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21 September 2021
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Meeting of the MED POL Focal Points

Teleconference, 27-28 May and 6-7 October 2021

Agenda item 12: Harmonization and standardization of IMAP Pollution Cluster Monitoring:
- **a) Monitoring Guidelines/Protocols for IMAP Common Indicators 13, 14, 17, 18, 20 and 23**
- **b) Monitoring Guidelines/Protocols for Analytical Quality Assurance and Reporting Monitoring Data for IMAP Common Indicators 13, 14, 17, 18 and 20**
- **c) Monitoring Guidelines/Protocols for Floating Microplastics**

Results of 2019 and 2020 Proficiency Tests on the Determination of Trace Elements and Organic Contaminants in Sediment and Biota Samples along with the Results of related Training Courses

UNEP/MAP
Athens, 2021

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Meeting of the Ecosystem Approach Correspondence Group on Pollution Monitoring

Videoconference, 26-28 April 2021

Agenda item 5: MEDPOL Proficiency Test on the Determination of Trace Elements in Sediment Sample (2019)

UNEP/MAP
Athens, 2021

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REPORT

MEDPOL PROFICIENCY TEST ON THE DETERMINATION OF TRACE ELEMENTS IN SEDIMENT SAMPLE

2019

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1. INTRODUCTION

The primary goal of the International Atomic Energy Agency's Environment Laboratories (IAEA-NAEL), and in particular the Environment Laboratories (NAEL), is to help Member States understand, monitor and protect the marine environment. Relevant activities comprise the organization of global inter-laboratory comparison, regional proficiency tests, the production of marine certified reference materials and development of recommended analytical methods for trace elements and organic pollutants analysis in marine samples. The Marine Environmental Studies Laboratory (MESL) of NAEL is actively assisting Member States with the organization of inter-laboratory comparisons and provision of certified reference materials.

The IAEA has a long collaboration with UNEP and its Program for the Assessment and Control of Pollution in the Mediterranean region (MED POL) which was initiated as the environmental assessment component of the Mediterranean Action Plan (MAP).

The MESL provides assistance to the designated MED POL monitoring laboratories via training (trace element, petroleum hydrocarbons and organochlorine compounds), provision of certified reference materials and organisation of targeted proficiency tests (PTs) on matrices of relevance to the marine monitoring studies.

The periodic external assessments of measurement performances of monitoring laboratories via interlaboratory comparisons (ILCs) and targeted proficiency tests (PTs) are of crucial interest for laboratories as they provide clear information of their measurement capabilities. These exercises are designed not only to monitor and demonstrate the performance and analytical capabilities of the participating laboratories, but also to identify gaps and problem areas where further development is needed.

This report describes the results of the PT on the determination of selected trace elements in sediment sample organised by the MESL in 2019 for the designated MED POL monitoring laboratories.

The IAEA officers responsible for this publication are S. Azemard, E. Vasilev, S. Sander. A. Trinkl from NAEL Terrestrial Laboratory was responsible for the management of the on-line reporting system.

SCOPE OF EXERCISE

In May 2019the MED POL Programme Officer contacted the National Focal Points of MED POL countries, requesting them to provide the names of the designated national laboratories, involved in MED POL monitoring activities. The final list of designated national laboratories, respectively participants in the organised by MESL targeted proficiency test for trace elements in marine environment, was established at the end of July 2019.

The test material, named ***IAEA-MESL-2019-02-TE-MEDPOL-PT*** sample, was sent to 19 designated monitoring laboratories from 17 countries in August 2019. Figure 1 shows the distribution of PT samples in MED POL countries, and the distribution per countries of received results.

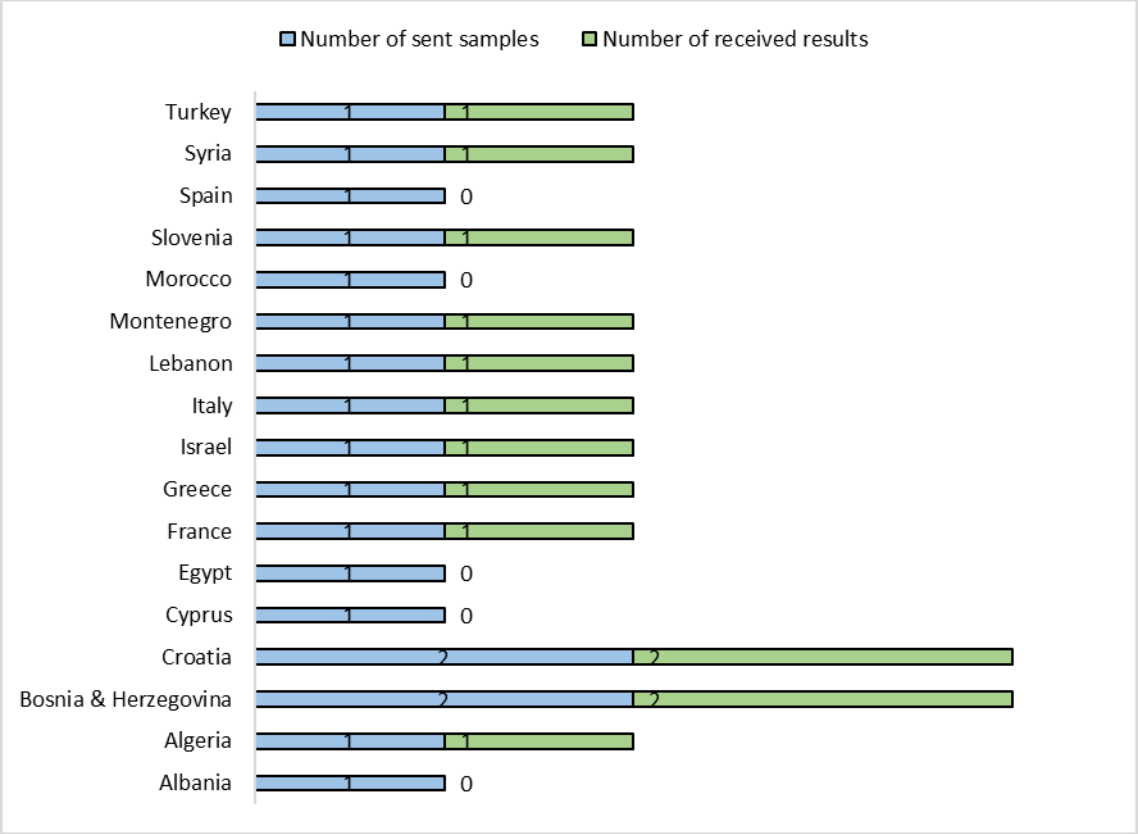


FIG. 1. Distribution per country of the MED POL PT sample

Participants were requested to apply their established analytical methods, usually used for MED POL monitoring studies, for the determination of total contents of the following IMAP EO9 mandatory (priority) elements: Cd, Hg and Pb as well as on some additional trace elements: Al, As, Co, Cr, Cu, Fe, Mn, Sr, V, and Zn in the test PT

sample (IAEA-MESL-2019-02-TE-MEPDOL-PT) as well as in one matrix matching quality control sample, sent to the MED POL laboratories together with the PT test sample.

The deadline for reporting the results back to the MESL was originally set to 31 October 2019. Finally, 14 from 19 (74%) monitoring laboratories proposed for participation in this proficiency sent their results back to the organisers in the requested deadlines.

Laboratories participating in the present exercise are listed in the Annex 1. Designated MED POL laboratories which didn't report the results are listed in the Annex 2.

2. MATERIAL

2.1. Preparation of the material

The sediment used for preparing IAEA-MESL-2019-02-TE-MEPDOL-PT sample was collected in a bay of the Caspian Sea; freeze dried, sieved at 100µm, mechanically homogenized and packed in amber glass bottles.

Homogeneity test were performed at the MESL following the requirements ISO 35 guidelines [1], using preliminary validated in MESL's trace elements laboratories analytical methodologies.

2.2. Assigned values and their uncertainties:

The assigned values and their associated uncertainties are presented in the Table 1.
The assigned values were calculated from the results reported by the participants in this PT and from the results obtained in the MESL with preliminary validated analytical methods. They were calculated according to the requirements of the ISO 17043 standard [2]. The robust statistics was applied as recommended in the ISO 13528 [3]. Kernel density was used as an appropriate method to represent the overall structure of the entire data set [4]. Several bimodality distributions were observed for Al, Cr, Cu, Mn and Pb, mainly connected to the incomplete digestion of the sediment sample. Therefore, only data reported with total digestion or non-destructive techniques were kept for derive the assigned values for above mentioned analytes. One laboratory reported negative results, rejected before starting the data treatment.

Expanded uncertainties were calculated according to the ISO standard 35 [1] applying the Eq. (1).

$$U = k \times \sqrt{u_{char}^2 + u_{stab}^2 + u_{hom}^2} \quad (1)$$

where:

k: coverage factor, *k*=2, represents level of confidence of about 95%

u_{hom} is the standard uncertainty, due to between unit inhomogeneity, evaluated by ANOVA [1]

u_{stab} is the standard uncertainty, due to long term stability of the sample. Based on our experience u_{stab} component was considered to have negligible contribution and was set at 1%.

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

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

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

All assigned values and expanded uncertainties are presented in Table 1.

TABLE 1: ASSIGNED VALUES FOR TRACE ELEMENTS IN THE MED POL PT SAMPLE

Element	Assigned Value (mg kg^{-1})	U (*k*=2) (mg kg^{-1})
Al	68.0×10^3	5.0×10^3
As	10.0	1.0
Cd	0.162	0.026
Co	14.0	1.6
Cr	88.4	8.7
Cu	30.0	2.9
Fe	39.2×10^3	3.9×10^3
Hg	0.470	0.034
Mn	870	83
Pb	26.7	2.9
V	127	15
Zn	97.4	7.8

3. EVALUATION OF RESULTS

3.1. Evaluation criteria:

Individual laboratory performance was evaluated with *z* and Zeta scores as recommended in the ISO guide 17043 [2]

$$z = \frac{x_{lab} - X_{ass}}{\sigma_p} \quad (3)$$

$$\text{zeta} = \frac{x_{lab} - X_{ass}}{\sqrt{u_{lab}^2 + u_{ass}^2}} \quad (4)$$

Where:

x_{lab} is the measurement result reported by participant

X_{ass} is the assigned value

σ_p is the target standard deviation or standard deviation for proficiency assessment

U_{ass} is the standard uncertainty of the assigned value

u_{lab} is the standard uncertainty reported by participant

The interpretation of a laboratory's performance was according to the following generally accepted criteria [2].:

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

***z*-score:** This score expresses the difference between the mean of the laboratory and the assigned value in the same unit. *z*-score represents a simple method of giving each participant a normalized performance score for the measurement bias of the respective measurement result. The standard deviation for the proficiency assessment (also called target standard deviation), σ_p, was set to be fit for purpose and was fixed to 12.5 % of the assigned values. The determination of target standard deviation was done on the basis of the outcome of previous ILCs organised by the MESL for the same population of laboratory. The appropriateness of this level of tolerated variability of results was confirmed by calculation of the robust standard deviation of the participants' results and the uncertainty of the assigned values for the respective measurements.

Zeta-Score: This score state if the participant result agrees with the assigned value within the respective uncertainties. The denominator of equation 4 is the combined uncertainty of the assigned value and the measurement uncertainty reported by the participant. When the uncertainties were not reported by, Zeta-score was not calculated.

3.2. Overview of the reported measurement results

14 laboratories provided 140 measurement results on the mass fractions of trace elements in the PT sample by the final deadline. Graphical presentations of z-score and Zeta-scores are presented in the Annex 3 together with a summary on the statistical evaluation of reported results for the respective trace element. Kernel density plots are presented in the Annex [4]. All results are reported by the laboratory code number only, to protect the Participants confidentiality. However, as agreed with the participants the laboratory codes will be shared with their MEDPOL National Focal Point as part of the capacity building and quality assurance programme of MEDPOL.

3.3. Laboratory results and scoring:

3.3.1 *z*-scores

The measurement performance of participating laboratories was assessed by *z*-scores. Obtained results are summarized in Table 2 and the z-scores are summarized in Table 4 and Figure 2. *z*-scores per element are presented in Table 5 and on Figure 3.

A total 135 *z*-scores were calculated. Overall 81% of reported measurement results were assessed as satisfactory, 2.2% as questionable and 17% as unacceptable. From 14 participating laboratories, 6 laboratories (43%) reported 100% of their measurement results with $|z| \leq 3$ and 5 laboratories (36%) were able to report 100% of their measurement results with $|z| \leq 2$. On the other hand, 2 laboratories reported less than 40% of their results with $|z| \leq 2$. This fact is probably reflecting the existing of unresolved analytical problems in those laboratories.

Extreme z-scores >7 have been obtained for about 8% of reported results. Some have been identified as unit error (laboratory 1), while some have been obtained for understandable negative results (laboratory 7).

3.3.2 Zeta-scores

The Zeta-score shows if the laboratory result agrees with the assigned value within the respective combined uncertainty. It should be mentioned that an unsatisfactory Zeta-score can be caused either by an incorrect measurement result or by an inappropriate estimation of the respective measurement uncertainty, or by both.

Obtained in this PT Zeta-score results are summarized in Table 3. Zeta-scores per participant are summarized in Table 6 and on Figure 4. Zeta-score per element are presented in Table 7 and in Figure 5.

About 66% of measurement results were reported with uncertainties. Zeta-scores were calculated for 9 of participating laboratories (64%), 5 of participating laboratories didn't report measurement uncertainties, which made the calculation of Zeta score impossible. One participant (laboratory code 2) did report only expanded uncertainty and *k* factor and for the for calculation of Zeta scores, expanded uncertainties were divided by the reported *k* factor in order to obtained combined uncertainty.

Eleven participants have evaluated uncertainties but only 9 laboratories, effectively reported results with their uncertainties. Different approaches were reported to estimate measurement uncertainties: 4 participants applied single validation approach, 2 laboratories used modelling approach, 2 laboratories were reporting measurement uncertainties, obtained via Nordtest approach, and 1 participant didn't provide the information on how it estimates uncertainties.

86.5% of the calculated Zeta-scores are considered as satisfactory and 4 laboratories reported 100% of their measurement results with Zeta-scores below 2. Two participating laboratories received satisfactory Zeta-score for less than 50% of reported results.

Overall, obtained results show that there are still remaining problems with the realistic estimation of the combined measurement uncertainty. Some laboratories have reported wrong information for the measurement uncertainties: Laboratory 1 reported very similar values for u and U and Laboratory 17 reported u and U in % instead of mg kg^{-1} (as requested).

It should be mentioned here that an unsatisfactory Zeta-score can also be caused by an inappropriate evaluation of the mass fraction of the respective trace element.

TABLE 2: ALL CALCULATED z-SCORES. Blue fonts are z-scores 2< | *z* | <3, and red highlighted fields being z-scores | *z* |>3.

Laboratory Code	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Pb	V	Zn
1	-7.99	15.05	18.16	-0.51	-3.79	-1.61	-7.99	0.49	-7.30	5.45		-0.98
2		-1.85	0.02	0.03	-3.20	-1.73		-1.62	-0.18	-0.83	-3.75	-0.52
5		0.54	1.70	0.93	-0.77	0.05		-3.10	-0.11	-0.66	-0.03	0.65
7	-4.28		-4843.42		-5.70	-1.77	-0.96		-0.35	-13.13		
8	-0.26	-1.76	-0.56		0.10	0.19	-0.14	1.74	-0.20	0.14		-0.70
9	0.22	0.47	-1.23	0.76	-0.09	0.28	0.09	0.38	-0.31	0.46	-0.44	0.35
10	-0.28	0.39	0.49	0.32	0.04	-0.94	-0.46	0.03	-0.49	0.19	0.45	-0.23
11		20.37	-5.02	-1.01	-3.90	-1.50	-1.05	-0.51	-0.29	1.33	-5.12	-0.92
12	-0.06		-1.55	0.48	-0.11	-1.09	-0.60	0.22	-0.60	0.46	-0.83	-0.25
14	-7.30	-0.30	9.00	0.19	1.93	0.70	1.90	-2.11	1.24	-0.56	-0.08	1.59
15		-0.27	-0.28	-0.21	0.52	0.28	0.08	0.67	0.35	0.70		0.00
17	0.57	-1.13		-3.28	1.04	-1.53	0.00		-0.09	-0.85	5.11	-1.74
18			0.40		-2.71	2.38	1.09		1.29			-0.23
19			-0.81					0.30		-3.34		

TABLE 3: ALL CALCULATED ZETA –SCORES. Blue fonts are Zeta-scores 2< │Zeta│ <3, and red highlighted fields being Zeta-scores │Zeta│>3.

Laboratory Code	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Pb	V	Zn
1	-27.04	0.65	0.70	-0.07	-0.90	-0.25	-19.84	0.06	-9.15	0.41		-0.14
2	-2.55		0.01	0.03	-4.45	-2.33		-1.89	-0.25	-0.99	-5.20	-0.64
5												
7												
8	-0.28	-2.37	-0.57		0.13	0.23	-0.19	2.35	-0.16	0.16		-0.96
9	0.40	0.75	-1.64	1.12	-0.16	0.42	0.14	0.63	-0.54	0.76	-0.68	0.59
10	-0.34	0.46	0.54	0.42	0.06	-1.37	-0.66	0.03	-0.69	0.24	0.56	-0.28
11												
12	-0.05		-1.91	0.62	-0.15	-1.70	-0.50	0.32	-0.89	0.30	-1.14	-0.31
14												
15		-0.44	-0.41	-0.23	1.03	0.62	0.15	0.28	0.66	1.08		0.00
17	1.94	-0.21		-0.80	1.64	-0.85	-0.01		-0.24	-0.42	9.60	-3.56
18												
19			-1.05					0.42		-6.75		

TABLE 4: SUMMARY OF OBTAINED z-SCORES PER LABORATORY

Laboratory Code	Number of results	$\lvert z \rvert \geq 3$	$2 < \lvert z \rvert < 3$	$\lvert z \rvert \leq 2$
1	11	64%	0%	36%
2	10	20%	0%	80%
5	10	10%	0%	90%
7	7	57%	0%	43%
8	10	0%	0%	100%
9	12	0%	0%	100%
10	12	0%	0%	100%
11	11	36%	0%	64%
12	11	0%	0%	100%
14	12	17%	8%	75%
15	10	0%	0%	100%
17	10	20%	0%	80%
18	6	0%	33%	67%
19	3	33%	0%	67%

TABLE 5: SUMMARY OF OBTAINED z-SCORES PER ELEMENT

Element	Participation	$\lvert z \rvert \geq 3$	$2 < \lvert z \rvert < 3$	$\lvert z \rvert \leq 2$
Al	93%	38%	0%	63%
As	57%	20%	0%	80%
Cd	57%	31%	0%	69%
Co	93%	10%	0%	90%
Cr	93%	31%	8%	62%
Cu	71%	0%	8%	92%
Fe	79%	9%	0%	91%
Hg	71%	9%	9%	82%
Mn	79%	8%	0%	92%
Pb	93%	23%	0%	77%
V	93%	38%	0%	63%
Zn	86%	0%	0%	100%

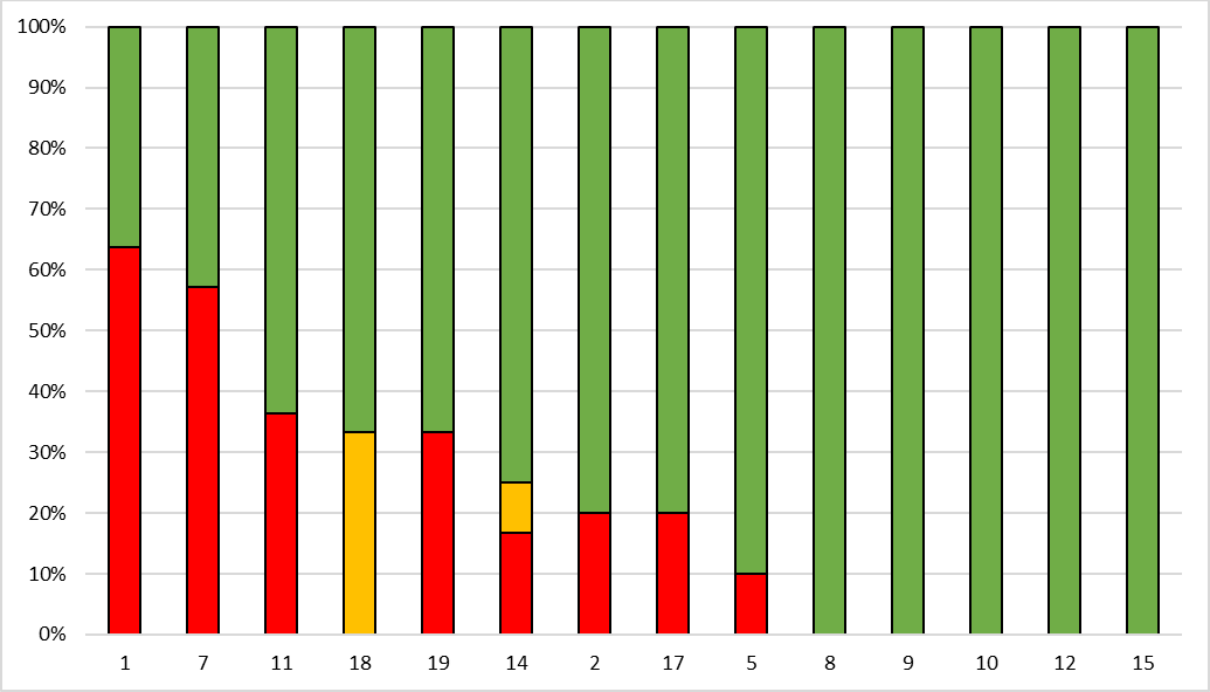


FIG. 2. Summary of obtained z-scores per participant

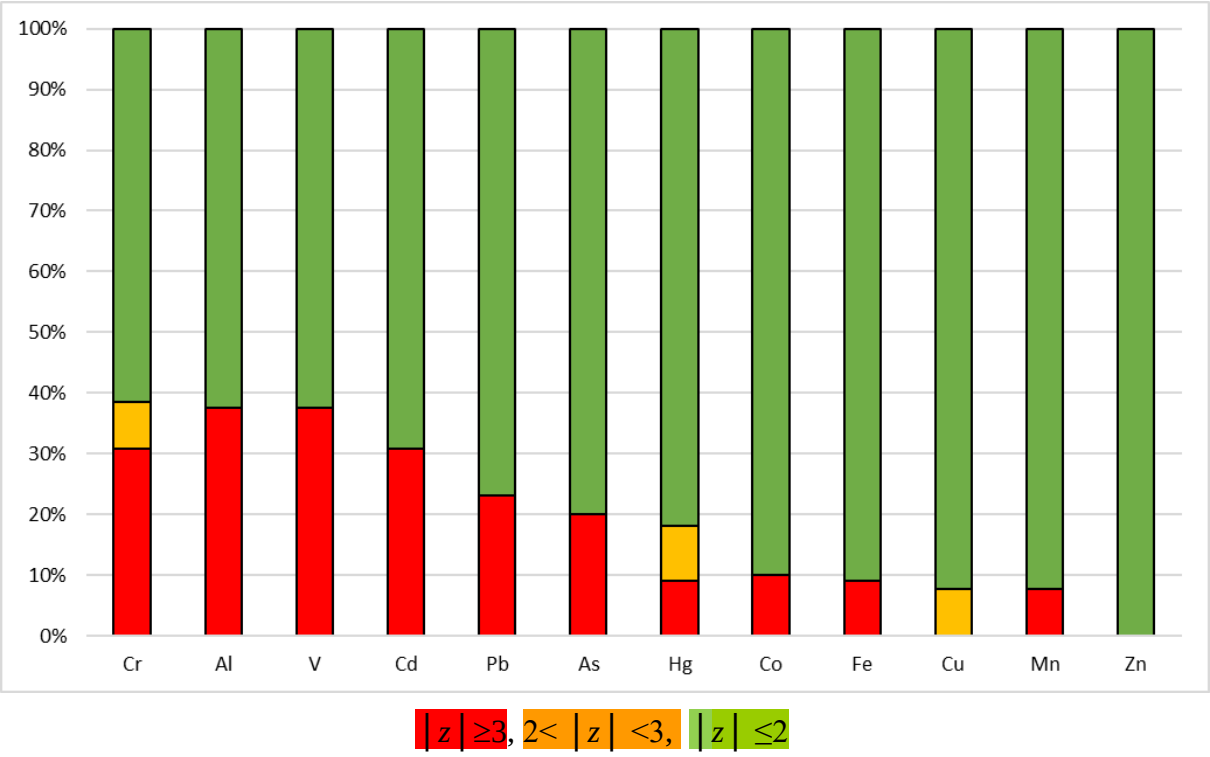


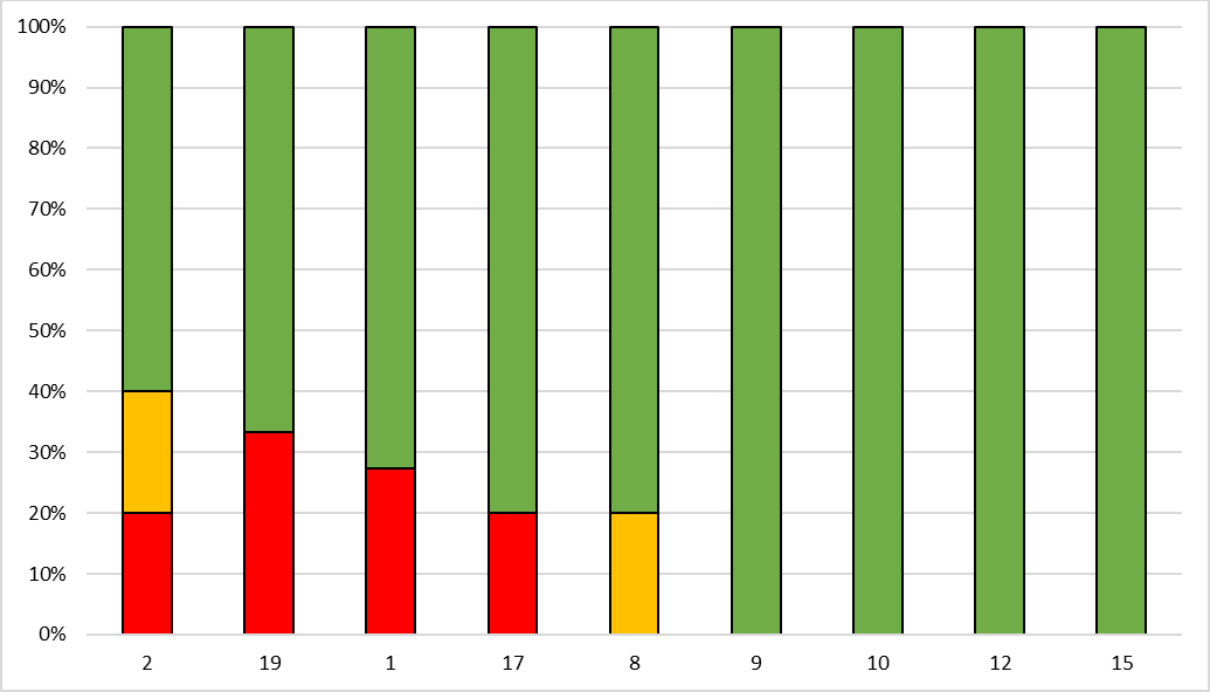
FIG. 3. Summary of obtained z-scores per element

TABLE 6: SUMMARY OF OBTAINED ZETA-SCORES PER LABORATORY

Laboratory Code	Number of results	|Zeta| ≥3	2< |Zeta| <3	|Zeta| ≤2
1	11	27%	0%	73%
2	10	20%	20%	60%
5				
7				
8	10	0%	20%	80%
9	12	0%	0%	100%
10	12	0%	0%	100%
11				
12	11	0%	0%	100%
14				
15	10	0%	0%	100%
17	10	20%	0%	80%
18				
19	3	33%	0%	67%

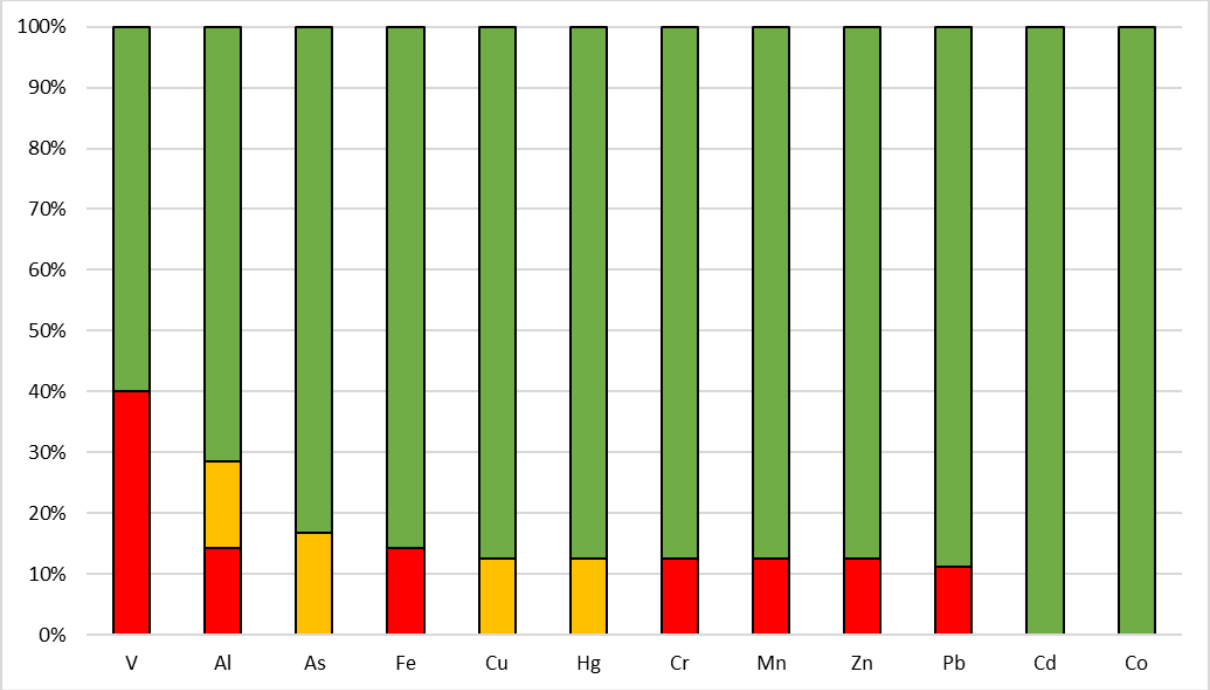
TABLE 7: SUMMARY OF OBTAINED ZETA-SCORE PER ELEMENT

Element	Participation	|Zeta| ≥3	2< |Zeta| <3	|Zeta| ≤2
Al	36%	14%	14%	71%
As	50%	0%	17%	83%
Cd	43%	0%	0%	100%
Co	50%	0%	0%	100%
Cr	57%	13%	0%	88%
Cu	57%	0%	13%	88%
Fe	57%	14%	0%	86%
Hg	57%	0%	13%	88%
Mn	57%	13%	0%	88%
Pb	64%	11%	0%	89%
V	57%	40%	0%	60%
Zn	50%	13%	0%	88%



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

FIG. 4. Summary of obtained Zeta-scores per participants



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

FIG. 5. Summary of obtained Zeta-scores per element

3.4. Sample treatment, use of CRM and recovery correction:

Most of participating in the MEDPOL PT laboratories applied microwave digestion, using mainly mixture of acid. Hydrofluoric acid is required for decomposition of the silicate lattice of a sediment matrix. Without the use of HF, the dissolution of a sediment sample will be incomplete, resulting in the observation of negatively biased concentrations for certain refractory elements, such as Al, Cr, and V (Figure 3 and Annex 3). Only 8 laboratories participating in the MED POL PT have used hydrofluoric acid in their sample preparation step. 6 participants were not using total digestion procedure and despite that 4 of them (1, 2, 7 and 11) have reported results for refractory elements (Al, Cr and V), unsurprisingly with unsatisfactory low biased results (i.e. z scores < - 3) for the mass fractions of Al, Cr and V.

For the total mercury determination 36% of laboratories used solid mercury analyser and didn't applied any sample preparation before the instrumental measurement. One laboratory has used XRF without any sample digestion before, except for the determination of Al and Fe mass fractions in the PT sample.

Freeze drying step was a part of sample processing procedure for the MEDPOL PT sample. Depending on local storage and humidity conditions, the PT sample might absorb water from the laboratory environment. As the moisture is an operationally dependent parameter, the procedure for moisture content determination in the PT sample was carefully developed and provided in the letter, describing details on the MED POL PT exercise. Oven drying for a separate portion of sediment sample at 110°C until constant weight was the recommended procedure for moisture determination. Only 3 participating laboratories have respected it, while the remaining participants applied in house developed protocol or didn't report the information on moisture content. The moisture content reported by the laboratories was in the range from 0.4 to 5%.

In order to provide traceable results and to confirm the validation of the methods used, designated MED POL laboratories have been systematically requested to analyse a CRM with a matrix and concentration range similar to the PT sample. CRMs used from the participating in the PT exercise designated laboratories, were generally selected according to the above described criteria: similar matrix and concentration range of the analytes of interest.

Out of the 14 data sets received, 5 laboratories didn't include quality control (QC) results in the reporting form, despite the fact that some of them are reporting the use of CRM in their

quality procedures. It should be noted that 2 participating laboratories, claiming to be accredited for this type of analyses didn't report any quality control results and evidences.

Nine laboratories reported recoveries, but only 4 of them claimed implementing correction for recovery for all, or part of reported trace elements mass fraction. Most participants have calculated recovery rates by using CRMs and few of them have used spike solution for the analytes of interest. Interestingly, a considerably high proportion of laboratories that didn't correct for recovery obtained satisfactory scorings. This is an indication that the laboratories have correctly estimated that the recoveries achieved with the used analytical procedures were not significantly different from 100%.

3.5. Analytical techniques used by participants:

Abbreviations of the instrumental techniques used in this exercise are given in Table 8. As it can be seen from Figure 6, ICP-MS is the most used instrumental technique, followed by AAS and ICP-OES.

TABLE 8: ANALYTICAL TECHNIQUES ABBREVIATIONS

Method Code	Instrumental Technique
AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectrometry
F-AAS	Flame Atomic Absorption Spectrometry
ET-AAS	Graphite Furnace Atomic Absorption Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
CV	Cold Vapour
XRF	X-ray fluorescence

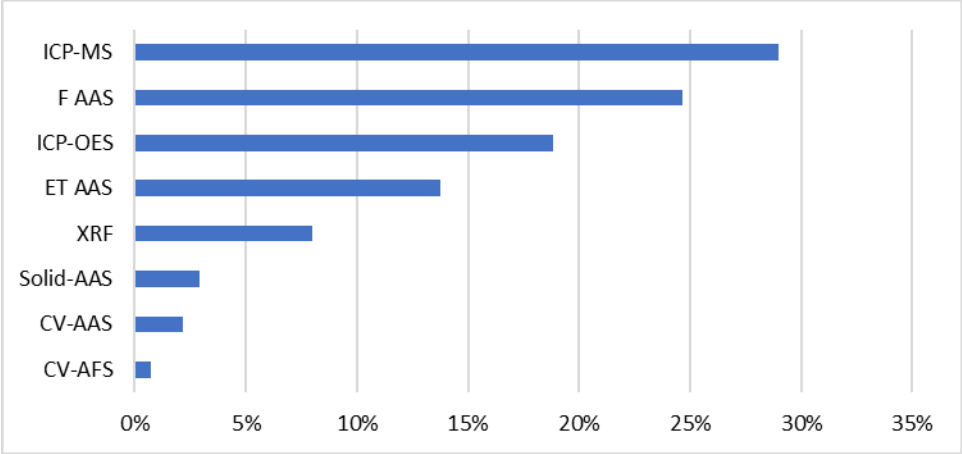


FIG. 6. Graphical distribution of instrumental techniques, applied in the present PT

3.6. Answer to the provided questionnaire:

Four laboratories didn't report any information in the questionnaire.

Nine laboratories claimed to be accredited, however 4 of them didn't report measurement uncertainties, which should be part of a result provided by an accredited laboratory.

Nine laboratories applied preliminary validated methods, while 11 participants declared to have quality system in place. Nine participants declare to be accredited, but only 2 of them are accredited for the analytes and matrix of this PT.

2 participants did not explain how they have assured the traceability of obtained results.

4. CONCLUSIONS AND RECOMMENDATIONS

Participation in MEDPOL proficiency test is considered as an educational activity. Participants are advised to review their data element-by-element, especially in the cases where the *z*-score or/and Zeta-score are above 2. The use of the *z*-scores will help to identify systematic errors in the measurement results (e.g. from calibration or reagent contamination) and should ultimately improve data quality.

In order to obtain a real estimation of laboratory performance, the proficiency test sample should be treated in exactly the same way as any routine test sample. Examples of 'poor practice' include:

- Getting the PT samples analysed by the most experienced analyst

- Reporting results considered to be the ‘best’ ones.

In the case of unsatisfactory performance each laboratory should carefully investigate the cause of the unsatisfactory scores (i.e. $|z| > 3$) and put in place the necessary corrective actions in order to prevent the problem to reoccur. This is one of the requirements for laboratories accredited according to the ISO/IEC 17025 standard.

The concept of recovery is not implemented in several laboratories and as a consequence the validation of the analytical methods, used by them is often questionable.

Five laboratories didn’t provide results for the use of CRMs in their analytical procedure, which means that the internal quality control in those laboratories is not in place.

Uncertainty of the measurement results in the MED POL PT exercise was calculated from 64% of the participants. Considering the Zeta-scores reported, we can conclude that the way of calculation and application of uncertainty concept is still questionable for some of the laboratories participating in the MEDPOL PT and further training on uncertainty of measurement results is highly desirable.

Five (26%) from 19 designated by the MED POL laboratories didn’t send the requested in the frame of MED POL PT results, which make the evaluation of their measurement performance impossible. One of them didn’t receive the test sample due to problem with transportation.

5. REFERENCES

[1] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide *35 (2005), Reference Materials-General and statistical principles for certification, ISO, Geneva, Switzerland.*

[2] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide *17043 (2010), Conformity assessment, general requirements for proficiency testing, ISO, Geneva, Switzerland.*

[3] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide *13528 (2005), Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons, ISO, Geneva, Switzerland.*

[4] ROYAL SOCIETY OF CHEMISTRY, Statistical Subcommittee of the Analytical Methods Committee (AMC), AMC Technical Brief: Representing data distributions with Kernel density estimates" 2006, www.rsc.org/amc.

Annex 1: List of MEDPOL designated participants that sent results

ALGERIA

Laboratories Regional Centre
Observatoire National de l'Envirnnement et du Développement Durable
ONEDD
11, Rue Mohamed Tazairt, Bab El Oued
16008 Alger

BOSNIA & HERZEGOVINA

Institut for Water
(Institut Za Vode Doo)
Miloša Obilića 51
76300 Bijeljina

Institute for Public Health FB&H
Vukovarska 46
88000 Mostar

CROATIA

Public Health Institute of County of Istra
Nazorova 23
52100 Pula

Institute of Public Health
Ljudevita Posavskog 7A
23000 Zadar

FRANCE

Laboratoire de Biogéochimie des Contaminants Métalliques
Rue de l'Ile d'Yeu
BP 21105
44311 Nantes

GREECE

Hellenic Centre for Marine Research
Institute of Oceanography
46.7km Athens-Sounio Av.
Mavro Lithari
19013 Anavyssos

ISRAEL

Israel Oceanographic & Limnological Research
Tel Shikmona
POBox 8030
3108001 Haifa

ITALY

ARPAV Veneto
Via Lissa 6
30171 Mestre (Venezia)

LEBANON

American University of Beirut
CCC-SRB Bldg, 3rd Floor, Room 303c
Bliss St Hamra
PO Box 11.0236 Riad El Solh
Beirut

MONTENEGRO

Centre for Ecotoxicological Research Podgorica
Bulevar Sarla de Gola 2
81000 Podgorica

SLOVENIA

National Laboratory of Health
Environment and Food
Prvomajska Ulica 1
2000 Maribor

SYRIA

Central Laboratories
Ministry of Local Administration and Environment
Kafar sosah- 17 Nesaan Street
po box 3773
963 Damascus

TURKEY

Çevre Referans Laboratuvarı
National Environmental Reference Laboratory
Haymana Yolu 5. Km.
Gölbaşı-Ankara

Annex 2: List of MEDPOL designated particpants that did not send results

ALBANIA

Agjencia Kombetare e Mjedisit
National Environment Agency (NEA)
Rruga Sami Frasheri nr 23 godina nr 4
Tirana

CYPRUS

State General Laboratory
44 Kimonos Str.
Stovolos
1451 Nicosia

EGYPT

Institute of Graduate Studies and Research
Alexandria University
163 El Horreya Avenue
Alexandria

NOTE : Did not received sample

MOROCCO

Laboratoire National des Etudes et de Surveillance de la Pollution
Av. Mohamed Ben Abdellah Erregragui Madinat
Al-Irfane
Rabat

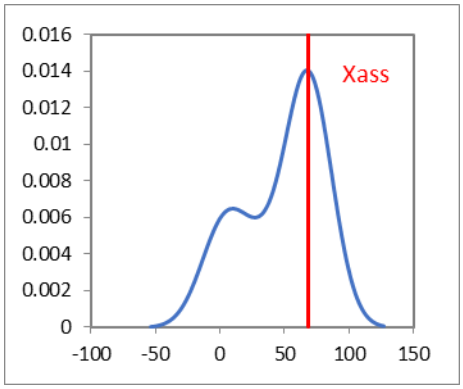
SPAIN

Instituto Espanol de Oceanografia (IEO)
Centro Oceanografico de Murcia
c/Varadero, 1
30740 San Pedro del Pinatar

Annex 3: Graphical representation

Reported data for Al in the IAEA-MESL-2019-02-TE

Kernel density Plot



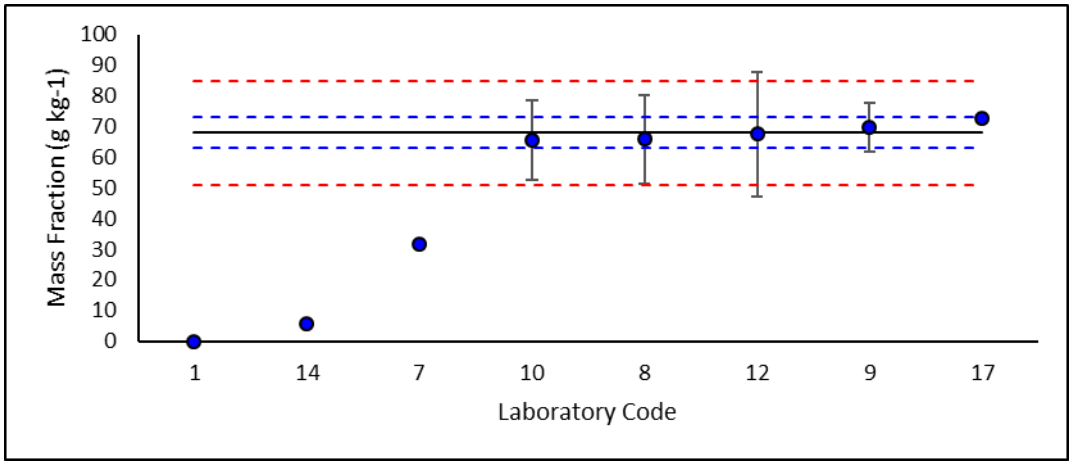
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	63%	0%	38%
Zeta-score	71%	14%	14%

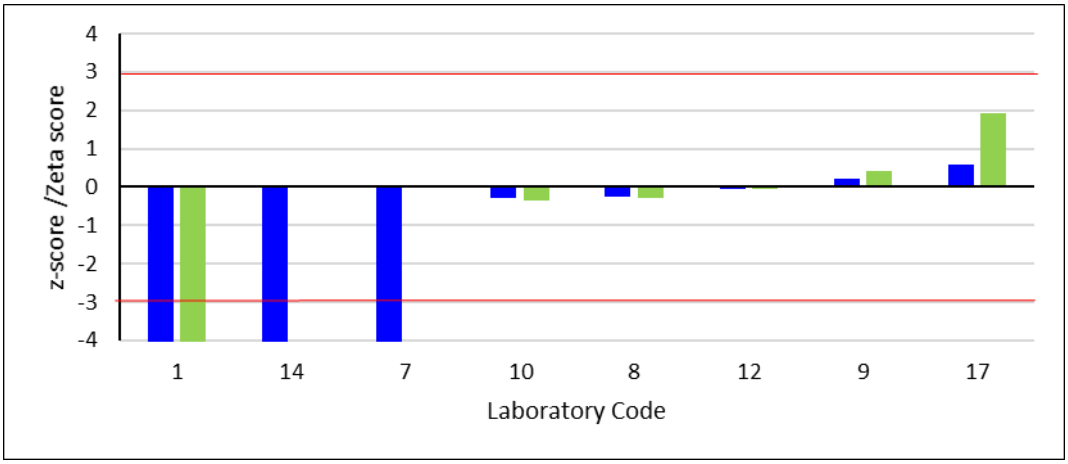
X_{Ass} g kg^{-1}	68.0
U_{Ass} (k=2) g kg^{-1}	5.0[1]
2σ_p g kg^{-1}	17.0
Number of results:	8
Number of methods:	4

Reported results and expanded uncertainties:

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

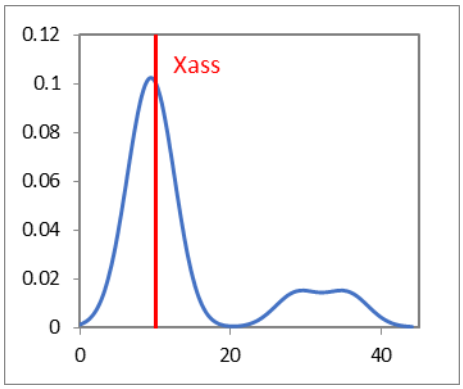


Performance evaluation: z-score Zeta-score



Reported data for As in the IAEA-MESL-2019-02-TE

Kernel density Plot



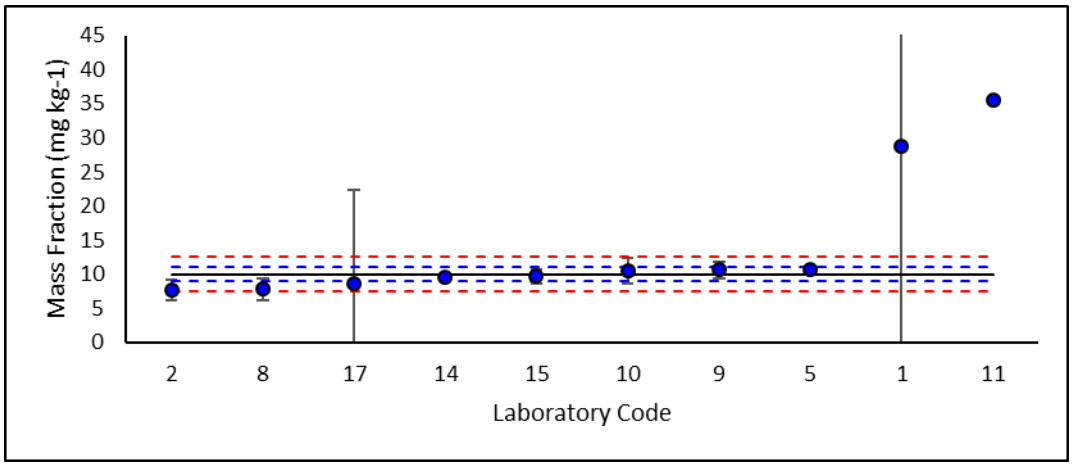
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	80%	0%	20%
Zeta-score	83%	17%	0%

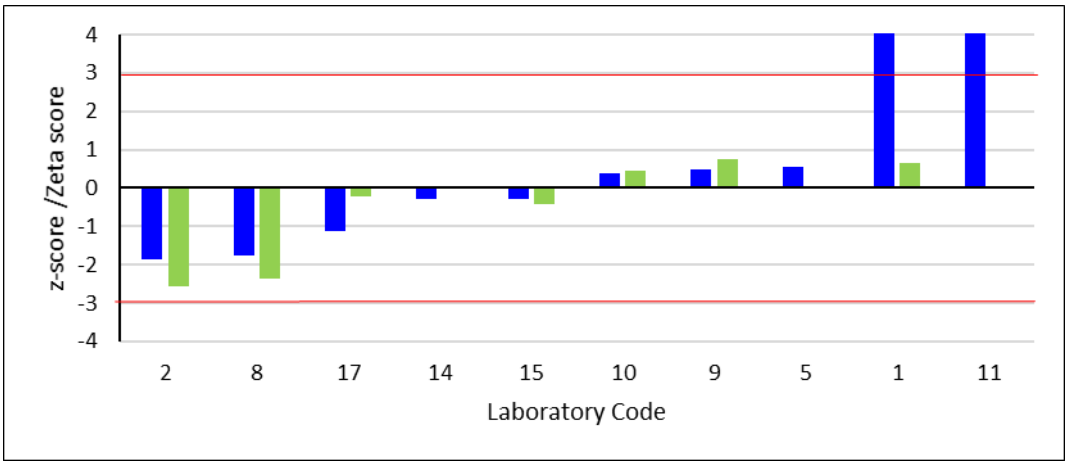
X_{Ass} mg kg^{-1}	10.0
U_{Ass} (k=2) mg kg^{-1}	1.0
$2\sigma_p$ mg kg^{-1}	2.5
Number of results:	10
Number of method:	4

Reported results and expanded uncertainties:

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

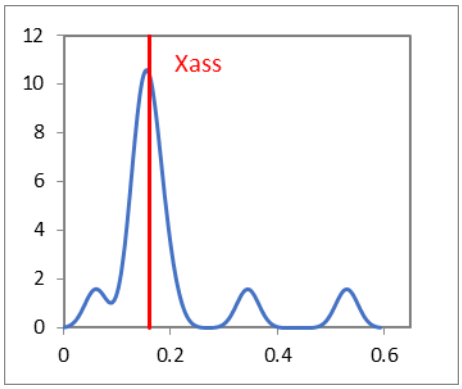


Performance evaluation: *z*-score Zeta-score



Reported data for Cd in the IAEA-MESL-2019-02-TE

Kernel density Plot



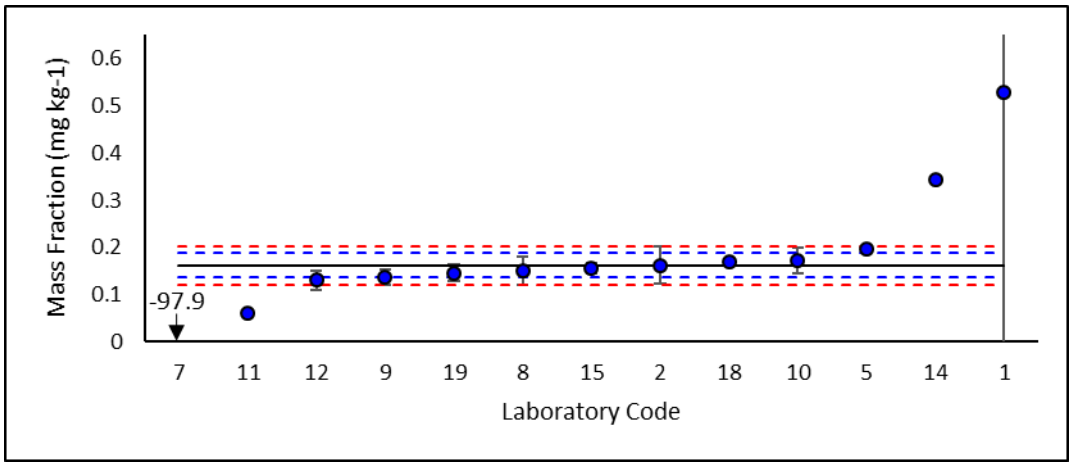
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	69%	0%	31%
Zeta-score	100%	0%	0%

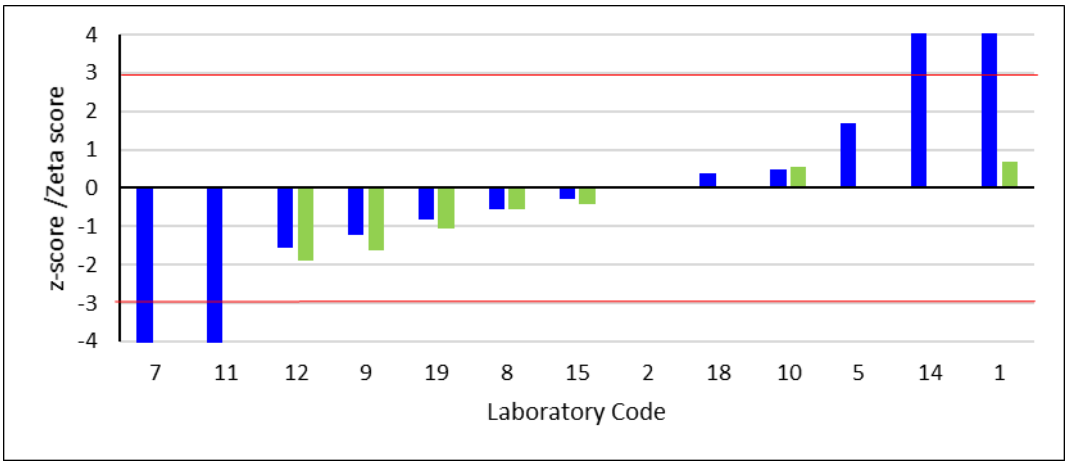
X_{Ass} mg kg^{-1}	0.162
U_{Ass} (k=2) mg kg^{-1}	0.026
$2\sigma_p$ mg kg^{-1}	0.040
Number of results:	13
Number of method:	3

Reported results and expanded uncertainties:

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

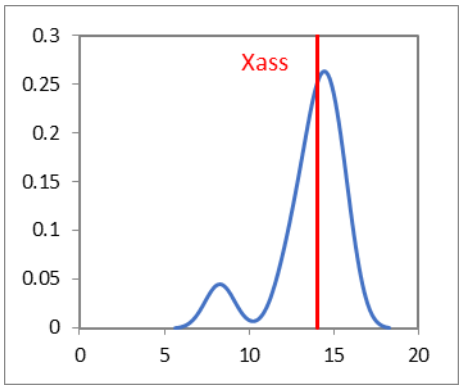


Performance evaluation: *z*-score Zeta-score



Reported data for Co in the IAEA-MESL-2019-02-TE

Kernel density Plot



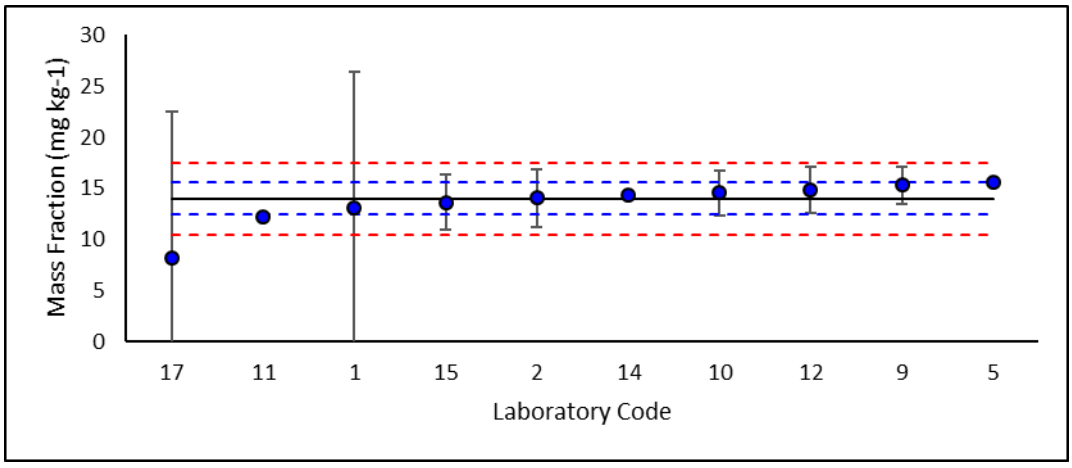
Summary of results:

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

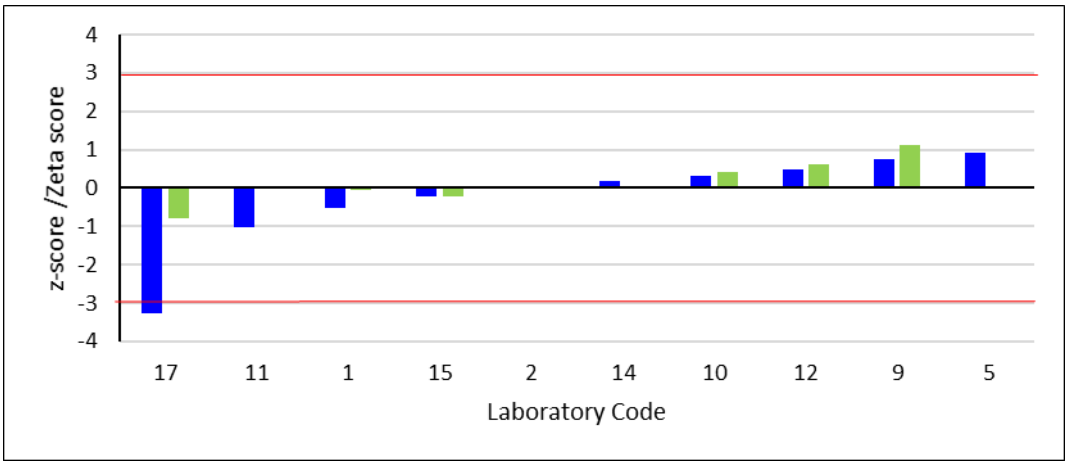
X_{Ass} mg kg^{-1}	14.0
U_{Ass} (k=2) mg kg^{-1}	1.6
$2\sigma_p$ mg kg^{-1}	3.5
Number of results:	10
Number of method:	5

Reported results and expanded uncertainties:

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

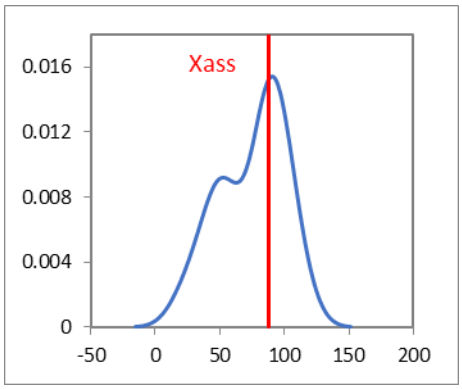


Performance evaluation: *z*-score Zeta-score



Reported data for Cr in the IAEA-MESL-2019-02-TE

Kernel density Plot



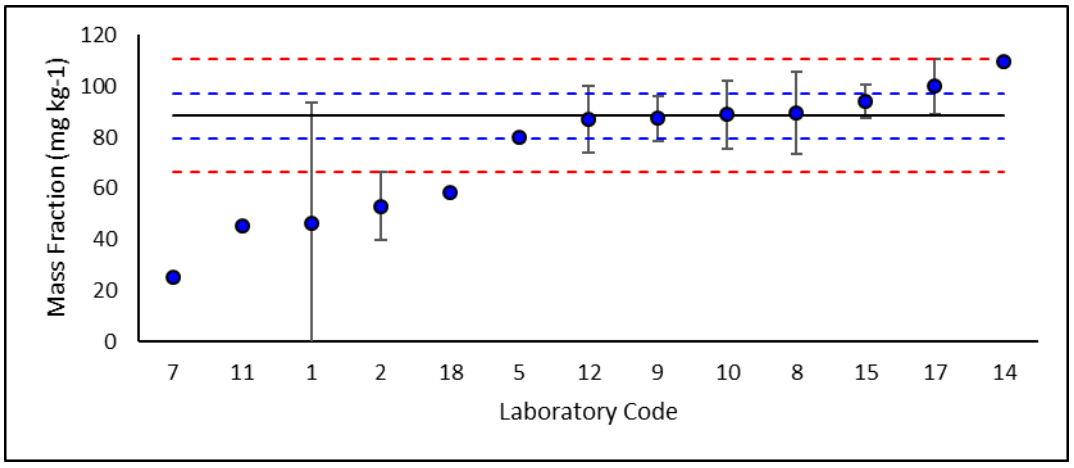
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	62%	8%	31%
Zeta-score	88%	0%	13%

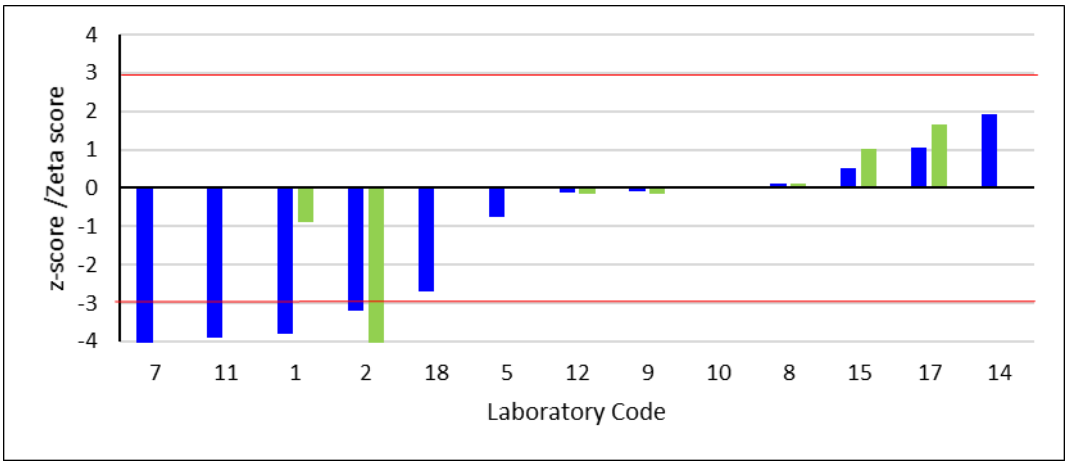
X_{Ass} mg kg^{-1}	88.4
U_{Ass} (k=2) mg kg^{-1}	8.7
$2\sigma_p$ mg kg^{-1}	22.1
Number of results:	13
Number of method:	5

Reported results and expanded uncertainties:

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

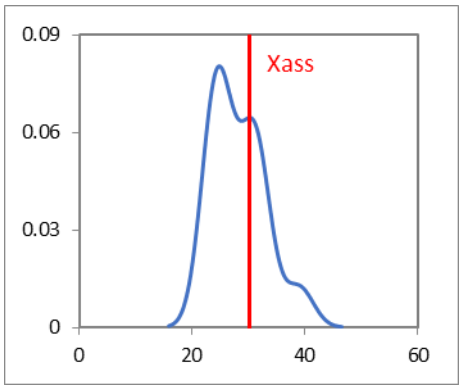


Performance evaluation: *z*-score Zeta-score



Reported data for Cu in the IAEA-MESL-2019-02-TE

Kernel density Plot



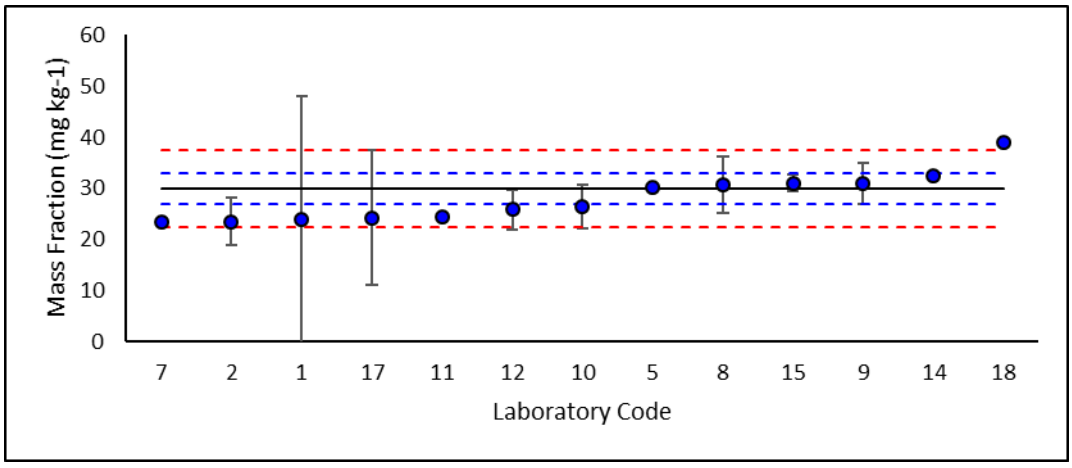
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	92%	8%	0%
Zeta-score	88%	13%	0%

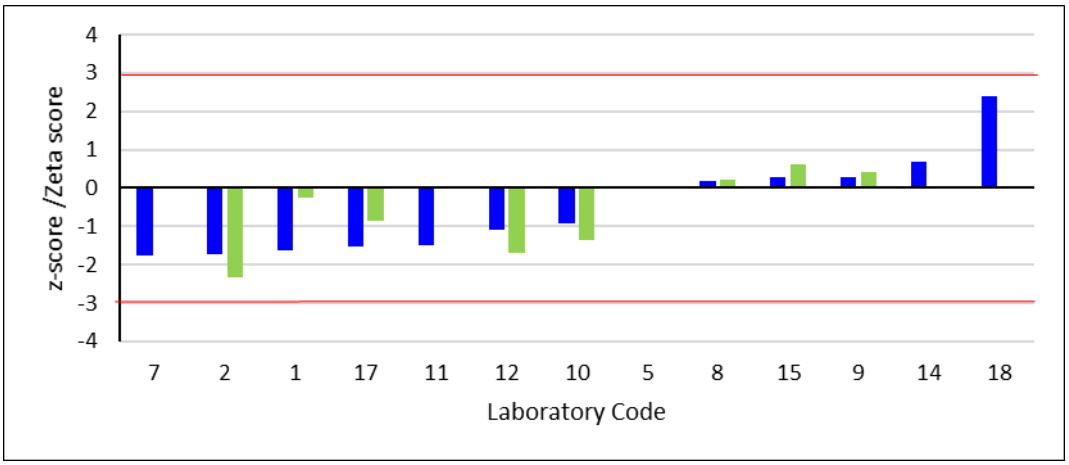
X_{Ass} mg kg^{-1}	30.1
U_{Ass} (k=2) mg kg^{-1}	2.9
$2\sigma_p$ mg kg^{-1}	7.5
Number of results:	13
Number of method:	5

Reported results and expanded uncertainties:

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

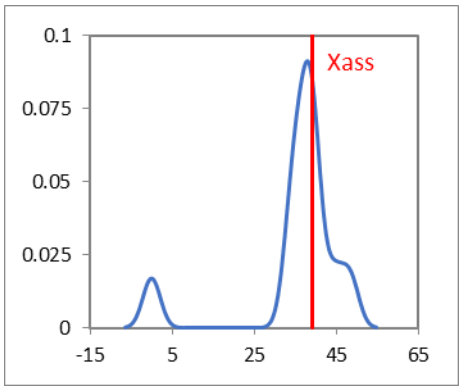


Performance evaluation: *z*-score Zeta-score



Reported data for Fe in the IAEA-MESL-2019-02-TE

Kernel density Plot



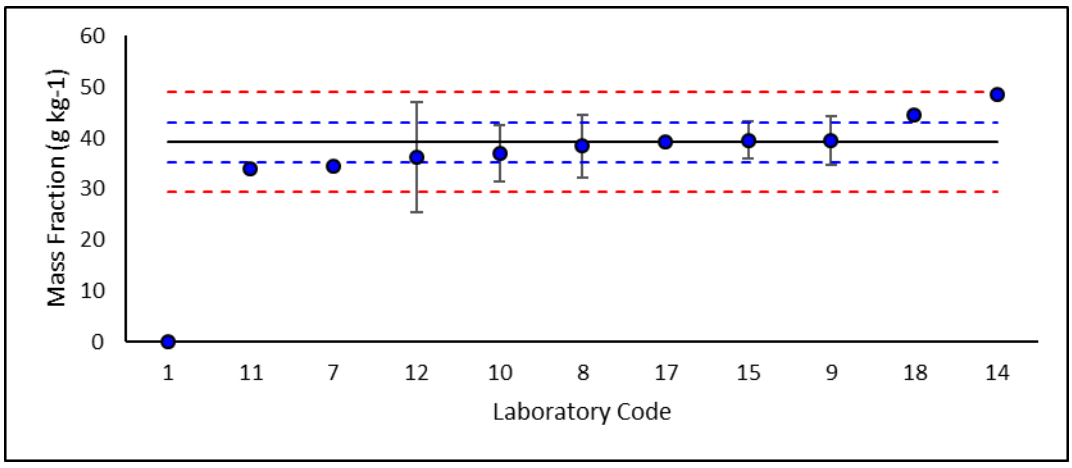
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	91%	0%	9%
Zeta-score	86%	0%	14%

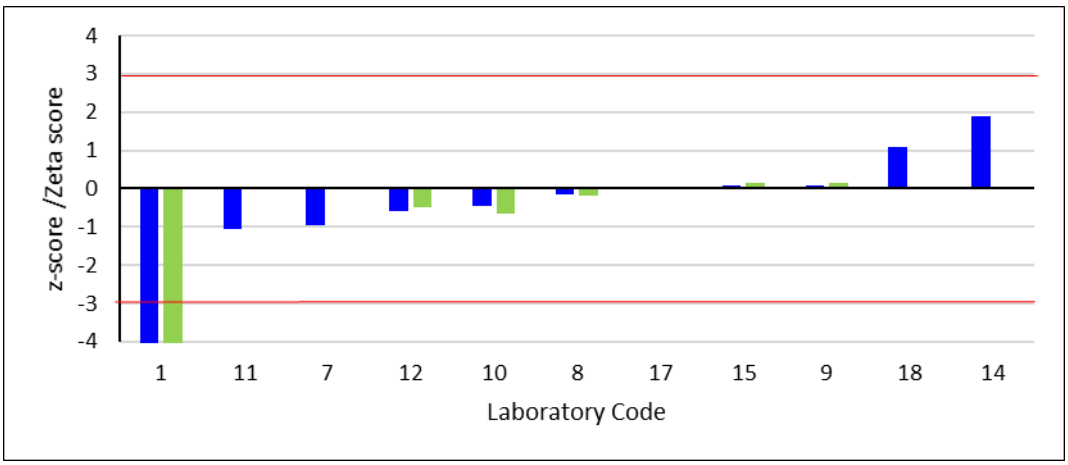
X_{Ass} g kg^{-1}	39.2
U_{Ass} (k=2) g kg^{-1}	3.9
$2\sigma_p$ g kg^{-1}	9.8
Number of results:	11
Number of method:	4

Reported results and expanded uncertainties:

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

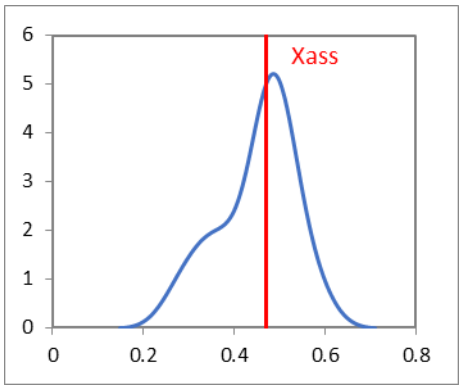


Performance evaluation: *z*-score Zeta-score



Reported data for Hg in the IAEA-MESL-2019-02-TE

Kernel density Plot



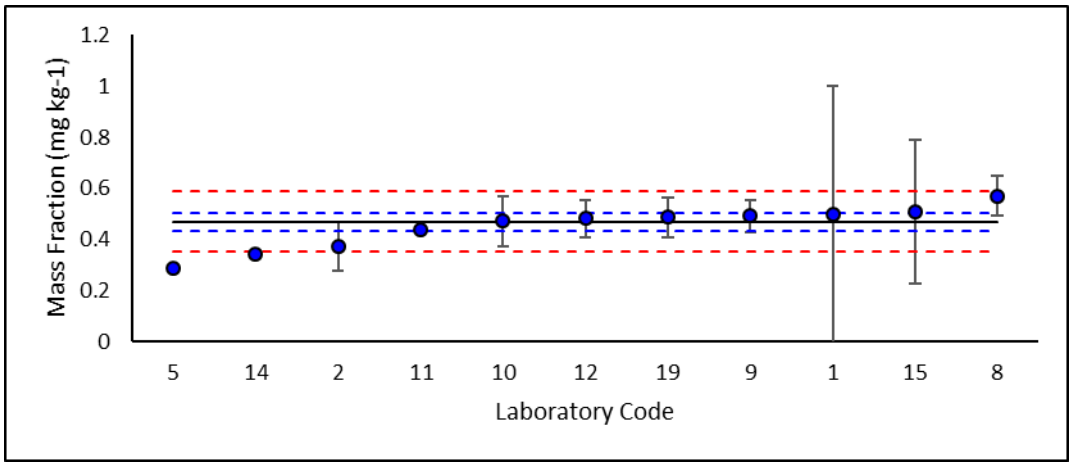
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	82%	9%	9%
Zeta-score	88%	13%	0%

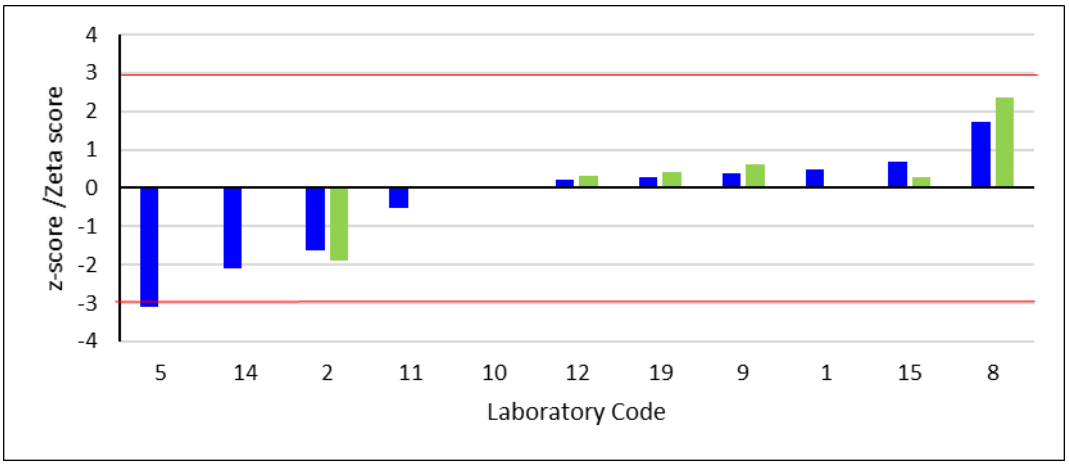
X_{Ass} mg kg^{-1}	0.470
U_{Ass} (k=2) mg kg^{-1}	0.034
$2\sigma_p$ mg kg^{-1}	0.120
Number of results:	11
Number of method:	4

Reported results and expanded uncertainties:

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

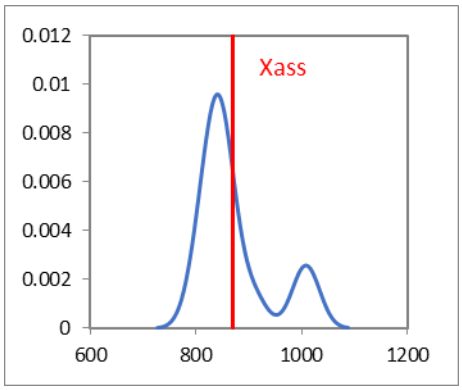


Performance evaluation: *z*-score Zeta-score



Reported data for Mn in the IAEA-MESL-2019-02-TE

Kernel density Plot



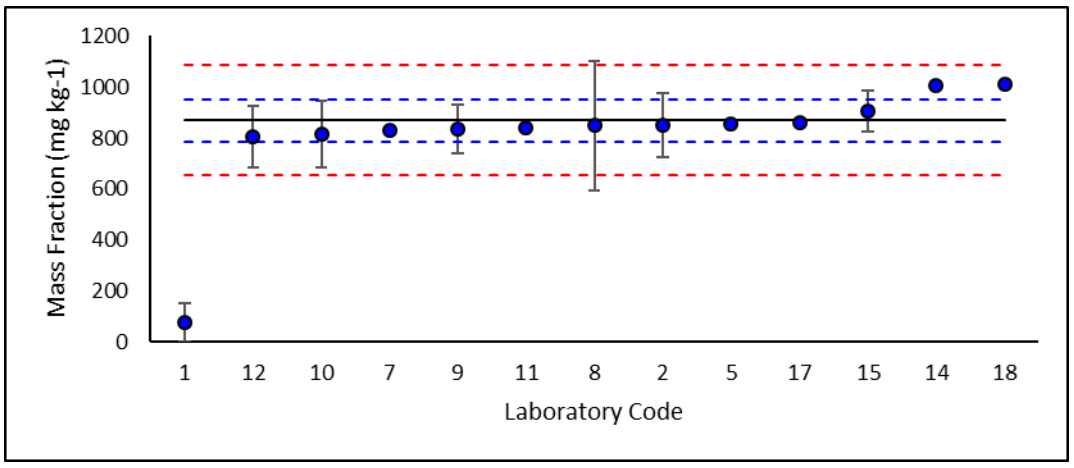
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	92%	0%	8%
Zeta-score	88%	0%	13%

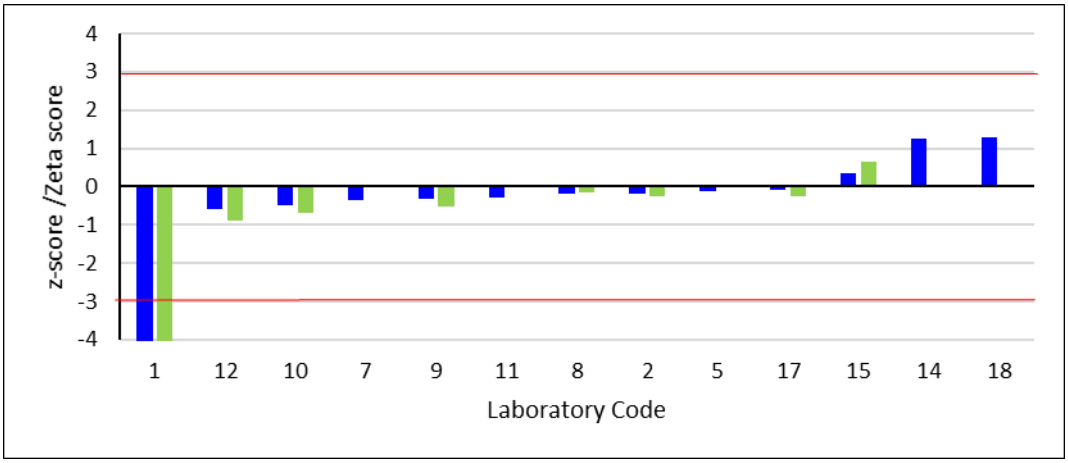
X_{Ass} mg kg^{-1}	870
U_{Ass} (k=2) mg kg^{-1}	83
$2\sigma_p$ mg kg^{-1}	217
Number of results:	13
Number of method:	4

Reported results and expanded uncertainties:

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

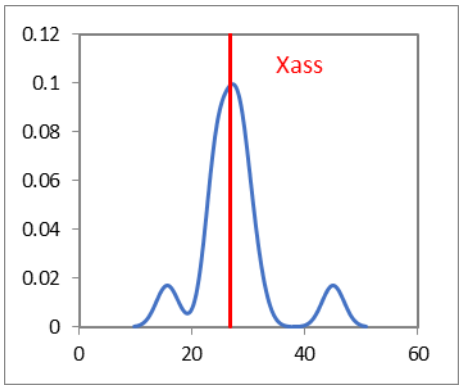


Performance evaluation: *z*-score Zeta-score



Reported data for Pb in the IAEA-MESL-2019-02-TE

Kernel density Plot



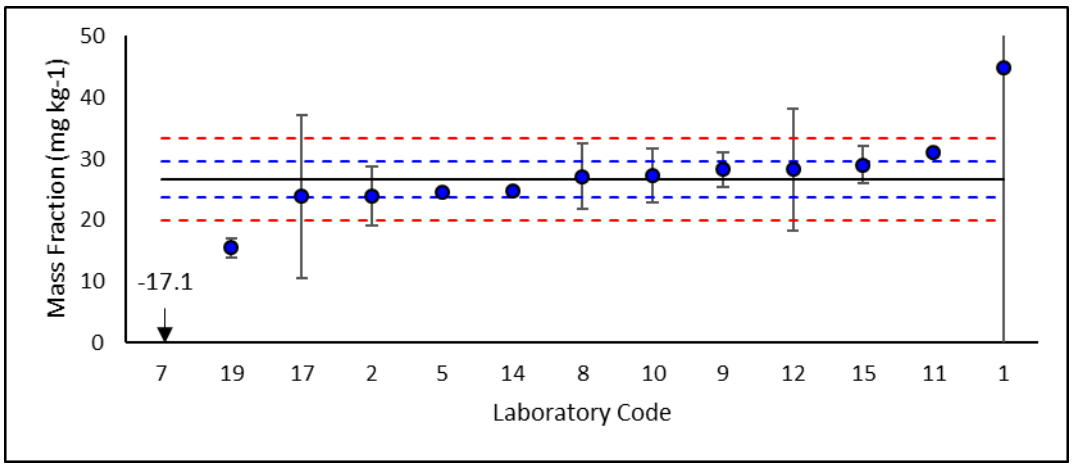
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	77%	0%	23%
Zeta-score	89%	0%	11%

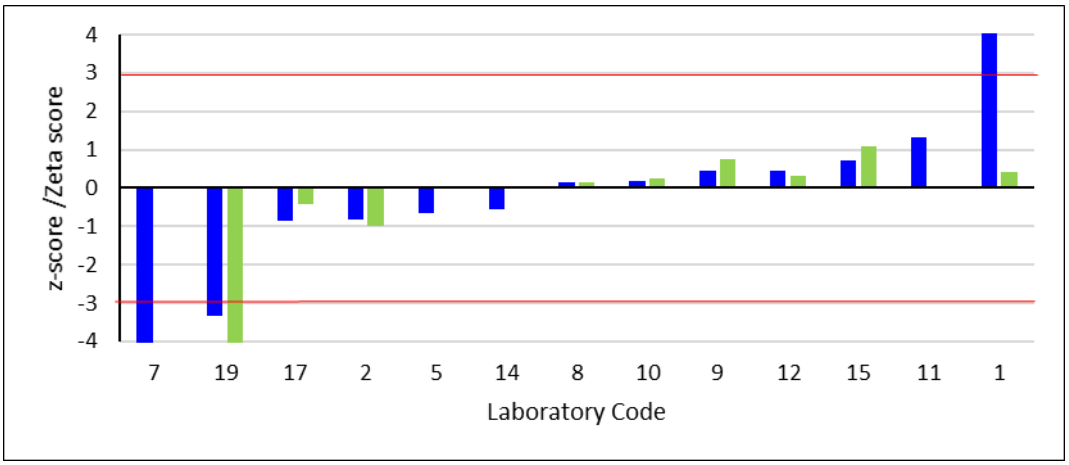
X_{Ass} mg kg^{-1}	26.7
U_{Ass} (k=2) mg kg^{-1}	2.9
$2\sigma_p$ mg kg^{-1}	6.7
Number of results:	13
Number of method:	5

Reported results and expanded uncertainties:

— X_{Cert} ; $\overset{\top}{\bullet}$ $X_{lab} \pm U_{lab}$; ---- $X_{Cert} \pm 2\sigma_p$; ---- $X_{Cert} \pm U_{Cert}(k=2)$

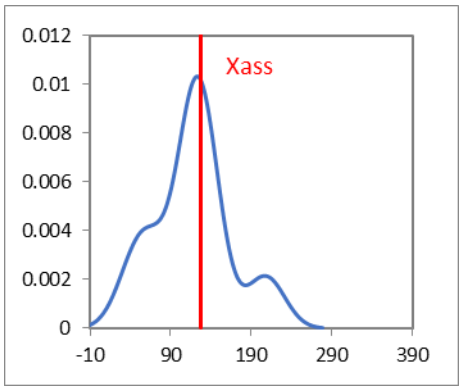


Performance evaluation: *z*-score Zeta-score



Reported data for V in the IAEA-MESL-2019-02-TE

Kernel density Plot



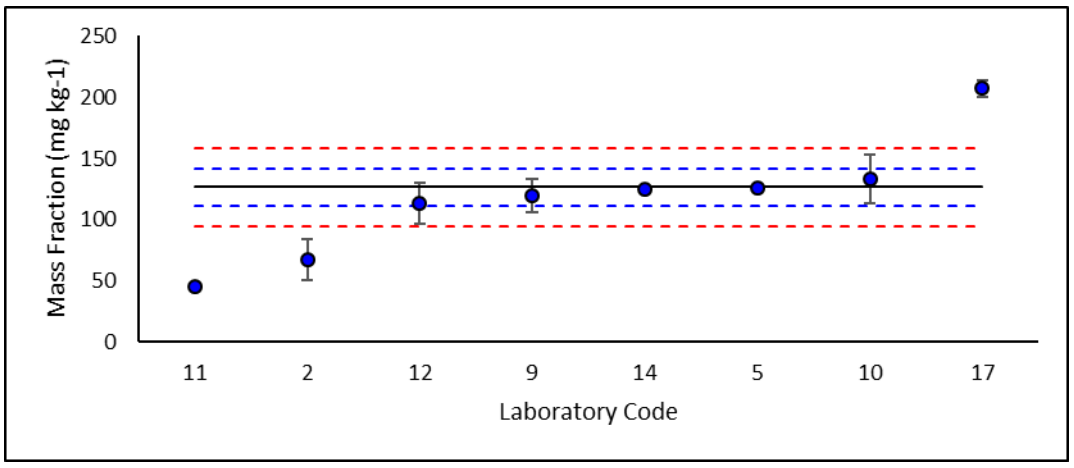
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	63%	0%	38%
Zeta-score	60%	0%	40%

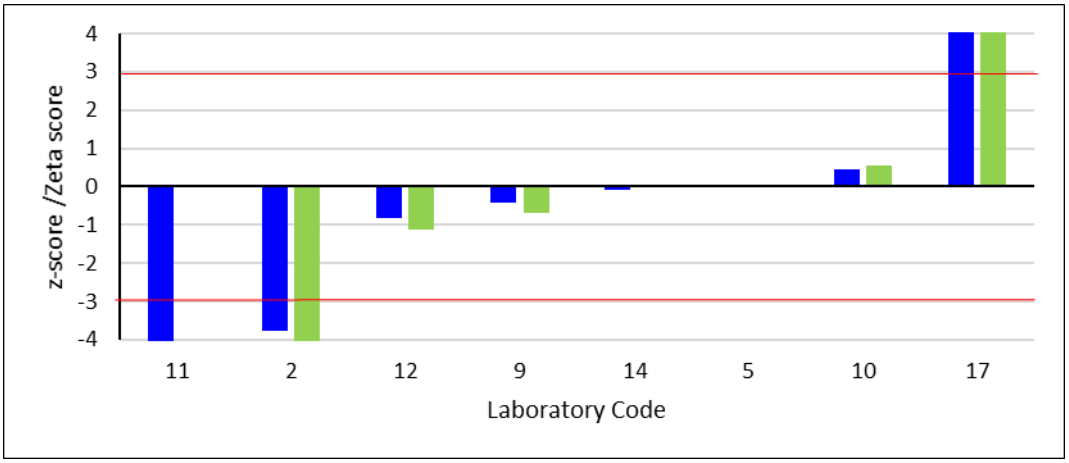
X_{Ass} mg kg^{-1}	127
U_{Ass} (k=2) mg kg^{-1}	15
$2\sigma_p$ mg kg^{-1}	32
Number of results:	8
Number of method:	4

Reported results and expanded uncertainties:

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

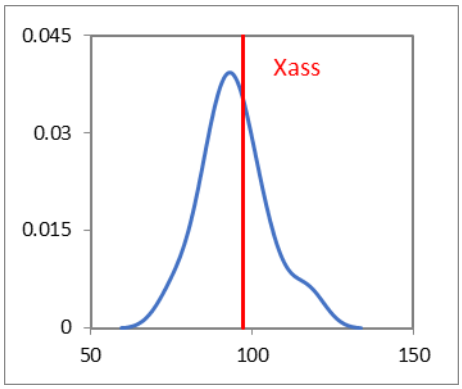


Performance evaluation: *z*-score Zeta-score



Reported data for Zn in the IAEA-MESL-2019-02-TE

Kernel density Plot



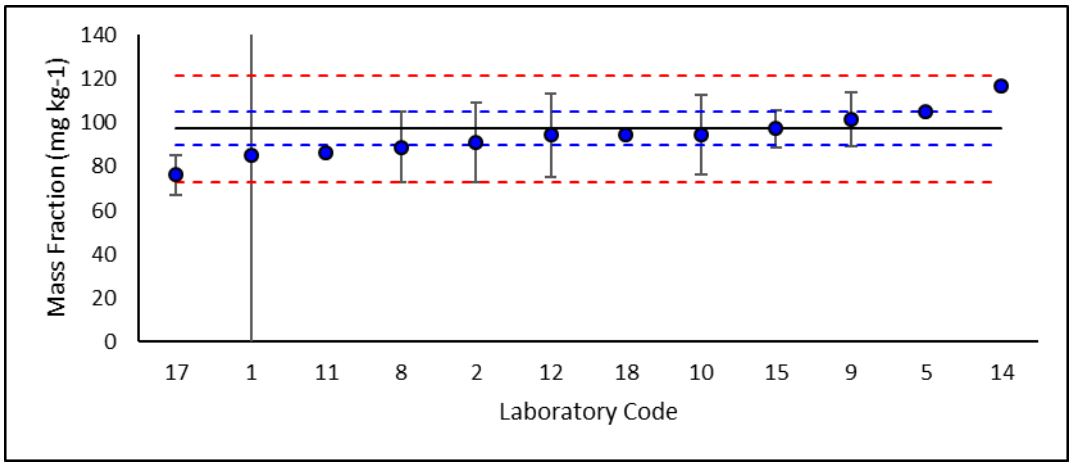
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	100%	0%	0%
Zeta-score	88%	0%	13%

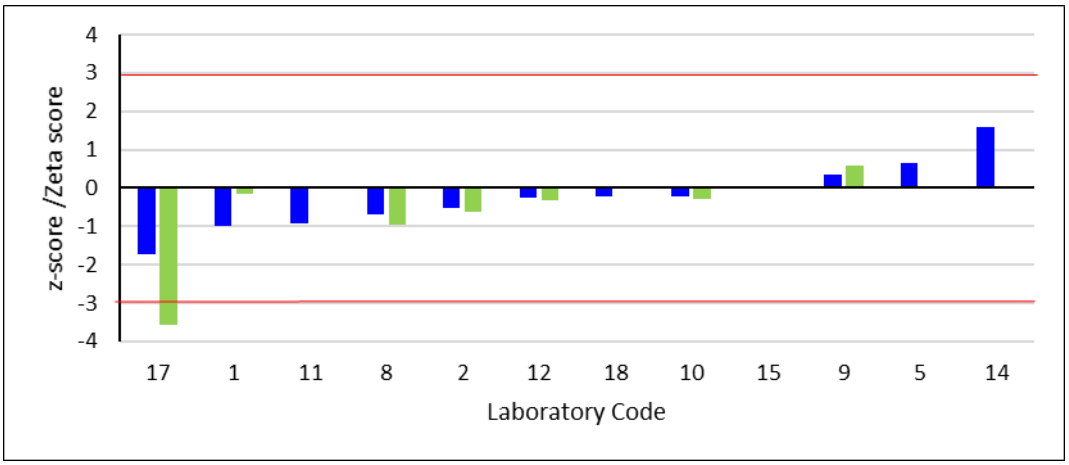
X_{Ass} mg kg^{-1}	97.4
U_{Ass} (k=2) mg kg^{-1}	7.8
$2\sigma_p$ mg kg^{-1}	24.3
Number of results:	12
Number of method:	4

Reported results and expanded uncertainties:

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



Performance evaluation: *z*-score Zeta-score



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ENVIRONMENT PROGRAMME
MEDITERRANEAN ACTION PLAN

26. March 2021
Original: English

Meeting of the Ecosystem Approach Correspondence Group on Pollution Monitoring

Videoconference, 26-28 April 2021

Agenda item 5: MEDPOL Proficiency Test on the Determination of Organochlorine Pesticides, PCBs and PAHs in Sediment sample (2019)

UNEP/MAP
Athens, 2021

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REPORT

MED POL PROFICIENCY TEST ON THE DETERMINATION OF ORGANOCHLORINE PESTICIDES, PCBs AND PAHS IN SEDIMENT SAMPLE IAEA-MEL-2019-01 PT/ORG

2019

Prepared in collaboration with:

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TABLE OF CONTENT

1. INTRODUCTION

The primary goal of the International Atomic Energy Agency's Environment Laboratories (IAEA-NAEL) is to assist Member States in the use of nuclear and non-nuclear analytical techniques to understand, monitor and protect the environment. The major impact exerted by large coastal cities on marine ecosystems is an issue of primary concern for the Agency and its Environment Laboratories. To this extent, it is noteworthy that marine pollution assessment depends on the accurate knowledge of contaminant concentrations in various environmental compartments.

NAEL has been assisting national laboratories and regional laboratory networks through the provision of Analytical Quality Control Services (AQCS) for the analysis of radionuclides, trace elements and organic compounds in marine samples since the early 1970's. Relevant activities comprise global inter-laboratory comparison exercises, regional proficiency tests, the production of marine reference materials and development of reference methods for trace elements and organic pollutants analysis in marine samples.

The IAEA has a long collaboration with UN Environment Programme/Mediterranean Action Plan (UN Environment/ MAP) and its Program for the Assessment and Control of Marine Pollution in the Mediterranean region (MEDPOL), which assists countries to implement programmes and measures to assess and eliminate marine pollution. The Marine Environmental Studies Laboratory (MESL) provides assistance to UN Environment/ MAP - MEDPOL in training (trace element, PAHs and organochlorine compounds), production of reference materials and by conducting interlaboratory studies and proficiency tests on matrices of relevance to marine monitoring.

This report describes the results of a Proficiency Test (PT) for the determination of organic contaminants in a marine sediment sample carried out in 2019 by MED POL designated laboratories.

The IAEA officers responsible for this publication are R. Cassi, I. Tolosa, S. Sander and A. Trinkl.

2. SCOPE OF EXERCISE

In May 2019 the MED POL Monitoring and Assessment Officer contacted the National Focal Points of MED POL countries, requesting them to provide the names of the designated national laboratories, involved in MED POL monitoring activities. The final list of designated national laboratories and contact persons for the targeted proficiency test for organochlorine pesticides, polychlorobiphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) was established at the end of July 2019. Consequently, a set of samples (bottles of sediment samples IAEA-MEL-2019-01 PT/ORG) were dispatched to 16 laboratories. All samples were sent in August 2019. The list of participating laboratories can be found in Annex 3.

Participants were requested to determine organochlorine pesticides, PCBs and PAHs, using the measurement procedures, usually applied for MED POL monitoring studies.

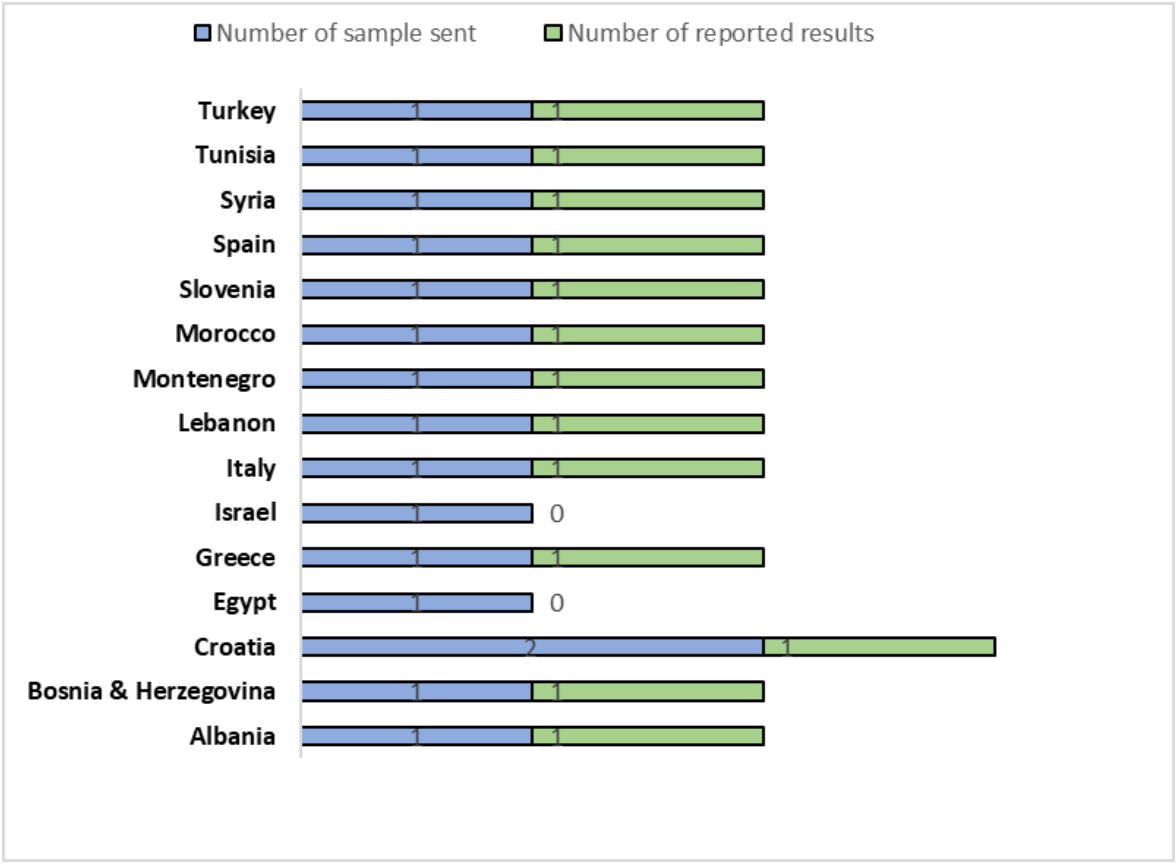

Figure. 1. Distribution per country of the MED POL PT sample

The deadline for reporting results was set for the 31st of October 2019, but it was extended to the 29th of November 2019, after request of several laboratories. Finally, 13 laboratories representing 81% of the 16 that received the test sample reported results (see figure 1). Seven laboratories reported results for both organochlorine pesticides, PCB congeners and PAHs, 5 laboratories reported results only for organochlorine pesticides and PCB congeners and 1 laboratory reported results only for PAHs.

3. MATERIAL

The blind PT sample IAEA-MEL-2019-01 PT/ORG is the Certified Marine Sediment Reference Material IAEA-459, which had been previously characterized through a characterization campaign [1]. Knowing "certified", and "information" values for the concentration of specified organochlorine pesticides, PCBs and PAHs, this PT yields more reliable data compared to an Inter Laboratory Comparison (ILC) done with a sample of unknown concentrations. Participants were asked to report data for selected organic contaminants listed in the CRM IAEA459, including some that are reported as "information" values. These organic contaminants are in line with those listed for the MEDPOL Common Indicator 17. The z-scores for this PT were only calculated for contaminants with "certified" values in IAEA459.

A marine sediment sample was collected in Han River estuary, South Korea. This sediment was dried, ground into powder and sieved at 125 μm.

The sieved sediment obtained, around 26 kg, with a particle size of less than 125 μm was homogenized by mixing it in a stainless-steel rotating homogenizer for three weeks. Then, aliquots of about 50 g were packaged into cleaned amber glass bottles with aluminium screw caps, labelled IAEA-459 and sealed with Teflon tape.

The between-bottle homogeneity of the material was assessed by determining the mass fraction of selected chlorinated pesticides, polychlorinated biphenyls, polybrominated diphenyl ethers and parent polycyclic aromatic hydrocarbons in sample aliquots of 10 bottle units randomly selected and analysed under repeatability conditions. The within–bottle homogeneity was assessed by 6 determinations of mass fractions of chlorinated pesticides, polychlorinated biphenyls (PCB), polybrominated diphenyl ethers (PDBE) and polycyclic aromatic hydrocarbons (PAH) in one bottle.

The coefficient of variation for the content of the major analytes between the 10 different sample bottles was below 10%. Thus, the material was considered sufficiently homogeneous for the PAHs, the organochlorinated and PBDEs compounds at 6 g sample size. The uncertainty contribution of possible inhomogeneity between bottles was estimated by applying the ANOVA-like approach [2,3], and it was lower than 11% for the certified analytes.

The selected certified and information values of organic contaminants used for this exercise can be found in Table 1 and 2. The complete reference sheet of IAEA459 can be found in Annex 2.

4. RESULTS AND EVALUATION

4.1. Data Reporting

Data were reported through the IAEA on-line reporting system. All participants were able to download their preliminary evaluation report (reporting assigned values, reported values and z-scores) at the end of December 2019 through the online portal.

4.2. Overview of Reported Analysis Results and Analytical Procedures

Participants' results for organochlorine pesticides and PCB congeners are listed in TABLE 1 and the results for PAHs in TABLE 2. In both tables the assigned and information values are indicated along with the "total error" for each compound.
All results are reported by the laboratory code number only, to protect the Participants confidentiality. However, as agreed with the participants the laboratory codes will be shared with their MEDPOL National Focal Point as part of the capacity building and quality assurance programme of MEDPOL.

The treatments of samples for the analysis of organochlorine pesticides and PCBs congeners are reported in TABLE 3 and the gas chromatography (GC) conditions for these analyses are reported in TABLE 4. The treatments of samples for the analysis of PAHs are reported in TABLE 5 and the instrumental conditions for these analyses are reported in TABLE 6.

To gain a better understanding of Participants laboratory procedures, for 2019 it was decided to collect information about the use of "surrogates standards", i.e. standards within the same class of organic contaminants spiked before the extraction to investigate the effect of sample pre-treatment, and the use of "internal standards" spiked just before the instrumental injection. Analysing the information collected it appeared evident that difference between the two type of standards and their use is still unclear to several Participants. It was decided to comment only on the use of internal standards/surrogates.

Quality parameters, i.e., if a QA/QC system is in place, if and which (Certified) Reference Material was used and if reference material data was reported, if the method used was validated, if the laboratory is accredited, and if the uncertainty was reported, for organochlorinated pesticides and PCB congeners and PAHs respectively reported by Participants, can be found in TABLES 7 and 8.

Unfortunately, despite the importance of such information, details regarding quality parameters were only seldom provided by Participants.

Figures 2 and 3 shows the graphic representations of key points of sample treatment and instrumental analyses for organochlorine pesticides and PCBs congeners and PAHs respectively.

TABLE 1. Reported results and certified and information values for organochlorine pesticides and PCB congeners in the sediment test sample (IAEA-459)

All results are in ng/g dry weight.

	Laboratory codes													
Analyte	**20**	**22**	**23**	**24**	**26**	**27**	**28**	**30**	**31**	**32**	**33**	**34**	**IAEA-459**	**Total error**
pp DDD	5.38	5.22	0.72	4.80	4.81	<2.0	4.33	2.96	1.71	.	.	.	3.00	0.60
pp DDE	7.11	5.14	3.29	.	0.81	2.33	3.83	.	2.68	.	.	.	3.60	0.51
pp DDT	2.82	3.30	1.66	.	12.8	<2.0	4.53	1.39	1.33	.	.	0.72	1.32	0.31
op DDT	.	.	.	.	.	<2.0	0.20	.	<0.5	.	.	0.15	0.35	0.08
PCB No 28	2.86	4.51	1.99	3.85	8.26	1.85	2.47	.	7.02	1.90	0.46	2.83	2.27	0.40
PCB No 52	3.68	2.18	.	1.45	676	2.55	2.47	2.56	4.49	0.95	7.36	2.65	2.38	0.45
PCB No 101	3.37	3.79	.	1.37	1.88	3.52	4.47	3.65	4.11	1.85	2.47	4.28	3.78	0.52
PCB No 105	.	.	.	.	.	.	1.27	.	.	0.50	.	1.44	1.29	0.22
PCB No 118	5.54	3.68	2.88	2.35	3.95	2.67	3.58	2.79	5.09	1.45	1.34	3.72	2.98	0.42
PCB No 138	3.73	5.08	2.00	0.75	2.59	3.49	4.58	2.68	3.56	1.20	3.22	4.23	3.25	0.60
PCB No 153	7.69	5.09	1.69	2.10	7.18	3.48	4.54	3.69	3.63	1.75	2.21	4.44	3.75	0.57
PCB No 156	.	.	.	.	.	.	0.27	.	.	0.10	.	0.34	0.34	0.05
PCB No 180	4.89	2.67	3.08	8.73	2.29	2.16	3.15	1.89	1.85	1.00	1.73	2.33	2.22	0.33
HCB*	.	.	.	2.95	.	<2.0	0.09	.	<0.5	0.10	16.5	0.15	0.15	0.03
ɣ HCH-Lindane*	1.18	0.39	.	0.46	0.06	<2.0	0.09	.	<0.5	.	4.70	0.11	0.18	0.04
Aldrin*	0.79	.	0.59	.	1.72	<2.0	0.05	.	.	.	.	.	0.10	0.05
Dieldrin*	4.03	.	.	12.5	0.39	<2.0	0.10	.	0.61	.	.	.	0.10	0.05

* Information value.

TABLE 2. Reported results and certified and information values for PAHs in the sediment test sample (IAEA-459)

All results are in ng/g dry weight.

Analyte	Laboratory codes								IAEA-459	Total error
	20	23	24	25	30	32	33	34		
Phenanthrene	2.08	13.9	.	19.2	28.8	31.1	270	23.2	33.9	5.19
Anthracene	2.56	10.7	.	6.32	5.17	5.73	6.25	3.07	6.00	0.90
Fluoranthene	8.36	50.0	.	15.4	33.7	37.2	8.80	17.7	37.3	4.90
Pyrene	7.31	57.6	.	19.6	40.9	43.2	3120	23.5	46.3	7.12
Chrysene and Triphenylene	.	.	.	.	24.6	32.4	.	10.0	27.5	5.47
Benzo(k)Fluoranthene	0.78	86.2	96.8	23.3	19.5	22.4	59.2	8.00	19.0	3.56
Benzo(a)Pyrene	3.84	79.8	114	31.7	22.8	26.3	28.4	6.77	22.7	3.56
Indeno(1.2.3-c.d) Pyrene	8.88	31.7	105	22.3	35.1	38.7	23.6	7.67	36.0	7.11
Benzo(g,h,i)Perylene	0.98	30.1	.	36.0	33.8	35.5	10.2	14.1	36.0	7.11
Chrysene*	3.66	27.9	.	89.8	.	.	3.34	.	18.4	2.70

* Information value.

TABLE 3. Treatment of samples performed by participants for organochlorine pesticides and PCBs

Lab. Code	Extraction	Solvent	Desulphurisation	Fractionation
20	Sonication	Acetone/n-Hexane	Copper	Florisil
22	Microwave assisted	Acetone/n-Hexane	Copper	None
23	Microwave assisted	n-Hexane/Dichloromethane	Copper	Silica/Alumina
24	Sohxlet	Acetone/n-Hexane		Florisil
26				Florisil
27	Shaking (solid/liquid extraction)	Acetone/n-Hexane		None
28	Sohxlet	n-Hexane/Dichloromethane		Silica
30	Sohxlet	n-Hexane/Dichloromethane	TBA (tetratbutylammonium)	Silica
31	Sohxlet	n-Hexane/Dichloromethane	Copper	Florisil
32	Sohxlet	n-Hexane/Dichloromethane	Copper	Alumina
33	Microwave assisted	Acetone/n-Hexane	None	Florisil
34	Quechers	Dichloromethane (DCM)	Copper	Other

TABLE 4. GC conditions used by participants for organochlorine pesticides and PCBs

Lab. Code	Use of Surrogates	Surrogates used	Use of Internal Std	Internal Std used	Injector Type	GC-Column	Detector Type
20	No		Yes	PCB 30	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/ECD
22	Yes	PCB 209 and 2 4 5 6-tetrachloro-m-xylene	Yes	pentachloronitrobenzene	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MSMS
23	Yes	PCB 29 PCB 198 and Chloropyrifos	Yes	Pentachloronitrobenzene	Split	Other	GC/ECD
24					Splitless	Other	GC/MS
26							GC-ECD
27	Yes	a sediment lab test sample	Yes	PCB 209	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/ECD and peak confirmation with dual column
28					Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MSMS
30	No		No	PCB 29 PCB 198 Epsilon HCH	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/ECD
31	Yes	PCB 29 PCB 193 Isodrine E-HCH	Yes	Pentachlororbenzene	Splitless	100% Dimethylpolysiloxane	GC/ECD
32					Splitless	Other	GC/ECD
33	No				Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
34	Yes		Yes		Splitless	Other	GC/HRMS

*With dual column confirmation

TABLE 5. Treatment of samples performed by participants for PAHs

Lab. Code	Extraction	Solvent	Desulphurisation	Fractionation
20	Sonication	Acetone/n-Hexane		Silica/Cyanopropyl
23	Microwave assisted	n-Hexane/Dichloromethane		Silica/Cyanopropyl
24	Sohxlet	Dichloromethane (DCM)		Florisil
25	Sohxlet	n-Hexane/Dichloromethane		Silica/Alumina
30	Sohxlet	n-Hexane/Dichloromethane		Silica
32	Sohxlet	Other		Silica
33	Microwave assisted	Acetone/n-Hexane	None	None
34				

TABLE 6. Instrumental conditions used by participants for PAHs

Lab. Code	Use of Surrogates	Surrogates used	Use of Internal Std	Internal Std used	Injector Type	GC-Column	Detector Type
20				CARB 429 IS Mix	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
23		Deuterated PAH acenaphthene d10 Phenanthrene d10 chrysene d12 perylene d12		fluorobromobenzene and 1 2 dichlorobenzene d4	Split	5% Phenyl 95% dimethyl arylene siloxane	GC/MS
24					Splitless	Other	GC/MS
25	Yes	octadecene	No		Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC-FID
30				Naphtalene D8 Acenaphtene D10 Phenantrene D10 Fluoranthene D10 Chrysene D12 Perylene D12	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
32				Napthd8 Acyd10 Phed10 Pyrd10 Chryd12 Perd12 BgPd12	Splitless	Other	GC/MS
33	No		No				HPLC
34							

TABLE 7. Quality parameters for organochlorinated pesticides and PCB congeners.

Laboratory Code	QA/QC System	Use of Certified Reference Material	Reference Material Used	Reported Reference Material Data	Validated Method	Accreditation	Reported Uncertainty
20	Yes	Yes	IAEA 417	Yes	No	No	Yes
22	Yes	Yes	MR-383	Yes	No	No	
23	Yes	Yes	IAEA Sediment 159	Yes	No	No	
24	Yes	No			Yes	Yes	Yes
26							
27	Yes	No			Yes	Yes	Yes
28	Yes	Yes			Yes	No	
30	Yes	Yes	IAEA 159	Yes	Yes	Yes	Yes
31	Yes	Yes	Sigma Aldrich	Yes	No	No	Yes
32							
33	Yes						Yes
34	Yes	No			Yes	Yes	Yes

TABLE 8. Quality parameters for PAHs.

Laboratory Code	QA/QC System	Use of Certified Reference Material	Reference Material Used	Reported Reference Material Data	Validated Method	Accreditation	Reported Uncertainty
20	Yes	Yes	IAEA 417		No	No	
23	Yes	Yes	IAEA Sediment 159	Yes	No	No	
24	Yes				Yes	Yes	Yes
25	No	Yes	IAEA-159		No	No	
30	Yes	Yes	IAEA 159	Yes	Yes	Yes	Yes
32		Yes	NIST 1941b		Yes	Yes	
33	Yes				Yes	Yes	Yes
34							Yes

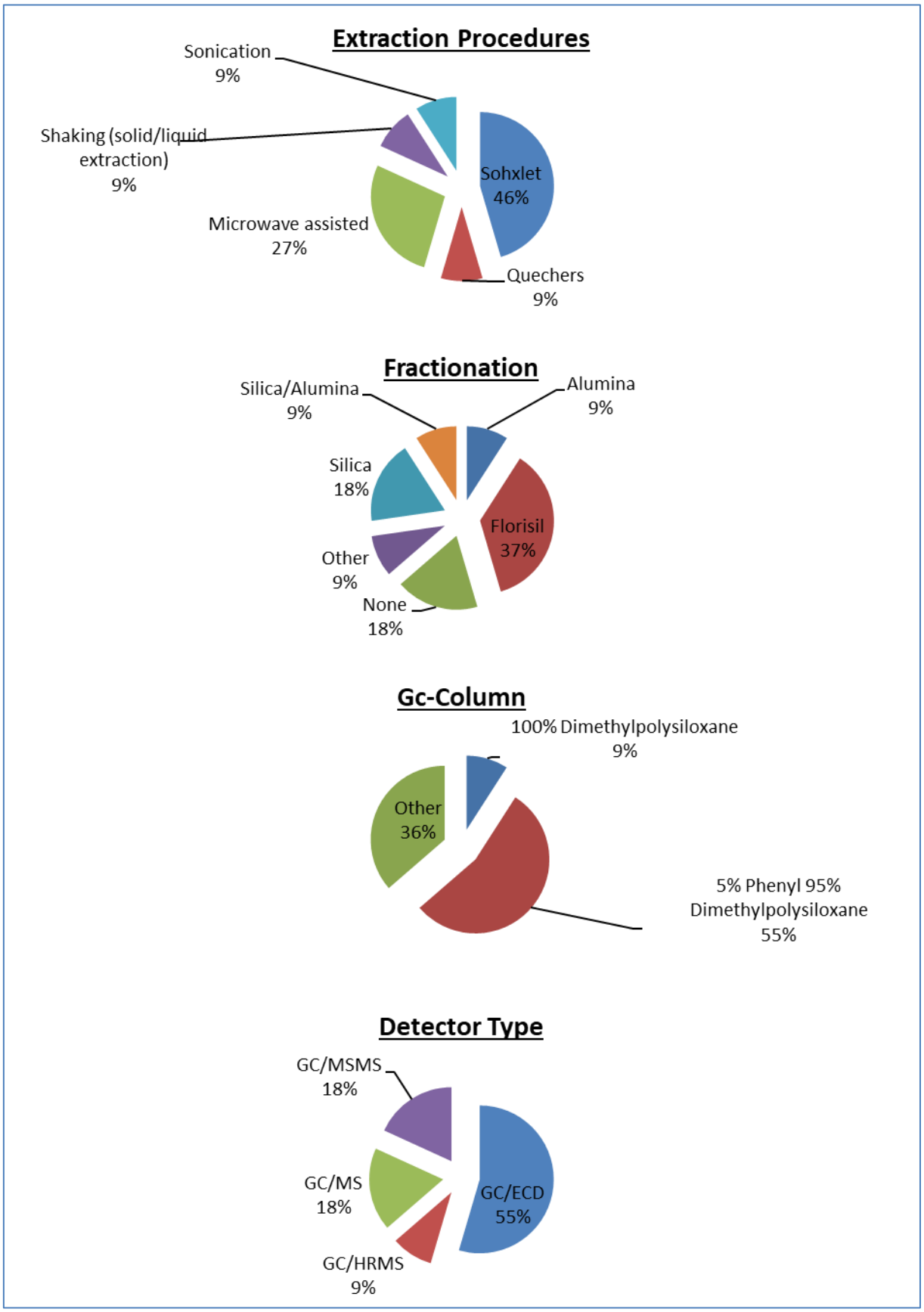

Figure 2. Graphic representation of sample treatment and instrumental conditions for organochlorine pesticides and PCB congeners.

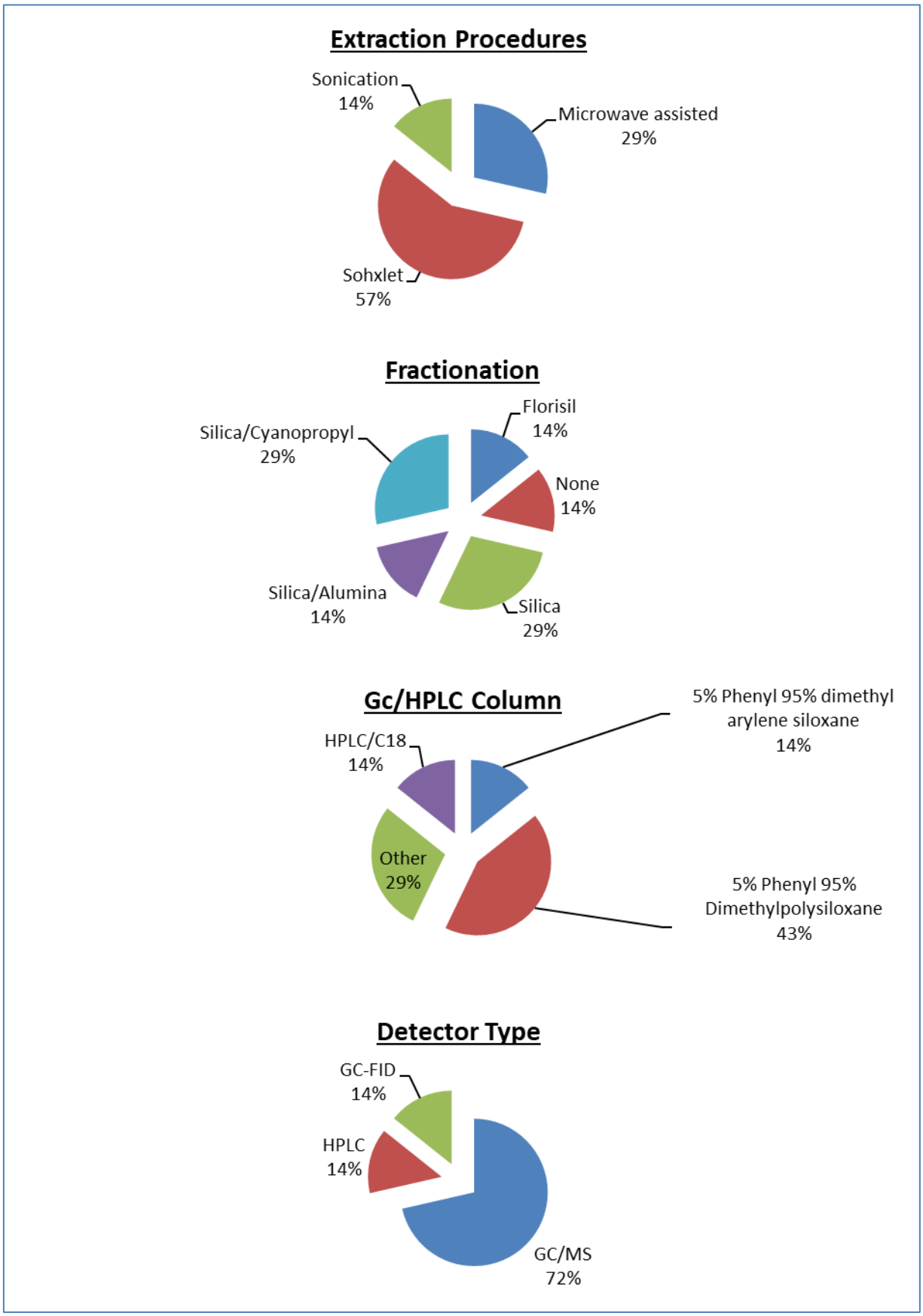

Figure 3. Graphic representation of sample treatment and instrumental conditions for PAHs

4.3. Evaluation Criteria

z-score: This score expresses the difference between the mean of the laboratory and the assigned value in the same unit. The z-score represents a simple method of giving each participant a normalized performance score for the measurement bias of the respective measurement result. Starting from 2019 it was decided to combine the target standard deviation for proficiency assessment (σ_p), usually set at 12.5% with the target uncertainty of the assigned value (u_a) for the calculation of the "Total error" according to the following formula:

$$Total\ error_a = \sqrt{u_a^2 + \sigma_p^2}$$

For the assessment of the laboratory performances, a *z*-score is calculated based on ISO/IEC 17043:2010 [2]:

$$z = (x_i - x_a) / Total\ error$$

Where:

- x_i is the reported values from participant of the analyte concentration in the sample;
- x_a is the assigned value;

Performance is considered acceptable if $|z| \leq 2$.

The measurement is regarded as questionable if $2 < |z| < 3$.

The measurement is regarded as out of control when $|z| \geq 3$.

This score represents a simple method of giving each participant a normalized performance score for bias. The procedure has been accepted as a standard by ISO/IUPAC [3, 4, 5].

The *z*-scores for participating laboratories can be found in TABLE 9 for chlorinated pesticides and PCB congeners and TABLE 10 for PAHs. The red shaded cells represent data to be considered as "out of control", the yellow shaded cells represent data to be considered as "questionable" and green shaded cells represent data to be considered "acceptable".

4.4. Laboratory Results and Scoring

TABLE 9. *Z*-scores for organochlorinated pesticides and PCB congeners

Analyte	Laboratory codes											
	20	22	23	24	26	27	28	30	31	32	33	34
pp DDD	4.0	3.7	-3.8	3.0	3.0		2.2	-0.1	-2.2			
pp DDE	6.9	3.0	-0.6		-5.5	-2.5	0.5		-1.8			
pp DDT	4.9	6.4	1.1		37		10.4	0.2	0.03			-2.0
op DDT							-1.9					-2.6
PCB No 28	1.5	5.6	-0.7	4.0	15	-1.1	0.5		12	-0.9	-4.5	1.4
PCB No 52	2.9	-0.4		-2.1	1504	0.4	0.2	0.4	4.7	-3.2	11	0.6
PCB No 101	-0.8	0.01		-4.6	-3.7	-0.5	1.3	-0.3	0.6	-3.7	-2.5	1.0
PCB No 105							-0.1			-3.5		0.7
PCB No 118	6.1	1.7	-0.2	-1.5	2.3	-0.7	1.4	-0.5	5.0	-3.6	-3.9	1.8
PCB No 138	0.8	3.0	-2.1	-4.2	-1.1	0.4	2.2	-0.9	0.5	-3.4	-0.05	1.6
PCB No 153	6.9	2.3	-3.6	-2.9	6.0	-0.5	1.4	-0.1	-0.2	-3.5	-2.7	1.2
PCB No 156							-1.2			-4.5		0.0
PCB No 180	8.2	1.4	2.6	20	0.2	-0.2	2.9	-1.0	-1.1	-3.7	-1.5	0.3

TABLE 10. Z-scores for PAHs

Analyte	Laboratory codes							
	20	23	24	25	30	32	33	34
Phenanthrene	-6.1	-3.8		-2.8	-1.0	-0.5	45.4	-2.1
Anthracene	-3.8	5.2		0.4	-0.9	-0.3	0.3	-3.3
Fluoranthene	-5.9	2.6		-4.5	-0.7	0.0	-5.8	-4.0
Pyrene	-5.5	1.6		-3.8	-0.8	-0.4	431.6	-3.2
Chrysene and Triphenylene					-0.5	0.9		-3.2
Benzo(k)Fluoranthene	-5.1	18.9	21.9	1.2	0.1	1.0	11.3	-3.1
Benzo(a)Pyrene	-5.3	16.0	25.8	2.5	0.0	1.0	1.6	-4.5
Indeno(1.2.3-c.d) Pyrene	-3.8	-0.6	9.7	-1.9	-0.1	0.4	-1.7	-4.0
Benzo(g,h,i)Perylene	-4.9	-0.8		0.0	-0.3	-0.1	-3.6	-3.1

5. EVALUATION OF RESULTS

5.1. Organochlorine Pesticides and PCB Congeners

Among all designated laboratories, 75% submitted results for organochlorine pesticides and PCB congeners.

Ten participants to the current PT reported to have a QA/QC system in place in their laboratory and 5 laboratories reported to use validated methods. More than 50% use internal standards/surrogates, and 5 laboratories reported their QA/QC results along with the test results. Laboratory number 30 provided all acceptable results. Four laboratories (27, 28, 31 and 34) reported more than 50% of acceptable results. Four laboratories (20, 24, 26 and 32) provided more than 50% of results "out of control".

All Participants filling the questionnaire stated having a QA/QC system in place in their laboratory, 50% stated using CRMs and 58% reported uncertainties along with their results. Most Participants reporting more than 50% outlying values either reported non using CRMs or failed to provide information about the use of CRMs.

Figure 4 reports a graphic representation of z-scores for organochlorine Pesticides and PCB congeners.

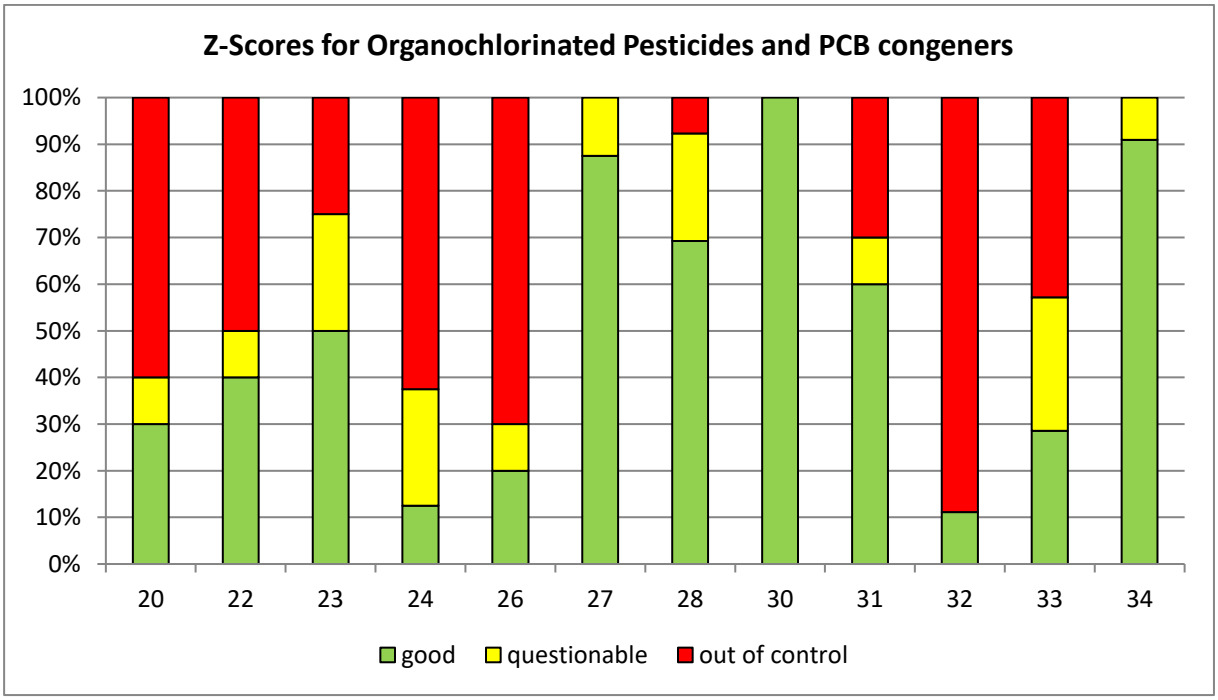

Figure 4. Graphic representation of laboratories z-scores for organochlorine pesticides and PCB congeners.

5.2. PAHs

Only 50% of the designated laboratories submitted results for PAHs.

Among the participants, laboratory number 30, 32 and 25 provided all acceptable and very few "questionable" or "outlying" results. Four laboratories (20, 24, 33 and 34) provided more than 50% of results "out of control".

About 60% of the participants reported to have a QA/QC system in place and to use internal standards/surrogates. Four laboratories representing 50% of the participants reported using validated methods and reported uncertainties for their measurements. Although 5 laboratories stated using CRMs only two of them reported their QA/QC data along with the test results. Laboratory 20 and 24, although having quality system in place and using CRMs or validated methods were not able to achieve acceptable performances. Unfortunately, laboratory 34 didn't report any information.

Figure 5 reports a graphic representation of z-scores for PAHs.

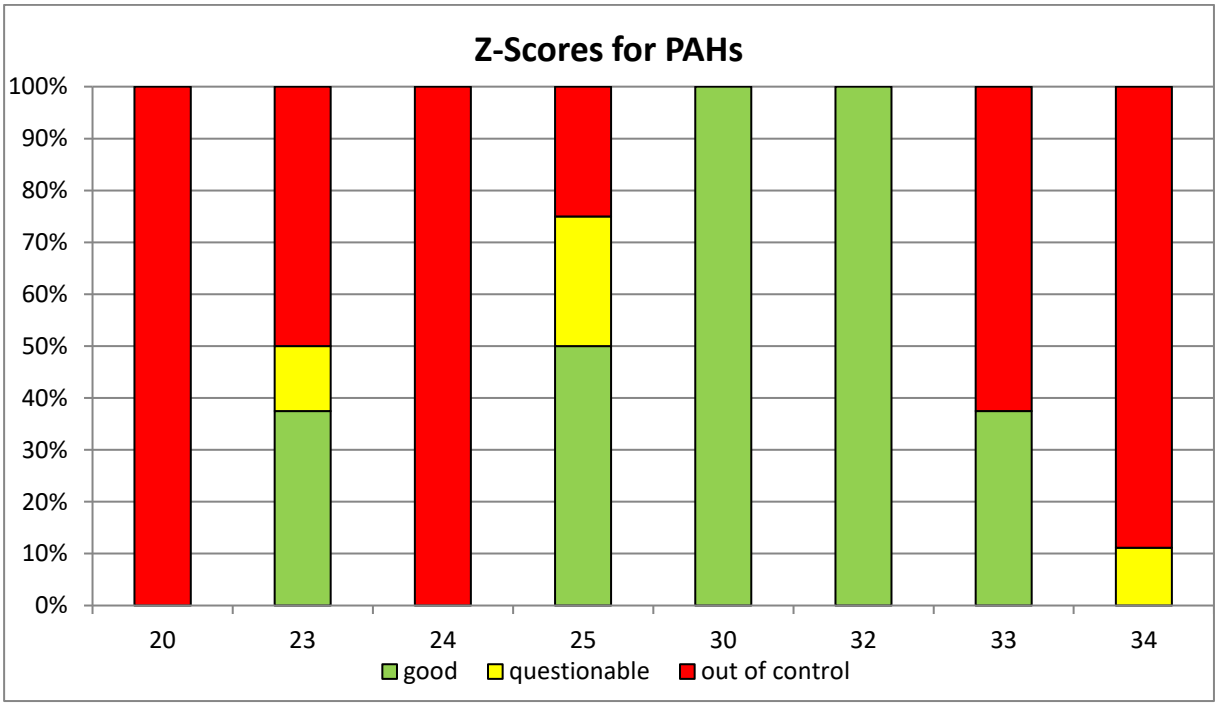

Figure 5. Graphic representation of laboratories z-scores for PAHs.

Figure 6 show the distributions of the values reported by participants for compounds for which only "information values" were available. As it is the case for other analytes, values reported by participants are sometimes spread over several orders of magnitude. This high interlaboratory variance reflects the heterogeneity of the participants group.

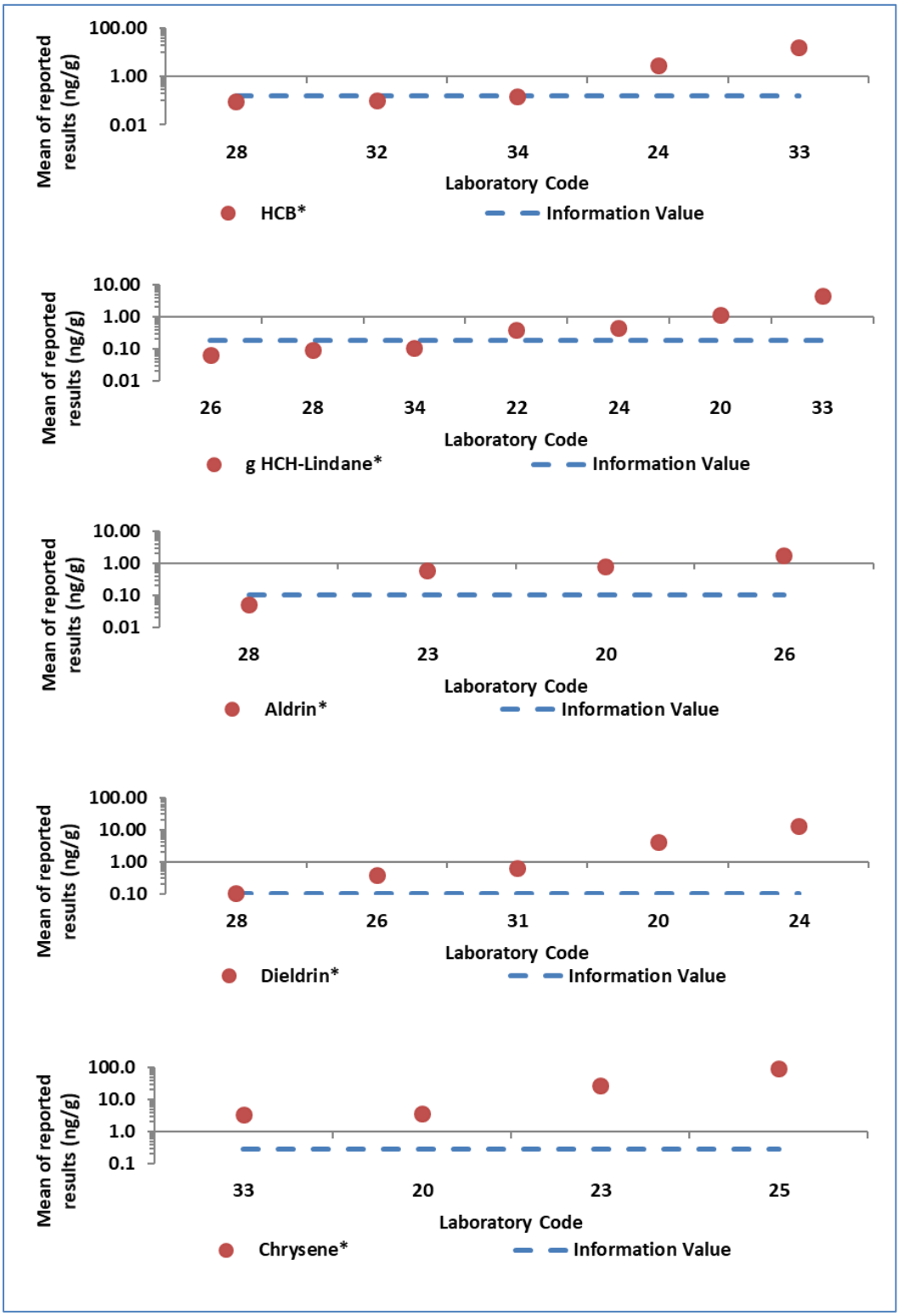

Figure.6. "Information values" reported by participants for organochlorine pesticides, PCB congeners and PAHs.

6. CONCLUSIONS AND RECOMMENDATIONS

Five participants, representing 42% of all the laboratories reporting results for organochlorine pesticides and PCB congeners, were able to produce all "acceptable" or very few "questionable" or outlying results, i.e. laboratories 27, 28, 30, 31 and 34. Five participants (i.e. laboratories 20, 22, 24, 26 and 32) , representing 42% of all the laboratories reporting results for organochlorine pesticides and PCB congeners, reported a high percentage of outlying or questionable results.

The z-scores distribution of most of the laboratories reporting data for organochlorine pesticides and PCB congeners show an inconsistent pattern. In many cases, for the same group of compounds, excellent z-scores values are reported for some compounds while for others z-scores are completely outlying. Such z-scores variation suggests that clean-up and fractionation should be optimized, and chromatographic peaks identity confirmed using multiple detection strategies (i.e. laboratories 20, 22, 24, 26 and 32). Carrying out the same analyses using different chromatographic columns or different detectors can, for example, overcome problems of co-elution and interferences very common in gas chromatographic analyses.

Three laboratories (number 24, 26 and 33) reported results which differed by more than one order of magnitude from the assigned or the information value. This may be due to a "reporting" mistake (for example: wrong unit conversion or wrong dataset reported) or due to more severe analytical issues which would require immediate root cause analysis and consequent corrective actions. These laboratories should verify that their units are correct. Three participants, representing 38% of all 8 laboratories reporting results for PAHs reported all or most "acceptable" results. Unfortunately, four participants, representing 50% of all 8 laboratories reporting results for PAHs, reported a high percentage of outlying or questionable results. In general best performing laboratories reported to have a quality system in place, to use internal standards/surrogates and validated methods and in some cases to be accredited. However, there are two examples of laboratories (24 and 33) that although being accredited and using validated methods were not able to provide acceptable results.

Like for organochlorine pesticides and PCB congeners, co-elution and interferences are very common sources of errors for PAHs analyses.

Both systematic and random errors may also be due to contamination issues. Solvents used for sample preparation and analysis should be of the highest purity available. Solvents quality should also be checked on regular base. Special care should also be taken during the evaporation

procedure of the solvent extracts to avoid dryness and losses of the more volatile contaminants. In this aspect, the use of internal standards/surrogates with similar polarity of the target analytes is fully recommended to compensate for these losses.

The use of reference materials and replicate samples are key points in every QA/QC system to produce quality results. Reference materials must match the test sample matrix and must undergo the same exact procedure of the test sample to be as effective as possible to avoid inaccuracy and precision issues.

Unfortunately, some participants reported data but did not fill the questionnaire or filled it only partially. Most of the participants, although using certified reference materials, failed to report their QA/QC data along with the test sample. This makes it impossible to get a better understanding where problems might be.

Although the participation to the annual proficiency test organized by MED POL is mandatory for MED POL laboratories, over the years, the participation rate has been very low.

However, while for the current 2019 PT, 75% of the designated laboratories submitted results for chlorinated compounds, the highest return since at least 2008, for PAHs the return was still only 50% and as such in about the same ratio than in previous years.

Given the importance of this PT exercises to test and demonstrate laboratory performances as required by ISO Guide 17025, the participation rate is still low, especially for PAHs.

Laboratories could also benefit more from the PT exercise if they provide all the key information requested through the questionnaire reporting file. In this context, details on the analytical procedures, e.g., careful listing of the individual internal standards/surrogates, quantification procedures (internal or external), will be useful to provide further feedback on the outlying results. It is also recommended that participants provide their data along with their estimates of uncertainty in accordance to the approach set forth in the basic Guide to the expression of uncertainty in measurement (GUM).

The knowledge on basic principles of metrology, e.g. method validation, traceability and uncertainty of measurement results, are still limited and laboratories that lack proficiency in this area should take action.

If a lack in infrastructure is hindering them to improve their results, including the unavailability of appropriate matrix CRMs they should seek advice from their MEDPOL national focal point.

Designated MED POL laboratories should only use validated measurement procedures for the analysis of samples within the realization of the MED POL monitoring programme of the country.

7. REFERENCES

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[2] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide 17043 (2010), Conformity assessment, general requirements for proficiency testing, ISO, Geneva, Switzerland.

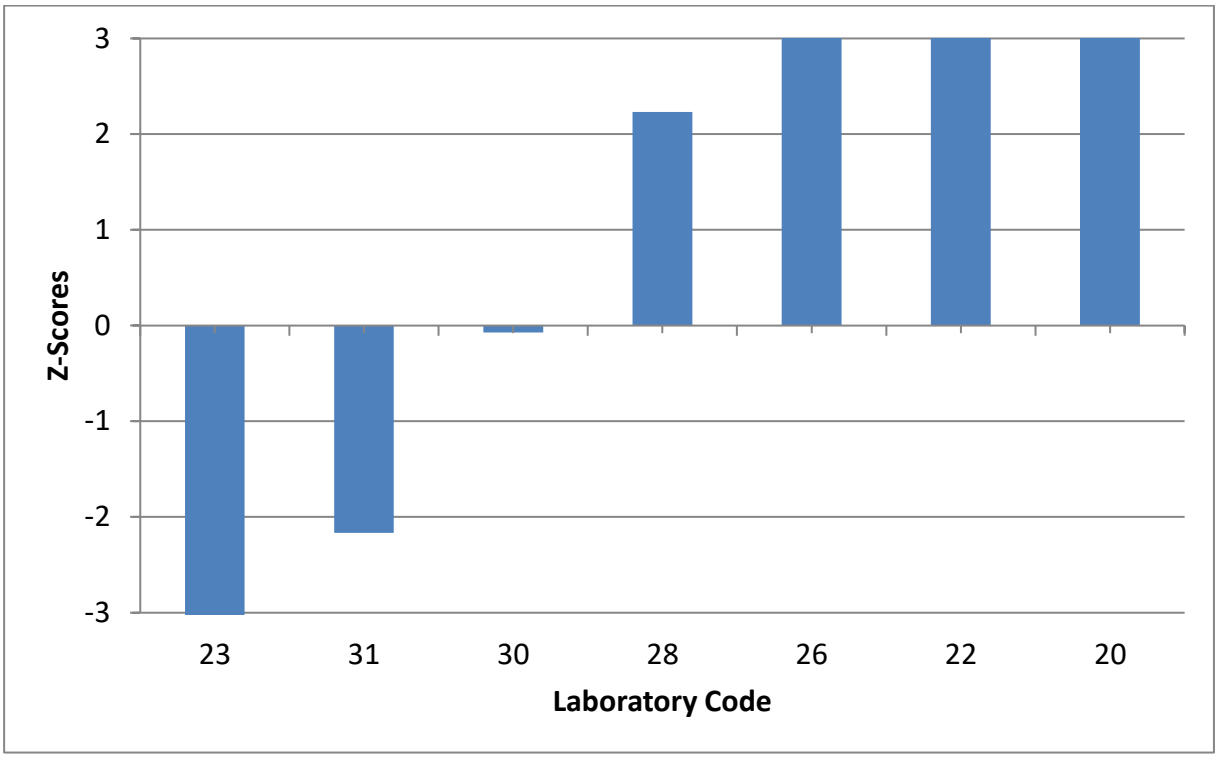
[3] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide 13528 (2005), Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons, ISO, Geneva, Switzerland.

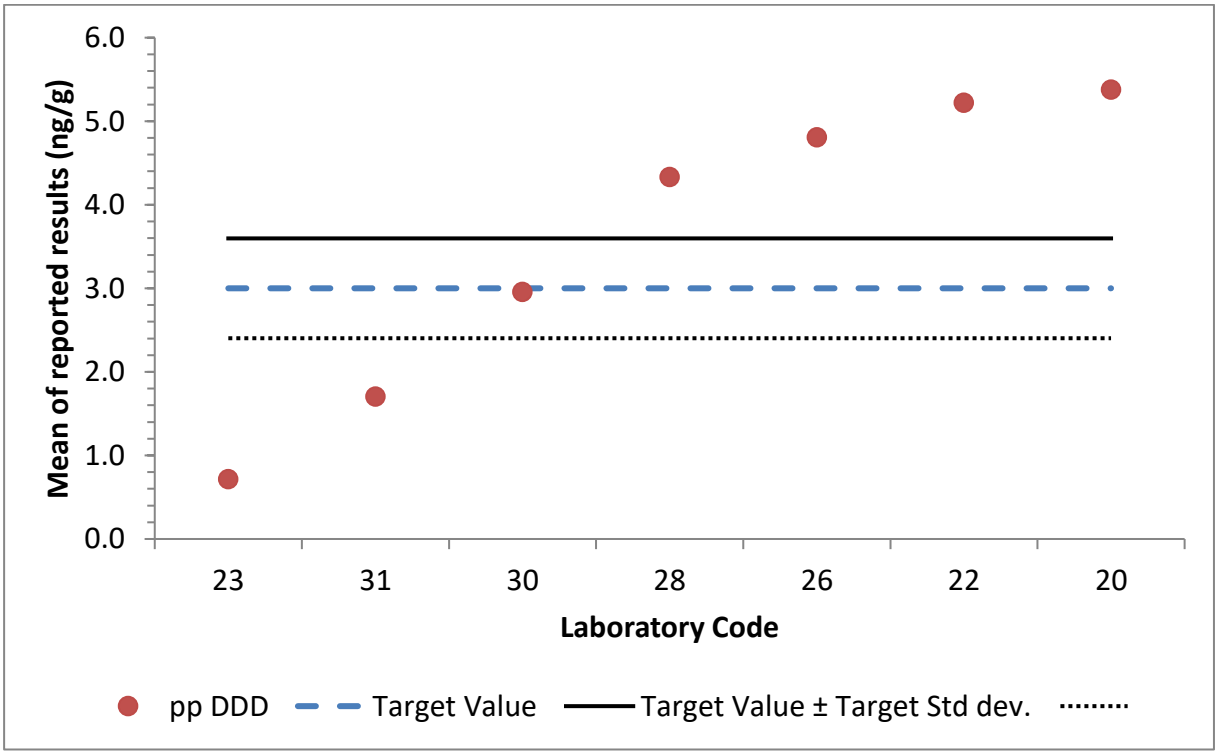
[4] Thompson and R. Wood (1993). The international harmonized protocol for the proficiency testing of (chemical) analytical laboratories. IUPAC/ISO/AOAC. *J. Pure. Appl. Chem*. **65**(9), 2123-2144.

[5] Thompson, M., Ellison, S. L. R. and R. Wood (2006). The international harmonized protocol for the proficiency testing of (chemical) analytical laboratories. IUPAC Technical report. *J. Pure. Appl. Chem*. **78**(1), 145-196.

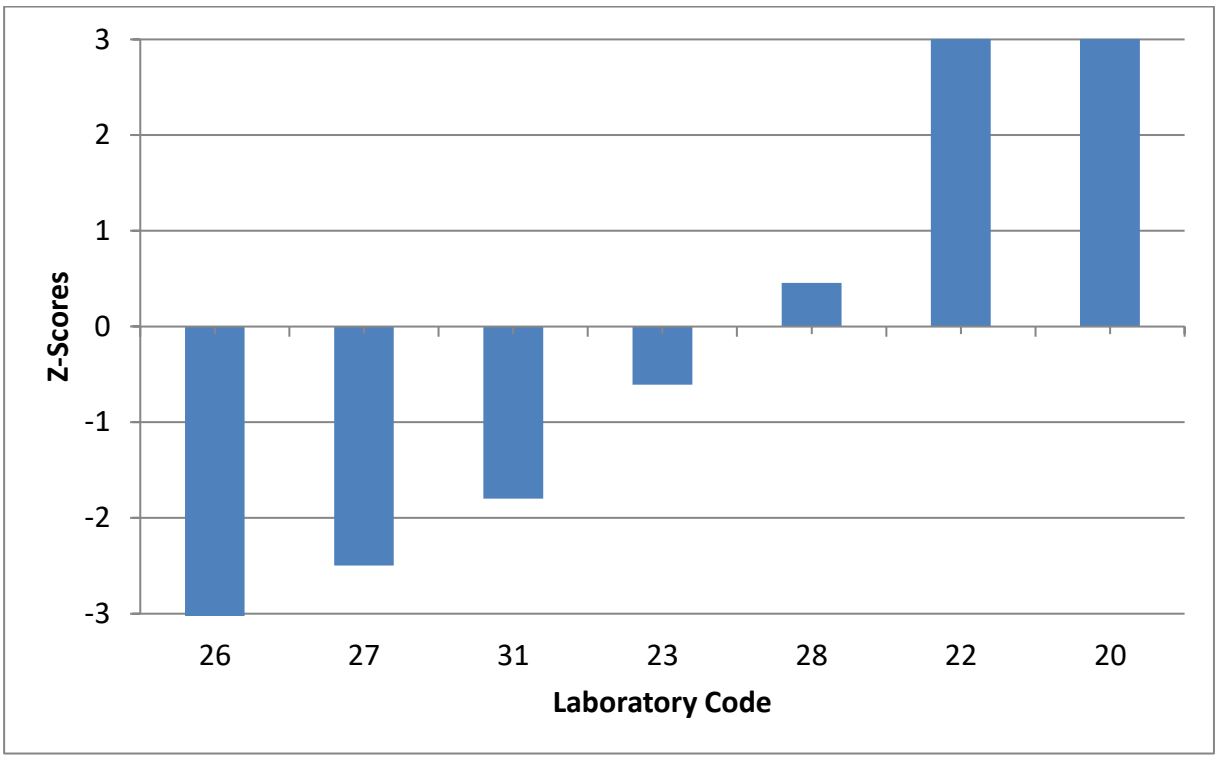
Annex 1: Graphic Representation of Laboratories Performances

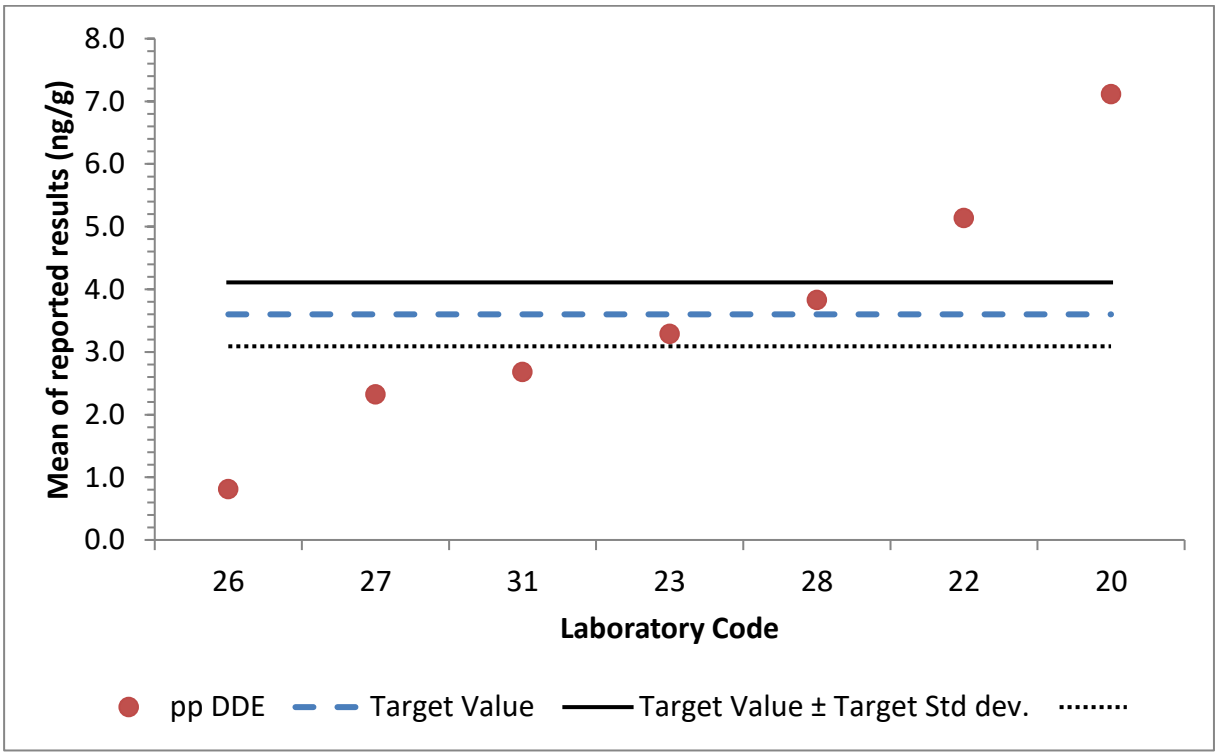
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR pp'DDD





GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR pp'DDE





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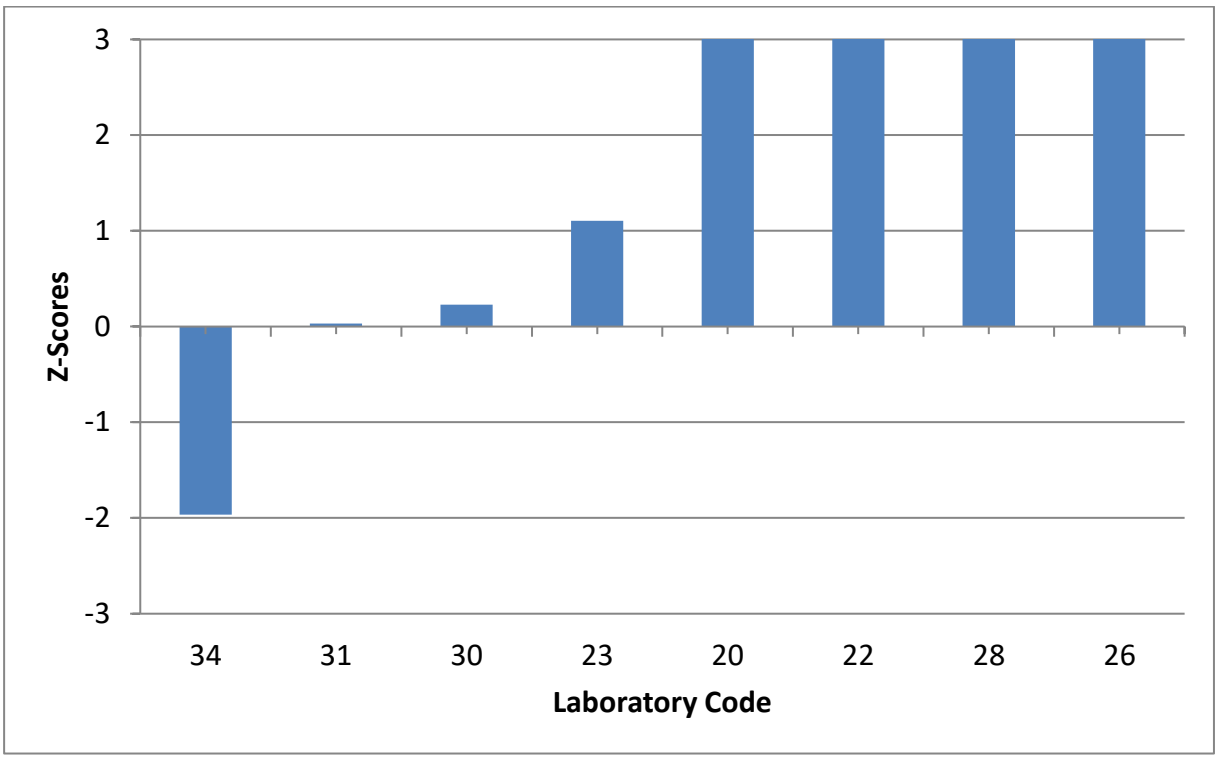
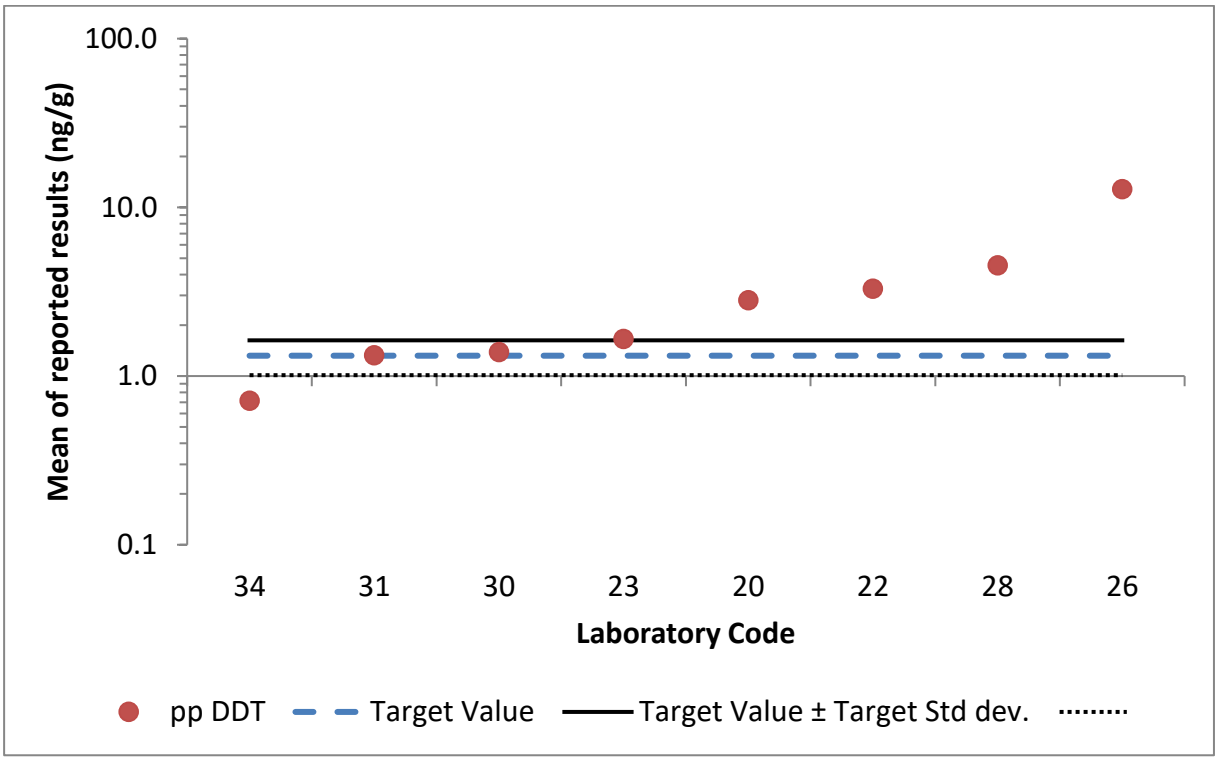
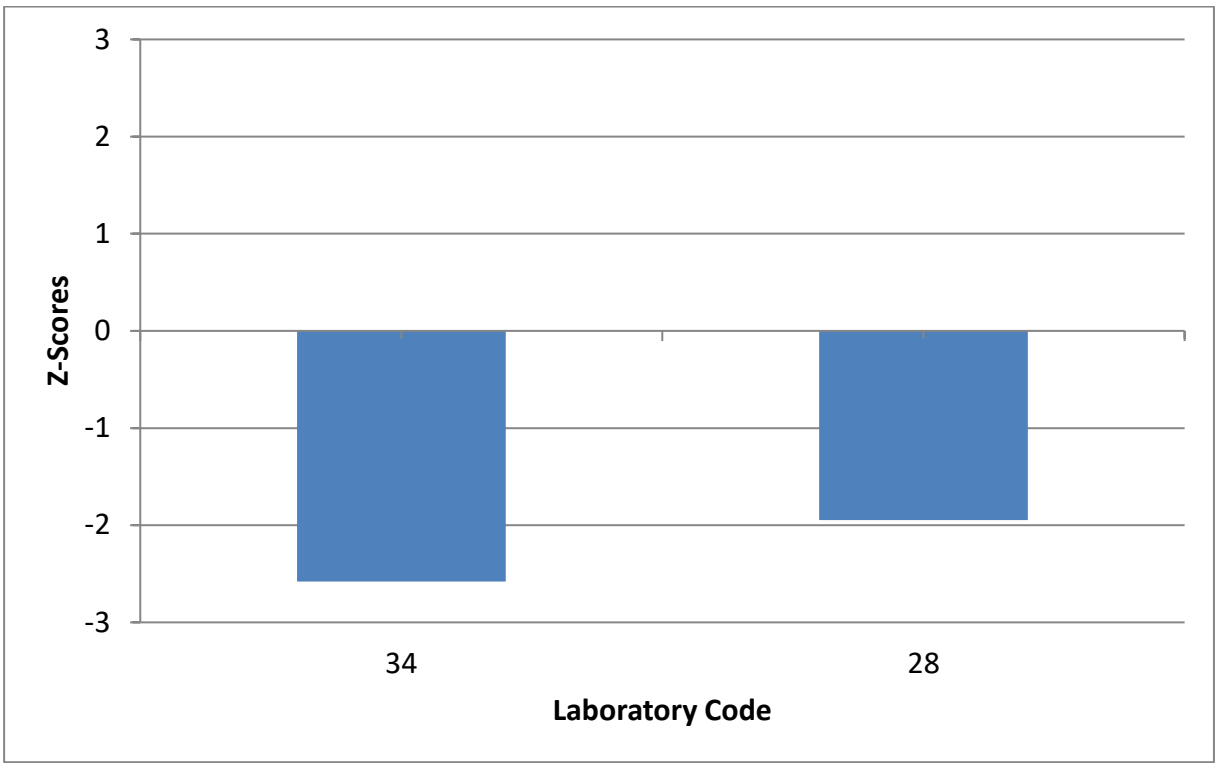
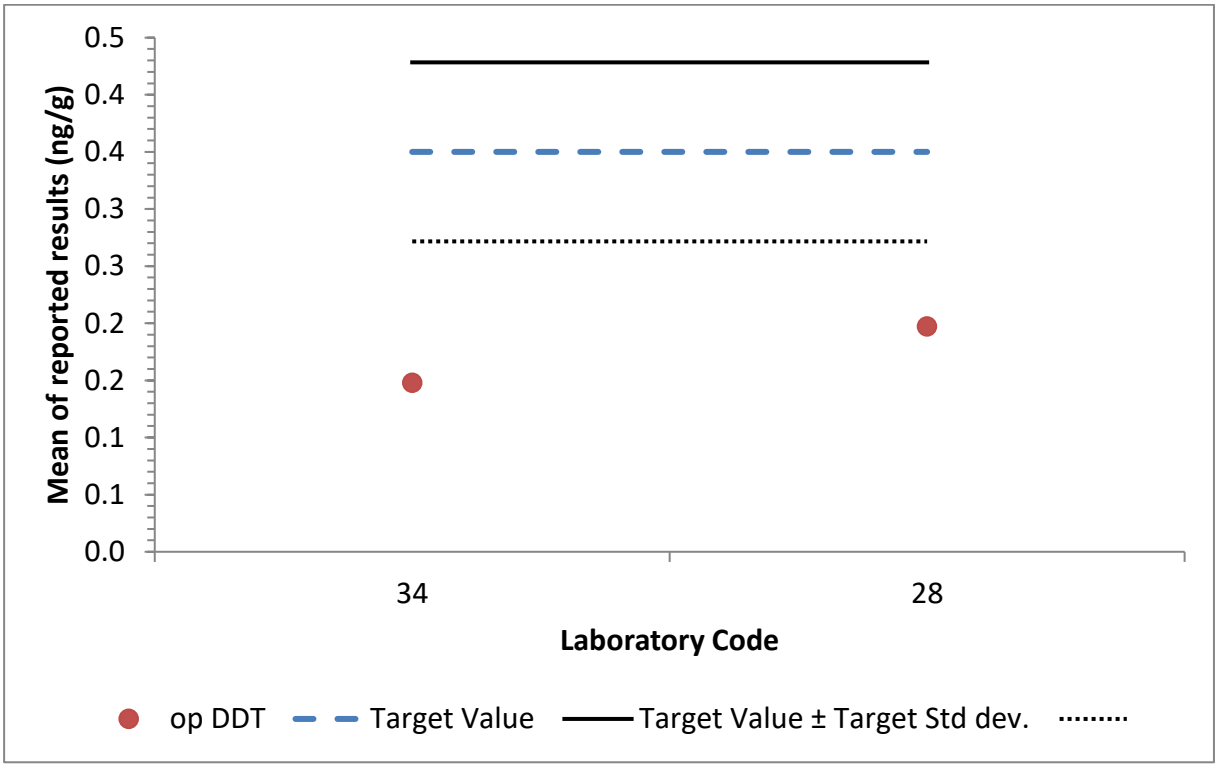




GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR op'DDT





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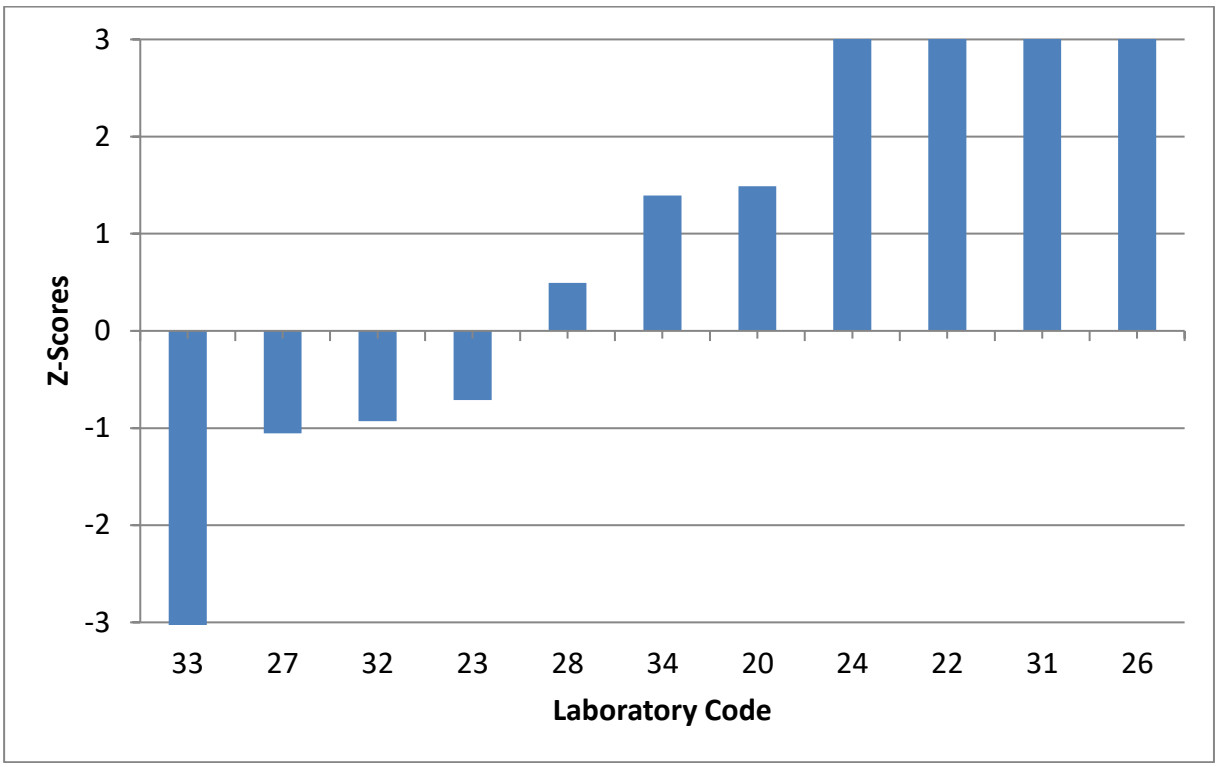

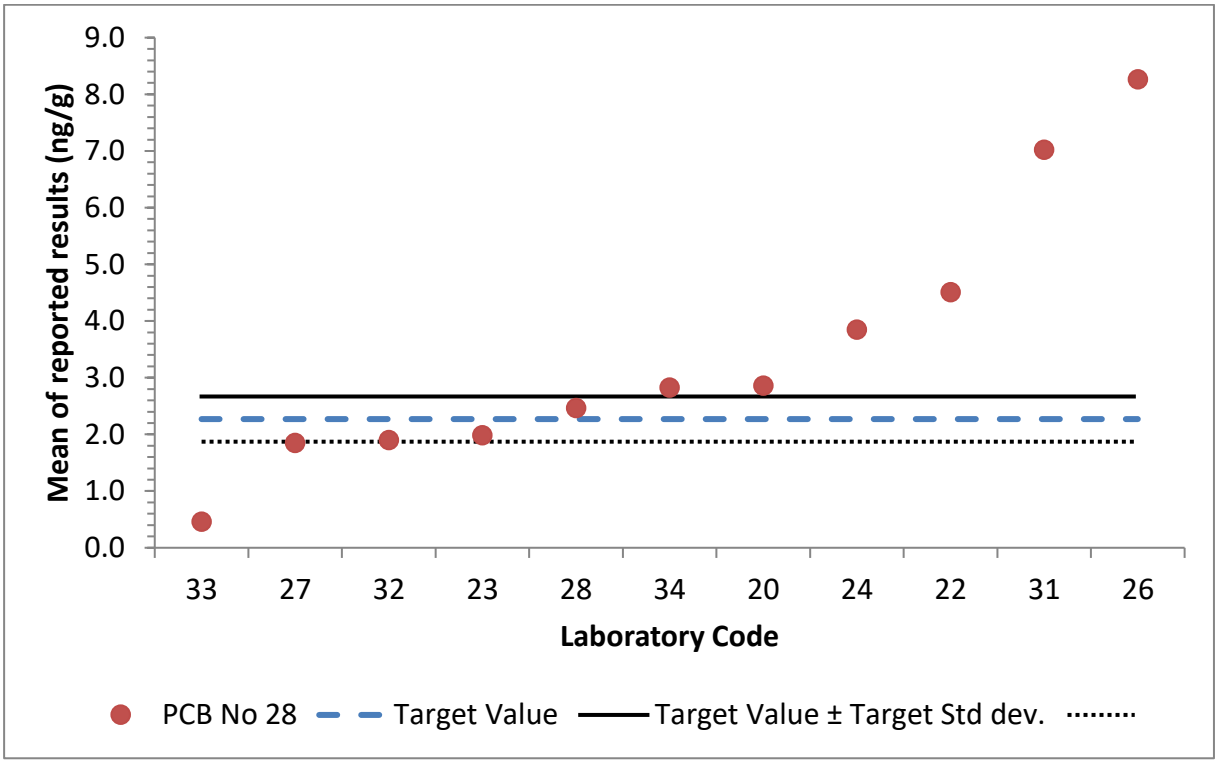

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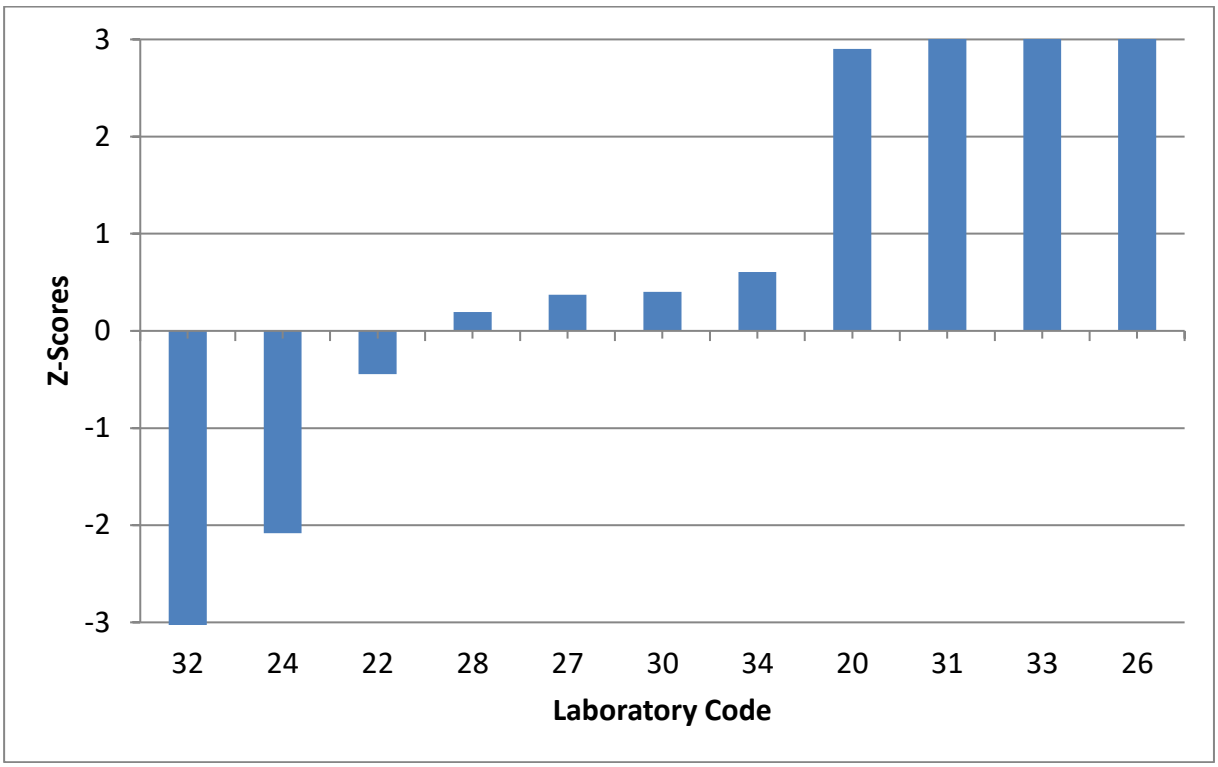

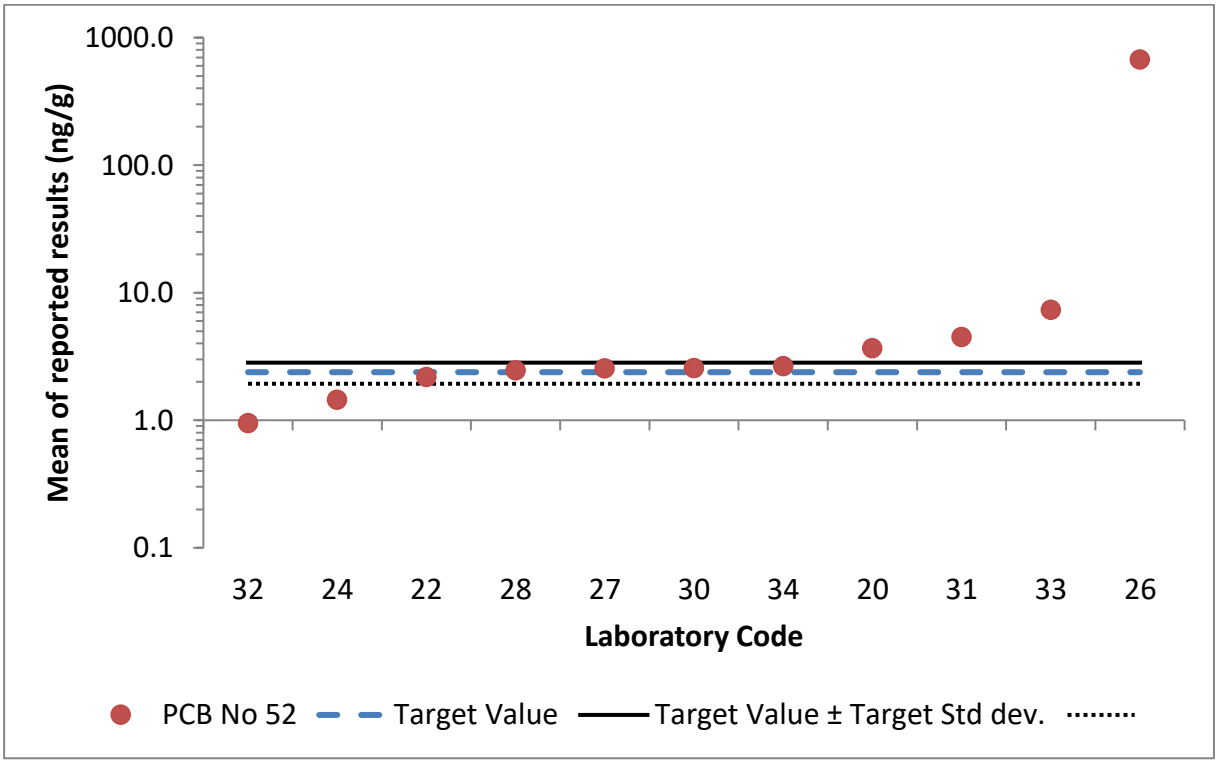

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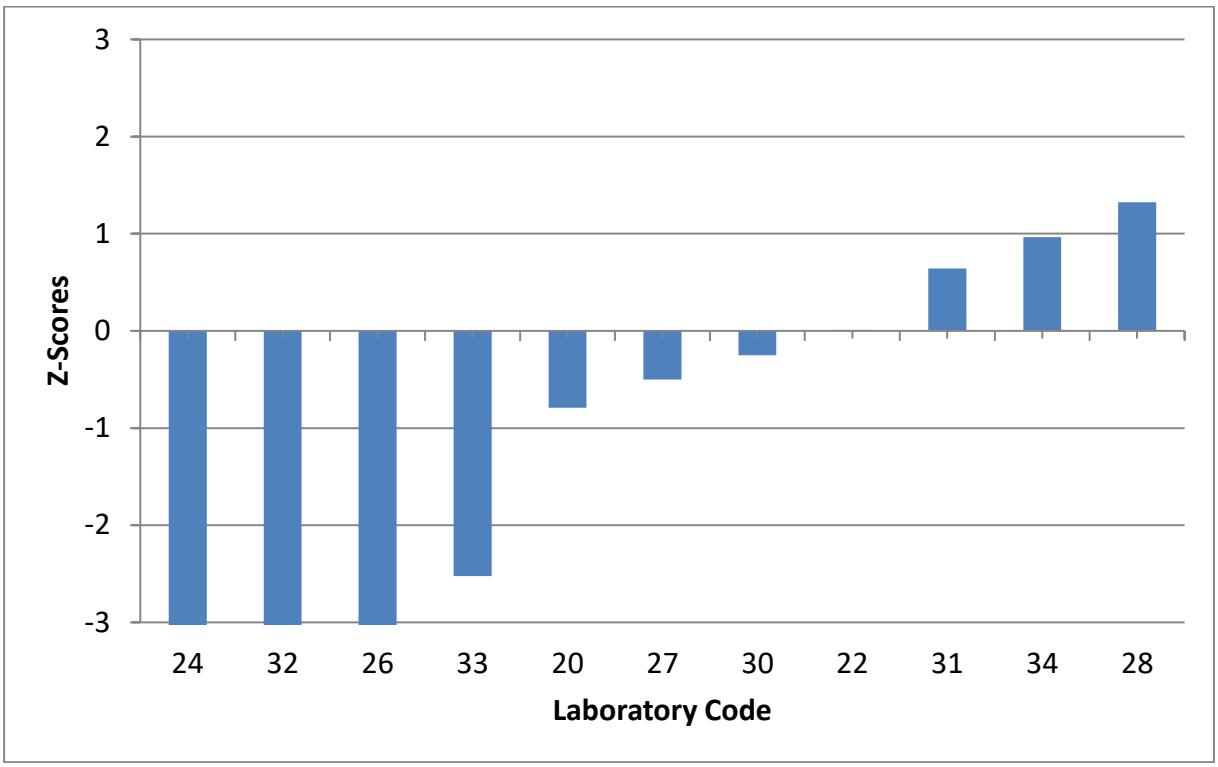

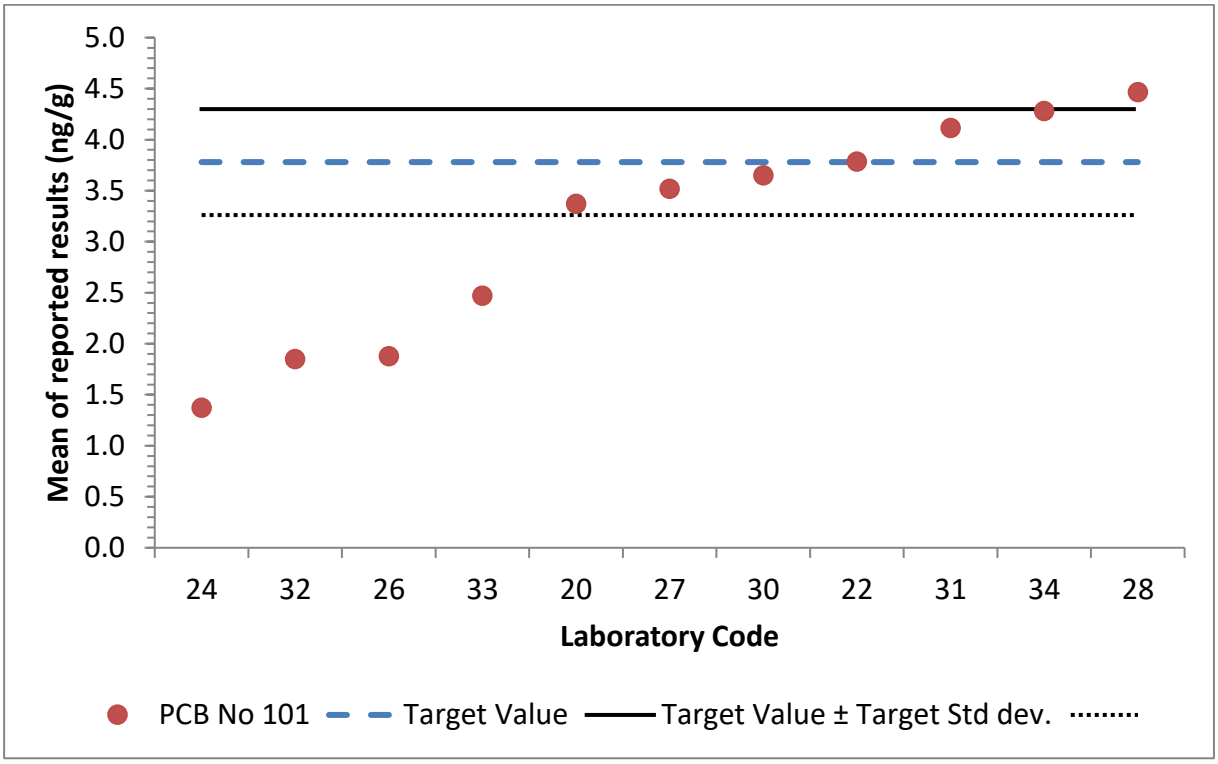

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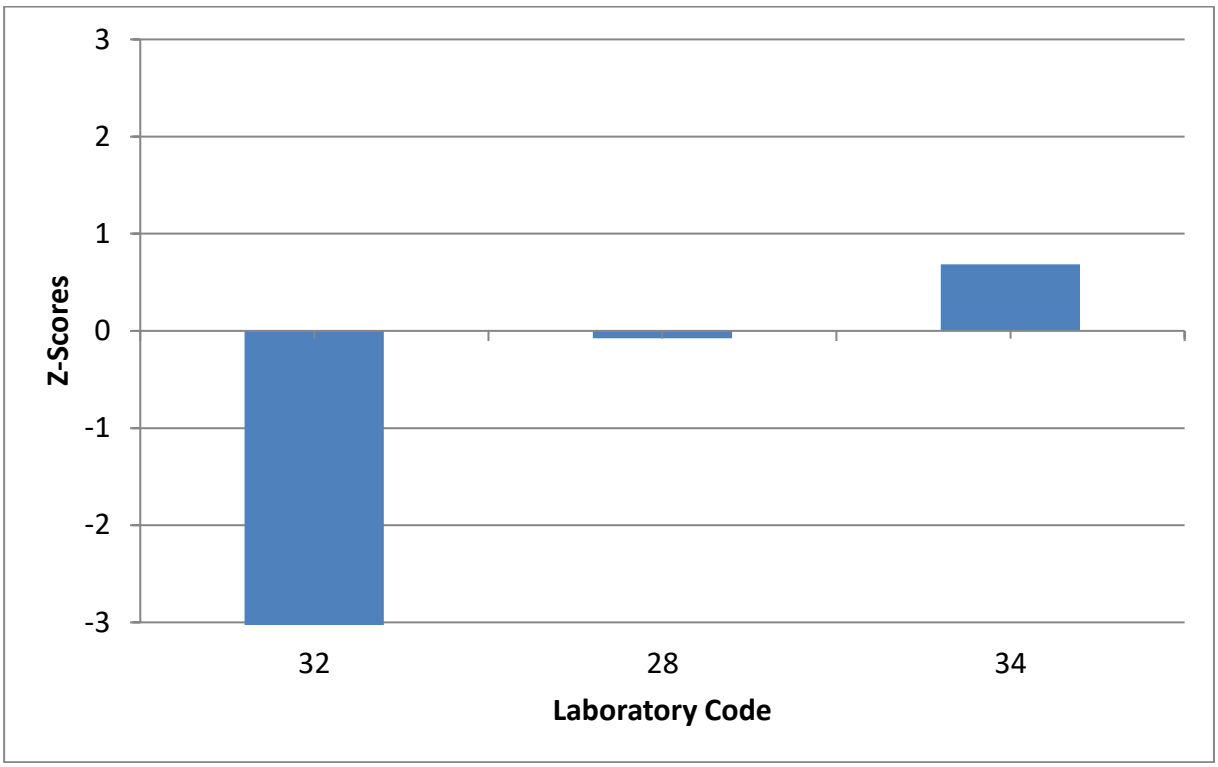

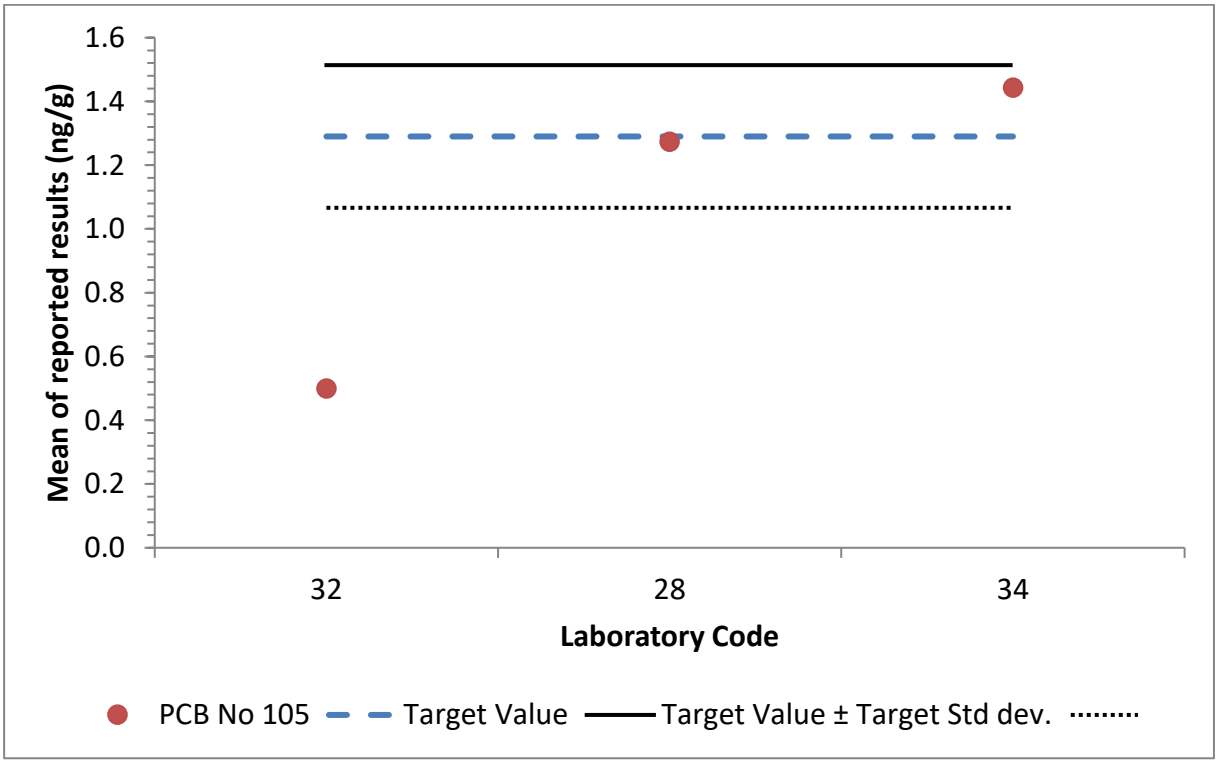

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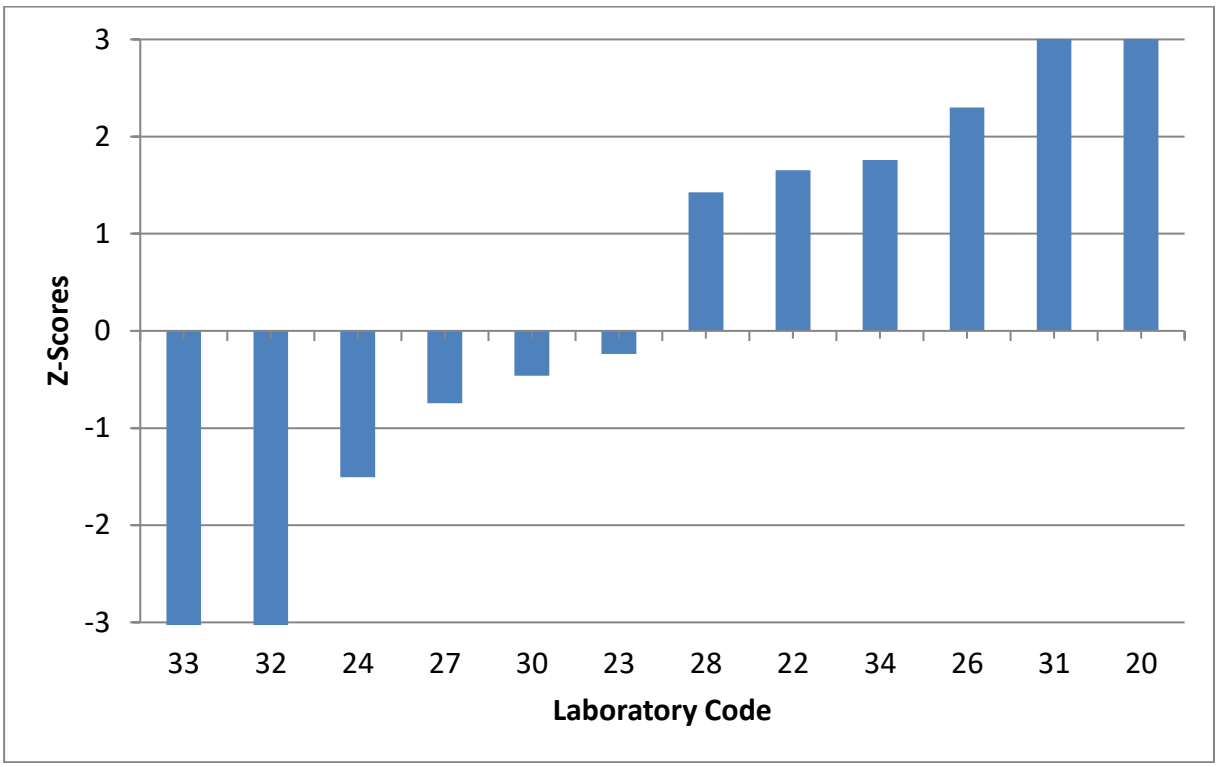

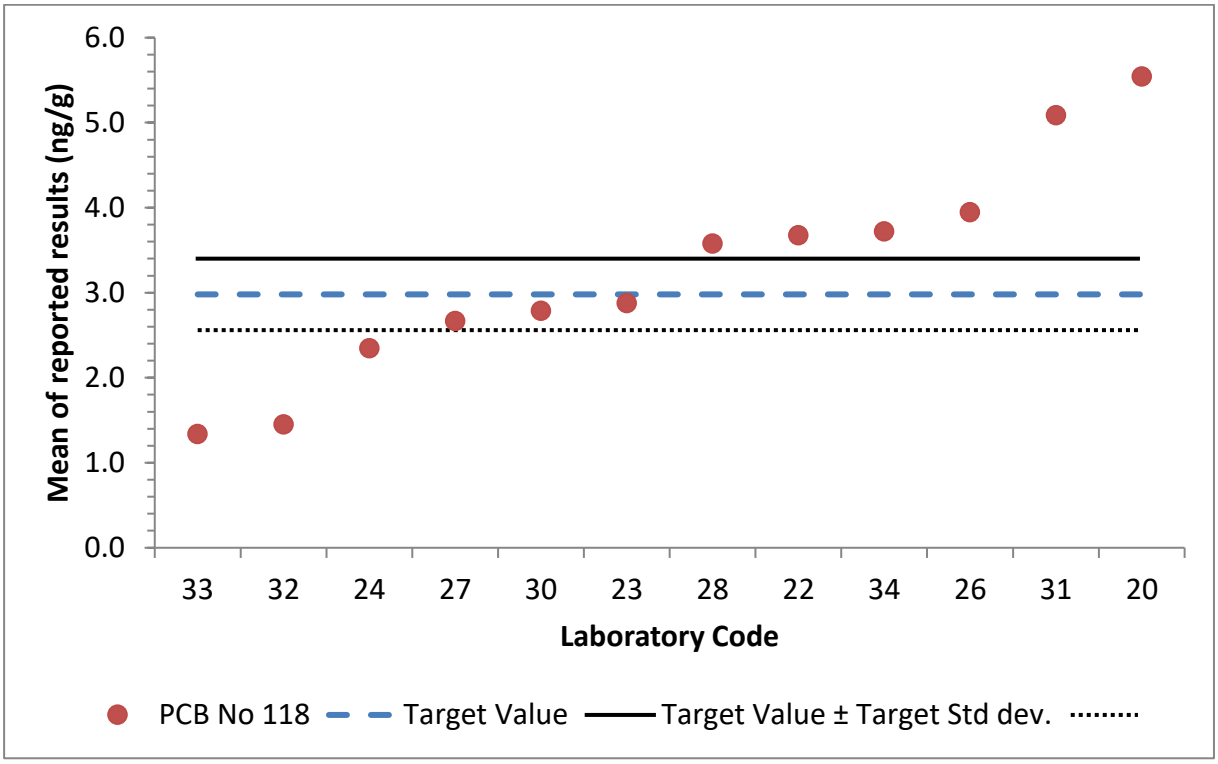

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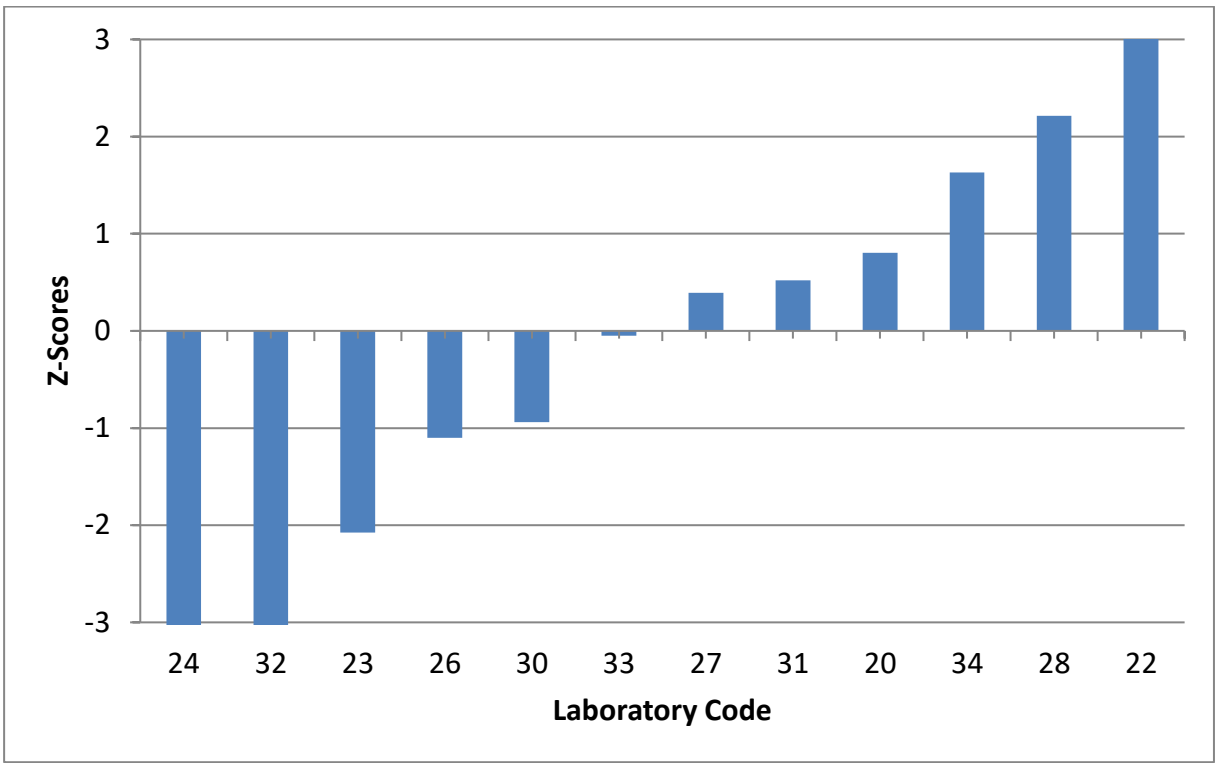

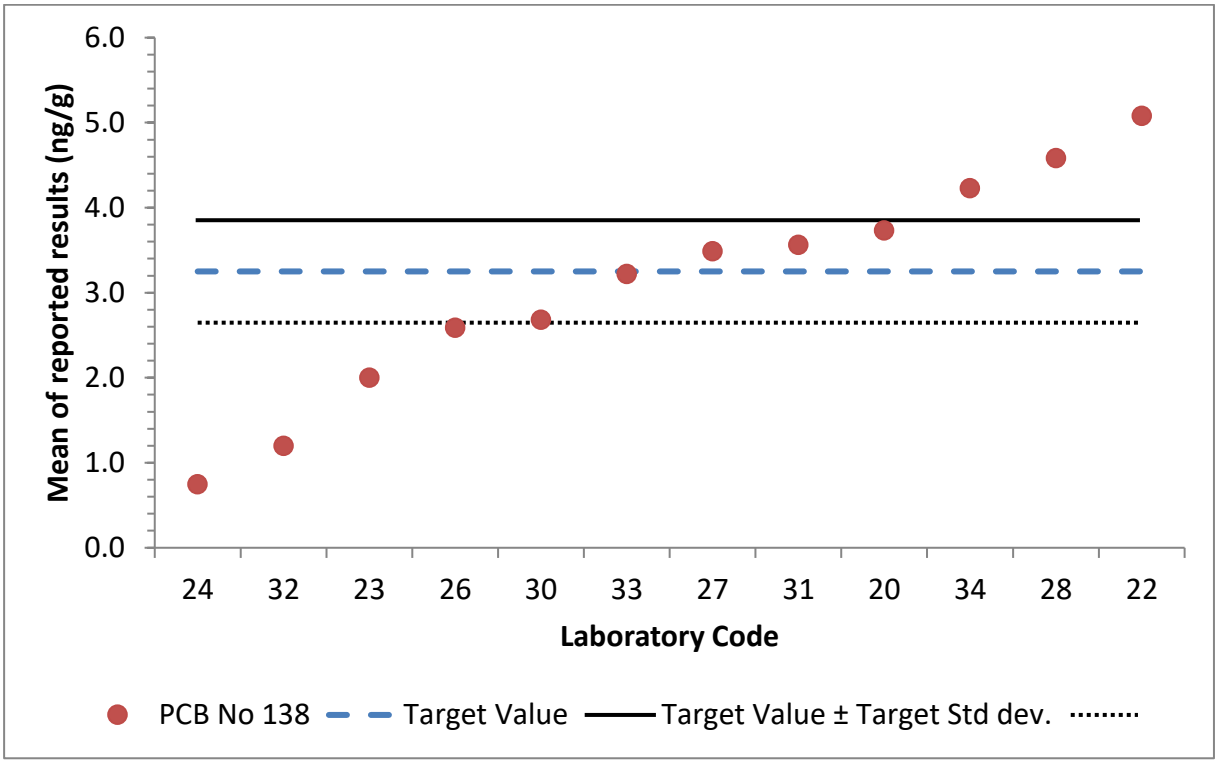

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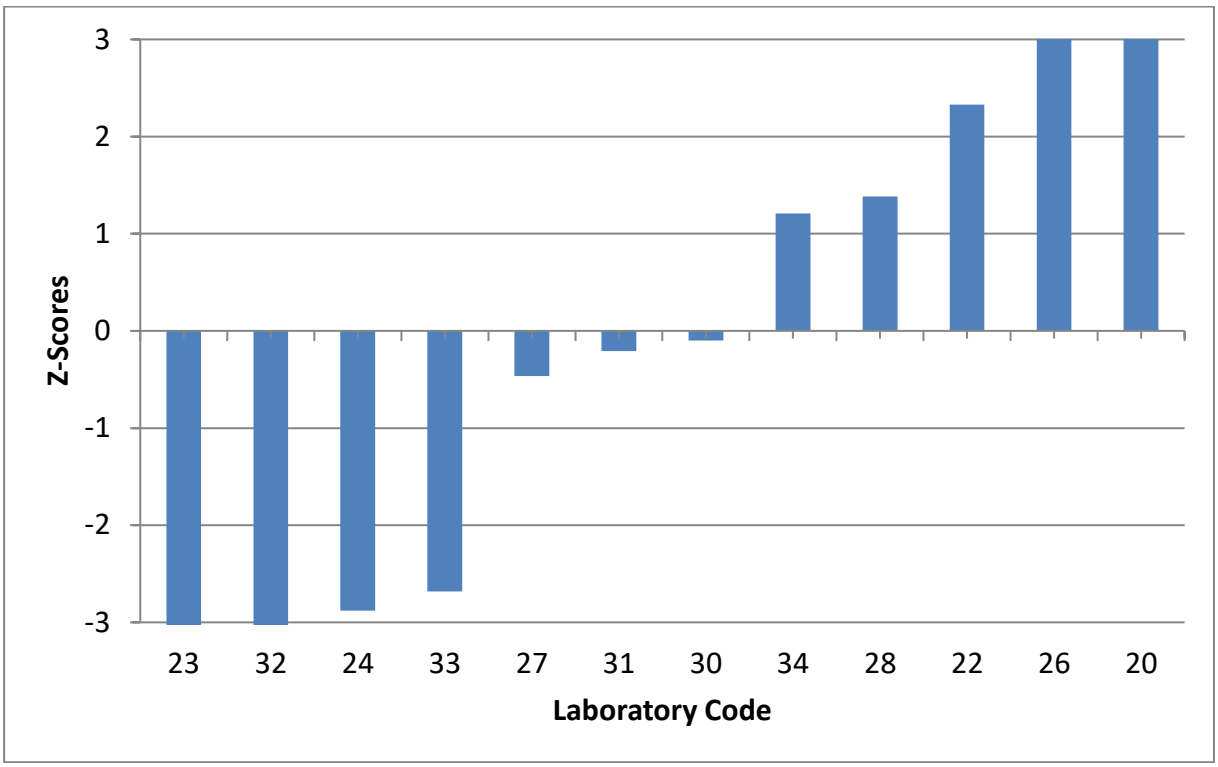

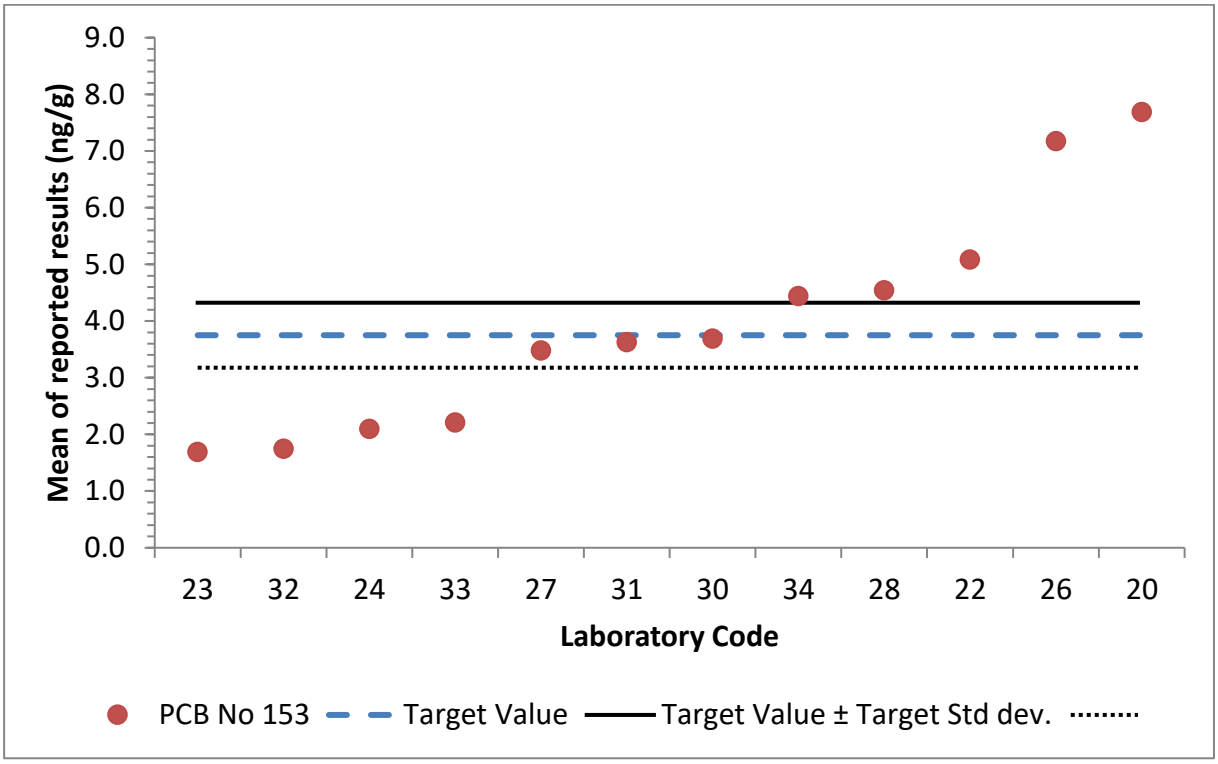

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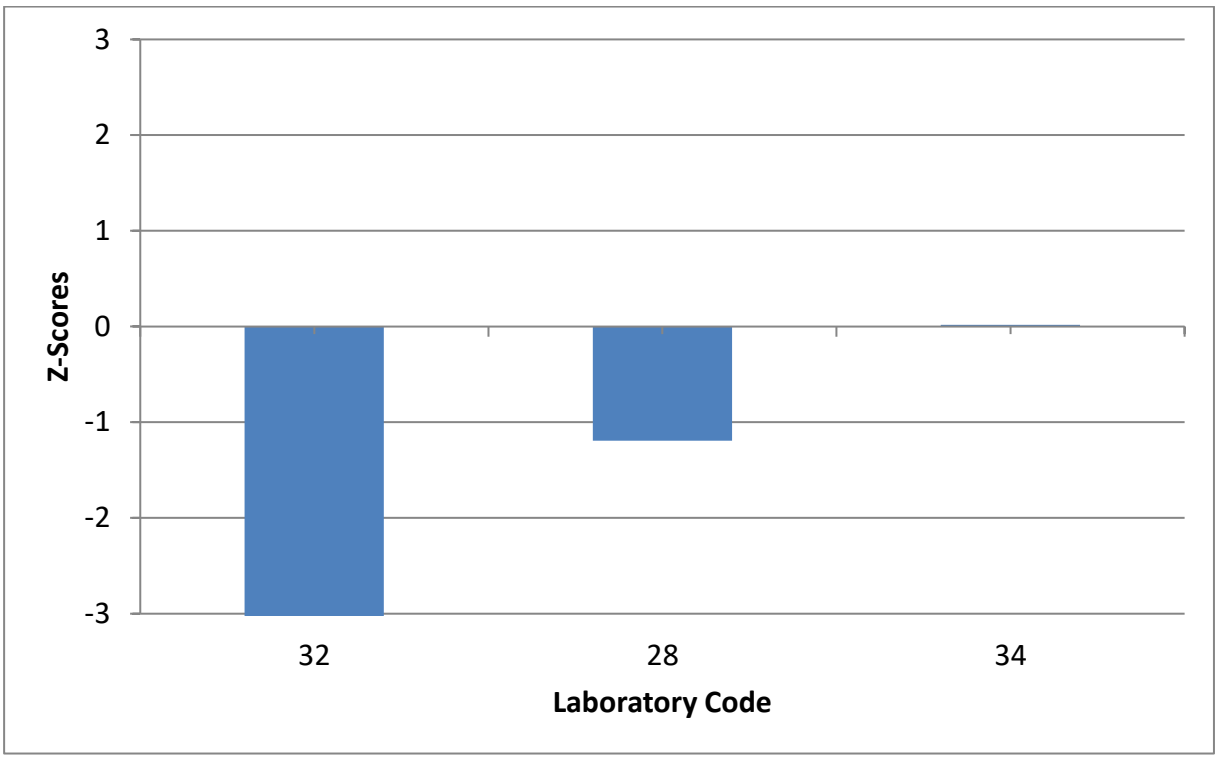

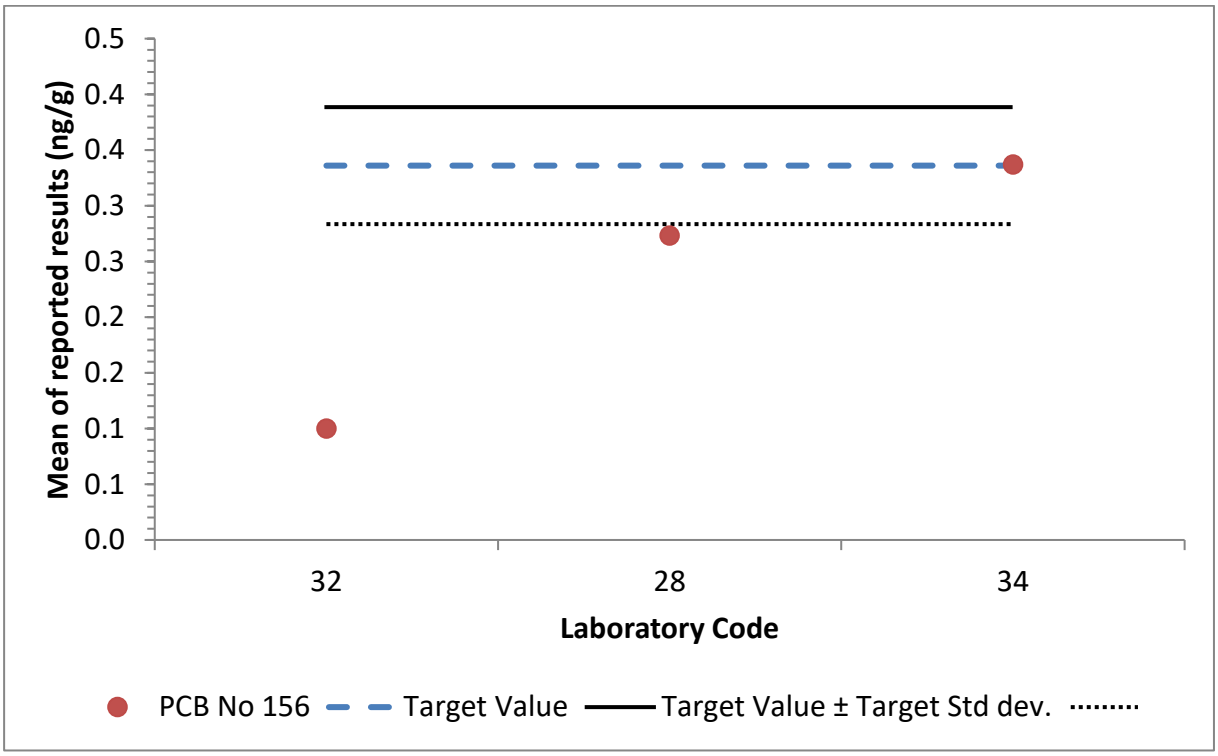

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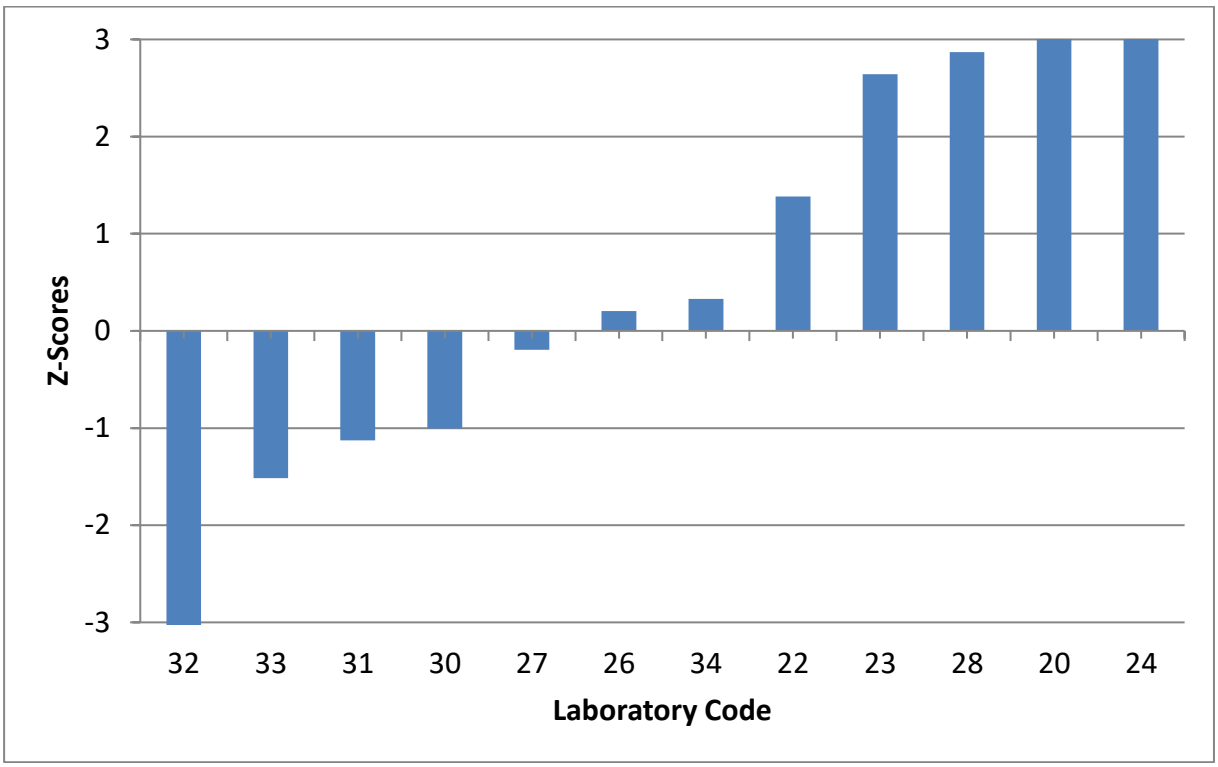

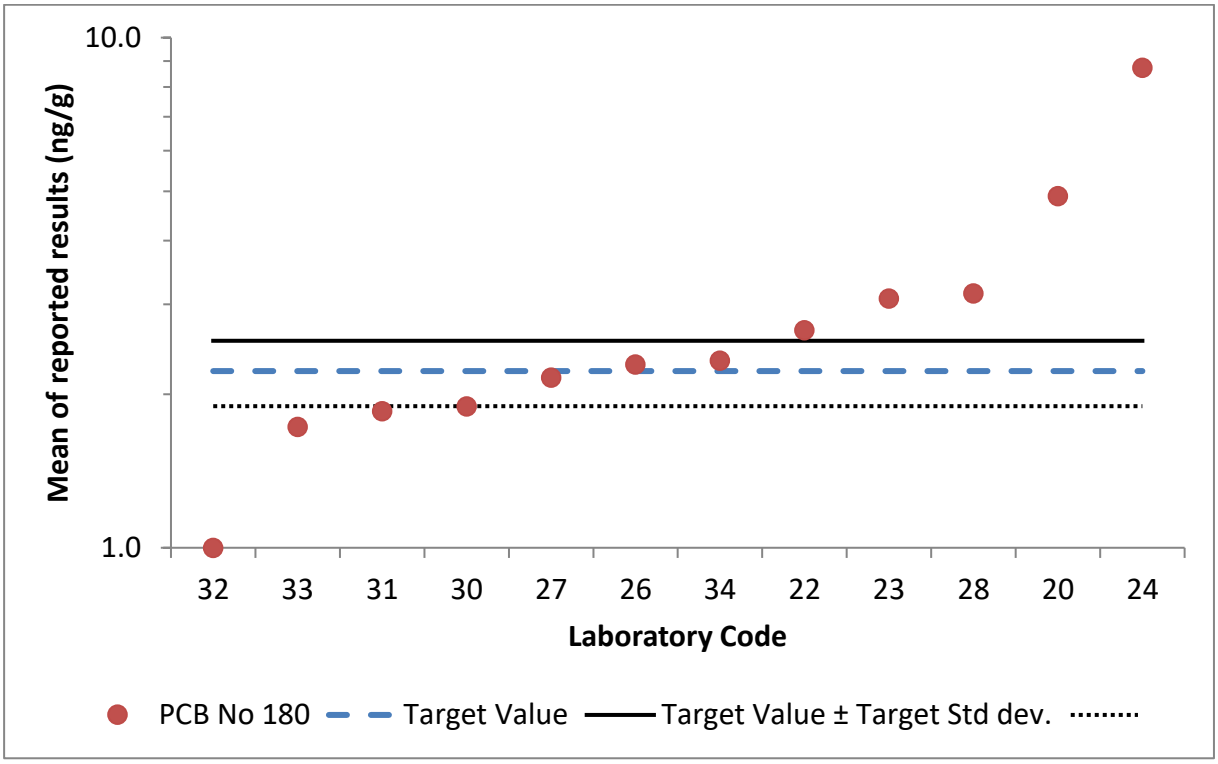

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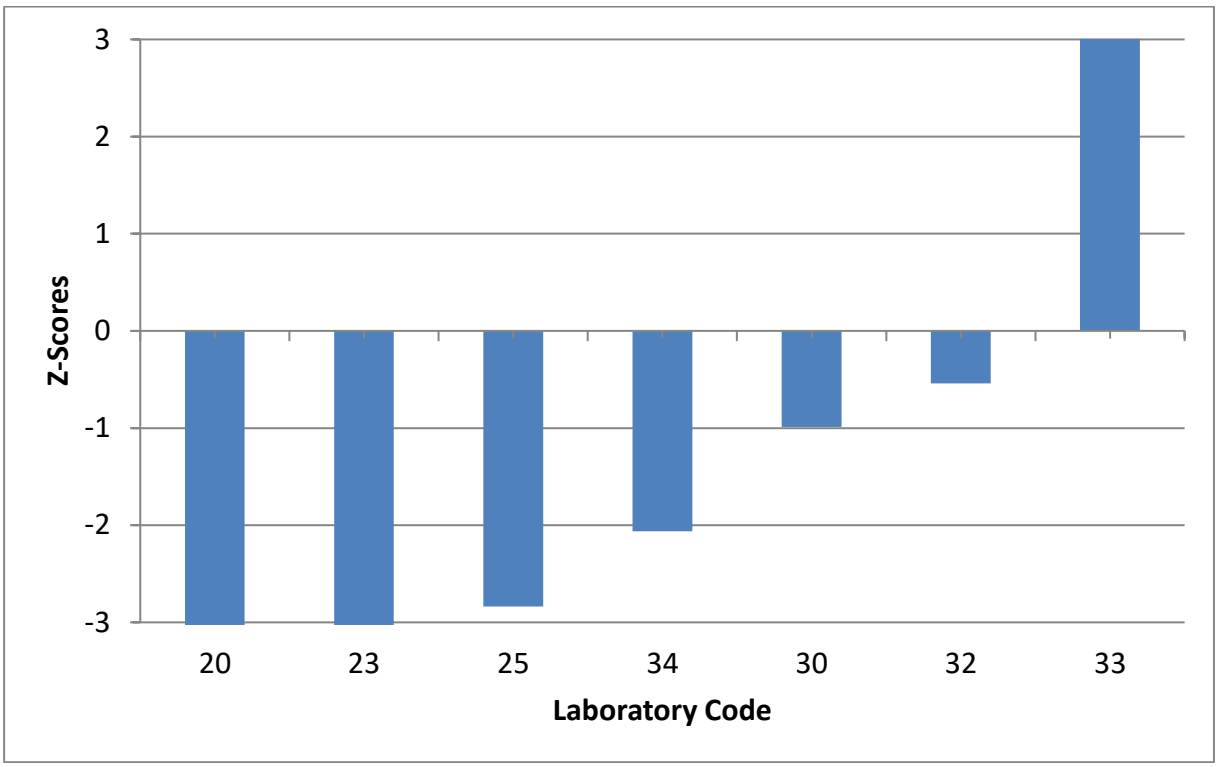

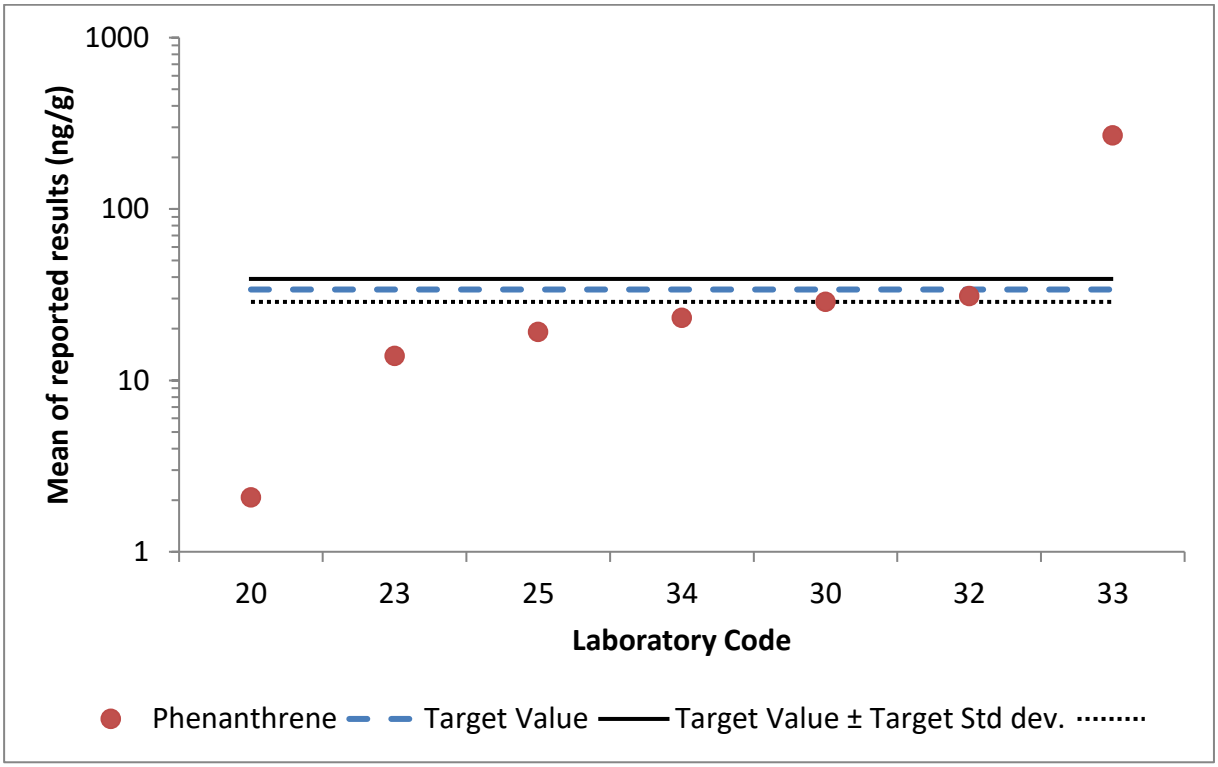

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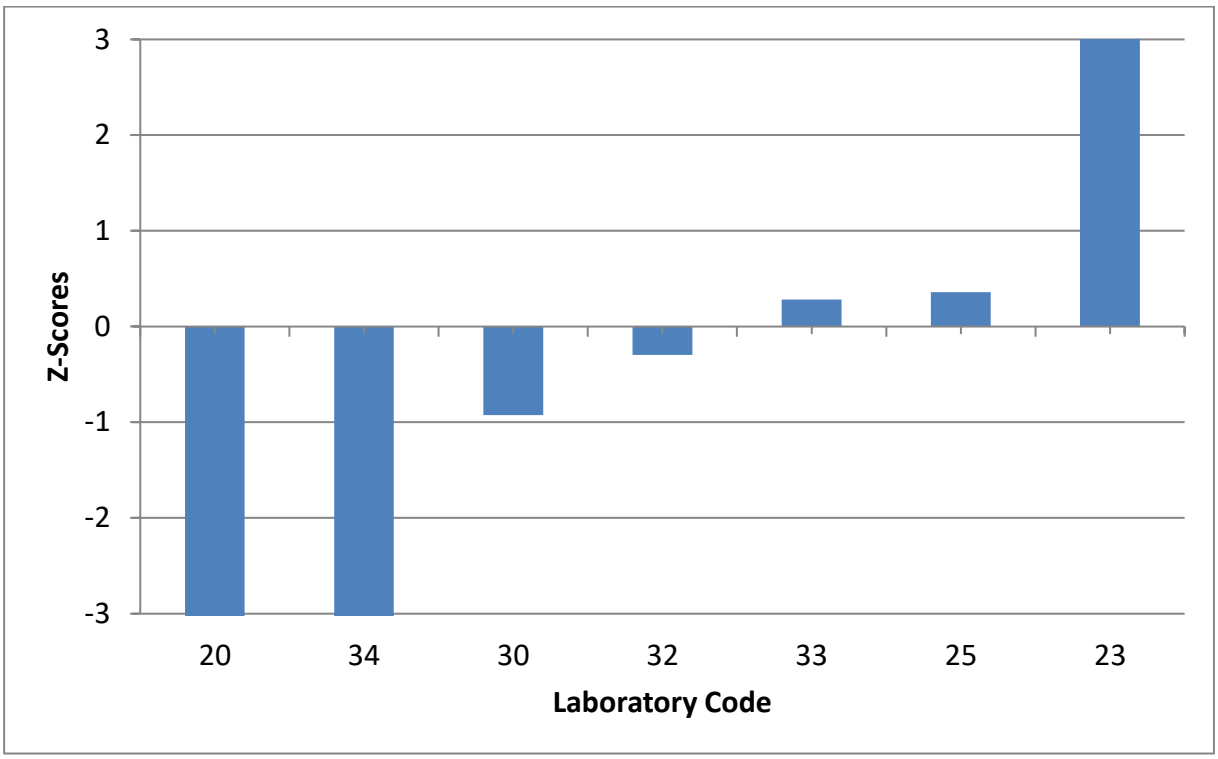

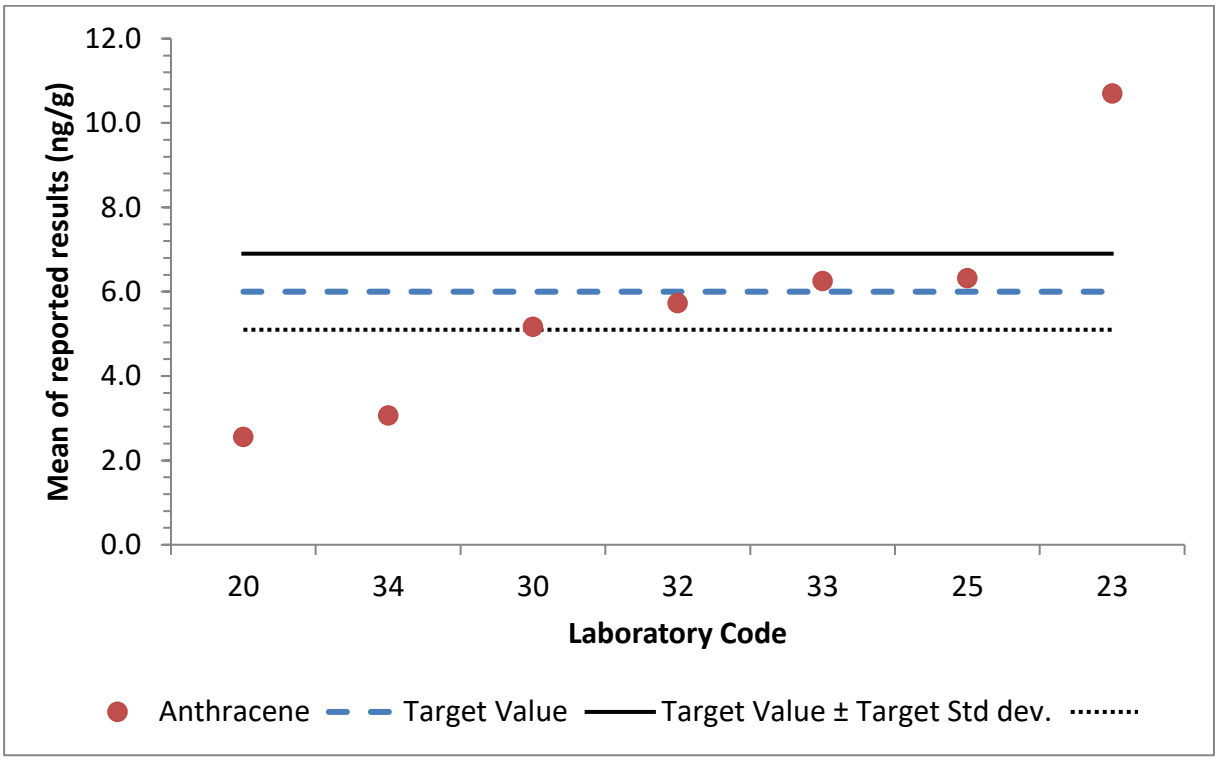

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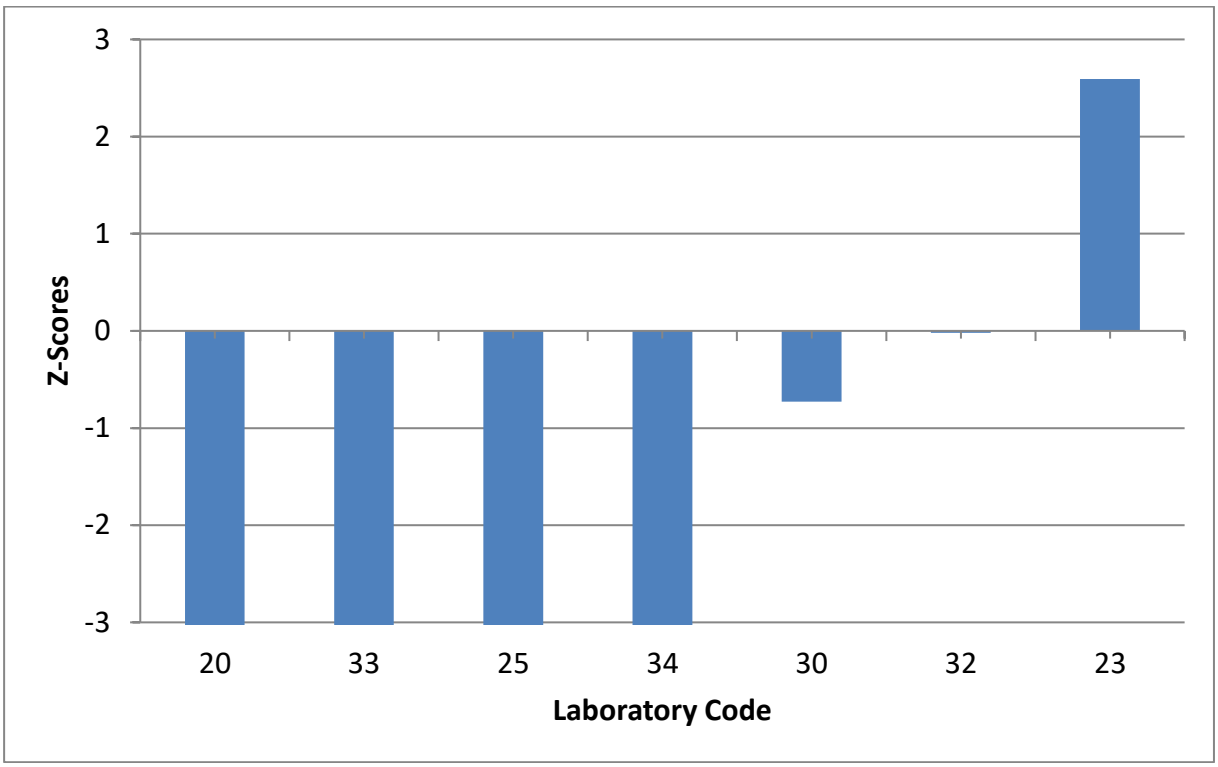

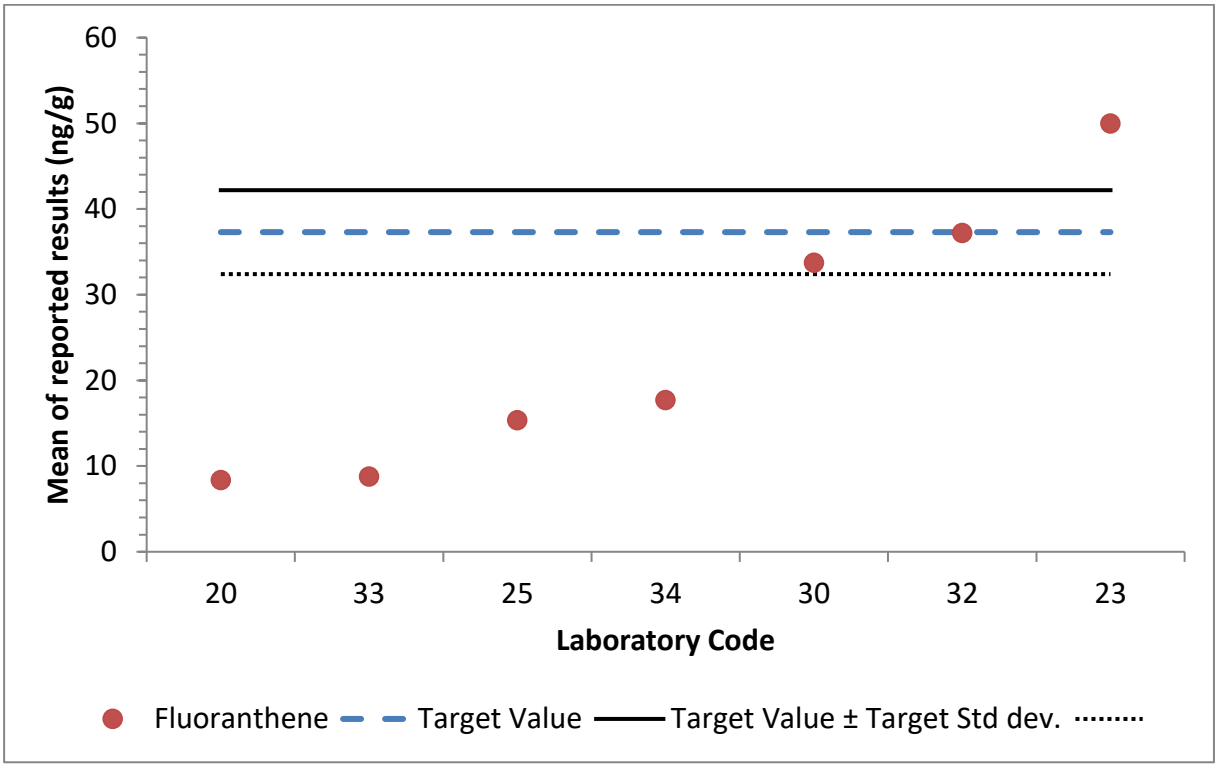

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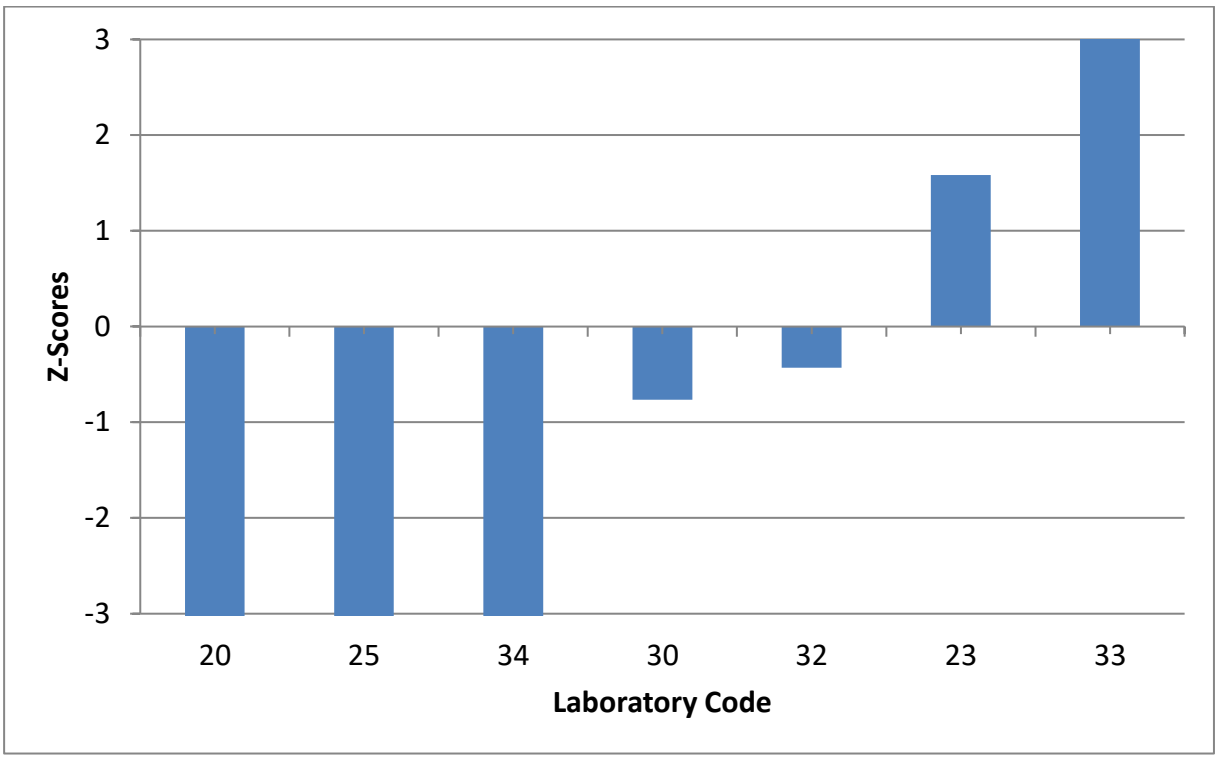
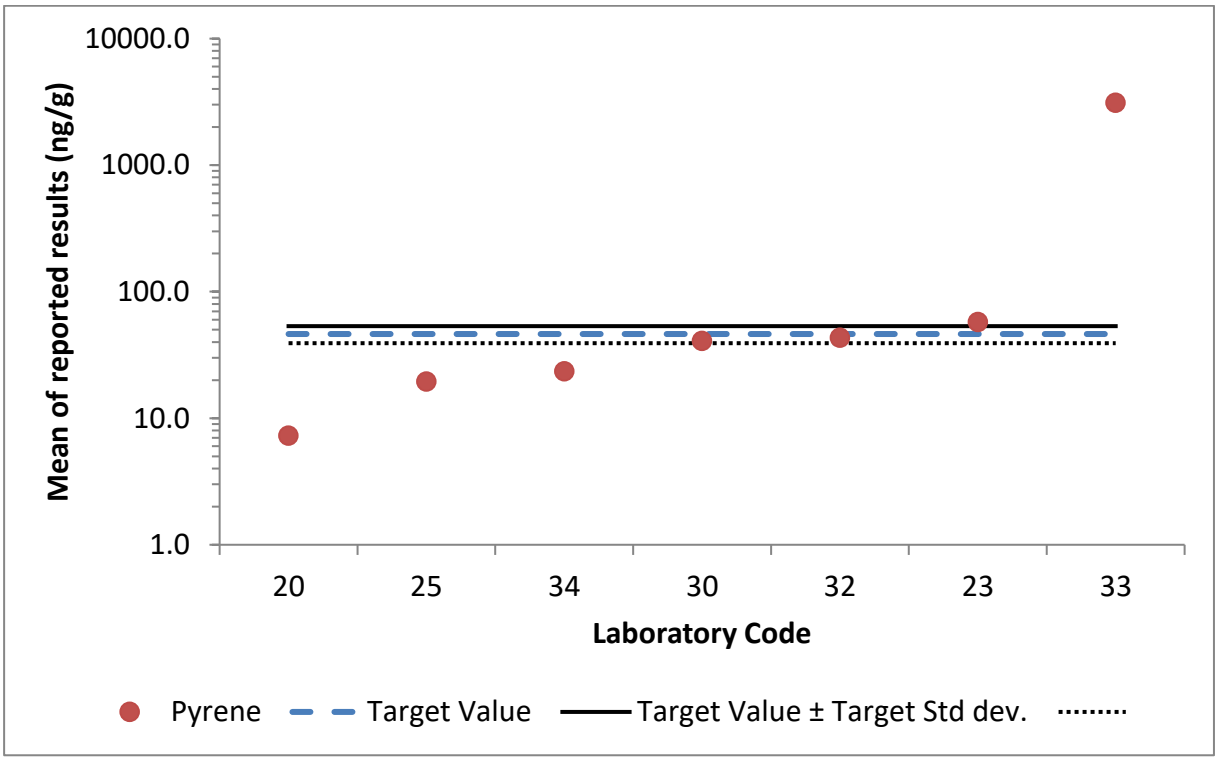
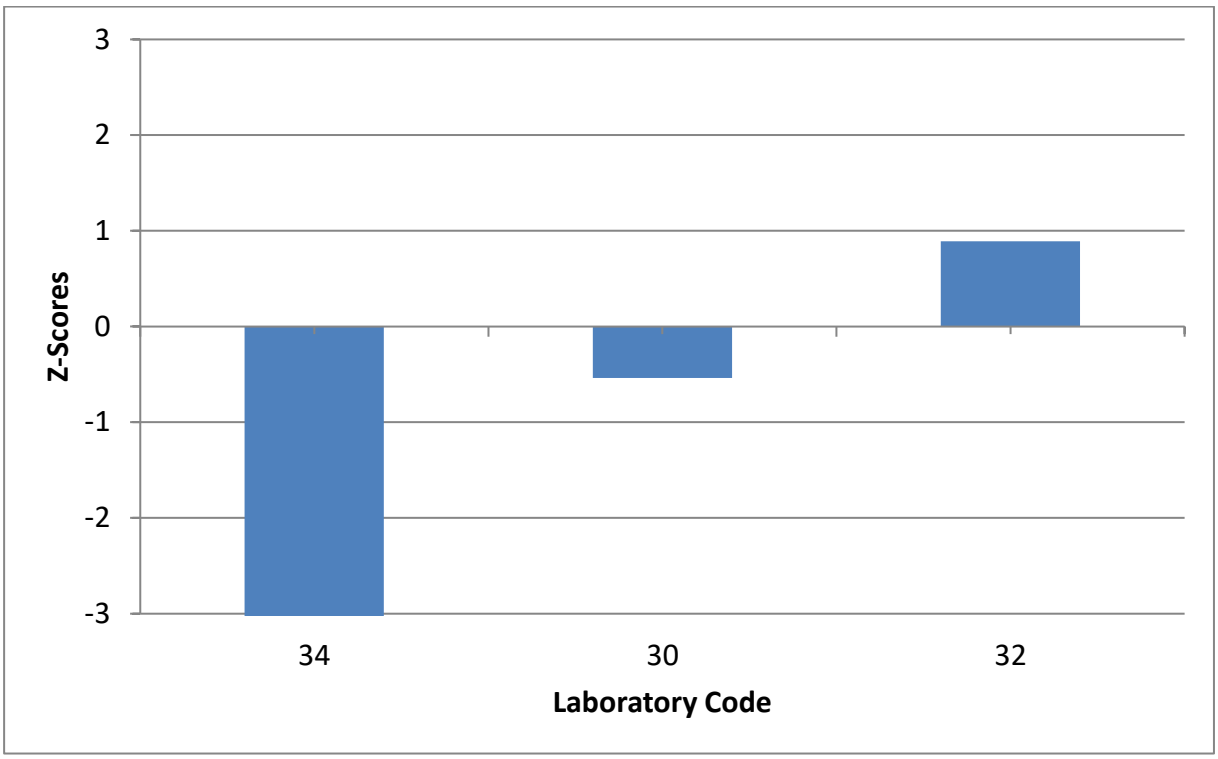
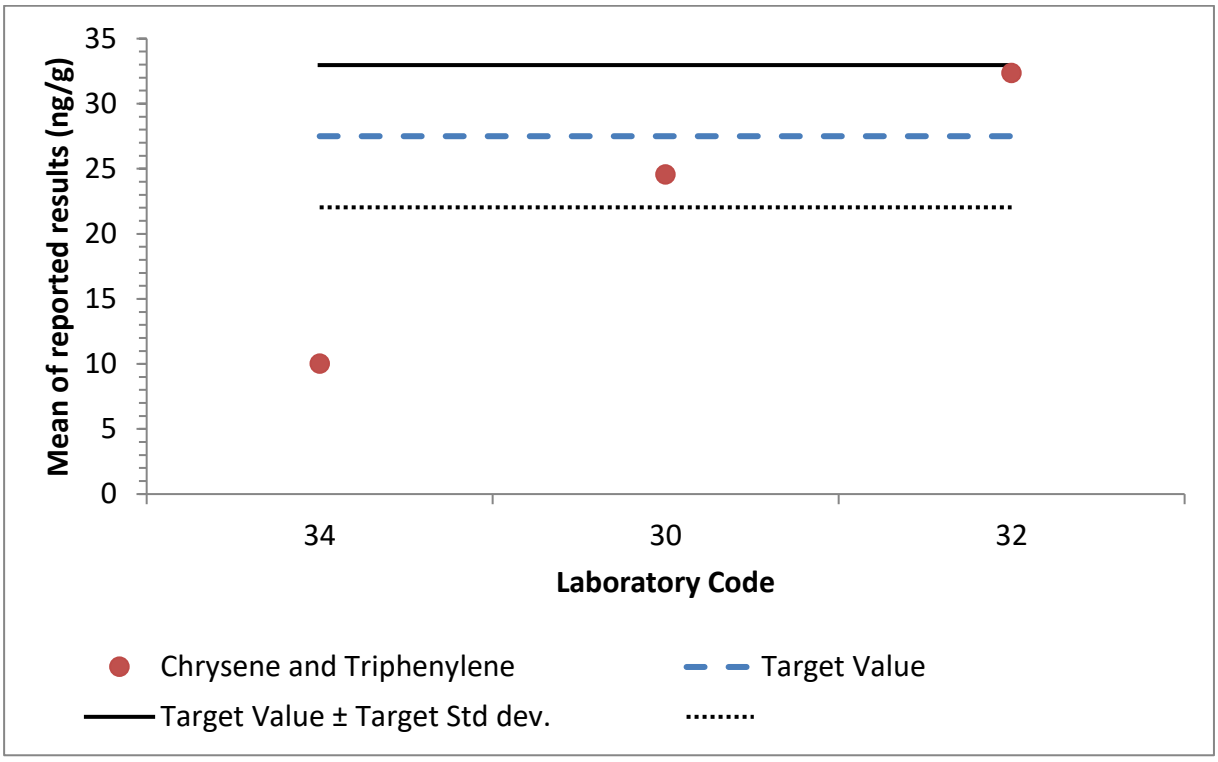


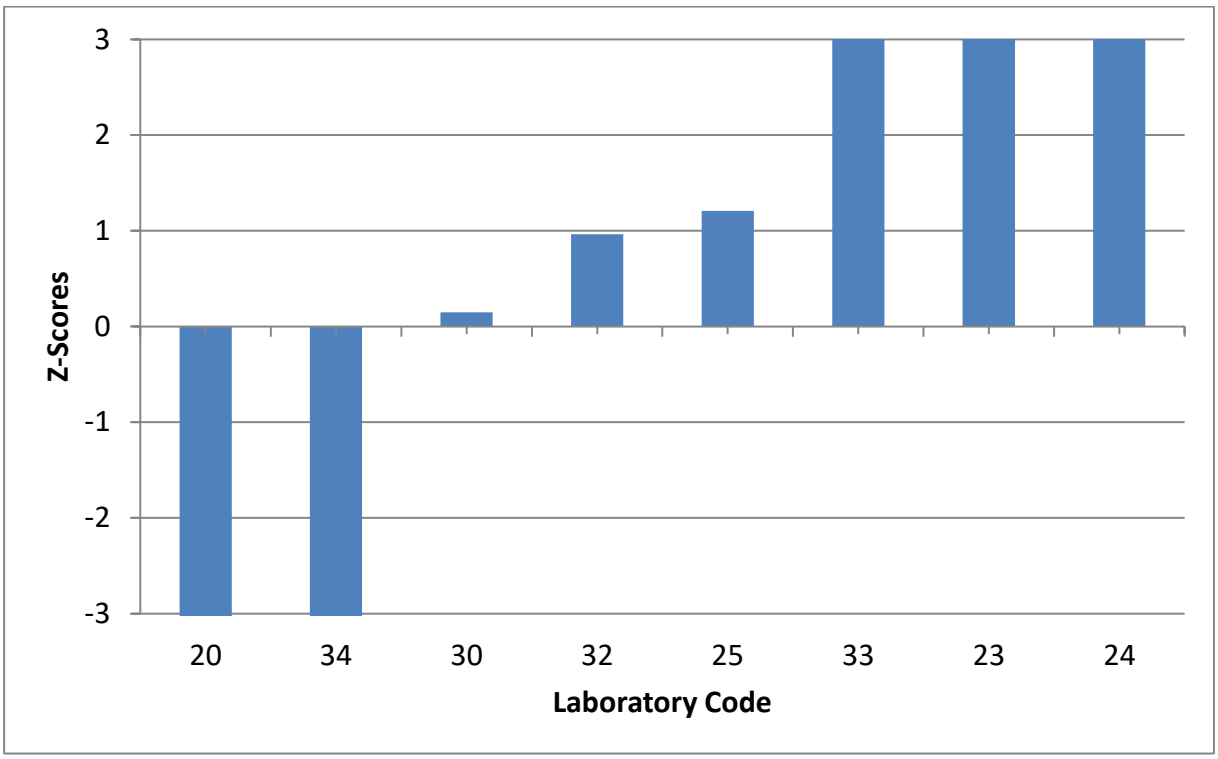


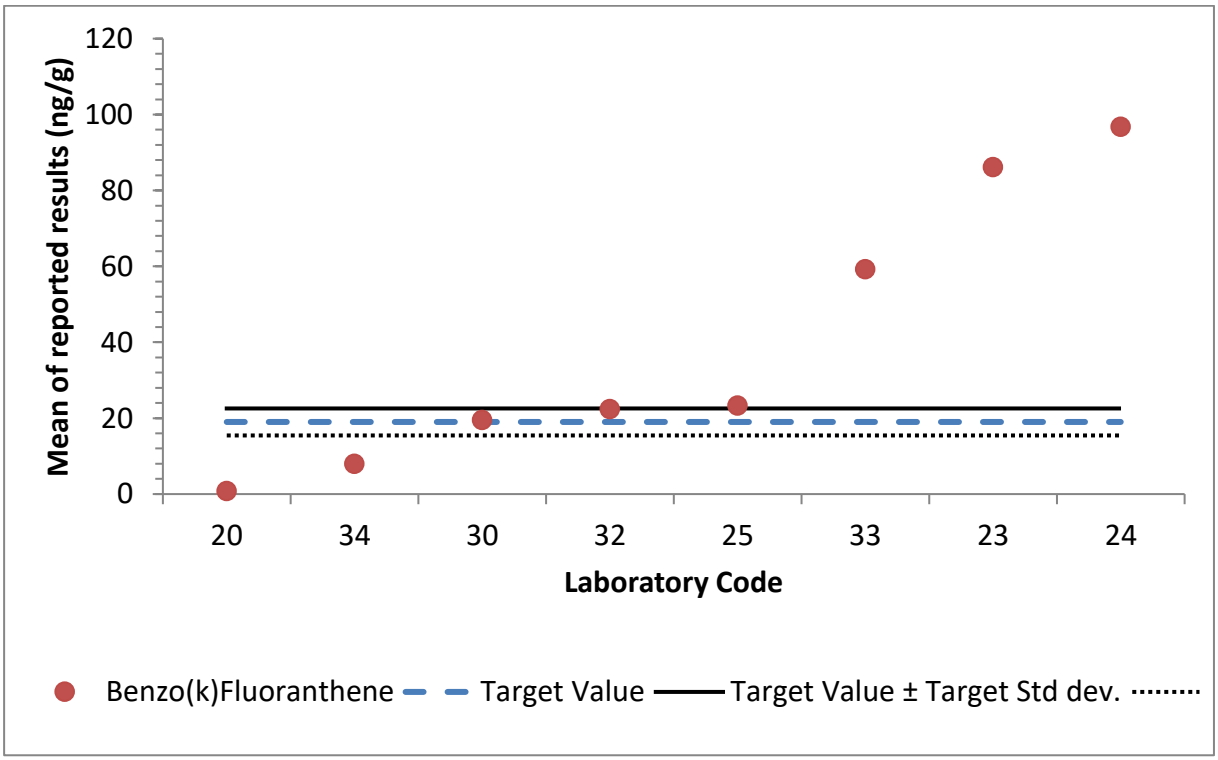
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR CHRYSENE (+ TRIPHENYLENE)



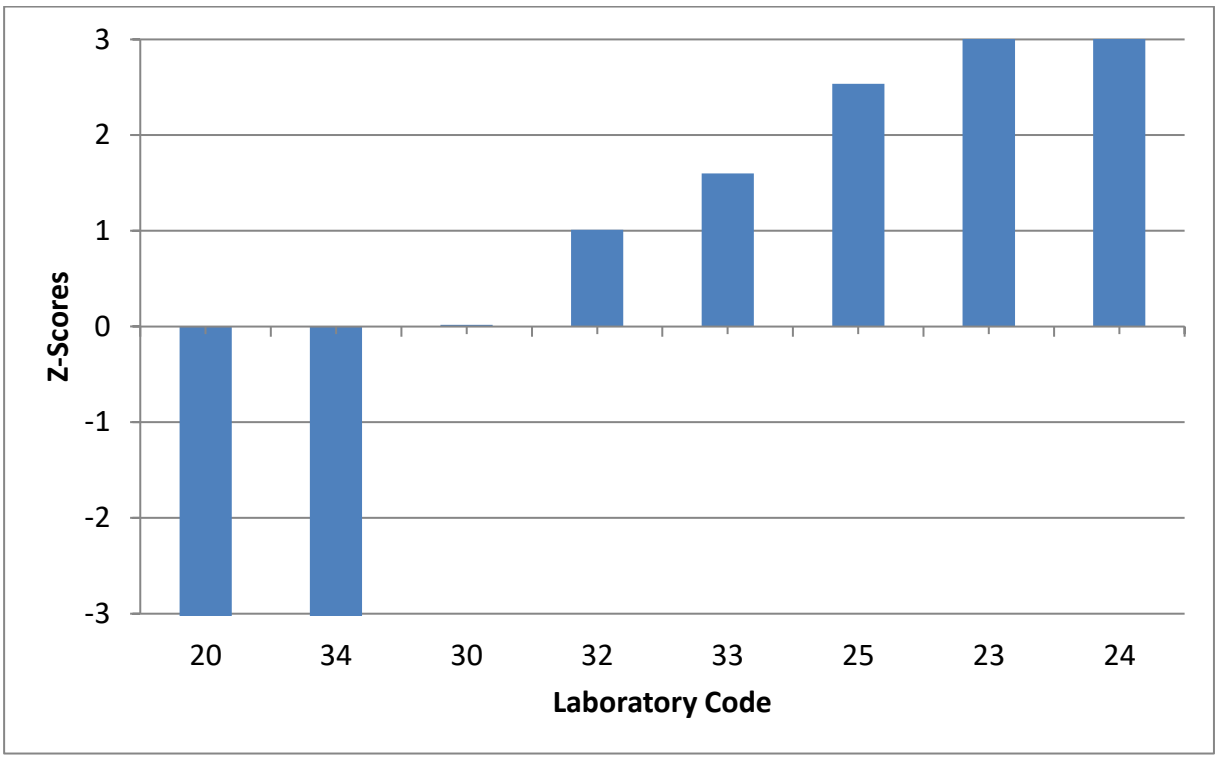


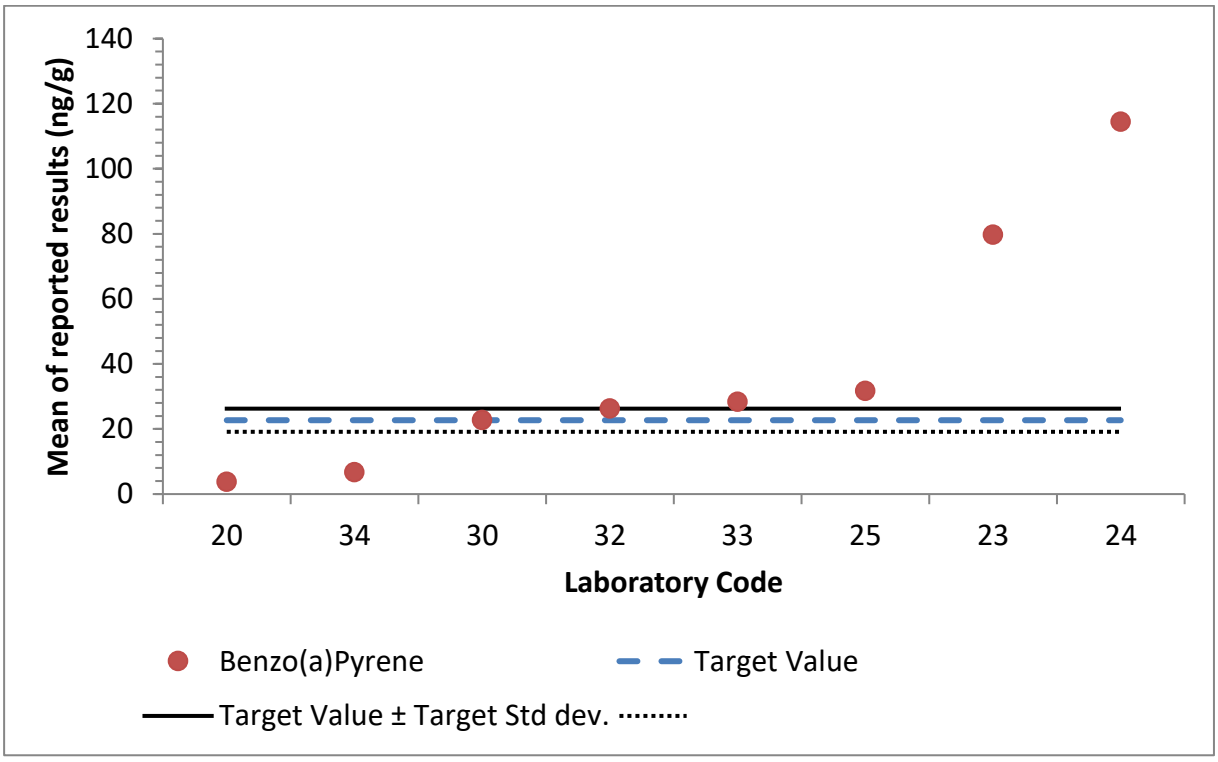
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [k] FLUORANTHENE



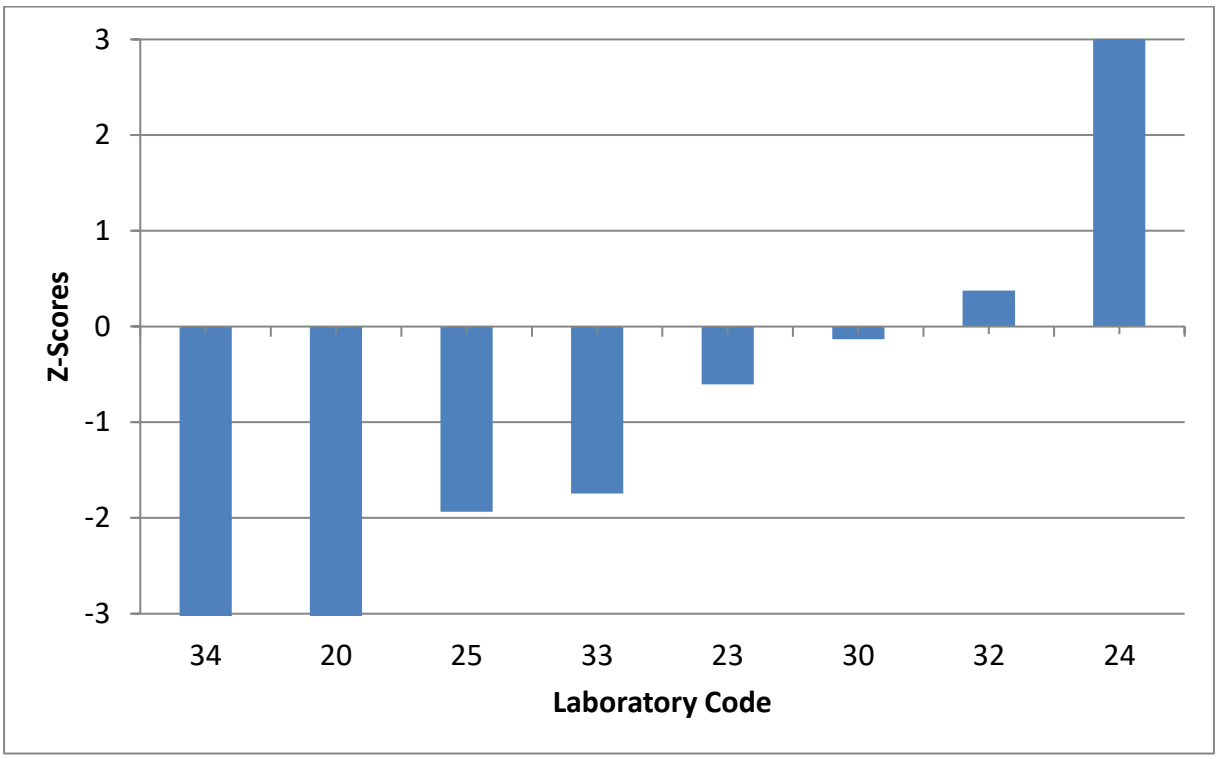


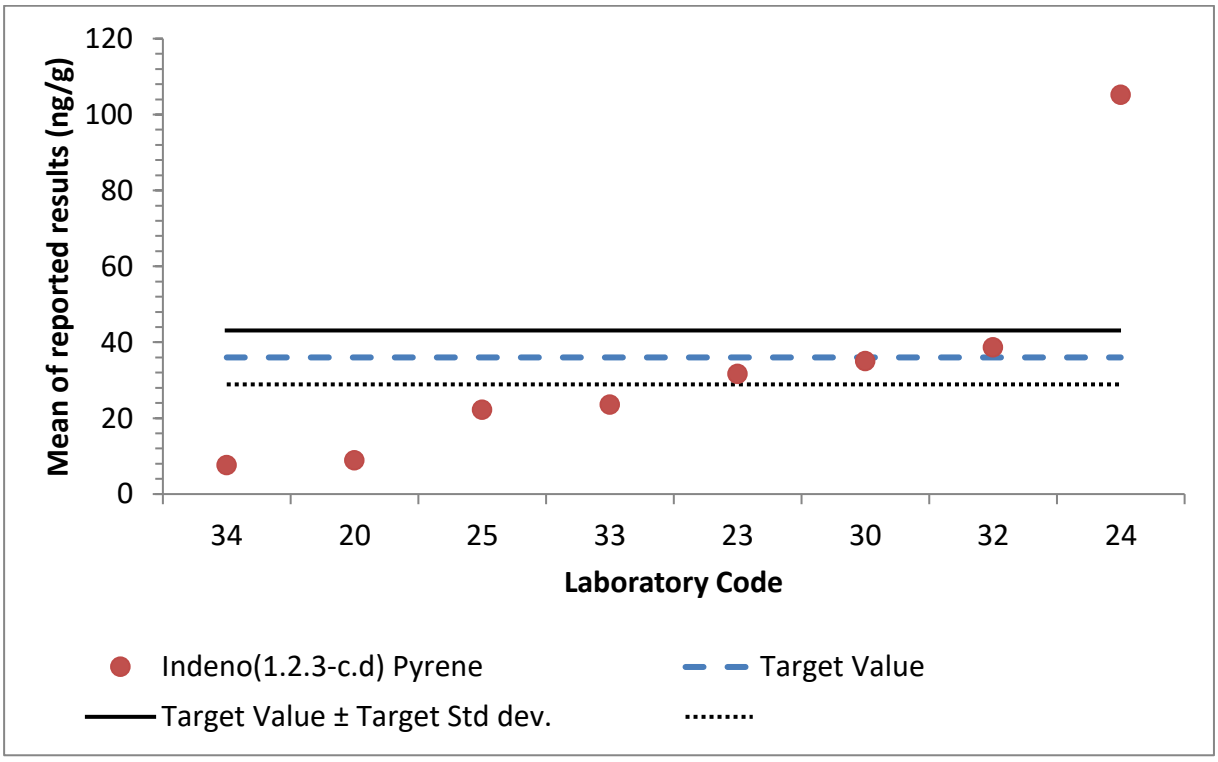
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [a] PYRENE



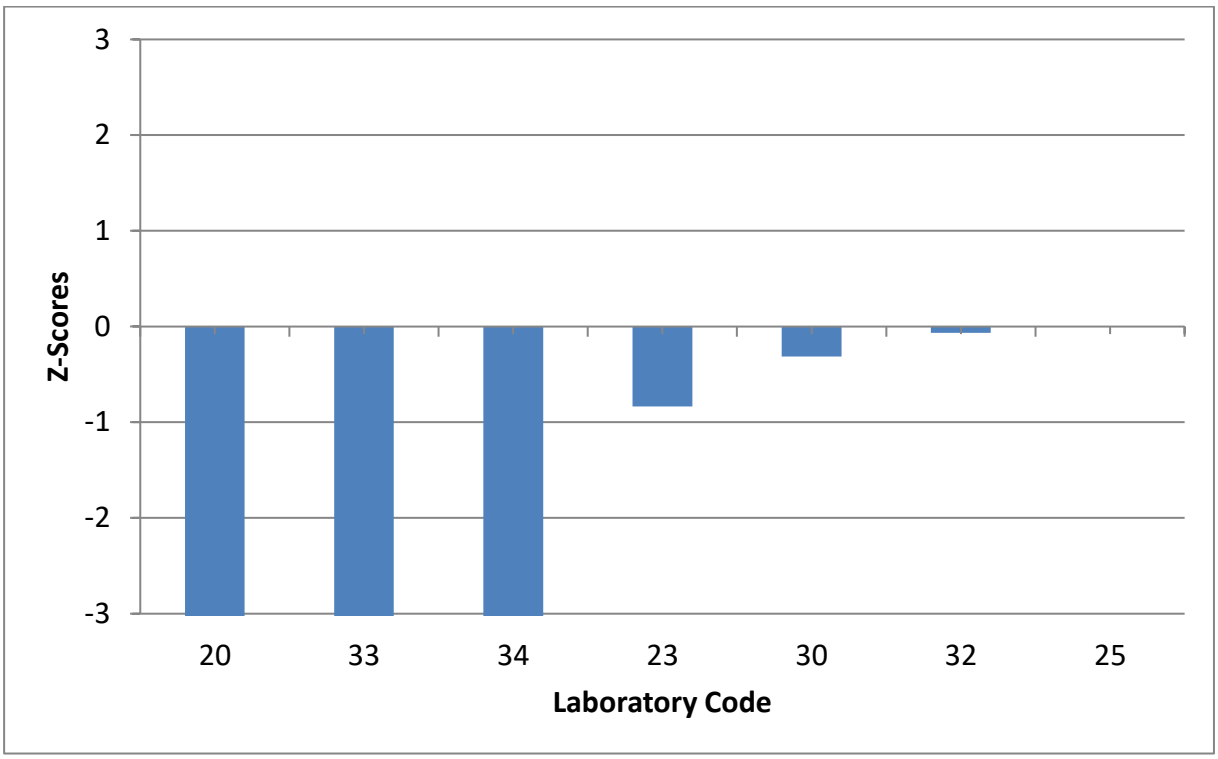


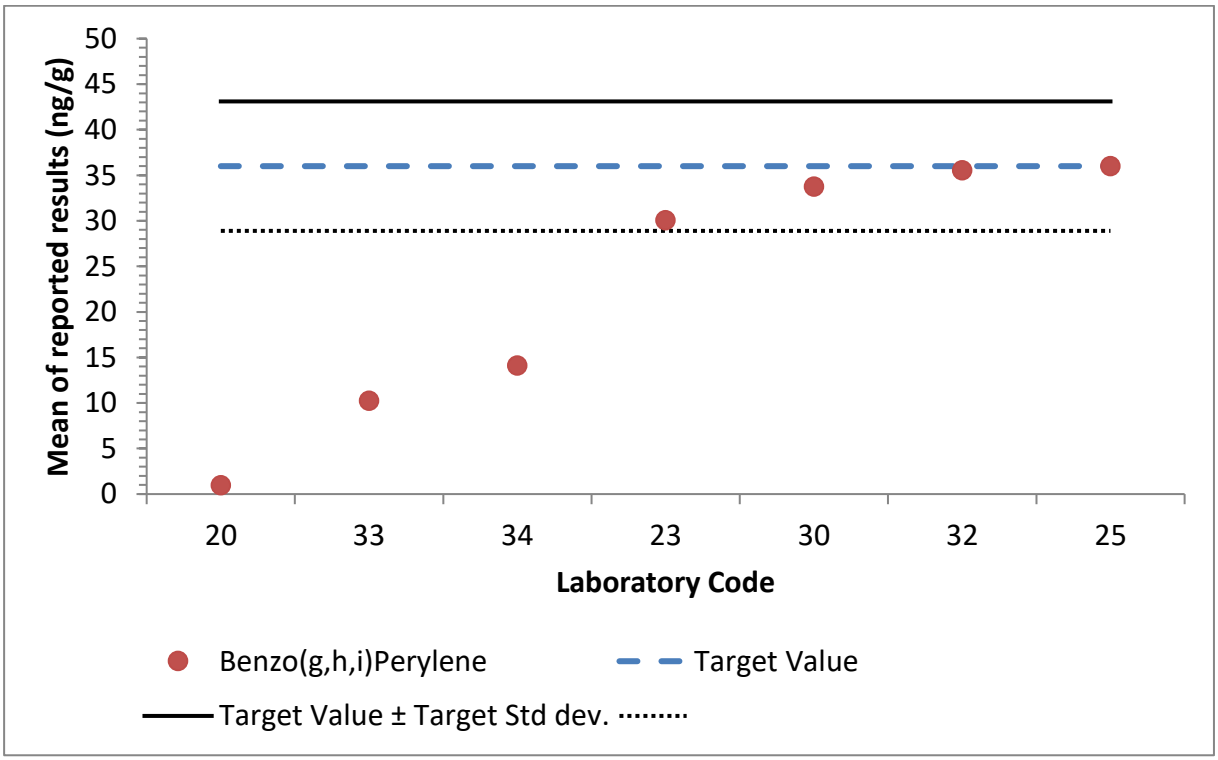
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR INDENO (1.2.3-cd) Pyrene





GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO (g,h,i) PERYLENE





Annex 2: IAEA-459 Refence Sheet

International Atomic Energy Agency
Department of Nuclear Sciences and Applications
IAEA Environment Laboratories

Vienna International Centre, P.O. Box 100, 1400 Vienna, Austria

REFERENCE SHEET

CERTIFIED REFERENCE MATERIAL

IAEA-459

MASS FRACTIONS OF POLYCYCLIC AROMATIC HYDROCARBONS, ORGANOCHLORINES AND POLYBROMINATED DIPHENYL ETHERS IN IAEA-459 MARINE SEDIMENT SAMPLE

Certified mass fraction values *(based on dry mass)*

Polycyclic Aromatic hydrocarbons

Analyte	Unit	Certified value[1]	Expanded uncertainty[2]
2-Methylnaphthalene	µg kg-1	15.5	5.0
1-Methylnaphthalene	µg kg-1	9.2	3.6
Acenaphthylene	µg kg-1	3.2	1.3
Fluorene	µg kg-1	4.7	1.9
Acenaphthene	µg kg-1	1.78	0.73
Dibenzothiophene	µg kg-1	9.4	1.8
Phenanthrene	µg kg-1	33.9	6.0
Anthracene	µg kg-1	6.0	1.0
Fluoranthene	µg kg-1	37.3	3.0
Pyrene	µg kg-1	46.3	8.3
Benz(a)anthracene	µg kg-1	19.3	4.3
Chrysene+triphenylene	µg kg-1	27.5	8.5
Benzo(b)fluoranthene	µg kg-1	44.1	9.3
Benzo(b+j) fluoranthene	µg kg-1	59	15
Benzo(k)fluoranthene	µg kg-1	19.0	5.3
Benzo(e)pyrene	µg kg-1	36	12
Benzo(a)pyrene	µg kg-1	22.7	4.3
Indeno[1,2,3-c,d]pyrene	µg kg-1	36	11
Benzo(g,h,i)perylene	µg kg-1	36	11

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

[2] Expanded uncertainty with a coverage factor k=2 estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [1], corresponding to the level of confidence of about 95%.

PCB congeners

Analyte	Unit	Certified value[1]	Expanded uncertainty[2]
PCB 28	µg kg-1	2.27	0.56
PCB 31	µg kg-1	2.41	0.60
PCB 44	µg kg-1	1.72	0.64
PCB 49	µg kg-1	2.64	0.40
PCB 52	µg kg-1	2.38	0.67
PCB 66	µg kg-1	3.10	0.81
PCB 87	µg kg-1	1.24	0.17
PCB 101	µg kg-1	3.78	0.43
PCB 105	µg kg-1	1.29	0.31
PCB 110	µg kg-1	3.70	0.68
PCB 118	µg kg-1	2.98	0.39
PCB 128	µg kg-1	0.62	0.11
PCB 138	µg kg-1	3.25	0.89
PCB 149	µg kg-1	2.88	0.51
PCB 151	µg kg-1	0.66	0.18
PCB 153	µg kg-1	3.75	0.66
PCB 156	µg kg-1	0.336	0.063
PCB 170	µg kg-1	1.02	0.22
PCB 180	µg kg-1	2.22	0.34
PCB 183	µg kg-1	0.72	0.27
PCB 187	µg kg-1	1.39	0.20
PCB 209	µg kg-1	0.199	0.067

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

[2] Expanded uncertainty with a coverage factor k=2 estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [1], corresponding to the level of confidence of about 95%.

Chlorinated pesticides

Analyte	Unit	Certified value[1]	Expanded uncertainty[2]
pp' DDE	µg kg-1	3.60	0.48
pp' DDD	µg kg-1	3.00	0.93
pp' DDT	µg kg-1	1.32	0.52
op DDE	µg kg-1	0.47	0.11
op DDD	µg kg-1	0.75	0.27
op DDT	µg kg-1	0.35	0.13

[1] The value is the robust mean of accepted sets of data, each set being obtained by different laboratory. The certified values are reported on dry mass basis and are traceable to the SI.
[2] Expanded uncertainty with a coverage factor k=2 estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [1], corresponding to the level of confidence of about 95%.

PBDE congeners

Analyte	Unit	Certified value[1]	Expanded uncertainty[2]
BDE 47	µg kg-1	0.177	0.060
BDE 99	µg kg-1	0.240	0.067
BDE 153	µg kg-1	0.097	0.022
BDE 183	µg kg-1	0.282	0.065
BDE 209	µg kg-1	10.8	2.9

[1] The value is the robust mean of accepted sets of data, each set being obtained by different laboratory. The certified values are reported on dry mass basis and are traceable to the SI.
[2] Expanded uncertainty with a coverage factor k=2 estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [1], corresponding to the level of confidence of about 95%.

Information mass fraction values *(based on dry mass)*

Polycyclic aromatic hydrocarbons

Analyte	Unit	Information value[1]	Expanded uncertainty[2]
Naphthalene	µg kg^{-1}	20.9	9.1
C2-Naphthalene	µg kg^{-1}	55	31
C3-Naphthalene	µg kg^{-1}	66	28
Biphenyl	µg kg^{-1}	10.5	2.6
C1-Fluorenes	µg kg^{-1}	11.1	--
C2-Fluorenes	µg kg^{-1}	21.9	--
C3-Fluorenes	µg kg^{-1}	30.1	--
C1-Dibenzothiophene	µg kg^{-1}	35.0	9.9
C2-Dibenzothiophene	µg kg^{-1}	63	23
C3-Dibenzothiophene	µg kg^{-1}	99	41
1methylphenanthrene	µg kg^{-1}	7.7	4.1
2methylphenanthrene	µg kg^{-1}	20	11
C1- Phen/Anth	µg kg^{-1}	45	21
C2- Phen/Anth	µg kg^{-1}	47	13
C3- Phen/Anth	µg kg^{-1}	39.1	8.1
C4- Phen/Anth	µg kg^{-1}	34	11
1methyl Pyrene	µg kg^{-1}	8.8	1.0
C1-Fluor/Pyrenes	µg kg^{-1}	43.6	8.9
C2-Fluor/Pyrenes	µg kg^{-1}	49.1	6.7
C3-Fluoranthenes/pyrenes	µg kg^{-1}	36.0	--
Chrysene	µg kg^{-1}	18.4	3.0
Triphenylene	µg kg^{-1}	8.0	--
C1-Chrysenes	µg kg^{-1}	34.9	4.7
C2-Chrysenes	µg kg^{-1}	50.0	9.4
C3-Chrysenes	µg kg^{-1}	39.7	5.1
Benzo(j)fluoranthene	µg kg^{-1}	20	11
Benzo(a)fluoranthene	µg kg^{-1}	7.0	5.0
Dibenz(a,h)anthracene	µg kg^{-1}	6.6	2.8
Perylene	µg kg^{-1}	32	18

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

[2] Expanded uncertainty with a coverage factor k=2 estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [1], corresponding to the level of confidence of about 95%.

PCB congeners

Analyte	Unit	Information value[1]	Expanded uncertainty[2]
PCB 8	µg kg-1	0.46	0.28
PCB 18	µg kg-1	1.11	0.53
PCB 95	µg kg-1	2.42	--
PCB 97	µg kg-1	1.42	0.42
PCB 99	µg kg-1	2.54	0.33
PCB 174	µg kg-1	0.90	0.10
PCB 177	µg kg-1	0.50	--
PCB 194	µg kg-1	0.47	0.30
PCB 195	µg kg-1	0.10	0.12
PCB 201	µg kg-1	0.184	0.038
PCB 206	µg kg-1	0.204	0.062

[1] The value is the robust mean of accepted sets of data, each set being obtained by different laboratory. The information values are reported on dry mass basis and are traceable to the SI.
[2] Expanded uncertainty with a coverage factor k=2 estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [1], corresponding to the level of confidence of about 95%.

Chlorinated pesticides

Analyte	Unit	Information value[1]	Expanded uncertainty[2]
HCB	µg kg^{-1}	0.153	0.058
α HCH	µg kg^{-1}	0.145	0.067
β HCH	µg kg^{-1}	0.136	0.083
γ HCH- Lindane	µg kg^{-1}	0.182	0.064
cis-Chlordane	µg kg^{-1}	0.05	–
trans-Chlordane	µg kg^{-1}	0.07	–
δ HCH	µg kg^{-1}	0.03	–
Heptachlor	µg kg^{-1}	0.15	–
Aldrin	µg kg^{-1}	<0.10	–
Dieldrin	µg kg^{-1}	0.10	–
Endrin	µg kg^{-1}	<0.03	–
cis-Nonachlor	µg kg^{-1}	0.06	–
trans-Nonachlor	µg kg^{-1}	0.01	–
α Endosulfan	µg kg^{-1}	0.06	–
β Endosulfan	µg kg^{-1}	0.05	–
Endosulfan sulfate	µg kg^{-1}	0.05	–

[1] The value is the robust mean of accepted sets of data, each set being obtained by different laboratory. The information values are reported on dry mass basis and are traceable to the SI.
[2] Expanded uncertainty with a coverage factor k=2 estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [1], corresponding to the level of confidence of about 95%.

PBDE congeners

Analyte	Unit	Information value[1]	Expanded uncertainty[2]
BDE 28	µg kg^{-1}	0.0213	0.0092
BDE 66	µg kg^{-1}	0.0100	0.0048
BDE 85	µg kg^{-1}	0.0092	0.0058
BDE 100	µg kg^{-1}	0.0293	0.0083
BDE 154	µg kg^{-1}	0.0252	0.0124

[1] The value is the robust mean of accepted sets of data, each set being obtained by different laboratory. The information values are reported on dry mass basis and are traceable to the SI.
[2] Expanded uncertainty with a coverage factor k=2 estimated in accordance with the JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [1], corresponding to the level of confidence of about 95%.

Origin and preparation of the material

A marine sediment sample was collected in Han River estuary, South Korea. This sediment was freeze-dried, ground and sieved at 125 µm.
The sieved sediment obtained, around 26 kg, with a particle size of less than 125 µm was homogenized by mixing it in a stainless steel rotating homogenizer for three weeks. Then, aliquots of about 50 g were packaged into cleaned amber glass bottles with aluminium screw caps, labelled IAEA-459 and sealed with Teflon tape.

Homogeneity of the material

The between-bottle homogeneity of the material was assessed by determining the mass fraction of selected chlorinated pesticides, polychlorinated biphenyls, polybrominated diphenyl ethers and parent polycyclic aromatic hydrocarbons in sample aliquots of 10 bottle units randomly selected and analysed under repeatability conditions. The within–bottle homogeneity was assessed by 6 determinations of mass fractions of chlorinated pesticides, polychlorinated biphenyls, polybrominated diphenyl ethers and polycyclic aromatic hydrocarbons in one bottle.

The coefficient of variation for the content of the major analytes between the 10 different sample bottles was below 10%. Thus the material was considered sufficiently homogeneous for the PAHs, the organochlorinated and PBDEs compounds at 6 g sample size. The uncertainty contribution of possible inhomogeneity between bottles was estimated by applying the ANOVA-like approach [2,3], and it was lower than 11% for the certified analytes.

Characterization study

The selection of participants for this certification exercise was based on the measurement performances demonstrated by laboratories in the previous IAEA inter-laboratory comparisons on marine sediments. Participants were requested to analyse chlorinated pesticides, PCB congeners, PBDE congeners and petroleum hydrocarbons by the analytical technique of their choice. They were also requested to make six separate determinations with the applied quality control procedures, including results for the organic contaminants in a CRM with a matrix similar to the candidate reference material.

The number of independent datasets obtained for PAHs, organochlorines and PBDEs was 10, 12 and 7, respectively.

The characterization of the PAHs was performed by using three different analytical techniques, gas chromatography/mass spectrometry (GC-MS), gas chromatography/high resolution mass spectrometry (GC-HRMS) and high performance liquid chromatography/fluorescence detector (HPLC–FLD).

The characterization of the PCBs was based on the application of five different analytical techniques, two-dimensional gas chromatography/electron capture detector (GCxGC-ECD), gas chromatography coupled to tandem mass spectrometry (GC-MS/MS), gas chromatography/mass spectrometry (GC-MS), gas chromatography/high resolution mass spectrometry (GC-HRMS) and gas chromatography/electron capture detector (GC-ECD).

The characterization of the PBDEs was based on the application of four different analytical techniques, gas chromatography/mass spectrometry by electron impact (GC-MS-EI), gas chromatography/mass spectrometry by negative ion chemical ionization (GC-MS-NICI), gas chromatography/high resolution mass spectrometry (GC-HRMS) and gas chromatography/electron capture detector (GC-ECD).

Assignment of values – Certification procedure

The determination of the assigned values and its standard uncertainty for organic contaminants in the IAEA-459 sample were derived applying the robust statistics approach and using the Algorithm A from the ISO standard 13528 [4].
The uncertainties associated with the assigned property values were conducted according to ISO Guide 35 [5]. The relative combined uncertainty of the assigned property value of the CRM involved combining the standard uncertainties associated with the characterization (u_{char}), homogeneity (u_{hom}), and stability (u_{stab}). These different contributions were combined to estimate the final standard uncertainty.
The robust mean of the laboratory means was assigned as certified value, for those compounds where the assigned value was derived from at least five datasets from at least two different analytical techniques, and its relative expanded uncertainty was less than 40 % of the assigned value. Assigned mass fraction values that did not fulfill the criteria of certification are considered information values.
The details concerning all reported results as well as the criteria for qualification as a certified, or information value are reported in "Certification of Polycyclic Aromatic Hydrocarbons, Organochlorine Compounds and Polybrominated Diphenyl Ethers Mass Fractions in IAEA-459 Sediment Sample" IAEA/AQ/52, IAEA, Vienna, 2017 [6]. The report may be downloaded free of charge from:

http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials/Organic_Contaminants_/index.htm
Based on the evidence on calibrators used, quality control procedures applied by the participating laboratories and their generally high quality performance in previous IAEA interlaboratory comparisons, the Certification Committee decided to accept these assigned values as certified or information values as presented in the Tables above.

Statement on metrological traceability, commutability, and uncertainty of assigned values

The property values assigned to the IAEA-459 reference material are calculated as mass fractions of chlorinated pesticides, PCB congeners, PBDE congeners, and PAHs expressed in the derived SI unit µg kg^{-1}. Evidence on metrological traceability to the SI Units of reference materials and calibrators used in the characterization process was provided by all laboratories in their reports. More details may be found in reference [6].

Expanded uncertainties with a coverage factor of k=2, corresponding to a level of confidence of approximately 95%, were calculated according to JCGM100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurement [1].

Intended use

This certified reference material is intended to be used as a quality control material for the assessment of a laboratory's analytical work, for the development and validation of analytical

procedures, and for quality assurance within a laboratory in the determination of chlorinated pesticides, PCBs, polybrominated diphenyl ethers and polycyclic aromatic hydrocarbons in sediment samples with very low concentration levels.

Instructions for use

The reference material is supplied in 50 g units. The minimum recommended sample size for analysis is 3 g.

Dry mass determination

The moisture content of the lyophilized sample as determined by drying to a constant mass at 105°C was found to be (2.8 ± 0.1)%. Since the moisture content can change with the ambient humidity and temperature, it is recommended that it always be determined in a separate sub-sample (not that taken for analysis) by drying to a constant mass (approximately 24 hours) at 105°C. Results should always be reported on a dry mass basis.

Handling and storage

The material should be stored in the dark at temperatures below 30°C.
Analysts are reminded to take appropriate precautions in order to avoid contamination of the material during handling.

Issue and period of validity

The original issue date of this reference material is March 2017. Based on experience with similar materials, the period of validity is March 2027. The IAEA is monitoring the long term stability of the material and customers will be informed in case of any observed change.

Legal disclaimer

The IAEA makes no warranties, expressed or implied, with respect to the data contained in this reference sheet and shall not be liable for any damage that may result from the use of such data.

Compliance with ISO Guide 31:2000

The content of this this IAEA Reference Sheet is in compliance with the ISO Guide 31:2000: Reference materials – Contents of certificates and labels [4].

Citation of this reference sheet

It is suggested to cite this reference sheet according to the following example, as appropriate to the citation format used: INTERNATIONAL ATOMIC ENERGY AGENCY, Reference Sheet for CRM IAEA-459, Mass fractions of Polycyclic aromatic hydrocarbons, organochlorines, and polybrominated diphenyl ethers in IAEA-459 marine sediment sample. IAEA, Vienna, 11 pp.

Note

Certified values as stated in this reference sheet may be updated if more information becomes available. Users of this material should ensure that the reference sheet in their possession is current.

The current version may be found in the IAEA's Reference Materials online catalogue:
http://nucleus.iaea.org/rpst/ReferenceProducts/ReferenceMaterials

Further information:

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[2] LINSINGER T., PAUWELS J., VAN DER VEEN A., SCHIMMEL H., LAMBERTY A., Homogeneity and stability of reference materials, Accredit. Qual. Assur. 6 1 (2001) 20–25.
[3] VAN DER VEEN A., LINSINGER T., PAUWELS J., Uncertainty calculations in the certification of reference materials. 2 Homogeneity study, Accredit. Qual. Assur. 6 1 (2001) 26–30.
[4] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, Statistical methods for use in proficiency testing by interlaboratory comparisons, ISO 13528:2005 (E), ISO, Geneva (2005).
[5] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, ISO Guide 35:2006, Reference Materials – General and Statistical Principles for Certification, ISO, Geneva (2006).
[6] INTERNATIONAL ATOMIC ENERGY AGENCY, Certification of Mass Fractions of Polycyclic Aromatic Hydrocarbons, Organochlorines and Polybrominated Diphenyl Ethers in IAEA-459 Marine Sediment Sample, IAEA Analytical Quality in Nuclear Applications Series No. 52 (IAEA/AQ/52), IAEA, Vienna (2017).

Mr Ales Fajgelj
Chair,
RM Certification Committee

Ms Imma Tolosa
Project Officer,
Marine Environmental Studies Laboratory

Annex 3: List of Participants:

MEDPOL designated participants that sent results

ALBANIA	
Agjencia Kombetare e Mjedisit National Environment Agency (NEA) Ruga Sami Frasheri nr 23 godina nr 4 Tirana	OCs
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CROATIA	
Public Health Institute of County of Istra Nazorova 23 52100 Pula	OCs
GREECE	
Hellenic Centre for Marine Research Institute of Oceanography 46.7km Athens-Sounio Av. Mavro Lithari 19013 Anavyssos	OCs, PAHs
ITALY	
ARPA Toscana Via G. Marradi 114 57126 Livorno	OCs, PAHs
LEBANON	
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SPAIN	
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SYRIA	
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Meeting of the Ecosystem Approach Correspondence Group on Pollution Monitoring

Videoconference, 26-28 April 2021

Agenda item 5: MEDPOL Proficiency Test on the Determination of Trace Elements in Fish Sample (2020)

UNEP/MAP
Athens, 2021

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REPORT

MEDPOL PROFICIENCY TEST
ON THE DETERMINATION OF TRACE ELEMENTS
IN FISH SAMPLE
IAEA-MEL-2020-TE MEDPOL

2020

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TABLE OF CONTENT

1. INTRODUCTION

The International Atomic Energy Agency's Environment Laboratories (IAEA-NAEL), and in particular the Environment Laboratories (NAEL), continues to help Member States understand, monitor and protect the marine environment. Relevant activities comprise the organization of global inter-laboratory comparison, regional proficiency tests, the production of marine certified reference materials and development of recommended analytical methods for trace elements and organic pollutants analysis in marine samples. The Marine Environmental Studies Laboratory (MESL) of NAEL is actively assisting Member States with the organization of inter-laboratory comparisons and provision of certified reference materials.

The IAEA has a long collaboration with UN Environment Programme/Mediterranean Action Plan (UNEP/ MAP) and its Program for the Assessment and Control of Pollution in the Mediterranean region (MED POL) which was initiated as the environmental assessment component of the Mediterranean Action Plan (MAP).

The MESL provides assistance to the designated IMAP competent laboratories via training (trace element, petroleum hydrocarbons and organochlorine compounds), provision of certified reference materials and organisation of targeted proficiency tests (PTs) on matrices of relevance to the marine monitoring studies.

The periodic external assessments of measurement performances of monitoring laboratories via interlaboratory comparisons (ILCs) and targeted proficiency tests (PTs) are of crucial interest for laboratories as they provide clear information of their measurement capabilities. These exercises are designed not only to monitor and demonstrate the performance and analytical capabilities of the participating laboratories, but also to identify gaps and problem areas where further development is needed.

This report describes the results of the PT on the determination of selected trace elements in fish sample organised by the MESL in 2020 for the designated IMAP Pollution Cluster competent laboratories. In line with the conclusions of the Meeting of the Ecosystem Approach Correspondence Group on Pollution Monitoring (April, 2019), this report is complemented with the individual evaluation reports for each specific laboratory that participated in 2020 PT, as well as the national reports. The individual reports have been shared by MESL with the laboratories, while the National

Reports for all 2020/2021 activities will be prepared for submission to MEDPOL Focal Points respectively to designated IMAP laboratories in November 2021.

The IAEA officers responsible for this publication are S. Azemard, E. Vasileva, Mr. A. Trinkl from NAEL Terrestrial Laboratory was responsible for the management of the on-line reporting system. This report has also been revised by the MED POL Monitoring and Assessment Officer, Jelena Knezevic and IAEA Scientific Secretary, Sylvia Sander.

2. SCOPE OF EXERCISE

In July 2020 the MED POL Monitoring and Assessment Officer contacted MEDPOL Focal Points of the Contracting Parties of Barcelona Convention that are eligible for participation in Proficiency Testing for IMAP CI 17, according to procedures of IAEA-MESL, requesting them to provide the names of the designated national laboratories, involved in implementation of IMAP CI 17. The final list of designated national laboratories, respectively participants in the organised by MESL targeted proficiency test for trace elements in marine environment, was established at the end of August 2020.

The test material, named ***IAEA-MEL-2020-TE MEDPOL*** sample, was sent to 18 designated monitoring laboratories from 15 countries. Figure 1 shows the distribution of PT samples in MED POL countries, and the distribution per countries of received results.

Participating laboratories, thereafter, also called participants received together with the sample an information sheet (see Annex 3) with information on expected concentration range of analytes, protocol for determination of moisture and explanation on expected reported results and information., Participants were requested to use their established analytical methods usually applied for IMAP /MED POL monitoring studies, for the determination of total contents of the mandatory elements: Cd, Hg and Pb and additional elements: As, Co, Cr, Cu, Fe, Mn, MeHg, Ni, and Zn in IAEA-MESL-2020-TE-MEPDOL-PT sample, as well as in one matrix matching quality control sample.

The deadline for reporting the results back to the MESL was originally set to 2 November 2020, but deadline was extended to 1st December. Finally, 15 out of 18

(83%) participating laboratories proposed for participation in this proficiency testing sent their results in the requested deadlines.

Laboratories participating in the present exercise are listed in the

Annex 1:

List of participants

Designated IMAP Competent laboratories that sent results

1. Designated IMAP competent laboratories which did not report the results are listed in the Annex 2.

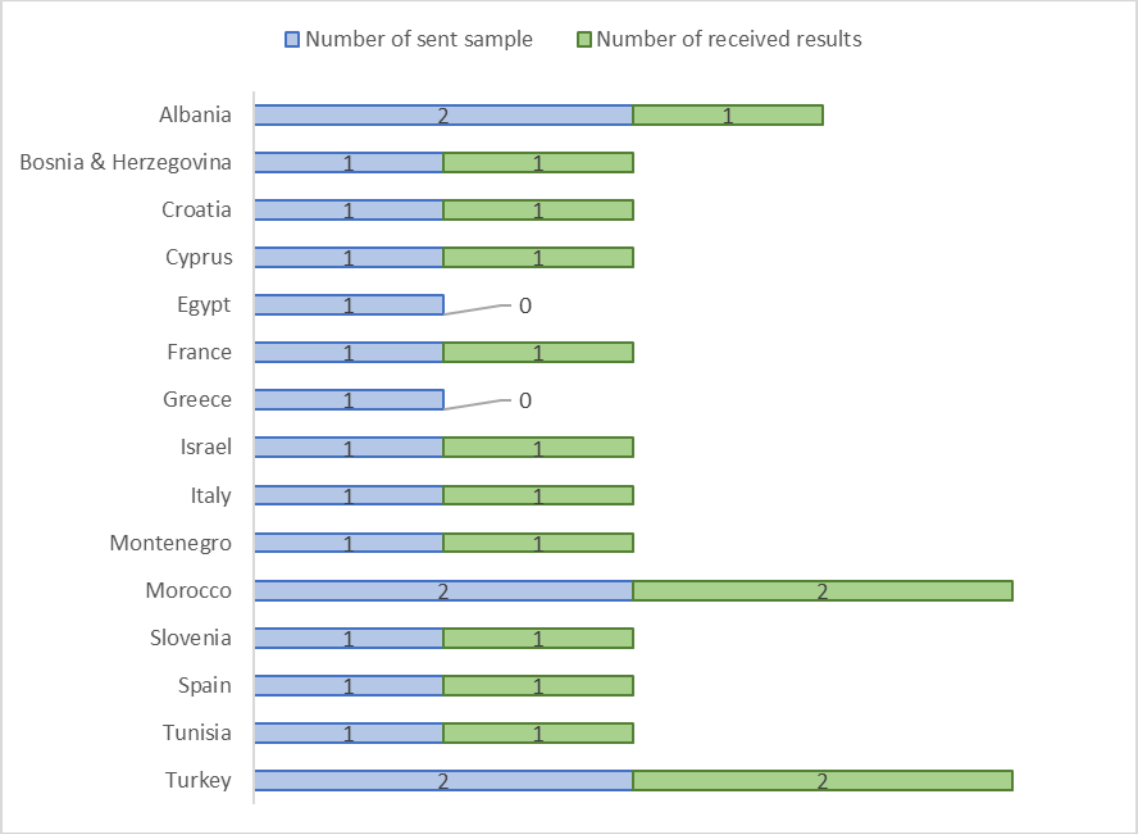


FIG. 1. Distribution per country of the MED POL PT sample

3. MATERIAL

3.1. Preparation of the material

Fish flesh homogenate from North Sea was used for preparing IAEA-MESL-2020-TE-MEPDOL-PT test sample The Fish flesh homogenate was freeze dried, sieved at 250µm, mechanically homogenized and packed in plastic sealed containers.

Homogeneity tests were performed at the MESL following the requirements ISO 35 guidelines [1], using preliminary validated in MESL's trace elements laboratories analytical methods.

3.2. Assigned values and their uncertainties

The assigned values for the trace element mass fractions of IAEA-MESL-2020-TE-MEPDOL-PT sample were calculated according to the requirements of the ISO 17043 standard [2]. The assigned values were calculated as Robust mean (ISO 13528 [3]) from the results reported by the participants in this PT and results obtained in the MESL with preliminarily validated analytical methods.

To ensure the best possible estimate of the assigned values, the following criteria have been set before applying robust statistics:

- Rejection of data reported without QC;
- Visual inspection of results, kernel density plot [4] to evaluate potential bimodality of distribution;
- Comparison with IAEA values as expert laboratory;
- Review of data based on technical validity.

As a results of dataset evaluation, some reported data have been excluded before applying robust statistics; details are shown in the table 1.

Table 1: REPORTED VALUES REJECTED BEFORE CALCULATION OF ROBUST MEANS

ANALYTE	LAB CODE	Comments
ALL	3	No QC, rejected all data before calculation of assigned values
As	13	Appears like extreme outlier, rejected
Co	8	Expected mass fraction (from IAEA) is < reported LOD
Pb	8, 14, 16	Bimodality Based on IAEA values the first mode is kept, and three values are rejected before applying robust statistics.

Expanded uncertainties of assigned values for trace element mass fractions were calculated according to the ISO standard 35 [1], using equation (Eq1).

$$U = k \times \sqrt{u_{char}^2 + u_{stab}^2 + u_{hom}^2} \qquad (1)$$

where:

k: coverage factor, *k* = 2, representing level of confidence of about 95%

u_{char} is the uncertainty of characterization, estimated according to the recommendations of the ISO 35 [1] using Eq. (2); u_{stab} is the standard uncertainty, due to long term stability of the sample. Based on our experience u_{stab} component was considered to have negligible contribution and was set at 1%;

u_{hom} is the standard uncertainty, due to between unit inhomogeneity, evaluated by ANOVA [1].

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

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

All assigned values (Xass) of trace element mass fractions, expanded uncertainties (U) and the standard deviation for the proficiency assessment (also called target standard deviation, see 4.2)), obtained in this study are presented in Table 2. For Cr expanded uncertainty was beyond 20%, therefore the value is given for information only and was not used for the evaluation of measurement performances of laboratories, participating in this PT.

TABLE 2: ASSIGNED VALUES FOR TRACE ELEMENTS IN THE PT SAMPLE

	Xass - Assigned Values (mg kg^{-1})	U (mg kg^{-1}) (k=2)	Target standard deviation(mg kg^{-1})
As	4.7	0.4	0.6
Cd	0.78	0.06	0.1
Co	0.063	0.009	0.008
Cr	*0.7*	*0.2*	*0.09*
Cu	3.9	0.2	0.5
Fe	137	16	17
Hg	0.115	0.009	0.014
Mn	6	0.4	0.8
Ni	0.6	0.12	0.07
Pb	0.051	0.007	0.006
Zn	103	4	13

4. EVALUATION OF RESULTS

4.1. Data Reporting

Data were reported through the IAEA on-line reporting system. Participants were asked to report data for trace elements ((as listed in information sheet) and to fill a questionnaire (see Annex 3)

All participants were able to download their draft preliminary evaluation report (reporting assigned values, reported values z and Zeta-scores) at the middle of December 2020 through the online portal.

All results disseminated in this report are only referring to a laboratory code number, to protect the Participants confidentiality. However, as agreed with the participants the laboratory codes will be shared with UNEP/MAP – MEDPOL and respective MEDPOL Focal Point as part of the capacity building and quality assurance programme of MEDPOL.

4.2. Evaluation criteria

Individual laboratory performance was evaluated with *z* and Zeta scores as recommended in the ISO guide 17043 [2]

$$z = \frac{x_{lab} - X_{ass}}{\sigma_p} \quad (3)$$

$$\text{zeta} = \frac{x_{lab} - X_{ass}}{\sqrt{u_{lab}^2 + u_{ass}^2}} \quad (4)$$

Where:

x_{lab} is the measurement result reported by participant;

X_{ass} is the assigned value of mass fractions for TEs in PT sample;

σ_p is the target standard deviation or standard deviation for proficiency assessment;

U_{ass} is the standard uncertainty of the assigned value;

u_{lab} is the standard uncertainty reported by participant.

The interpretation of a laboratory's performance was according to the following generally accepted criteria [2].:

$|z \text{ or Zeta}| \leq 2$ Satisfactory

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

***z*-score:** This score expresses the difference between the reported mass fraction of the laboratory and the assigned mass fraction in the same unit for each analyte. *z*-score represents a simple method of giving each participant a normalized performance score for the measurement bias of the respective measurement result. The standard deviation for the proficiency assessment (also called target standard deviation), σ_p, was set to be fit for purpose and was fixed to 12.5 % of the assigned values. The determination of target standard deviation was done on the basis of the outcome of previous ILCs organised by the MESL for the same population of laboratory. The appropriateness of this level of tolerated variability of results was confirmed by calculation of the robust standard deviation of the participants' results and the uncertainty of the assigned values for the respective measurements.

Zeta-Score: This score state if the participant result agrees with the assigned value within the respective uncertainties. The denominator of equation 4 is the combined uncertainty of the assigned value and the measurement uncertainty reported by the participant. When the uncertainties were not reported by participating laboratories, Zeta-score was not calculated.

4.3. Overview of the reported measurement results

15 laboratories provided results for the analysis of the PT sample by the final deadline, comprising 114 measurement results. Graphical presentations of z-score and Zeta-scores are presented in Annex 2 with a summary on the statistical evaluation of reported results for the respective trace element. Kernel density plots [4] are also presented in Annex 2.

4.4. Laboratory results and scoring

4.4.1 *z*-scores

The measurement performance of participating laboratories was assessed by *z*-scores. Obtained results are summarized in Table 3 and on Figure 2 and 3. The number of evaluated analytes per participant is displayed in Figure 2.

A total 104 *z*-scores were calculated. Overall, 87% of reported measurement results were assessed as satisfactory, 2% as questionable and 12% as unsatisfactory. From 15 participating laboratories, 8 laboratories (53%) reported 100% of their measurement results with $|z| \leq 2$ and all laboratories except 1 could report at least half of their results evaluated as satisfactory. Extreme z-scores >7 have been obtained for about 7% of reported results.

Nickel, lead and cobalt are analytes with higher percentage of unsatisfactory z scores probably reflecting unresolved analytical problems with those analytes at low levels.

4.4.2 Zeta-scores

The Zeta-score shows if the laboratory result agrees with the assigned value within the respective combined uncertainty. It should be mentioned that an unsatisfactory Zeta-score can be caused either by an incorrect measurement result or by an inappropriate estimation of the respective measurement uncertainty, or by both.

Zeta-score results obtained in this PT are summarized in Table 4 and presented in in Figure 4 and 5. The number of evaluated analytes per participant is displayed in Figure 4.

About 67% of measurement results were reported with uncertainties. Zeta-scores were calculated for 10 of participating laboratories (66%), 5 of participating laboratories (33%) did not report measurement uncertainties, which made the calculation of Zeta score impossible. It should be noted that 2 out of 5 laboratories that did not provide uncertainties claim to be accredited against ISO 17025.

74% of the calculated Zeta-scores are considered as satisfactory but only 2 laboratories reported 100% of their results with Zeta-scores below 2. The results show that there are still remaining problems with the realistic estimation of the combined measurement uncertainty. Some laboratories have reported unrealistically small uncertainties (i.e less than 2.5%)

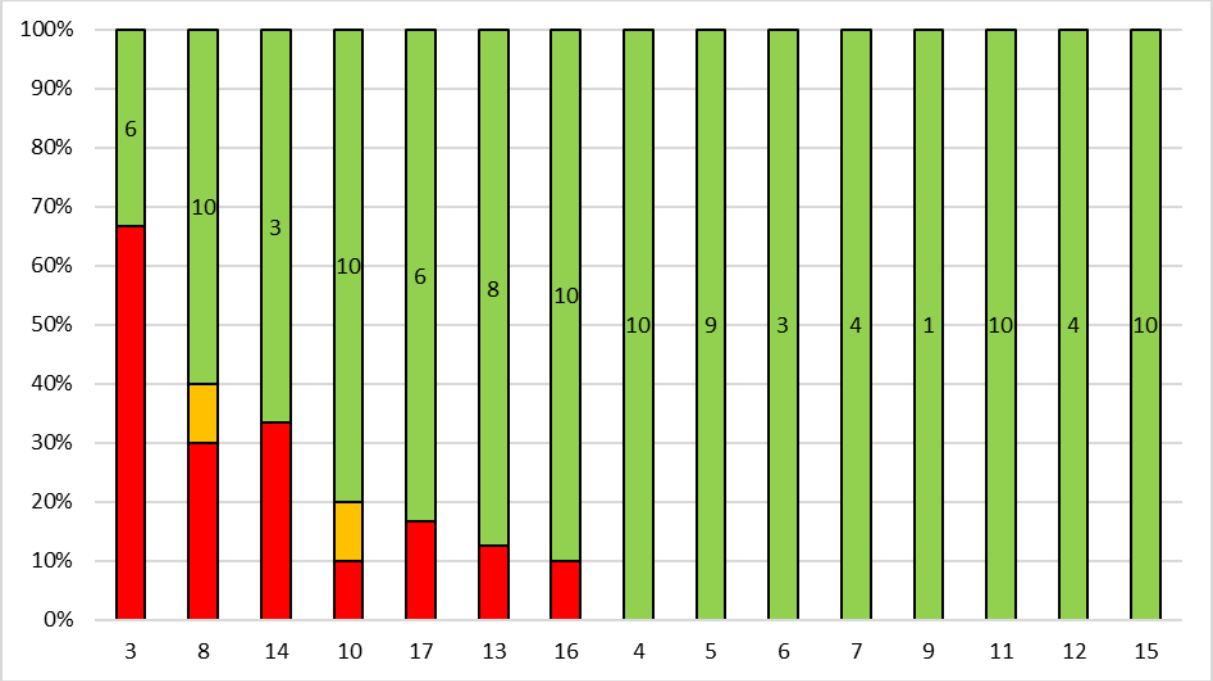
It should be mentioned here that an unsatisfactory Zeta-score can also be caused by an inappropriate evaluation of the mass fraction of the respective trace element.

TABLE 3: ALL CALCULATED z-SCORES. Blue fonts are z-scores 2< | *z* | <3, and red highlighted fields being z-scores | *z* |>3.

Lab. Code	As	Cd	Co	Cu	Fe	Hg	Mn	Ni	Pb	Zn
3		17.79	515.17	-3.54	-0.04		0.00			-3.59
4	-1.45	0.28	-0.38	0.13	-0.54	0.33	0.21	1.83	1.20	-0.13
5	1.86	0.67	-1.02	0.14	0.53		1.42	-0.71	-0.99	1.51
6		0.99				0.93			-0.43	
7	-0.04	-0.63				-0.31			1.22	
8	1.30	0.07	12.28	0.41	-0.06	2.43	0.09	-4.13	25.99	-0.16
9						-0.70				
10	-0.10	-0.20	1.06	-0.26	2.82	-0.35	-0.01	9.73	0.05	-0.08
11	0.42	0.61	-1.09	-0.57	0.31	1.23	-0.09	0.23	-0.05	0.13
12					-0.90	-0.30	-0.96			0.58
13	-6.11	-0.17		1.75	-0.11	-1.02	-0.60		-1.27	0.24
14		-1.75				-0.28			37.33	
15	-0.14	-0.48	0.72	-0.08	-0.66	0.09	0.30	-0.76	0.52	0.26
16	-1.41	-0.24	-0.63	0.27	-0.13	-1.76	0.18	1.13	28.55	-0.86
17		-3.03		-0.31	0.05	1.67	-0.56			-0.26

TABLE 4: ALL CALCULATED ZETA –SCORES. Blue fonts are Zeta-scores 2< │Zeta│ <3, and red highlighted fields being Zeta-scores │Zeta│>3.

Lab. Code	As	Cd	Co	Cu	Fe	Hg	Mn	Ni	Pb	Zn
3										
4										
5	3.10	1.27	-1.60	0.30	0.84		2.62	-0.81	-1.42	3.03
6		1.54				1.65			-0.41	
7										
8	2.71	0.22	21.62	1.79	-0.12	7.83	0.33	-4.90	15.38	-0.55
9						-2.45				
10	-0.15	-0.22	1.03	-0.40	2.34	-0.51	-0.02	5.10	0.05	-0.10
11	1.05	1.09	-1.71	-2.06	0.52	2.28	-0.24	0.26	-0.06	0.42
12										
13	-12.08	-0.22		2.18	-0.12	-1.25	-1.02		-1.38	0.45
14		-4.45				-0.29			17.50	
15	-0.28	-1.01	1.13	-0.21	-1.27	0.21	0.78	-0.87	0.67	0.68
16										
17		-7.45		-0.61	0.08	1.07	-1.14			-0.54



c. Summary of obtained z-scores per participant, number are total number of evaluated analytes

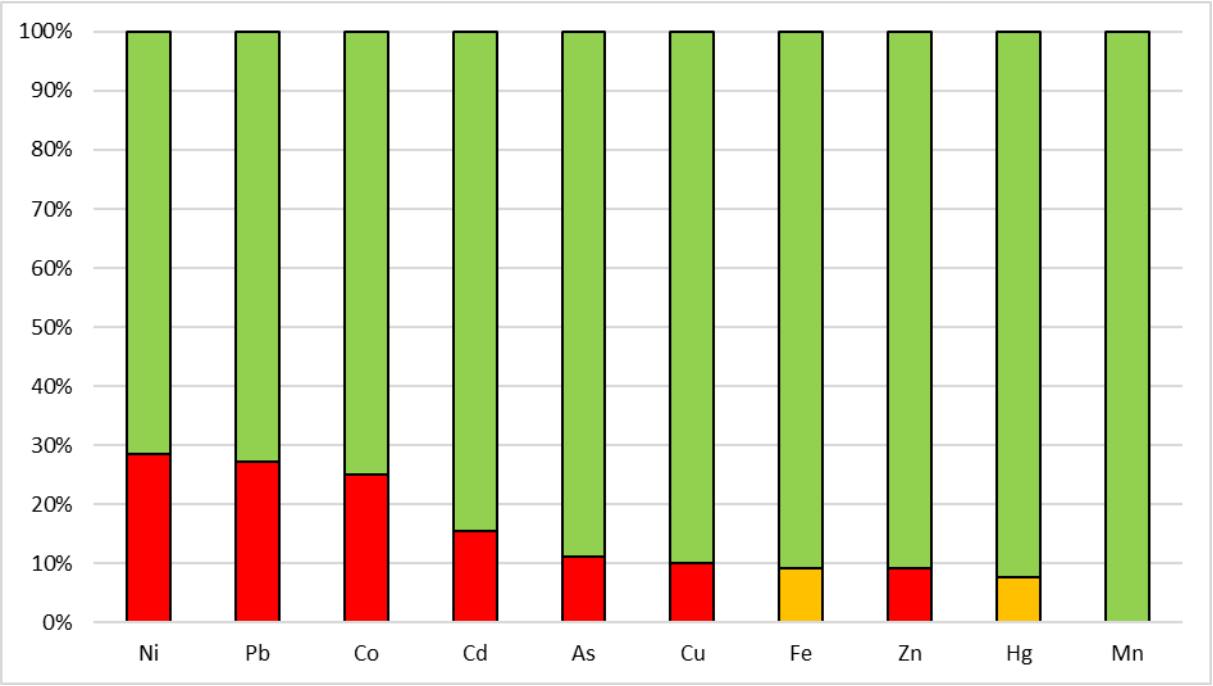


FIG. 2. Summary of obtained z-scores per element

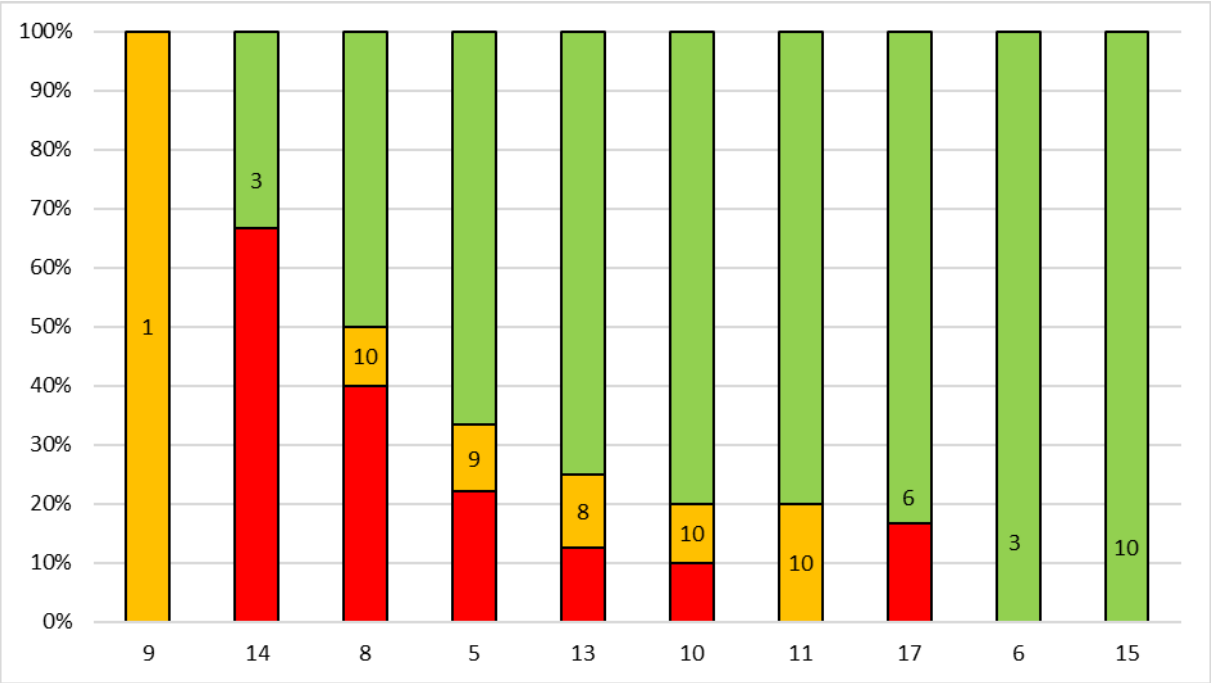


FIG. 3. Summary of obtained Zeta-scores per participants number are total number of evaluated analytes

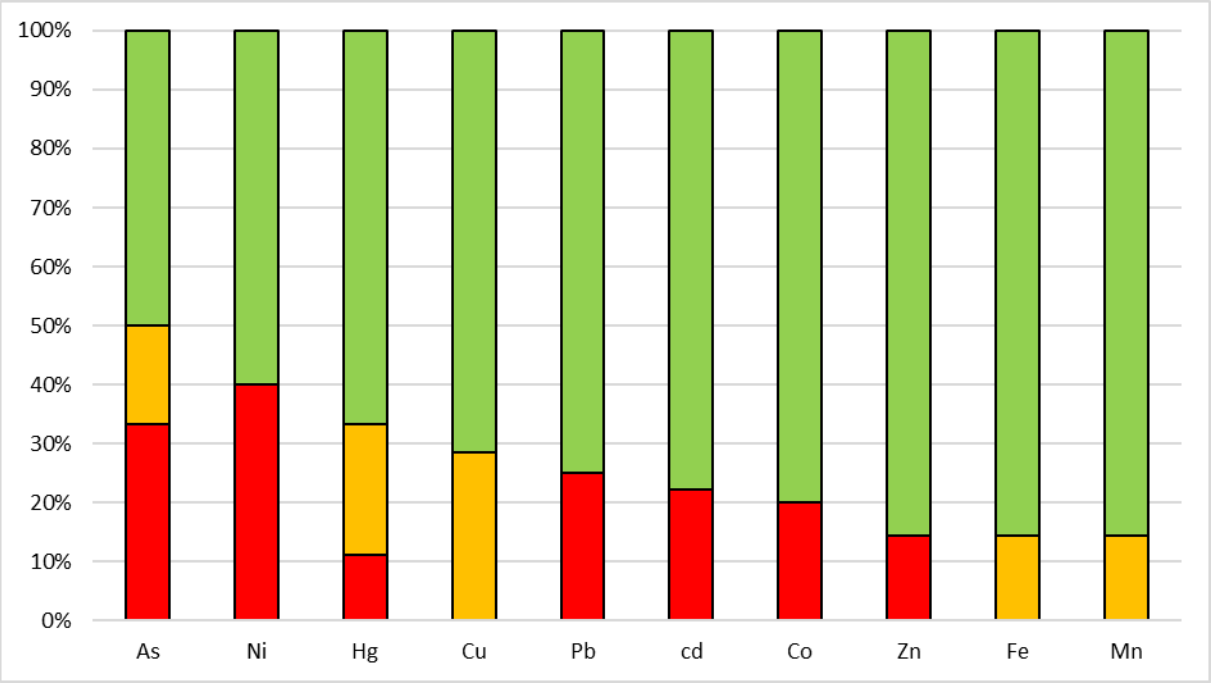


FIG. 4. Summary of obtained Zeta-scores per element

4.5. Sample treatment, use of CRM and recovery correction

All participating IMAP competent laboratories applied microwave digestion, using nitric acid with or without addition of hydrogen peroxide. For total mercury determination 46% of laboratories used solid mercury analyser and did not apply any sample preparation before the instrumental measurement.

Freeze drying step was a part of sample processing procedure for the IAEA-MESL-2020-TE-MEPDOL-PT sample. Depending on local storage and humidity conditions, the PT sample might absorb water from the laboratory environment. As the moisture is an operationally dependent parameter, the procedure for moisture content determination in the PT sample was carefully developed and provided in the information sheet, describing details on the MED POL/MESL PT exercise. Oven drying for a separate portion of sediment sample at 85°C until constant weight was the recommended procedure for moisture determination. Only 5 participating laboratories have respected this procedure, while most of the remaining participants applied in house developed protocol. One participant declared not to correct for moisture. The moisture content reported by the laboratories was in the range from 1 to 9%.

In order to provide traceable results and to confirm the validation of the methods used, designated IMAP competent laboratories have been systematically requested to analyse a CRM with a matrix and concentration range similar to the PT sample. CRMs used from the participating laboratories in the PT exercise, were generally selected accordingly. Out of the 15 data sets received, only 1 participant (laboratory 3) did not include quality control (QC) results in the reporting form.

Eight laboratories reported recoveries, but only 1 of them claimed implementing correction for recovery for all, or part of reported trace elements mass fraction. Interestingly, a considerably high proportion of laboratories that did not correct for recovery obtained satisfactory scorings. This is an indication that the laboratories have correctly estimated that the recoveries achieved with the used analytical procedures were not significantly different from 100%.

4.6. Analytical techniques used by participants:

Abbreviations of the instrumental techniques used in this exercise are given in Table 5. As it can be seen from Figure 6, ICP-MS is the most used instrumental technique, followed by ICP-OES. Solid mercury analyser represents about half of reported results for mercury.

TABLE 5: ANALYTICAL TECHNIQUES ABBREVIATIONS

Method Code	Instrumental Technique
AAS	Atomic Absorption Spectrometry
AFS	Atomic Fluorescence Spectrometry
F	Flame
ET	Graphite Furnace
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
CV	Cold Vapour
MP-AES	Microwave Plasma Atomic Emission Spectrometry

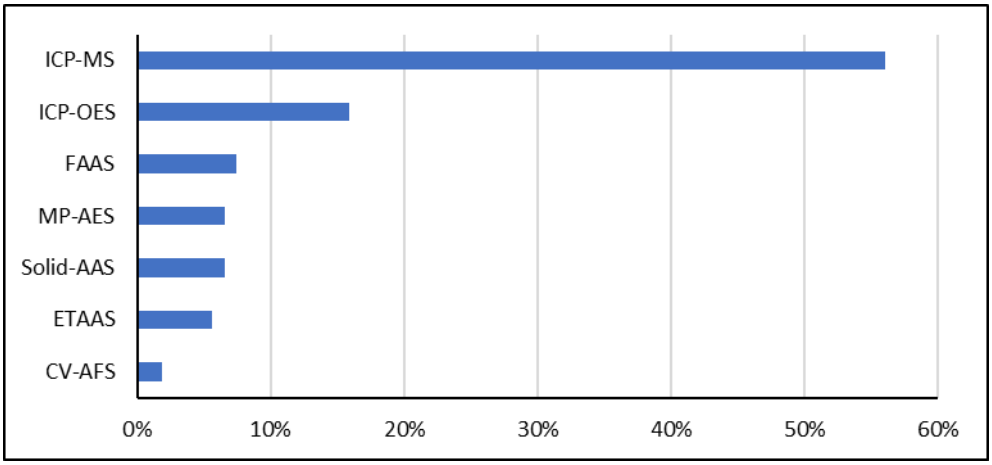


FIG. 5. Graphical distribution of instrumental techniques, applied in the present PT

4.7. Answer provided to the questionnaire

As mentioned in 4.1, participants were requested to answer a questionnaire (Annex 3), to reply to questions on analytical methods used and quality assurance measured taken to assure the traceability of their results. Two laboratories did not report any information in the questionnaire.

Seven laboratories claimed to be accredited, however 2 of them were not reporting measurement uncertainties and also did not claim using a validated method, both of which should be part of a result provided by an accredited laboratory. Two out of the seven accredited laboratories are however not accredited for biological matrix, while one is accredited only for Hg.

Ten laboratories applied preliminary validated methods, and 10 participants declared to have quality system in place. Out of seven laboratories not reporting their limits of detection and quantification, three claimed to use validated methods which should imply the estimation of those parameters.

Four participants did not explain how they have assured the traceability of obtained results.

5. CONCLUSIONS AND RECOMMENDATIONS

The MEDPOL/MESL proficiency tests is part of the capacity building activity for IMAP competent laboratories. To make the most of this activity, participants are advised to review their data element-by-element, especially in the cases where the *z*-score or/and Zeta-score are above 2. The use of the *z*-scores will help to identify systematic errors in the measurement results (e.g. from calibration or reagent contamination) and should ultimately improve data quality.

To get a realistic estimation of the laboratory's performance, the proficiency test sample should be treated in exactly the same way as any routine test sample. Examples of 'poor practice' include:

- Having the PT samples analysed by the most experienced analyst;
- Reporting only the 'best' results, rather than all.

In the case of unsatisfactory performance each laboratory should carefully investigate the cause of the unsatisfactory scores (i.e. $|z| > 3$) and put in place the necessary corrective actions to prevent the problem reoccurring. This is one of the requirements for laboratories accredited according to the ISO/IEC 17025 standard.

The concept of recovery is still not implemented in several laboratories and consequently the validation of the analytical methods, used by them is often questionable.

All except one laboratory provided results for the use of CRMs in their analytical procedure, which means that the internal quality control in those laboratories is in place.

In the MED POL PT exercise the uncertainty of measurement results was calculated from 67% of the participants. Considering the Zeta-scores reported, we can conclude that the way of calculation and application of uncertainty concept is still questionable for some of the laboratories participating in the MEDPOL PT and further training on uncertainty of measurement results is highly recommended.

Three (16%) from 18 designated MED POL laboratories did not send the PT results by the deadline, which make the evaluation of their measurement performance impossible.

Two national laboratory mission visits were conducted in early 2020 by MESL experts. The focus of the gap-finding visits was aimed at the identification of technical (e.g. acquisition of laboratory equipment) and knowledge needs to strengthen the understanding for applying the analytical methods and good laboratory practices in line with the requirements of IMAP Common Indicator 17.

6. REFERENCES

[1] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide *35 (2005), Reference Materials-General and statistical principles for certification, ISO, Geneva, Switzerland.*

[2] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide *17043 (2010), Conformity assessment, general requirements for proficiency testing, ISO, Geneva, Switzerland.*

[3] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide *13528 (2005), Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons, ISO, Geneva, Switzerland.*

[4] ROYAL SOCIETY OF CHEMISTRY, Statistical Subcommittee of the Analytical Methods Committee (AMC), AMC Technical Brief: Representing data distributions with Kernel density estimates" 2006, www.rsc.org/amc.

Annex 1:

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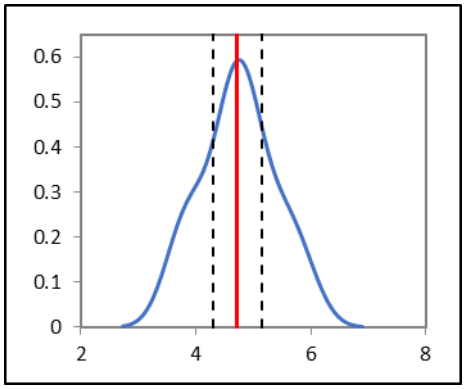
Annex 2:

Graphical representation

Reported data for As in IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



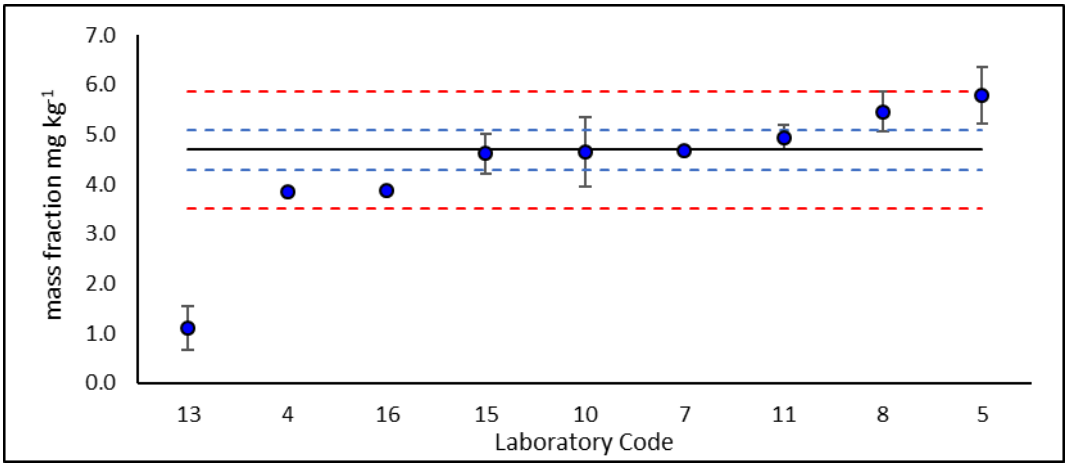
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	89%	0%	11%
Zeta-score	50%	17%	33%

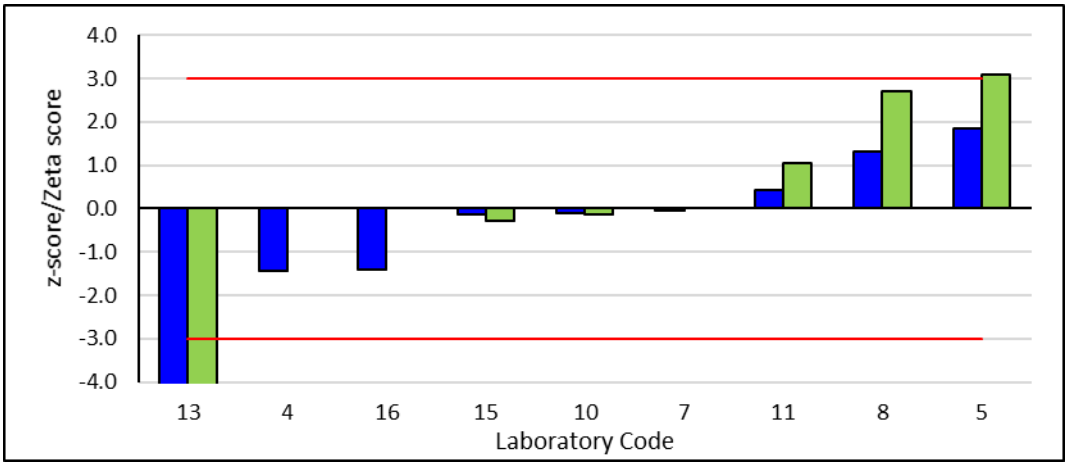
X_{Ass} mg kg^{-1}	4.7
U_{Ass} (k=2) mg kg^{-1}	0.4
$2\sigma_p$ mg kg^{-1}	1.2
Number of results:	9
Number of methods:	3

Reported results and expanded uncertainties:

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

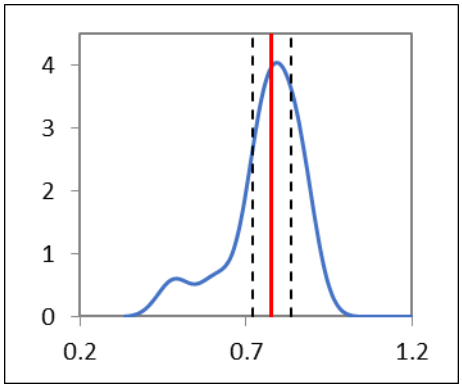


Performance evaluation: z-score Zeta-score



Reported data for Cd in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



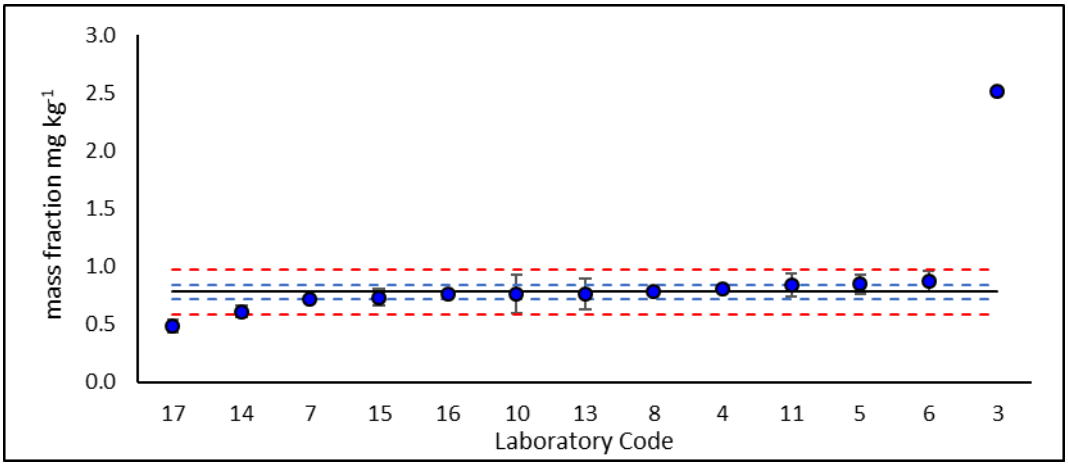
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	85%	0%	15%
Zeta-score	78%	0%	22%

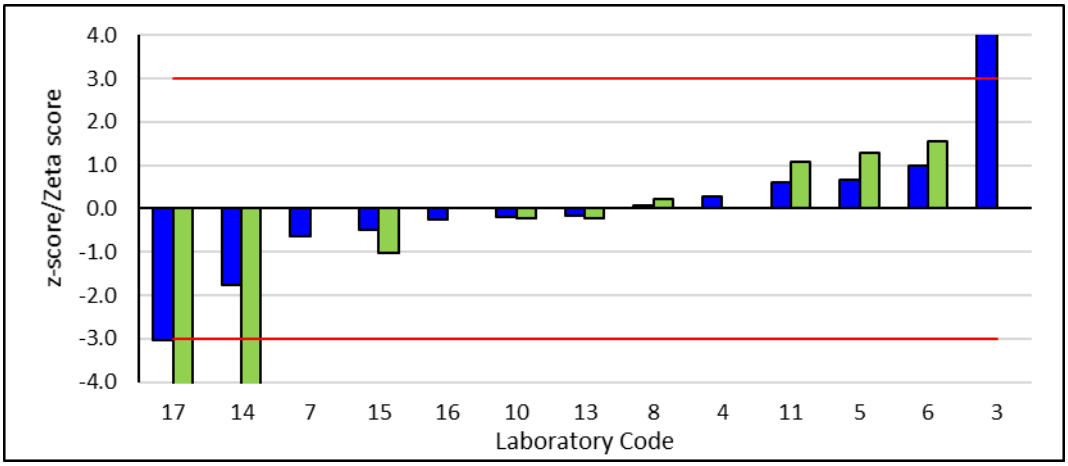
X_{Ass} mg kg^{-1}	0.78
U_{Ass} (k=2) mg kg^{-1}	0.06
$2\sigma_p$ mg kg^{-1}	0.19
Number of results:	13
Number of methods:	5

Reported results and expanded uncertainties:

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

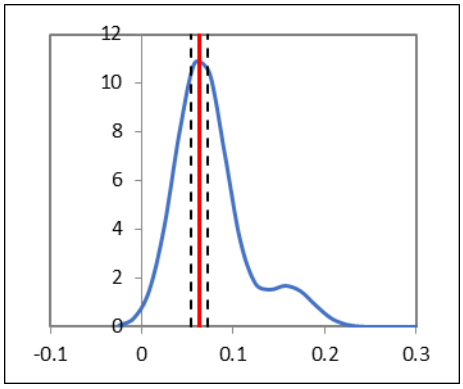


Performance evaluation: z-score Zeta-score



Reported data for Co in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



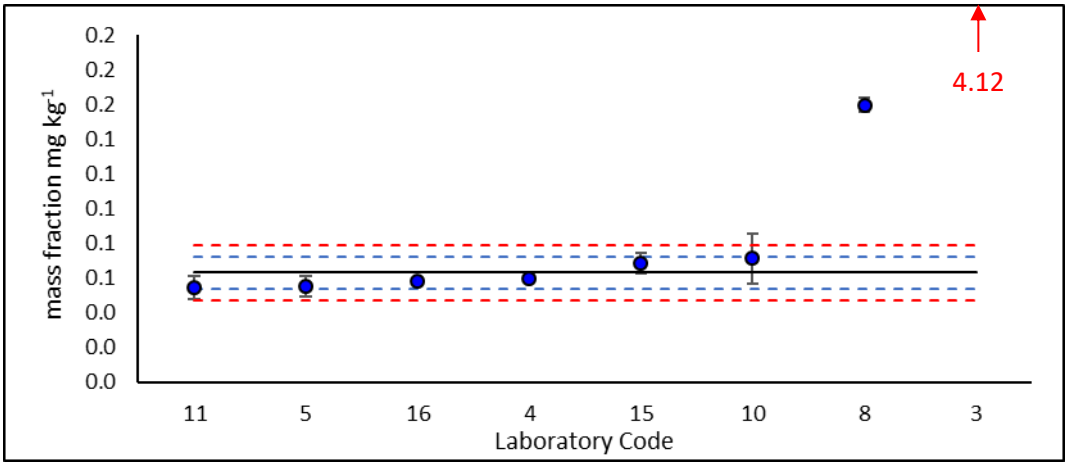
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	75%	0%	25%
Zeta-score	80%	0%	20%

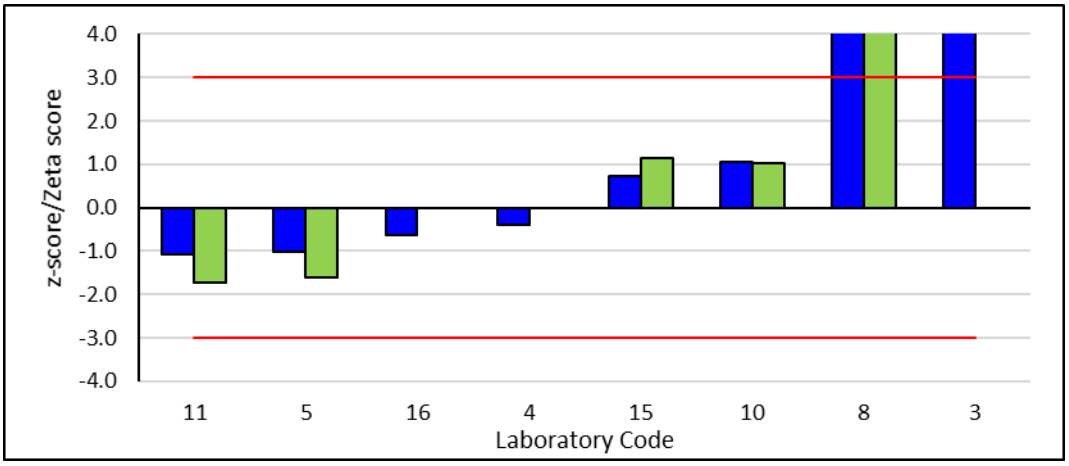
X_{Ass} mg kg^{-1}	0.063
U_{Ass} (k=2) mg kg^{-1}	0.009
$2\sigma_p$ mg kg^{-1}	0.016
Number of results:	8
Number of methods:	3

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)

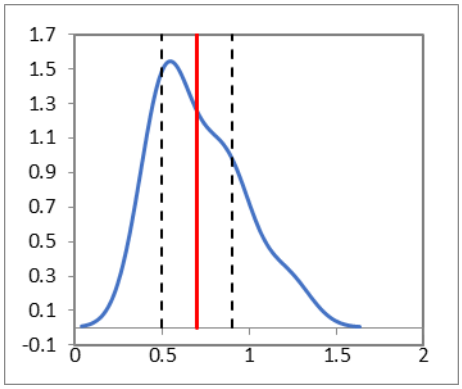


Performance evaluation: z-score Zeta-score



Reported data for Cr in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot

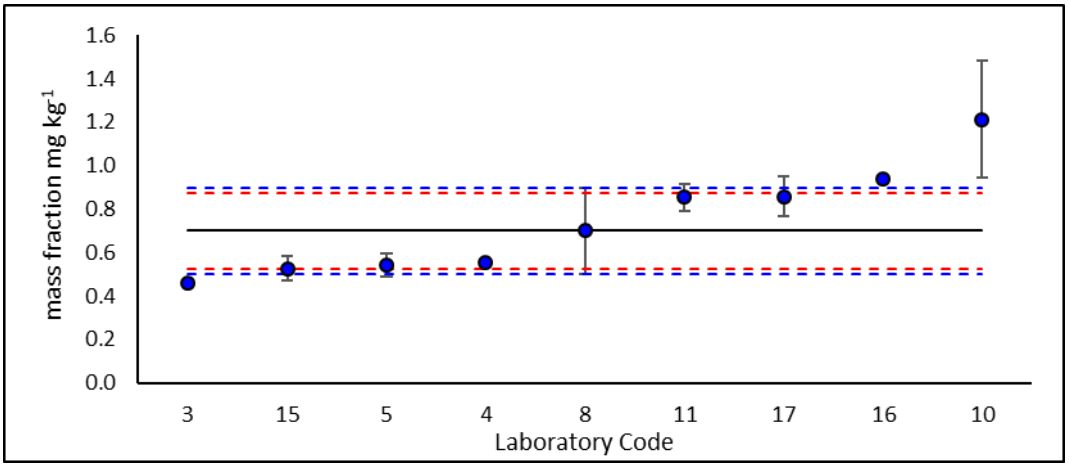


Summary of results:

X_{info} mg kg^{-1}	0.7
U_{Info} (k=2) mg kg^{-1}	0.2
$2\sigma_p$ mg kg^{-1}	0.16
Number of results:	9
Number of methods:	3

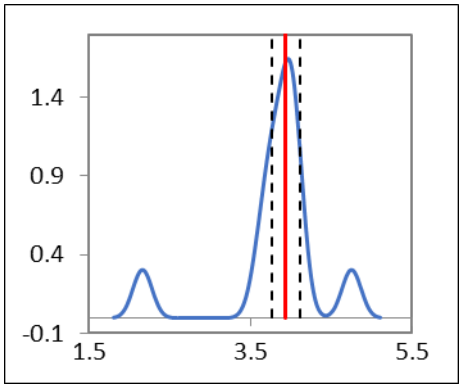
Reported results and expanded uncertainties:

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



Reported data for Cu in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



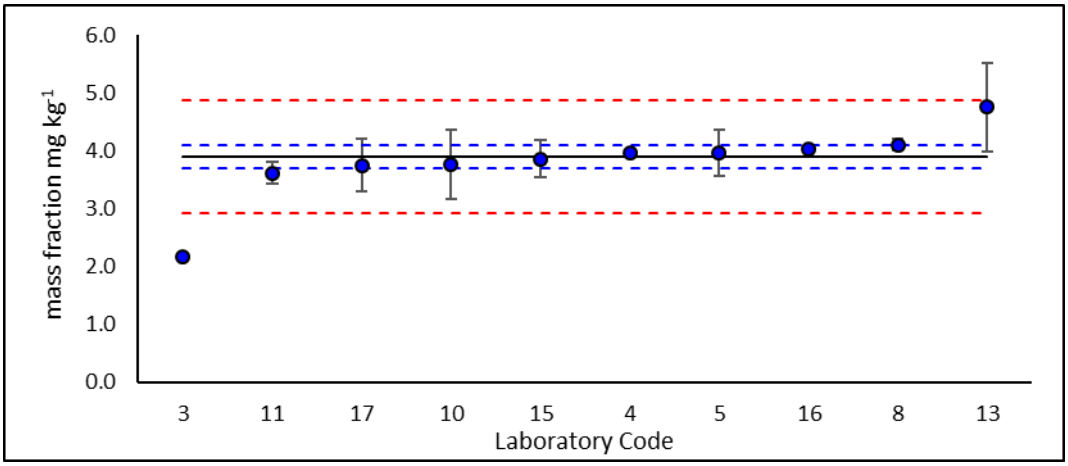
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	90%	0%	10%
Zeta-score	71%	29%	0%

X_{Ass} mg kg^{-1}	3.9
U_{Ass} (k=2) mg kg^{-1}	0.2
$2\sigma_p$ mg kg^{-1}	0.1
Number of results:	10
Number of methods:	4

Reported results and expanded uncertainties:

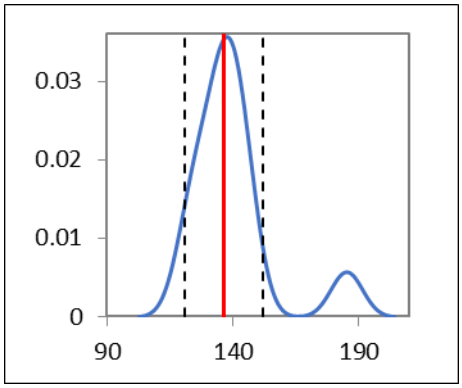
— X_{Ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{Ass} \pm 2\sigma_p$; ---- $X_{Ass} \pm U_{Ass}$ (k=2)



Performance evaluation: z-score Zeta-score

Reported data for Fe in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



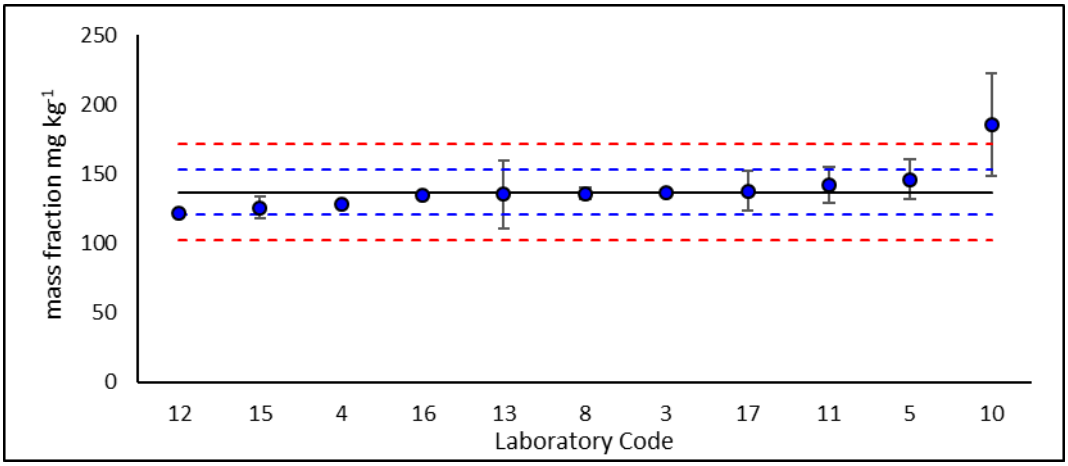
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	91%	9%	0%
Zeta-score	86%	14%	0%

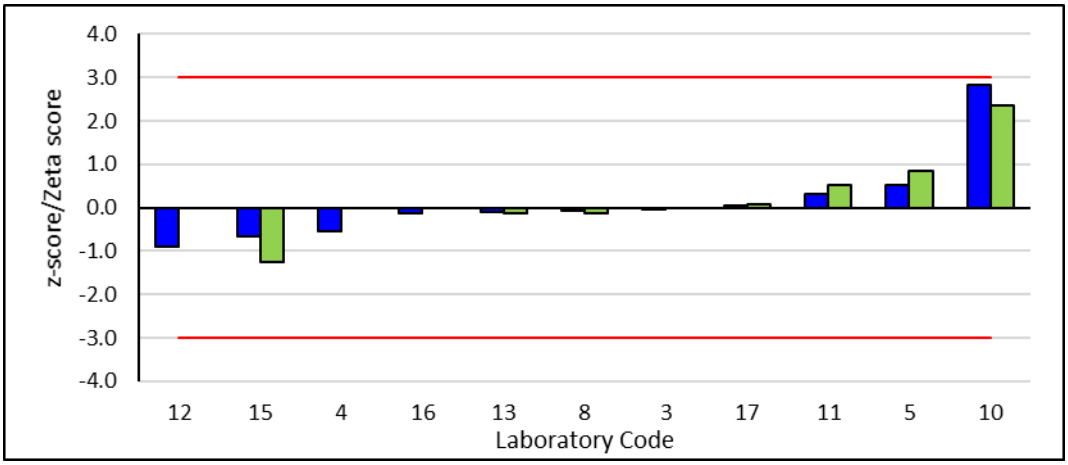
X_{Ass} mg kg^{-1}	137
U_{Ass} (k=2) mg kg^{-1}	16
$2\sigma_p$ mg kg^{-1}	34
Number of results:	11
Number of methods:	4

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)

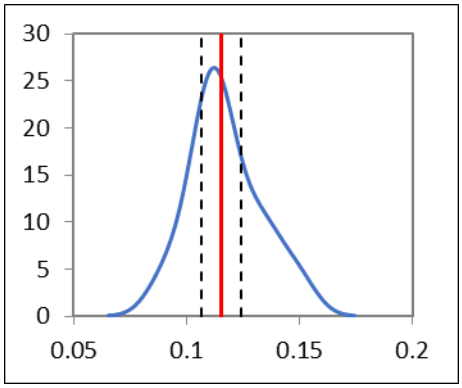


Performance evaluation: z-score Zeta-score



Reported data for Hg in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



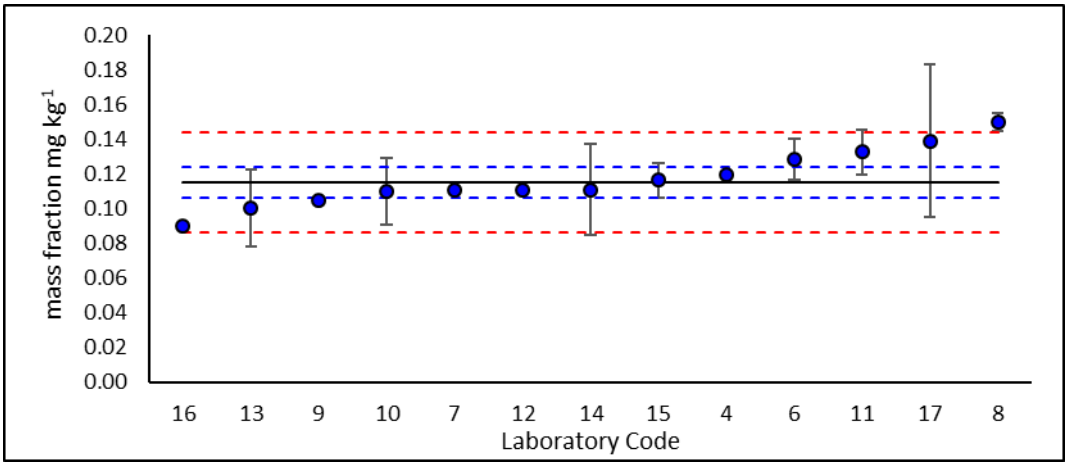
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	92%	8%	0%
Zeta-score	67%	22%	11%

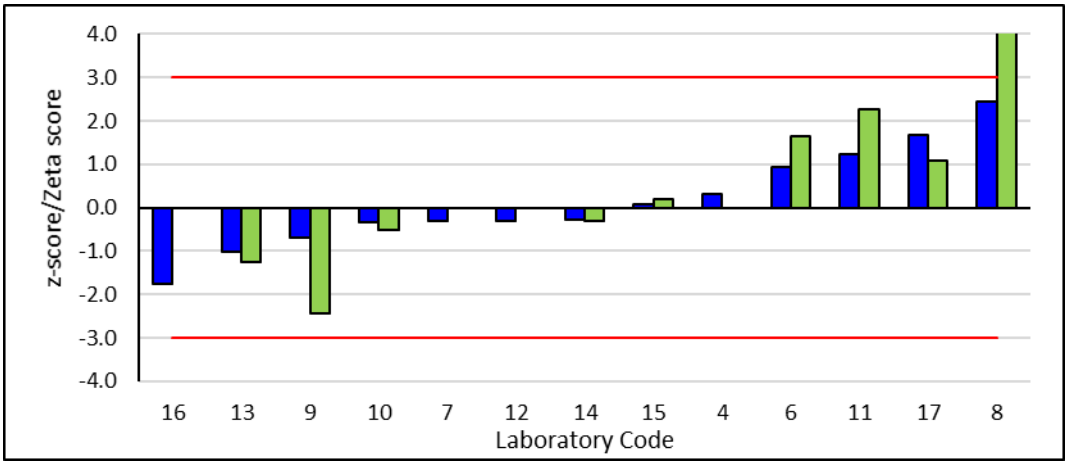
X_{Ass} mg kg^{-1}	0.115
U_{Ass} (k=2) mg kg^{-1}	0.009
$2\sigma_p$ mg kg^{-1}	0.029
Number of results:	13
Number of methods:	4

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)

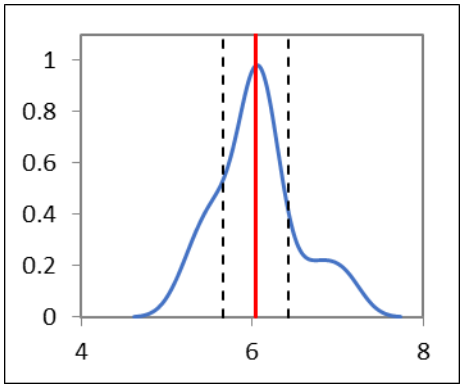


Performance evaluation: z-score Zeta-score



Reported data for Mn in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



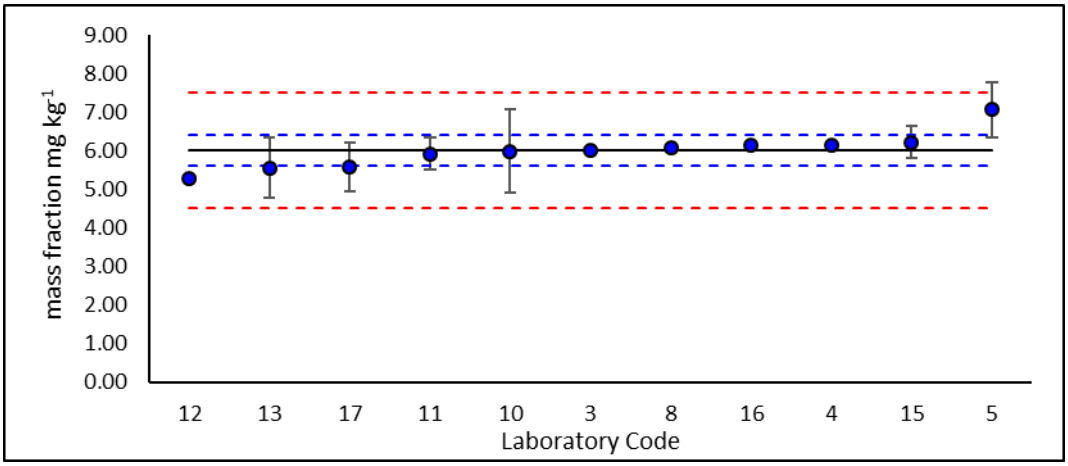
Summary of results:

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

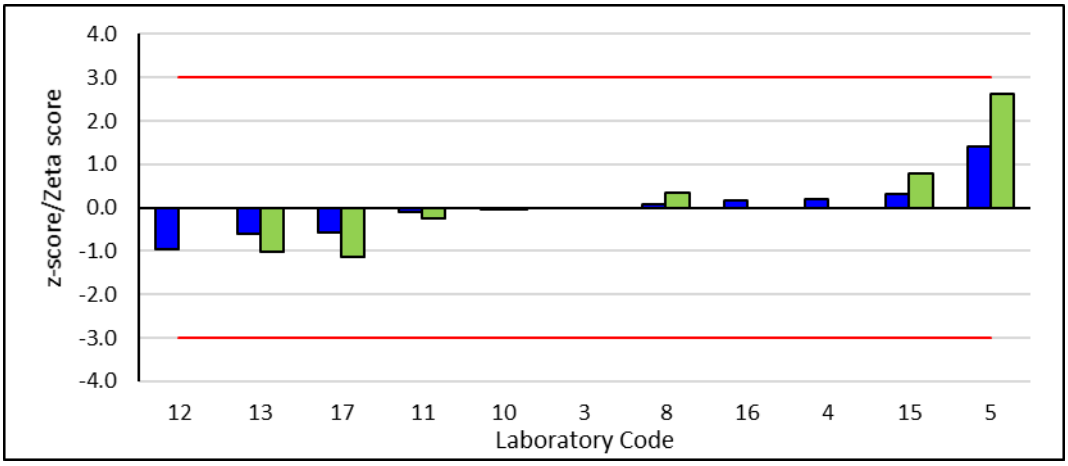
X_{Ass} mg kg^{-1}	6.0
U_{Ass} (k=2) mg kg^{-1}	0.4
$2\sigma_p$ mg kg^{-1}	1.5
Number of results:	11
Number of methods:	4

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)

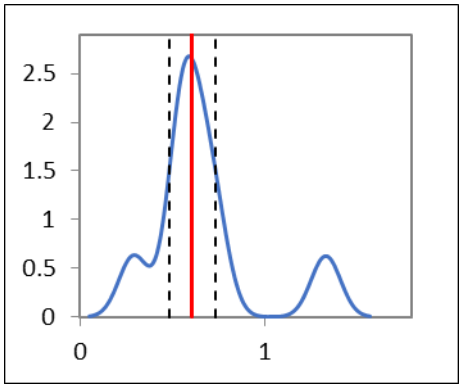


Performance evaluation: z-score Zeta-score



Reported data for Ni in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



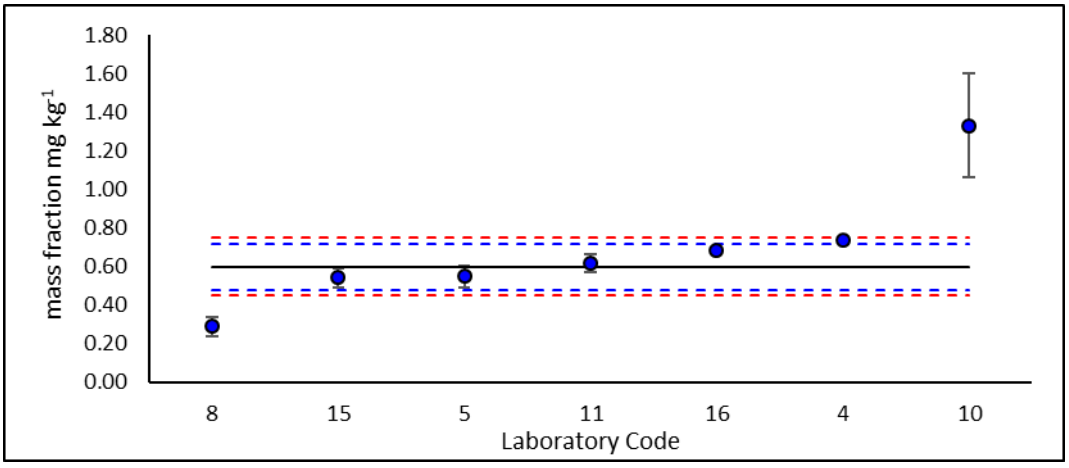
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	71%	0%	29%
Zeta-score	60%	0%	40%

X_{Ass} mg kg^{-1}	0.60
U_{Ass} (k=2) mg kg^{-1}	0.12
$2\sigma_p$ mg kg^{-1}	0.15
Number of results:	7
Number of methods:	2

Reported results and expanded uncertainties:

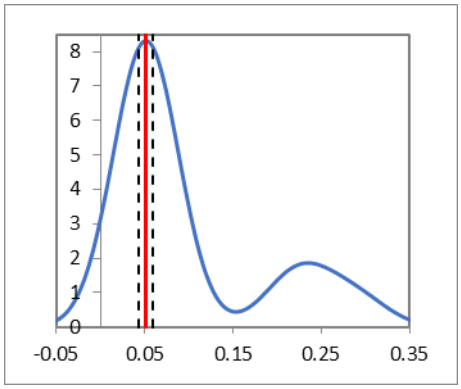
— X_{Ass} ; $X_{lab} \pm U_{lab}$; ---- $X_{Ass} \pm 2\sigma_p$; ---- $X_{Ass} \pm U_{Ass}$ (k=2)



Performance evaluation: z-score Zeta-score

Reported data for Pb in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



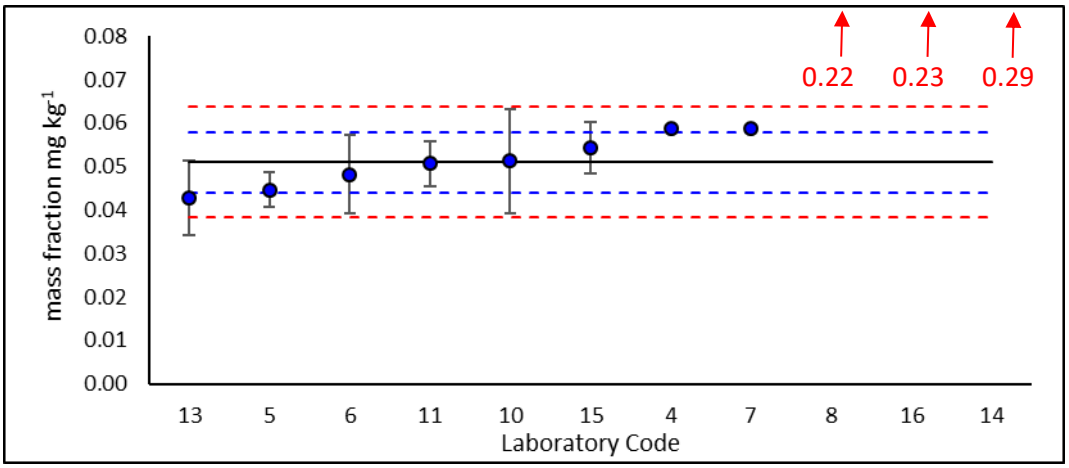
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	73%	0%	27%
Zeta-score	75%	0%	25%

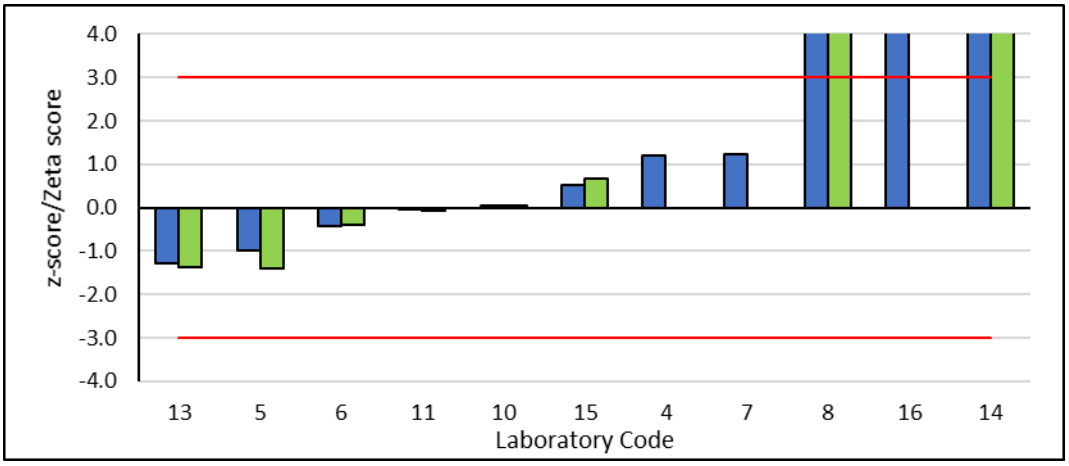
X_{Ass} mg kg^{-1}	0.051
U_{Ass} (k=2) mg kg^{-1}	0.007
$2\sigma_p$ mg kg^{-1}	0.013
Number of results:	11
Number of methods:	3

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)

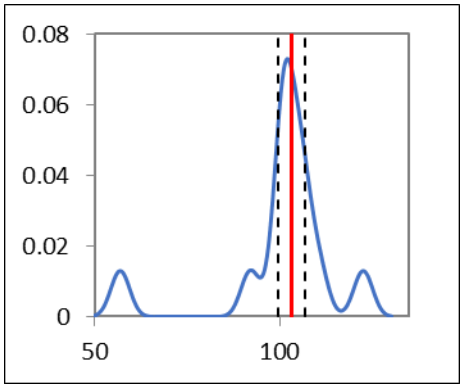


Performance evaluation: z-score Zeta-score



Reported data for Zn in the IAEA-MESL-2020-TE-MEPDOL-PT

Kernel density Plot



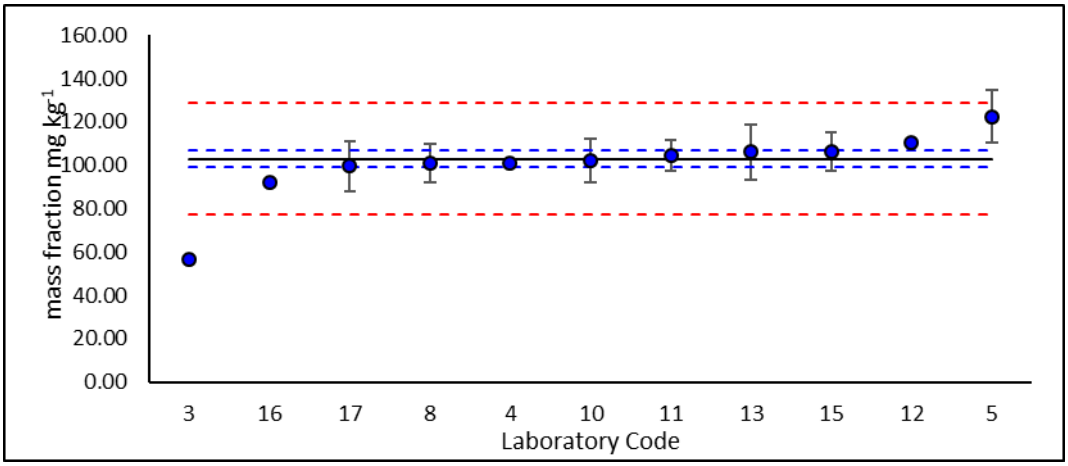
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	91%	0%	9%
Zeta-score	86%	0%	14%

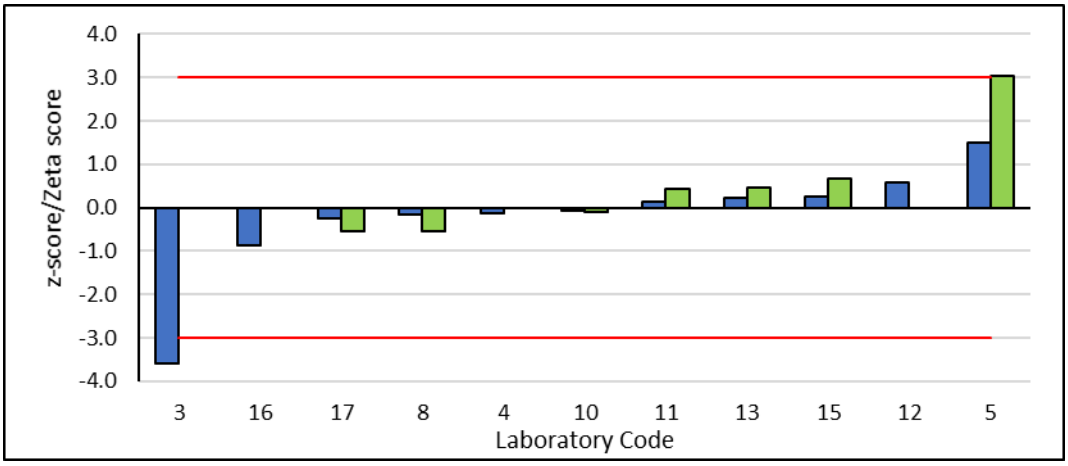
X_{Ass} mg kg^{-1}	103
U_{Ass} (k=2) mg kg^{-1}	4
$2\sigma_p$ mg kg^{-1}	26
Number of results:	11
Number of methods:	4

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



Annex 3:

Document sent to participants

INFORMATION SHEET: IAEA-MESL-2021-01-ILC-TE-BIOTA

TRACE ELEMENTS IN FISH

PLEASE READ THIS INFORMATION CAREFULLY BEFORE STARTING THE ANALYSES AND FILLING IN THE ONLINE DATA REPORTING FORM!

The present exercise is specifically organized for the determination of **trace elements in fish sample: IAEA-MESL-2021-01-ILC-TE-BIOTA**

Description of the material

IAEA-MESL-2021-01-ILC-TE-BIOTA is a fish flesh homogenate sample from North Sea; freeze dried, sieved at 250µm, mechanically homogenized and packed in plastic sealed containers.

Moisture content

The material can easily pick up moisture during storage. It is therefore necessary that the water content of the material is determined at the time of analysis in a separate sub-sample (i.e., not that taken for analysis) by **drying to a constant weight at 85˚C** (usually at least 24 hours).

PLEASE NOTE THAT ALL RESULTS ARE TO BE REPORTED ON A DRY MASS BASIS.

Instruction for use:

The sample should be kept in original bottle and mixed well before each use. A minimum sample of 0.3g should is required for analytical determination of all trace elements except mercury were subsamples of 0.05 g can be use.

Elements to be determined

Participants are requested to use their established analytical methods for the determination of **total contents** of the **mandatory** elements: **Cd, Hg and Pb** in IAEA-MESL-2020-TE-MEPDOL-PT sample.

In addition, when possible IAEA MESL will also evaluate results for some additional analytes, As, Co, Cr, Cu, Fe, MeHg, Mn, Ni and Zn.

Expected range of concentration:

- Fe, Zn: > 50 mg kg^{-1}
- Co, Cr, Cu, Mn, Ni: <10 mg kg^{-1}
- Cd, Hg, MeHg, Pb: < 1 mg kg^{-1}

Analytical quality control

Procedures of quality control and laboratory quality assurance are recommended to be applied.

The results of the analyses of a matrix matching quality control (QC) sample **must be reported** together with the results from the PT sample.

Reporting of results

1. Participants **MUST** report results together with a short **description of the method** and their **QA/QC procedures** using the IAEA on-line reporting system. User name, password and instructions for the on-line reporting will be sent to participant by email about 2 weeks before the deadline.

2. The participants are requested to make **three independent determinations** for each element in the PT sample.

3. The participant **MUST** answer to all questions during the reporting:

    - Moisture determination procedure
    - Sample preparation procedure
    - Instrumental method used for the quantitative determination of requested elements
    - Information on the validation of the method used
    - Statement on traceability of obtained measurement results (standards, reference material used, etc.)
    - Calculation of results and combined uncertainty
    - Recovery and correction for recovery
    - Quality control procedures (control charts, etc.).

4. For **each** element the participants **MUST** report:

    - **The results of each independent determination**; reported as net values (i.e., after correcting for blanks, etc.), leaving as many significant figures as

justified by the precision of the method used. **The results should be reported using the unit specified on the reporting form on a dry mass basis**.

- Uncertainties (standard combined and expanded) **in the same specified unit**
- Coverage factor
- The result of the matrix matching QC sample
- The recovery
- The detection and quantification limit in the **specified unit**

OTHER NOTES

1. If an element is not detected by the method used, it should not be reported but associated results of QC material, detection and quantification limits **must be** to allow evaluation of less than values by MESL. If not, the analyte will be evaluated as not determined by participant in the final evaluation report.

2. One report containing the results and statistical evaluation of the proficiency test data will be issued and sent to participants after the finalization of the exercise. Each participant or working group will be identified with a code number and the identity of this number will be revealed only to the respective participant, and, since this activity is part of the MED POL quality assurance of monitoring data program, their respective MEDPOL National Focal Point.

3. Two weeks before the deadline, the organizers of the Proficiency Test will send to all participating laboratories a deadline reminder and further instructions for the on-line submission of results by email.

Questionnaire:

- Description of sample preparation
- Description of calibration strategy
- Did you apply recovery correction?
- How did you calculate recovery?
- Do you usually report uncertainties?
- If yes, what is your coverage factor?
- How did you estimate uncertainties?
- How do you assure traceability of your results?
- Did you correct your results for moisture?
- Description of protocol used for determination of moisture content
- If you did not correct for moisture explain why
- Did you used validated method?
- Did you used CRM for validation?
- Did you used CRM for calibration?
- Do you have a quality system in place?
- If yes, please describe
- Are you accredited?
- If yes, please provide details of your accreditation
- Do you have further comments?

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Meeting of the Ecosystem Approach Correspondence Group on Pollution Monitoring

Videoconference, 26-28 April 2021

Agenda item 5: MEDPOL Proficiency Test on the Determination of Organochlorine Pesticides, PCBs and PAHs in Sediment sample (2020)

UNEP/MAP
Athens, 2021

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REPORT

MED POL PROFICIENCY TEST ON THE DETERMINATION OF ORGANOCHLORINE PESTICIDES, PCBs AND PAHS IN SEDIMENT SAMPLE IAEA-MEL-2020-01 PT/ORG

2020

Prepared in collaboration with:

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1. INTRODUCTION

The International Atomic Energy Agency's Environment Laboratories (IAEA-NAEL) continues to assist Member States in the use of nuclear and non-nuclear analytical techniques to understand, monitor and protect the environment. The major impact exerted by large coastal cities on marine ecosystems is an issue of primary concern for the Agency and its Environment Laboratories. To this extent, it is noteworthy that marine pollution assessment depends on the accurate knowledge of contaminant concentrations in various environmental compartments.

NAEL has been assisting national laboratories and regional laboratory networks through the provision of Analytical Quality Control Services (AQCS) for the analysis of radionuclides, trace elements and organic compounds in marine samples since the early 1970's. Relevant activities comprise global inter-laboratory comparison exercises, regional proficiency tests, the production of reference materials and development of reference methods for trace elements and organic pollutants analysis in marine samples.

The IAEA has a long collaboration with UN Environment Programme/Mediterranean Action Plan (UNEP/ MAP) and its Program for the Assessment and Control of Marine Pollution in the Mediterranean region (MED POL), which assists countries to implement programmes and measures to assess and eliminate marine pollution. The Marine Environmental Studies Laboratory (MESL) provides assistance to UNEP/MAP-MED POL in training (trace element, polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds), production of reference materials and by conducting interlaboratory studies and proficiency tests on matrices of relevance to marine monitoring.

This report describes the results of a Proficiency Test (PT) for the determination of organic contaminants in a marine sediment sample carried out in 2020 by designated IMAP Competent laboratories. In line with the conclusions of the Meeting of the Ecosystem Approach Correspondence Group on Pollution Monitoring (April, 2019), this report is complemented with the individual evaluation reports for each specific laboratory that participated in 2020 PT, as well as the national reports. The individual reports have been shared by MESL with the laboratories, while the National Reports for all 2020/2021 activities will be prepared for submission to MEDPOL Focal Points respectively to designated IMAP laboratories in November 2021.

The IAEA officers responsible for this publication are R. Cassi, I. Tolosa, S. Sander and A. Trinkl.

2. SCOPE OF EXERCISE

In July 2020 the MED POL Monitoring and Assessment Officer contacted MEDPOL Focal Points of the Contracting Parties of Barcelona Convention that are eligible for participation in Proficiency Testing for IMAP CI 17, according to procedures of IAEA-MESL, requesting them to provide the names of the designated national laboratories, involved in implementation of IMAP CI 17. The final list of designated national laboratories and contact persons for the targeted proficiency test for organochlorine pesticides, polychlorobiphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) was established at the end of August 2020. Consequently, a set of samples (bottles of sediment samples IAEA-MEL-2020-01 PT/ORG) were dispatched to 15 laboratories. All samples were sent in between August and September 2020. The list of participating laboratories can be found in Annex 2.

Participating laboratories, thereafter, also called participants, were requested to determine organochlorine pesticides, PCBs and PAHs, using the measurement procedures, usually applied for IMAP/MED POL monitoring studies.

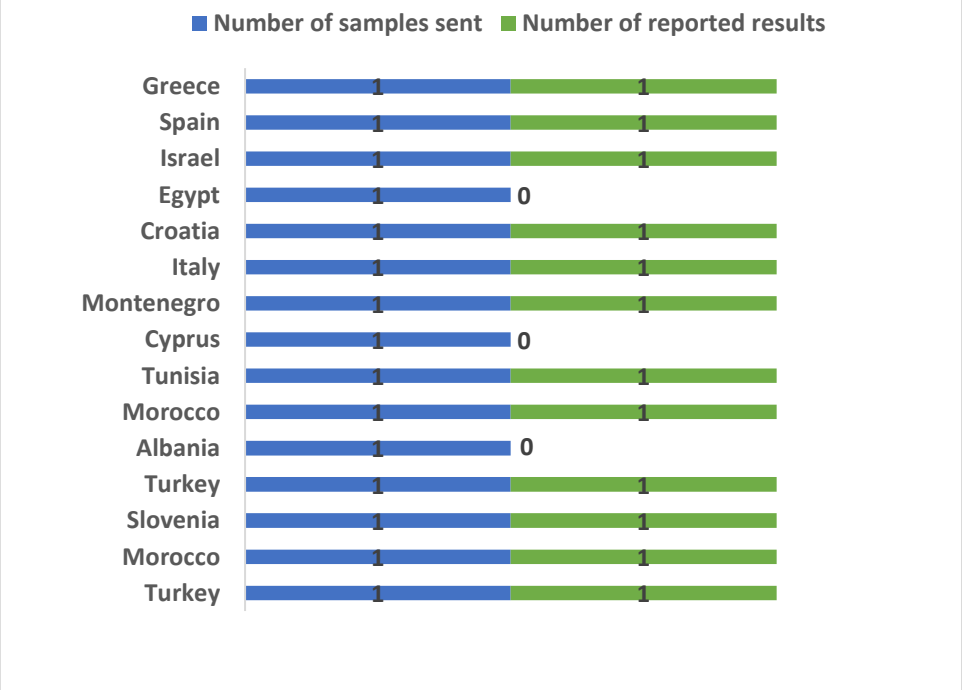

Figure. 1. Distribution per country of the MED POL PT sample

The deadline for reporting results was set for the 2 November 2020, but it was extended to the 15th of November 2020, after the request of several laboratories. Finally, 12 laboratories sent their results within the requested deadlines representing 80% of 15 participating laboratories

that received the test sample reported results (see figure 1). Six laboratories reported results for both organochlorine pesticides, PCB congeners and PAHs, 4 laboratories reported results only for organochlorine pesticides and PCB congeners and 2 laboratory reported results only for PAHs.

3. MATERIAL

3.1. Preparation of the material

The blind PT IAEA-MEL-2020-01 PT/ORG sample was collected from the intertidal mudflats of the Tagus estuary (Portugal) for use as an intercomparison material. This sediment was deep-frozen, freeze- dried, ground and sieved through a 150 μm stainless steel sieve. This sediment fraction was further homogenized by mixing in a stainless-steel rotating drum for two weeks. Then, aliquots of about 40 g were packed into glass bottles with aluminium screw caps and sealed with Teflon tape

The homogeneity of the material for organochlorine compounds and PAHs was assessed by determining the concentration of selected compounds (PCBs, chlorinated pesticides and PAHs) in 10 sample aliquots taken randomly in the bulk of the powder. A one-way variance analysis of the results indicated that the material can be considered as homogeneous.

3.2. Assigned values and associated uncertainties of the PT sample

The PT sample was previously characterized through a worldwide intercomparison exercise resulting on the production of the Marine Sediment Reference Material IAEA-408 [1]. The original data set was revaluated according to the requirements of the ISO 17043 standard [2], using the robust statistics and further reassessed according to the analytical methodologies validated in the MESL organic laboratories. The robust statistics, which provide high resistance to the influence of extreme outlying values were applied following the recommendations of ISO 13528 [3].

The uncertainties associated with the new assigned property values of the PT IAEA-MEL-2020-01 PT/ORG sample were conducted according to ISO Guide 35 [4], combining the standard uncertainties associated with the characterization (u_{char}), homogeneity (u_{hom}) and long-term stability (u_{stab}). Because the uncertainty component derived from the long-term stability was insignificant and assumed to be zero, the final expanded uncertainty was a combination of the other two contributions using the law of propagation of uncertainty as shown:

$$U = k \times \sqrt{u_{char}^2 + u_{hom}^2}$$

where k is the coverage factor of 2, representing a confidence level of 95%,

u_{hom} was set at 5%,

u_{char} was calculated as described in ISO 13528 [3] using:

$$u_{char} = 1.25 \times \frac{s^*}{\sqrt{p}}$$

where: s* is the robust standard deviation and p is the number of participating laboratories.

The new assigned concentration values and their associated uncertainties for the target chlorinated pesticides and PCBs congeners in the PT sample are shown in Table 1.

TABLE 1. Assigned values and associated uncertainties for the target chlorinated pesticides and PCBs congeners in the PT sample

Compounds	p	Assigned value (µg kg^{-1})	u_{char} (µg kg^{-1})	u_{hom} (µg kg^{-1})	U (k=2) (µg kg^{-1})
HCB	24	0.46	0.05	0.02	0.11
Lindane	13	0.20	0.02	0.01	0.05
pp' DDE	33	1.38	0.15	0.07	0.32
pp' DDD	25	0.85	0.10	0.04	0.22
pp' DDT	20	0.76	0.10	0.04	0.22
op DDT	3	<0.1	--	--	--
Dieldrin	13	0.35	0.06	0.02	0.13
Aldrin	7	<0.1	--	--	--
PCB No 28	14	0.73	0.14	0.04	0.30
PCB No 52	17	0.66	0.11	0.03	0.23
PCB No 101	23	1.24	0.15	0.06	0.32
PCB No 105	9	0.55	0.08	0.03	0.16
PCB No 118	21	1.22	0.14	0.06	0.31
PCB No 138	23	1.66	0.21	0.08	0.45
PCB No 153	21	1.71	0.24	0.09	0.51
PCB No 156	4	0.35	0.03	0.02	0.08
PCB No 180	20	1.04	0.07	0.05	0.18

The new assigned concentration values and their associated uncertainties for the target PAHs in the PT sample are shown in Table 2

TABLE 2. Assigned values and associated uncertainties for the target PAHs compounds in the PT sample

Compounds	p	Assigned value (µg kg^{-1})	u_{char} (µg kg^{-1})	u_{hom} (µg kg^{-1})	U (k=2) (µg kg^{-1})
Phenanthrene	15	35	4.3	1.73	9.2
Anthracene	8	11	2.3	0.53	4.8
Fluoranthene	19	93	16.9	4.67	35.0
Pyrene	17	76	9.6	3.78	20.7
Chrysene	15	40	6.8	1.99	14.1
Benzo [a] Pyrene	13	46	7.1	2.28	14.9
Benzo [k] Fluoranthene	7	39	10.9	1.97	22.2
Benzo [g,h,i] Perylene	11	34	7.7	1.70	15.8
Indeno[1,2,3-cd] Pyrene	7	43	6.1	2.15	13.0

4. RESULTS AND EVALUATION

4.1. Data Reporting

Data were reported through the IAEA on-line reporting system. Participants were asked to report data for selected organic contaminants listed in the IAEA408. These organic contaminants represent list of mandatory contaminants as defined for IMAP Common Indicator 17. All participants were able to download their preliminary evaluation report (reporting assigned values, reported values and z-scores) at the middle of December 2020 through the online portal.

4.2. Evaluation Criteria

The performance of each participant was evaluated with the **z-score** which expresses the difference between the mean of the laboratory and the assigned value in the same unit. The z-score represents a simple method of giving each participant a normalized performance score for the measurement bias of the respective measurement result. Starting from 2019 it was decided to combine the target standard deviation for proficiency assessment (σ_p), usually set at 12.5% with the target uncertainty of the assigned value (u_a) for the calculation of the "Total error" according to the following formula:

$$Total\ error_{\,a} = \sqrt{u_a^2 + \sigma_p^2}$$

For the assessment of the laboratory performances, a *z*-score is calculated based on ISO/IEC 17043:2010 [2]:

$$z = (x_i - x_a) / \text{Total error}_a$$

Where:

- x_i is the reported values from participant of the analyte concentration in the sample;
- x_a is the assigned value;

Performance is considered satisfactory if $|z| \leq 2$.

The measurement is regarded as questionable if $2 < |z| < 3$.

The measurement is regarded as unsatisfactory when $|z| \geq 3$.

This score represents a simple method of giving each participant a normalized performance score for bias. The procedure has been accepted as a standard by ISO/IUPAC [3, 5, 6].

Zeta-scores, are is not included in this report on the proficiency testing for the organic contaminants because most of the participating laboratories do not provide uncertainty values and therefore Zeta-score cannot be calculated. In addition, because of the complexity of the organic analyses procedures, uncertainties provided by most of the participating laboratories are not realistic and zeta-score is not yet relevant for the evaluation of organic contaminants.

4.3. Overview of the reported measurement results and scoring

Participants' results for organochlorine pesticides and PCB congeners are listed in TABLE 3 and the results for PAHs in TABLE 4. In both tables the assigned values of concentrations for organochlorine pesticides and PCB congeners in PT sample are indicated along with the "total error" for each compound, as it is further indicated in section 4.2.

All results are reported only by the laboratory code number, to protect the Participants confidentiality. However, as agreed with the participants the laboratory codes will be shared with UNEP/MAP – MEDPOL and respective MEDPOL Focal Point as part of the capacity building and quality assurance programme of MEDPOL.

The *z*-scores for participating laboratories can be found in TABLE 5 for chlorinated pesticides and PCB congeners and in TABLE 6 for PAHs. The red shaded cells represent data to be considered as "unsatisfactory", the yellow shaded cells represent data to be considered as "questionable" and green shaded cells represent data to be considered "satisfactory".

TABLE 3. Reported results and assigned concentration values for organochlorine pesticides and PCB congeners in the sediment test sample.

All results are in µg kg^{-1} dry weight.

Analyte	Laboratory codes										Assigned value	Total error
	1	2	3	4	6	9	10	11	13	14		
pp DDD	1.06	.	<1.00	1.51	.	1.50	1.11	8.37	5.00	0.50	0.85	0.152
pp DDE	1.71	0.18	1.10	0.36	0.15	1.43	1.32	9.13	9.60	1.67	1.4	0.236
pp DDT	1.07	0.55	<1.00	15.59	0.56	.	0.78	9.59	.	0.54	0.76	0.146
op DDT	.	.	<1.00	.	.	.	<0.13	0.63	.	.	<0.1	.
PCB No 28	0.51	.	<1.00	1.15	.	.	.	1.48	.	0.74	0.73	0.175
PCB No 52	0.65	.	<1.00	7.41	.	.	0.86	1.21	.	0.55	0.66	0.141
PCB No 101	1.30	.	1.04	4.07	.	1.20	2.20	1.64	.	1.28	1.24	0.223
PCB No 105	.	.	.	.	.	.	0.59	1.01	.	0.56	0.55	0.106
PCB No 118	1.37	.	1.08	0.85	.	1.27	1.56	2.47	.	1.39	1.22	0.217
PCB No 138	2.99	.	1.84	5.14	.	1.63	1.41	3.40	.	2.10	1.66	0.305
PCB No 153	2.08	2.61	1.68	1.66	0.26	2.03	1.74	3.21	.	2.02	1.71	0.332
PCB No 156	.	.	.	.	.	.	0.14	0.72	.	0.15	0.35	0.058
PCB No 180	1.35	.	1.09	0.96	.	1.16	1.14	2.38	.	1.19	1.04	0.158
HCB	.	.	<1.00	.	.	.	0.31	0.26	5.78	0.29	0.46	0.078
γ-HCH-Lindane	0.20	.	<1.00	1.39	.	.	0.19	2.99	.	.	0.2	0.035
Aldrin	.	.	<1.00	1.36	.	.	<0.13	2.50	5.00	.	<0.1	.
Dieldrin	0.31	.	<1.00	0.32	.	.	0.29	1.46	6.37	.	0.35	0.080

TABLE 4. Reported results and concentration assigned values for PAHs in the sediment test sample

All results are in µg kg^{-1} dry weight.

Analyte	Laboratory codes								Assigned value	Total error
	1	3	4	7	9	10	13	15		
Phenanthrene	42.8	17.0	29.5	3.01	33.8	30.4	19.5	35.1	35	6.3
Anthracene	13.9	5.00	5.32	14.7	9.46	9.60	9.00	9.07	11	2.7
Fluoranthene	84.3	51.7	47.5	4.13	78.0	76.8	50.0	91.8	93	21.0
Pyrene	72.8	41.7	60.6	3.01	70.6	67.6	41.5	74.7	76	14.0
Chrysene and Triphenylene*	52.1	21.7	34.8	21.7	36.5	32.9	45.2	56.2	40	8.7
Benzo(k)Fluoranthene	35.1	21.7	41.6	1.27	28.7	24.8	54.5	33.9	39	12.2
Benzo(a)Pyrene	48.8	28.3	39.8	5.44	45.6	38.9	48.0	52.7	46	9.4
Indeno(1.2.3-c.d) Pyrene	49.9	26.7	32.5	6.91	51.5	43.4	11.7	62.2	43	8.4
Benzo(g,h,i)Perylene	47.1	31.7	31.5	1.62	41.7	41.0	8.92	12.0	34	9.0

*The peaks of Chrysene and the one of Triphenylene tend to coelute and are very difficult to separate in the commonly used 5% phenylmethylsilicone GC capillary column.

After examining the GC columns used by the participants, it was decided to evaluate the data reported for “Chrysene” as “Chrysene + Triphenylene” to be more accurate.

TABLE 5. *Z*-scores for organochlorinated pesticides and PCB congeners

Analyte	Laboratory codes									
	1	2	3	4	6	9	10	11	13	14
pp DDD	1.36		**	4.4		4.3	1.7	49.6	27.4	-2.3
pp DDE	1.30	-5.2	-1.3	-4.4	-5.3	0.1	-0.3	32.7	34.7	1.1
pp DDT	2.11	-1.4	**	101.8	-1.4		0.2	60.6		-1.5
op DDT			**				**	*		
PCB No 28	-1.24		**	2.4				4.3		0.04
PCB No 52	-0.05		**	47.7			1.4	3.9		-0.8
PCB No 101	0.25		-0.9	12.7		-0.2	4.3	1.8		0.2
PCB No 105							0.4	4.3		0.1
PCB No 118	0.68		-0.7	-1.7		0.2	1.6	5.7		0.8
PCB No 138	4.38		0.6	11.4		-0.1	-0.8	5.7		1.4
PCB No 153	1.12	2.7	-0.1	-0.2	-4.4	1.0	0.1	4.5		0.9
PCB No 156							-3.6	6.4		-3.5
PCB No 180	1.97		0.3	-0.5		0.8	0.6	8.5		1.0
HCB			**				-1.9	-2.6	67.7	-2.2
g HCH-Lindane	-0.08		**	33.7			-0.2	79.2		
Aldrin			**	*			**	*	*	
Dieldrin	-0.54		**	-0.4			-0.7	14.0	75.6	

*Recommended values for Aldrin and op DDT are both < 0.1 ng/g. Laboratories that reported values for Aldrin and op DDT received a “unsatisfactory” z-score.

**Values reported as “< detection limit” are considered “satisfactory” if the corresponding assigned value is equal or inferior to the reported detection limit.

TABLE 6. Z-scores for PAHs

Analyte	Laboratory codes							
	1	3	4	7	9	10	13	15
Phenanthrene	1.2	-2.8	-0.9	-5.1	-0.2	-0.7	-2.4	0.02
Anthracene	1.1	-2.2	-2.1	1.4	-0.6	-0.5	-0.7	-0.7
Fluoranthene	-0.4	-2.0	-2.2	-4.2	-0.7	-0.8	-2.0	-0.1
Pyrene	-0.2	-2.5	-1.1	-5.2	-0.4	-0.6	-2.5	-0.1
Chrysene and Triphenylene	1.4	-2.1	-0.6	-2.1	-0.4	-0.8	0.6	1.9
Benzo(k)Fluoranthene	-0.3	-1.4	0.2	-3.1	-0.8	-1.2	1.3	-0.4
Benzo(a)Pyrene	0.3	-1.9	-0.7	-4.3	-0.05	-0.8	0.2	0.7
Indeno(1.2.3-c.d) Pyrene	0.8	-1.9	-1.2	-4.3	1.0	0.05	-3.7	2.3
Benzo(g,h,i)Perylene	1.5	-0.3	-0.3	-3.6	0.9	0.8	-2.8	-2.5

4.4. Analytical methodologies used by the participants

The treatments of samples for the analysis of organochlorine pesticides and PCBs congeners are reported in TABLE 7 and the instrumental conditions for these analyses are reported in TABLE 8. The treatments of samples for the analysis of PAHs are reported in TABLE 9 and the instrumental conditions for these analyses are reported in TABLE 10.

To gain a better understanding of Participants laboratory procedures, since 2019 it was decided to collect information about the use of "surrogates standards", i.e. standards within the same class of organic contaminants spiked before the extraction to investigate the effect of sample pre-treatment, and the use of "internal standards" spiked just before the instrumental injection. Analysing the information collected it appeared evident that difference between the two type of standards and their use is still unclear to several Participants. It was decided to comment only on the use of internal standards/surrogates.

Quality parameters, i.e., if a QA/QC system is in place, if and which (Certified) Reference Material was used and if reference material data was reported, if the method used was validated, if the laboratory is accredited, and if the uncertainty was reported, for organochlorinated pesticides and PCB congeners and PAHs respectively reported by Participants, can be found in TABLES 11 and 12.

Despite the importance of key quality parameter information, only some participants provided all of the information requested..

Figures 2 and 3 shows the graphic representations of key points of sample treatment and instrumental analyses for organochlorine pesticides and PCBs congeners and PAHs respectively.

TABLE 7. Treatment of samples performed by participants for organochlorine pesticides and PCBs

Lab. Code	Extraction	Solvent	Desulphurisation	Fractionation
1	Microwave assisted	Acetone/n-Hexane	Copper	Florisil
2	Microwave assisted	n-Hexane	Mercury	Florisil
3	Shaking (solid/liquid extraction)	Acetone/n-Hexane	Silver nitrate	None
4	Sonication	Acetone/n-Hexane	Mercury	Florisil
6	Microwave assisted	n-Hexane/Dichloromethane	Mercury	Florisil
9	Sohxlet	n-Hexane/Dichloromethane	TBA (tetratbutylammonium)	Florisil
10	Quechers	Other	Copper	None
11	PE	Dichloromethane	Gel Permeation Chromatography	
13	Sohxlet	n-Hexane/Dichloromethane	None	Florisil
14	Sohxlet	n-Hexane/Dichloromethane	Copper	Silica

TABLE 8. Use of surrogates/internal standards and instrumental conditions used by participants for organochlorine pesticides and PCBs

Lab. Code	Use of Surrogates	Surrogates used	Use of Internal Std	Internal Std used	Injector Type	GC-Column	Detector Type
1	Yes	PCB29 and PCB198 for OCPs and PCBs	No		PTV	5% Phenyl 95% Dimethylpolysiloxane	GC/MSMS
2	Yes	PCB29	No		Splitless	Other	GC/MS
3	Yes	a sediment lab sample	No	e-HCH PCB209	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/ECD*
4	Yes	1-Bromo 2-NitroBenzen	Yes		Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/ECD
6	Yes	PCB29 endosulfan id4 Naphthalene-d8	No		Splitless	Other	GC/MS
9	No		Yes	epsilon-HCH PCB 29 PCB198 PCB209	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
10	Yes	HCB ppDDE ppDDT marcati	Yes	DCBF	MMI	5% Phenyl 95% Dimethylpolysiloxane	GC/MSMS
11							GC/MS
13	No		No		Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
14			Yes		Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MSMS

*With dual column confirmation

TABLE 9. Treatment of samples performed by participants for PAHs

Lab. Code	Extraction	Solvent	Desulphurisation	Fractionation
1	Microwave assisted	Acetone/n-Hexane		Silica
3	Shaking (solid/liquid extraction)	n-Hexane/Dichloromethane		None
4	Sonication	Acetone/n-Hexane		None
7	Sohxlet	n-Hexane/Dichloromethane		Silica/Alumina
9	Sohxlet	n-Hexane/Dichloromethane	TBA (tetratbutylammonium)	Alumina
10	ASE	n-Hexane/Dichloromethane	None	Silica
13	Sohxlet	n-Hexane/Dichloromethane	None	Florisil
15	Sohxlet	n-Hexane/Dichloromethane	Other	Silica

TABLE 10. Use of surrogates/internal standards and instrumental conditions used by participants for PAHs

Lab. Code	Use of Surrogates	Surrogates used	Use of Internal Std	Internal Std used	Injector Type	GC-Column	Detector Type
1	Yes	PAH Mix 31 deuterated			PTV	5% Phenyl 95% Dimethylpolysiloxane	GC/MSMS
3			Yes	PhenanthreneD10 ChryseneD12 PeryleneD12	Splitless	Other	GC/MS
4			Yes	Deuterium PAHs	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
7	Yes	Cadalene	No		Splitless		GC, Other
9	No		Yes	Naphthalene d8 Acenaphthene d10 Phenanthrene d10 fluoranthene d10 chrysene d12 perylene d12	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
10	Yes	surrogate std EPA 8270 method	Yes	internal standard EPA 8270 method	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
13	No		No		Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
15	Yes	Deuterated PAHs			Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS

TABLE 11. Quality parameters for organochlorinated pesticides and PCB congeners.

Laboratory Code	QA/QC System	Use of Certified Reference Material	Reference Material Used	Reported Reference Material Data	Validated Method	Accreditation	Reported Uncertainty
1	Yes	Yes	MS2-2017-1	Yes	Yes	No	No
2	No	No		No	No	No	No
3	Yes	No			Yes	Yes	Yes
4	Yes	Yes	IAEA 417			No	Yes
6	Yes	No		No	No	No	No
9	Yes	Yes	IAEA 459	Yes	Yes	Yes	Yes
10	Yes	Yes	Clean soil reference material EDF-5183 CIL	Yes	Yes	No	Yes
11							Yes
13	No	Yes				No	No
14	Yes	Yes	IAEAMEL_2019.02OC	Yes	Yes		No

TABLE 12. Quality parameters for PAHs.

Laboratory Code	QA/QC System	Use of Certified Reference Material	Reference Material Used	Reported Reference Material Data	Validated Method	Accreditation	Reported Uncertainty
1	Yes	Yes	QPH094MS	Yes	Yes	No	Yes
3	Yes	No		No	Yes	No	Yes
4	Yes	Yes	IAEA 417	No		No	Yes
7		Yes	IAEA-159	Yes	No	No	No
9	Yes	Yes	IAEA 459	Yes	Yes	Yes	Yes
10	Yes	Yes	Unichim IPAs22	Yes	Yes	Yes	Yes
13	No			No			No
15	Yes	Yes	NIST1941b	Yes	Yes	Yes	Yes

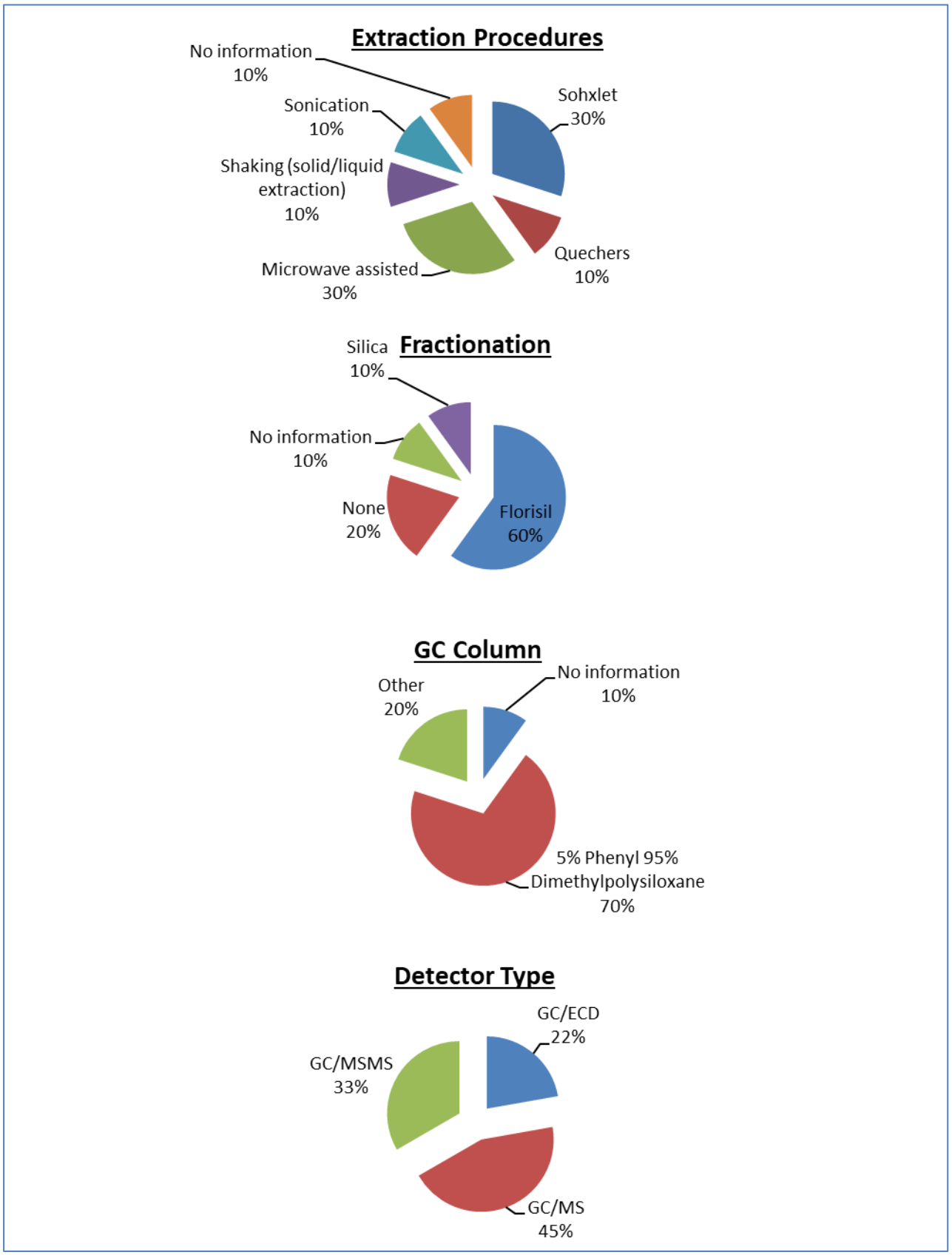

Figure 2. Graphic representation of sample treatment and instrumental conditions for organochlorine pesticides and PCB congeners.

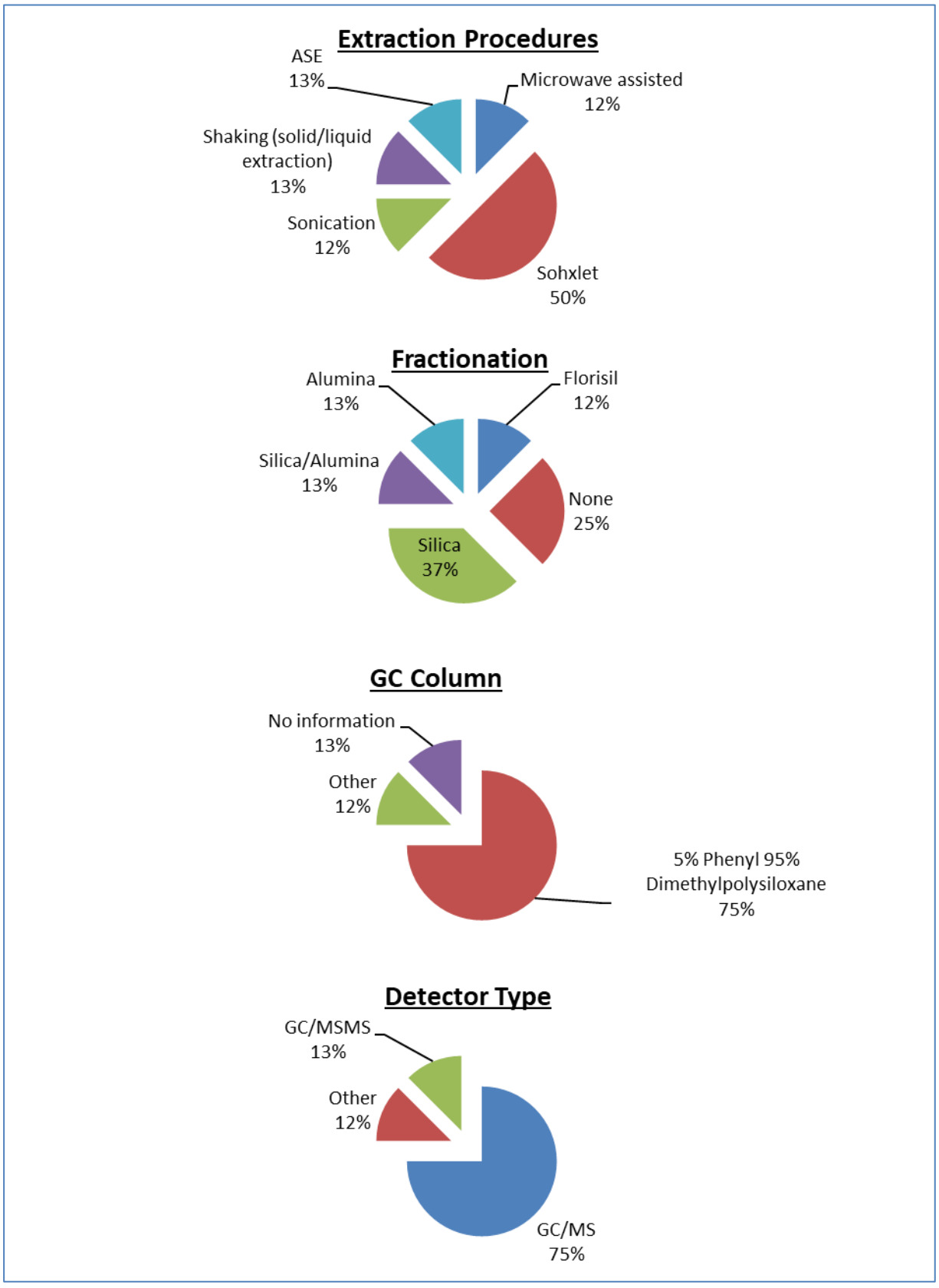

Figure 3. Graphic representation of sample treatment and instrumental conditions for PAHs

5. EVALUATION OF RESULTS

5.1. Organochlorine Pesticides and PCB Congeners

Among all designated laboratories, 67% submitted results for organochlorine pesticides and PCB congeners.

Table 13 reports the number of results and z-scores distribution per Participant for organochlorinated pesticides and PCB congeners.

TABLE 13. Number of results reported and z-scores distribution for organochlorinated pesticides and PCB congeners

Laboratory code	Number of Results	$\|z\| \geq 3$	$2 < \|z\| < 3$	$\|z\| \leq 2$
1	12	8%	8%	83%
2	3	33%	33%	33%
3	15	0%	0%	100%
4	13	62%	8%	31%
6	3	67%	0%	33%
9	7	14%	0%	86%
10	16	13%	0%	88%
11	17	88%	6%	6%
13	5	100%	0%	0%
14	13	8%	15%	77%

Laboratory number 3 provided all satisfactory results taking in account that most of their reported values were under their limit of detection. Four laboratories (1, 9, 10 and 14) reported more than 50% of satisfactory results. Four laboratories (4, 6, 11 and 13) provided more than 50% of results unsatisfactory.

Seven participants of the current PT reported to have a QA/QC system in place in their laboratory; 5 laboratories reported to use validated methods and 4 laboratories reported their QA/QC results along with the test results (laboratories 1, 9, 10 and 14). All laboratories used internal standards/surrogates, except laboratories 11 and 13.

Among the 7 Participants having a QA/QC system in place in their laboratory, 70 % stated using CRMs and 60% reported uncertainties along with their results.

Most Participants reporting more than 50% outlying values either reported non using CRMs or failed to provide information about the use of CRMs.

Figure 4 reports a graphic representation of z-scores for organochlorine pesticides and PCB congeners.

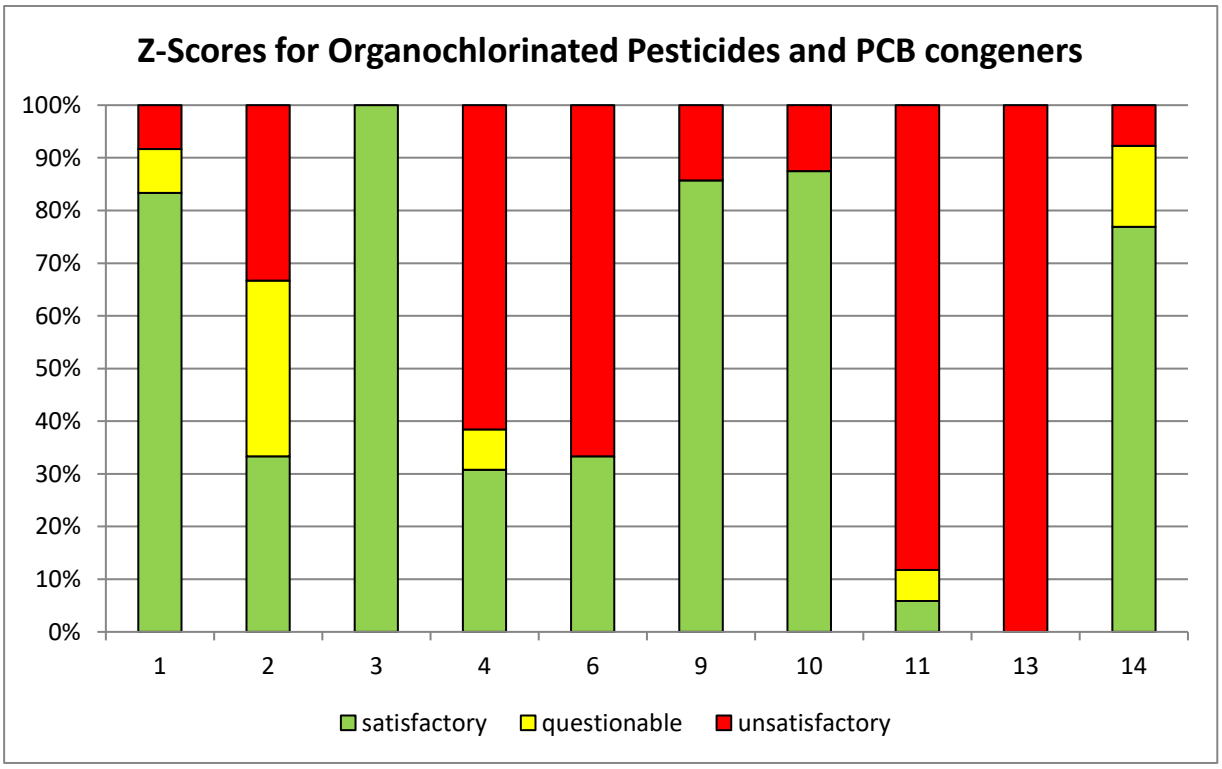

Figure 4. Graphic representation of laboratories z-scores for organochlorine pesticides and PCB congeners.

5.2. PAHs

Among all designated laboratories, only 53% submitted results for PAHs.

Table 14 reports the number of results and z-scores distribution per Participant for PAHs. Among the participants, laboratory number 1, 4, 9, 10 and 15 provided all satisfactory and very few "questionable" results. Laboratory number 7 provided more than 75% of results unsatisfactory.

TABLE 14. Number of results reported and z-scores distribution for PAHs

Laboratory code	Number of Results	$\|z\| \geq 3$	$2 < \|z\| < 3$	$\|z\| \leq 2$
1	9	0%	0%	100%
3	9	0%	44%	56%
4	9	0%	22%	78%
7	9	78%	11%	11%
9	9	0%	0%	100%
10	9	0%	0%	100%
13	9	11%	44%	44%
15	9	0%	22%	78%

Among the participants, 75% reported to have a QA/QC system in place (laboratories 1, 3, 4, 9, 10 and 15); five laboratories (1, 3, 9, 10, 15) representing 63% of the participants reported to use validated methods; 88% stated to use internal standards/surrogates, and 75% reported uncertainties for their measurements (laboratories 1, 3, 4, 9, 10, 15). Six laboratories stated using CRMs and 5 of them (laboratories 1, 7, 9, 10, 15) reported their QA/QC data along with the test results

Figure 5 reports a graphic representation of z-scores for PAHs.

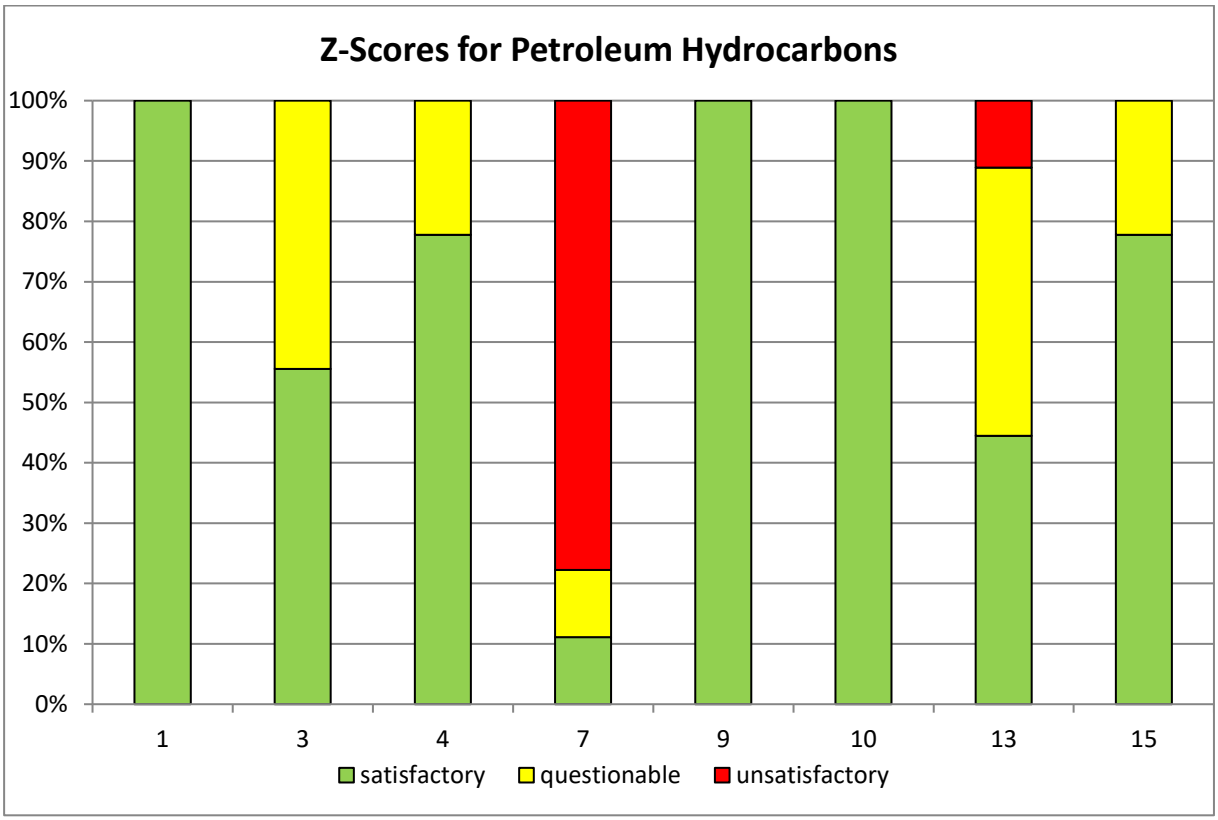

Figure 5. Graphic representation of laboratories z-scores for PAHs.

6. CONCLUSIONS AND RECOMMENDATIONS

Five participants, representing 50% of all the laboratories reporting results for organochlorine pesticides and PCB congeners, were able to produce all "satisfactory" or very few "questionable" or outlying results, i.e. laboratories 1, 3, 9, 10 and 14. Four participants (i.e. laboratories 4, 6, 11 and 13) , representing 40% of all the laboratories reporting organochlorine pesticides and PCB congeners, exhibited a high percentage of outlying or questionable results.

The z-score distribution of most laboratories reporting data for organochlorine pesticides and PCB congeners, are inconsistent. In many cases, for the same group of compounds, excellent z-scores values are reported for some compounds while for others, z-scores are completely outlying. Such z-scores variation suggests that clean-up and fractionation should be optimized, and chromatographic peaks identity confirmed using multiple detection strategies (i.e. laboratories 2, 4, 6 and 9). Carrying out the same analyses using different chromatographic columns or different detectors can, for example, overcome problems of co-elution and interferences very common in gas chromatographic analyses.

Three laboratories (number 4, 11 and 13) reported some results which differed by one order of magnitude from the assigned value. This may be due to a "reporting" mistake (for example: wrong unit conversion or wrong dataset reported) or due to more severe analytical issues which would require immediate root cause analysis and consequent corrective actions. These laboratories should verify their analytical procedures and their data reporting units.

Five participants, representing 63% of all 8 laboratories reporting results for PAHs reported all or most "satisfactory" results. Unfortunately, one participant (laboratory number 7) reported almost all outlying or questionable results. In general, best performing laboratories reported to have a quality system in place, to use internal standards/surrogates and validated methods and in some cases to be accredited.

Similar to organochlorine pesticides and PCB congeners, co-elution and interferences are very common sources of errors for PAHs analyses.

Both systematic and random errors may also be due to contamination issues. Solvents used for sample preparation and analysis should be of the highest purity available. Solvents quality should also be checked on regular base. Special care should also be taken during the evaporation procedure of the solvent extracts to avoid dryness and losses of the more volatile contaminants. In this aspect, the use of internal standards/surrogates with physico-chemical properties similar to the target analytes is fully recommended to compensate for these losses.

The use of reference materials and replicate samples are key points in every QA/QC system to produce accurate results. Reference materials must match the test sample matrix and must undergo the same exact procedure of the test sample to be as effective as possible to avoid inaccuracy and precision issues.

Unfortunately, some participants reported data but did not fill the questionnaire or filled it only partially. Most of the participants, although using certified reference materials, failed to report their QA/QC data along with the test sample. This makes it impossible to get a better understanding where problems might be.

Although the participation to the annual proficiency test organized by MED POL is mandatory for MED POL laboratories, over the years, the participation rate has been very low, especially considering the importance of this PT exercises to test and demonstrate laboratory performances as required by ISO Guide 17025. Moreover, as it has often been the case in previous years, also for 2020 many Participants reported only few results for organochlorine pesticides and PCB congeners. We would like to remind that these organic contaminants are in line with those listed for the MEDPOL Common Indicator 17 and every MEDPOL laboratory should be able to measure them.

However, given the exceptional circumstances imposed by the pandemic spread of Covid-19 and the subsequent lockdowns, participation rates of 67% and 53% for organochlorine pesticides/PCB congeners and PAHs respectively, can be considered as a reasonable outcome.

Laboratories could also benefit more from the PT exercise if they provide all the key information requested through the questionnaire reporting file. In this context, details on the analytical procedures, e.g., careful listing of the individual internal standards/surrogates, quantification procedures (internal or external), will be useful to provide further feedback on the outlying results. It is also recommended that participants provide their data along with their estimates of uncertainty in accordance to the approach set forth in the basic Guide to the expression of uncertainty in measurement (GUM).

The knowledge on basic principles of metrology, e.g. method validation, traceability and uncertainty of measurement results, are still limited and laboratories that lack proficiency in this area should take action.

We continue to observe that the accessibility of appropriate CRMs and analytical infrastructure is hindering the improvement of results in certain laboratories which should be addressed at national level.

It is further recommended that designated MED POL laboratories should only use validated measurement procedures for the analysis of samples within the realization of the MED POL monitoring programme of the country.

Two national laboratory mission visits were conducted in early 2020 by MESL experts. The focus of the gap-finding visits was aimed at the identification of technical (e.g. acquisition of laboratory equipment) and knowledge needs to strengthen the understanding for applying the analytical methods and good laboratory practices in line with the requirements of IMAP Common Indicator 17.

7. REFERENCES

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[2] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide 17043 (2010), Conformity assessment, general requirements for proficiency testing, ISO, Geneva, Switzerland.

[3] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide 13528 (2005), Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons, ISO, Geneva, Switzerland.

[4] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, ISO Guide 35:2006, Reference Materials – General and Statistical Principles for Certification, ISO, Geneva (2006).

[5] Thompson and R. Wood (1993). The international harmonized protocol for the proficiency testing of (chemical) analytical laboratories. IUPAC/ISO/AOAC. *J. Pure. Appl. Chem*. **65**(9), 2123-2144.

[6] Thompson, M., Ellison, S. L. R. and R. Wood (2006). The international harmonized protocol for the proficiency testing of (chemical) analytical laboratories. IUPAC Technical report. *J. Pure. Appl. Chem*. **78**(1), 145-196.

Annex 1:
List of Participants

Designated IMAP Competent laboratories that sent results

CROATIA	
Teaching Institute of Public Health of PGZ Kreslimirova 52a 51000 Rijeka	OCs
GREECE	
Hellenic Centre for Marine Research Institute of Oceanography 46.7km Athens-Sounio Av. Mavro Lithari 19013 Anavyssos	PAHs
ISRAEL	
Israel Oceanographic & Limnological Research (IOLR) 1st Hubert Humphrey Tel Shikmona 2650100 Haifa	OCs, PAHs
ITALY	
ARPAE – Emilia Romagna Via Alberoni, 17/19 48121 Ravenna	OCs, PAHs
MONTENEGRO	
Centre for Ecotoxicological Research Podgorica Bulevar Sarla de Gola 2 81000 Podgorica	OCs, PAHs
MOROCCO	
Laboratoire National des Etudes et de Surveillance de la Pollution Département de l'Environnement - Ministère de l'Energie, des Mines et de l'Environnement Avenue Mohammed Ben Abdellah Erregragui Madinat Al Irfane 10112 Agdal- Rabat	OCs
Institut National d'Hygiène Ministère de la Santé 27, avenue Iben Batouta BP 769 10112 Agdal- Rabat	OCs

SLOVENIA	
National Laboratory of Health Environment and Food Prvomajska Ulica 1 2000 Maribor	OCs, PAHs
SPAIN	
Instituto Espanol de Oceanografia (IEO) Centro Oceanografico de Murcia c/Varadero, 1 30740 San Pedro del Pinatar	OCs
TUNISIA	
Institut National des Sciences et Technologies de la Mer (INSTM) Port de Pêche La Goulette 2060 La Goulette	PAHs
TURKEY	
Ministry of Environment and Urbanization Çevre Referans Laboratuvarı National Environmental Reference Laboratory Haymana Yolu 5. Km. 06830 Gölbaşı-Ankara	OCs, PAHs
Scientific and Technological Research Council of Turkey Marmara Research Center Environment and Clean Production Institute TUBITAK Gebze Yerleskesi Marmara Arastirma Merkeri Cevre ve Temiz Uretim Enstitusu 41470 Gebze/KOCAELI	OCs, PAHs

Designated IMAP competent laboratories that did not send

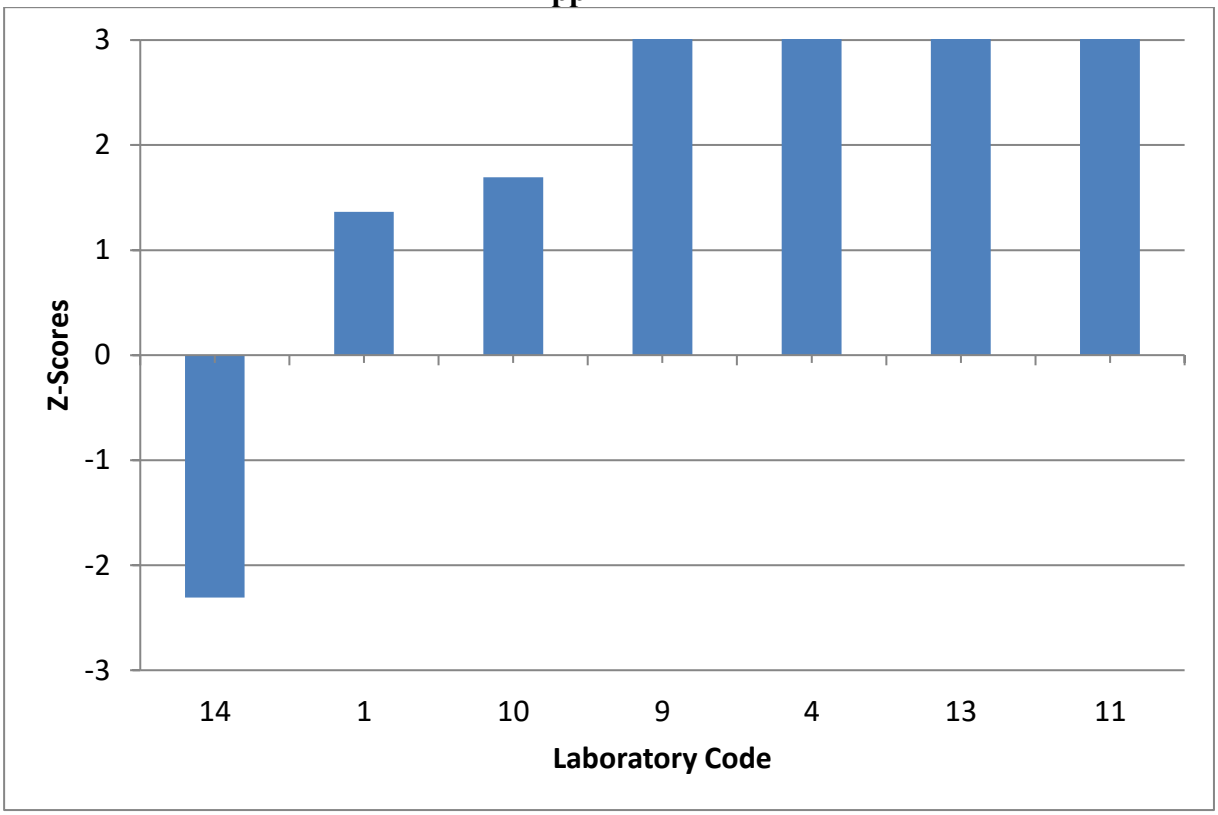
ALBANIA
Agjencia Kombetare e Mjedisit National Environment Agency (NEA) Ruga Sami Frasheri nr 23 godina nr 4 Tirana
CYPRUS
State General Laboratory (SGL) 44 Kimonos Street 1451 Nicosia
EGYPT
National Institute of Oceanography and Fisheries Kayet Bay, Elanfoushy 56621 Alexandria

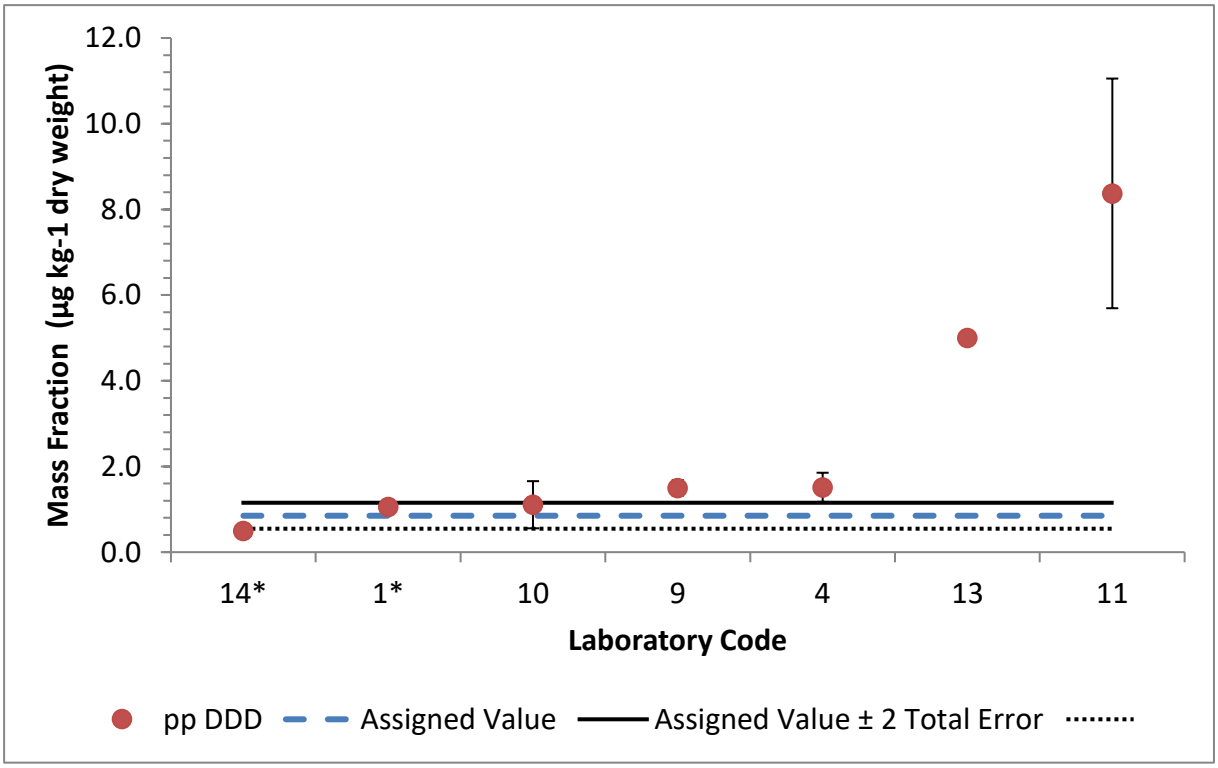
Annex 2:
Graphic Representation of Laboratories Performances

Graphic Representation of Laboratories Performances

The mean concentration values reported by the participants for the target analytes are plotted with their associated reported uncertainties, excepting laboratories labelled with "*" for which we estimated their associated uncertainty as $2 \times \frac{s}{\sqrt{n}}$ where s is the standard deviation and n is the number of measurements reported by participants.

GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR pp'DDD





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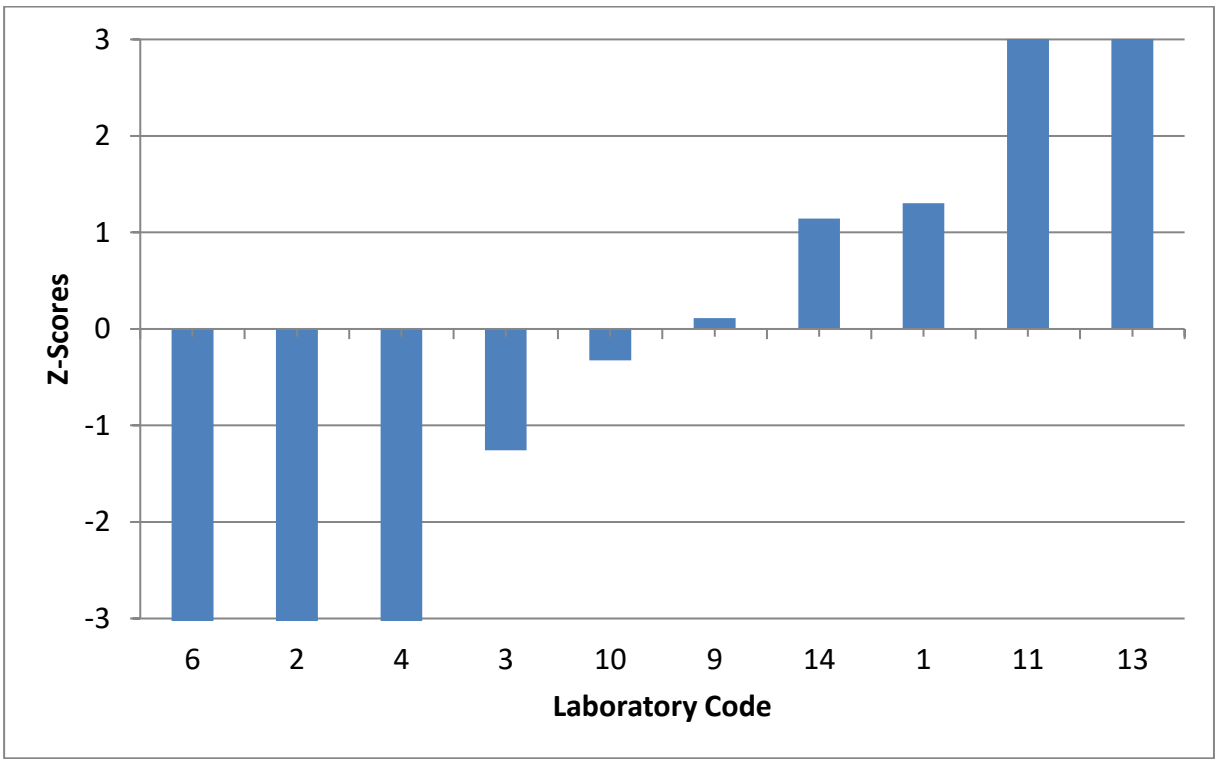

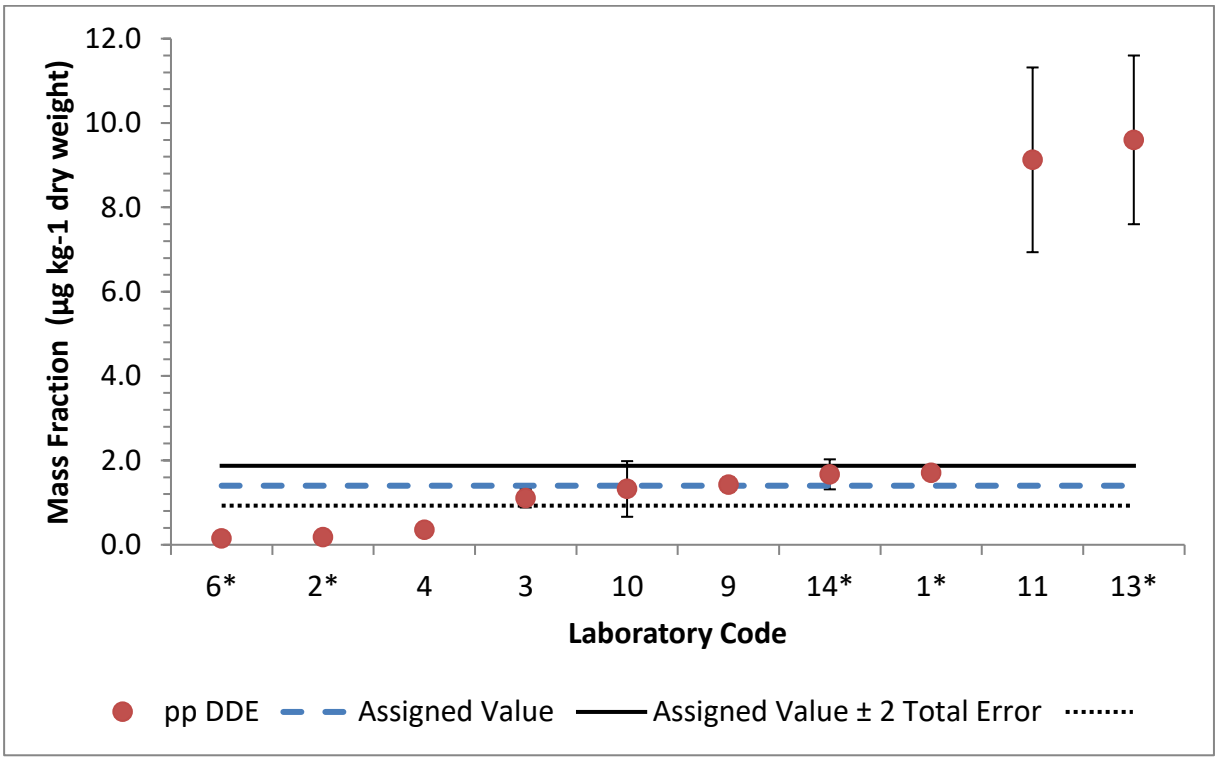

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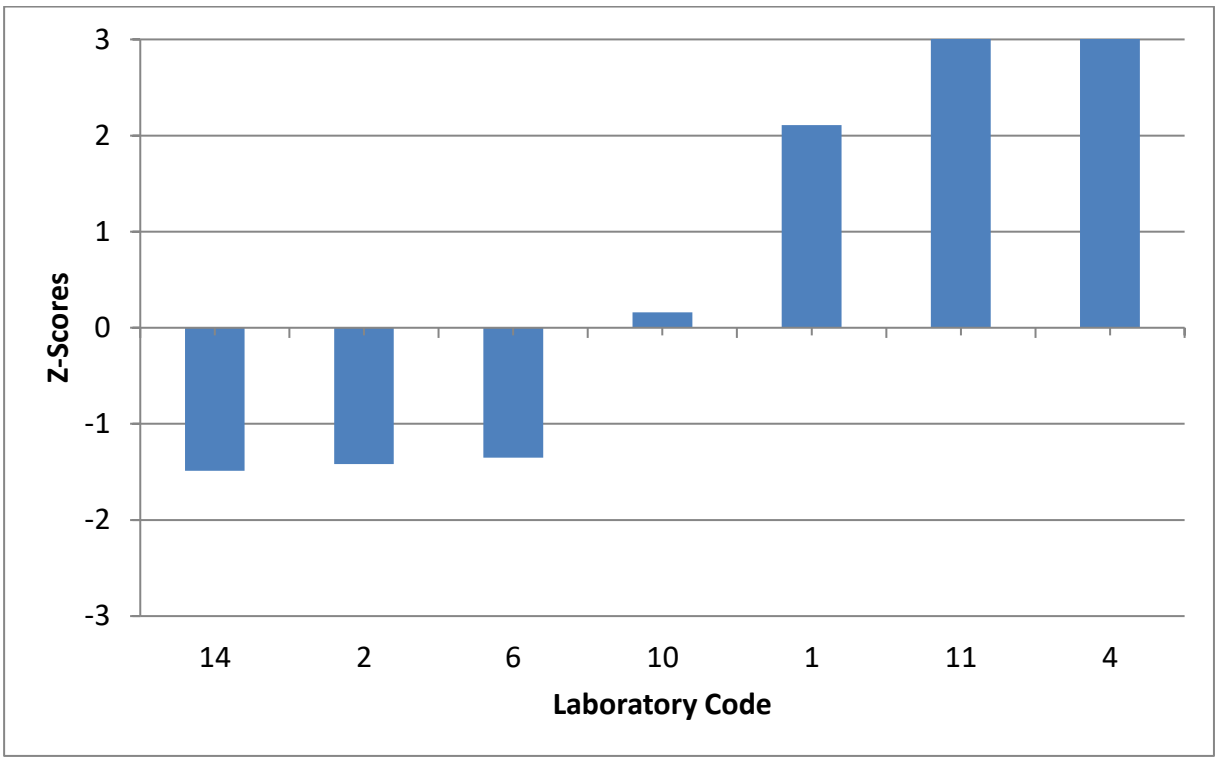

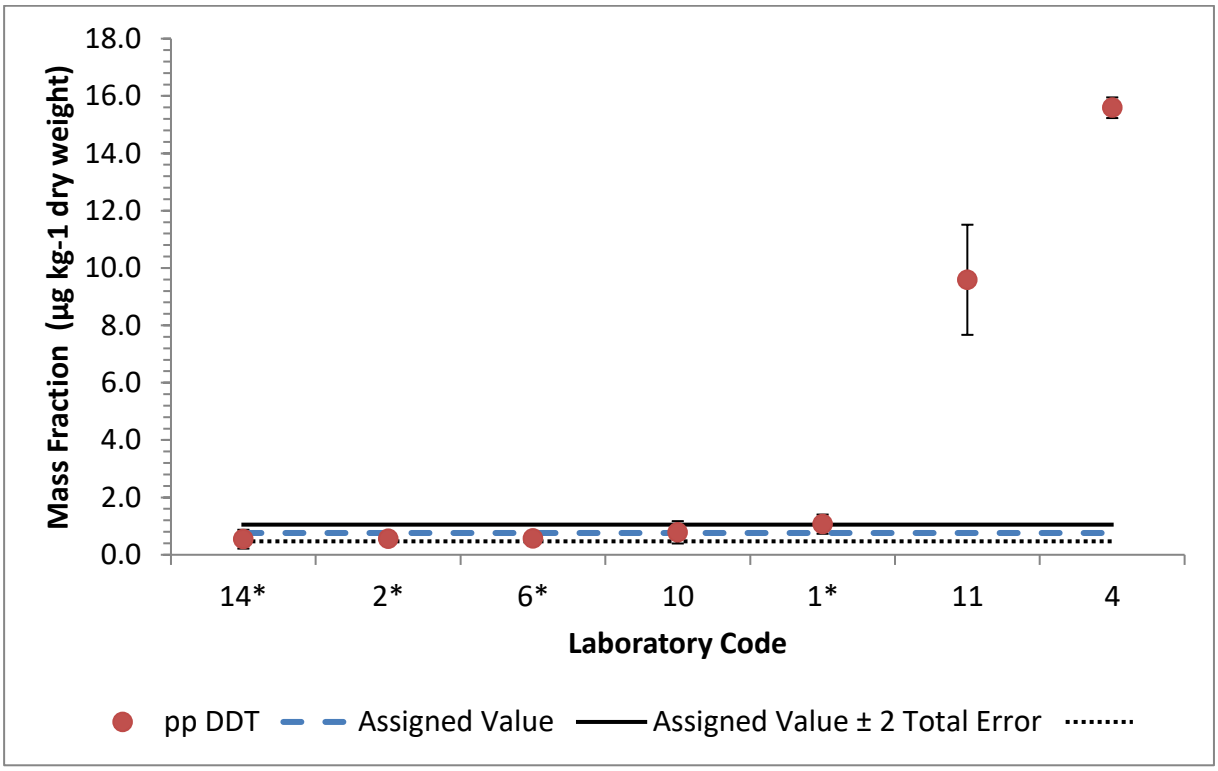

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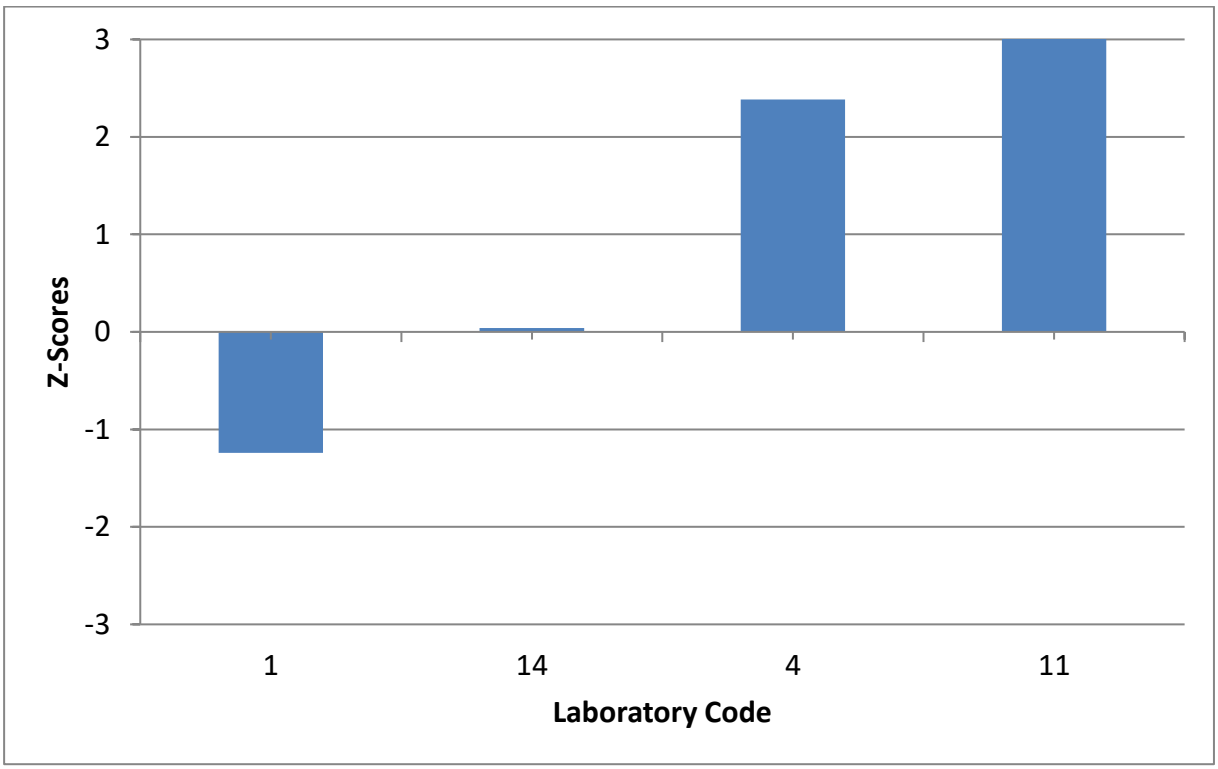

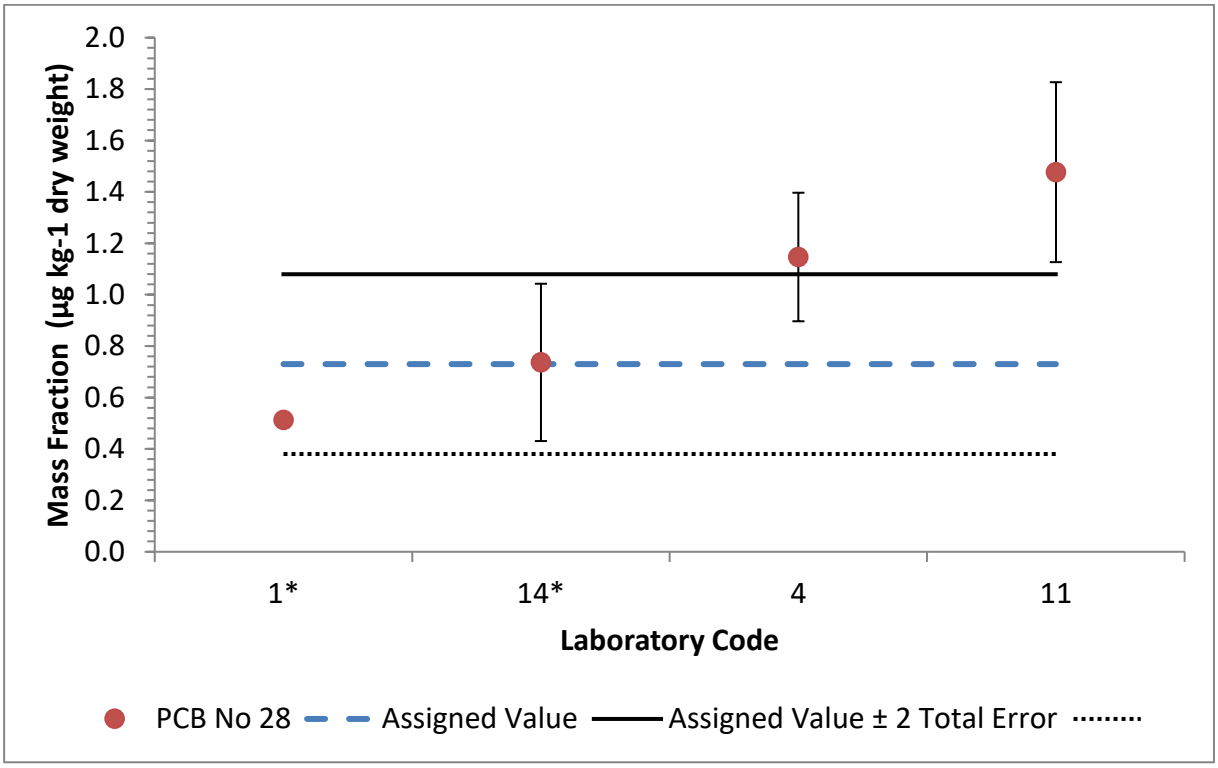

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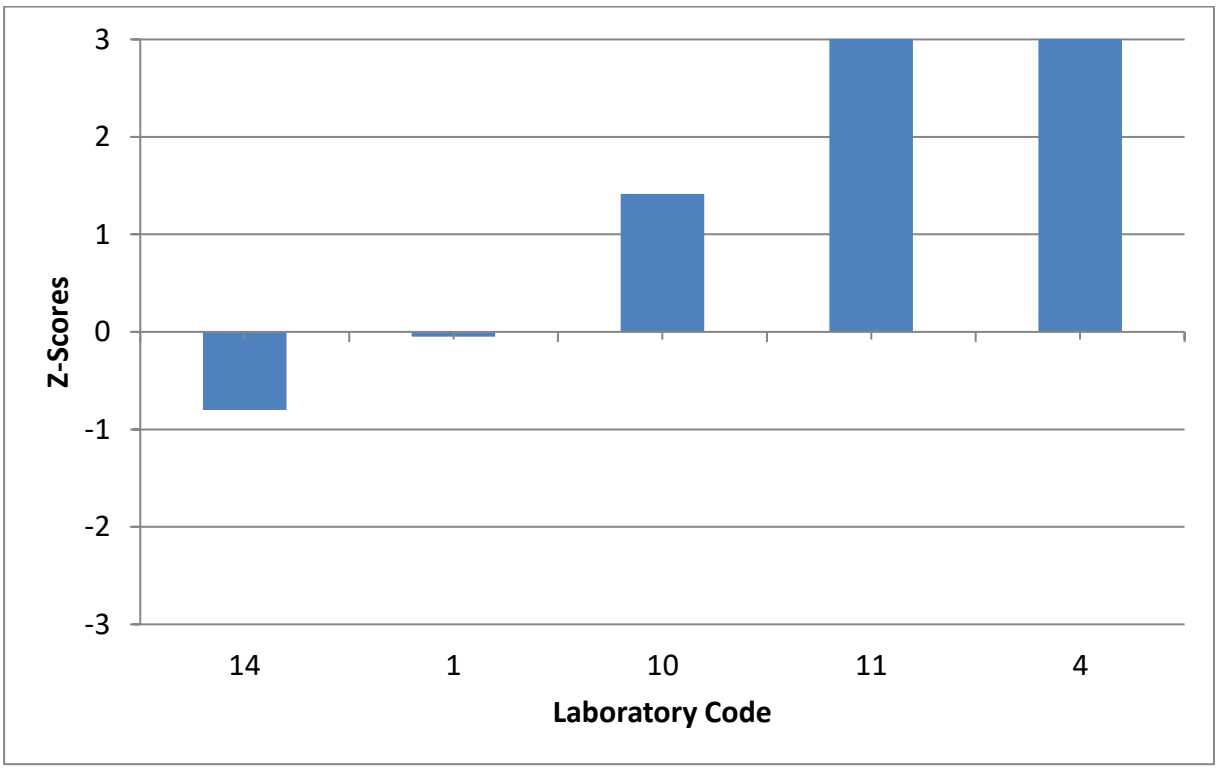

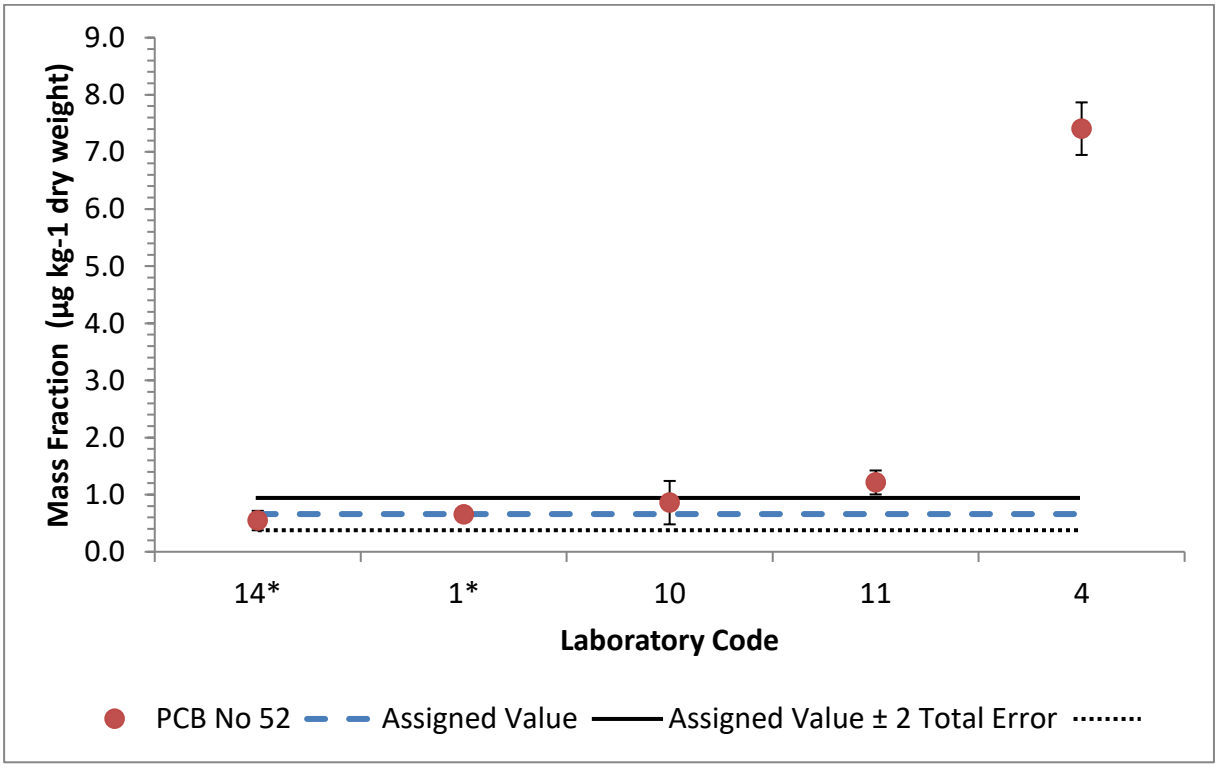

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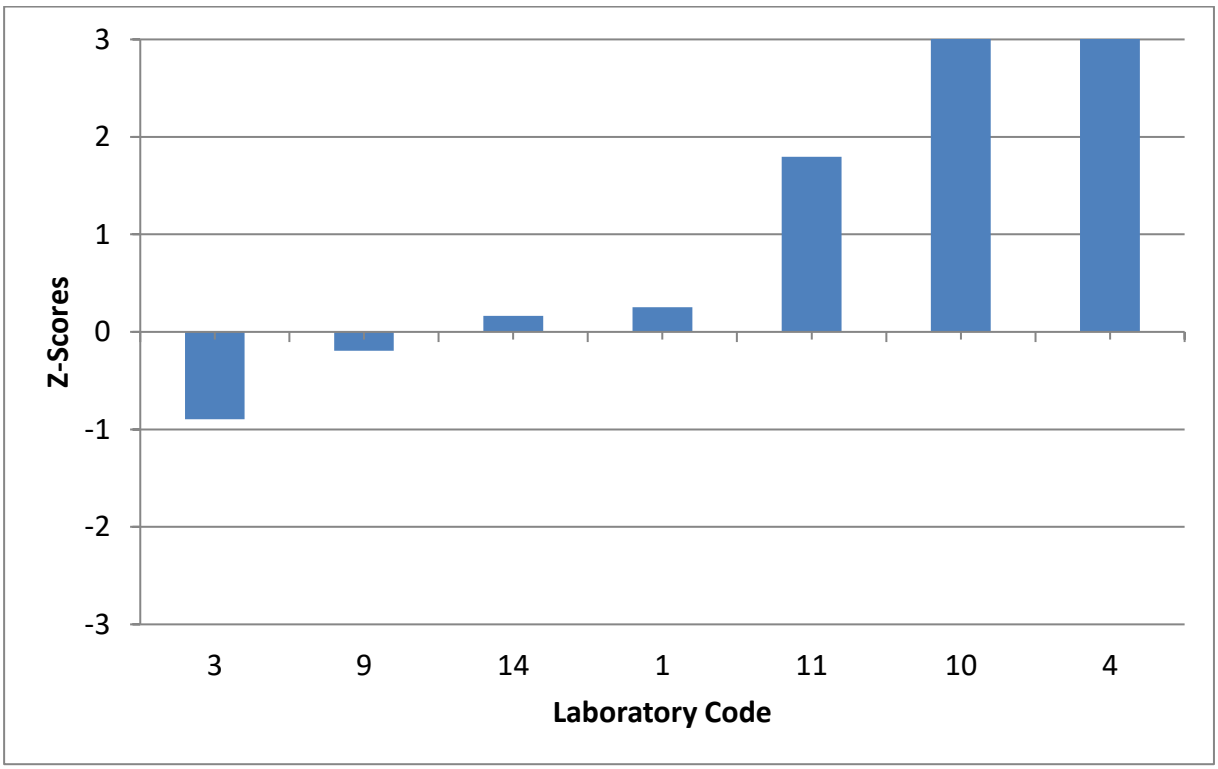

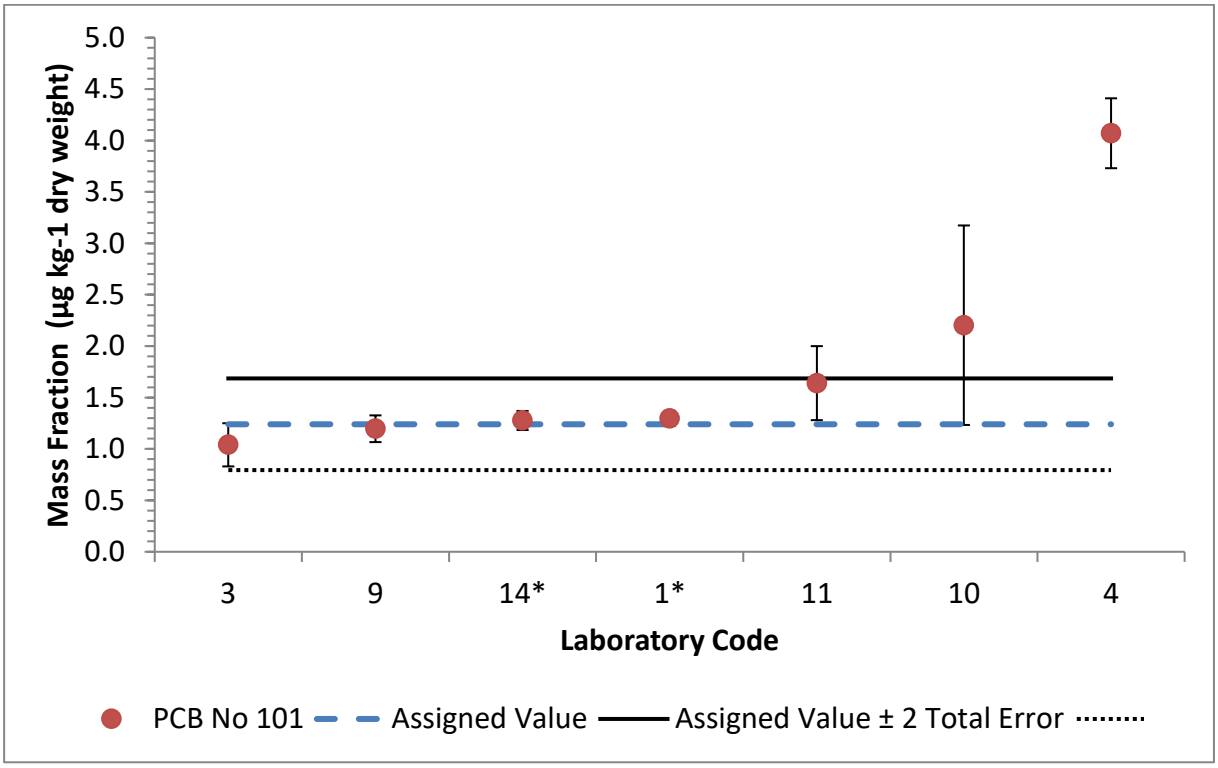

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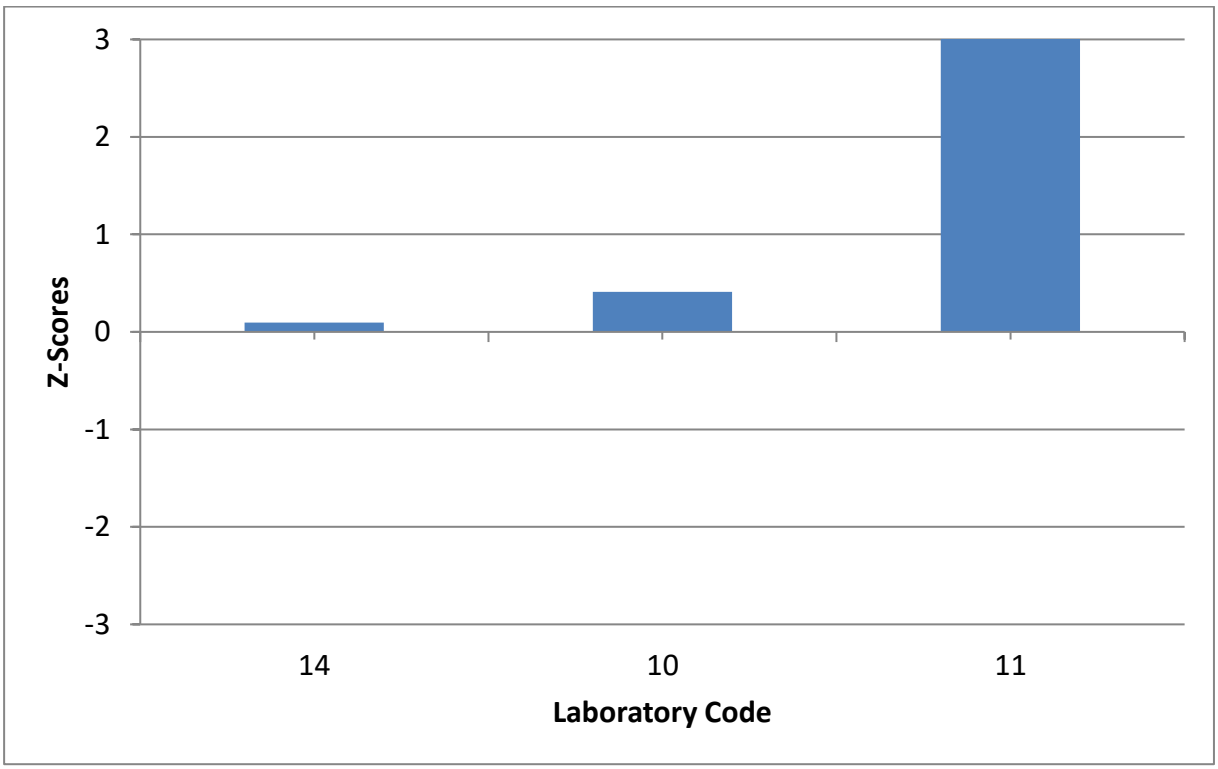

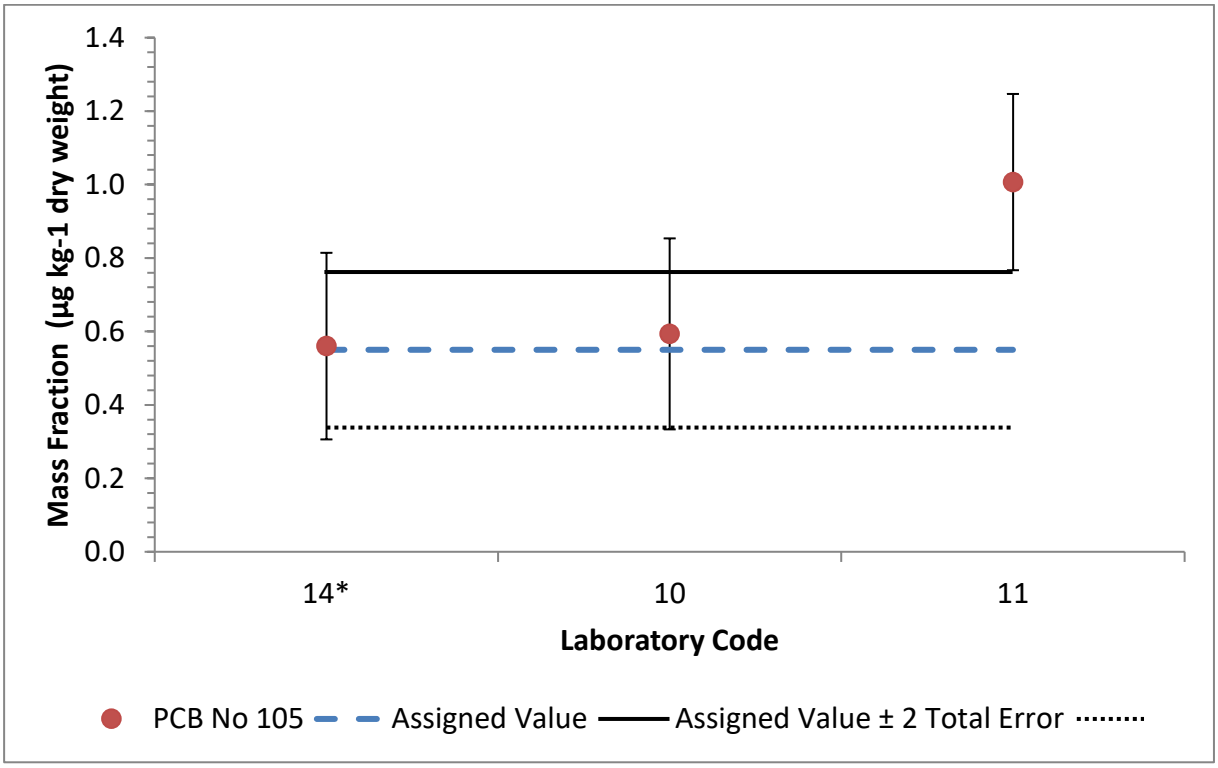

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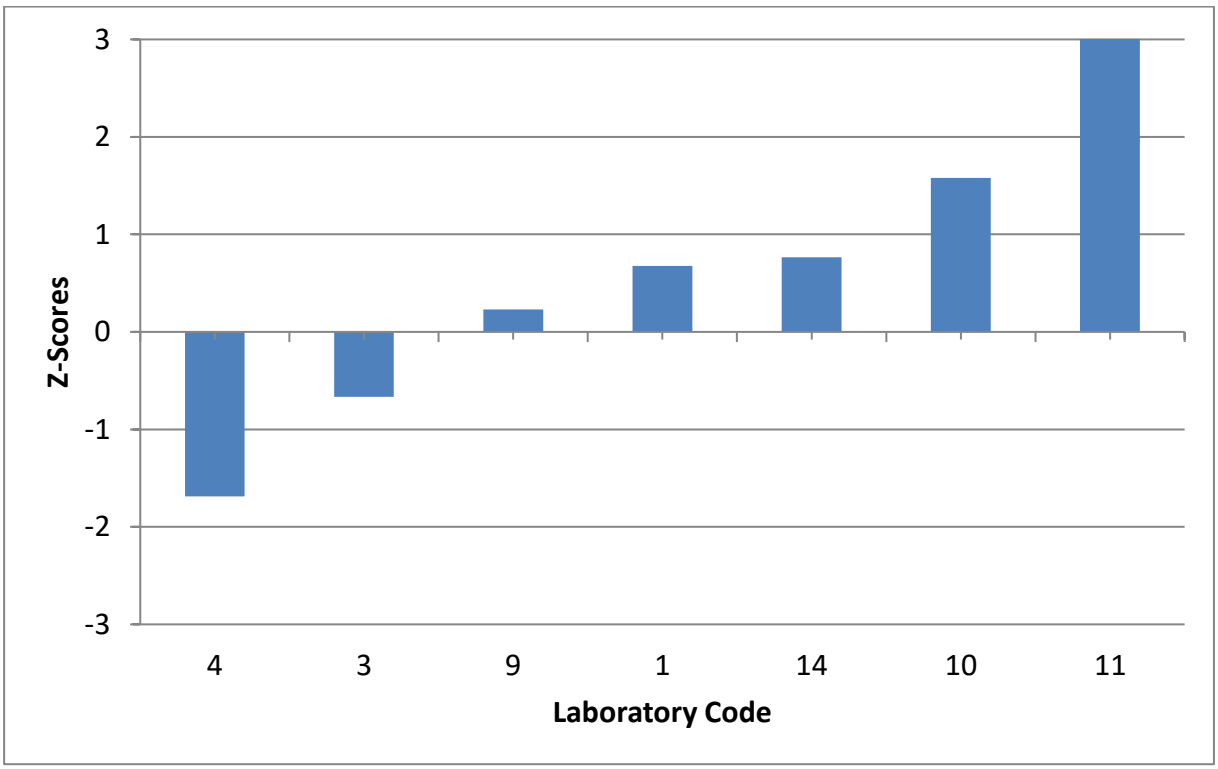

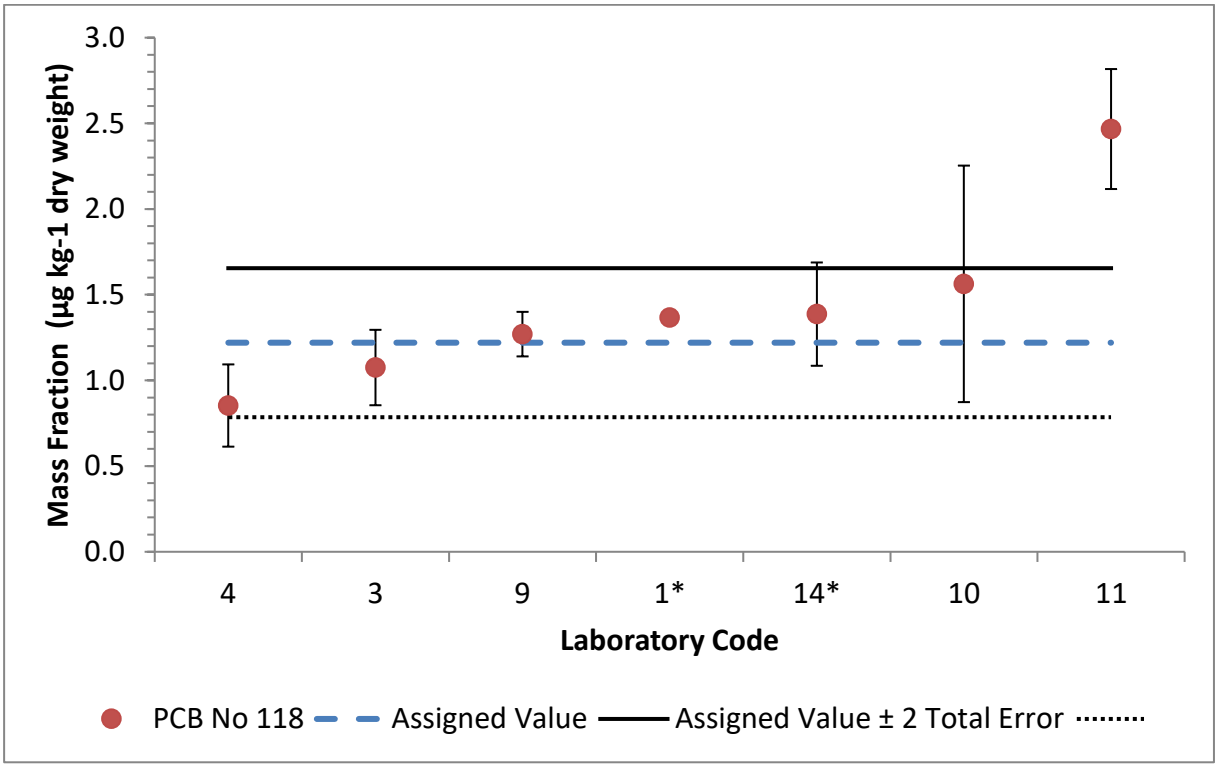

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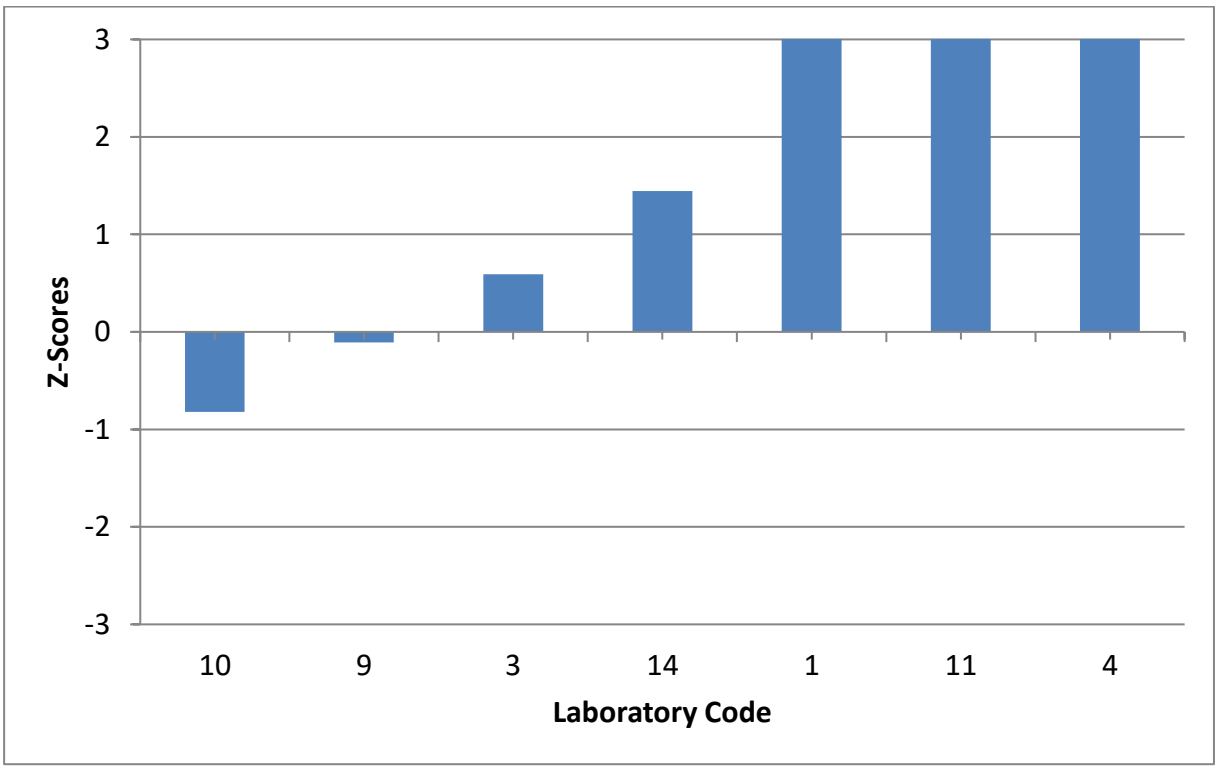

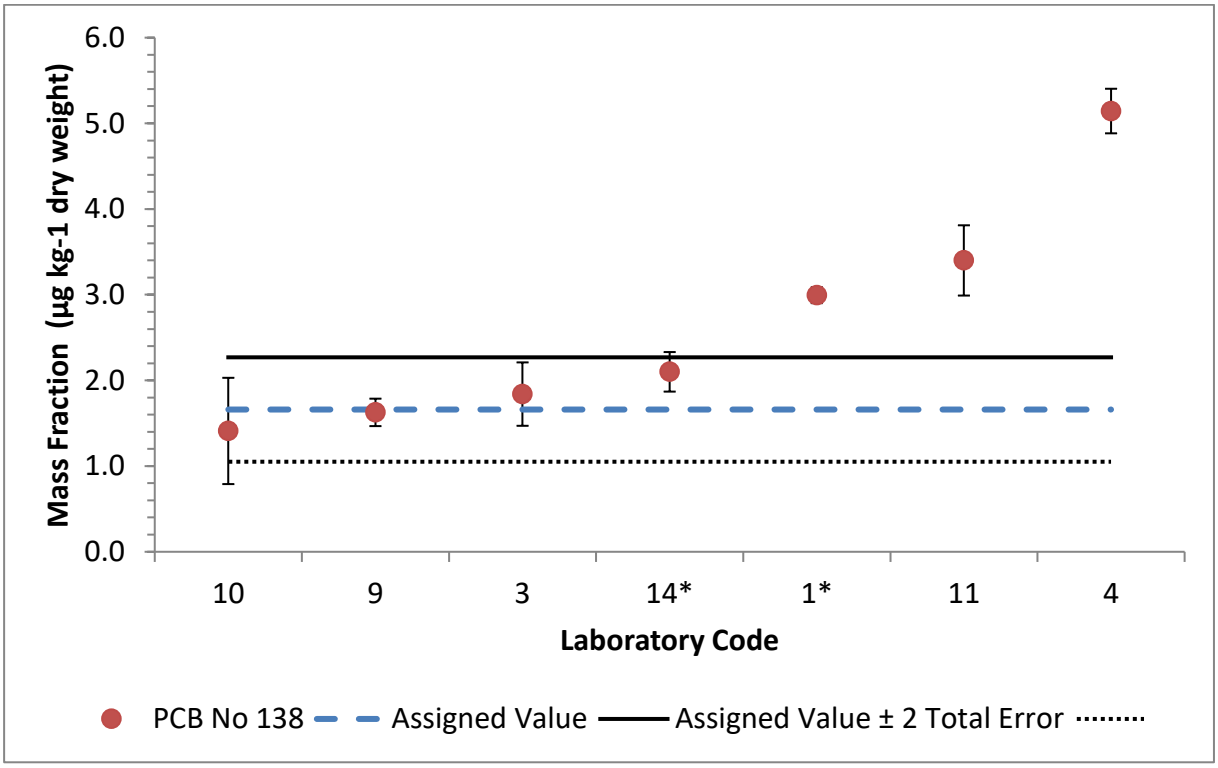

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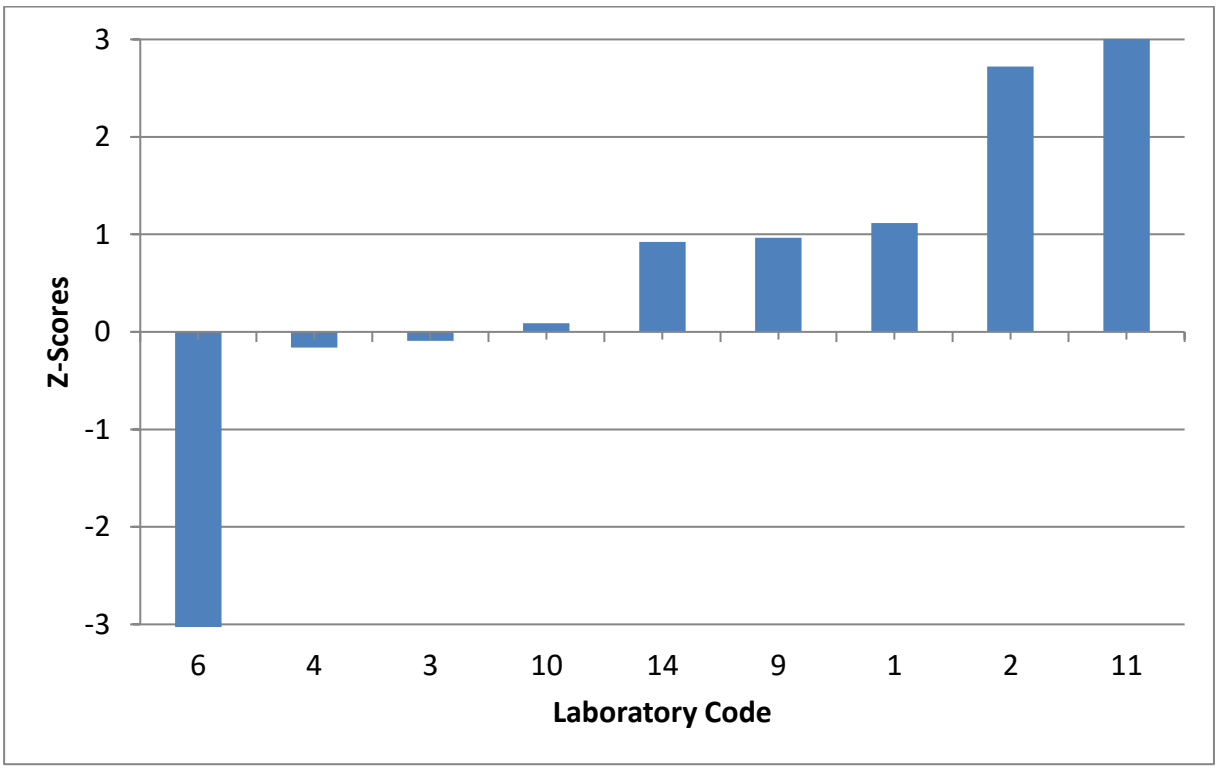

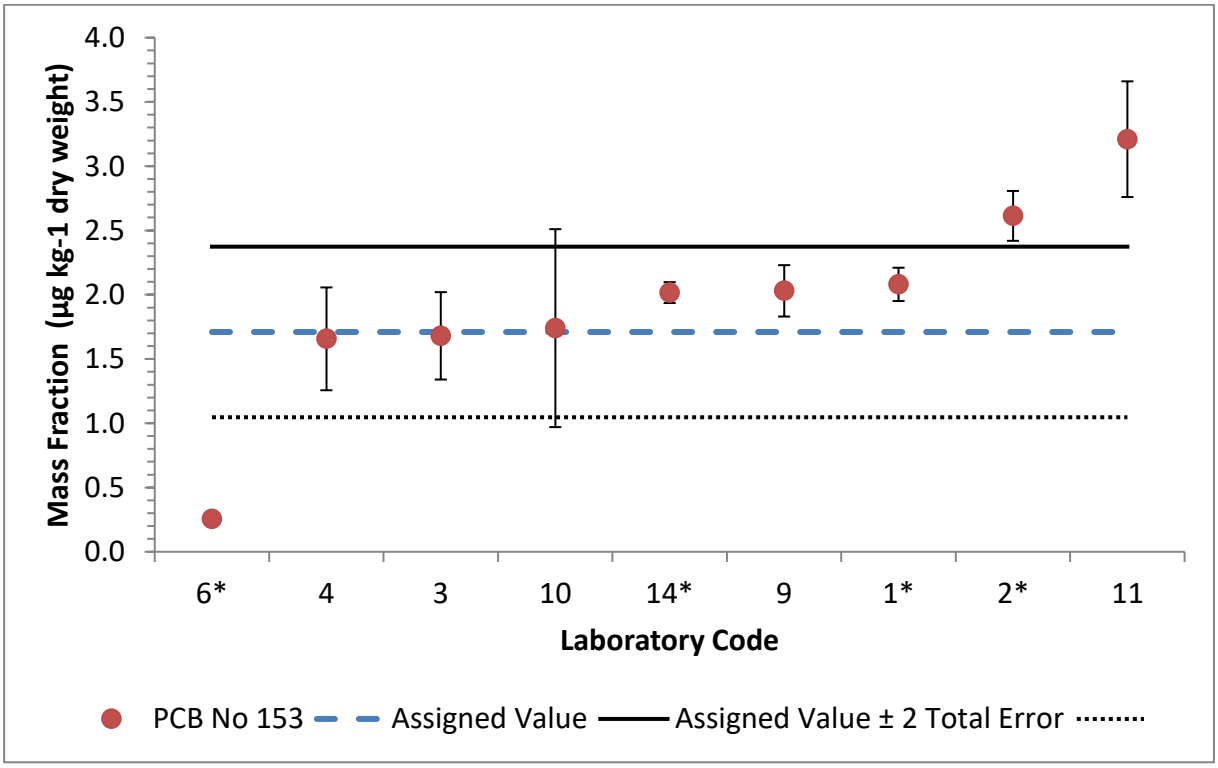

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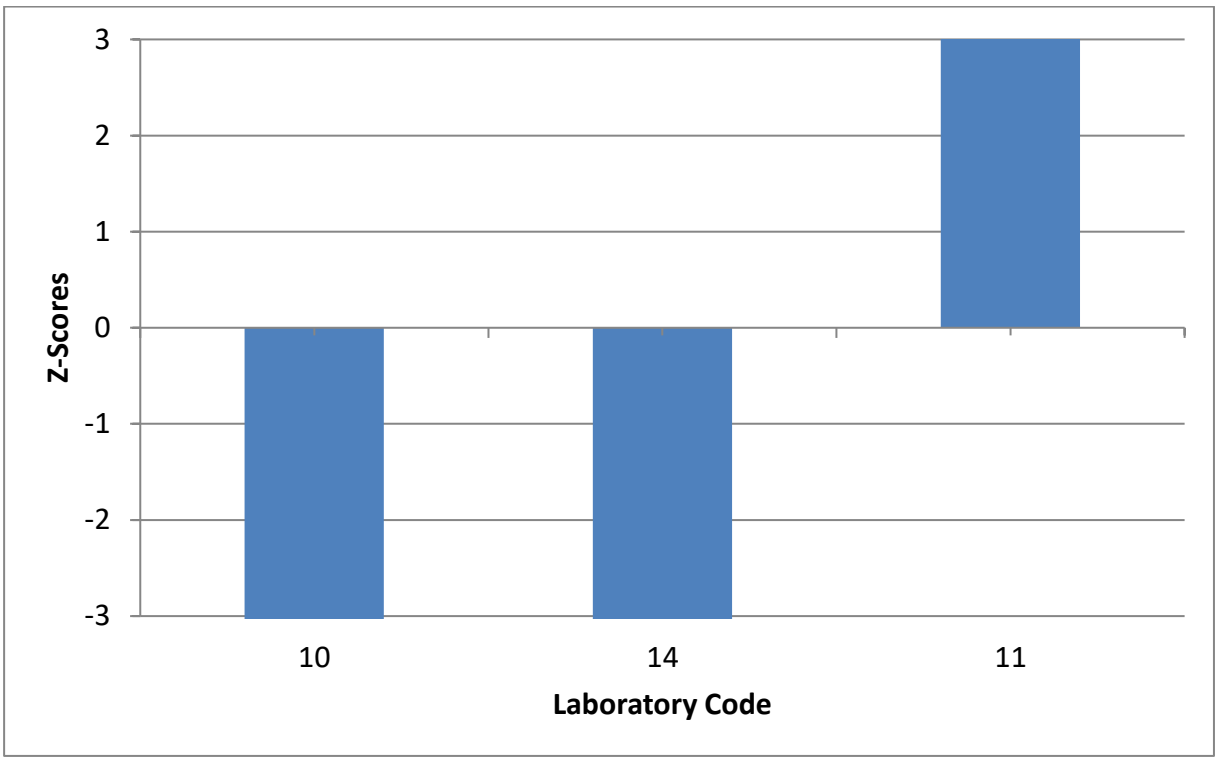

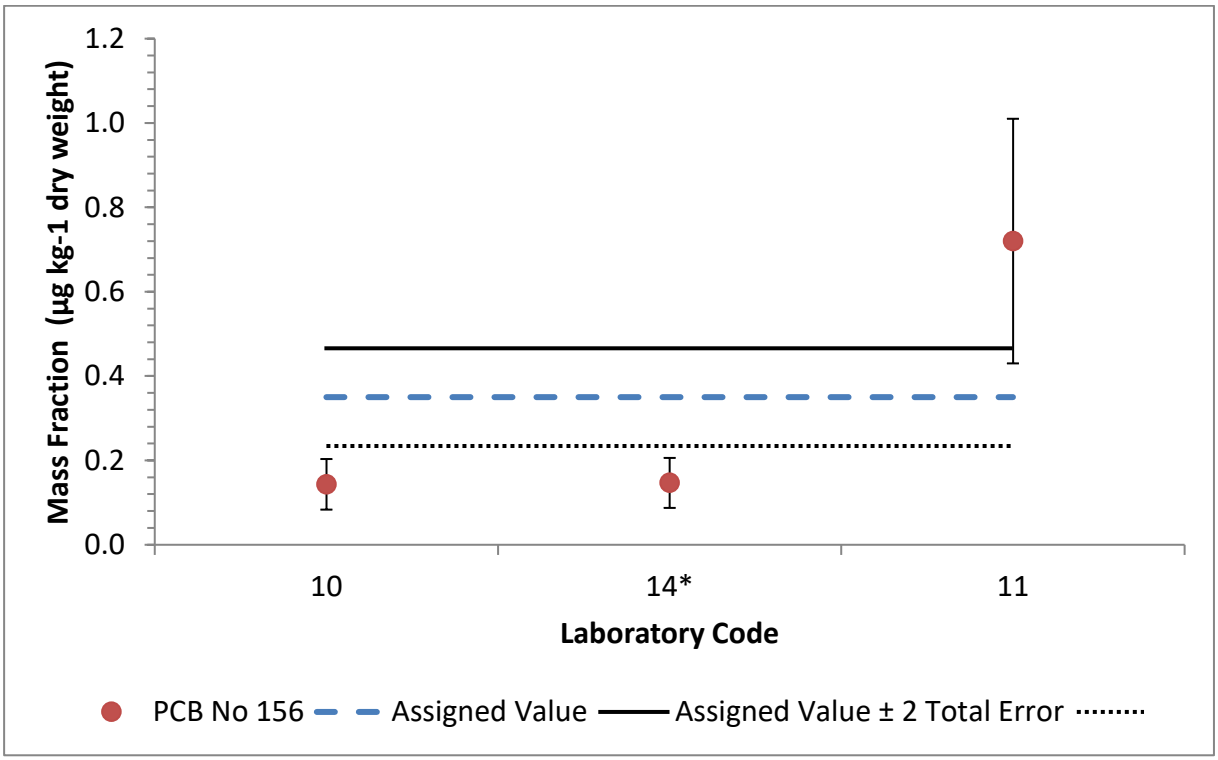

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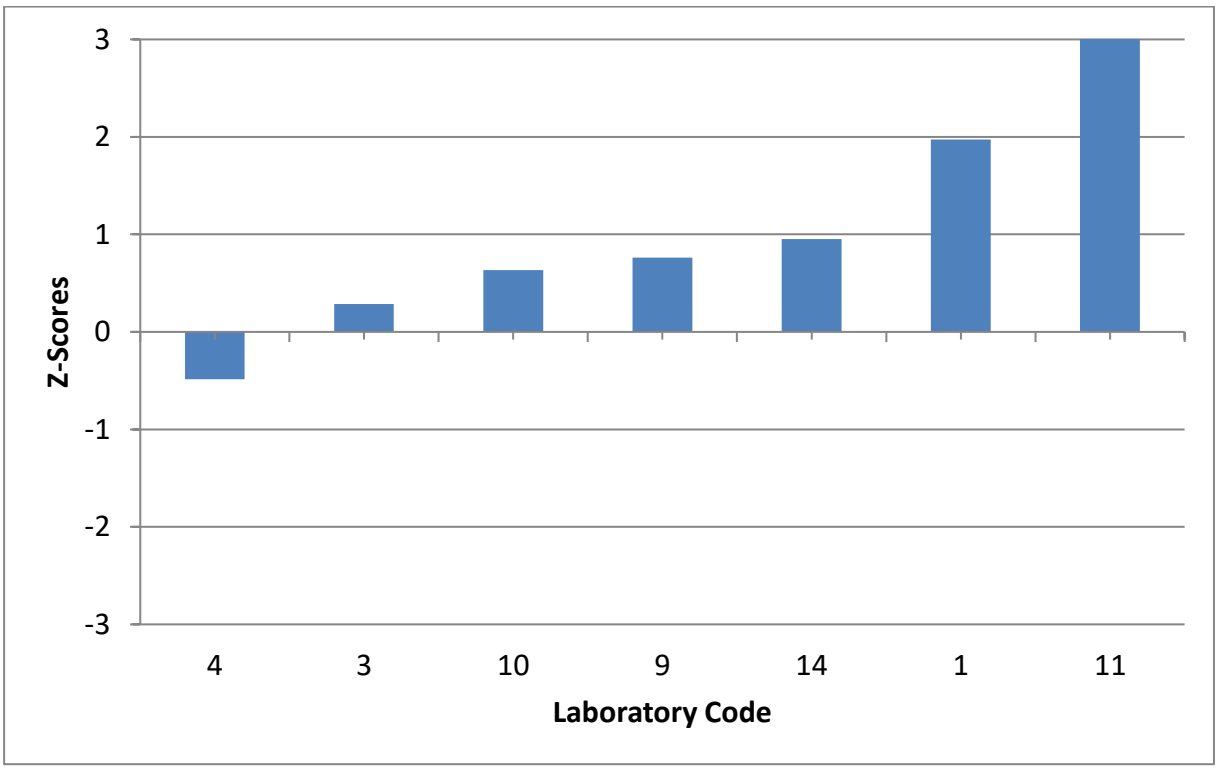

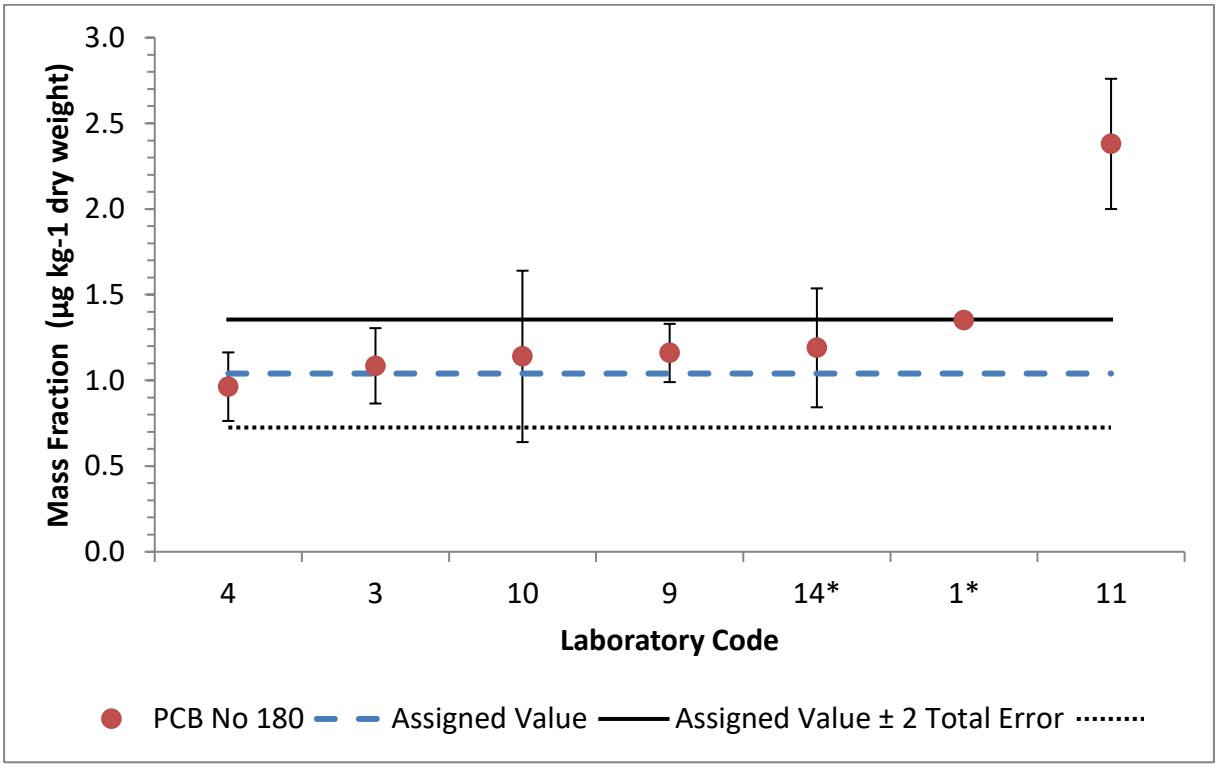

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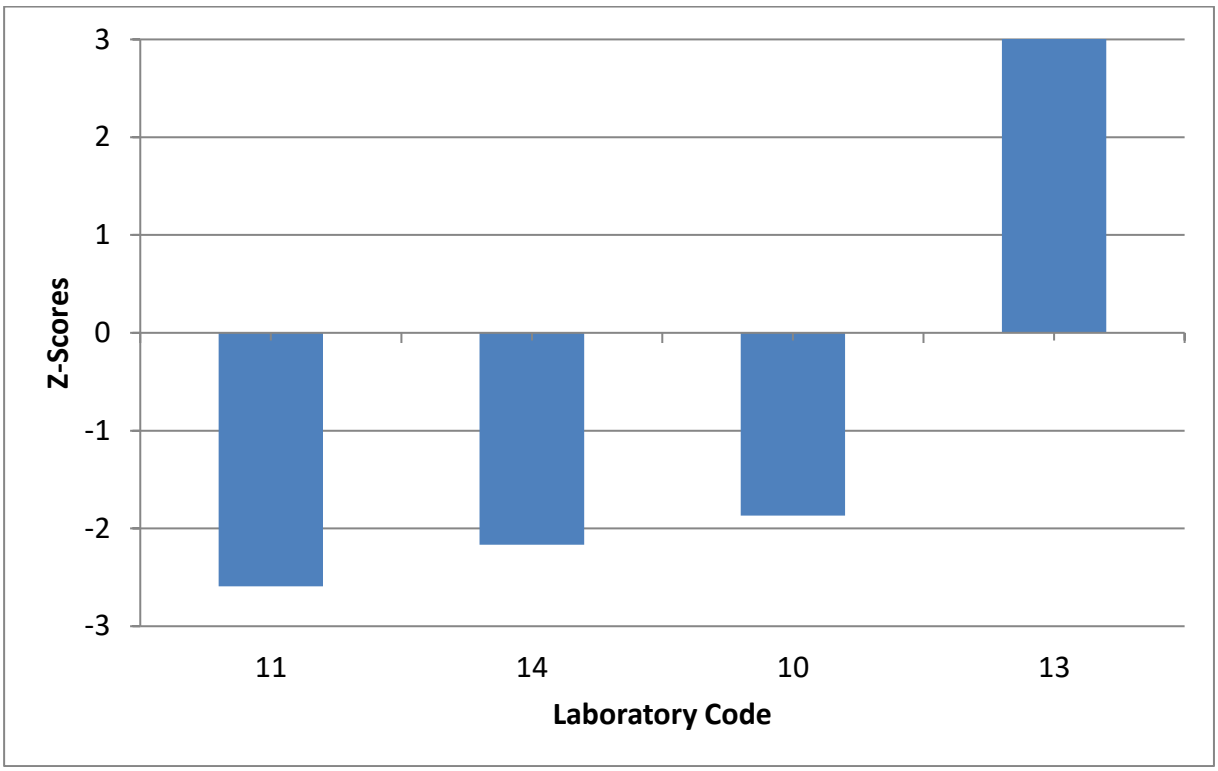

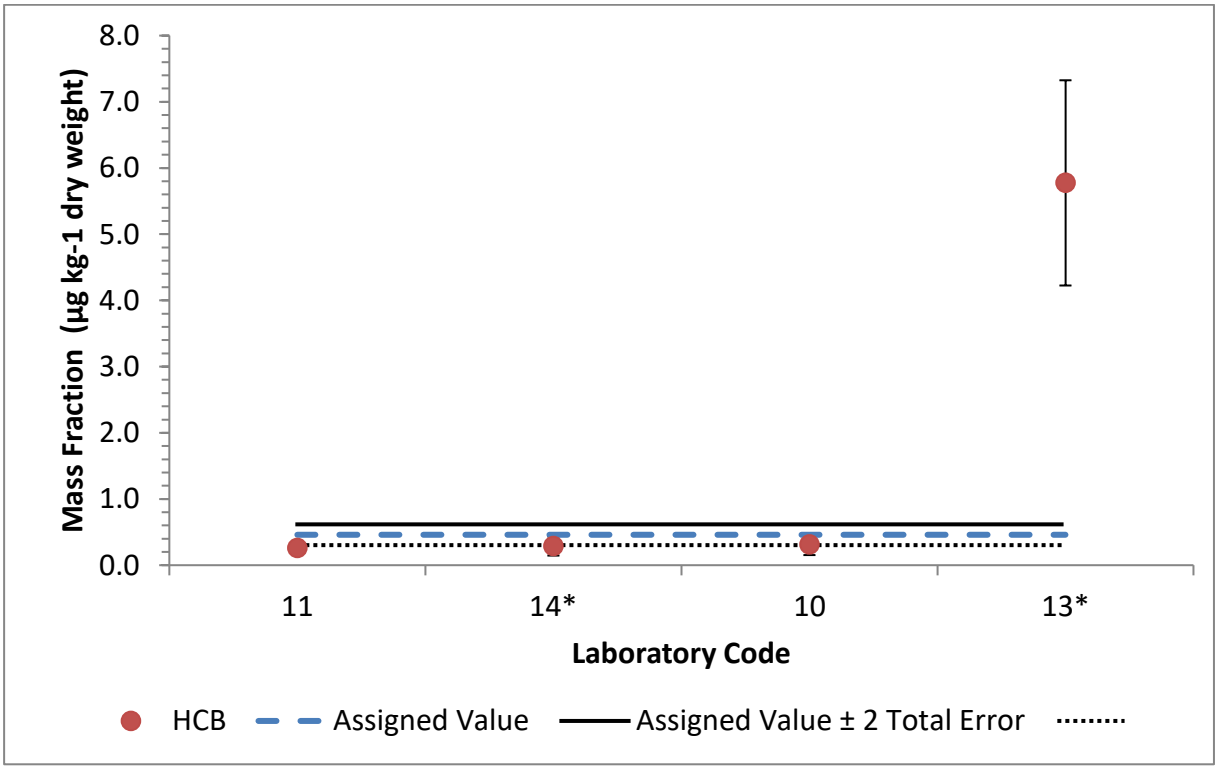

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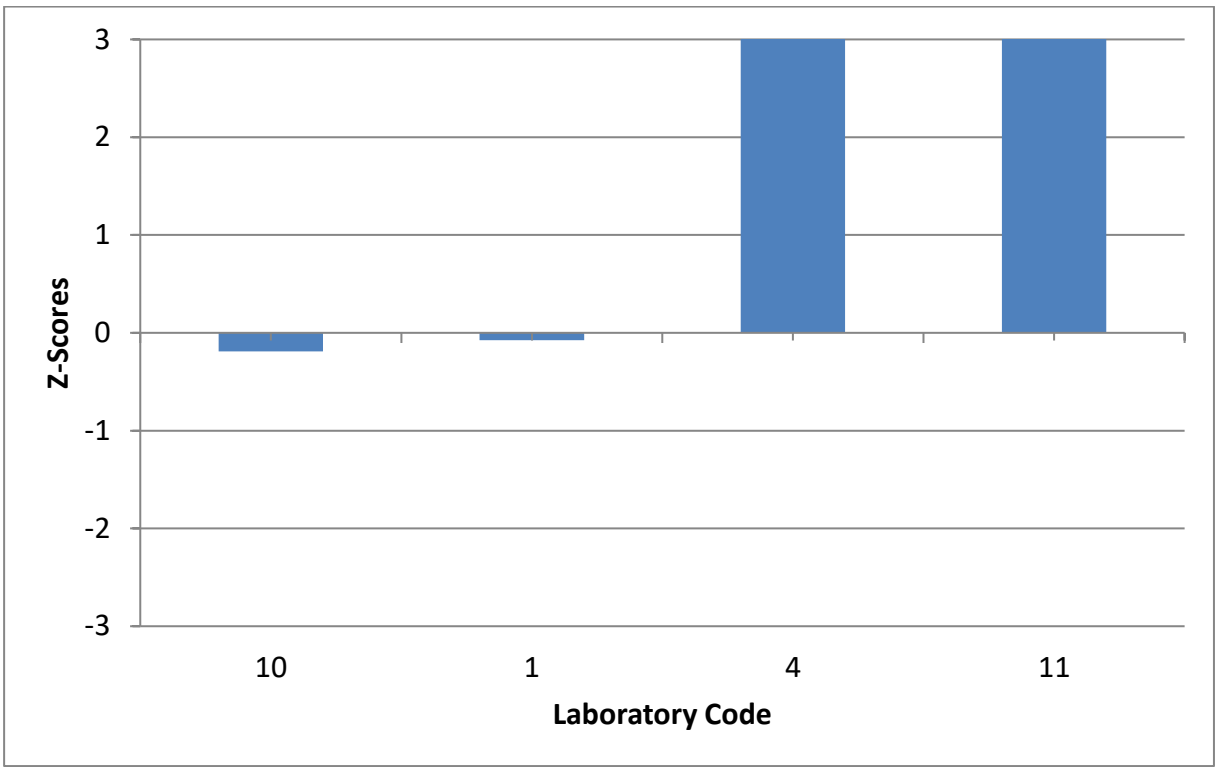

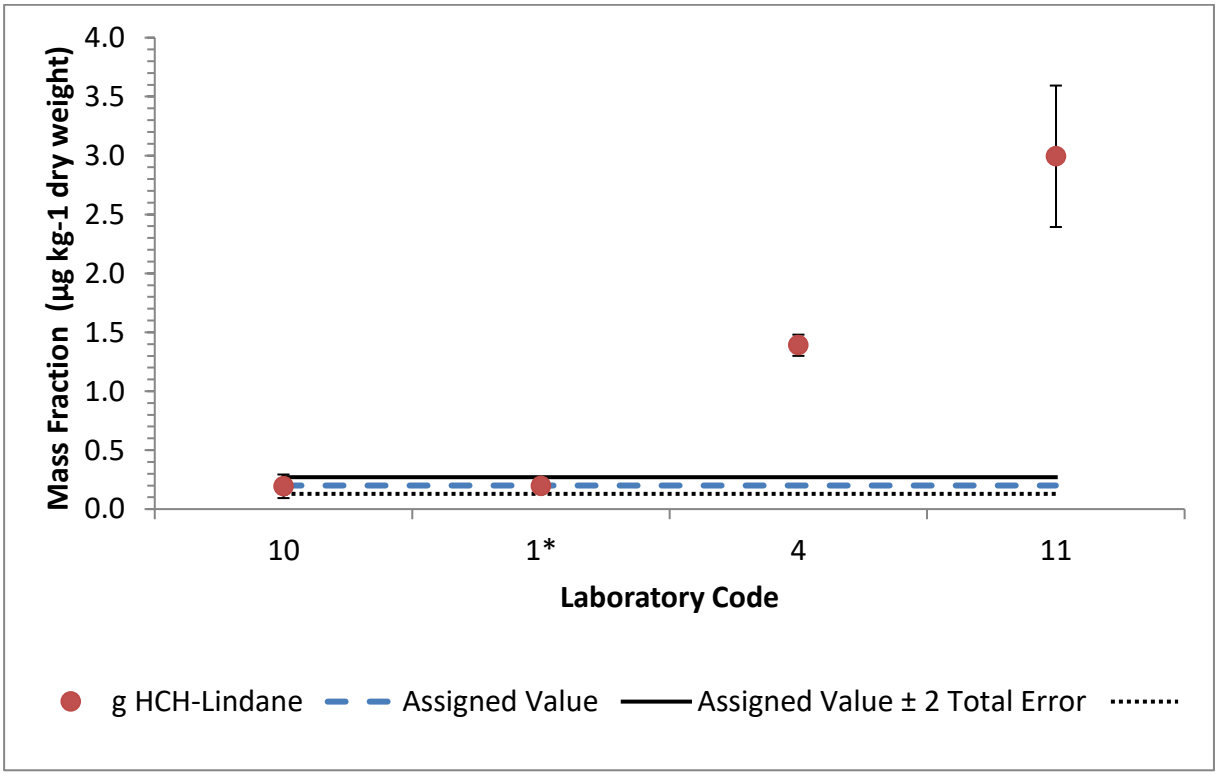

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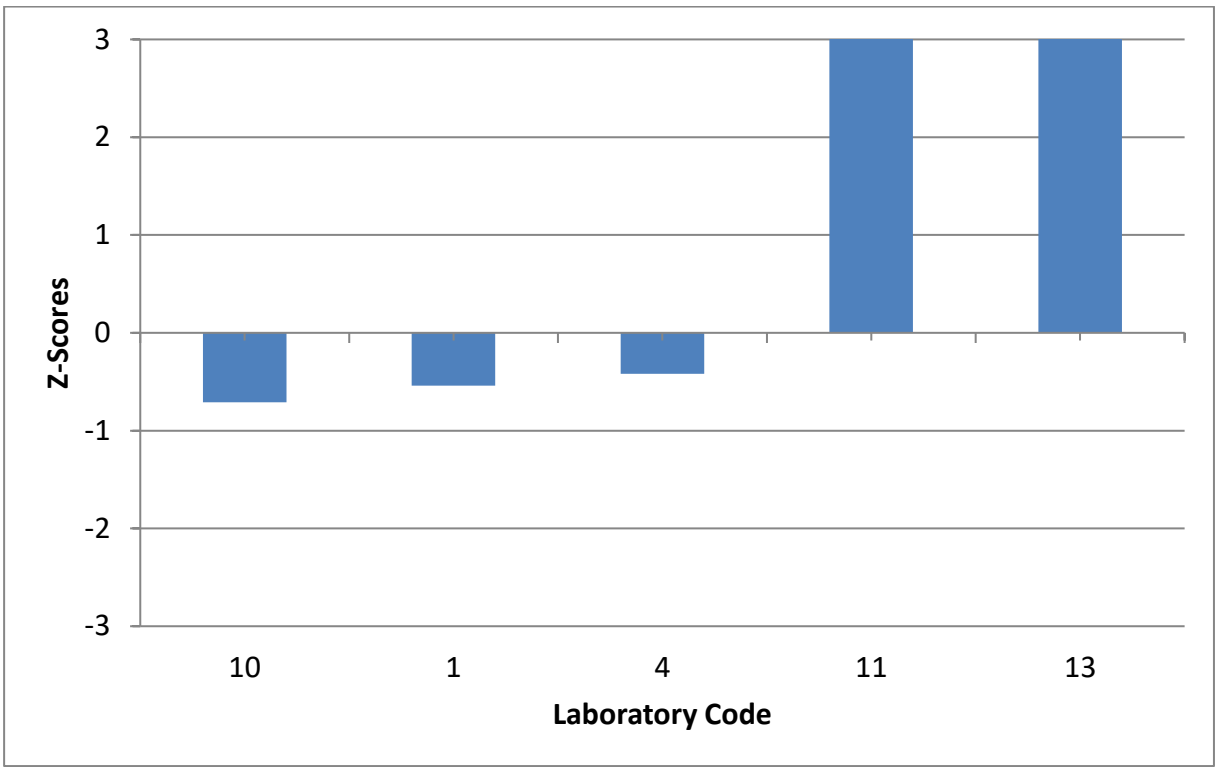

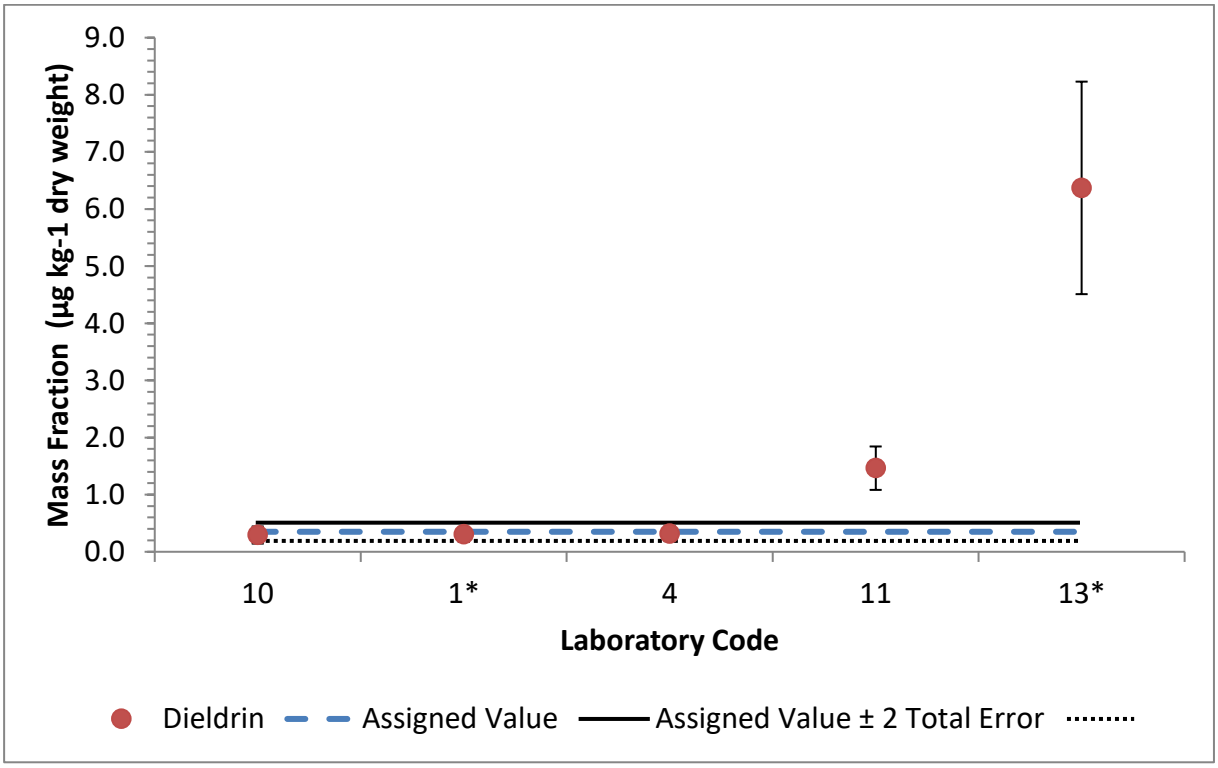

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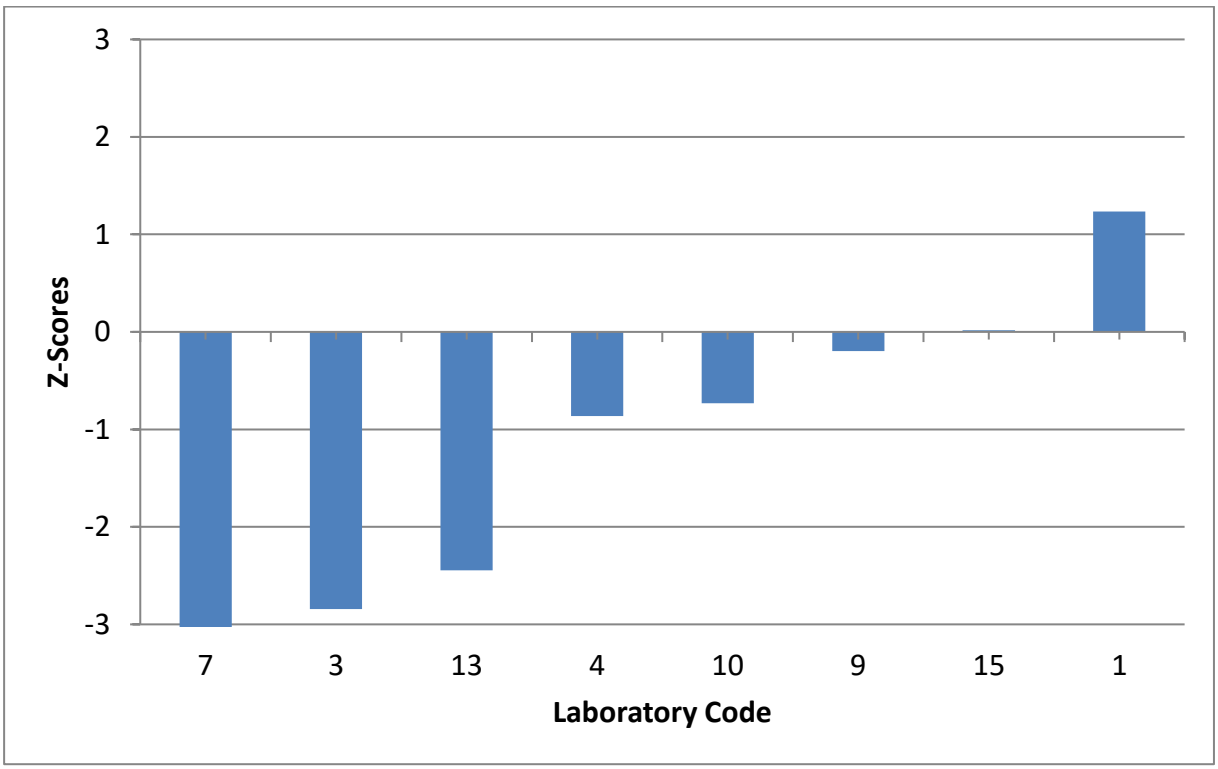

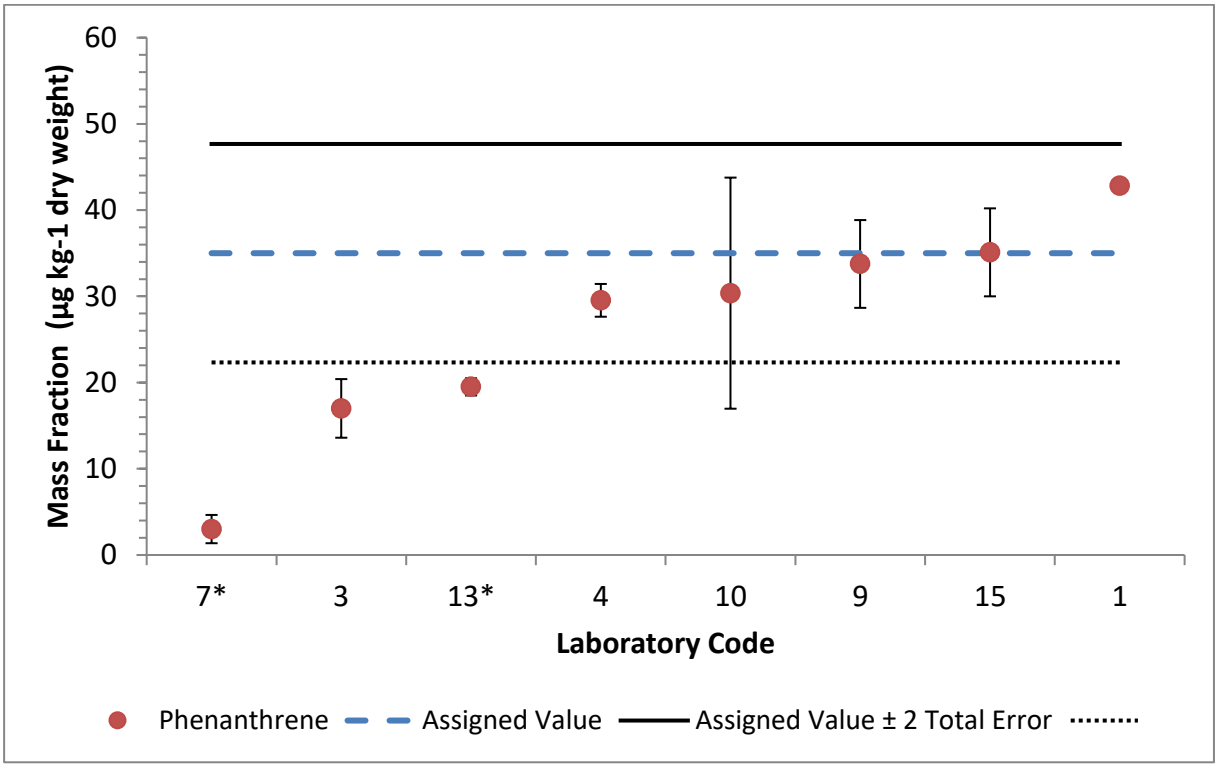

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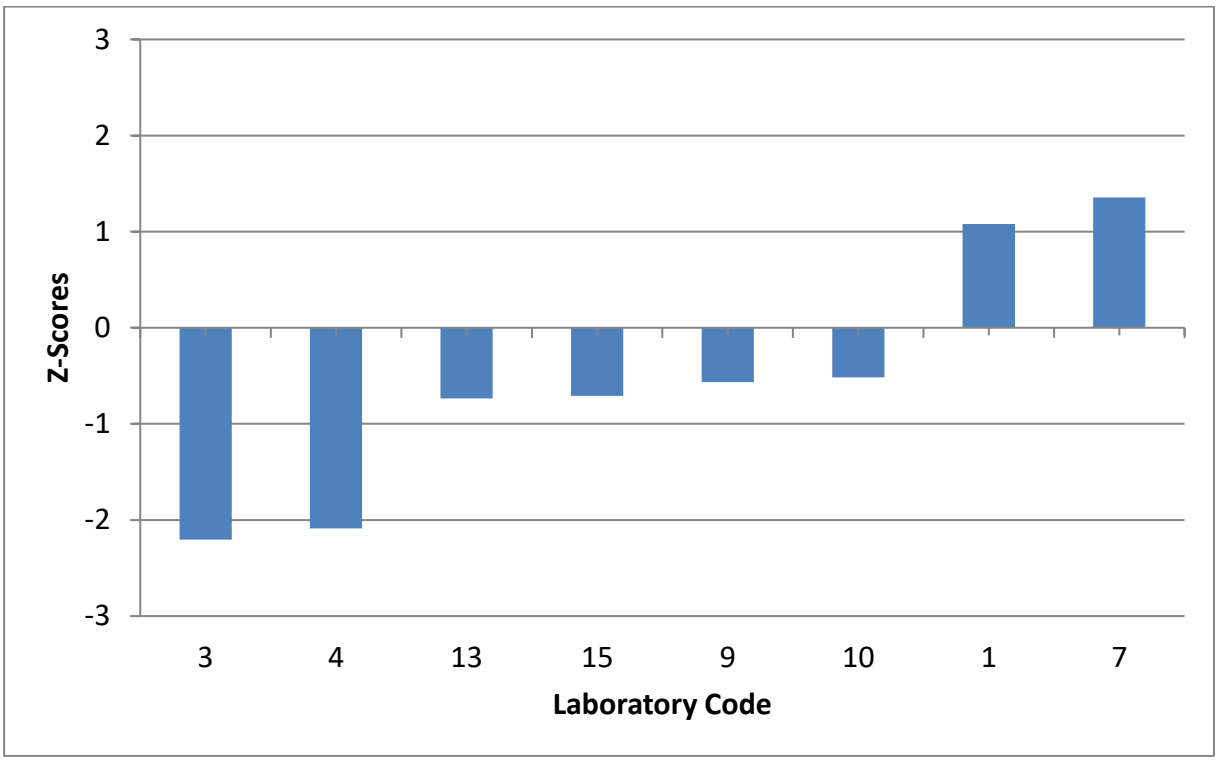

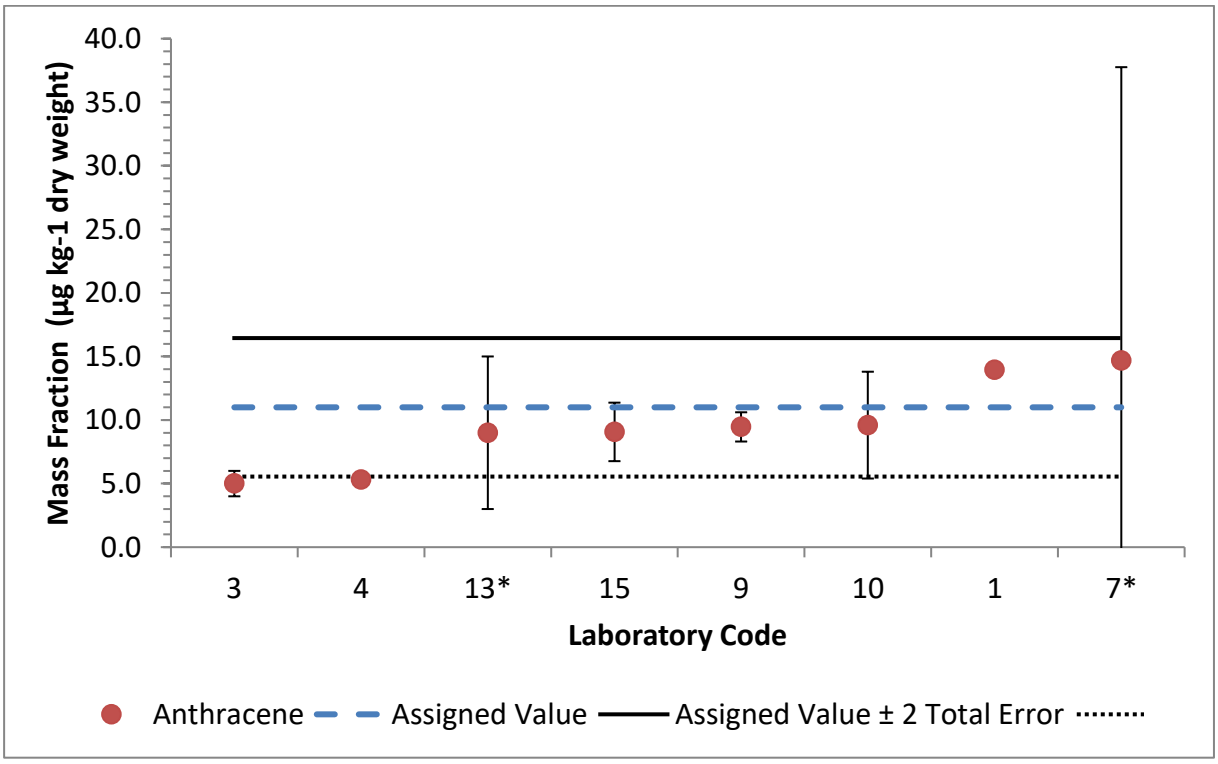

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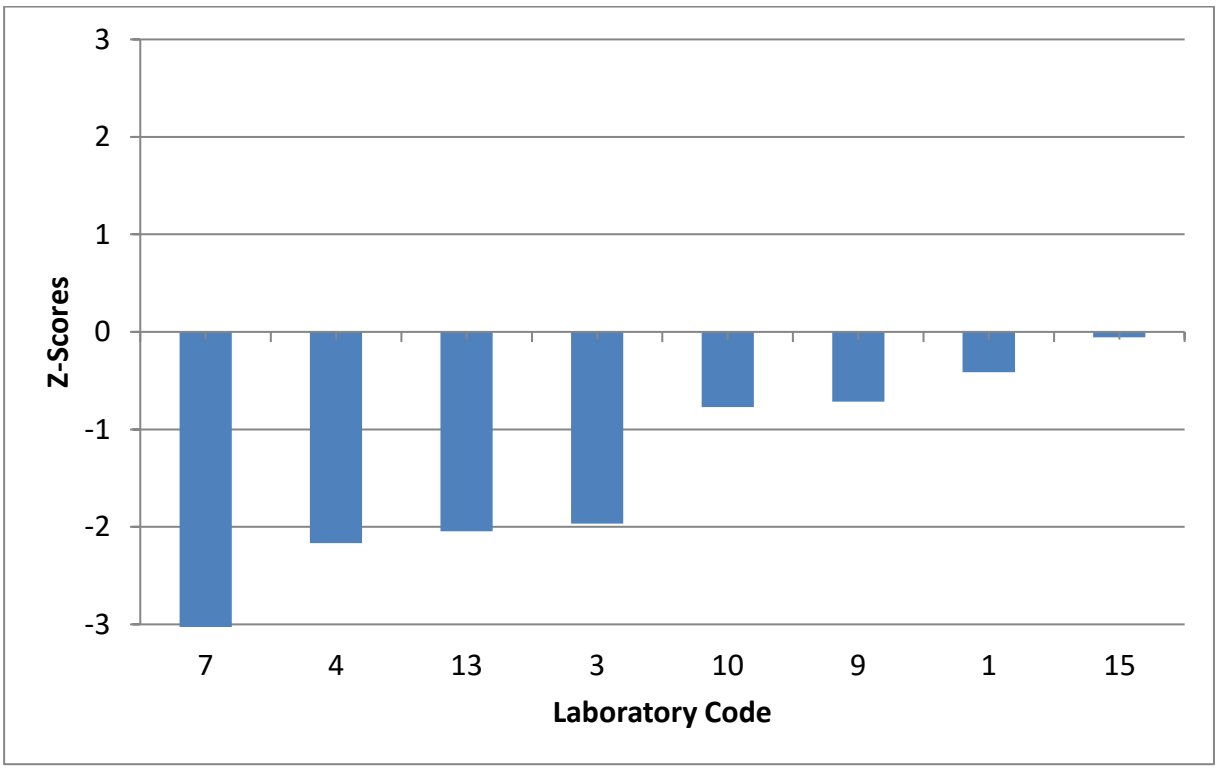

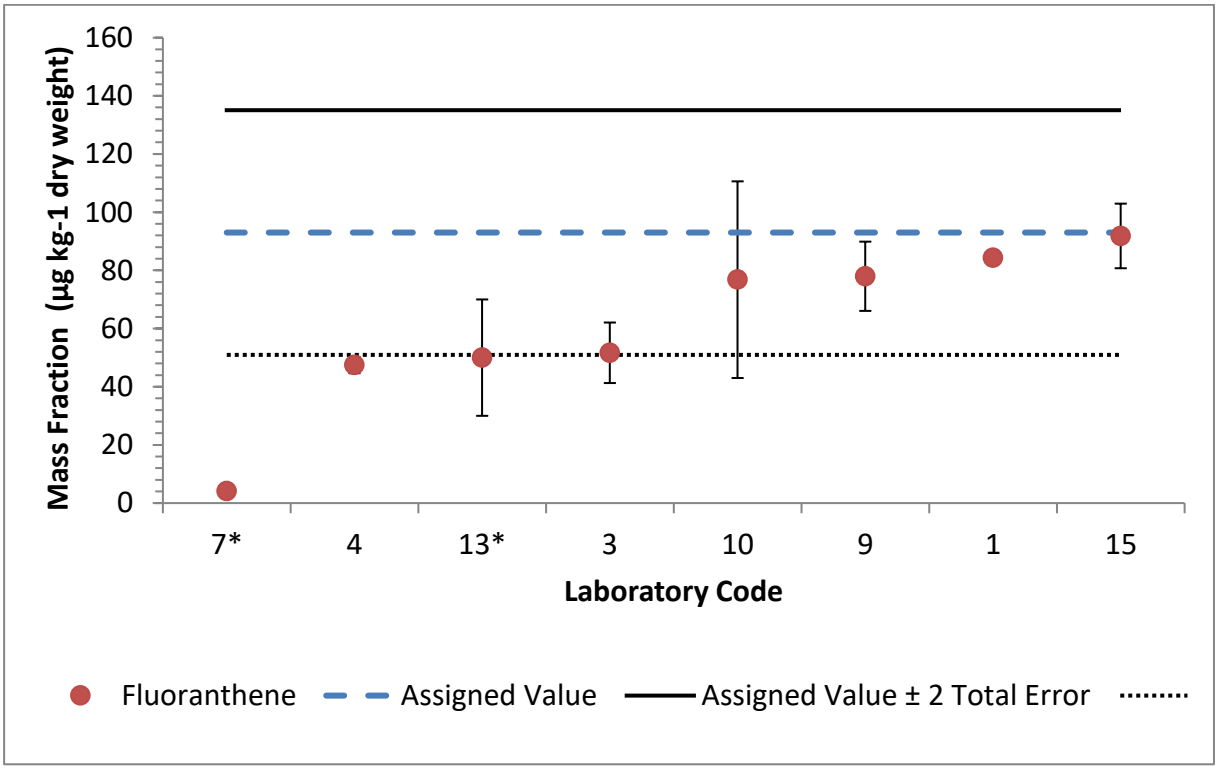

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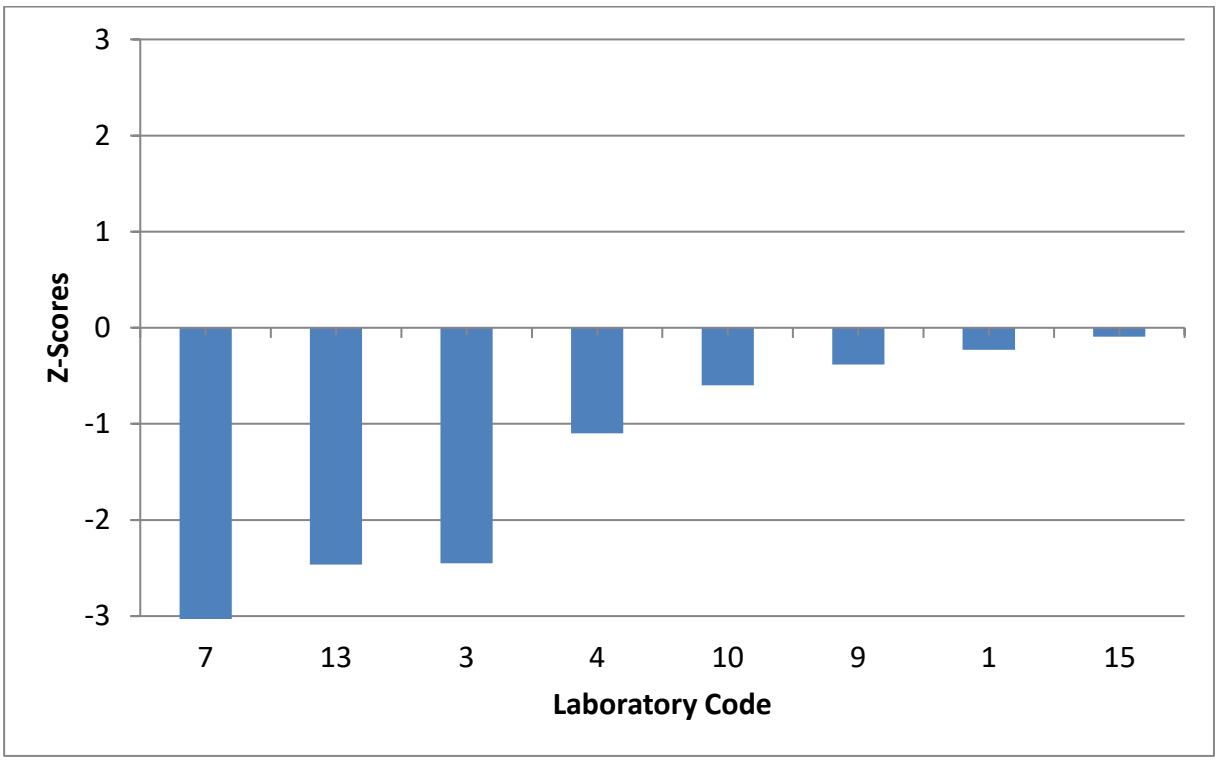

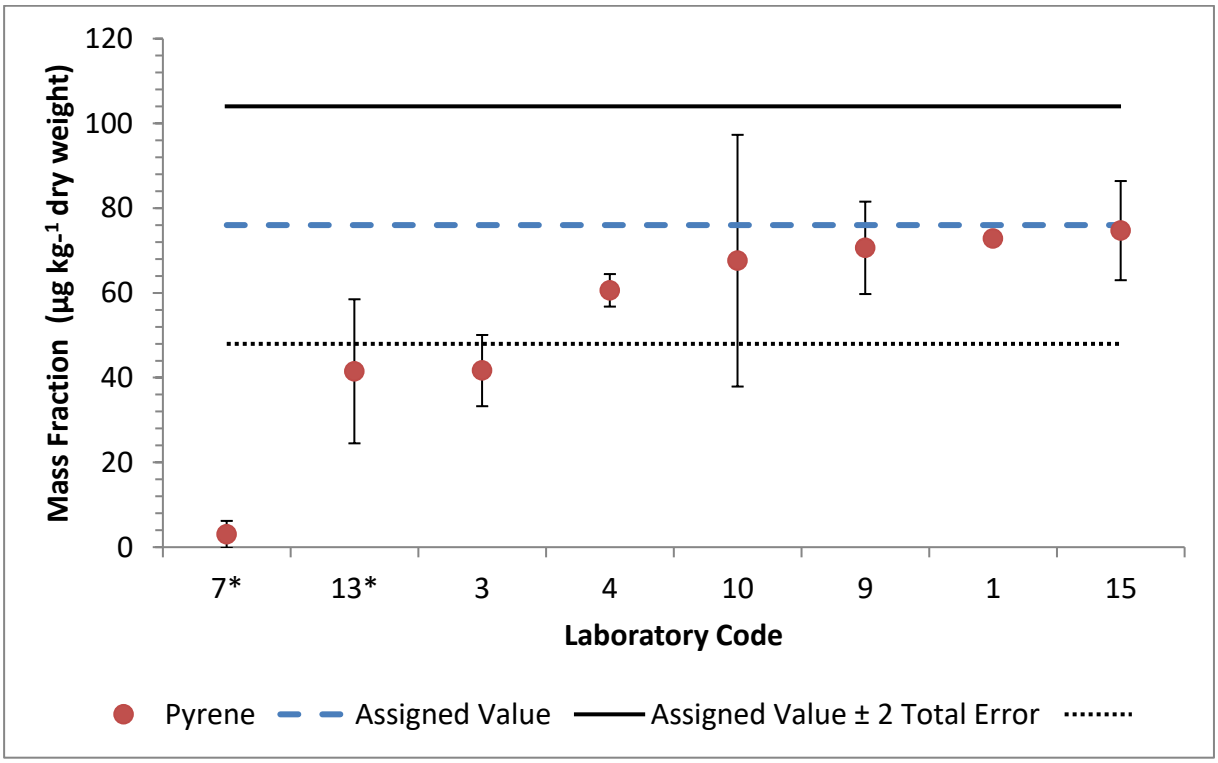

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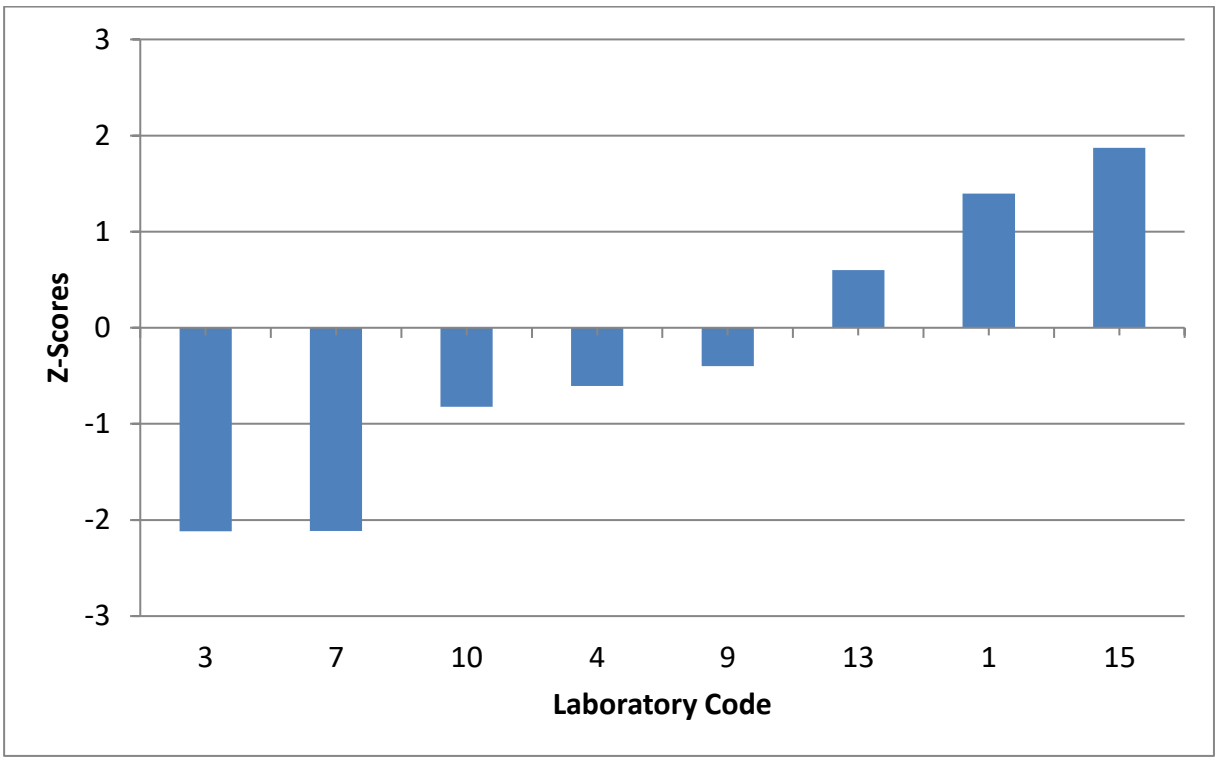

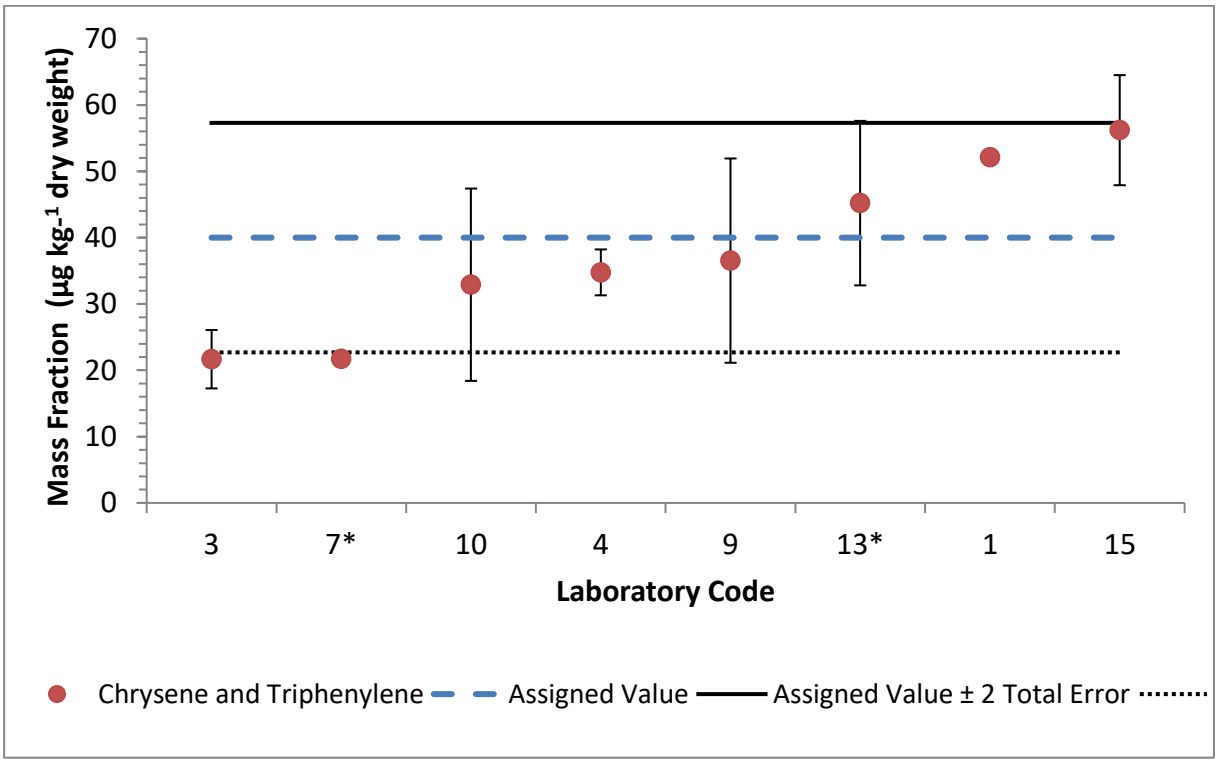

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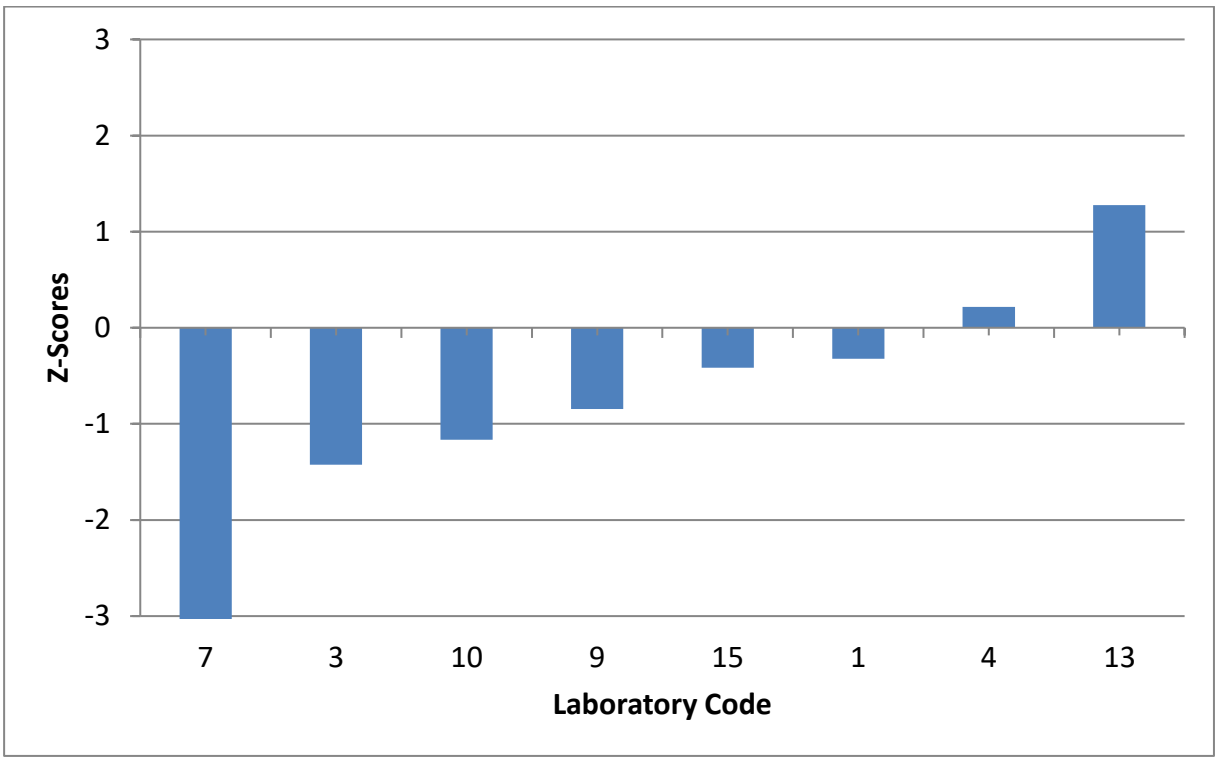

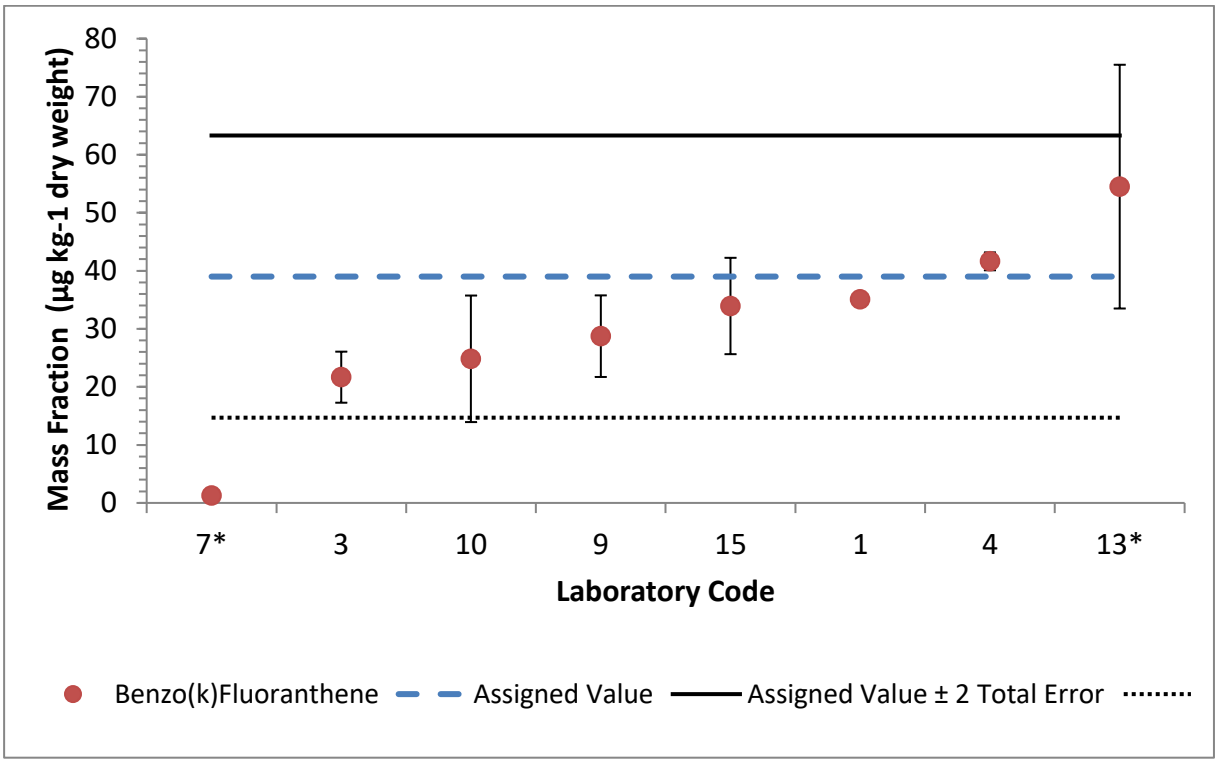

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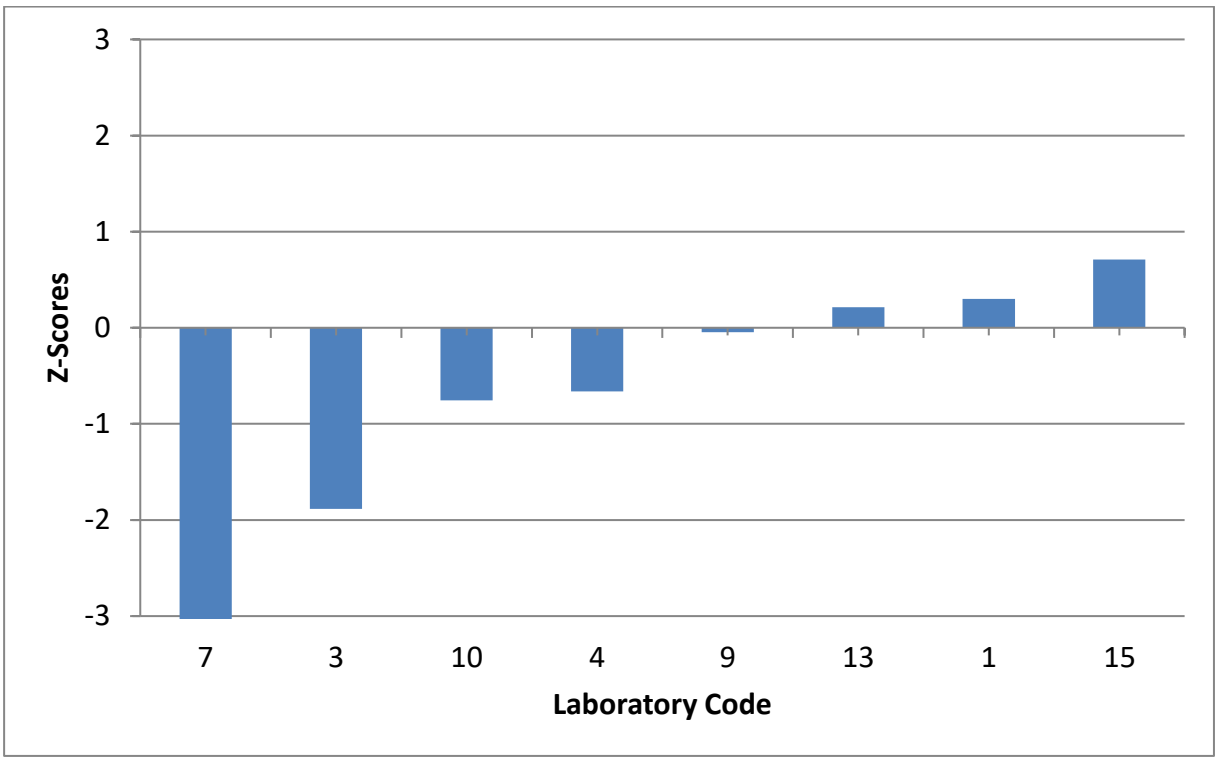

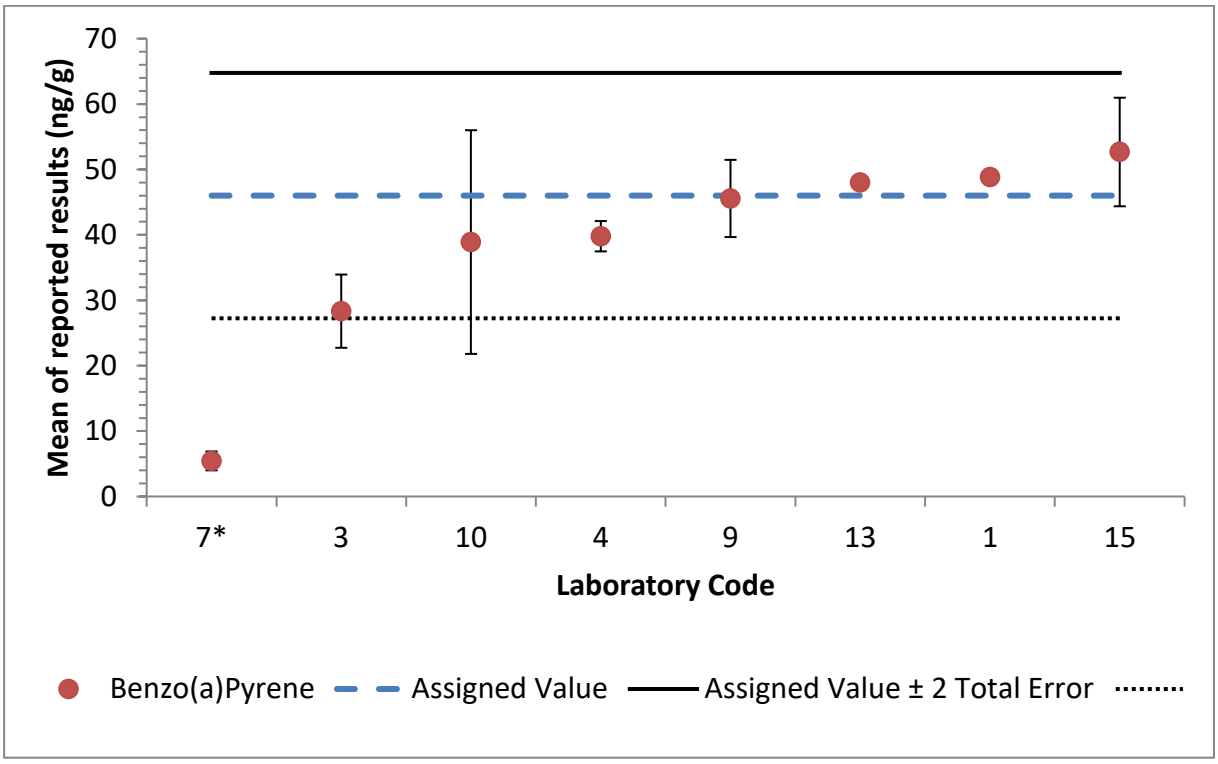

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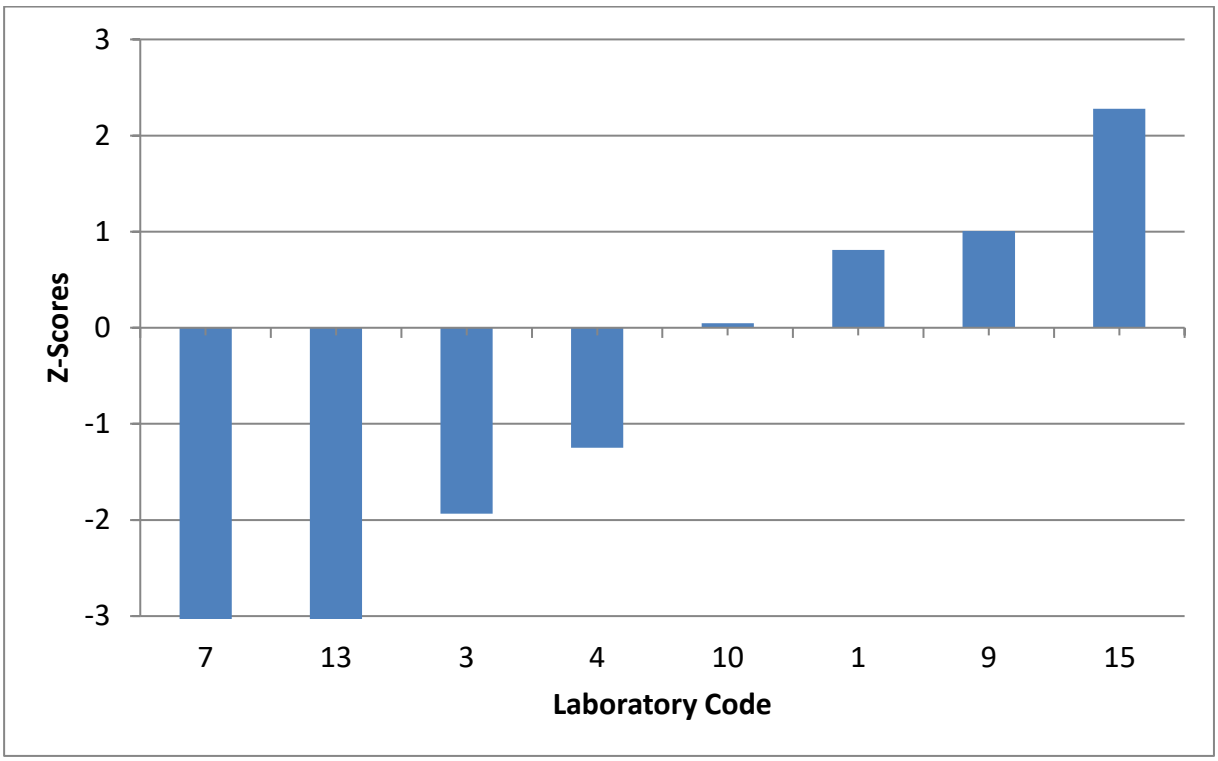

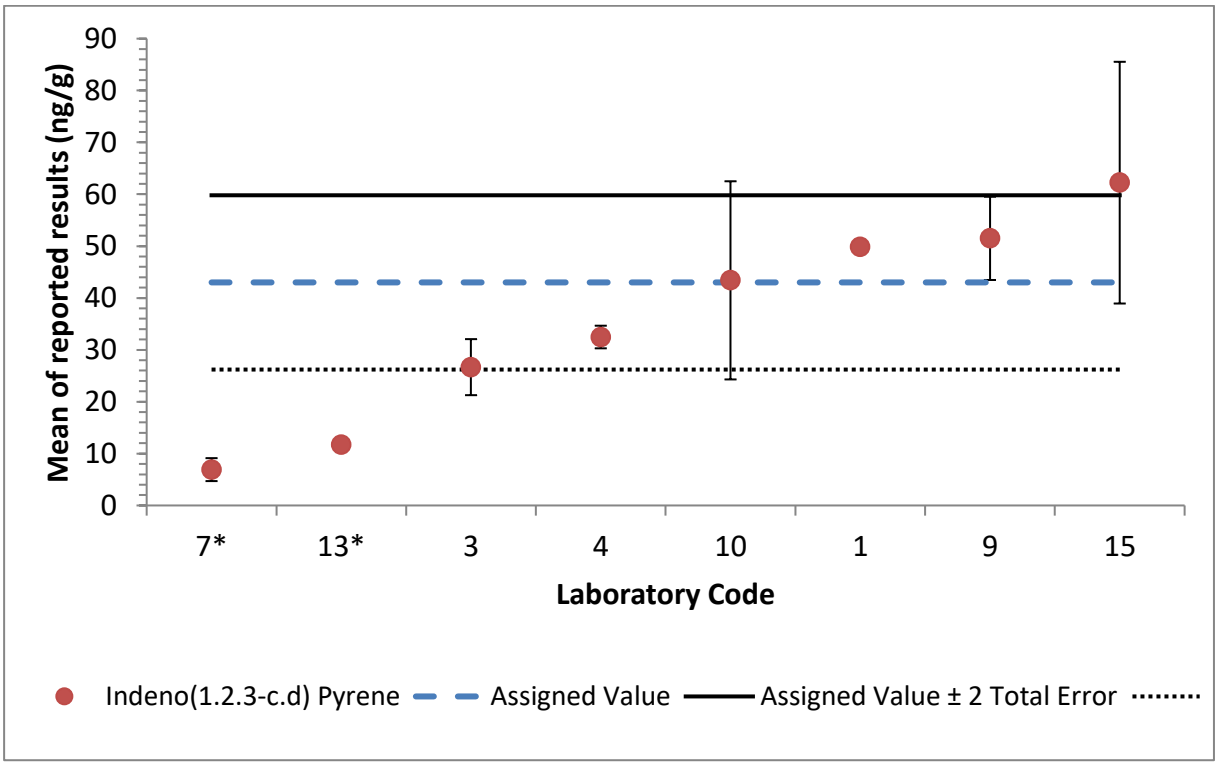

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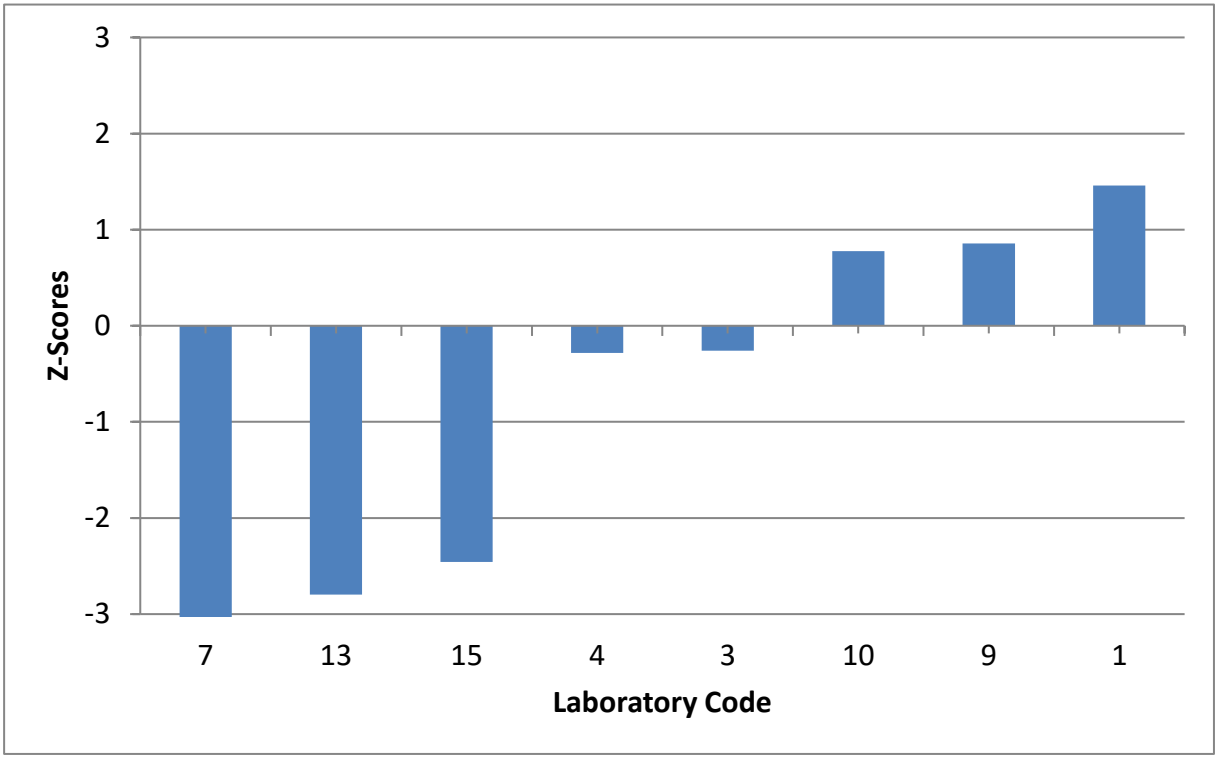

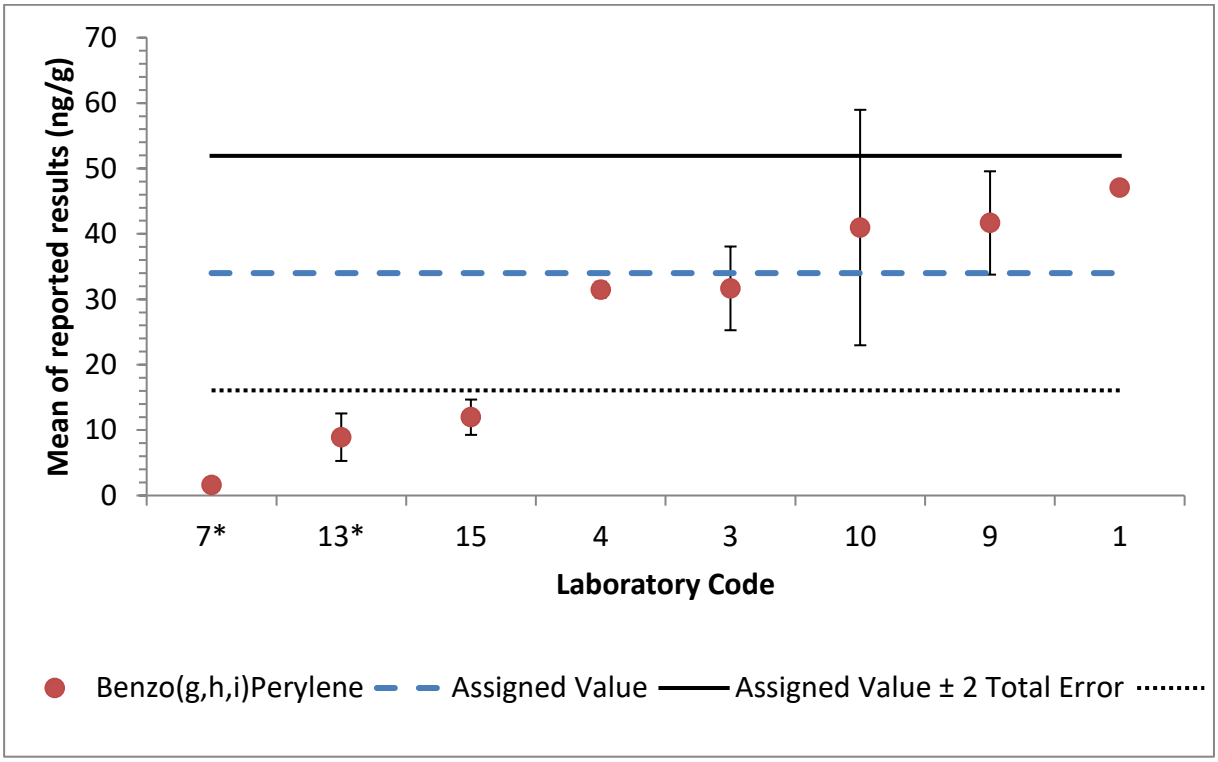

UNITED NATIONS

EP

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UNEP

UNITED NATIONS
ENVIRONMENT PROGRAMME
MEDITERRANEAN ACTION PLAN

26. March 2021
Original: English

Meeting of the Ecosystem Approach Correspondence Group on Pollution Monitoring

Videoconference, 26-28 April 2021

Agenda item 5: Report on Training Course for Trace Elements (2019)

UNEP/MAP
Athens, 2021

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TRAINING COURSE ON THE ANALYTICAL TECHNIQUES FOR THE DETERMINATION OF TRACE ELEMENTS IN ENVIRONMENTAL SAMPLES

Organized by:

International Atomic Energy Agency-Environment Laboratories
4 Quai Antoine 1er, MC 98000 MONACO

2 – 13 September 2019

IAEA-EL staff involved:

E. Vasileva-Veleva, Research Scientist
S. Azemard, Laboratory Technician
A-M. Orani, Laboratory Technician
P. Mandjukov, Consultant MESL
S. Sander, MESL Section Head
L. Barilaro-Hamonic, Team assistant

Prepared in collaboration with:

CONTENTS

TRAINING COURSE ON THE ANALYTICAL TECHNIQUES FOR THE DETERMINATION OF TRACE ELEMENTS IN ENVIRONMENTAL SAMPLES

1. Background

A training course on the analysis of trace elements in marine environmental samples was organized in NAEL/MESL on behalf of MEDPOL, for participants from Mediterranean laboratories involved in the UNEP/Mediterranean Action Plan - MEDPOL marine pollution monitoring program in the framework of the Land-based sources (LBS) Protocol of the Barcelona Convention.

A letter describing the course content was sent out beginning of May 2019 to all MEDPOL National Focal Points, inviting them to nominate candidates for the training course from their respective countries.

The selection process of trainees was performed fully in line with the recommendations and conclusions of the Meeting of CorMon on Pollution Monitoring that was held from 1 to 2 April 2018 in Podgorica. Namely the selection of the six successful candidates was done jointly by MESL staff and the MEDPOL monitoring and assessment officer, by applying the following criteria:

- The selection process included consultations of MED POL Monitoring and Assessment Officer with the MED POL Focal Points of respective Contracting Parties regarding their need to participate in Training Course;
- The nominated candidates had to be staff members of the national laboratories that the national focal point would also designate them for participation in 2019 Proficiency Tests.
- The nominated candidates would have to be able to apply knowledge, built during 2019 Training Courses on trace elements analysis, in their regular work related to the sampling and assessment determination of trace elements in marine biota and sediment samples; use and maintenance of analytical equipment, selection of the appropriate reference materials, as well as quality assurance of monitoring data produced by their respective national laboratories participating in the MEDPOL IV/IMAP monitoring programme.
- The nominated candidates would need to have sufficiently good English language proficiency as the courses are held in English.

Additional information was requested in the nomination form on the i) education, ii) employment and employer's relation to the MEDPOL programme, iii) English proficiency (again!), iv) country distribution and v) overall merit of the nominees. After the reception of

the nominations and taking into consideration the training capacity of the laboratories, 6 participants from 6 different countries (Albania, Bosnia & Herzegovina, Croatia, Morocco, Syria, Turkey) were invited to attend the Training Course in NAEL, Monaco. Invitation letters to the participants were sent by IAEA/NAEL-MESL on 17 June 2019. The nominee from Syria did not receive his visa in time and the runner up from Montenegro was unable to accept the nomination on the short notice of only 2 weeks. Therefore only 5 participants were able to come to the course.

The course was held from 2 to 13 of September 2019.

Introductions to the basic concepts of trace elements analysis for monitoring studies, as well as, the principles of sample preparation methodology and moisture determination were presented to the participants in the training course. Lectures were dedicated on the analytical techniques (e.g. Flame Atomic Absorption Spectrometry, Graphite Furnace Atomic Absorption Spectrometry, and Inductively Coupled Plasma Mass Spectrometry as well as to the hyphenated technique (Cold Vapour Atomic Fluorescence Spectrometry-CV-AFS), applied for trace elements and mercury speciation analysis in marine samples. The most important concepts of measurement science-metrology in chemistry as validation of measurement procedure, use of certified reference materials, traceability and uncertainty of measurement results were also presented. The exercise on the estimation of measurement uncertainty for the AAS determination of lead in sediment sample using modelling approach was developed and all tutorial materials were provided to the participants. One of the theoretical sessions was dedicated to the sampling, sampling planning and strategies, samples preservation and storage. The uncertainty on samplings, which is the dominating contributor to the total uncertainty was discussed in detail. This was a new topic for most of participants in the training course.

During the practical session of the training course, the complete procedures on marine sample preparation and the quantification of trace elements in sediments and biota samples was demonstrated. All practical exercises were followed by a round-table discussion in order to answer questions from trainees and to compare proposed protocols with protocols applied in trainees' laboratories

A link was provided to the course participants including all lectures, practical sessions and additional information such as recommended methods.

2. Evaluation

A questionnaire was distributed to the trainees to receive feedback on the organization, content and structure of the training. The course was found to be useful and valuable and trainees' needs were met. E.g., 80% of participants indicated that their overall impression of the training course was excellent and 20% declared that it was better than expected. 100% of participants indicated that their needs were met and that they will be better able to do their job after attending this course. The balance between lectures, practical lab and computer sessions was found to be correct. However, some participants expressed to have appreciated more time in the laboratory to apply the newly accrued knowledge. The questionnaires and the summary of the evaluation forms can be found at the end of this report.

3. Conclusion and Recommendations

The theoretical knowledge on the good laboratory practice, sampling, different analytical techniques for trace element analysis and quality assurance principles were presented. Knowledge obtained during the training course was very well accepted from all participants, as their theoretical background was at the level requested for this training.

Practical exercises were also very well accepted by all trainees and they were very actively involved during the practical part of the training course.

Not all participants had the correct practical background for the training. One trainee reported to only occasionally work on the monitoring of trace elements in marine sediments. A second trainee apparently only worked on biota samples for general for food safety control. Even though most of the participants were familiar with at least one of the analytical techniques discussed during the training course, the fact that their work is mainly focused on non-marine matrices (drinking, waste and fresh waters) makes the training in its actual form questionable. One trainee reported that they only use ICP-OES, an analytical technique not included in the training course. All of this means that the capacity built during the training might not directly be beneficial for the MEDPOL programme.

The insufficient level of English language was a serious obstacle for three of the trainees (60%) to follow lectures and to be fully involved in the practical sessions. Two out of five participants

had a sufficiently high level of English, allowing proper communication during the training. Communication with one of the participants was only possible in French.

Although, in line with the conclusions and recommendations of the Meeting of CorMon on Pollution Monitoring that was held from 1 to 2 April 2018 in Podgorica, Montenegro, it was requested that the national laboratories nominated by focal points had participated in the 2018 MEDPOL PT and that they would be nominated for the 2019 MEDPOL PT, both criteria were not fulfilled for all laboratories. Thus, despite our efforts to link both activities, the training course and the PT in order to have high capacity building impact, this concept was not fully implemented by the national focal points.

Recommendations:

- ✓ The selection procedure for the participants in MEDPOL training course may need to be further improved and selection criteria, as provided in chapter 1, further adjusted.
- ✓ Language tests should be introduced as the integral part of the selection process.
- ✓ The communication with the selected participants, their background, needs and expectations from the training should be done before the training course by the MESL with involvement of MEDPOL Monitoring and Assessment Officer, if need be. This will help in the preparation of more relevant for the selected participants training program.
- ✓ MEDPOL focal points should only nominate candidates that are actively involved in implementation of Pollution and Marine Litter Cluster of IMAP/MEDPOL monitoring programme therefore being staff members of the laboratories responsible for IMAP implementation at national level.
- ✓ Additional efforts are needed to ensure the laboratories participating in the TCs are those taking part in PTs in order to make the most of the training received, as recommended by the Meeting of CorMon on Pollution Monitoring
- ✓ MEDPOL Focal Points should follow up more closely with the nominated national laboratories participating in the implementation of MEDPOL IV/IMAP monitoring programme and experts participating in the TC for trace elements, including a follow up on the results and related recommendations of the Proficiency Testing, with a view

of further supporting national efforts to implement the QA/QC measures for the marine monitoring data reported to MEDPOL.

- ✓ MESL recommends that the list of national IMAP competent laboratories is regularly updated and shared with the MEDPOL Monitoring and Assessment Officer in order for MESL to undertake a simplified selection process that is fully in line with such updated list.

4. List of participants

PARTICIPANTS OF THE TRAINING COURSE ON THE ANALYTICAL TECHNIQUES FOR THE DETERMINATION OF TRACE ELEMENTS IN ENVIRONMENTAL SAMPLES

ALBANIA

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Ms Ilknur Sirimoglu Environmental Reference Laboratory Ministry of Environment and Urbanisation Mustafa Kemal Mahalles Eskisehir Devlet Yolu 9. KM N°278 06830 ANKARA	E-mail: ilknur.sirimoglu@csb.gov.tr

5. Course outline

MEDPOL training course on the Analytical Techniques for the Determination of Trace Elements in Environmental Samples

IAEA – Environment Laboratories, Monaco
2 – 13 September 2019

IAEA Atoms For Peace Environment Laboratories
UN environment United Nations Environment Programme
MAP Mediterranean Action Plan Barcelona Convention

COURSE OUTLINE

(Note: Owing to parallel scientific meetings at MEL, the chronology of lectures and practical sessions is liable to change)

MONDAY 2 SEPTEMBER

9:00 – 12:00	Welcome to IAEA Environment Laboratories Monaco.	*Mr David Osborn DIR-NAEL*
	Housekeeping (Health and Safety).	*Mr Hussein Ramadan Head - Engineering and Electronics Support (EES)*
	Introduction to the MEDPOL IMAP monitoring programme. Presentation of the Marine Environment Laboratories and their activities.	*Ms Sylvia Sander Laboratory Head-MESL*
	Coffee/tea break	
	Self-introduction of participants and their laboratory, and expectations from the training course.	*All participants*
	Group photos.	
	Administrative matters.	*Ms Leslie Barilaro-Hamonic Team Assistant-MESL*

13:30 – 15:30	Visit of the other Marine Environment Laboratories	
	13:30 – 14:15 Visit of the Radiometrics Laboratory (RML).	*Mr Paul Morris* *Acting Section Head-RML*
	14:15 – 15:00 Visit of the Radioecology Laboratory (REL).	*Mr Peter Swarzenski* *Section Head-REL* *Ms Imma Tolosa* *Research Scientist*
TUESDAY 3 SEPTEMBER		
9:00 – 12:00	**THEORETICAL SESSION** Trace Elements Determination for monitoring studies. Sample preparation for trace element analysis in sediments and biological samples. Mineralization techniques. Moisture determination.	*Ms Emilia Vasileva* *Research Scientist*
13:00 – 17:00	**PRACTICAL SESSION** Inorganic Laboratory Orientation. Dry oven moisture determination in biota sample.	*Ms Sabine Azemard* *Ms Anna Maria Orani* *Laboratory Technicians*
WEDNESDAY 4 SEPTEMBER		
9:00 – 12:00	**TEORITICAL SESSION** ICP-MS Spectrometry - Main principles and application for trace element analysis of Environment Samples. Reliable Measurement Results. Proper use of Certified Reference Materials.	*Ms Emilia Vasileva* *Research Scientist*
13:00 – 17:00	**PRACTICAL SESSION** Sample preparation: mineralization of biological and sediment samples for trace element analysis. Dilution of sediment and biota digests to appropriate, specified volumes. Flame Atomic Absorption Spectrometry and application of the method for determination of trace elements in marine samples. Preparation of calibration curve for Zn by Flame Atomic Absorption Spectrometry.	*Ms Sabine Azemard* *Laboratory Technician* *Ms Anna Maria Orani* *Laboratory Technician*

THURSDAY 5 SEPTEMBER

9:00 – 12:00 **TEORITICAL SESSION** *Ms Emilia Vasileva, Research Scientist*

Uncertainty of measurement results.

Basic statistics for uncertainty estimation and method validation.

Practical exercise on uncertainty estimation.
Case study: Determination of Pb in soil by GF-AAS.

13:00 – 17:00 **PRACTICAL SESSION** *Ms Sabine Azemard, Laboratory Technician*

Determination of Zinc by Flame Atomic Absorption Spectrometry in biota and sediment samples. Data treatment.
Determination of Cu by Graphite Furnace Atomic Absorption Spectrometry in biota. Calibration curve. Data treatment.

FRIDAY 6 SEPTEMBER

9:00 – 17:00 **PRACTICAL SESSION** *Ms Sabine Azemard, Laboratory Technician*

Development of temperature programs for the determination of Cd in sediment by GF-AAS.
Optimization of furnace parameters.
Standard addition method.
Spectral interferences corrections.

MONDAY 9 SEPTEMBER

9:00 – 12:00 **THEORETICAL SESSION** *M. Petko Mandjukov, Consultant MESL*

Sampling and sample storage in the case of trace element analysis.
Introduction to the determination of trace elements by Flame Atomic Absorption Spectrometry (AAS).

14:00 – 17:00	**PRACTICAL SESSION**	*Mr Roberto Cassi* *Mr David Huertas* *Laboratory Technicians*
	Sampling principles and techniques. Sample storage, transport and pre-treatment. Sample preparation: dissection of biological samples (fish, mussels, oysters).	

TUESDAY 10 SEPTEMBER

9:00 – 13:00	**THEORITICAL SESSION**	*Mr Petko Mandjukov* *Consultant MESL*
	Introduction to the determination of trace elements by Graphite Furnace-AAS (GF-AAS) and Solid Sampling AAS. Method validation. Practical exercise on method validation. Case study: Determination of Pb in soil by GF-AAS.	
14:00 – 17:00	**PRACTICAL SESSION**	*Mr Roberto Cassi* *Mr David Huertas* *Laboratory Technicians*
	Sampling field trip. Demonstration on sediment and water sampling techniques. Sample storage.	

WEDNESDAY 11 SEPTEMBER

9:00 – 17:00	**PRACTICAL SESSION**	
	Development of method for the determination of Cd in biota sample by ICP-MS.	*Ms Anna Maria Orani* *Laboratory Technician*
	Determination of Cu in sediments and biota samples by Solid sampling CS HR AAS	*Ms Anna Maria Orani* *Laboratory Technician* *Ms Petko Mandjukov* *Consultant MESL*

THURSDAY 12 SEPTEMBER

9:00 – 12:00	**PRACTICAL SESSION**	*Ms Sabine Azemard* *Ms Anna Maria Orani* *Laboratory Technicians*
	Determination of organic Hg by AMA Calibration curves. Data treatment. Case study: Determination of organic Hg mass fraction in marine biota sample.	

13:00 – 17:00	Determination of Hg in biota samples by CV AFS	*Ms Sabine Azemard* *Ms Anna Maria Orani* *Laboratory Technicians*

FIRDAY 13 SEPTEMBER

9:00 – 12:00	**CLOSURE OF THE TRAINING COURSE**	
	Presentations by trainees: 1) Reflections on the training course, • Theoretical part, • Laboratory experiments. 2) How will the newly gained knowledge be implemented in home laboratory:	*All course participants*
	Closing remarks. Certificates	*Mr David Osborn* *DIR-NAEL* *(or alternate)*
13:00 – 17:00	Visit of the Oceanographic Museum, Monaco.	*All course participants*

6. Theoretical sessions

Introductions to the basic concepts of trace elements analysis for monitoring studies, as well as, the principles of sample preparation methodology and moisture determination were presented to the participants in the training course. Following lectures were dedicated on the analytical techniques (e.g. Flame Atomic Absorption Spectrometry, Graphite Furnace Atomic Absorption Spectrometry, and Inductively Coupled Plasma Mass Spectrometry as well as to the hyphenated technique (Cold Vapour Atomic Fluorescence Spectrometry-CV-AFS), applied for trace elements and mercury speciation analysis in marine samples. The most important concepts of measurement science-metrology in chemistry as validation of measurement procedure, use of certified reference materials, traceability and uncertainty of measurement results were also presented. The exercise on the estimation of measurement uncertainty for the AAS determination of lead in sediment sample using modelling approach was developed and all tutorial materials were provided to the participants. One of the theoretical sessions was dedicated to the sampling, sampling planning and strategies, samples preservation and storage. The uncertainty on samplings, which is the dominating contributor to the total uncertainty was discussed in detail. This was a new topic for most of participants in the training course.

During the practical session of the training course, the complete procedures on marine sample preparation and the quantification of trace elements in sediments and biota samples was demonstrated. More details on the practical part of the course are given in the Practical session section.

A link (https://share.iaea.org/pub/index.php/s/0YJwmnuEJvucPI3 - Password: monaco) was provided to the course participants including all lectures, practical sessions and additional information such as recommended methods. Please not that this link was only valid for a limited amount o time due to IT security purposes.

7. Practical sessions

The laboratory training was devised in three parts: sample preparation, instrumental measurement and calculation of obtained results.

All practical exercises were followed by a round-table discussion in order to answer questions from trainees and to compare proposed protocols with protocols applied in trainees' laboratories.

1) SAMPLE PREPARATION

The session on sample preparation started with the dissection of fish and mussel, followed by the collection of water and sediment samples during a field trip on a small boat.

Trainees performed a microwave digestion of the biota and sediment samples using a microwave technique. The moisture determination was performed for biota samples and appeared to be done as a routine for all participants performing determination of trace elements in sediment and biota samples.

2) ATOMIC ABSORPTION SPECTROMETRY (AAS)

a) Determination of Zn mass fraction in sediment samples by Flame AAS

This session started with basic calculations of element mass fractions in calibration solutions and analysed samples in order to verify that all participants are familiar with them.

Trainees were requested to prepare standard solutions for Zn, using "matrix matching" approach. The concepts for "matrix matching" of all solutions and calibration blank were not clear for all participants.

b) Determination of Cd mass fraction biological material by graphite furnace AAS (ETAAS)

Basic optimisation of the temperature program for the ETAAS using a matrix modifier was demonstrated. The basic steps of one ETAAS program were discussed and introduced. The aching curve was produced for a sample and a standard, using a conventional program and a matrix modifier.

Biota samples, together with QC samples and procedural blanks were analysed, using the developed temperature program. The possibility for preparation and implementation of automatic quality control (QC) checks in the measurement sequence was demonstrated. The

basic calculation of post-digestion standard addition approach was demonstrated again, as it was not clear for some of the participants in the training.

The calculation of characteristic mass as a routine check for sensitivity of the method was performed.

c) Demonstration of permanent modification and rapid temperature program

The demonstration of permanent matrix modification was done for the determination of cadmium in a biota sample. The use of permanent modification with iridium followed by "rapid temperature program" was explained and shown to the participants. None of the trainees were familiar with this type of program.

The mass fraction of cadmium in the biota sample was also determined with a "conventional" matrix modifier and "conventional" four stage temperature program. The results for mass fraction of Cd in biota sample obtained with "rapid" and "conventional" programs were compared.

d) Determination of Cu in sediments and biota samples by Solid Sampling CS HR AAS

This practical session was intended to get the participants familiar with the analysis of trace elements in solid sediments and biota samples, by High Resolution Continuous Source AAS. The advantages of direct analysis on solid sample, the use of fast programs and of a new approach based on calibration using a solid CRMs, were discussed with the trainees. The participants had the opportunity to perform analysis by themselves, comment the obtained high-resolution spectra and learn about the advantages/disadvantages of this approach compared with conventional AAS analyses. None of the participant was familiar with this specific approach and all of them appeared to be rather interested.

3) COLD VAPOR ATOMIC FLUORESCENT SPECTROMETRY (CV-AFS)

Determination of total mercury by CV- AFS

The cold vapor AFS, with double gold trap amalgamation was demonstrated with standard solutions and digested sediment samples. The exercise was mainly based on discussion of different type of instrument available for cold vapor and on specific sample preparation (mainly on preservation limitation) that should be applied.

4) SOLID MERCURY ANALYSER (AMA)

Total and organic mercury mass fractions in marine biota samples using solid mercury analyser (AMA)

One half day was dedicated to the determination of total mercury mass fraction in fish samples, using a solid mercury analyser. Calibration using liquid standard and solid CRM were demonstrated. The application of specific extraction method for organic mercury in biota was explained in detail but not demonstrated as majority of trainees did not have solid mercury analyser.

5) INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS)

Development of method for the determination of Cd in biota by ICP-MS and external calibration

During this practical session an example of the determination of cadmium in different replicates of one fish sample and one biota CRM was used to demonstrate the method development and application of ICP-MS technique for trace elements monitoring studies. The optimization of the measurement method covered: checking the general instrument condition, selection of proper internal standard, selection of proper Cd isotopes, explanation of different types of spectral interferences and their correction, checking the procedural blanks, analysis of certified reference materials as QC samples.

The ICP-MS session included proper gravimetric dilution of digested samples and gravimetric preparation of standard solution for external calibration. Additionally, simple calculation of the exact dilution factors and conversion of results from µg/kg (in the digested solutions) to mg/kg (in dry samples) was also included. The results obtained with different Cd isotopes were discussed and compared. The importance of possible contamination in trace elements analysis by ICP-MS and the evaluation of detection limits were underlined. None of the

participants had experience with ICP-MS technique as they do not have this kind of instrumentation in their respective laboratories.

6) CALCULATIONS AND REPORTING OF RESULTS

Basic calculations of obtained results in mg/kg mass fraction were performed and the concept of procedural and instrumental blanks, recovery and detection limits discussed and applied. As the use of modelling approach, prescribed by ISO Guide 17025, for the Expression of Uncertainty in Measurement (GUM) was explained in detail during the theoretical session, the estimation of uncertainty using control chart and validation parameter was applied on results obtained from the practical sessions.

8. Certificates of participation

IAEA Atoms For Peace Environment Laboratories

UN environment United Nations Environment Programme

MAP Mediterranean Action Plan Barcelona Convention

CERTIFICATE OF PARTICIPATION

Sabrie PICARI

National Environment Agency (NEA)

Tirana, Albania

attended the training course

Analytical Techniques for the Determination of Trace Elements in Environmental Samples

2 – 13 September 2019
IAEA MONACO

Organized by

UNEP/MAP - MED POL & IAEA-NAEL

Marine Environmental Studies Laboratory

Trainers

Ms S. Azemard
Ms A.M. Orani
Ms E. Vasileva
Mr P. Mandjukov

David Osborn
Director - IAEA Environment Laboratories

IAEA Atoms For Peace Environment Laboratories

UN environment United Nations Environment Programme

MAP Mediterranean Action Plan Barcelona Convention

CERTIFICATE OF PARTICIPATION

Branimir DRINOVAC

Institute for Public Health

Mostar, Bosnia & Herzegovina

attended the training course

Analytical Techniques for the Determination of Trace Elements in Environmental Samples

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David Osborn
Director - IAEA Environment Laboratories

IAEA Atoms For Peace Environment Laboratories

UN environment United Nations Environment Programme

MAP Mediterranean Action Plan Barcelona Convention

CERTIFICATE OF PARTICIPATION

Ozren GROZDANIC

Public Health Institute of County of Istria

Pula, Croatia

attended the training course

Analytical Techniques for the Determination of Trace Elements in Environmental Samples

2 – 13 September 2019
IAEA MONACO

Organized by

UNEP/MAP - MED POL & IAEA-NAEL

Marine Environmental Studies Laboratory

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Ms S. Azemard
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Ms E. Vasileva
Mr P. Mandjukov

David Osborn
Director - IAEA Environment Laboratories

IAEA Atoms For Peace Environment Laboratories

UN environment United Nations Environment Programme

MAP Mediterranean Action Plan Barcelona Convention

CERTIFICATE OF PARTICIPATION

Rajaa ESSAIDI

National Laboratory of Environment

Rabat, Morocco

attended the training course

Analytical Techniques for the Determination of Trace Elements in Environmental Samples

2 – 13 September 2019
IAEA MONACO

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Ms E. Vasileva
Mr P. Mandjukov

David Osborn
Director - IAEA Environment Laboratories

IAEA Atoms For Peace Environment Laboratories

UN environment United Nations Environment Programme

MAP Mediterranean Action Plan Barcelona Convention

CERTIFICATE OF PARTICIPATION

Ilknur SIRIMOGLU

Environmental Reference Laboratory

Ankara, Turkey

attended the training course

Analytical Techniques for the Determination of Trace Elements in Environmental Samples

2 – 13 September 2019
IAEA MONACO

Organized by

UNEP/MAP - MED POL & IAEA-NAEL

Marine Environmental Studies Laboratory

Trainers

Ms S. Azemard
Ms A.M. Orani
Ms E. Vasileva
Mr P. Mandjukov

David Osborn
Director - IAEA Environment Laboratories

9. Training course evaluation questionnaires

IAEA

INTERNATIONAL ATOMIC ENERGY AGENCY
MARINE ENVIRONMENT LABORATORIES
MARINE ENVIRONMENTAL STUDIES LABORATORY

TRAINING EVALUATION QUESTIONNAIRE

Dear Participant, the purpose of this evaluation form is to collect the participants' opinions about the entire programme. This information will be very helpful in planning future courses. Please do not leave any question unanswered. Thank you.

Participant's name: SABRIE PICARI

Participant's nationality: ALBANIA

Institute Name & Address: The National ENVIRONMENTAL AGENCY (AKM)

What is your overall impression of the training course?

☒ Excellent ☐ Satisfactory ☐ Poor ☐ Better than expected

Do you feel that this training met your needs? (if NOT, please, explain)

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you feel that you will be better able to do your job after attending this course?

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you have a better attitude to your job having completed this course?

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

Would you recommend that others in your field should attend this course?

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you think that similar workshops with other topics would be useful?

☒ Yes ☐ No

If YES, please indicate relevant topics:
☐ Trace elements by ICP-OES ☐ Trace elements by ICP-MS
☐ Others (specify) GF-AAS

TRAINING CONTENT

How do you rate the balance of theoretical and practical material in the workshop?

☐ Too theoretical ☒ Good balance ☐ Too practical

How do you rate the balance of lectures, group discussions, and group exercises?

☒ Good ☐ Too many lectures ☐ Too many discussion sessions

How do you rate the training's length?

☐ Too short ☒ Just right ☐ Too long

How did you feel about the pacing of the course?

☐ Too fast ☒ Just right ☐ Too slow

How do you rate the training's sequence?

☐ Very well sequenced ☒ Suitable ☐ Poorly sequenced

How helpful were the group exercises?

☒ Very helpful ☐ Helpful ☐ Not helpful

Did you have enough skills practice time?

☒ Yes ☐ No ☐ Uncertain

How valuable was the training content to your current job?

☒ Very valuable ☐ Of some value ☐ No real value

What did you like best about the training course? (Strongest aspects)

Sampling and sample preparation for my...

What did you like least about the training course? (Weakest aspects)

Uncertain, calculator

What do you think should be dropped from this course?

~~You are very very good~~

Comments about the course contents:

You are very, very good together (INORG) Groups.

INSTRUCTIONAL MATERIAL (on CD ROM)

In your opinion, was the number of handouts you received during the course sufficient?

☒ Just right ☐ Too few ☐ Too many

How do you rate the quality of the handout material?

☒ High quality ☐ Sufficient ☐ Below expectation

LABORATORIES AND FACILITIES

Did you like the seating arrangements of the conference room?

☒ Yes ☐ No ☐ No opinion

How do you rate the practical sessions?

☒ Excellent ☐ Very good ☐ Fair ☐ Poor

Do you think the number of participants in the workshop was:

☐ Too many ☒ Too few ☐ Just right

Comments about laboratory sessions: This is very interesting. work in the lab. I advice work in the lab and practicale: - Sampling - Sample preparation etc.

What is your overall evaluation of the course?

☒ Excellent ☐ Very good ☐ Fair ☐ Poor

QUESTIONS FOR THE CERTIFICATE OF PROFICIENCY

1. Which of the following statements regarding CRMs is NOT correct?

❒ CRMs should be used for calibration only
❒ CRMs should be stored according to the manufacturer' instructions
❒ Sampling of CRMs should take into account prescribed minimum amounts, if stated
❒ Degradation of CRMs due to bioactivity should be avoided
❒ CRMs should always be accompanied by a certificate

2. A CRM does NOT necessarily need to have:

❒ low cost
❒ stability
❒ stated uncertainty
❒ values assigned to the material
❒ demonstrated homogeneity

3. Which (of the following) information is NOT necessarily included in the certificate of a CRM?

❒ Prescribed experimental protocol
❒ A statement of traceability
❒ Uncertainty of the certified value
❒ Signature or name of certifying officer
❒ Sample number

4. In order to provide evidence of the traceability of a measurement result it is sufficient to:

❒ Document the traceability of the result to a stated reference
❒ Report the result in SI unit
❒ Participate successfully in a Proficiency Testing Scheme
❒ Use a Reference Material
❒ Calibrate the critical measurement equipment once a year

5. What is your definition for trace element?

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.....
.....

Thank you for taking the time to respond to this survey.
Your input is very valuable to us!

IAEA

INTERNATIONAL ATOMIC ENERGY AGENCY
MARINE ENVIRONMENT LABORATORIES
MARINE ENVIRONMENTAL STUDIES LABORATORY

TRAINING EVALUATION QUESTIONNAIRE

Dear Participant, the purpose of this evaluation form is to collect the participants' opinions about the entire programme. This information will be very helpful in planning future courses. Please do not leave any question unanswered. Thank you.

Participant's name: Branimir Drinovac

Participant's nationality: Bosnia and Herzegovina (Croatian)

Institute Name & Address: Institute for Public Health Federation of Bosnia and Herzegovina

What is your overall impression of the training course?

☐ Excellent ☐ Satisfactory ☐ Poor ☒ Better than expected

Do you feel that this training met your needs? (if NOT, please, explain)

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

.....

Do you feel that you will be better able to do your job after attending this course?

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you have a better attitude to your job having completed this course?

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

Would you recommend that others in your field should attend this course?

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you think that similar workshops with other topics would be useful?

☒ Yes ☐ No

If YES, please indicate relevant topics:
☐ Trace elements by ICP-OES ☒ Trace elements by ICP-MS
☐ Others (specify)

.....

TRAINING CONTENT

How do you rate the balance of theoretical and practical material in the workshop?

☐ Too theoretical ☒ Good balance ☐ Too practical

How do you rate the balance of lectures, group discussions, and group exercises?

☒ Good ☐ Too many lectures ☐ Too many discussion sessions

How do you rate the training's length?

☐ Too short ☒ Just right ☐ Too long

How did you feel about the pacing of the course?

☒ Too fast ☐ Just right ☐ Too slow

How do you rate the training's sequence?

☐ Very well sequenced ☒ Suitable ☐ Poorly sequenced

How helpful were the group exercises?

☒ Very helpful ☐ Helpful ☐ Not helpful

Did you have enough skills practice time?

☒ Yes ☐ No ☐ Uncertain

How valuable was the training content to your current job?

☒ Very valuable ☐ Of some value ☐ No real value

What did you like best about the training course? (Strongest aspects)

Correlation between theoretical and practical training was very good. Lecturers and consultants did great job.

What did you like least about the training course? (Weakest aspects)

In my opinion there are no ~~weak~~ weak aspects of the training course.

What do you think should be dropped from this course?

Nothing should be dropped for this course.

Comments about the course contents:

Course contents are constructed so well and allow expansion of knowledge and improvement analytical skills.

INSTRUCTIONAL MATERIAL (on CD ROM)

In your opinion, was the number of handouts you received during the course sufficient?

☒ Just right ☐ Too few ☐ Too many

How do you rate the quality of the handout material?

☐ High quality ☒ Sufficient ☐ Below expectation

LABORATORIES AND FACILITIES

Did you like the seating arrangements of the conference room?

☒ Yes ☐ No ☐ No opinion

How do you rate the practical sessions?

☐ Excellent ☒ Very good ☐ Fair ☐ Poor

Do you think the number of participants in the workshop was:

☐ Too many ☐ Too few ☒ Just right

Comments about laboratory sessions:

Laboratory is very well equipped. Technicians and consultant possess vaject knowledge and experience and it was pleasure to cooperate with them.

What is your overall evaluation of the course?

☒ Excellent ☐ Very good ☐ Fair ☐ Poor

QUESTIONS FOR THE CERTIFICATE OF PROFICIENCY

1. Which of the following statements regarding CRMs is NOT correct?

☒ CRMs should be used for calibration only
☐ CRMs should be stored according to the manufacturer' instructions
☐ Sampling of CRMs should take into account prescribed minimum amounts, if stated
☐ Degradation of CRMs due to bioactivity should be avoided
☐ CRMs should always be accompanied by a certificate

2. A CRM does NOT necessarily need to have:

☒ low cost
☐ stability
☐ stated uncertainty
☐ values assigned to the material
☐ demonstrated homogeneity

3. Which (of the following) information is NOT necessarily included in the certificate of a CRM?

☒ Prescribed experimental protocol
☐ A statement of traceability
☐ Uncertainty of the certified value
☐ Signature or name of certifying officer
☐ Sample number

4. In order to provide evidence of the traceability of a measurement result it is sufficient to:

☒ Document the traceability of the result to a stated reference
☐ Report the result in SI unit
☐ Participate successfully in a Proficiency Testing Scheme
☐ Use a Reference Material
☐ Calibrate the critical measurement equipment once a year

5. What is your definition for trace element?

From the health safety point of view trace elemt is a
contamt which can damage human health if it passes in
large concentration in ~~the~~ environmental and food samples.

Thank you for taking the time to respond to this survey.
Your input is very valuable to us!

IAEA International Atomic Energy Agency Marine Environment Laboratories

INTERNATIONAL ATOMIC ENERGY AGENCY
MARINE ENVIRONMENT LABORATORIES
MARINE ENVIRONMENTAL STUDIES LABORATORY

TRAINING EVALUATION QUESTIONNAIRE

Dear Participant, the purpose of this evaluation form is to collect the participants' opinions about the entire programme. This information will be very helpful in planning future courses. Please do not leave any question unanswered. Thank you.

Participant's name: OZREN GRGIČANIĆ

Participant's nationality: CROATIAN

Institute Name & Address: INSTITUTE OF PUBLIC HEALTH OF COUNTY OF ISTRIA (ZZJZIZ), PULA

What is your overall impression of the training course?

☑ Excellent ☐ Satisfactory ☐ Poor ☐ Better than expected

Do you feel that this training met your needs? (if NOT, please, explain)

☑ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you feel that you will be better able to do your job after attending this course?

☑ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you have a better attitude to your job having completed this course?

☑ Yes ☐ To some extent ☐ Uncertain ☐ No

Would you recommend that others in your field should attend this course?

☑ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you think that similar workshops with other topics would be useful?

☑ Yes ☐ No

If YES, please indicate relevant topics:

☑ Trace elements by ICP-OES ☑ Trace elements by ICP-MS

☐ Others (specify)

TRACE METALS IN SEAWATER

TRAINING CONTENT

How do you rate the balance of theoretical and practical material in the workshop?

☐ Too theoretical ☑ Good balance ☐ Too practical

How do you rate the balance of lectures, group discussions, and group exercises?

☑ Good ☐ Too many lectures ☐ Too many discussion sessions

How do you rate the training's length?

☐ Too short ☑ Just right ☐ Too long

How did you feel about the pacing of the course?

☐ Too fast ☑ Just right ☐ Too slow

How do you rate the training's sequence?

☐ Very well sequenced ☑ Suitable ☐ Poorly sequenced

How helpful were the group exercises?

☑ Very helpful ☐ Helpful ☐ Not helpful

Did you have enough skills practice time?

☑ Yes ☐ No ☐ Uncertain

How valuable was the training content to your current job?

☑ Very valuable ☐ Of some value ☐ No real value

What did you like best about the training course? (Strongest aspects)

THE OPPORTUNITY TO LEARN FROM PEOPLE IN THE LAB THAT ARE REAL EXPERTS IN THEIR FIELD AND THEIR WILL TO SHARE WITH US VERY VALUABLE "TIPS AND TRICS"

What did you like least about the training course? (Weakest aspects)

UNCERTAINTY BUDGET WAS ONLY THEORETICAL, IT MIGHT BE BETTER IF HAD THE CHANCE TO BUILD OUR OWN UNDER SUPERVISION

What do you think should be dropped from this course?

NOTHING

Comments about the course contents:

EVERYTHING WAS EXTREMELY WELL ORGANIZED AND THOUGHT-THROUGH.

INSTRUCTIONAL MATERIAL (on CD ROM)

In your opinion, was the number of handouts you received during the course sufficient?

☑ Just right ☐ Too few ☐ Too many

How do you rate the quality of the handout material?

☑ High quality ☐ Sufficient ☐ Below expectation

LABORATORIES AND FACILITIES

Did you like the seating arrangements of the conference room?

☑ Yes ☐ No ☐ No opinion

How do you rate the practical sessions?

☑ Excellent ☐ Very good ☐ Fair ☐ Poor

Do you think the number of participants in the workshop was:

☐ Too many ☐ Too few ☑ Just right

Comments about laboratory sessions:

SIMPLY GREAT. SABINE AND ANNA-MARIA HELPED A LOT WITH THE PROBLEMS IN OUR LABS AND CLARIFIED MANY THINGS.

What is your overall evaluation of the course?

☑ Excellent ☐ Very good ☐ Fair ☐ Poor

QUESTIONS FOR THE CERTIFICATE OF PROFICIENCY

1. Which of the following statements regarding CRMs is NOT correct?

- ☐ CRMs should be used for calibration only
- ☐ CRMs should be stored according to the manufacturer' instructions
- ☐ Sampling of CRMs should take into account prescribed minimum amounts, if stated
- ☑ Degradation of CRMs due to bioactivity should be avoided
- ☐ CRMs should always be accompanied by a certificate

2. A CRM does NOT necessarily need to have:

- ☑ low cost
- ☐ stability
- ☐ stated uncertainty
- ☐ values assigned to the material
- ☐ demonstrated homogeneity

3. Which (of the following) information is NOT necessarily included in the certificate of a CRM?

- ☑ Prescribed experimental protocol
- ☐ A statement of traceability
- ☐ Uncertainty of the certified value
- ☐ Signature or name of certifying officer
- ☐ Sample number

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- ☑ Document the traceability of the result to a stated reference
- ☑ Report the result in SI unit
- ☐ Participate successfully in a Proficiency Testing Scheme
- ☐ Use a Reference Material
- ☐ Calibrate the critical measurement equipment once a year

5. What is your definition for trace element?

ELEMENTS PRESENT IN THE SAMPLE IN LOW CONCENTRATION.
.....
.....
.....

Thank you for taking the time to respond to this survey.
Your input is very valuable to us!

IAEA
International Atomic Energy Agency
Marine Environment Laboratories

INTERNATIONAL ATOMIC ENERGY AGENCY
MARINE ENVIRONMENT LABORATORIES
MARINE ENVIRONMENTAL STUDIES LABORATORY

TRAINING EVALUATION QUESTIONNAIRE

Dear Participant, the purpose of this evaluation form is to collect the participants' opinions about the entire programme. This information will be very helpful in planning future courses. Please do not leave any question unanswered. Thank you.

Participant's name: Rajaa ESSADI

Participant's nationality: Morocco

Institute Name & Address: the national laboratory for studies and Monitoring of pollution

What is your overall impression of the training course?

☑ Excellent ☐ Satisfactory ☐ Poor ☐ Better than expected

Do you feel that this training met your needs? (if NOT, please, explain)

☑ Yes ☐ To some extent ☐ Uncertain ☐ No

.....

Do you feel that you will be better able to do your job after attending this course?

☑ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you have a better attitude to your job having completed this course?

☑ Yes ☐ To some extent ☐ Uncertain ☐ No

Would you recommend that others in your field should attend this course?

☑ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you think that similar workshops with other topics would be useful?

☑ Yes ☐ No

If YES, please indicate relevant topics:
☑ Trace elements by ICP-OES ☐ Trace elements by ICP-MS
☐ Others (specify)

.....

TRAINING CONTENT

How do you rate the balance of theoretical and practical material in the workshop?

☐ Too theoretical ☑ Good balance ☐ Too practical

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☑ Good ☐ Too many lectures ☐ Too many discussion sessions

How do you rate the training's length?

☐ Too short ☑ Just right ☐ Too long

How did you feel about the pacing of the course?

☐ Too fast ☑ Just right ☐ Too slow

How do you rate the training's sequence?

☑ Very well sequenced ☐ Suitable ☐ Poorly sequenced

How helpful were the group exercises?

☑ Very helpful ☐ Helpful ☐ Not helpful

Did you have enough skills practice time?

☑ Yes ☐ No ☐ Uncertain

How valuable was the training content to your current job?

☑ Very valuable ☐ Of some value ☐ No real value

What did you like best about the training course? (Strongest aspects)

j'ai bien aimé la partie pratique

What did you like least about the training course? (Weakest aspects)

R.A.S

What do you think should be dropped from this course?

R.A.S

Comments about the course contents:

été très bénéfique et riches des informations

INSTRUCTIONAL MATERIAL (on CD ROM)

In your opinion, was the number of handouts you received during the course sufficient?

☑ Just right ☐ Too few ☐ Too many

How do you rate the quality of the handout material?

☑ High quality ☐ Sufficient ☐ Below expectation

LABORATORIES AND FACILITIES

Did you like the seating arrangements of the conference room?

☑ Yes ☐ No ☐ No opinion

How do you rate the practical sessions?

☑ Excellent ☐ Very good ☐ Fair ☐ Poor

Do you think the number of participants in the workshop was:

☐ Too many ☐ Too few ☑ Just right

Comments about laboratory sessions:

What is your overall evaluation of the course?

☑ Excellent ☐ Very good ☐ Fair ☐ Poor

QUESTIONS FOR THE CERTIFICATE OF PROFICIENCY

1. Which of the following statements regarding CRMs is NOT correct?

☑ CRMs should be used for calibration only
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3. Which (of the following) information is NOT necessarily included in the certificate of a CRM?

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4. In order to provide evidence of the traceability of a measurement result it is sufficient to:

☑ Document the traceability of the result to a stated reference
☐ Report the result in SI unit
☐ Participate successfully in a Proficiency Testing Scheme
☒ Use a Reference Material
☒ Calibrate the critical measurement equipment once a year

5. What is your definition for trace element?

Les éléments trace sont des élément très sensible, on doit les analyses avec précaution en utilisant les connaissance acquises durant cette formation (partie pratique)

Thank you for taking the time to respond to this survey.
Your input is very valuable to us!

IAEA

INTERNATIONAL ATOMIC ENERGY AGENCY
MARINE ENVIRONMENT LABORATORIES
MARINE ENVIRONMENTAL STUDIES LABORATORY

TRAINING EVALUATION QUESTIONNAIRE

Dear Participant, the purpose of this evaluation form is to collect the participants' opinions about the entire programme. This information will be very helpful in planning future courses. Please do not leave any question unanswered. Thank you.

Participant's name: ÜNSAL SIRIMOĞLU

Participant's nationality: TURKEY

Institute Name & Address: MINISTRY OF ENVIRONMENT AND URBANISATION/
THE ENVIRONMENT REFERENCE LABORATORY - ANKARA / TURKEY

What is your overall impression of the training course?

☒ Excellent ☐ Satisfactory ☐ Poor ☐ Better than expected

Do you feel that this training met your needs? (if NOT, please, explain)

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you feel that you will be better able to do your job after attending this course?

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you have a better attitude to your job having completed this course?

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

Would you recommend that others in your field should attend this course?

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

Do you think that similar workshops with other topics would be useful?

☒ Yes ☐ No

If YES, please indicate relevant topics:

☐ Trace elements by ICP-OES ☐ Trace elements by ICP-MS

☒ Others (specify)

Validation, Verification, Uncertainty

TRAINING CONTENT

How do you rate the balance of theoretical and practical material in the workshop?

☐ Too theoretical ☒ Good balance ☐ Too practical

How do you rate the balance of lectures, group discussions, and group exercises?

☒ Good ☐ Too many lectures ☐ Too many discussion sessions

How do you rate the training's length?

☐ Too short ☒ Just right ☐ Too long

How did you feel about the pacing of the course?

☐ Too fast ☒ Just right ☐ Too slow

How do you rate the training's sequence?

☐ Very well sequenced ☒ Suitable ☐ Poorly sequenced

How helpful were the group exercises?

☒ Very helpful ☐ Helpful ☐ Not helpful

Did you have enough skills practice time?

☒ Yes ☐ No ☐ Uncertain

How valuable was the training content to your current job?

☒ Very valuable ☐ Of some value ☐ No real value

What did you like best about the training course? (Strongest aspects)

The helpful attitude of all instructors.....

.....

What did you like least about the training course? (Weakest aspects)

.....

.....

What do you think should be dropped from this course?

.....
.....

Comments about the course contents:

.....
.....
.....

INSTRUCTIONAL MATERIAL (on CD ROM)

In your opinion, was the number of handouts you received during the course sufficient?

☒ Just right ☐ Too few ☐ Too many

How do you rate the quality of the handout material?

☐ High quality ☒ Sufficient ☐ Below expectation

LABORATORIES AND FACILITIES

Did you like the seating arrangements of the conference room?

☒ Yes ☐ No ☐ No opinion

How do you rate the practical sessions?

☐ Excellent ☒ Very good ☐ Fair ☐ Poor

Do you think the number of participants in the workshop was:

☐ Too many ☐ Too few ☒ Just right

Comments about laboratory sessions:

.....
.....
.....

What is your overall evaluation of the course?

☐ Excellent ☒ Very good ☐ Fair ☐ Poor

QUESTIONS FOR THE CERTIFICATE OF PROFICIENCY

1. Which of the following statements regarding CRMs is NOT correct?

- [x] CRMs should be used for calibration only
- [ ] CRMs should be stored according to the manufacturer' instructions
- [ ] Sampling of CRMs should take into account prescribed minimum amounts, if stated
- [ ] Degradation of CRMs due to bioactivity should be avoided
- [ ] CRMs should always be accompanied by a certificate

2. A CRM does NOT necessarily need to have:

- [x] low cost
- [ ] stability
- [ ] stated uncertainty
- [ ] values assigned to the material
- [ ] demonstrated homogeneity

3. Which (of the following) information is NOT necessarily included in the certificate of a CRM?

- [x] Prescribed experimental protocol
- [ ] A statement of traceability
- [ ] Uncertainty of the certified value
- [ ] Signature or name of certifying officer
- [x] Sample number

4. In order to provide evidence of the traceability of a measurement result it is sufficient to:

- [x] Document the traceability of the result to a stated reference
- [x] Report the result in SI unit
- [x] Participate successfully in a Proficiency Testing Scheme
- [x] Use a Reference Material
- [x] Calibrate the critical measurement equipment once a year

5. What is your definition for trace element?

The element which concentration is low.

Thank you for taking the time to respond to this survey.
Your input is very valuable to us!

10. Evaluation of participants' questionnaire

1. What is your overall impression of the training course ?

80% Excellent ❒ Satisfactory ❒ Poor 20% Better than expected

2. Do you feel that this training met your needs ? (if NOT, please, explain)

100% Yes ❒ To some extent ❒ Uncertain ❒ No

3. Do you feel that you will be better able to do your job after attending this course?

100% Yes ❒ To some extent ❒ Uncertain ❒ No

4. Do you have a better attitude to your job having completed this course ?

100% Yes ❒ To some extent ❒ Uncertain ❒ No

5. Would you recommend that others in your field should attend this course ?

100% Yes ❒ To some extent ❒ Uncertain ❒ No

6. Do you think that similar workshops with other topics would be useful ?

100% Yes ❒ No

If YES, please indicate relevant topics:

20% Trace elements by ICP-MS
20% Trace elements by ICP-OES
20% GF-AAS
20% Trace elements in seawater
20% Validation, verification, uncertainty

7. How do you rate the balance of theoretical and practical material in the workshop ?

❒ Too theoretical 100% Good balance ❒ Too practical

8. How do you rate the balance of lectures, group discussions, and group exercises ?

100% Good 1 x Too many lectures ❒ Too many discussion sessions

9. How do you rate the training's length ?

❒ Too short 100% Just right ❒ Too long

10. How did you feel about the pacing of the course ?

20% Too fast 80% Just right ❒ Too slow

11. How do you rate the training's sequence ?

20% Very well sequenced 80% Suitable ❒ Poorly sequenced

12. How helpful were the group exercises ?

100% Very helpful ❒ Helpful ❒ Not helpful

13. Did you have enough skills practice time ?

100% Yes ❒ No ❒ Uncertain

14. How valuable was the training content to your current job ?

100% Very valuable ❒ Of some value ❒ No real value

UNITED NATIONS

EP

UNEP/MED WG.492/Inf. 8

UNEP

UNITED NATIONS
ENVIRONMENT PROGRAMME
MEDITERRANEAN ACTION PLAN

26. March 2021
Original: English

Meeting of the Ecosystem Approach Correspondence Group on Pollution Monitoring

Videoconference, 26-28 April 2021

Agenda item 5: Report on Training Course for Organic Contaminants (2019)

UNEP/MAP
Athens, 2021

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TRAINING COURSE
ON THE ANALYSIS OF ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS IN ENVIRONMENTAL SAMPLES

Organized by:

International Atomic Energy Agency-Environment Laboratories
4 Quai Antoine 1er, MC 98000 MONACO

2 - 13 September 2019

IAEA-EL staff involved:

I. Tolosa, Research Scientist
R. Cassi, Laboratory Technician
D. Huertas, Laboratory Technician
S. Choyke, Associate Analytical Chemist
S. Sander, MESL Section Head
L. Barilaro-Hamonic, Team assistant

Prepared in collaboration with:

UN environment
United Nations Environment Programme

MAP
Mediterranean Action Plan
Barcelona Convention

CONTENTS

TRAINING COURSE ON THE ANALYSIS OF ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS IN ENVIRONMENTAL SAMPLES

1. Background

A training course on the analysis of Organochlorinated Pesticides (OCs) and Polychlorinated Biphenyls (PCBs) in marine environmental samples was organized in NAEL/MESL on behalf of the UN Environment Programme/Mediterranean Action Plan (UN Environment/MAP) - Programme for the Assessment and Control of Marine Pollution in the Mediterranean Sea (MEDPOL), referred to henceforth as MEDPOL, for participants from Mediterranean laboratories involved in the MEDPOL marine pollution monitoring program in the framework of the Land-based sources (LBS) Protocol of the Barcelona Convention.

A letter describing the course content was sent out beginning of May 2019 to all MEDPOL National Focal Points, inviting them to nominate candidates from their respective countries. MESL received 6 nominations of candidates for analysis of Organochlorinated Pesticides (OCs) and Polychlorinated Biphenyls (PCBs) in marine environmental samples. The selection of the six successful candidates was done jointly by MESL staff and the MEDPOL monitoring and assessment officer, by applying the following criteria:

- The nominated candidates must be staff members of the national laboratories that will be designated for participation in 2019 Proficiency Tests.
- The nominated candidates have to be able to apply knowledge, to be built during 2019 Training Courses on organic contaminants, in their regular work related to sampling and assessment; use and maintenance of analytical equipment, selection of the appropriate reference materials, as well as quality assurance of monitoring data produced by their respective national laboratories participating in the MEDPOL IV/IMAP monitoring programme.
- The nominated candidates need to have sufficiently good English language proficiency as the courses will be held in English. Additionally information was requested in the nomination form on the i) education, ii) employment and employers relation to the MEDPOL programme, iii) English proficiency, iv) country distribution and v) overall merit of the nominees. Invitation letters were sent to the participants by IAEA/NAEL-MESL on 17 June 2019. The selected candidates were from Albania, Bosnia & Herzegovina, Croatia, Lebanon, Morocco and Tunisia. The course took place from 2nd to 13th September 2019.

The Training Course began with an introduction to the basic concepts and terminology on persistent organic contaminants analysis. Then the principles of sample preparation methodologies for sediments and biological materials were presented to the participants. Several lectures were dedicated to the high-resolution gas chromatography techniques used for organochlorinated and other organic contaminants in marine samples, and on quality assurance/quality control principles. The most important concepts of measurement science - metrology in chemistry -

validation of measurement procedure, use of reference materials, and uncertainty of measurement results, were also discussed.

During the practical session of the Training Course, the procedures of marine samples preparation and quantification of polychlorinated biphenyls and organochlorinated pesticides in sediments and biota, using gas chromatography coupled to the electron capture detector, was demonstrated. Two kinds of unknown samples were used for the laboratory demonstrations: sediment sample (IAEA 417) and biota sample (IAEA 432).
To set a working pace that everyone could follow the entire laboratory procedures for both sediment and biota samples were prepared before the training course and the most important phases were highlighted. Intermediate steps and corresponding intermediate samples and solutions were prepared beforehand by the trainers. During the course the trainees were shown the entire procedures, but they focused their attention and performed only the most important phases under strict supervision and with the help of the trainers. This methodology, which avoids long waiting times, was welcomed by all trainees.
At the end of the course the identity of the samples was revealed, and results were compared with Reference Materials assigned values.

A sampling field trip was organized for the demonstration of marine sediment and water sampling techniques. During the sea-going field mission, the procedures for surface sediment (grab sampler), surface water and water profile sampling (Niskin bottle) were shown to the trainees, who could appreciate how samples are collected and handled following the strictest procedures ensuring the highest quality of samples.

Theoretical and practical sessions were also devoted to sample preparation, storage, transport and pre-treatment of the samples. Within the practical section, biological samples, as fish and mussels, were dissected by the participants and they were trained on the precautions to be taken during the removal of soft tissue from the organisms to avoid contamination from dissection tools, reagents, laboratory environment and the person carrying out the procedure.

During both, theoretical lectures and practical exercises in the laboratory, analytical methodologies, instrument optimization, quality assurance and quality control and quantitative calculations were discussed in detail. The details on the practical part of the course are given in the Practical Session section.
Trainees were provided with a certificate stating their participation in the training course. They were supplied with online links to shared folders containing methodologies, useful literature and the computer exercises they finalized during the course (https://share.iaea.org/pub/index.php/s/iOYQx49Q8J386db - password: monaco)

The program of the course, trainees' evaluations and examples of data produced are included in this report.

2. Evaluation

The experience of participants of the 2019 MEDPOL training course on the analysis of Organochlorinated Pesticides (OCs) and Polychlorinated Biphenyls (PCBs) in marine environmental samples in the field of organic contaminant analysis varied greatly within the group of participants, and not all of them were directly involved in sediments and biota matrices or this type of contaminant analyses in their institutions. This year, almost all participants showed the required minimum level of English to follow the entire training course without the need of translating constantly into French or other languages. This has been a big improvement from other years' experience. All participants showed a lot of interest in the laboratory part and had enough laboratory knowledge to understand the different steps of the analytical procedures, including the importance for obtaining accurate results in the analysis of organochlorinated compounds and pesticides in environmental matrices (sediment and biota). All of them were interested in implementing the learned procedures in their home laboratories and were keen to find out different solutions to make it possible. Also, all laboratories' trainees provided results in the 2018 MEDPOL PT for chlorinated compounds, except Lebanon and Tunisia. Nevertheless, Lebanon participated in previous MEDPOL PTs (2015-2017) and Tunisia reported result for PAHs in 2018 MEDPOL PT.

A questionnaire was distributed to the trainees to receive feedback on the organization, content and structure of the training. Overall the course was, rated as excellent by 100% (6/6). 83% (5/6) of participants thought that the course met their needs and another 17% (1/6) considered that to some extent, so in general they felt they will be better able to do their job after attending this course (67% replied yes and 33% to some extent). Although the balance of lectures, group discussions and group exercises were found to be correct, most participants wished to have more practical time in the laboratory to apply the newly learned knowledge. The questionnaires can be found in pages 45-66.

3. Conclusion and Recommendations

The training course on the analysis of Organochlorinated Pesticides (OCs) and Polychlorinated Biphenyls (PCBs) in marine environmental samples was beneficial for all participating trainees. In the MESL, each participant had a chance to observe and apply validated analytical protocols with a strict quality assurance system in place, following the Eurachem guidelines* and according to the ISO 17025**. Most participants acknowledged that they will have to improve or modify their laboratory procedures to reach a quality of analysis required for the MEDPOL monitoring program.

Although most participants were familiar with concepts like internal standards, reference materials and quality assurance, they showed genuine interest and commitment to improve the quality of their work. More advanced participants took advantage of discussing specific problems with fellow trainees and MESL staff providing the training. This year, all laboratories trainees participating in the organic contaminants TC had sufficient English proficiency. In this respect, we consider that the nomination process of this year has improved significantly compared to the previous years where laboratories' trainees never provided data results for the PT MEDPOL exercises. It was followed by a selection process of trainees, which was done fully in line with the recommendations and conclusions of the Meeting of CorMon on Pollution Monitoring that was held from 1 to 2 April 2018 in Podgorica, Montenegro, including consultations of MED POL Monitoring and Assessment Officer with the MED POL Focal Points of respective Contracting Parties regarding their need to participate in Training Course; a stricter selection of participants representing the laboratories that are identified by their respective MED POL Focal Points as the competent national entities for IMAP implementation, and that thereby also participate in Proficiency Testing organized by MESL within the cooperation with MED POL; good English proficiency of the participants. Despite these clear criteria one participant of this course was from a laboratory that later on was declared not to be an IMAP laboratory. While MESL and the MEDPOL officer are doing their best to select participants complying with criteria accepted by the COP it is the responsibility of the national focal points to nominate the correct laboratories. Therefore, MEDPOL Focal Points should continue to make all possible efforts to ensure nominated participants of the TC are with adequate background and from laboratories actively participating in national marine environment monitoring programs within the implementation of IMAP/ MEDPOL IV. Similarly, additional efforts are needed to ensure the laboratories participating in TCs are those taking part in PTs in order to make the most of the training received. Focus should be on laboratory experience to benefit most from the capacity building efforts provided.
MESL recommends that the list of national IMAP competent laboratories is regularly updated and shared with the MEDPOL Monitoring and Assessment Officer in order for MESL to undertake a simplified selection process that is fully in line with such updated list.

Several of the participants complained about the lack of funds for buying analytical standards, reference materials and maintaining the good performance of their equipment.

Based on the experience from this training course, expert missions to national designated laboratories participating in national marine environment monitoring programs for IMAP/MEDPOL IV are under preparation as to assist at laboratories with greatest needs to improve their QA/QC and data quality. Given the fact that some laboratories need to build up expertise and infrastructure to be able to provide good quality data especially for organic contaminants, this should include the identification of technical (e.g. acquisition of laboratory equipment, analytical standards, reference materials) and knowledge needs. These missions have been planned in close consultations of MED POL with MEDPOL Focal Points. They should also include direct participation of MED POL Focal Points in expert missions of MESL as to reinforce the importance and motivation.

MEDPOL Focal Points should follow up more closely with national laboratories participating in the implementation of the IMAP MEDPOL IV/monitoring program and experts participating in the TC organized for organic compounds, with a view of further supporting national efforts to implement the QA/QC measures, including results and related recommendations of the Proficiency Testing organized by MESL in close collaboration with MED POL, in order to warrant good quality of monitoring data reported to MEDPOL.

*B. Magnusson and U. Örnemark (eds) Eurachem Guide : The Fitness for Purpose of Analytical Methods -A laboratory Guide to Method Validation and Related Topics (2 nd ed. 2014).

**INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, ISO/IEC 17025:2017. General requirements for the competence of testing and calibration laboratories, Geneva, (2017).

4. List of participants

TRAINING WORKSHOP ON THE ANALYSIS OF ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS IN ENVIRONMENTAL SAMPLES FOR MEDPOL

ALBANIA	
Ms Gjystina FUSHA National Environment Agency (NEA) Unit №04, Rruga Sami Frasheri Tirana	gjystinafusha@ymail.com
BOSNIA & HERZEGOVINA	
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CROATIA	
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TUNISIA	
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5. Course outline

MEDPOL training course on the Analysis of Organochlorine Pesticides and Polychlorinated Biphenyls in Environmental Samples

IAEA – Environment Laboratories, Monaco
2 – 13 September 2019

COURSE OUTLINE

(Note: Owing to parallel scientific meetings at MEL, the chronology of lectures and practical sessions is liable to change)

MONDAY 2 SEPTEMBER

9:00 – 12:00	Welcome to IAEA Environment Laboratories Monaco.	*Mr David Osborn DIR-NAEL*
	Housekeeping (Health and Safety).	*Mr Hussein Ramadan Head - Engineering and Electronics Support (EES)*
	Introduction to the MEDPOL IMAP monitoring programme. Presentation of the Marine Environment Laboratories and their activities.	*Ms Sylvia Sander Laboratory Head-MESL*
	Coffee/tea break	
	Self-introduction of participants and their laboratory, and expectations from the training course.	*All participants*
	Group photos.	
	Administrative matters.	*Ms Leslie Barilaro-Hamonic Team Assistant-MESL*

13:30 – 15:30	Visit of the other Marine Environment Laboratories	
	13:30 – 14:15 Visit of the Radiometrics Laboratory (RML).	*Mr Paul Morris* *Acting Section Head-RML* *Mr Peter Swarzenski* *Section Head-REL*
	14:15 – 15:00 Visit of the Radioecology Laboratory (REL).	*Ms Emilia Vasileva* *Research Scientist*
15:30 – 16:00	Analytical Methods for Organic Contaminants. Introduction to computer sessions.	*Mr Roberto Cassi* *Laboratory Technician*

TUESDAY 3 SEPTEMBER

9:00 – 17:00	**PRACTICAL SESSION**	*Mr Roberto Cassi* *Mr David Huertas* *Laboratory Technicians*
	Extraction of sediment and biological samples with microwave oven. Filtration of samples and blank. Activation of copper. Removal of sulfur from sediment samples and blank.	
	THEORETICAL SESSION	*Ms Imma Tolosa* *Research Scientist*
	Sources, properties and fate of organochlorinated compounds (OCs). The past, the present, and the future. Analytical techniques for the determination of OCs. Extraction and clean-up methods.	

WEDNESDAY 4 SEPTEMBER

9:00 – 17:00	**PRACTICAL SESSION**	*Mr Roberto Cassi* *Mr David Huertas* *Laboratory Technicians*
	Sample concentration: rotatory evaporator, multi-evaporator and nitrogen stream. Solid Phase Extraction (SPE) column chromatography for sediment samples. Elution and concentration of all fractions obtained. Transfer of samples and calibrating standards in auto- injector vials. Spiking of internal standards for Gas Chromatography (GC). Instrumental Injection GC with Electron Capture Detector (ECD).	

THURSDAY 5 SEPTEMBER

09:00 – 12:30 — **THEORETICAL SESSION** — *Mr Imma Tolosa, Research Scientist*

Quantitative determination of OCs by GC-ECD.
Confirmation analyses. Quantitative determination of OCs by GC-MS.
Quality assurance/quality control requirements.

14:00 – 17:00 — **PRACTICAL SESSION** — *Mr Roberto Cassi, Mr David Huertas, Laboratory Technicians*

Determination of lipid content for biological samples.
Sample clean-up using sulfuric acid.

FRIDAY 6 SEPTEMBER

9:00 – 13:00 — **PRACTICAL SESSION** — *Mr Roberto Cassi, Mr David Huertas, Laboratory Technicians*

Solid Phase Extraction (SPE) column chromatography for biological samples. Elution and concentration of the third fraction. Transfer of samples and calibrating standards in auto- injector vials. Spiking of GC internal standards. Instrumental Injection (GC-ECD).

14:00 – 17:00 — **PRACTICAL SESSION** — *Mr Roberto Cassi, Mr David Huertas, Laboratory Technicians; Ms Imma Tolosa, Research Scientist*

GC-ECD maintenance and troubleshooting.
GC-MS confirmation analyses.

MONDAY 9 SEPTEMBER

9:00 – 12:00 — **THEORETICAL SESSION** — *Ms Imma Tolosa, Research Scientist*

High resolution gas chromatography (HPLC), theory and instrumentation.
Set up of GC-MS for confirmation analyses of organochlorinated compounds.

14:00 – 17:00	**PRACTICAL SESSION** Sampling principles and techniques. Sample storage, transport and pre-treatment. Sample preparation: dissection of biological samples (fish, mussels, oysters).	*Mr Roberto Cassi* *Mr David Huertas* *Laboratory Technicians*

TUESDAY 10 SEPTEMBER

9:00 – 13:00	**PRACTICAL SESSION** Sampling field trip. Demonstration of sediment and water sampling techniques. Sample storage.	*Mr Roberto Cassi* *Mr David Huertas* *Laboratory Technicians*
14:00 – 17:00	**THEORETICAL SESSION** The stationary phase. Capillary columns. Sample introduction. Detectors. Temperature effects.	*Ms Imma Tolosa* *Research Scientist*

WEDNESDAY 11 SEPTEMBER

9:00 – 12:00	**THEORETICAL SESSION** Quantifying Uncertainty. Assessing Linear Calibration.	*Ms Sarah Choyke* *Associate Chemist*
13:00 – 17:00	**COMPUTER SESSION** Introduction to GC-ECD data retreatment software. Peak identification and integration. Use of spreadsheet for data quantification.	*Mr Roberto Cassi* *Mr David Huertas* *Laboratory Technicians*

THURSDAY 12 SEPTEMBER

9:00 – 17:00

COMPUTER SESSION

Mr Roberto Cassi
Mr David Huertas
Laboratory Technicians

Data quantification of organochlorine compounds.
Determination and use of limits of detection.
Evaluation of organochlorinated results on sediment samples, QA/QC of data obtained.

THEORETICAL SESSION

Uncertainty estimation by the "Nordtest approach".

Ms Imma Tolosa
Research Scientist
Ms Sarah Choyke
Associate Chemist

FRIDAY 13 SEPTEMBER

9:00 – 12:00

CLOSURE OF THE TRAINING COURSE

Presentations by trainees:

1) Reflections on the training course,
   - Theoretical part,
   - Laboratory experiments
2) How will the newly gained knowledge be implemented in home laboratory:

All course participants

Questionnaires.
Closing remarks.
Certificates.

Mr David Osborn
DIR-NAEL
(or alternate)

13:00 – 17:00 Visit of the Oceanographic Museum, Monaco.

All course participants

6. Theoretical session

Within the theoretical sessions, introductions to the basic concepts on terminology, sources, properties and behaviour of organochlorinated compounds in the environment were presented to the participants. Also detailed talks on the principles of sample preparation methodologies for sediments and biological materials for analyzing persistent organic pollutants (POPs) were provided in line with the practical sessions organized in the laboratory. Several lectures were dedicated to the high-resolution gas chromatography techniques, the electron capture detector (ECD) and mass spectrometry (GC-MS) used for organochlorinated and other organic contaminants in marine samples. In the framework of quality assurance/quality control principles, the key concepts of measurement science - metrology in chemistry - validation of measurement procedures, use of reference materials, and uncertainty of measurement results were also presented, discussed and further practiced with the computers.

A link (https://share.iaea.org/pub/index.php/s/0YJwmnuEJvucPI3 - Password: monaco) was provided to the course participants including the training course laboratory manuals, the practical sessions on quantification data and additional keys guides for working with organic contaminants, gas chromatography techniques and quality assurance.

7. Practical session

Practical sessions were organized to show the most critical aspects in each step of the analytical procedure and the data analyses. They included and covered the following "hands-on" procedures:

Microwave oven extraction and surrogate standards spiking

Special focus was given to the spiking of surrogate standards to increase the accuracy of quantification of the target compounds using the internal standard method. Each trainee was able to repeat the critical step several times until they were confident with the spiking procedure.

Evaporation of solvent extract

Rotatory evaporator was demonstrated and applied by the trainees to concentrate the organic extracts of the samples. A multi-vaporator was also introduced to the trainees and careful evaporation under nitrogen gas was done to prepare the final extracts for gas chromatography analyses.

Sulphur clean-up in sediment extracts

Sulphur in the sediment extract must be eliminated to avoid interferences before quantification of the final extract, especially if done by gas chromatography coupled to electron capture detector (GC/ECD). The activated copper procedure was used for the removal of Sulphur. The full procedure including the careful activation of the copper, and the complete removal of acid and water was practiced, and critical steps pointed out to the trainees.

Separation techniques by solid-phase extraction (SPE)

The fractionation of the different organochlorine compounds was performed by pipetting the concentrated organic extract on the SPE column and eluting the column with sequential volumes of solvents of increasing polarity. Every trainee performed the fractionation of the extracts on individual SPE columns of Florisil and Silica adsorbent.

Measurement of lipid content and lipid cleanup in biota samples

The extractable organic matter of the biological samples, mainly consisting of lipids was observed and quantified gravimetrically using a microbalance, in order to calculate the aliquot of sample extract that can be cleaned-up by SPE adsorption chromatography

The extracts were subsequently separated into two aliquots: The first aliquot was treated with sulphuric acid, to destroy the interfering lipids before cleaning up the sample over a Florisil SPE. As some organochlorinated pesticides may degrade with acid, the second aliquot of the extract was cleaned up using an alternative procedure with a Silica SPE column before the Florisil SPE column.

Preparation of calibration standards and sample vials for instrumental injection

The final purified samples were transferred to vials and appropriate GC-internal standards were carefully spiked by the trainees before the instrumental analyses. Preparation of the calibrating standards were also done. Special care was devoted to the use of the Pasteur pipettes and volumetric syringes.

Quantitative determination by gas chromatography and electron capture detector (GC-ECD)

The gas chromatography data retreatment software was demonstrated for peak identification and integration. Calibration curves by internal calibration using the appropriate surrogate standards were shown and verified by the trainees. The concepts of method blank, recoveries and detection limits were implemented and tested by the trainees. An example of a typical computer session is shown in figures 1 to 7.

Confirmation by GC-MS

The set-up of the monitoring program for quantification and confirmation of the organochlorinated compounds by GC/MS using the total scan and selected ion monitoring acquisition was explained within the acquisition program on the equipment.

Quality control charts and estimation of uncertainties

Guidelines on how to plot the internal quality control charts were provided and the results of the calculated data were assessed by plotting them on the quality control charts of the laboratory (Fig. 8-11), following the Eurochem guidelines (Eurochem 2014). The estimation of the uncertainty of the measurements, which is a requirement of the ISO 17025 for accredited laboratories, was explained in detail during the lectures and practical examples of calculation using the Nordtest approach were performed.

Emphasis was also given to the major problem associated with the PCB results, which can be the lack of separation of several important congeners on the classical stationary phase commonly used in the GC determination of PCBs. Improvements to reduce the risk of erroneous data due to co-elution were shown to be achieved using two capillary columns with different polarities, length and internal diameter.

Maintenance and troubleshooting of the GC-ECD

The high-resolution gas chromatography, theory and instrumentation, including the stationary phases, the sample injector, detectors and temperature effects were explained in detail during the lectures. A practical demonstration of the maintenance of the GC, including the change of the glass liner, O-ring, septum and gold ring was shown. Also, the procedure on how to cut the capillary columns and install them into the injector and detector was explained. All trainees had the opportunity to practice the cutting of the capillary columns with the appropriate tool and asses their correct cutting using magnifiers.

Sampling, storage, transport and dissection of samples

As mentioned in the introduction of this report, trainees were also able to participate in a field sampling mission to understand and practice the good use of sampling techniques to obtain better environmental samples to analyze organochlorinated compounds (OCs) and pesticides, as well as PAHs. During the trip they have learned how to sample using different procedures, keep a good storage system and be able to transport safely and in good conditions samples to the laboratory. This is the first critical step in order to obtain better results in their analysis. In addition, also a dissection session was organized to show and let them practice collection of different parts of fish and mussels for the analysis of OCs, pesticides and PAHs. All trainees had the possibility to practice this dissection exercise with one fish and a mussel.

8. Example of computer session and data produced including quality control charts

Figure 1. Description of the calibration strategy and formulas used for quantitative calculations.

INTERNAL CALIBRATION

This method is based on the use of a *surrogate* which is defined as a non-interfering compound added to a sample in known concentration to eliminate the need to measure the sample size in quantitative analysis and for correction of instrumental variation.
In this method, the surrogate is added to each sample. The ratio of the areas of the surrogate and analyte are then used to construct the calibration curve.
In a multiple point internal calibration each analysis contains the surrogate whose total amount is kept constant and the analyte of interest whose amount covers the range of concentrations expected.
A multiple points relative response factor (RRF) calibration curve is established for analytes of interest for each working batch. A RRF is determined, for each analyte, for each calibration level using the following equation:

$$RRF\,(X) = \frac{\text{Area (X)}}{\text{Area (SU)}} \text{ x } \frac{\text{Qty (SU)}}{\text{Qty (X)}}$$

Where:
Area (X) = the area of the analyte to be measured (target compound)
Area (SU) = the area of the specific surrogate
Qty (X) = the known quantity of the analyte in the calibration solution
Qty (SU) = the known quantity of the surrogate in the calibration solution

The relative response factors determined for each calibration level are averaged to produce a mean relative response factor (mRRF) for each analyte. The percent relative standard deviation (%RSD) for all response factors must be less than or equal to 15%, for each analyte.

$$\%RSD = \frac{\text{Standard deviation of the RRFs}}{\text{Average of the RFs}} \text{ x } 100$$

SAMPLES QUANTIFICATION

Sample analyte concentrations are calculated based on the quantity and response of the surrogate.
The following equation gives the amount of analyte in the solution analysed.

$$Qty\,(\text{X}) = \text{Qty (SU)} \text{ x } \frac{\text{Area (X)}}{\text{Area (SU)}} \text{ x } \frac{1}{\text{m}RRF\,(X)}$$

Where:
Qty (X) = the unknown quantity of the analyte in the sample
Qty (SU) = the known quantity of the surrogate added to the sample
Area (X) = the area of the analyte
Area (SU) = the area of the surrogate
mRRF (X) = the average response factor of the analyte
Sample analyte concentrations are then calculated by dividing the amount found (Qty) by the grams of samples extracted

Figure 2. Example of quantitative calculation of relative response factors (RRF) for fractions 1, 2 and 3. At F1: HCB, PCB-28, PCB-52 and PCB-101 were calculated using PCB-29 SU. The others using PCB-198 SU.

OCs - F1

	CALIBRATION CURVE-1				
	Conc. (pg/µl)	**Volume (µl)**	**Qty Spiked (pg)**	**Area**	**RRF**
TCMX (GC-IS)	1000	10	10000	16724	
HCB	10	100	1000	1730	2.97
PCB-29 SU	25	100	2500	1456	0.35
PCB-28	10	100	1000	743	1.28
PCB-52	10	100	1000	558	0.96
PCB-101	10	100	1000	797	1.37
ppDDE	10	100	1000	1345	1.14
PCB-118	10	100	1000	1000	0.85
PCB-153	10	100	1000	917	0.78
ppDDT	10	100	1000	938	0.79
PCB-138	10	100	1000	1124	0.95
PCB-180	10	100	1000	1307	1.11
PCB-198 SU	25	100	2500	2950	0.71

OCs - F2

	CALIBRATION CURVE-1				
	Conc. (pg/µl)	**Volume (µl)**	**Qty Spiked (pg)**	**Area**	**RRF**
TCMX (GC-IS)	1000	10	10000	16965	
Lindane	10	100	1000	1523	1.53
E-HCH - SU	25	100	2500	2491	0.59
ppDDD	10	100	1000	1157	1.16

OCs - F3

	CALIBRATION CURVE-1				
	Conc. (pg/µl)	**Volume (µl)**	**Qty Spiked (pg)**	**Area**	**RRF**
TCMX (GC-IS)	1000	10	10000	18251	
Endosulfan LD40 - SU	25	100	2500	3703	0.81
a-Endosulfan	10	100	1000	1454	0.98
Dieldrin	10	100	1000	1766	1.19
Endrin	10	100	1000	1343	0.91
b-Endosulfan	10	100	1000	1653	1.12

Figure 3. Average of relative response factors (RRFs) from the 3 calibration levels (10, 50 and 100 pg/µl) and percentage relative standard deviation (%RSD) for fractions 1, 2 and 3. At F1: HCB, PCB-28, PCB-52 and PCB-101 were calculated using PCB-29 SU. The others using PCB-198 SU.

Mean RRF	SD	%RSD		
			Compound	**Mean RRF**
2.6	0.32	12.3	HCB	2.6
0.4	0.01	4.1	PCB-29 SU	0.4
1.1	0.14	12.9	PCB-28	1.1
0.8	0.16	20.8	PCB-52	0.8
1.1	0.25	23.4	PCB-101	1.1
1.1	0.05	4.3	ppDDE	1.1
0.7	0.14	19.6	PCB-118	0.7
0.6	0.13	21.6	PCB-153	0.6
0.8	0.07	8.4	ppDDT	0.8
0.8	0.12	14.6	PCB-138	0.8
1.0	0.13	14.0	PCB-180	1.0
0.7	0.03	4.1	PCB-198 SU	0.7

Mean RRF	SD	%RSD		
			Compound	**Mean RRF**
1.5	0.07	4.5	Lindane	1.5
0.6	0.02	2.9	E-HCH - SU	0.6
1.0	0.13	12.6	ppDDD	1.0

Mean RRF	SD	%RSD		
			Compound	**Mean RRF**
0.8	0.02	2.6	Endosulfan LD40 - SU	0.8
0.9	0.06	7.0	a-Endosulfan	0.9
1.1	0.07	6.3	Dieldrin	1.1
0.8	0.11	13.8	Endrin	0.8
1.0	0.08	8.0	b-Endosulfan	1.0

Figure 4. Example of quantitative calculation of the procedural blank sample for fractions 1, 2 and 3.

	BLANK					
	Conc. (pg/µl)	**Vol. (µl)**	**Qty Spiked (pg)**	**Area**	**Qty Found (pg)**	**SU % REC**
TCMX (GC-IS)	1000	10	10000	10091		
HCB				168	333	
PCB-29 SU	100	100	10000	1942	5330	53
PCB-28				90	418	
PCB-52				101	668	
PCB-101				128	608	
ppDDE				198	297	
PCB-118				681	1622	
PCB-153				89	234	
ppDDT				156	329	
PCB-138				165	332	
PCB-180				82	142	
PCB-198 SU	100	100	10000	6077	8180	82

	BLANK					
	Conc. (pg/µl)	**Vol. (µl)**	**Qty Spiked (pg)**	**Area**	**Qty Found (pg)**	**SU % REC**
TCMX (GC-IS)	1000	10	10000	7620		
Lindane				23	46	
E-HCH - SU	100	100	10000	3392	7407	74
ppDDD				74	214	

	BLANK					
	Conc. (pg/µl)	**Vol. (µl)**	**Qty Spiked (pg)**	**Area**	**Qty Found (pg)**	**SU % REC**
TCMX (GC-IS)	1000	10	10000	7407		
Endosulfan LD40 - SU	100	100	10000	3990	6821	68
a-Endosulfan				40	109	
Dieldrin				44	100	
Endrin				52	168	
b-Endosulfan				35	85	

Figure 5. Example of quantitative calculation of a reference material sample (IAEA-417) for fractions 1, 2 and 3.

grams extracted	8.11

	SAMPLE-1 FRACTION 1							
	Conc. (pg/µl)	**Vol. (µl)**	**Qty Spiked (pg)**	**Area**	**Qty Found (pg)**	**Blank-substr (pg)**	**Conc. (ng/g)**	**SU % REC**
TCMX (GC-IS)	1000	10	10000	9727				
HCB				6095	8600	8268	1.02	
PCB-29 SU	100	100	10000	2724	7759			78
PCB-28				11547	38078	37660	4.64	
PCB-52				26269	124263	123595	15.24	
PCB-101				89030	301914	301306	37.15	
ppDDE				106779	174410	174113	21.47	
PCB-118				135480	350872	349249	43.06	
PCB-153				108475	311347	311113	38.36	
ppDDT				66709	209849	209520	25.83	
PCB-138				198725	435619	435287	53.67	
PCB-180				73023	136829	136687	16.85	
PCB-198 SU	100	100	10000	5590	7807			78

	SAMPLE-1 FRACTION 2							
	Conc. (pg/µl)	**Vol. (µl)**	**Qty Spiked (pg)**	**Area**	**Qty Found (pg)**	**Blank-substr (pg)**	**Conc. (ng/g)**	**SU % REC**
TCMX (GC-IS)	1000	10	10000	8527				
Lindane				1026	1736	1689	0.21	
E-HCH - SU	100	100	10000	4070	7942			79
ppDDD				76500	185366	185152	22.83	

	SAMPLE-1 FRACTION 3							
	Conc. (pg/µl)	**Vol. (µl)**	**Qty Spiked (pg)**	**Area**	**Qty Found (pg)**	**Blank-substr (pg)**	**Conc. (ng/g)**	**SU % REC**
TCMX (GC-IS)	1000	10	10000	6068				
Endosulfan LD40 - SU	100	100	10000	3332	6955			70
a-Endosulfan				690	2270	2270	0.28	
Dieldrin				3903	10538	10538	1.30	
Endrin				954	3655	3655	0.45	
b-Endosulfan				5383	15781	15781	1.95	

Figure 6. Table of quantitative calculation of a sediment reference material sample (IAEA-417) performed by the trainees. Results include mean, standard deviation and relative standard deviation (ng/g d.w.)

Compound	IAEA-417 Sample 1	IAEA-417 Sample 2	IAEA-417 Sample 3	Mean (ng/g)	Standard Deviation (ng/g)	Relative Standard Deviation (%)	Reference Value (ng/g)	Expanded Uncertainty (ng/g)
PCB-28	4.50	4.64	4.81	4.65	0.13	3%	5.70	1.00
PCB-52	14.85	15.24	15.98	15.36	0.47	3%	17.00	2.50
PCB-101	36.00	37.15	38.73	37.29	1.12	3%	42.00	4.90
PCB-118	39.16	43.06	42.65	41.62	1.75	4%	43.00	5.60
PCB-138	49.91	53.67	51.74	51.77	1.54	3%	45.00	6.60
PCB-153	36.20	38.36	37.57	37.38	0.89	2%	39.00	5.80
PCB-180	18.19	16.85	18.06	17.70	0.60	3%	16	2.2
HCB	0.97	1.02	1.03	1.01	0.03	3%	1.20	0.30
Lindane	0.20	0.21	0.22	0.21	0.01	4%	0.54	0.15
ppDDE	19.63	21.47	21.01	20.70	0.78	4%	14.00	1.90
ppDDD	22.86	22.83	28.68	24.79	2.75	11%	21.00	2.90
ppDDT	16.25	25.83	18.43	20.17	4.10	20%	19.00	3.20

Figure 7. Table of quantitative calculation of a biota reference material sample (IAEA-432) performed by the trainees. Results include mean, standard deviation and relative standard deviation (ng/g d.w.)

Compound	IAEA-432 Sample 1	IAEA-432 Sample 2	IAEA-432 Sample 3	Mean (ng/g)	Standard Deviation (ng/g)	Relative Standard Deviation (%)	Reference Value (ng/g)	Standard Deviation (ng/g)
PCB-28	0.20	0.29	0.21	0.23	0.04	17%	0.3	0.3
PCB-52	0.36	0.50	0.48	0.45	0.06	13%	1.2	1.2
PCB-101	1.40	1.45	1.46	1.44	0.03	2%	1.2	0.5
PCB-118	1.27	1.23	1.28	1.26	0.02	2%	1.1	0.4
PCB-138	2.69	2.59	2.61	2.63	0.04	2%	2.2	0.8
PCB-153	3.77	3.72	3.64	3.71	0.05	1%	2.8	1.0
PCB-180	0.15	0.17	0.20	0.17	0.02	11%	0.2	0.1
HCB	0.36	0.37	0.33	0.35	0.02	5%	0.2	0.1
Lindane	0.15	0.14	0.14	0.14	0.01	5%	0.58	0.54
ppDDE	2.89	3.12	3.03	3.01	0.10	3%	2.1	1.0
ppDDD	0.94	0.83	0.79	0.86	0.06	7%	0.88	0.49
ppDDT	0.39	0.74	0.36	0.50	0.17	34%	0.7	0.5

Figure 8. Quality control chart (QC) for PCB-52 in IAEA-417 sediment reference material (ng/g d.w).

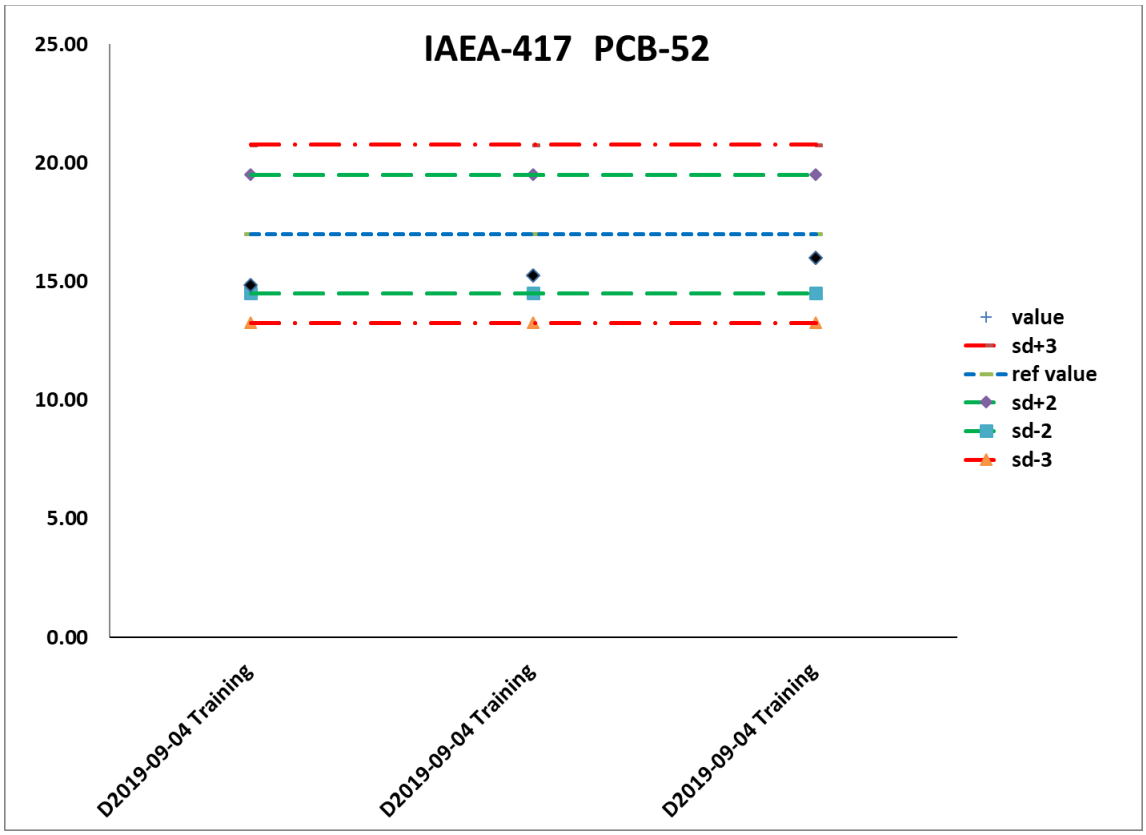


Figure 9. Quality control chart (QC) for p,p-'DDD in IAEA-417 sediment reference material (ng/g d.w).

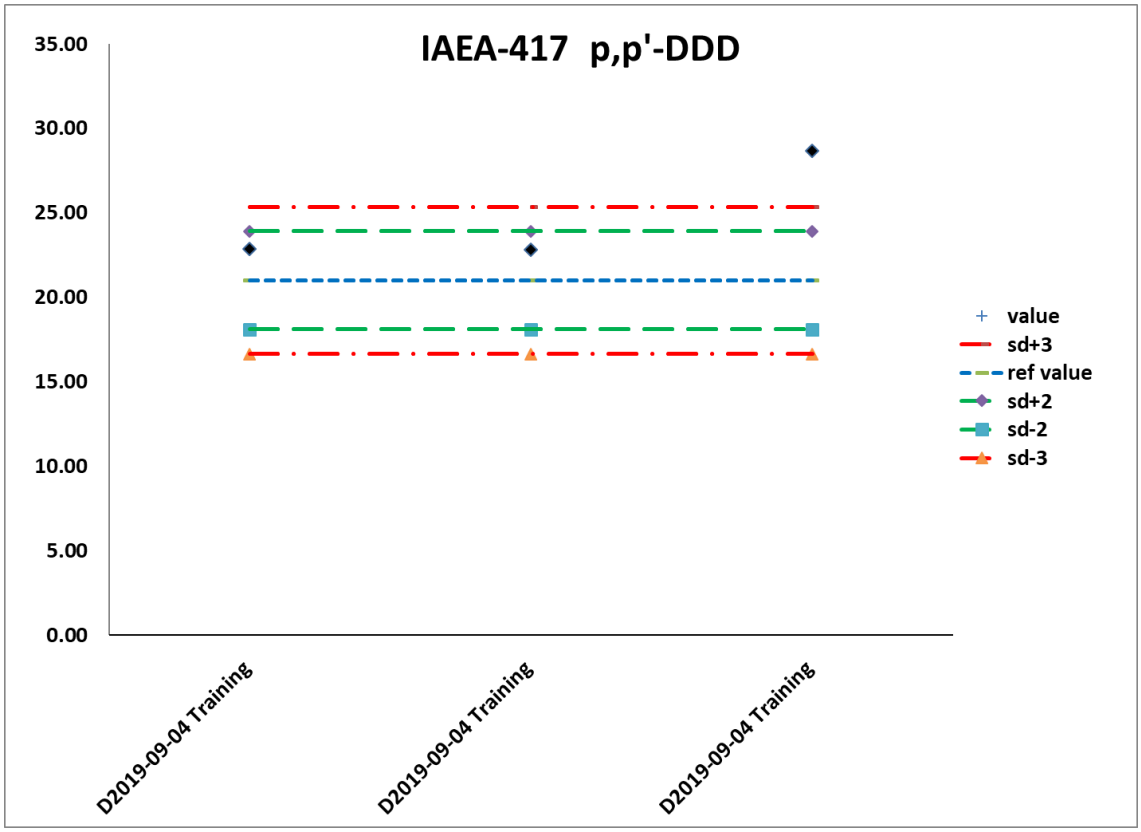


Figure 10. Quality control chart (QC) for PCB-101 in IAEA-432 biota reference material (ng/g d.w).

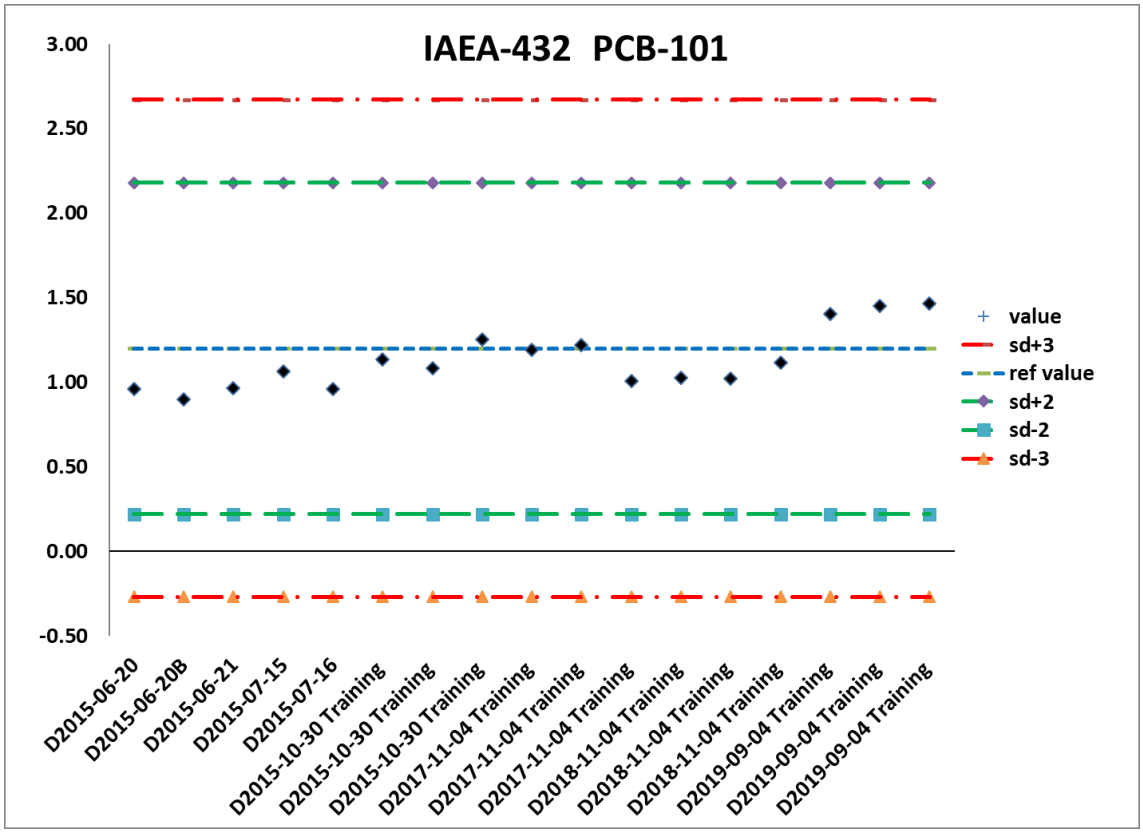
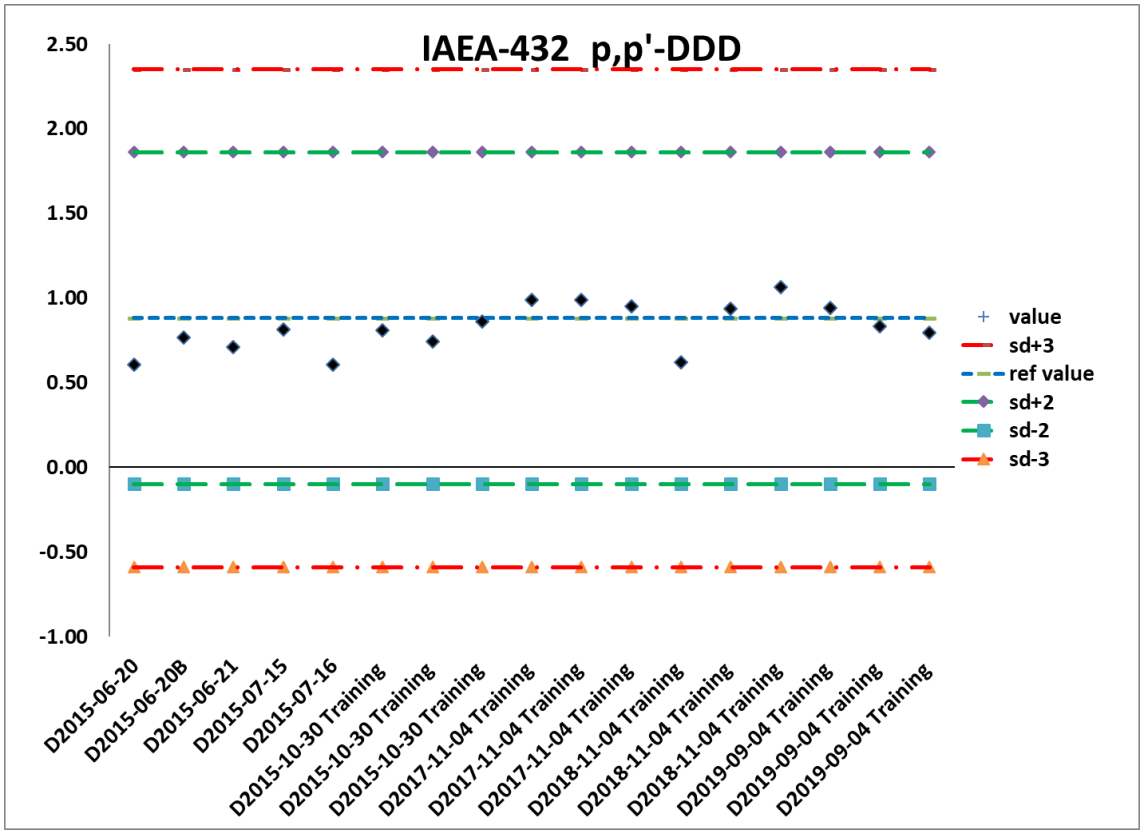


Figure 11. Quality control chart (QC) for p,p-'DDD in IAEA-432 biota reference material (ng/g d.w).



9. Certificates of participation

IAEA Atoms For Peace Environment Laboratories

UN environment United Nations Environment Programme

MAP Mediterranean Action Plan Barcelona Convention

CERTIFICATE OF PARTICIPATION

Gjystina FUSHA

National Environment Agency (NEA)

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Analysis of Organochlorine Pesticides and Polychlorinated Biphenyls in Environmental Samples

2 – 13 September 2019
IAEA MONACO

Organized by

UNEP/MAP - MED POL & IAEA-NAEL

Marine Environmental Studies Laboratory

Trainers

Ms I. Tolosa
Ms E. Vasileva
Mr R. Cassi
Ms S. Choyke
Mr D. Huertas

David Osborn
Director - IAEA Environment Laboratories

IAEA Atoms For Peace Environment Laboratories

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Rabat, Morocco

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Lasaad CHOUBA

Institut National des Sciences et Technologies de la Mer (INSTM)

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10. Training course evaluation questionnaires

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INTERNATIONAL ATOMIC ENERGY AGENCY

ENVIRONMENT LABORATORIES

MARINE ENVIRONMENTAL STUDIES LABORATORY

TRAINING COURSE EVALUATION QUESTIONNAIRE

Training Course organized for MED POL program on the
Analysis of Organochlorine Pesticides and Polychlorinated Biphenyls in Environmental Samples
MONACO
(2-13 September 2019)

Dear Participant,
The purpose of this evaluation form is to collect the participants' opinions about the entire programme.
This information will be very helpful in planning future courses. Please do not leave any question unanswered.

Participant's name: GJYSTINA.....

Participant's country: ALBANIA.....

1. What is your overall reaction to the workshop?

[X] Excellent [ ] Better than expected [ ] Satisfactory [ ] Poor

2. Do you feel that the workshop met your needs? ***(If NOT, please explain)***

[ ] Yes [X] To some extent [ ] Uncertain [ ] No

.....

.....

3. Do you feel that you will be better able to do your job after attending this course ?

[ ] Yes [X] To some extent [ ] Uncertain [ ] No

4. Do you have a better attitude about your job thanks to this course ?

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

5. Would you recommend to others in your field to attend this course?

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

6. In your opinion, the number of participants in the workshop was:

[X] Just right [ ] Too few [ ] Too many

7. Do you think that similar workshops with other topics would be useful?

[X] Yes [ ] No

If YES, please recommend topics:

[ ] Other pesticides [X] Heavy metals [ ] Others *(specify)*.....

8. How do you rate the balance of lectures, group discussion, and group exercises ?

[ ] Too many lectures [ ] Too many discussions [X] Good

9. How helpful were the group exercises ?

[X] Very helpful [ ] Helpful [ ] Not helpful

10. What do you think of the speed of the course ?

[X] Too fast [ ] Just right [ ] Too slow

11. Did you have enough skills practice time ?

[ ] Yes [X] No [ ] Uncertain

WORKSHOP CONTENT

12. What did you like best about the workshop course ? (strongest aspects)

Practical session

13. What did you like least about the workshop course ? (weakest aspects)

Two weeks is very short hearing, especially for practical session.

14. What do you think should be dropped from this workshop course ?

Nothing.

15. How do you rate the workshop length ?

[ ] Just right [X] Too short [ ] Too long

16. What's your opinion on the workshop content sequence ?

[ ] Very well sequenced [X] Suitable [ ] Poorly sequenced

17. How valuable was the workshop content to your current job ?

[ ] Very valuable [X] Some value [ ] No real value

18. How do you rate the balance of theoretical and practical sessions ?

[ ] Too theoretical [X] Good balance [ ] Too practical

19. Comments about the course contents :

INSTRUCTIONAL MATERIAL

20. In your opinion, was the number of handouts you received sufficient ?

[ ] Just right [X] Too few [ ] Too many

21. How do you rate the quality of the handout material ?

[X] High quality [ ] Sufficient [ ] Below expectations

LABORATORY AND FACILITIES

22. How do you rate the laboratory sessions ?

[ ] Excellent [X] Very good [ ] Good [ ] Fair [ ] Poor

23. Comments about laboratory sessions:

.....
.....
.....

24. Did you like the seating arrangements of the class room ?

[X] Yes [ ] No [ ] Uncertain

25. How do you rate the service (breaks, lunch, etc.) ?

[ ] Excellent [X] Very good [ ] Good [ ] Fair [ ] Poor

26. What is your overall evaluation of the course ?

[ ] Excellent [X] Very good [ ] Good [ ] Fair [ ] Poor

Thank you for taking the time to answer this questionnaire.
Your input is really valuable to us!

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(2-13 September 2019)

Dear Participant,
The purpose of this evaluation form is to collect the participants' opinions about the entire programme.
This information will be very helpful in planning future courses. Please do not leave any question unanswered.

Participant's name: ALEKSANDAR ELEZ

Participant's country: BOSNIA AND HERZEGOVINA

1. What is your overall reaction to the workshop?

[X] Excellent [ ] Better than expected [ ] Satisfactory [ ] Poor

2. Do you feel that the workshop met your needs? ***(If NOT, please explain)***

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

.....

.....

3. Do you feel that you will be better able to do your job after attending this course ?

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

4. Do you have a better attitude about your job thanks to this course ?

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

5. Would you recommend to others in your field to attend this course?

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

6. In your opinion, the number of participants in the workshop was:

[X] Just right [ ] Too few [ ] Too many

7. Do you think that similar workshops with other topics would be useful?

[X] Yes [ ] No

If YES, please recommend topics:

[X] Other pesticides [X] Heavy metals [X] Others *(specify)*..... BROMINATED FLAME RETARDANTS, AQUATIC ECOSYSTEM TOXICITY ASSESSMENT

8. How do you rate the balance of lectures, group discussion, and group exercises ?

[ ] Too many lectures [ ] Too many discussions [X] Good

9. How helpful were the group exercises ?

[X] Very helpful [ ] Helpful [ ] Not helpful

10. What do you think of the speed of the course ?

[ ] Too fast [X] Just right [ ] Too slow

11. Did you have enough skills practice time ?

[X] Yes [ ] No [ ] Uncertain

WORKSHOP CONTENT

12. What did you like best about the workshop course ? (strongest aspects)

ALL PRACTICAL SESSIONS.

13. What did you like least about the workshop course ? (weakest aspects)

14. What do you think should be dropped from this workshop course ?

NOTHING SHOULD BE DROPPED, THE CONTENT OF THE WORKSHOP IS EXCELLENT.

15. How do you rate the workshop length ?

[X] Just right [ ] Too short [ ] Too long

16. What's your opinion on the workshop content sequence ?

[X] Very well sequenced [ ] Suitable [ ] Poorly sequenced

17. How valuable was the workshop content to your current job ?

[X] Very valuable [ ] Some value [ ] No real value

18. How do you rate the balance of theoretical and practical sessions ?

[ ] Too theoretical [X] Good balance [ ] Too practical

19. Comments about the course contents :

1. EXCELLENT COMMUNICATION BEFORE THE START OF THE WORKSHOP.

2. LECTURERS (FOR PRACTICAL EXERCISE AND THEORETICAL LECTURES) KIND AND READY TO COOPERATE.

3. ALL OTHER STAFF KIND AND READY TO COOPERATE.

THANKS FOR EVERYTHING. I ENJOYED THIS WORKSHOP!

THE VIEW FROM KITCEH IS AMAZING! ☺

THE PARTICIPANTS WHO PARTICIPATED IN THE WORK SHOP ARE FRIENDLY.

I HOPE TO VISIT YOU IN THE FUTURE.

INSTRUCTIONAL MATERIAL

20. In your opinion, was the number of handouts you received sufficient ?

[X] Just right [ ] Too few [ ] Too many

21. How do you rate the quality of the handout material ?

[X] High quality [ ] Sufficient [ ] Below expectations

LABORATORY AND FACILITIES

22. How do you rate the laboratory sessions ?

[X] Excellent [ ] Very good [ ] Good [ ] Fair [ ] Poor

23. Comments about laboratory sessions:

STAFF FRIENDLY, ANSWERED FOR ALL QUESTIONS.
THEIR PRACTICAL WORK IS EXCELLENT.

24. Did you like the seating arrangements of the class room ?

[X] Yes [ ] No [ ] Uncertain

25. How do you rate the service (breaks, lunch, etc.) ?

[ ] Excellent [X] Very good [ ] Good [ ] Fair [ ] Poor

26. What is your overall evaluation of the course ?

[X] Excellent [ ] Very good [ ] Good [ ] Fair [ ] Poor

Thank you for taking the time to answer this questionnaire.
Your input is really valuable to us!

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TRAINING COURSE EVALUATION QUESTIONNAIRE

Training Course organized for MED POL program on the
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MONACO
(2-13 September 2019)

Dear Participant,
The purpose of this evaluation form is to collect the participants' opinions about the entire programme.
This information will be very helpful in planning future courses. Please do not leave any question unanswered.

Participant's name: IVA FINDRLE

Participant's country: CROATIA

1. What is your overall reaction to the workshop?

[X] Excellent [ ] Better than expected [ ] Satisfactory [ ] Poor

2. Do you feel that the workshop met your needs? ***(If NOT, please explain)***

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

EVEN THOUGH WE HAVE NO ACCESS TO SOME INSTRUMENTS AT HOME, YOU'VE EXPLAINED THE BASICS SO WE CAN DO IT THE BEST WITH WHAT WE HAVE.

3. Do you feel that you will be better able to do your job after attending this course ?

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

4. Do you have a better attitude about your job thanks to this course ?

[ ] Yes [X] To some extent [ ] Uncertain [ ] No

5. Would you recommend to others in your field to attend this course?

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

6. In your opinion, the number of participants in the workshop was:

[X] Just right [ ] Too few [ ] Too many

7. Do you think that similar workshops with other topics would be useful?

[X] Yes [ ] No

If YES, please recommend topics:

[X] Other pesticides [ ] Heavy metals [ ] Others *(specify)*.....

8. How do you rate the balance of lectures, group discussion, and group exercises ?

[ ] Too many lectures [ ] Too many discussions [X] Good

9. How helpful were the group exercises ?

[X] Very helpful [ ] Helpful [ ] Not helpful

10. What do you think of the speed of the course ?

[ ] Too fast [X] Just right [ ] Too slow

11. Did you have enough skills practice time ?

[ ] Yes [ ] No [X] Uncertain

I KNOW THERE IS NO TIME, BUT MAYBE I WOULD LIKE IF WE DID OUR OWN PARALEL SO WE CAN COMPARE OUR OWN RESULTS AND TALK ABOUT IT.

WORKSHOP CONTENT

12. What did you like best about the workshop course ? (strongest aspects)

YOU ANSWERED ALL MY QUESTIONS, EXPLAINED EVERYTHING IN DETAILS AND AS MANY TIMES WE NEEDED. WE SAW EVERYTHING IN PRACTISE, NOT ONLY IN THEORY.

13. What did you like least about the workshop course ? (weakest aspects)

THE FACT WE DIDN'T GET TO ANALYSE OUR OWN SAMPLE FROM THE BEGINING TILL THE END.

14. What do you think should be dropped from this workshop course ?

NOTHING. IN MY OPINION EVERYTHING WAS PERFECTLY BALANCED

15. How do you rate the workshop length ?

[X] Just right [ ] Too short [ ] Too long

16. What's your opinion on the workshop content sequence ?

[ ] Very well sequenced [X] Suitable [ ] Poorly sequenced

17. How valuable was the workshop content to your current job ?

[X] Very valuable [ ] Some value [ ] No real value

18. How do you rate the balance of theoretical and practical sessions ?

[ ] Too theoretical [X] Good balance [ ] Too practical

19. Comments about the course contents :

INSTRUCTIONAL MATERIAL

20. In your opinion, was the number of handouts you received sufficient ?

[X] Just right [ ] Too few [ ] Too many

21. How do you rate the quality of the handout material ?

[X] High quality [ ] Sufficient [ ] Below expectations

LABORATORY AND FACILITIES

22. How do you rate the laboratory sessions ?

[X] Excellent [ ] Very good [ ] Good [ ] Fair [ ] Poor

23. Comments about laboratory sessions:

EVERYTHING WAS EXPLAINED IN DETAILS, ALL MY QUESTIONS WAS ANSWERED, AND WE HAD A LOT OF EXAMPLES IN REAL LIFE → WHAT COULD HAPPEN AND HOW TO SOLVE THE PROBLEM.

24. Did you like the seating arrangements of the class room ?

[X] Yes [ ] No [ ] Uncertain

25. How do you rate the service (breaks, lunch, etc.) ?

[X] Excellent [ ] Very good [ ] Good [ ] Fair [ ] Poor

26. What is your overall evaluation of the course ?

[X] Excellent [ ] Very good [ ] Good [ ] Fair [ ] Poor

Thank you for taking the time to answer this questionnaire.
Your input is really valuable to us!

THANK YOU FOR INVITING US! :)

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Dear Participant,
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Participant's name: CAROL SUKHN

Participant's country: LEBANON

1. What is your overall reaction to the workshop?

[✓] Excellent [ ] Better than expected [ ] Satisfactory [ ] Poor

2. Do you feel that the workshop met your needs? *(If NOT, please explain)*

[✓] Yes [ ] To some extent [ ] Uncertain [ ] No

.....

.....

WORKSHOP CONTENT

12. What did you like best about the workshop course ? (strongest aspects)

latest determination of OCP + PCB in sediment and biota, remembrance of what I already knew and extra tips from here and there to conduct the procedure.

13. What did you like least about the workshop course ? (weakest aspects)

The hand outs were small in some instance we could not see much of some important slide, but I covered this by taking photos

14. What do you think should be dropped from this workshop course ?

No dropping

15. How do you rate the workshop length ?

[X] Just right [ ] Too short [ ] Too long

16. What's your opinion on the workshop content sequence ?

[X] Very well sequenced [ ] Suitable [ ] Poorly sequenced

17. How valuable was the workshop content to your current job ?

[X] Very valuable [ ] Some value [ ] No real value

18. How do you rate the balance of theoretical and practical sessions ?

[ ] Too theoretical [X] Good balance [ ] Too practical

19. Comments about the course contents :

I liked the overall structure. I would recommend to do the sampling in first week just in case weather gets bad in last weeks and sustains for few days. People then might miss out completely on a very important aspect of the training. I am grateful for invitation and for

hosting us, I will use the 8 hours of sampling Theoretical Dissection and outing in my observation of my international certificate of sampling. I felt so welcome and everybody was nice thank you all. for being such good host and for your courtesy I personally would like to be back for routine medical testing on ICCMS.

Suggestions: Lockers outside so we can put our stuff everyday

INSTRUCTIONAL MATERIAL

20. In your opinion, was the number of handouts you received sufficient ?

[✓] Just right [ ] Too few [ ] Too many

21. How do you rate the quality of the handout material ?

[ ] High quality [✓] Sufficient [ ] Below expectations

LABORATORY AND FACILITIES

22. How do you rate the laboratory sessions ?

[✓] Excellent [ ] Very good [ ] Good [ ] Fair [ ] Poor

23. Comments about laboratory sessions:

Well done, asked all the questions I wanted to ask, liked the discussion part

24. Did you like the seating arrangements of the class room ?

[✓] Yes [ ] No [ ] Uncertain

25. How do you rate the service (breaks, lunch, etc.) ?

[✓] Excellent [ ] Very good [ ] Good [ ] Fair [ ] Poor

26. What is your overall evaluation of the course ?

[✓] Excellent [ ] Very good [ ] Good [ ] Fair [ ] Poor

Thank you

Thank you for taking the time to answer this questionnaire.
Your input is really valuable to us!

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Participant's name: Nassima LAMBARKI EL ALLIOUI

Participant's country: MAROC

1. What is your overall reaction to the workshop?

[X] Excellent [ ] Better than expected [ ] Satisfactory [ ] Poor

2. Do you feel that the workshop met your needs? ***(If NOT, please explain)***

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

.....

.....

3. Do you feel that you will be better able to do your job after attending this course ?

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

4. Do you have a better attitude about your job thanks to this course ?

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

5. Would you recommend to others in your field to attend this course?

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

6. In your opinion, the number of participants in the workshop was:

[X] Just right [ ] Too few [ ] Too many

7. Do you think that similar workshops with other topics would be useful?

[X] Yes [ ] No

If YES, please recommend topics:

[X] Other pesticides [ ] Heavy metals [ ] Others *(specify)*... Organophosphate, HAP et les résidus de médicaments.

8. How do you rate the balance of lectures, group discussion, and group exercises ?

[ ] Too many lectures [ ] Too many discussions [ ] Good

9. How helpful were the group exercises ?

[ ] Very helpful [ ] Helpful [ ] Not helpful

10. What do you think of the speed of the course ?

[ ] Too fast [X] Just right [ ] Too slow

11. Did you have enough skills practice time ?

[X] Yes [ ] No [ ] Uncertain

WORKSHOP CONTENT

12. What did you like best about the workshop course ? (strongest aspects)

La qualité de la présentation des formateurs est bonne.
La compétence des formateurs qui est très excellente

13. What did you like least about the workshop course ? (weakest aspects)

R.A.S.

14. What do you think should be dropped from this workshop course ?

R.A.S.

15. How do you rate the workshop length ?

[X] Just right [ ] Too short [ ] Too long

16. What's your opinion on the workshop content sequence ?

[ ] Very well sequenced [X] Suitable [ ] Poorly sequenced

17. How valuable was the workshop content to your current job ?

[ ] Very valuable [X] Some value [ ] No real value

18. How do you rate the balance of theoretical and practical sessions ?

[ ] Too theoretical [X] Good balance [ ] Too practical

19. Comments about the course contents :

Le programme de cette formation a été bien étudié et préparé.
Il contient la partie théorique et expérimentale.
de la préparation des échantillons, Dosage et la
maintenance de l'équipement
Je souhaite que cette formation contient les séances
concernant LC/MS/MS

Ainsi je vous demande de m'envoyer les échantillons
inter comparaison avec un matériau de référence.

- je vous demande de former par groupe
~~francophone~~ qui parle en français (francophone)

Cette formation m'a permis d'acquérir de bonnes connaissances
concernant l'extraction du sédiment et bio-accumulation
le calcul des résultats.

- En conclusion, je tiens à remercier ~~les formateurs~~ l'ensemble
des formateurs pour leur accueil, assistance et effort
fournis durant la période de la formation.

INSTRUCTIONAL MATERIAL

20. In your opinion, was the number of handouts you received sufficient ?

[X] Just right [ ] Too few [ ] Too many

21. How do you rate the quality of the handout material ?

[X] High quality [ ] Sufficient [ ] Below expectations

LABORATORY AND FACILITIES

22. How do you rate the laboratory sessions ?

[ ] Excellent [X] Very good [ ] Good [ ] Fair [ ] Poor

23. Comments about laboratory sessions:

Les séances de laboratoire ont été effectuées dans de bonnes conditions. Elles ont été animées par du personnel qui a bien expliqué tout les étapes d'analyses des échantillons et toutes avant la maintenance du GC.

24. Did you like the seating arrangements of the class room ?

[X] Yes [ ] No [ ] Uncertain

25. How do you rate the service (breaks, lunch, etc.) ?

[ ] Excellent [ ] Very good [X] Good [ ] Fair [ ] Poor

26. What is your overall evaluation of the course ?

[X] Excellent [ ] Very good [ ] Good [ ] Fair [ ] Poor

Thank you for taking the time to answer this questionnaire.
Your input is really valuable to us!

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Dear Participant,
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This information will be very helpful in planning future courses. Please do not leave any question unanswered.

Participant's name: CHOUBA

Participant's country: TUNISIA

1. What is your overall reaction to the workshop?

[X] Excellent [ ] Better than expected [ ] Satisfactory [ ] Poor

2. Do you feel that the workshop met your needs? ***(If NOT, please explain)***

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

.....

.....

3. Do you feel that you will be better able to do your job after attending this course ?

[ ] Yes [X] To some extent [ ] Uncertain [ ] No

4. Do you have a better attitude about your job thanks to this course ?

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

5. Would you recommend to others in your field to attend this course?

[X] Yes [ ] To some extent [ ] Uncertain [ ] No

6. In your opinion, the number of participants in the workshop was:

[X] Just right [ ] Too few [ ] Too many

7. Do you think that similar workshops with other topics would be useful?

[X] Yes [ ] No

If YES, please recommend topics:

[X] Other pesticides [ ] Heavy metals [ ] Others *(specify)*..... Organophosphate HAP

8. How do you rate the balance of lectures, group discussion, and group exercises ?

[ ] Too many lectures [ ] Too many discussions [X] Good

9. How helpful were the group exercises ?

[X] Very helpful [ ] Helpful [ ] Not helpful

10. What do you think of the speed of the course ?

[ ] Too fast [X] Just right [ ] Too slow

11. Did you have enough skills practice time ?

[X] Yes [ ] No [ ] Uncertain

WORKSHOP CONTENT

12. What did you like best about the workshop course ? (strongest aspects)

Good competence of staff.

13. What did you like least about the workshop course ? (weakest aspects)

Better to have all presentation (powerpoint).

14. What do you think should be dropped from this workshop course ?

No things specially.

15. How do you rate the workshop length ?

[X] Just right [ ] Too short [ ] Too long

16. What's your opinion on the workshop content sequence ?

[ ] Very well sequenced [X] Suitable [ ] Poorly sequenced

17. How valuable was the workshop content to your current job ?

[ ] Very valuable [X] Some value [ ] No real value

Project: Sample.

18. How do you rate the balance of theoretical and practical sessions ?

[ ] Too theoretical [X] Good balance [ ] Too practical

19. Comments about the course contents :

1) Better to access for maintenance equipment

2) Use the same equipments in our laboratory if possible.

3) This periode is very difficult to found hotels etc...

4) Thank You for all Secretariat: Training course

INSTRUCTIONAL MATERIAL

20. In your opinion, was the number of handouts you received sufficient ?

[X] Just right [ ] Too few [ ] Too many

21. How do you rate the quality of the handout material ?

[ ] High quality [X] Sufficient [ ] Below expectations

LABORATORY AND FACILITIES

22. How do you rate the laboratory sessions ?

[X] Excellent [ ] Very good [ ] Good [ ] Fair [ ] Poor

23. Comments about laboratory sessions:

Thank you for all staff.

24. Did you like the seating arrangements of the class room ?

[X] Yes [ ] No [ ] Uncertain

25. How do you rate the service (breaks, lunch, etc.) ?

[ ] Excellent [X] Very good [ ] Good [ ] Fair [ ] Poor

26. What is your overall evaluation of the course ?

[X] Excellent [ ] Very good [ ] Good [ ] Fair [ ] Poor

Thank you for taking the time to answer this questionnaire.
Your input is really valuable to us!

11. Evaluation of participants' questionnaire

1. ***What is your overall reaction to the workshop?***

[100%] Excellent [] Better than expected [ ] Satisfactory [ ] Poor

2. ***Do you feel that the workshop met your needs? (If NOT, please explain)***

[83%] Yes [17%] To some extent [ ] Uncertain [ ] No

3. ***Do you feel that you will be better able to do your job after attending this course?***

[67%] Yes [33%] To some extent [ ] Uncertain [ ] No

4. ***Do you have a better attitude about your job thanks to this course?***

[67%] Yes [33%] To some extent [ ] Uncertain [ ] No

5. ***Would you recommend to others in your field to attend this course?***

[100%] Yes [ ] To some extent [ ] Uncertain [ ] No

6. ***In your opinion, the number of participants in the workshop was:***

[100%] Just right [ ] Too few [ ] Too many

7. ***Do you think that similar workshops with other topics would be useful?***

[100%] Yes [ ] No

If YES, please recommend topics:

[4] Other pesticides [2] Heavy metals [3] Others *(specify): PAH, BFRs*

8. ***How do you rate the balance of lectures, group discussion, and group exercises?***

[] Too many lectures [ ] Too many discussions [83%] Good

9. ***How helpful were the group exercises?***

[67%] Very helpful [17%] Helpful [ ] Not helpful

10. ***What do you think of the speed of the course?***

[17%] Too fast [83%] Just right [ ] Too slow

11. ***Did you have enough skills practice time?***

[66%] Yes [17%] No [17%] Uncertain

WORKSHOP CONTENT

15. How do you rate the workshop length?

[83%] Just right [17%] Too short [ ] Too long

16. What's your opinion on the workshop content sequence?

[33%] Very well sequenced [67%] Suitable [ ] Poorly sequenced

17. How valuable was the workshop content to your current job?

[50%] Very valuable [50%] Some value [ ] No real value

18. How do you rate the balance of theoretical and practical sessions?

[] Too theoretical [100%] Good balance [ ] Too practical

INSTRUCTIONAL MATERIAL

20. In your opinion, was the number of handouts you received sufficient?

[83%] Just right [17%] Too few [ ] Too many

21. How do you rate the quality of the handout material?

[67%] High quality [33%] Sufficient [ ] Below expectations

LABORATORY AND FACILITIES

22. How do you rate the laboratory sessions?

[67%] Excellent [33%] Very good [ ] Good [ ] Fair [ ] Poor

24. Did you like the seating arrangements of the class room?

[100%] Yes [ ] No [] Uncertain

25. How do you rate the service (breaks, lunch, etc.)?

[33%] Excellent [50%] Very Good [17%] Good [ ] Fair [ ] Poor

26. What is your overall evaluation of the course?

[83%] Excellent [17%] Very good [] Good [ ] Fair [ ] Poor

Note: Questions that required comments were not reported.