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Athens, Greece, 9 September 2019

Agenda Item 6: IMAP Pilot Info System and Related Quality Assurance Issues; Data Standards and Data Dictionaries; MAP Data Management Policy

Reports on Organization of 2017 and 2018 Proficiency Tests and Training Courses on Organic Compounds and Trace Elements

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Agenda item 4: Progress achieved regarding the implementation of the Programme of Work 2018-2019 related to land-based pollution and governance themes

Reports on organization of 2017 and 2018 proficiency tests and training courses on organic compounds and trace elements

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Meeting of the Ecosystem Approach Correspondence Group on Pollution Monitoring

Podgorica, Montenegro, 2-3 April 2019

Agenda Item 5: Marine Pollution Monitoring Regional Data Base and Related Quality Assurance Issues; Data Standards and Data Dictionaries

Reports on Organization of 2017 and 2018 Proficiency Tests and Training Courses on Organic Compounds and Trace Elements

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

IAEA
Atoms For Peace
Environment Laboratories

REPORT

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

January 2018

Prepared in collaboration with:

UNEP MAP MEDPOL

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1. INTRODUCTION

The primary goal of the International Atomic Energy Agency's Environment Laboratories (IAEA-NAEL) and in particular of the Marine Environmental Study Laboratory (MESL) is to help Member States understanding, monitoring and protecting the marine environment. Many laboratories are involved in the development and validation of new analytical methods, in investigations of the environmental impact of human activities, or are providing services to other organizations. As the scientific conclusions need to be based on valid and internationally comparable measurement results and to provide policy makers with correct information on the state of the environment, it is indispensable to ensure the good quality of measurement results, produced by each laboratory.

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 inter-laboratory comparisons (ILCs) and targeted proficiency tests (PTs) on matrices of relevance to the marine monitoring studies.

In order to assure reliability of analytical data for monitoring studies, one essential aspect of quality assurance and quality control is the periodic external assessments of measurement performance via interlaboratory comparisons (ILCs) and proficiency tests (PTs). The participation in the ILCs and/or PT's is important not only for checking the accuracy of laboratory's analytical results, but also for the evaluation of its analytical performance.

This report describes the results of the PT on the determination of selected trace elements in marine sediment sample organised by the MESL in 2017 for the designated MED POL monitoring laboratories.

The IAEA officers responsible for this publication are S. Azemard, E. Vasileva and A. Trinkl.

2. SCOPE OF EXERCISE

In September 2017 the 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 September 2017.

The test material, named ***IAEA-MESL-2017-01-TE*** sample, was sent to 38 designated laboratories from 15 countries beginning of October 2017. Figure 1 shows the distribution of PT sediment samples in MED POL countries.

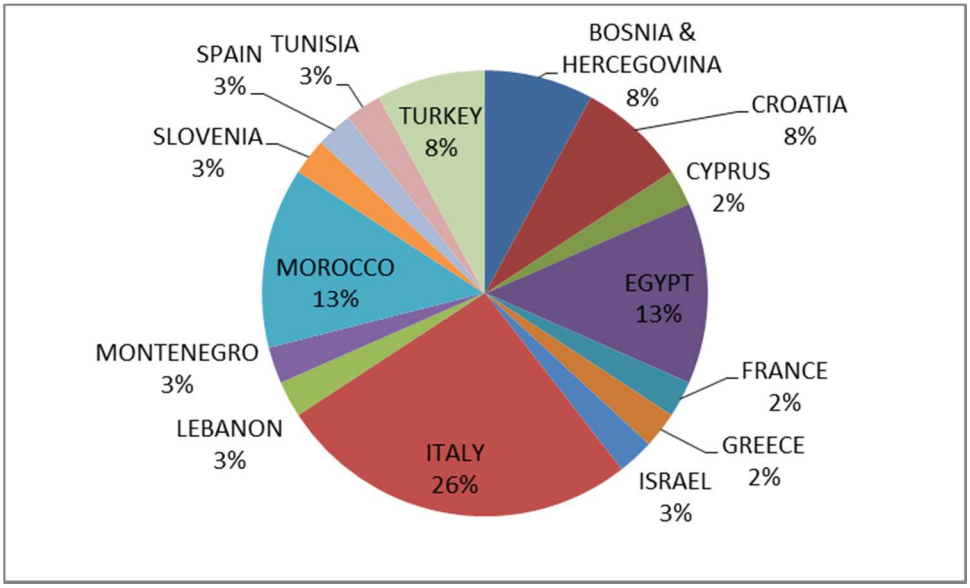


FIG. 1. Distribution per country of the MED POL PT sediment sample

Participants were requested to determine as many trace elements as possible from the following list: Al, As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Pb, Sr, V and Zn, using the measurement procedures, they usually apply for MED POL monitoring studies.

The deadline for reporting the results back to the MESL was originally set to 11 of December 2017. Finally, 22 from 38 (58%) test laboratories designated for participation in this proficiency sent their results by the requested deadlines.

Laboratories participating in the present exercise are listed in the Annex 1. Designated MED POL laboratories which did not report the results are listed in the Annex 2.

3. MATERIAL

The sediment used for the preparation of the IAEA-MESL-2017-01-TE sample was collected, freeze dried, sieved first at 1mm, ball milled and sieved again at 70µm. After homogenization of the sample, subsamples of around 4g were packed in polyethylene containers.

The initially performed tests for distribution of reported results showed bimodality for Al, Cr, Mn, Pb and V, linked to the sample preparation mode (addition or not of HF acid for total digestion of silicates, present in the sediment sample). Only results obtained after applying sample digestion procedure, including addition of HF or XRF instrumental method were retained for the calculation of the robust mean.

Homogeneity tests (within bottles and between bottles) for the IAEA-MESL-2017-01-TE sample were performed at MESL, using preliminary validated analytical method.

The assigned values and their associated uncertainties, presented in Table 1, were calculated according to the requirements of the ISO 35 guidelines [1]. Assigned values were set as the robust mean of the results, obtained by participants and MESL [2]. Expanded uncertainties were calculated according to the equation 1 [2].

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

where:

k: coverage factor equal to 2, representing a level of confidence of about 95%

u_{hom} is the standard uncertainty due to between units inhomogeneity.

u_{stab} is the standard uncertainty due to long-term stability of the sample. As the PT sample was prepared more than 10 years ago, u_{stab} component was considered to have negligible contribution and was not further propagated during the estimation of the total combined uncertainty.

u_{char} is the uncertainty related with characterisation estimated as described in ISO 13528 [2] using the equation 2:

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

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

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	20.0×10^3	2.7×10^3
As	6.79	1.10
Cd	0.141	0.015
Co	4.17	0.50
Cr	35.9	4.4
Cu	10.4	1.6
Fe	18.9×10^3	2.6×10^3
Hg	0.034	0.004
Mn	222	28
Pb	11.3	1.3
Sr	68.1	12.4
V	39.3	6.9
Zn	44.8	7.0

4. EVALUATION OF RESULTS

4.1. Evaluation criteria:

Individual laboratory performance is expressed as z and Zeta scores as recommended in the ISO guide 13528 [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 evaluated according to the following generally accepted limits:

	$\lvert z \text{ or Zeta} \rvert \leq 2$	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 laboratories. 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 measurants.

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.

4.2. Overview of the reported measurement results

22 laboratories provided results for the analysis of the PT sample by the final deadline, comprising 207 analytical results. Graphical presentations of z-score and Zeta-scores are presented in the Annex 3 with a summary of the statistical evaluation of reported results for the respective trace element. Kernel density plots (if more than 8 reported measurement results) [3] are also presented in the Annex 3.

All reported measurement results are compiled in the Annex 4. Some of them have been rounded to the appropriate number of significant figures.

4.3. Laboratory results and scoring:

4.3.1 *z*-scores

The measurement performance of participating laboratories was assessed by *z*-scores. A total 207 *z*-scores were calculated. Overall 73% of reported measurement results were assessed as satisfactory, 12% as questionable and 15% as unacceptable. From 22 participating laboratories, 6 laboratories (27%) reported 100% of their measurement results with $|z| \leq 3$. 4 laboratories (18%) were able to report 100% of their measurement results with $|z| \leq 2$. On the other hand, 3 laboratories (14%) reported more than 40% of the unsatisfactory results. This fact is probably reflecting the existing unresolved analytical problems in those laboratories.

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.

The reported Al, Cr, Mn, Pb and V biases are most probably linked to the protocol for the sample preparation and the lack of complete digestion. As a result almost all unsatisfactory *z*-scores, obtained for the refractory elements (Al, Cr, Mn, Pb and V) were negative, and in addition bimodality was observed on the kernel density plot.

4.3.2 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 its measurement uncertainty, or by both.

About 58% of measurement results were reported with uncertainties. Zeta-scores were calculated for 12 of participating laboratories (54%), 10 laboratories didn't report measurement uncertainties.

65% of the calculated Zeta-scores are considered as satisfactory. This result is comparable with the results obtained from the MED POL PT exercise from the previous year. Only 2 laboratories could report 100% of their results with Zeta-scores below 2. 3 participating laboratories received satisfactory Zeta-score for less than 50% of reported results. Obtained results show that there are still remaining problems with the realistic estimation of the combined measurement uncertainty.

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.

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.

TABLE 2: ALL CALCULATED z-SCORES. Grey fields 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	Sr	V	Zn
2	0.52	3.09	-0.07	0.23	-0.57	0.04	0.12		0.35	-0.52			-0.18
5			0.65	-1.66		-0.01	-1.00	0.96	-4.25	**-2.36**			-1.40
6	-3.60	-0.84	-0.39	0.19	0.07	0.51	-0.15	-0.15	-1.28	**-2.28**		-1.11	1.83
8	-0.65	6.03	0.23	1.09	1.76	1.36	1.58	0.60	0.75	0.31	-1.70	-0.81	1.04
11	0.60	-0.21	0.38		0.44	-0.26	0.44	0.60	-0.91	-0.66			-1.47
12	1.34	0.57	3.80	**2.03**	1.28	**-2.07**	1.09	**-2.95**	0.82	0.02	0.54	1.42	-0.12
14								-0.73					
19	-1.73				0.33	7.56	-1.75		-0.25				1.01
20							9.24	-0.35	-0.26				-0.38
22	-0.49	-1.26	3.48	**-2.70**	-4.52	-1.00	0.14	4.39	-3.59	0.01		**-2.20**	-0.77
24			-0.88					-0.66		0.38			
26		-0.18	-0.26	0.64	-3.69	**-2.22**		-1.29		-3.36		-3.66	**-2.35**
27	-3.93	-1.23	-0.26	-0.58	**-2.43**	0.05	**-2.63**		-1.04	**-2.47**		**-2.77**	0.26
28			-0.30		-0.42	**2.02**	0.31	3.36	0.22	-0.36			-0.17
30	-5.81	-1.06	-3.09	-1.11	-3.09	-0.80	-1.57	0.68	-3.53	-1.58		-3.96	1.96
32		-1.42	-0.26	-0.29	**-2.64**	-0.33	-0.65	-0.86	**-2.77**	**-2.01**		**-2.99**	-0.92
34	0.08	**2.85**		0.32	-0.59	-3.53	-8.00		-1.17	-0.17	-0.49	-0.36	-0.90
35	**-2.93**	-1.48	0.12	-0.59	-1.58	-1.03	0.24	1.63	-1.30	**-2.73**		-1.25	**-2.25**
36	0.65		-0.39	0.13	-0.15	-0.65	0.23	-0.74	0.26	0.80		0.65	-0.11
37	-1.51	26.86	337.35	0.13	0.43	-0.01	**2.90**	29.32	**2.77**	8.23	3.42	0.88	4.96
38	0.21	-0.34	0.18	0.49	-0.17	8.39	-0.07	-1.86	-0.07	-0.65		-0.07	**2.48**
39					1.47	36.23	0.36		-1.39	30.61			

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

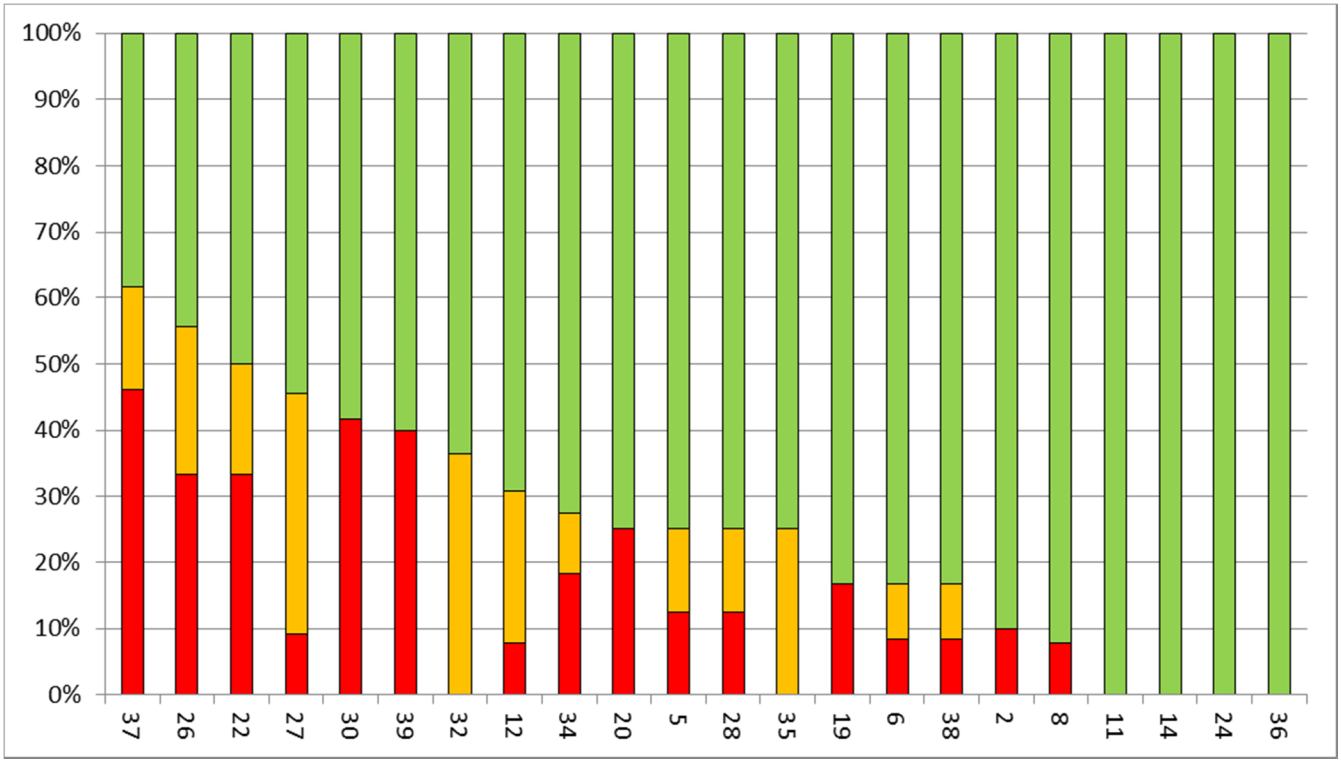
Laboratory Code	Al	As	Cd	Co	Cr	Cu	Fe	Hg	Mn	Pb	Sr	V	Zn
2													
5													
6													
8	-1.20	**2.26**	0.53	1.77	3.42	**2.19**	**2.63**	1.24	1.33	0.67	-1.96	-0.87	1.61
11	1.06	-0.26	0.78		0.85	-0.38	0.80	0.89	-1.61	-1.38			**-2.32**
12	**2.02**	0.71	4.45	**2.66**	1.89	**-2.95**	1.62	-3.45	1.15	0.04	0.66	1.73	-0.16
14													
19													
20													
22													
24			-0.83					-1.09		0.34			
26													
27	-5.79	-1.30	-0.29	-0.65	-3.27	0.05	-3.45		-1.22	-3.43		-3.15	0.25
28			-0.31		-0.69	**2.61**	0.51	3.17	0.37	-0.55			-0.23
30	-10.39	-1.38	**-2.55**	**-2.05**	-5.18	-0.44	**-2.55**	0.14	-6.73	-1.95		-5.48	3.06
32		-1.62	-0.32	-0.39	-3.55	-0.38	-0.81	-1.00	-4.33	**-2.84**		-3.59	-1.03
34	0.09	1.65		0.04	-1.03	-3.70	-14.72		**-2.33**	-0.03	-0.67	-0.45	-1.35
35	-5.26	**-2.20**	0.17	-1.13	-3.04	-1.58	0.20	1.27	**-2.46**	-5.19		-1.73	-3.12
36	0.46		-0.55	0.17	-0.12	-0.79	0.17	-0.58	0.32	0.49		0.68	-0.12
37													
38													
39					**2.17**	15.61	0.04		**-2.30**	15.53			

TABLE 4: SUMMARY OF OBTAINED z-SCORES PER LABORATORY

Laboratory Code	Number of results	$\lvert z \rvert \geq 3$	$2 < \lvert z \rvert < 3$	$\lvert z \rvert \leq 2$
2	10	10.0%	0.0%	90.0%
5	8	12.5%	12.5%	75.0%
6	12	8.3%	8.3%	83.3%
8	13	7.7%	0.0%	92.3%
11	10	0.0%	0.0%	100.0%
12	13	7.7%	23.1%	69.2%
14	1	0.0%	0.0%	100.0%
19	6	16.7%	0.0%	83.3%
20	4	25.0%	0.0%	75.0%
22	12	33.3%	16.7%	50.0%
24	3	0.0%	0.0%	100.0%
26	9	33.3%	22.2%	44.4%
27	11	9.1%	36.4%	54.5%
28	8	12.5%	12.5%	75.0%
30	12	41.7%	0.0%	58.3%
32	11	0.0%	36.4%	63.6%
34	11	18.2%	9.1%	72.7%
35	12	0.0%	25.0%	75.0%
36	11	0.0%	0.0%	100.0%
37	13	46.2%	15.4%	38.5%
38	12	8.3%	8.3%	83.3%
39	5	40.0%	0.0%	60.0%

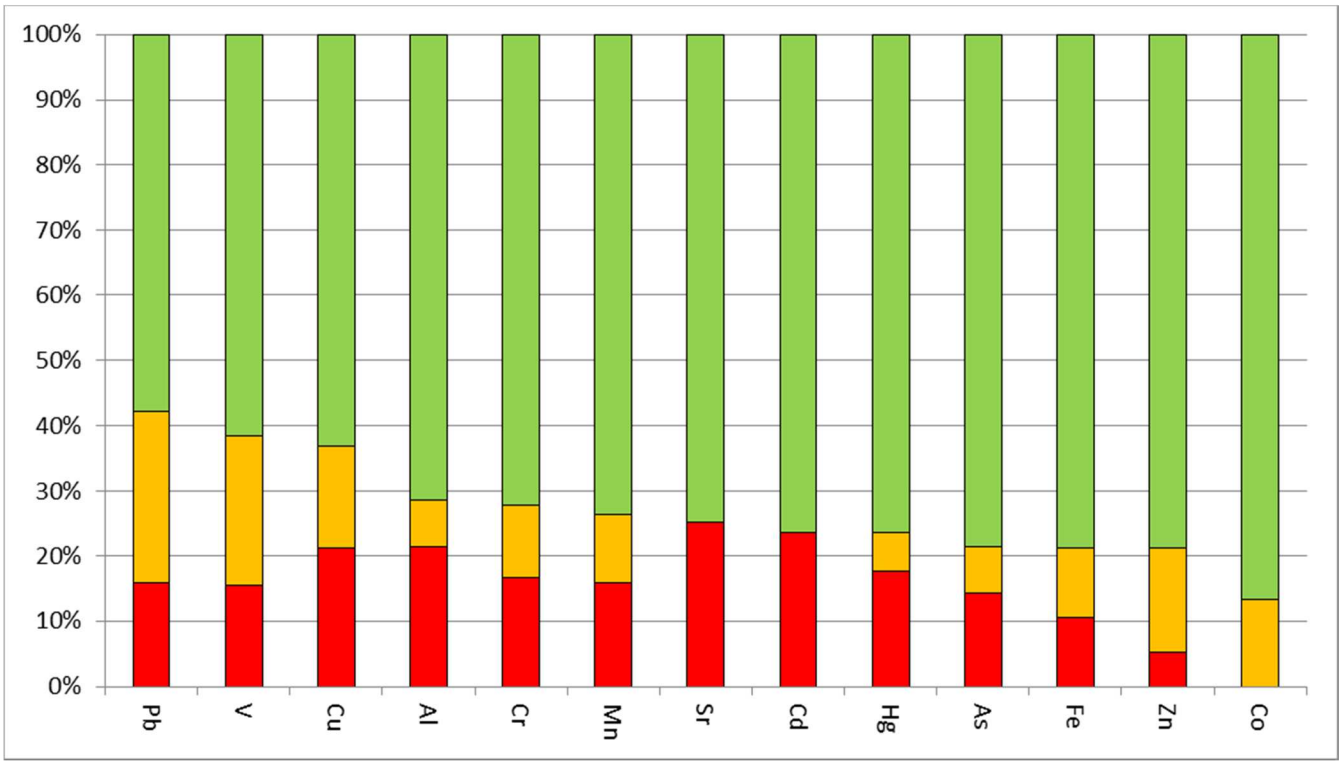
TABLE 5: SUMMARY OF OBTAINED z-SCORES PER ELEMENT

Element	Participation	$\lvert z \rvert \geq 3$	$2 < \lvert z \rvert < 3$	$\lvert z \rvert \leq 2$
Al	64%	21%	7%	71%
As	64%	14%	7%	79%
Cd	77%	24%	0%	76%
Co	68%	0%	13%	87%
Cr	82%	17%	11%	72%
Cu	86%	21%	16%	63%
Fe	86%	11%	11%	79%
Hg	77%	18%	6%	76%
Mn	86%	16%	11%	74%
Pb	86%	16%	26%	58%
Sr	18%	25%	0%	75%
V	59%	15%	23%	62%
Zn	86%	5%	16%	79%



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

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



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

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
2	0			
5	0			
6	0			
8	13	8%	23%	69%
11	10	0%	10%	90%
12	13	15%	23%	62%
14	0			
19	0			
20	0			
22	0			
24	3	0%	0%	100%
26	0			
27	11	45%	0%	55%
28	8	13%	13%	75%
30	12	42%	25%	33%
32	11	27%	9%	64%
34	11	18%	9%	73%
35	12	33%	17%	50%
36	11	0%	0%	100%
37	0			
38	0			
39	5	40%	40%	20%

TABLE 7: SUMMARY OF OBTAINED ZETA-SCORE PER ELEMENT

Element	Participation	|Zeta| ≥3	2< |Zeta| <3	|Zeta| ≤2
Al	36%	38%	13%	50%
As	36%	0%	25%	75%
Cd	45%	10%	10%	80%
Co	36%	0%	25%	75%
Cr	50%	45%	9%	45%
Cu	50%	18%	27%	55%
Fe	50%	18%	18%	64%
Hg	41%	22%	0%	78%
Mn	50%	18%	27%	55%
Pb	55%	25%	8%	67%
Sr	14%	0%	0%	100%
V	36%	38%	0%	63%
Zn	45%	20%	10%	70%

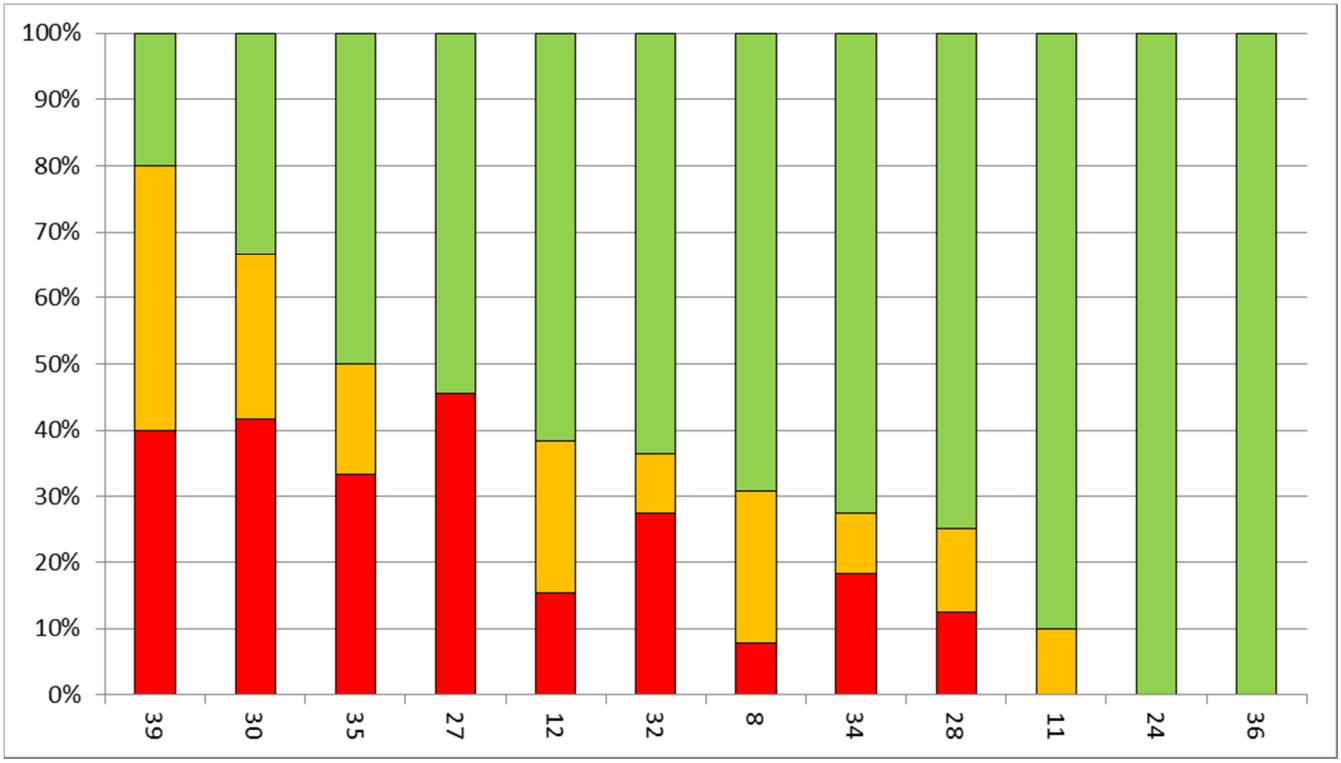


FIG. 4. Summary of obtained Zeta-scores per participants

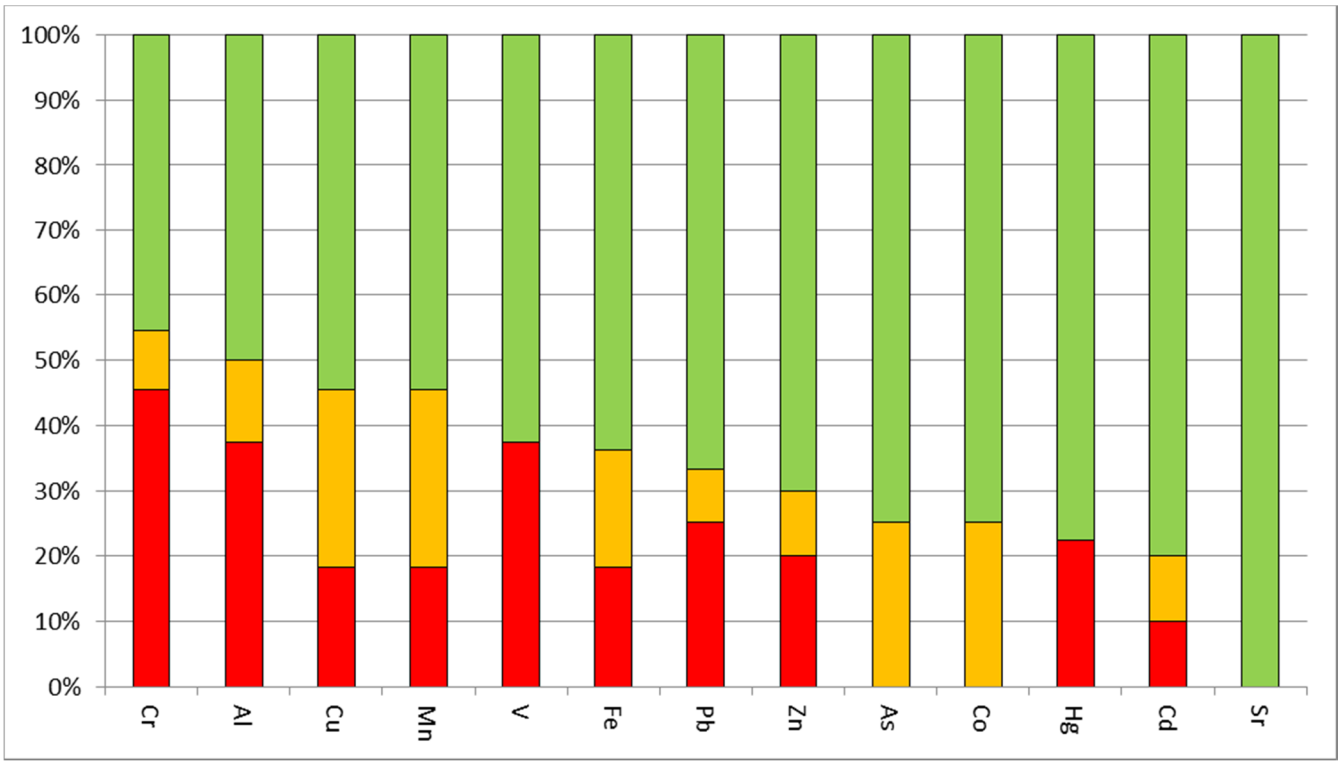


FIG. 5. Summary of obtained Zeta-scores per element

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

Hydrofluoric acid is required for decomposition of the silicate lattice of a sediment matrix. Without 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, Mn, Pb, V and Sr (Figure 3 and Annex 3). Only 13 laboratories participating in the MED POL PT used HF in their sample preparation step or have applied XRF detection technique.

Freeze drying step is a part of sample processing procedure of PT sediment 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 marine sediment 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 protocol for moisture determination. Only 3 participating laboratories have respected it, other participants have applied their in-house developed method (dry oven at 105°C).

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. With exception of 4 participants, using non matrix matching CRMs (mussel, water, soil), all others have used CRMs with similar matrix composition or sediment samples from the previous MED POL PTs.

Out of the 31 data sets received, only 2 laboratories didn't include quality control (QC) results in the reporting form, which is one noticeable improvement.

10 participating laboratories (45%) implemented correction for recovery for all, or part of reported measurement results. Most of the participants have calculated recovery rates by using CRMs. 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 methods were not significantly different from 100%.

4.5. 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 (63% of reported data), followed by AAS (22%) and ICP-OES (6%).

TABLE 8: INSTRUMENTAL TECHNIQUES ABBREVIATIONS

Method Code	Instrumental Technique
AAS	Atomic Absorption 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
Hyd	Hydride Generation

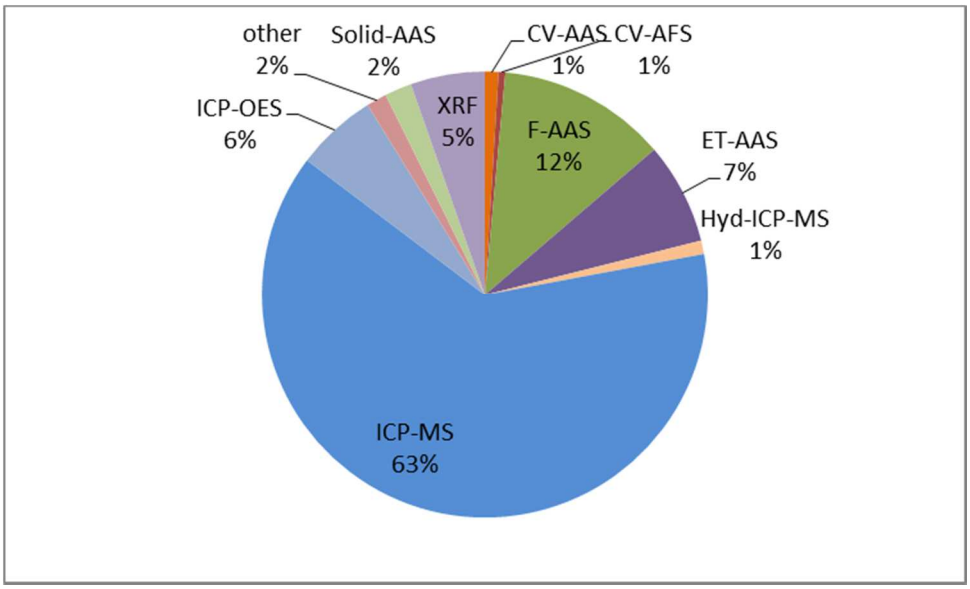


FIG. 6. Graphical distribution of instrumental techniques, applied in the present PT

4.6. Answer to the provided questionnaire:

6 laboratories claimed to be accredited, however 2 of them didn't report measurement uncertainties, which should be part of the measurement result, provided by an accredited laboratory. In total 12 participating laboratories (54%) reported results for the estimated combined uncertainty, and 11 of them (91%) provide uncertainty as a routine practice. Different approaches were used to estimate measurement uncertainties; 5 participants applied single validation approach, 4 laboratories used modelling approach, and 2 were reporting measurement uncertainties, obtained via their participation in the relevant ILC's. 3 of participating MED POL laboratories reported the standard deviation of analised replicates instead of combined uncertainties, which is leading to serious underestimation of combined measurement uncertainty.

10 laboratories applied preliminary validated methods, while only 11 participants declared to have quality system in place.

4 participants did not explain how they have assured the traceability of obtained results, although some of them declared to be accredited, and to have a quality system in place.

5. 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 of produced in the respective laboratory results.

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 reoccurring. This is one of the requirements for laboratories accredited according to the ISO/IEC 17025 standard.

Many laboratories didn't use hydrofluoric acid in the sample preparation step and could not achieve total digestion. As a consequence, only 64% of participants have provided satisfactory results for Al and other refractory elements. In the cases of monitoring studies, when the evaluation of the anthropogenic contributions is requested, Al is often used for the "normalisation" of the natural trace element content variability and for the accounting of grain size effects corrections for different sediment samples [4]. Therefore the accurate determination of Al is with particular importance for the pollution monitoring studies.

10 out of 22 laboratories are correcting all, or one part of their results for recovery rates. All of them are using CRM for calculation of recovery. 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.

Only two 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.

Some participants didn't apply the prescribed protocol for moisture content correction and as the moisture is operationally dependent parameter, they obtained biased measurement results.

Uncertainty of measurement results in the MED POL PT exercise was calculated from approximately half part 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 and further training on uncertainty of measurement results is highly desirable.

16 (42%) from 38 designated by the MED POL laboratories didn't send the requested in the frame of MED POL Proficiency Test results, which make the evaluation of their measurement performance impossible. Samples send to Egypt were apparently retained in customs and could not be claimed and distributed in time by the national focal point representative.

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 *13528 (2005), Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons, ISO, Geneva, Switzerland..*

[3] 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.

[4] INTERNATIONAL ATOMIC ENERGY AGENCY, Manual for geochemical analyses of sediment and suspended particulate matter. Reference method 63, UNEP/FAO/IOC (1995).

Annex 1: List of MEDPOL designated participants that sent results

CROATIA

Grozdan KUSPILIC	Institute Oceanography & Fisheries Laboratory of Chemical Oceanography and Sedimentology Setaliste Ivana Mestrovica 63 HR-21000 Split
Silvana MLADINOV	County of Istria Public Health Institute Dept for Health Ecology Vladimir Nazora 23 HR-52100 Pula
Paula ZURGA	Teaching Public Health Institute Dept for Health Ecology Kresimirova 52a HR-51000 Rijeka

FRANCE

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

GREECE

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ISRAEL

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ARPAB Basillicata
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Guido SPINELLI

ARPA Toscana
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LLC Center for ecotoxicological research-
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81000 Podgorica

MOROCCO

M. BENAMMI

Lab. De Recherche et d'Analyses Techniques et Scientifiques de la Gendarmerie Royale
Résidence de la Gendarmerie Royale
Temara
Rabat

F Zohra BOUTHIR

Institut National de Recherche Halieutique (INRH)
Laboratoire de Chimie
Dept. QSMM
Bd Sidi Abderhmanne
20030 Casablanca

Lalla KHADIJA GHEDDA	Office National de l'Electricité et de l'Eau – Branche Eau Avenue Mohamed Belhassan El Ouazzani Station de traitement Direction Contrôle Qualité des Eaux 10220 Rabat

SLOVENIA

Urska CERVEK	National Lab. For Health, Environment and Food Prvomajska Ulica 1 2000 Maribor

SPAIN

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

TUNISIA

Lassâad CHOUBA	INSTM, Departement Pollution Laboratoire Milieu Marin Métaux Traces, Pesticides et Hydrocarbures Port de Peche La Goulette 2060 LA GOULETTE

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Hakan ATABAY

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41470 Gebze-Kocaeli

Süleyman TUGRUL

METU-Institute of Marine Sciences
ODTU Deniz Bilimleri Enstitusu
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Annex 2: List of MEDPOL designated particpants that did not send results

BOSNIA & HERCEGOVINA

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Slađana ŠARAC	Institute for public health FB&H Department of Environmental Health Vukovarska 46, 88000 Mostar
Nezafeta SEJDIC	Sava River Watershed Agency Water quality Laboratory ul. Hamdije Ćemerlića 39a 71000 Sarajevo

CYPRUS

Stelios GIANNOPOULOS	State General Laboratory 44 Kimonos Str. 1451 Nicosia

EGYPT

Mai AHMED	CCC lab. (EEAA) 30 Misr Helwan El-Zyrae Road Maadi PO Box 11728 Cairo
Mohamed Gamal EL-DEIN HASANEIN	Tanta Lab. (EEAA)

Rehab EL-NOUBY	Mansoura Lab. (EEAA)
Samir NASR	Institute for Graduate studies and Research Alexandria University 163 Horriya Ave, Shatby Alexandria
Sameh REYAD	Alexandria Lab. (EEAA)

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Alessandro PEDEMONTE,	ARPA Liguria Laboratorio di Genova Via Bombrini 8 IT-16149 Genova

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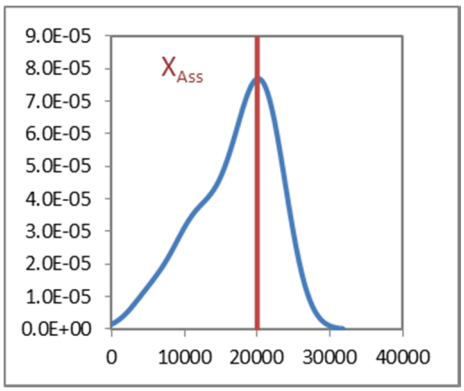
Madinat El Irfane
Rabat

Annex 3: Graphical representation

Reported data for Al in the IAEA-MESL-2017-01-TE

Kernel density Plot



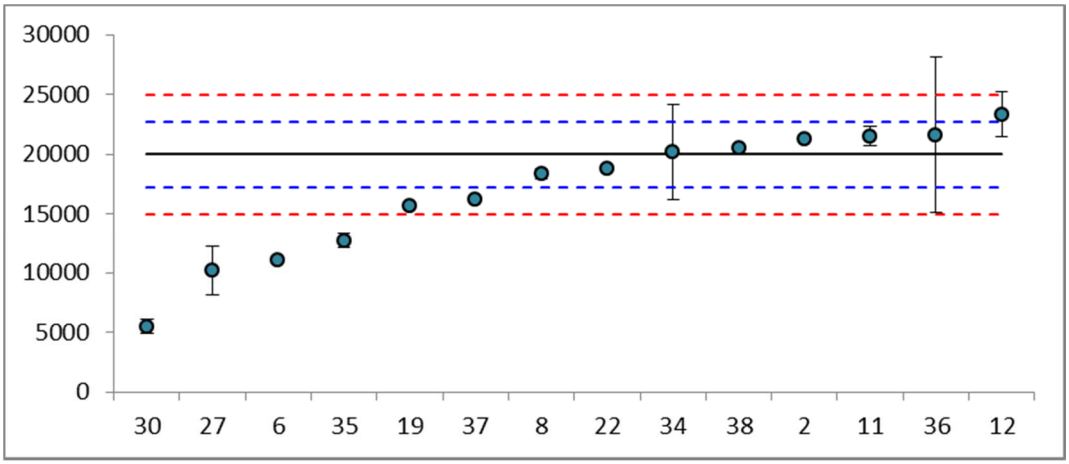
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	71%	21%	7%
Zeta-score	50%	13%	38%

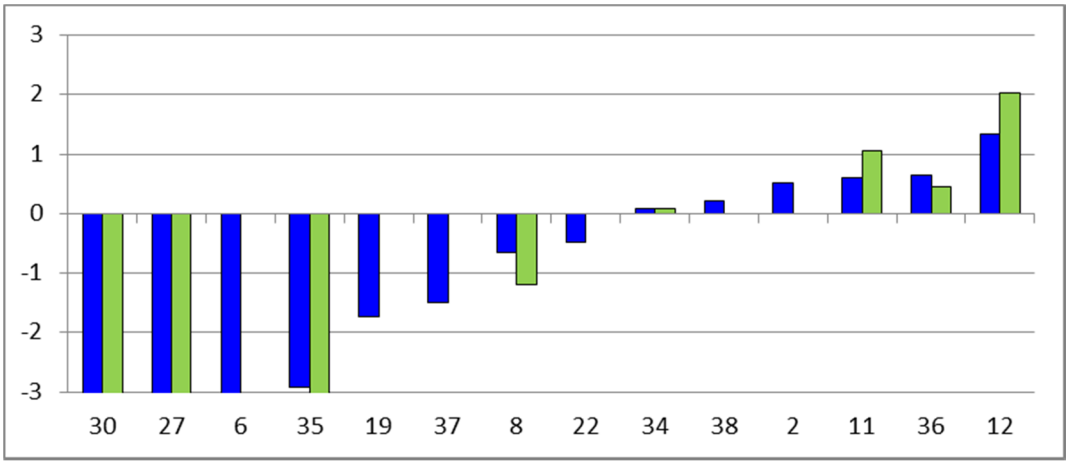
X_{Ass} mg kg^{-1}	20.0×10^3
U_{Ass} (k=2) mg kg^{-1}	2.7×10^3
$2\sigma_p$ mg kg^{-1}	5.0
Number of results:	14
Number of method:	5

Reported results and expanded uncertainties:

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

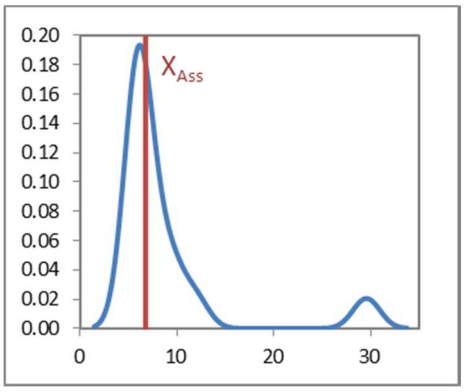


Performance evaluation: *z*-score Zeta-score



Reported data for As in the IAEA-MESL-2017-01-TE

Kernel density Plot



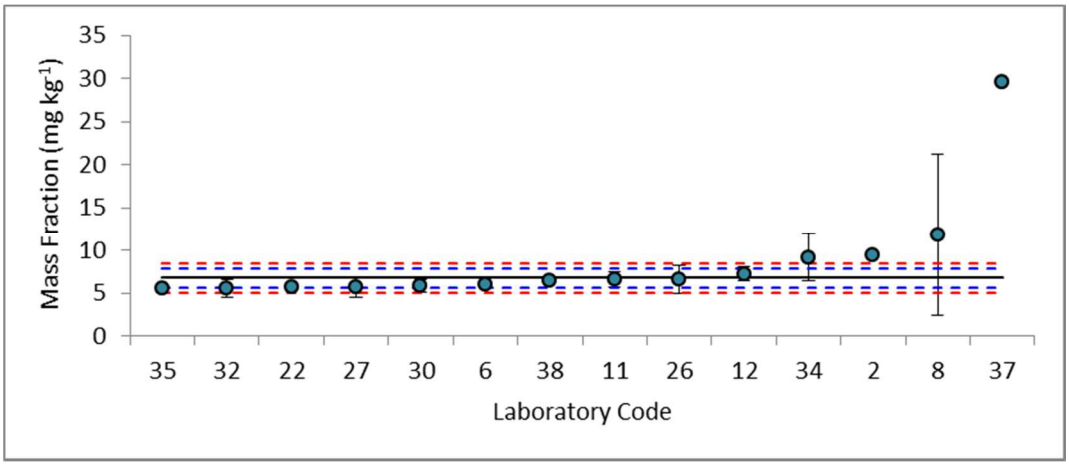
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	79%	7%	14%
Zeta-score	75%	25%	0%

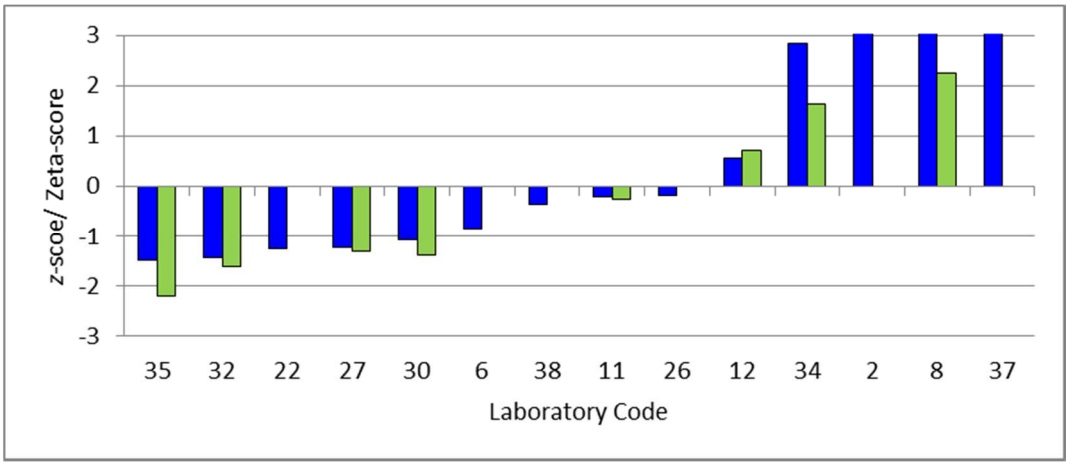
X_{Ass} mg kg^{-1}	6.79
U_{Ass} (k=2) mg kg^{-1}	1.10
$2\sigma_p$ mg kg^{-1}	1.70
Number of results:	14
Number of method:	5

Reported results and expanded uncertainties:

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

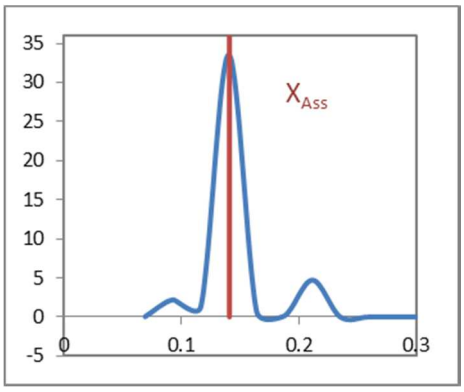


Performance evaluation: *z*-score Zeta-score



Reported data for Cd in the IAEA-MESL-2017-01-TE

Kernel density Plot



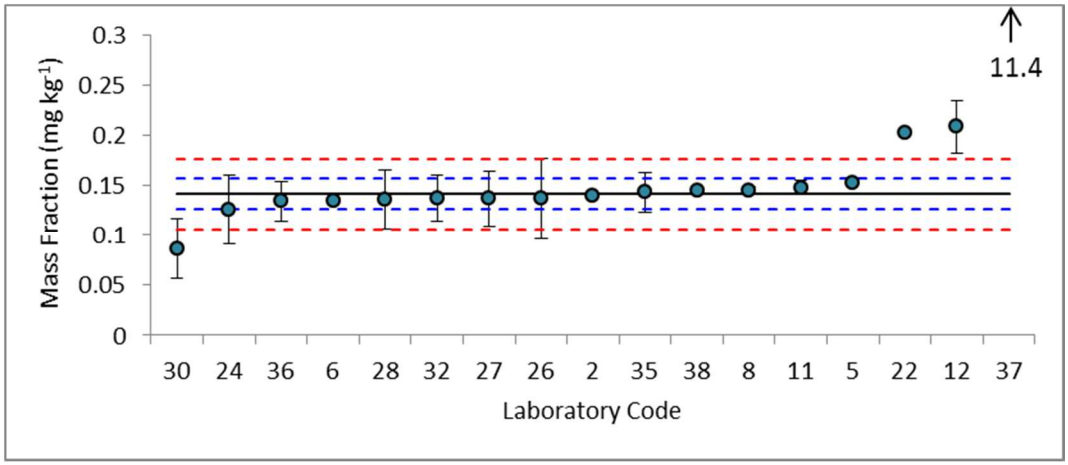
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	76%	0%	24%
Zeta-score	80%	10%	10%

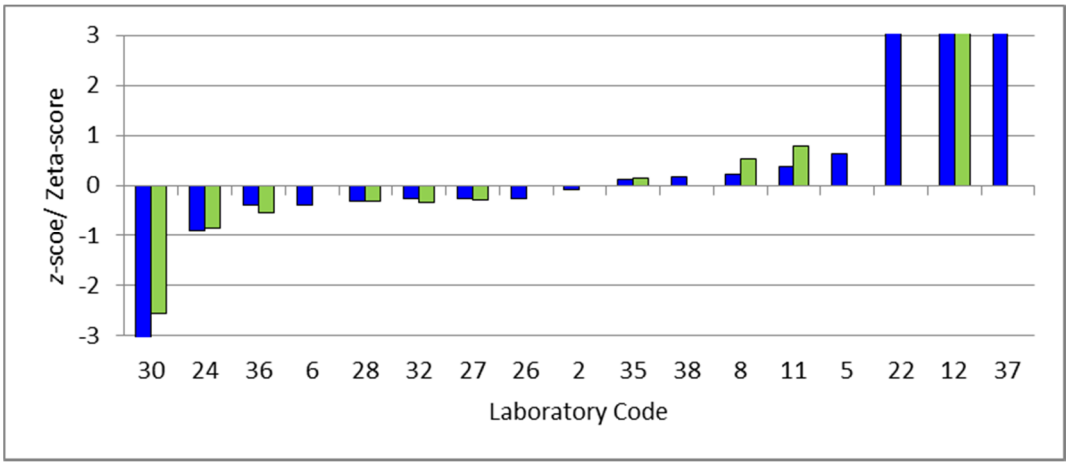
X_{Ass} mg kg^{-1}	0.141
U_{Ass} (k=2) mg kg^{-1}	0.015
$2\sigma_p$ mg kg^{-1}	0.035
Number of results:	17
Number of method:	3

Reported results and expanded uncertainties:

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

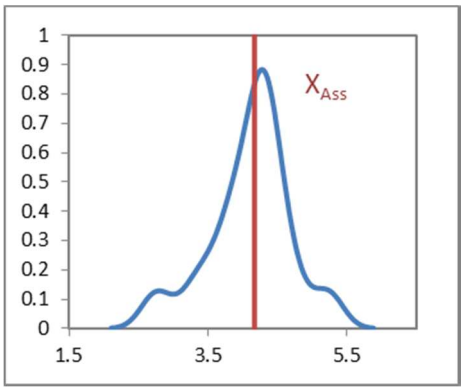


Performance evaluation: *z*-score Zeta-score



Reported data for Co in the IAEA-MESL-2017-01-TE

Kernel density Plot



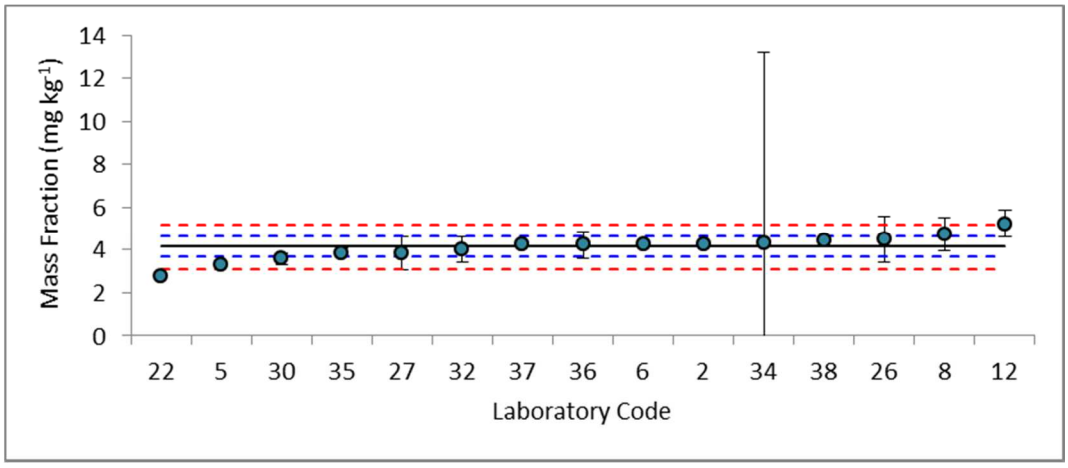
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	87%	13%	0%
Zeta-score	75%	25%	0%

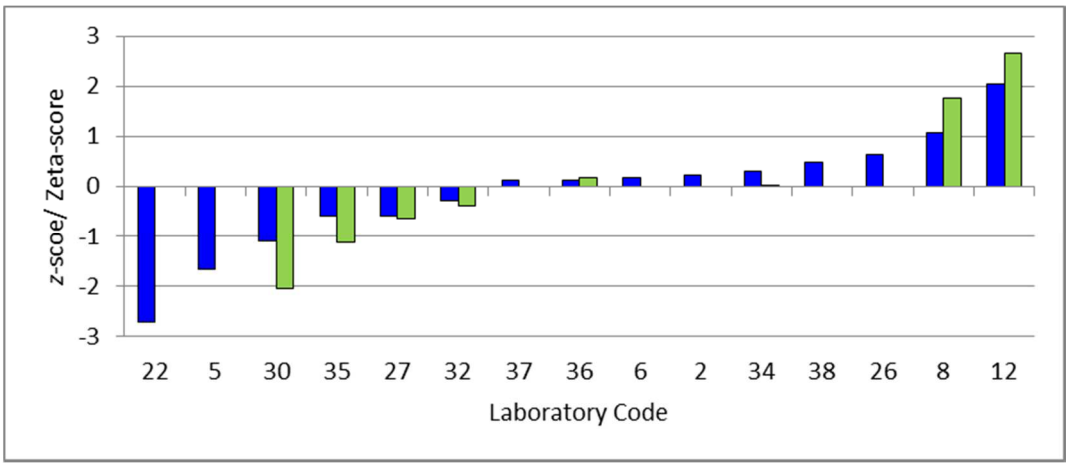
X_{Ass} mg kg^{-1}	4.17
U_{Ass} (k=2) mg kg^{-1}	0.50
$2\sigma_p$ mg kg^{-1}	1.01
Number of results:	15
Number of method:	5

Reported results and expanded uncertainties:

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

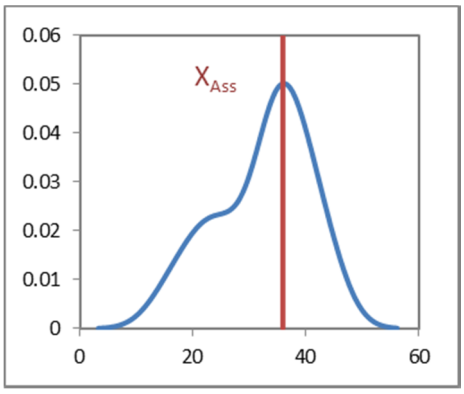


Performance evaluation: *z*-score Zeta-score



Reported data for Cr in the IAEA-MESL-2017-01-TE

Kernel density Plot



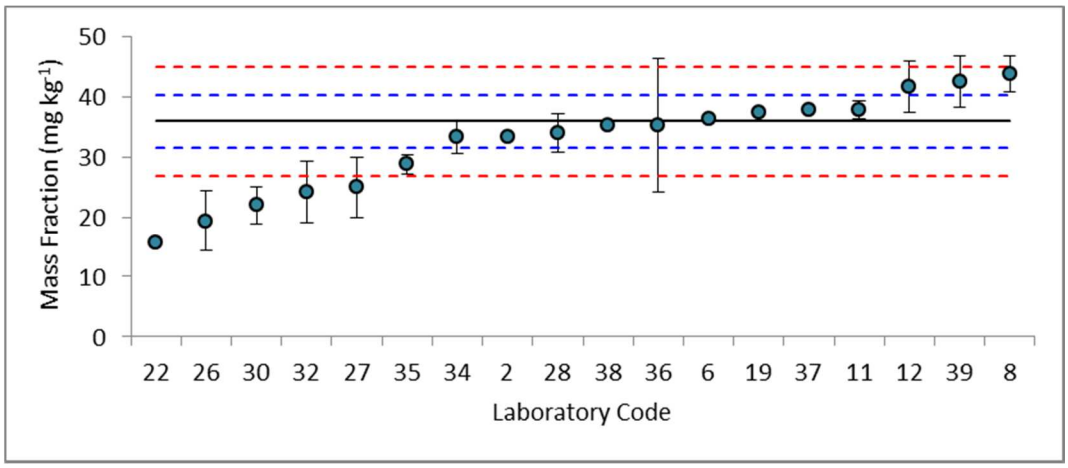
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	72%	11%	17%
Zeta-score	45%	9%	45%

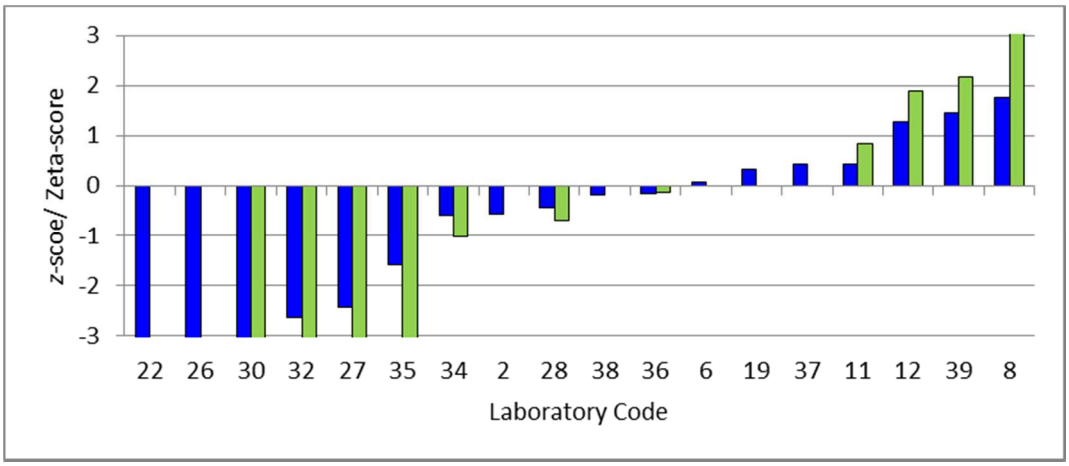
X_{Ass} mg kg^{-1}	35.9
U_{Ass} (k=2) mg kg^{-1}	4.4
$2\sigma_p$ mg kg^{-1}	9.0
Number of results:	18
Number of method:	5

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)

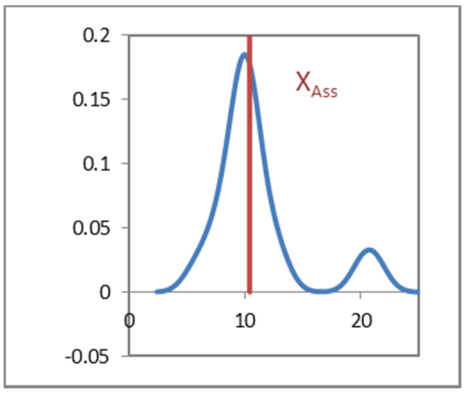


Performance evaluation: *z*-score Zeta-score



Reported data for Cu in the IAEA-MESL-2017-01-TE

Kernel density Plot



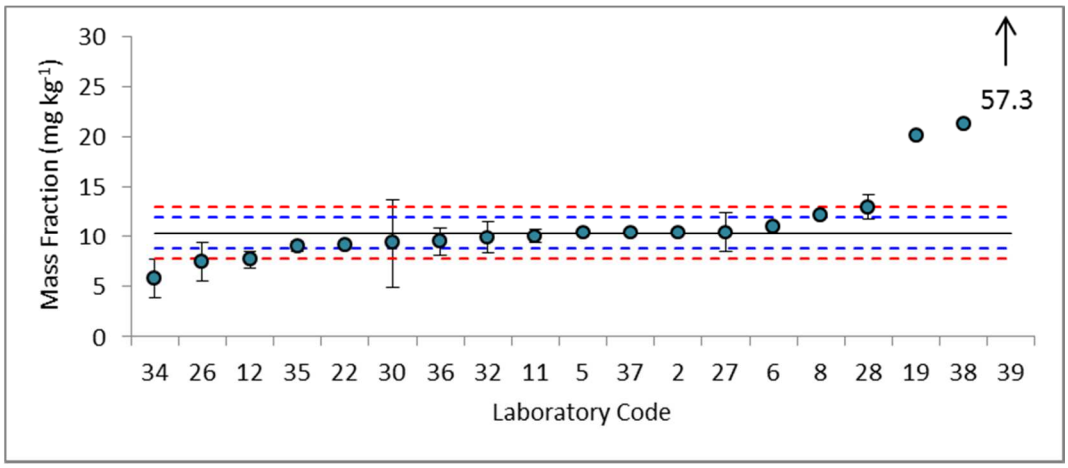
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	63%	16%	21%
Zeta-score	55%	27%	18%

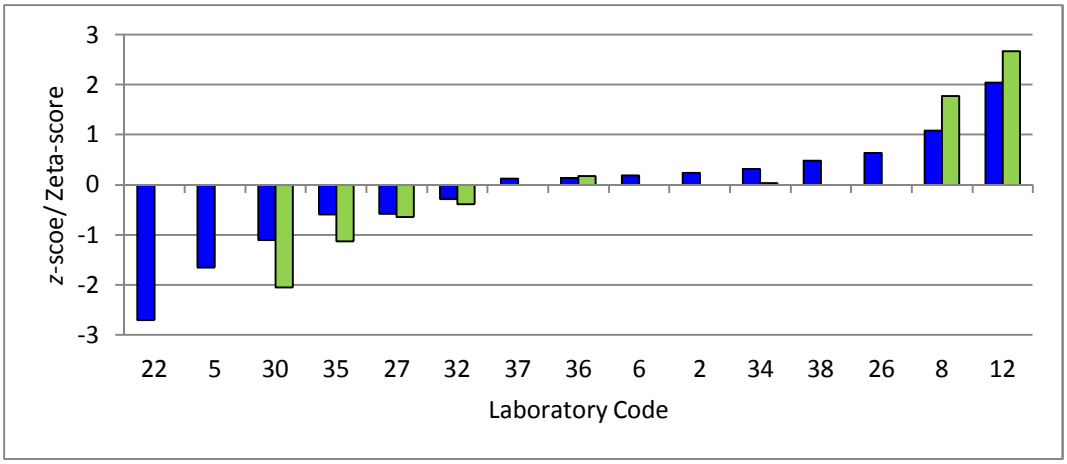
X_{Ass} mg kg^{-1}	10.4
U_{Ass} (k=2) mg kg^{-1}	1.6
$2\sigma_p$ mg kg^{-1}	2.6
Number of results:	19
Number of method:	5

Reported results and expanded uncertainties:

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

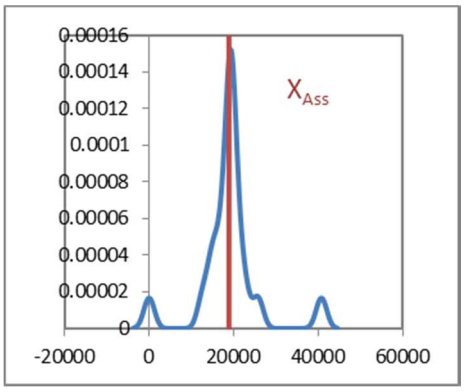


Performance evaluation: *z*-score Zeta-score



Reported data for Fe in the IAEA-MESL-2017-01-TE

Kernel density Plot



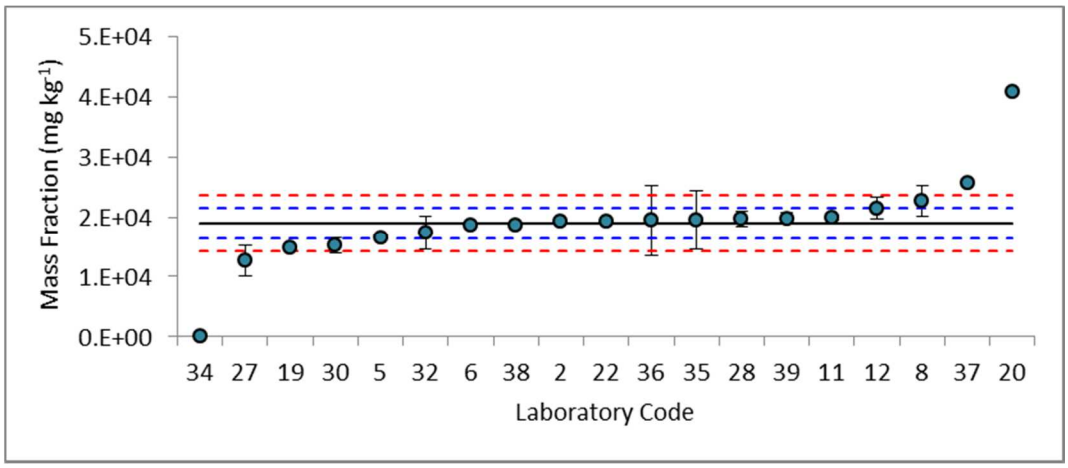
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	79%	11%	11%
Zeta-score	64%	18%	18%

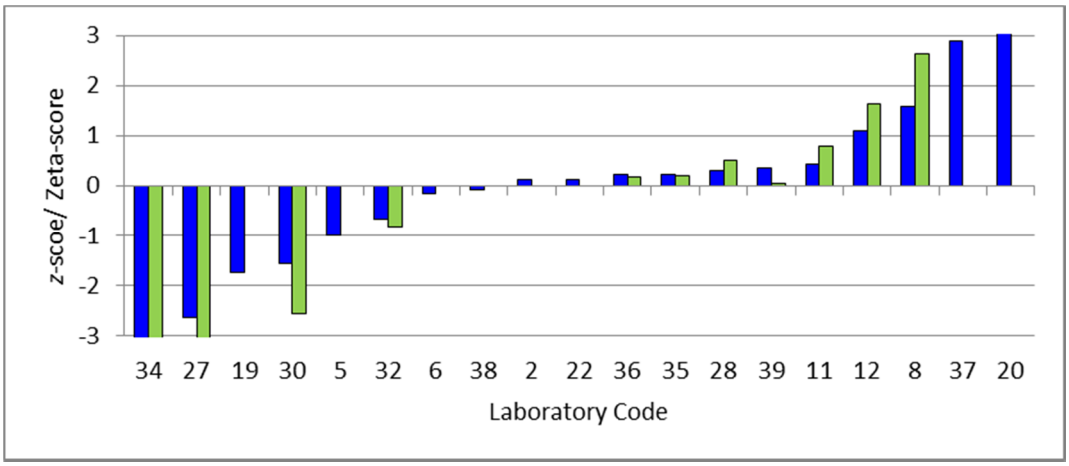
X_{Ass} mg kg^{-1}	18.9×10^3
U_{Ass} (k=2) mg kg^{-1}	2.5×10^3
$2\sigma_p$ mg kg^{-1}	4.7×10^3
Number of results:	19
Number of method:	4

Reported results and expanded uncertainties:

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

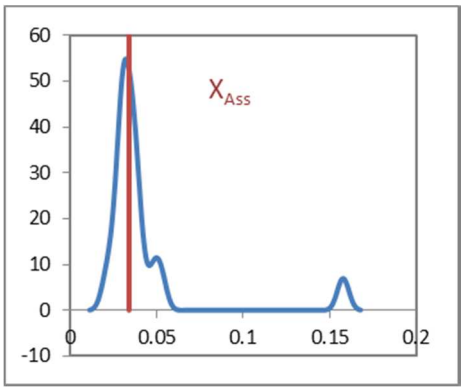


Performance evaluation: *z*-score Zeta-score



Reported data for Hg in the IAEA-MESL-2017-01-TE

Kernel density Plot



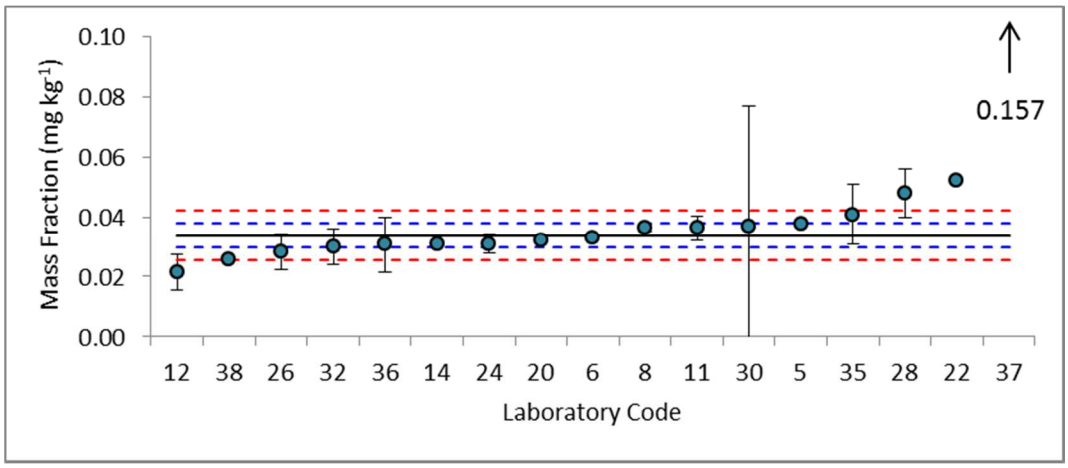
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	76%	6%	18%
Zeta-score	78%	0%	22%

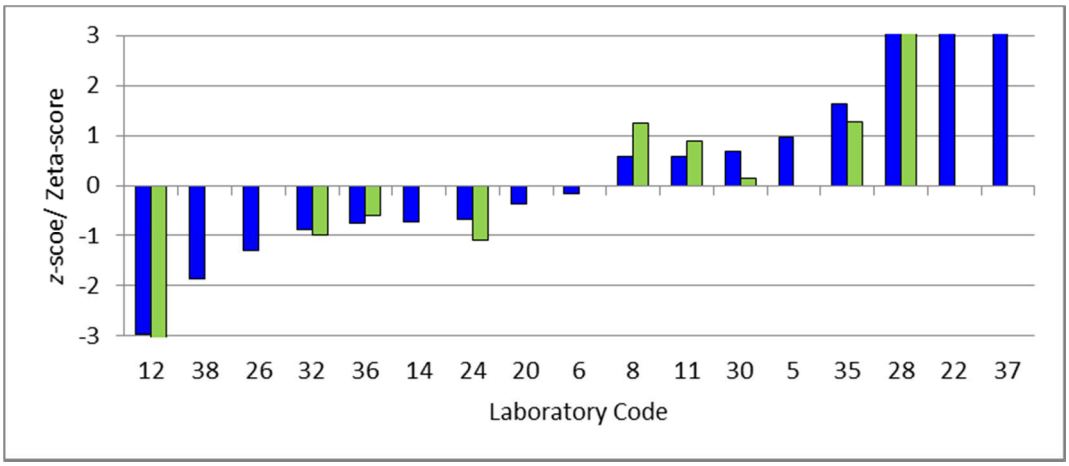
X_{Ass} mg kg^{-1}	0.034
U_{Ass} (k=2) mg kg^{-1}	0.004
$2\sigma_p$ mg kg^{-1}	0.008
Number of results:	17
Number of method:	5

Reported results and expanded uncertainties:

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

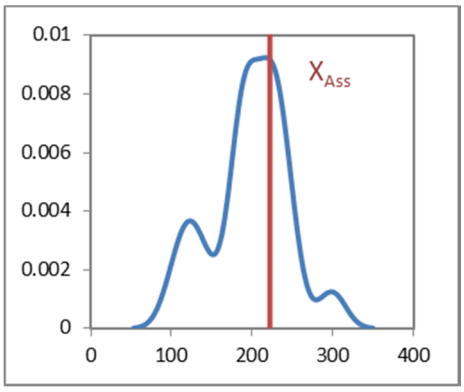


Performance evaluation: *z*-score Zeta-score



Reported data for Mn in the IAEA-MESL-2017-01-TE

Kernel density Plot



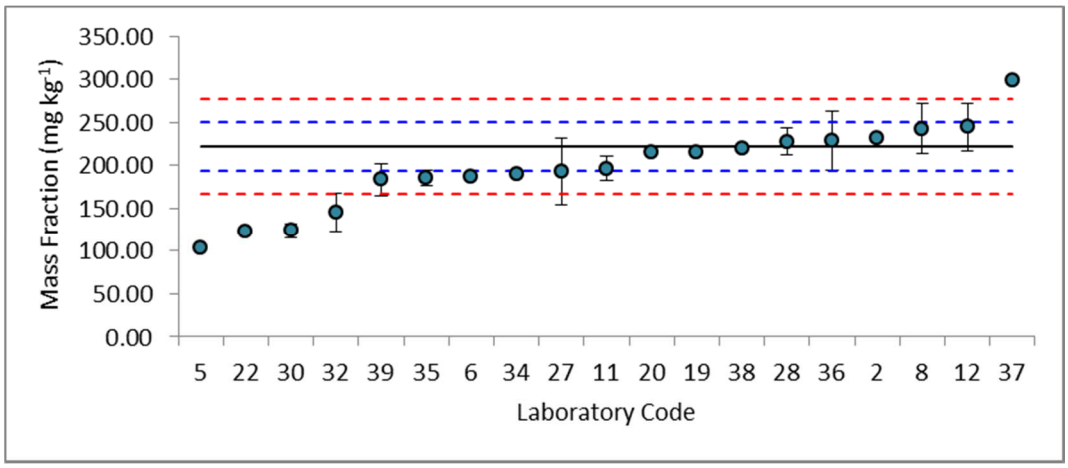
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	74%	11%	16%
Zeta-score	55%	27%	18%

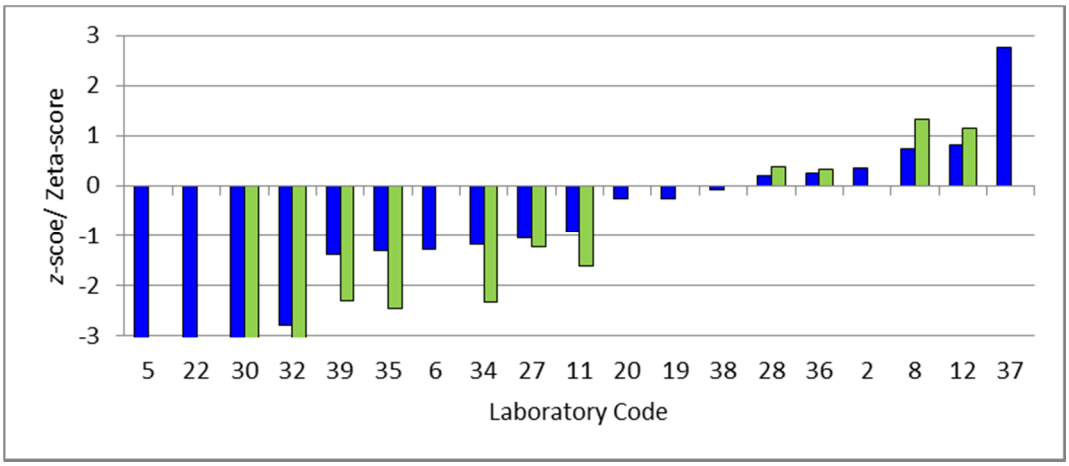
X_{Ass} mg kg^{-1}	222
U_{Ass} (k=2) mg kg^{-1}	28
$2\sigma_p$ mg kg^{-1}	55
Number of results:	19
Number of method:	5

Reported results and expanded uncertainties:

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

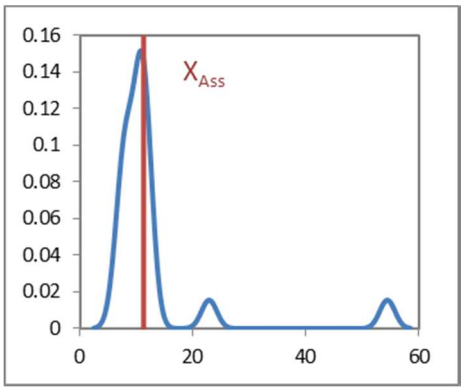


Performance evaluation: *z*-score Zeta-score



Reported data for Pb in the IAEA-MESL-2017-01-TE

Kernel density Plot



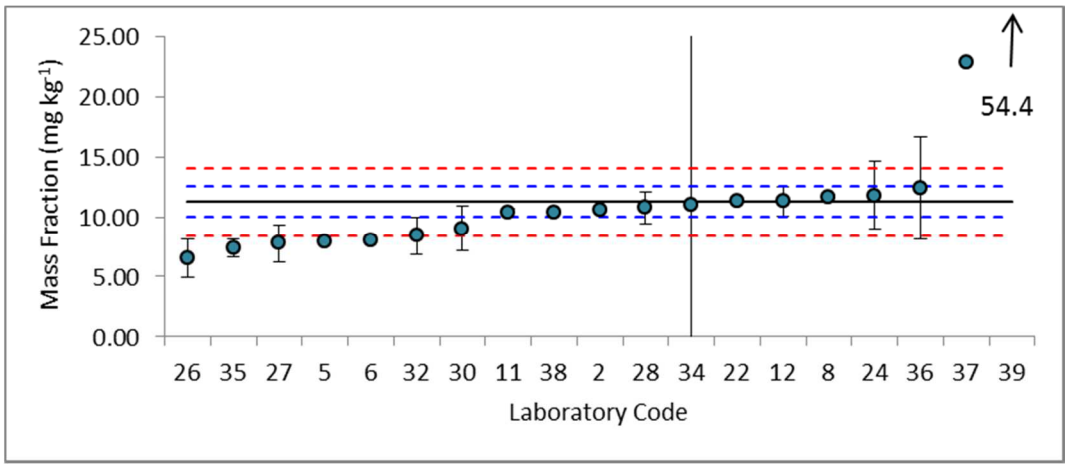
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	71%	21%	7%
Zeta-score	58%	26%	16%

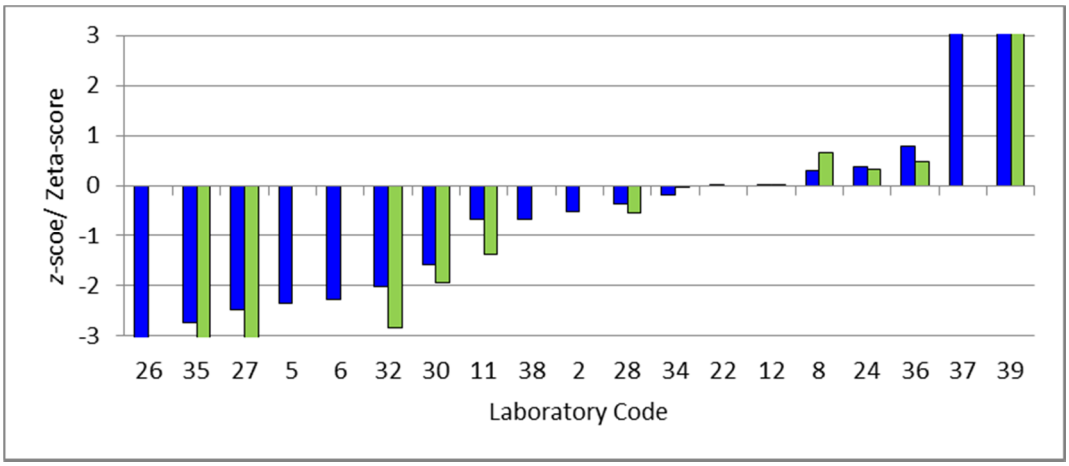
X_{Ass} mg kg^{-1}	11.3
U_{Ass} (k=2) mg kg^{-1}	1.3
$2\sigma_p$ mg kg^{-1}	2.8
Number of results:	19
Number of method:	5

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 Sr in the IAEA-MESL-2017-01-TE

Note: Kernel density Plot for Sr not available, as less than 8 measurement results were reported.

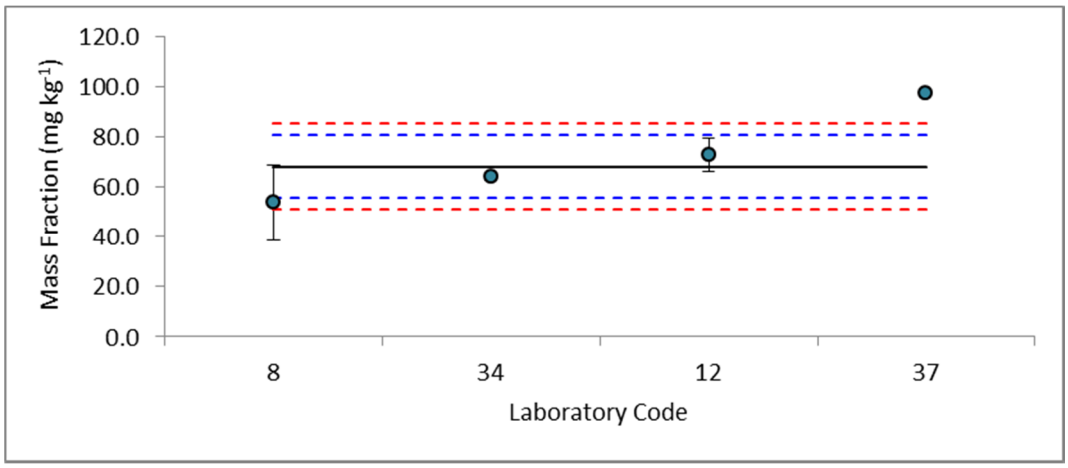
Summary of results:

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

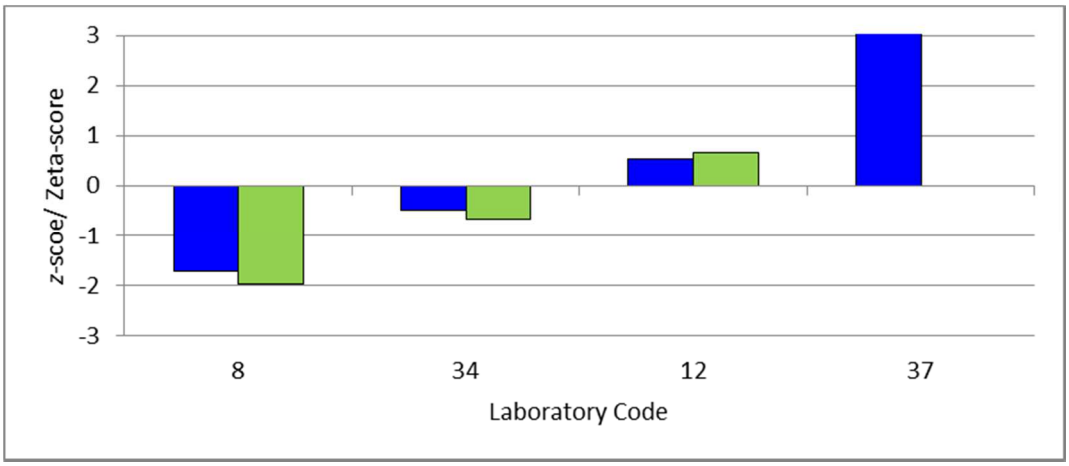
X_{Ass} mg kg^{-1}	68.1
U_{Ass} (k=2) mg kg^{-1}	12.4
$2\sigma_p$ mg kg^{-1}	17.0
Number of results:	4
Number of method:	2

Reported results and expanded uncertainties:

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

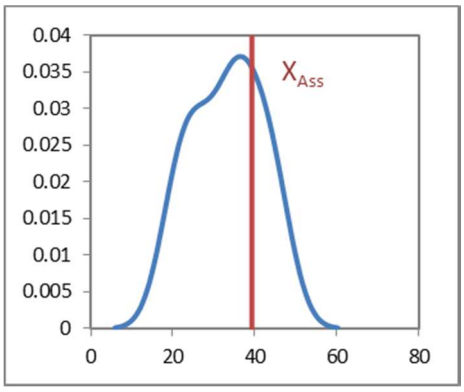


Performance evaluation: *z*-score Zeta-score



Reported data for V in the IAEA-MESL-2017-01-TE

Kernel density Plot



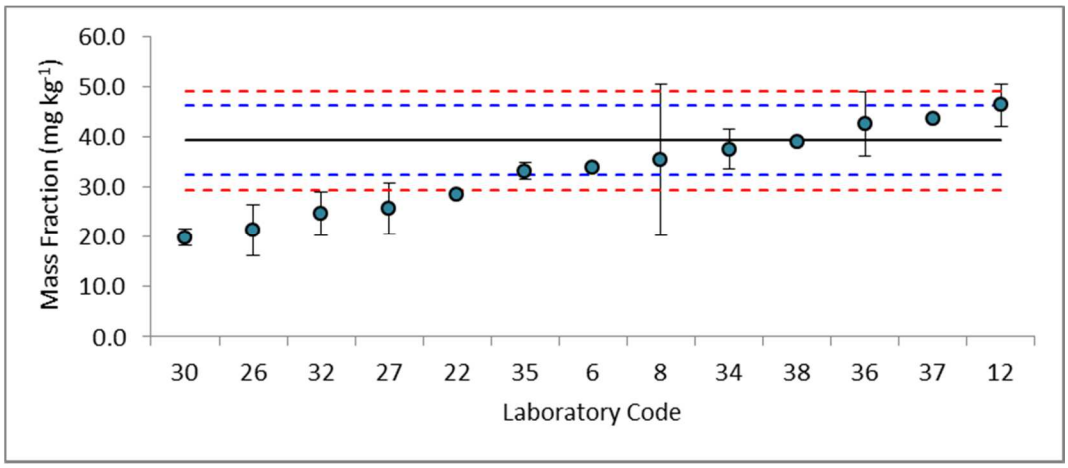
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	62%	23%	15%
Zeta-score	63%	0%	37%

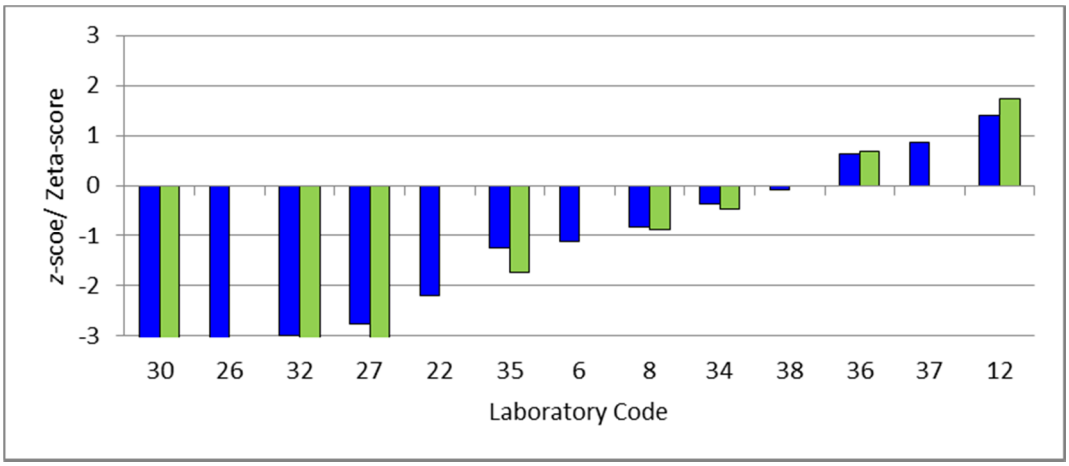
X_{Ass} mg kg^{-1}	39.3
U_{Ass} (k=2) mg kg^{-1}	6.9
$2\sigma_p$ mg kg^{-1}	9.8
Number of results:	13
Number of method:	4

Reported results and expanded uncertainties:

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

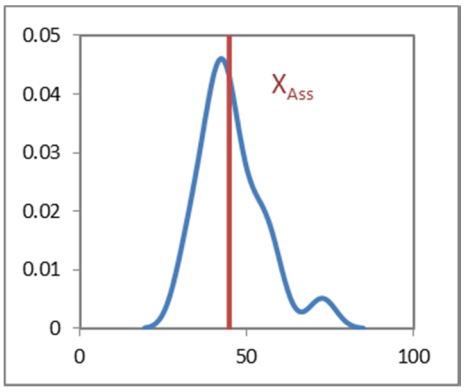


Performance evaluation: *z*-score Zeta-score



Reported data for Zn in the IAEA-MESL-2017-01-TE

Kernel density Plot



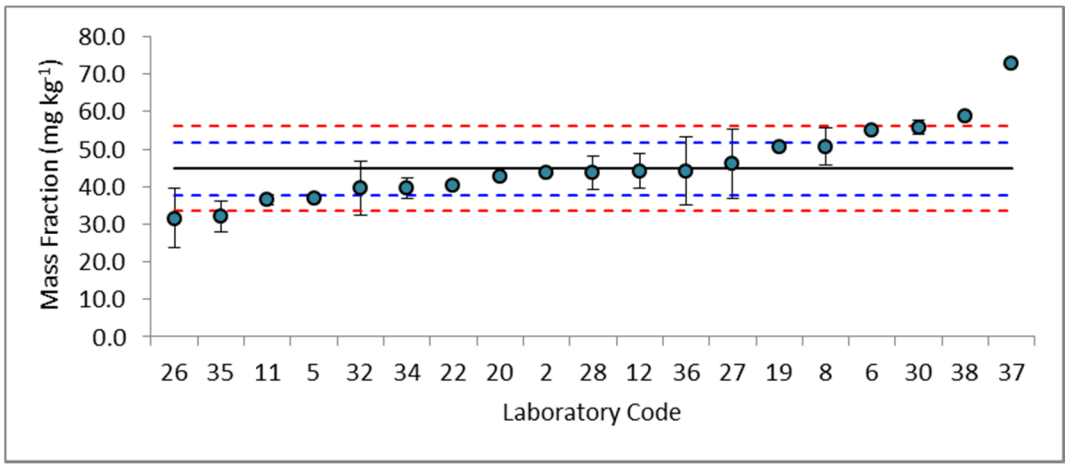
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	79%	5%	16%
Zeta-score	70%	10%	20%

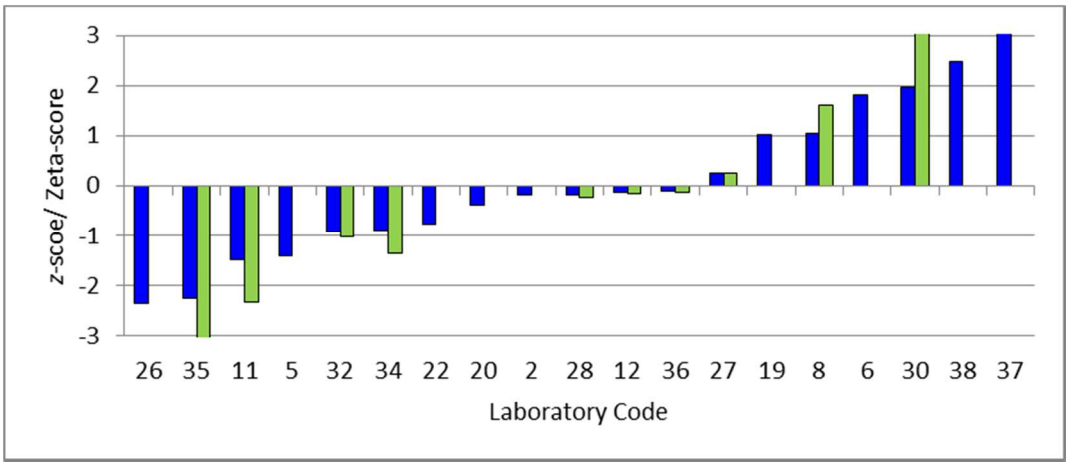
X_{Ass} mg kg^{-1}	44.8
U_{Ass} (k=2) mg kg^{-1}	7.0
$2\sigma_p$ mg kg^{-1}	11.2
Number of results:	19
Number of method:	4

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



Annex 4: Data reported by participants

TABLE 9: RESULTS AS REPORTED BY PARTICIPANTS. Mean and expanded uncertainty given in mg kg^{-1}

Analyte	Laboratory code	Mean	Expanded uncertainty	Method	CRM
Al	2	21300		ICP-MS	IAEA 158
Al	6	10987		ET-AAS	IAEA MESL 2015
Al	8	18357	424	ICP-MS	MESS-3
Al	11	21493	812	F-AAS	IAEA 458
Al	12	23333	1868	ICP-OES	NIST 2702
Al	19	15662		F-AAS	IAEA 433
Al	22	18756		ICP-MS	IAEA 457
Al	27	10161	2032	ICP-MS	
Al	30	5485	621	ICP-MS	MESS-3
Al	34	20200	4000	XRF	PACS-2
Al	35	12679	573	ICP-MS	TH-2
Al	36	21625	6488	ICP-MS	MESS-3
Al	37	16220		ICP-MS	NIST 2780
Al	38	20520		ICP-MS	IAEA 158
As	2	9.41		ICP-MS	IAEA 158
As	6	6.07		ET-AAS	IAEA 405
As	8	11.9	9.4	ICP-MS	MESS-3
As	11	6.60	0.87	ET-AAS	MESS-4
As	12	7.27	0.80	ICP-MS	NIST 2702
As	22	5.71		Hyd-ICP-MS	IAEA 457
As	26	6.63	1.70	ICP-OES	
As	27	5.74	1.16	ICP-MS	lgc aq513
As	30	5.88	0.70	ICP-MS	MESS-3
As	32	5.58	1.00	ICP-MS	ERM - CC141
As	34	9.20	2.73	XRF	PACS-2

TABLE 9: RESULTS AS REPORTED BY PARTICIPANTS (CONT.)

Analyte	Laboratory code	Mean	Expanded uncertainty	Method	CRM
As	35	5.53	0.32	ICP-MS	TH-2
As	37	29.6		ICP-MS	NIST 2780
As	38	6.49		ICP-MS	IAEA 158
Cd	2	0.140		ICP-MS	IAEA 158
Cd	5	0.153		ICP-MS	IAEA 433
Cd	6	0.134		ET-AAS	IAEA MESL 2015
Cd	8	0.145	0.004	ICP-MS	MESS-3
Cd	11	0.148	0.007	ET-AAS	IAEA 458
Cd	12	0.208	0.026	ICP-MS	NIST 2702
Cd	22	0.203		ICP-MS	IAEA 457
Cd	24	0.126	0.034	ICP-MS	IAEA 158
Cd	26	0.137	0.040	ICP-OES	
Cd	27	0.137	0.028	ICP-MS	lgc aq 513
Cd	28	0.136	0.030	ET-AAS	IAEA 433
Cd	30	0.087	0.030	ICP-MS	MESS-3
Cd	32	0.137	0.023	ICP-MS	ERM - CC141
Cd	35	0.143	0.020	ICP-MS	TH-2
Cd	36	0.134	0.020	ICP-MS	MESS-3
Cd	37	6.10		ICP-MS	NIST 2780
Cd	38	0.144		ICP-MS	IAEA 158
Co	2	4.29		ICP-MS	IAEA 158
Co	5	3.30		ICP-MS	IAEA 433
Co	6	4.27		ET-AAS	IAEA 405
Co	8	4.73	0.80	ICP-MS	MESS-3
Co	12	5.23	0.62	ICP-MS	NIST 2702
Co	22	2.76		Hyd-ICP-MS	IAEA 457
Co	26	4.50	1.10	ICP-OES	

TABLE 9: RESULTS AS REPORTED BY PARTICIPANTS (CONT.)

Analyte	Laboratory code	Mean	Expanded uncertainty	Method	CRM
Co	27	3.87	0.78	ICP-MS	lgc aq 513
Co	30	3.59	0.26	ICP-MS	MESS-3
Co	32	4.02	0.60	ICP-MS	ERM - CC141
Co	34	4.33	8.89	XRF	PACS-2
Co	35	3.86	0.22	ICP-MS	TH-2
Co	36	4.24	0.64	ICP-MS	MESS-3
Co	37	4.23		ICP-MS	NIST 2780
Co	38	4.42		ICP-MS	IAEA 158
Cr	2	33.3		ICP-MS	IAEA 158
Cr	6	36.2		ET-AAS	IAEA 405
Cr	8	43.8	3.0	ICP-MS	MESS-3
Cr	11	37.9	1.5	ET-AAS	IAEA 458
Cr	12	41.6	4.2	ICP-MS	NIST 2702
Cr	19	37.4		F-AAS	IAEA 433
Cr	22	15.6		ICP-MS	IAEA 457
Cr	26	19.3	5.0	ICP-OES	
Cr	27	25.0	5.0	ICP-MS	lgc aq 513
Cr	28	34.0	3.2	ET-AAS	IAEA 433
Cr	30	22.0	3.1	Not reported	MESS-3
Cr	32	24.1	5.1	ICP-MS	ERM - CC141
Cr	34	33.2	2.8	XRF	PACS-2
Cr	35	28.8	1.6	ICP-MS	TH-2
Cr	36	35.2	11.0	ICP-MS	MESS-3
Cr	37	37.8		ICP-MS	NIST 2780
Cr	38	35.1		ICP-MS	IAEA 158
Cr	39	42.5	4.2	F-AAS	
Cu	2	10.4		ICP-MS	IAEA 158

TABLE 9: RESULTS AS REPORTED BY PARTICIPANTS (CONT.)

Analyte	Laboratory code	Mean	Expanded uncertainty	Method	CRM
Cu	5	10.4		ICP-MS	IAEA 433
Cu	6	11.0		F-AAS	IAEA MESL 2015
Cu	8	12.1	0.1	ICP-MS	MESS-3
Cu	11	10.0	0.7	F-AAS	MESS-4
Cu	12	7.68	0.86	ICP-OES	NIST 2702
Cu	19	20.2		F-AAS	IAEA 433
Cu	22	9.08		ICP-MS	IAEA 457
Cu	26	7.50	1.90	ICP-OES	
Cu	27	10.4	2.0	ICP-MS	lgc aq 513
Cu	28	13.0	1.2	ET-AAS	IAEA 433
Cu	30	9.34	4.45	ICP-MS	MESS-3
Cu	32	9.95	1.59	ICP-MS	ERM - CC141
Cu	34	5.80	1.89	XRF	PACS-2
Cu	35	9.04	0.50	ICP-MS	TH-2
Cu	36	9.53	1.40	ICP-MS	MESS-3
Cu	37	10.4		ICP-MS	NIST 2780
Cu	38	21.3		ICP-MS	IAEA 158
Cu	39	57.4	5.8	F-AAS	
Fe	2	19190		ICP-MS	IAEA 158
Fe	5	16543		ICP-MS	IAEA 433
Fe	6	18558		F-AAS	IAEA 405
Fe	8	22637	2624	ICP-MS	MESS-3
Fe	11	19935	358	F-AAS	IAEA 458
Fe	12	21480	1862	ICP-OES	BCR 6677
Fe	19	14772		F-AAS	IAEA 433
Fe	20	40749		F-AAS	IAEA 405
Fe	22	19224		ICP-MS	IAEA 457

TABLE 9: RESULTS AS REPORTED BY PARTICIPANTS (CONT.)

Analyte	Laboratory code	Mean	Expanded uncertainty	Method	CRM
Fe	27	12679	2536	ICP-MS	
Fe	28	19643	1296	F-AAS	IAEA 433
Fe	30	15200	1360	ICP-MS	MESS-3
Fe	32	17367	2780	ICP-MS	IAEA MESL 2013 02 PT TM
Fe	34	1.87	0.66	XRF	PACS-2
Fe	35	19465	4957	ICP-MS	TH-2
Fe	36	19453	5836	ICP-MS	MESS-3
Fe	37	25746		ICP-MS	
Fe	38	18729		ICP-MS	IAEA 158
Fe	39	19760	993	F-AAS	
Hg	5	0.038		ICP-MS	IAEA 433
Hg	6	0.033		Solid-AAS	IAEA MESL 2014
Hg	8	0.036	0.001	ICP-MS	MESS-3
Hg	11	0.036	0.004	CV-AFS	NIST 2702
Hg	12	0.021	0.006	Solid-AAS	NIST 2702
Hg	14	0.031		Solid-AAS	NIST 2976
Hg	20	0.032		Solid-AAS	IAEA 405
Hg	22	0.052		ICP-MS	IAEA 457
Hg	24	0.031	0.003	Solid-AAS	IAEA 158
Hg	26	0.028	0.006	CV-AAS	
Hg	28	0.048	0.008	CV-AAS	IAEA 433
Hg	30	0.037	0.040	ICP-MS	MESS-3
Hg	32	0.030	0.006	Solid-AAS	IAEA MESL 2013 02 PT TM
Hg	35	0.041	0.010	ICP-MS	TH-2
Hg	36	0.031	0.009	Solid-AAS	MESS-3
Hg	37	0.158		ICP-MS	NIST 2780
Hg	38	0.026		Solid-AAS	IAEA 158

TABLE 9: RESULTS AS REPORTED BY PARTICIPANTS (CONT.)

Analyte	Laboratory code	Mean	Expanded uncertainty	Method	CRM
Mn	2	232		ICP-MS	IAEA 158
Mn	5	104		ICP-MS	IAEA 433
Mn	6	186		ET-AAS	IAEA 405
Mn	8	243	29	ICP-MS	MESS-3
Mn	11	197	14	F-AAS	MESS-4
Mn	12	245	28	ICP-OES	NIST 2702
Mn	19	215		F-AAS	IAEA 433
Mn	20	215		F-AAS	IAEA 405
Mn	22	122		ICP-MS	IAEA 457
Mn	27	193	39	ICP-MS	lgc aq 513
Mn	28	228	16	F-AAS	IAEA 433
Mn	30	124	8	ICP-MS	MESS-3
Mn	32	145	22	ICP-MS	ERM - CC141
Mn	34	189	1	XRF	PACS-2
Mn	35	186	9	ICP-MS	TH-2
Mn	36	229	34	ICP-MS	MESS-3
Mn	37	299		ICP-MS	NIST 2780
Mn	38	220		ICP-MS	IAEA 158
Mn	39	183	18	F-AAS	
Pb	2	10.5		ICP-MS	IAEA 158
Pb	5	7.94		ICP-MS	IAEA 433
Pb	6	8.05		Not reported	IAEA 405
Pb	8	11.7	0.2	ICP-MS	MESS-3
Pb	11	10.3	0.4	ET-AAS	MESS-4
Pb	12	11.3	1.2	ICP-MS	NIST 2702
Pb	22	11.3		ICP-MS	IAEA 457
Pb	24	11.8	2.8	ICP-MS	IAEA 158

TABLE 9: RESULTS AS REPORTED BY PARTICIPANTS (CONT.)

Analyte	Laboratory code	Mean	Expanded uncertainty	Method	CRM
Pb	26	6.53	1.60	ICP-OES	
Pb	27	7.79	1.56	ICP-MS	lgc aq 513
Pb	28	10.8	1.3	ET-AAS	IAEA 433
Pb	30	9.04	1.88	ICP-MS	MESS-3
Pb	32	8.43	1.52	ICP-MS	ERM - CC141
Pb	34	11.0	14.9	XRF	PACS-2
Pb	35	7.42	0.72	ICP-MS	TH-2
Pb	36	12.4	4.3	ICP-MS	MESS-3
Pb	37	22.9		ICP-MS	NIST 2780
Pb	38	10.3		ICP-MS	IAEA 158
Pb	39	54.4	5.4	F-AAS	
Sr	8	53.7	15.0	ICP-MS	MESS-3
Sr	12	72.8	6.6	ICP-MS	NIST 2702
Sr	34	64.0	1.3	XRF	PACS-2
Sr	37	97.3		ICP-MS	NIST 2780
V	6	33.8		ET-AAS	IAEA MESL 2015
V	8	35.3	15.0	ICP-MS	MESS-3
V	12	46.3	4.2	ICP-MS	NIST 2702
V	22	28.5		ICP-MS	IAEA 457
V	26	21.3	5.0	ICP-OES	
V	27	25.7	5.2	ICP-MS	lgc aq 513
V	30	19.9	1.7	ICP-MS	MESS-3
V	32	24.6	4.4	ICP-MS	
V	34	37.5	3.9	XRF	PACS-2
V	35	33.2	1.7	ICP-MS	TH-2
V	36	42.5	6.4	ICP-MS	MESS-3
V	37	43.6		ICP-MS	NIST 2780

TABLE 9: RESULTS AS REPORTED BY PARTICIPANTS (CONT.)

Analyte	Laboratory code	Mean	Expanded uncertainty	Method	CRM
V	38	39.0		ICP-MS	IAEA 158
Zn	2	43.8		ICP-MS	IAEA 158
Zn	5	37.0		ICP-MS	IAEA 433
Zn	6	55.1		F-AAS	IAEA MESL 2015
Zn	8	50.7	5.0	ICP-MS	MESS-3
Zn	11	36.6	1.3	F-AAS	IAEA 458
Zn	12	44.2	4.6	ICP-MS	NIST 2702
Zn	19	50.5		F-AAS	IAEA 433
Zn	20	42.7		F-AAS	IAEA 405
Zn	22	40.5		ICP-MS	IAEA 457
Zn	26	31.7	8.0	ICP-OES	
Zn	27	46.3	9.2	ICP-MS	lgc aq 513
Zn	28	43.9	4.4	F-AAS	IAEA 433
Zn	30	55.8	1.7	ICP-MS	MESS-3
Zn	32	39.7	7.1	ICP-MS	ERM - CC141
Zn	34	39.8	2.8	XRF	PACS-2
Zn	35	32.2	4.1	ICP-MS	TH-2
Zn	36	44.2	9.0	ICP-MS	MESS-3
Zn	37	72.6		ICP-MS	NIST 2780
Zn	38	58.7		ICP-MS	IAEA 158

REPORT
ANALYTICAL PERFORMANCE STUDY FOR MEDPOL: DETERMINATION OF CHLORINATED PESTICIDES, PCBs AND PETROLEUM HYDROCARBONS IN SEDIMENT SAMPLE
IAEA-MEL-2017-01 PT/ORG

REPORT

ANALYTICAL PERFORMANCE STUDY FOR MEDPOL: DETERMINATION OF CHLORINATED PESTICIDES, PCBs AND PETROLEUM HYDROCARBONS IN SEDIMENT SAMPLE IAEA-MEL-2017-01 PT/ORG

January 2018

Prepared in collaboration with:

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THE ANALYTICAL PERFORMANCE STUDY FOR MEDPOL: DETERMINATION OF CHLORINATED PESTICIDES, PCBs AND PETROLEUM HYDROCARBONS IN SEDIMENT SAMPLE IAEA-MEL-2017-01 PT/ORG

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 UNEP/Mediterranean Action Plan 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, petroleum hydrocarbons 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 for the determination of organic contaminants in a marine sediment sample carried out in 2017 by MEDPOL designated laboratories.

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

2. SCOPE OF EXERCISE

At the request of MEDPOL, all national coordinators for the MEDPOL programme were contacted in September 2017 to nominate their national laboratories involved in MED POL monitoring activities. Consequently, a set of samples (31 bottles of sediment samples IAEA-MEL-2017-01 PT/ORG) were dispatched to the 31 laboratories listed in Table 1. All the samples were sent in October 2017.

The sample dispatched is the Marine Sediment Reference Material IAEA-383 previously characterized through a worldwide interlaboratory comparison (ILC) exercise [1]. Because the sample contains known concentrations of chlorinated pesticides, PCBs and petroleum hydrocarbons, the proficiency test yields more accurate data rather than an ILC done with samples of unknown concentrations. The target compounds that were requested to be analyzed by the participants were previously reassessed in our laboratories and their new revised assigned values, both “recommended” and “information” values are shown in the Annexes. Z-scores were only calculated for “recommended values”.

The deadline for reporting results and consequently starting to draft the report was fixed for the 24 of November 2017, but it was postponed to the 11th of December 2017 to allow more laboratories participating in the exercise.

At the closure of the exercise, only 16 laboratories (52%) submitted their results. Ten laboratories reported results for both chlorinated pesticides, PCB congeners and petroleum hydrocarbons, 15 laboratories reported results only for chlorinated pesticides and PCB congeners and 1 laboratory reported results only for petroleum hydrocarbons.

3. ON LINE REPORTING SYSTEM

For 2017 an online reporting system was implemented allowing Participants to enter themselves their data on a dedicated web site. Participants received instructions for the online reporting system as well as a username and a password in November 2017. The use of the on-line reporting system allowed participants to download their preliminary evaluation report (reporting assigned values, reported values and z-scores). Preliminary evaluation reports were available for downloading late January 2018.

TABLE 1. LIST OF LABORATORIES WHERE THE SAMPLES WERE SENT AND ORGANIC CONTAMINANT FAMILY THEY REPORTED RESULTS BACK.

BOSNIA & HERZEGOVINA

Dr Milenko SAVIC **OC, PAHs**
Institut za vode doo Bijeljina
Miloša Obilića 51
76300 Bijeljina

CROATIA

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Ms Silvana MLADINOV **OC**
County of Istria
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Vladimir Nazora 23
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Ms Jadranka SANGULIN
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Dept for Health Ecology
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23000 Zadar

CYPRUS

Mr Militsa HADJIGEORGIOU
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44 Kimonos Str,
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EGYPT

Prof Ahmed Moustafa Hassan EL-NEMR
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ARPA Puglia
Dipartimento Provinciale di Bari
Via Caduti di Tutte le Guerre 7
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Mr Achille PALMA **OC, PAHs**
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Participants' results for chlorinated pesticides and PCB congeners are listed in TABLE 2 and the results for petroleum hydrocarbons in TABLE 3. In both tables the new assigned and information values are indicated along with the target standard deviation (12.5%) for each compound.
All results are reported by the laboratory code number only to protect the Participants confidentiality.

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

The treatments of samples for the analysis of petroleum hydrocarbons are reported in TABLE 6 and the instrumental conditions for these analyses are reported in TABLE 7.

Some laboratories that reported data but didn't provide information for treatment of samples and GC conditions were not included in tables 4, 5, 6 and 7. One laboratory that provided information for treatment of samples and GC conditions but didn't report any measurement was not included in tables 4, 5, 6 and 7.

Figures 1 and 2 shows the graphic representations of key points of sample treatment and instrumental analyses for chlorinated pesticides and PCBs congeners and petroleum hydrocarbons respectively.

TABLE 2. REPORTED RESULTS FOR CHLORINATED PESTICIDES AND PCB CONGENERS IN THE SEDIMENT TEST SAMPLE (IAEA-383)

All results are in ng/g dry weight.

Analyte	Laboratory codes															IAEA-383	Trgt Stdev**
	8	10	13	14	15	16	19	21	24	25	26	27	28	31	32		
HCB	37	.	.	12	59	39	.	.	47	84	45	.	.	77	57	38	4.75
pp DDE	1.0	.	1.5	0.2	1.2	1.3	29	1.3	0.9	1.0	1.8	.	.	2.8	.	1.20	0.15
PCB No 28	1.2	.	.	1.4	.	1.1	318	1.1	.	3.0	2.6	2.4	.	.	1.0	1.00	0.13
PCB No 31	0.9	.	.	.	.	.	94	.	.	.	.	.	.	.	.	0.76	0.10
PCB No 44	.	1.9	.	.	1.3	.	70	.	.	.	.	.	.	.	.	1.10	0.14
PCB No 52	2.6	2.6	.	1.4	3.4	2.7	9.3	2.1	.	2.0	3.5	2.9	2.8	2.6	2.6	2.50	0.31
PCB No 101	2.0	3.3	.	1.2	3.7	4.4	142	2.9	.	5.4	6.7	5.2	4.6	2.5	3.4	2.90	0.36
PCB No 105	1.0	.	.	.	.	1.1	.	1.8	.	1.9	1.3	1.2	.	.	.	0.99	0.12
PCB No 118	3.3	2.7	.	.	2.9	4.0	802	5.3	.	6.0	3.6	3.6	7.6	.	3.0	3.30	0.41
PCB No 128	0.9	.	.	.	.	.	.	0.7	.	.	0.8	0.9	.	0.7	.	0.63	0.08
PCB No 138	4.6	3.4	.	1.4	3.6	6.4	72	4.3	.	6.6	12.6	4.1	4.4	3.8	3.8	4.40	0.55
PCB No 149	2.7	2.0	.	.	2.5	.	282	.	.	.	.	3.5	.	3.0	.	3.20	0.40
PCB No 153	5.8	3.6	.	1.5	4.2	6.0	286	6.6	.	8.5	6.1	5.5	11.1	5.0	4.1	4.30	0.54
PCB No 170	1.6	1.8	.	.	.	.	379	1.1	.	.	.	1.7	.	1.3	.	0.82	0.10
PCB No 180	3.6	2.1	.	1.0	2.6	3.9	363	2.7	.	4.5	6.6	3.4	5.4	2.5	2.4	2.50	0.31
PCB No 183	0.6	.	.	.	.	.	.	0.6	.	.	.	0.7	.	0.5	.	0.47	0.06
PCB No 187	1.6	.	.	.	.	.	.	.	.	.	.	1.8	.	.	.	1.30	0.16
PCB No 110*	2.9	.	.	.	.	.	.	.	.	.	.	4.0	.	3.2	.	2.4*	0.30
PCB No 194*	.	3.5	.	.	.	.	125	0.8	.	.	.	.	.	.	0.6	0.54*	0.07
pp DDD*	1.3	.	1.3	0.5	0.9	0.9	32	0.8	0.5	1.8	0.9	.	.	0.9	.	1.8*	0.23
pp DDT*	0.4	.	0.4	0.2	.	0.1	9.1	1.1	0.2	0.6	0.5	.	.	.	.	2.4*	0.30
Lindane*	0.7	.	0.2	0.2	.	.	68	.	0.3	0.1	0.2	.	.	17.9	.	0.46*	0.06

*Information value; ** target standard deviation of IAEA-383

TABLE 3. REPORTED RESULTS FOR PETROLEUM HYDROCARBONS IN THE SEDIMENT TEST SAMPLE (IAEA-383)

All results are in ng/g dry weight.

Analyte	Laboratory codes											IAEA-383	Trgt Stdev
	3	8	10	13	15	21	25	26	27	28	31		
n-C17	160	.	.	.	117	72	.	.	.	.	.	380	48
Naphthalene	29	36	.	81	65	88	84	.	66	240	.	96	12
Acenaphthylene	20	28	154	56	60	72	3.3	85	48	196	46	47	5.9
Acenaphthene	11	19	9.4	16	18	20	0.9	15	14	130	18	16	2.0
Fluorene	23	21	16	25	22	31	37	24	30	121	29	27	3.4
Anthracene	26	19	22	27	26	30	33	42	32	150	24	30	3.8
Phenanthrene	96	71	115	138	143	141	187	146	166	735	129	160	20
2 Methyl Phenanthrene	14	.	.	.	.	12	.	.	.	.	.	31	3.9
1 Methyl Phenanthrene	15	.	.	.	.	13	.	.	.	.	.	24	3.0
Fluoranthene	135	123	211	222	269	240	272	266	330	321	225	290	36
Pyrene	156	100	190	223	246	259	272	245	295	3154	224	280	35
Benz [a] Anthracene	42	52	70	80	109	104	180	89	143	7707	62	105	13
Chrysene (+Triphenylene)	77	78	110	145	156	161	283	167	144	.	220	170	21
Benzo [e] Pyrene	33	128	.	.	.	205	.	119	167	.	187	160	20
Benzo [a] Pyrene	47	64	54	85	104	144	146	107	127	4884	148	120	15
Benzo[b+j]fluoranthene	109	159	139	185	221	333	136	215	248	.	167	150	19
Benzo [k] Fluoranthene	30	34	58	54	72	82	39	72	85	126	84	73	9.1
Perylene	.	25	.	.	.	66	.	60	53	.	39	58	7.3
Benzo [g,h,i] Perylene	28	107	107	164	166	172	330	185	222	278	126	190	24
Indeno[1,2,3-cd]pyrene	26	80	95	124	125	117	153	96	169	1102	125	150	19
n-C18*	43	.	.	.	47	40	.	.	.	.	.	83*	10
Phytane*	21	.	.	.	.	35	.	.	.	.	.	57*	7
Pristane*	16	.	.	.	.	26	.	.	.	.	.	87*	11
1 Methyl Naphthalene*	11	20	.	.	21	46	.	.	.	.	.	14*	2
Dibenz[a,h]anthracene*	36	18	36	25	24	21	33	23	38	312	20	20*	3

*Information value; ** target standard deviation of IAEA-383

TABLE 4. CHLORINATED COMPOUNDS AND PCBs - TREATMENT OF SAMPLES

Lab. Code	Extraction	Solvent	Clean-up	Fractionation	Desulphurication
10	Microwave assisted	n-Hexane/Dichloromethane	SPE	Florisil	Copper
13	Microwave assisted	Acetone/n-Hexane	Other	Florisil	Copper
14	Sohxlet	n-Hexane/Dichloromethane	None	Florisil	Copper
15	Sohxlet	n-Hexane/Dichloromethane	SPE	None	
16	Sohxlet	n-Hexane/Dichloromethane	Other	Silica/Alumina	Copper
19	Microwave assisted	Acetone/n-Hexane	SPE	Florisil	Copper
21	Sohxlet	n-Hexane/Dichloromethane	SPE	Alumina	Copper
24	Quechers	Other	SPE	Other	TBA (tetratbutylammonium)
25	Shaking (solid/liquid extraction)	Acetone	None	Florisil	Copper
26	Quechers	Other	SPE	Other	Copper
28	Microwave assisted	Acetone/n-Hexane	None		
31	ASE	n-Hexane/Dichloromethane	None	None	None
32	Shaking (solid/liquid extraction)	Acetone/n-Hexane	SPE	Florisil	

TABLE 5. GC CONDITIONS - CHLORINATED PESTICIDES AND PCBs

Lab. Code	Use of Internal Standard	Internal Standards used	Injector Type	Gc-Column	Detector Type
10	Yes	Pentachloronitrobenzene	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
13	Yes	PCB198 PCB29	Split		GC/MSMS
14	Yes		Splitless	100% Dimethylpolysiloxane	GC/ECD
15	Yes	PCB 29 PCB 198 epsilon-HCH	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
16			Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
19	Yes	PCB 30 1 Bromo 2 nitrobenzene	Splitless	Other	GC/ECD
21	Yes		Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/ECD
24	Yes	decachlorobiphenyl	MMI	5% Phenyl 95% Dimethylpolysiloxane	GC/MSMS
25	Yes		Splitless	Other	GC/MSMS
26	Yes	All compounds 13C labeled	Splitless	Other	GC/MS
28	No		Splitless		GC/MS
31	Yes	alpha HCH D6 mix deuterated PAH	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
32	Yes	PCB 209	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/ECD and peak confirmation with dual column

TABLE 6. PETROLEUM HYDROCARBONS - TREATMENT OF SAMPLES

Lab. Code	Extraction	Solvent	Clean-up	Fractionation	Desulphurication
10	Microwave assisted	n-Hexane/Dichloromethane	SPE	Silica	
3	Soxhlet	n-Hexane/Dichloromethane	Other	Silica/Alumina	
31	ASE	n-Hexane/Dichloromethane	None	None	None
28	Microwave assisted	Acetone/n-Hexane	None	None	None
8	ASE	n-Hexane/Dichloromethane	GPC		
15	Soxhlet	n-Hexane/Dichloromethane	SPE	Alumina	
26	ASE	Acetone/n-Hexane	None	None	
21	Soxhlet	Other	Other	Silica	
25	Shaking (solid/liquid extraction)	Acetone	None	Florisil	Copper
13	Microwave assisted	Acetone/n-Hexane	Other	Silica	Copper

TABLE 7. INSTRUMENTAL CONDITIONS – PETROLEUM HYDROCARBONS

Lab. Code	Use of Internal Standard	Internal Standards used	Injector Type	GC/HPLC-Column	Detector Type
10	Yes	o terphenyl and 1 chlorooctadecane	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
3	Yes		Splitless	Other	GC/MS
31	Yes	mix Deuterated PAH	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
28	No		Other	C18	HPLC-FLD
8	No		Other	C18	HPLC-FLD
15	Yes	Naphtalene-d8 Acenaphthene-d10 Phenanthrene-d10 Fluoranthene-d10 Chrysene-d12 Perylene-d12 C19-d40	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
26	Yes	Deuterated compounds of all PAH quantified	Splitless	50% Phenyl 50% dimethylpolysiloxane	GC/MS
21	Yes	Deuterated PAH	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
25			Splitless	Other	GC/MSMS
13	Yes	Acenaphthene D10 Phenanthrene D10 Chrysene D12 Napthhalene D8 Perylene D12	Split		GC/MSMS

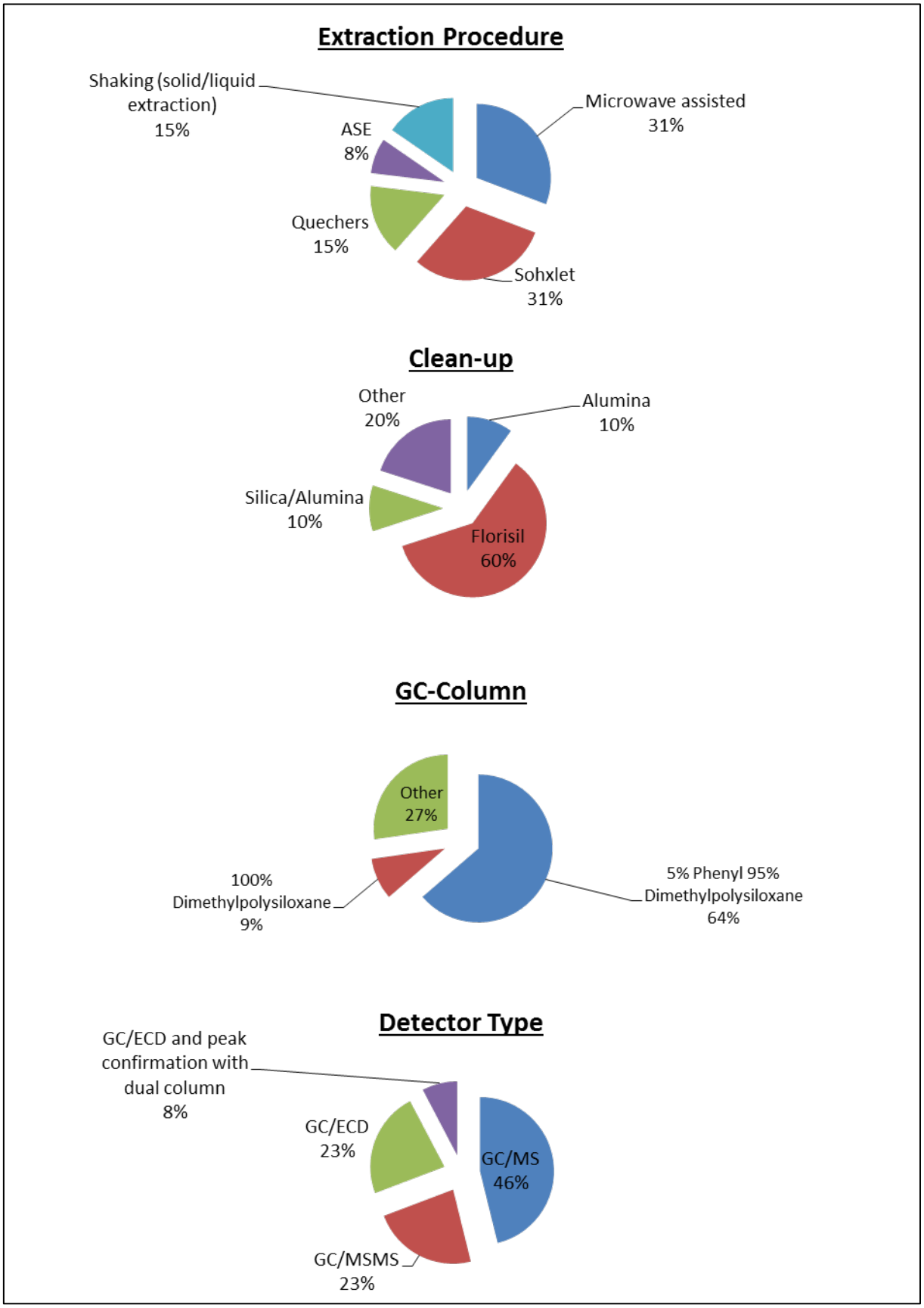


FIG.1. Graphic representation of sample treatment and instrumental conditions for chlorinated pesticides and PCB congeners.

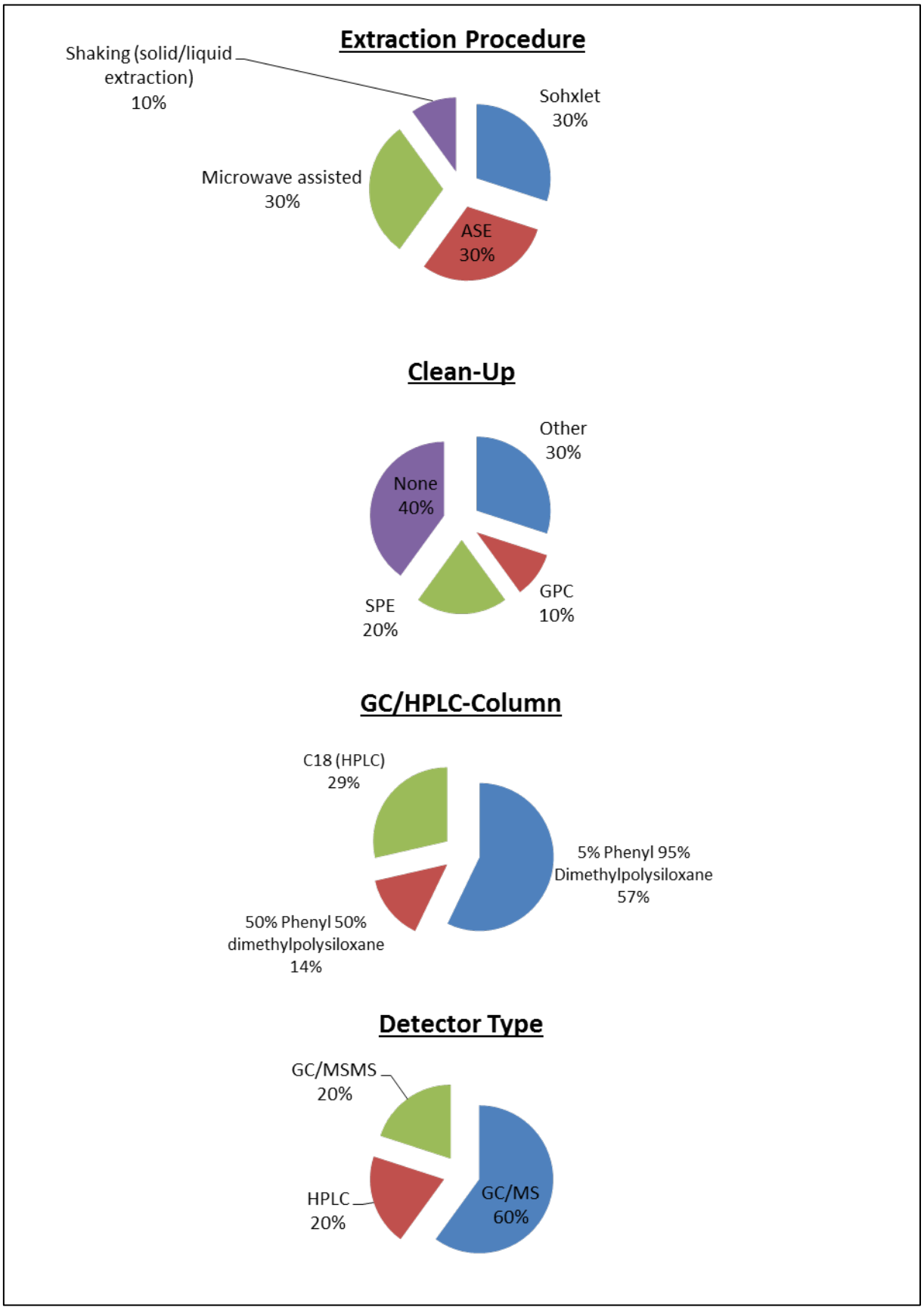


FIG.2. Graphic representation of sample treatment and instrumental conditions for Petroleum Hydrocarbons

4. EVALUATION CRITERIA

For the assessment of the laboratory performances, a *z*-score is calculated according to the ISO guide 13528 [2]:

$$z = (x_i - x_a)/ \sigma_p$$

Where:

- x_i is the reported values from participant of the analyte concentration in the sample;
- x_a is the assigned value;
- σ_p is the standard deviation for proficiency assessment,

This score effectively expresses the difference between the robust mean of the laboratory and the assigned value in unit σ_p .

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 [2, 3, 4].

The standard deviation for proficiency assessment for all target compounds, σ_p, was set at 12.5% in this exercise.

The *z*-scores for participating laboratories can be found in TABLE 8 for chlorinated pesticides and PCB congeners and TABLE 9 for petroleum hydrocarbons. 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”.

TABLE 8. *z*-SCORES FOR CHLORINATED PESTICIDES AND PCB CONGENERS

Analyte	Laboratory codes														
	8	10	13	14	15	16	19	21	24	25	26	27	28	31	32
HCB	-0.2			-5.5	4.3	0.3			1.96	9.8	1.5			8.3	4.0
pp DDE	-1.4		2.3	-6.5	0.1	0.8	186	0.8	-1.97	-1.4	3.9			10.6	
PCB No 28	1.3			3.01		1.1	2536	1.1		15.6	13.0	11.0			0.1
PCB No 31	1.8						986								
PCB No 44		5.9			1.8		502								
PCB No 52	0.2	0.4		-3.4	2.98	0.5	22	-1.2		-1.6	3.1	1.1	0.9	0.5	0.4
PCB No 101	-2.6	1.2		-4.8	2.2	4.0	383	-0.1		6.8	10.4	6.2	4.6	-1.1	1.5
PCB No 105	0.4					0.9		6.5		7.0	2.2	1.9			
PCB No 118	-0.1	-1.5			-1.0	1.8	1937	4.8		6.6	0.6	0.8	10.4		-0.6
PCB No 128	2.8							1.2			1.6	3.9		1.3	
PCB No 138	0.3	-1.8		-5.5	-1.4	3.6	122	-0.2		3.9	15.0	-0.5	0.02	-1.0	-1.0
PCB No 149	-1.1	-3.1			-1.7		697					0.7		-0.5	
PCB No 153	2.9	-1.4		-5.2	-0.2	3.2	524	4.3		7.7	3.3	2.3	12.6	1.4	-0.3
PCB No 170	7.3	9.2					3687	2.5				8.4		4.9	
PCB No 180	3.6	-1.1		-4.7	0.2	4.6	1154	0.5		6.3	13.2	3.03	9.3	-0.04	-0.4
PCB No 183	2.04							2.9				4.5		0.2	
PCB No 187	1.6											3.2			

TABLE 9. *z*-SCORES FOR PETROLEUM HYDROCARBONS

Analyte	Laboratory codes										
	3	8	10	13	15	21	25	26	27	28	31
n-C17	-4.6				-5.5	-6.5					
Naphthalene	-5.6	-5.0		-1.2	-2.6	-0.7	-1.0		-2.5	12.0	
Acenaphthylene	-4.6	-3.2	18.3	1.5	2.3	4.3	-7.4	6.5	0.2	25.4	-0.1
Acenaphthene	-2.7	1.3	-3.3	-0.1	0.8	1.96	-7.6	-0.5	-0.8	57.0	1.2
Fluorene	-1.1	-1.8	-3.4	-0.7	-1.6	1.0	2.9	-0.9	0.8	27.8	0.7
Anthracene	-1.1	-3.01	-2.2	-0.8	-1.0	0.04	0.7	3.2	0.6	31.9	-1.6
Phenanthrene	-3.2	-4.5	-2.2	-1.1	-0.9	-1.0	1.3	-0.7	0.3	28.8	-1.6
2 Methyl Phenanthrene	-4.4					-5.0					
1 Methyl Phenanthrene	-3.01					-3.7					
Fluoranthene	-4.3	-4.6	-2.2	-1.9	-0.6	-1.4	-0.5	-0.6	1.1	0.9	-1.8
Pyrene	-3.6	-5.1	-2.6	-1.6	-1.0	-0.6	-0.2	-1.0	0.4	82.1	-1.6
Benz [a] Anthracene	-4.8	-4.1	-2.7	-1.9	0.3	-0.1	5.7	-1.3	2.9	579	-3.3
Chrysene (+Triphenylene)	-4.4	-4.3	-2.8	-1.2	-0.7	-0.4	5.3	-0.1	-1.2		2.3
Benzo [e] Pyrene	-6.4	-1.6				2.2		-2.05	0.3		1.3
Benzo [a] Pyrene	-4.8	-3.7	-4.4	-2.3	-1.1	1.6	1.8	-0.8	0.5	318	1.8
Benzo[b+j]fluoranthene	-2.2	0.5	-0.6	1.9	3.8	9.8	-0.8	3.5	5.2		0.9
Benzo [k] Fluoranthene	-4.7	-4.3	-1.7	-2.1	-0.1	0.9	-3.8	-0.2	1.3	5.8	1.2
Perylene		-4.6				1.0		0.2	-0.7		-2.6
Benzo [g,h,i] Perylene	-6.8	-3.5	-3.5	-1.1	-1.0	-0.7	5.9	-0.2	1.3	3.7	-2.7
Indeno[1,2,3-cd]pyrene	-6.6	-3.8	-3.0	-1.4	-1.3	-1.8	0.1	-2.9	1.0	51	-1.4

5. EVALUATION OF RESULTS

CHLORINATED PESTICIDES AND PCB CONGENERS

Among all designated laboratories, only 48% submitted results for chlorinated pesticides and PCB congeners.

Only 11 participants to the current PT reported to have a QA/QC system in place in their laboratory and 8 laboratories reported to use validated methods. More than 60% use Internal Standards, but only 3 Laboratories, representing 20%, reported their QA/QC results along with the test results.

Laboratory number 24 provided all acceptable results; but reported only two values. Seven laboratories (8, 10, 15, 16, 21, 31 and 32) reported more than 50% of acceptable results. Four laboratories (25, 26, 27 and 28) provided more than 50% of results "out of control". Laboratories number 14 and 19 reported all outlying results.

Most of the participants reporting more than 50% outlying values reported not using CRMs for their analyses, despite of having a QA/QC system in place in their laboratories.

Figure 3 reports a graphic representation of z-scores for chlorinated Pesticides and PCB congeners.

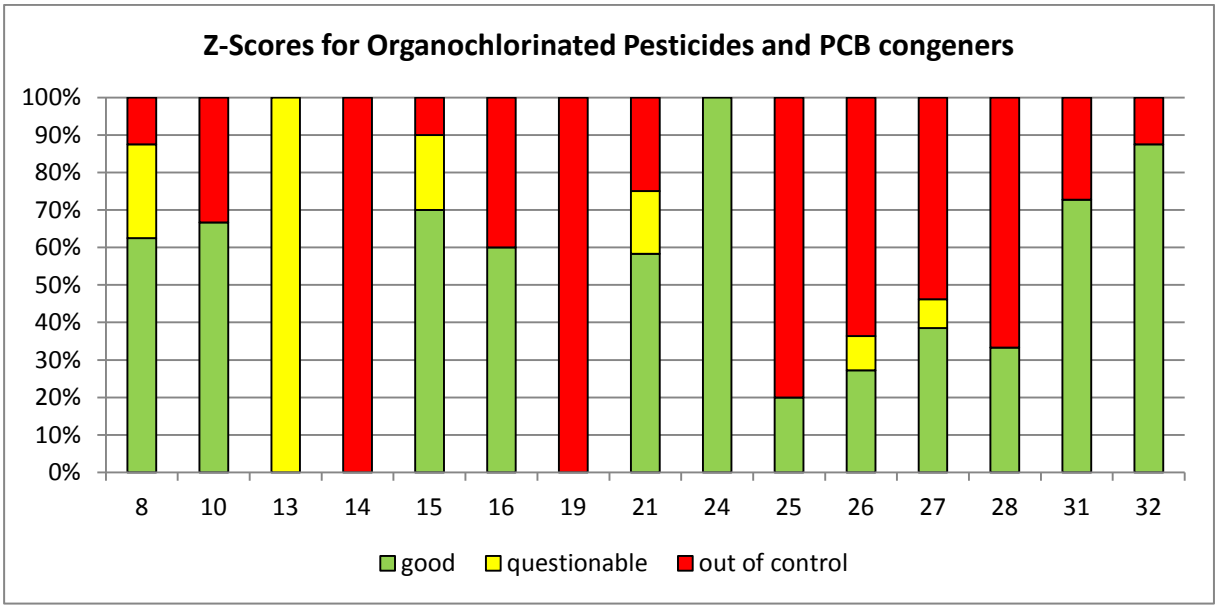


FIG.3. Graphic representation of laboratories z-scores for chlorinated pesticides and PCB congeners.

PETROLEUM HYDROCARBONS

Only 35% of the designated Laboratories submitted results for petroleum hydrocarbons.

Among the participants, Laboratory number 13 and 27 provided all acceptable and very few "questionable" results. Five Laboratories (15, 21, 25, 26 and 31) reported more than 50% of acceptable results. Three Laboratories (3, 8 and 28) 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. Only three Laboratories reported their QA/QC data along with the test results.

Figure 4 reports a graphic representation of z-scores for petroleum hydrocarbons.

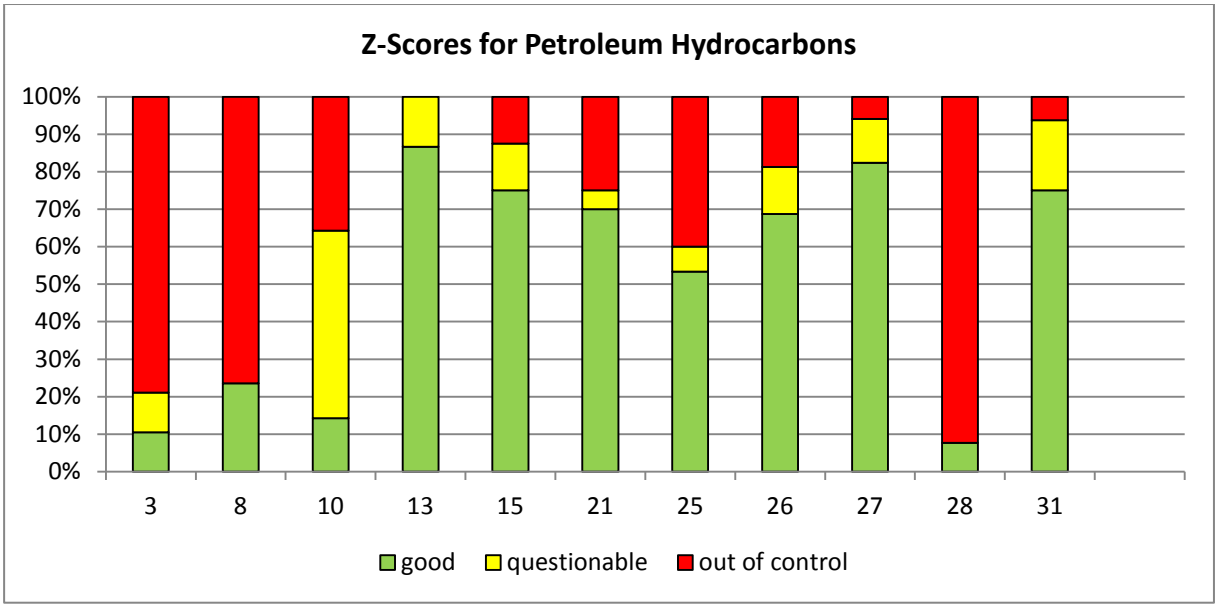


FIG. 4. Graphic representation of laboratories z-scores for petroleum hydrocarbons.

Figure 5 and 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.

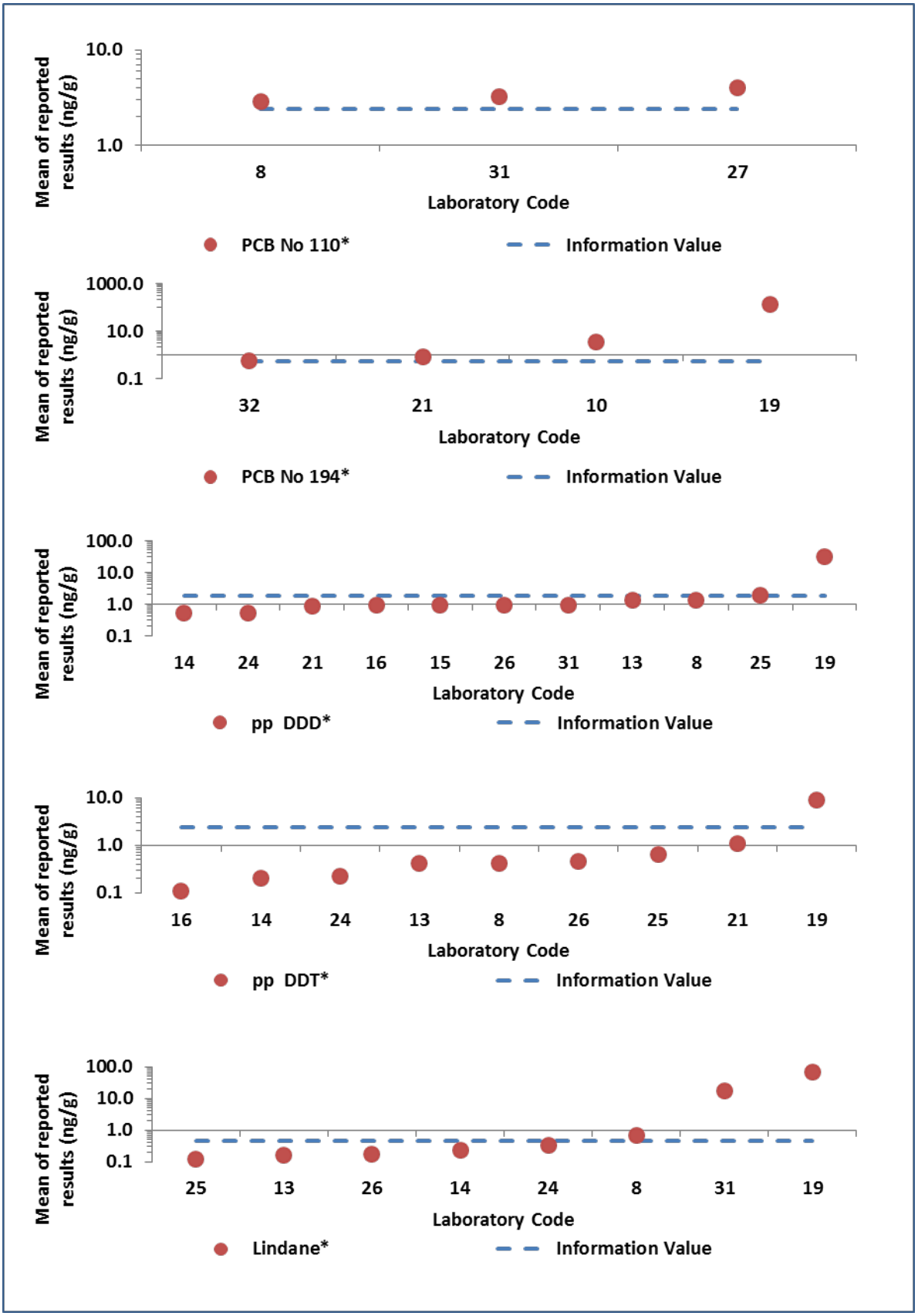


FIG.5. "Information values" reported by participants for chlorinated pesticides and PCB congeners.

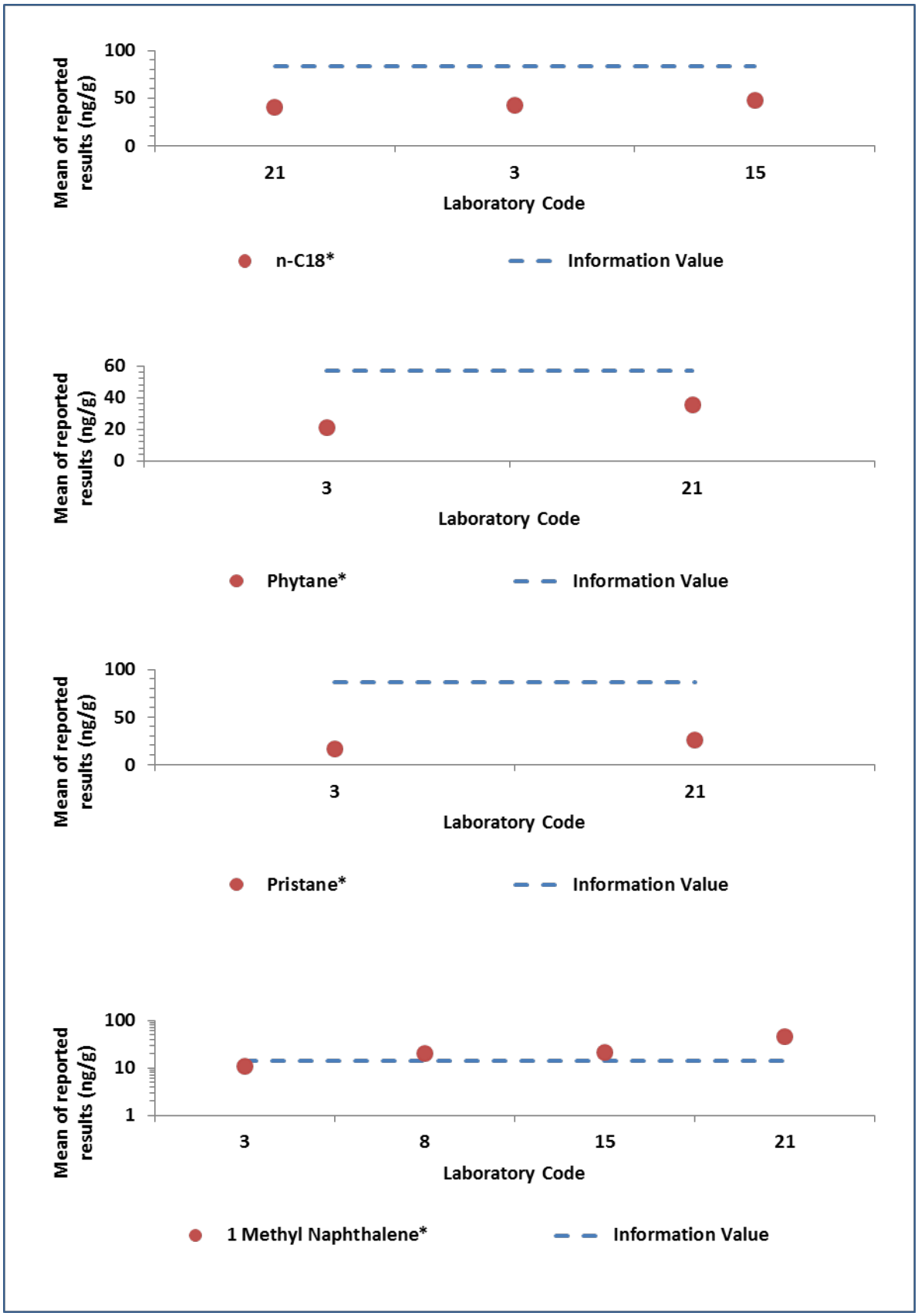


FIG.6. "Information values" reported by participants for petroleum hydrocarbons.

6. CONCLUSIONS AND RECOMMENDATIONS

Eight participants, representing 53% of all the Laboratories reporting results for chlorinated pesticides and PCB congeners, were able to produce all “acceptable” and few “questionable” results. Six participants, representing 40% of all the Laboratories reporting results for chlorinated 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 chlorinated pesticides and PCB congeners show an inconsistent pattern. In many cases, for the same group of compounds, excellent z-scores values are reported along with z-scores that 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.

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.

In one case (Laboratory number 19) reported results were off by more than one order of magnitude. This may be due to a “reporting” mistake (for example: wrong unit conversion or wrong data-set reported) or due to more severe analytical issues which would require immediate root cause analysis and consequent corrective actions.

Results for petroleum hydrocarbons confirmed the positive trend in Laboratories performances starting with 2016 exercise. Even though 3 Laboratories provided most or all outlying results, 7 participants, representing 64% of all the Laboratories reporting results for petroleum hydrocarbons, reported all or most acceptable results and in many cases their results showed very good accuracy all over the compounds range.

On the other hand, Laboratories that provided mostly outlying results were often very far off the assigned values.

In general best performing Laboratories reported to have a quality system in place, to use internal standards and validated methods and in some cases to be accredited. However, there are several examples of Laboratories that although having a quality system and being accredited were not able to provide acceptable results.

Like for chlorinated pesticides and PCB congeners, co-elution and interferences are very common sources of errors for petroleum hydrocarbons 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.

The use of Reference Materials and replicate samples are key points in every QA/QC system in order 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 in avoiding accuracy and precision issues.

Unfortunately, some Participants reported data but didn't 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.

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

For the current PT, 52% of the designated Laboratories submitted results for chlorinated compounds and 35% for petroleum hydrocarbons. The rate of participation to this PT is unfortunately low and worse than the last two exercises (2015 and 2016).

Although some Participants communicated upfront their difficulty to participate to this year exercise due to instrumental and/or manpower unavailability, most of the non-participating Laboratories did not participate in 2016 exercise either.

This low participation rate is discouraging given the importance of such exercises to test and demonstrate laboratory performances as required by ISO Guide 17025.

7. REFERENCES

[1] INTERNATIONAL ATOMIC ENERGY AGENCY, World-wide and Regional intercomparison for the determination of organochlorine compounds and petroleum hydrocarbons and sterols in the Sediment Sample IAEA-383, IAEA Analytical Quality in Nuclear Applications Series.

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

[3] 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.

[4] 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.

8. ANNEXES

- List of the target chlorinated pesticides and PCBs congeners with their new revised assigned values and target confidence interval in test sample IAEA-383
- List of the target Petroleum Hydrocarbon compounds with their new revised assigned values and target confidence interval in test sample IAEA-383
- Graphic representation of Laboratories performances

- List of the target chlorinated pesticides and PCBs congeners with their new revised assigned values and target confidence Interval (assigned value ± 2 target standard deviation) in test sample IAEA-383

Analyte	Assigned value [ng/g]	Target confidence Interval [ng/g]
HCB	38	29 - 48
pp'DDE	1.20	0.90 - 1.50
PCB No 28	1.00	0.75 - 1.25
PCB No 31	0.76	0.57 - 0.95
PCB No 44	1.10	0.83 - 1.38
PCB No 49	1.10	0.83 - 1.38
PCB No 52	2.50	1.88 - 3.13
PCB No 101	2.90	2.18 - 3.63
PCB No 105	0.99	0.74 - 1.24
PCB No 118	3.30	2.48 - 4.13
PCB No 128	0.63	0.47 - 0.79
PCB No 138	4.40	3.30 - 5.50
PCB No 149	3.20	2.40 - 4.00
PCB No 153	4.30	3.23 - 5.38
PCB No 170	0.82	0.62 - 1.03
PCB No 180	2.50	1.88 - 3.13
PCB No 183	0.47	0.35 - 0.59
PCB No 187	1.30	0.98 - 1.63
PCB No 209	2.10	1.58 - 2.63
PCB No 110*	2.40	1.80 - 3.00
PCB No 194*	0.54	0.41 - 0.68
pp DDD*	1.80	1.35 - 2.25
pp DDT*	2.40	1.80 - 3.00
Lindane*	0.46	0.35 - 0.58

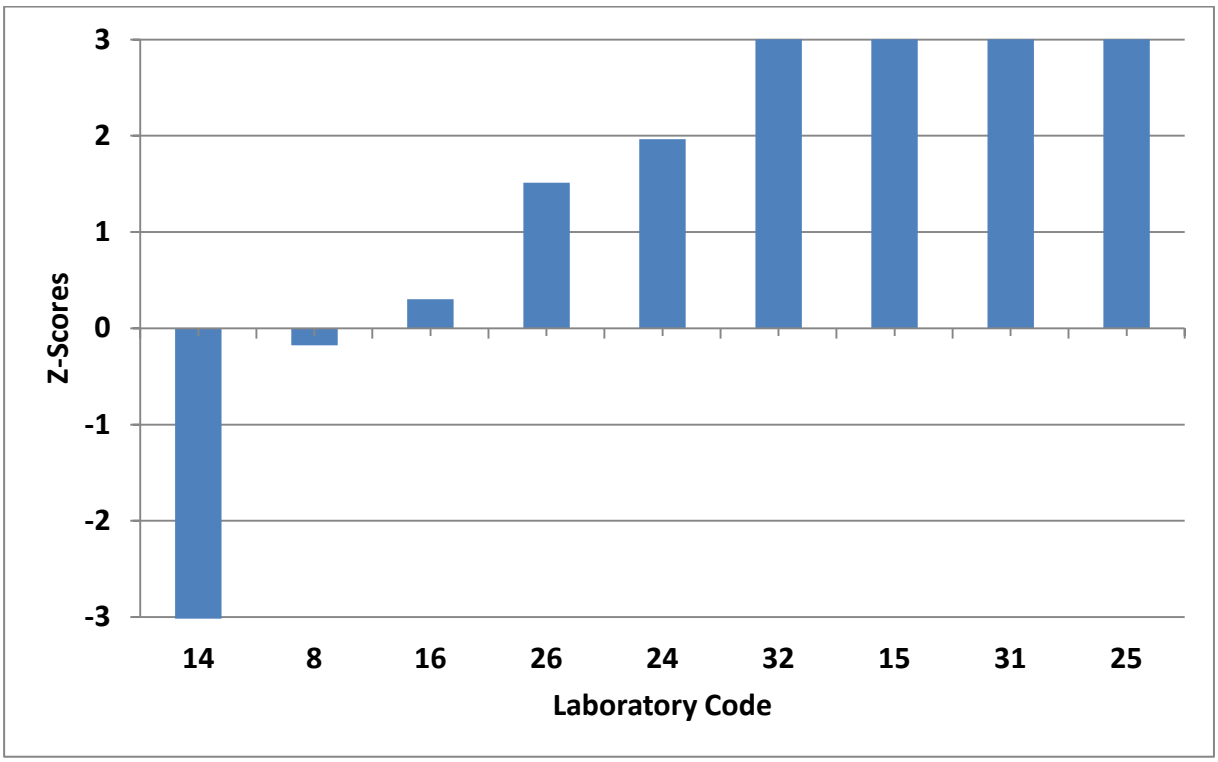
*Information values

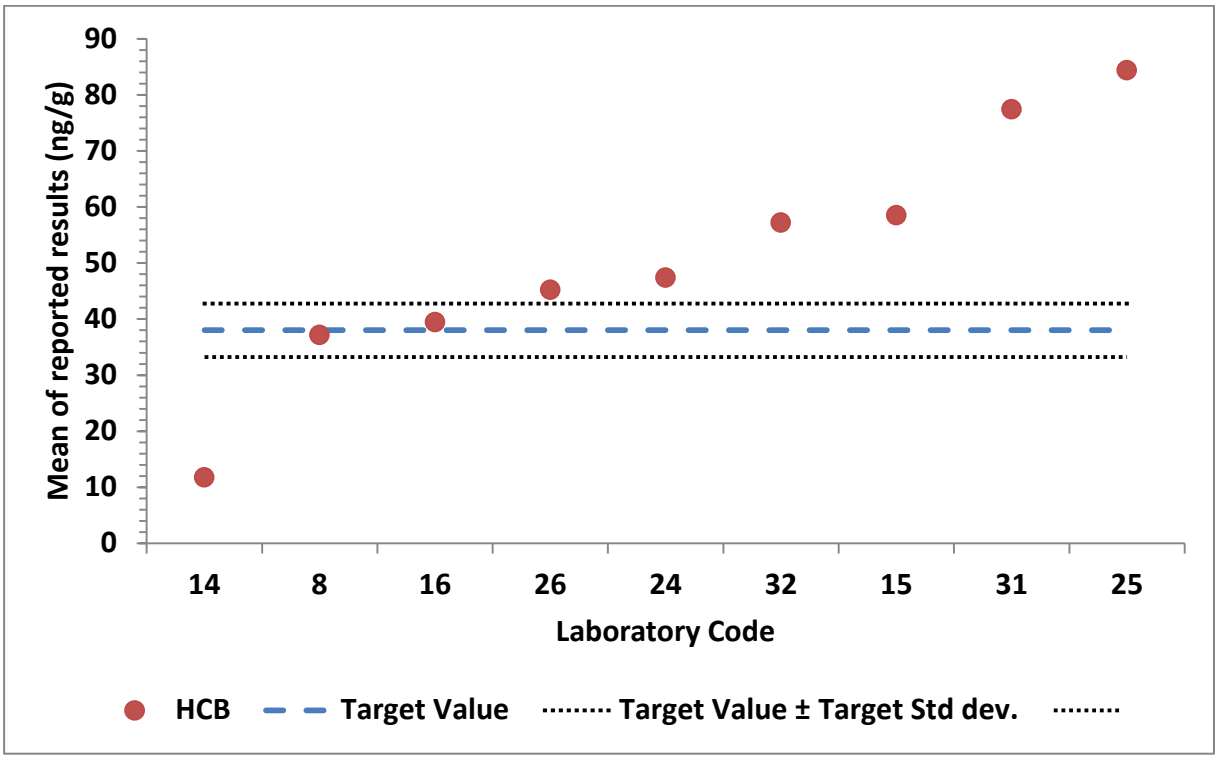
- List of the target Petroleum Hydrocarbon compounds with their new revised assigned values and target confidence Interval (assigned value ± 2 target standard deviation) in test sample IAEA-383

Analyte	Assigned value [ng/g]	Target confidence Interval [ng/g]
n-C17	380	285 - 475
Naphthalene	96	72 - 120
Acenaphthylene	47	35 - 59
Acenaphthene	16	12 - 20
Fluorene	27	20 - 34
Anthracene	30	23 - 38
Phenanthrene	160	120 - 200
2 Methyl Phenanthrene	31	23 - 39
1 Methyl Phenanthrene	24	18 - 30
Fluoranthene	290	218 - 363
Pyrene	280	210 - 350
Benz [a] Anthracene	105	79 - 131
Chrysene (+Triphenylene)	170	128 - 213
Benzo [e] Pyrene	160	120 - 200
Benzo [a] Pyrene	120	90 - 150
Benzo[b+j]fluoranthene	150	113 - 188
Benzo [k] Fluoranthene	73	55 - 91
Perylene	58	44 - 73
Benzo [g,h,i] Perylene	190	143 - 238
Indeno[1,2,3-cd]pyrene	150	113 - 188
n-C18*	83	62 - 104
Phytane*	57	43 - 71
Pristane*	87	65 - 109
1 Methyl Naphthalene*	14	11 -18
Dibenz[a,h]anthracene*	20	15 - 25

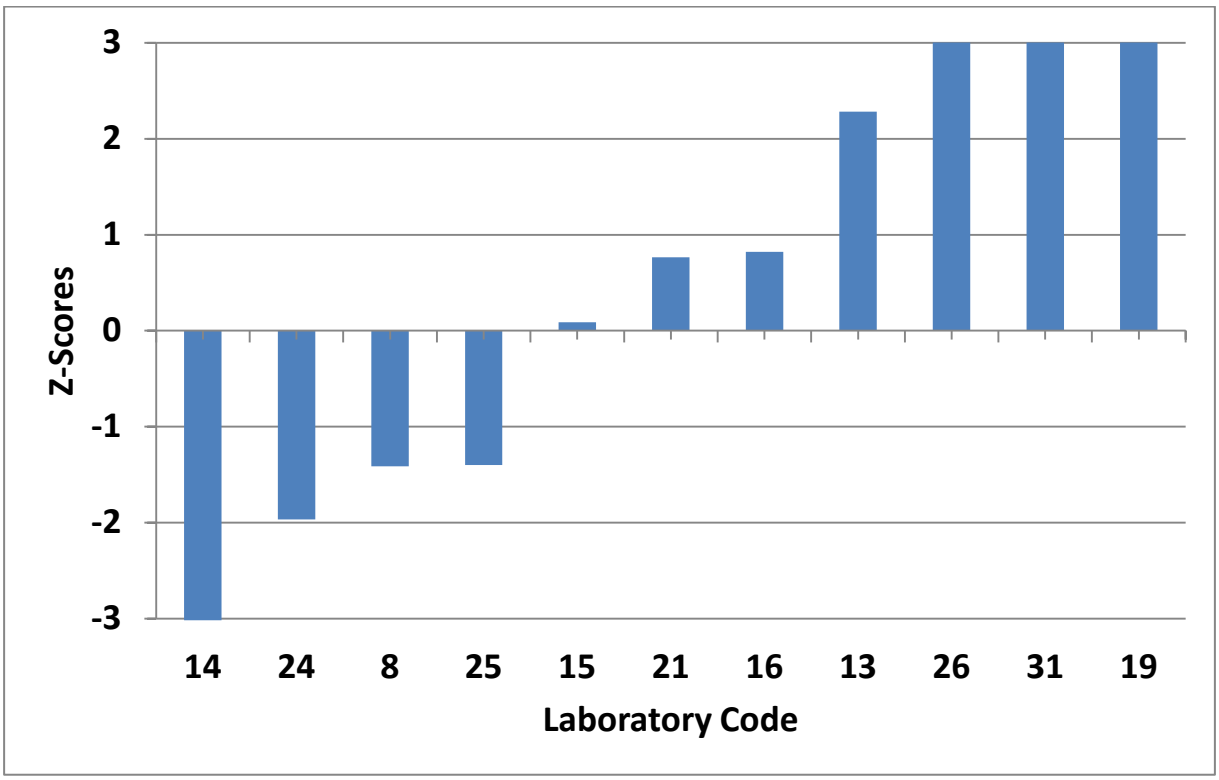
*Information values

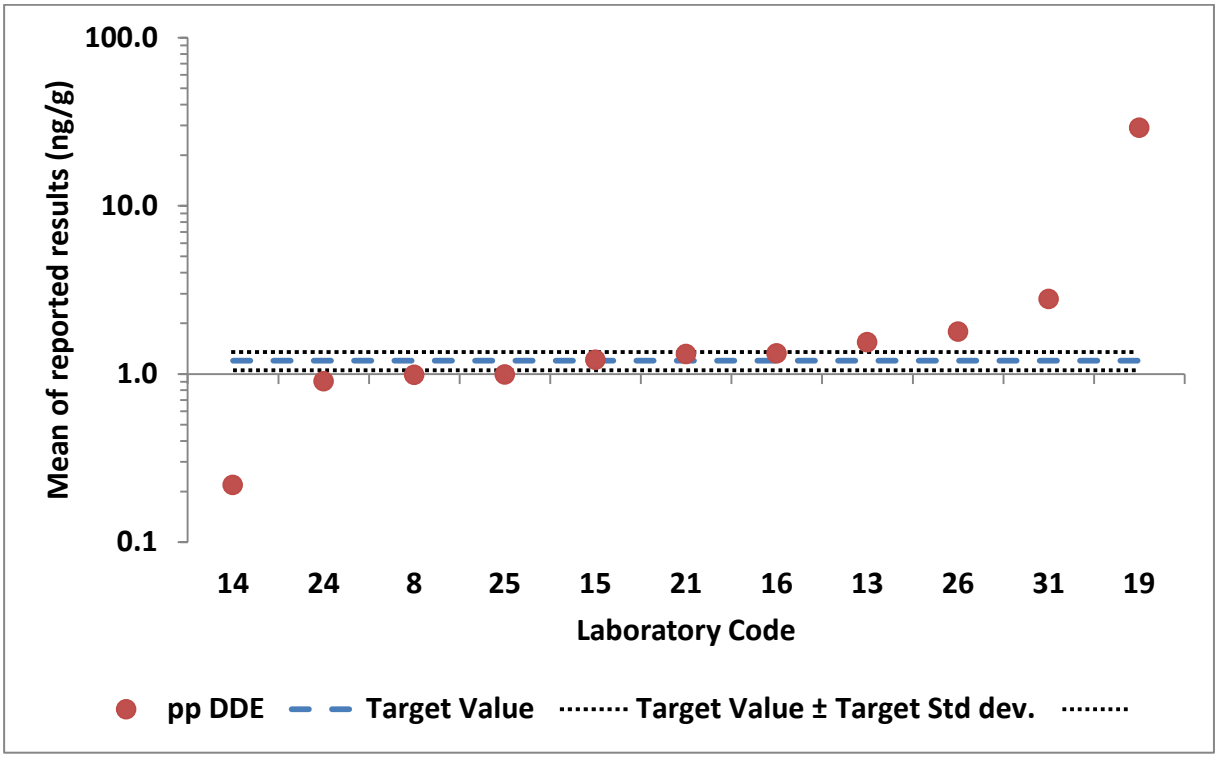
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR HCB





GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR pp'DDE





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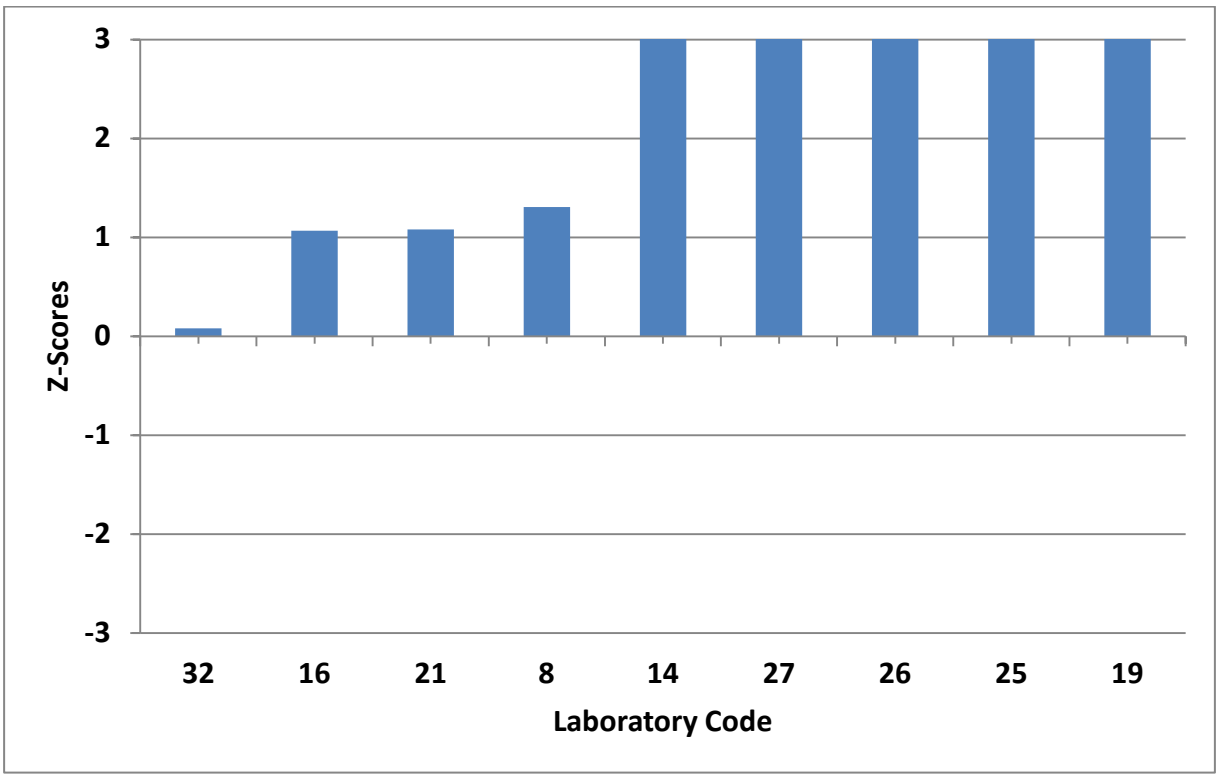

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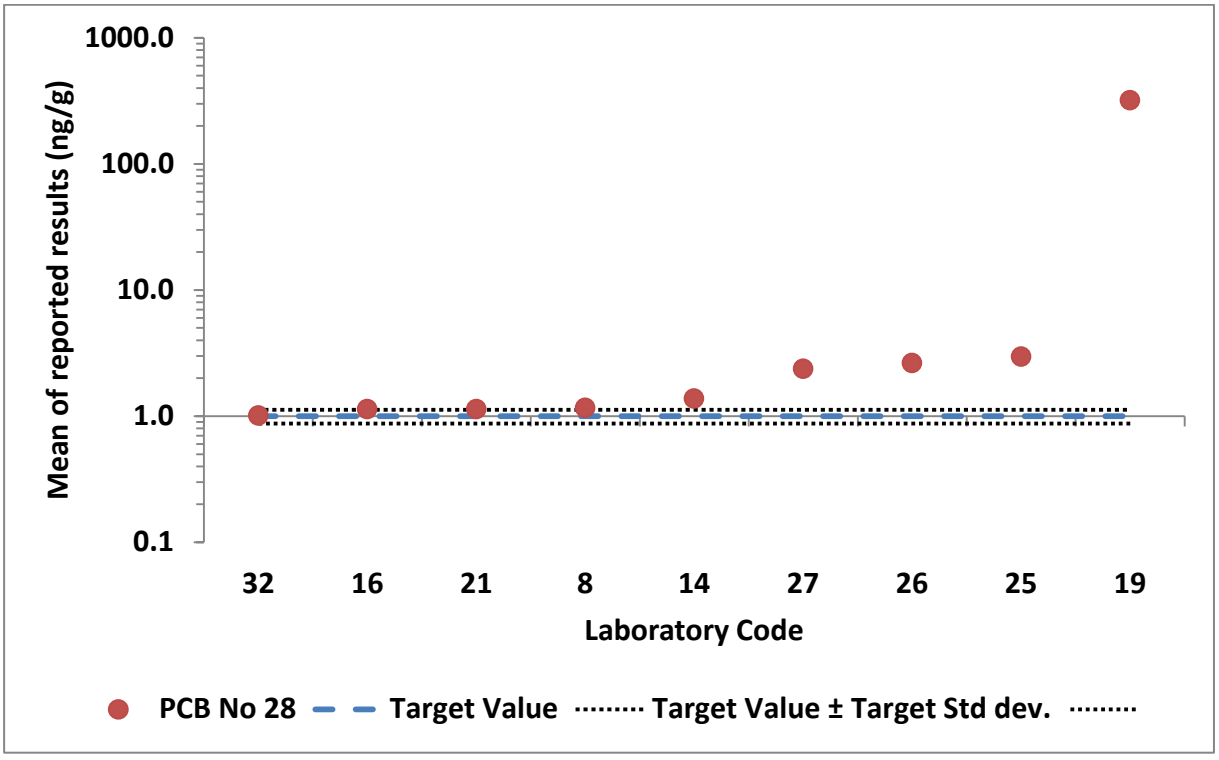

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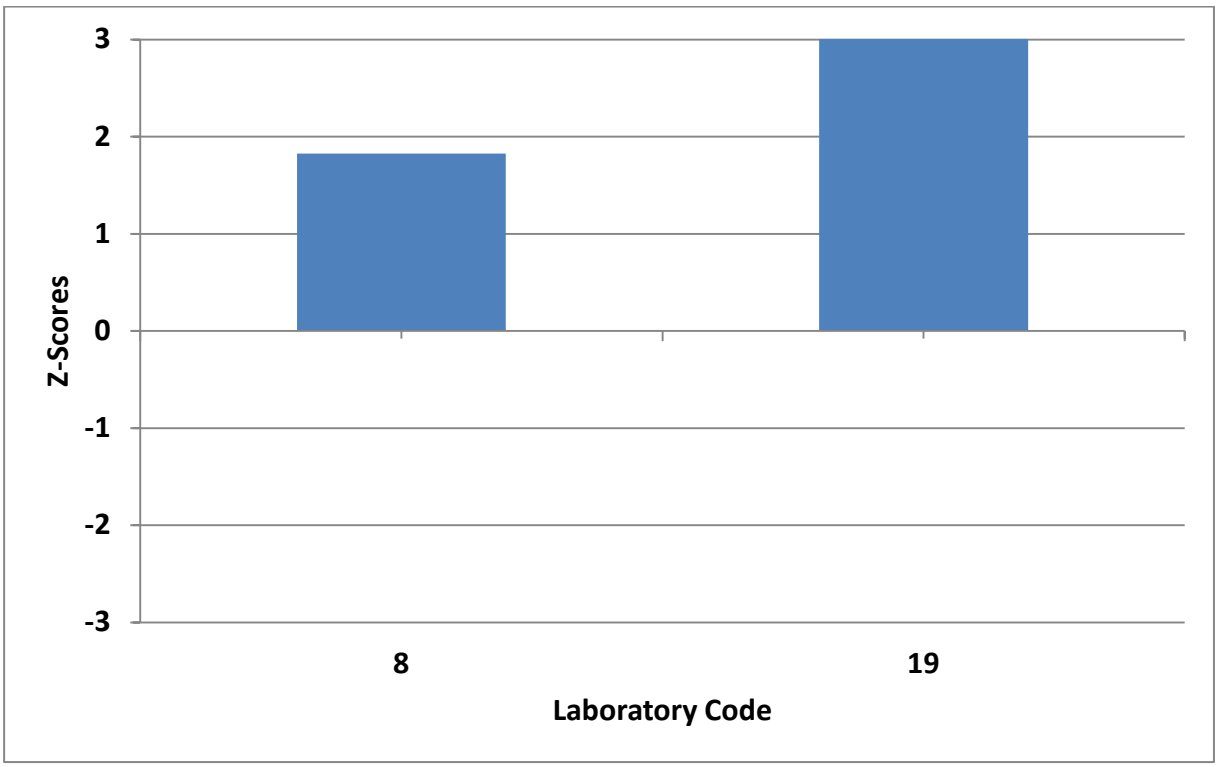

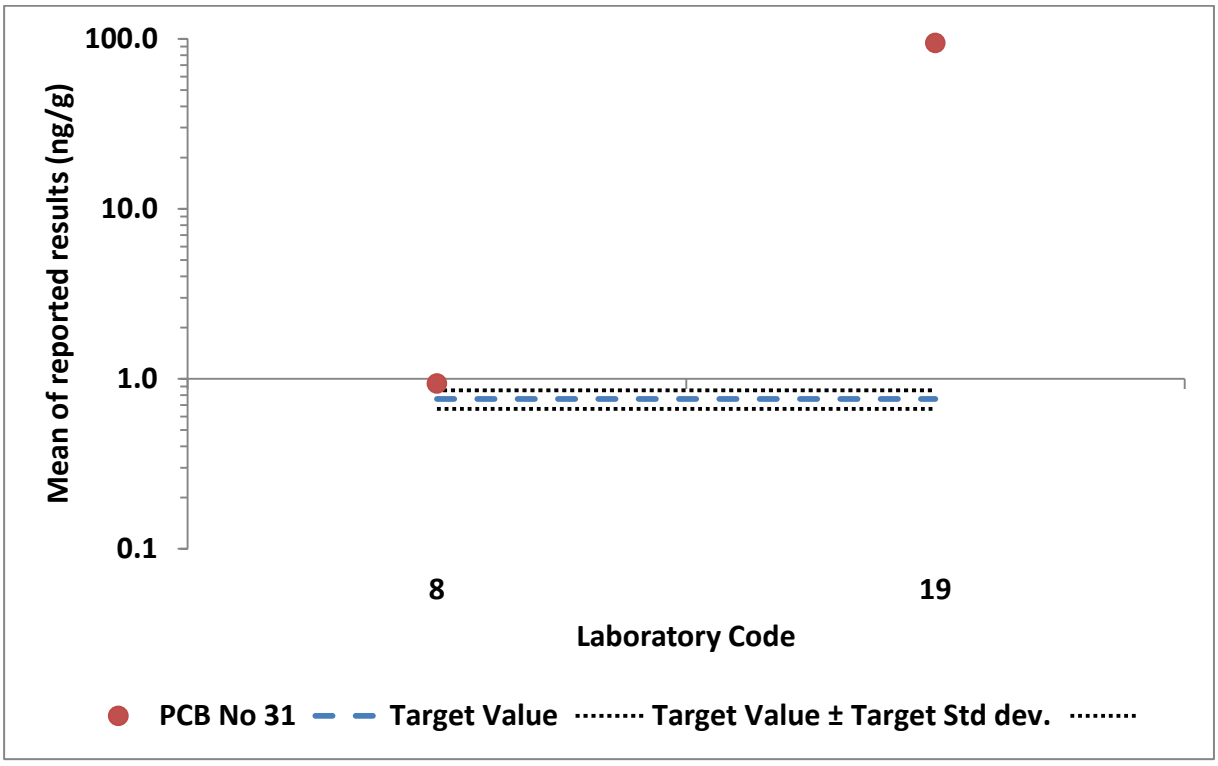

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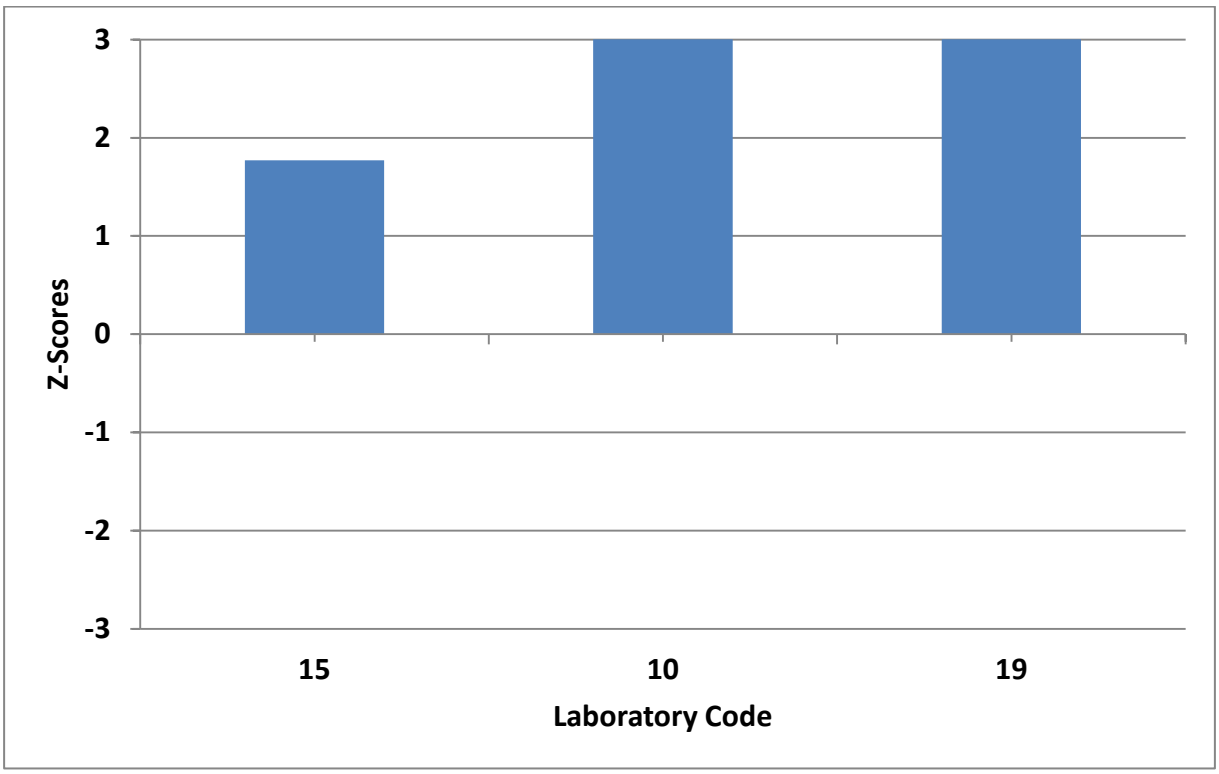

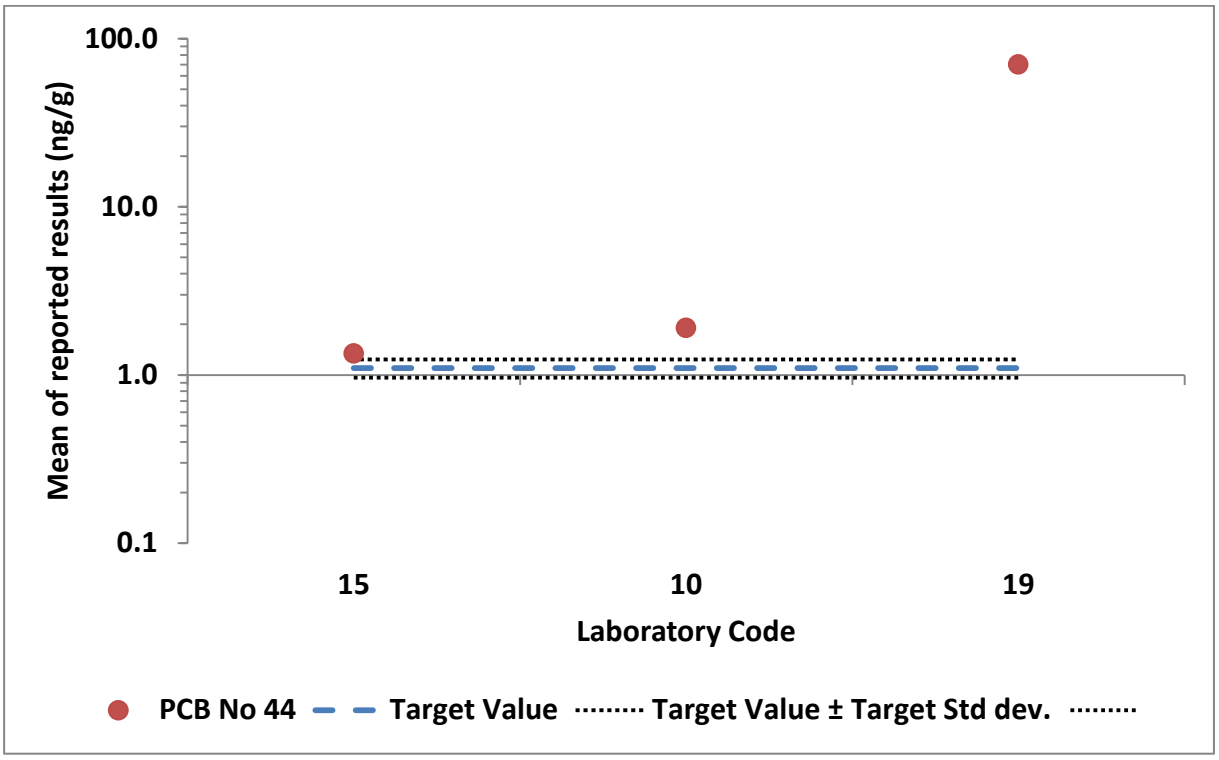

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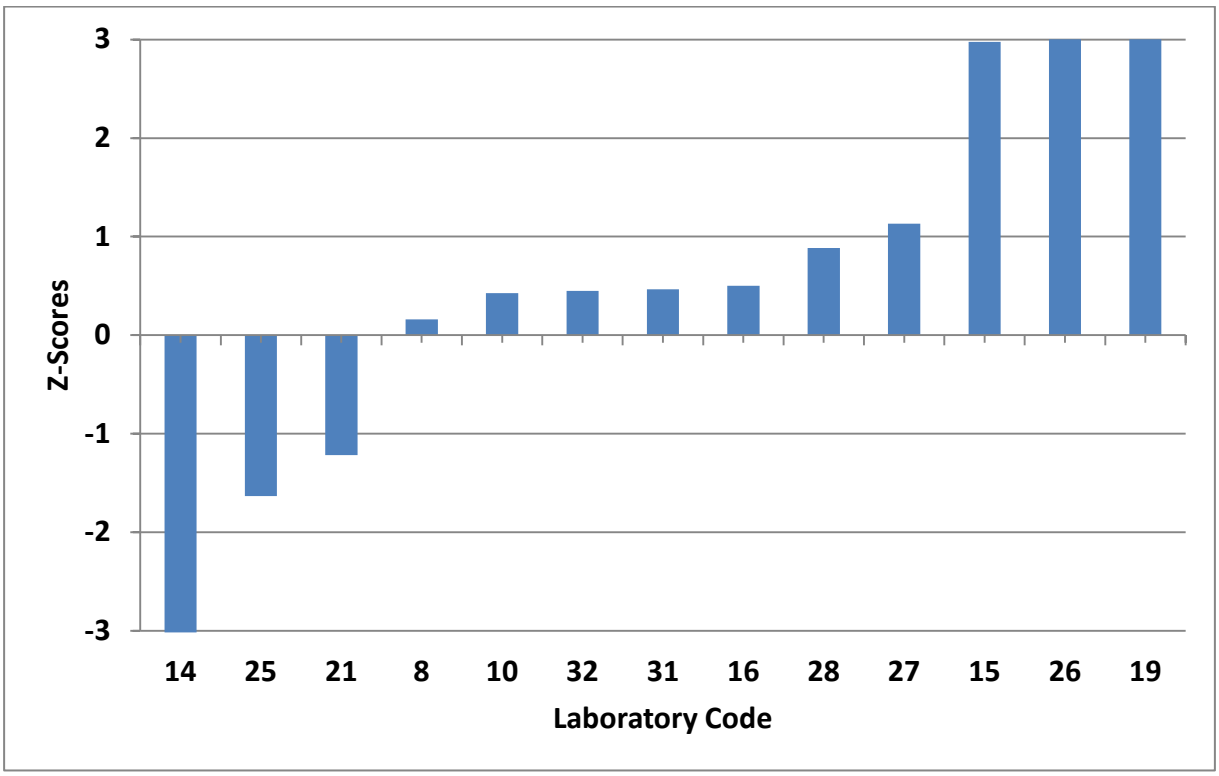

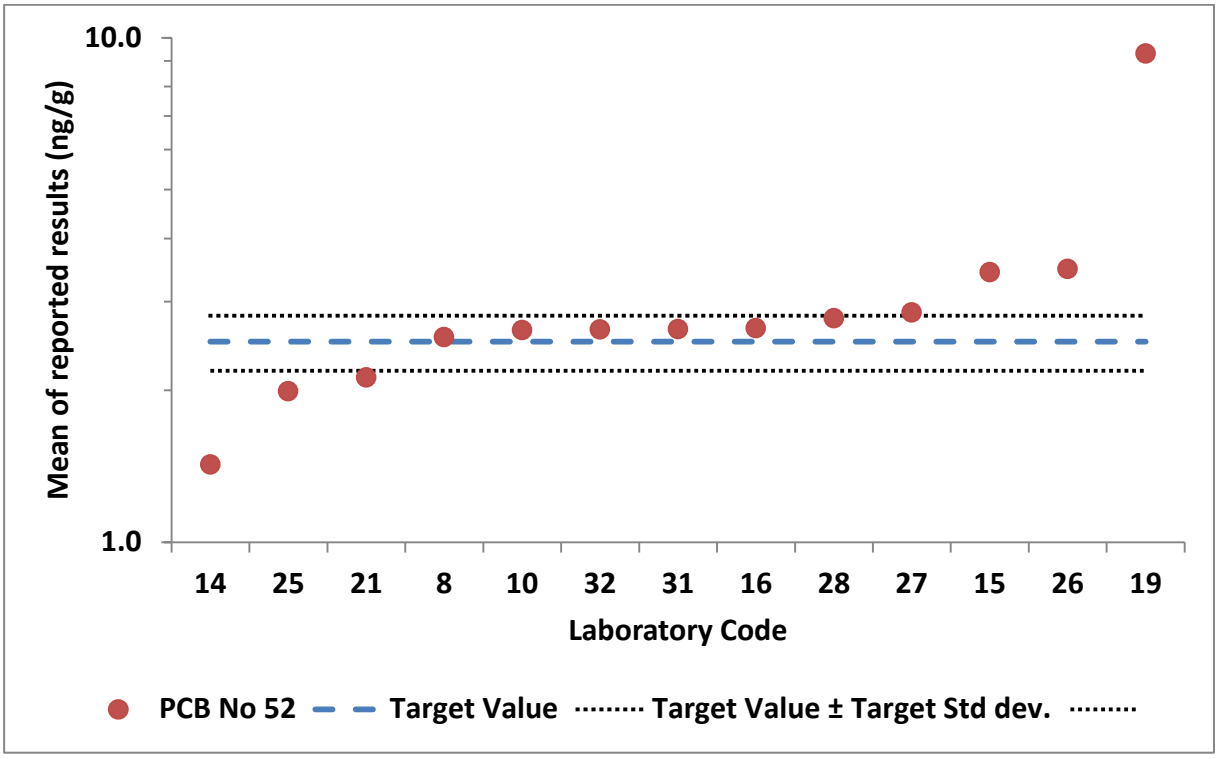

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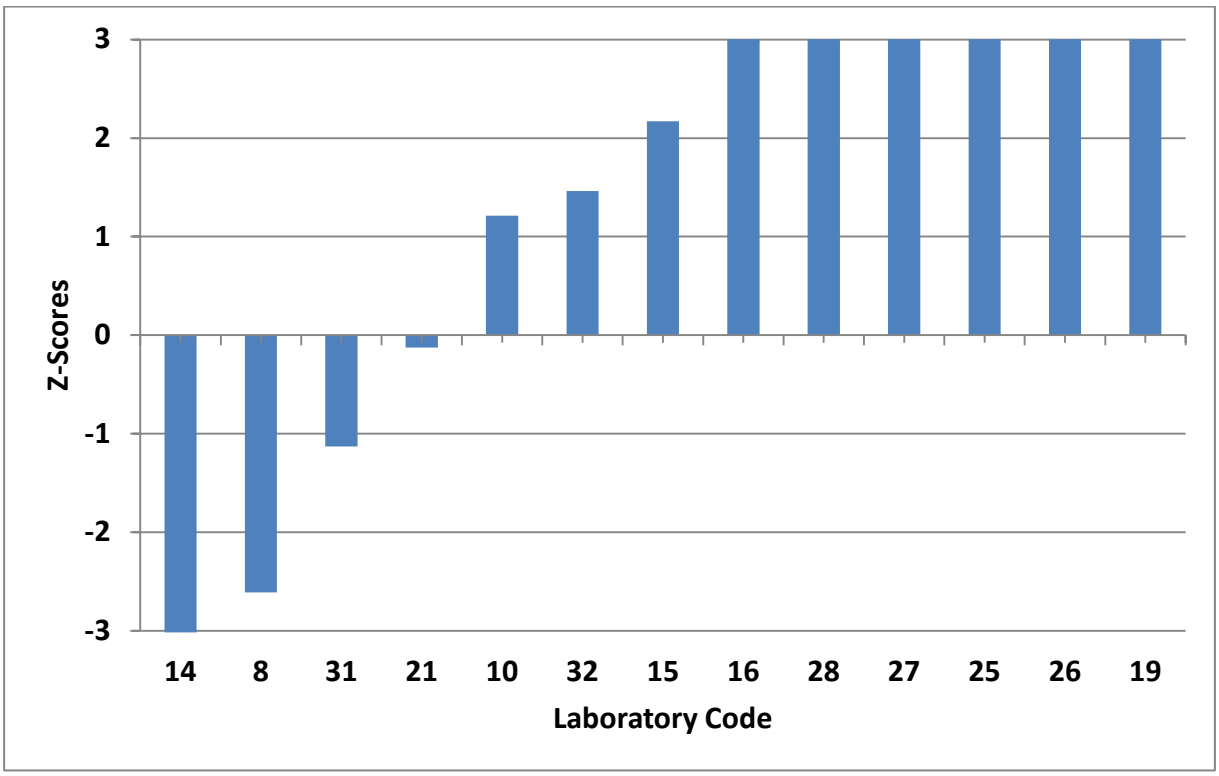

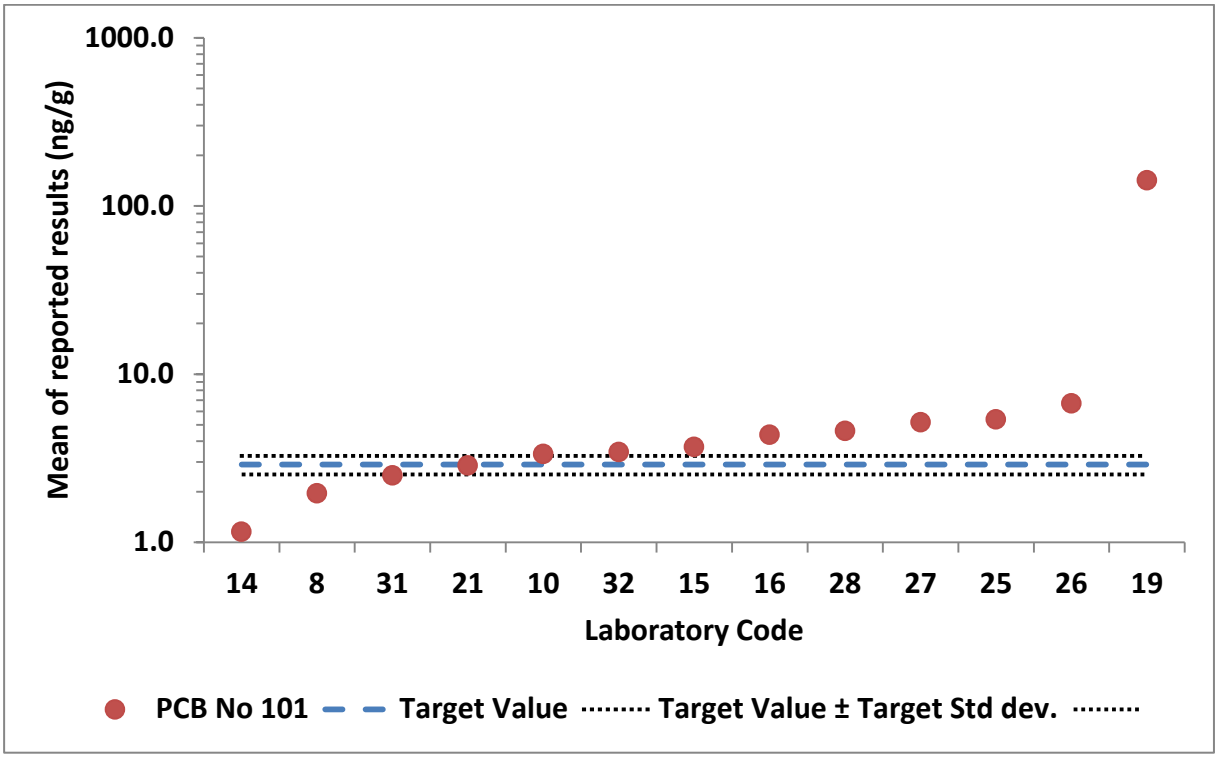

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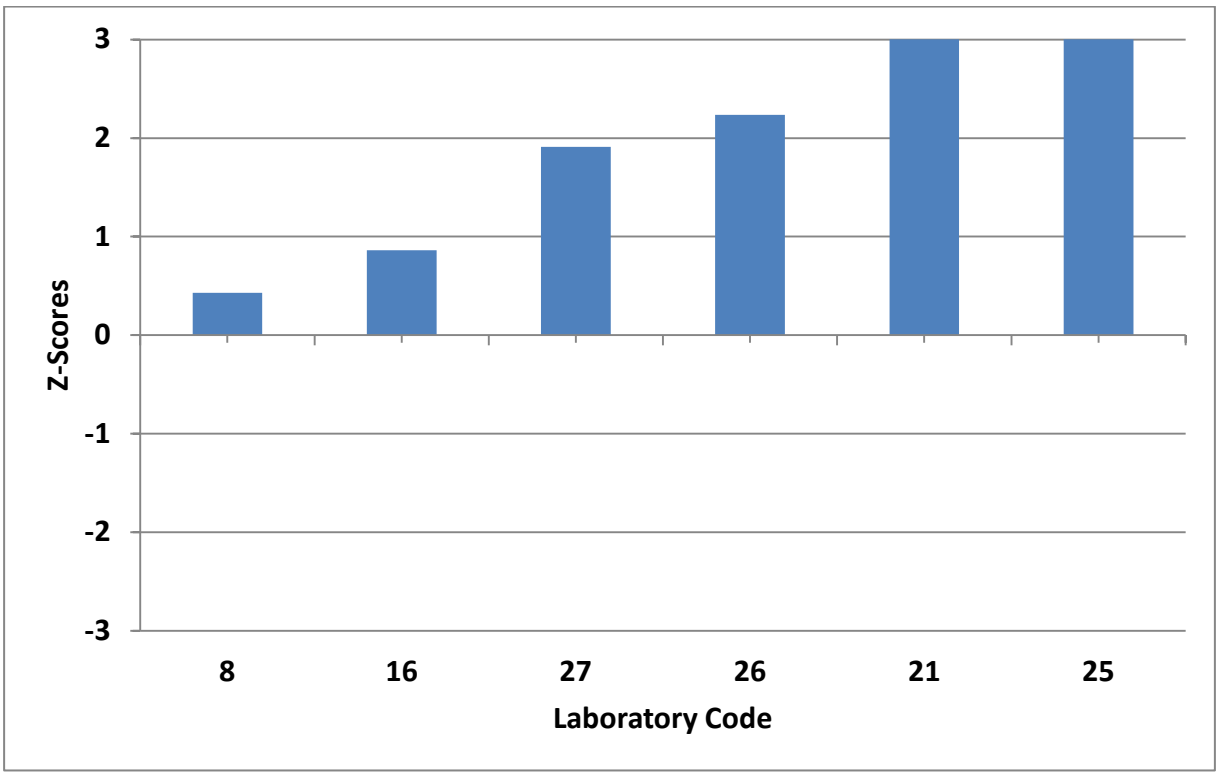

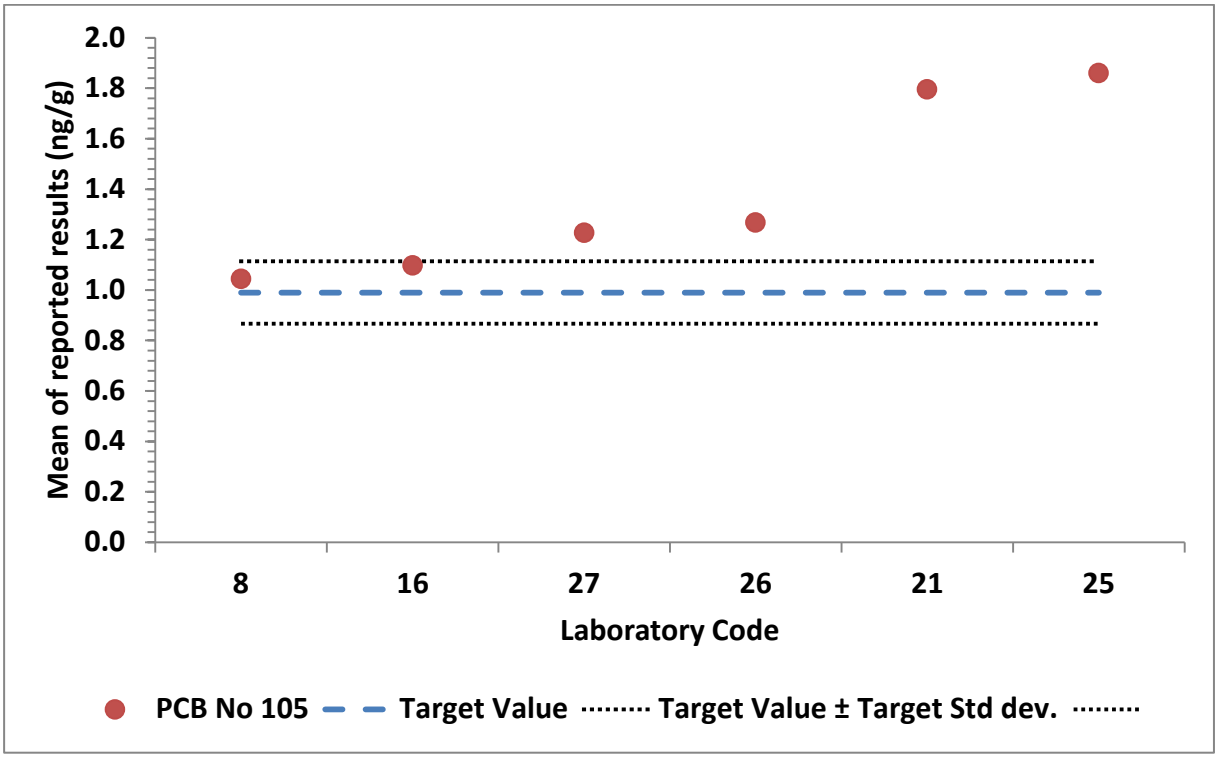

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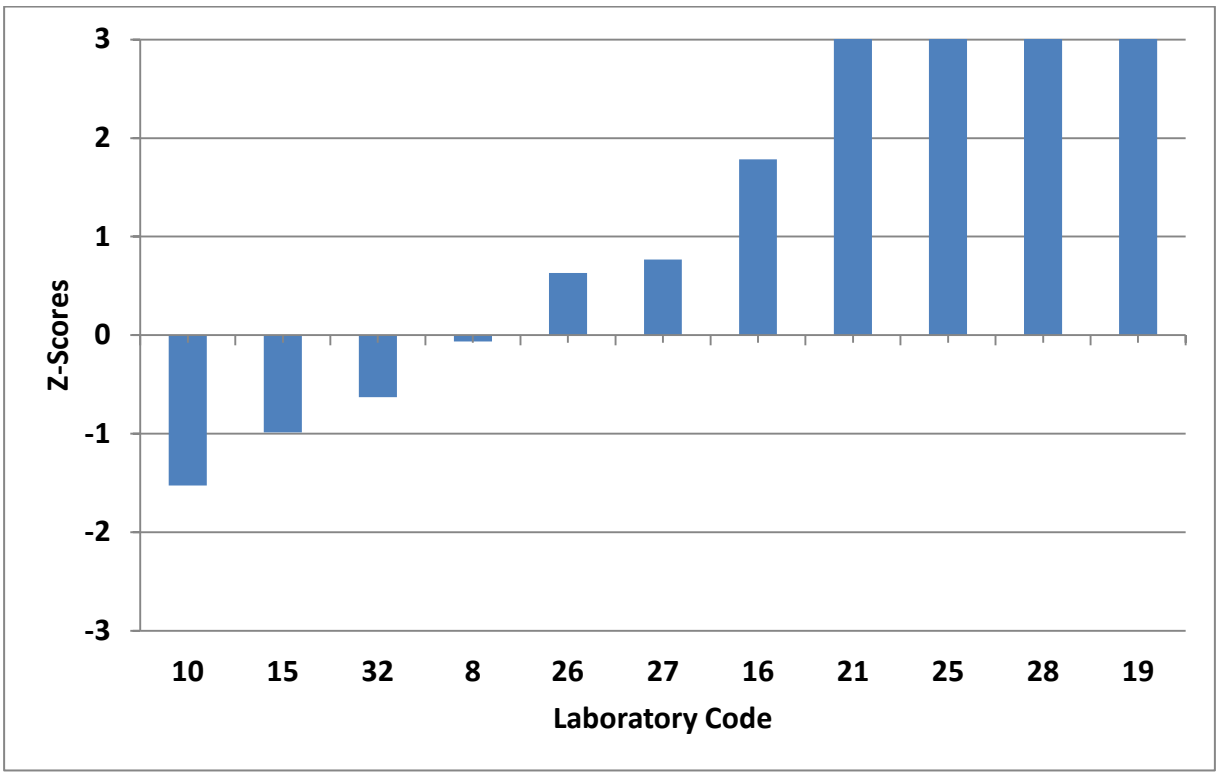

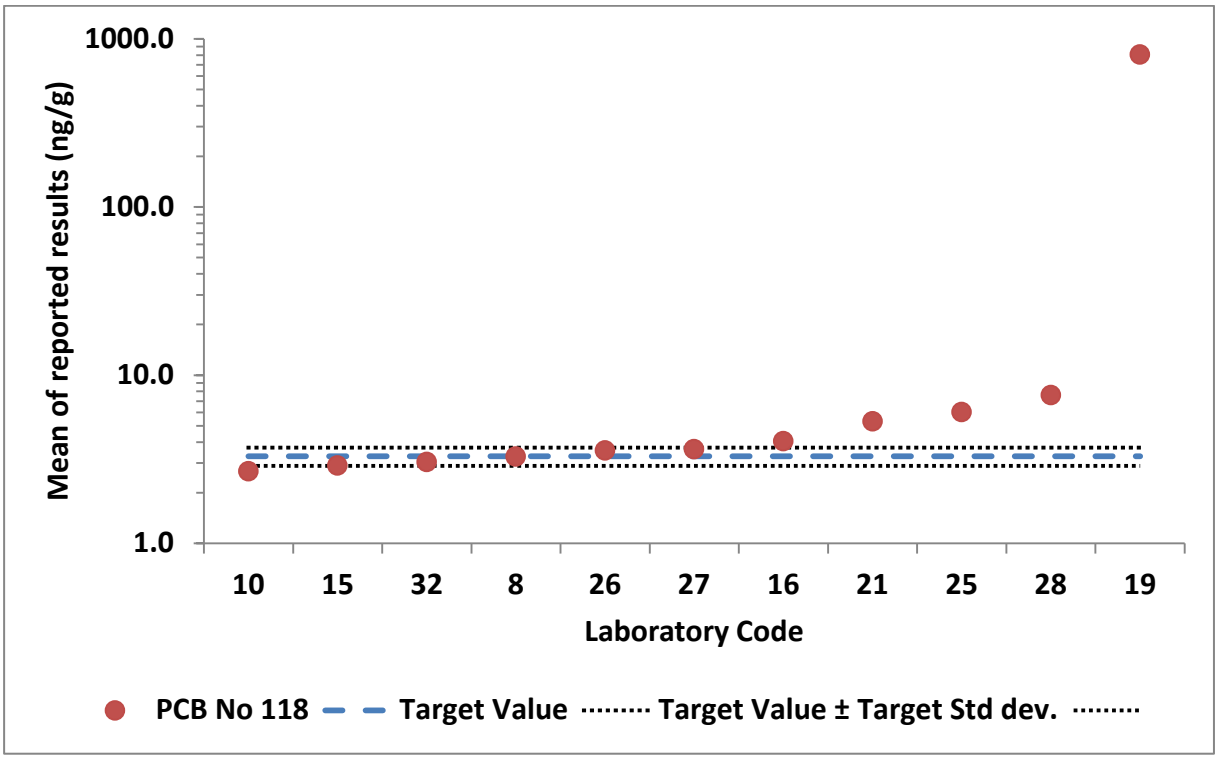

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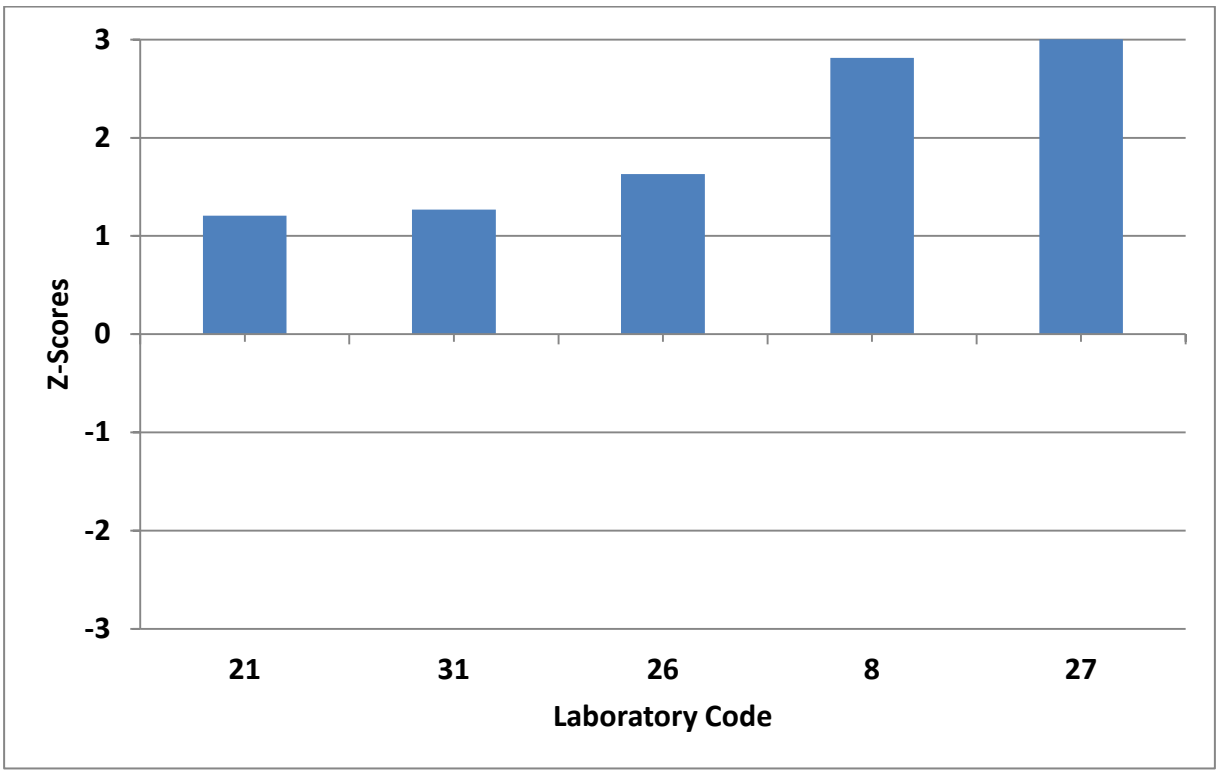

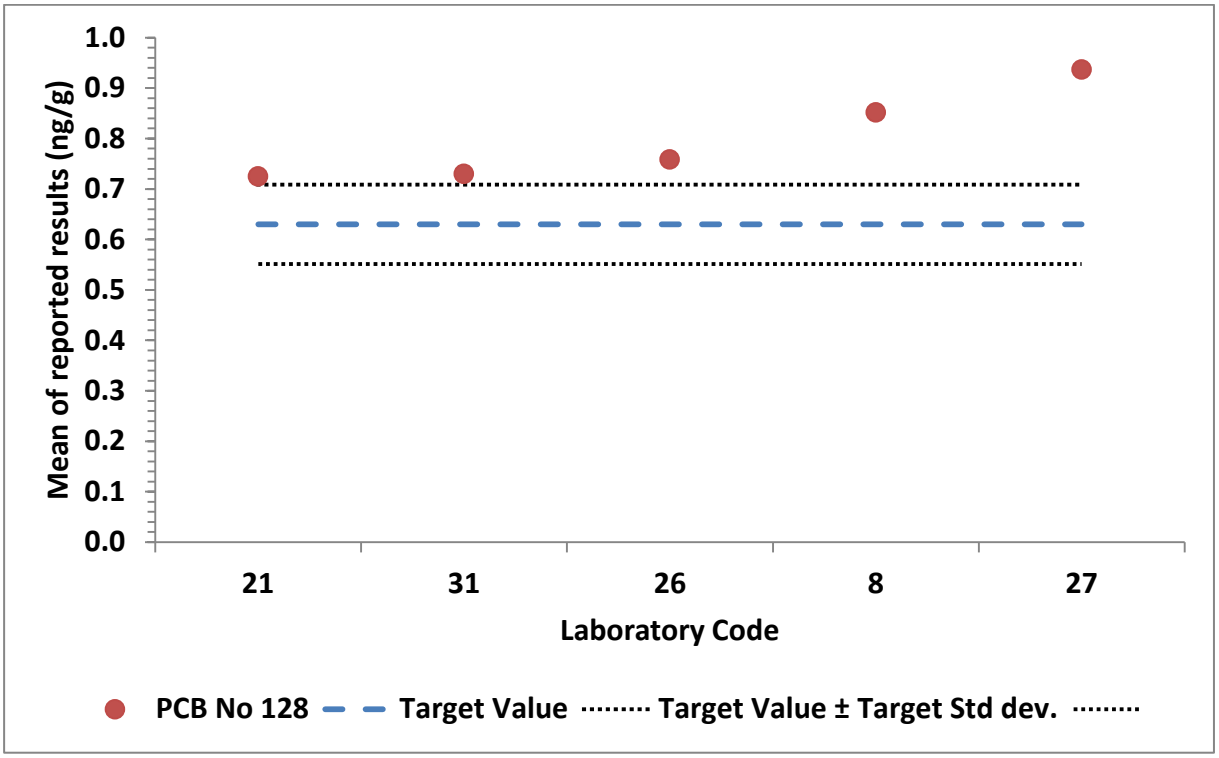

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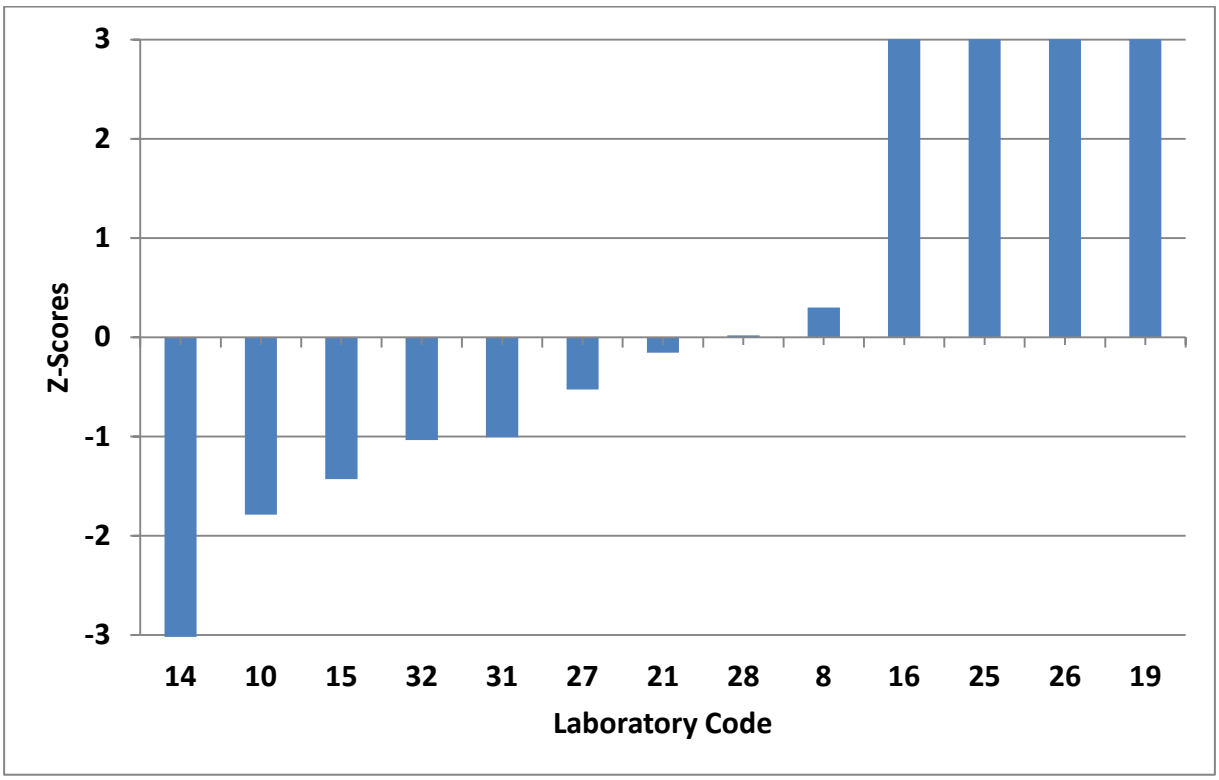
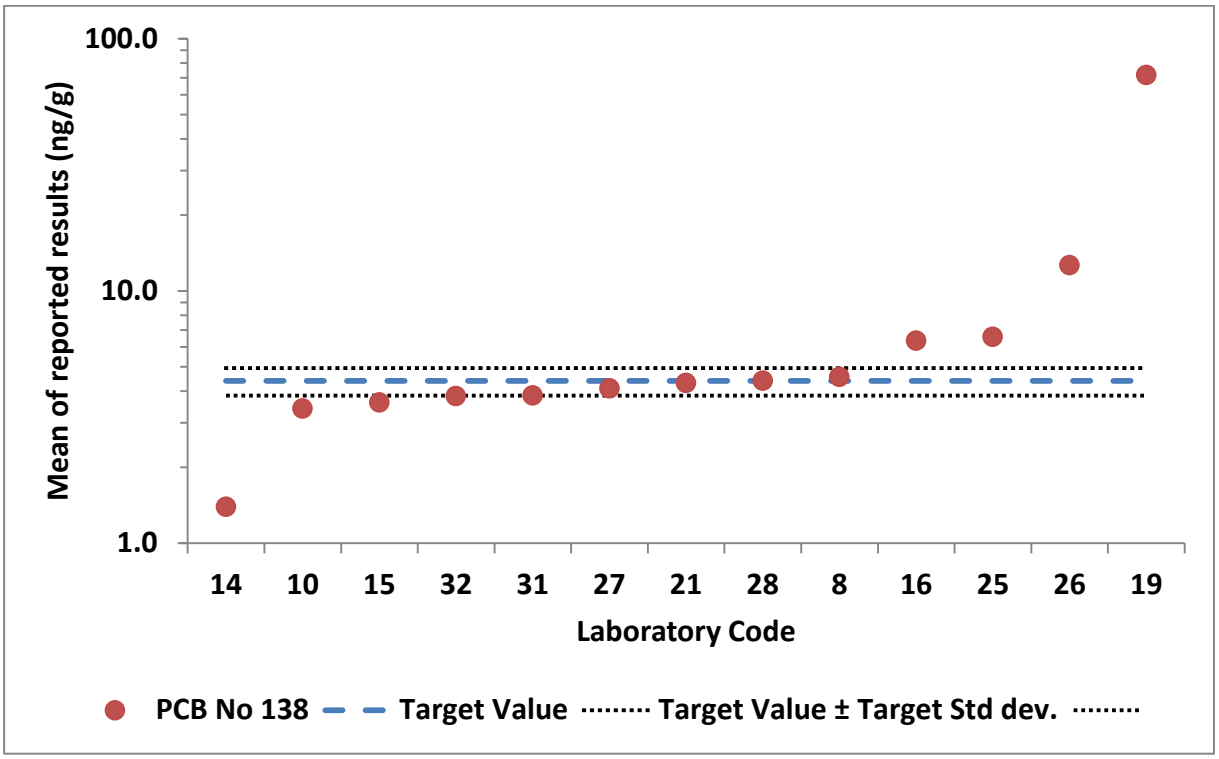
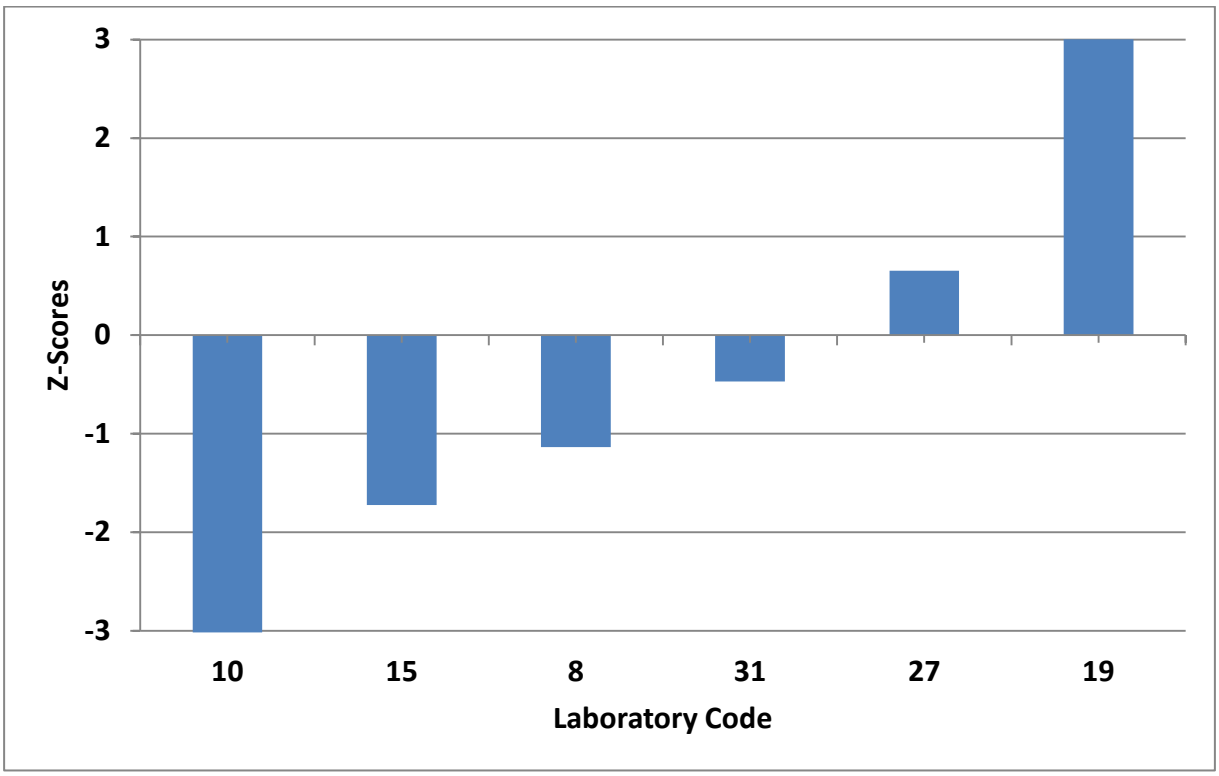
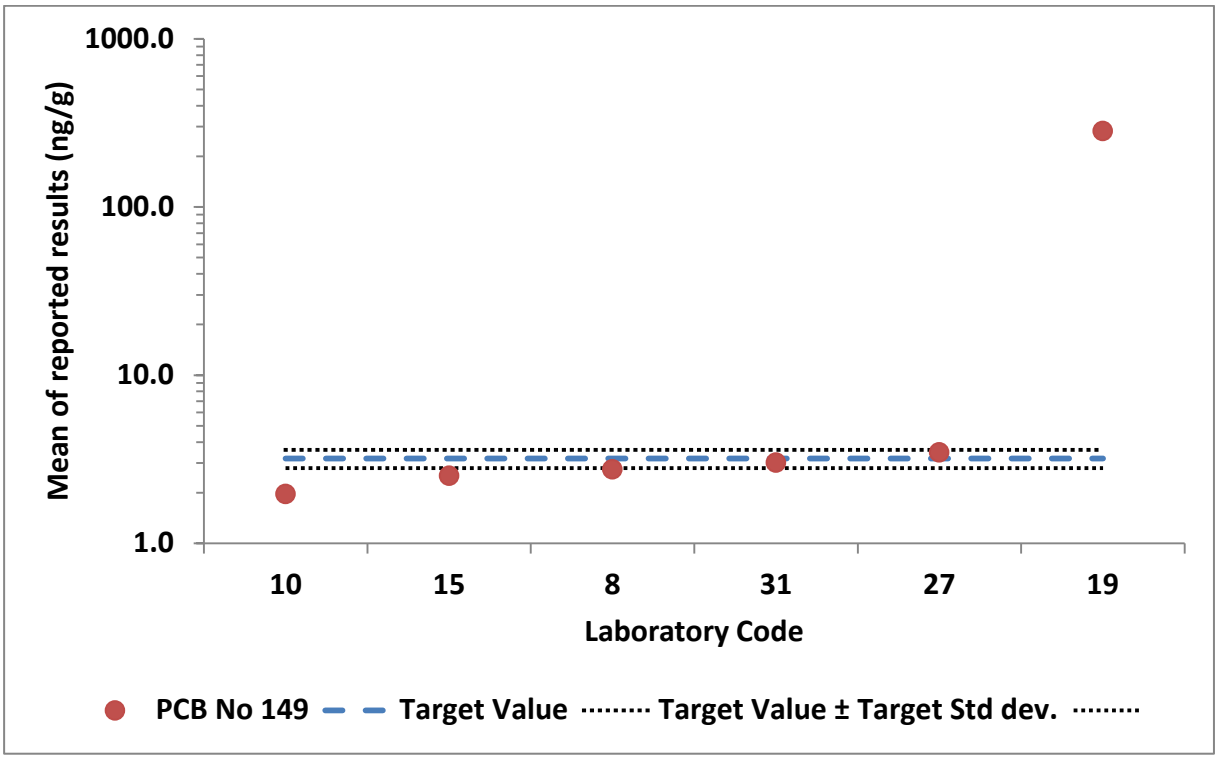


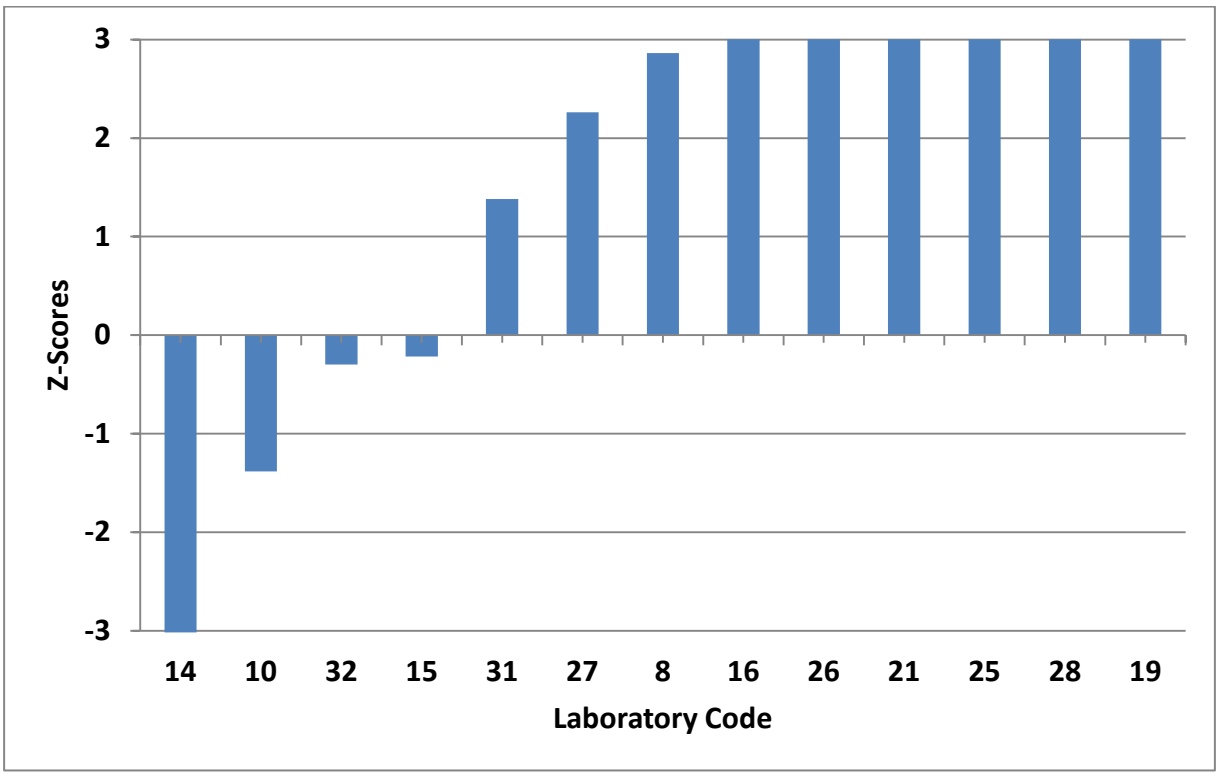


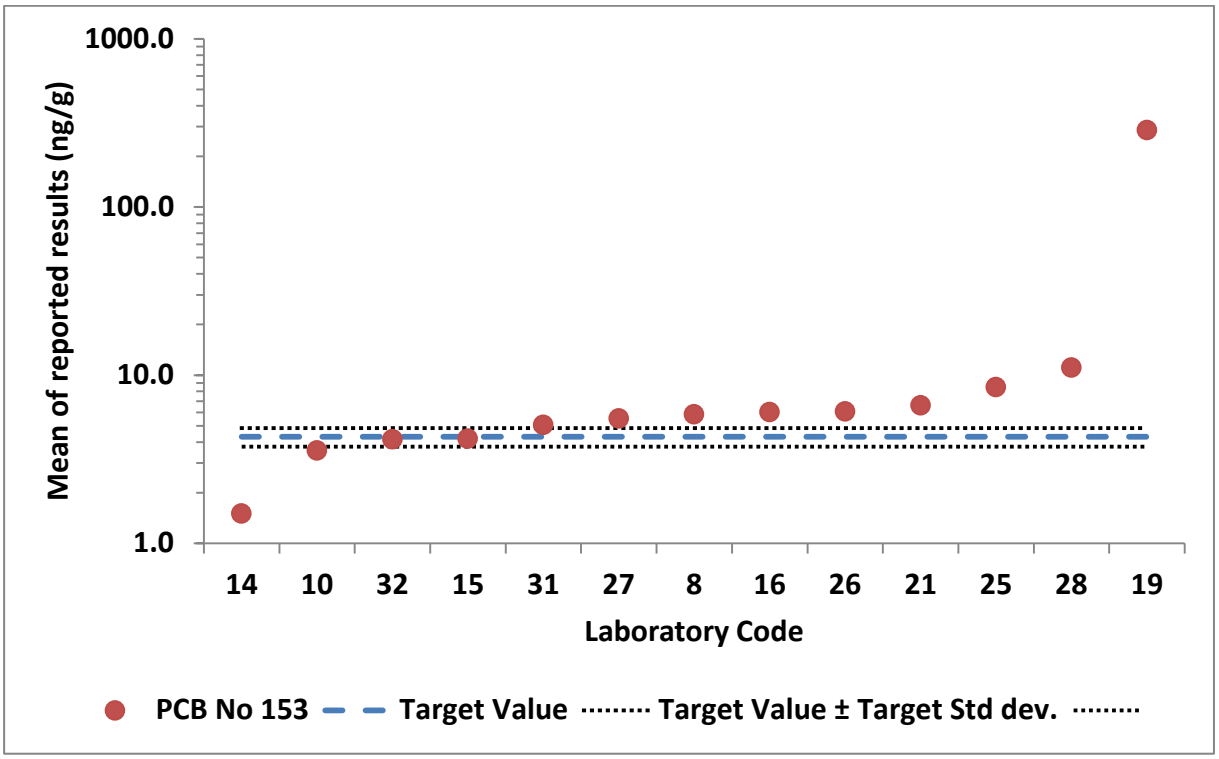
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR PCB 149



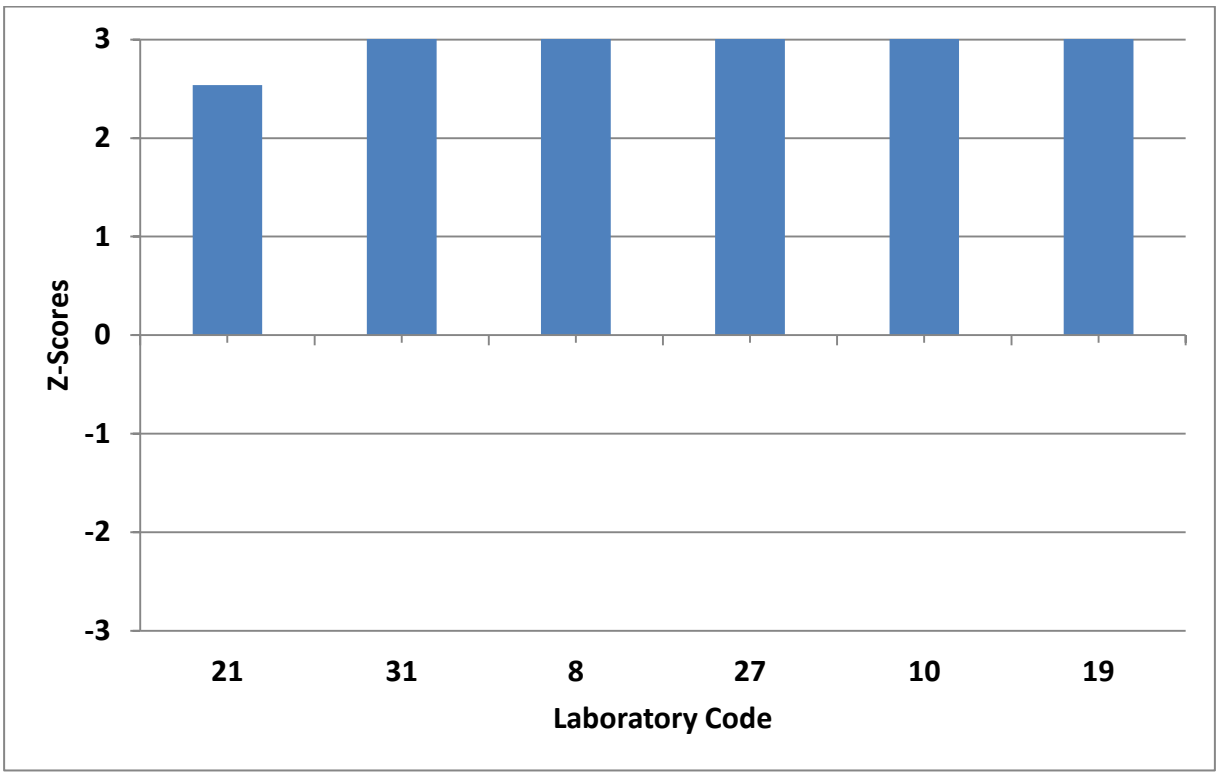


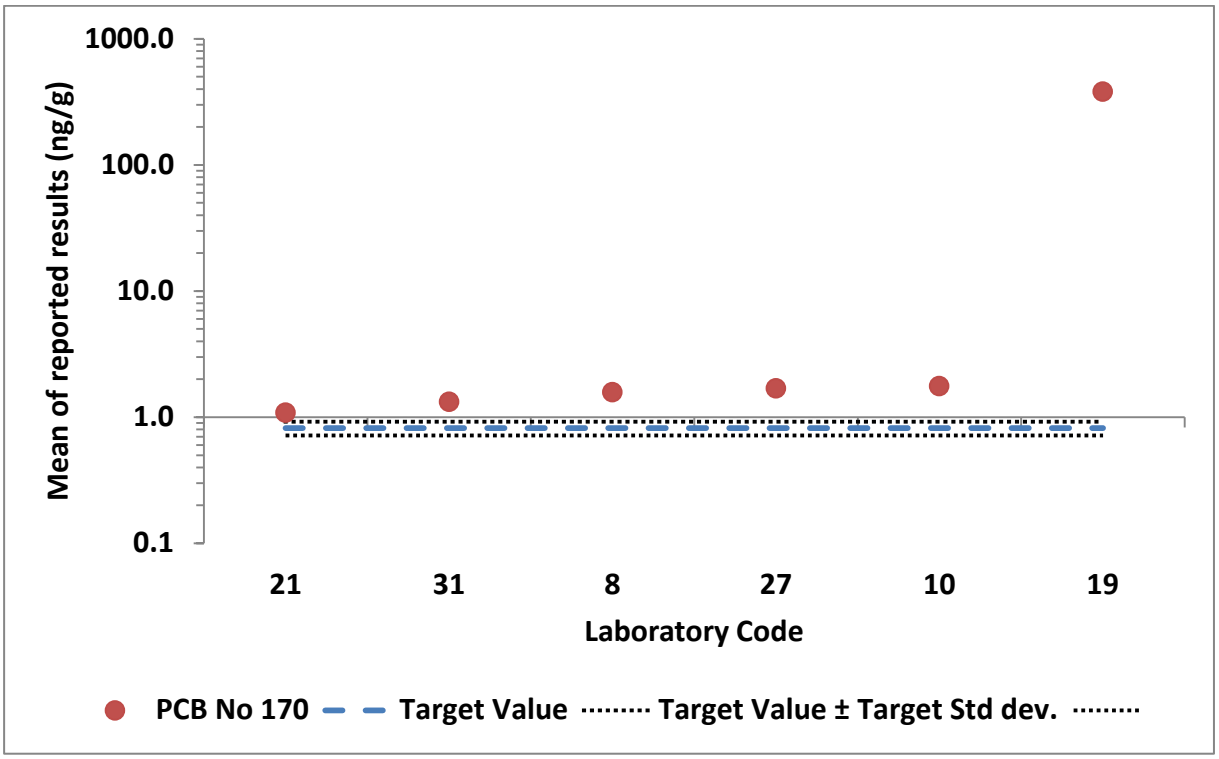
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR PCB 153



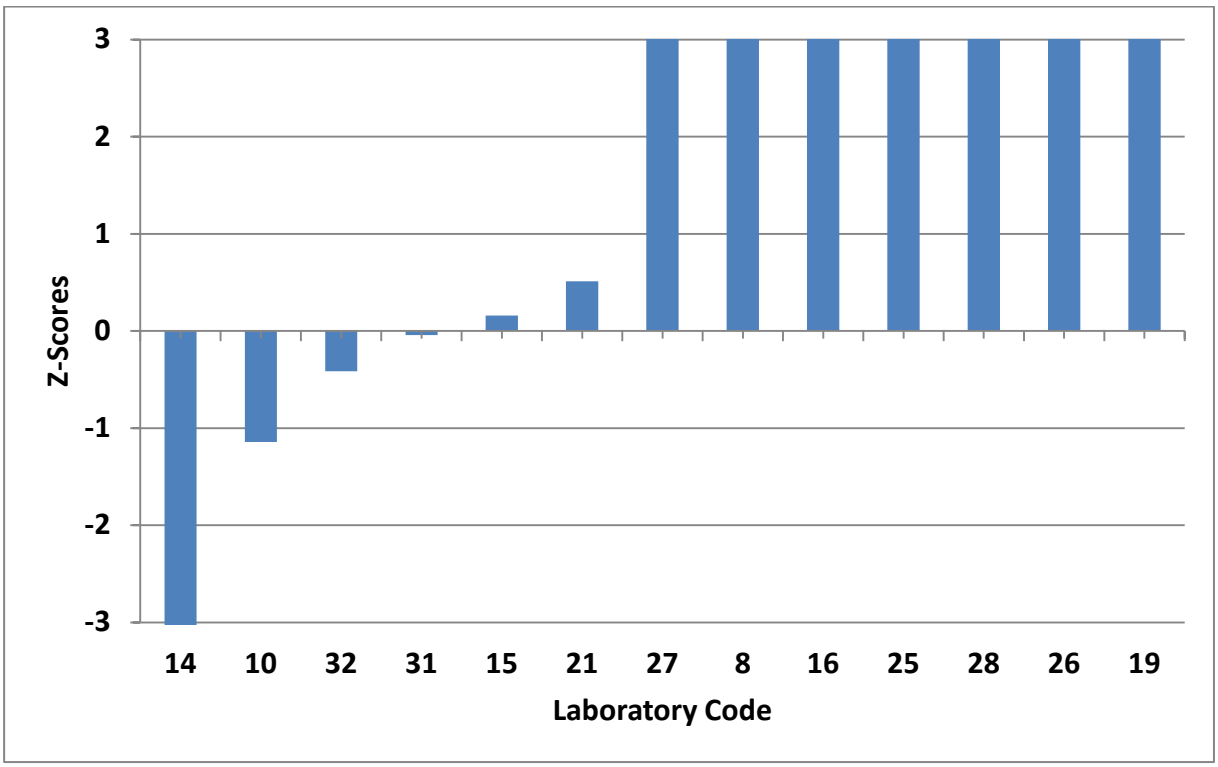


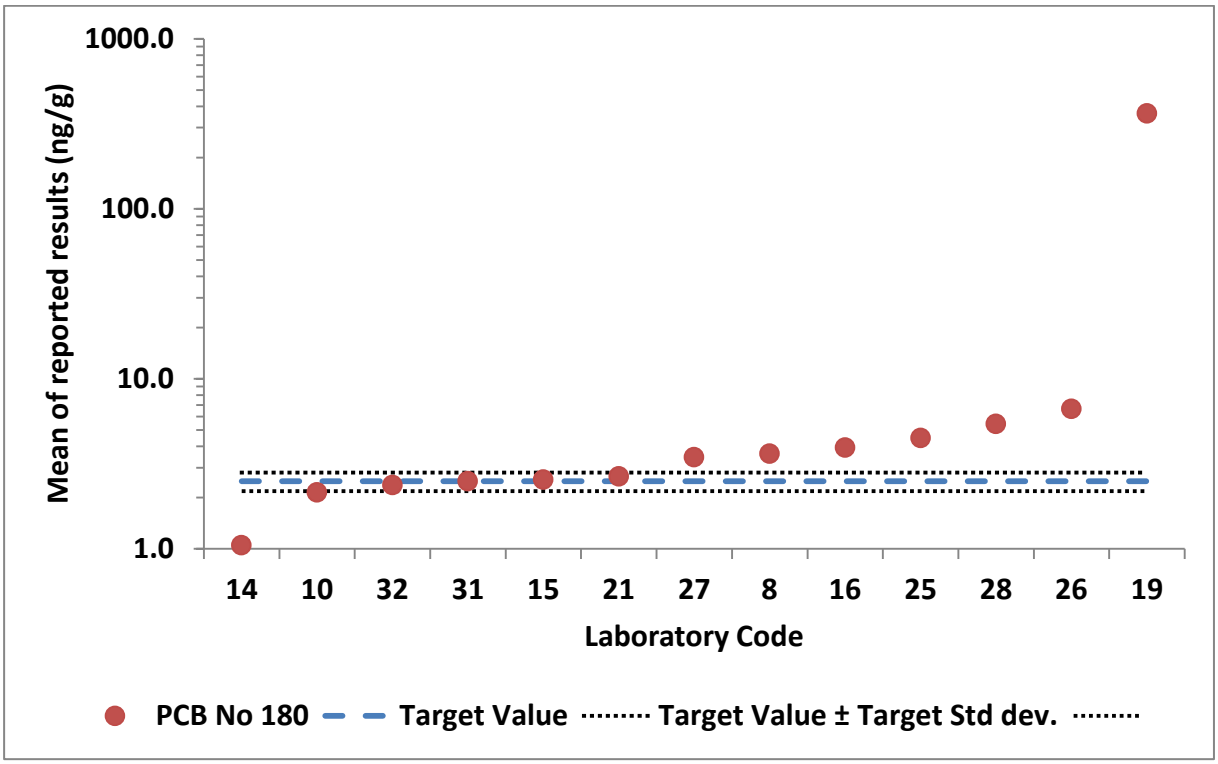
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR PCB 170



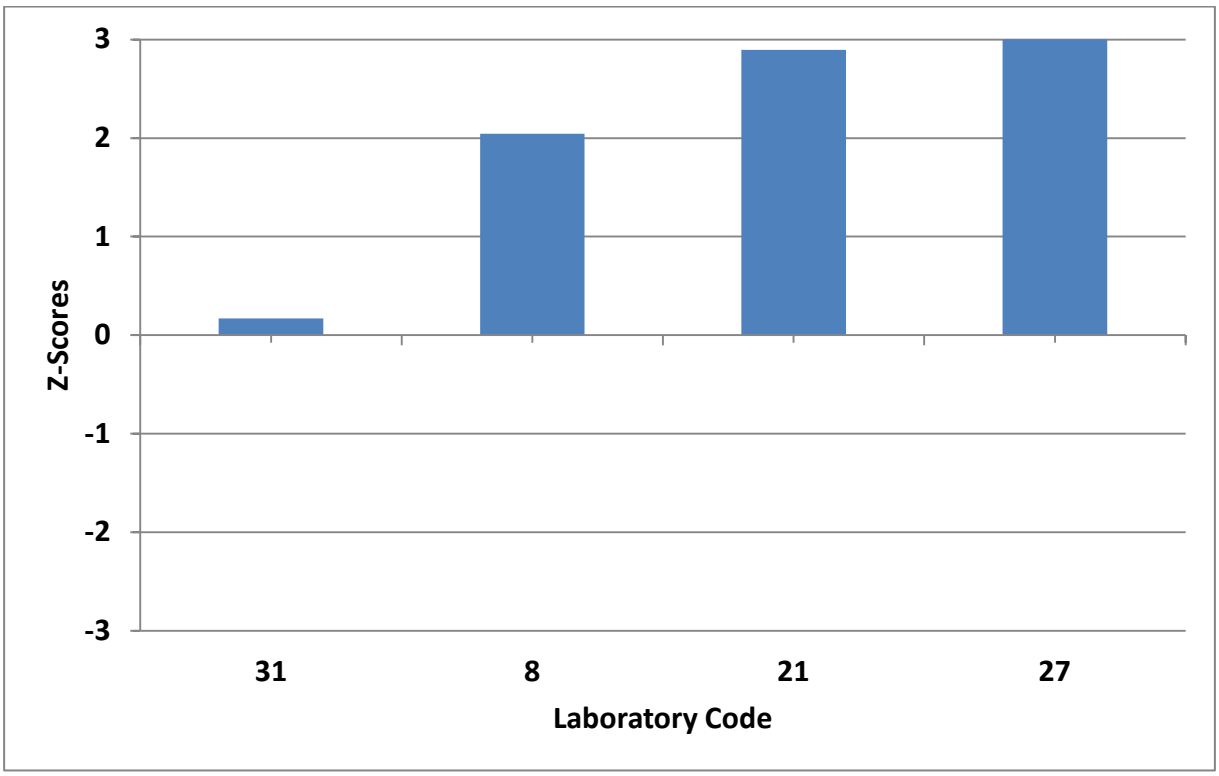


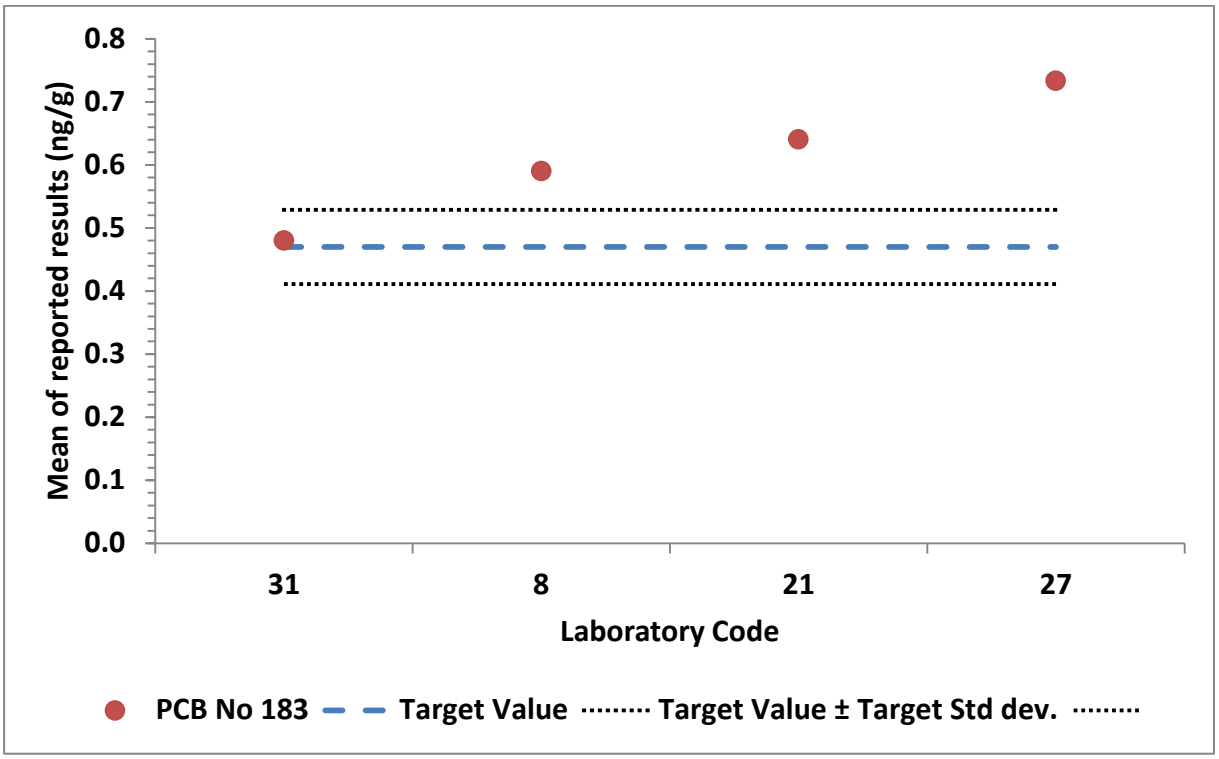
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR PCB 180



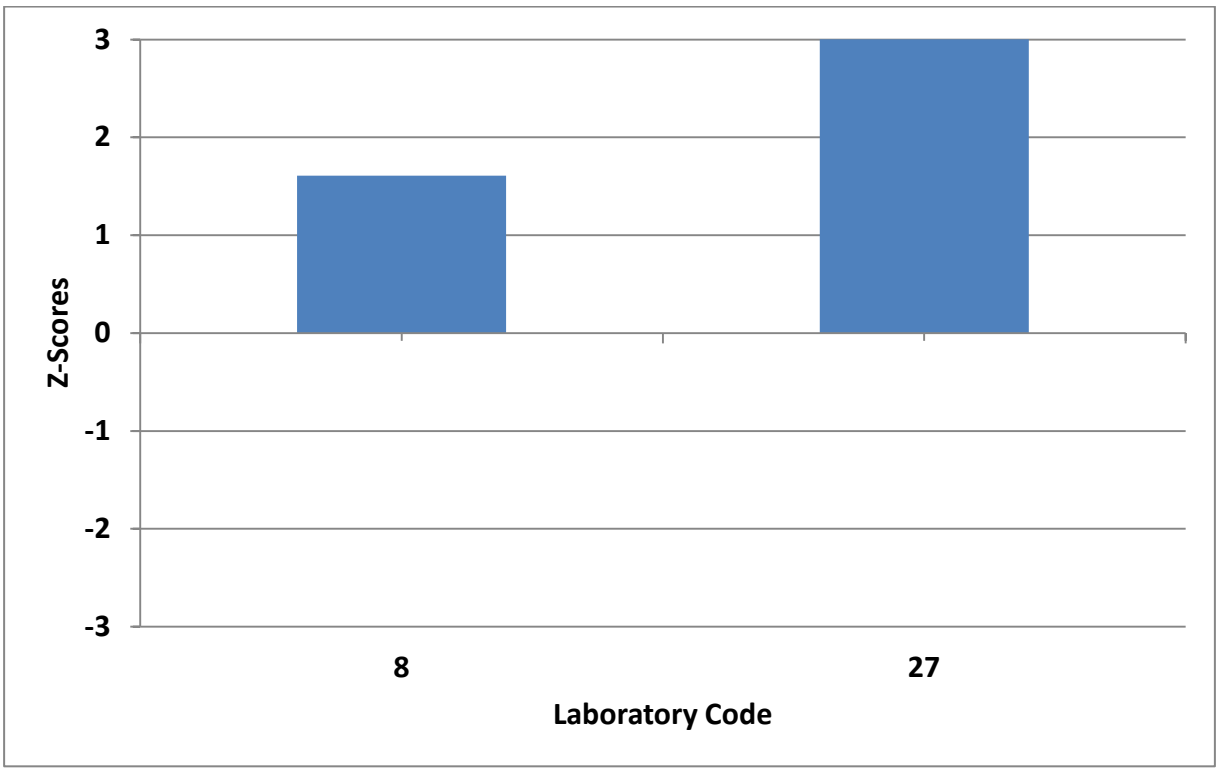


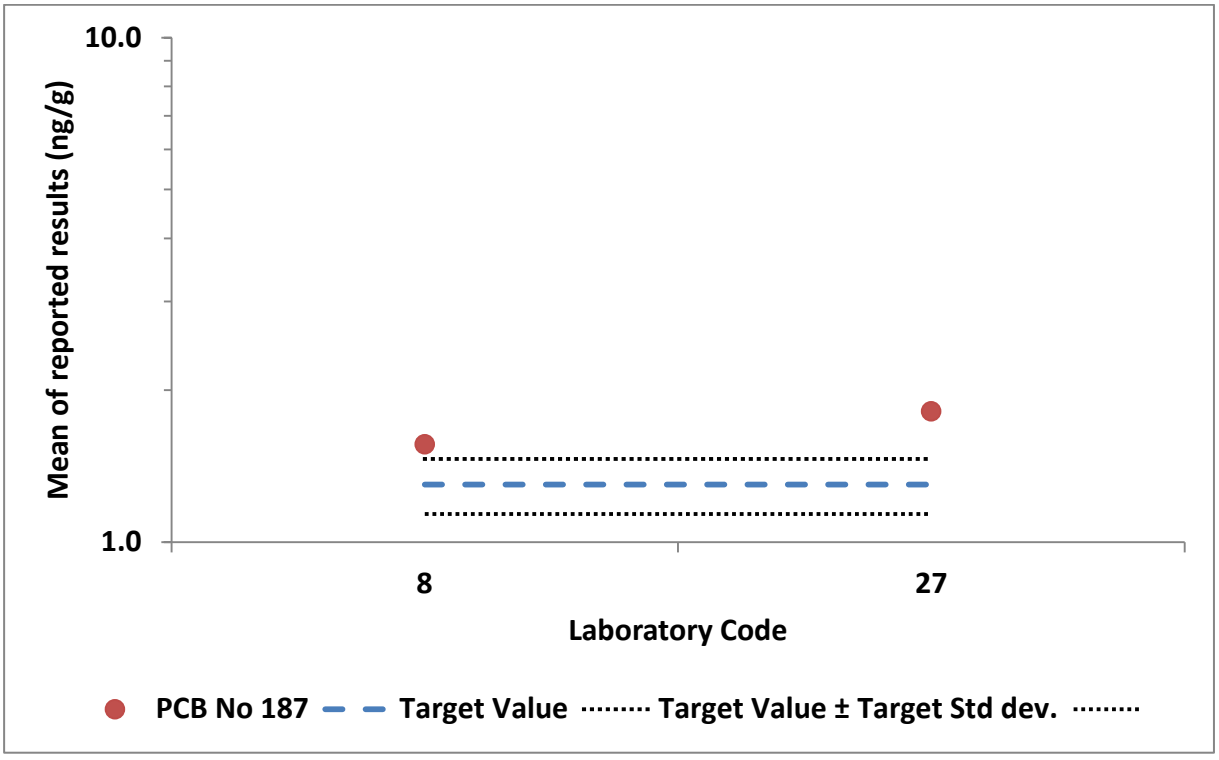
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR PCB 183



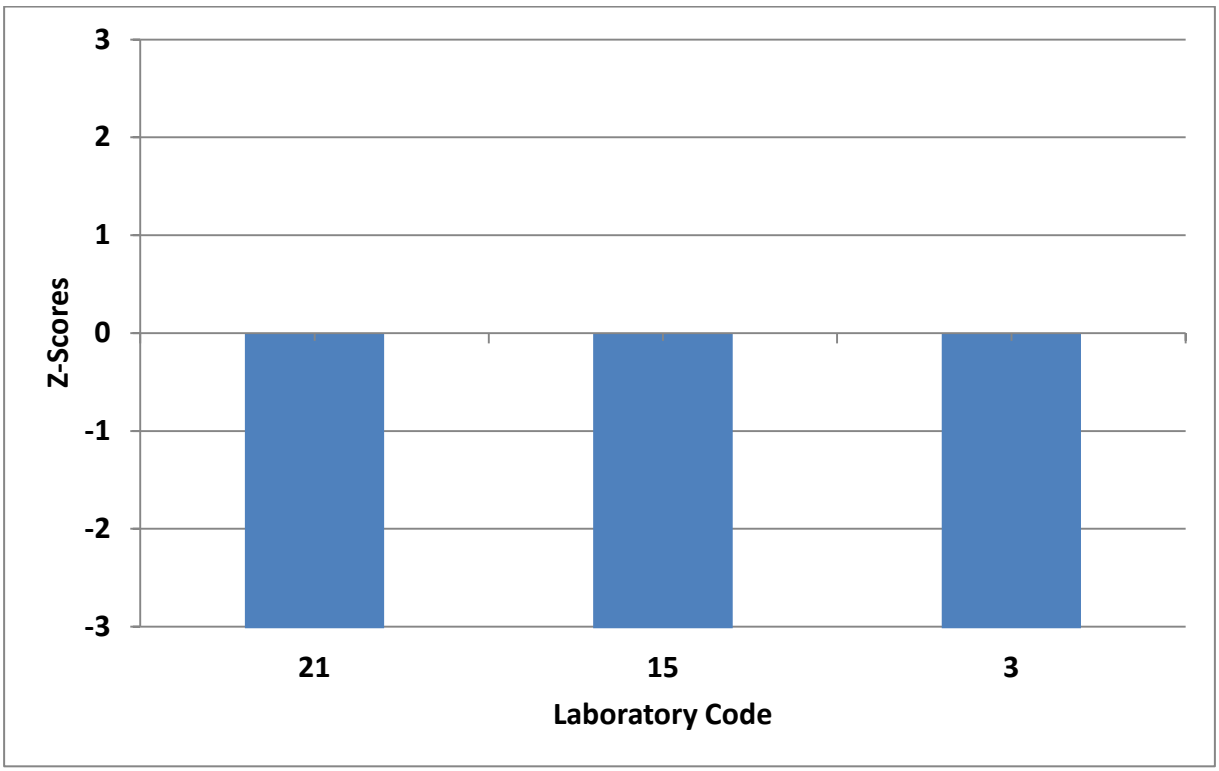


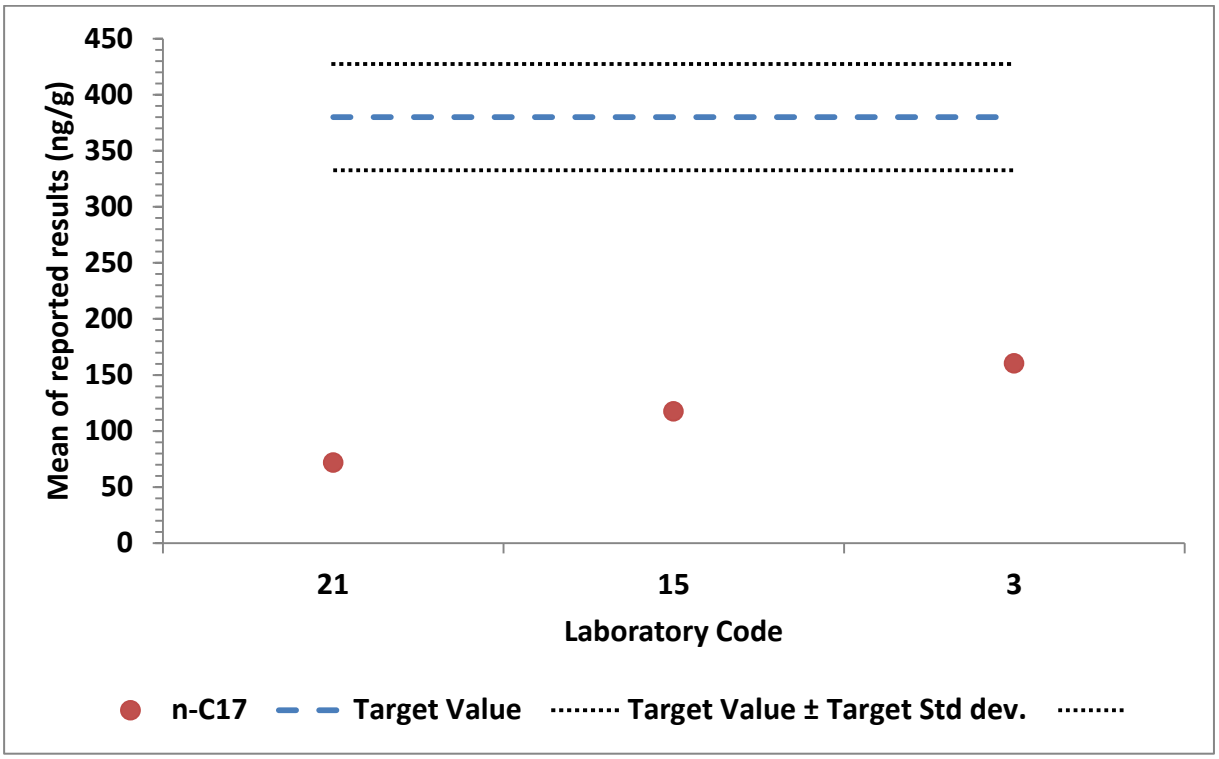
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR PCB 187



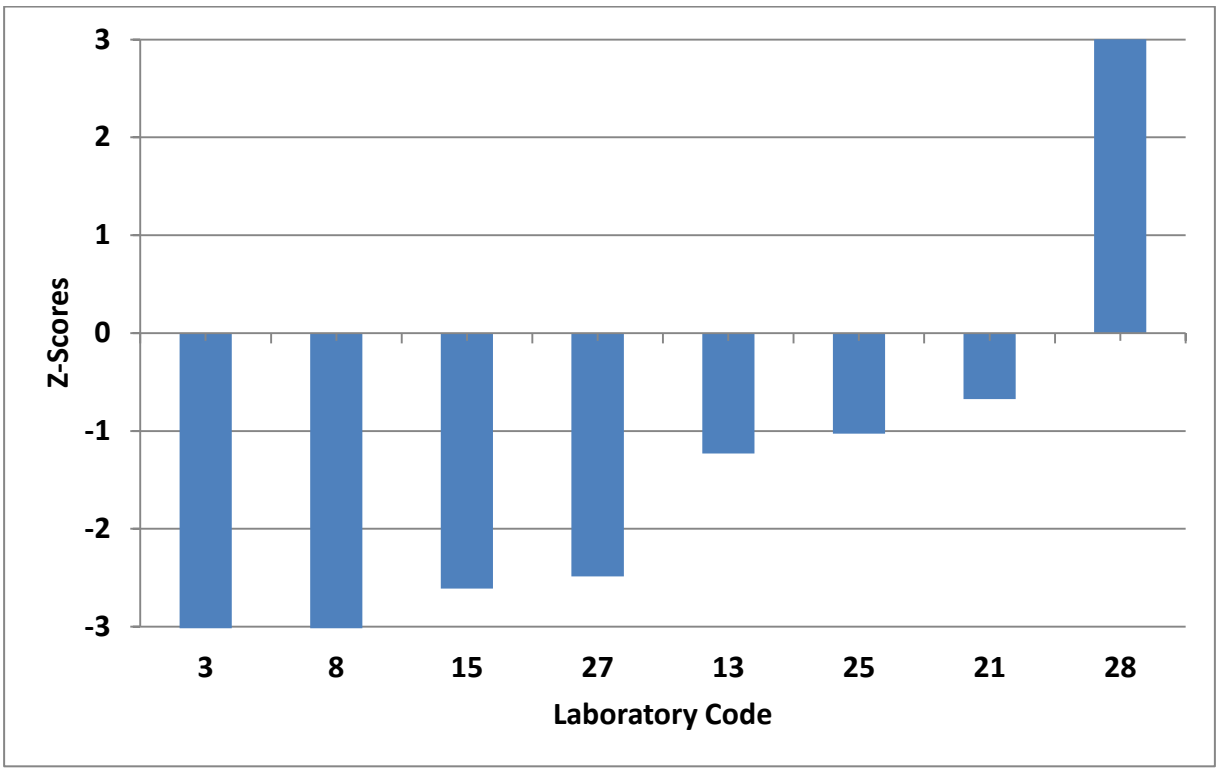


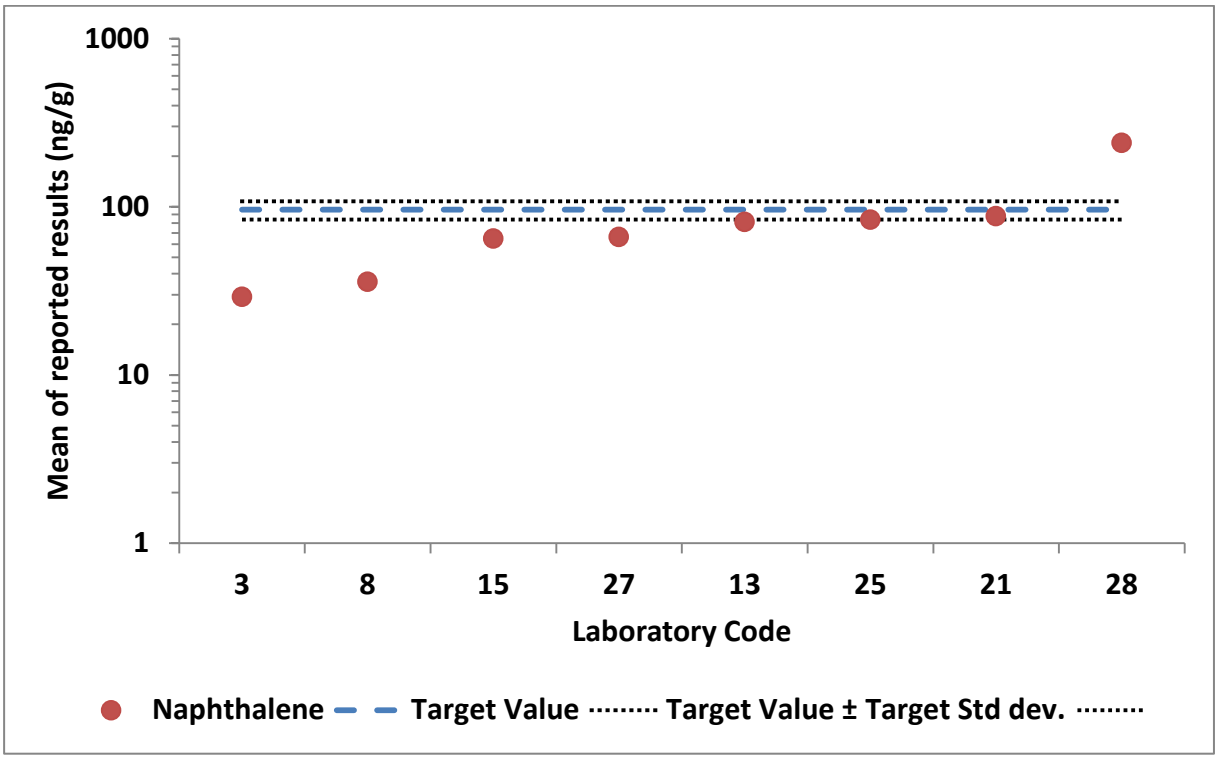
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR C-17



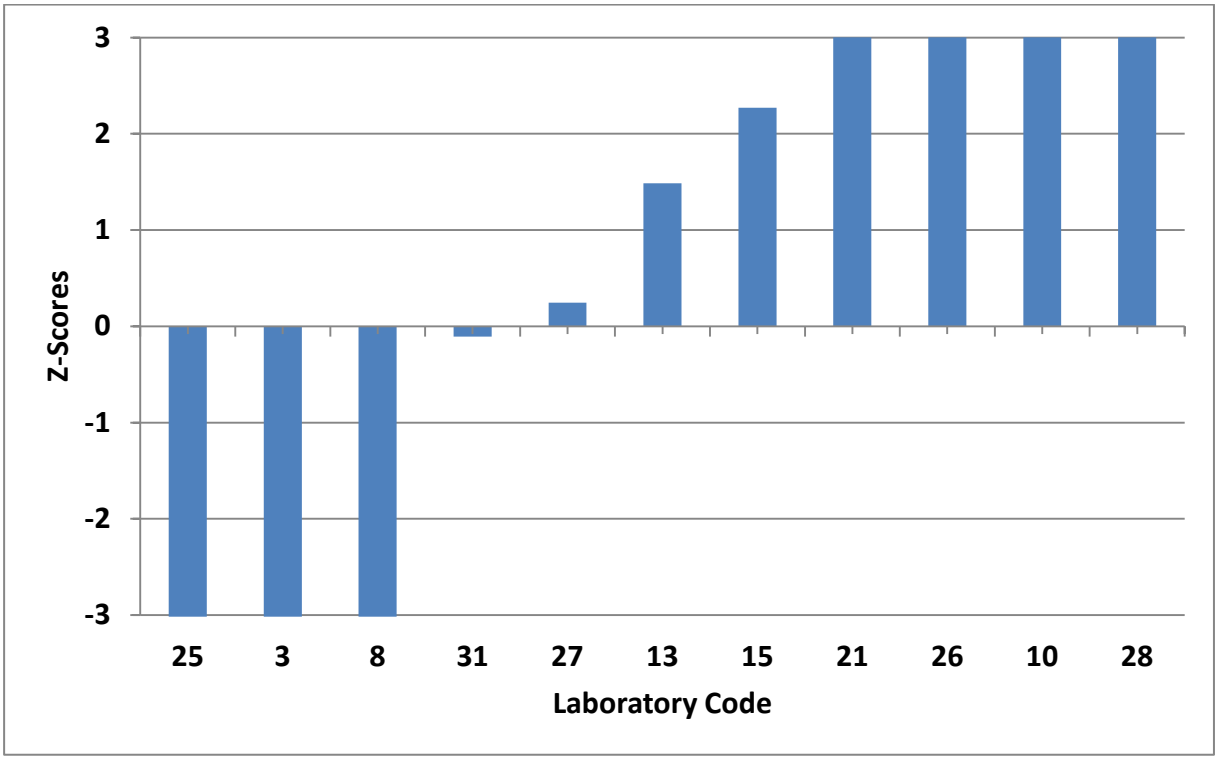


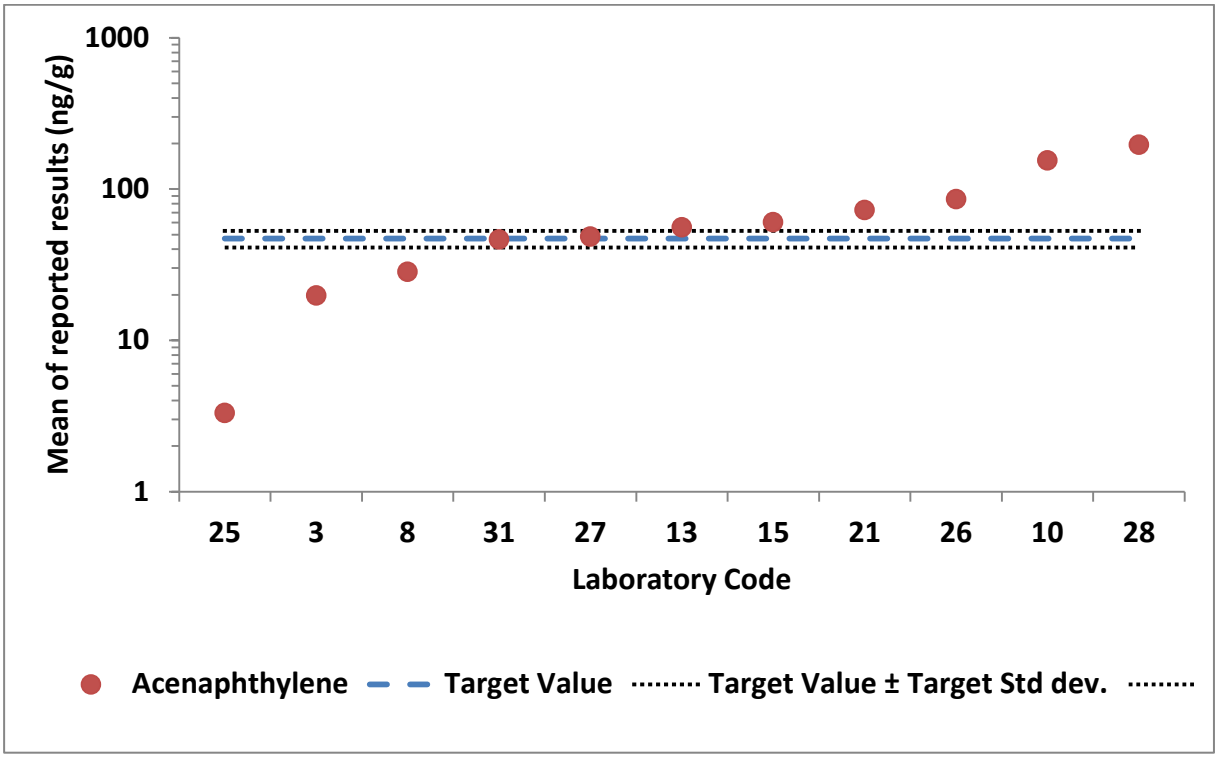
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR NAPHTHALENE



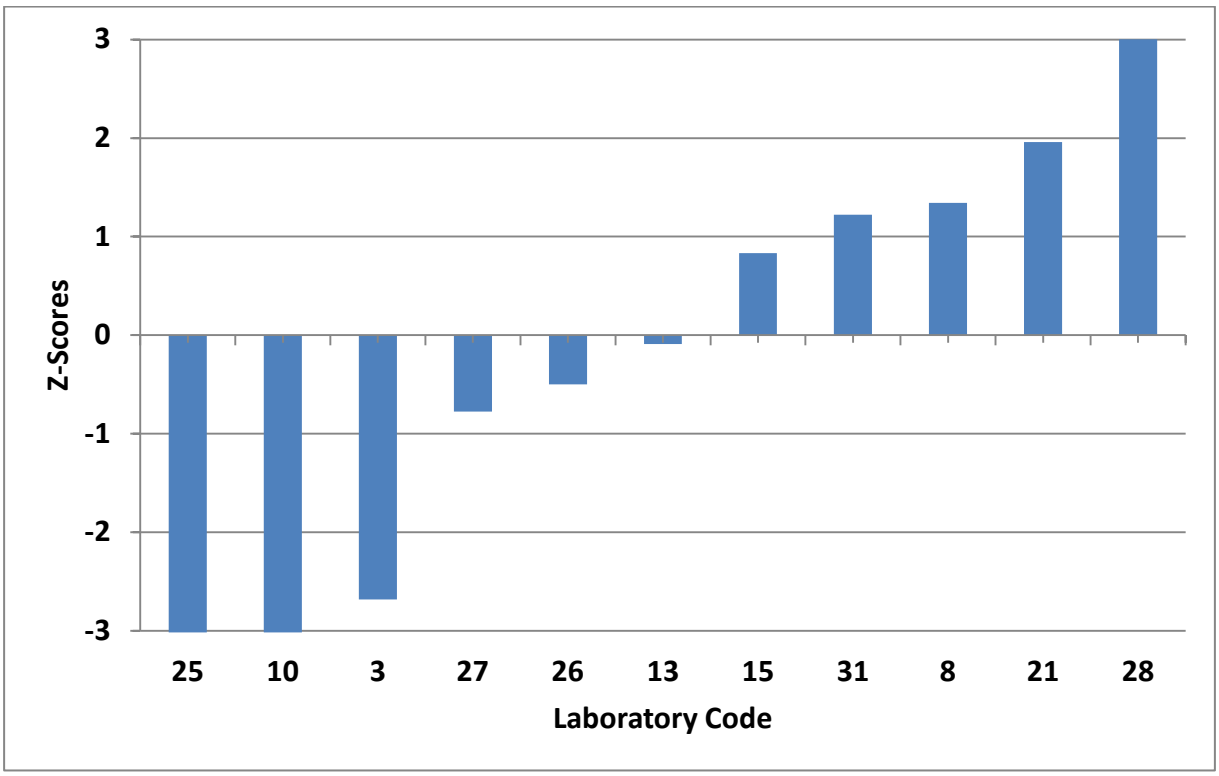


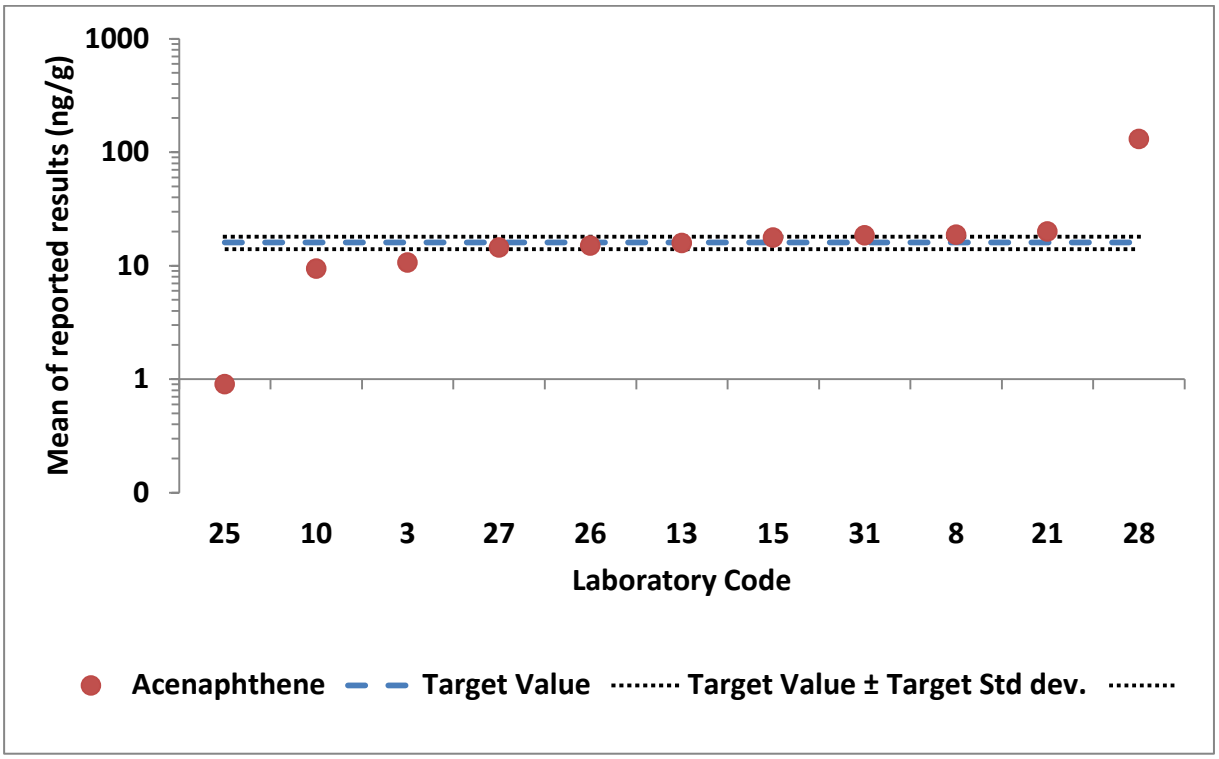
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR ACENAPHTYLENE



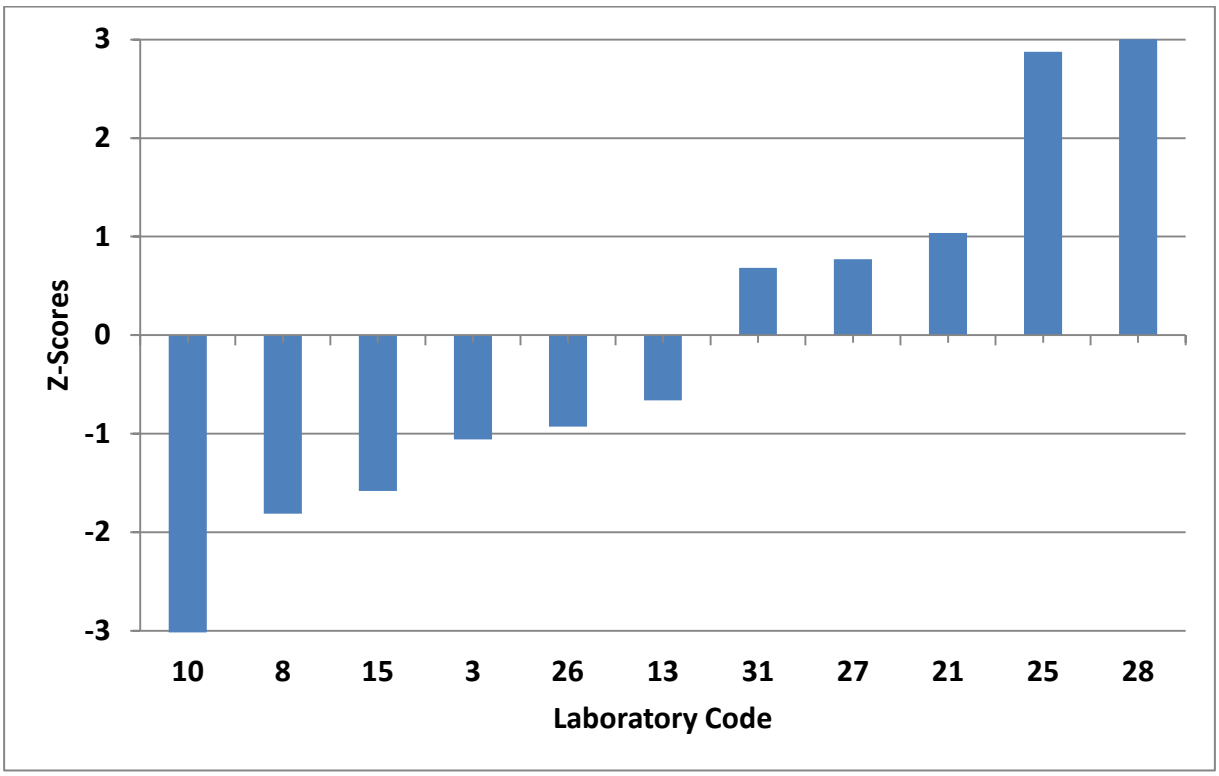


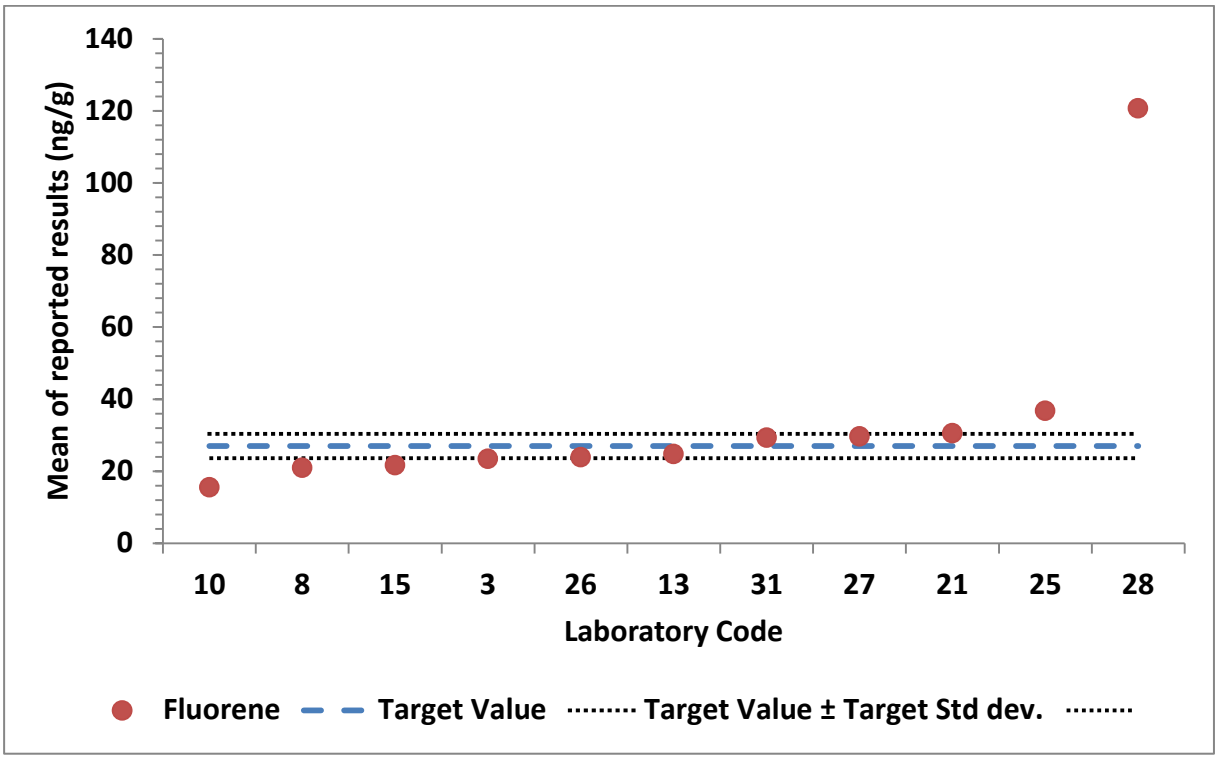
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR ACENAPHTENE



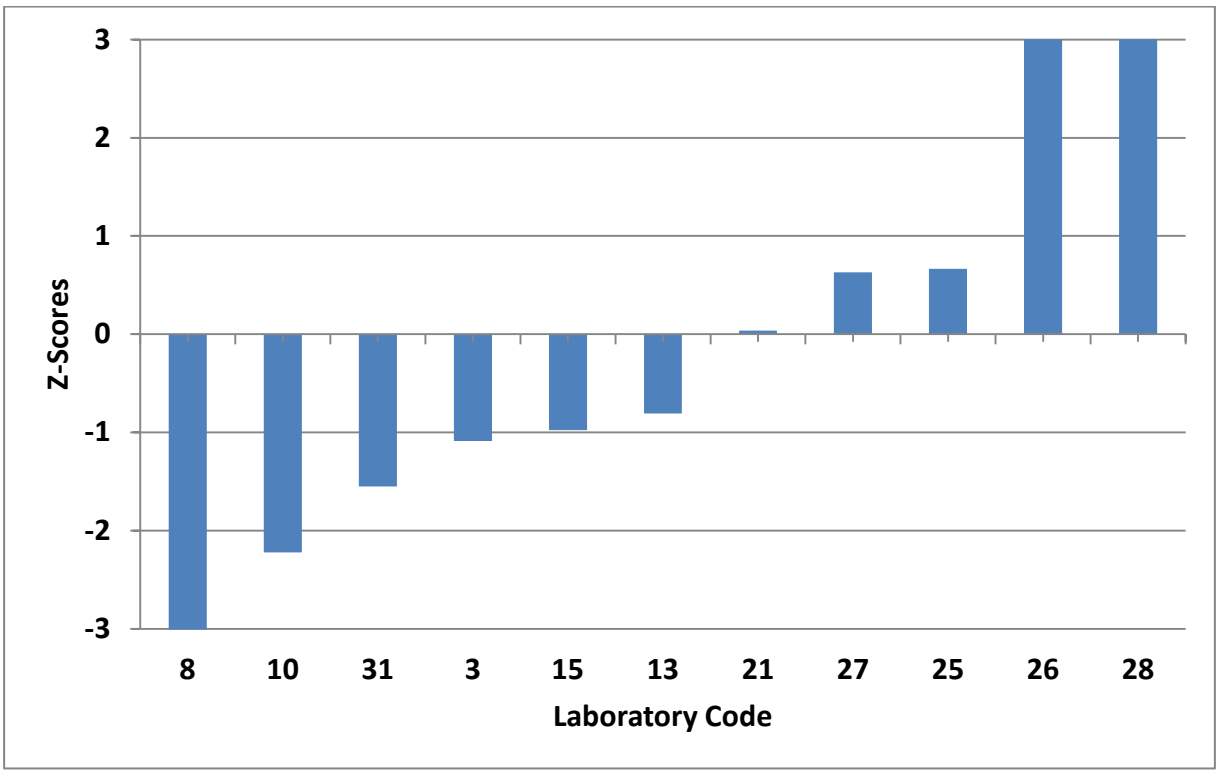


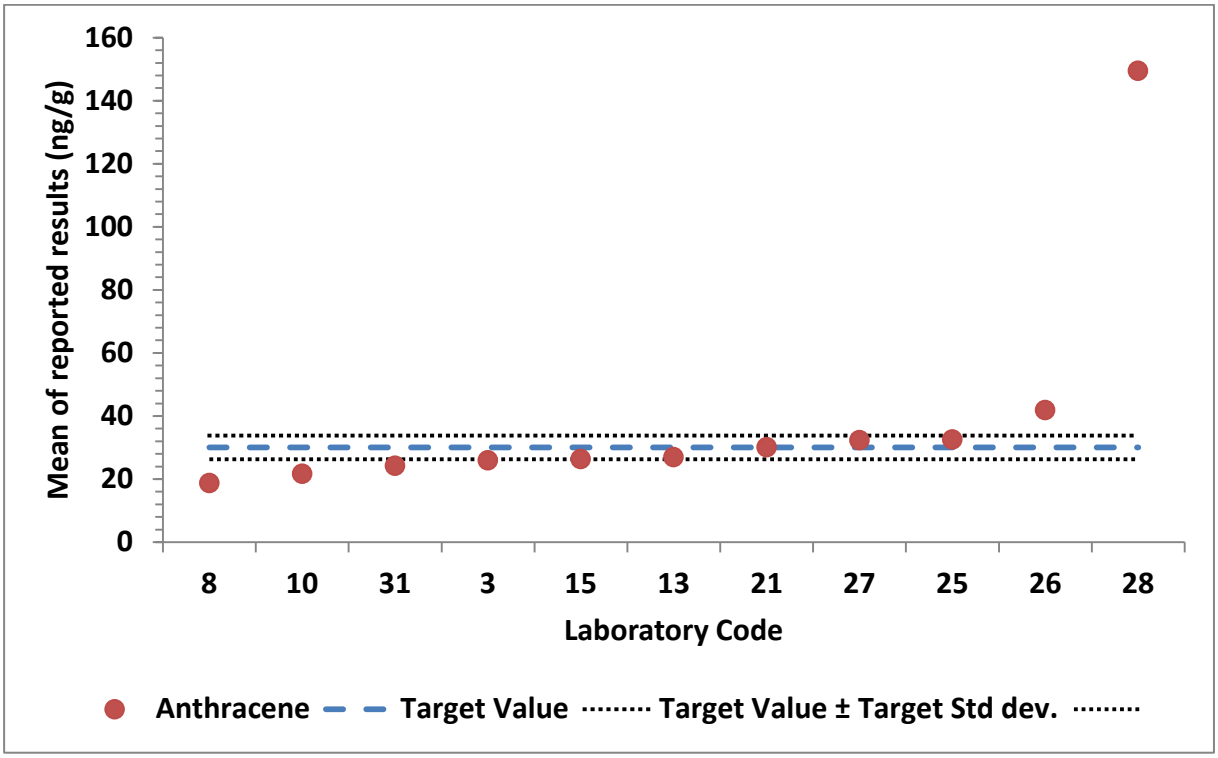
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR FLUORENE



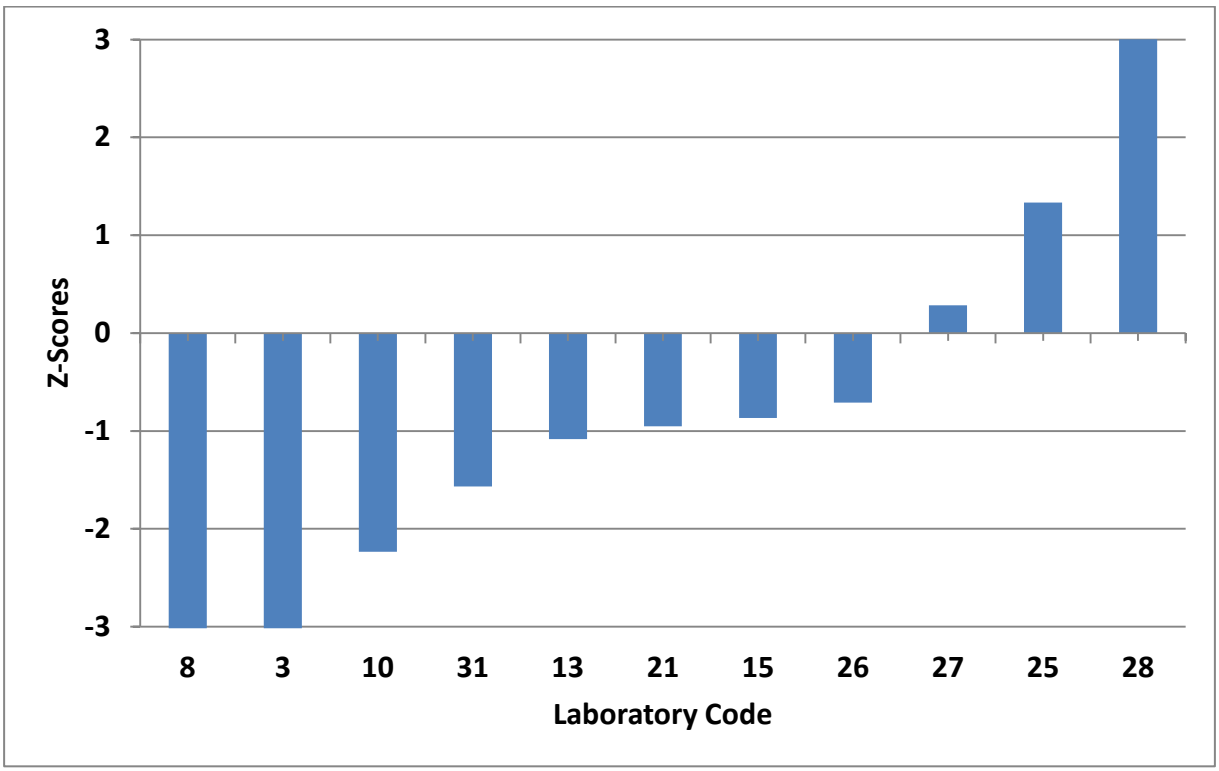


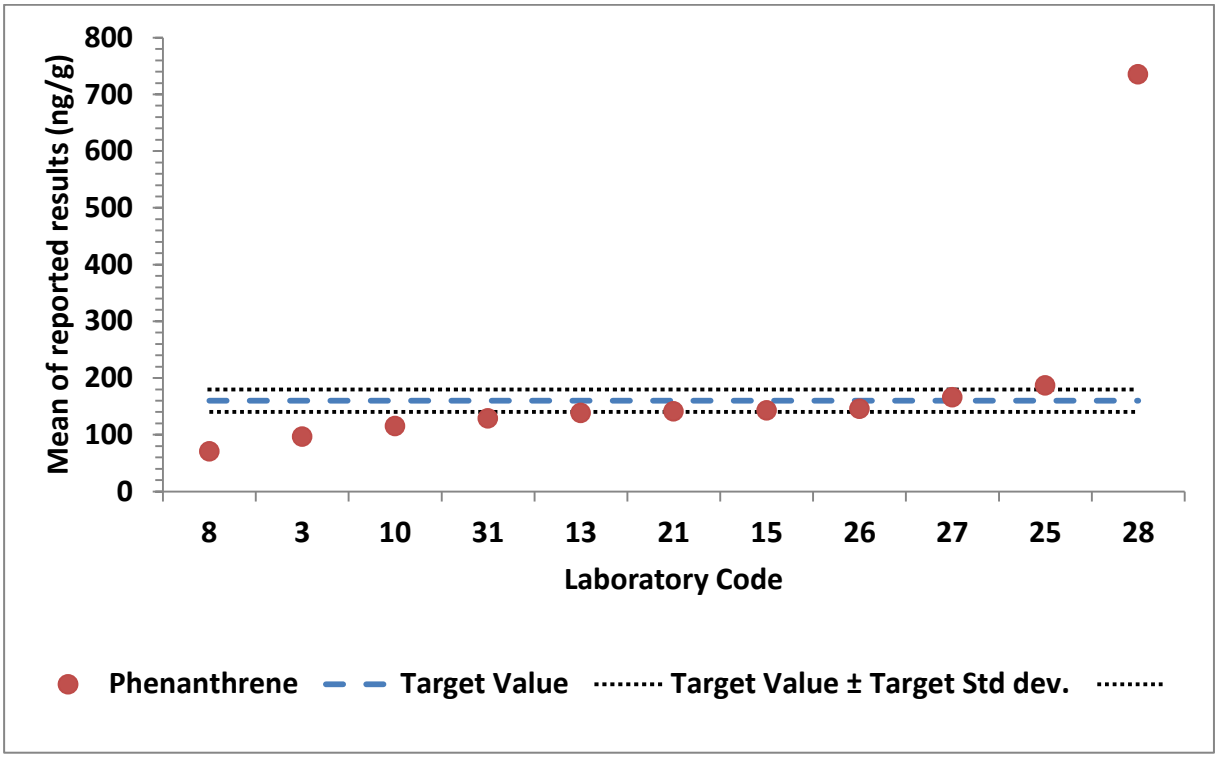
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR ANTHRACENE



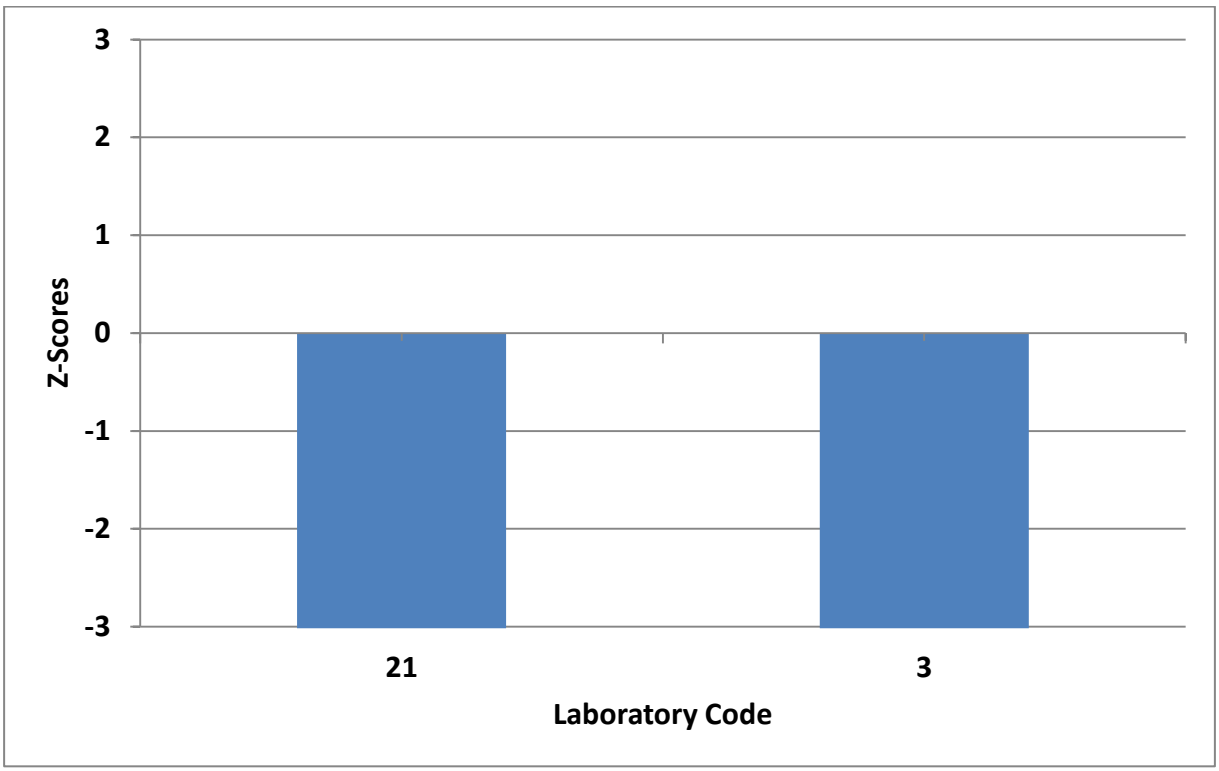


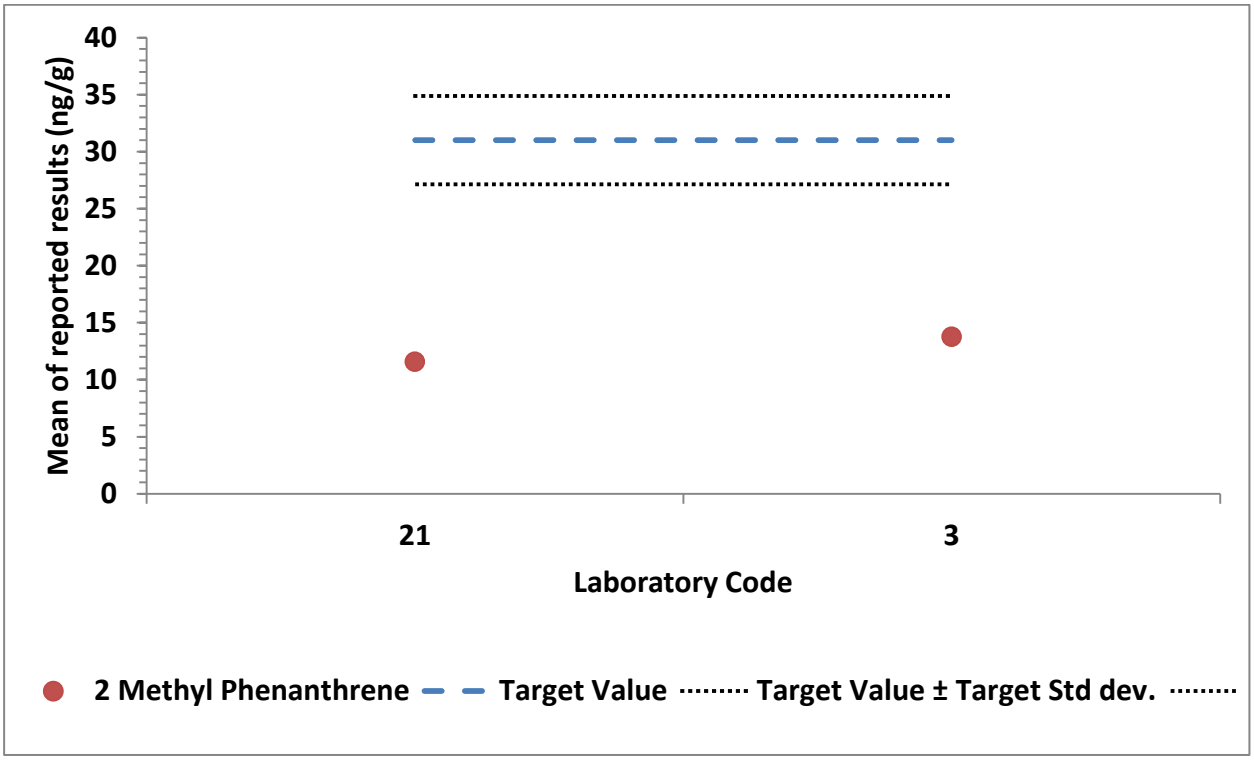
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR PHENANTHRENE



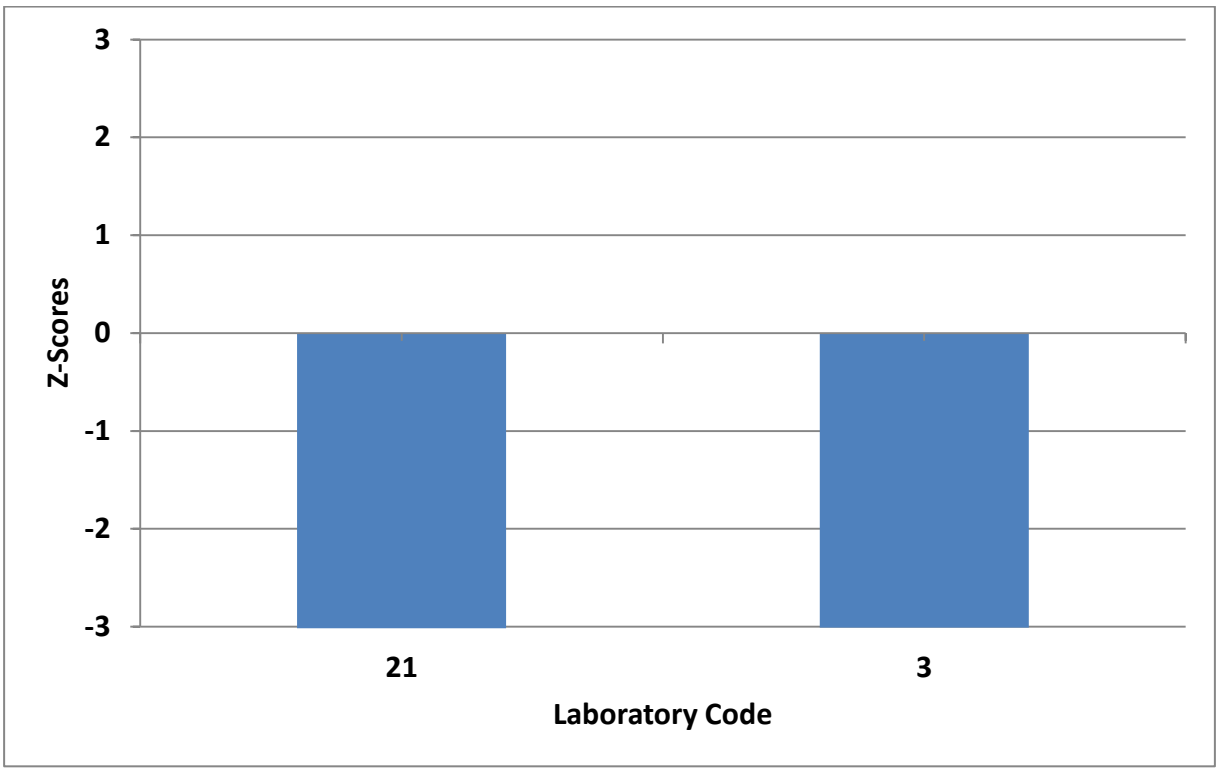


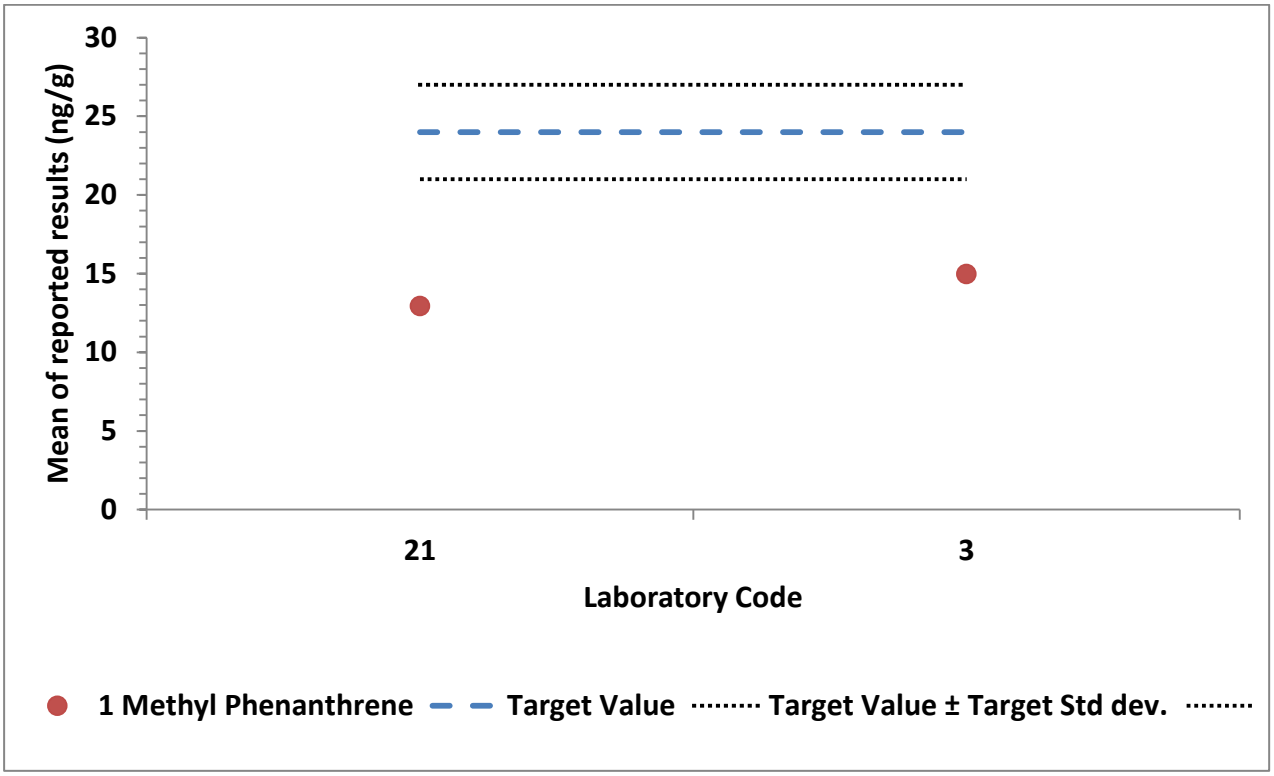
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR 2-METHYL PHENANTHRENE



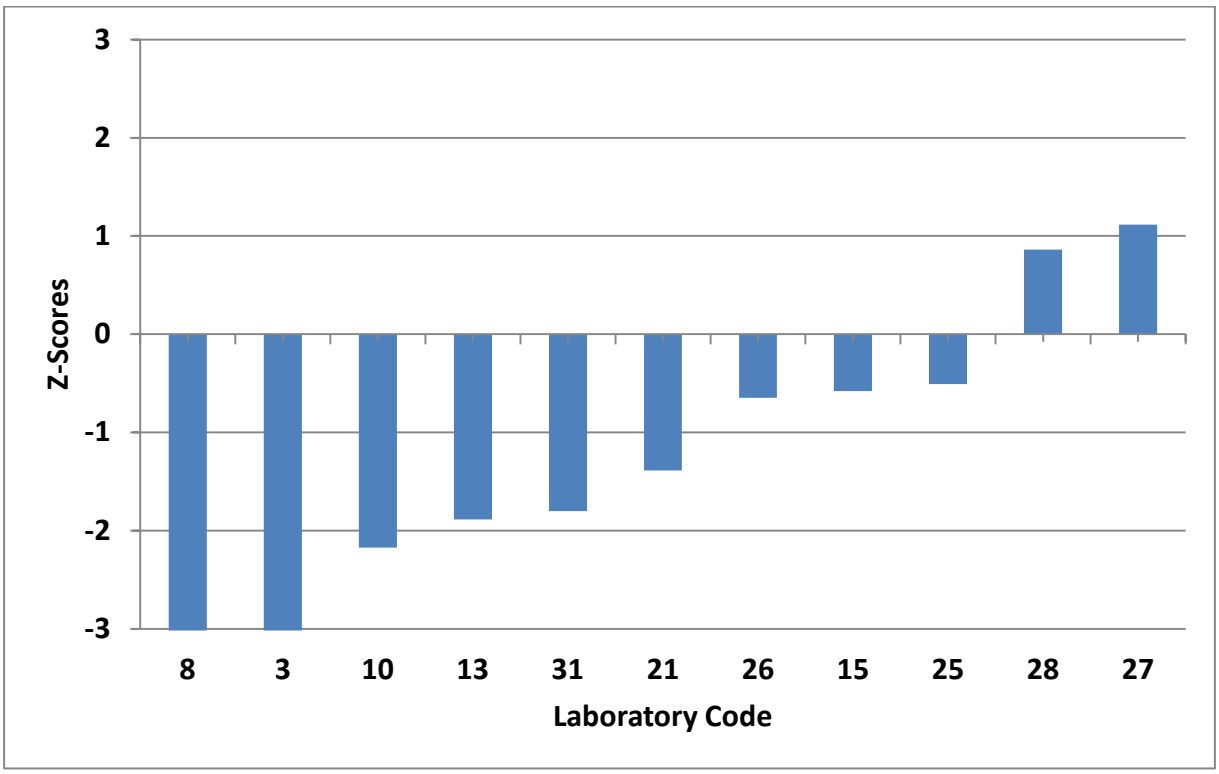


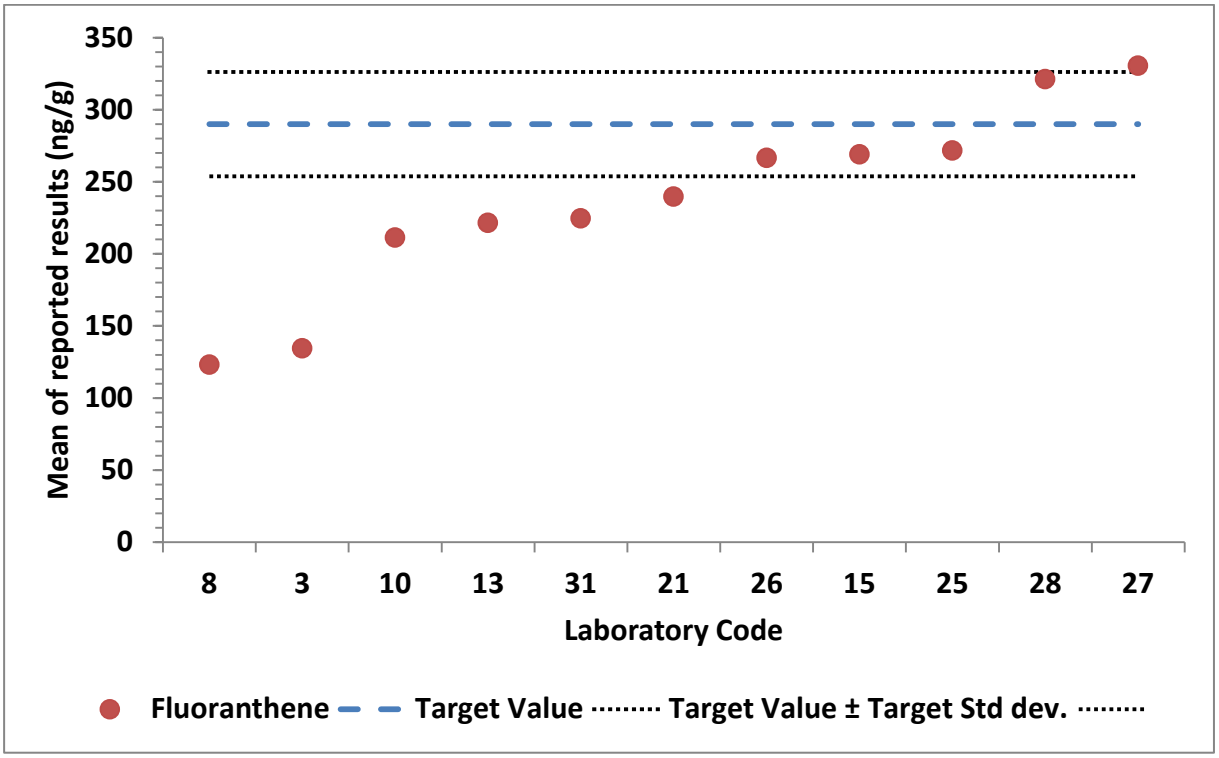
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR 1-METHYL PHENANTHRENE



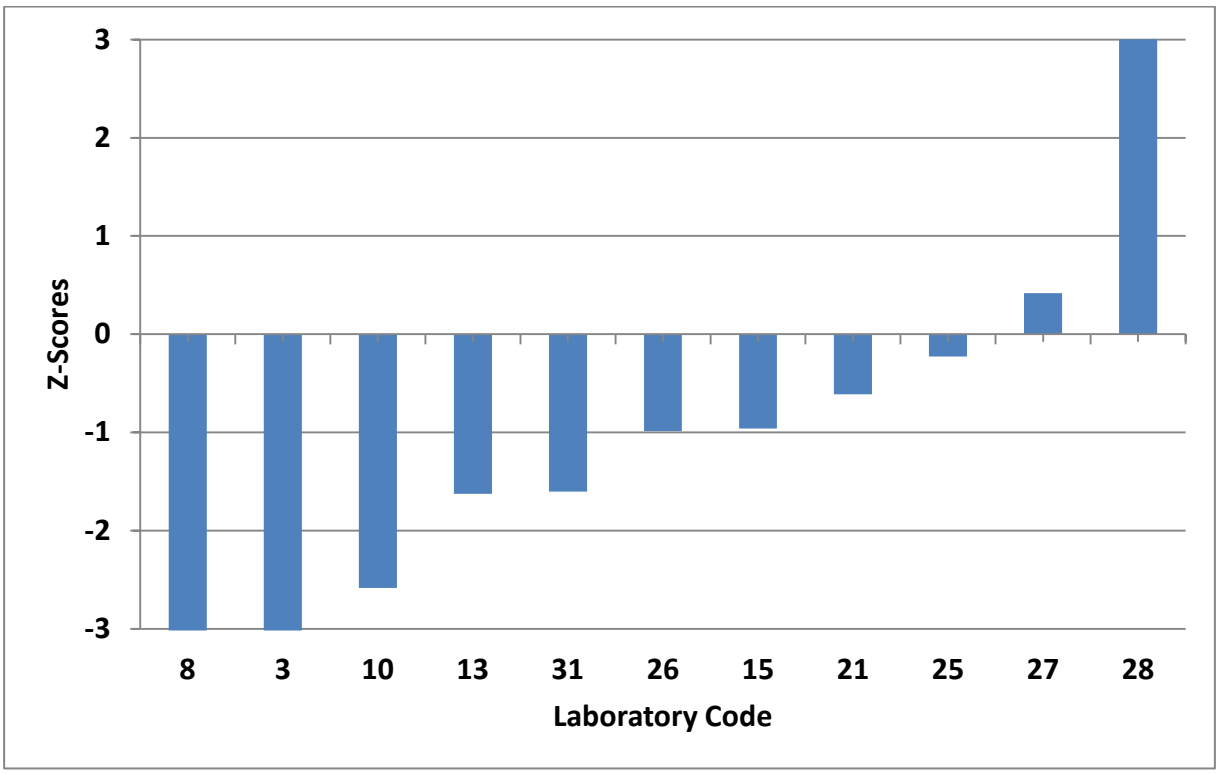


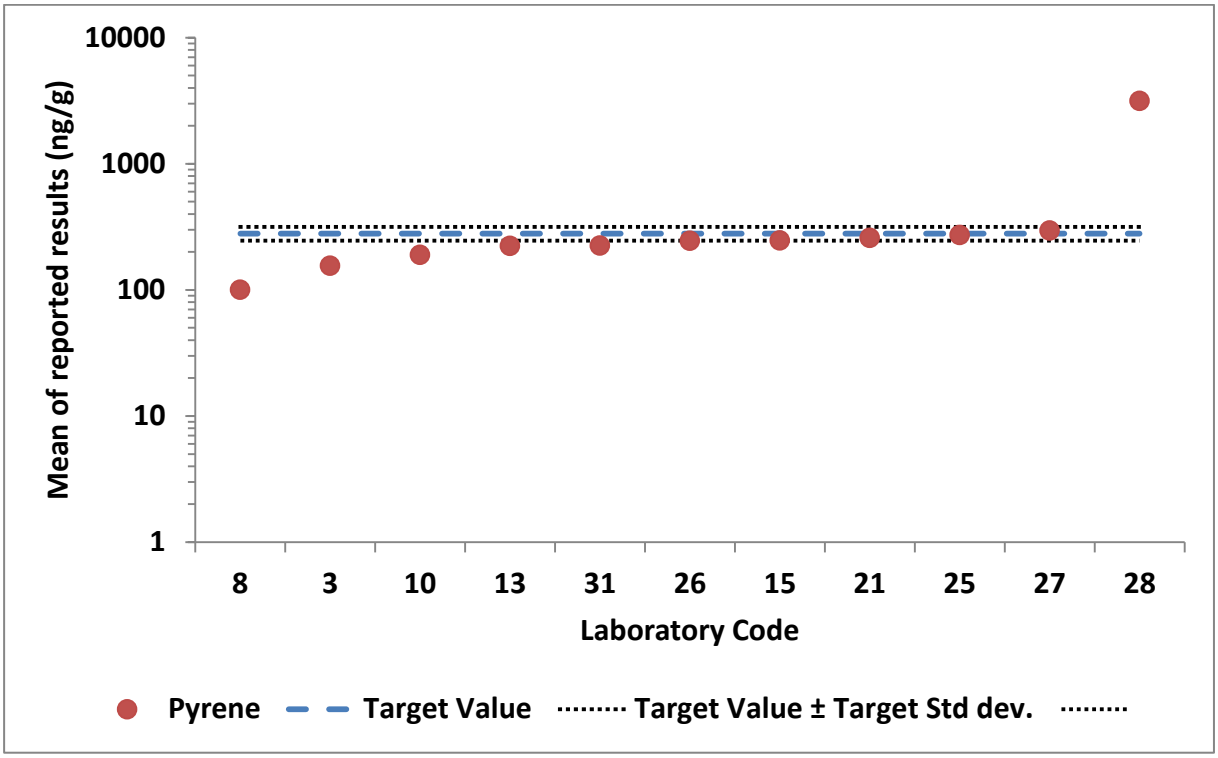
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR FLUORANTHENE



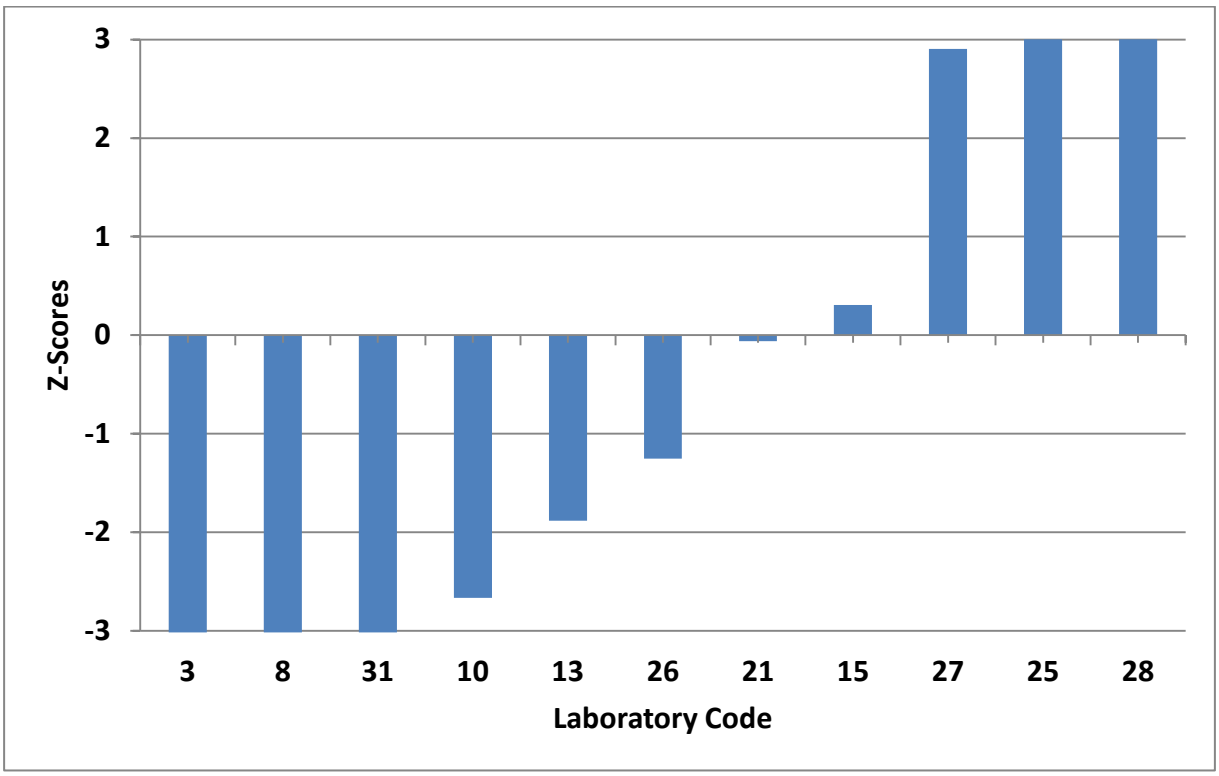


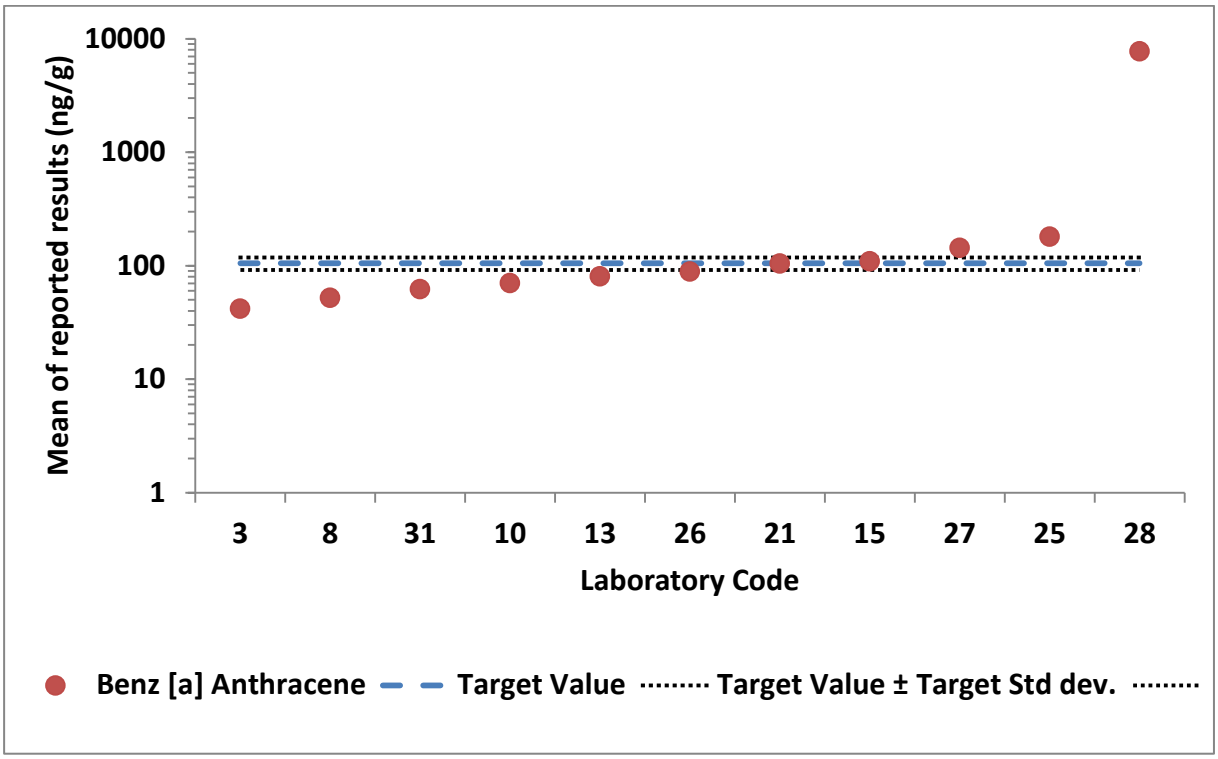
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR PYRENE



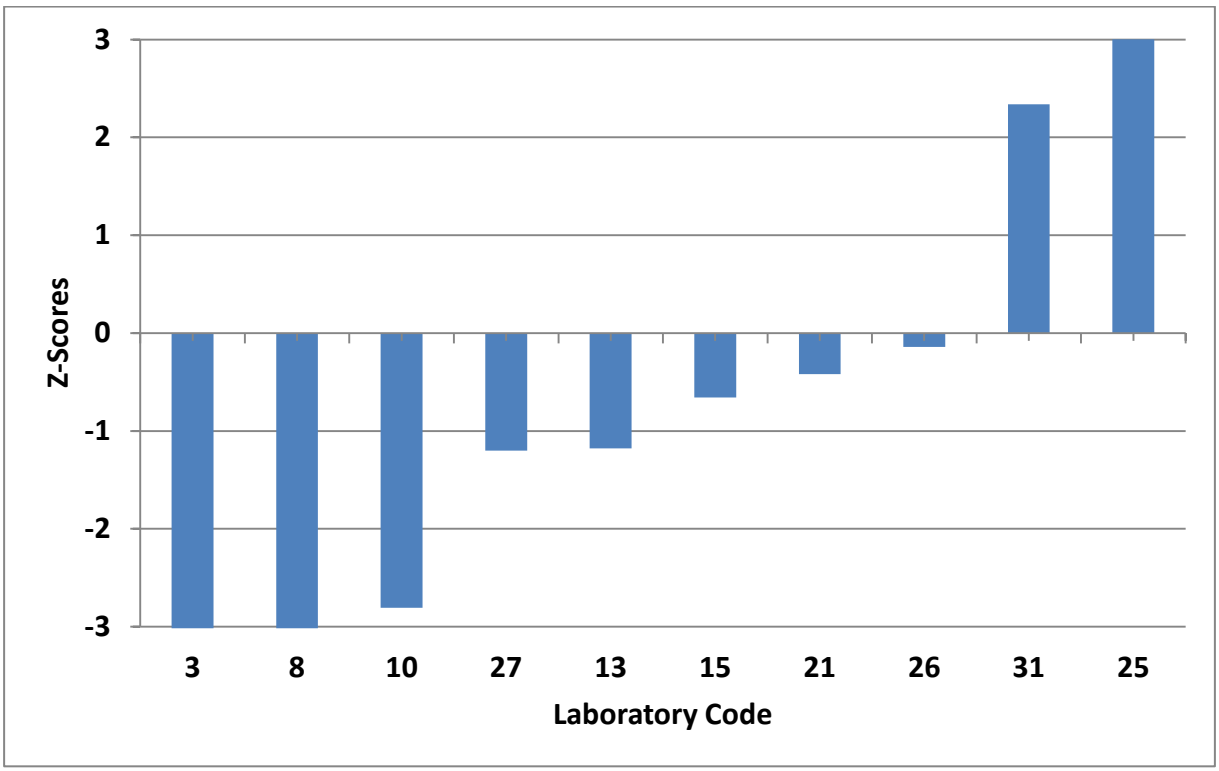


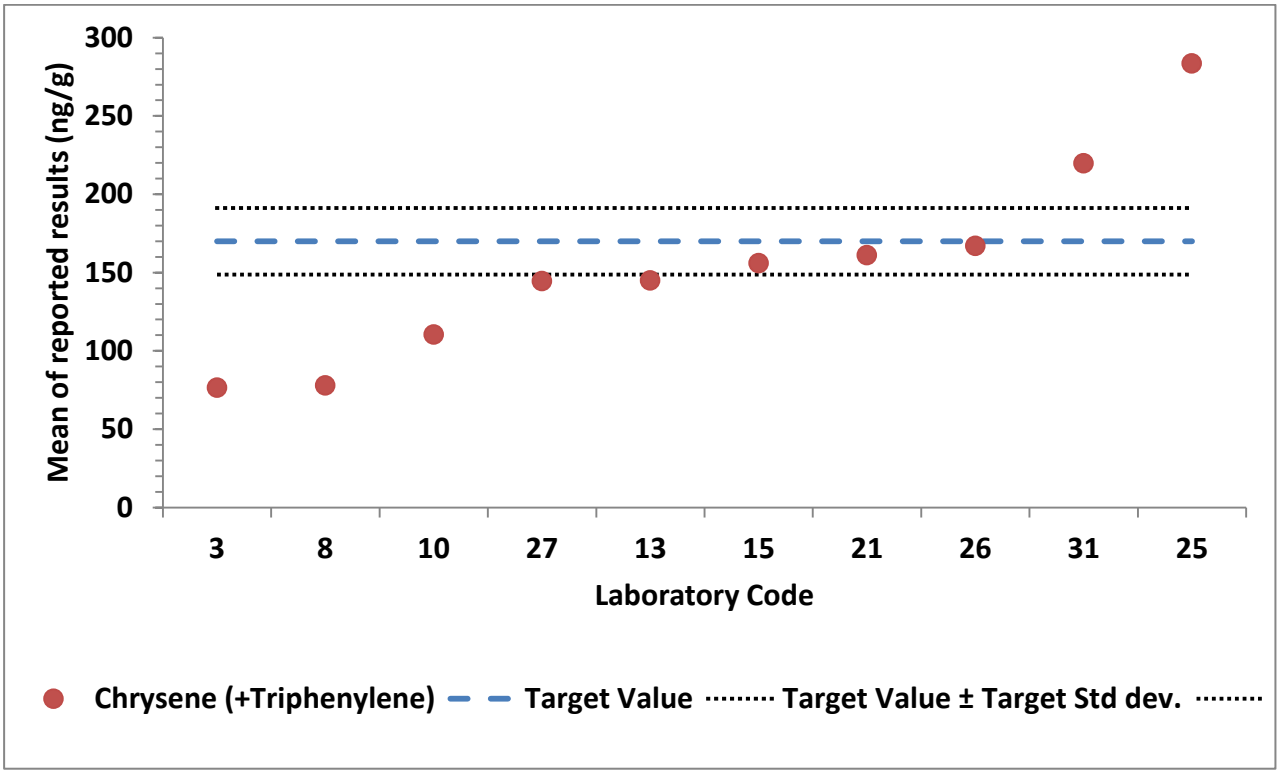
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZ [a] ANTHRACENE



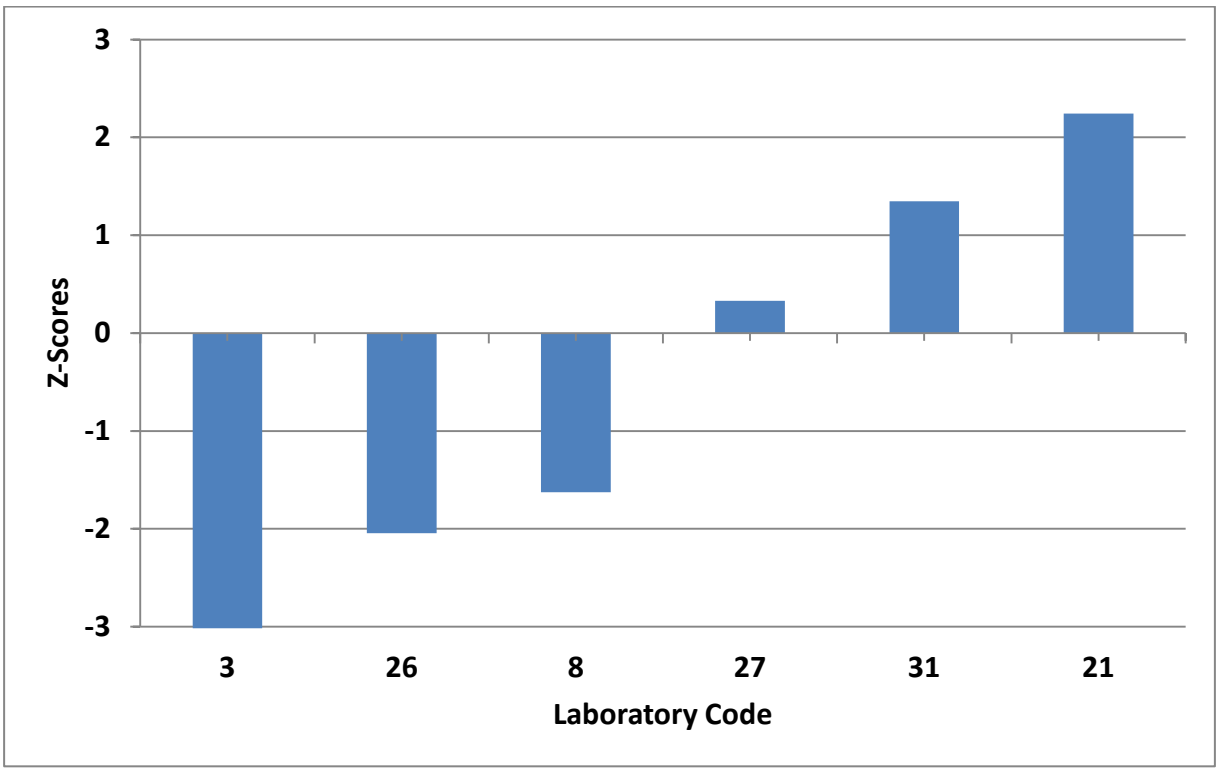


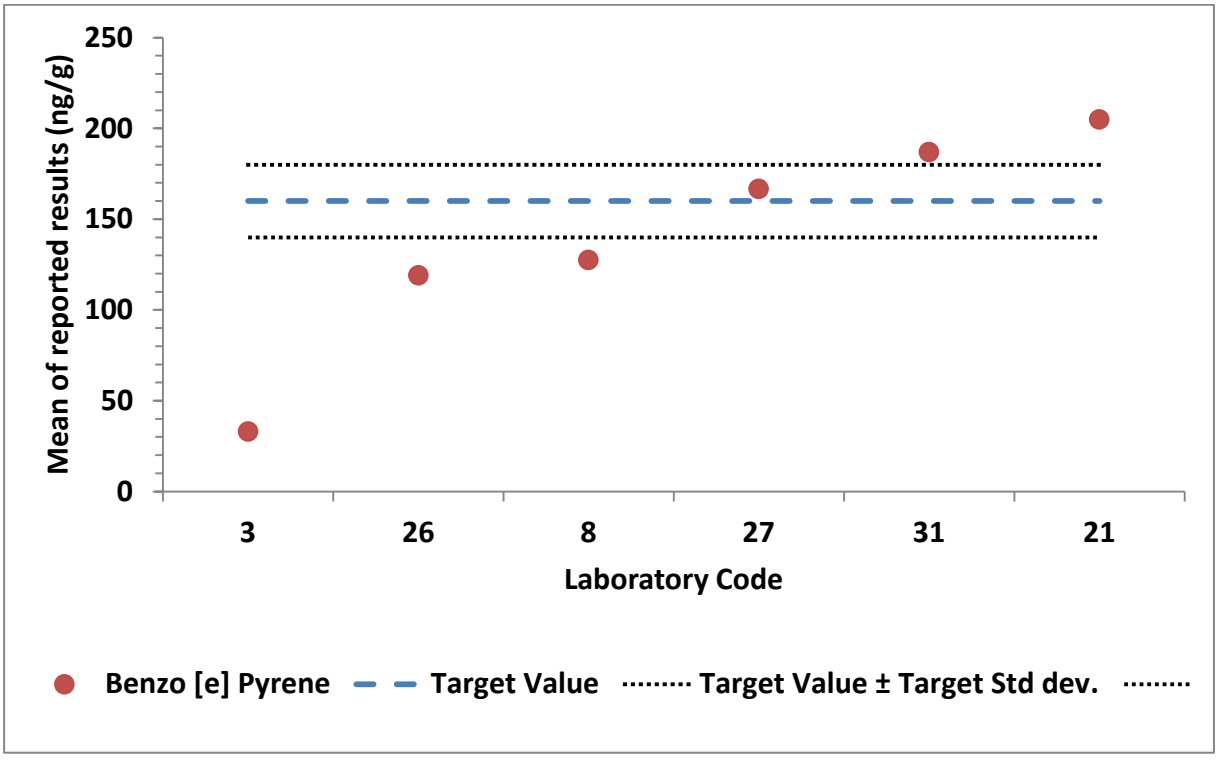
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR CHRYSENE (+ TRIPHENYLENE)



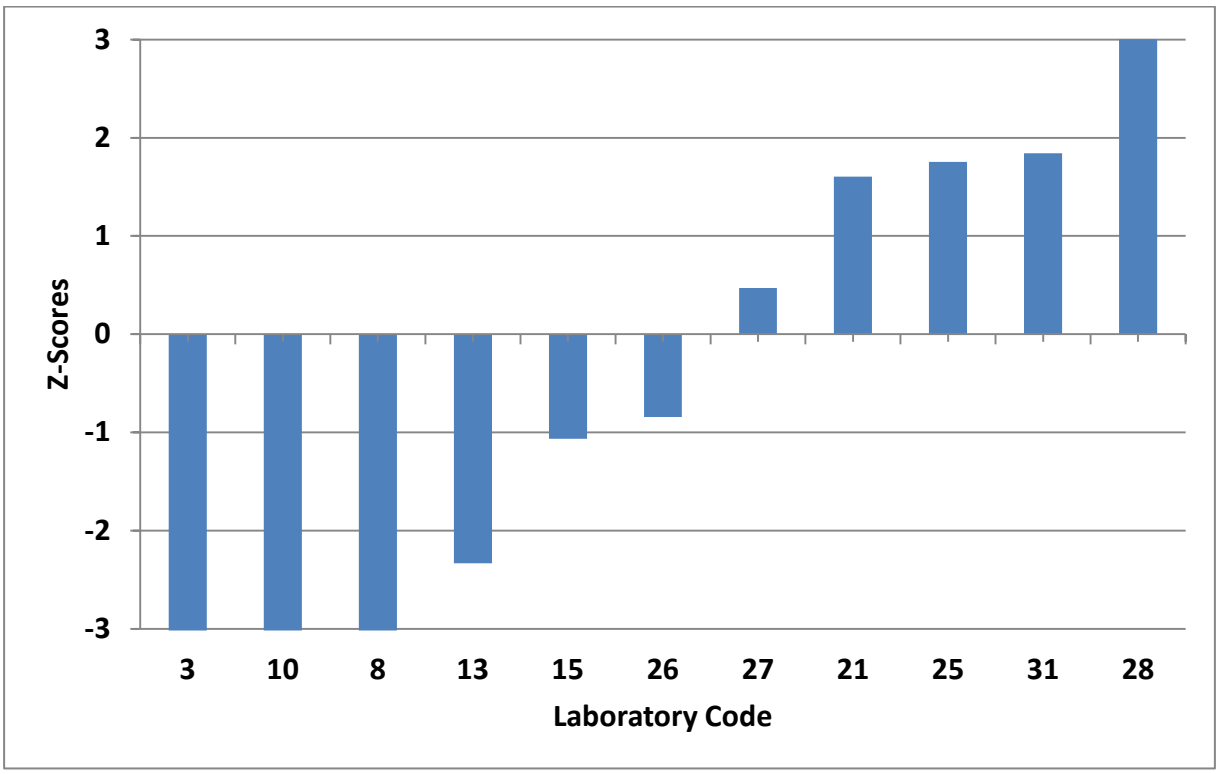


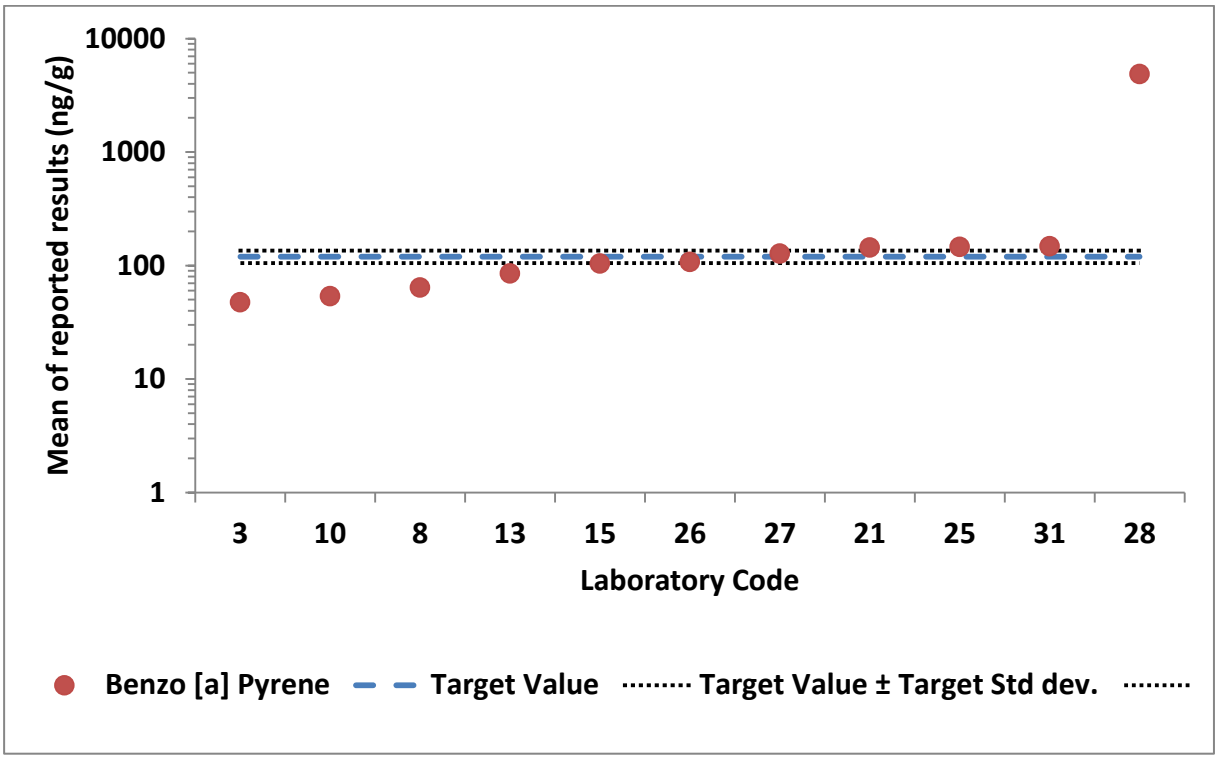
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [e] PYRENE



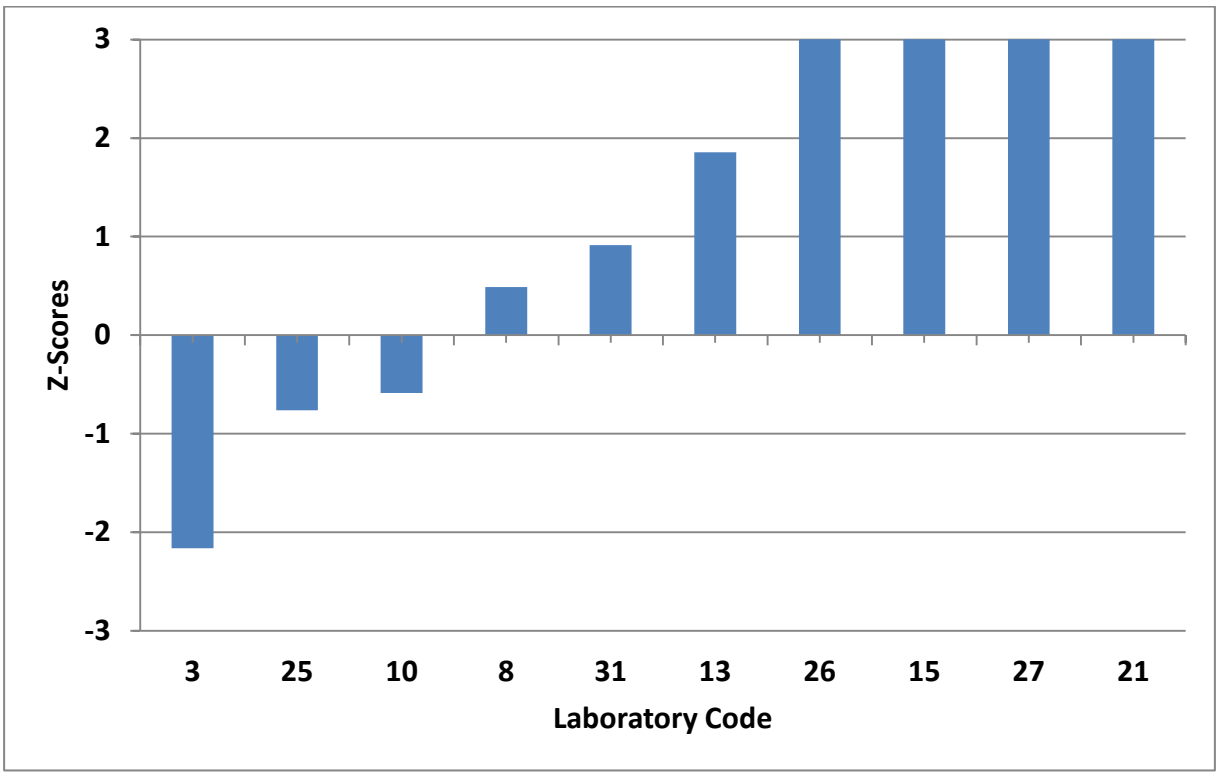


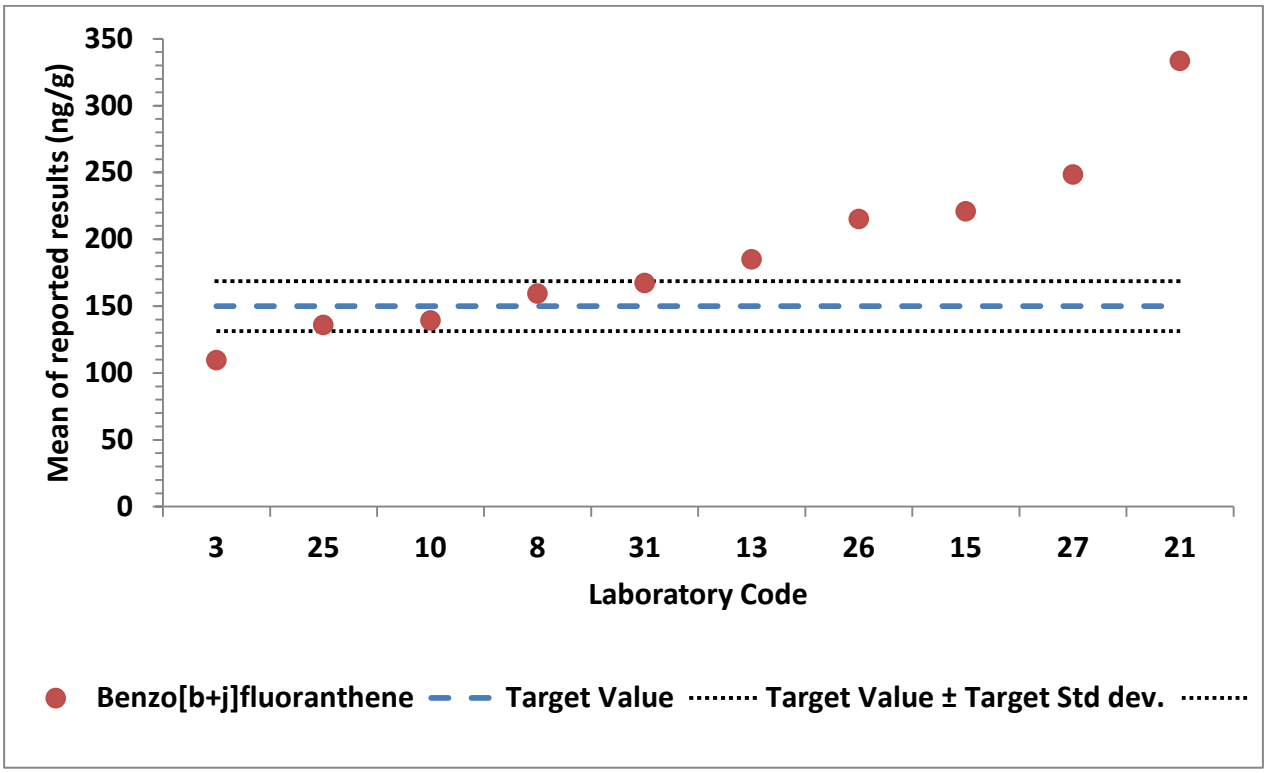
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [a] PYRENE



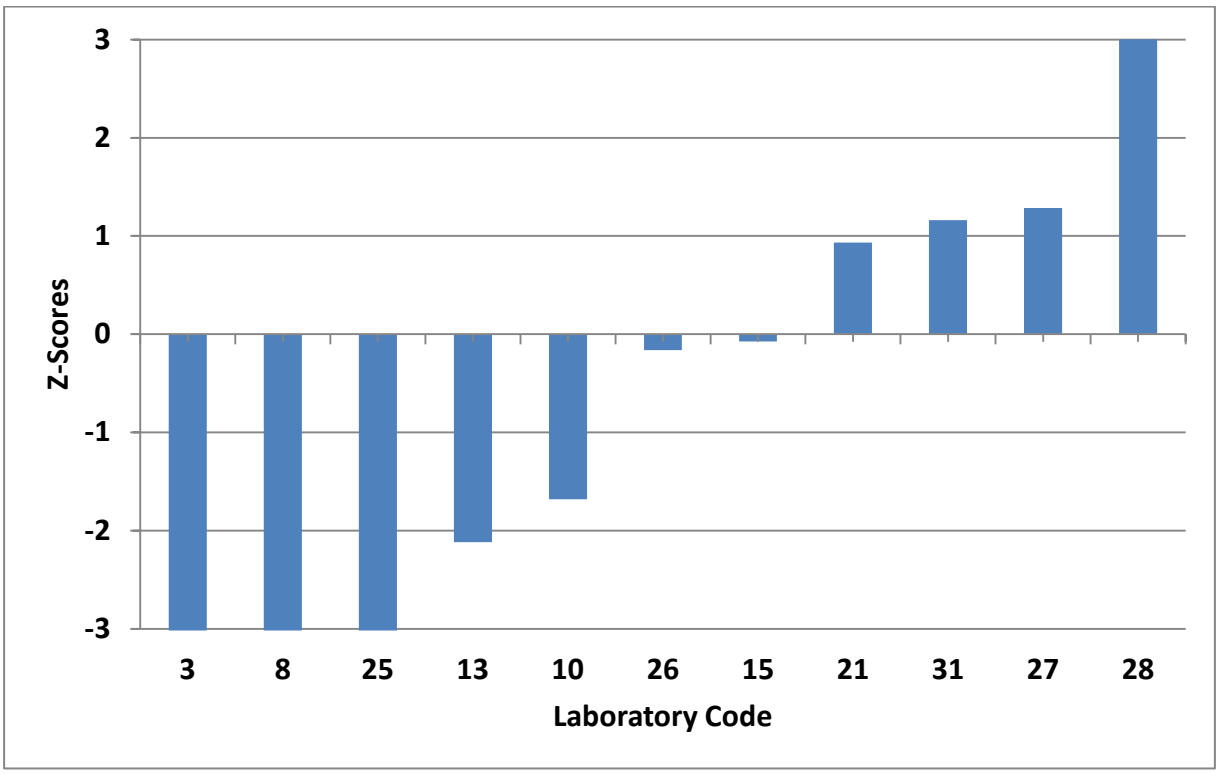


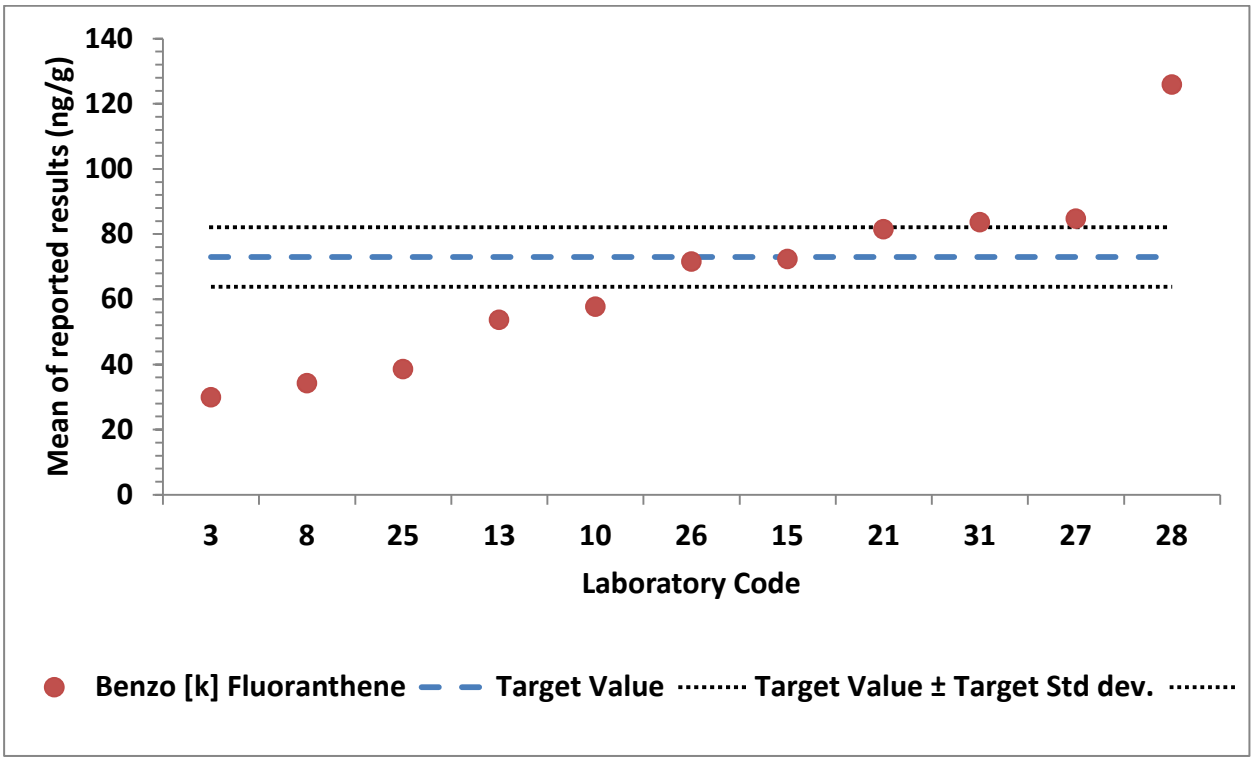
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [b+j] FLUORANTHENE



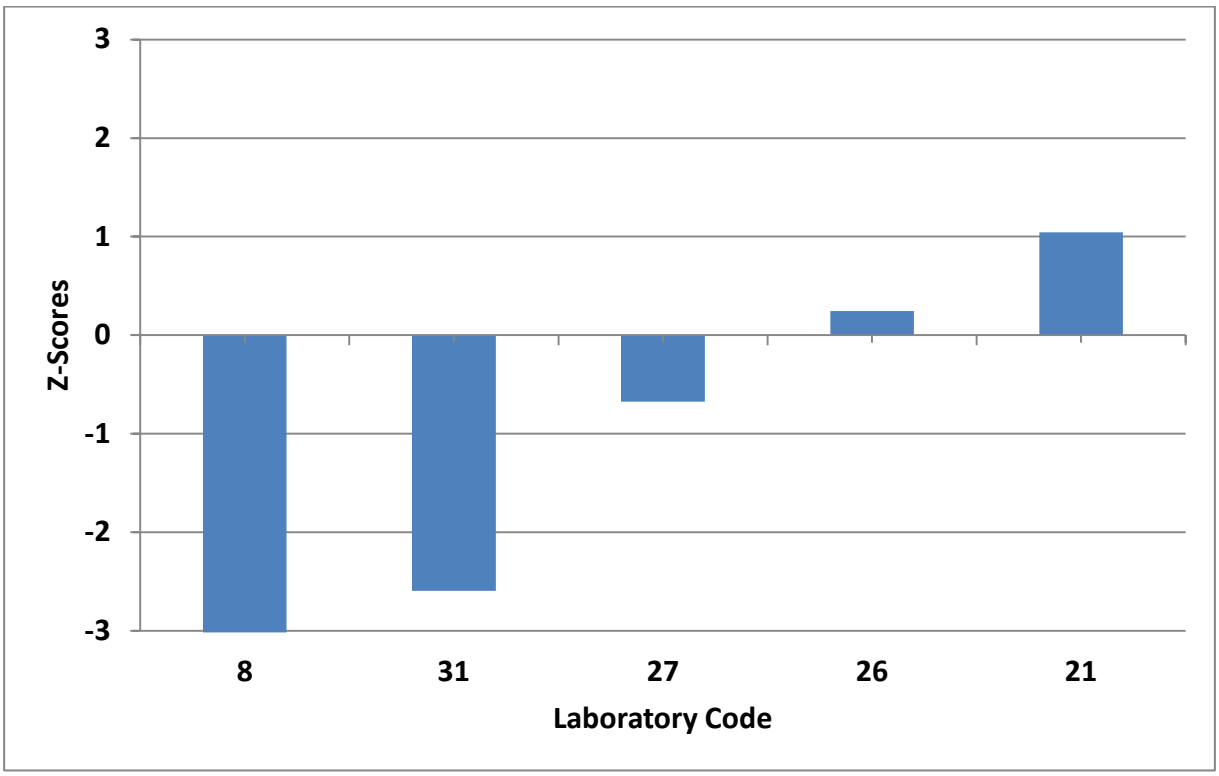


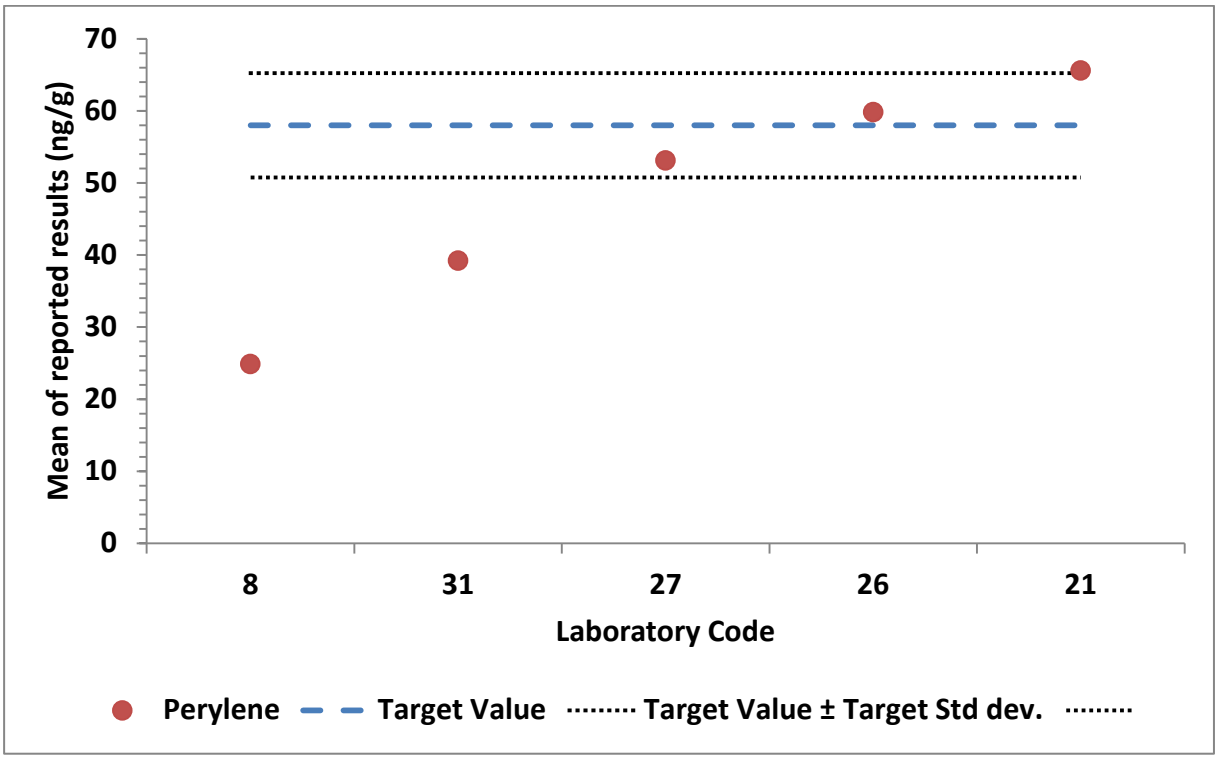
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [k] FLUORANTHENE



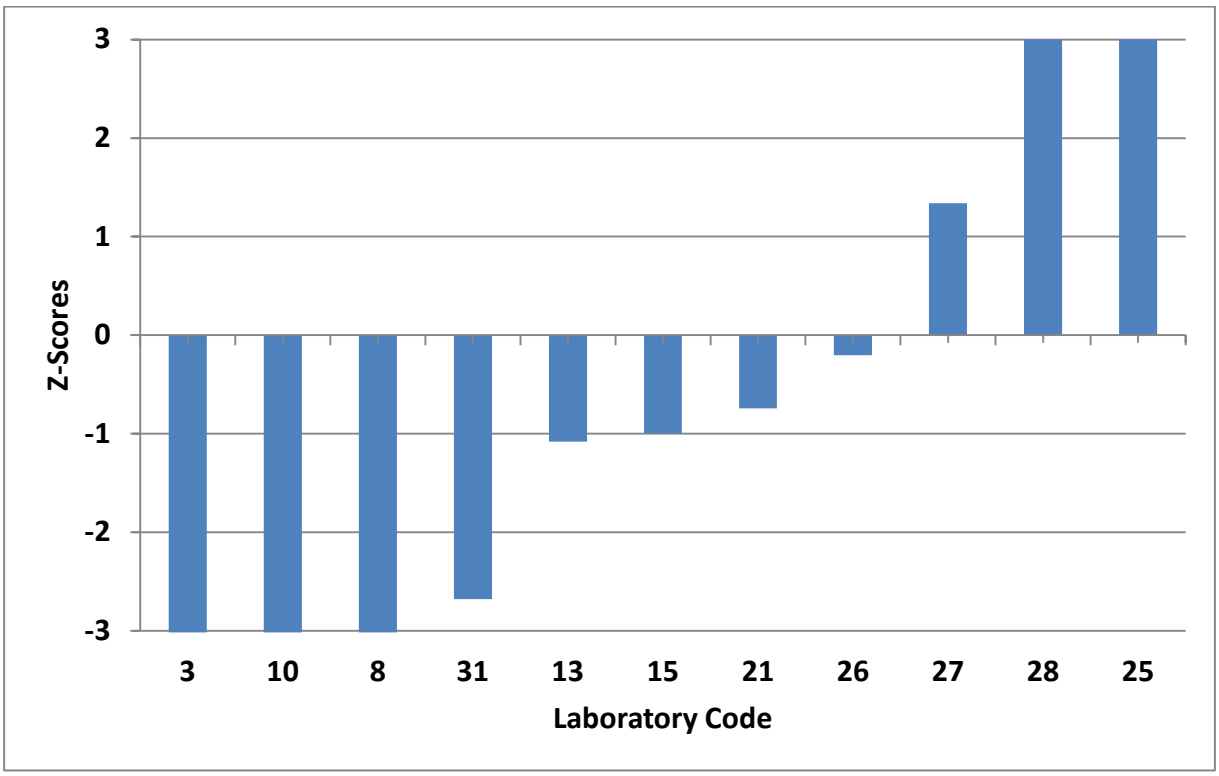


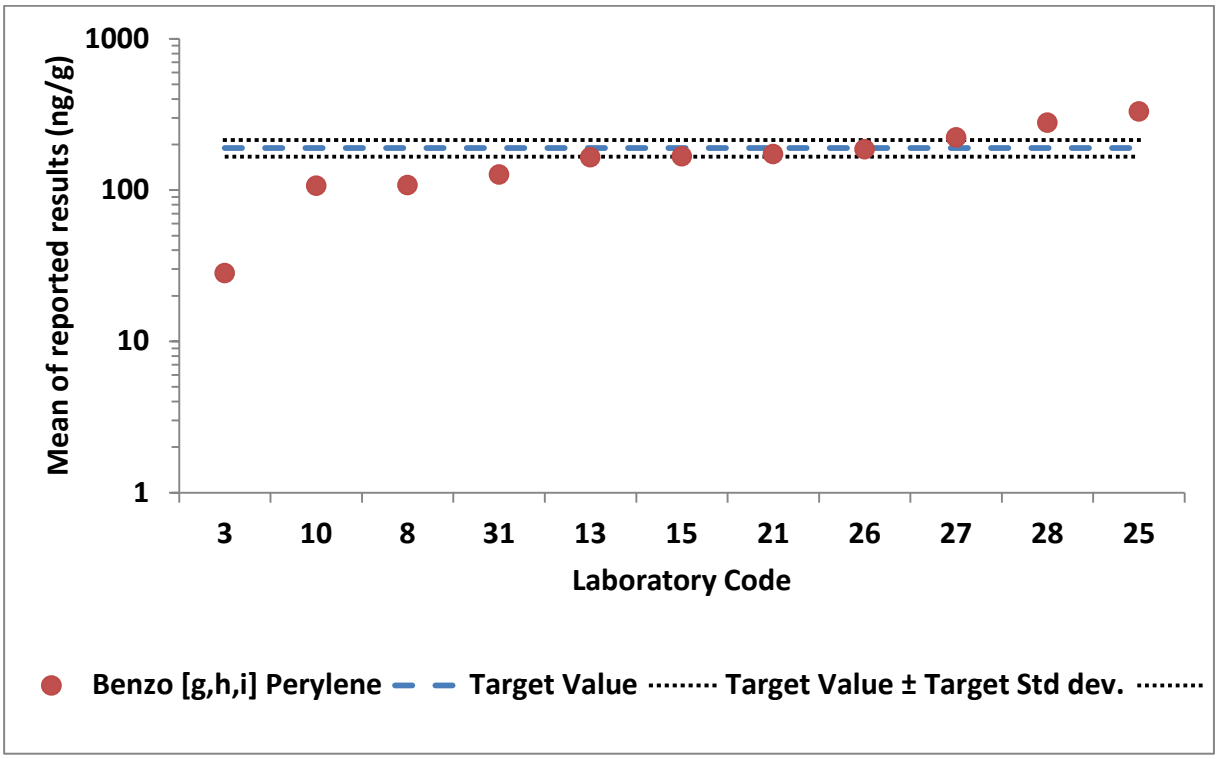
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR PERYLENE



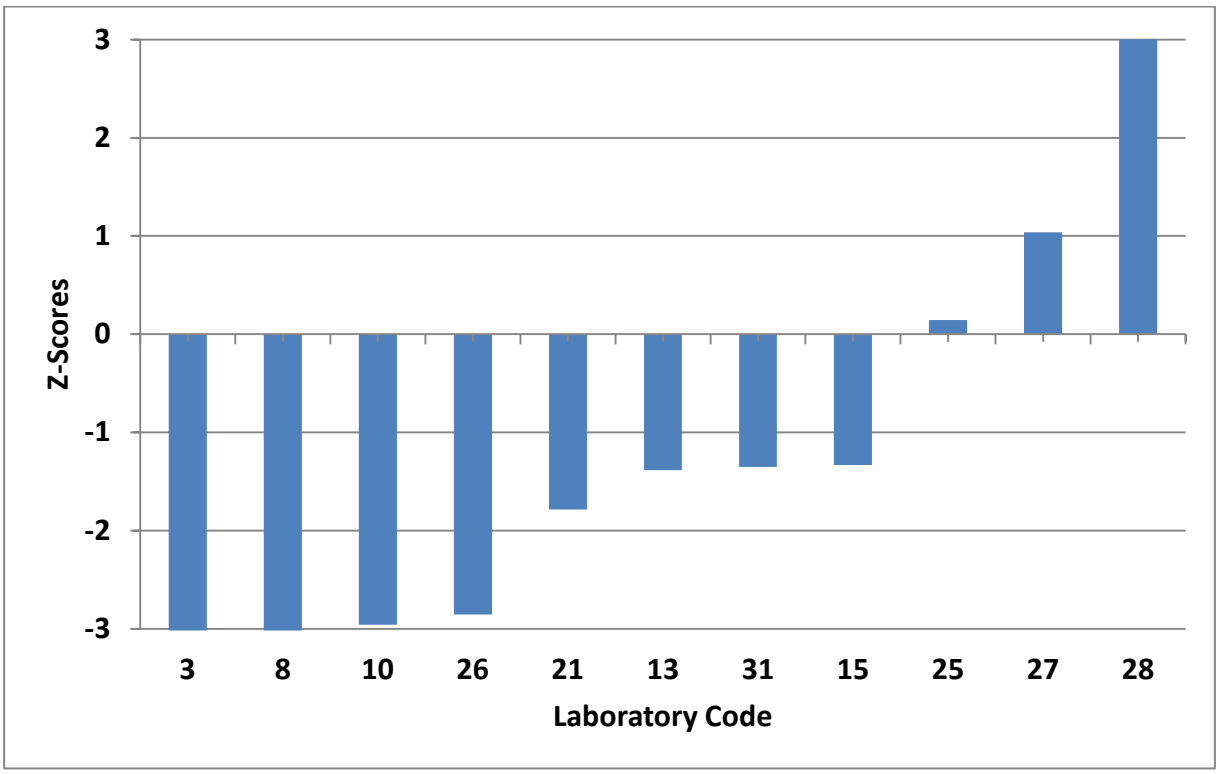


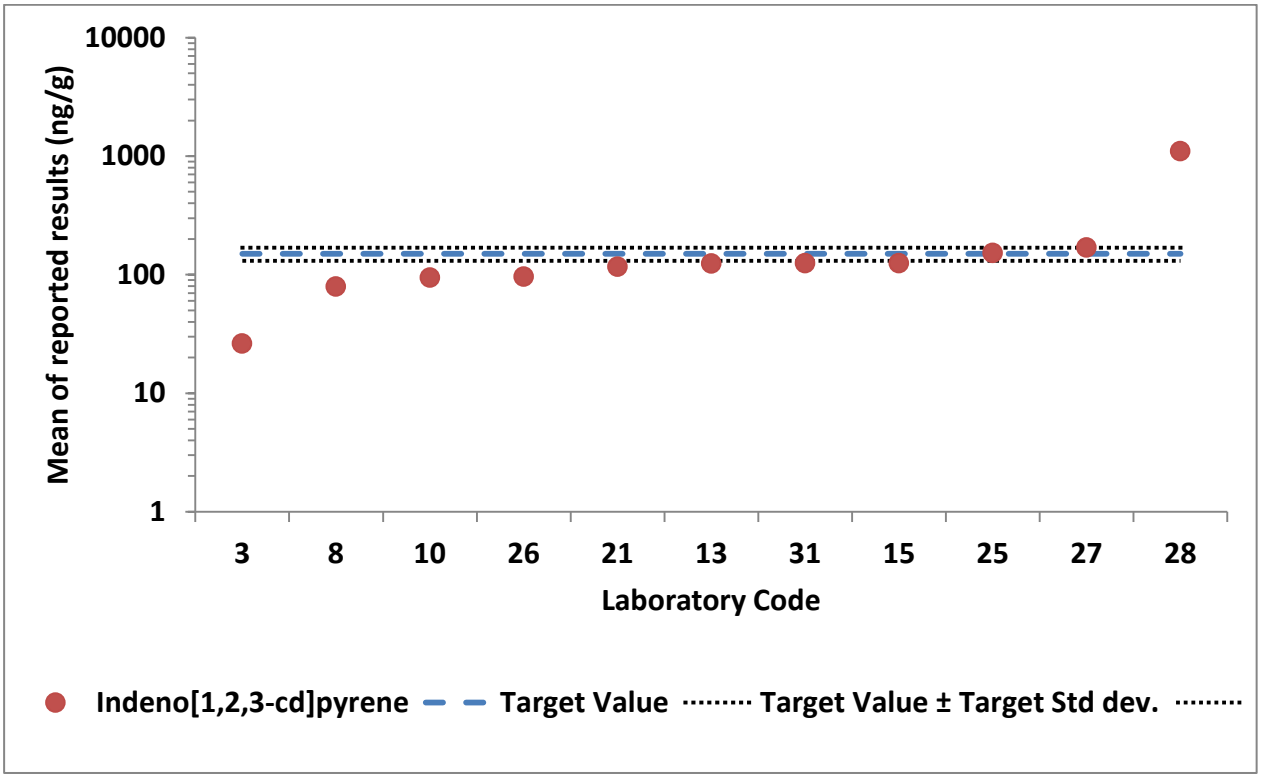
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [g,h,i] PERYLENE





GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR INDENO [1,2,3-cd] PYRENE





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

TRAINING WORKSHOP
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

30 October - 10 Novembre 2017

IAEA-EL staff involved:

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

Prepared in collaboration with:

CONTENTS

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

Background

A training course on the analysis of trace elements in marine environmental samples was organized in NAEL/MESL on behalf of MED POL, for participants from Mediterranean laboratories involved in the UNEP/Mediterranean Action Plan - MED POL 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 in June 2017 to all MED POL National Focal Points, inviting them to nominate candidates for the training course from their respective countries. After the reception of the nominations and taking into consideration the training capacity of the laboratories, 6 participants from 6 different countries (Algeria, Croatia, Egypt, Morocco, Tunisia, Turkey) were selected by MED POL and invited to attend the Training Course in NAEL, Monaco. Invitation letters to the participants were sent by IAEA/NAEL-MESL on the 11th of September 2017. Unfortunately two participants, one from Algeria and one from Egypt, could not obtain their Visa in due time and they were not able to attend the Training Course.

The course was scheduled from 30 of October to 10 of November 2017.

Detailed program of the course is presented page 15.

Evaluation

At the end of the course a questionnaire was distributed to the trainees in order to collect their feedbacks on training organization, content and structure. The course was found to be useful and valuable and trainees' needs were met. Although the balance of lectures, group discussions and group exercises was found to be correct, most participants expressed the interest to have more practical work in the laboratory and apply new methodologies. The evaluation forms are presented in the Annex 2.

Conclusion and general remarks

The theoretical knowledge on the good laboratory practice, different analytical techniques for trace element analysis and quality assurance principles (use of certified reference material, internal and external quality control, validation, uncertainty and traceability of measurement results), obtained during the training course were beneficial for all participants in the training course.

Practical exercises were beneficial only for some participants and the main reasons for that are described below:

- ✓ Some of participants are usually not directly involved in laboratory work, which made questionable the efficiency of the training course for them.
- ✓ The differences in the level of background knowledge of participants created difficulties both for the training officers and for participants.
- ✓ The insufficient level of English language was one obstacle for some of trainees to follow the lectures and slow down the entire training, due to the need for parallel explanation in French language.

It should also be added that despite the strong recommendations for participation of trainees' laboratories in the on-going proficiency test for MEDPOL, the laboratories of Morocco and Croatia did not send any results.

Further recommendations:

- ✓ The selection of participants in MEDPOL training course should to be improved and some constant criteria for selection (language level, laboratory experience) to be respected.

LIST OF PARTICIPANTS

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

CROATIA	
Ms Ivana BORZIC Public Health Institute Split - Dalmatia County Vukovarska 46 SPLIT	E-mail: ivana_hr2003@yahoo.com
MOROCCO	
Mr Sliman HSSAISOUNE Laboratoire National des Etudes et de Surveillance de la Pollution (LNESP) N°9, Avenue Al Araar 420/1 Secteur 16, Hay Riad RABAT	E-mail: hssaissoune_sliman1@yahoo.fr
TUNISIA	
Ms Amira RJEIBI National Institute of Science and Technology (INSTM) Port de la Goulette LA GOULETTE	E-mail: rjaibi.amira@gmail.com
TURKEY	
Mr Osman TANER Ministry of Environment and Urbanization Mustafa Kemal Mahallesi Eskişehir Devlet Yolu (Dumlupınar Bulvarı) 9. km. No: 278 ÇANKAYA / ANKARA	E-mail: osman.taner@csb.gov.tr

COURSE OUTLINE

MED POL TRACE ELEMENTS ANALYSIS TRAINING COURSE

IAEA – Environment Laboratories, Monaco

30 Oct. – 10 Nov. 2017

COURSE OUTLINE

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

MONDAY 30 OCTOBER

9:00 – 09:05	Welcome to IAEA Environment Laboratories Monaco.	*Mr David Osborn* *DIR-NAEL* *(or alternate)*
09:05 – 09:30	Presentation of MESL and its activities.	*Ms Sylvia Sander* *Section Head MESL*
09:30 – 09:45	Laboratory Safety and Security.	*Mr Jean-François Comanducci* *Head - EES*
09:45 – 10:00	Coffee break	
10:00 – 11:30	Self-introduction of participants and expectations from the Training Course.	*All participants*
11:30 – 12:00	Visit of the REL laboratories	*Mr Marc Métian* *Research Scientist*
14:00 – 14:30	Visit of the RML laboratories	*Ms Martina Rozmaric Macefat* *Research Scientist*

TUESDAY 31 OCTOBER

9:00 – 12:00	**THEORETICAL SESSION** Trace Elements Analysis. 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** *Ms Sabine Azemard, Laboratory Technician*

Inorganic Laboratory Orientation.
Dry oven moisture determination in biota sample.

WEDNESDAY 1 NOVEMBER

9:00 – 11:00 **THEORETICAL SESSION** *Ms Emilia Vasileva, Research Scientist*

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

11:00 – 17:00 **PRACTICAL SESSION** *Ms Sabine Azemard, Laboratory Technician*

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.

THURSDAY 2 NOVEMBER

9:00 – 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 3 NOVEMBER

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 6 NOVEMBER

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

Application of metrology concepts for uncertainty and traceability of measurement results.
Study case: AAS determination of lead in sediments.

14:00 – 17:00 **PRACTICAL SESSION** *Mr Roberto Cassi, Mr David Huertas, Laboratory Technician*

Lecture on Sampling Principles and Techniques.
Samples storing, transport and pre-treatment.
Sample preparation: Dissection of biological samples (fish, mussels, oysters).

TUESDAY 7 NOVEMBER

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

Validation of Analytical Method.
ICP-MS Spectrometry- Main Principles and application for trace element analysis of Environment Samples.

13:30 – 17:00 **PRACTICAL SESSION** *Mr Roberto Cassi, Ms Anna Maria Orani, Laboratory Technician*

Sampling field trip.
Demonstration on sediment and water sampling techniques.
Samples storing.

WEDNESDAY 8 NOVEMBER

9:00 – 12:00 **PRACTICAL SESSION** *Ms Sabine Azemard, Laboratory Technician*

Determination of Mercury in sea water by CV AFS.
Optimization of instrument parameters.
Calibration curve. Data treatment.

13:00 – 17:00 *Ms Anna Maria Orani, Laboratory Technician*

Development of method for the determination of Cd in biota sample by ICP-MS.

THURSDAY 9 NOVEMBER

9:00 – 12:00 **PRACTICAL SESSION** — *Ms Sabine Azemard, Ms Anna Maria Orani, Laboratory Technician*

Determination of Mercury by AMA and solid sampling AAS.
Calibration curves.
Data treatment.
Case study: determination of Mercury mass fraction in sediment sample.

13:00 – 17:00 **PRACTICAL SESSION** — *Ms Anna Maria Orani, Laboratory Technician*

Determination of Cu in sediment and biota samples by Solid Sampling CS HR AAS.

FIRDAY 10 NOVEMBER

9:00 – 10:00 **THEORETICAL SESSION** — *Ms Emilia Vasileva, Research Scientist*

Reliable measurement results.

10:00 – 12:00 **CLOSURE OF THE TRAINING COURSE** — *Ms Sylvia Sander, Section Head MESL*

Questionnaire - Presentation of results - Closing discussion - Course evaluation.

Presentation by trainees: — *All participants*

- Theoretical part
- Laboratory experiments.

Closing remarks. — *Mr David Osborn, DIR-NAEL (or alternate)*
Certificates for participation and photos session.

13:00 – 17:00 Visit to the Oceanographic Museum, Monaco. — *All participants*

PRACTICAL SESSIONS

The laboratory session 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 samples preparation started with dissection of fish and mussel, followed by the collection of water and sediment samples.

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)

- <u>Determination of Cu mass fraction in biota samples by Flame AAS</u>

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 gravimetrical standard solutions for Cu, using "matrix matching" approach. The concepts for "matrix matching" of all solutions and calibration blank were not clear for all participants.

After the optimisation of the instrument the use of non-linear versus linear algorithm for calibration (as a possibility for improving the sensitivity of the instrument and achieving linear conditions without further sample dilution) was demonstrated.

- Determination of Cu 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 optimisation of the graphite furnace included the alignment of the graphite furnace and the auto-sampler. The basic steps of one ETAAS program were discussed and introduced. The ashing curve was produced for a sample and a standard.
Biota samples, together with QC samples and procedural blanks were analysed, using the developed temperature program. The possibility for preparation and implementation of automatics 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.

- 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 showed to 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 "conventional" matrix modifier and "conventional" four stage temperature program. The results for mass fraction of Cd in biota sample obtained with fast and conventional programs were compared.

3. Total Mercury by Cold Vapour AAS: Application to digested sediment solutions

4. Sample preparation and instrumental determination of mass fraction of total mercury in digested biological and sediment samples with in vial purge cold vapour atomic fluorescence spectrometry was demonstrated in detail.

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

One full day was dedicated to the determination of total mercury mass fraction in fish samples, using a solid mercury analyser. After the application of the appropriate extraction method the mass fraction of the organic mercury in the same samples was determined, too.

6. 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 optimisation of the measurement method covered: checking the general instrument condition, selecting appropriate isotopes, explanation of the correction for spectral interferences, checking the procedural blanks, analysis of the 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 and evaluating of detection limit were underlined.

7. 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 as prescribed by ISO Guide to 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 obtained from practical session results.

THEORETICAL SESSIONS

An introduction to the basic concepts and terminology of trace elements analysis, as well as, the principles of sample preparation methodology and moisture determination was presented to the participants.

In the training course on trace element analysis, the principles of sample preparation methodology and moisture determination, were presented and lectures were dedicated to the analytical techniques (e.g. Atomic Absorption Spectrometry-AAS, Inductively Coupled Plasma Mass Spectrometry–ICP-MS and Direct Mercury Analyser -AMA), and to hyphenated analytical techniques (Cold Vapour Atomic Fluorescence Spectrometry-CV-AFS), which are used for trace elements and mercury speciation analysis in marine samples. Lectures also included quality assurance, internal and external quality control principles. The most important concepts of measurement science, metrology in chemistry, validation of measurement procedure, use of certified reference materials, traceability and uncertainty of measurement results were also presented. Practical 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.

All theoretical presentations were followed by a round-table discussion in order to answer questions from trainees and to clarify unclear theoretical points.

During the practical session of the training course, the complete procedures on marine samples preparation and the quantification of trace elements in sediments and biota, using AAS, ICP-MS and AMA instrumentations was demonstrated.

The obtained results and more details on the practical part of the course are given in the Practical session section.

CERTIFICATS OF PARTICIPATION

UNEP

MAP

MEDPOL

IAEA
Atoms For Peace
Environment
Laboratories

CERTIFICATE OF PARTICIPATION

Ms Ivana BORZIC

The Public Health Institute
of Split-Dalmatian County
Split, Croatia

attended the training course:

Analytical Techniques for the Determination of Trace Elements in Environmental Samples

30 October – 10 November 2017
IAEA MONACO

Organized by

UNEP/MAP - MED POL & IAEA-NAEL

Trainers

Ms E. Vasileva
Ms A.-M. Orani
Ms S. Azemard
Mr R. Cassi, Mr D. Huertas

Marine Environmental Studies Laboratory

INTERNATIONAL ATOMIC ENERGY AGENCY
ENVIRONMENT LABORATORIES
MONACO

David Osborn
Director - IAEA Environment Laboratories

UNEP

MAP

MEDPOL

IAEA
Atoms For Peace
Environment
Laboratories

CERTIFICATE OF PARTICIPATION

Mr Sliman HSSAISOUNE

Laboratoire National des Etudes et de Surveillance de la Pollution (LNESP)

Rabat, Morocco

attended the training course:

Analytical Techniques for the Determination of Trace Elements in Environmental Samples

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Laboratories

CERTIFICATE OF PARTICIPATION

Ms Amira RJEIBI

National Institute of Marine Science and Technology

(INSTM)

La Goulette, Tunisia

attended the training course:

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Director - IAEA Environment Laboratories

UNEP

MAP

MEDPOL

IAEA
Atoms For Peace
Environment
Laboratories

CERTIFICATE OF PARTICIPATION

Mr Osman TANER

Ministry of Environment and Urbanisation

Environment Reference Laboratory

Ankara, Turkey

attended the training course:

Analytical Techniques for the Determination of Trace Elements in Environmental Samples

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Trainers

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INTERNATIONAL ATOMIC ENERGY AGENCY
ENVIRONMENT LABORATORIES
MONACO

TRAINING COURSE EVALUATION QUESTIONNAIRES

INTERNATIONAL ATOMIC ENERGY AGENCY

ENVIRONMENT LABORATORIES

MARINE ENVIRONMENTAL STUDIES LABORATORY

TRAINING COURSE EVALUATION QUESTIONNAIRE

Training Course organized for MED POL program on the
Analytical Techniques for the Determination of Trace Elements in Environmental Samples
MONACO
(30 October to 10 November 2017)

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: IVANA BORZIĆ

Participant's nationality: CROATIAN

Institute Name & Address: THE PUBLIC HEALTH INSTITUTE OF SPLIT - DALMATIAN COUNTY

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

☒ Excellent ☐ Satisfactory ☐ Poor ☐ Better than expected

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

☒ 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 ☐ To some extent ☐ Uncertain ☐ No

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

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

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

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

6. **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)...GC-MS/MS.....

TRAINING CONTENT

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

☐ Too theoretical ☒ Good balance ☐ Too practical

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

☒ Good ☐ Too many lectures ☐ Too many discussion sessions

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

☐ Too short ☒ Just right ☐ Too long

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

☐ Too fast ☒ Just right ☐ Too slow

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

☒ Very well sequenced ☐ Suitable ☐ Poorly sequenced

12. **How helpful were the group exercises ?**

☒ Very helpful ☐ Helpful ☐ Not helpful

13. Did you have enough skills practice time ?

☒ Yes ☐ No ☐ Uncertain

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

☐ Very valuable ☒ Of some value ☐ No real value

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

I MOST LIKED THE WAY GOOD ORGANIZATION AND A GOOD BALANCE BETWEEN LECTURES AND PRACTICAL WORK

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

/

17. What do you think should be dropped from this course?

/

18. Comments about the course contents:

TO BE HONEST WITH YOU I LEARNED MORE IN THESE TWO WEEKS ABOUT VALIDATION OF METHODS THAN ~~MONTHS~~ FROM MY COLLEAGUES, BUT THAT'S BECAUSE WE DON'T GO TO OFTEN ON PROFESIONAL EDUCATIONS

INSTRUCTIONAL MATERIAL (on CD ROM)

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

☒ Just right ☐ Too few ☐ Too many

20. How do you rate the quality of the handout material ?

☒ High quality ☐ Sufficient ☐ Below expectation

LABORATORIES AND FACILITIES

21. Did you like the seating arrangements of the conference room ?

☒ Yes ☐ No ☐ No opinion

22. How do you rate the practical sessions ?

☒ Excellent ☐ Very good ☐ Fair ☐ Poor

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

☐ Too many ☐ Too few ☒ Just right

24. Comments about laboratory sessions:

LABORATORY SESSIONS WAS VERY GOOD. SABINE AND ANA WAS ARE VERY NICE AND THEY HAVE A GREAT KNOWLEDGE ABOUT THEIR INSTRUMENTS

25. What is your overall evaluation of the course ?

☐ Excellent ☒ Very good ☐ Fair ☐ Poor

QUESTIONS FOR THE CERTIFICATE OF PROFICIENCY

I. **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

II. **A CRM does NOT necessarily need to have:**

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

III. **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 ✓
- [ ] Sample number ✓

IV. **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 ✓
- [ ] 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?

IN ANALYTICAL CHEMISTRY, A TRACE ELEMENTS ARE ONE WHOSE AVERAGE CONCENTRATION IS LESS THAN 100 ppm.

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

INTERNATIONAL ATOMIC ENERGY AGENCY

ENVIRONMENT LABORATORIES

MARINE ENVIRONMENTAL STUDIES LABORATORY

TRAINING COURSE EVALUATION QUESTIONNAIRE

Training Course organized for MED POL program on the
Analytical Techniques for the Determination of Trace Elements in Environmental Samples
MONACO
(30 October to 10 November 2017)

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: Sliman HSSAISSOUNE

Participant's nationality: Moroccan

Institute Name & Address: I.N.E.S.P. Rue Ben Abdellah Ezzaraqui Madinat Al Irfane Rabat

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

☑ Excellent ☐ Satisfactory ☐ Poor ☐ Better than expected

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

☑ Yes ☐ To some extent ☐ Uncertain ☐ No

.....

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

☑ Yes ☐ To some extent ☐ Uncertain ☐ No

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☑ Yes ☐ To some extent ☐ Uncertain ☐ No

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☑ Yes ☐ To some extent ☐ Uncertain ☐ No

6. **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

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

☐ Too theoretical ☑ Good balance ☐ Too practical

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

☑ Good ☐ Too many lectures ☐ Too many discussion sessions

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

☐ Too short ☑ Just right ☐ Too long

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

☑ Too fast ☐ Just right ☐ Too slow

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

☑ Very well sequenced ☐ Suitable ☐ Poorly sequenced

12. **How helpful were the group exercises ?**

☑ Very helpful ☐ Helpful ☐ Not helpful

13. Did you have enough skills practice time ?

☑ Yes ☐ No ☐ Uncertain

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

☐ Very valuable ☑ Of some value ☐ No real value

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

- Lovely staf and competent
- Methodology of working

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

Nemt

17. What do you think should be dropped from this course?

Sampling.

18. Comments about the course contents:

The course contents is reach for me. I learn some new skills that i need in my new work in the Laboratory (LNESR).

INSTRUCTIONAL MATERIAL (on CD ROM)

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

☑ Just right ☐ Too few ☐ Too many

20. How do you rate the quality of the handout material ?

☑ High quality ☐ Sufficient ☐ Below expectation

LABORATORIES AND FACILITIES

21. Did you like the seating arrangements of the conference room ?

☑ Yes ☐ No ☐ No opinion

22. How do you rate the practical sessions ?

☑ Excellent ☐ Very good ☐ Fair ☐ Poor

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

☐ Too many ☐ Too few ☑ Just right

24. Comments about laboratory sessions:

For the Laboratory Sessions there is many things internship: Preparation of Samples, Calibration Curves

25. What is your overall evaluation of the course ?

☑ Excellent ☐ Very good ☐ Fair ☐ Poor

QUESTIONS FOR THE CERTIFICATE OF PROFICIENCY

I. **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
- [x] Degradation of CRMs due to bioactivity should be avoided
- [x] CRMs should always be accompanied by a certificate

II. **A CRM does NOT necessarily need to have:**

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

III. **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
- [ ] Sample number

IV. **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
- [x] Use a Reference Material
- [x] Calibrate the critical measurement equipment once a year

5. What is your definition for trace element?

Is the elements with the concentration is bellow order of ppm

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

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

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

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

☒ Yes ☐ To some extent ☐ Uncertain ☐ No

6. **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

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

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☒ Too short ☐ Just right ☐ Too long

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

☒ Too fast ☐ Just right ☐ Too slow

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

☒ Very well sequenced ☐ Suitable ☐ Poorly sequenced

12. **How helpful were the group exercises ?**

☒ Very helpful ☐ Helpful ☐ Not helpful

13. Did you have enough skills practice time ?

☒ Yes ☐ No ☐ Uncertain

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

☒ Very valuable ☐ Of some value ☐ No real value

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

- Digestion d'échantillonnage for déterminate of trace métals and digestion of biota, préparation des standard, détermination des métaux traces par les différents instruments (Cu, Cd, Hg), charte de contrôle...

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

- Tout a été bien réussie pour améliorer mes connaissances pour les analyses et le dosage des métaux traces.

17. What do you think should be dropped from this course?

Tout est important, rien à éviter

18. Comments about the course contents:

le cours est bien enrichie par définit, méthodes de calculs, présentation les appareils

INSTRUCTIONAL MATERIAL (on CD ROM)

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

☒ Just right ☐ Too few ☐ Too many

20. How do you rate the quality of the handout material ?

☒ High quality ☐ Sufficient ☐ Below expectation

LABORATORIES AND FACILITIES

21. Did you like the seating arrangements of the conference room ?

☒ Yes ☐ No ☐ No opinion

22. How do you rate the practical sessions ?

☒ Excellent ☐ Very good ☐ Fair ☐ Poor

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

☐ Too many ☐ Too few ☒ Just right

24. Comments about laboratory sessions:

Je tiens à remercier tout le membre de l'I.A.E.A pour les efforts fournis pour cette formation, ravis de vous connaître toutes les personnes. Merci.

25. What is your overall evaluation of the course ?

☒ Excellent ☐ Very good ☐ Fair ☐ Poor

QUESTIONS FOR THE CERTIFICATE OF PROFICIENCY

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IV. **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
- ☐ Rèport 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?

Ce sont des métaux lourds toxiques s'ils dépassent un seuil et dont certain sont radioactifs. Ces métaux se trouvent dans l'air, végétaux, organismes, eau, ayant comme une origine principale les activités et les apports anthropiques.

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

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

☑ Yes ☐ To some extent ☐ Uncertain ☐ No

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

☑ Yes ☐ To some extent ☐ Uncertain ☐ No

6. **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

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☐ Too theoretical ☑ Good balance ☐ Too practical

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☐ Too short ☑ Just right ☐ Too long

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

☐ Too fast ☑ Just right ☐ Too slow

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

☐ Very well sequenced ☑ Suitable ☐ Poorly sequenced

12. **How helpful were the group exercises ?**

☐ Very helpful ☑ Helpful ☐ Not helpful

LABORATORIES AND FACILITIES

21. Did you like the seating arrangements of the conference room ?

☑ Yes ☐ No ☐ No opinion

22. How do you rate the practical sessions ?

☐ Excellent ☑ Very good ☐ Fair ☐ Poor

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

☑ Too many ☐ Too few ☐ Just right

24. Comments about laboratory sessions:

Yes

25. What is your overall evaluation of the course ?

☐ Excellent ☑ Very good ☐ Fair ☐ Poor

13. Did you have enough skills practice time ?

☑ Yes ☐ No ☐ Uncertain

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

☑ Very valuable ☐ Of some value ☐ No real value

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

Device applications and theoretical information are very nice.

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

Individual device applications with participant

17. What do you think should be dropped from this course?

No.

18. Comments about the course contents:

The distribution of subjects is sufficient for a time interval of 2 weeks

INSTRUCTIONAL MATERIAL (on CD ROM)

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

☑ Just right ☐ Too few ☐ Too many

20. How do you rate the quality of the handout material ?

☑ High quality ☐ Sufficient ☐ Below expectation

QUESTIONS FOR THE CERTIFICATE OF PROFICIENCY

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- ☐ 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?

Concentration range is referred to as elements with ppm and lower values

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

REPORT

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

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

Organized by:

International Atomic Energy Agency-Environment Laboratories
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30 October - 10 Novembre 2017

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CONTENTS

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

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 MED POL, for participants from Mediterranean laboratories involved in the UNEP/Mediterranean Action Plan - MED POL 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 in June 2017 to all MED POL National Focal Points, inviting them to nominate candidates from their respective countries in order to participate in the training course. After the reception of the nominations and taking into consideration the training capacity of the laboratories, six (6) participants from 5 different countries (Algeria, Croatia, Morocco, Tunisia, Turkey) were selected by MED POL and invited to attend the Training Course in NAEL, Monaco. Invitation letters to the participants were sent by IAEA/NAEL-MESL on the 11th of September 2017. Unfortunately the participant from Algeria could not obtain her Visa in due time and was not able to attend the Training Course.
The course was implemented from 30 October to 10 November 2017.

The group of participants was very heterogeneous (in terms of age and occupation) and not all of them were directly involved in this type of analyses in their institutions. In order to set a working pace that everyone could follow the entire laboratory procedures for both sediment and biota samples were accurately analyzed 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.

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 was unanimously welcomed by the trainees. While beginners were able to learn and practice new procedures and techniques more advanced trainees took the opportunity to exchange information and opinion on a broad range of topics.

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 383) and biota sample (IAEA 432). At the end of the course the identity of the samples were 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 under-water 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.
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 details. The details on the practical part of the course are given in the Practical Session section.

Evaluation

At the end of the course a questionnaire was distributed to the trainees in order to collect their feedbacks on training organization, content and structure. The course was, unanimously, found to be useful and valuable and trainees' needs were met. Although the balance of lectures, group discussions and group exercises was found to be correct, most participants wished to have more practical time in the laboratory to apply the newly learned knowledge.

Conclusion

The training course was beneficial for the all the trainees. Each participant had a chance to see the application of strict analytical protocols and the quality system in place in MESL and in most cases they realized they will have to improve or modify their laboratory procedures.

Although most participants were only partially familiar with concepts like Internal Standards, Reference Materials and Quality Assurance, they showed genuine interest and commitment to improve the quality of their work.

Because of the diversity of trainees' background and actual occupation some practical sessions and group exercises like results calculation and data quantification took longer than foreseen. Computer sessions were included in the training course to meet the needs of both beginners and more skilled trainees.

Trainees were provided with a Certificate stating their participation in the Training Course. They were supplied with CD-ROMs containing Reference Methods available and useful literature and lectures.

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

General conclusion from NAEL/MESL teaching staff:
The heterogeneity of the background of the participants of the 2017 MEDPOL training course on the analysis of Organochlorinated Pesticides (OCs) and Polychlorinated Biphenyls (PCBs) in marine environmental samples made it very challenging to keep the level of the course high enough to ensure benefit to the participants and their home laboratories. In the future, an attempt should be made to improve the nomination and selection process for participants in the MEDPOL training course. We propose to make the national focal points more aware of the consequences it can have on the course if some key criteria for selection (language level, laboratory experience) are not strictly applied.
Alternatively it may be beneficial to offer two different types of course – one for beginners and one for specialists.

PRACTICAL WORK SESSION

Practical sessions were organized to show the main critical aspects in each step of the analytical procedure and in the data analyses instrumentation. They included and covered the following “hands-on” step procedures:

- Microwave oven extraction and surrogate standards spiking

Special focus was given to the spiking of surrogate standards in order to increase accuracy on the quantification of the target compounds by the internal standard method. Each trainee was able to repeat the critical step several times until he was confident with the spiking procedure.

- Evaporation of solvent extract

Rotatory evaporator was shown and used by the trainees to concentrate the organic extracts of the samples. A multievaporator was also shown to the trainees and careful evaporation under nitrogen gas was shown and used to prepare the final extracts for gas chromatography analyses.

- Sulphur clean-up in sediment extracts

Sulphur in the sediment extract must be completely eliminated to avoid interferences before quantification of the final extract, especially by gas chromatography coupled to electron capture detector (GC/ECD). The Sulphur removal procedure was performed by careful activation of copper, and the overall procedure on preparation of the activated copper was performed in detail to show to the trainees the critical points of the process (activation of copper and complete removal of acid and water).

- Separation techniques by solid-phase extraction (SPE).

The fractionation of the different organochlorine compounds was performed by deposing the concentrated organic extract on top of 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 or lipid content of the biological samples was shown and determined gravimetrically in a microbalance to calculate the aliquot of extract sample that could be cleanup by adsorption chromatography on a SPE column.

The extracts were then separated into two aliquots: First aliquot was treated with sulphuric acid, to destroy the interfering lipids before the separation technique on Florisil SPE was performed. As some organochlorinated pesticides may degradate with acid, the other aliquot of the extract was cleaned using an alternative procedure, 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 shown 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 computer session is shown in Fig. 1-7.

- 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 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).

The estimation of the uncertainty of the measurements 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 exhibition on the maintenance of the gas chromatography, including the change of glass liner, o-ring, septum and gold ring was shown. Also the procedure on how to cut and install the capillary columns 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 with magnifiers.

EXAMPLE OF COMPUTER SESSION AND DATA PRODUCED INCLUDING QUALITY CONTROL CHARTS

Figure 1. Description of 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 in order 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 analyses 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**	**13384**	
HCB	10	100	1000	2249	3.37
PCB-29 SU	**25**	**100**	**2500**	**1668**	**0.50**
PCB-28	10	100	1000	862	1.29
PCB-52	10	100	1000	640	0.96
PCB-101	10	100	1000	830	1.24
ppDDE	10	100	1000	1478	1.48
PCB-118	10	100	1000	925	0.92
PCB-153	10	100	1000	888	0.89
ppDDT	10	100	1000	541	0.54
PCB-138	10	100	1000	1116	1.11
PCB-180	10	100	1000	1180	1.18
PCB-198 SU	**25**	**100**	**2500**	**2504**	**0.75**

OCs - F2

	CALIBRATION CURVE-1				
	Conc. (pg/µl)	**Volume (µl)**	**Qty Spiked (pg)**	**Area**	**RRF**
TCMX (GC-IS)	**1000**	**10**	**10000**	**16775**	
Lindane	10	100	1000	2121	1.58
E-HCH - SU	**25**	**100**	**2500**	**3346**	**0.80**
ppDDD	10	100	1000	1840	1.37

OCs - F3

	CALIBRATION CURVE-1				
	Conc. (pg/µl)	**Volume (µl)**	**Qty Spiked (pg)**	**Area**	**RRF**
TCMX (GC-IS)	**1000**	**10**	**10000**	**11142**	
Endosulfan LD40 - SU	**25**	**100**	**2500**	**3081**	**1.11**
a-Endosulfan	10	100	1000	1230	1.00
Dieldrin	10	100	1000	1519	1.23
Endrin	10	100	1000	1154	0.94
b-Endosulfan	10	100	1000	1388	1.13

Figure 3. Average of the RRFs from the 3 calibration levels 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**
3.3	0.06	1.9	HCB	3.3
0.5	**0.02**	**3.8**	**PCB-29 SU**	0.5
1.2	0.09	7.0	PCB-28	1.2
0.8	0.15	18.8	PCB-52	0.8
1.1	0.16	14.5	PCB-101	1.1
1.4	0.09	6.8	ppDDE	1.4
0.8	0.13	16.9	PCB-118	0.8
0.7	0.13	17.0	PCB-153	0.7
0.6	0.03	4.6	ppDDT	0.6
1.0	0.12	12.3	PCB-138	1.0
1.1	0.10	9.7	PCB-180	1.1
0.8	**0.06**	**7.4**	**PCB-198 SU**	0.8

Mean RRF	SD	%RSD		
			Compound	**Mean RRF**
1.5	0.11	7.4	Lindane	1.5
0.8	**0.02**	**3.0**	**E-HCH - SU**	0.8
1.2	0.12	9.4	ppDDD	1.2

Mean RRF	SD	%RSD		
			Compound	**Mean RRF**
1.3	**0.21**	**16.4**	**Endosulfan LD40 - SU**	1.3
0.9	0.10	11.6	a-Endosulfan	0.9
1.1	0.12	10.9	Dieldrin	1.1
0.8	0.10	11.9	Endrin	0.8
1.0	0.13	13.1	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**	**SU % REC**
TCMX (GC-IS)	**1000**	**10**	**10000**	**7305**		
HCB				477	641	
PCB-29 SU	**100**	**100**	**10000**	**2234**	**5941**	**59**
PCB-28				29	108	
PCB-52				50	286	
PCB-101				39	164	
ppDDE				16	22	
PCB-118				30	71	
PCB-153				53	131	
ppDDT				99	318	
PCB-138				50	93	
PCB-180				25	42	
PCB-198 SU	**100**	**100**	**10000**	**5469**	**9175**	**92**

	BLANK					
	Conc. (pg/µl)	**Vol. (µl)**	**Qty Spiked (pg)**	**Area**	**Qty Found**	**SU % REC**
TCMX (GC-IS)	**1000**	**10**	**10000**	**5161**		
Lindane				22	42	
E-HCH - SU	**100**	**100**	**10000**	**3517**	**8279**	**83**
ppDDD				19	43	

	BLANK					
	Conc. (pg/µl)	**Vol. (µl)**	**Qty Spiked (pg)**	**Area**	**Qty Found**	**SU % REC**
TCMX (GC-IS)	**1000**	**10**	**10000**	**4763**		
Endosulfan LD40 - SU	**100**	**100**	**10000**	**4106**	**6853**	**69**
a-Endosulfan				70	193	
Dieldrin				127	283	
Endrin				63	186	
b-Endosulfan				73	181	

Figure 5. Example of quantitative calculation of a reference material sample (IAEA-383) for fractions 1, 2 and 3.

grams extracted	3.16

	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**	**5900**				
HCB				119466	164800	164159	51.95	
PCB-29 SU	**100**	**100**	**10000**	**2178**	**7171**			**72**
PCB-28				322	1221	1114	0.35	
PCB-52				1239	7202	6916	2.19	
PCB-101				2860	12276	12112	3.83	
ppDDE				2695	4370	4348	1.38	
PCB-118				3062	8870	8799	2.78	
PCB-153				4436	13377	13246	4.19	
ppDDT				589	2323	2005	0.63	
PCB-138				6217	14206	14113	4.47	
PCB-180				4527	9507	9465	3.00	
PCB-198 SU	**100**	**100**	**10000**	**4469**	**9283**			**93**

	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**	**9720**				
Lindane				497	535	493	**0.16**	
E-HCH - SU	**100**	**100**	**10000**	**6354**	**7942**			**79**
ppDDD				2143	2716	2674	**0.85**	

	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**	**4981**				
Endosulfan LD40 - SU	**100**	**100**	**10000**	**4300**	**6862**			**69**
a-Endosulfan				157	414	222	**0.07**	
Dieldrin				579	1229	946	**0.30**	
Endrin				235	663	477	**0.15**	
b-Endosulfan				228	542	361	**0.11**	

Figure 6. Table of quantitative calculation of a sediment reference material sample (IAEA-383) performed by the trainees. Results include mean, standard deviation and relative standard deviation (ng/g d.w.)

Compound	IAEA-383 Sample 1	IAEA-383 Sample 2	IAEA-383 Sample 3	Mean (ng/g)	Standard Deviation (ng/g)	Relative Standard Deviation (%)	Updated Reference Value (ng/g)	Target Standard Deviation (ng/g)
PCB-28	0.35	0.45	0.51	0.44	0.06	15%	0.93	0.12
PCB-52	2.19	2.24	2.16	2.20	0.04	2%	1.73	0.22
PCB-101	3.83	3.79	4.03	3.88	0.10	3%	2.90	0.36
PCB-118	2.78	2.74	2.50	2.68	0.12	5%	2.73	0.34
PCB-138	4.47	4.39	4.07	4.31	0.17	4%	4.41	0.55
PCB-153	4.19	4.26	3.88	4.11	0.16	4%	4.09	0.51
PCB-180	3.00	2.94	2.78	2.90	0.09	3%	2.99	0.37
HCB	51.95	45.76	46.83	48.18	2.70	6%	43.34	5.42
Lindane	0.16	0.17	0.17	0.17	0.01	4%	0.16	0.02
ppDDE	1.38	1.37	1.26	1.33	0.05	4%	1.38	0.17
ppDDD	0.85	0.94	0.84	0.88	0.05	6%	0.87	0.11
ppDDT	0.63	0.44	0.65	0.57	0.10	17%	1.03	0.13
Dieldrin	0.30	0.38	0.25	0.31	0.06	18%	0.22	0.03
Endrin	0.15	0.23	0.16	0.18	0.03	19%	0.07	0.01
a-Endosulfan	0.07	0.07	0.10	0.08	0.02	19%	0.01	0.00
b-Endosulfan	0.11	0.26	0.26	0.21	0.07	33%	-	-

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	0.43	0.49	0.32	0.41	0.07	17%	0.32	0.26
PCB-52	1.11	1.14	1.04	1.10	0.05	5%	1.20	1.20
PCB-101	1.19	1.22	1.00	1.14	0.10	8%	1.20	0.49
PCB-118	0.79	0.89	0.89	0.86	0.04	5%	1.09	0.42
PCB-138	2.53	2.31	2.46	2.43	0.09	4%	2.20	0.84
PCB-153	3.40	3.28	3.28	3.32	0.06	2%	2.80	0.99
PCB-180	0.30	0.22	0.24	0.25	0.03	12%	0.20	0.11
HCB	0.11	0.06	0.10	0.09	0.03	29%	0.20	0.10
Lindane	0.14	0.19	0.19	0.17	0.03	15%	0.58	0.54
ppDDE	2.96	2.66	3.11	2.91	0.19	6%	2.10	1.00
ppDDD	0.99	0.99	0.95	0.98	0.02	2%	0.88	0.49
ppDDT	1.56	1.41	1.46	1.48	0.08	5%	0.67	0.46

Figure 8. Quality control chart (QC) for PCB-180 in IAEA-383 sediment reference material (ng/g d.w).

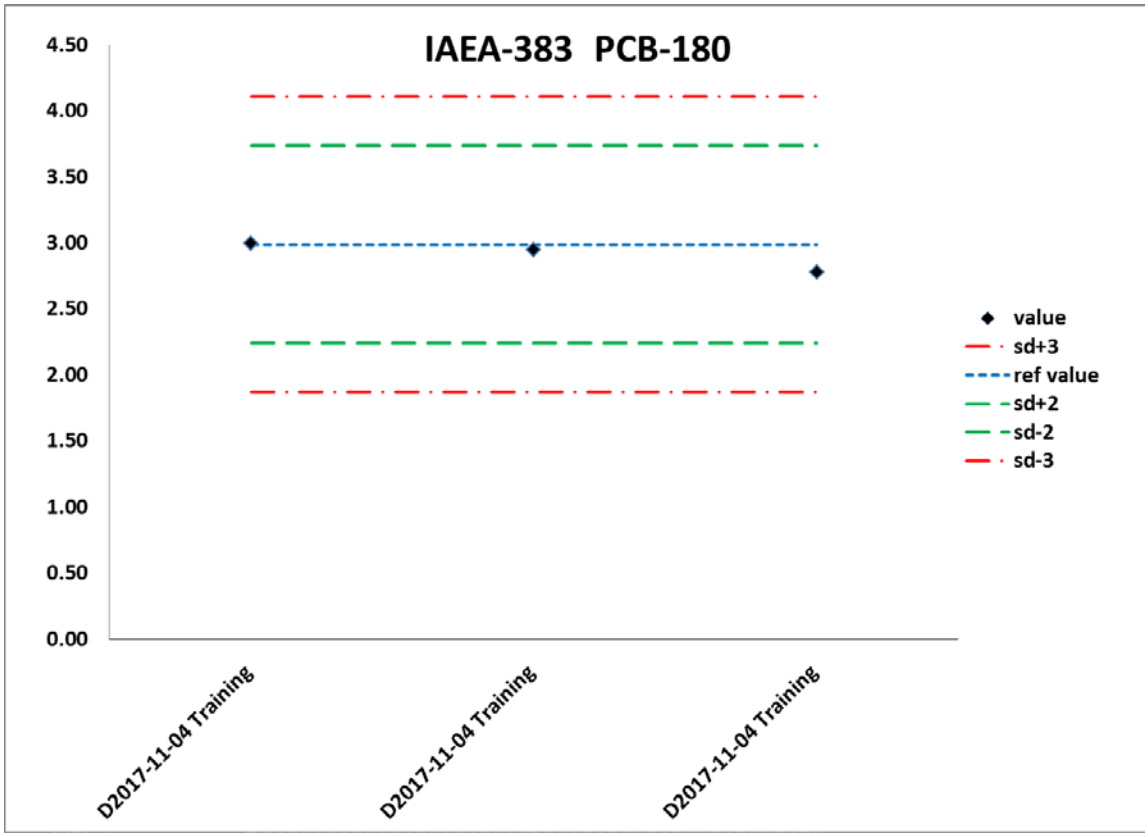


Figure 9. Quality control chart (QC) for p,p-'DDE in IAEA-383 sediment reference material (ng/g d.w).

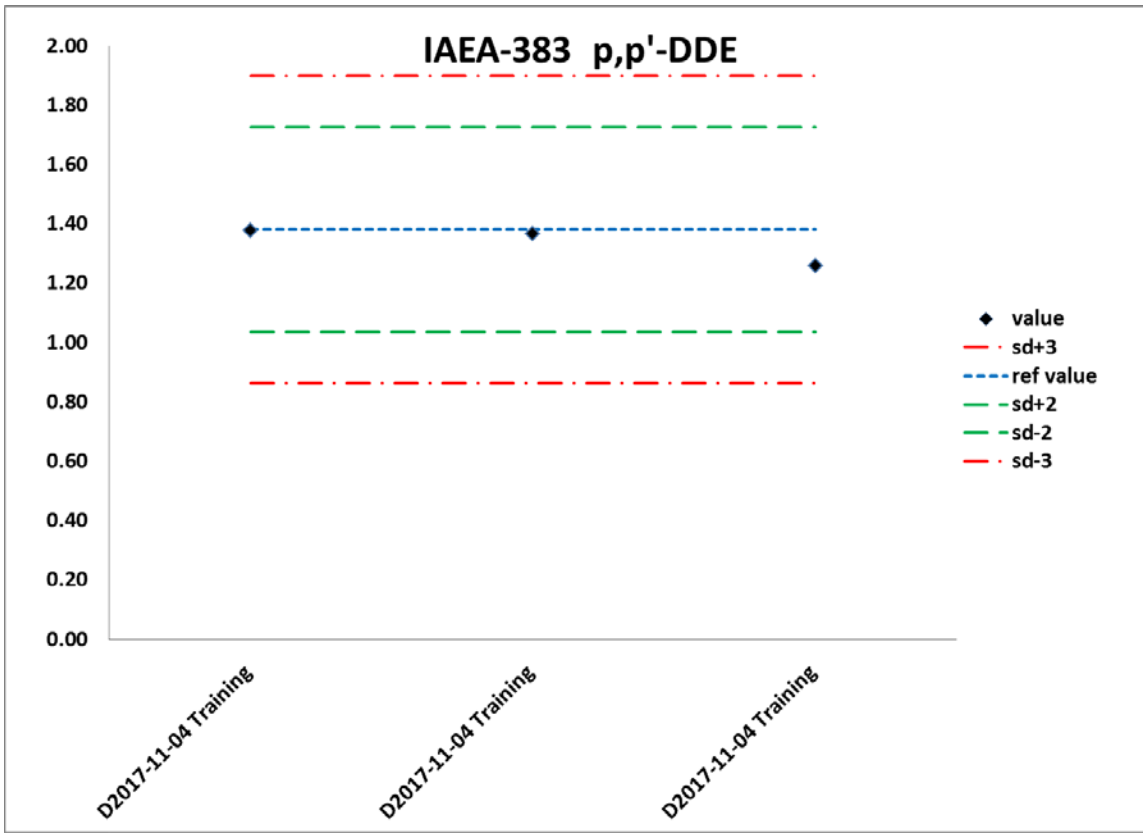


Figure 10. Quality control chart (QC) for PCB-28 in IAEA-432 biota reference material (ng/g d.w).

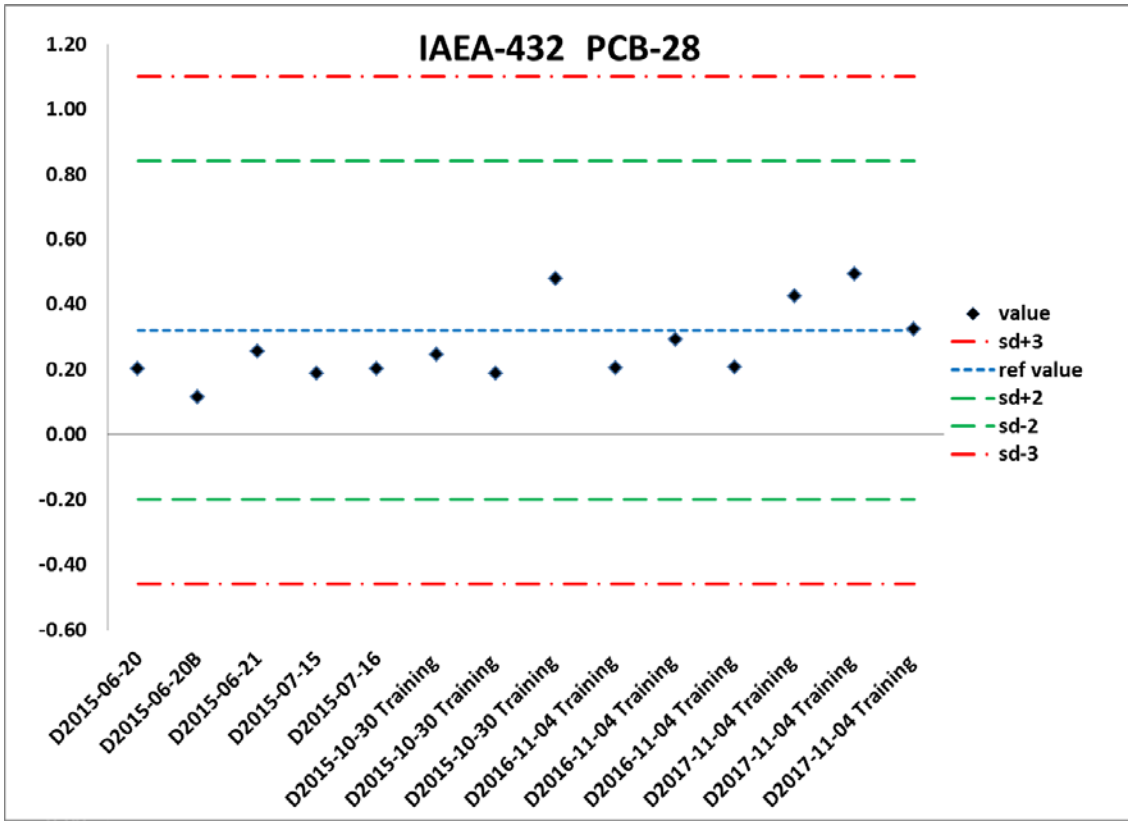
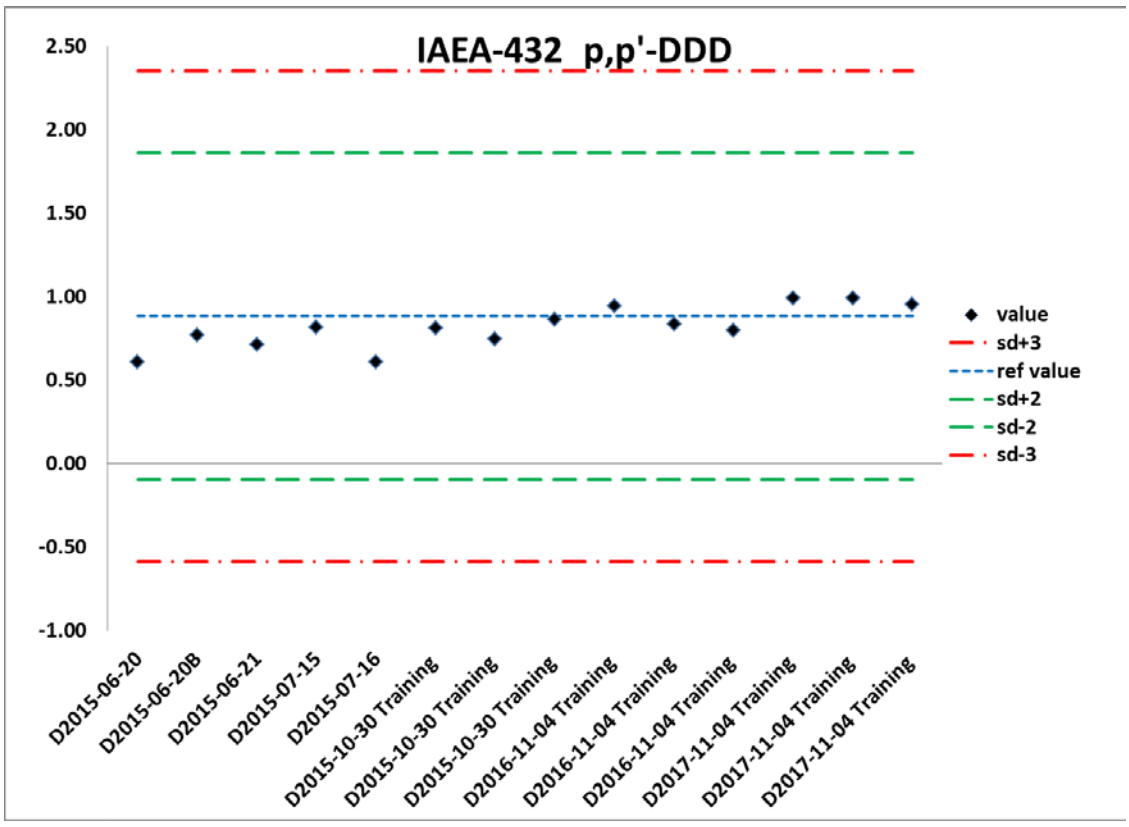


Figure 11. Quality control chart (QC) for p,p-'DDD in IAEA-432 biota reference material (ng/g d.w).



LIST OF PARTICIPANTS

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

CROATIA	
Ms Jelena KORON Public Health Institute County of Istria Nazorova 23 PULA	Email: ekologija2@zzjziz.hr
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TUNISIA	
Mr Fourat AKROUT National Institute of Science and Technology (INSTM) Port de la Goulette LA GOULETTE	Email: fouratakrout@yahoo.fr
TURKEY	
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COURSE OUTLINE

MED POL ORGANIC CONTAMINANTS ANALYSIS TRAINING COURSE

IAEA – Environment Laboratories, Monaco

30 Oct. – 10 Nov. 2017

COURSE OUTLINE

(Liable to modifications upon request)

MONDAY 30 OCTOBER

9:00 – 09:05	Welcome to IAEA Environment Laboratories Monaco.	*Mr David Osborn DIR-NAEL (or alternate)*
09:05 – 09:30	Presentation of MESL and its activities.	*Ms Sylvia Sander Section Head MESL*
09:30 – 09:45	Laboratory Safety and Security.	*Mr Jean-François Comanducci Head - EES*
09:45 – 10:00	Coffee break	
10:00 – 11:30	Self-introduction of participants and expectations from the Training Course.	*All participants*
11:30 – 12:00	Visit of the REL laboratories	*Mr Marc Métian Research Scientist*
14:00 – 14:30	Visit of the RML laboratories	*Ms Martina Rozmaric Macefat Research Scientist*
14:30 – 17:00	Analytical Methods for Organic Contaminants. Introduction to computer sessions.	*Mr Roberto Cassi Laboratory Technician*
	Sources, properties and fate of organochlorinated compounds (OCs). The past, the present, and the future.	*Ms Imma Tolosa Research Scientist*

TUESDAY 31 OCTOBER

9:00 – 17:00 **PRACTICAL SESSION**

Mr Roberto Cassi
Mr David Huertas
Laboratory Technician

Extraction of sediment and biological samples with microwave oven. Filtration of samples and blank. Activation of copper. Removal of sulfur on sediment samples and blank.

THEORETICAL SESSION

Ms Imma Tolosa
Research Scientist

Analytical techniques for the determination of OCs. Extraction and clean-up methods.
Quantitative determination of OCs by GC-ECD.

WEDNESDAY 1 NOVEMBER

9:00 – 17:00 **PRACTICAL SESSION**

Mr Roberto Cassi
Mr David Huertas
Laboratory Technician

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 GC internal standards. Instrumental Injection (GC-ECD).

THURSDAY 2 NOVEMBER

09:00 – 12:30 **THEORETICAL SESSION**

Mr Imma Tolosa
Research Scientist

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 Technician

Determination of lipid content for biological samples. Samples clean-up using sulfuric acid.

FRIDAY 3 NOVEMBER

9:00 – 13:00 **PRACTICAL SESSION**

Mr Roberto Cassi
Mr David Huertas
Laboratory Technician

Solid Phase Extraction (SPE) column chromatography for biological samples (F3). 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 Technician

GC-ECD maintenance and troubleshooting.
Set up of GC-MS for confirmation analyses of organochlorinated compounds.

Ms Imma Tolosa
Research Scientist

MONDAY 6 NOVEMBER

9:00 – 12:00 **THEORETICAL SESSION**

Ms Emilia Vasileva
Research Scientist

Application of metrology concepts for uncertainty and traceability of measurement results.
Study case: AAS determination of lead in sediments.

14:00 – 17:00 **PRACTICAL SESSION**

Mr Roberto Cassi
Mr David Huertas
Laboratory Technician

Lecture on Sampling Principles and Techniques.
Samples storing, transport and pre-treatment.
Sample preparation: Dissection of biological samples (fish, mussels, oysters).

TUESDAY 7 NOVEMBER

9:00 – 13:00 **PRACTICAL SESSION**

Mr Roberto Cassi
Mr David Huertas
Laboratory Technician

Sampling field trip.
Demonstration on sediment and water sampling techniques, samples storing, data reporting.

14:00 – 17:00 **THEORETICAL SESSION**

Ms Imma Tolosa
Research Scientist

High resolution gas chromatography, theory and instrumentation.

WEDNESDAY 8 NOVEMBER

9:00 – 12:00	**THEORETICAL SESSION**	*Ms Imma Tolosa* *Research Scientist*
	The stationary phase. Capillary columns. Sample introduction. Detectors. Temperature effects.	
13:00 – 17:00	**COMPUTER SESSION**	
	Introduction to GC-ECD data retreatment software. Peaks identification and integration. Use of Spreadsheet for data quantification.	*Mr Roberto Cassi* *Mr David Huertas* *Laboratory Technician*

THURSDAY 9 NOVEMBER

9:00 – 17:00	**PRACTICAL SESSION**	*Mr Roberto Cassi* *Mr David Huertas* *Laboratory Technician*
	Data quantification of organochlorine compounds. Determination and use of limits of detection. Evaluation of organochlorinated results on sediment samples, QA/QC of data obtained.	
	Uncertainty estimation by the " Nordtest approach"	*Ms Imma Tolosa* *Research Scientist*

FIRDAY 10 NOVEMBER

9:00 – 10:00	**THEORETICAL SESSION**	*Ms Emilia Vasileva* *Research Scientist*
	Reliable measurement results.	
10:00 – 12:00	**CLOSURE OF THE TRAINING COURSE**	*Ms Sylvia Sander* *Section Head MESL*
	Questionnaire - Presentation of results - Closing discussion - Course evaluation.	
	Presentation by trainees: • Theoretical part • Laboratory experiments.	*All participants*
	Closing remarks. Certificates for participation and photos session.	*Mr David Osborn* *DIR-NAEL* *(or alternate)*
13:00 – 17:00	Visit to the Oceanographic Museum, Monaco.	*All participants*

CERTIFICATES OF PARTICIPATION

UNEP

MAP

MEDPOL

IAEA
Atoms For Peace
Environment
Laboratories

CERTIFICATE OF PARTICIPATION

Mr Fourat AKROUT

National Institute of Marine Science and Technology

(INSTM)

La Goulette, Tunisia

attended the training course:

Analysis of Organochlorine Pesticides and Polychlorinated Biphenyls in Environmental Samples

30 October – 10 November 2017
IAEA MONACO

Organized by

UNEP/MAP - MED POL & IAEA-NAEL

Trainers

Ms I. Tolosa
Mr D. Huertas
Mr R. Cassi
Ms E. Vasileva

Marine Environmental Studies Laboratory

David Osborn
Director - IAEA Environment Laboratories

INTERNATIONAL ATOMIC ENERGY AGENCY
ENVIRONMENT LABORATORIES
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CERTIFICATE OF PARTICIPATION

Ms Nursel CALOVA

Ministry of Environment and Urbanisation

Environment Reference Laboratory

Ankara, Turkey

attended the training course:

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Ms Jelena KORON

Public Health Institute

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CERTIFICATE OF PARTICIPATION

Mr Moulay Lahcen OUAHIDI

Laboratoire National des Etudes et de Surveillance de la Pollution (LNESP)

Rabat, Morocco

attended the training course:

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Ms Saida ZAZA

Office National de l'Electricité et de l'Eau potable – Branche eau (ONEE)

Rabat, Morocco

attended the training course:

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INTERNATIONAL ATOMIC ENERGY AGENCY
ENVIRONMENT LABORATORIES
MONACO

David Osborn
Director - IAEA Environment Laboratories

EVALUATION OF TRAINING BY PARTICIPANTS

1. *What is your overall reaction to the workshop?*

[80%] Excellent [20%] Better than expected [ ] Satisfactory [ ] Poor

2. *Do you feel that the workshop met your needs? (If NOT, please explain)*

[80%] Yes [20%] To some extent [ ] Uncertain [ ] No

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

[60%] Yes [40%] To some extent [ ] Uncertain [ ] No

4. *Do you have a better attitude about your job thanks to this course?*

[100%] Yes [ ] To some extent [ ] Uncertain [ ] No

5. *Would you recommend to others in your field to attend this course?*

[80%] Yes [] To some extent [ ] Uncertain [20%] No

6. *In your opinion, the number of participants in the workshop was:*

[80%] Just right [20%] Too few [ ] Too many

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

[80%] Yes [20%] No

If YES, please recommend topics:

[2] Other pesticides [] Heavy metals

[2]Others *(specify) : Organotin compounds, PAH's,*

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

[ ] Too many lectures [20%] Too many discussions [80%] Good

9. *How helpful were the group exercises?*

[60%] Very helpful [40%] Helpful [ ] Not helpful

10. *What do you think of the speed of the course?*

[20%] Too fast [80%] Just right [ ] Too slow

11. *Did you have enough skills practice time?*

[80%] Yes [20%] No [ ] Uncertain

WORKSHOP CONTENT

15. How do you rate the workshop length?

[100%] Just right [ ] Too short [20%] Too long

16. What's your opinion on the workshop content sequence?

[100%] Very well sequenced [ ] Suitable [ ] Poorly sequenced

17. How valuable was the workshop content to your current job?

[100%] Very valuable [ ] Some value [ ] No real value

18. How do you rate the balance of theoretical and practical sessions?

[20%] Too theoretical [60%] Good balance [20%] Too practical

INSTRUCTIONAL MATERIAL

20. In your opinion, was the number of handouts you received sufficient?

[80%] Just right [ ] Too few [20%] Too many

21. How do you rate the quality of the handout material?

[100%] High quality [ ] Sufficient [ ] Below expectations

LABORATORY AND FACILITIES

22. How do you rate the laboratory sessions?

[60%] Excellent [40%] 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.)?

[40%] Excellent [20%] Very Good [40%] Good [ ] Fair [ ] Poor

26. What is your overall evaluation of the course?

[80%] Excellent [20%] Very good [] Good [ ] Fair [ ] Poor

Note: Questions that required comments were not reported.

TRAINING COURSE EVALUATION QUESTIONNAIRES

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Environment Laboratories

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
(30 October to 10 November 2017)

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: AKROUT FOURAT

Participant's country: TUNISIE

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?**

[ ] Yes [ ] To some extent [ ] Uncertain [X] 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 [ ] Heavy metals [ ] Others *(specify)* Hydrocarbures aromatiques

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)

a practical Sessions because, we work in laboratory to analyzing

13. What did you like least about the workshop course ? (weakest aspects)

14. What do you think should be dropped from this workshop course ?

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 [ ] Good balance [X] Too practical

19. Comments about the course contents :

the Course contents its Very good for me

INSTRUCTIONAL MATERIAL

20. In your opinion, was the number of handouts you received sufficient ?

[ ] Just right [ ] Too few [X] 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 is very good

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!

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
(30 October to 10 November 2017)

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: NURSEL CALOVA

Participant's country: TURKEY

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 [ ] Heavy metals [ ] Others *(specify)*.....

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

[ ] Too many lectures [X] Too many discussions [ ] Good

9. **How helpful were the group exercises ?**

[ ] Very helpful [X] 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 [ ] Uncertain

WORKSHOP CONTENT

12. What did you like best about the workshop course ? (strongest aspects)

The workshop course ; application of their work

13. What did you like least about the workshop course ? (weakest aspects)

Maybe, the device usage should be increased

14. What do you think should be dropped from this workshop course ?

I think ; the course is enough

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 ?

[x] Too theoretical [ ] Good balance [ ] Too practical

19. Comments about the course contents :

The course is good But, Distribution of subjects is sufficient for a five weeks ~~for~~ ~~the~~ interval

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:

Very good the laboratory sessions

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 for taking the time to answer this questionnaire.
Your input is really valuable to us!

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(30 October to 10 November 2017)

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: JELENA KORON

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

.....

.....

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)*.....

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)

I liked how everybody was always available and ready to help in any way. I liked that it was a good mixture of theorical and practical part.

13. What did you like least about the workshop course ? (weakest aspects)

I don't have any remarks about this workshop.

14. What do you think should be dropped from this workshop course ?

For me, it was a good balance between theory and practice I would not drop anything.

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 :

Thank you for the beautiful time in Navacchio, everybody was really helpfull. I learned a lot on how to improve my work and how to manage my results.

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:

I learned that I had gaps in my knowledge and in my work in the laboratory which is so very helpfull in the way that I can fix it and improve. My every question was answered.

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.
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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: OUAHFDI Nouday Lahcen

Participant's country: MAROC

1. What is your overall reaction to the workshop?

[ ] Excellent [X] 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:**

[ ] Just right [X] Too few [ ] Too many

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

[ ] Yes [X] No

If YES, please recommend topics:

[ ] 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 ?**

[ ] Very helpful [X] 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)

Les techniques de methode d'analyses, les cours sont très importantes avec une concordance

13. What did you like least about the workshop course ? (weakest aspects)

Je pense que les cours theoriques et pratiques sont très entrecoupés et très riche.

14. What do you think should be dropped from this workshop course ?

Des exercices semilaires pour le traitement des données.

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 :

Les cours sont très importants et riches avec des bonnes theories plus pour les pratiques, formation ciblé et conforme avec ma carriere professionnelle donc il va m'aider à développer mes Competance dans le domaine d'analyses de recherche.

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:

très importante et methodique et bien organiser avec
avec la meilleur technique d'analyse

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 ?

[ ] Excellent [x] Very good [ ] Good [ ] Fair [ ] Poor

Thank you for taking the time to answer this questionnaire.
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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: ZAZA Saida

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)*..... Mycocystins (toxins algals)

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)

Le cours est très bénéfique et enrichissant et personnellement j'étais agréablement surprise par la disponibilité et le dévouement de encadrants et de tout le personnel. Merci beaucoup

13. What did you like least about the workshop course ? (weakest aspects)

Rien à signaler. Nothing.

14. What do you think should be dropped from this workshop course ?

A mon avis il y a le développement de la technologie, il faut élargir la formation à d'autres techniques tels LC-MS/MS, GC-MS/MS et à d'autres composés émergents

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 :

La formation était bénéfique et enrichissante sur tous les plans humainement, j'étais agréablement surprise et tout au long de ce cours (théorique et pratique) j'étais gâtée et mise à table à toutes les étapes nécessaires en vue de l'analyse pour obtenir à un résultat fiable.
Donc la formation était satisfaisante à tous le niveau.

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:

La session était riche, beaucoup d'information, ciblée et méthodique. L'encadrement était très bien fait et je suis très satisfaite.

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!

REPORT
MED POL PROFICIENCY TEST
ON THE DETERMINATION OF TRACE ELEMENTS IN MUSSEL SAMPLE

IAEA
Atoms For Peace
Environment Laboratories

REPORT

MED POL PROFICIENCY TEST ON THE DETERMINATION OF TRACE ELEMENTS IN MUSSEL SAMPLE

January 2019

Prepared in collaboration with:

UN environment
United Nations Environment Programme

MAP
Mediterranean Action Plan
Barcelona Convention

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E-mail: NAEL-MESL.Contact-Point@iaea.org

TABLE OF CONTENT

1. INTRODUCTION

Since 1960s IAEA has been providing help to its Member States (MS) in the field of data quality and quality assurance. In order to support MS in their marine monitoring activities, but also in the domain of food safety, Marine Environment Studies Laboratory (MESL) has produced Certified Reference Materials (CRM's) characterized for trace elements and methylmercury using samples of marine origin (biota and sediments), and organized interlaboratory comparison (ILC's).

The IAEA has a long collaboration with the UN Environment Programme (UN Environment) and its Programme 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.

In order to assure reliability of analytical data for monitoring studies, one essential aspect of quality assurance and quality control is the periodic external assessments of measurement performance via proficiency tests (PTs). The participation of designated MED POL monitoring laboratories in PTs is important for the evaluation of their analytical performance.

This report describes the results of the PT on the determination of selected trace elements in mussel sample organised by the MESL in 2018 for the designated MED POL monitoring laboratories.

The IAEA officers responsible for this publication are S. Azemard, E. Vasileva, S. Sander and A. Trinkl.

2. SCOPE OF EXERCISE

In July 2018 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 trace elements in the marine environment, organised by MESL, was established at the end of September 2018.

The test material, named ***IAEA-MESL-2018-02-TE-MEDPOL-PT*** sample, was sent to 46 designated monitoring laboratories from 17 countries at the end of September 2018. However, only 35 laboratories returned results. Figure 1 shows the number of PT samples sent to MED POL countries, and the number of received at MESL results per country.

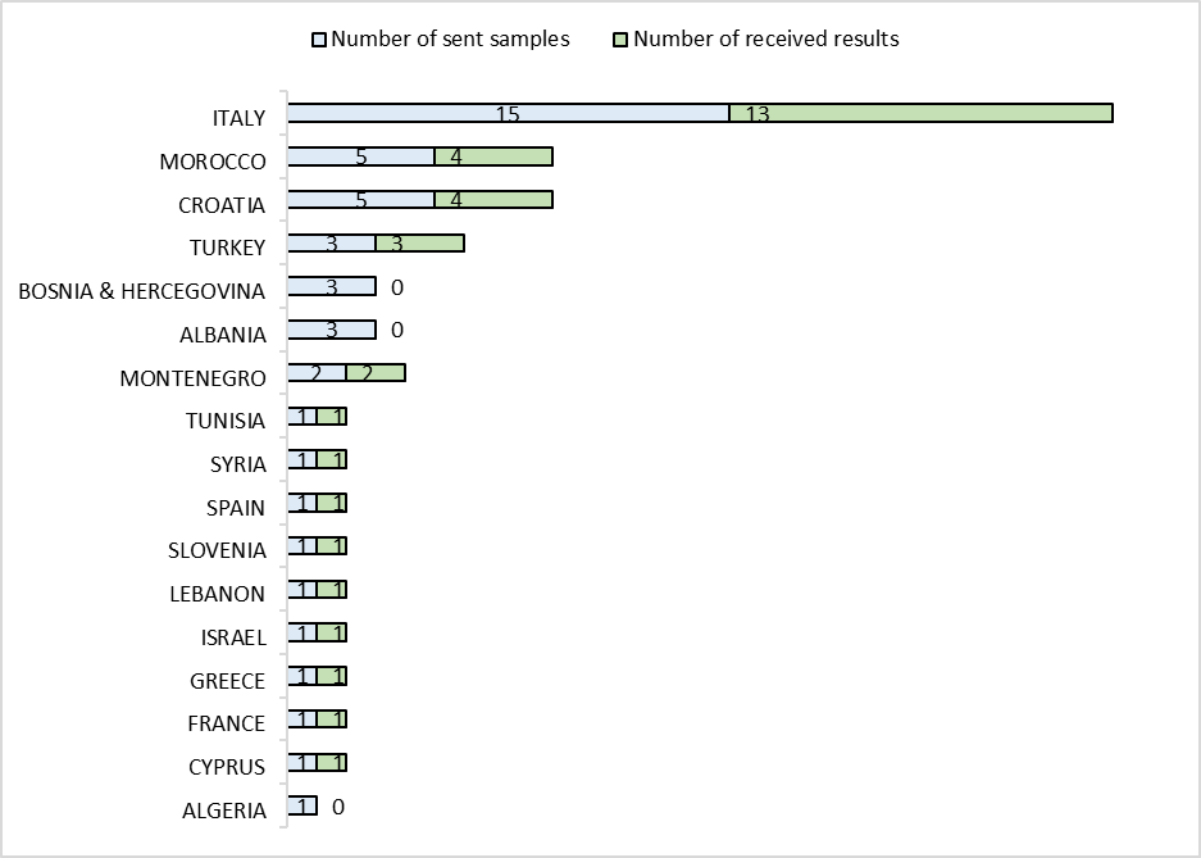


FIG. 1. Distribution of MED POL samples versus reported to the PT organiser results per country. Seven samples were returned to MESL unclaimed by the laboratory.

Participants were requested to determine as many trace elements as possible from the following list: As, Cd, Co, Cu, Fe, Hg, Mn, Pb, Sr and Zn, using the measurement procedures, usually applied for MED POL monitoring studies.

The deadline for reporting the results back to the MESL was originally set to 3rd December but was extended to 9th December 2018, after request from several participating laboratories. Finally, 35 monitoring laboratories sent their results by the extended deadline, which is 76% of the 46 nominated laboratories and 87% of the laboratories that actually received the sample.

Laboratories participating in the present exercise are listed in the **Error! Reference s ource not found.**2. Designated MED POL laboratories which didn't receive or report the results are listed in the

3. All participating in the MED POL PT exercise received a lab code to anonymise the results shown in this report.

3. MATERIAL

3.1. Preparation of the material

A large quantity of mussel (Mytilus galloprovincialis species) were collected in Anse de Carteau, Port Saint Louis du Rhône (43°20"S, 5°10'E), France, by the Institute of Radioprotection and Nuclear Safety (IRSN, France). The shells were removed, and the fresh soft parts and internal fluids separated from the raw mussels. The sample was freeze-dried, ground to a powder, sieved at 200 μm, and then homogenized. The sub-samples of about 10g were bottled and each bottle introduced in cleaned sealed plastic containers. Bottles were sterilized at 25 kGy in the IAEA irradiation facility.

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

3.2. Assigned values and their uncertainties

The assigned values and their associated uncertainties are presented in the Table 1. They were calculated according to the requirements of the ISO 17043 standard [2]. Assigned

values were set as the robust mean [3] of the reported by participants results and results obtained in the MESL with preliminary validated analytical methods. Expanded uncertainties were calculated according to the ISO standard 35 [1]. using Eq. (1).

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

where:

k: coverage factor, *k*=2, representing 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 not further propagated during the estimation of the total combined uncertainty.

u_{char} is the uncertainty of characterization, estimated according to the recommendations of the ISO 35 [3] 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})
As	13.6	1.6
Cd	0.373	0.044
Co	0.688	0.084
Cu	4.70	0.54
Fe	167	18
Hg	0.090	0.012
Mn	11.1	1.2
Pb	1.15	0.14
Sr	77.1	13
Zn	124	14

4. EVALUATION OF RESULTS

4.1. 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 the laboratory, the Zeta-score was not calculated.

4.2. Overview of the reported measurement results

35 laboratories provided results for the analysis of the PT sample by the final deadline, comprising 276 measurement results. Graphical presentations of z-score and Zeta-scores are presented in the Annex 3 with a summary on the statistical evaluation of reported results for the respective trace element. Kernel density plots are also presented in the Annex [4].

4.3. Laboratory results and scoring

4.3.1 *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 of 276 *z*-scores were calculated. Overall 85% of reported measurement results were assessed as satisfactory, 9% as questionable and 7% as unacceptable. From 35 participating laboratories, 23 laboratories (66%) reported 100% of their measurement results with $|z| \leq 3$ and 18 laboratories (51%) were able to report 100% of their measurement results with $|z| \leq 2$. On the other hand, 3 laboratories reported less than 40% of their results with $|z| \leq 2$. This fact is probably reflecting the existence of unresolved analytical problems in those laboratories.

4.3.2 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 both.

PT Zeta-score results are summarized in Table 3. Zeta-scores per designated national laboratories are summarized in Table 6 and on Figure 4. Zeta-scores per element are presented in Table 7 and in Figure 5.

About 60% of measurement results were reported with uncertainties. Zeta-scores were calculated for 21 of participating laboratories (60%), 14 of participating laboratories didn’t report measurement uncertainties, which made the calculation of Zeta score impossible. Laboratories can familiarize themselves with the concept how to estimate combined uncertainties [5]

In total 21 participating laboratories (60%) reported results for the estimated combined uncertainty, and 9 of them (43%) provide uncertainty as a routine daily practice. Different approaches were used to estimate measurement uncertainties: 7 participants applied single validation approach, 4 laboratories used modelling approach, and 3 laboratories were reporting measurement uncertainties, obtained via their participation in the relevant ILC’s. Two of participating MED POL laboratories reported the standard

deviation of replicates, which is only part of combined uncertainty. This lack of understanding of uncertainty concept is leading to serious underestimation of combined measurement uncertainty.

87% of the calculated Zeta-scores are considered as satisfactory and 10 laboratories reported 100% of their results with Zeta-scores below 2. Two participating laboratories received satisfactory Zeta-score for less than 50% of reported results. Obtained results show that there are still remaining problems with the realistic estimation of the combined measurement uncertainty.

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. Grey fields are *z*-scores 2< | *z* | <3, and red highlighted fields being z-scores | *z* |>3 .

Laboratory Code	As	Cd	Co	Cu	Fe	Hg	Mn	Pb	Sr	Zn
1		-1.23		0.45	-1.68	-0.73	-0.44	3.48		7.47
3		1.22		0.20	0.53	0.49	0.06			0.77
4	-0.41	-0.95	-0.04	-0.46	0.46	-2.25	-0.62	0.25	-0.91	0.74
5	0.44	-0.42	0.21	-1.25	0.59	1.31	0.29	1.39		-0.83
6	-0.23	0.84	-0.46	1.07	-0.44		0.25	1.85		0.59
8						0.27				
9	0.32	0.76	0.40	-0.28	0.53	0.62	-0.46	-0.75		0.17
11		8.73		2.76	2.49	13.33	0.55	-6.68		-1.39
12	-1.47	0.72	-1.29	0.40	-0.45	-0.06	0.59	-3.55	0.02	0.37
13		-2.10				-0.56		-2.47		
14	-2.67	0.62	-1.02	1.49	-2.85	-0.67	-1.81	1.15	-2.06	-2.30
15	0.41	0.14	-0.48	-0.74	-0.14	-0.95	-0.34	0.21	0.74	0.22
16		1.15				-0.95		0.07		
17	0.78	-0.15	-0.92	-0.97	-0.93	-0.74	-0.51	1.33		-0.11
18	2.06	0.22	-0.40	-0.27	-0.29		-0.46	-1.04	1.63	1.12
19	-1.21	0.61		0.60	-0.57	-0.27	0.26	-4.16		0.75
20	-5.78	2.68	2.50	4.01	-0.06	163.26	2.98	18.78		-0.86
23	1.01	-2.55	1.33	0.62		12.47	0.53	-0.26		-2.34
24		-1.50		-1.89	-0.48		-0.48			-0.30
25	-1.30	-0.69	-0.30	-0.33	-2.52	4.03	-1.28	-0.55		-0.91
26		0.79	1.24	0.45	1.69	-0.53	1.31	-0.07		1.35
27	-0.43	-2.14	1.25	-0.43	0.56	1.87	0.79	-0.53		-1.18
30	0.24	-0.71	-1.14	-0.70	-0.33	-0.30	-0.53	-0.14		-0.98

Laboratory Code	As	Cd	Co	Cu	Fe	Hg	Mn	Pb	Sr	Zn
31	-0.88	-0.78	-1.02		1.64		0.53	0.23		-1.10
32	-0.09	-0.13	0.40	-0.14	-0.47	-1.57	-0.53	0.24		0.19
33	-0.06	-1.34	-0.37	1.24	-0.08	-0.86	-0.41	-0.37	-0.73	0.32
35						-1.39				
36	1.65	0.44	1.84	0.28	0.16	-2.58	0.29	-0.79	-0.88	0.04
37	0.78	-0.42	-1.22	-0.23	-0.21	0.86	-0.80	0.07		0.35
38			26.77	-0.48	0.71		0.01	0.16		-0.76
40	-0.08	0.19	-0.24	-0.78	-1.05	-1.39	-0.64	1.23	-1.58	-0.64
43	-0.01	0.44	-0.40	1.01	-0.01	-1.78	-0.01	0.05	-0.07	0.03
44	2.78	0.77	2.39	2.76	1.33	0.41	2.35	-0.72	4.07	1.96
45	-0.18	1.26	0.55	1.62	-0.75	-2.13	-0.19	12.82		1.38
46	-0.92	0.87	-4.05	-2.04	-0.46	3.26	0.12	1.28		0.22

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

Laboratory Code	As	Cd	Co	Cu	Fe	Hg	Mn	Pb	Sr	Zn
1		-2.61						3.32		
3		1.04		0.34	0.89	0.62	0.11			1.21
4	-0.84	-2.00	-0.04	-0.89	0.89	-3.51	-1.37	0.33	-1.29	1.08
5										
6										
8										
9	0.66	0.44	0.50	-0.60	1.22	0.07	-1.05	-1.10		0.38
11										
12		0.72						-3.56		
13										
14										
15	0.51	0.21	-0.63	-1.19	-0.19	-1.26	-0.47	0.28	0.77	0.32
16		0.54				-1.11		0.03		
17										
18										
19	-1.56	0.58		0.56	-0.69	-0.28	0.29	-6.44		0.84
20										
23	0.63	-3.26	0.93	0.55		2.63	0.48	-0.26		-3.05
24										
25										
26		1.23	1.84	0.72	2.61	-0.71	2.05	-0.11		2.08
27										
30	0.21	-0.72	-1.20	-0.68	-0.31	-0.29	-0.51	-0.13		-1.00

Laboratory Code	As	Cd	Co	Cu	Fe	Hg	Mn	Pb	Sr	Zn
31	-1.04	-0.88	-1.20		1.55		0.55	0.24		-1.31
32	-0.19	-0.09	0.70	-0.07	-0.86	-1.23	-1.06	0.24		0.40
33	-0.06	-1.65	-0.48	1.41	-0.11	-0.93	-0.57	-0.34	-0.79	0.37
35										
36	2.62	0.84	3.68	0.58	0.35	-4.59	0.66	-1.49	-1.24	0.09
37										
38			13.15	-1.03	1.65		0.03	0.33		-1.41
40	-0.08	0.20	-0.26	-0.90	-1.28	-1.70	-0.74	1.16	-1.70	-0.75
43	-0.01	0.68	-0.67	1.50	-0.01	-1.24	-0.02	0.07		0.04
44	2.29	0.43	1.40	1.99	1.66	0.21	2.02	-0.59	3.53	2.33
45	-0.14	0.66	0.31	1.07	-0.64	-1.40	-0.15	2.45		0.93
46	-0.79	0.44	-4.26	-3.57	-0.98	1.20	0.25	1.11		0.39

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	7	29%	0%	71%
3	6	0%	0%	100%
4	10	0%	10%	90%
5	9	0%	0%	100%
6	8	0%	0%	100%
8	1	0%	0%	100%
9	9	0%	0%	100%
11	7	43%	29%	29%
12	10	10%	0%	90%
13	3	0%	67%	33%
14	10	0%	40%	60%
15	10	0%	0%	100%
16	3	0%	0%	100%
17	9	0%	0%	100%
18	9	0%	11%	89%
19	8	13%	0%	88%
20	9	44%	33%	22%
23	8	13%	25%	63%
24	5	0%	0%	100%
25	9	11%	11%	78%
26	8	0%	0%	100%
27	9	0%	11%	89%
30	9	0%	0%	100%
31	7	0%	0%	100%
32	9	0%	0%	100%
33	10	0%	0%	100%
35	1	0%	0%	100%
36	10	0%	10%	90%
37	9	0%	0%	100%
38	6	17%	0%	83%
40	10	0%	0%	100%
43	10	0%	0%	100%
44	10	10%	40%	50%
45	9	11%	11%	78%
46	9	22%	11%	67%

TABLE 5: SUMMARY OF OBTAINED z-SCORES PER ELEMENT

Element	Participation	$\lvert z \rvert \geq 3$	$2 < \lvert z \rvert < 3$	$\lvert z \rvert \leq 2$
As	71%	4%	12%	84%
Cd	91%	3%	13%	84%
Co	74%	8%	8%	85%
Cu	86%	3%	10%	87%
Fe	86%	0%	10%	90%
Hg	86%	17%	10%	73%
Mn	89%	0%	6%	94%
Pb	89%	19%	3%	77%
Sr	29%	10%	10%	80%
Zn	89%	3%	6%	90%

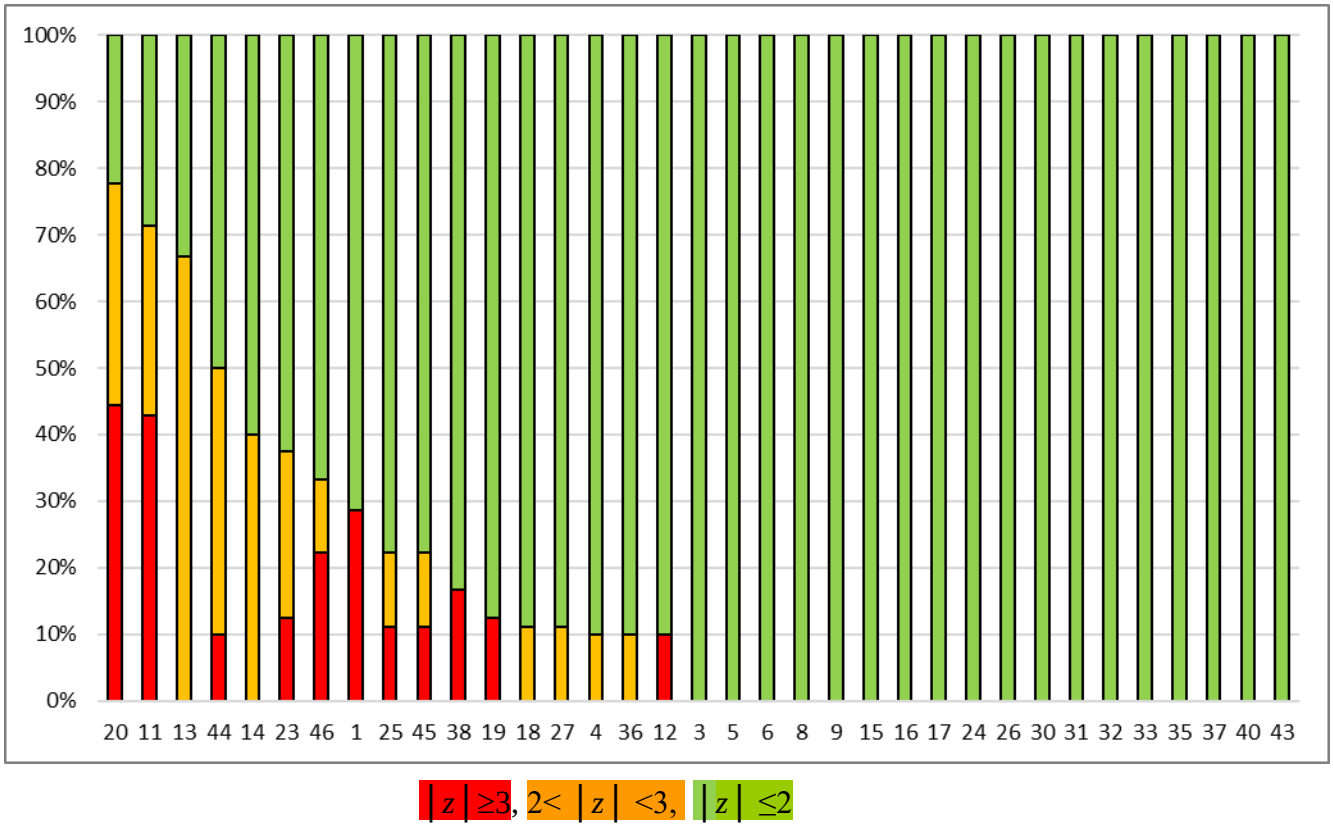


FIG. 2. Summary of obtained z-scores per participant, based on 35 laboratories providing in total 276 results

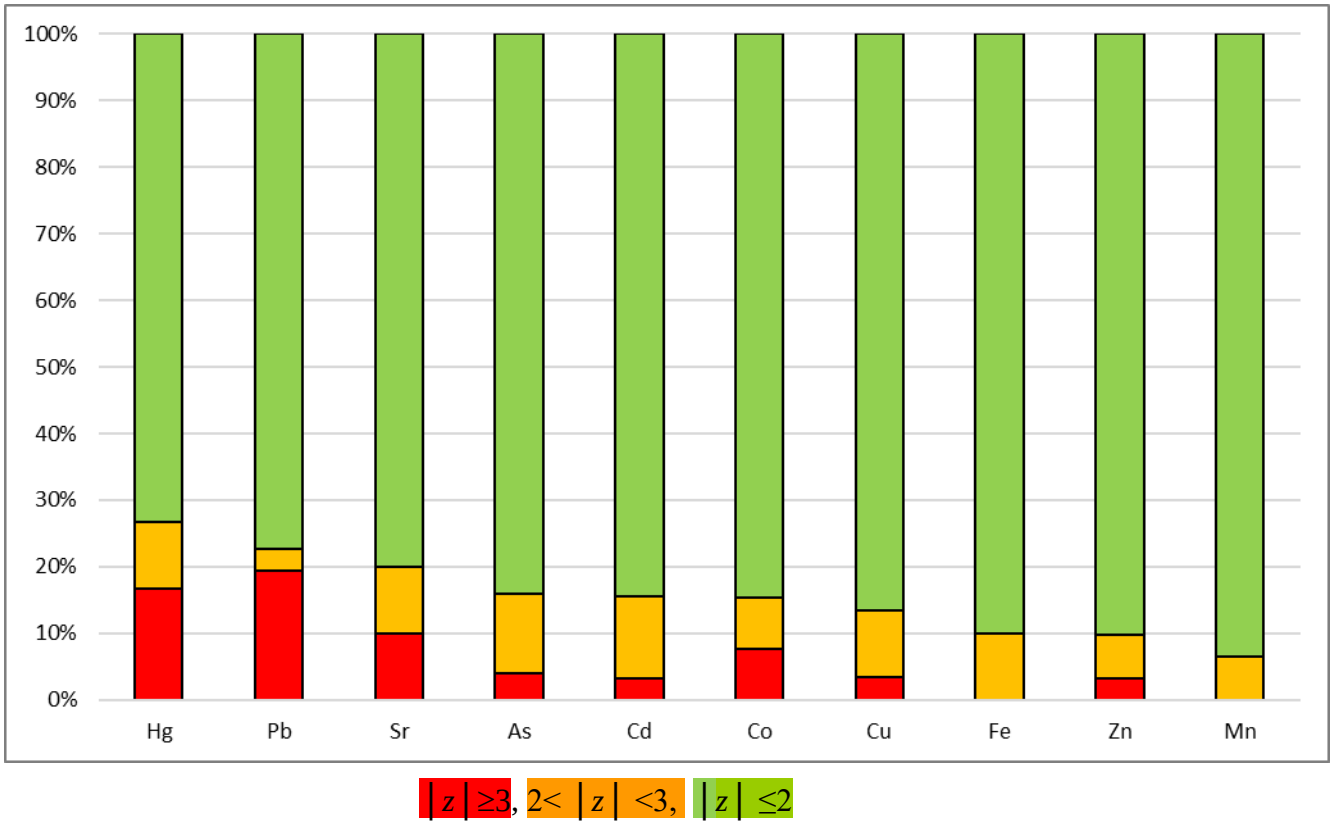


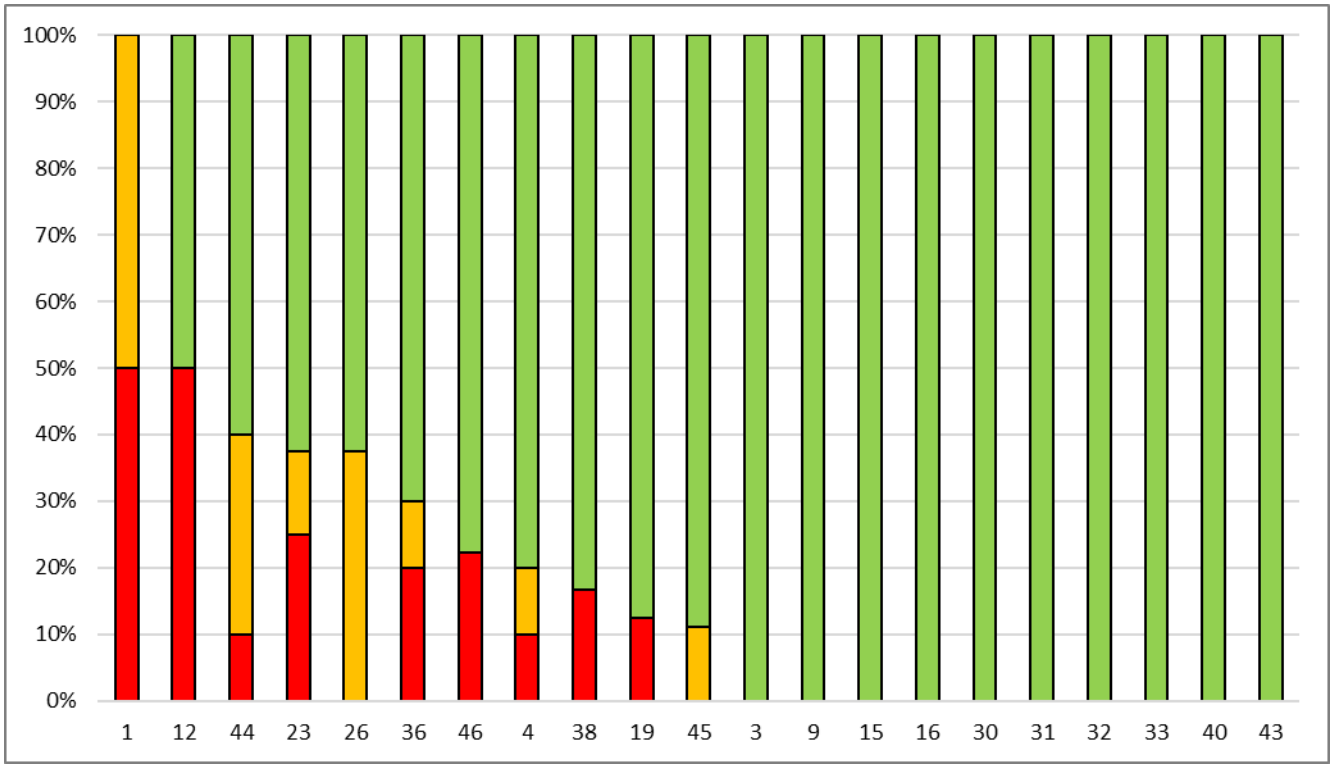
FIG. 3. Summary of obtained z-scores per element, based on 35 laboratories providing in total 276 results

TABLE 6: SUMMARY OF OBTAINED ZETA-SCORES PER LABORATORY

Laboratory Code	Number of results	|Zeta| ≥3	2< |Zeta| <3	|Zeta| ≤2
1	2	50%	50%	0%
3	6	0%	0%	100%
4	10	10%	0%	90%
5	0			
6	0			
8	0			
9	9	0%	0%	100%
11	0			
12	2	50%	0%	50%
13	0			
14	0			
15	10	0%	0%	100%
16	3	0%	0%	100%
17	0			
18	0			
19	8	13%	0%	88%
20	0			
23	8	25%	13%	63%
24	0			
25	0			
26	8	0%	38%	63%
27	0			
30	9	0%	0%	100%
31	7	0%	0%	100%
32	9	0%	0%	100%
33	10	0%	0%	100%
35	0			
36	10	20%	10%	70%
37	0			
38	6	17%	0%	83%
40	10	0%	0%	100%
43	9	0%	0%	100%
44	10	10%	30%	60%
45	9	0%	11%	89%
46	9	22%	0%	78%

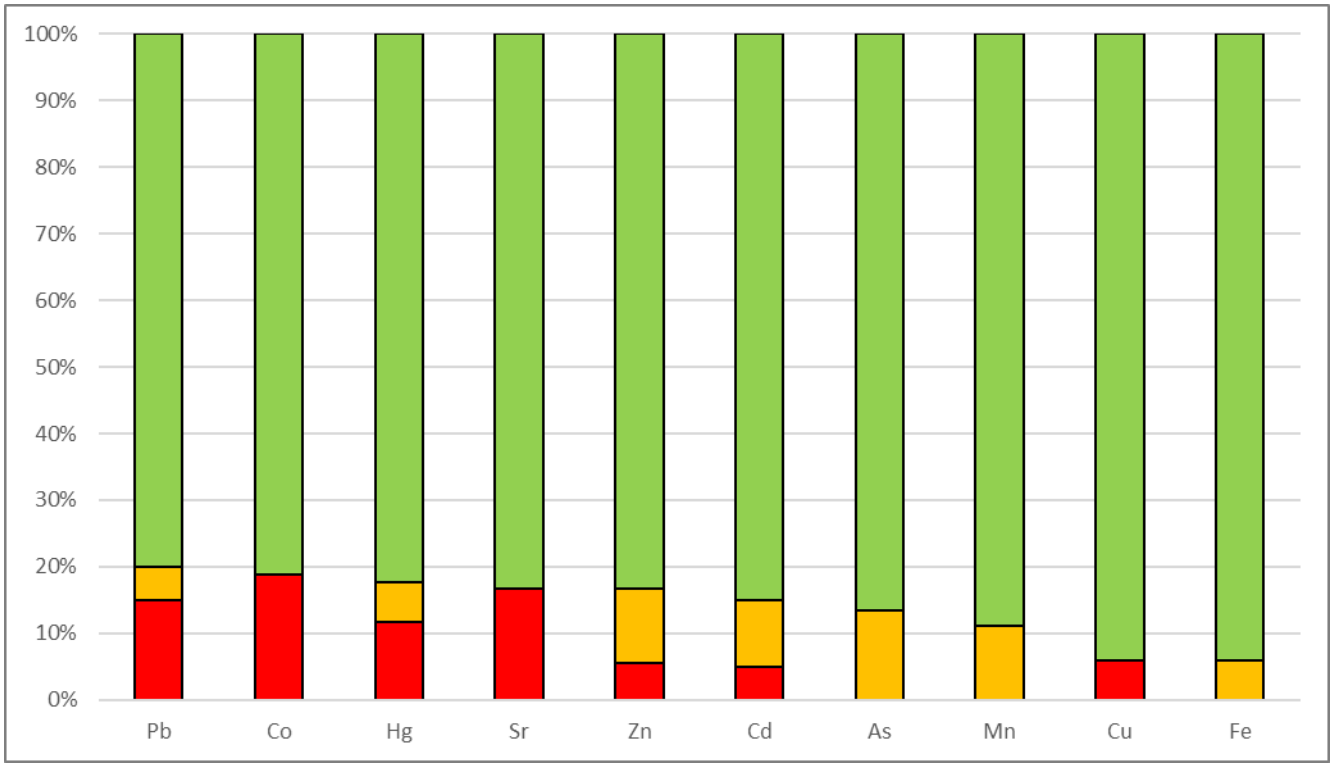
TABLE 7: SUMMARY OF OBTAINED ZETA-SCORE PER ELEMENT

Element	Participation	|Zeta| ≥3	2< |Zeta| <3	|Zeta| ≤2
As	43%	0%	13%	87%
Cd	57%	5%	5%	90%
Co	46%	19%	0%	81%
Cu	49%	6%	0%	94%
Fe	49%	0%	6%	94%
Hg	49%	12%	6%	82%
Mn	51%	0%	11%	89%
Pb	57%	15%	5%	80%
Sr	17%	17%	0%	83%
Zn	51%	6%	11%	83%



| 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, based on 21 laboratories providing in total 164 results

4.4. Sample treatment, use of CRM and recovery correction

Most of participating in the MED POL PT laboratories applied microwave digestion, using mainly nitric acid, pure, or mixed with other acids, or hydrogen peroxide. For the total mercury determination almost 45% of laboratories used a solid mercury analyser and did not perform any sample preparation before the instrumental measurement.

Freeze drying step was a part of sample processing procedure for the MED POL 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 mussel sample at 85°C until constant weight was the recommended procedure for moisture determination. Only 10 participating laboratories adhered to this recommendation. Nine laboratories did not correct their results for moisture content, whereas the remaining 26 participants applied in-house developed protocols or did not report information on moisture content. The moisture content reported by the laboratories was in the range from 2 to 7%.

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 designated laboratories participating in the PT exercise, were generally selected according to the above described criteria. With exception of 5 participants, using non-matrix matching CRMs (water, sediment), all others used CRMs with similar matrix composition or sediment samples from the previous MED POL PTs.

Out of the 35 data sets received, 12 laboratories did not 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 3 participating laboratories, claiming to be accredited for this type of analyses, did not report any quality control results and evidences.

Fifteen laboratories reported recoveries, but only 5 of them claimed to apply recovery correction factors for all, or part of the reported trace elements mass fraction. Participants calculated recoveries by using CRMs or internal standards. 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%.

4.5. 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 (58% of reported data), followed by AAS (21%) and ICP-OES (11%).

TABLE 8: ANALYTICAL TECHNIQUES ABBREVIATIONS

Method Code	Instrumental Technique
AAS	Atomic Absorption 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
MP AES	Microwave plasma Optical Emission Spectrometry
Hyd	Hydride Generation

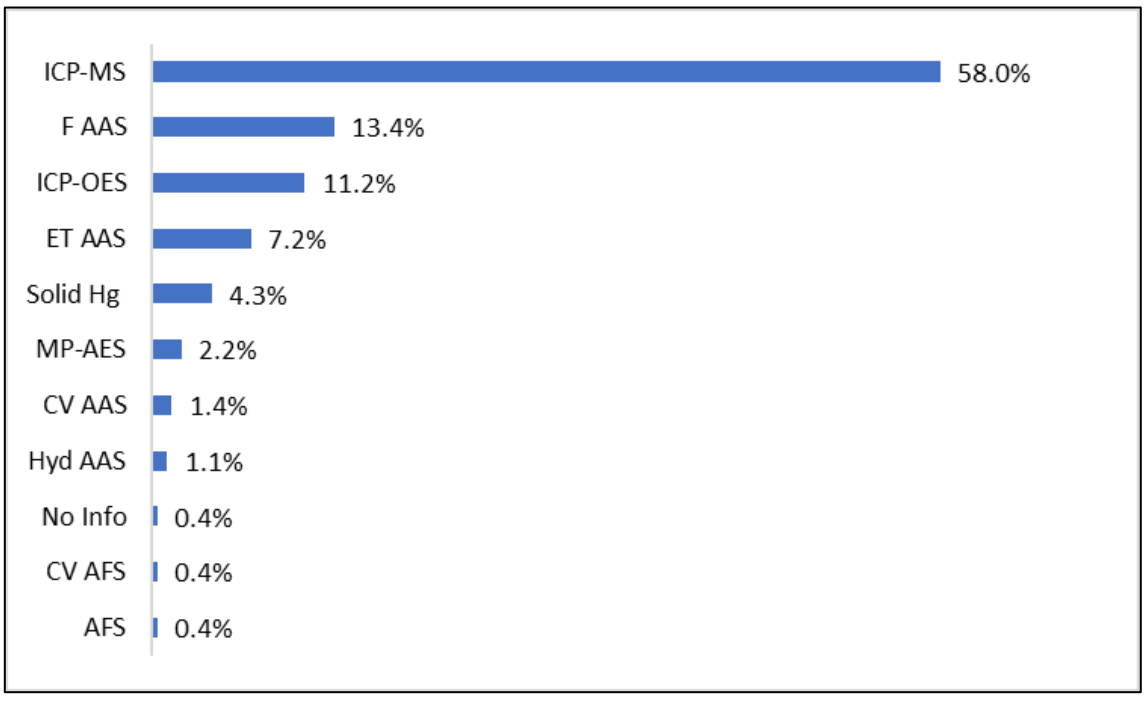


FIG. 6. Graphical distribution of instrumental techniques, applied in the present PT

4.6. Answer to the provided questionnaire

A questionnaire was provided at the time of reporting the results to obtain background information necessary for evaluation of the performance of the participating MED POL designated laboratories. Information was requested about the sample preparation, calibration, recovery, uncertainty statement and coverage factor and traceability. Further questions on the moisture content, the protocol and correction were asked. Regarding the quality assurance system in place it was required to state if a validated procedure was applied, if and which certified reference material was used and if, and which quality system was in place and if the laboratory is accredited and what this accreditation comprises. There was also a field for additional comments.

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

Twelve laboratories claimed to be accredited, but not all of them are accredited for the sediment matrix and the analytes, requested to by determined in this PT exercise. However, two of them didn't report measurement uncertainties, which should be part of a result provided by an accredited laboratory.

13 laboratories applied preliminary validated methods, while 18 participants declared to have quality system in place.

12 participants did not explain how they have assured the traceability of obtained results, although some of them declared to be accredited, and to have a quality system in place.

5. CONCLUSIONS AND RECOMMENDATIONS

Participation in MED POL 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 reoccurring. 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 a consequence the validation of the analytical methods, used by them is often questionable.

Twelve 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.

Some participants did not apply the prescribed protocol for moisture content correction and as the moisture is operationally dependent parameter, they obtained biased measurement results.

Uncertainty of the measurement results in the MED POL PT exercise was calculated from 60% 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 MED POL PT and further training on uncertainty of measurement results is highly desirable.

Of the 46 laboratories designated by the MED POL laboratories, 39 received the sample and 7 samples were returned to MESL as 'unclaimed'. Laboratories should review their receiving samples procedure. Four of the 39 laboratories that apparently received the sample did not return data for this MED POL PT, which obviously makes the evaluation of their measurement performance impossible.

The completion of the questionnaire, provided during the reporting of results, is an essential and obligatory part of the PT and should be completed to allow for an objective evaluation of the measurement performance of MEDPOL designated laboratories and for an appropriate feedback to MEDPOL.

The knowledge on basic principles of metrology in chemistry, 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 or the unavailability of appropriate matrix CRMs are hindering designated MEDPOL laboratories them to improve their measurement performances, 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.

To assist participating laboratories a technical paper on the guidelines recommended by MED POL for the analysis and the quality assurance procedures will be available in the near future.

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.*

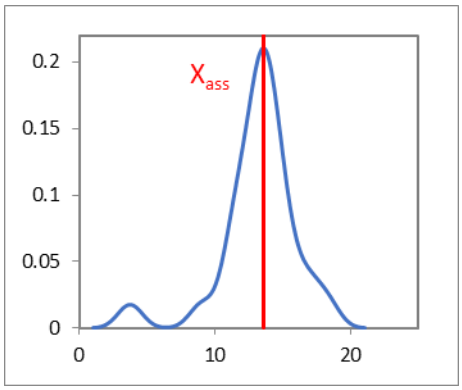
[4] ROYAL SOCIETY OF CHEMISTRY, Statistical Subcommittee of the Analytical Methods Committee (AMC), AMC Technical Brief: Representing data distributions with Kernel density estimates" 2006, www.rsc.org/amc.

[5] JOINT COMMITTEE FOR GUIDES IN METROLOGY, ISO/GUM Evaluation of measurement data – Guide to the expression of uncertainty in measurement, 2008.

Annex 1: Graphical representation

Reported data for As in the IAEA-MESL-2018-02-TE

Kernel density Plot



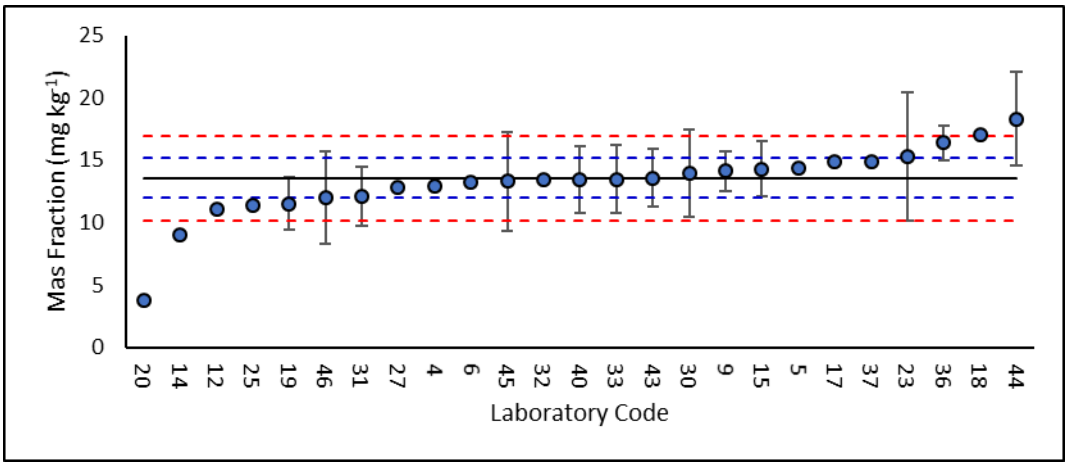
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	84%	12%	4%
Zeta-score	87%	13%	0%

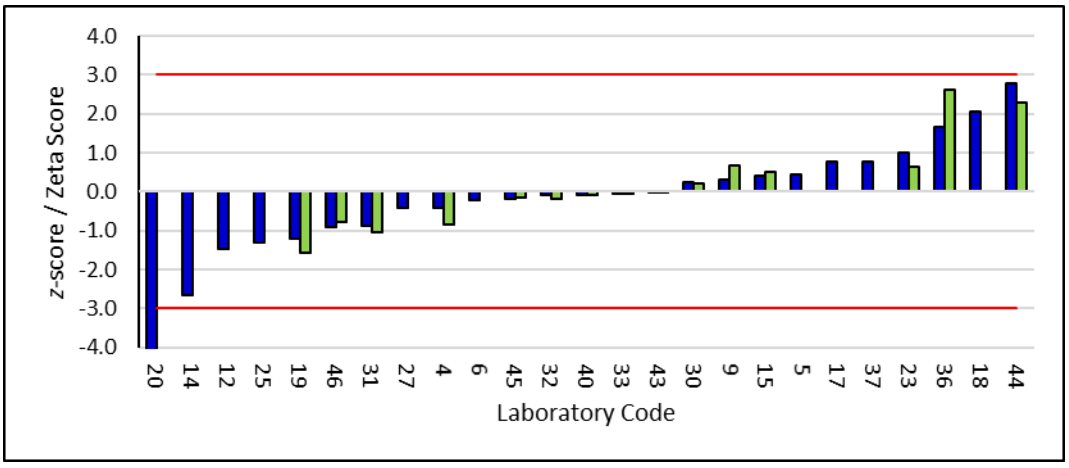
X_{Ass} mg kg^{-1}	13.6
U_{Ass} (k=2) mg kg^{-1}	1.6
$2\sigma_p$ mg kg^{-1}	3.4
Number of results:	25
Number of method:	4

Reported results and expanded uncertainties:

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

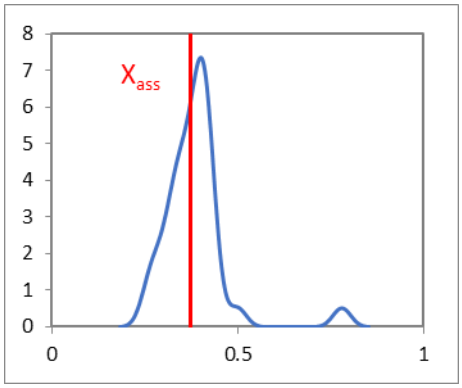


Performance evaluation: *z*-score Zeta-score



Reported data for Cd in the IAEA-MESL-2018-01-TE

Kernel density Plot



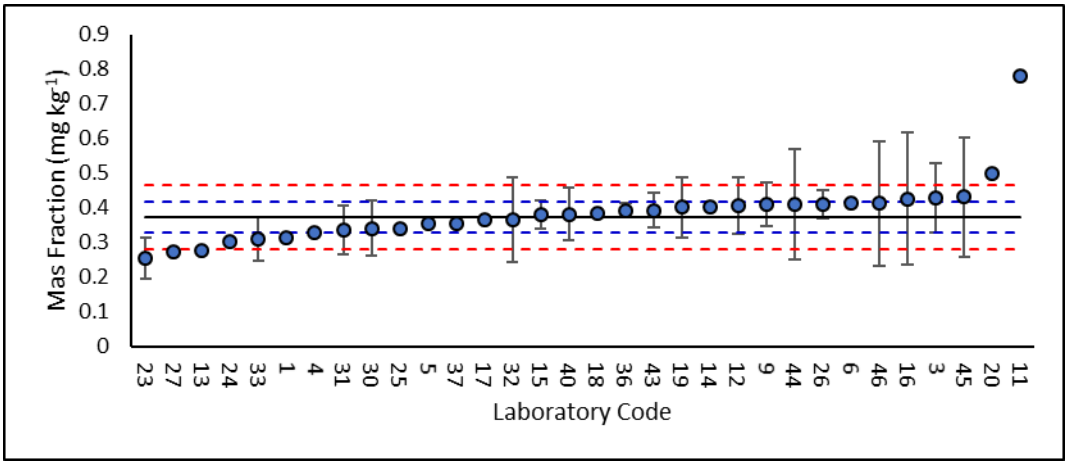
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	84%	13%	3%
Zeta-score	90%	5%	5%

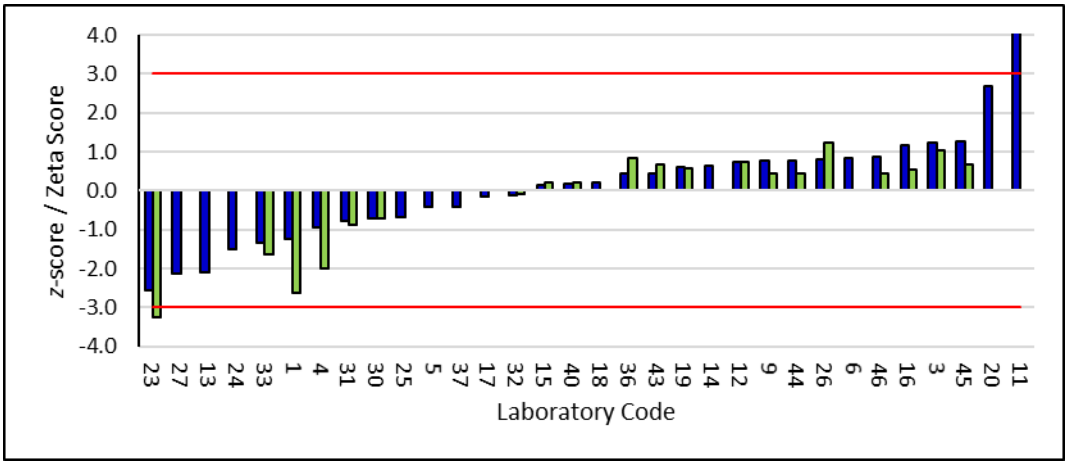
X_{Ass} mg kg^{-1}	0.373
U_{Ass} (k=2) mg kg^{-1}	0.044
$2\sigma_p$ mg kg^{-1}	0.093
Number of results:	32
Number of method:	5

Reported results and expanded uncertainties:

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

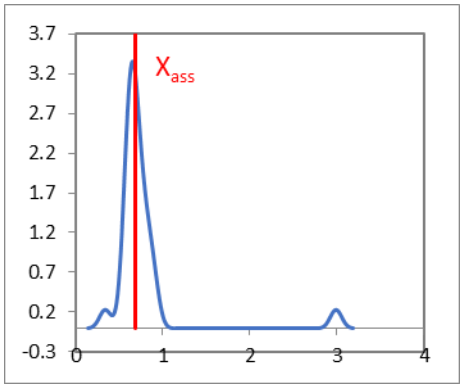


Performance evaluation: z-score Zeta-score



Reported data for Co in the IAEA-MESL-2018-02-TE

Kernel density Plot



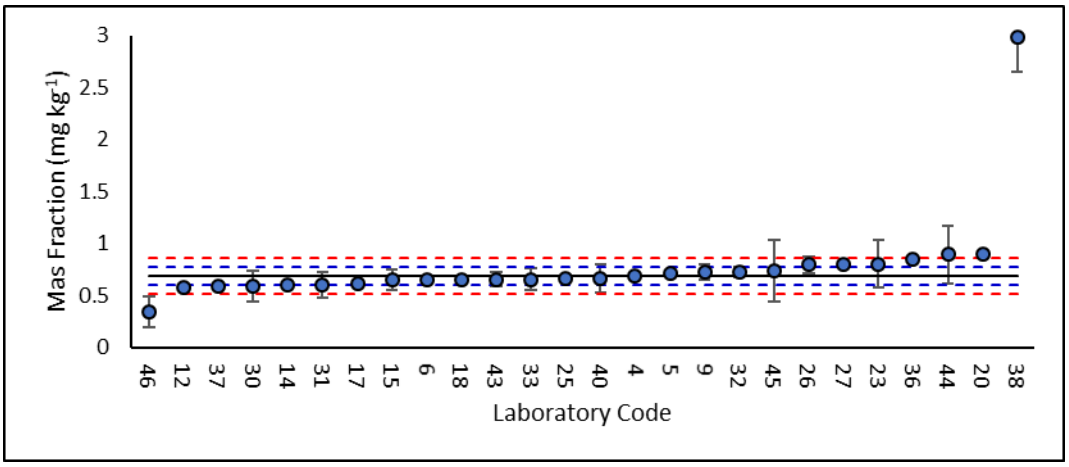
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	85%	8%	8%
Zeta-score	91%	0%	19%

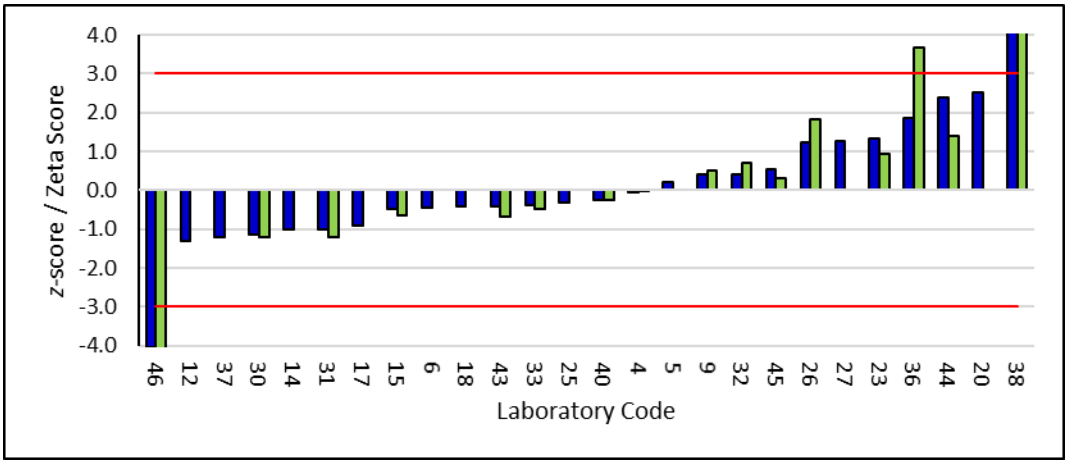
X_{Ass} mg kg^{-1}	0.688
U_{Ass} (k=2) mg kg^{-1}	0.084
$2\sigma_p$ mg kg^{-1}	0.172
Number of results:	26
Number of method:	4

Reported results and expanded uncertainties:

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

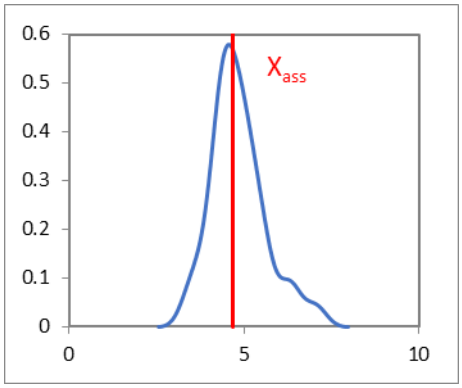


Performance evaluation: z-score Zeta-score



Reported data for Cu in the IAEA-MESL-2018-02-TE

Kernel density Plot



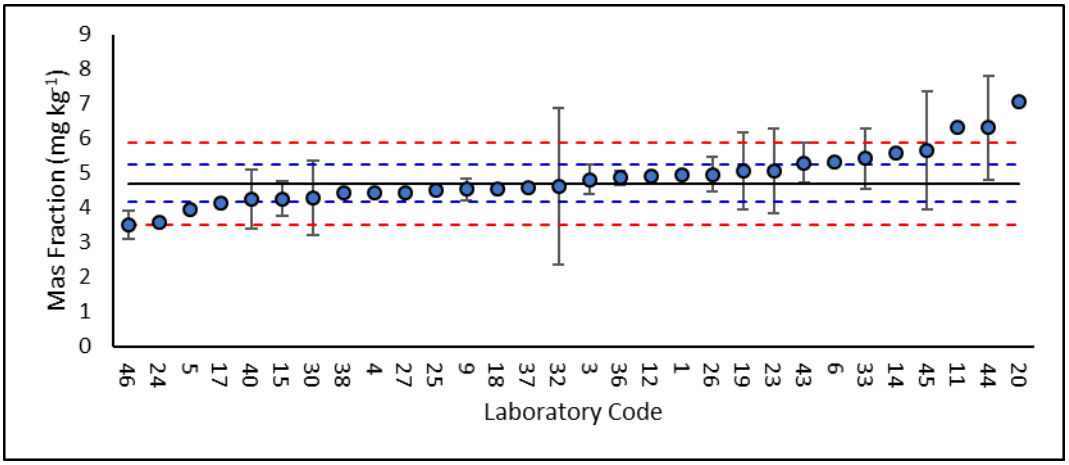
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	87%	10%	3%
Zeta-score	94%	0%	6%

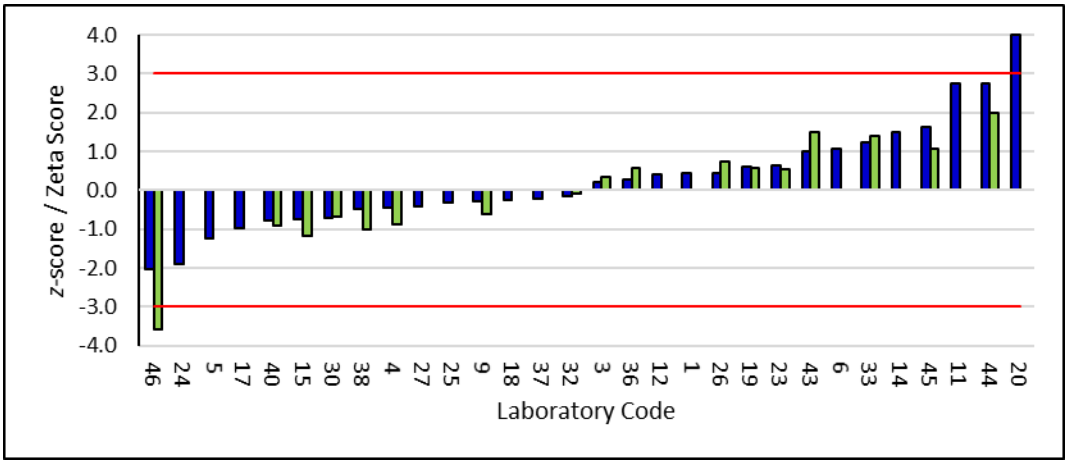
X_{Ass} mg kg^{-1}	4.70
U_{Ass} (k=2) mg kg^{-1}	0.54
$2\sigma_p$ mg kg^{-1}	1.17
Number of results:	30
Number of method:	5

Reported results and expanded uncertainties:

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

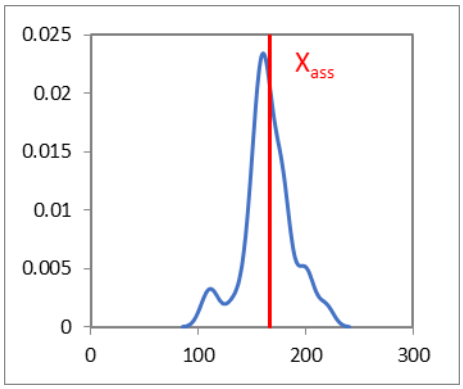


Performance evaluation: z-score Zeta-score



Reported data for Fe in the IAEA-MESL-2018-02-TE

Kernel density Plot



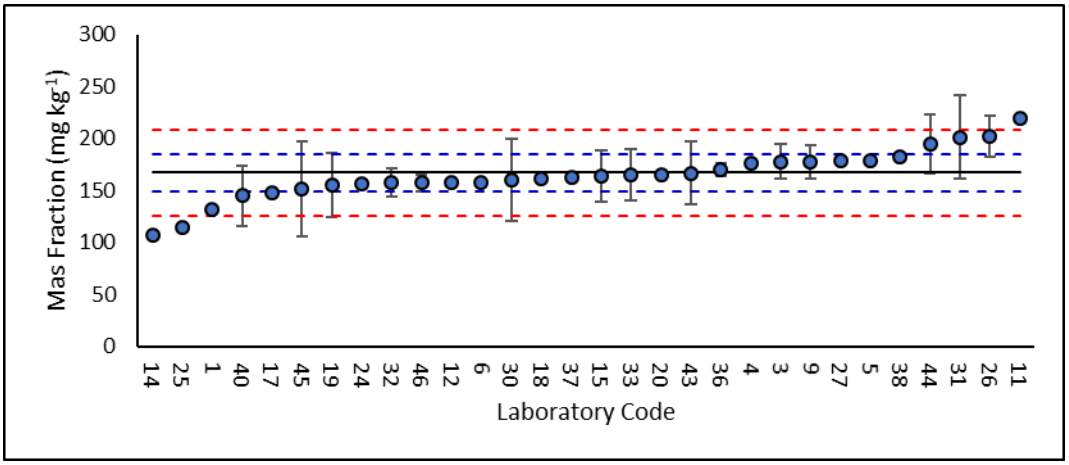
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	90%	10%	0%
Zeta-score	94%	6%	0%

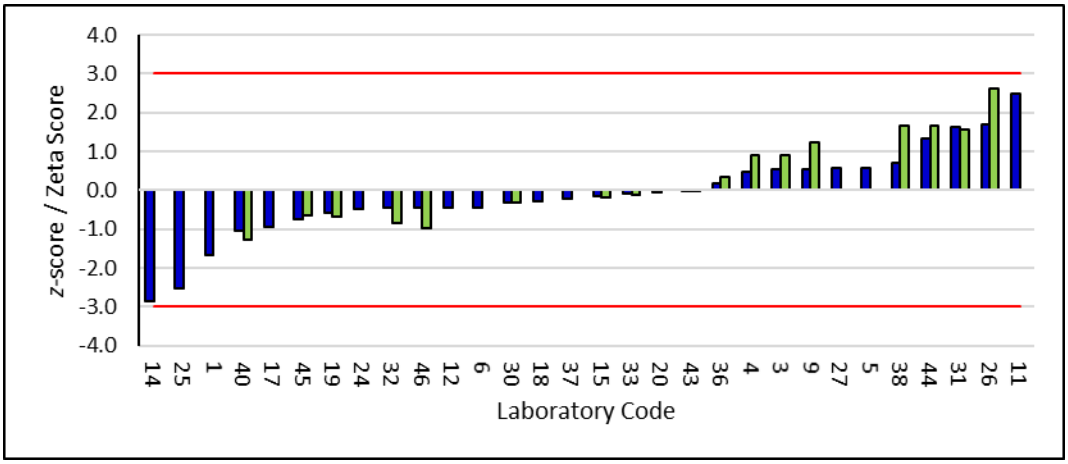
X_{Ass} mg kg^{-1}	167
U_{Ass} (k=2) mg kg^{-1}	18
2σ_p mg kg^{-1}	42
Number of results:	30
Number of method:	5

Reported results and expanded uncertainties:

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

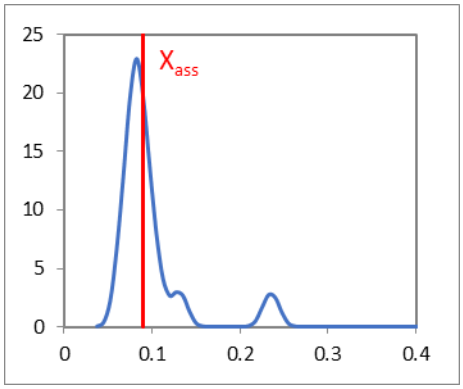


Performance evaluation: z-score Zeta-score


4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
-3.0
-4.0
z-score / Zeta Score
14 25 1 40 17 45 19 24 32 46 12 6 30 18 37 15 33 20 43 36 4 3 9 27 5 38 44 31 26 11
Laboratory Code

Reported data for Hg in the IAEA-MESL-2018-02-TE

Kernel density Plot



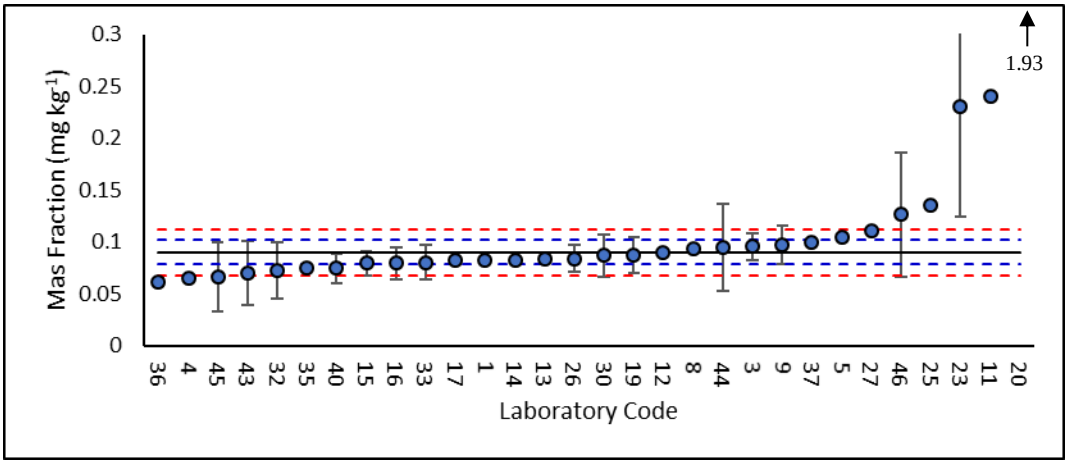
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	73%	10%	17%
Zeta-score	82%	6%	12%

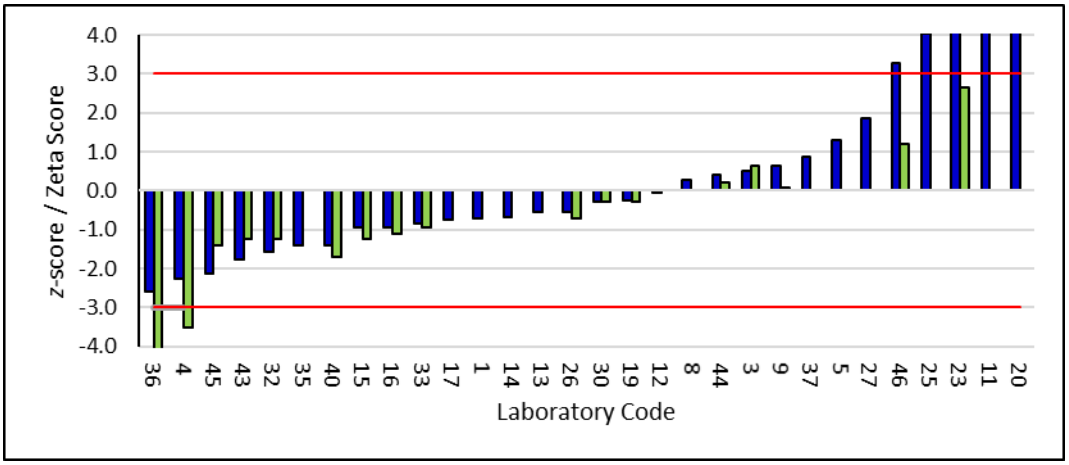
X_{Ass} mg kg^{-1}	0.090
U_{Ass} (k=2) mg kg^{-1}	0.012
$2\sigma_p$ mg kg^{-1}	0.022
Number of results:	30
Number of method:	6

Reported results and expanded uncertainties:

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

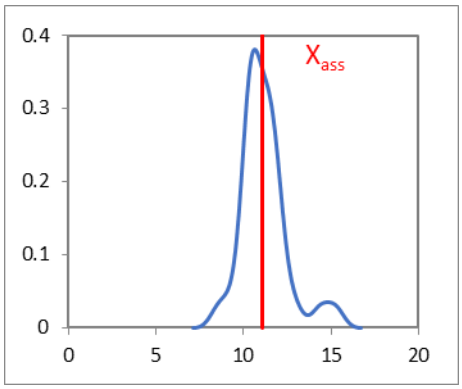


Performance evaluation: *z*-score Zeta-score



Reported data for Mn in the IAEA-MESL-2018-02-TE

Kernel density Plot



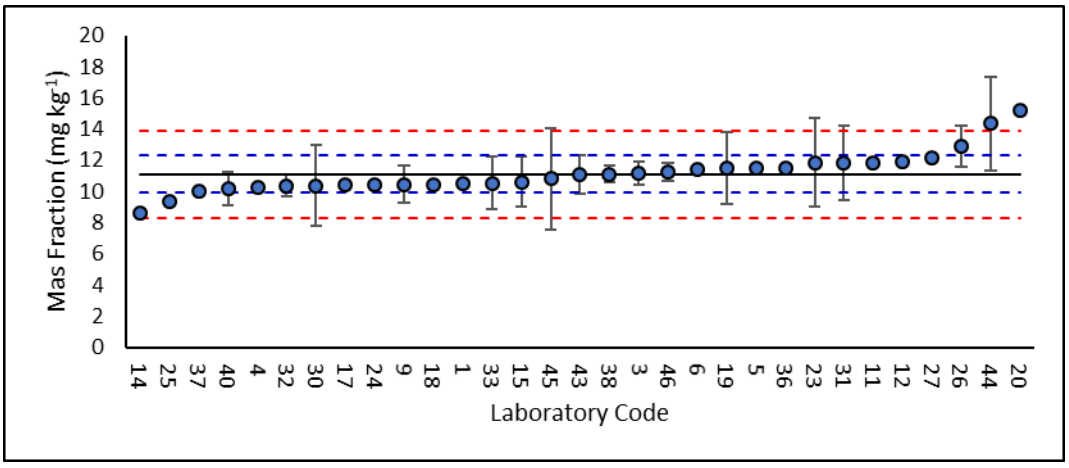
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	94%	6%	0%
Zeta-score	89%	11%	0%

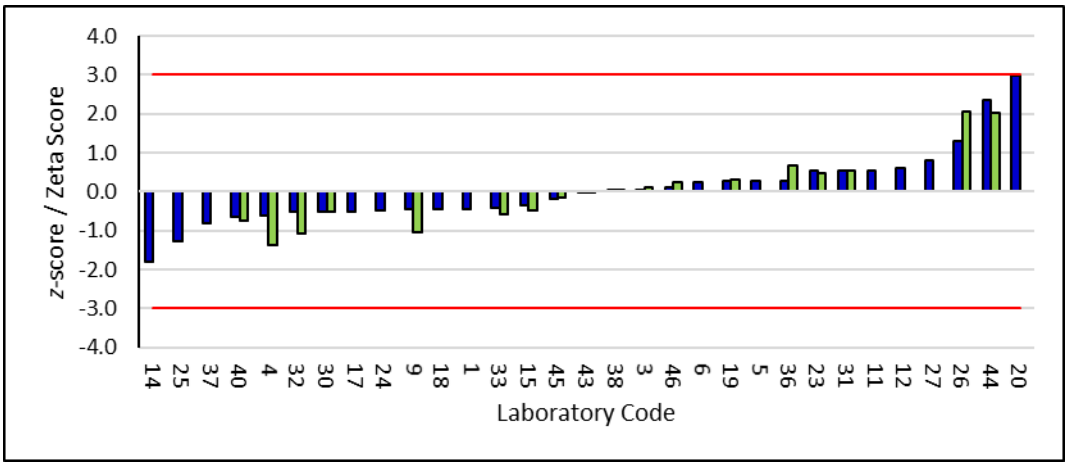
X_{Ass} mg kg^{-1}	11.1
U_{Ass} (k=2) mg kg^{-1}	1.2
$2\sigma_p$ mg kg^{-1}	2.8
Number of results:	31
Number of method:	5

Reported results and expanded uncertainties:

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

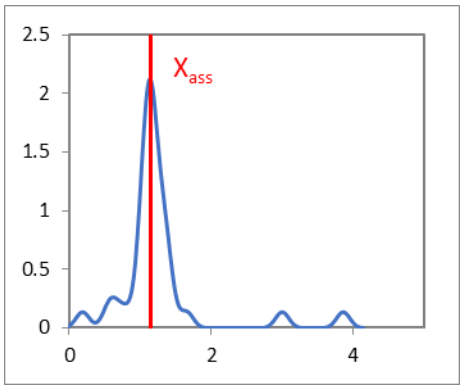


Performance evaluation: *z*-score Zeta-score



Reported data for Pb in the IAEA-MESL-2018-02-TE

Kernel density Plot



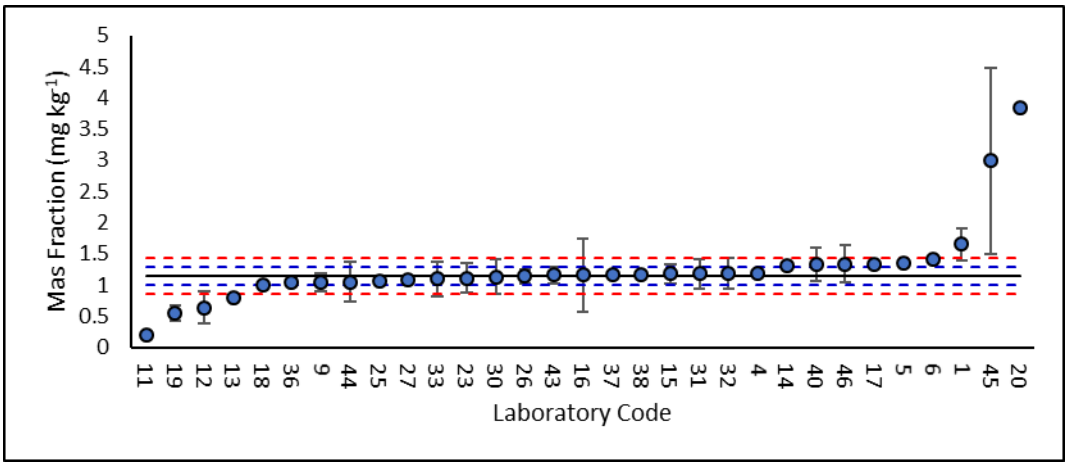
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	77%	3%	19%
Zeta-score	80%	5%	15%

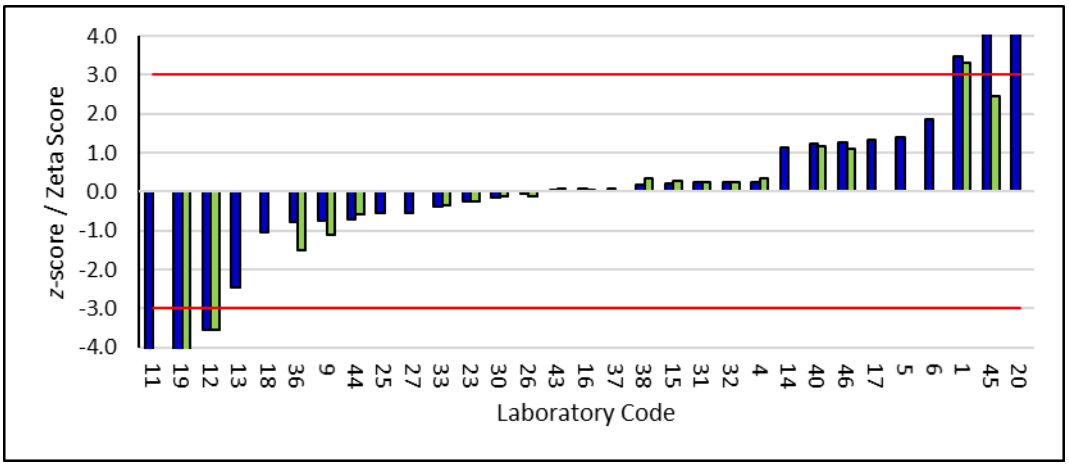
X_{Ass} mg kg^{-1}	1.15
U_{Ass} (k=2) mg kg^{-1}	0.14
$2\sigma_p$ mg kg^{-1}	0.28
Number of results:	31
Number of method:	5

Reported results and expanded uncertainties:

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

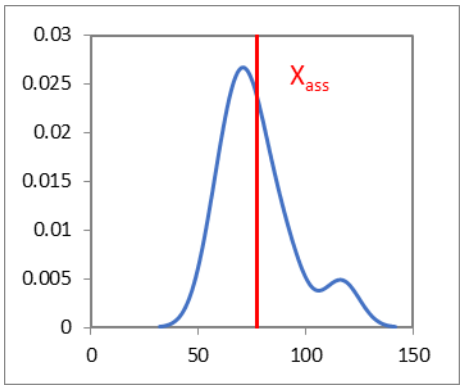


Performance evaluation: *z*-score Zeta-score



Reported data for Sr in the IAEA-MESL-2018-02-TE

Kernel density Plot



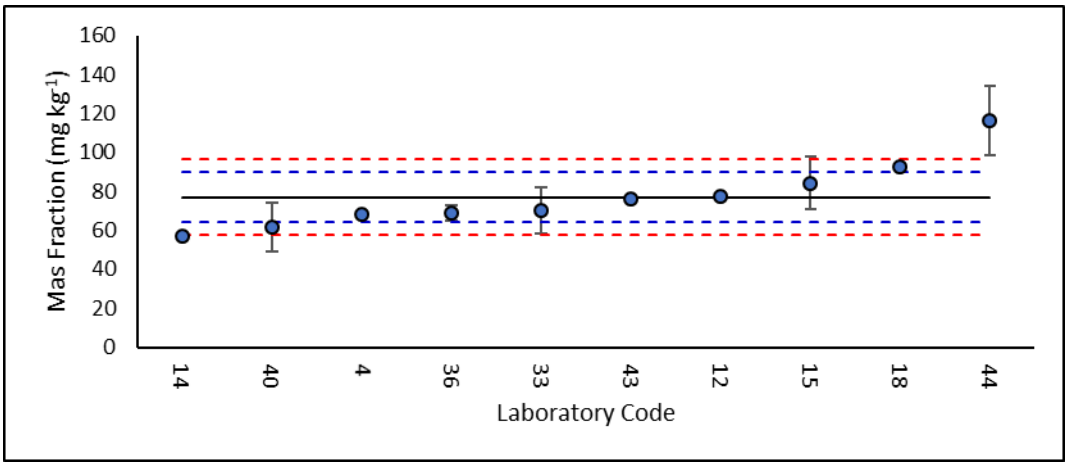
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	80%	10%	10%
Zeta-score	83%	0%	17%

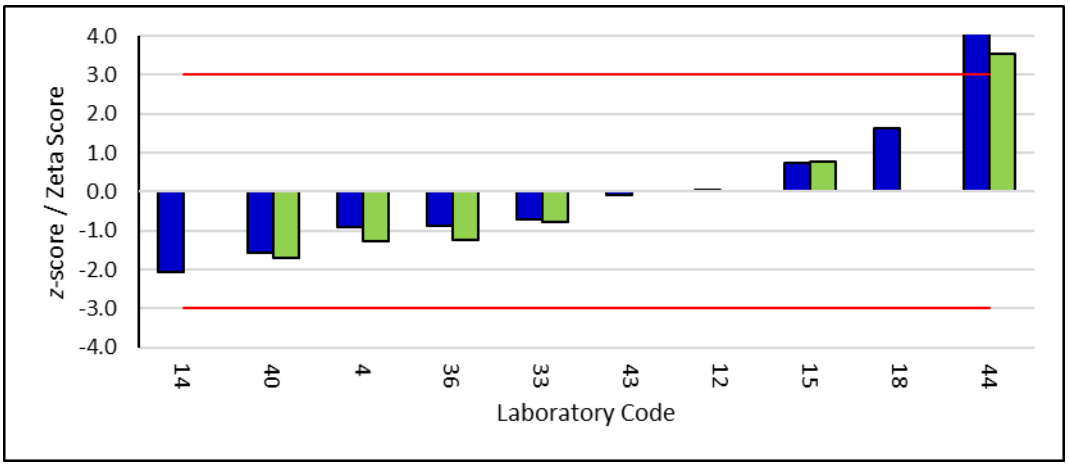
X_{Ass} mg kg^{-1}	77.1
U_{Ass} (k=2) mg kg^{-1}	13
$2\sigma_p$ mg kg^{-1}	31
Number of results:	10
Number of method:	3

Reported results and expanded uncertainties:

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

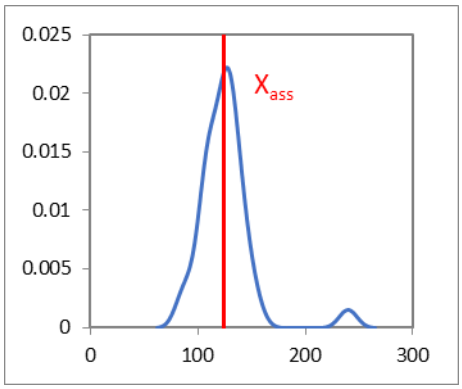


Performance evaluation: *z*-score Zeta-score



Reported data for Zn in the IAEA-MESL-2018-02-TE

Kernel density Plot



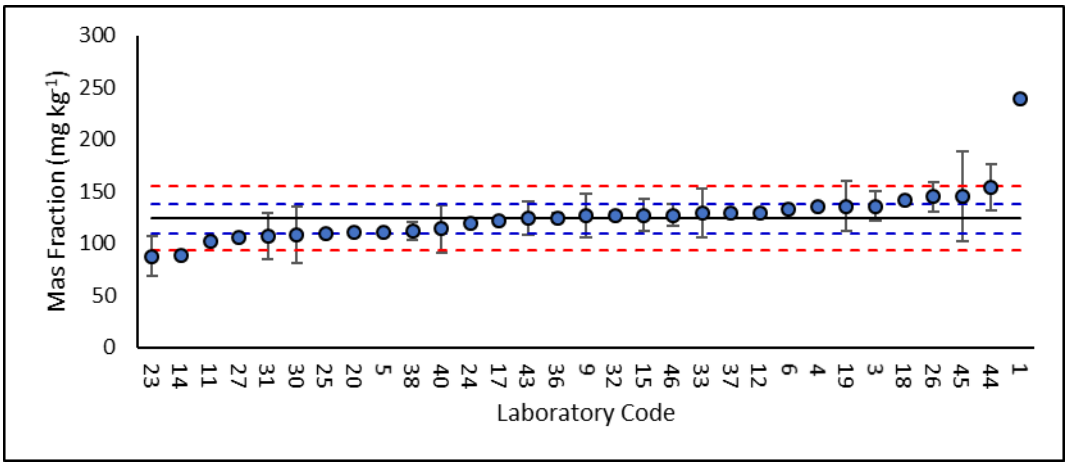
Summary of results:

	Satisfactory	Questionable	Unsatisfactory
z-score	90%	6%	3%
Zeta-score	83%	11%	6%

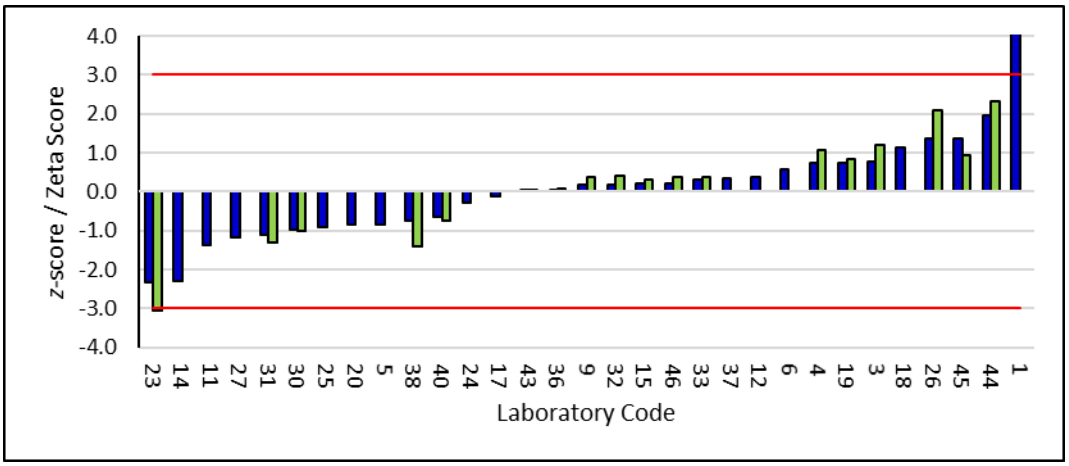
X_{Ass} mg kg^{-1}	124
U_{Ass} (k=2) mg kg^{-1}	14
$2\sigma_p$ mg kg^{-1}	31
Number of results:	31
Number of method:	4

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



REPORT
MED POL PROFICIENCY TEST
ON THE DETERMINATION OF ORGANOCHLORINE PESTICIDES, PCBs AND PETROLEUM HYDROCARBONS
IN BIOTA SAMPLE
IAEA-MEL-2018-02 PT/ORG

IAEA
Atoms For Peace
Environment Laboratories

REPORT

MED POL PROFICIENCY TEST ON THE DETERMINATION OF ORGANOCHLORINE PESTICIDES, PCBs AND PETROLEUM HYDROCARBONS IN BIOTA SAMPLE IAEA-MEL-2018-02 PT/ORG

January 2019

Prepared in collaboration with:

UN environment
United Nations Environment Programme

MAP
Mediterranean Action Plan
Barcelona Convention

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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, petroleum hydrocarbons 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 biota sample carried out in 2018 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 July 2018 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, PCBs and petroleum hydrocarbons the marine environment, organised by MESL, was established at the end of September 2018. Consequently, a set of samples (35 bottles of biota samples IAEA-MEL-2018-02 PT/ORG) were dispatched to the 35 laboratories listed in Appendix 1. All samples were sent in September 2018.

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

The deadline for reporting results was set for the 3rd of December 2018, but it was extended to the 7th of December 2018, after request of several laboratories. Finally, 22 laboratories (63%) submitted their results, which is only 63% of the 35 laboratories that received the samples. Eleven laboratories reported results for both organochlorine pesticides, PCB congeners and petroleum hydrocarbons, 7 laboratories reported results only for organochlorine pesticides and PCB congeners and 4 laboratory reported results only for petroleum hydrocarbons.

3. MATERIAL

The blind PT sample IAEA-MEL-2018-02 PT/ORG is the Marine Biota Reference Material IAEA-451, which had been previously characterized through a worldwide interlaboratory comparison (ILC) exercise [1]. Knowing "certified", "recommended" and "information" values for the concentration of specified organochlorine pesticides, PCBs and petroleum hydrocarbons, this PT yields more reliable data compared to an ILC done with a sample of unknown concentrations. Participants were asked to report data for all organic contaminants listed in the CRM IAEA451, including those that are reported as "recommended" and "information" values. However, z-scores for this PT were only calculated for contaminants with "certified" values in IAEA451.

Briefly, 60 kg of Tumid Venus clams (Gafrarium tumidum) were collected in Noumea, New Caledonia. The organisms were dissected, and the soft tissues were deep-frozen, freeze dried, ground into powder and sieved through a 250 μm stainless steel sieve. The sieved biota fraction with a particle size of less than 250 μm was homogenized by mixing it in a stainless-steel rotating homogenizer for three weeks.

The homogeneity of the material was confirmed by determining the concentration of some representative analytes in ten replicates taken randomly in the bulk of the powder

The certified, recommended and information values of organic contaminants can be found in Table 1 and 2, and in the reference sheet of IAEA451 in Annex 2

4. RESULTS AND EVALUATION

4.1. Data Reporting

Data were either reported through the IAEA on-line reporting system or off-line in an excel file sent to MESL staff. The 'off-line' reporting was done by participants who had problems accessing the 'on-line' portal. Once those results were uploaded by IAEA-NAEL staff, participants were asked to validate their data and finalize their submission as necessary for the evaluation. All participants were able to download their preliminary evaluation report (reporting assigned values, reported values and z-scores) at the end of December 2018 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 petroleum hydrocarbons in TABLE 2. In both tables the assigned and information values are indicated along with the target standard deviation (12.5%) for each compound.

All results are reported by the laboratory code number only to protect the Participants confidentiality.

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 petroleum hydrocarbons are reported in TABLE 5 and the instrumental conditions for these analyses are reported in TABLE 6

Laboratories that reported data but didn't provide information for treatment of samples and GC conditions were not included in TABLES 3, 4, 5 and 6. Figures 1 and 2 shows the graphic representations of key points of sample treatment and instrumental analyses for organochlorine pesticides and PCBs congeners and petroleum hydrocarbons respectively.

TABLE 1. Reported results and certified, recommended and information values for organochlorine pesticides and PCB congeners in the biota test sample (IAEA-451)

All results are in ng/g dry weight.

	Laboratory codes																		IAEA -451	TSD[1]
Analyte	**2**	**5**	**7**	**9**	**11**	**12**	**14**	**16**	**17**	**18**	**21**	**24**	**25**	**26**	**27**	**29**	**32**	**33**		
Dieldrin	2.85	2.99	.	323	280	8.1	.	0.87	.	.	<3	.	1.1	.	1.4	.	2.8	1.9	1.88	0.24
HCB	.	<0.33	.	.	2205	9.1	2.1	0.35	.	.	<1	.	<0.5	.	0.18	.	.	<0.1	0.39	0.05
PCB No 28	126	0.09	0.10	.	261	3.3	.	0.24	0.53	8.2	<1	0.42	2.4	.	0.64	0.79	0.8	0.18	0.85	0.11
PCB No 101	66	0.65	0.32	.	645	13.4	3.0	1.14	1.64	48	<1	1.6	3.0	1.4	1.3	2.2	1.93	0.77	1.74	0.22
PCB No 105	.	0.18	.	.	.	.	1.5	0.22	0.30	.	.	.	.	.	0.50	.	.	<0.1	0.49	0.06
PCB No 110	.	0.36	0.90	.	.	.	.	0.82	0.60	.	.	.	.	.	.	.	.	0.41	0.88	0.11
PCB No 118	235	0.58	0.20	.	255	0.71	1.2	0.83	0.86	39	<3	0.74	.	0.83	2.4	1.0	1.4	0.45	1.01	0.13
PCB No 128	.	0.46	.	.	.	.	0.55	0.56	0.96	.	.	.	.	.	.	.	.	0.65	0.49	0.06
PCB No 138	253	3.41	2.6	.	244	5.4	3.1	4.9	5.8	36	4.2	6.0	3.4	4.3	5.2	5.3	7.6	5.9	5.30	0.66
PCB No 149	.	2.30	1.1	.	.	2.4	.	3.6	3.5	.	.	.	.	2.8	.	.	.	2.8	3.33	0.42
PCB No 153	296	9.73	2.2	.	370	7.8	16	12	9.5	26	9.7	8.9	5.7	9.7	8.8	8.5	20	11	8.59	1.1
PCB No 170	.	2.75	0.79	.	.	2.0	3.5	3.2	3.1	.	.	.	.	.	.	.	.	4.5	3.05	0.38
PCB No 180	220	6.69	2.3	.	111	6.1	8.8	8.2	6.6	43	6.0	6.0	4.3	7.5	6.7	5.8	15	7.1	6.56	0.82
PCB No 183	.	1.46	0.39	.	.	.	1.8	5.6	1.4	.	.	.	.	.	.	.	.	0.56	1.82	0.23
PCB No 187	.	3.75	0.33	.	.	.	.	1.9	3.2	.	.	.	.	.	.	.	.	2.8	3.97	0.50
PCB No 194	.	1.46	.	.	.	2.4	1.8	.	.	.	.	.	.	1.3	.	.	.	.	1.45	0.18
PCB No 206	.	0.16	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	0.24	0.03
Lindane*	1.03	<0.33	.	253	2758	0.36	0.38	0.36	.	.	<1	0.22	3.4	.	0.10	.	0.09	<0.1	0.56	0.07
pp DDD*	5.22	<0.33	.	7.8	85	1.2	0.61	0.34	.	.	<1	0.26	2.3	0.52	1.7	1.2	0.64	2.7	0.99	0.12
pp DDE*	2.87	<1	.	137	.	0.48	1.9	0.98	.	.	<3	0.63	<0.5	0.88	1.6	0.95	0.76	2.0	1.73	0.22
pp DDT*	16	<0.33	.	171	.	7.7	.	0.21	.	.	<3	0.22	<0.5	.	1.7	.	.	<0.1	1.34	0.17
PCB No 31*	.	0.04	.	.	.	4.1	.	0.15	0.53	.	.	.	.	.	.	.	.	0.13	0.29	0.04
PCB No 44**	.	0.06	.	.	.	0.74	.	.	.	.	.	.	.	0.21	.	.	.	.	0.40	0.05
PCB No 49**	.	0.14	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	0.92	0.12
PCB No 52*	439	0.16	0.10	.	812	3.3	0.50	0.53	0.51	19	<1	0.45	35	0.97	0.58	0.45	0.68	0.27	0.82	0.10
PCB No 209**	1.62	0.07	.	.	.	0.73	.	.	.	.	.	.	.	.	.	.	.	.	0.15	0.02

[1] TSD = Target Standard Deviation, *Recommended value; ** Information value.

TABLE 2. Reported results and certified, recommended and information values for petroleum hydrocarbons in the biota test sample (IAEA-451)

All results are in ng/g dry weight.

	Laboratory codes														IAEA-451	TSD[1]
Analyte	**5**	**7**	**9**	**10**	**11**	**14**	**15**	**16**	**17**	**18**	**26**	**28**	**31**	**33**		
n-C17	.	.	.	.	.	.	.	.	.	.	.	.	134	303	373	47
Naphthalene	.	21	16	14	61	10	6	.	4.4	.	.	285	6.4	24	15	1.9
Phenanthrene	<12	.	17	30	36	19	11	9.2	18	6.5	19	.	6.4	18	16	2.0
Fluoranthene	26	34	69	76	173	55	77	35	46	116	56	12	9.3	45	49	6.2
Pyrene	21	29	60	32	183	42	27	28	33	.	42	.	24	38	40	5.0
Benz [a] Anthracene	13	7.3	24	18	19	24	20	27	12	53	19	.	1.5	18	19	2.4
Chrysene (+Triphenylene)	21	20	40	23	11	47	35	34	21	19	43	11	19	43	27	3.4
Benzo [a] Pyrene	11	8.7	20	12	46	19	12	12	11	120	16	.	15	13	18	2.3
Benzo[b+j]fluoranthene	42	18	.	14	35	63	42	45	33	.	.	.	1.2	45	36	4.5
Benzo [k] Fluoranthene	13	8.7	25	14	10	20	12	79	10	43	16	.	2.6	14	15	1.8
Benzo [g,h,i] Perylene	19	13	37	14	8.7	19	17	37	20	110	23	.	1.4	20	20	2.4
Dibenz[a,h]anthracene	3.9	<1.0	8.0	43	15	5.0	3.8	.	4.6	101	6.0	.	26	4.5	5.3	0.67
n-C18**	.	.	.	.	.	.	.	.	.	.	.	.	18	194	232	29
Phytane**	.	.	.	.	.	.	.	.	.	.	.	.	17	141	51	6.3
Pristane**	.	.	.	.	.	.	.	.	.	.	.	.	17	55	67	8.3
1 Methyl Naphthalene**	.	.	.	.	.	10	.	.	.	.	6.1	.	20	14	5.0	0.62
1 Methyl Phenanthrene**	.	.	.	.	.	6.6	.	.	.	.	.	.	11	21	5.3	0.66
2 Methyl Phenanthrene**	.	.	.	.	.	8.5	.	.	.	.	.	.	.	26	18	2.2
Acenaphthene**	.	.	4.6	.	1442	1.5	0.5	.	1.2	692	.	.	18	2.4	2.2	0.27
Acenaphthylene*	.	.	.	.	24	4.5	1.0	.	2.7	745	5.0	.	5.0	3.8	2.0	0.25
Fluorene**	.	.	12	7	1445	7.1	0.8	.	4.0	292	2.8	.	34	3.4	2.6	0.33
Anthracene*	<1.33	.	<4	<3	761	2.3	15	.	1.8	250	3.1	22	10	3.6	5.1	0.63
Benzo [e] Pyrene*	.	.	36	.	12	33	.	18	22	.	.	.	1.2	22	21	2.6
Indeno[1,2,3-cd]pyrene*	18	5.8	<4	30	20	21	16	.	18	253	24	.	5.6	22	24	2.9

[1] TSD = Target Standard Deviation, *Recommended value; ** Information value.

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

Lab. Code	Extraction	Solvent	Clean-up	Fractionation
2	Shaking (solid/liquid extraction)	n-Hexane	Sulphuric Acid (H2SO4)	Florisil
5	ASE	Toluene/Acetone	Sulphuric Acid (H2SO4)	Silica, Florisil, Carbon/Florisil
7	Sonication	Acetone/n-Hexane	GPC	None
9	ASE	Dichloromethane (DCM)	None	None
11	Sohxlet	Dichloromethane (DCM)	SPE	Florisil
12	Sohxlet	n-Hexane/Dichloromethane	Sulphuric Acid (H2SO4)	Florisil
16	Quechers	Other	SPE	Other
17	ASE	n-Hexane/Dichloromethane	Silica	None
18	Microwave assisted	Acetone/n-Hexane	None	None
21	Shaking (solid/liquid extraction)	n-Hexane, Cyclohexane and Acetone	SPE	Florisil
24	Microwave assisted	Acetone/n-Hexane	Sulphuric Acid (H2SO4)	Florisil
25	Quechers	Acetonitrile	SPE	None
26	Sohxlet	n-Hexane	SPE	Silica
27	Sohxlet	n-Hexane/Dichloromethane	Other	Silica
29	Sohxlet	n-Hexane/Dichloromethane	Sulphuric Acid (H2SO4)	Florisil
32	Sohxlet	n-Hexane/Dichloromethane	Sulphuric Acid (H2SO4)	Florisil
33	ASE	n-Hexane/Dichloromethane	GPC	None

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

Lab. Code	Use of Internal Standard	Internal Standards used	Injector Type	GC-Column	Detector Type
2	yes	EPA 8081	Split	Other	GC/ECD
5	yes	13C mass labelled standard	Splitless	HT8PCBAr	GC/HRMS
7	No		PTV	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
9	No		Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/ECD
11	No		Splitless	DB5ms	GC/MS
12	yes	PCB 30	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/ECD
16	yes	All analytes 13C labelled	PTV	Other	GC/MSMS
17	yes	Std Int EPA 1948 Surrogato 7 marcati	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MSMS
18	No	no	Splitless	Other	GC/MS
21	yes	PCB 209	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/ECD *
24	yes	Dr Ehrenstorfer GmbH PCB No29 Ultra Scientific BZ198	PTV	5% Phenyl 95% Dimethylpolysiloxane	GC/MSMS
25	yes	PCB 29 Epsilon HCH PCB 193	Splitless	100% Dimethylpolysiloxane	GC/ECD
26	yes	Epsilon HCH - PCB 29 - PCB 198	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/ECD
27	yes	PCB155	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MSMS
29	No		Split	5% Phenyl 95% Dimethylpolysiloxane	GC/ECD
32	yes	pentachloronitrobenzene	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MSMS
33	yes	mix PCB labelled	MMI	5% Phenyl 95% dimethyl arylene siloxane	GC/MSMS

*With dual column confirmation

TABLE 5. Treatment of samples performed by participants for petroleum hydrocarbons

Lab. Code	Extraction	Solvent	Clean-up	Fractionation
5	ASE	Acetone/n-Hexane	SPE	None
7	Shaking (solid/liquid extraction)	Other	None	None
9	Sonication	acetonitrile	None	HPLC chromatography
10	ASE	n-Hexane/Dichloromethane	Other	Silica
11	Sohxlet	Dichloromethane (DCM)	SPE	Florisil
14	Sohxlet	Other	Other	Silica/Alumina
15	Microwave assisted	Methanol	None	Silica/Alumina
16	ASE	Acetone/n-Hexane	SPE	Silica
17	ASE	n-Hexane/Dichloromethane	Other	Silica
18	Microwave assisted	Acetone/n-Hexane	None	None
26	Sohxlet	n-Hexane/Dichloromethane	Silica	Silica
31	Sohxlet	Methanol	Other	Silica/Alumina
33	ASE	n-Hexane/Dichloromethane	GPC	None

TABLE 6. Instrumental conditions used by participants for petroleum hydrocarbons

Lab. Code	Use of Internal Standard	Internal Standards/surrogates used	Injector Type	GC/HPLC-Column	Detector Type
5	Yes	13C mass labelled standard	Splitless	PAH select (Agilent)	GC/MSMS
7	No			C18	HPLC
9	No		On-column	HypersilGreenPAH	HPLC
10	Yes	7-methylbenzo(a)pyrene		Other	HPLC
11			Splitless	DB5ms	GC/MS
14	Yes	Napthalened8 Acenapthened10 Phenanthrened10 Pyrened10 Chrysened12 Perylened12 BenzoPerylened12	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
15	Yes		Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
16	Yes	PAH Deuterated	Splitless	50% Phenyl 50% dimethyl arylene siloxane	GC/MS
17	Yes	Std Int EPA 8270 Surrogato 8270	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
18	No	no		C18	HPLC
26	Yes	Internal Standard Mix Naphtalene D8 Acenaphtene D10 Phenanthrene D10 Fluoranthene D10 Chrysene D12 Perylene D12	Splitless	5% Phenyl 95% Dimethylpolysiloxane	GC/MS
31	Yes		Splitless	5% Phenyl 95% Dimethylpolysiloxane	Other
33	Yes	mix PAH labelled	Other	DB5ms	GC/MSMS

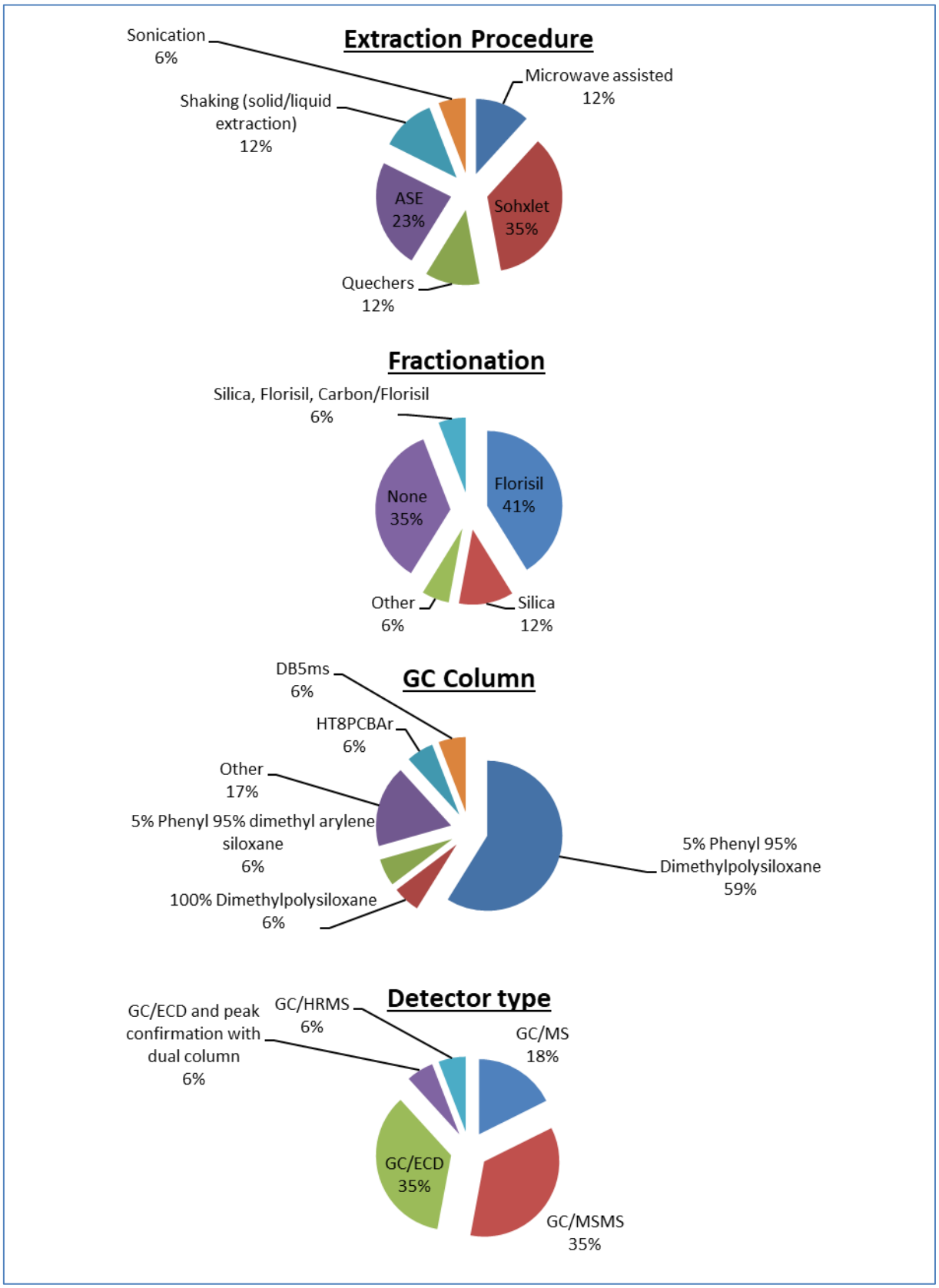


Figure.1. Graphic representation of sample treatment and instrumental conditions for organochlorine pesticides and PCB congeners.

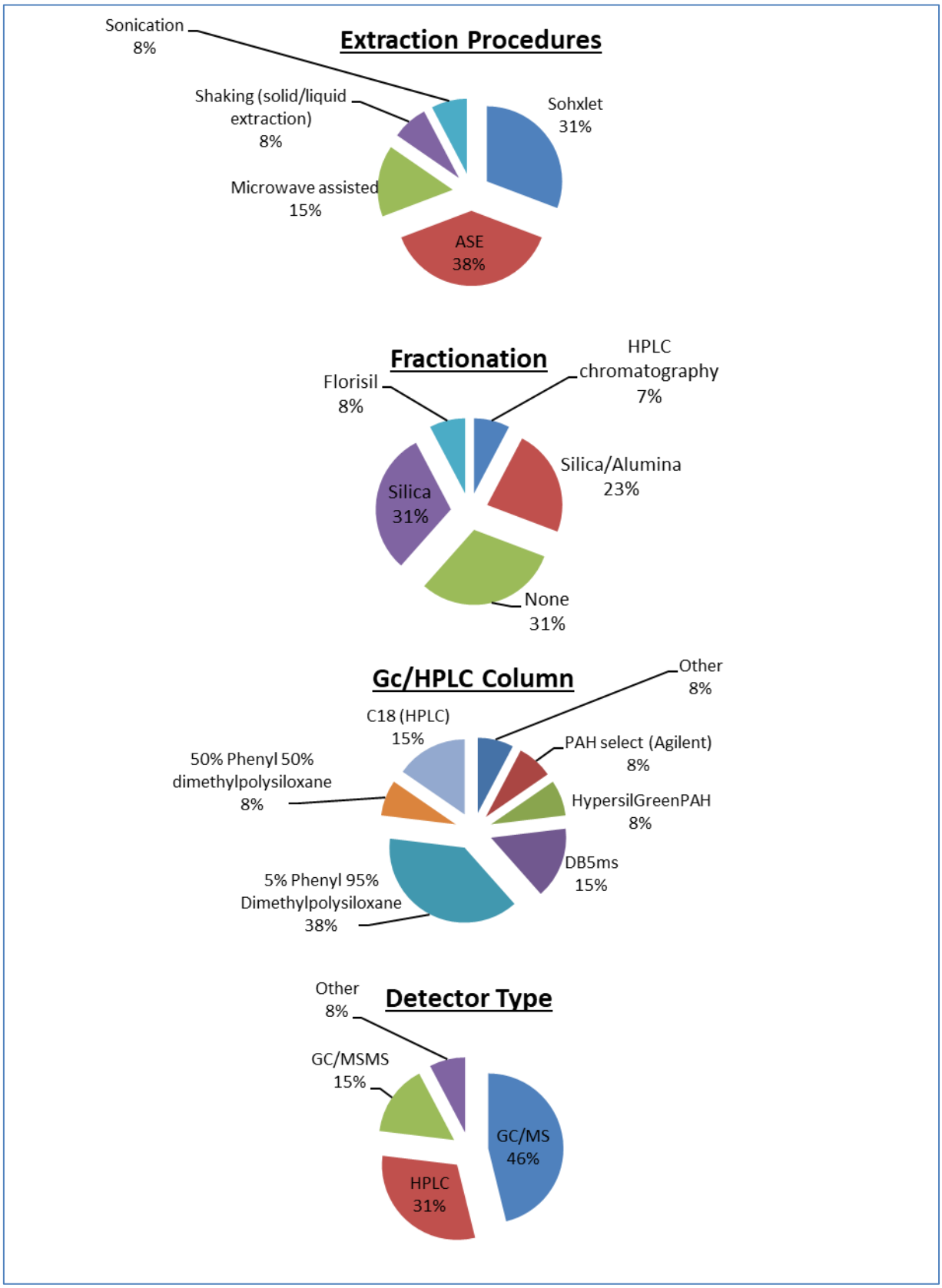


Figure.2. Graphic representation of sample treatment and instrumental conditions for Petroleum Hydrocarbons

4.3. Evaluation Criteria

For the assessment of the laboratory performances, a *z*-score is calculated according to the ISO guide 13528 [2]:

$$z = (x_i - x_a)/ \sigma_p$$

Where:

- x_i is the reported values from participant of the analyte concentration in the sample;
- x_a is the assigned value;
- σ_p is the standard deviation for proficiency assessment,

This score effectively expresses the difference between the robust mean of the laboratory and the assigned value in unit σ_p .

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 [2, 3, 4].

The standard deviation for proficiency assessment for all target compounds, σ_p, was set at 12.5% in this exercise.

The *z*-scores for participating laboratories can be found in TABLE 7 for chlorinated pesticides and PCB congeners and TABLE 8 for petroleum hydrocarbons. 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 7. *Z*-scores for organochlorinated pesticides and PCB congeners

Analyte	Laboratory codes																	
	2	5	7	9	11	12	14	16	17	18	21	24	25	26	27	29	32	33
Dieldrin	4	4.7		1366	1183	26		-4.3					-3.2		-2.1		4.1	0.2
HCB					45223	179	35	-0.9							-4.2			
PCB No 28	1178	-7.2	-7.1		2448	23		-5.7	-3.0	70		-4.0	15		-2.0	-0.6	-0.3	-6.3
PCB No 101	295	-5.0	-6.5		2959	53	5.7	-2.8	-0.5	210		-0.8	5.7	-1.4	-1.8	1.9	0.9	-4.5
PCB No 105		-5.1					16	-4.4	-3.2						0.2			
PCB No 110		-4.8	0.2					-0.5	-2.5									-4.3
PCB No 118	1856	-3.4	-6.4		2014	-2.4	1.6	-1.4	-1.2	305		-2.2		-1.4	11	0.2	2.9	-4.5
PCB No 128		-0.4					0.9	1.2	7.7									2.6
PCB No 138	374	-2.8	-4.1		360	0.1	-3.3	-0.6	0.7	46	-1.7	1.0	-2.9	-1.5	-0.1	-0.1	3.5	0.9
PCB No 149		-2.5	-5.3			-2.2		0.6	0.5					-1.2				-1.2
PCB No 153	268	1.1	-6.0		337	-0.7	6.6	3.4	0.8	17	1.0	0.3	-2.7	1.1	0.2	-0.1	11	2.3
PCB No 170		-0.8	-5.9			-2.8	1.1	0.4	0.2									3.8
PCB No 180	260	0.2	-5.2		127	-0.6	2.7	2.0	0.1	44	-0.7	-0.6	-2.8	1.1	0.2	-1.0	9.7	0.6
PCB No 183		-1.6	-6.3				-0.2	17	-1.6									-5.5
PCB No 187		-0.4	-7.3					-4.1	-1.5									-2.4
PCB No 194		0.1				5.3	1.8							-0.9				
PCB No 206		-2.7																

TABLE 8. Z-scores for petroleum hydrocarbons

Analyte	Laboratory codes													
	5	7	9	10	11	14	15	16	17	18	26	28	31	33
n-C17													-5.13	-1.50
Naphthalene		3.4	0.7	-0.5	25	-2.6	-5.0		-5.6			146	-4.6	5.0
Phenanthrene			0.5	7.4	10	1.6	-2.3	-3.4	1.3	-4.7	1.6		-4.7	0.9
Fluoranthene	-3.8	-2.5	3.2	4.3	20	0.9	4.5	-2.3	-0.5	11	1.1	-6.1	-6.5	-0.6
Pyrene	-3.7	-2.2	4.0	-1.6	29	0.4	-2.6	-2.5	-1.4		0.4		-3.3	-0.5
Benz [a] Anthracene	-2.7	-5.0	2.0	-0.6	-0.3	2.1	0.4	3.4	-3.1	14.3	0.0		-7.4	-0.5
Chrysene (+Triphenylene)	-1.6	-2.2	3.9	-1.1	-4.7	6.1	2.4	2.0	-1.8	-2.4	4.8	-4.7	-2.5	4.7
Benzo [a] Pyrene	-3.2	-4.2	0.8	-2.6	12	0.2	-2.7	-2.9	-3.2	45	-0.9		-1.3	-2.3
Benzo[b+j]fluoranthene	1.4	-3.9		-4.8	-0.1	6.1	1.3	2.1	-0.6				-7.7	2.1
Benzo [k] Fluoranthene	-1.0	-3.3	5.8	-0.5	-2.5	2.8	-1.7	35.1	-2.4	16	0.8		-6.6	-0.6
Benzo [g,h,i] Perylene	-0.3	-2.5	7.2	-2.1	-4.4	-0.1	-1.1	7.3	0.2	37	1.4		-7.4	0.1
Dibenz[a,h]anthracene	-2.1		4.0	56.2	15	-0.5	-2.4		-1.1	143	1.0		31	-1.3

5. EVALUATION OF RESULTS

5.1. Organochlorine Pesticides and PCB Congeners

Among all designated laboratories, only 51% submitted results for organochlorine pesticides and PCB congeners.

Only 13 participants to the current PT reported to have a QA/QC system in place in their laboratory and 6 laboratories reported to use validated methods. More than 70% use internal standards, and 7 laboratories reported their QA/QC results along with the test results.

Laboratory number 21, 26 and 29 provided all acceptable results. Four laboratories (16, 17, 24 and 27) reported more than 50% of acceptable results. Three laboratories (7, 25 and 32) provided more than 50% of results "out of control". Four laboratories (2, 9, 11 and 18) reported all outlying results.

Most of the participants reporting more than 50% outlying values reported neither using CRMs for their analyses nor having a QA/QC system in place in their laboratories.

Figure 3 reports a graphic representation of z-scores for organochlorine Pesticides and PCB congeners.

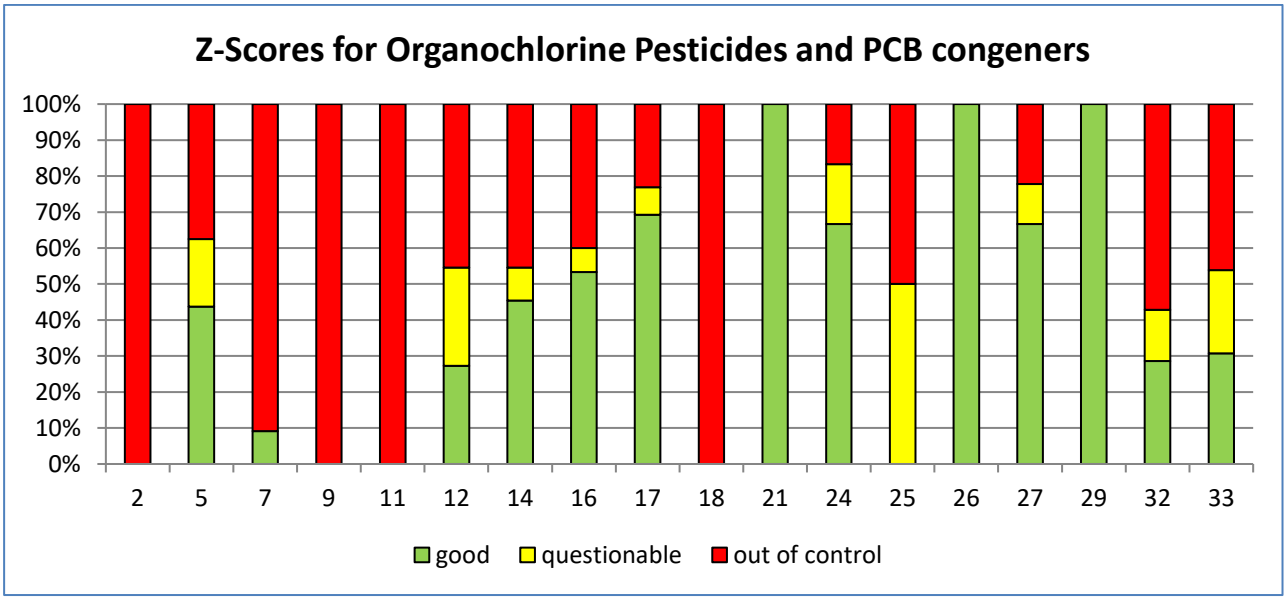


Figure 3. Graphic representation of laboratories z-scores for organochlorine pesticides and PCB congeners.

5.2. Petroleum Hydrocarbons

Only 43% of the designated laboratories submitted results for petroleum hydrocarbons.

Among the participants, laboratory number 14, 17, 26 and 33 provided all acceptable and very few “questionable” or “outlying” results. Six laboratories (7, 9, 11, 18, 28 and 31) provided more than 50% of results “out of control”.

About 70% of the participants reported to have a QA/QC system in place and to use internal standards. About half of the participants reported using validated methods. Only three laboratories (17, 26 and 31) reported their QA/QC data along with the test results. Two laboratories among the worst performing (9 and 18) reported using neither internal standards nor reference materials. Laboratory 31, although using internal standards and refence materials was not able to achieve acceptable performances. Unfortunately, laboratory 28 didn’t report any information.

Figure 4 reports a graphic representation of z-scores for petroleum hydrocarbons.

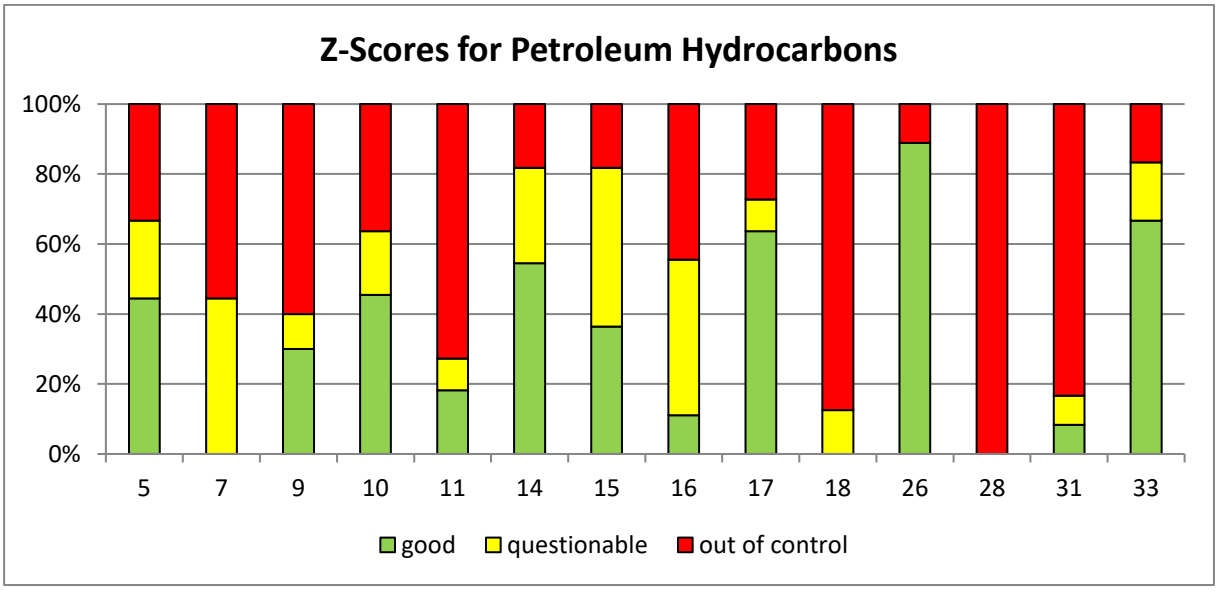


Figure 4. Graphic representation of laboratories z-scores for petroleum hydrocarbons.

Figure 5 and 6 show the distributions of the values reported by participants for the most analyzed 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.

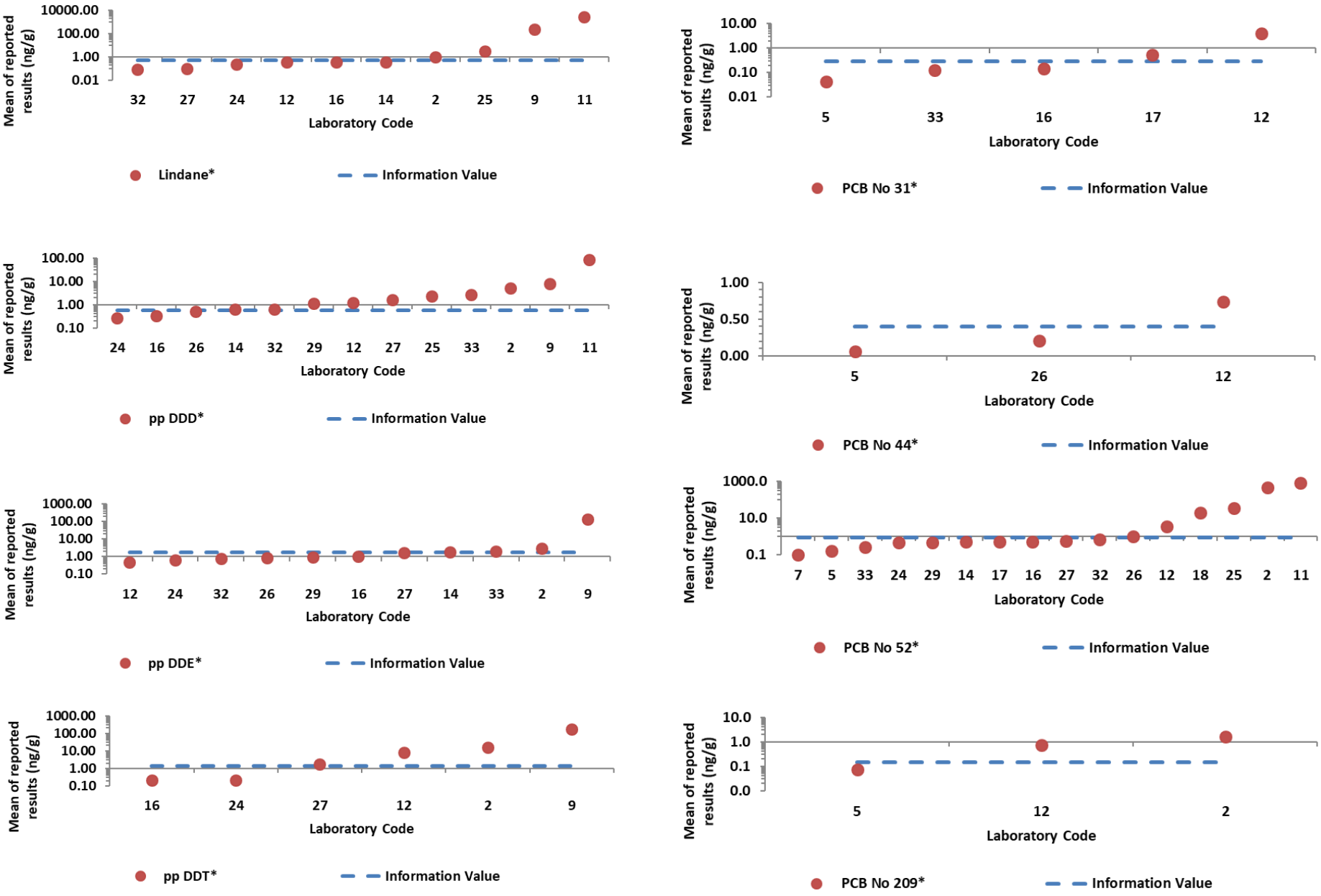


Figure.5. "Information values" reported by participants for organochlorine pesticides and PCB congeners.

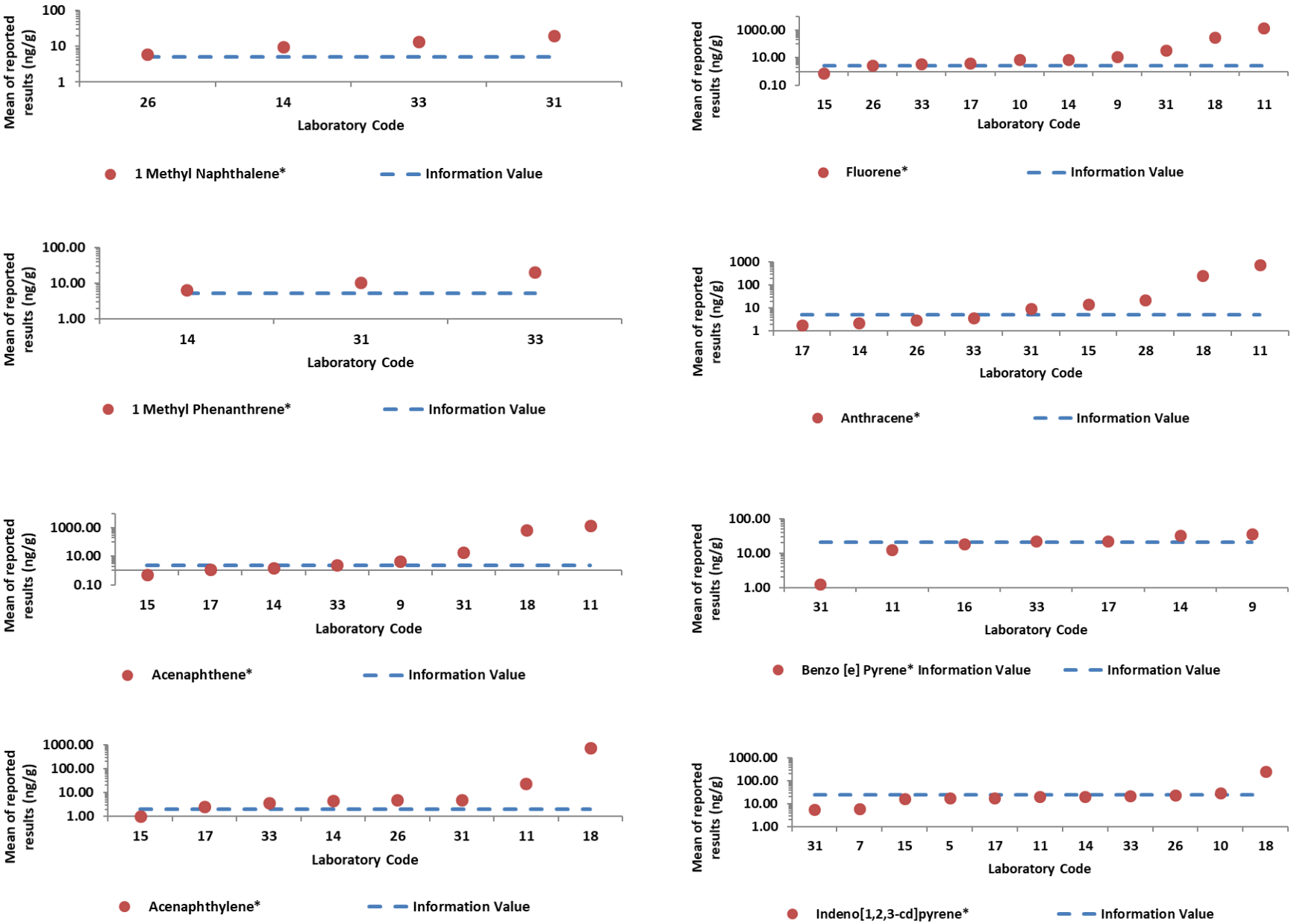


Figure 6. "Information values" reported by participants for petroleum hydrocarbons.

6. CONCLUSIONS AND RECOMMENDATIONS

Six participants, representing 33% 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 17, 21, 24, 26, 27 and 29. Six participants (i.e. laboratories 2, 7, 9, 11, 18 and 32) , representing 33% 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 along with z-scores that 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 7, 12, 14, 25 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 2, 9 and 11) reported results which differed by more than one order of magnitude from the assigned value. This may be due to a "reporting" mistake (for example: wrong unit conversion or wrong data-set 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. Four participants, representing 27% of all 15 laboratories reporting results for petroleum hydrocarbons reported all or most "acceptable" results. Unfortunately, six participants, representing 40% of all 15 laboratories reporting results petroleum hydrocarbons, 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 and validated methods and in some cases to be accredited. However, there are two examples of laboratories (11 and 18) 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 petroleum hydrocarbons analyses. Analyzing biological samples is in general more challenging than analyzing sediment samples due to presence of lipids. Lipids are extracted along with target compounds and can interfere separation and quantification of analytes. To avoid interferences from lipids the cleanup and separation procedures must be optimized.

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 surrogate standards/internal standards 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 in avoiding accuracy 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.

For the current PT, 51% of the designated laboratories submitted results for chlorinated compounds and 43% for petroleum hydrocarbons. The rate of participation to this PT is unfortunately low and in line with 2017 exercise when participation rates for chlorinated compounds and petroleum hydrocarbons were 48% and 35% respectively. Only 6 among the 11 newly nominated laboratories for 2018 exercise reported values.

Although some participants communicated upfront their difficulty to participate to this year exercise due to instrumental and/or manpower unavailability, some non-participating laboratories did not participate in 2017 exercise neither and did not communicate the reasons for non-participation.

This low participation rate is a problem given the importance of such exercises to test and demonstrate laboratory performances as required by ISO Guide 17025.

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 surrogates/internal standards, 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.

To assist participating laboratories a technical paper on the guidelines recommended by MED POL for the analysis and the quality assurance procedures will be available in the near future.

7. REFERENCES

[1] INTERNATIONAL ATOMIC ENERGY AGENCY, World-wide and Regional laboratory comparison on the determination of organochlorine compounds, polybrominated diphenyl ethers and petroleum hydrocarbons in IAEA-451 clam (*Gafrarium tumidum*) sample, IAEA Analytical Quality in Nuclear Applications Series No. 28 (IAEA/AQ/28, IAEA, Vienna (2013)

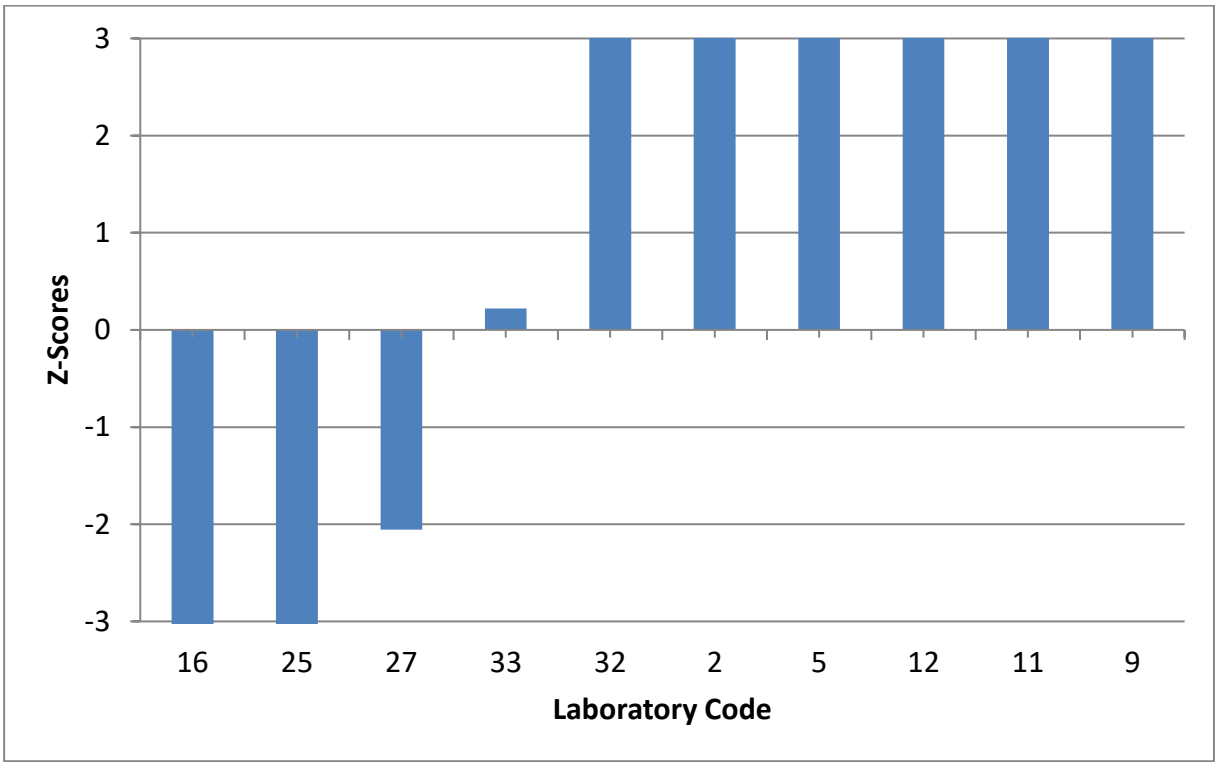
[2] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide 13528 (2005), Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons, ISO, Geneva, Switzerland.

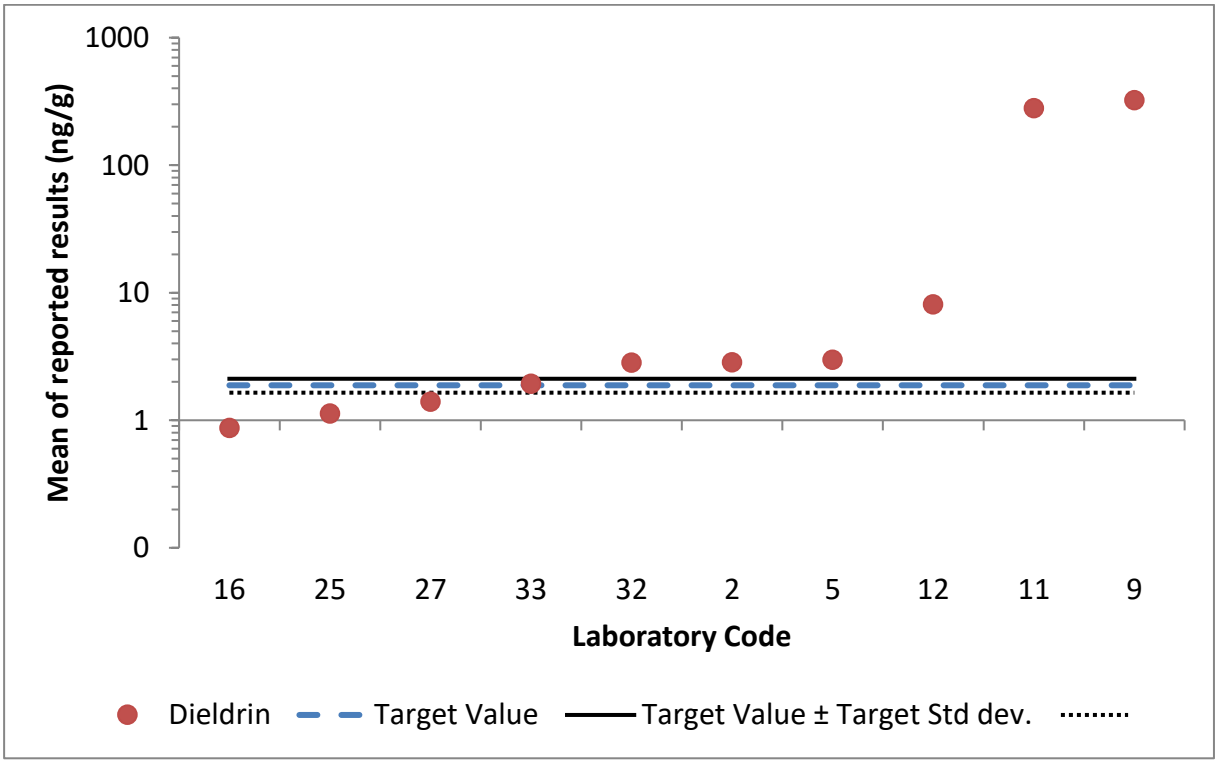
[3] Thompson and R. Wood (1993). The international harmonized protocol for the proficiency testing of (chemical) analytical laboratories. IUPAC/ISO/AOAC. *J. Pure. Appl. Chem*. **65**(9), 2123-2144.

[4] 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 DIELDRIN





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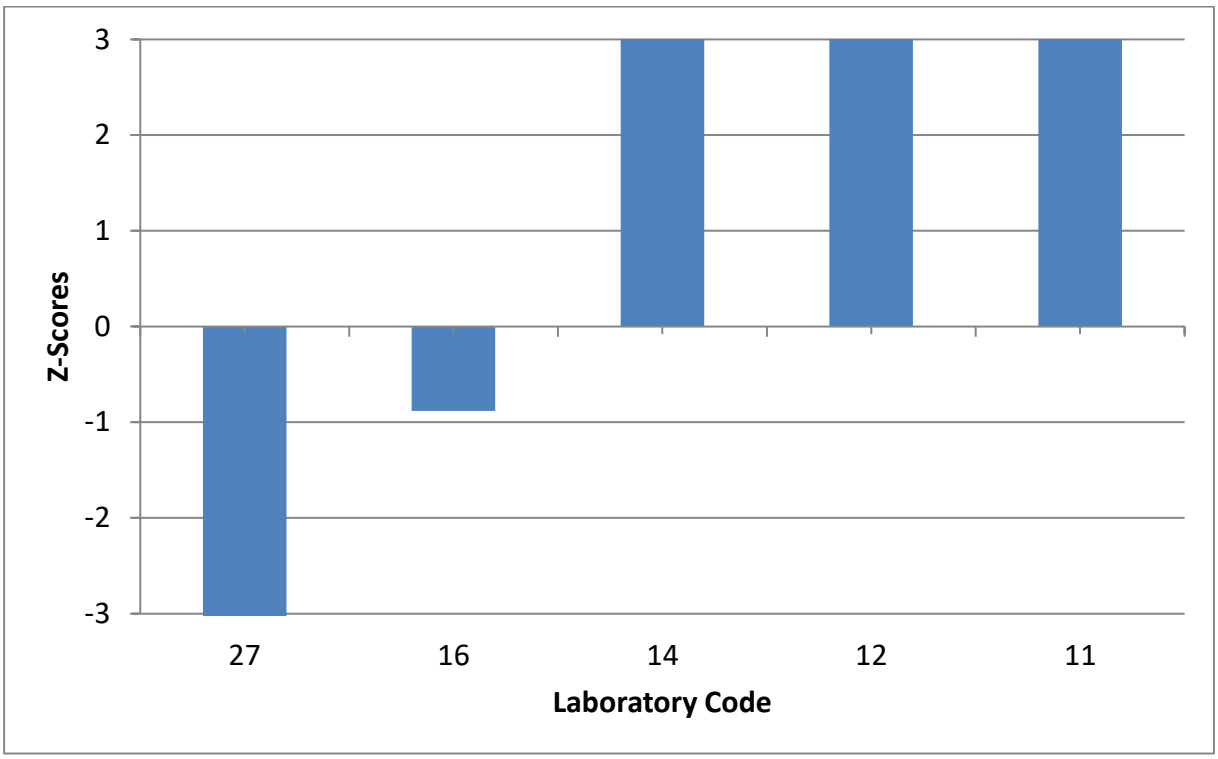

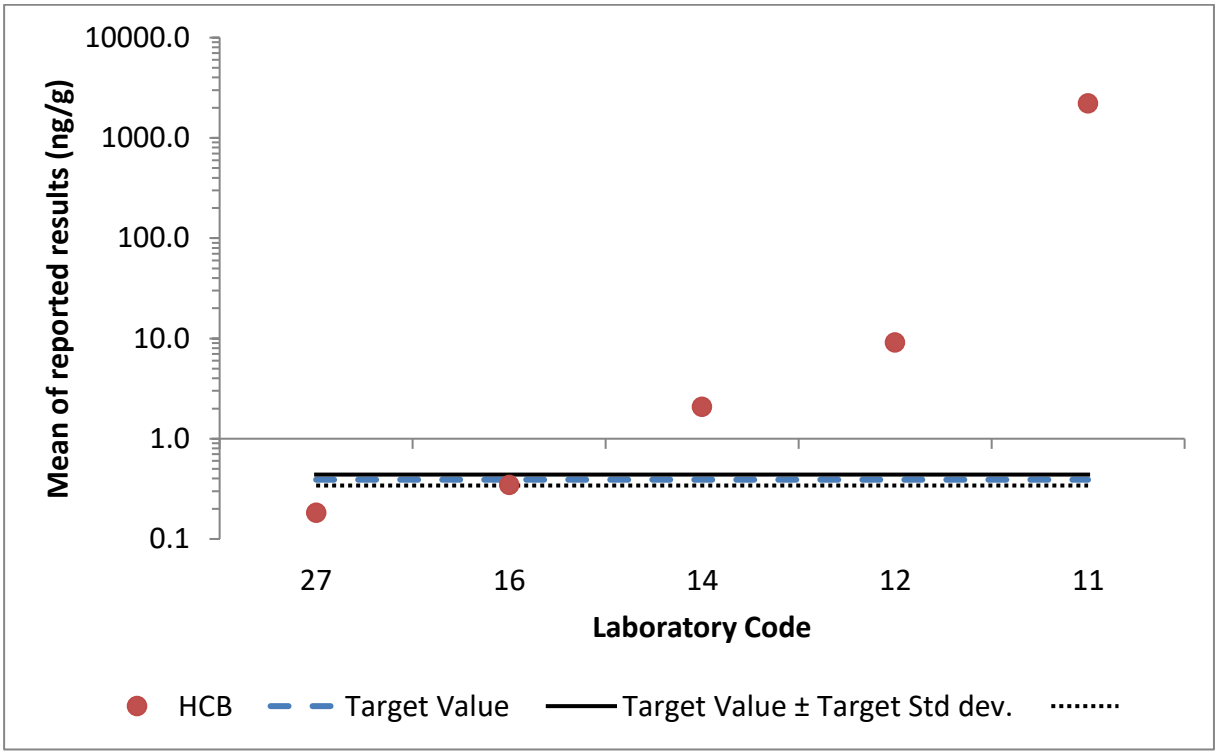

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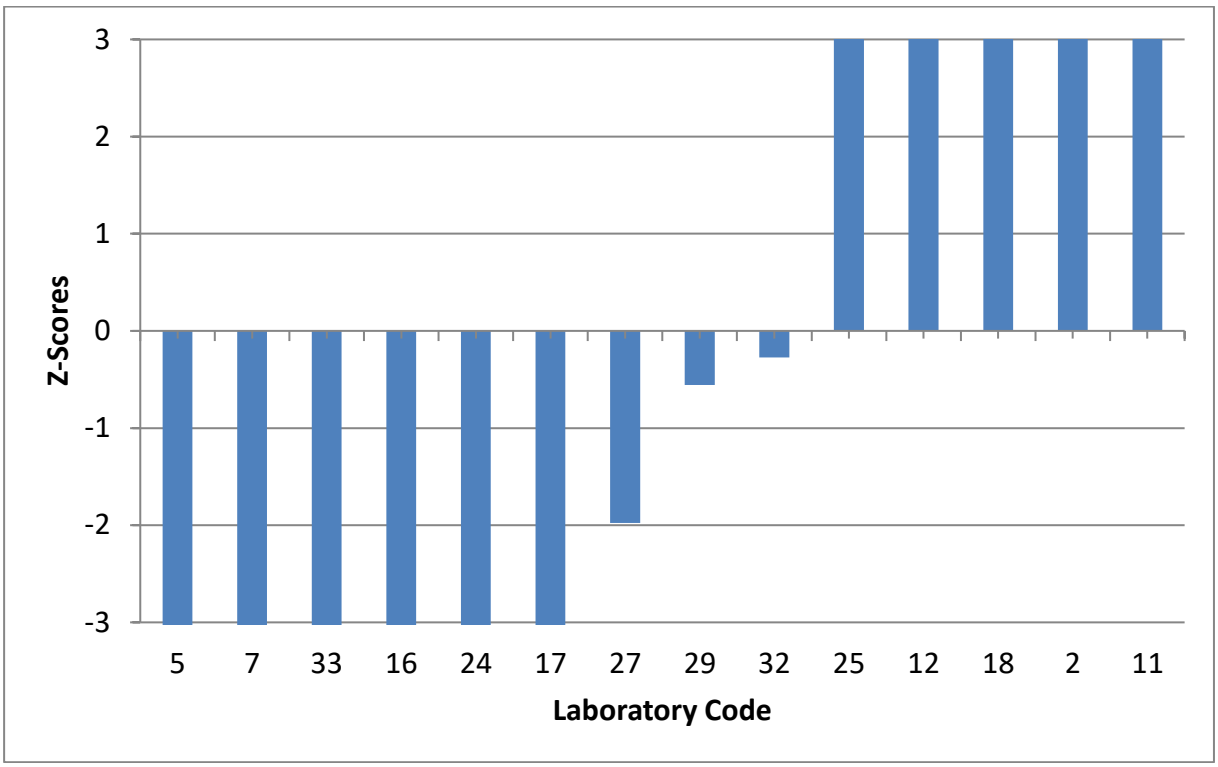

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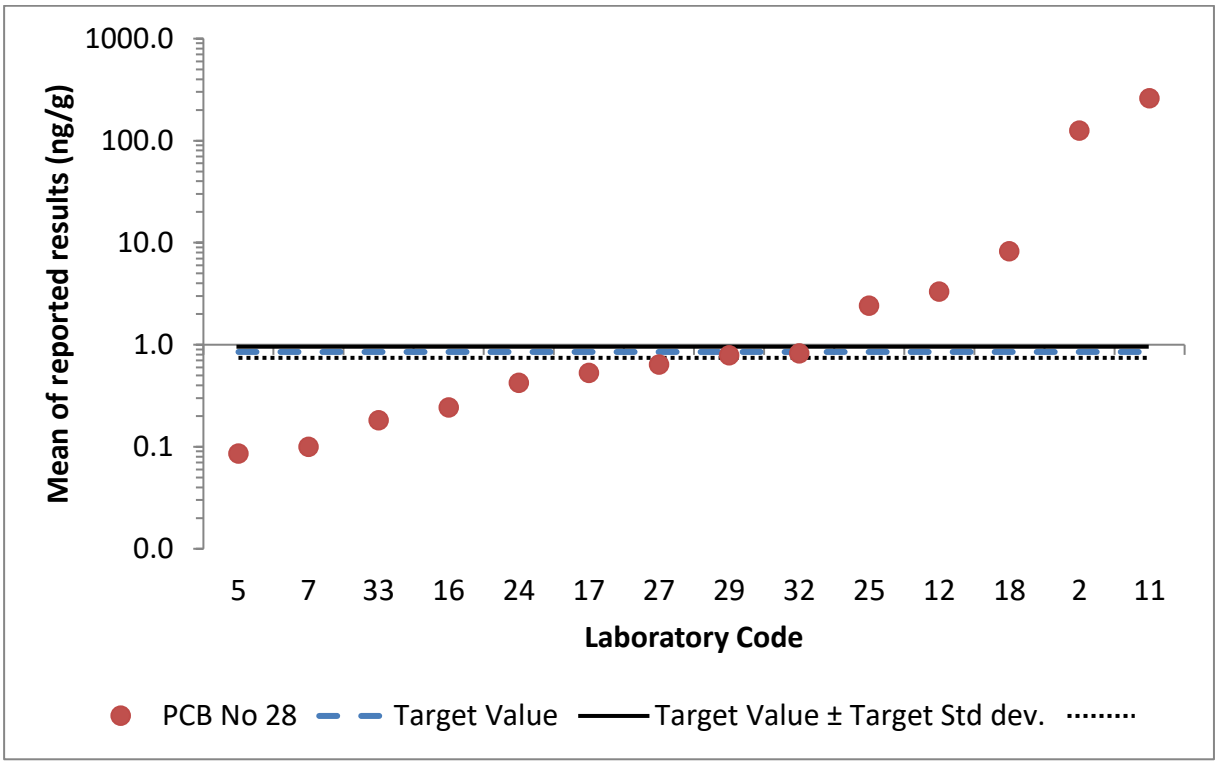

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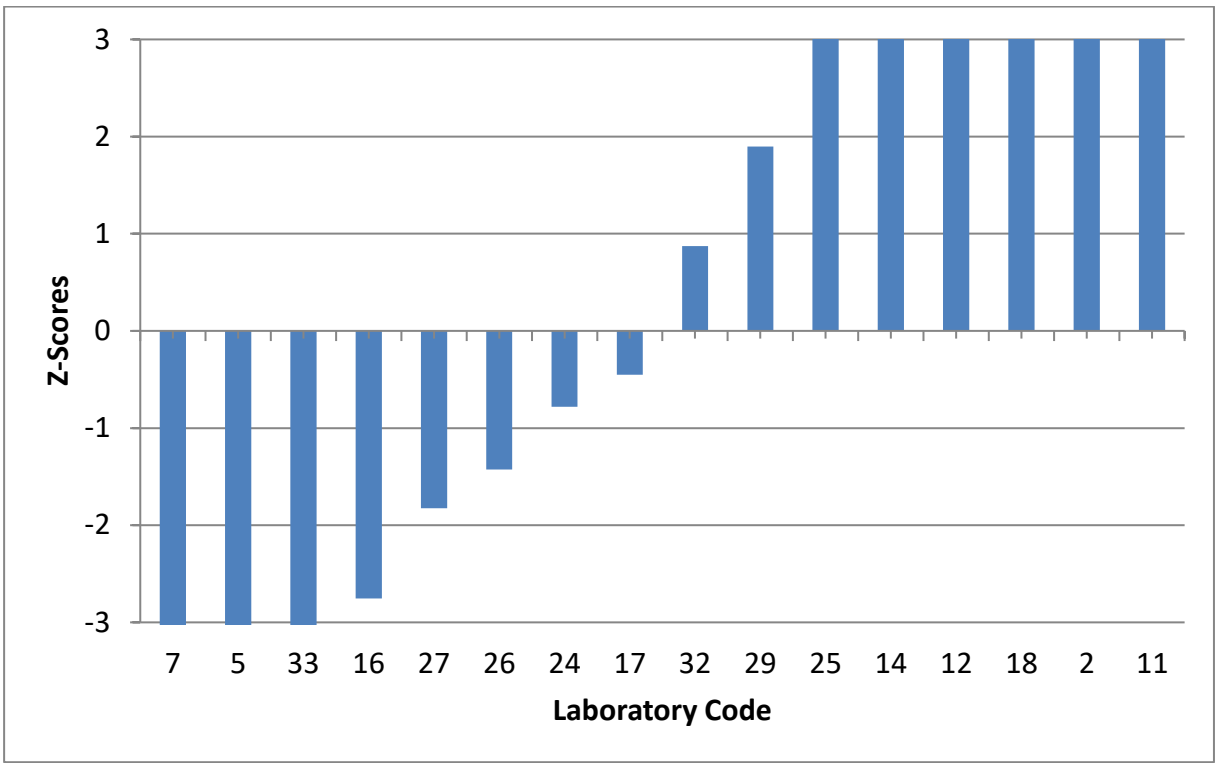

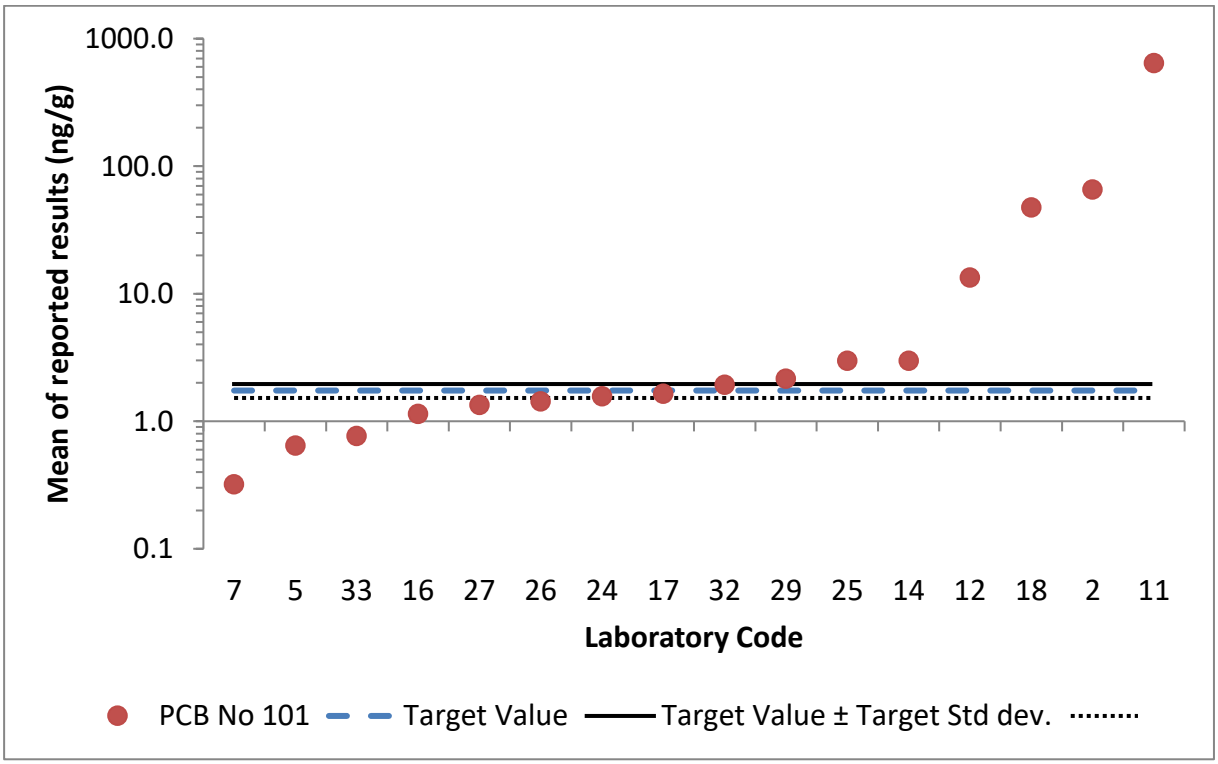

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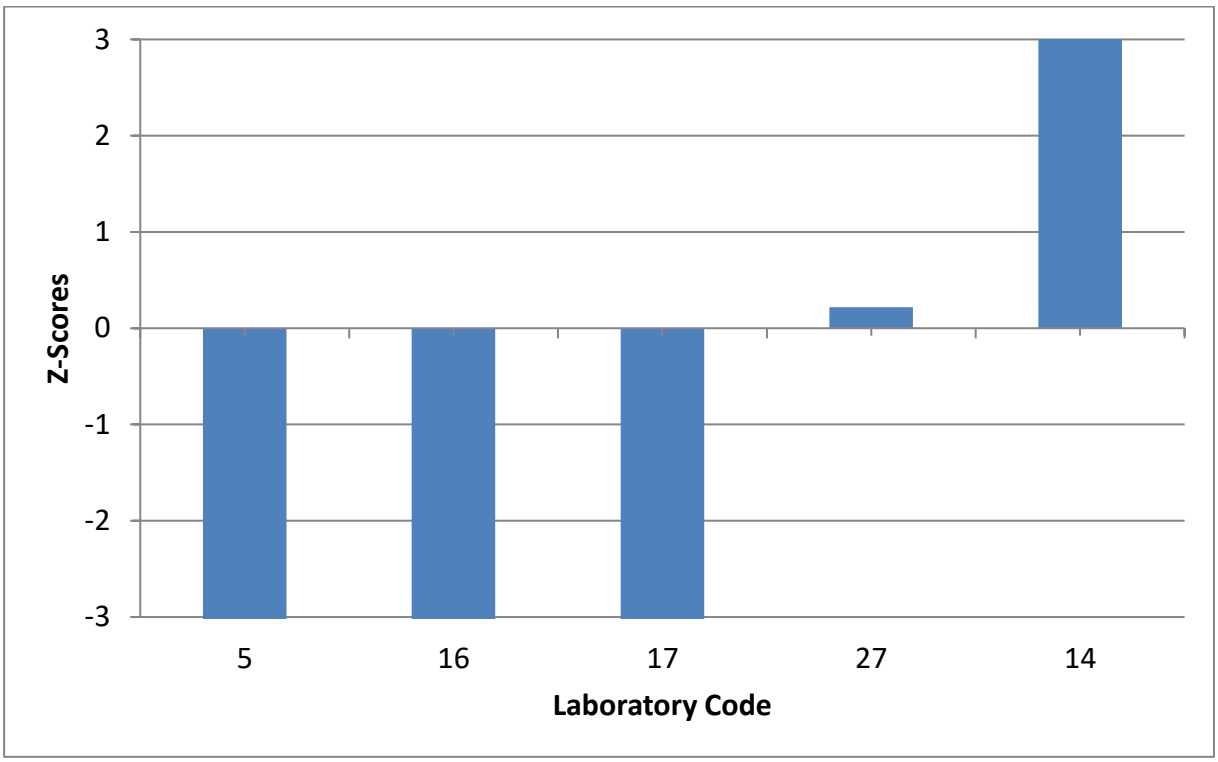

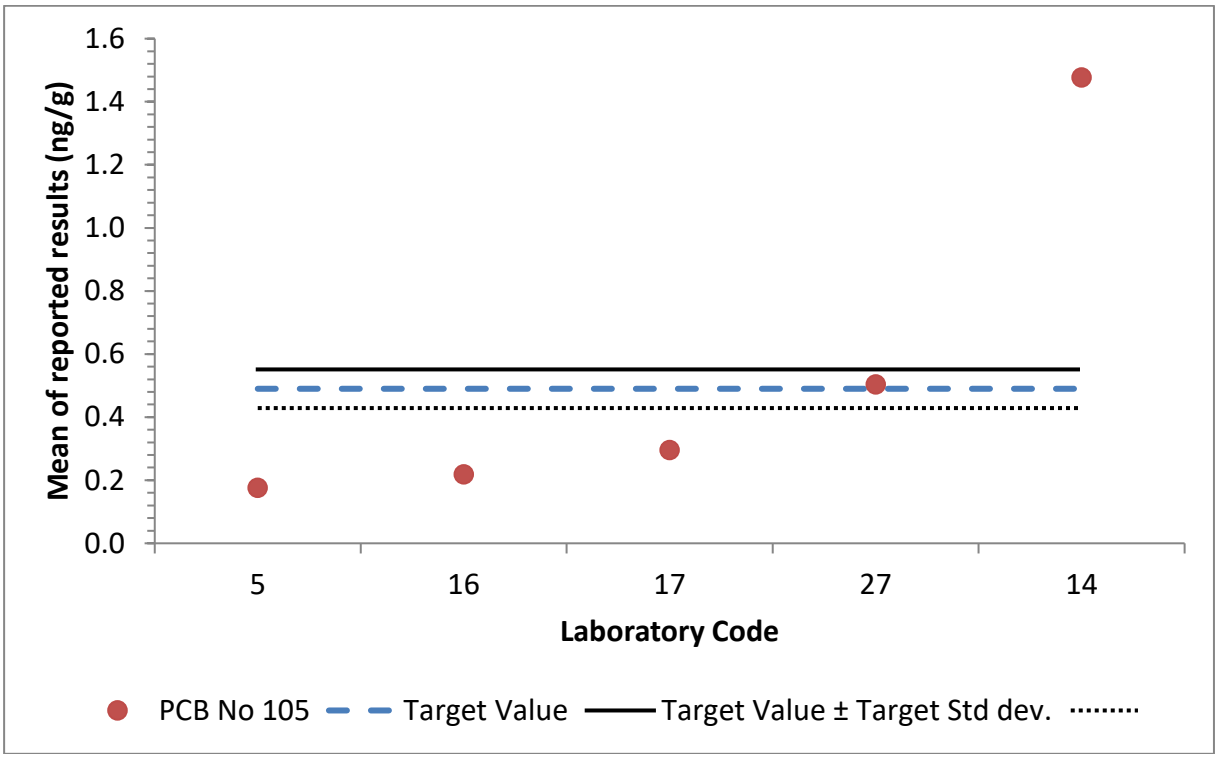

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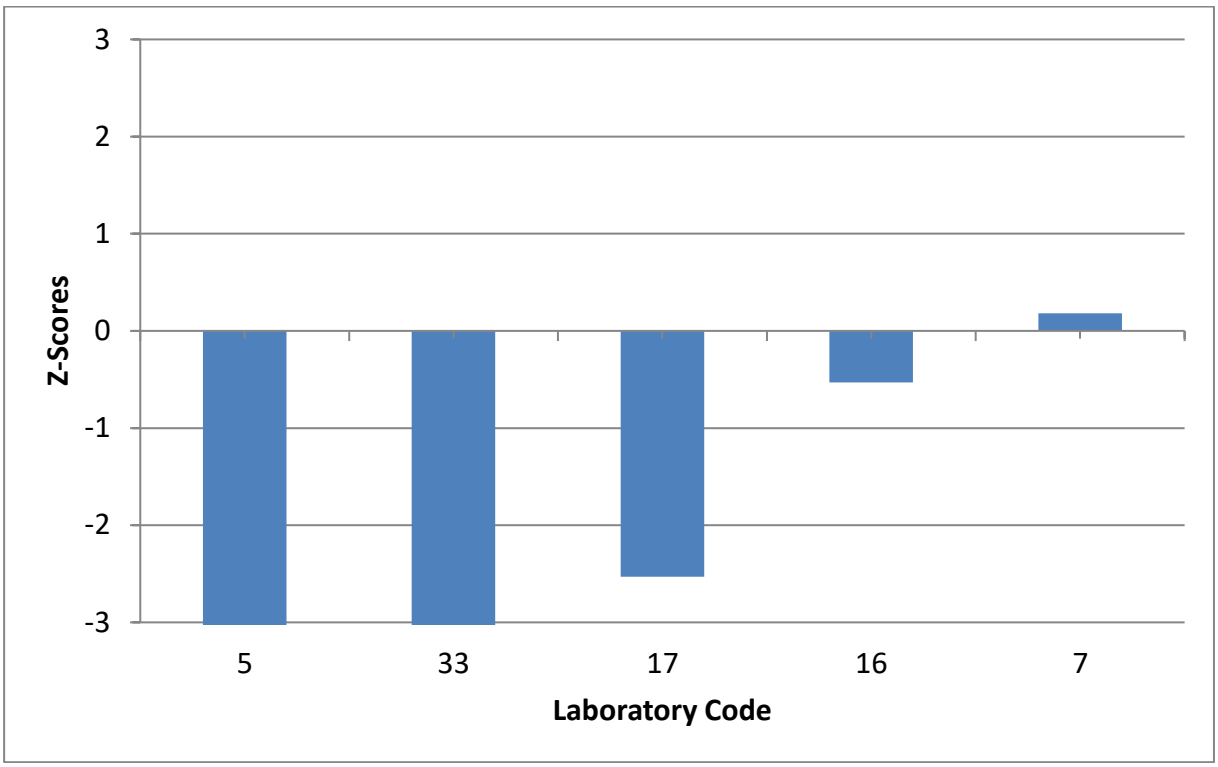

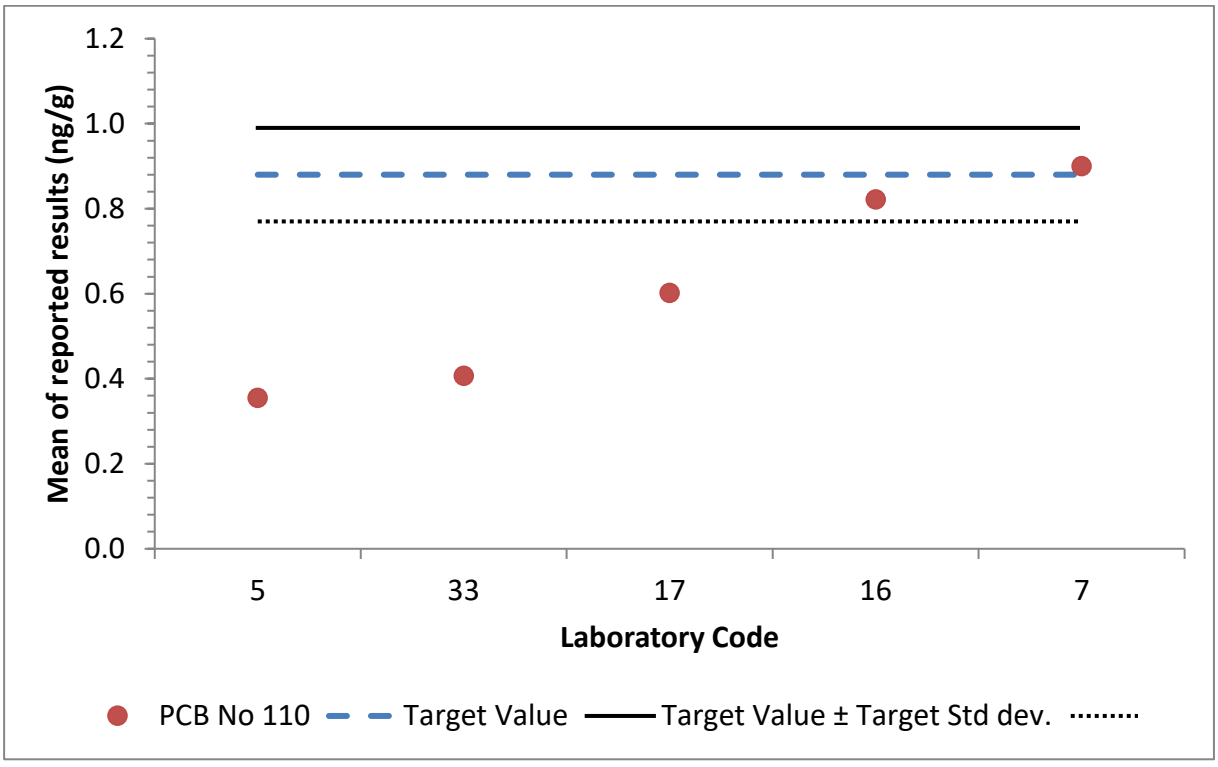

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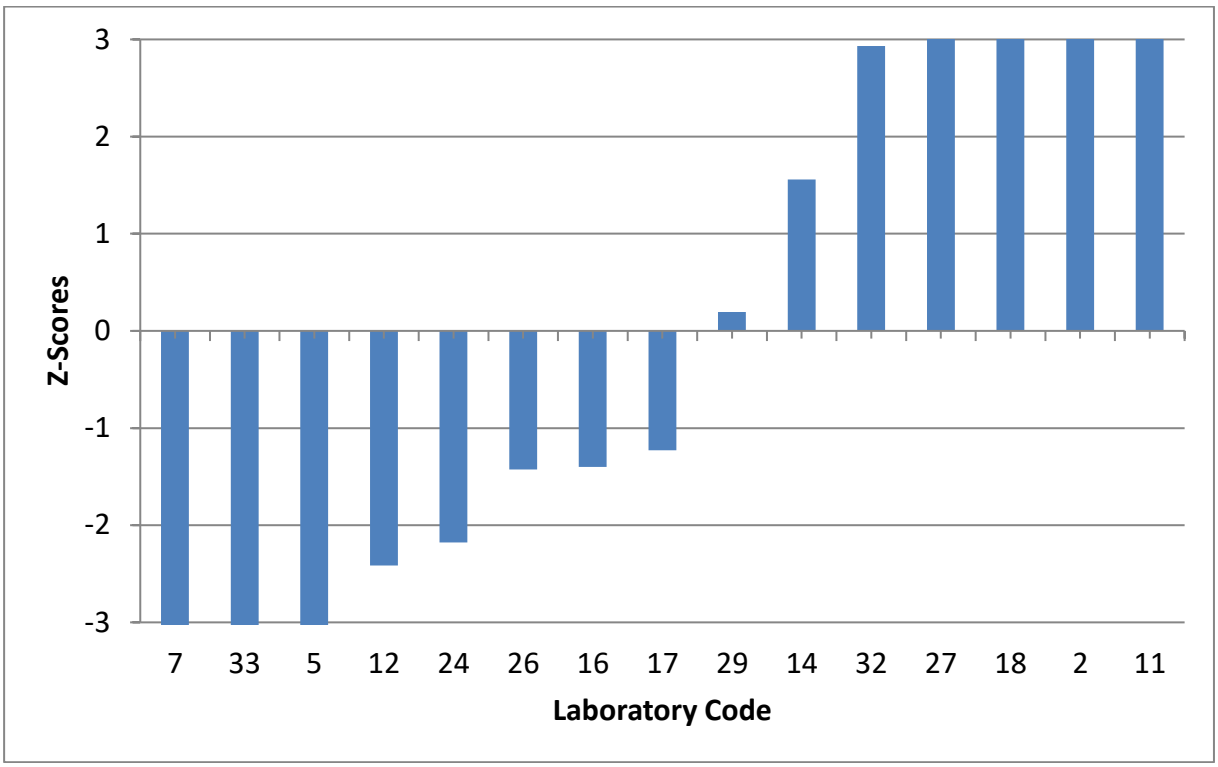

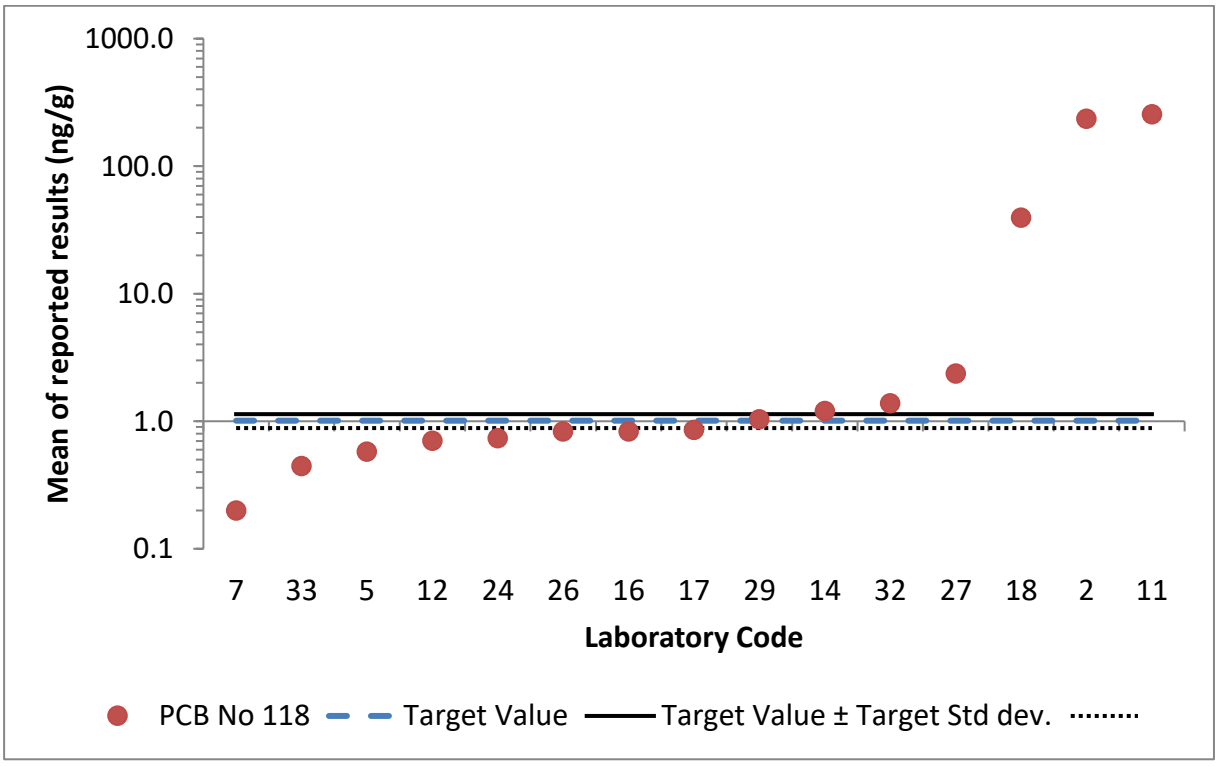

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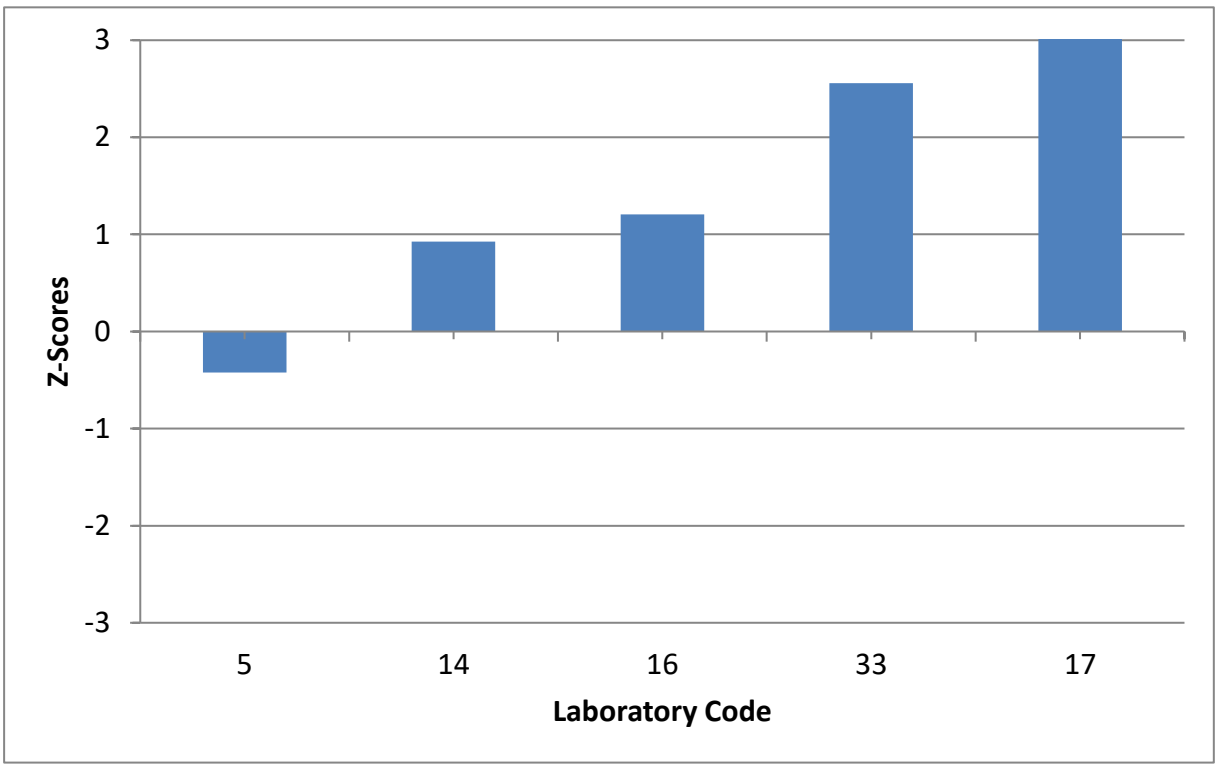

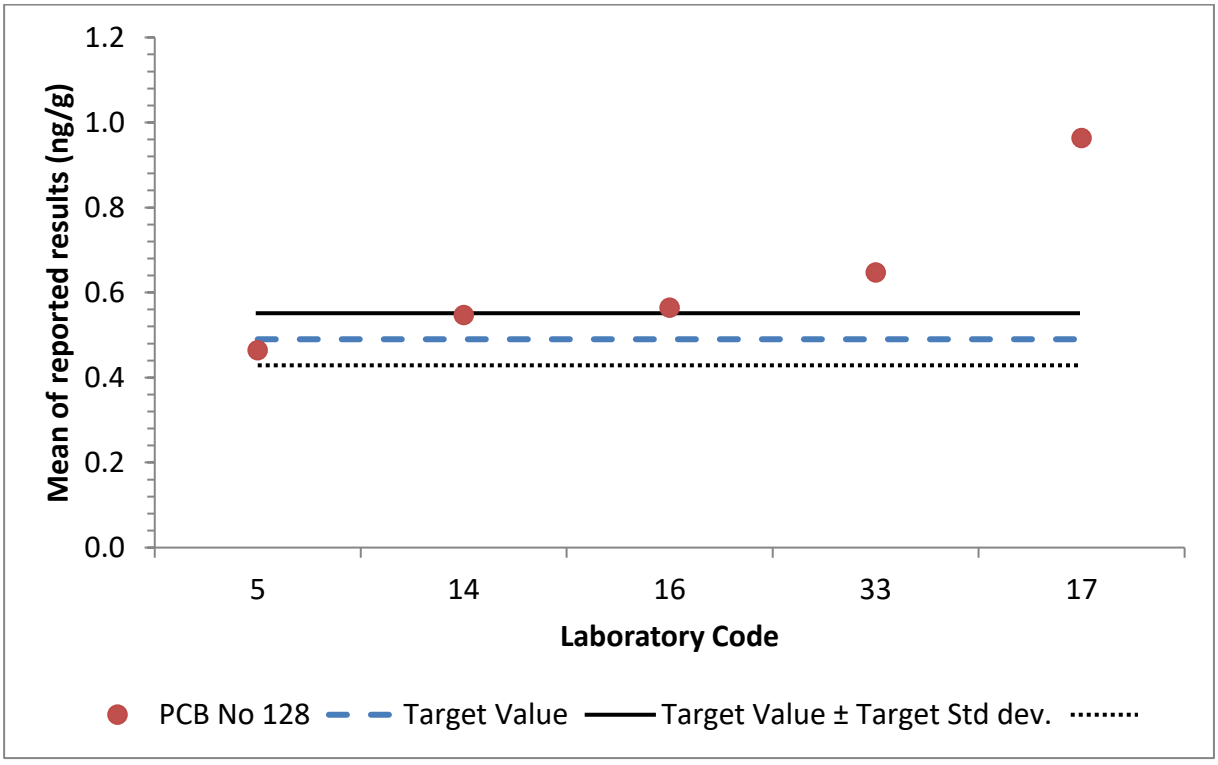

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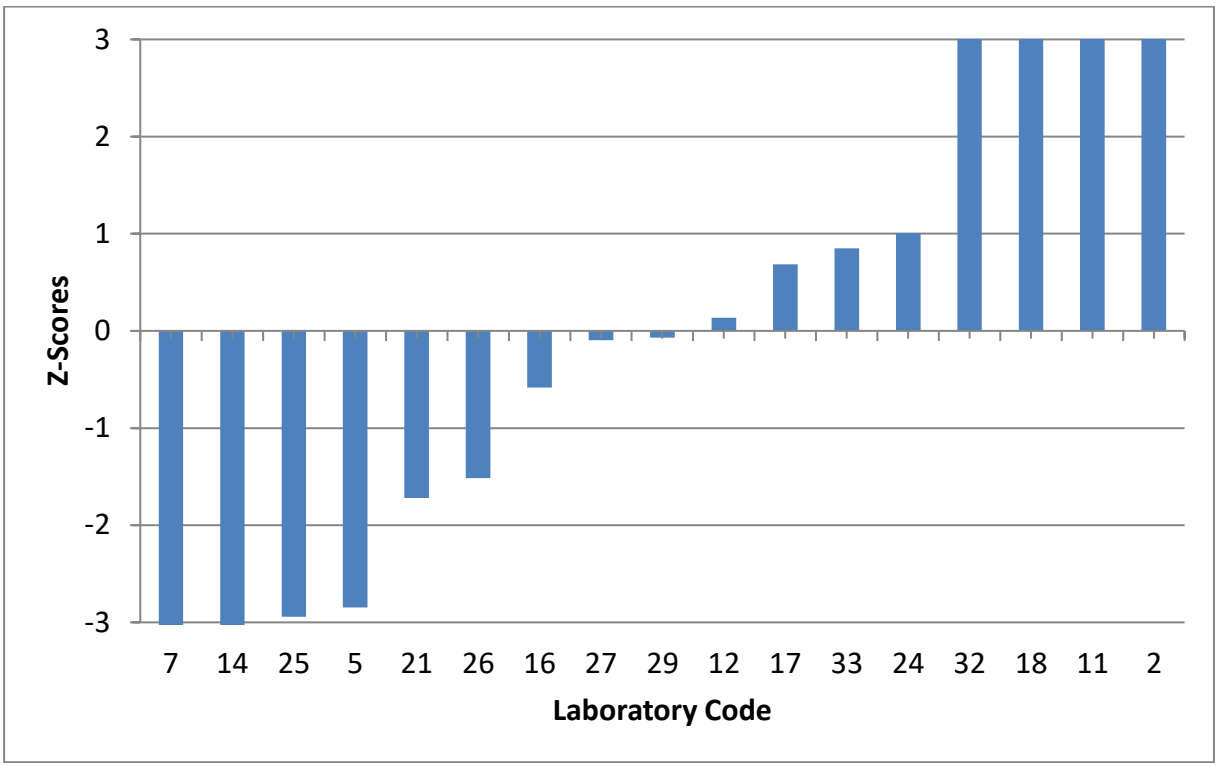

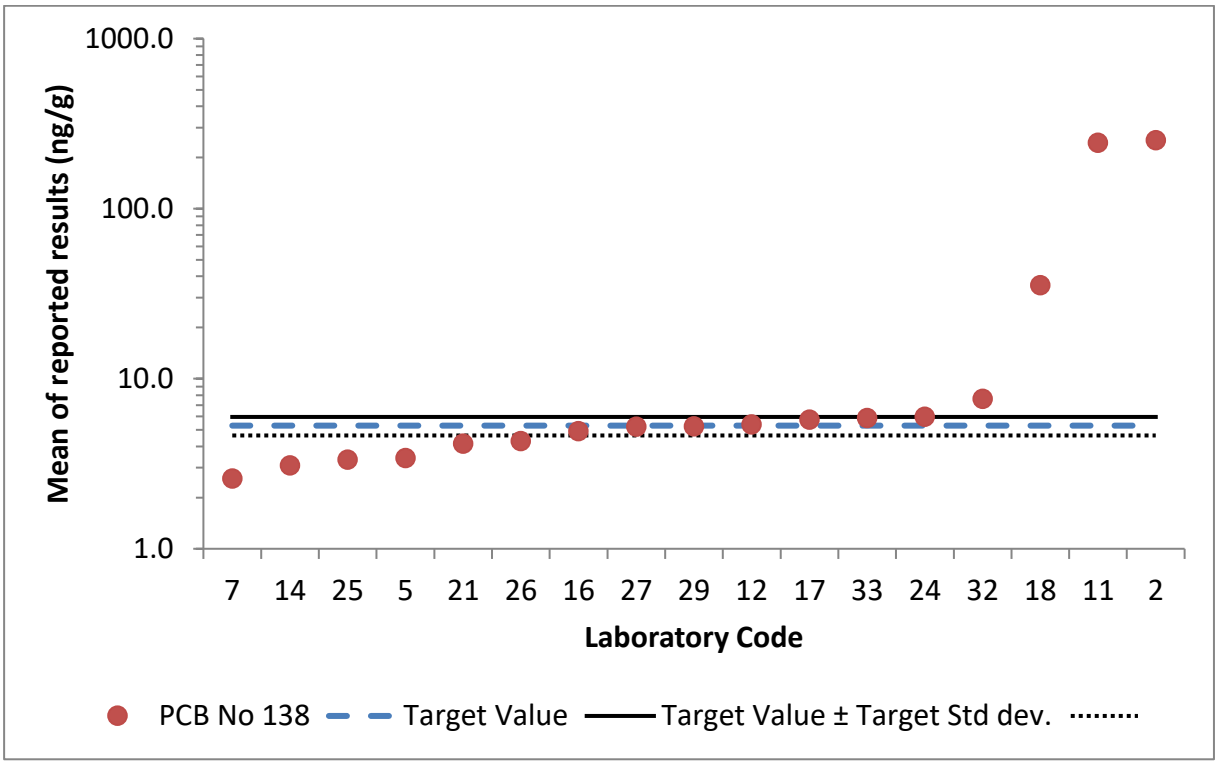

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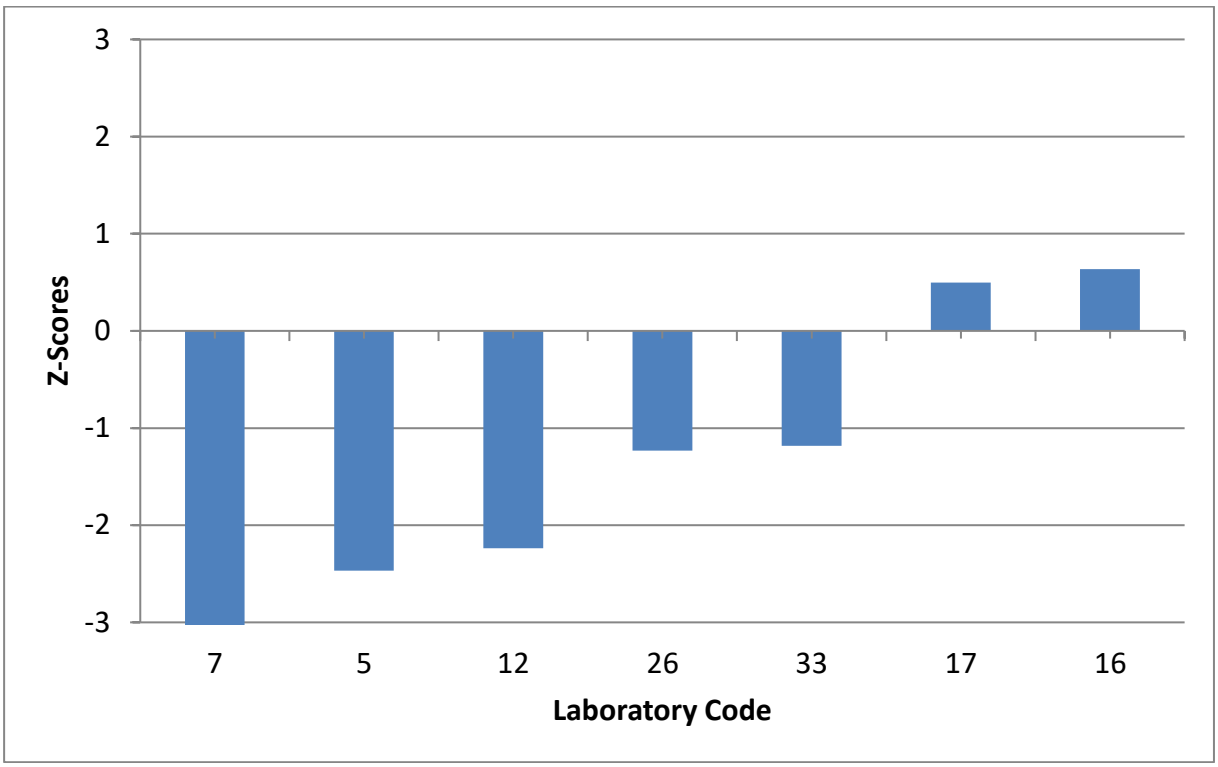

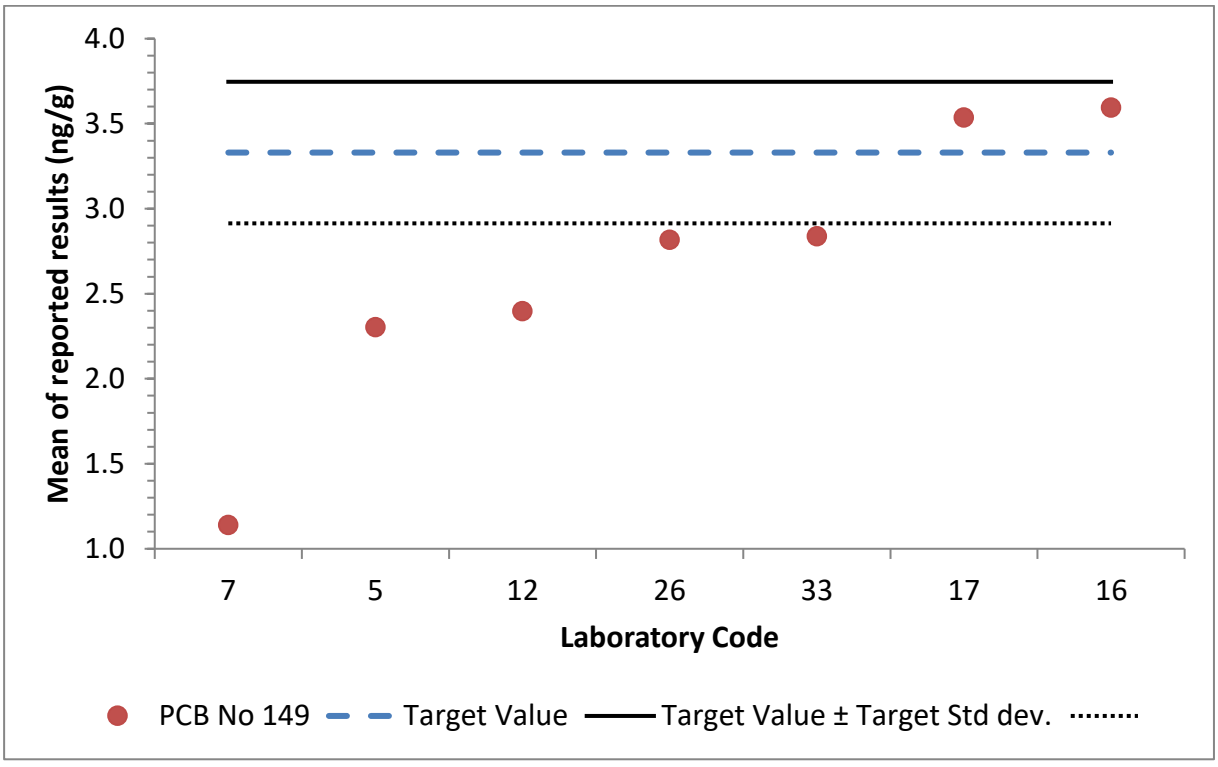

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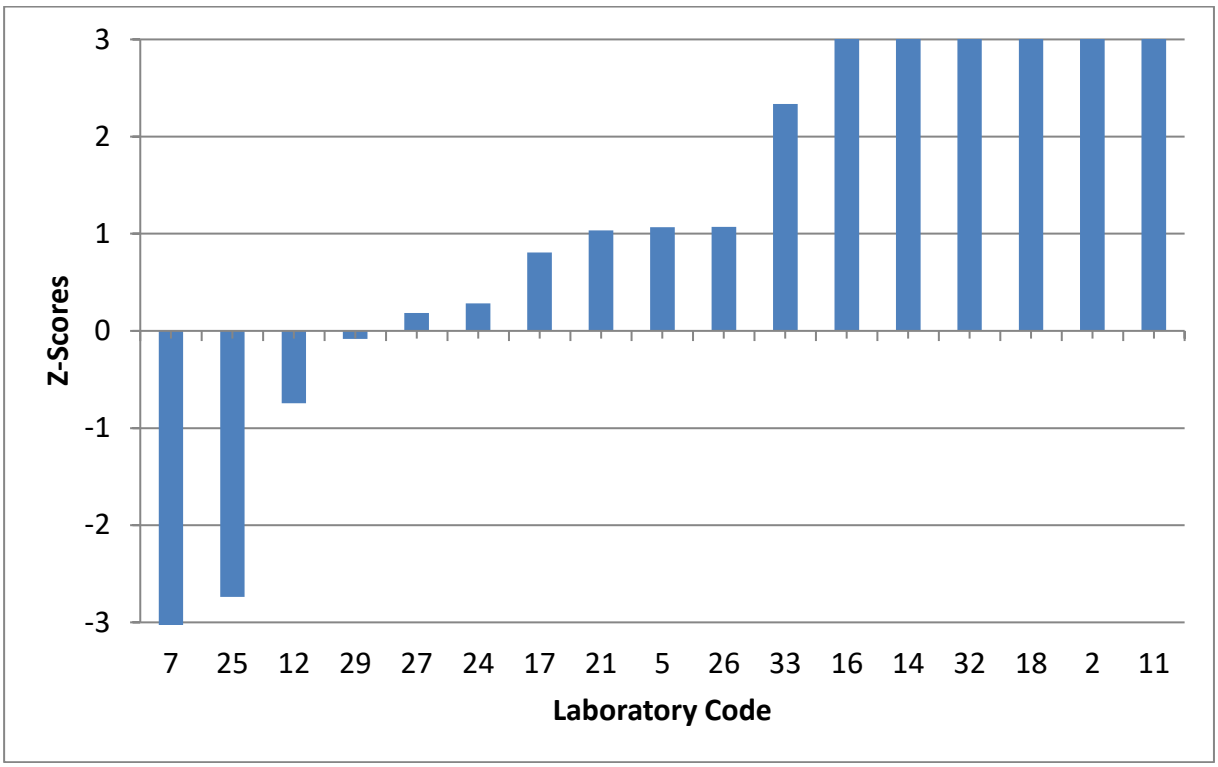

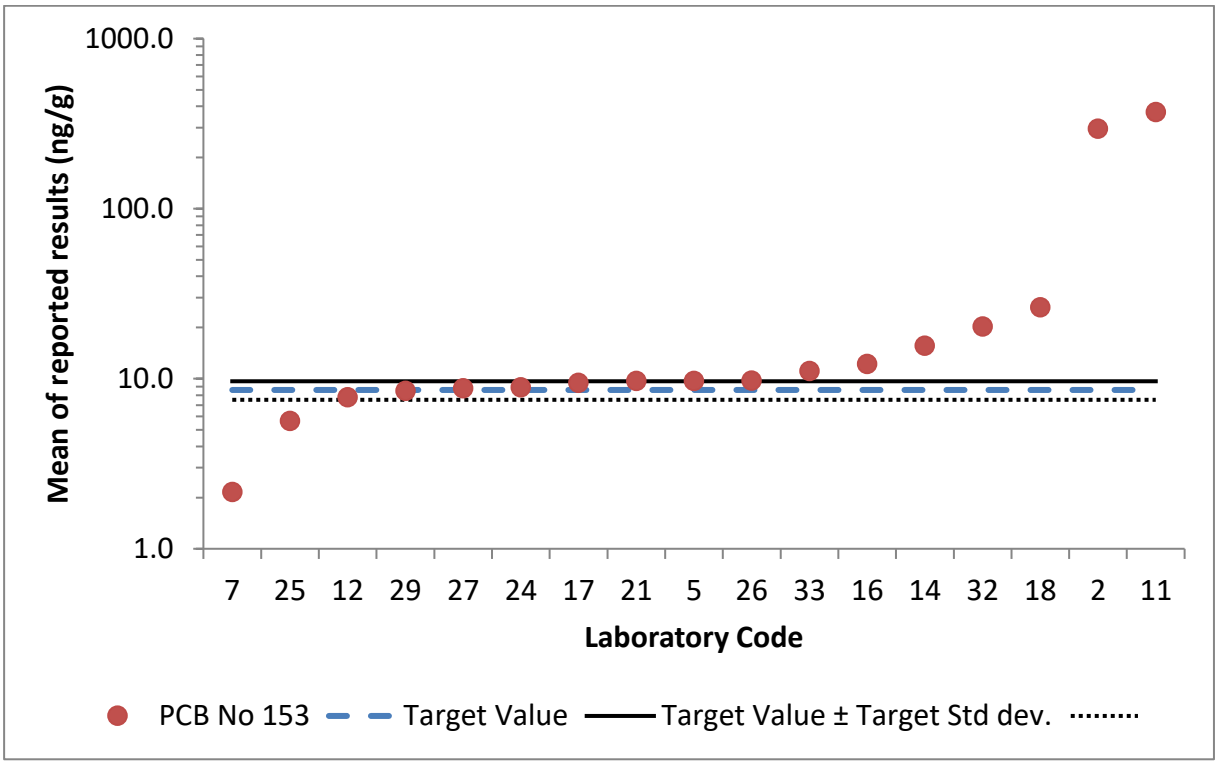

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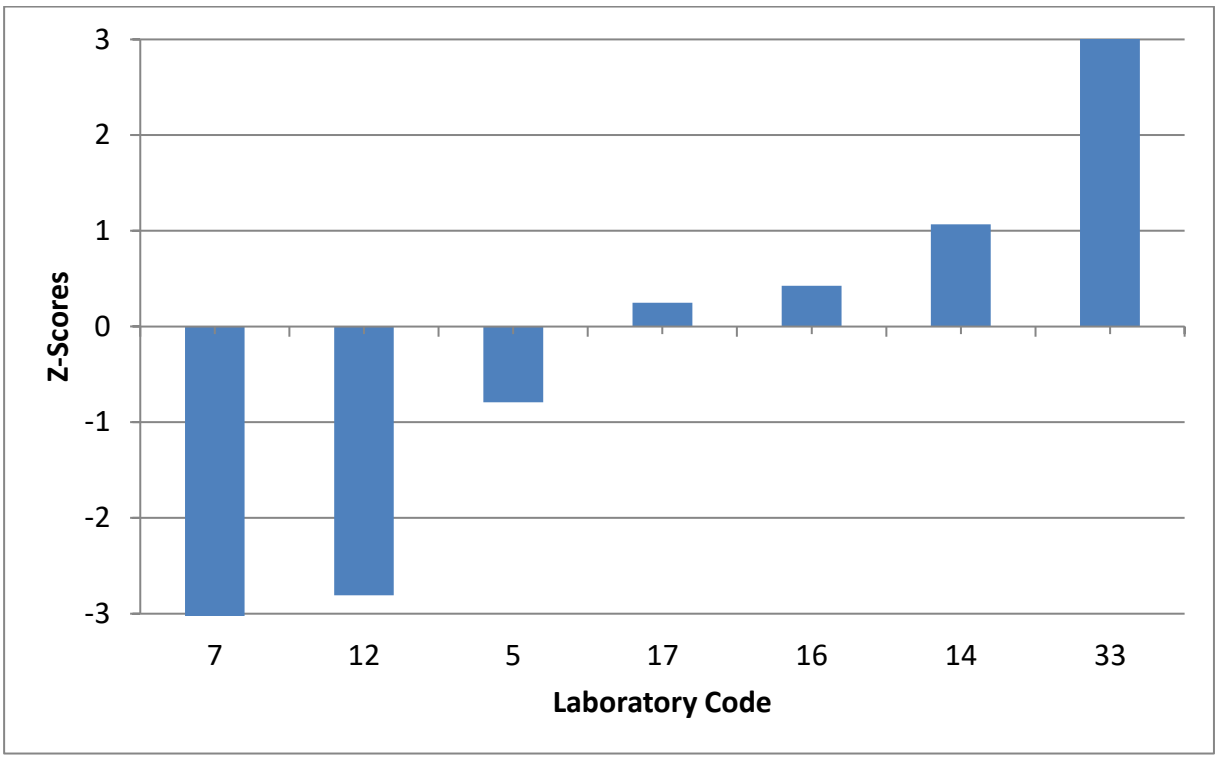

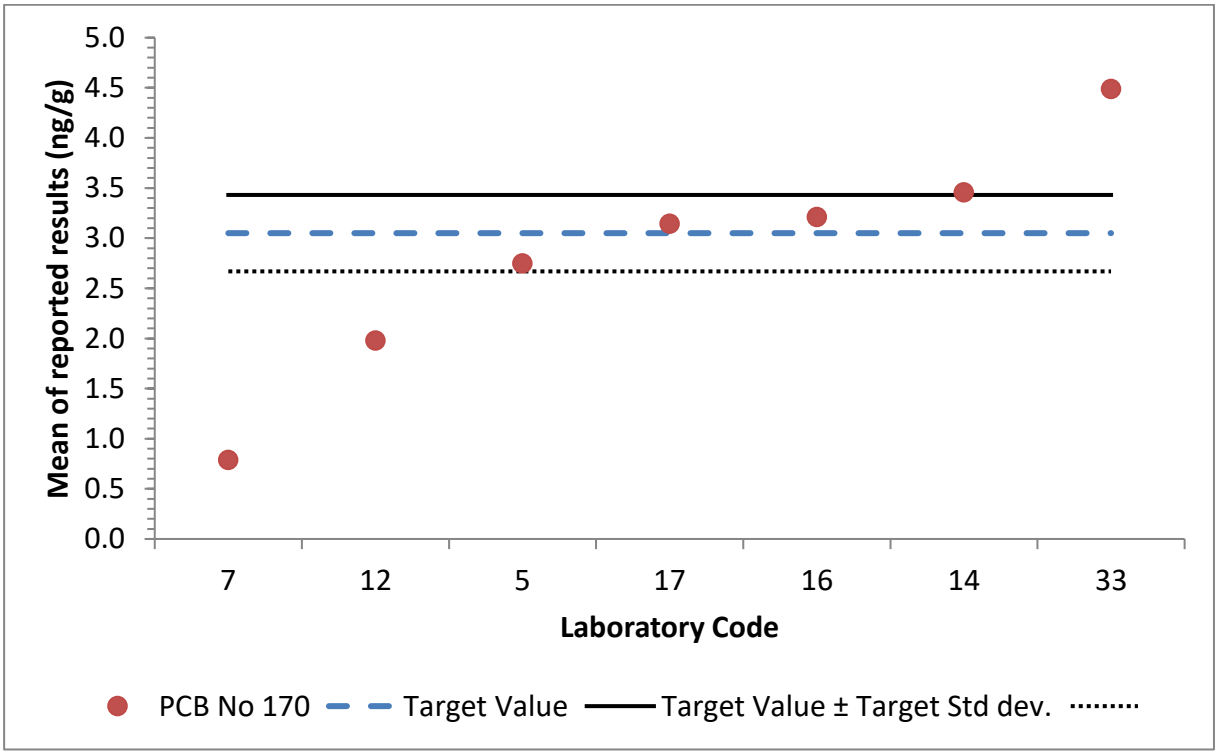

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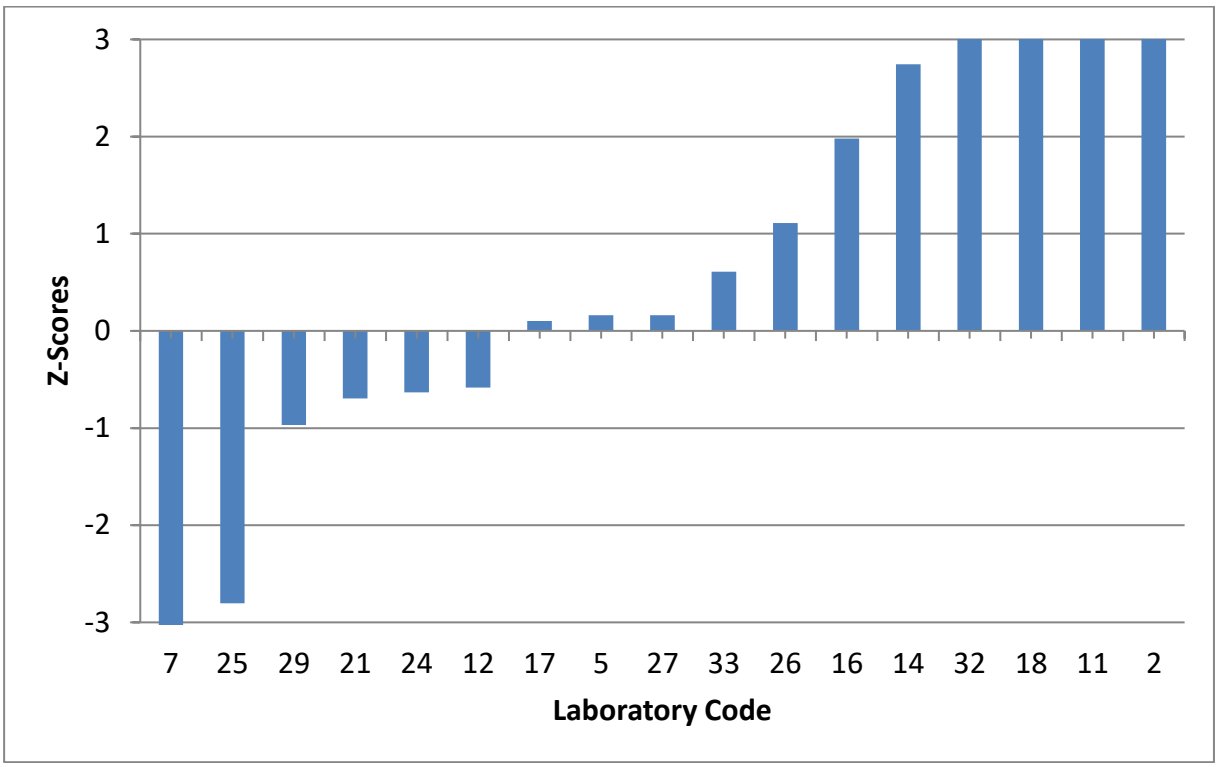

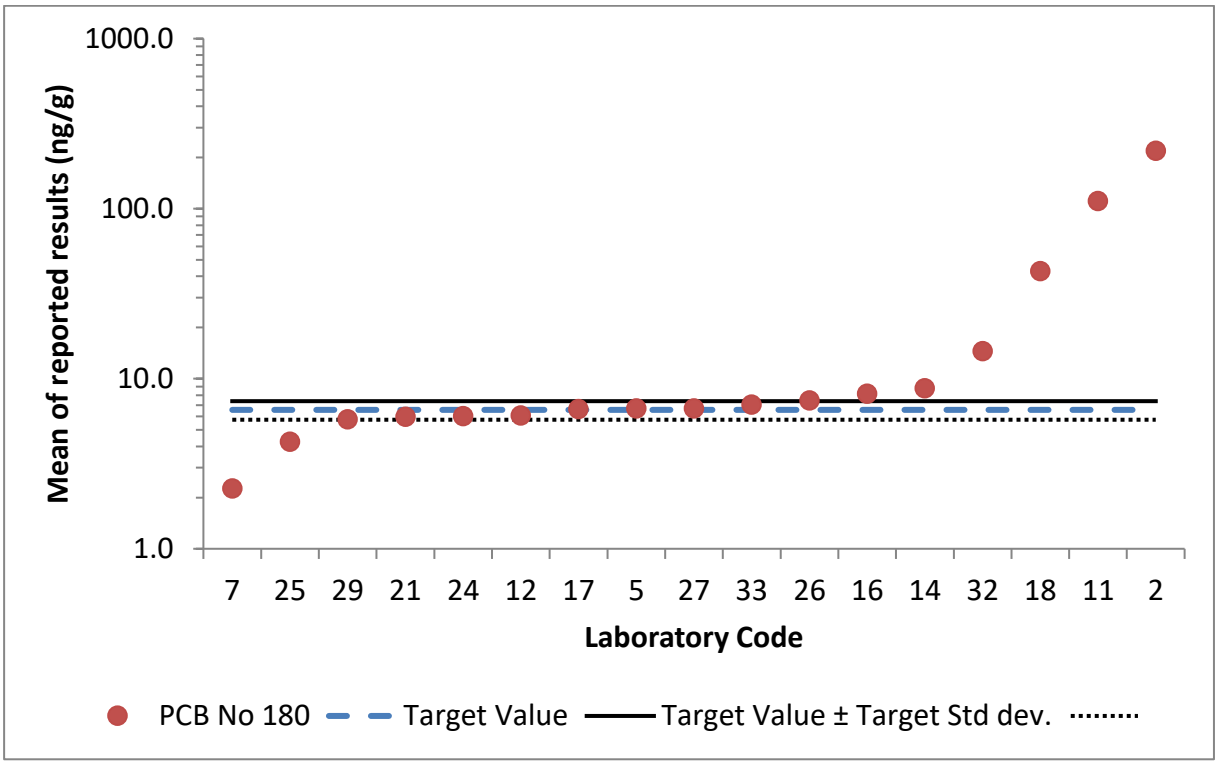

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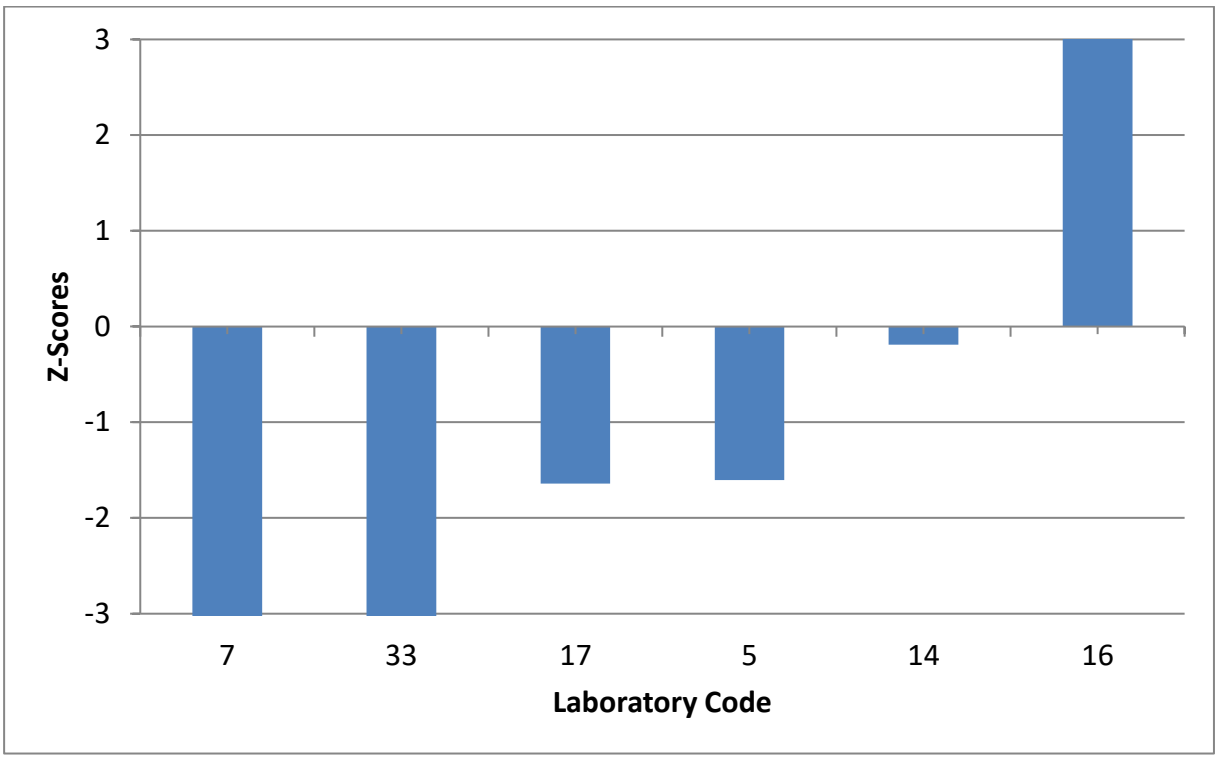

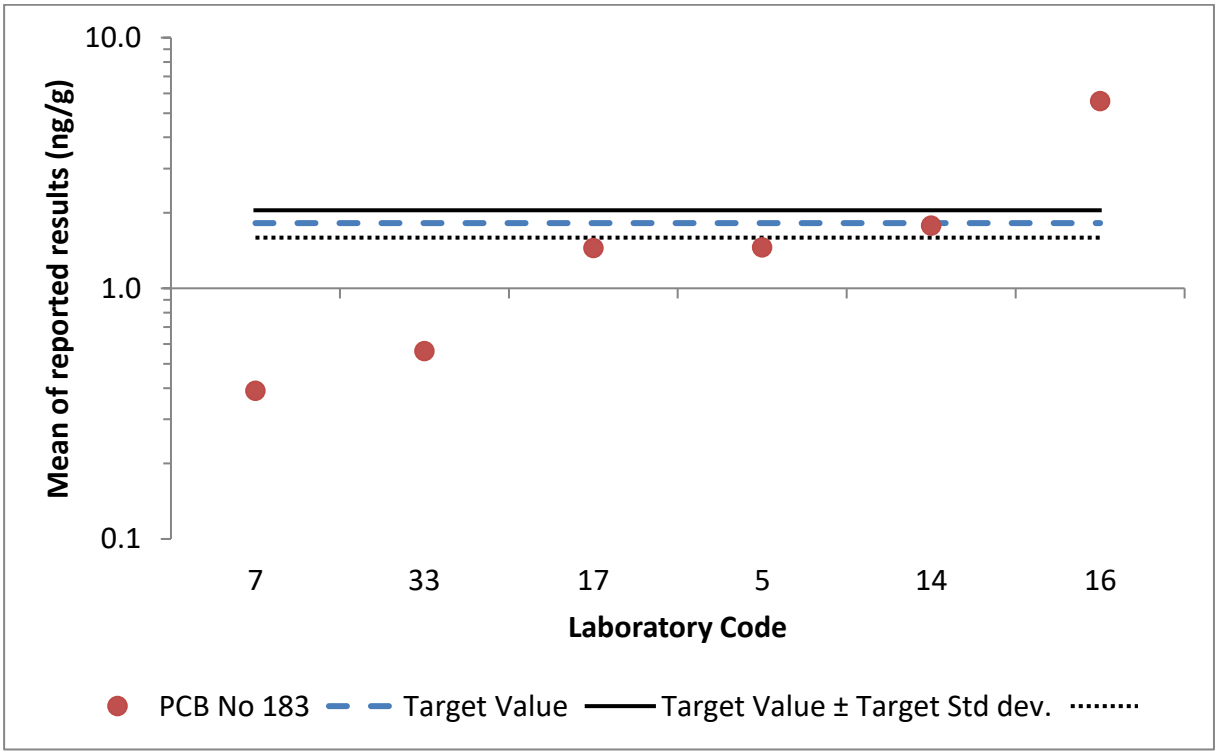

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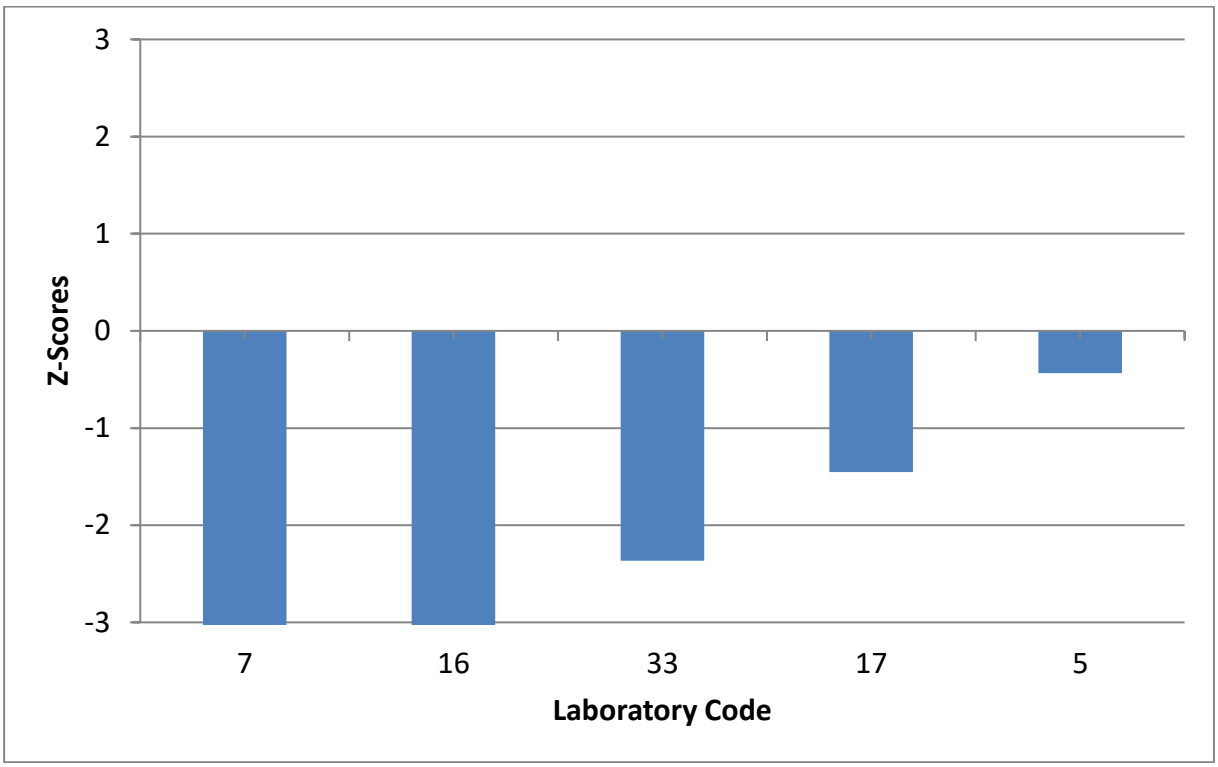

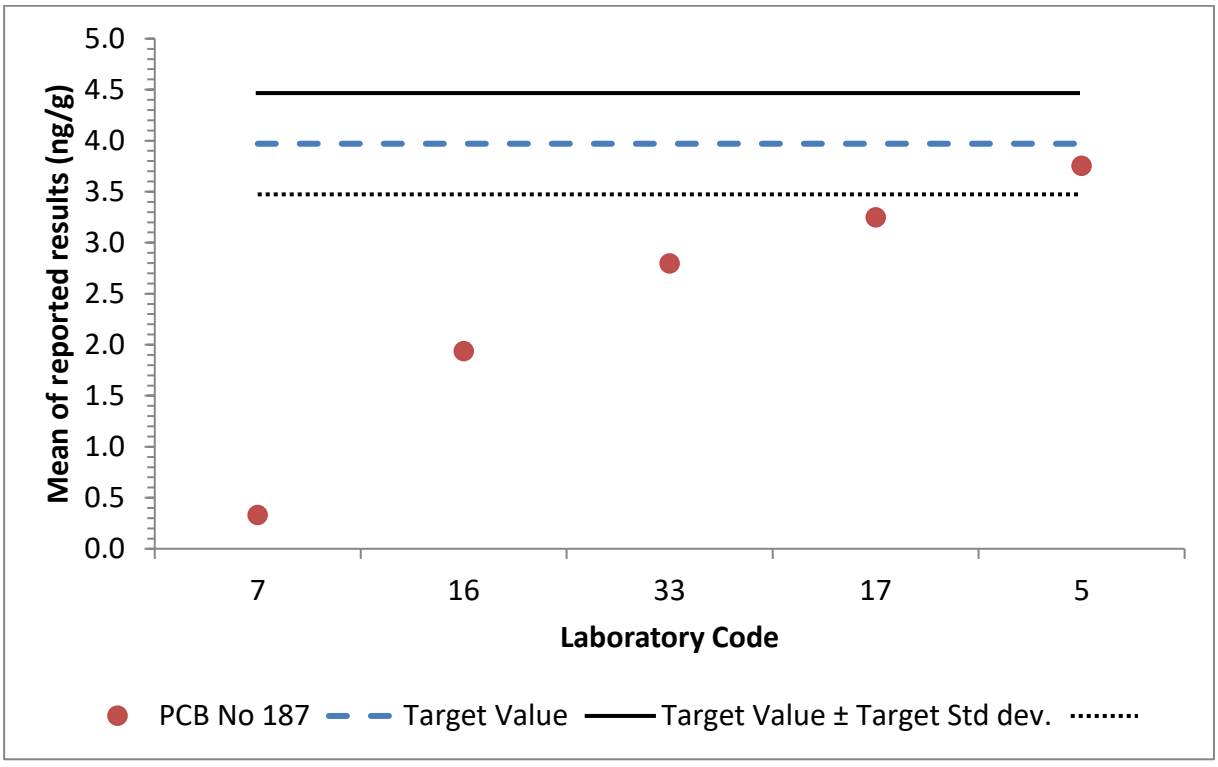

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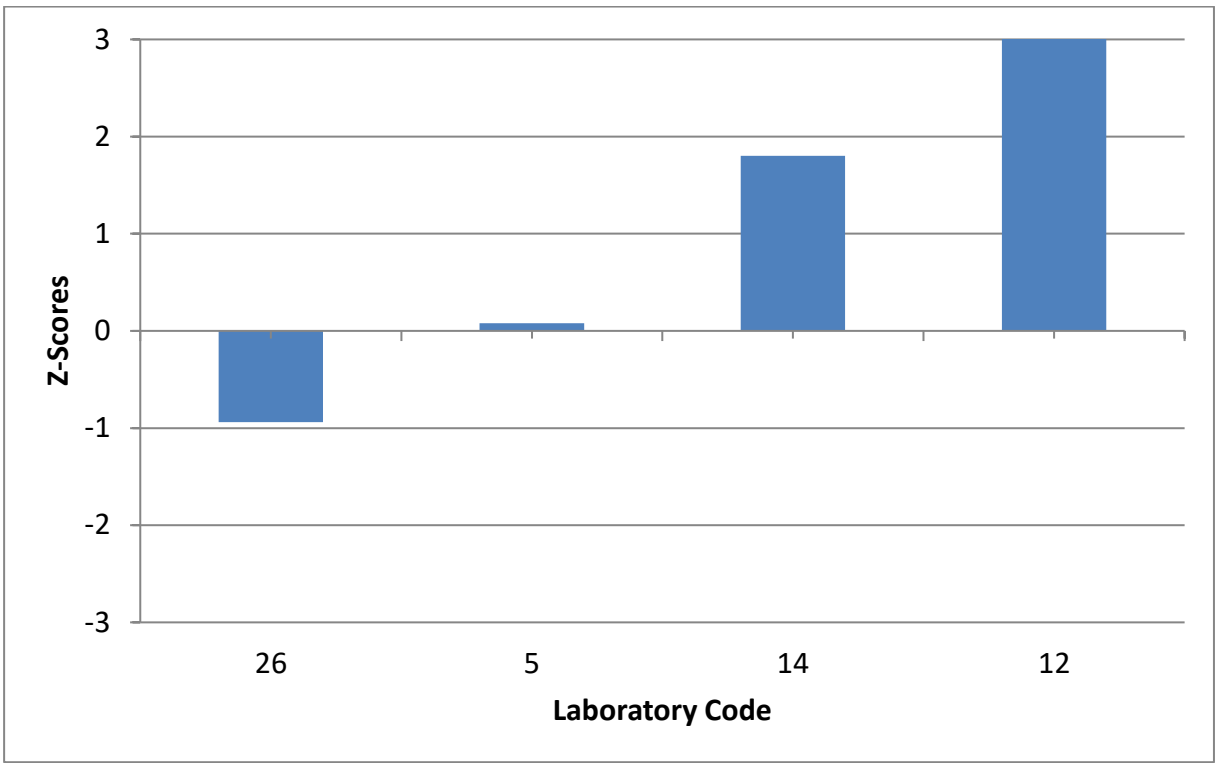

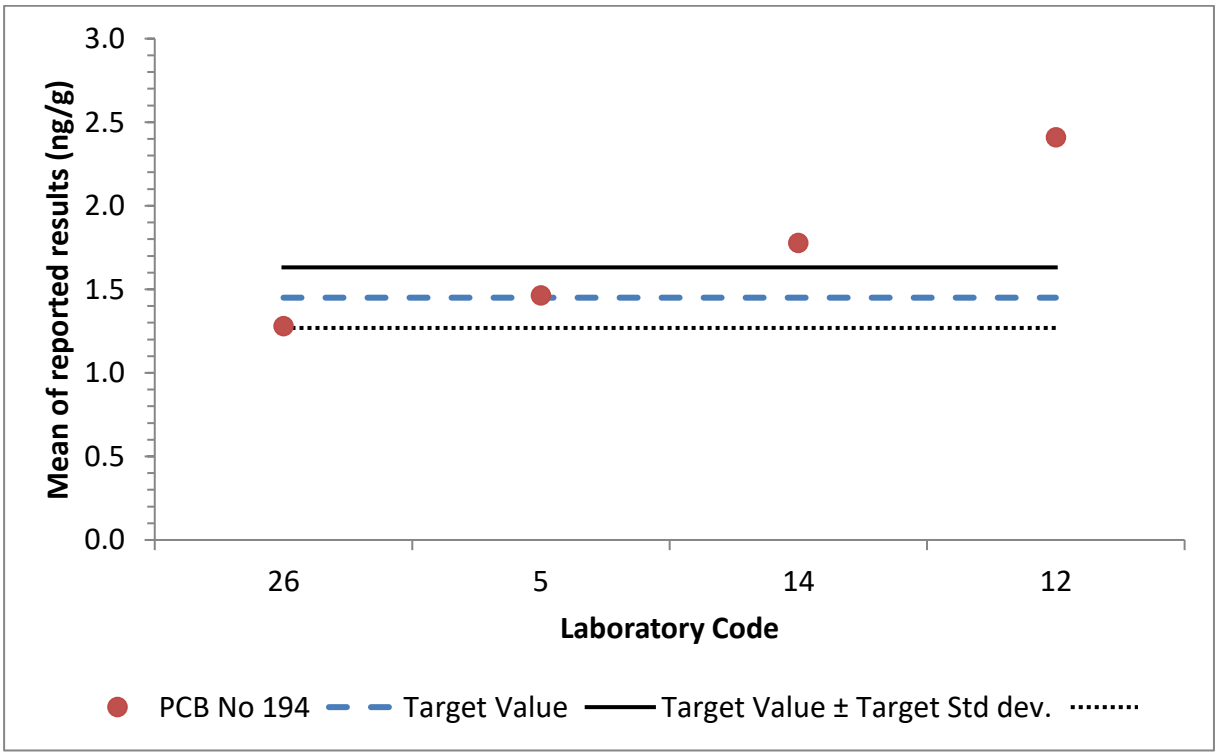

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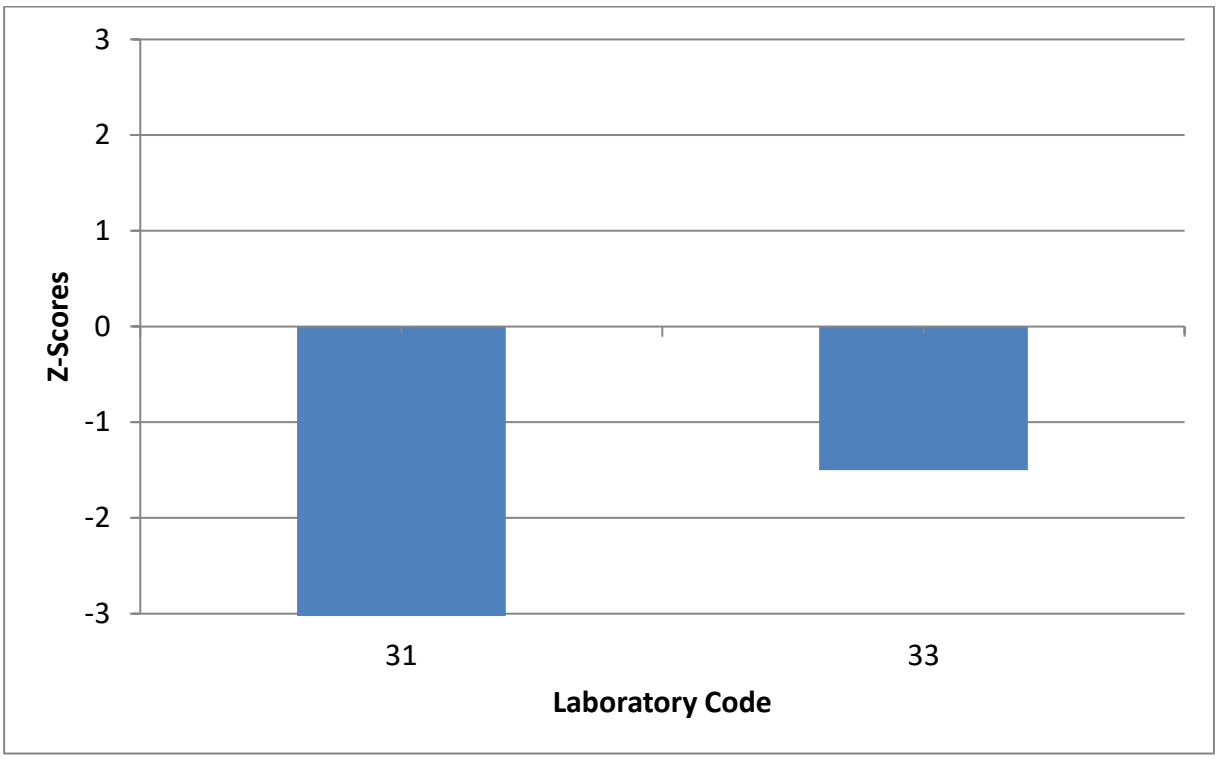

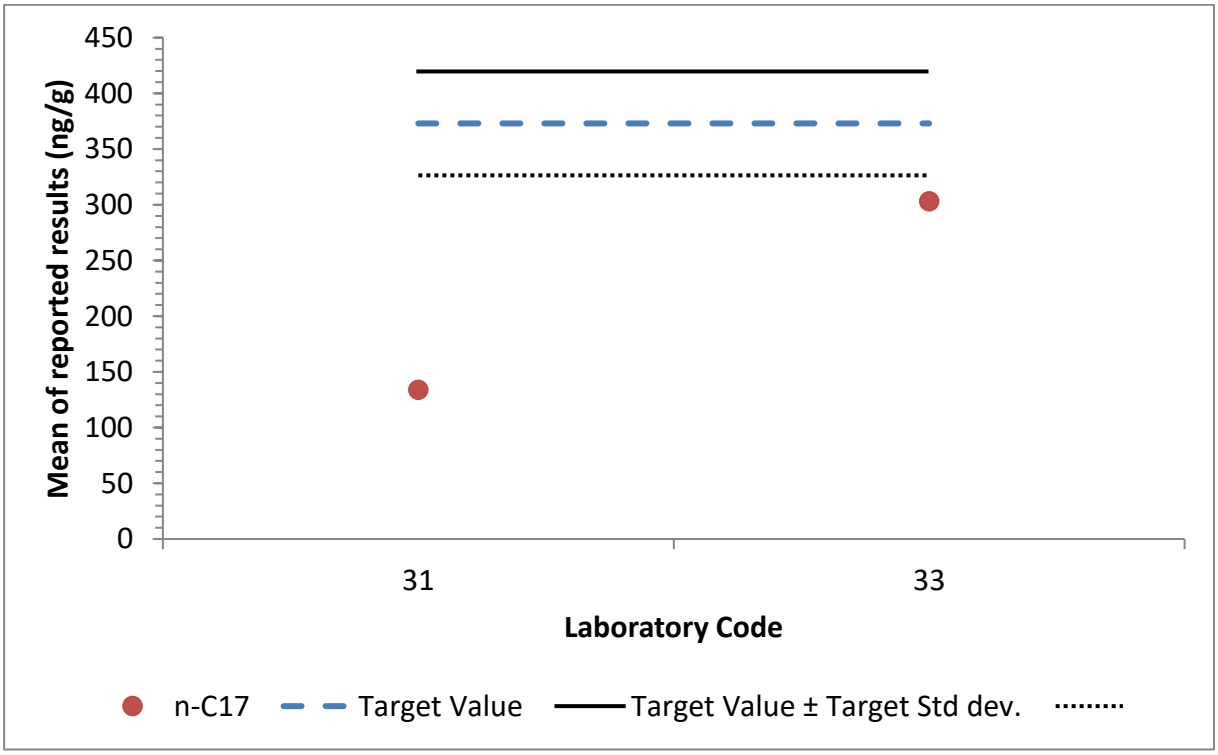

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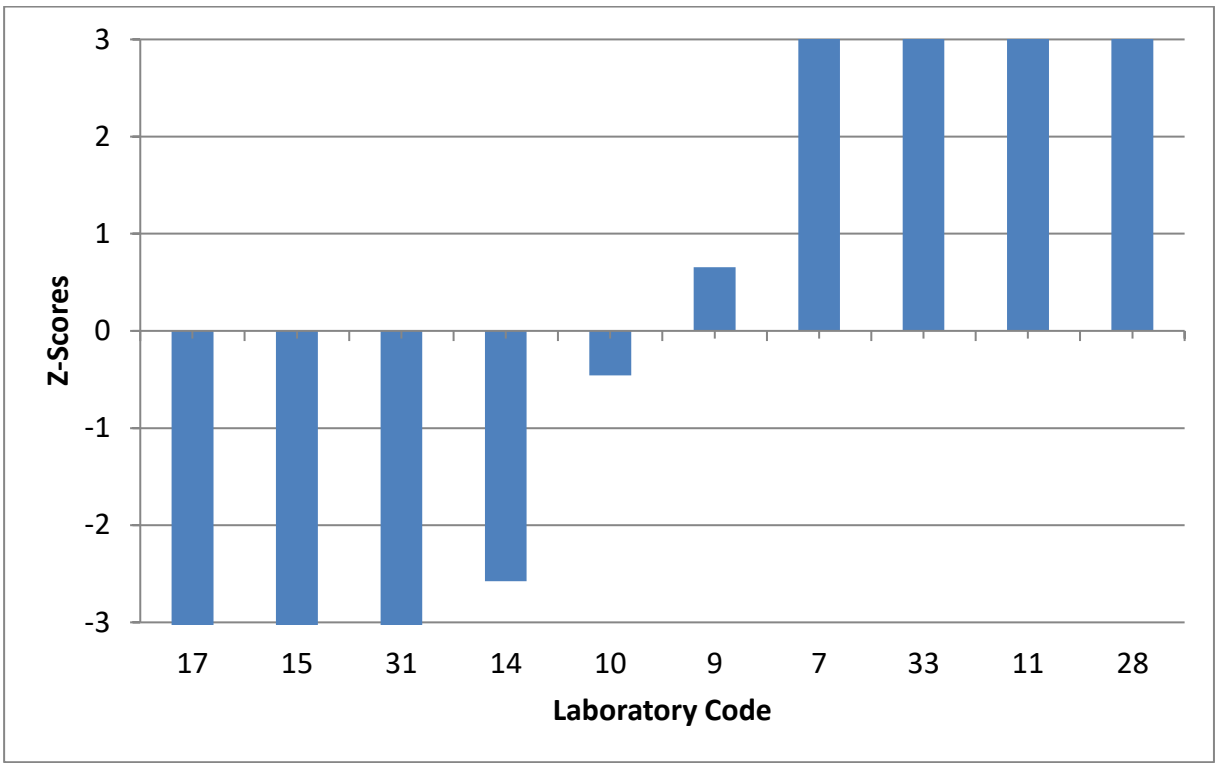

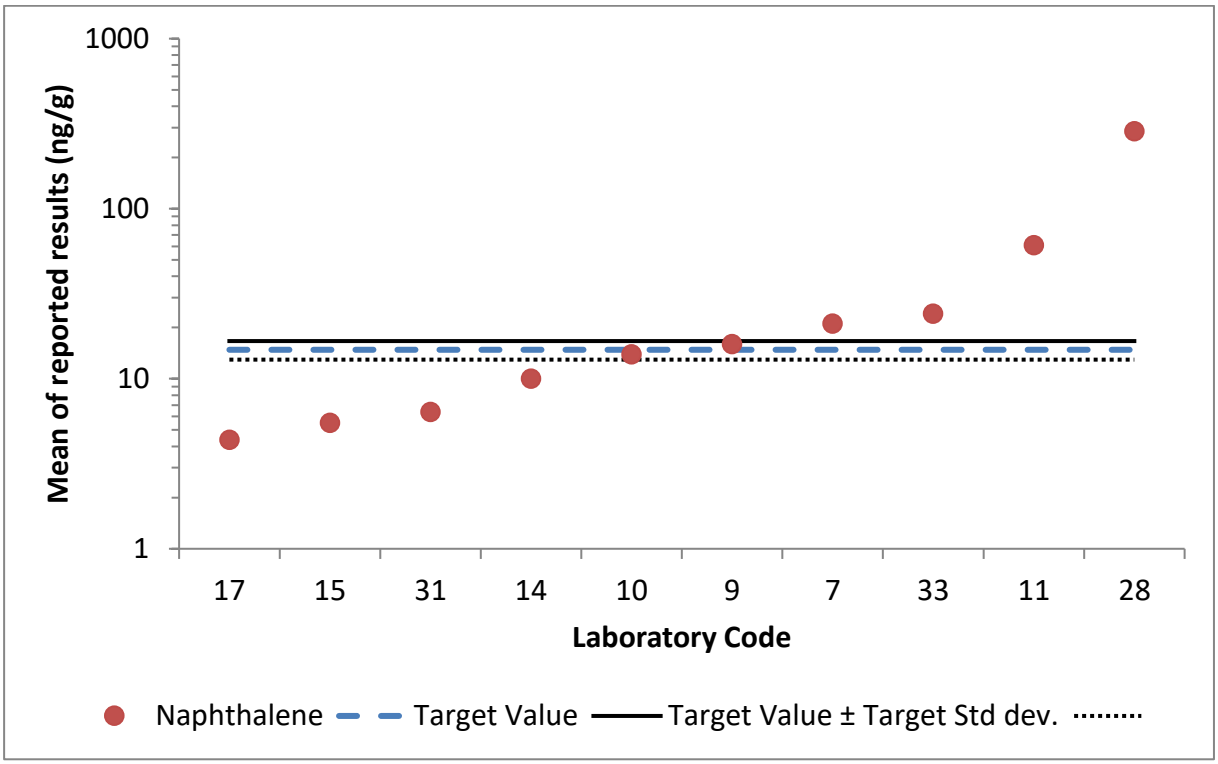

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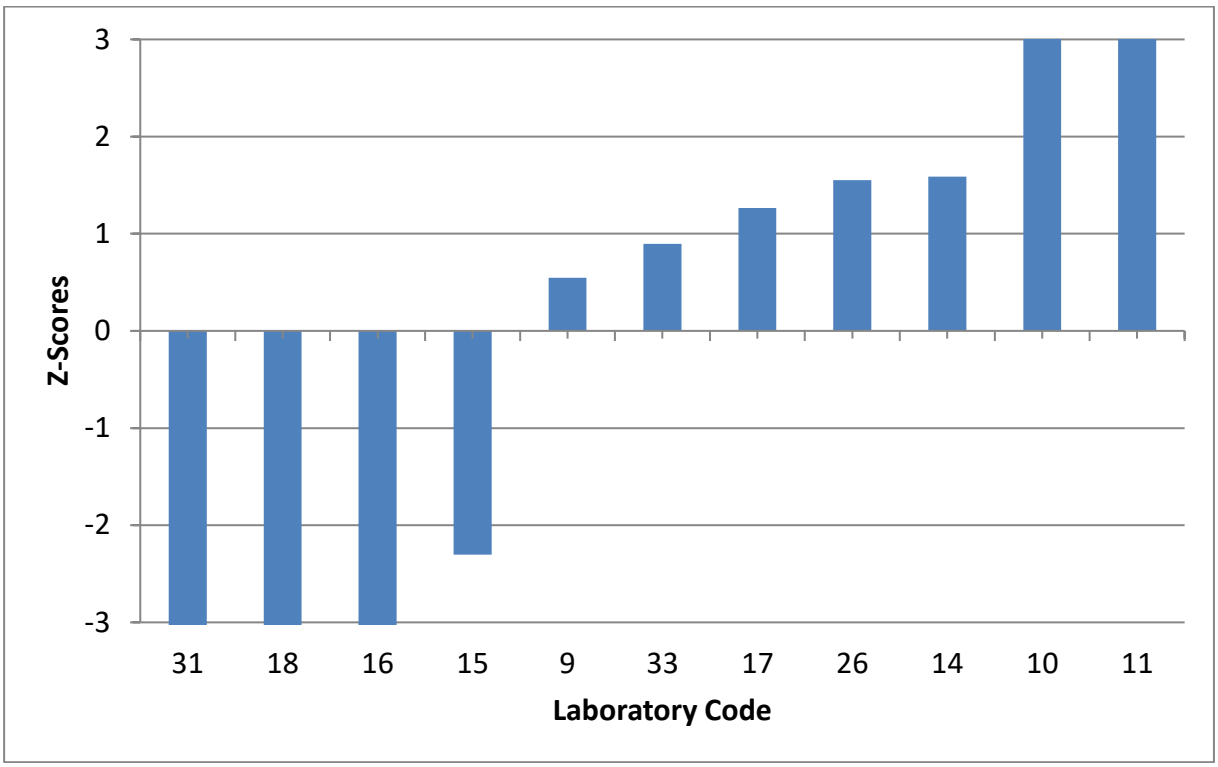

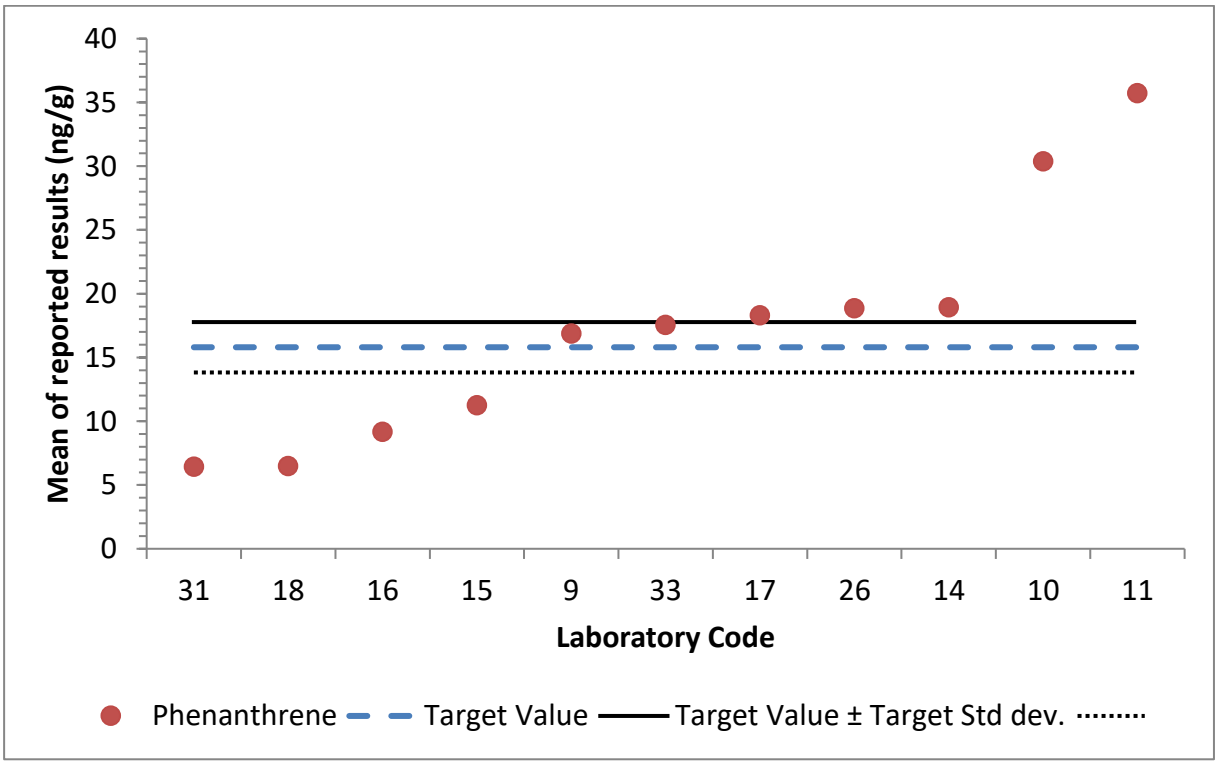

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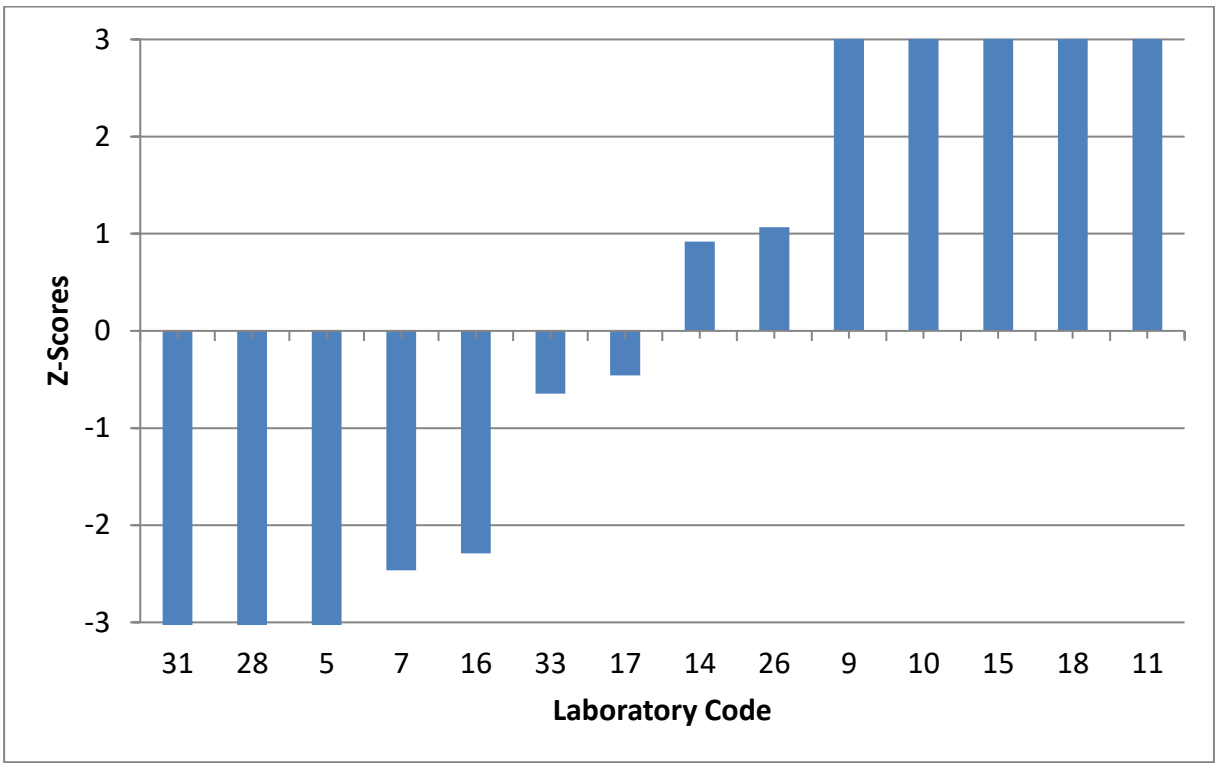

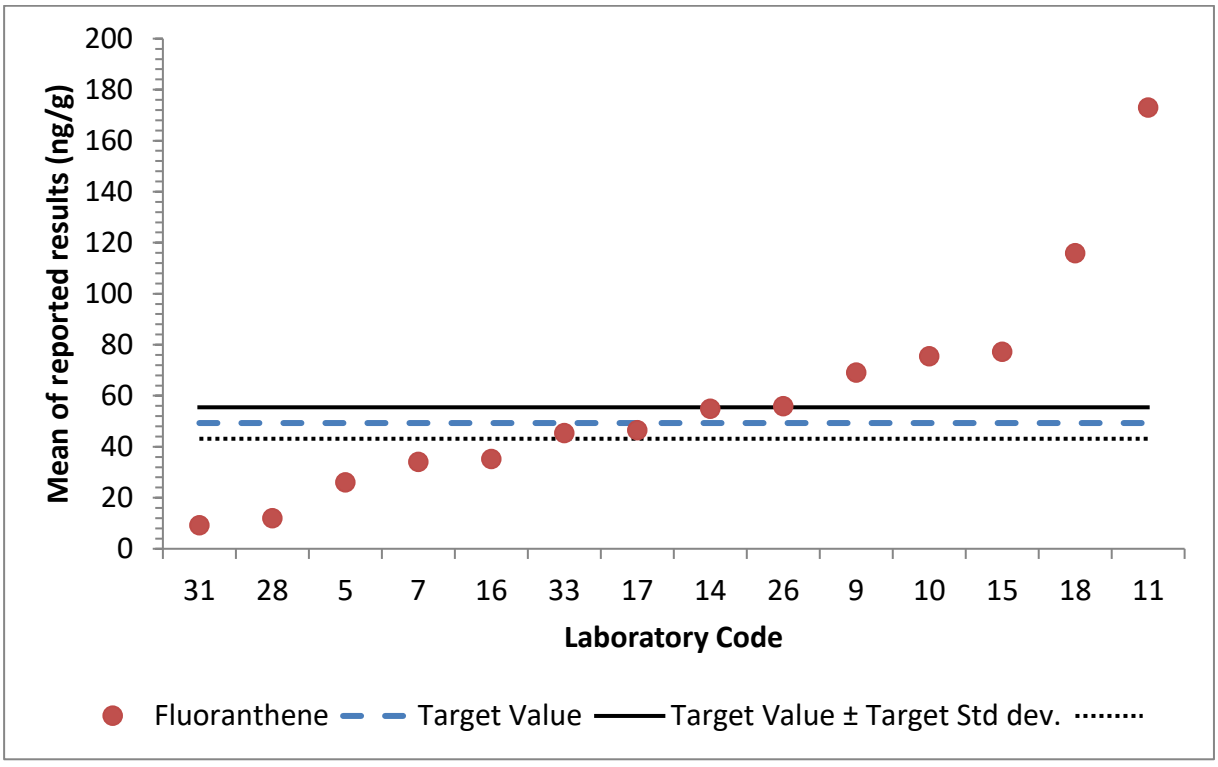

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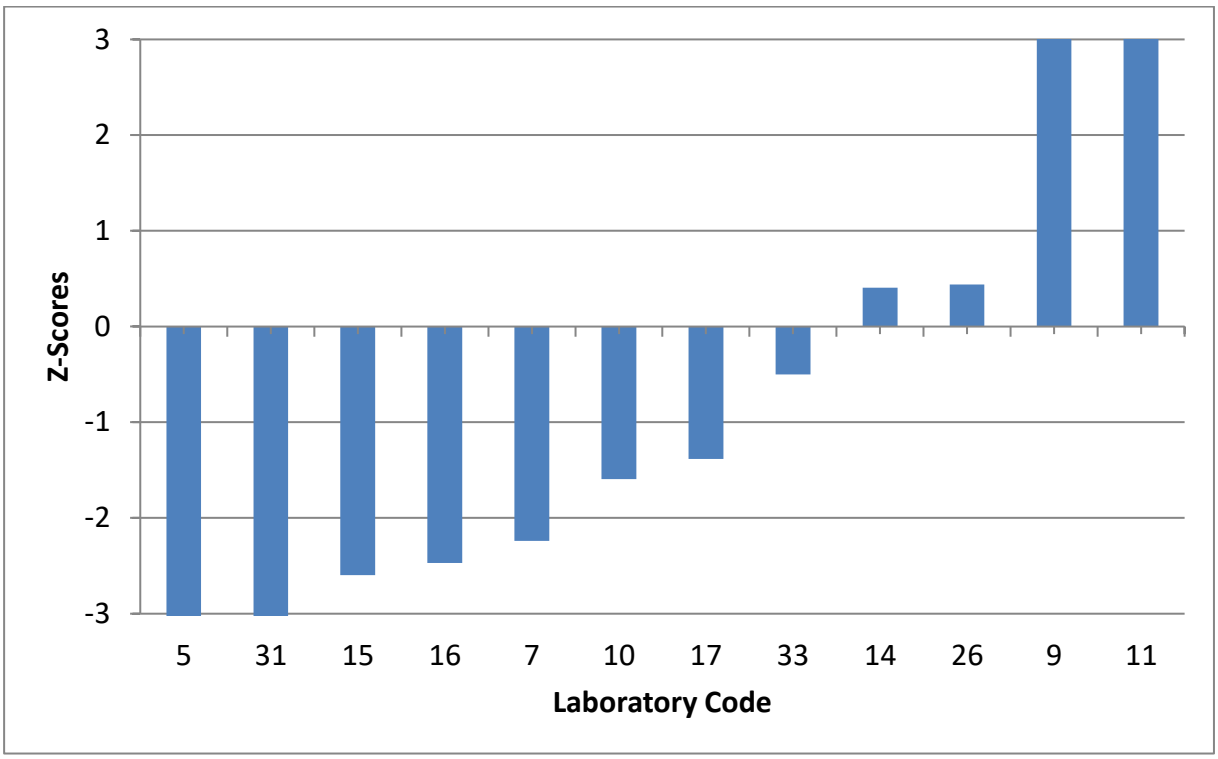

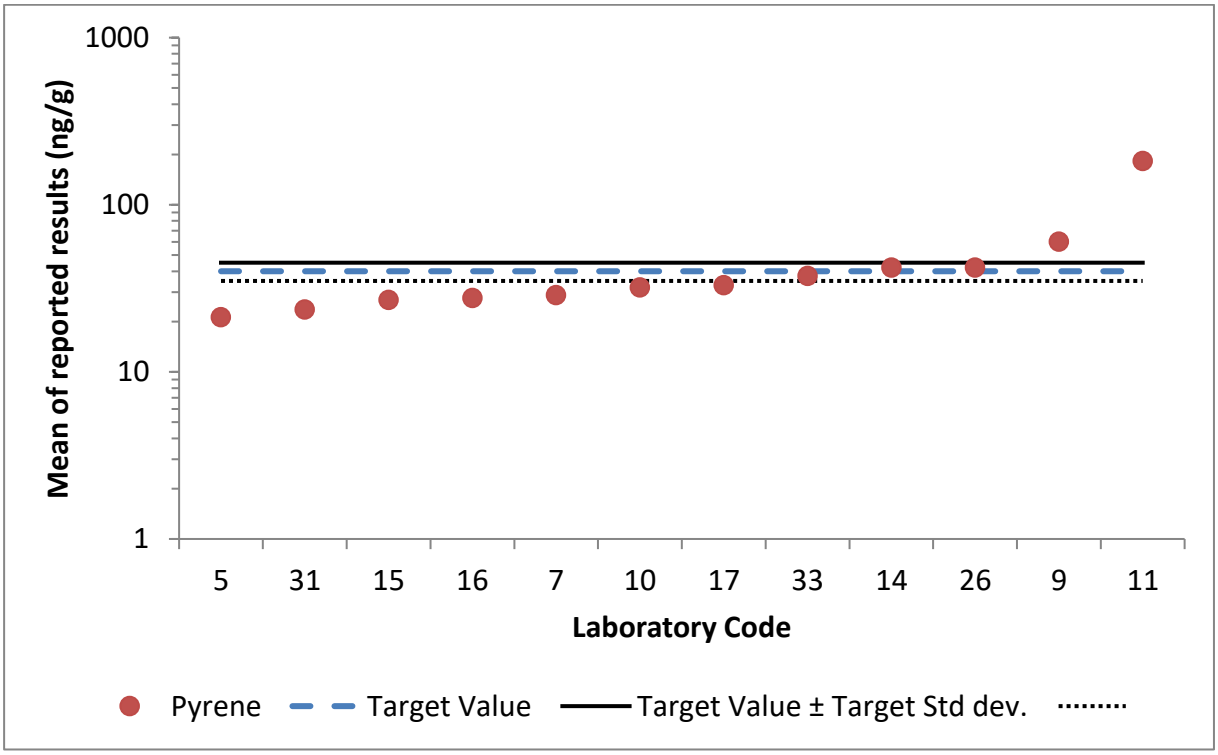

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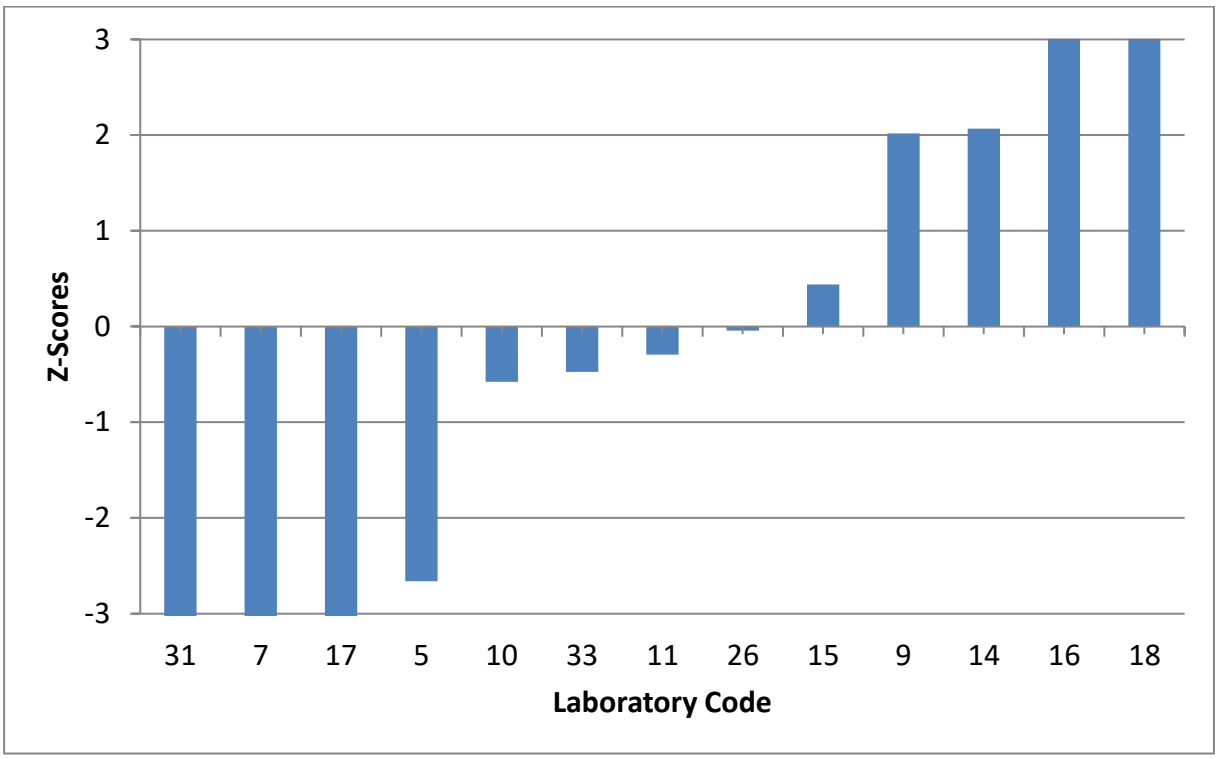
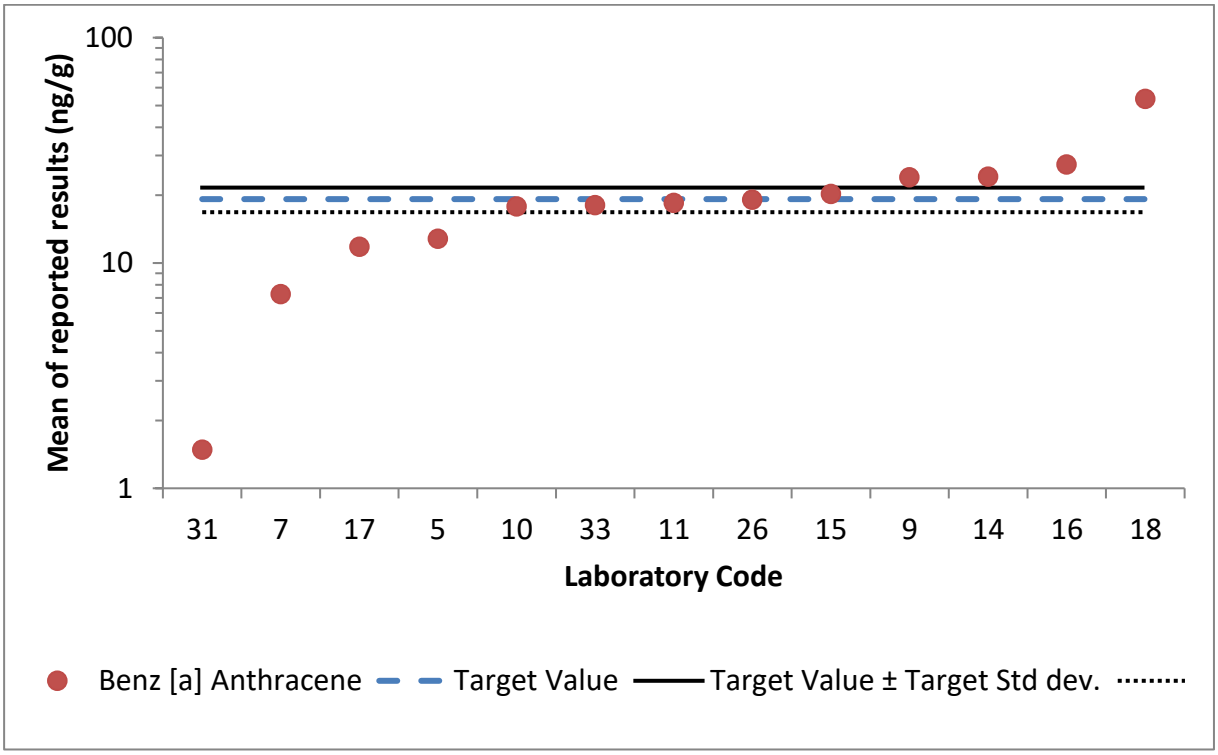
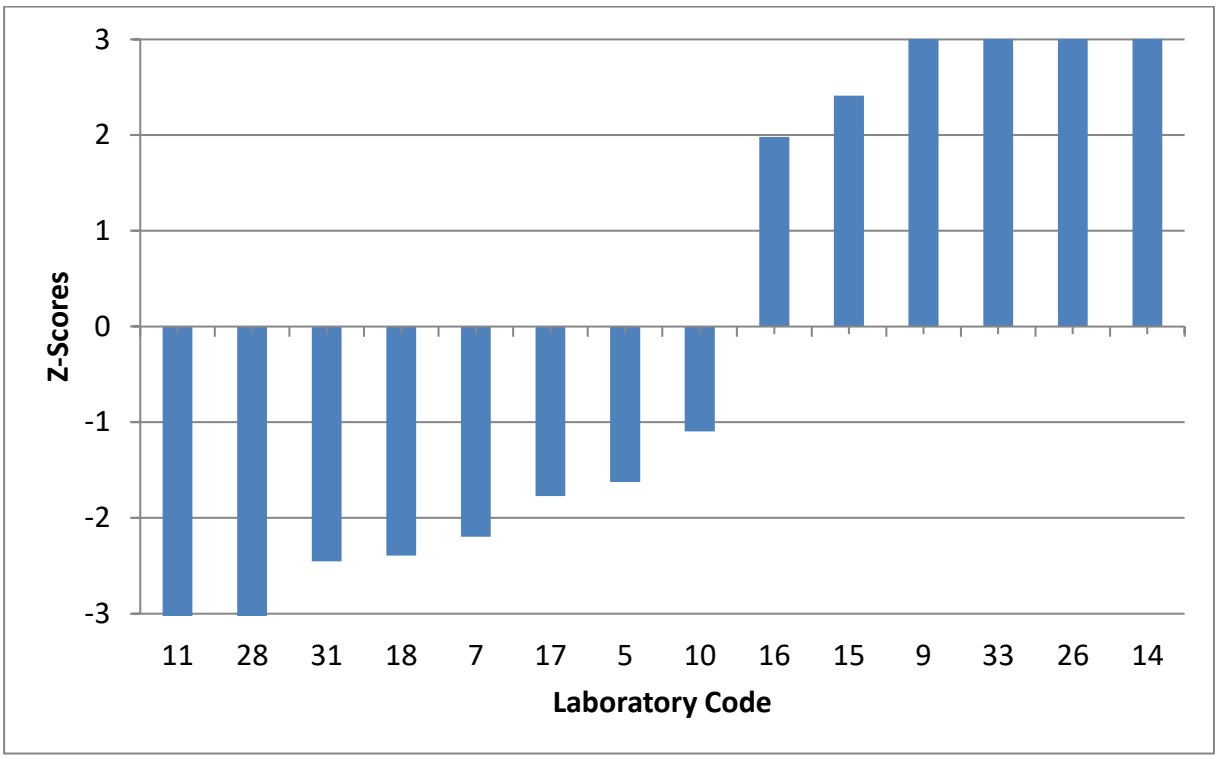
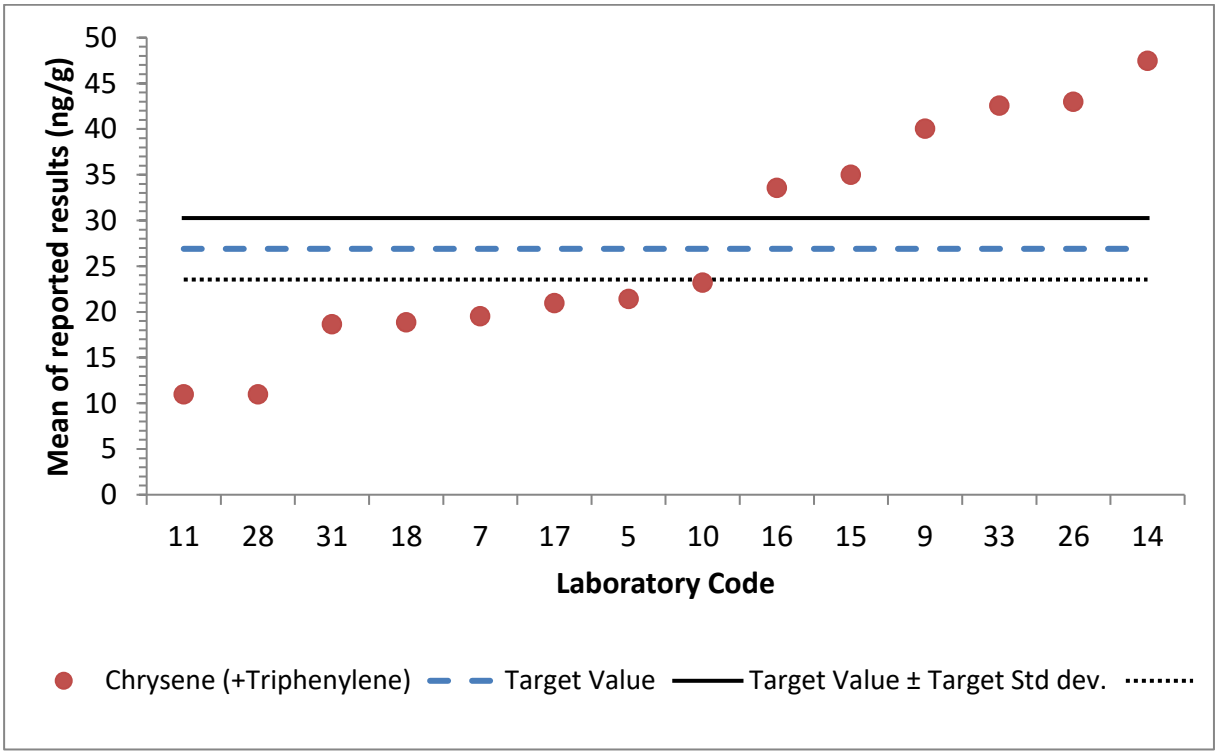


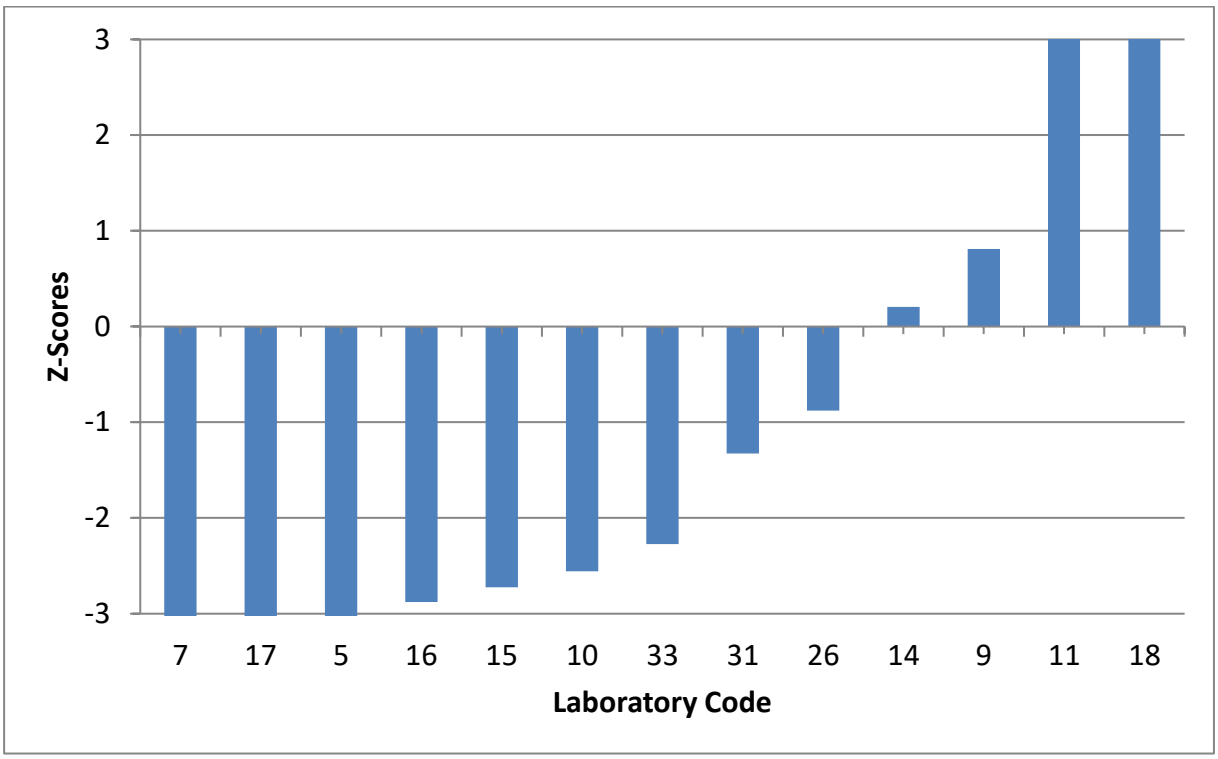


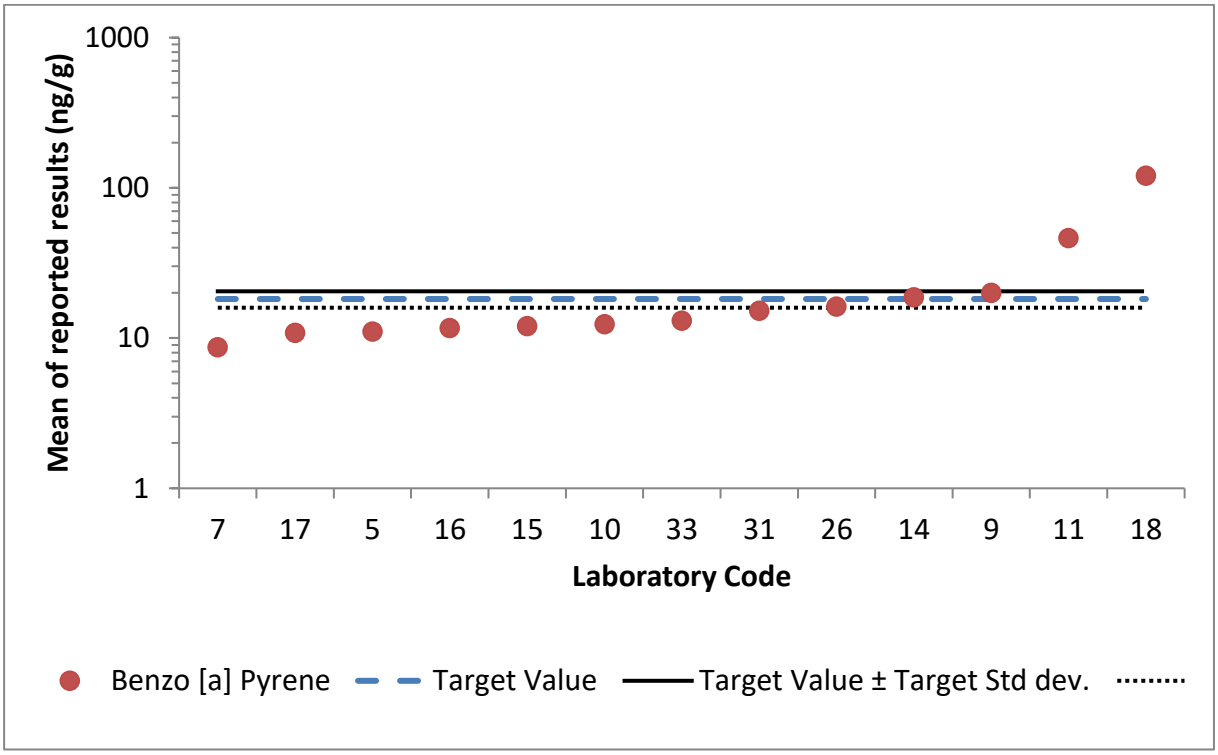
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR CHRYSENE (+ TRIPHENYLENE)



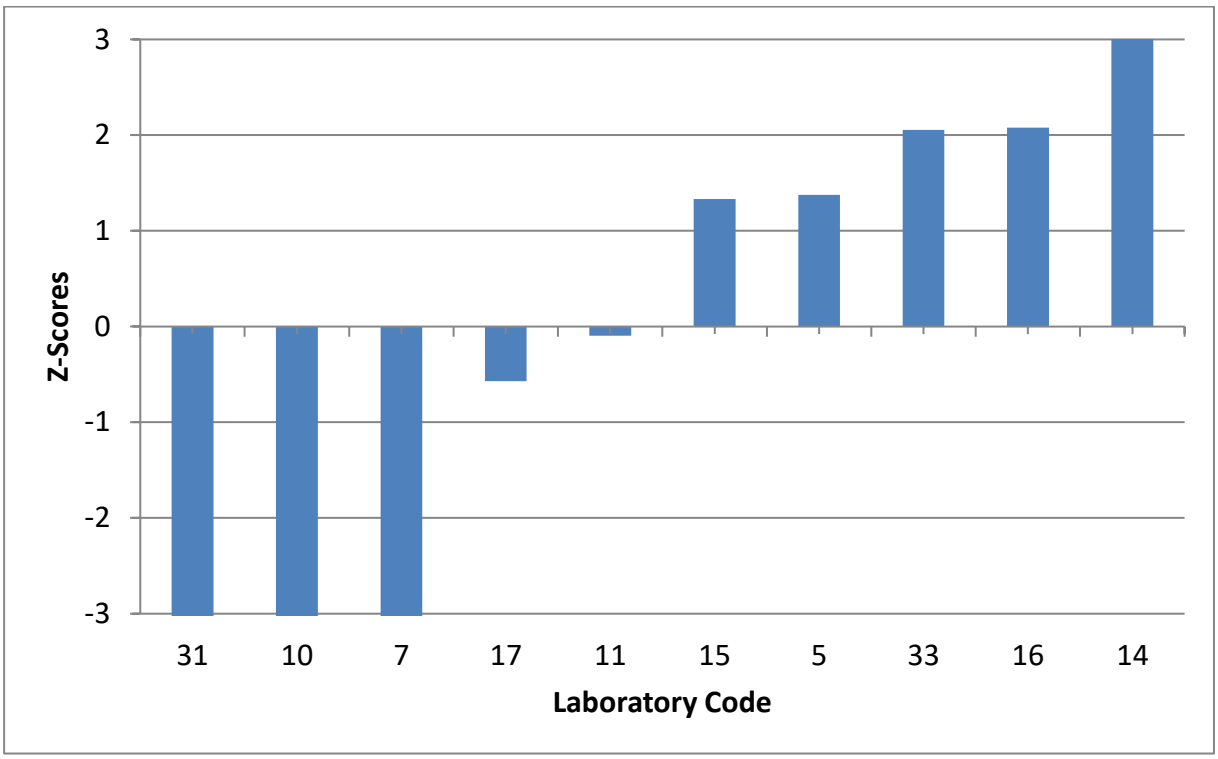


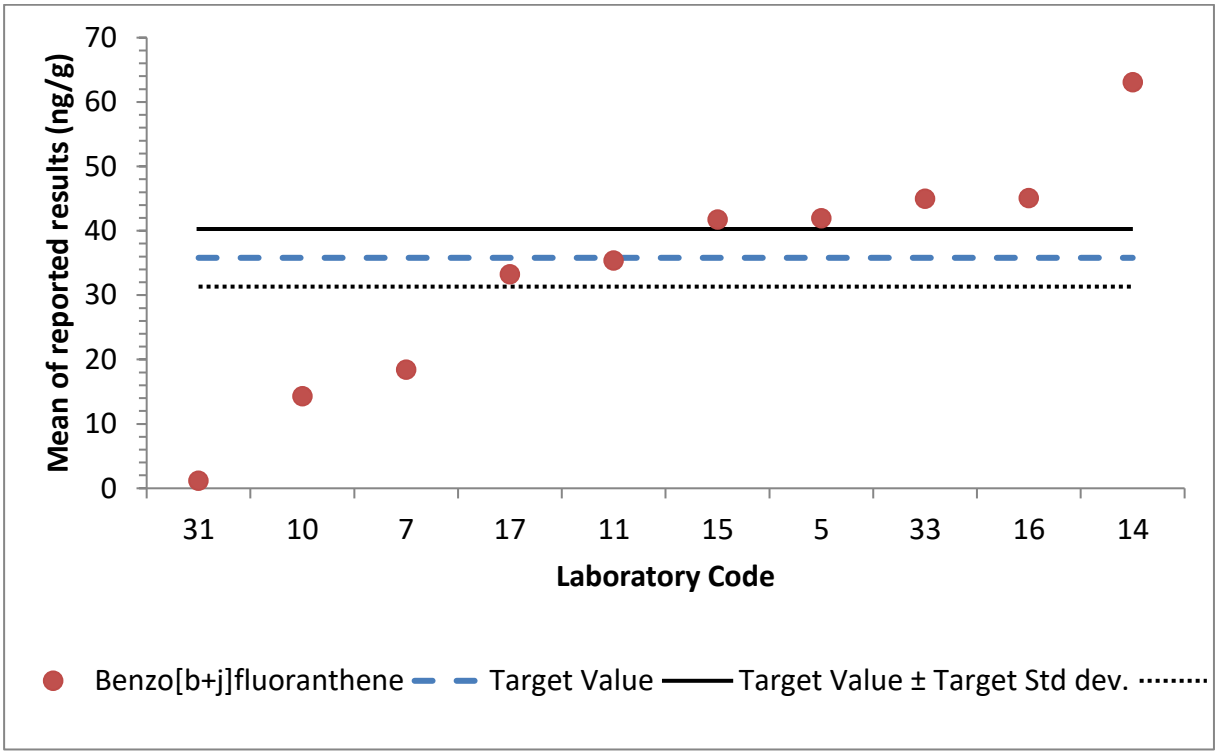
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [a] PYRENE



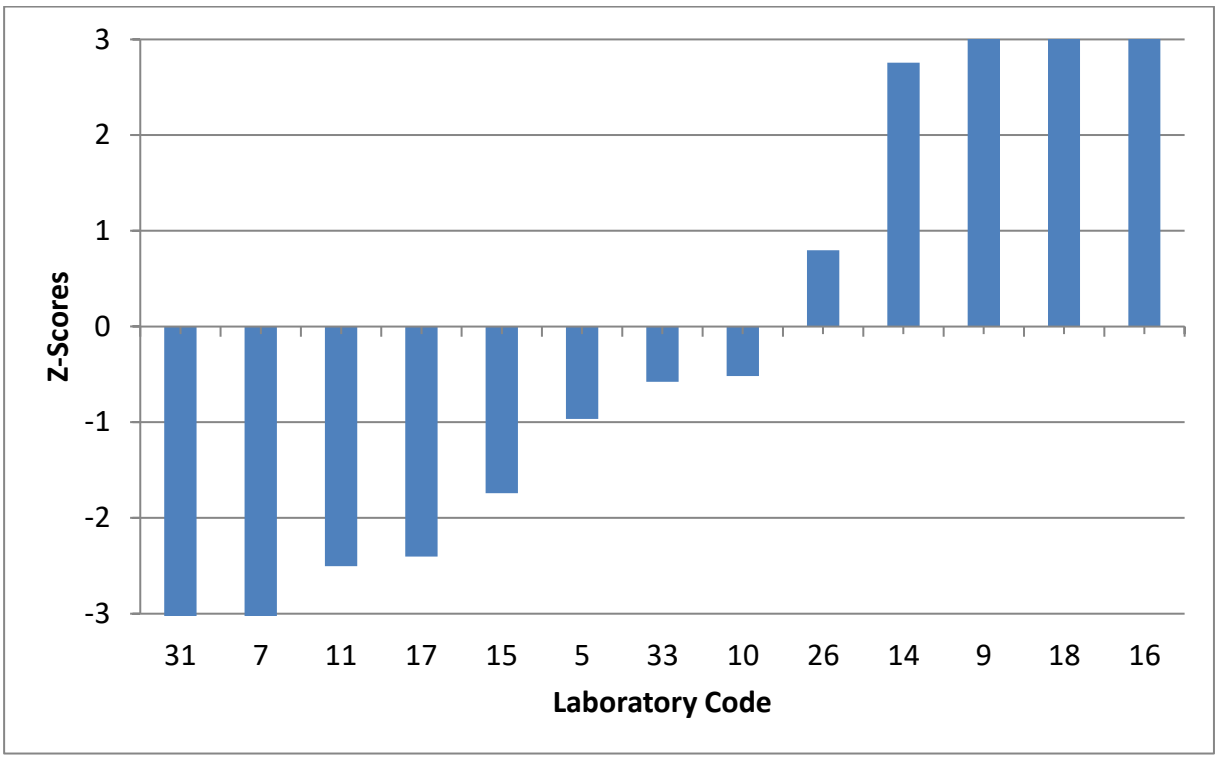


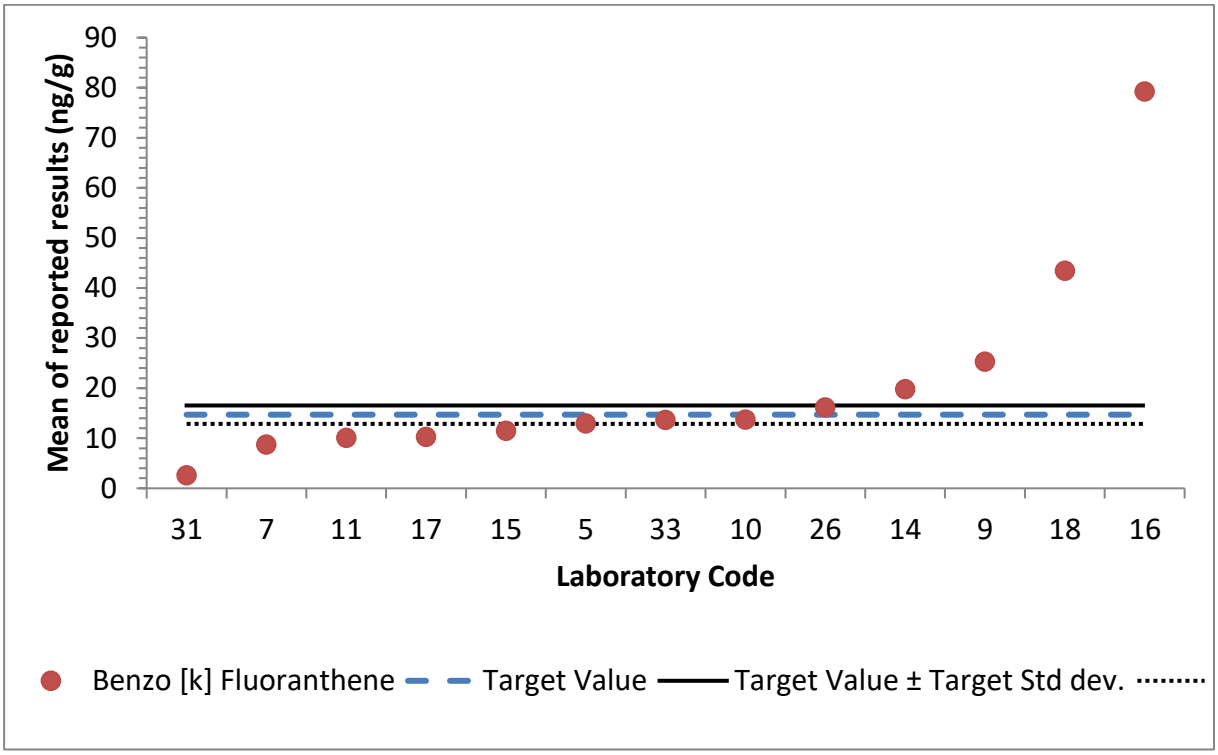
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [b+j] FLUORANTHENE



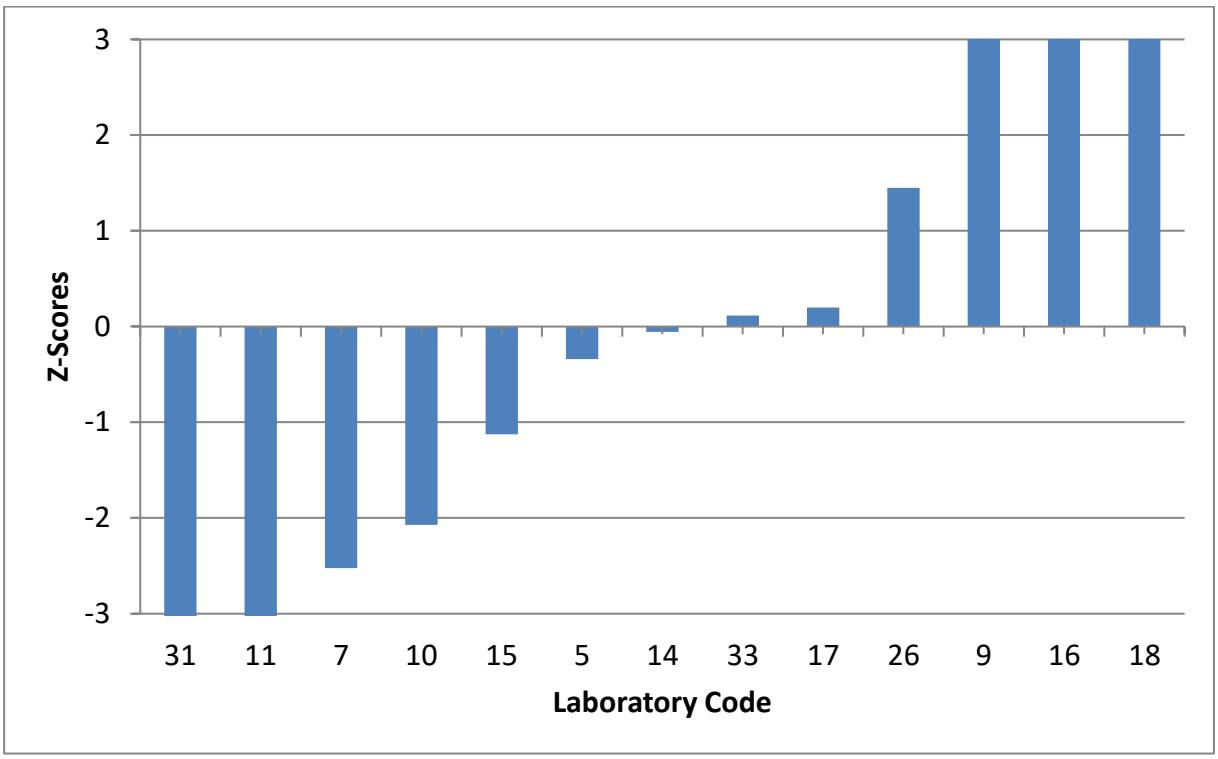


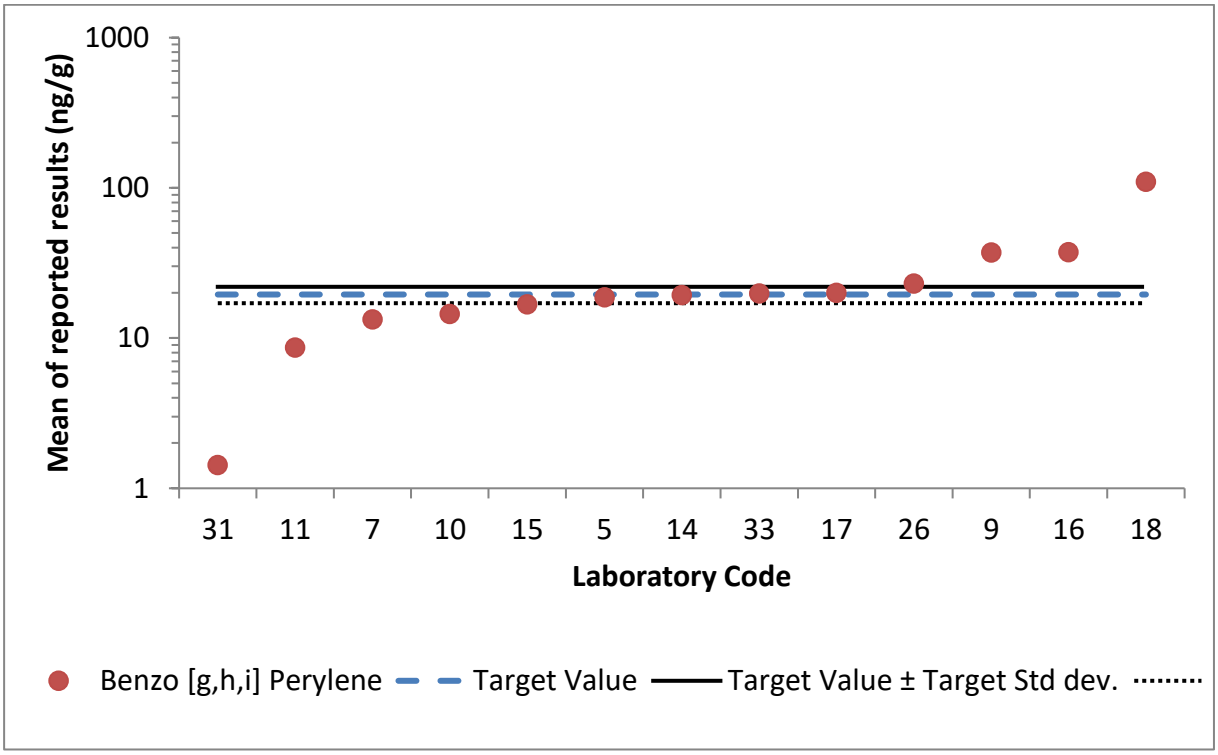
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [k] FLUORANTHENE



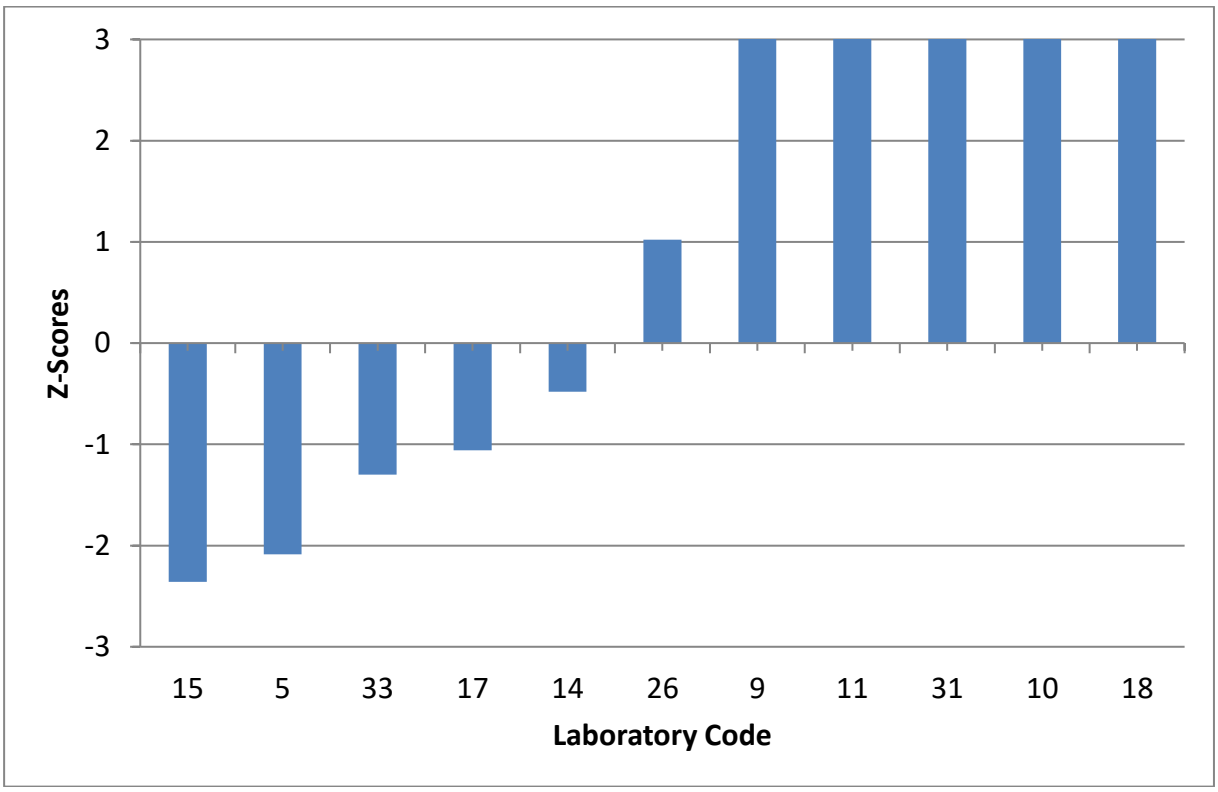


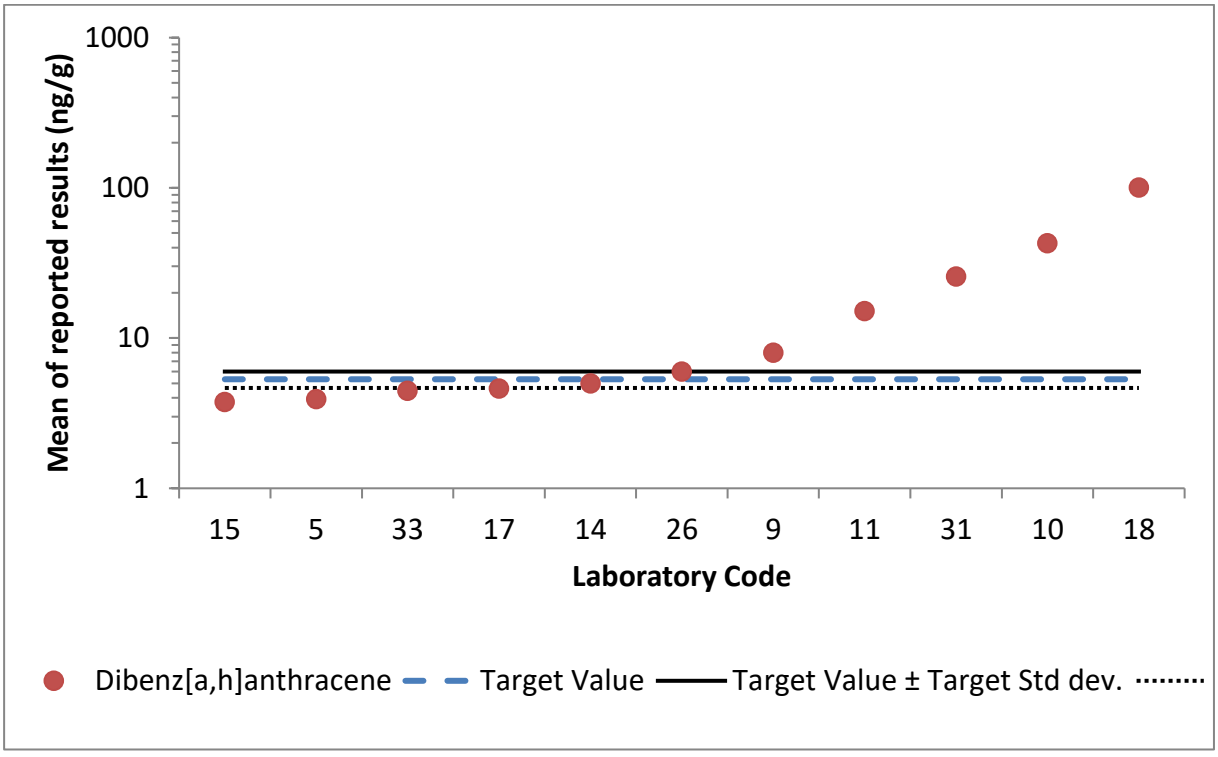
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [g,h,i] PERYLENE





GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR DIBENZ [a, h] ANTHRACENE





Annex 2: IAEA-451 Refence Sheet

IAEA
International Atomic Energy Agency
Atoms for Peace

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-451

MASS FRACTIONS OF ORGANOCHLORINE COMPOUNDS, POLYBROMINATED DIPENYL ETHERS AND PETROLEUM HYDROCARBONS IN CLAM (*Gafrarium tumidum*)

Certified mass fraction values
(based on dry mass)

Chlorinated pesticides

Analyte	Unit	Certified value[1]	Expanded uncertainty[2]
EOM	mg g^{-1}	42.2	4.4
HCB	ng g^{-1}	0.39	0.04
Dieldrin	ng g^{-1}	1.88	0.16
α-Chlordane	ng g^{-1}	0.56	0.04
γ-Chlordane	ng g^{-1}	0.46	0.13
Aroclor 1260	ng g^{-1}	53.2	4.0

Certified mass fraction values

(based on dry mass)

PCB congeners

Analyte	Certified value[1] [ng g^{-1}]	Expanded uncertainty[2] [ng g^{-1}]
PCB 28	0.85	0.09
PCB 95	0.58	0.10
PCB 101	1.74	0.14
PCB 105	0.49	0.12
PCB 110	0.88	0.13
PCB 118	1.01	0.08
PCB 128	0.49	0.04
PCB 138	5.30	0.58
PCB 149	3.33	0.42
PCB 153	8.59	0.78
PCB 170	3.05	0.40
PCB 174	1.32	0.07
PCB 177	0.94	0.10
PCB 180	6.56	1.20
PCB 183	1.82	0.22
PCB 187	3.97	0.26
PCB 194	1.45	0.09
PCB 206	0.24	0.03

PBDE

Analyte	Certified value[1] [ng g^{-1}]	Expanded uncertainty[2] [ng g^{-1}]
PBDE 100	0.23	0.04

(1) Robust mean of the accepted data sets, each set being obtained by a different laboratory and/or a different method of determination.

(2) Estimated expanded uncertainty with a coverage factor k=2, corresponding to a level of confidence of approximately 95%, as defined in the Evaluation of measurement data – Guide to the expression of uncertainty in measurement JCGM100:2008 [1].

Certified mass fraction values

(based on dry mass)

Petroleum hydrocarbons

Analyte	Unit	Certified value[1]	Expanded uncertainty[2]
EOM	mg g^{-1}	36.7	6.4
Total aliphatics	µg g^{-1}	244	34
n-C_{17}	ng g^{-1}	373	44
Naphthalene	ng g^{-1}	14.8	1.2
Phenanthrene	ng g^{-1}	15.8	5.6
Chrysene	ng g^{-1}	26.9	2.0
Fluoranthene	ng g^{-1}	49.3	3.2
Pyrene	ng g^{-1}	40.0	4.6
Benzo[b]fluoranthene	ng g^{-1}	35.8	6.2
Benzo[k]fluoranthene	ng g^{-1}	14.7	3.2
Benz[a]anthracene	ng g^{-1}	19.2	1.3
Benzo[a]pyrene	ng g^{-1}	18.2	2.4
Benzo[g,h,i]perylene	ng g^{-1}	19.5	2.4
Dibenz[a,h]anthracene	ng g^{-1}	5.32	1.36

Recommended mass fraction values

(based on dry mass)

Chlorinated pesticides and PCB congeners

Analyte	Mass fraction[1] [ng g^{-1}]	Expanded uncertainty[2] [ng g^{-1}]
α-HCH	0.78	0.14
γ-HCH (Lindane)	0.56	0.05
pp' DDE	1.73	0.22
pp' DDD	0.99	0.22
pp' DDT	1.34	0.22
Heptachlor	2.07	0.22
Aldrin	0.87	0.10
α-Endosulfan	1.20	0.20
PCB 31	0.29	0.02
PCB 52	0.82	0.04
PCB 195	0.45	0.03

PBDEs

Analyte	Mass fraction[1] [ng g^{-1}]	Expanded uncertainty[2] [ng g^{-1}]
PBDE 47	0.99	0.16
PBDE 154	0.17	0.03
PBDE 209	0.94	0.18

Petroleum hydrocarbons

Analyte	Unit	Mass fraction[1]	Expanded uncertainty[2]
Unresolved Aliphatics	µg g^{-1}	237	44
Σ *n*-Alkanes [C_{14}-C_{34}]	µg g^{-1}	2.85	0.48
Anthracene	ng g^{-1}	5.07	1.10
Benzo[e]pyrene	ng g^{-1}	20.8	2.8
Indeno[1,2,3-cd]pyrene	ng g^{-1}	23.8	1.2
Acenaphthylene	ng g^{-1}	2.01	0.40

(1) Robust mean of the accepted data sets, each set being obtained by a different laboratory and/or a different method of determination.
(2) Estimated expanded uncertainty with a coverage factor k=2, corresponding to a level of confidence of approximately 95%, as defined in the Evaluation of measurement data – Guide to the expression of uncertainty in measurement JCGM100:2008 [1].

Information mass fraction values

(based on dry mass)

Chlorinated pesticides and PCB congeners

Analyte	Mass fraction(*) [ng g^{-1}]
op DDE	4.34
op DDT	0.32
Heptachlor Epoxide	0.73
Endrin	4.60
β-Endosulfan	2.60
Endosulfan sulfate	1.95
trans-Nonachlor	0.15
Aroclor 1254	34.3
PCB 8	1.44
PCB 18	0.58
PCB 44	0.40
PCB 49	0.92
PCB 66	0.45

Chlorinated pesticides and PCB congeners (cont.)

Analyte	Mass fraction(*) [ng g^{-1}]
PCB 70	0.65
PCB 87	0.31
PCB 99	1.21
PCB 151	1.54
PCB 156	0.56
PCB 157	0.40
PCB 167	0.34
PCB 189	0.21
PCB 209	0.15

PBDEs

Analyte	Mass fraction(*) [ng g^{-1}]
PBDE 28	0.07
PBDE 66	0.05
PBDE 85	0.11
PBDE 99	0.81
PBDE 153	0.11
PBDE 183	0.09

Petroleum hydrocarbons

Analyte	Unit	Mass fraction(*)
UVF Chrysene eq.	µg g^{-1}	12.1
Resolved aliphatics	µg g^{-1}	20.0
n-C_{18}	ng g^{-1}	232
Pristane	ng g^{-1}	66.7
Phytane	ng g^{-1}	50.7
Total aromatics	µg g^{-1}	5.17
Resolved aromatics	µg g^{-1}	0.55
1-Methylnaphthalene	ng g^{-1}	4.98
1-Methylphenanthrene	ng g^{-1}	5.3
2-Methylphenanthrene	ng g^{-1}	17.6

Petroleum hydrocarbons (cont.)

Analyte	Unit	Mass fraction(*)
Fluorene	ng g^{-1}	2.62
Acenaphthene	ng g^{-1}	2.18

(*) Information values are robust means of the results from at least four laboratories participating in the interlaboratory comparison [2].

Origin and preparation of the material

60 kg of Tumid Venus clams (*Gafrarium tumidum*) were collected in Noumea, New Caledonia. The organisms were dissected and the soft tissues were deep-frozen, freeze dried, ground into powder and sieved through a 250 µm stainless steel sieve.
The sieved biota fraction with a particle size of less than 250 µm was homogenized by mixing it in a stainless steel rotating homogenizer for three weeks. Then, aliquots of about 20 g were packaged in amber glass bottles with aluminum screw caps, labeled IAEA-451 and sealed with Teflon tape.

Characterization study

The IAEA-451 candidate reference material was characterized in an interlaboratory comparison (ILC).
94 laboratories (including the IAEA's Marine Environmental Studies Laboratory, Monaco) from 51 countries reported results.
Participants were requested to analyse chlorinated pesticides, PCBs, PBDEs and petroleum hydrocarbons by the analytical technique of their choice. They were also requested to make at least one, but preferably three separate determinations for each compound and to report the results together with a short description of the method used.

Assignment of values – Certification procedure

The assigned values were established on the basis of statistically valid results submitted by laboratories which had participated in an international interlaboratory comparison organized by the IAEA Environment Laboratories, Monaco, in 2009. The details concerning all reported results as well as the criteria for qualification as a certified, recommended or information value are reported in "World-wide and regional laboratory comparison on the determination of organochlorine compounds, polybrominated diphenyl ethers and petroleum hydrocarbons in IAEA-451 clam (*Gafrarium tumidum*) sample", IAEA/AQ/28, IAEA, Monaco, 2013 [2]. 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, recommended or information as presented in the Tables above.

Statement on metrological traceability and uncertainty of assigned values

The property values assigned to the IAEA-451 reference material are calculated as mass fractions of chlorinated pesticides, PCBs, PBDEs, aliphatic hydrocarbons and PAHs expressed in the derived SI units µg g^{-1}, mg g^{-1} and ng g^{-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 [2].

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 petroleum hydrocarbons in biota samples.

Instructions for use

Homogeneity of the material

The homogeneity of the material was checked by determining the concentration of some representative analytes (chlorinated pesticides, PCBs, polybrominated diphenyl ethers and petroleum hydrocarbons) in ten replicate analyses taken randomly in the bulk of the powder. A one-way variance analysis indicated that the material can be considered homogenous.

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 (5.1 $\pm$ 0.3)%. 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.

Recommended minimum test portion

The reference material is supplied in 20 g units. The recommended sample size for analysis is 2 g for petroleum hydrocarbons and 3 g for organochlorine pesticides, PCBs and polybromodiphenyl ethers, respectively.

Handling and storage

The material should be stored in the dark and kept in a refrigerator.
Analysts are reminded to take appropriate precautions in order to avoid contamination of the material during handling.

Issue and expiry date

The original issue date of this reference material is **January 2013**. The expiry date is **January 2023**. 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 [3].

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-451, Mass fractions of organochlorine compounds, polybrominated diphenyl ethers and petroleum hydrocarbons in clam (*Gafrarium tumidum*). IAEA, Vienna, 8 pp. (The latest version published applies, see "Note" below).

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

Tel.: 377 97 97 72 72
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E-mail: NAEL-MESL.Contact-Point@iaea.org

REFERENCES

[1] JOINT COMMITTEE FOR GUIDES IN METROLOGY (JGCM), Evaluation of Measurement data - Guide to the Expression of Uncertainty in Measurement, JGCM 100:2008 (GUM with minor corrections), (2008). http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf

[2] INTERNATIONAL ATOMIC ENERGY AGENCY, World-wide and regional laboratory comparison on the determination of organochlorine compounds, polybrominated diphenyl ethers and petroleum hydrocarbons in IAEA-451 clam (*Gafrarium tumidum*) sample, IAEA Analytical Quality in Nuclear Applications Series No. 28 (IAEA/AQ/28), IAEA, Vienna (2013) *(in press)*.

[3] INTERNATIONAL ORGANIZATION FOR STANDARDIZATION, Reference materials – Contents of certificates and labels, ISO Guide 31: 2000, ISO, Geneva (2000).

Mr Ales Fajgelj
Chair,
RM Certification Committee

Ms Chantal Cattini
Project Officer,
Marine Environmental Studies Laboratory

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

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

29 October - 9 November 2018

IAEA-EL staff involved:

E. Vasileva-Veleva, Research Scientist
S. Azemard, Laboratory Technician
A-M. Orani, Laboratory Technician
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 the UN Environment Programme/Mediterranean Action Plan (UN Environment/MAP) - Programme for the Assessment and Control of Marine Pollution in the Mediterranean Sea (MED POL), referred to henceforth as MED POL, for participants from Mediterranean laboratories involved in the MED POL 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 in July 2018 to all MED POL National Focal Points, inviting them to nominate candidates for the training course from their respective countries. MESL received 11 nominations of candidates for the training course on the analytical techniques for the determination of trace elements in environmental samples. Six candidates were selected by the MED POL coordinator in collaboration with MESL staff, based on the information given about their i) education, ii) employment and employers relation to the MED POL 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 13 August 2018. The selection of an Algerian candidate was withdrawn after the candidate did not reply in a timely manner making it impossible for them to receive a visa. The next candidate on the waiting list was invited instead, so that the maximum number of funded participants took part in the course. The six participants were from Albania, Cyprus, Israel, Montenegro [2] and Turkey.

The course took place from 29 October to 9 November 2018.

The theoretical and practical knowledge on good laboratory practice (GLP), different analytical techniques for trace element analysis, and quality assurance principles were presented during the training course. On special request of the trainees several additional lectures on metrology in chemistry and quality assurance and quality control (QA/QC, use of certified reference material, procedure validation, uncertainty and traceability of measurement results) were added to the theoretical part of the training course after the start of the course, which requested rearrangements on a day-to-day basis of the preliminary prepared and final training program, which is presented in on page 15.

2. Evaluation

While all participants had the correct technical background for the course, the participant from Turkey was lacking English proficiency and was therefore struggling to follow the course. Only two of the participants knew that their laboratory was involved in the MED POL monitoring program, but neither these two, nor the other four, were aware that they are doing analysis themselves for the MED POL monitoring programme.

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., 100% of participants indicated that their overall impression of the training course was excellent, 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 good. However, some participants expressed to have appreciated more time in the laboratory to apply the newly accrued knowledge. Several trainees recommended that practical sessions could be conducted with a smaller number of participants in the future. A summary of the evaluation forms can be found at the end of this report.

3. Conclusion and Recommendations

All participants had the correct technical background for the course and were exceptionally enthusiastic. However, despite asking in the nomination form how the work of the candidate relates to UN Environment/MAP MED POL programme to the training course offered, and only selecting candidates that indicated with relation to the programme, none of the actual participants was apparently directly involved in laboratory analysis for MED POL monitoring programme. This makes the training questionable, meaning that the capacity built in participants' laboratories may not directly benefit the MED POL programme.

The participants were all very satisfied with the course, especially after their request for more QA/QC training was positively responded to and additional lectures and practical sessions were organized at short notice.

Recommendations:

Laboratories and MED POL focal points should only nominate training course candidates that are actively involved in the MED POL monitoring programme!

MED POL Focal Points should 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 programmes within the implementation of MED POL IV/IMAP. Similarly, 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.

The selection procedure for the participants in MED POL training course should to be further improved and only candidates that are actively involved in the MEDPOL monitoring selected. Communication with the selected participants on their background, needs and expectations from the training should start as soon as possible after selection to help adjusting the training content as good as possible to the participants needs, and consequently achieve the best outcome.

MED POL Focal Points should follow up more closely with national laboratories participating in the implementation of MED POL IV/IMAP monitoring programme and experts participating in the TC organized for trace elements, with a view of further supporting national efforts to implement the QA/QC measures in order to warrant good quality of monitoring data reported to MED POL.

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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5. Course outline

MED POL TRACE ELEMENTS ANALYSIS TRAINING COURSE

IAEA – Environment Laboratories, Monaco

29 Oct. – 9 Nov. 2018

COURSE OUTLINE

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

MONDAY 29 OCTOBER

9:00 – 12:00	Welcome to IAEA Environment Laboratories Monaco.	*Mr David Osborn DIR-NAEL (or alternate)*
	Laboratory Safety and Security.	*Mr Hussein Ramadan Head - EES*
	Presentation of MESL and its activities.	*Ms Sylvia Sander Laboratory Head - MESL*
	Self-introduction of participants and expectations from the Training Course.	*All participants*
	Visit of the EL laboratories.	*Ms Leslie Barilaro-Hamonic Team Assistant MESL*
14:00 – 17:00	Administrative matters.	*Ms Leslie Barilaro-Hamonic Team Assistant MESL*

TUESDAY 30 OCTOBER

9:00 – 13:00	**THEORETICAL SESSION** Trace elements determination for monitoring studies. Sample preparation for trace element analysis in sediments and biological samples. Mineralization techniques. Moisture determination. Sampling and sample storage in the case of trace element analysis.	*Ms Emilia Vasileva Research Scientist*
14:00 – 17:00	**PRACTICAL SESSION** Inorganic Laboratory Orientation. Dry oven moisture determination in biota sample.	*Ms Sabine Azemard Ms Anna Maria Orani Laboratory Technician*

WEDNESDAY 31 OCTOBER

9:00 – 14:00 — **TEORITICAL SESSION** — *Ms Emilia Vasileva, Research Scientist*

Introduction to the determination of trace elements by Flame Atomic Absorption Spectrometry (AAS) and Graphite Furnace- Atomic Absorption Spectrometry (GF-AAS).

Method Validation

Uncertainty and traceability of measurement results.

14:30 – 17:00 — **PRACTICAL SESSION** — *Ms Sabine Azemard, Ms Anna Maria Orani, Laboratory Technician*

Sample preparation: mineralization of biological and sediment samples for trace element analysis.
Dilution of sediment and biota digests to appropriate, specified volumes.
Flame AAS and application of the method for the determination of trace elements in marine samples.
Preparation of calibration curve for Zn by Flame AAS.

THURSDAY 01 NOVEMBER

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

Determination of Zinc by Flame AAS in biota and sediment samples. Data treatment.
Determination of Cu by GF-AAS in biota sample. Calibration curve. Data treatment.

FRIDAY 02 NOVEMBER

9:00 – 14:00 — **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.

MONDAY 05 NOVEMBER

9:00 – 13:00	**THEORETICAL SESSION** Inductively Coupled Plasma -Mass Spectrometry (ICP-MS) - Main Principles and application for trace element analysis of Environment Samples. Proper use of Certified Reference Materials	*Ms Emilia Vasileva* *Research Scientist*
14:00 – 17:00	**PRACTICAL SESSION** Sampling principles and techniques. Samples storing, transport and pre-treatment. Sample preparation: dissection of biological samples (fish, mussels, oysters).	*Mr Roberto Cassi* *Mr. David Huertas* *Laboratory Technician*

TUESDAY 06 NOVEMBER

9:00 – 13:00	**PRACTICAL SESSION** Determination of mercury in seawater by Cold Vapor Atomic Fluorescent Spectrometry (CV-AFS). Optimization of instrument parameters. Calibration curve. Data treatment.	*Ms Sabine Azemard* *Laboratory Technician*
14:00 – 17:00	**PRACTICAL SESSION** Sampling field trip. Demonstration on sediment and water sampling techniques. Samples storing.	*Mr Roberto Cassi* *Laboratory Technician* *Mr David Huertas* *Laboratory Technician*

WEDNESDAY 07 NOVEMBER

9:00 – 12:00	**PRACTICAL SESSION** Development of method for the determination of Cd in biota sample by ICP-MS.	*Ms Anna Maria Orani* *Laboratory Technician*
13:00 – 17:00	**THEORETICAL SESSION** Reliable Measurement Results. Internal Quality Control	*Ms Emilia Vasileva* *Research Scientist*

THURSDAY 08 NOVEMBER		
9:00 – 12:00	**PRACTICAL SESSION**	
	Determination of total and organic Hg by Advanced Mercury Analyzer (AMA). Calibration curves. Data treatment. Case study: Determination of total and organic Hg mass fraction in marine biota sample.	*Ms Sabine Azemard* *Ms Anna Maria Orani* *Laboratory Technician*
13:00 – 17:00	**THEORETICAL SESSION**	
	Basic Statistics Estimation of measurement uncertainty- how to build uncertainty budget. Case study: AAS determination of Pb in sediments	*Ms Emilia Vasileva* *Research Scientist*
FIRDAY 09 NOVEMBER		
9:00 – 12:00	**CLOSURE OF THE TRAINING COURSE**	
	Presentation about MEDPOL. Barcelona Convention: The Ecosystem Approach in the Mediterranean Sea.	*Ms Jelena Knezevic* *Monitoring and Assessment Officer* *UN Environment/MAP*
	Feedback from course participants: Short presentation by participants about the course (teams or individuals). Course evaluation survey.	*All course participants*
	Closing remarks. Award of certificates and photos.	*Mr David Osborn* *DIR-NAEL (or alternate)* *& Ms Jelena Knezevic* *UN Environment/MAP*
13:00 – 17:00	Visit to the Oceanographic Museum, Monaco.	

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. Subsequent lectures were dedicated to analytical techniques, e.g. Flame Atomic Absorption Spectrometry, Graphite Furnace Atomic Absorption Spectrometry, Inductively Coupled Plasma Mass Spectrometry, as well as to the hyphenated technique, such as Cold Vapor Atomic Fluorescence Spectrometry-CV-AFS, applied for trace elements and mercury speciation analysis in marine samples during the practical part of MED POL training course.

Provided lectures also included quality assurance, internal and external quality control principles. Special focus was given to QA/QC procedures necessary and recommended by ISO guide 17025*. The most important concepts of measurement science, metrology in chemistry, validation of measurement procedure, use of certified reference materials, traceability and uncertainty of measurement results were presented. Practical 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.

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.

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

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.

a) 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.

b) Atomic Absorption Spectrometry (AAS)

- Determination of Cu 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 gravimetrical standard solutions for Cu, using "matrix matching" approach. The concepts for "matrix matching" of all solutions and calibration blank were not clear for all participants.
A specific exercise was performed to demonstrate a practical way of determining the method detection limits using a low-level solution. This was not performed as routine for most of the participants.

- 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 ashing 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.

- 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.

c) Determination of total mercury by cold vapor techniques

The cold vapor AFS, with double gold trap amalgamation was quickly 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.

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

One full day was dedicated to the determination of total mercury mass fraction in fish samples, using a solid mercury analyser. After the application of the appropriate extraction method the mass fraction of the organic mercury in the same samples was determined, too. None of the participants were familiar with the use of specific extraction for organic mercury.

e) 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 the correction for spectral interferences, checking the procedural blanks, analysis of the 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. Two trainees demonstrated to be already proficient in the use of ICP-MS in their routine work, while for others it was a new experience.

f) 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. Evaluation of training by participants

Training Course organized for MED POL program on the
Analytical Techniques for the Determination of Trace Elements in Environmental Samples
MONACO
(29 October to 9 November 2018)

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

6 x Excellent ❒ Satisfactory ❒ Poor ❒ Better than expected

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

6 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?

6 x Yes ❒ To some extent ❒ Uncertain ❒ No

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

6 x Yes ❒ To some extent ❒ Uncertain ❒ No

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

6 x Yes ❒ To some extent ❒ Uncertain ❒ No

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

6 x Yes ❒ No

If YES, please indicate relevant topics:

4 x Trace elements by ICP-OES 4 x Trace elements by ICP-MS
1 x Others (specify):
QA and QC of analysis in determination of trace elements.

TRAINING CONTENT

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

2 x Too theoretical 4 x Good balance ❒ Too practical

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

5 x Good 1 x Too many lectures ❒ Too many discussion sessions

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

❒ Too short 6 x Just right ❒ Too long

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

2 x Too fast 4 x Just right ❒ Too slow

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

4 x Very well sequenced 2 x Suitable ❒ Poorly sequenced

12. How helpful were the group exercises ?

5 x Very helpful 1 x Helpful ❒ Not helpful

13. Did you have enough skills practice time ?

2 x Yes 3 x No 1 x Uncertain

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

6 x Very valuable ❒ Of some value ❒ No real value

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

- High level of the trainers both in theoretical and practical sessions.
- Opportunities to discuss and share information with others (participants and trainers).
- See the whole way from sampling to the results, practice in sediment and biota analysis.
- Lectures on uncertainty, validation and QC.
- Gives an overall idea on how trace elements on different equipment can be handle.

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

- Group should be smaller during the practical sessions in the laboratories.
- Too many theoretical sessions / Not enough practical sessions.

17. What do you think should be dropped from this course?

- Theoretical lectures about the instruments.

18. Comments about the course contents:

- Very useful, helpful both lectures and practical sessions for practices in their laboratories.
- Very well organized, very good training course.

INSTRUCTIONAL MATERIAL (on CD ROM)

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

5 x Just right 1 x Too few ❒ Too many

20. How do you rate the quality of the handout material ?

5 x High quality 1 x Sufficient ❒ Below expectation

LABORATORIES AND FACILITIES

21. Did you like the seating arrangements of the conference room ?

6 x Yes ❒ No ❒ No opinion

22. How do you rate the practical sessions ?

4 x Excellent 2 x Very good ❒ Fair ❒ Poor

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

2 x Too many ❒ Too few 4 x Just right

24. Comments about laboratory sessions:

- Very useful.
- Excellent (professional) training.
- Group too large for the practical sessions into the laboratories.

25. What is your overall evaluation of the course ?

6 x Excellent ❒ Very good ❒ Fair ❒ Poor

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

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

Organized by:

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

29 October - 09 Novembre 2018

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 FOR MEDPOL

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 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 (MED POL), referred to henceforth as MED POL, for participants from Mediterranean laboratories involved in the MED POL 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 in July 2018 to all MED POL 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. All 6 candidates were selected by the MED POL coordinator in collaboration with MESL staff, as the information given about their i) education, ii) employment and employers relation to the MEDPOL programme, iii) English proficiency, iv) country distribution and v) overall merit of the nominees seemed appropriate. Invitation letters were sent to the participants by IAEA/NAEL-MESL on 13 August 2018. The selected candidates were from Algeria, Bosnia & Herzegovina, Cyprus, Morocco, Tunisia, Turkey. Unfortunately, the participant from Tunisia cancelled her participation for medical reasons only on the first day of the course. The course took place from 29 October to 09 November 2018.

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 459) 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.
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.

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

2. Evaluation

The experience of participants of the 2018 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 this type of analyses in their institutions. This heterogeneity of the background of the participants made it very challenging to keep the level of the course high enough to ensure benefit to all the participants and their home laboratories. Because of the diversity of trainees' background and their actual role in their home laboratories some practical sessions and group exercises like results calculation and data quantification took longer than planned. Computer sessions were included in the training course to meet the needs of both beginners and more skilled trainees.

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 80% (4/5) and very good (20%). 100% of participants thought that the course met their needs and that they felt they will be better able to do their job after attending this course. Although the balance of lectures, group discussions and group exercises was 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 was beneficial for the all 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 MED POL monitoring programme.

Although most participants were only partially 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.

In the future the nomination process needs to be further improved to make sure that the right people from laboratories actually providing analysis data to the MED POL monitoring programmes are receiving the training. Focus should be on laboratory experience to benefit most from the capacity building efforts provided.

Based on the experience from this training course, expert missions to national designated laboratories participating in national marine environment monitoring programmes for MED POL IV/IMAP should be organized and aimed 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) and knowledge needs. These missions should be supported by the MED POL Focal Points to reinforce the importance and motivation.

MED POL Focal Points should follow up more closely with national laboratories participating in implementation of MED POL IV/IMAP monitoring programme and experts participating in the TC organized for organic compounds, with a view of further supporting national efforts to implement the QA/QC measures in order to warrant good quality of monitoring data reported to MED POL.

MED POL Focal Points should 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 programmes within the implementation of MED POL IV/IMAP. 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.

*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. Course outline

MED POL ORGANIC CONTAMINANTS ANALYSIS TRAINING COURSE

IAEA – Environment Laboratories, Monaco
29 Oct. – 9 Nov. 2018

COURSE OUTLINE

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

MONDAY 29 OCTOBER

9:00 – 12:00	Welcome to IAEA Environment Laboratories Monaco.	*Mr David Osborn* *DIR-NAEL* *(or alternate)*
	Safety and Security. General Housekeeping.	*Mr Hussein Ramadan* *Head - EES*
	Presentation of the Marine Environment Study Laboratories (MESL) and its activities.	*Ms Sylvia Sander* *Laboratory Head - MESL*
	Self-introduction of participants and expectations from the Training Course.	*All participants*
14:00 – 17:00	Visit of the other Marine Environment Laboratories.	*Ms Leslie Barilaro-Hamonic* *Team Assistant MESL*
	14:30 Visit of the section of RML **15:00** Visit of the section of REL	
	Analytical Methods for Organic Contaminants. Introduction to computer sessions.	*Mr Roberto Cassi* *Laboratory Technician*

TUESDAY 30 OCTOBER

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 31 OCTOBER

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 1 NOVEMBER

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 2 NOVEMBER

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 5 NOVEMBER

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**

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 6 NOVEMBER

9:00 – 13:00 **PRACTICAL SESSION**

Mr Roberto Cassi
Mr David Huertas
Laboratory Technicians

Sampling field trip.
Demonstration of sediment and water sampling techniques.
Sample storage.

14:00 – 17:00	**THEORETICAL SESSION**	*Ms Imma Tolosa* *Research Scientist*
	The stationary phase. Capillary columns. Sample introduction. Detectors. Temperature effects.	

WEDNESDAY 7 NOVEMBER

9:00 – 12:00	**THEORETICAL SESSION**	*Ms Sarah Choyke* *Associate Chemist*
	Quantifying Uncertainty. Assessing Linear Calibration.	
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 8 NOVEMBER

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 9 NOVEMBER

9:00 – 12:00	**CLOSURE OF THE TRAINING COURSE**	
	Presentation about MEDPOL. Barcelona Convention: The Ecosystem Approach in the Mediterranean Sea.	*Ms Jelena Knezevic* *Monitoring and Assessment Officer* *UN Environment* *Mediterranean Action Plan*
	Feedback from course participants: Short presentation by participants about the course (teams or individuals). Course evaluation survey.	*All course participants*
	Closing remarks. Award of certificates and photos.	*Mr David Osborn* *DIR-NAEL (or alternate)* *& Ms Jelena Knezevic* *UN Environnent/MAP*
13:00 – 17:00	Visit of the Oceanographic Museum, Monaco.	*All course participants*

5. 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.

6. 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**	**15334**	
HCB	10	100	1000	2733	3.53
PCB-29 SU	**100**	**100**	**10000**	**7745**	**0.51**
PCB-28	10	100	1000	966	1.25
PCB-52	10	100	1000	793	1.02
PCB-101	10	100	1000	1054	1.36
ppDDE	10	100	1000	1897	1.38
PCB-118	10	100	1000	1176	0.85
PCB-153	10	100	1000	1102	0.80
ppDDT	10	100	1000	715	0.52
PCB-138	10	100	1000	1314	0.95
PCB-180	10	100	1000	1693	1.23
PCB-198 SU	**100**	**100**	**10000**	**13794**	**0.90**

OCs - F2

	CALIBRATION CURVE-1				
	Conc. (pg/µl)	**Volume (µl)**	**Qty Spiked (pg)**	**Area**	**RRF**
TCMX (GC-IS)	**1000**	**10**	**10000**	**16144**	
Lindane	10	100	1000	2115	1.50
E-HCH - SU	**100**	**100**	**10000**	**14064**	**0.87**
ppDDD	10	100	1000	2025	1.44

OCs - F3

	CALIBRATION CURVE-1				
	Conc. (pg/µl)	**Volume (µl)**	**Qty Spiked (pg)**	**Area**	**RRF**
TCMX (GC-IS)	**1000**	**10**	**10000**	**15835**	
Endosulfan LD40 - SU	**100**	**100**	**10000**	**18177**	**1.15**
a-Endosulfan	10	100	1000	2098	1.15
Dieldrin	10	100	1000	2388	1.31
Endrin	10	100	1000	1250	0.69
b-Endosulfan	10	100	1000	2137	1.18

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**
3.5	0.13	3.8	HCB	3.5
0.4	**0.05**	**10.8**	**PCB-29 SU**	0.4
1.2	0.11	9.0	PCB-28	1.2
0.9	0.13	15.2	PCB-52	0.9
1.2	0.14	12.0	PCB-101	1.2
1.3	0.06	4.9	ppDDE	1.3
0.7	0.12	17.5	PCB-118	0.7
0.7	0.10	14.8	PCB-153	0.7
0.5	0.05	9.3	ppDDT	0.5
0.9	0.06	6.5	PCB-138	0.9
1.1	0.15	14.1	PCB-180	1.1
0.9	**0.03**	**3.1**	**PCB-198 SU**	0.9

Mean RRF	SD	%RSD		
			Compound	**Mean RRF**
1.5	0.03	1.8	Lindane	1.5
0.9	**0.01**	**1.3**	**E-HCH - SU**	0.9
1.3	0.13	10.2	ppDDD	1.3

Mean RRF	SD	%RSD		
			Compound	**Mean RRF**
1.1	**0.01**	**0.6**	**Endosulfan LD40 - SU**	1.1
1.0	0.12	11.8	a-Endosulfan	1.0
1.2	0.11	8.8	Dieldrin	1.2
0.6	0.08	12.8	Endrin	0.6
1.0	0.12	11.1	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**	**7305**		
HCB				25	32	
PCB-29 SU	**100**	**100**	**10000**	**2234**	**6799**	**68%**
PCB-28				29	110	
PCB-52				50	257	
PCB-101				39	146	
ppDDE				16	23	
PCB-118				30	77	
PCB-153				53	141	
ppDDT				99	338	
PCB-138				50	101	
PCB-180				25	43	
PCB-198 SU	**100**	**100**	**10000**	**5469**	**8417**	**84%**

	BLANK					
	Conc. (pg/µl)	**Vol. (µl)**	**Qty Spiked (pg)**	**Area**	**Qty Found (pg)**	**SU % REC**
TCMX (GC-IS)	**1000**	**10**	**10000**	**5161**		
Lindane				22	42	
E-HCH - SU	**100**	**100**	**10000**	**3517**	**7751**	**78%**
ppDDD				19	41	

	BLANK					
	Conc. (pg/µl)	**Vol. (µl)**	**Qty Spiked (pg)**	**Area**	**Qty Found (pg)**	**SU % REC**
TCMX (GC-IS)	**1000**	**10**	**10000**	**4763**		
Endosulfan LD40 - SU	**100**	**100**	**10000**	**4106**	**7526**	**75%**
a-Endosulfan				70	167	
Dieldrin				127	259	
Endrin				63	255	
b-Endosulfan				73	170	

Figure 5. Example of quantitative calculation of a reference material sample (IAEA-459) for fractions 1, 2 and 3.

grams extracted	4.61

	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**	**6577**				
HCB				459	735	704	0.15	
PCB-29 SU	**100**	**100**	**10000**	**1781**	**6023**			**60%**
PCB-28				1976	9369	9259	2.01	
PCB-52				1661	10608	10351	2.25	
PCB-101				4010	18684	18538	4.02	
ppDDE				6403	11285	11262	2.44	
PCB-118				3550	11502	11425	2.48	
PCB-153				4636	15499	15358	3.33	
ppDDT				357	2947	2609	0.57	
PCB-138				5032	12916	12815	2.78	
PCB-180				4211	9186	9143	1.98	
PCB-198 SU	**100**	**100**	**10000**	**4337**	**7414**			**74%**

	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**	**5228**				
Lindane				712	2127	2085	**0.45**	
E-HCH - SU	**100**	**100**	**10000**	**2271**	**4942**			**49%**
ppDDD				3999	13658	13617	**2.95**	

	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**	**5342**				
Endosulfan LD40 - SU	**100**	**100**	**10000**	**4079**	**6667**			**67%**
a-Endosulfan				85	204	37	**0.01**	
Dieldrin				317	651	391	**0.08**	
Endrin				126	513	257	**0.06**	
b-Endosulfan				84	196	26	**0.01**	

Figure 6. Table of quantitative calculation of a sediment reference material sample (IAEA-459) performed by the trainees. Results include mean, standard deviation and relative standard deviation (ng/g d.w.)

Compound	IAEA-459 Sample 1	IAEA-459 Sample 2	IAEA-459 Sample 3	Mean (ng/g)	Standard Deviation (ng/g)	Relative Standard Deviation (%)	Reference Value (ng/g)	Expanded Uncertainty (ng/g)
PCB-28	2.46	2.01	2.03	2.17	0.21	9%	2.27	0.56
PCB-52	2.29	2.25	2.18	2.24	0.04	2%	2.38	0.67
PCB-101	4.00	4.02	3.64	3.89	0.18	5%	3.78	0.43
PCB-118	2.65	2.48	2.59	2.58	0.07	3%	2.98	0.39
PCB-138	3.04	2.78	2.93	2.92	0.11	4%	3.25	0.89
PCB-153	3.35	3.33	3.35	3.34	0.01	0%	3.75	0.66
PCB-180	1.98	1.98	1.96	1.97	0.01	1%	2.22	0.34
HCB	0.15	0.15	0.10	0.13	0.02	16%	0.15	0.06
Lindane	0.42	0.45	0.47	0.45	0.02	4%	0.18	0.06
ppDDE	2.83	2.44	2.27	2.51	0.23	9%	3.60	0.48
ppDDD	3.72	2.95	4.79	3.82	0.76	20%	3.00	0.93
ppDDT	0.23	0.57	0.45	0.41	0.14	34%	1.32	0.52

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	0.52	0.51	0.49	0.51	0.01	2%	0.32	0.26
PCB-52	1.12	1.15	1.03	1.10	0.06	6%	1.20	1.20
PCB-101	1.02	1.02	1.12	1.05	0.04	4%	1.20	0.49
PCB-118	1.01	0.91	0.90	0.94	0.05	5%	1.09	0.42
PCB-138	2.35	2.25	2.22	2.28	0.05	2%	2.20	0.84
PCB-153	3.28	3.09	3.13	3.17	0.08	3%	2.80	0.99
PCB-180	0.12	0.12	0.10	0.11	0.01	8%	0.20	0.11
HCB	0.15	0.15	0.16	0.15	0.01	5%	0.20	0.10
Lindane	0.33	0.13	0.19	0.21	0.08	38%	0.58	0.54
ppDDE	2.99	2.82	2.65	2.82	0.14	5%	2.10	1.00
ppDDD	0.62	0.94	1.06	0.87	0.18	21%	0.88	0.49
ppDDT	0.56	0.78	0.63	0.66	0.08	12%	0.67	0.46

Figure 8. Quality control chart (QC) for PCB-153 in IAEA-459 sediment reference material (ng/g d.w).

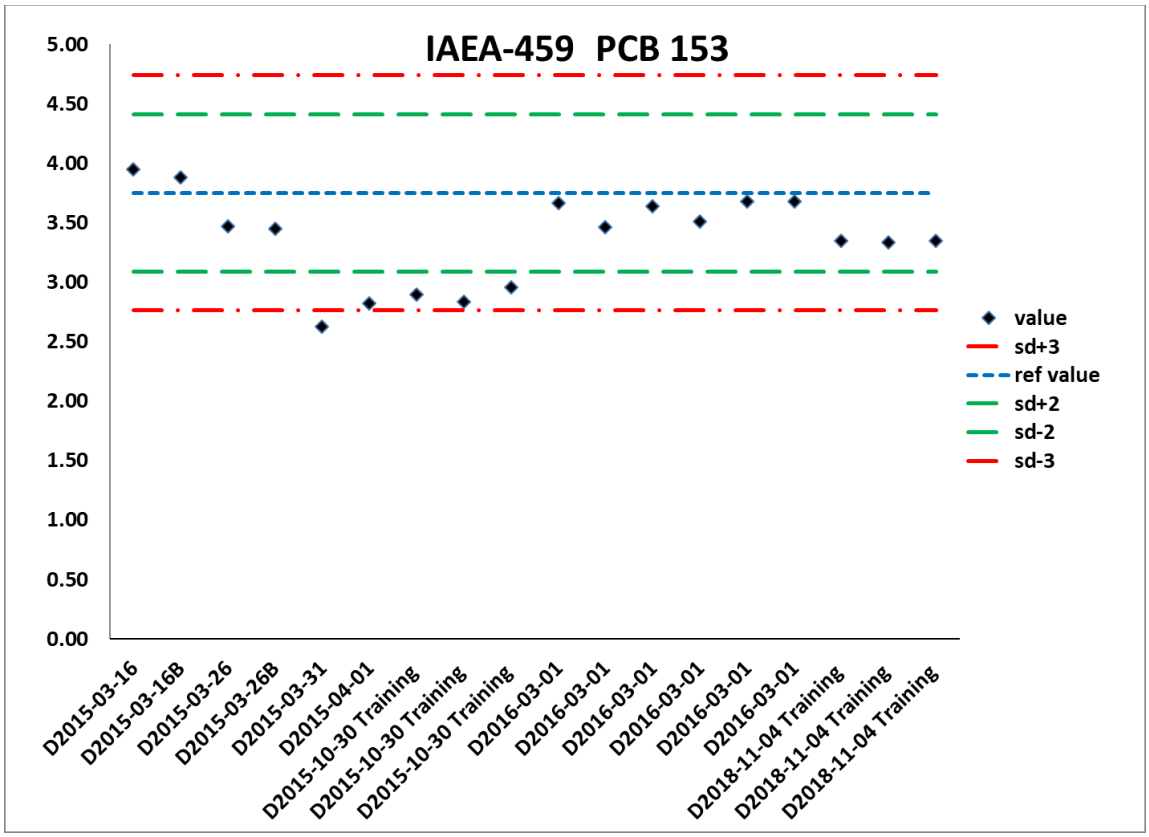


Figure 9. Quality control chart (QC) for p,p-'DDD in IAEA-459 sediment reference material (ng/g d.w).

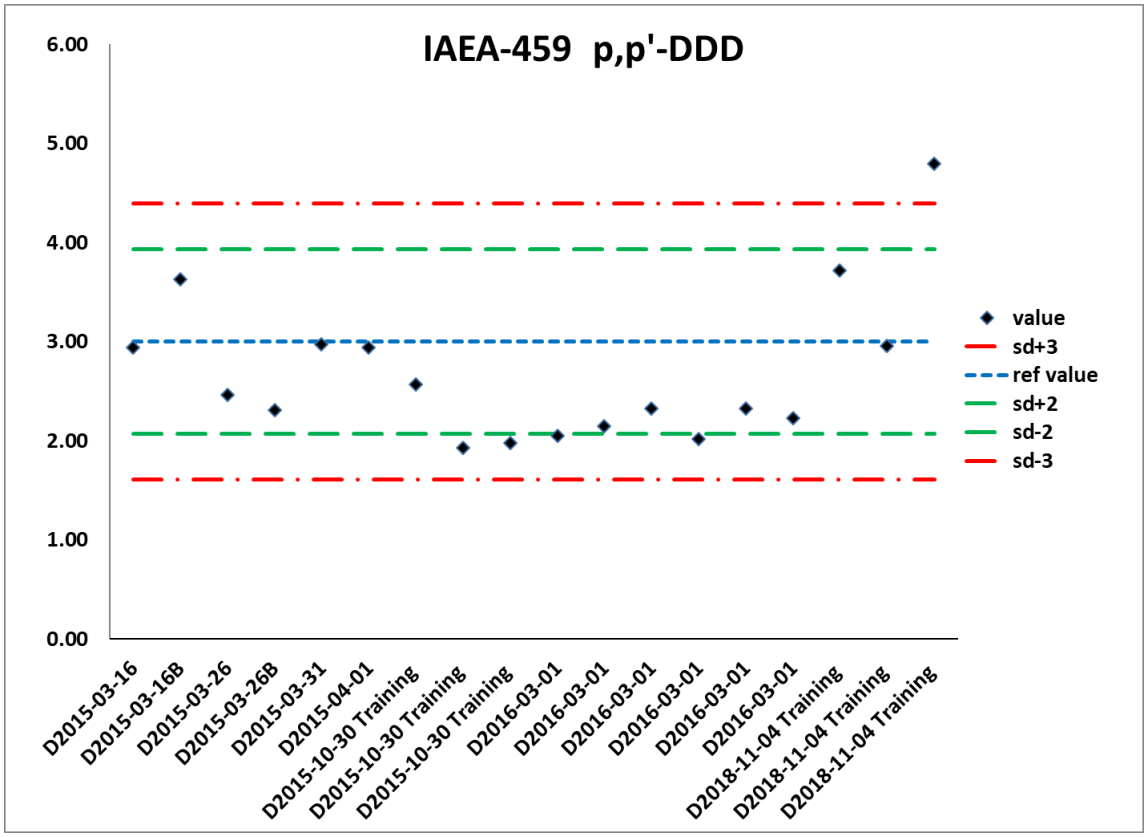


Figure 10. Quality control chart (QC) for PCB-28 in IAEA-432 biota reference material (ng/g d.w).

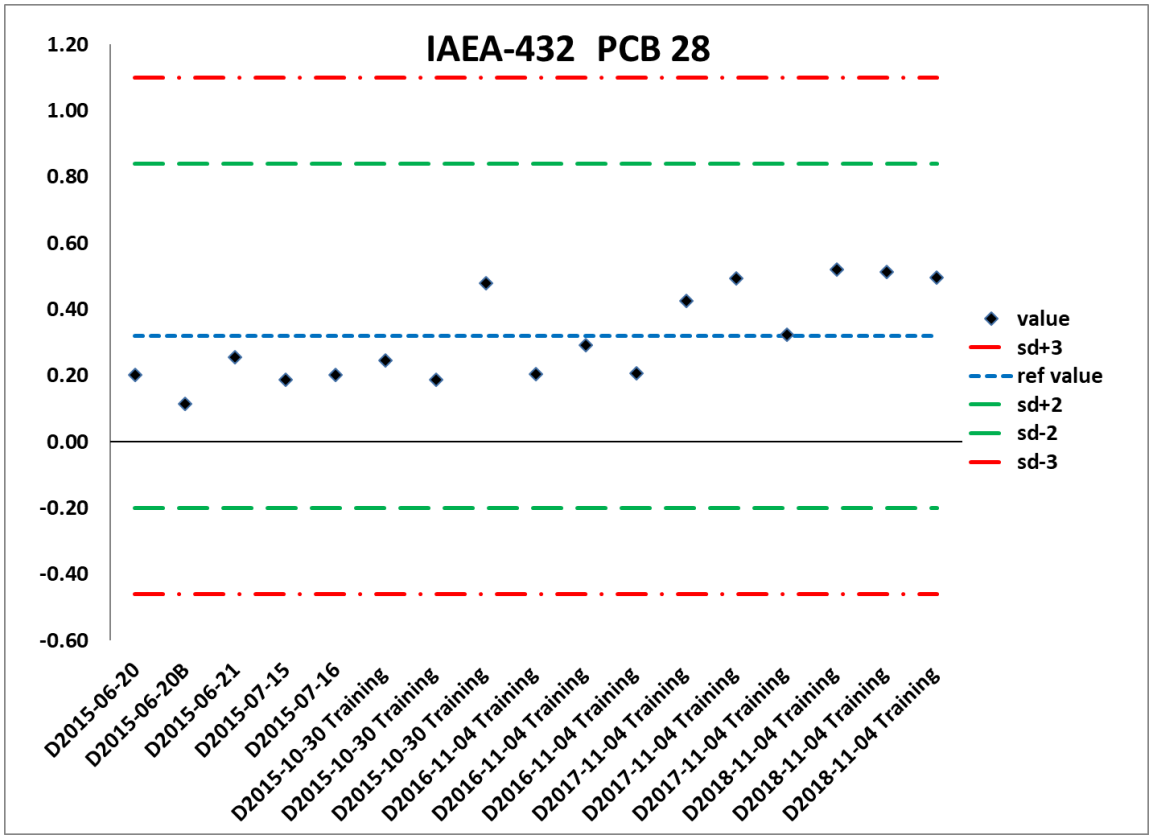
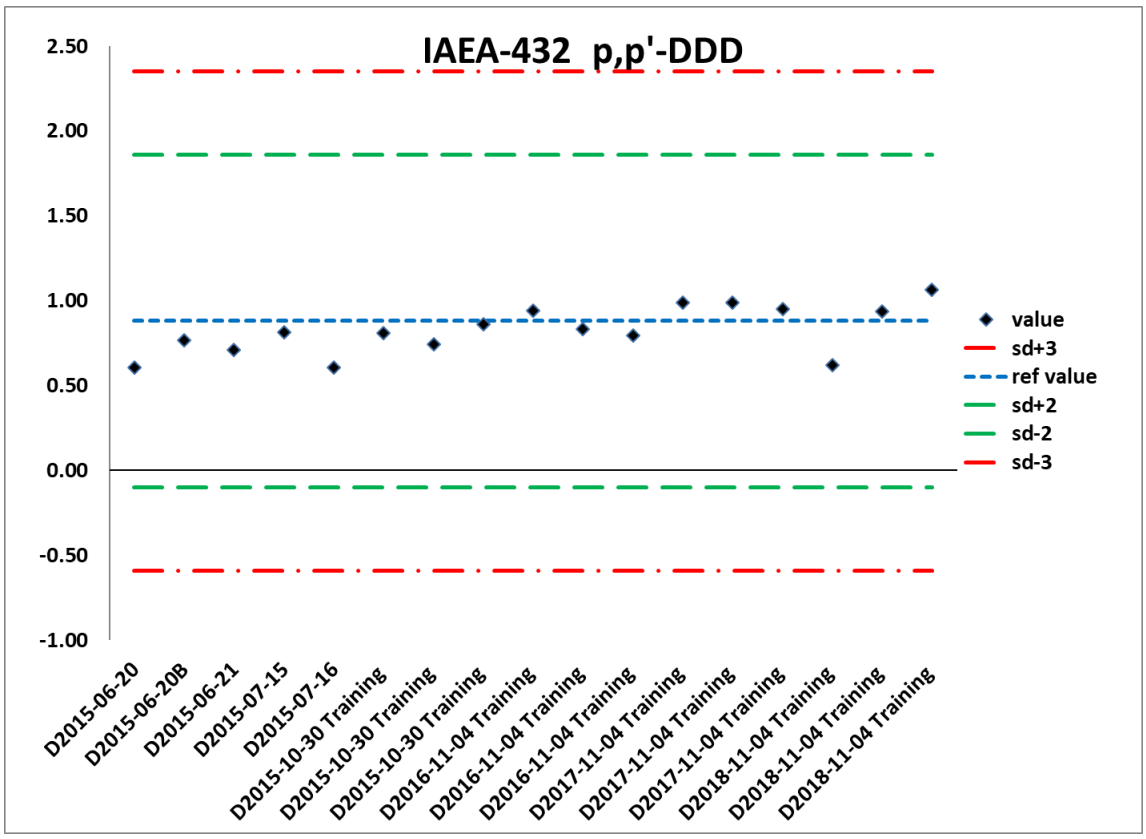


Figure 11. Quality control chart (QC) for p,p-'DDD in IAEA-432 biota reference material (ng/g d.w).



7.Summary of evaluations by participants

1. *What is your overall reaction to the workshop?*

[40%] Excellent [60%] Better than expected [ ] Satisfactory [ ] Poor

2. *Do you feel that the workshop 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 about your job thanks to this course?*

[100%] Yes [ ] 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 [2] Others *(specify) : PAH's*

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

[60%] Too many lectures [ ] Too many discussions [40%] Good

9. ***How helpful were the group exercises?***

[100%] Very helpful [ ] Helpful [ ] Not helpful

10. ***What do you think of the speed of the course?***

[20%] Too fast [80%] Just right [ ] Too slow

11. ***Did you have enough skills practice time?***

[100%] Yes [ ] No [ ] Uncertain

WORKSHOP CONTENT

15. How do you rate the workshop length?

[80%] Just right [20%] Too short [ ] Too long

16. What's your opinion on the workshop content sequence?

[100%] Very well sequenced [ ] Suitable [ ] Poorly sequenced

17. How valuable was the workshop content to your current job?

[100%] Very valuable [ ] Some value [ ] No real value

18. How do you rate the balance of theoretical and practical sessions?

[20%] Too theoretical [80%] Good balance [ ] Too practical

INSTRUCTIONAL MATERIAL

20. In your opinion, was the number of handouts you received sufficient?

[100%] Just right [ ] Too few [ ] Too many

21. How do you rate the quality of the handout material?

[20%] High quality [80%] Sufficient [ ] Below expectations

LABORATORY AND FACILITIES

22. How do you rate the laboratory sessions?

[80%] Excellent [20%] Very good [ ] Good [ ] Fair [ ] Poor

24. Did you like the seating arrangements of the class room?

[80%] Yes [ ] No [20%] Uncertain

25. How do you rate the service (breaks, lunch, etc.)?

[40%] Excellent [60%] Very Good [40%] Good [ ] Fair [ ] Poor

26. What is your overall evaluation of the course?

[80%] Excellent [20%] Very good [] Good [ ] Fair [ ] Poor

Note: Questions that required comments were not reported.