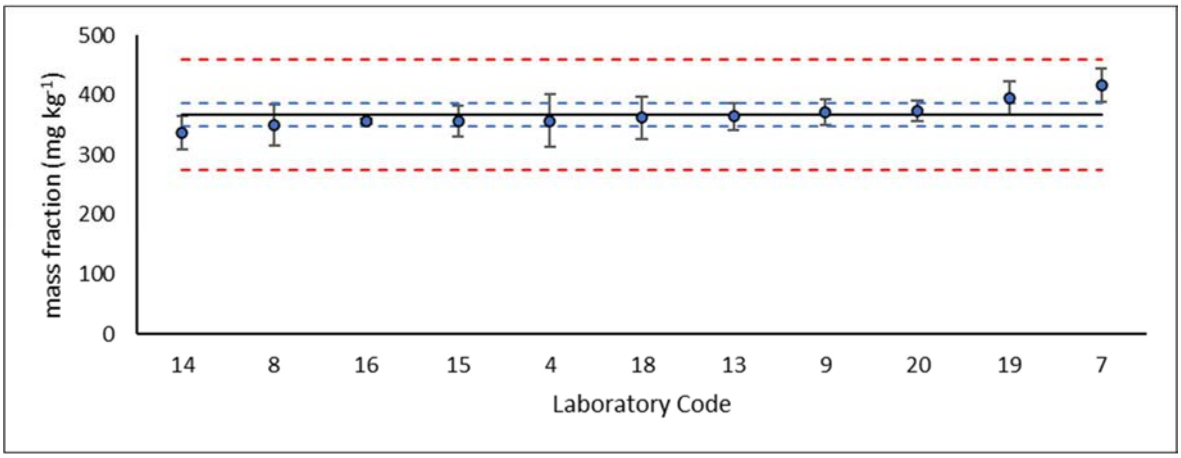


FIG. 43. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 44. Reported results and expanded uncertainties.

A.20. EVALUATION OF REPORTED DATA FOR Na

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	89%	0%	11%

X_{Ass}:	23.91 g kg^{-1}
U_{Ass} (k=2):	0.88 g kg^{-1}
$2\sigma_p$:	5.98 g kg^{-1}
Number of results:	9
Number of method:	3

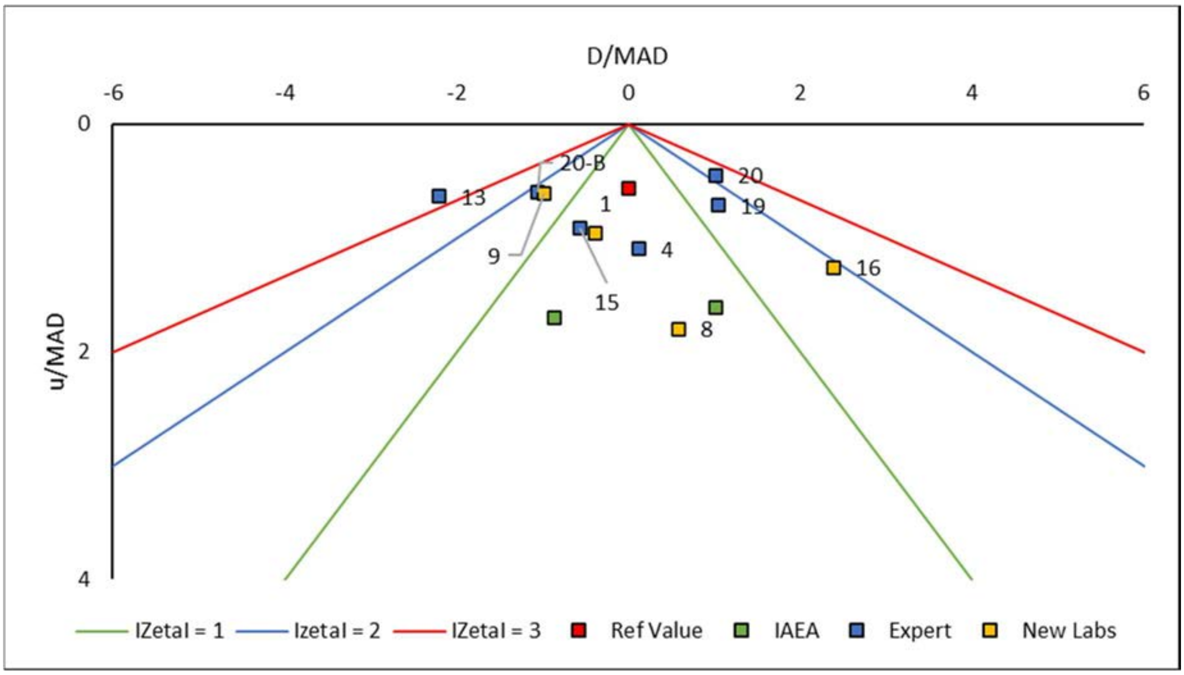
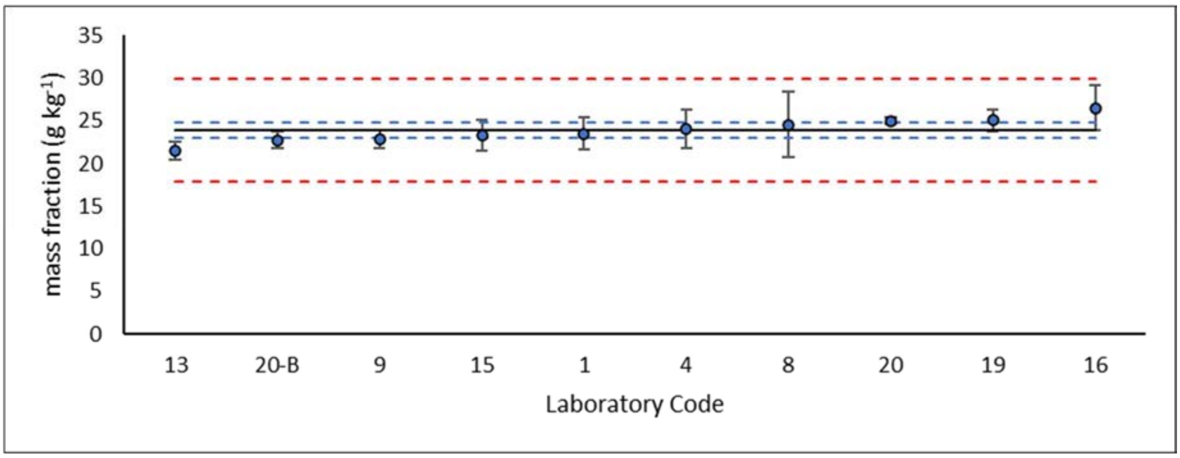


FIG. 45. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 46. Reported results and expanded uncertainties.

A.21. EVALUATION OF REPORTED DATA FOR Nd

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	83%	17%	0%

X_{Ass}:	25.1 mg kg^{-1}
U_{Ass} (k=2):	2.6 mg kg^{-1}
$2\sigma_P$:	6.3 mg kg^{-1}
Number of results:	6
Number of method:	2

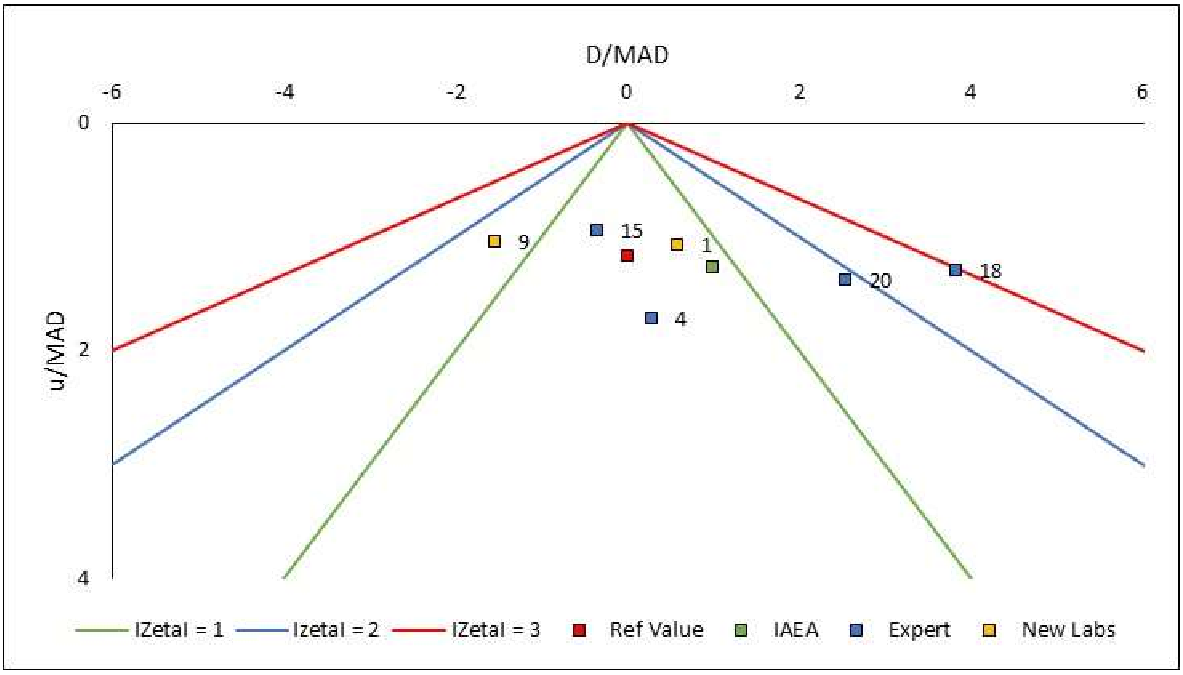
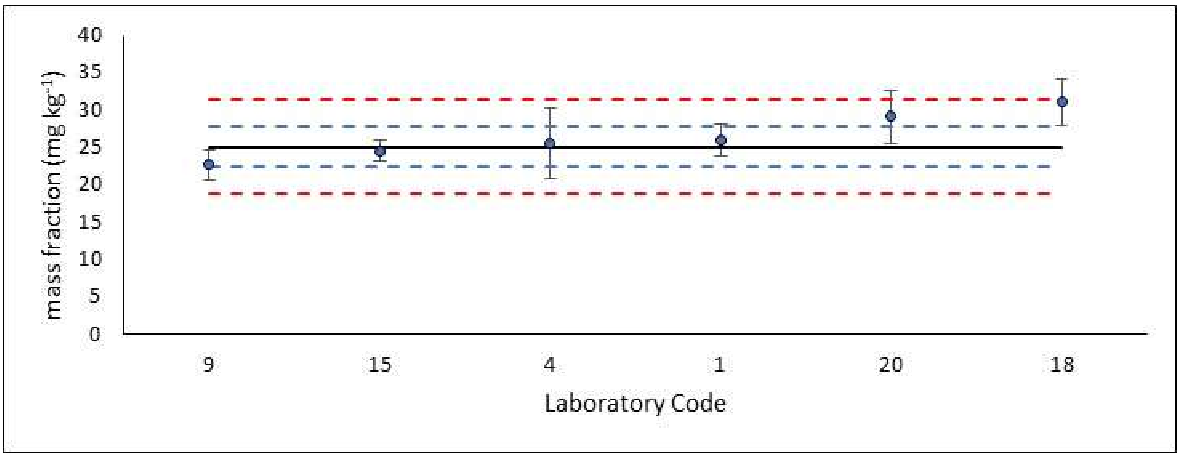


FIG. 47. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 48. Reported results and expanded uncertainties.

A.22. EVALUATION OF REPORTED DATA FOR Ni

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	57%	29%	14%

X_{Ass}:	31.1 mg kg^{-1}
U_{Ass} (k=2):	2.1 mg kg^{-1}
$2\sigma_p$:	7.8 mg kg^{-1}
Number of results:	7
Number of method:	2

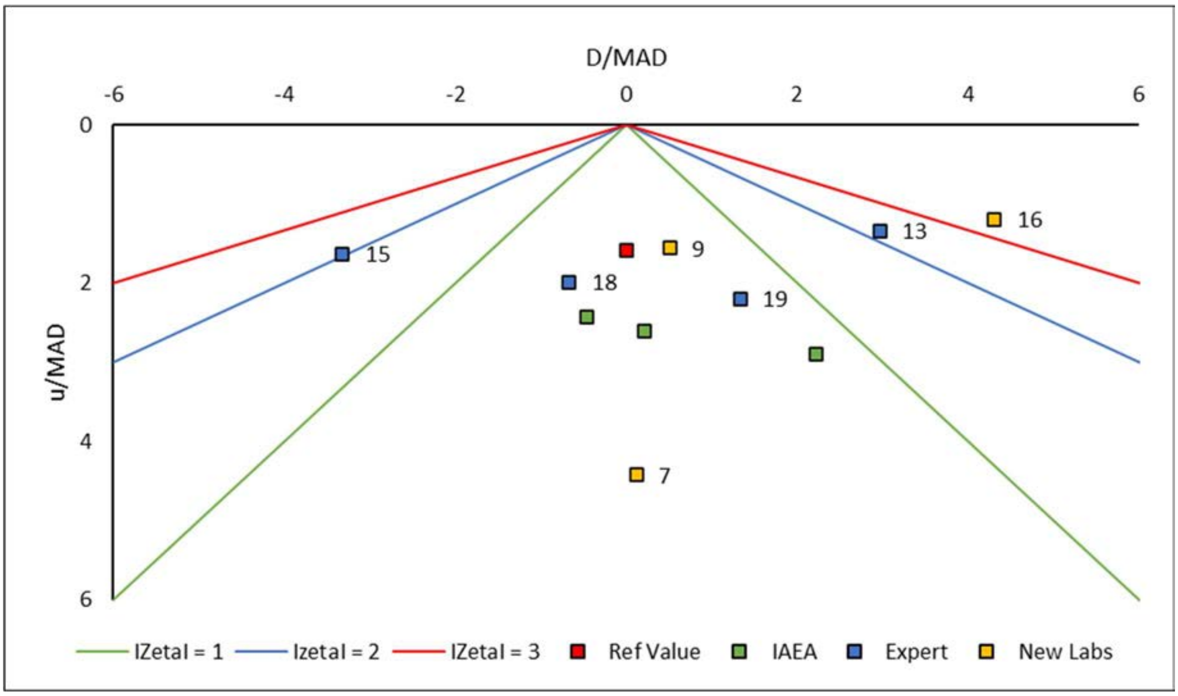
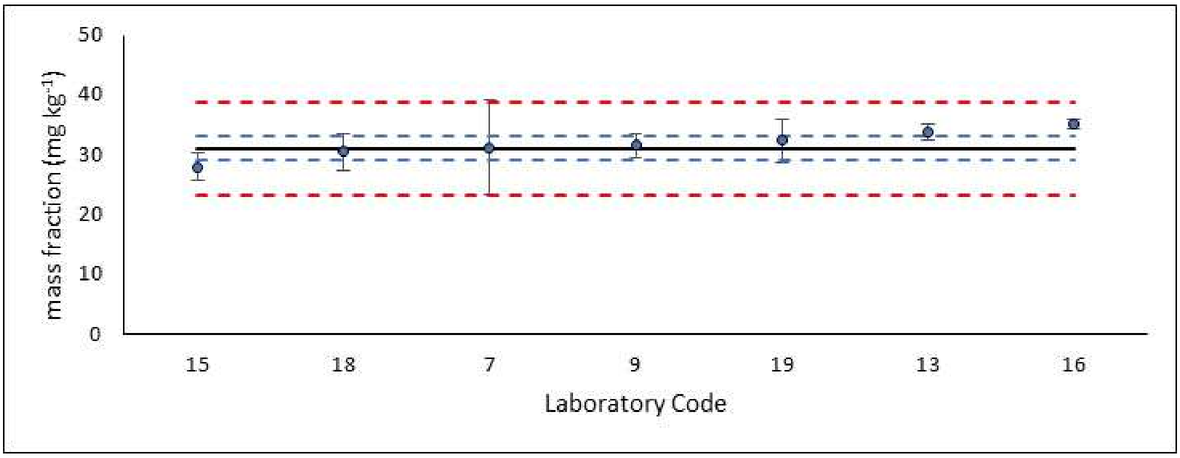


FIG. 49. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 50. Reported results and expanded uncertainties.

A.23. EVALUATION OF REPORTED DATA FOR Pb

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	75%	25%	0%
Zeta-score	88%	0%	13%

X_{Ass}:	41.0 mg kg^{-1}
U_{Ass} (k=2):	5.2 mg kg^{-1}
$2\sigma_p$:	10.3 mg kg^{-1}
Number of results:	8
Number of method:	

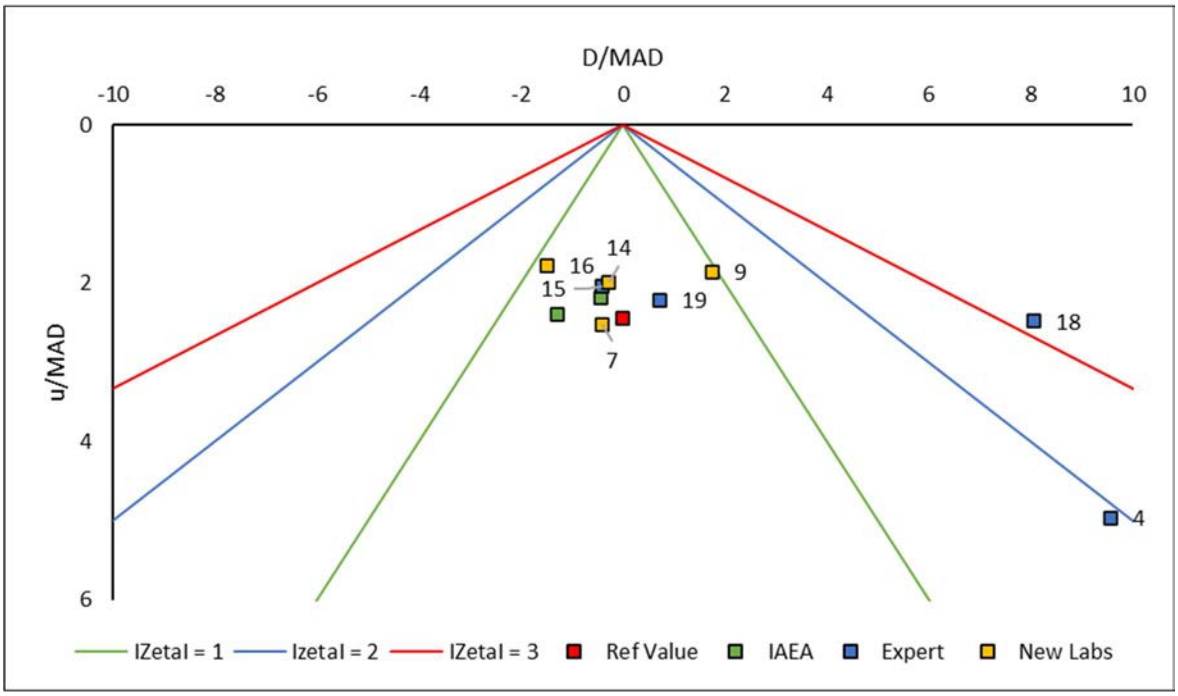
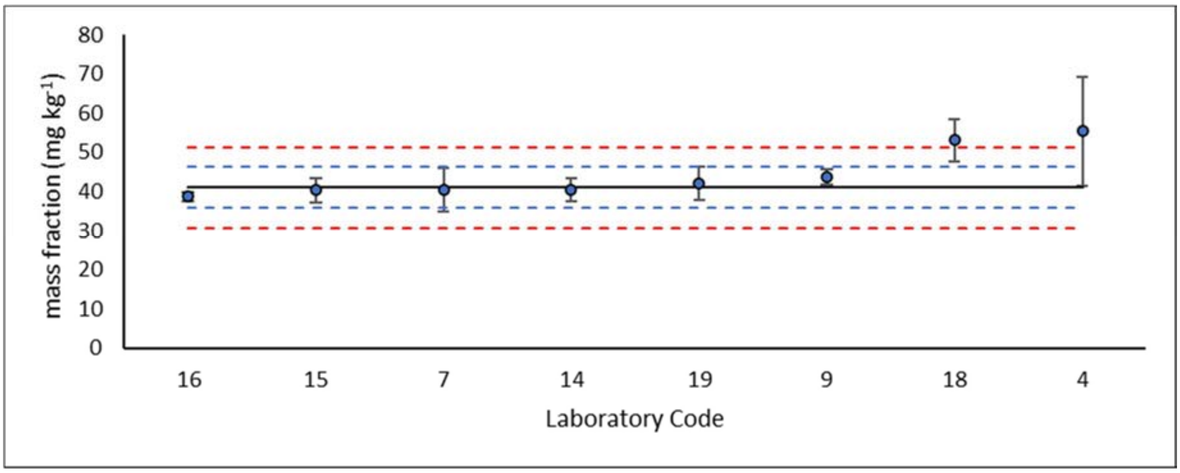


FIG. 51. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 52. Reported results and expanded uncertainties.

A.24. EVALUATION OF REPORTED DATA FOR Rb

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	86%	0%	14%

X_{Ass}:	87.4 mg kg^{-1}
U_{Ass} (k=2):	7.2 mg kg^{-1}
2σ_P:	21.9 mg kg^{-1}
Number of results:	7
Number of method:	2

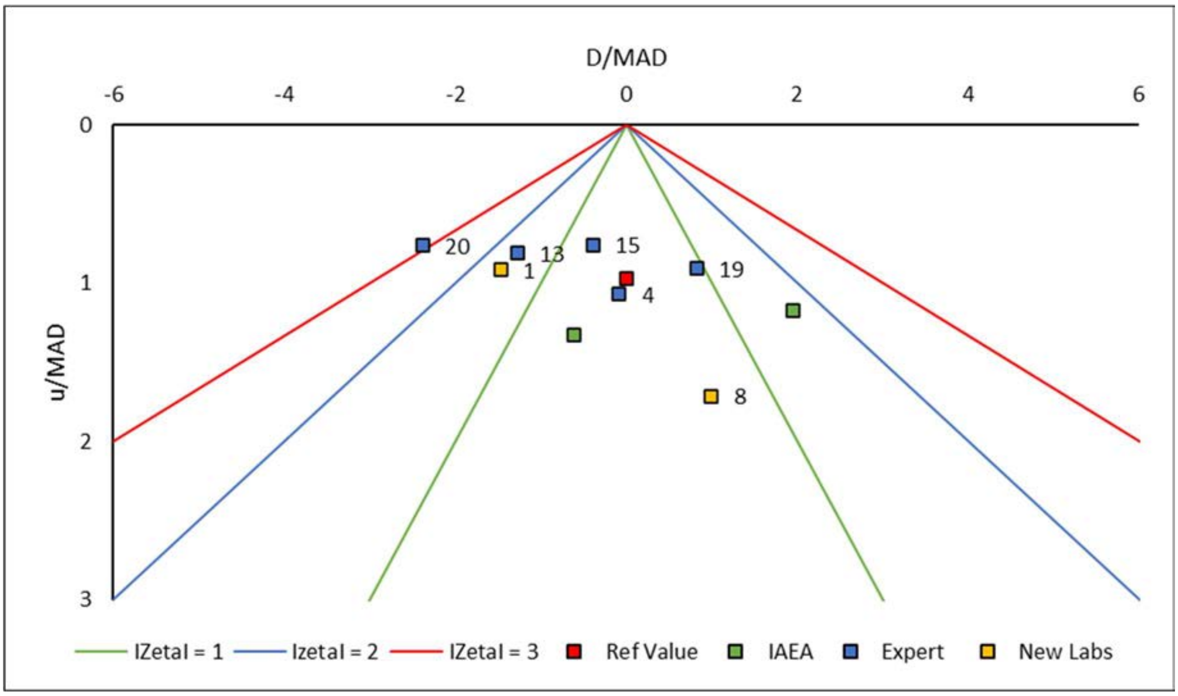
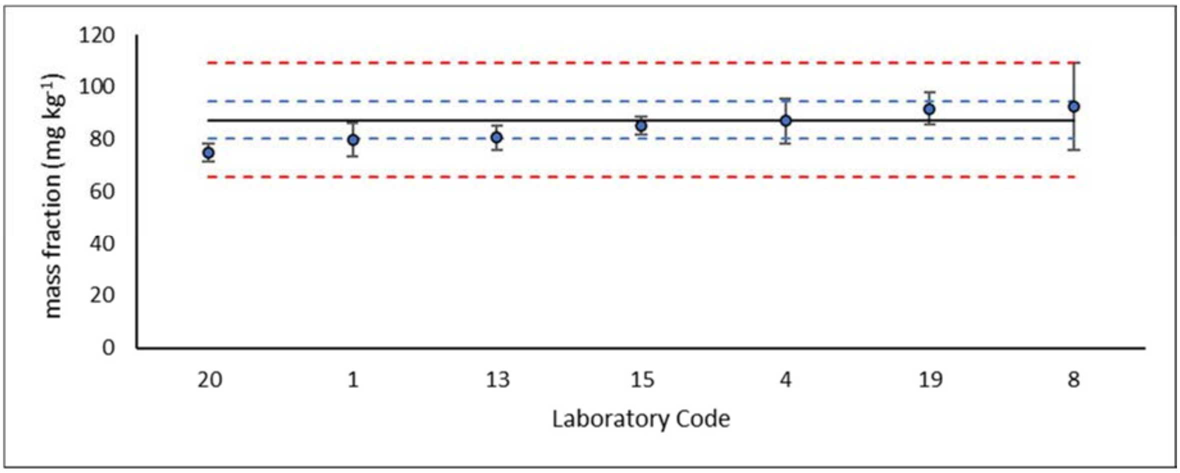


FIG. 53. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 54. Reported results and expanded uncertainties.

A.25. EVALUATION OF REPORTED DATA FOR Sc

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	8.20 mg kg^{-1}
U_{Ass} (k=2):	0.84 mg kg^{-1}
$2\sigma_P$:	2.05 mg kg^{-1}
Number of results:	4
Number of method:	1

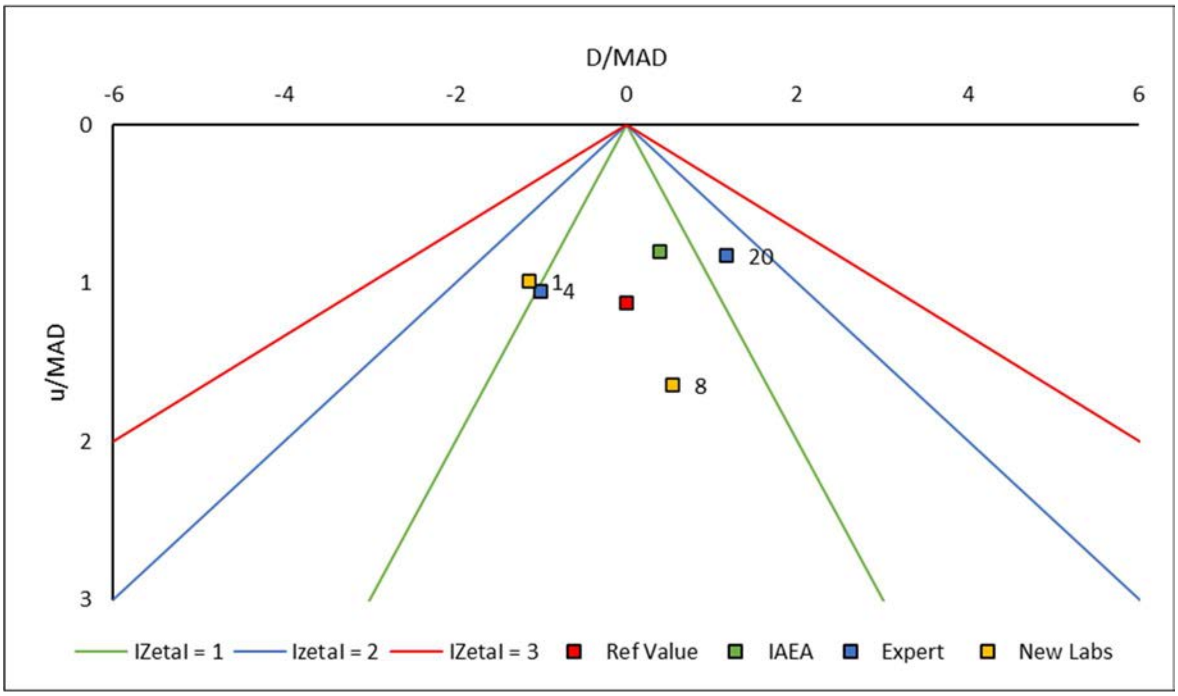
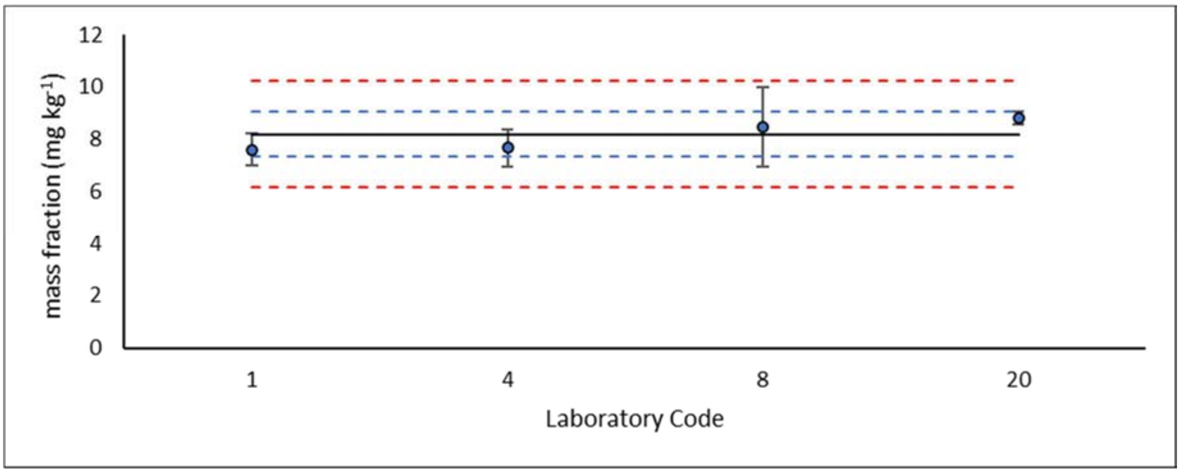


FIG. 55. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 56. Reported results and expanded uncertainties.

A.26. EVALUATION OF REPORTED DATA FOR Sm

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	4.64 mg kg^{-1}
U_{Ass} (k=2):	0.52 mg kg^{-1}
$2\sigma_p$:	1.16 mg kg^{-1}
Number of results:	6
Number of method:	2

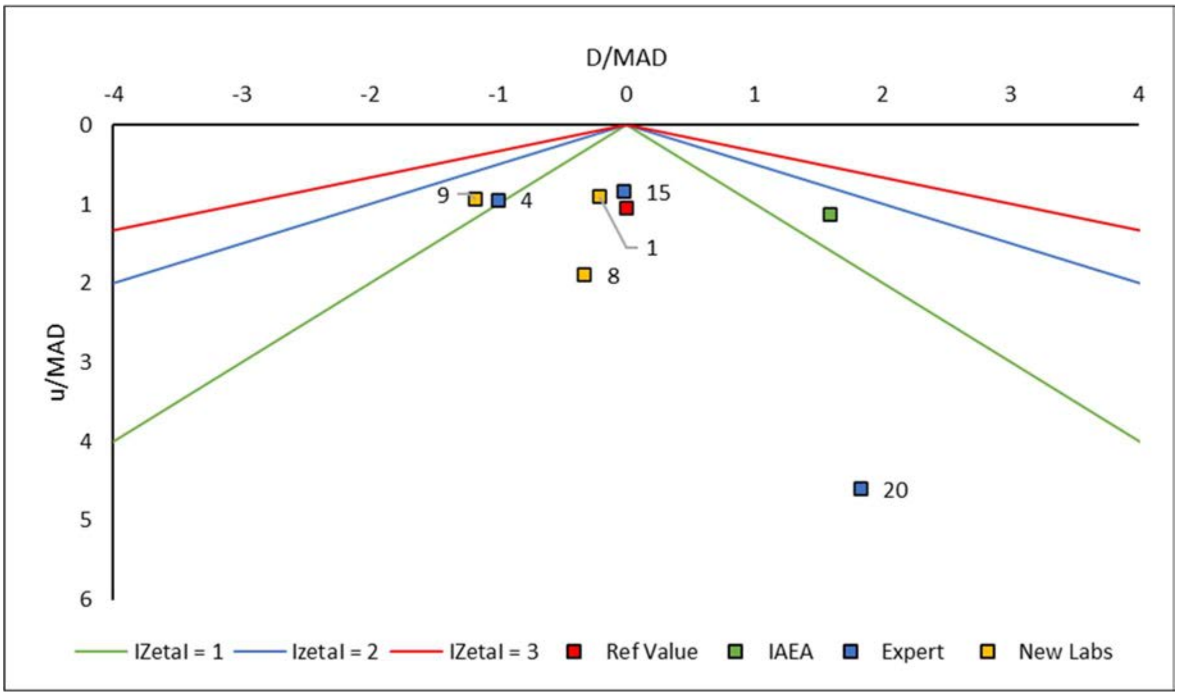
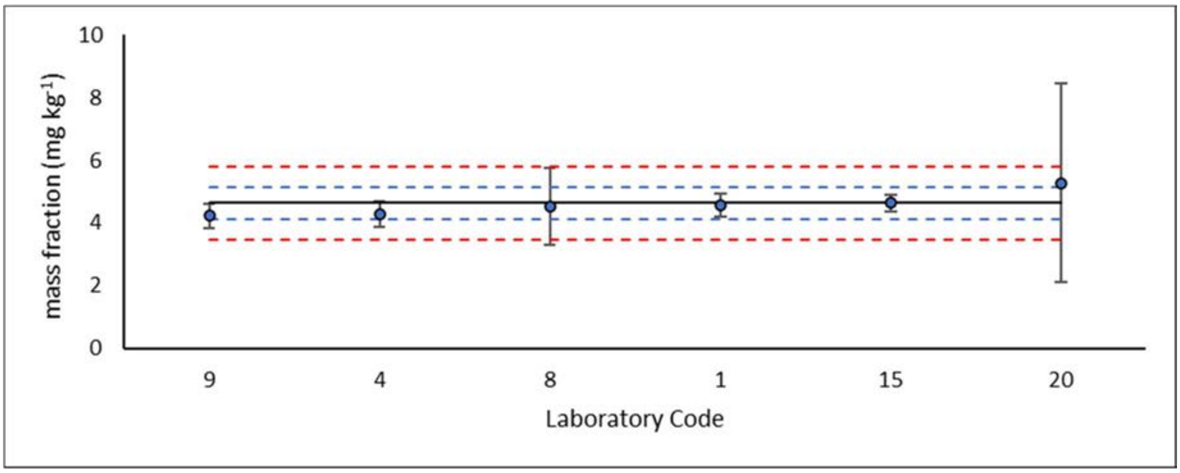


FIG. 57. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 58. Reported results and expanded uncertainties.

A.27. EVALUATION OF REPORTED DATA FOR Sr

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	478 mg kg^{-1}
U_{Ass} (k=2):	54 mg kg^{-1}
$2\sigma_p$:	120 mg kg^{-1}
Number of results:	7
Number of method:	3

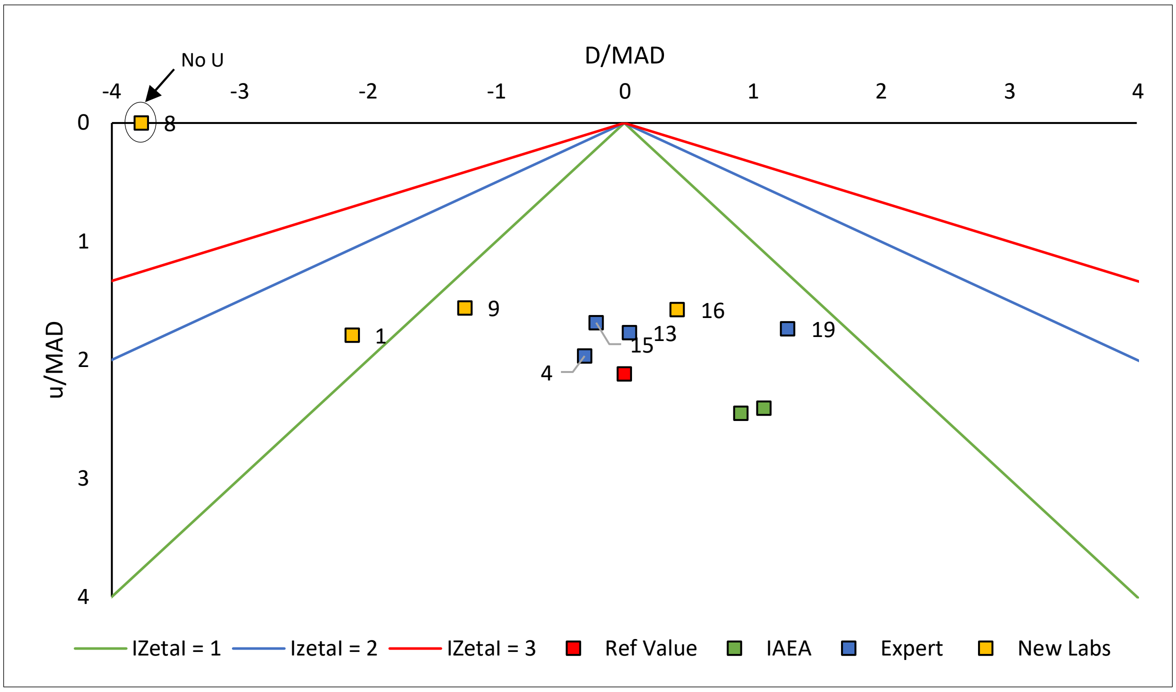
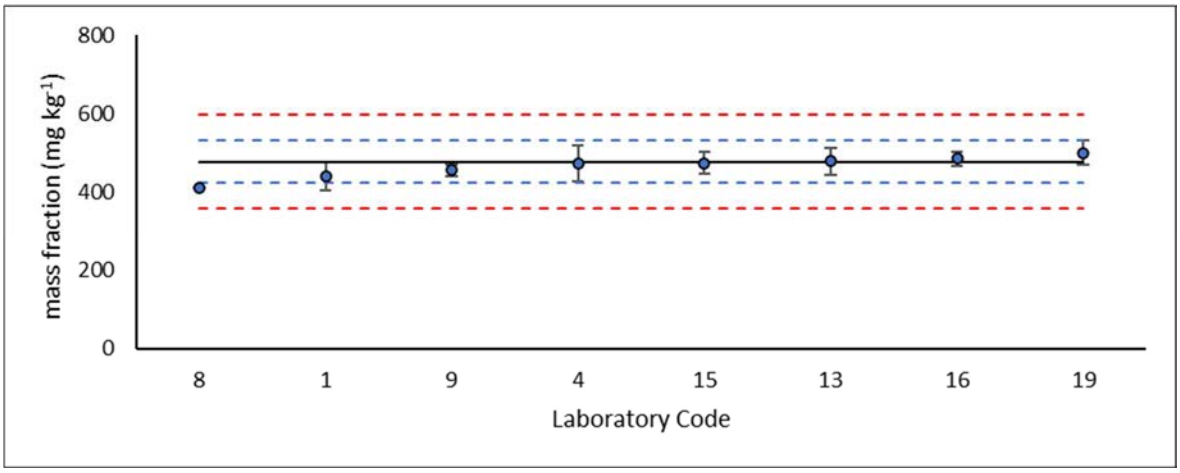


FIG. 59. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 60. Reported results and expanded uncertainties.

A.28. EVALUATION OF REPORTED DATA FOR Ta

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	80%	20%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	0.984 mg kg^{-1}
U_{Ass} (k=2):	0.14 mg kg^{-1}
$2\sigma_P$:	0.25 mg kg^{-1}
Number of results:	5
Number of method:	2

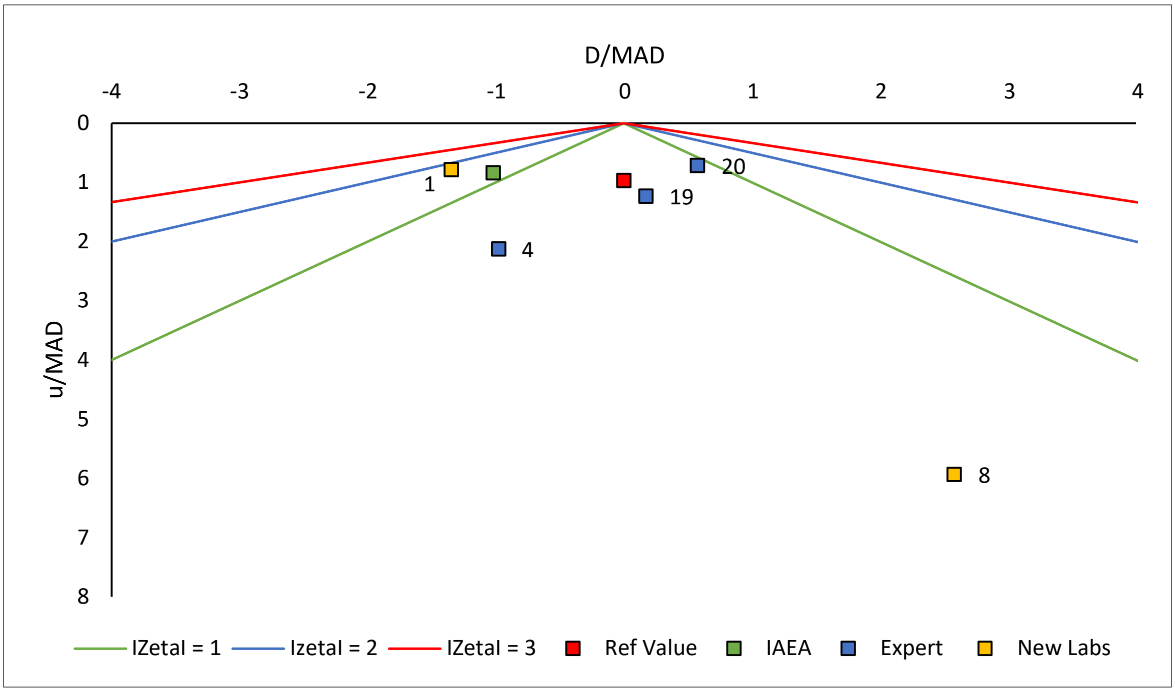
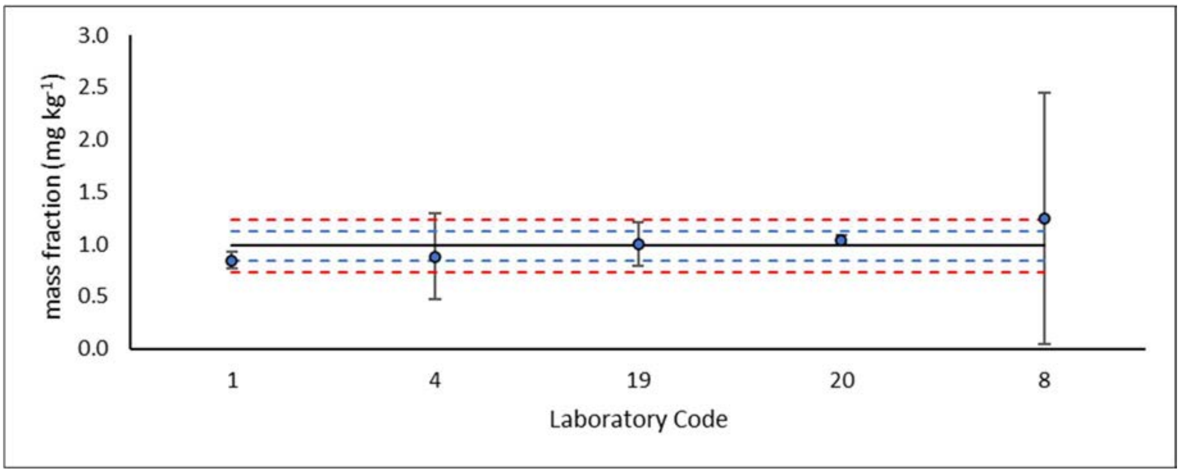


FIG. 61. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 62. Reported results and expanded uncertainties.

A.29. EVALUATION OF REPORTED DATA FOR Tb

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	0.633 mg kg^{-1}
U_{Ass} (k=2):	0.061 mg kg^{-1}
$2\sigma_P$:	0.158 mg kg^{-1}
Number of results:	7
Number of method:	2

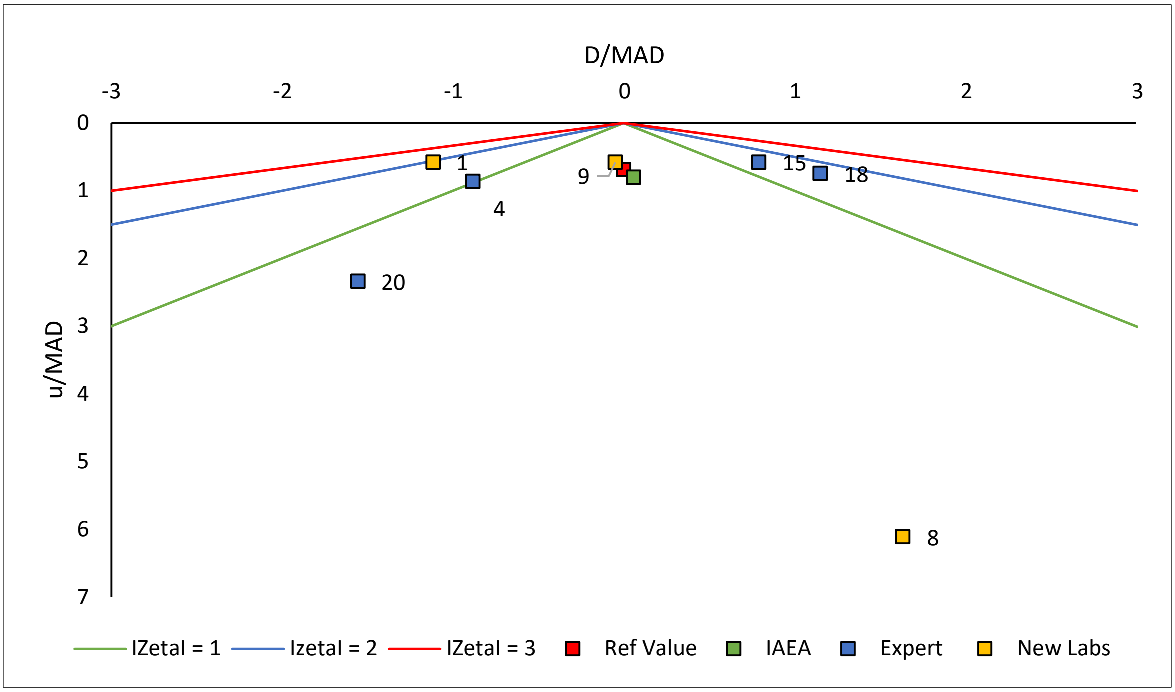
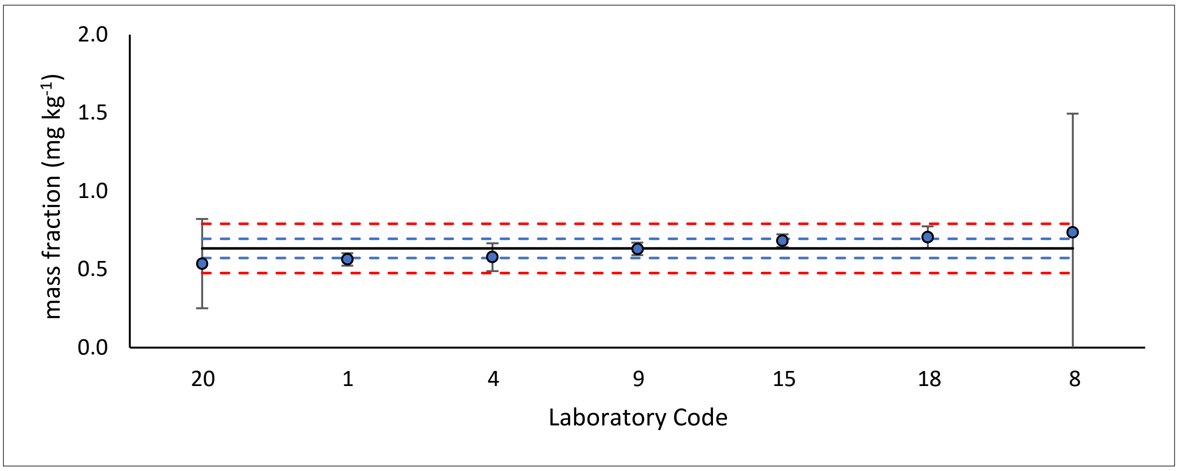


FIG. 63. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 64. Reported results and expanded uncertainties.

A.30. EVALUATION OF REPORTED DATA FOR Th

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	8.39 mg kg^{-1}
U_{Ass} (k=2):	0.64 mg kg^{-1}
$2\sigma_p$:	2.10 mg kg^{-1}
Number of results:	4
Number of method:	1

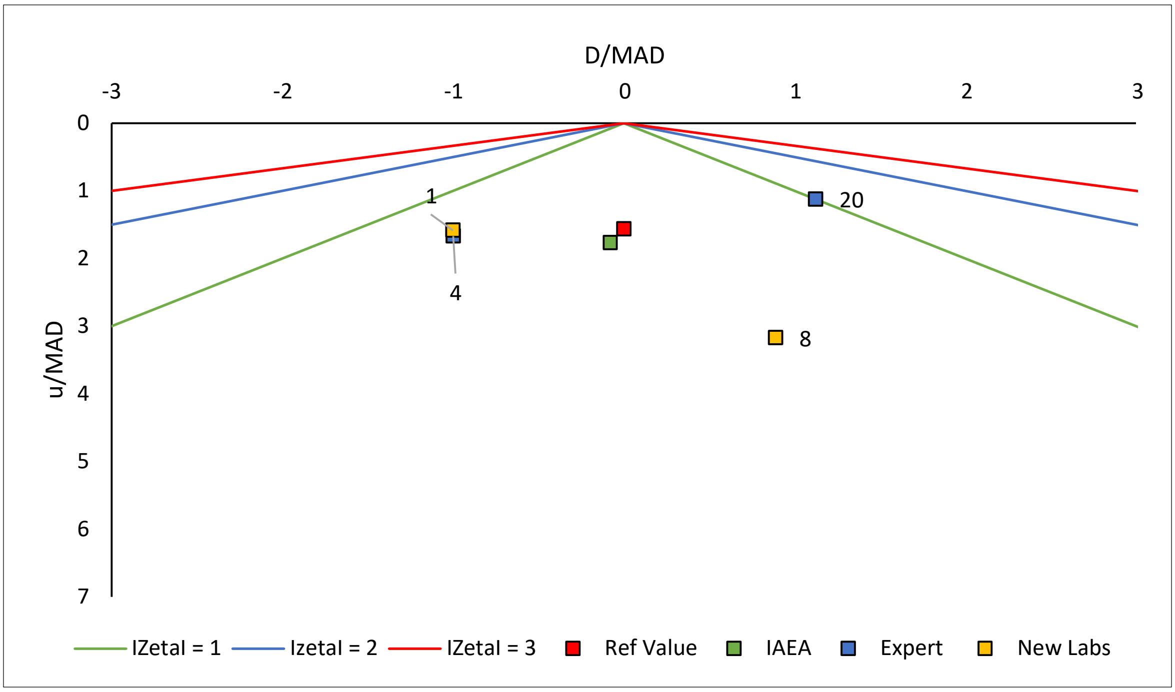
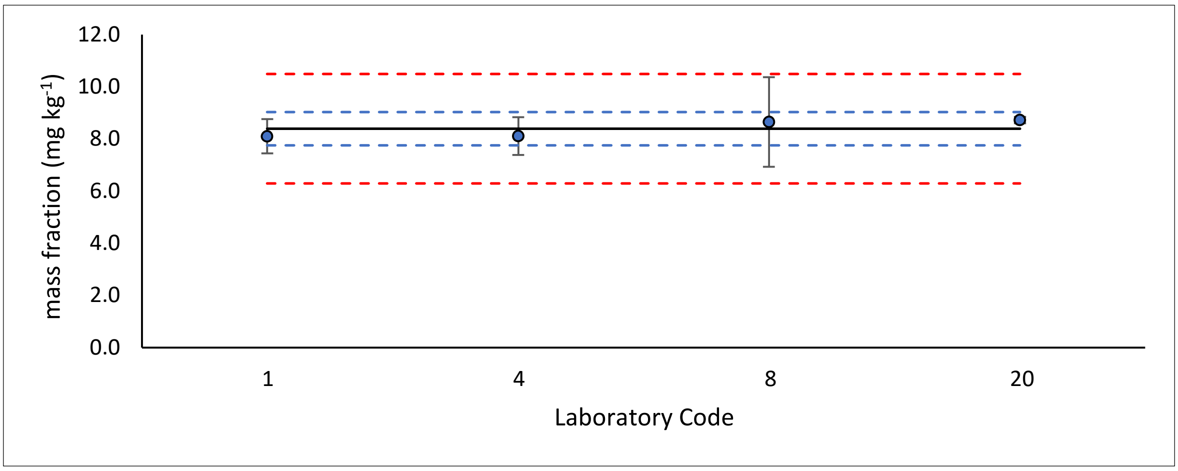


FIG. 65. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 66. Reported results and expanded uncertainties.

A.31. EVALUATION OF REPORTED DATA FOR Ti

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	3.29 g kg^{-1}
U_{Ass} (k=2):	0.59 g kg^{-1}
$2\sigma_p$:	0.82 mg kg^{-1}
Number of results:	7
Number of method:	3

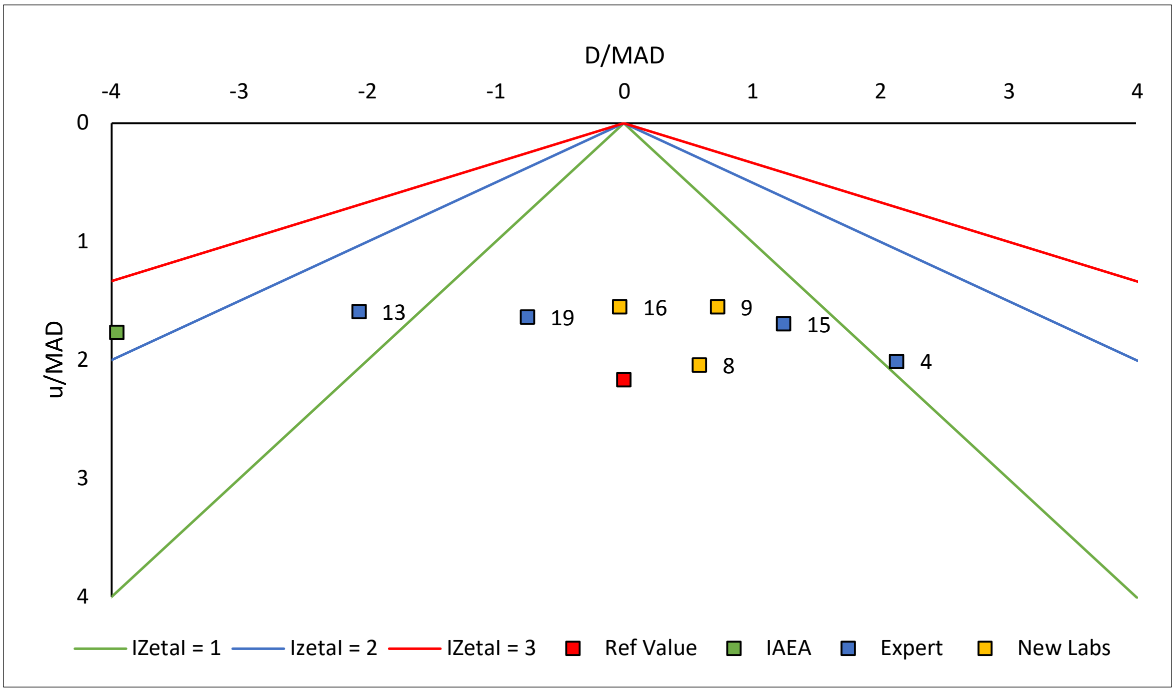
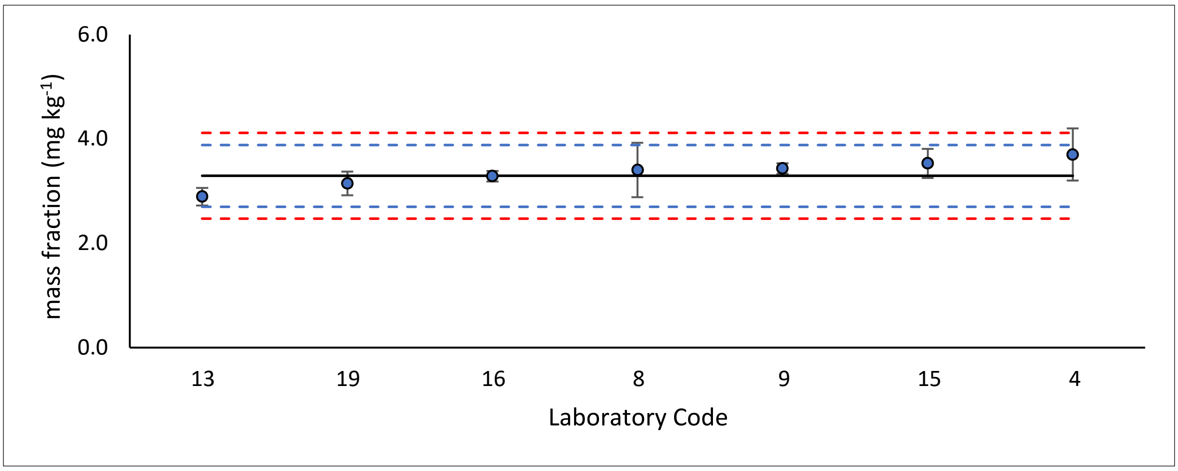


FIG. 67. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 68. Reported results and expanded uncertainties.

A.32. EVALUATION OF REPORTED DATA FOR U

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	2.40 mg kg^{-1}
U_{Ass} (k=2):	0.33 mg kg^{-1}
$2\sigma_p$:	0.60 mg kg^{-1}
Number of results:	7
Number of method:	2

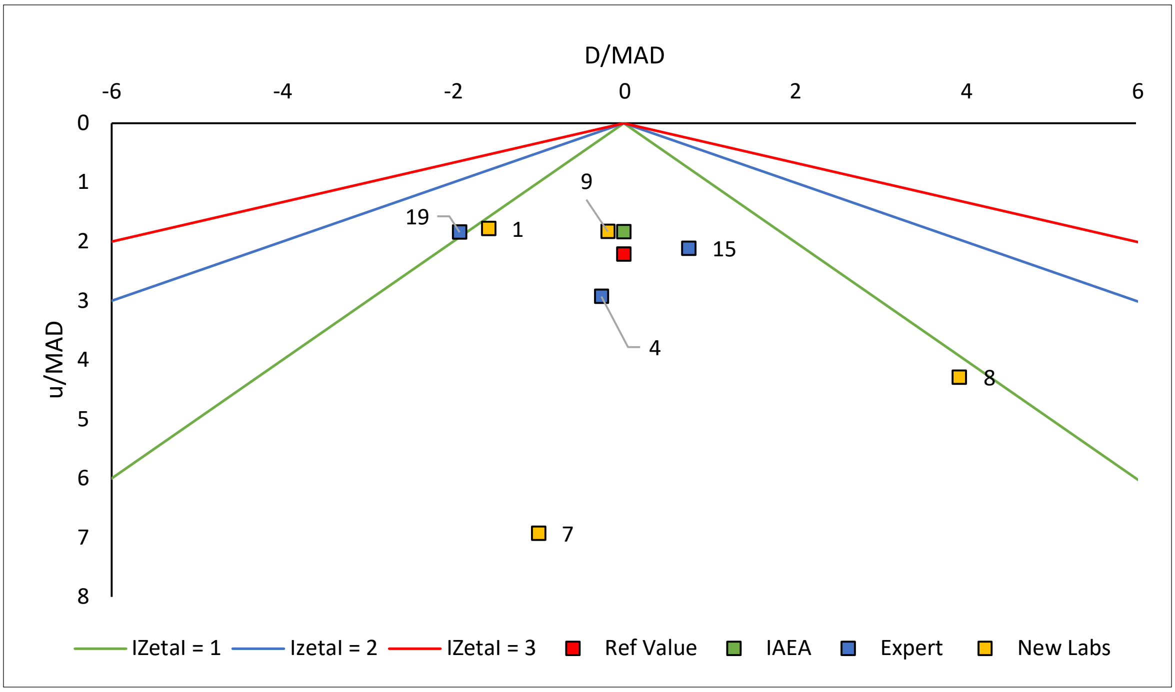
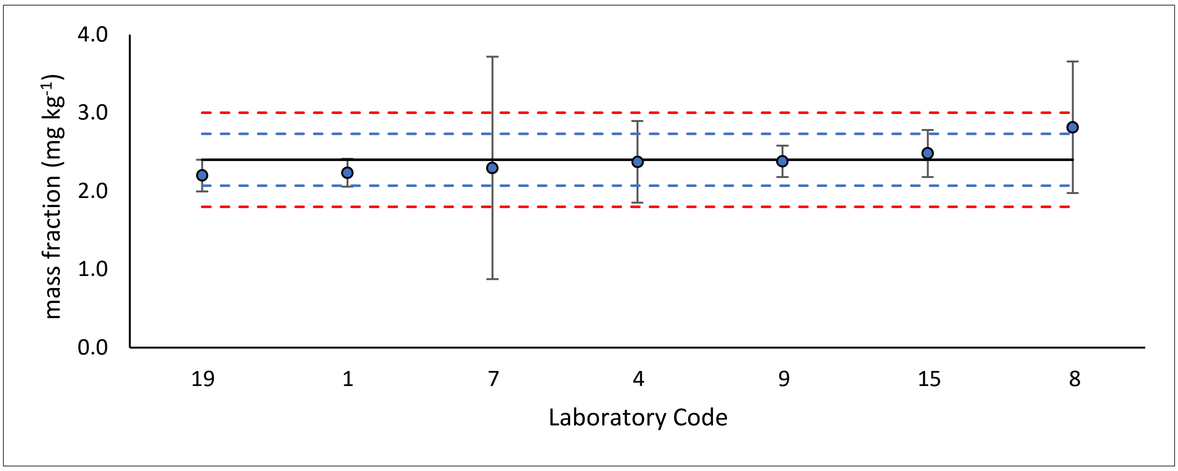


FIG. 69. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 70. Reported results and expanded uncertainties.

A.33. EVALUATION OF REPORTED DATA FOR V

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	90%	10%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	74.1 mg kg^{-1}
U_{Ass} (k=2):	5.2 mg kg^{-1}
$2\sigma_p$:	18.5 mg kg^{-1}
Number of results:	10
Number of method:	3

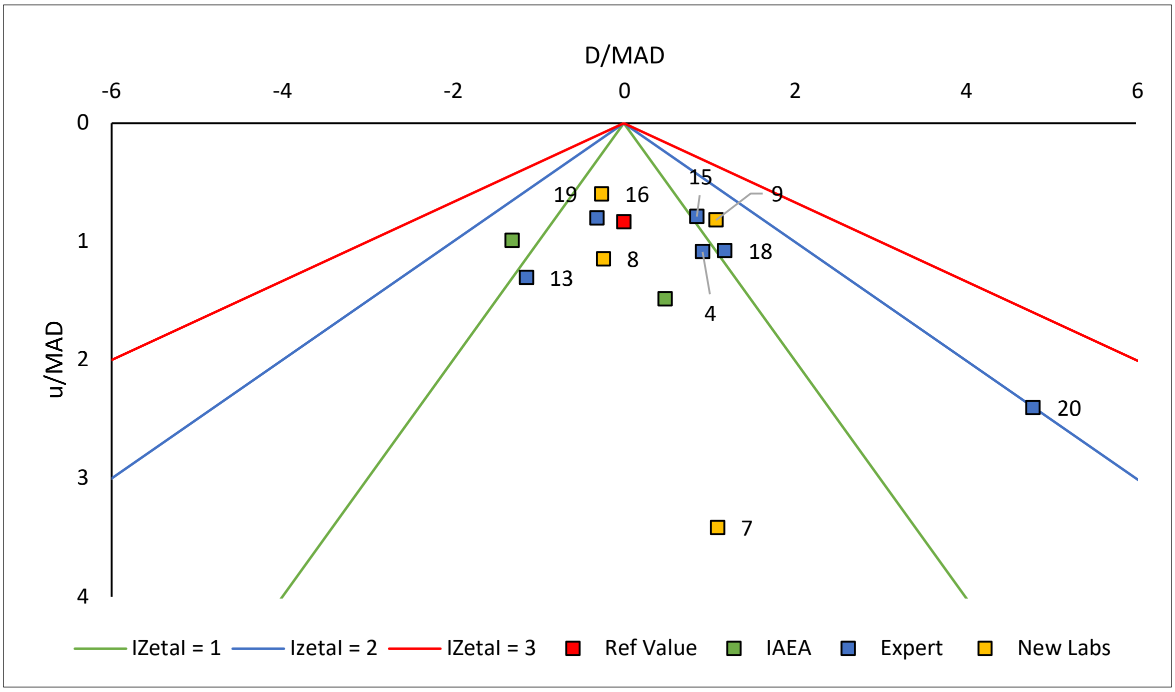
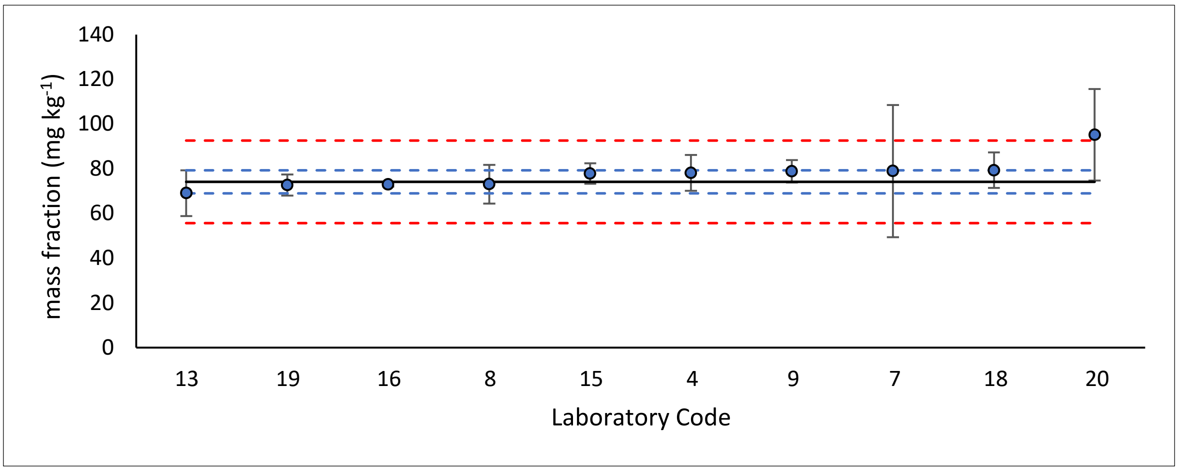


FIG. 71. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 72. Reported results and expanded uncertainties.

A.34. EVALUATION OF REPORTED DATA FOR Y

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	17.1 mg kg^{-1}
U_{Ass} (k=2):	1.1 mg kg^{-1}
$2\sigma_P$:	4.3 mg kg^{-1}
Number of results:	4
Number of method:	2

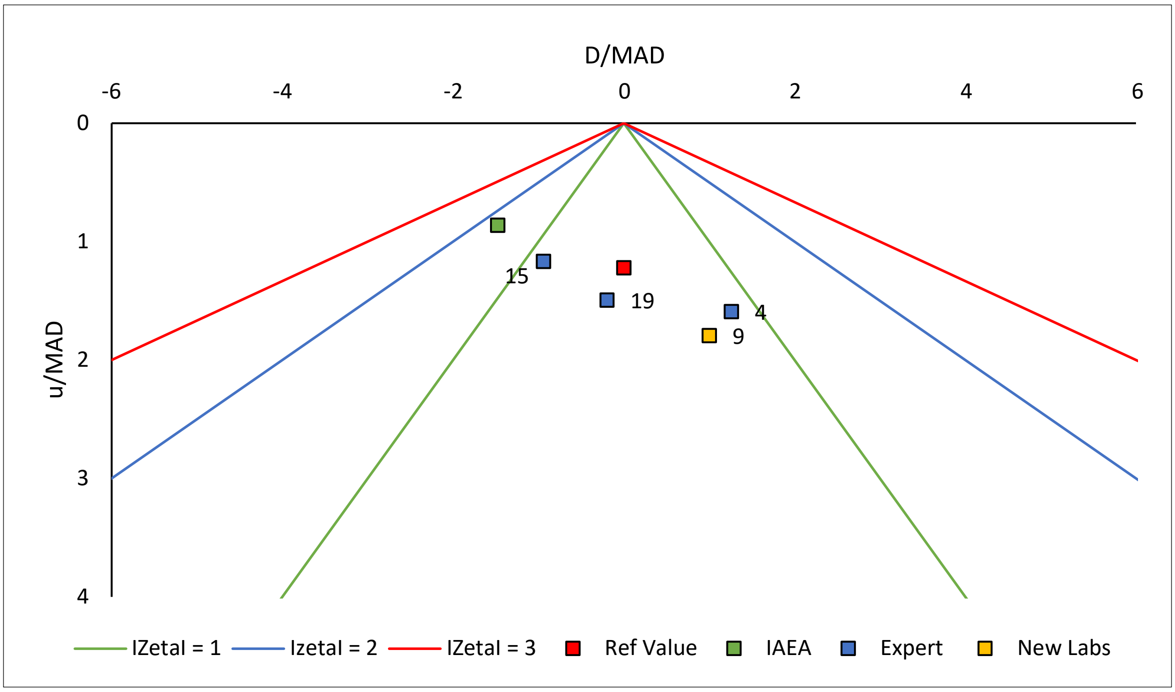
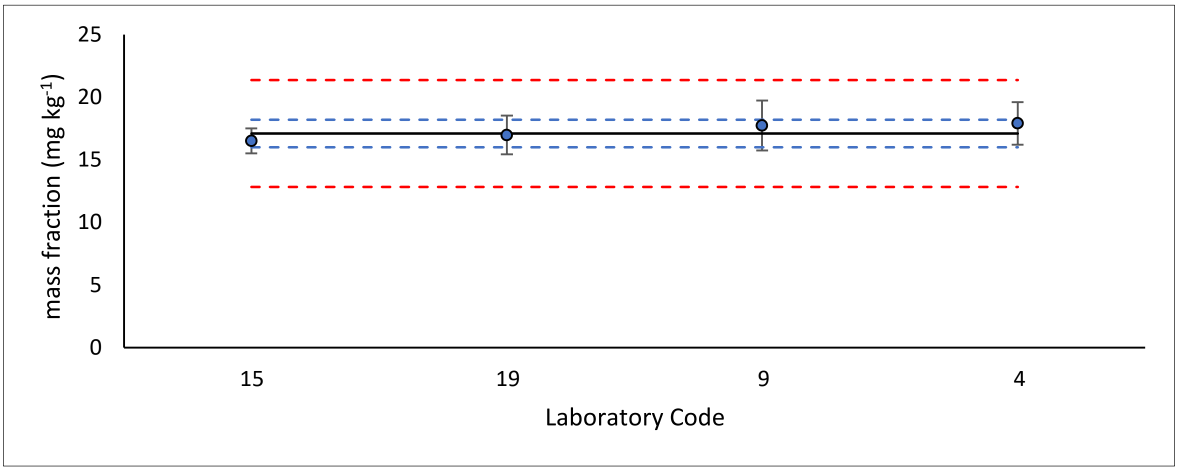


FIG. 73. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 74. Reported results and expanded uncertainties.

A.35. EVALUATION OF REPORTED DATA FOR Yb

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	100%	0%	0%

X_{Ass}:	2.02 mg kg^{-1}
U_{Ass} (k=2):	0.24 mg kg^{-1}
$2\sigma_p$:	0.51 mg kg^{-1}
Number of results:	7
Number of method:	2

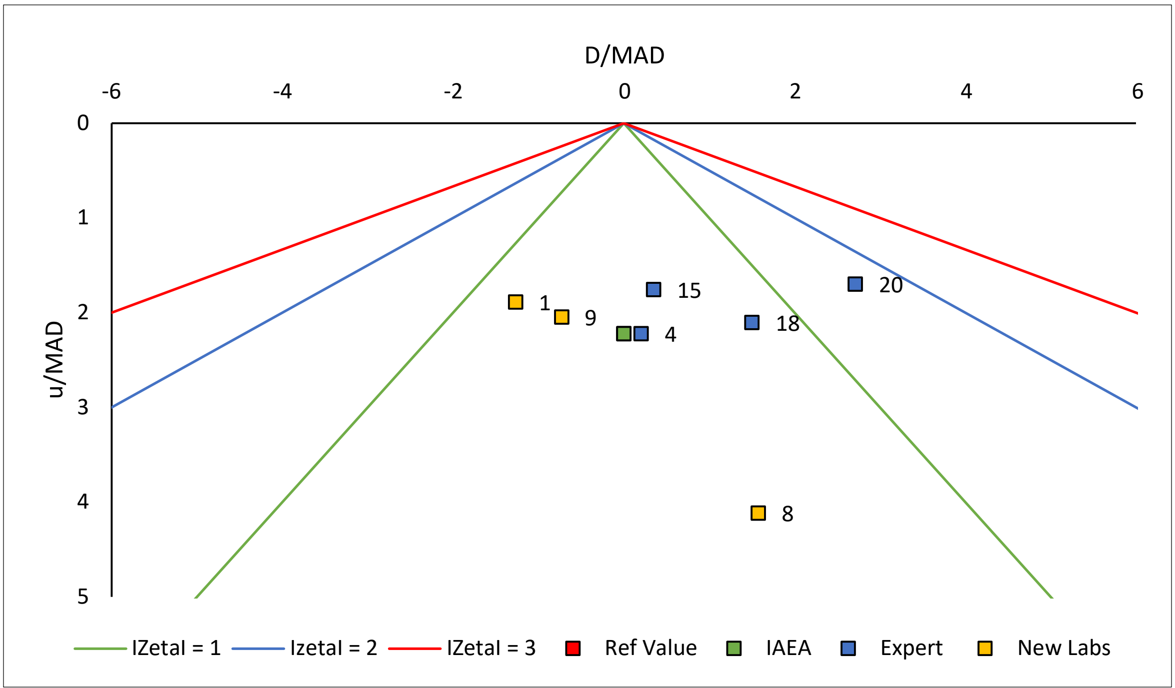
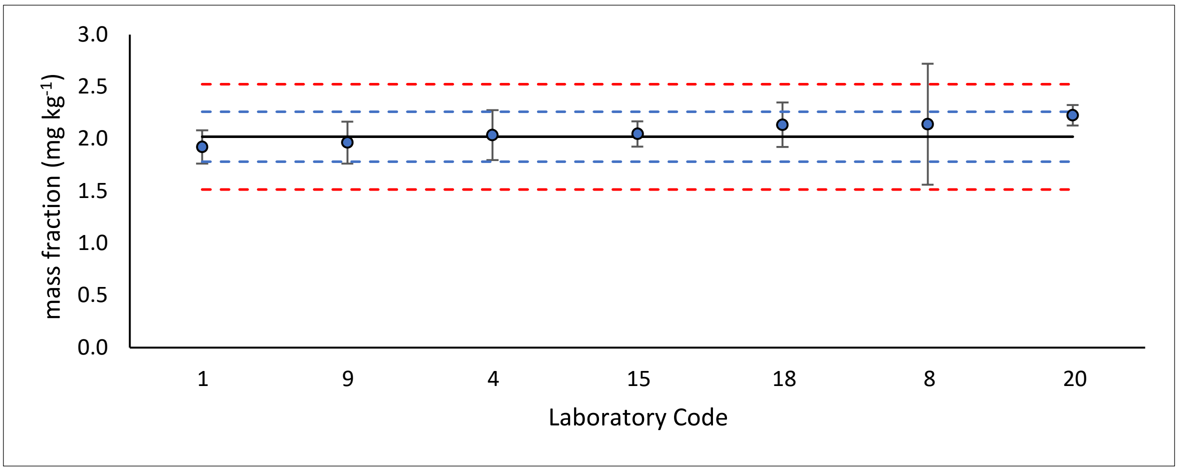


FIG. 75. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 76. Reported results and expanded uncertainties.

A.36. EVALUATION OF REPORTED DATA FOR Zn

Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	91%	0%	9%
Zeta-score	91%	0%	9%

X_{Ass}:	141 mg kg^{-1}
U_{Ass} (k=2):	18 mg kg^{-1}
$2\sigma_p$:	35 mg kg^{-1}
Number of results:	11
Number of method:	4

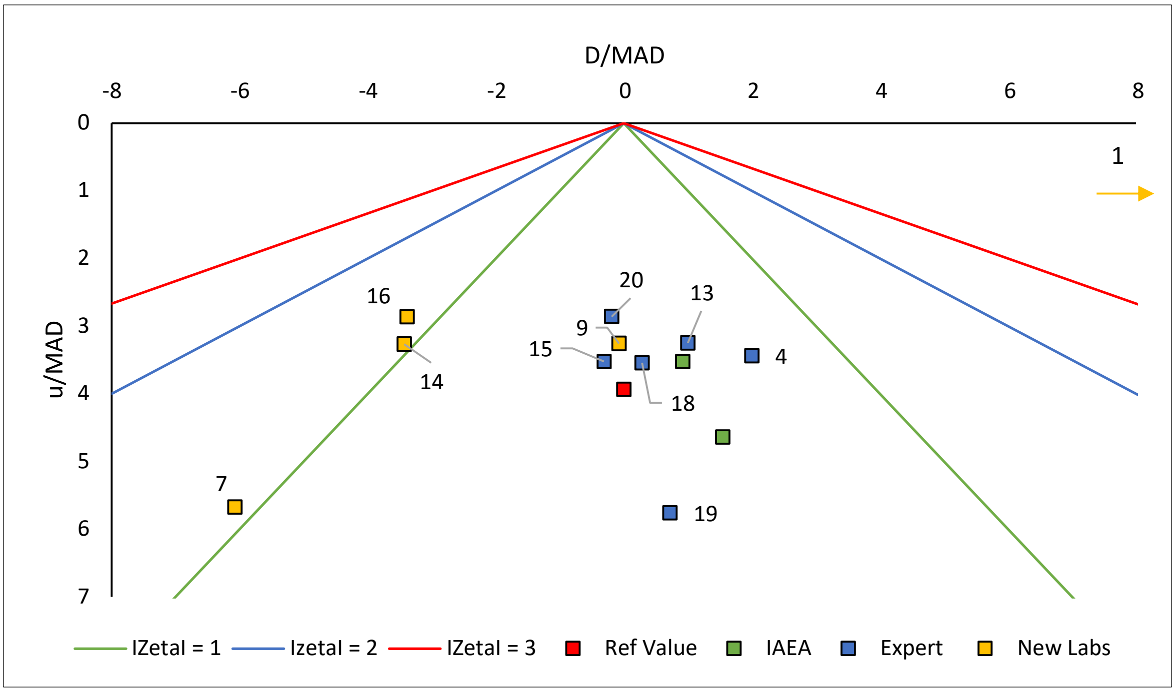
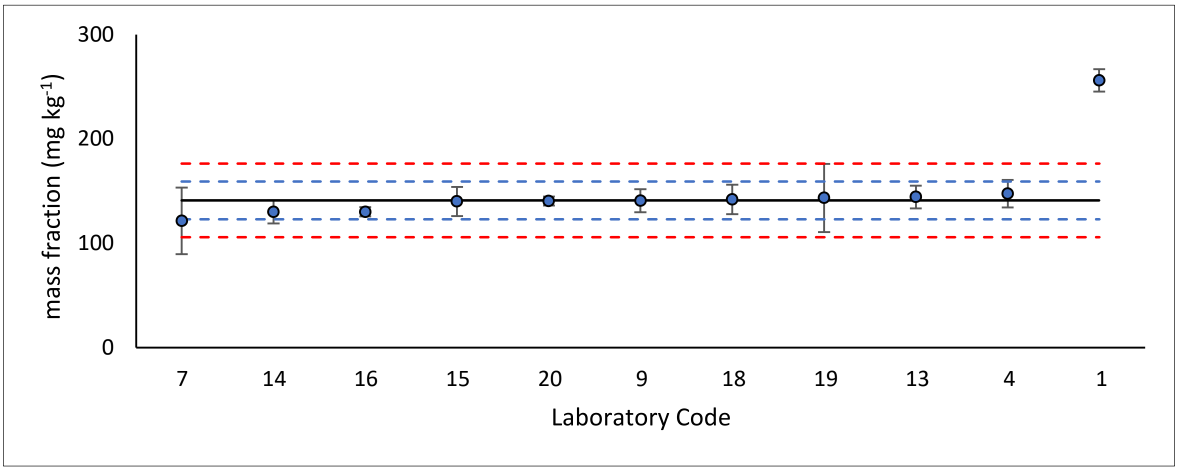


FIG. 77. PomPlot: Numbers are laboratory codes. (See Section 4. for more details).



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

FIG. 78. Reported results and expanded uncertainties.

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