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

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IAEA
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Laboratories

REPORT

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

2019

Prepared in collaboration with:

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1. INTRODUCTION

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

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

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

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

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

2. SCOPE OF EXERCISE

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

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

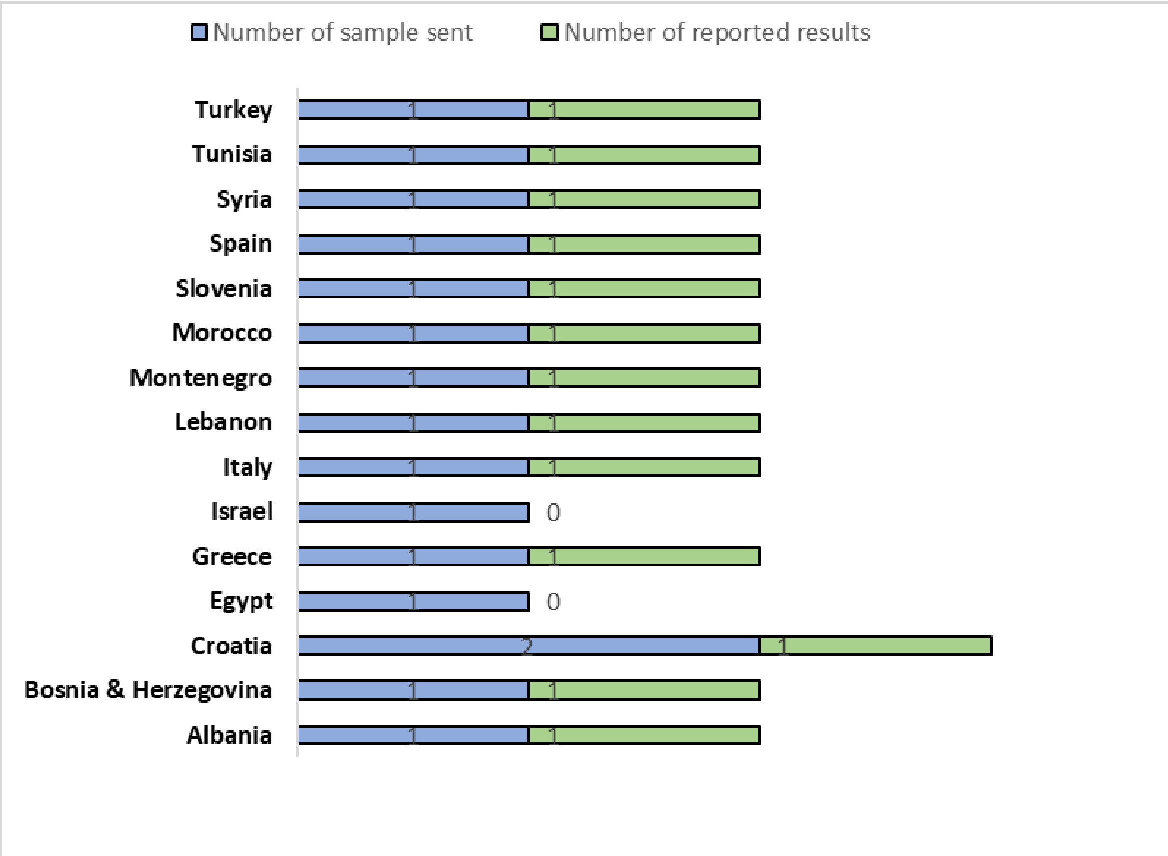


Figure. 1. Distribution per country of the MED POL PT sample

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

3. MATERIAL

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

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

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

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

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

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

4. RESULTS AND EVALUATION

4.1. Data Reporting

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

4.2. Overview of Reported Analysis Results and Analytical Procedures

Participants' results for organochlorine pesticides and PCB congeners are listed in TABLE 1 and the results for PAHs in TABLE 2. In both tables the assigned and information values are indicated along with the "total error" for each compound.

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

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

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

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

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

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

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

All results are in ng/g dry weight.

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

* Information value.

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

All results are in ng/g dry weight.

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

* Information value.

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

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

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

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

*With dual column confirmation

TABLE 5. Treatment of samples performed by participants for PAHs

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

TABLE 6. Instrumental conditions used by participants for PAHs

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

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

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

TABLE 8. Quality parameters for PAHs.

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

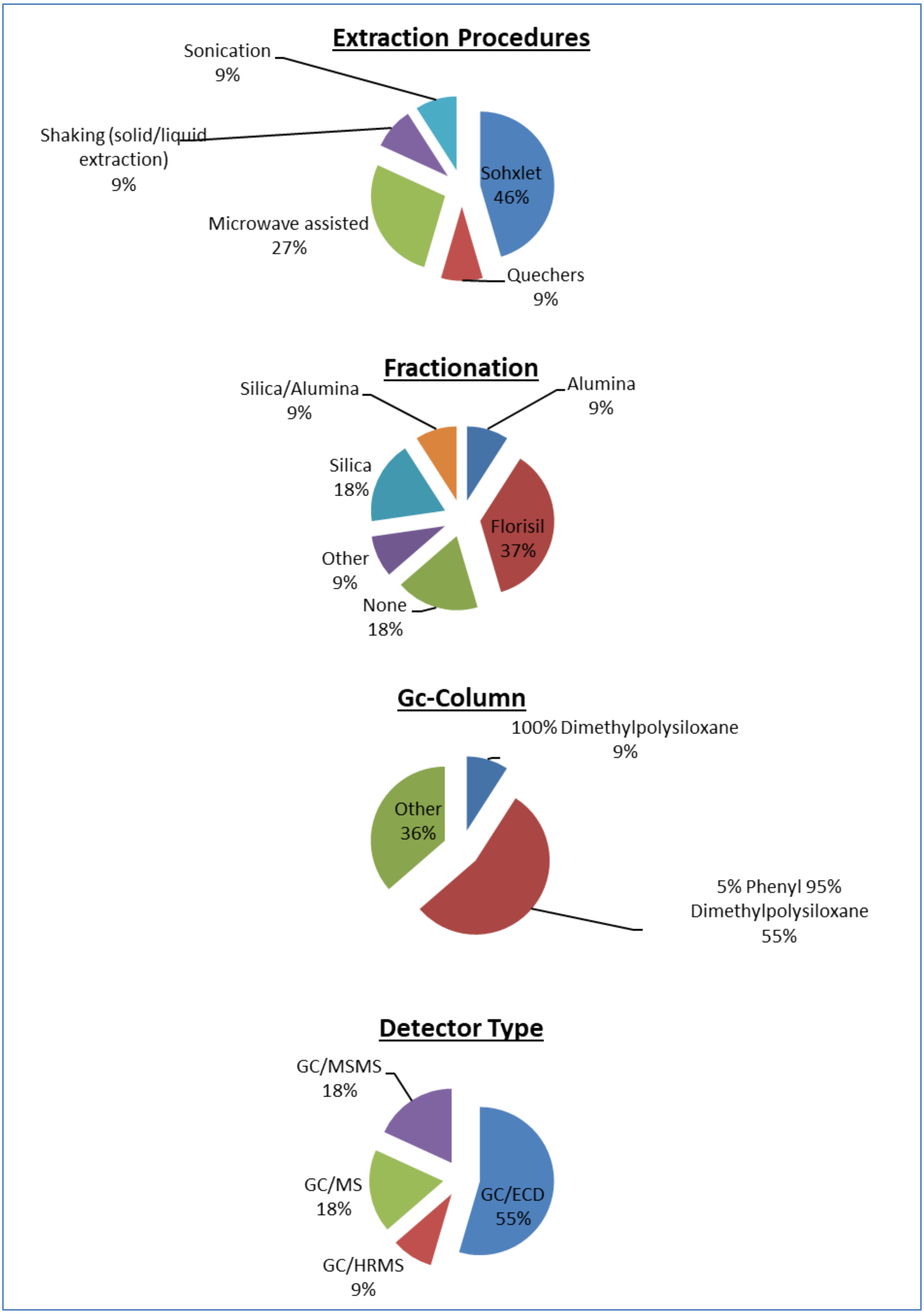


Figure 2. Graphic representation of sample treatment and instrumental conditions for organochlorine pesticides and PCB congeners.

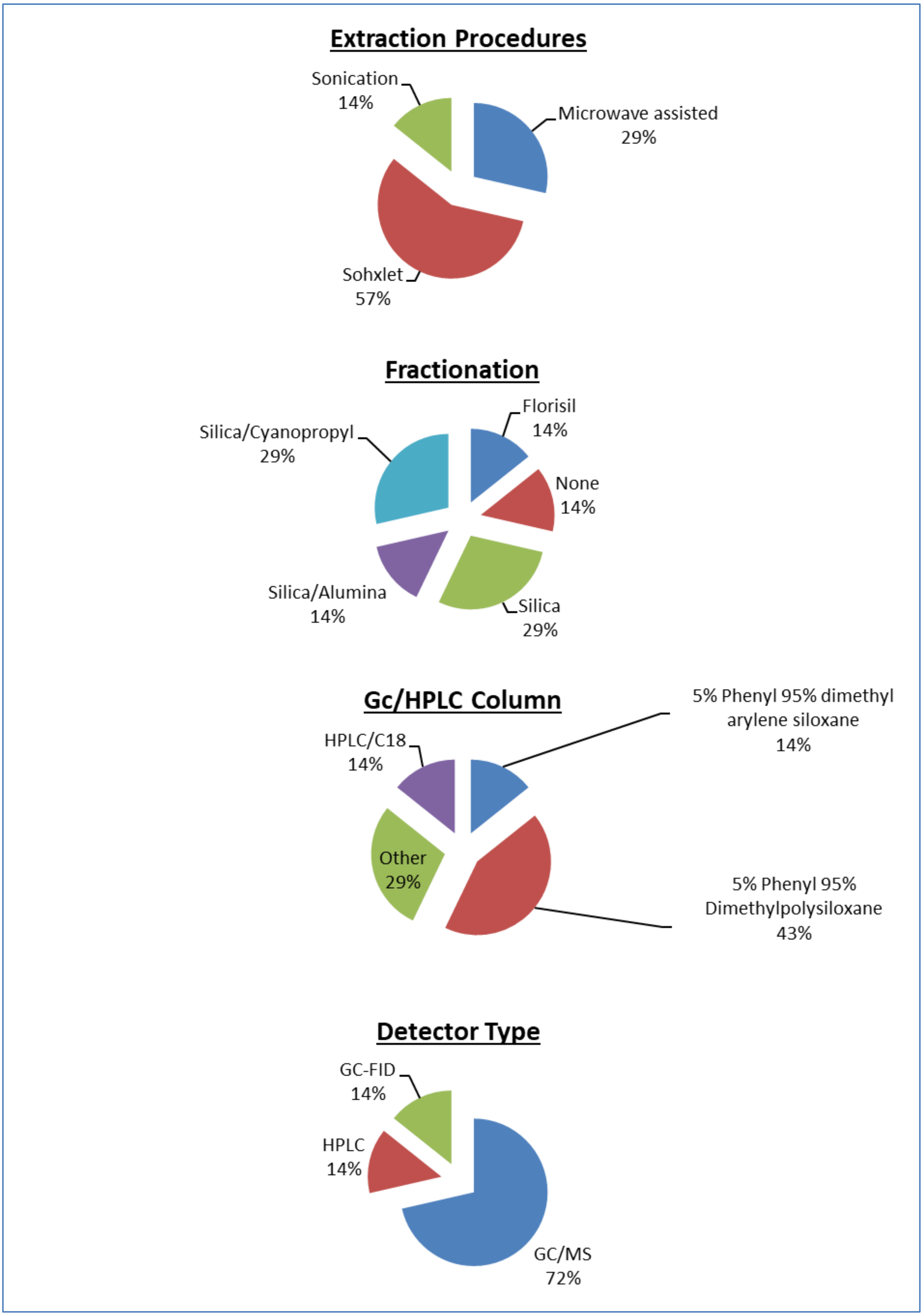


Figure 3. Graphic representation of sample treatment and instrumental conditions for PAHs

4.3. Evaluation Criteria

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

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

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

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

Where:

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

Performance is considered acceptable if $|z| \leq 2$.
The measurement is regarded as questionable if $2 < |z| < 3$.
The measurement is regarded as out of control when $|z| \geq 3$.
This score represents a simple method of giving each participant a normalized performance score for bias. The procedure has been accepted as a standard by ISO/IUPAC [3, 4, 5].

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

4.4. Laboratory Results and Scoring

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

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

TABLE 10. Z-scores for PAHs

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

5. EVALUATION OF RESULTS

5.1. Organochlorine Pesticides and PCB Congeners

Among all designated laboratories, 75% submitted results for organochlorine pesticides and PCB congeners.
Ten participants to the current PT reported to have a QA/QC system in place in their laboratory and 5 laboratories reported to use validated methods. More than 50% use internal standards/surrogates, and 5 laboratories reported their QA/QC results along with the test results. Laboratory number 30 provided all acceptable results. Four laboratories (27, 28, 31 and 34) reported more than 50% of acceptable results. Four laboratories (20, 24, 26 and 32) provided more than 50% of results "out of control".

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

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

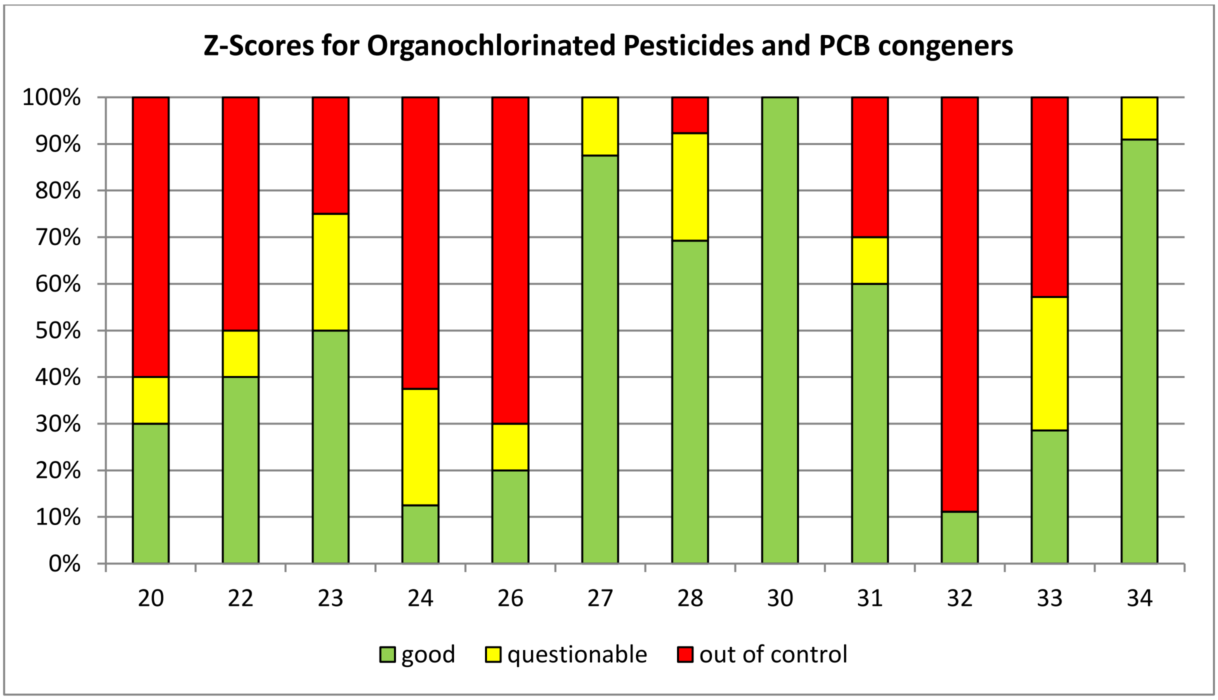


Figure 4. Graphic representation of laboratories z-scores for organochlorine pesticides and PCB congeners.

5.2. PAHs

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

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

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

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

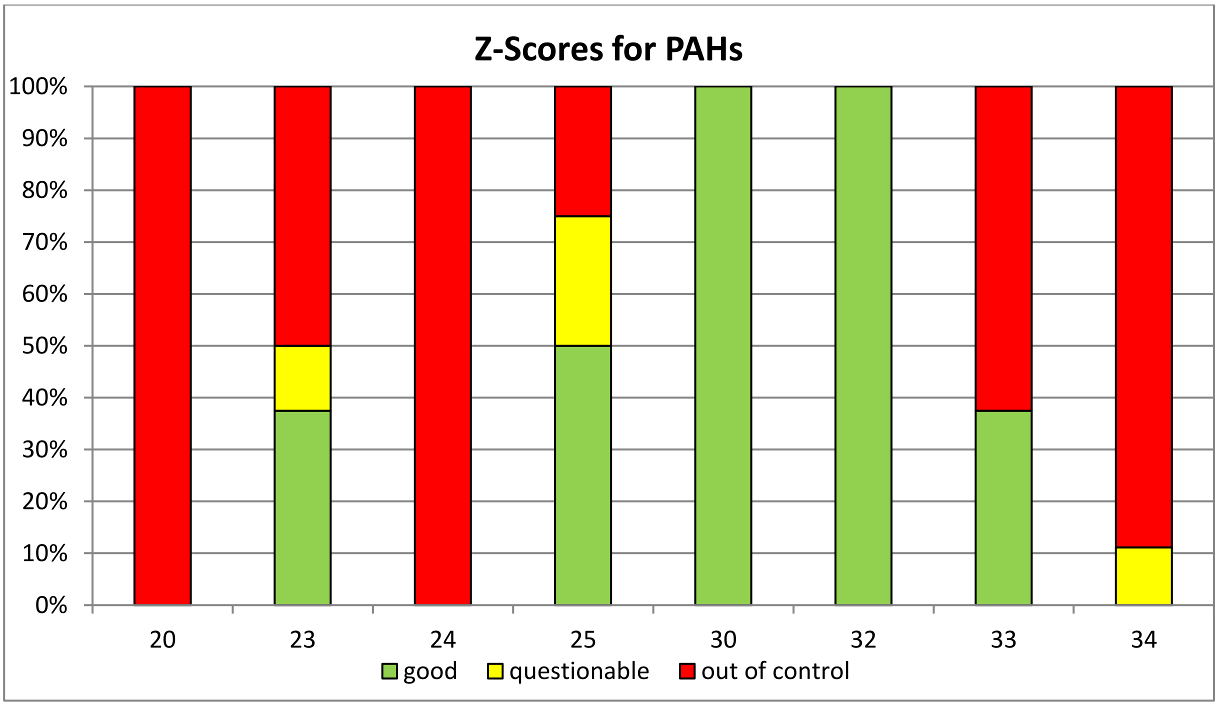


Figure 5. Graphic representation of laboratories z-scores for PAHs.

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

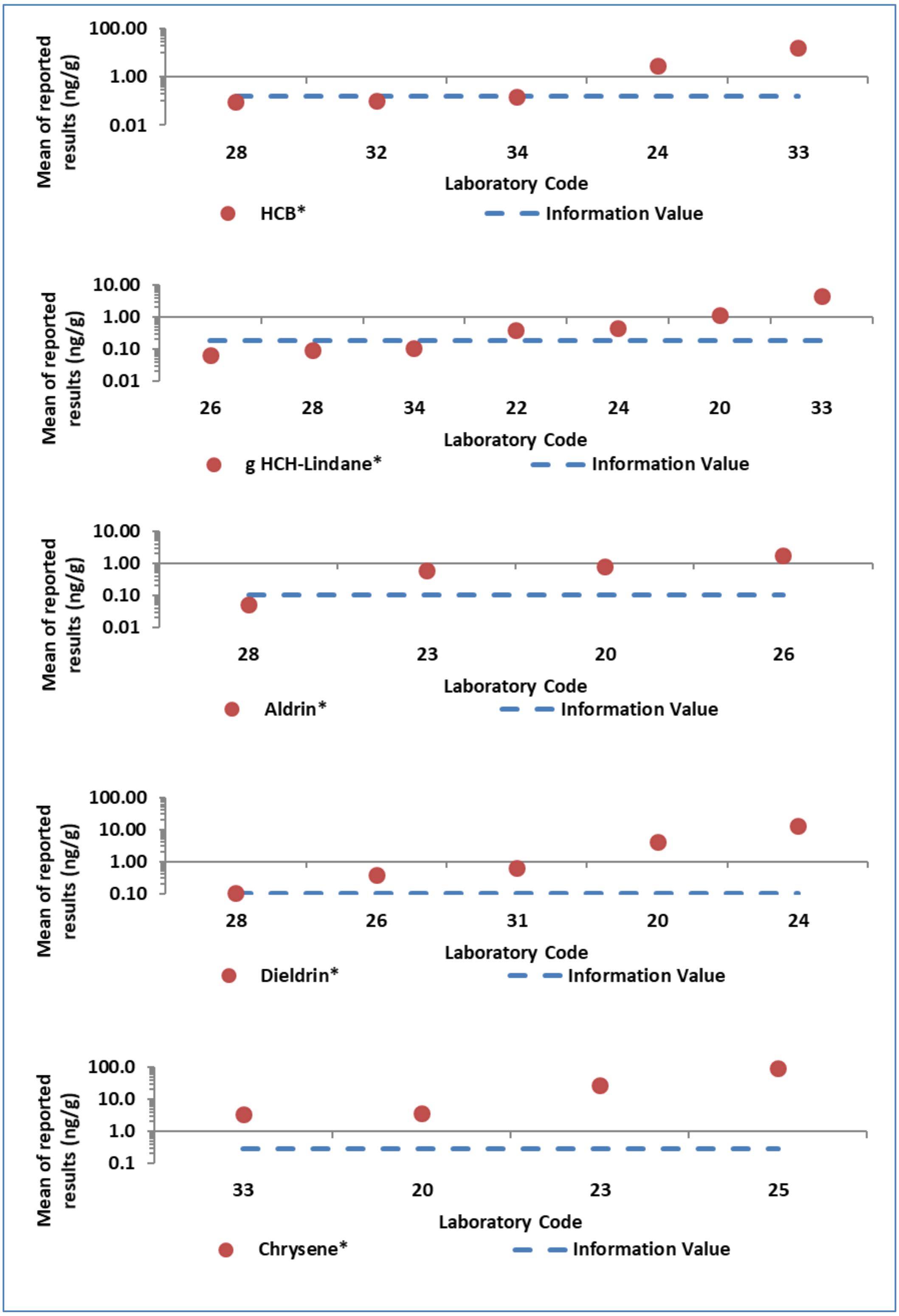


Figure.6. "Information values" reported by participants for organochlorine pesticides, PCB congeners and PAHs.

6. CONCLUSIONS AND RECOMMENDATIONS

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

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

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

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

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

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

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

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

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

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

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

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

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

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

7. REFERENCES

[1] INTERNATIONAL ATOMIC ENERGY AGENCY, (IAEA/AQ/52) (2017). Certification of mass fractions of polycyclic aromatic hydrocarbons, organochlorines and polybrominated diphenyl ethers in IAEA-459 marine sediment sample, IAEA Analytical Quality in Nuclear Applications Series No. 52, IAEA, Vienna

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

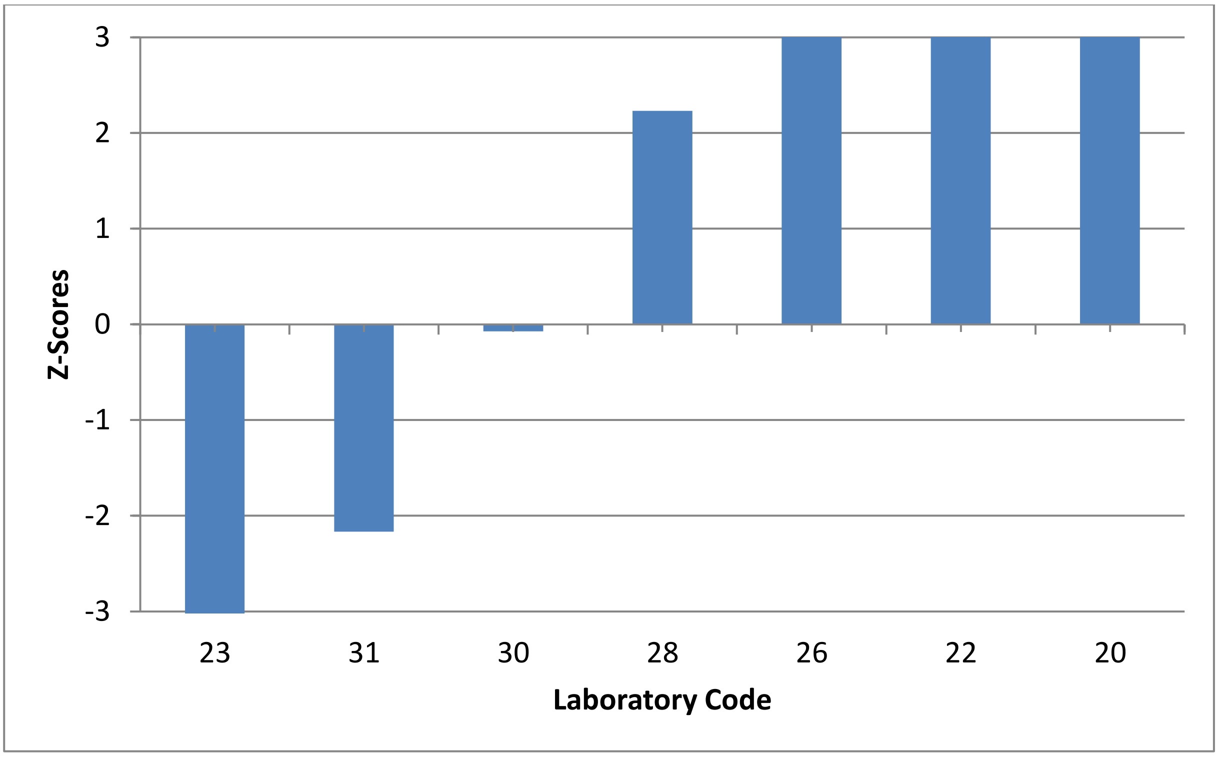
[3] INTERNATIONAL ORGANISATION FOR STANDARDISATION, Guide 13528 (2005), Statistical Methods for Use in Proficiency Testing by Interlaboratory Comparisons, ISO, Geneva, Switzerland.

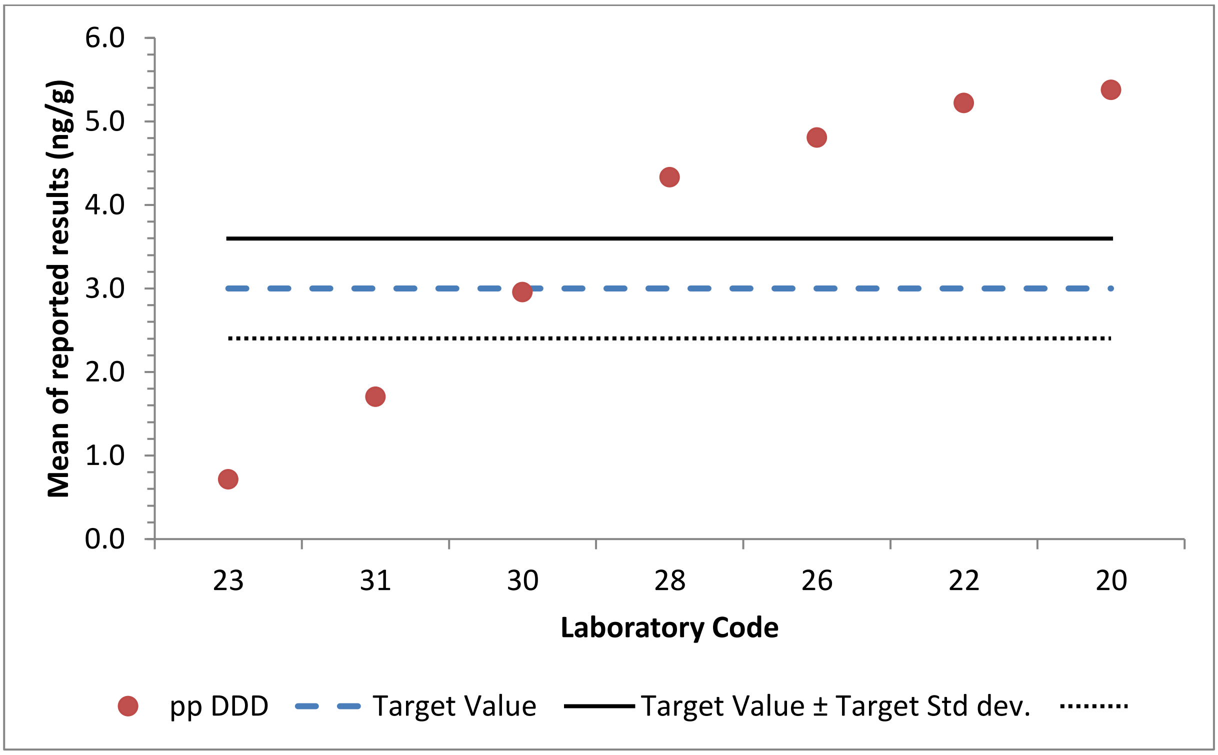
[4] Thompson and R. Wood (1993). The international harmonized protocol for the proficiency testing of (chemical) analytical laboratories. IUPAC/ISO/AOAC. *J. Pure. Appl. Chem*. **65**(9), 2123-2144.

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

Annex 1: Graphic Representation of Laboratories Performances

GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR pp'DDD





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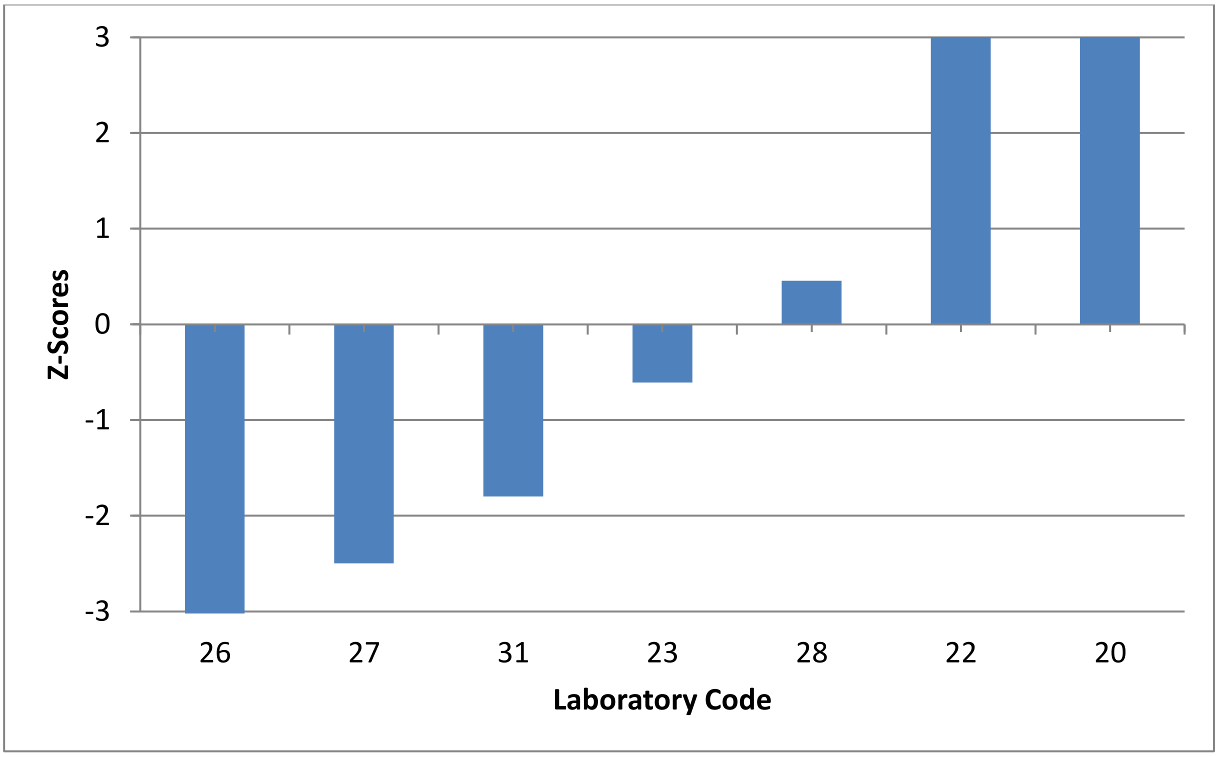

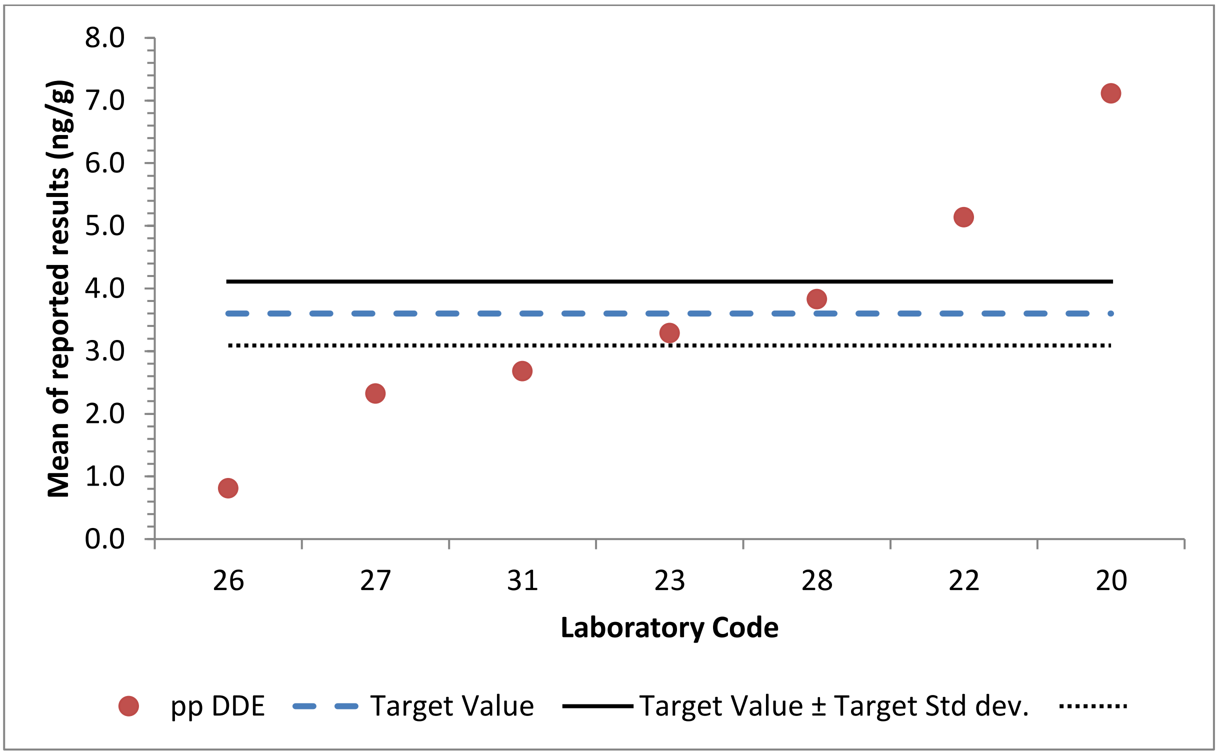

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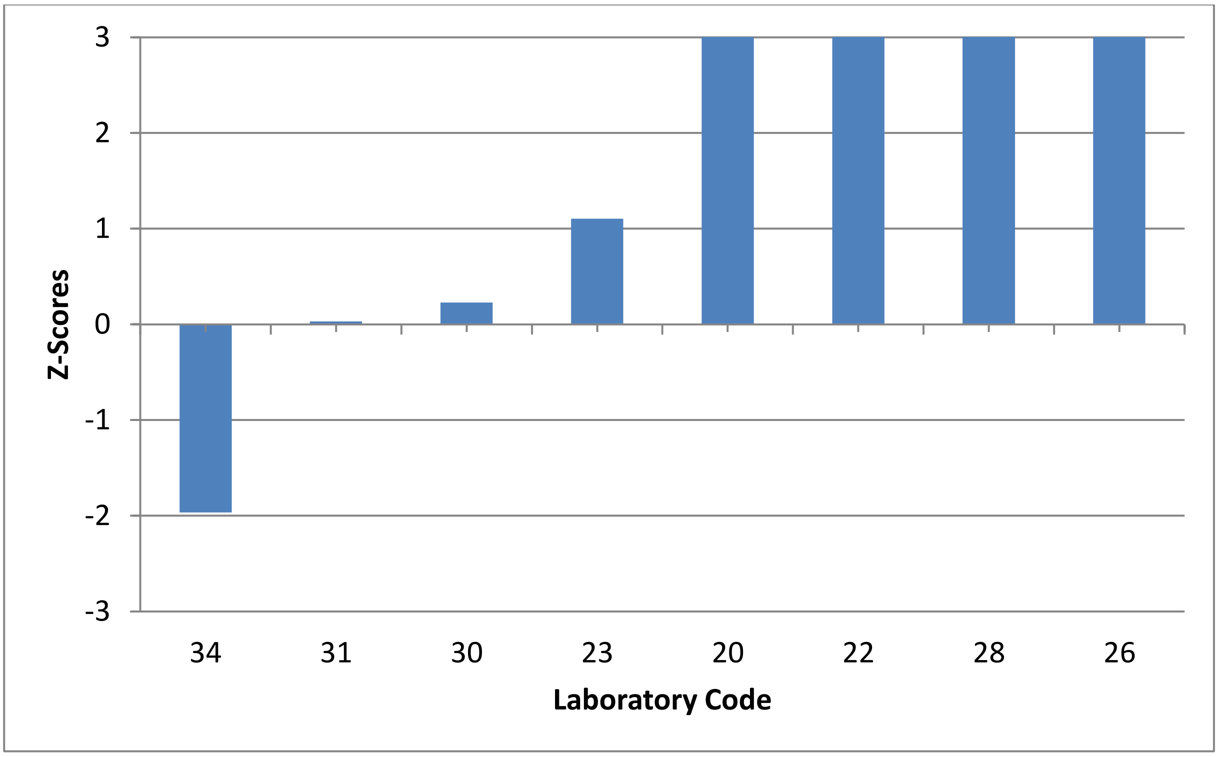

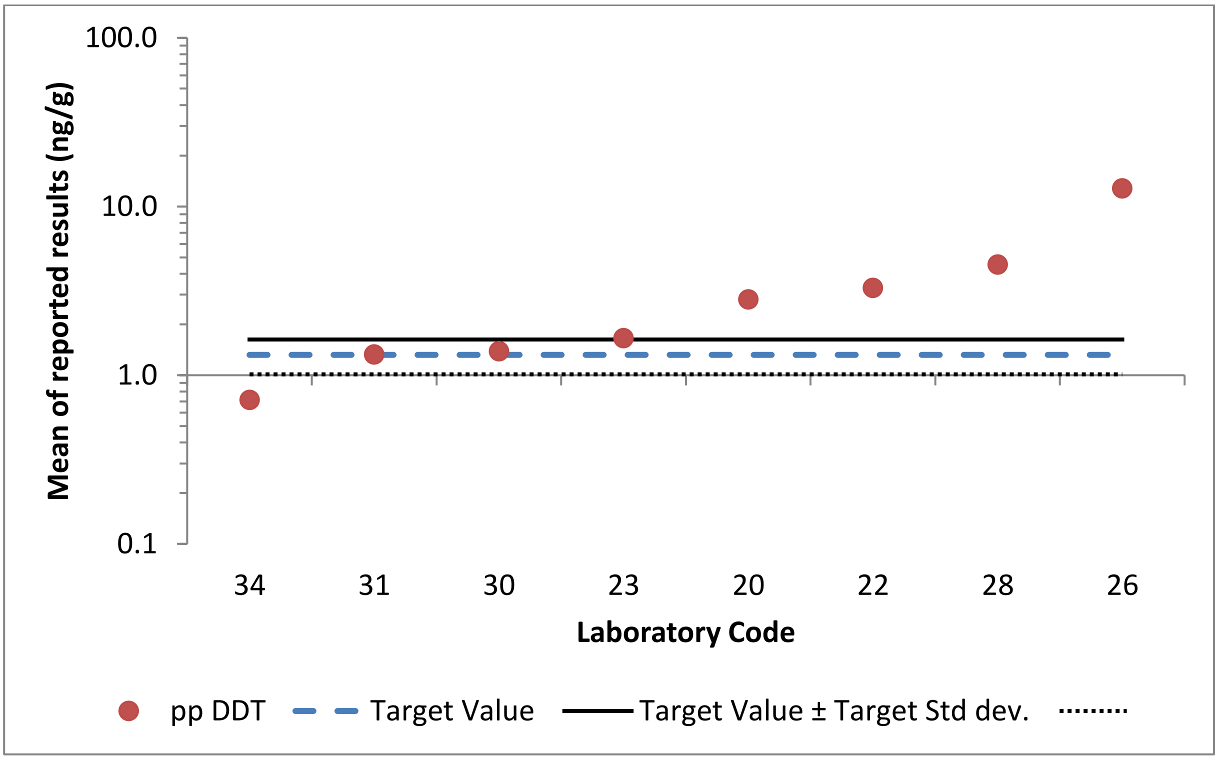

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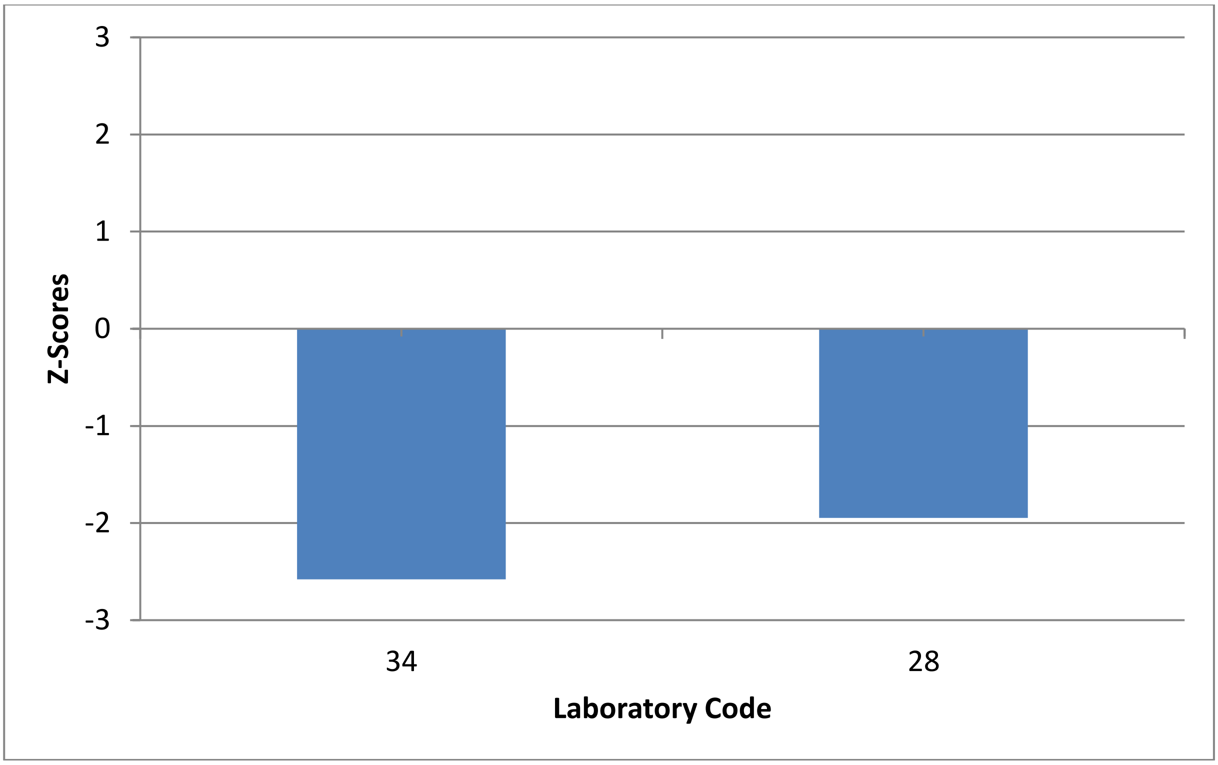
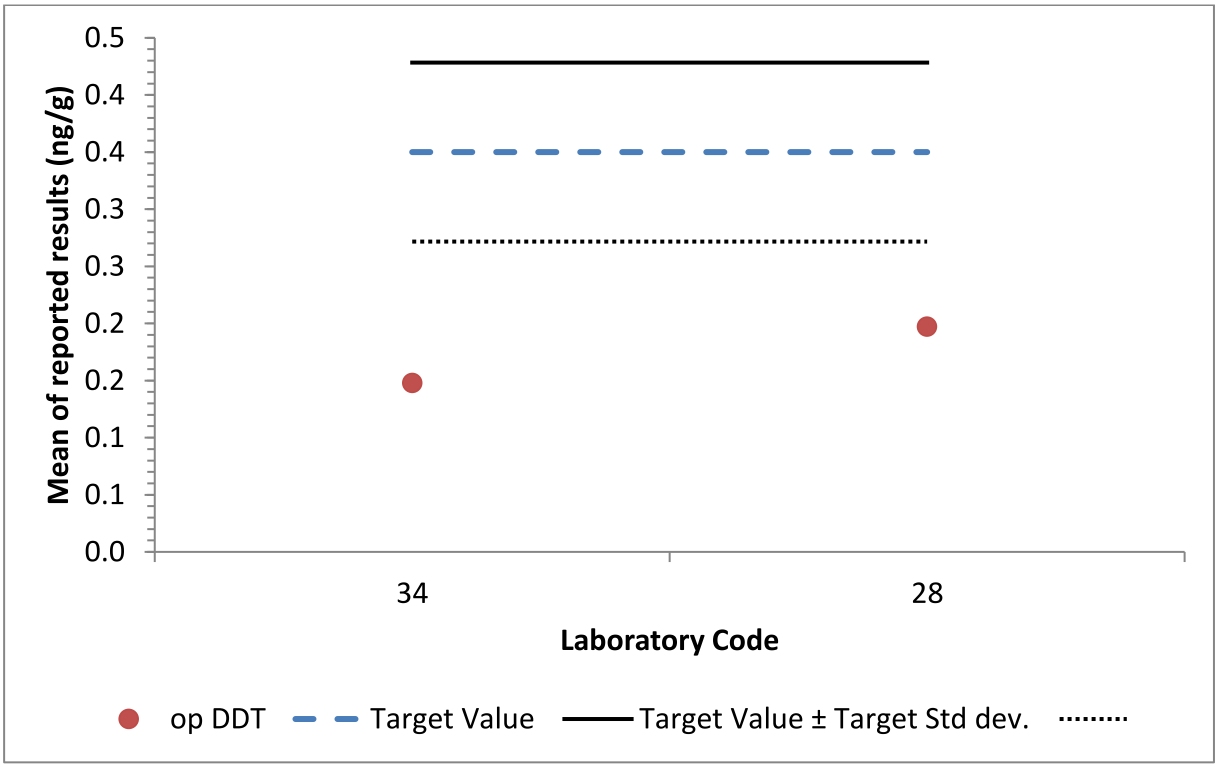
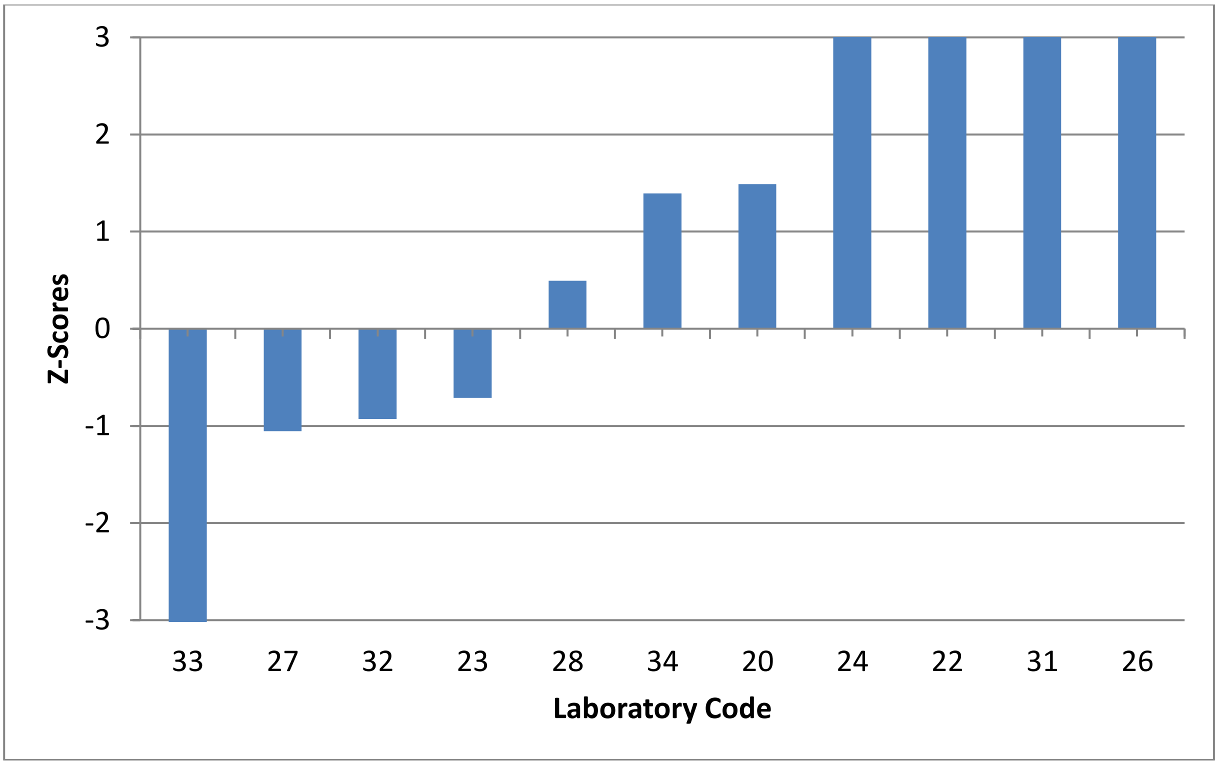
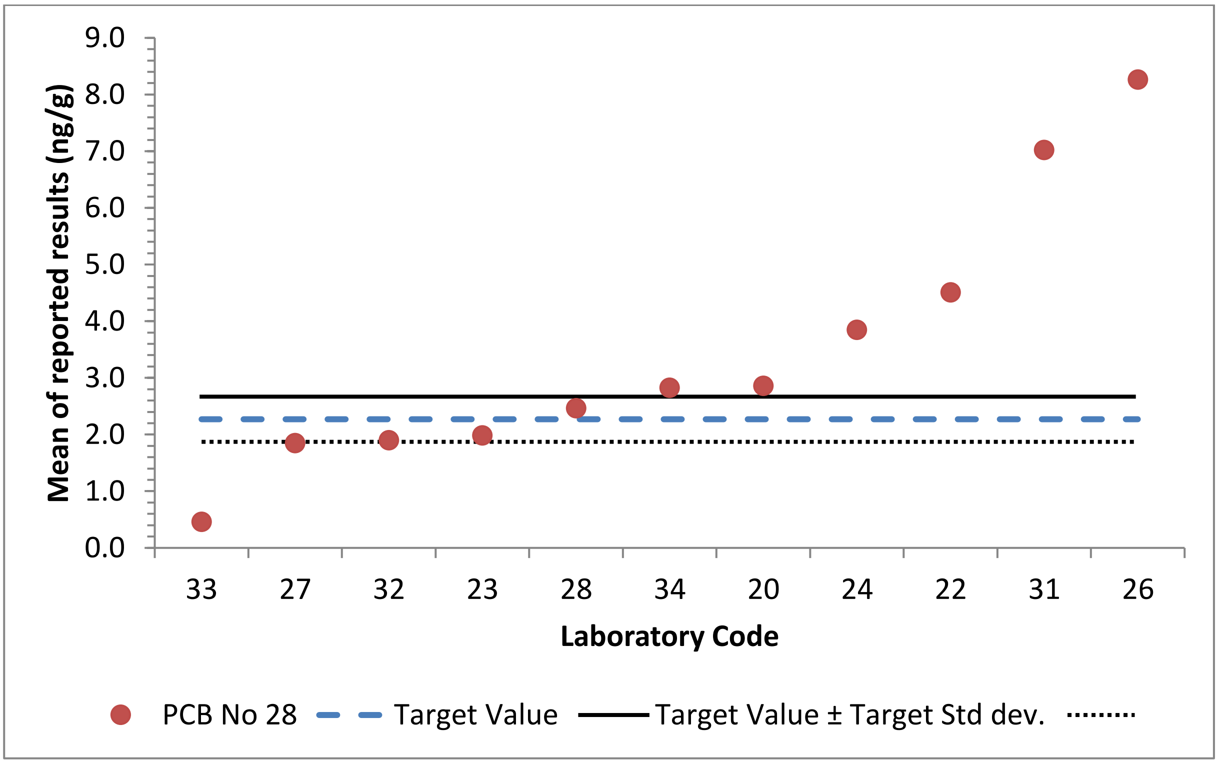




GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR PCB 28





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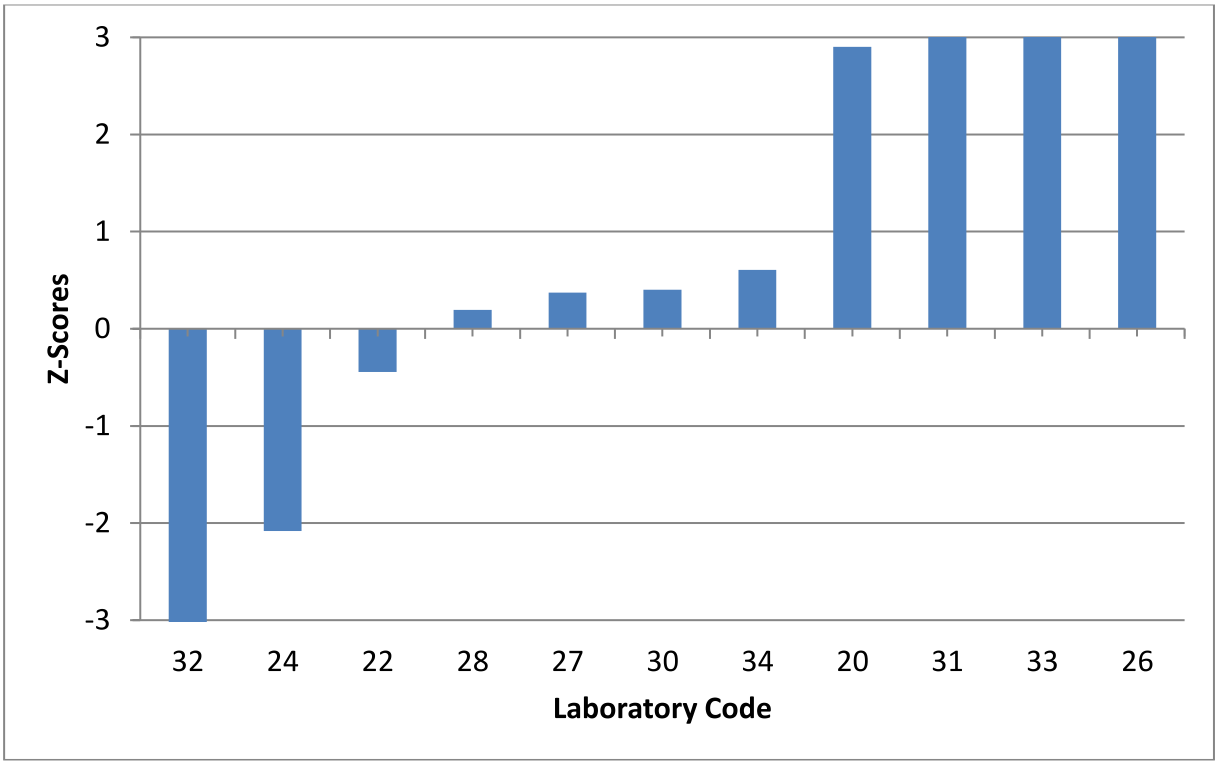

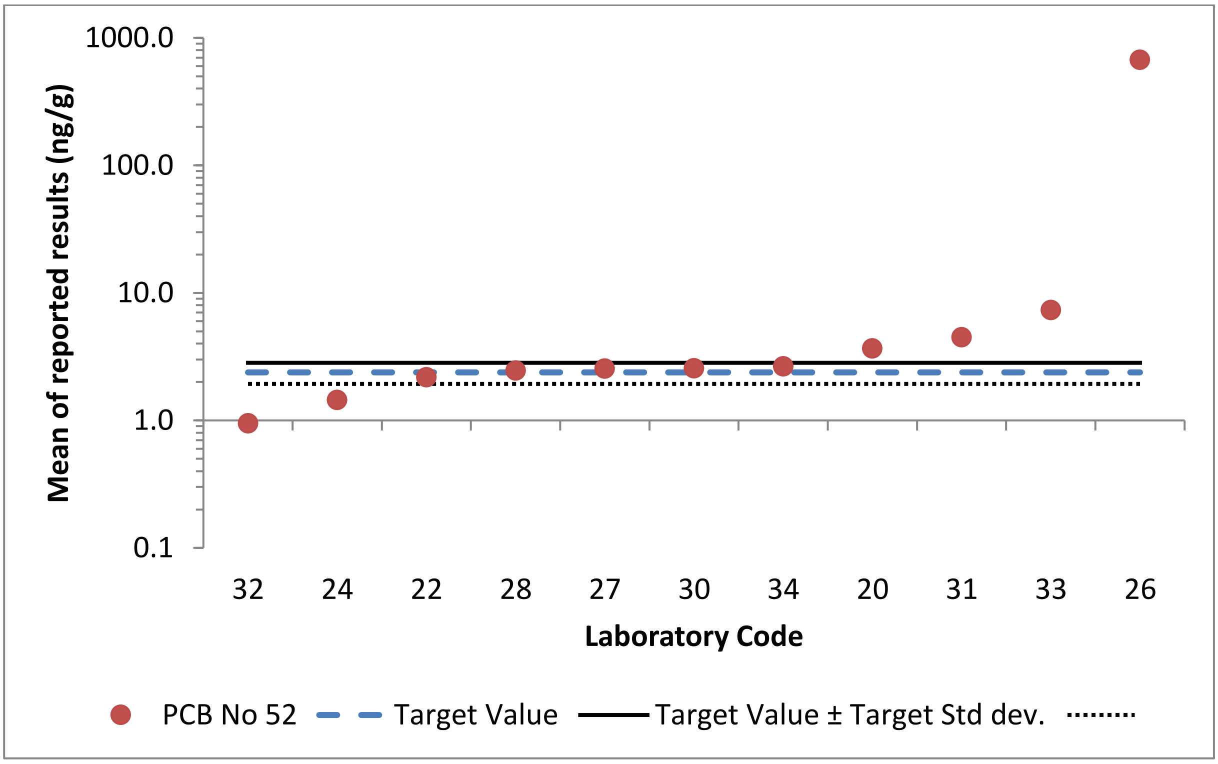

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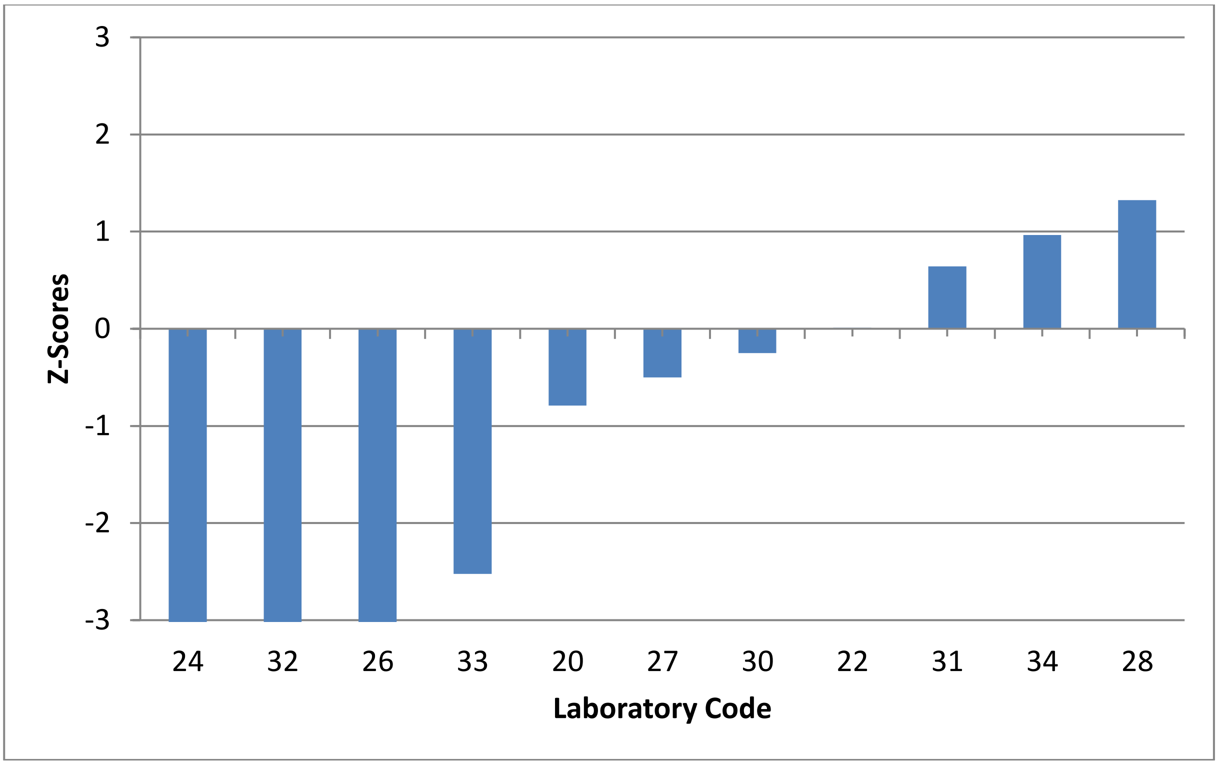

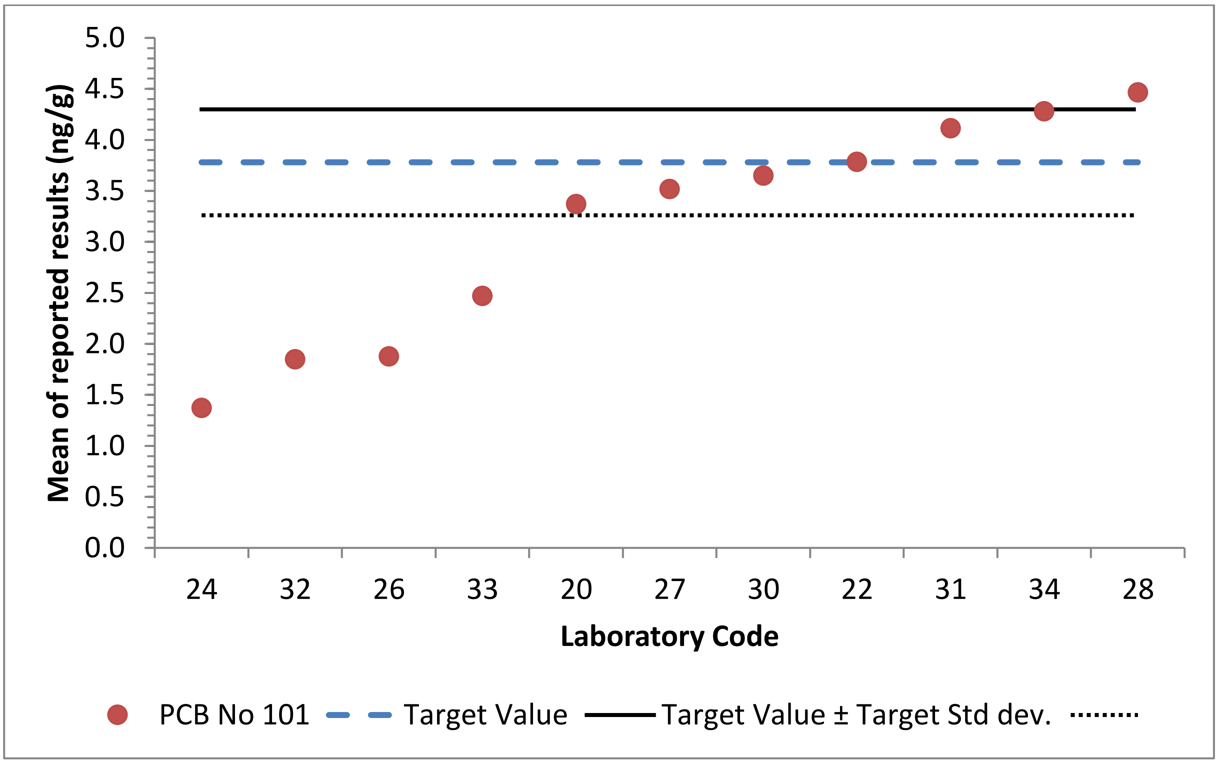

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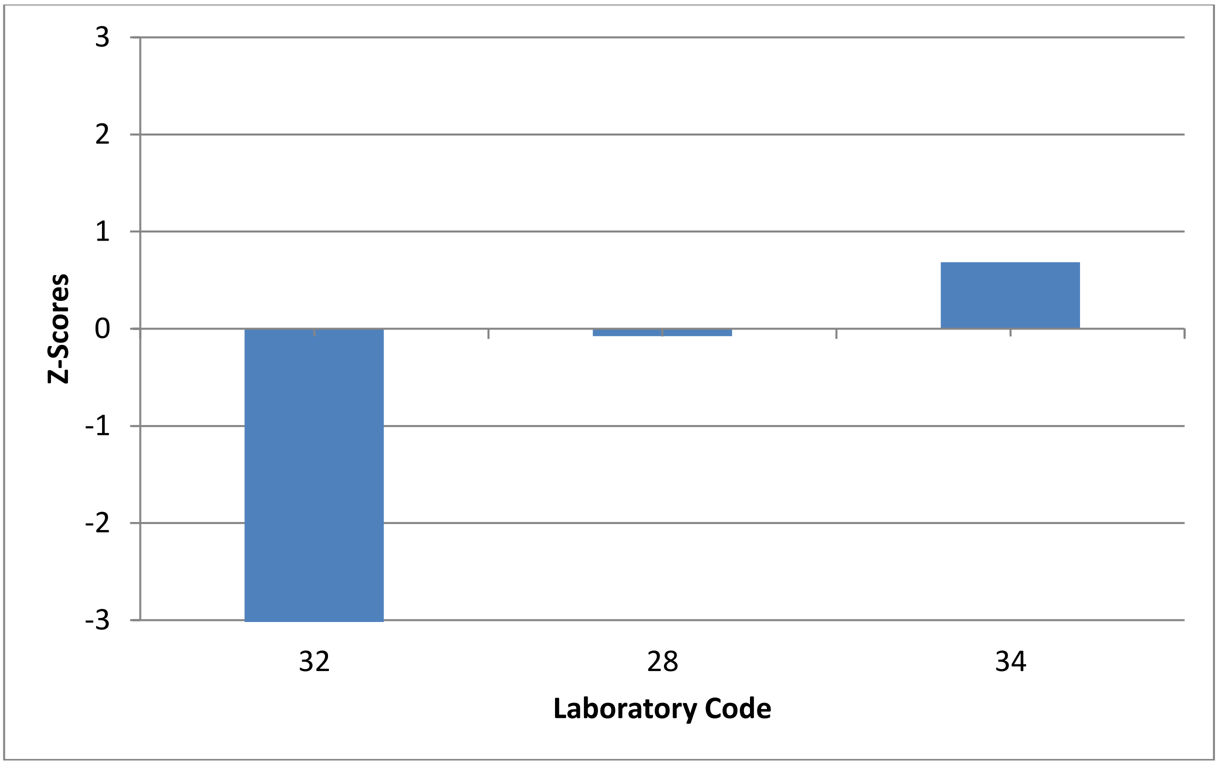

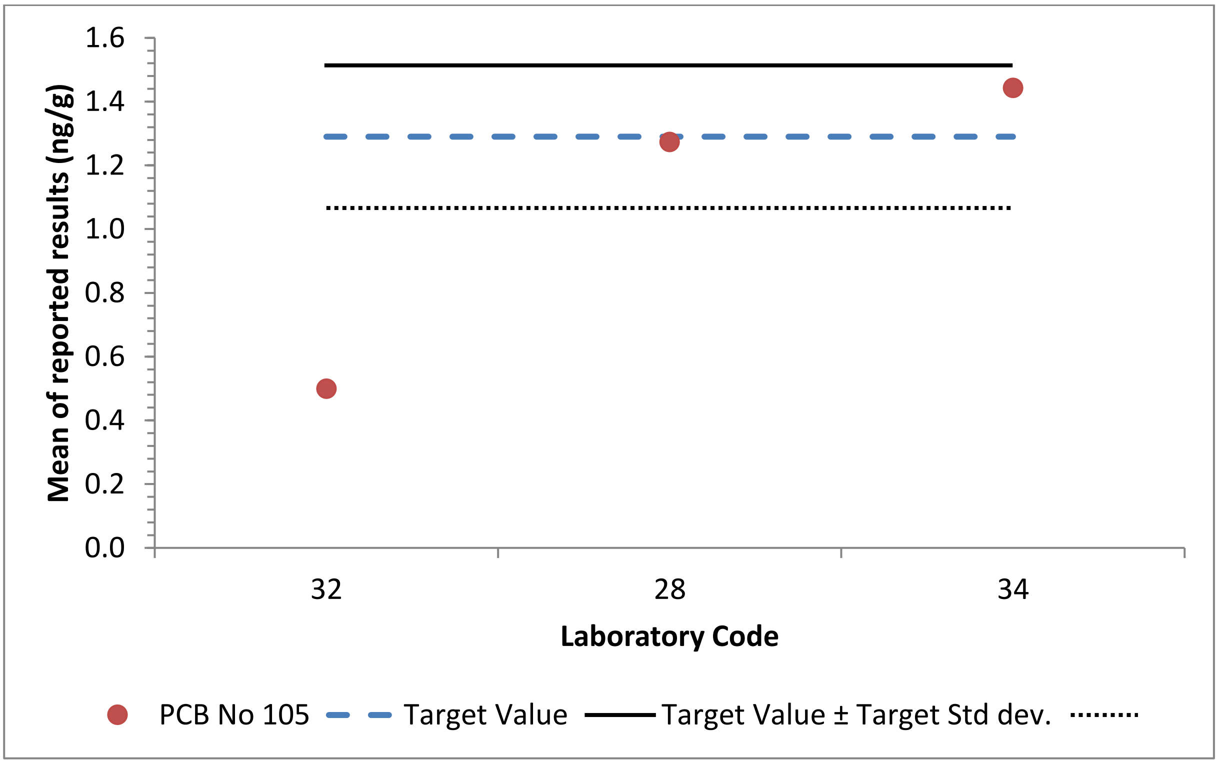

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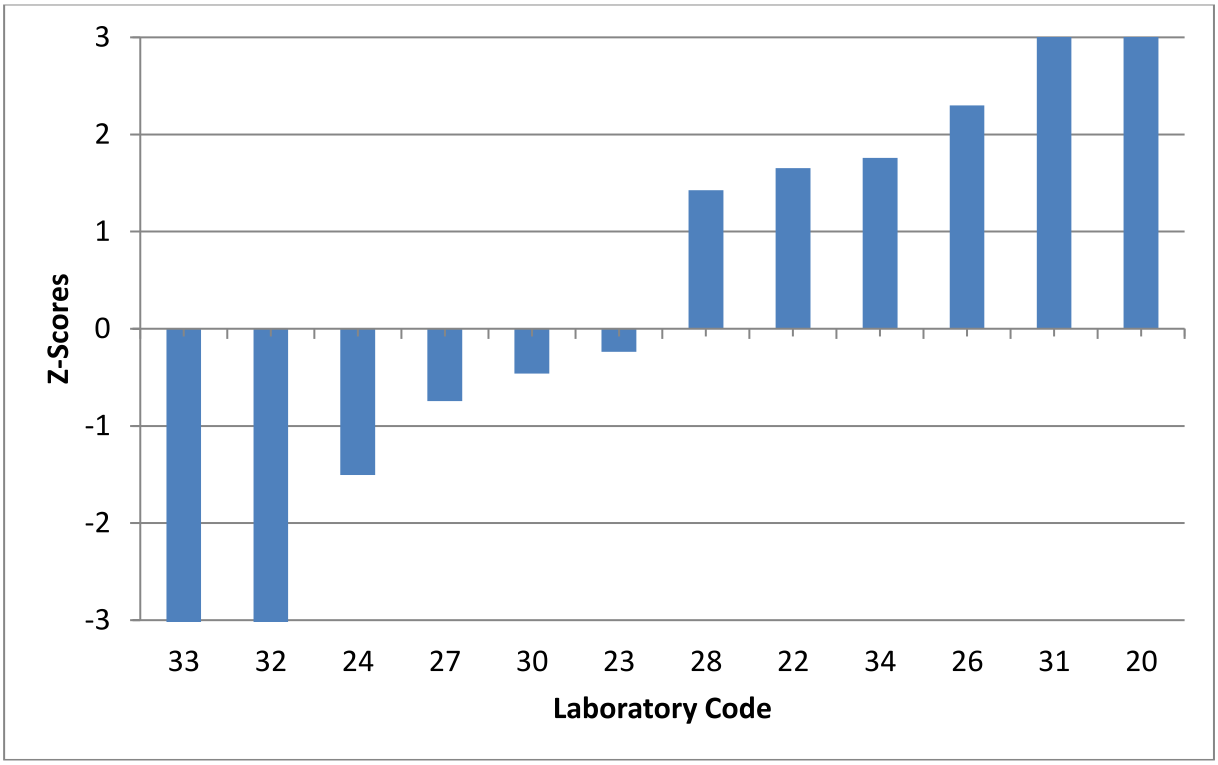

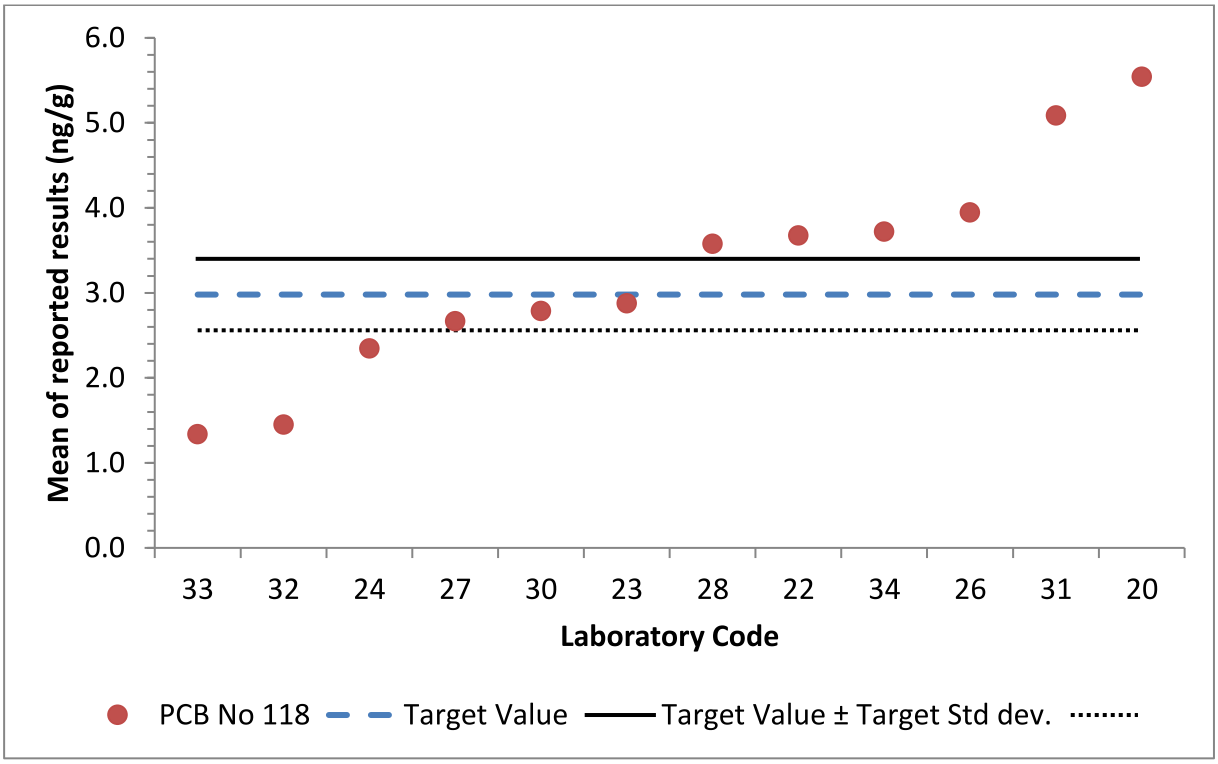

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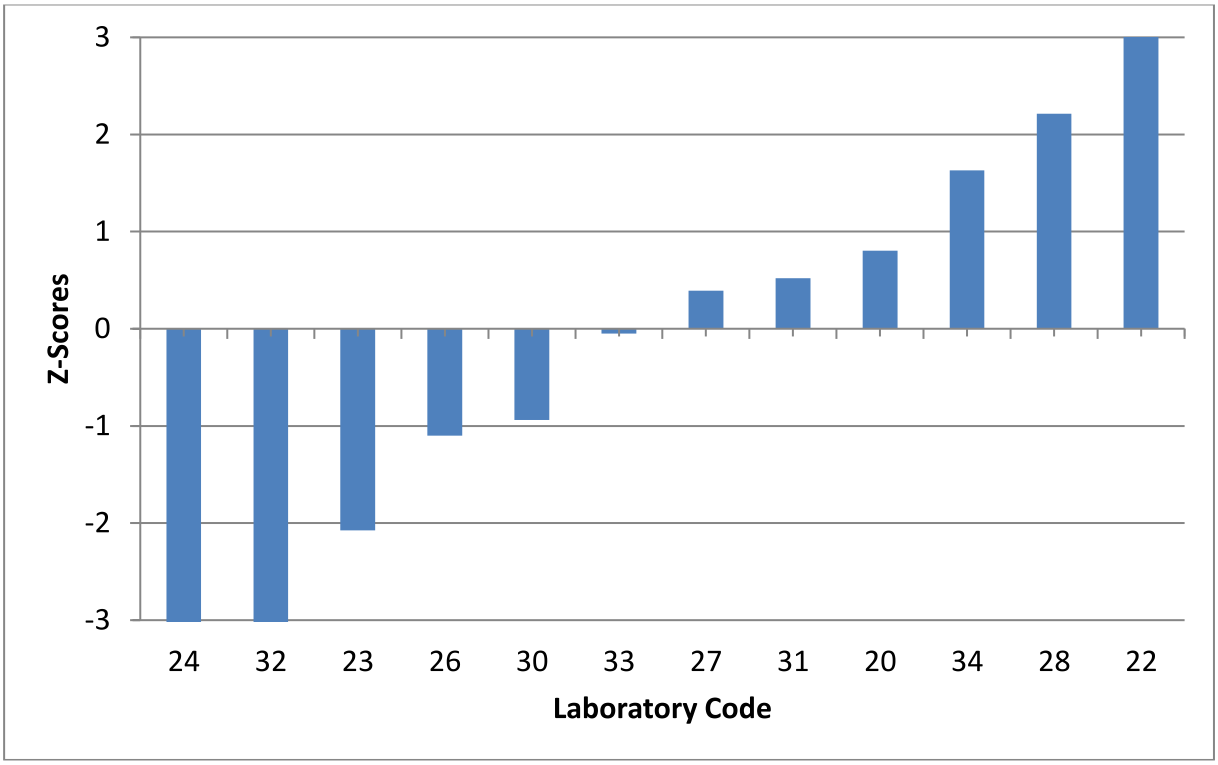

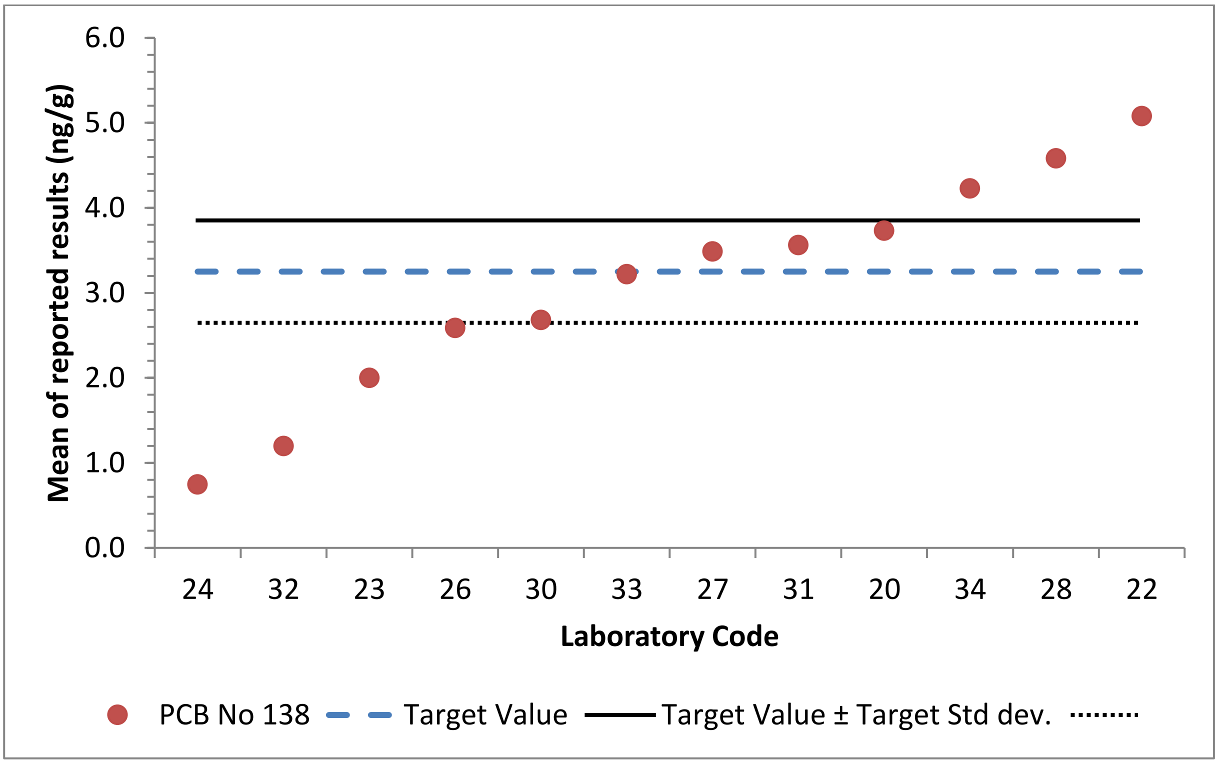

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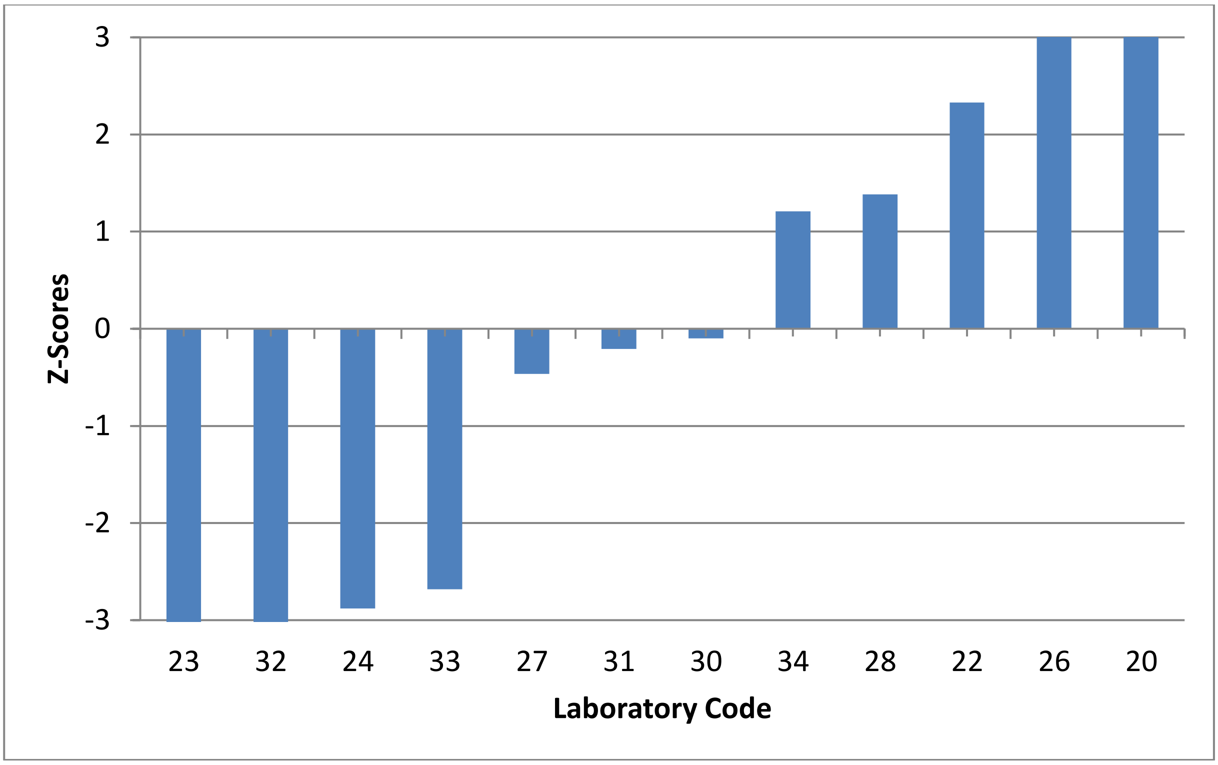

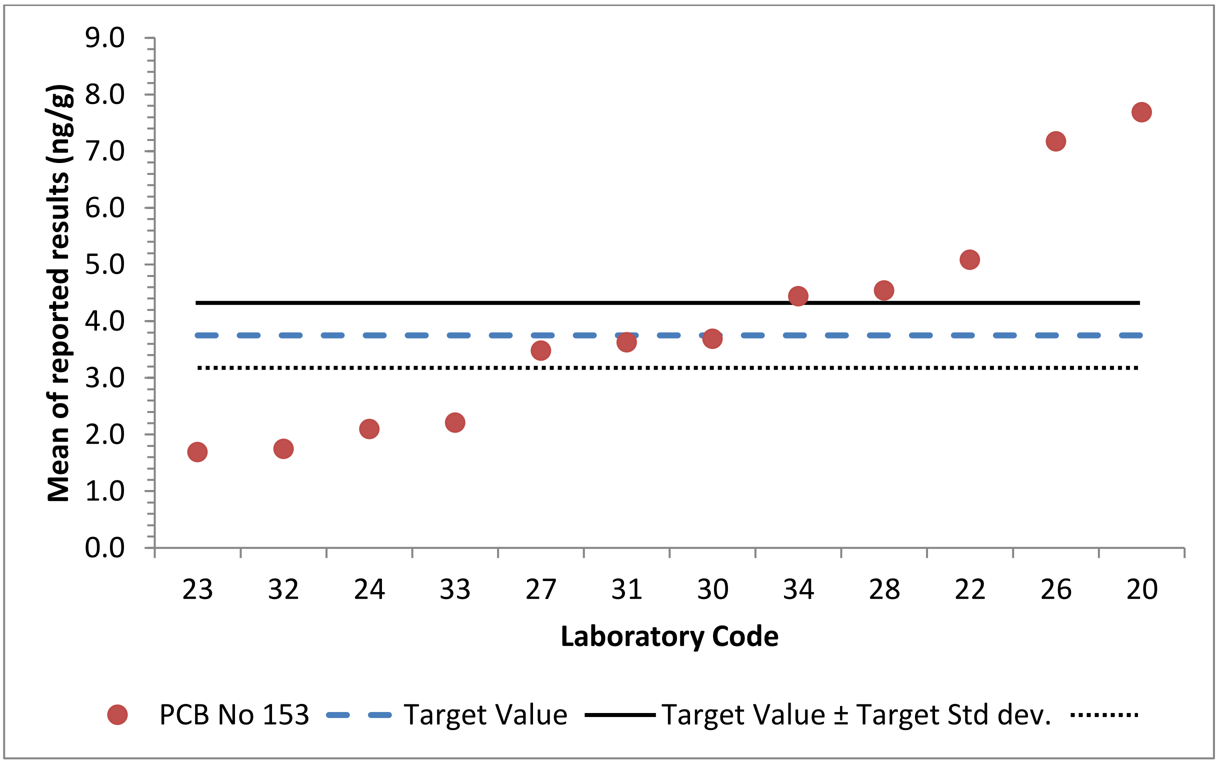

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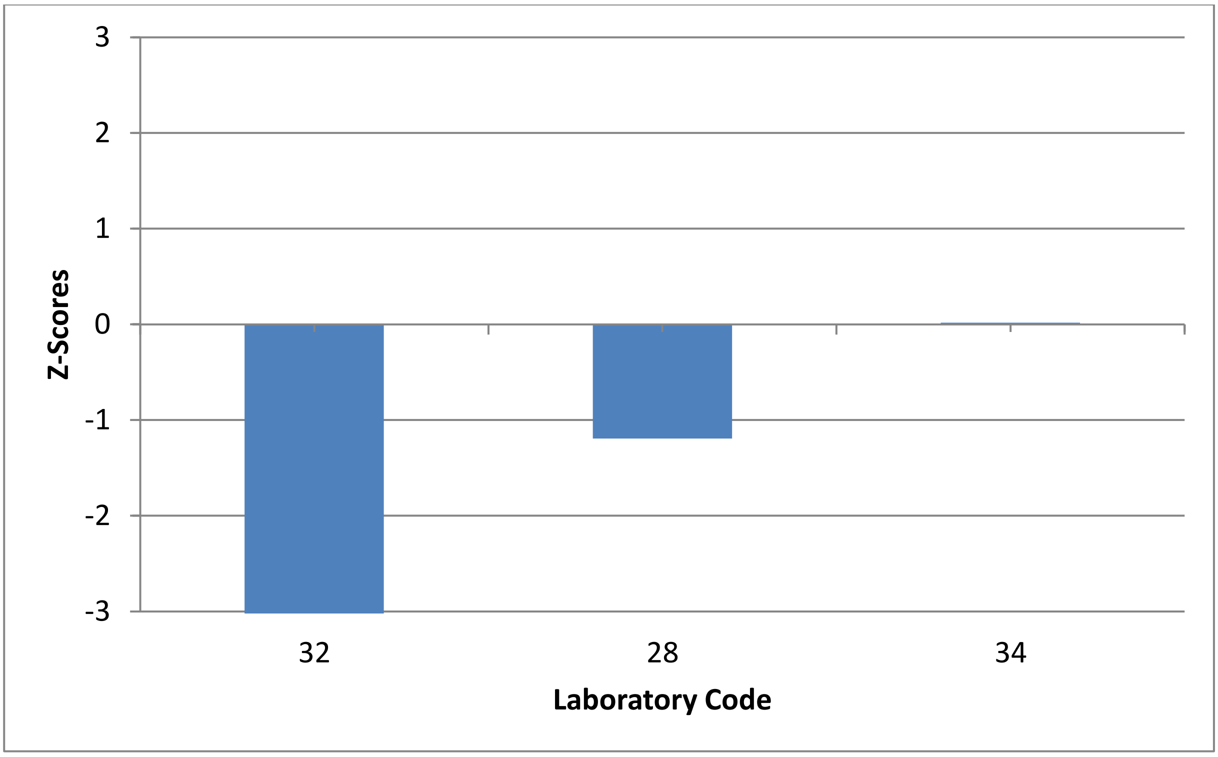

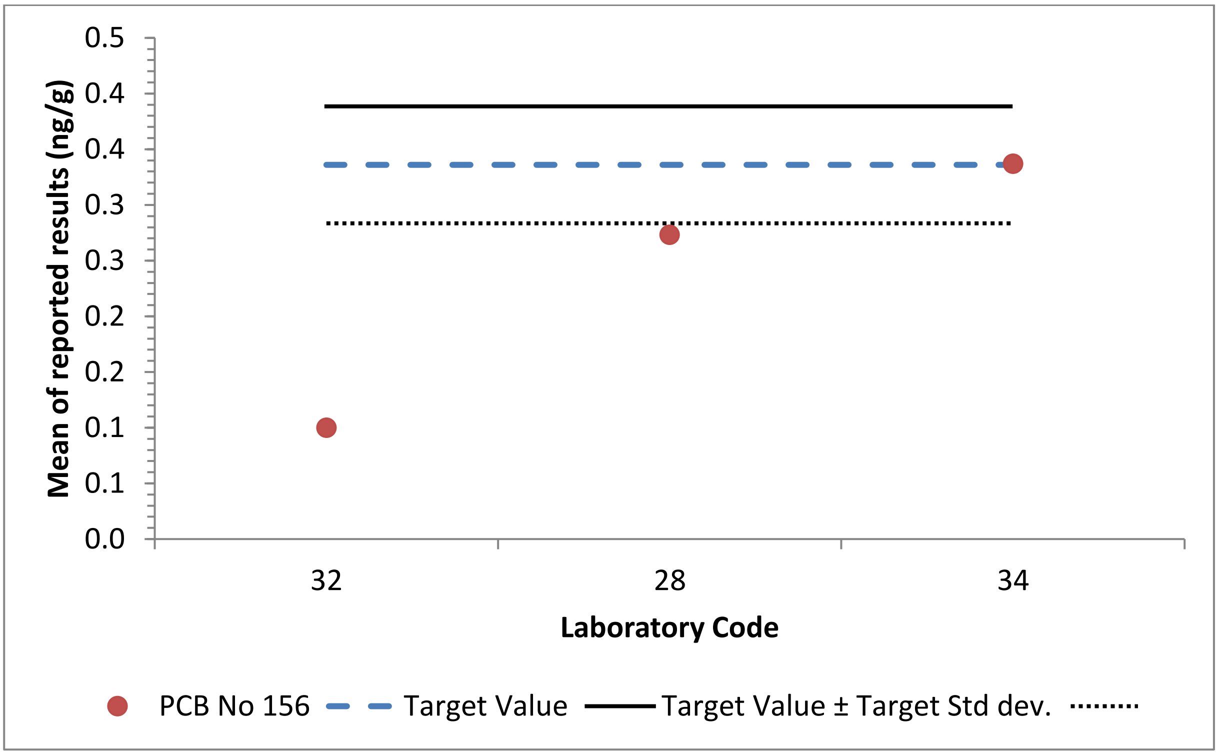

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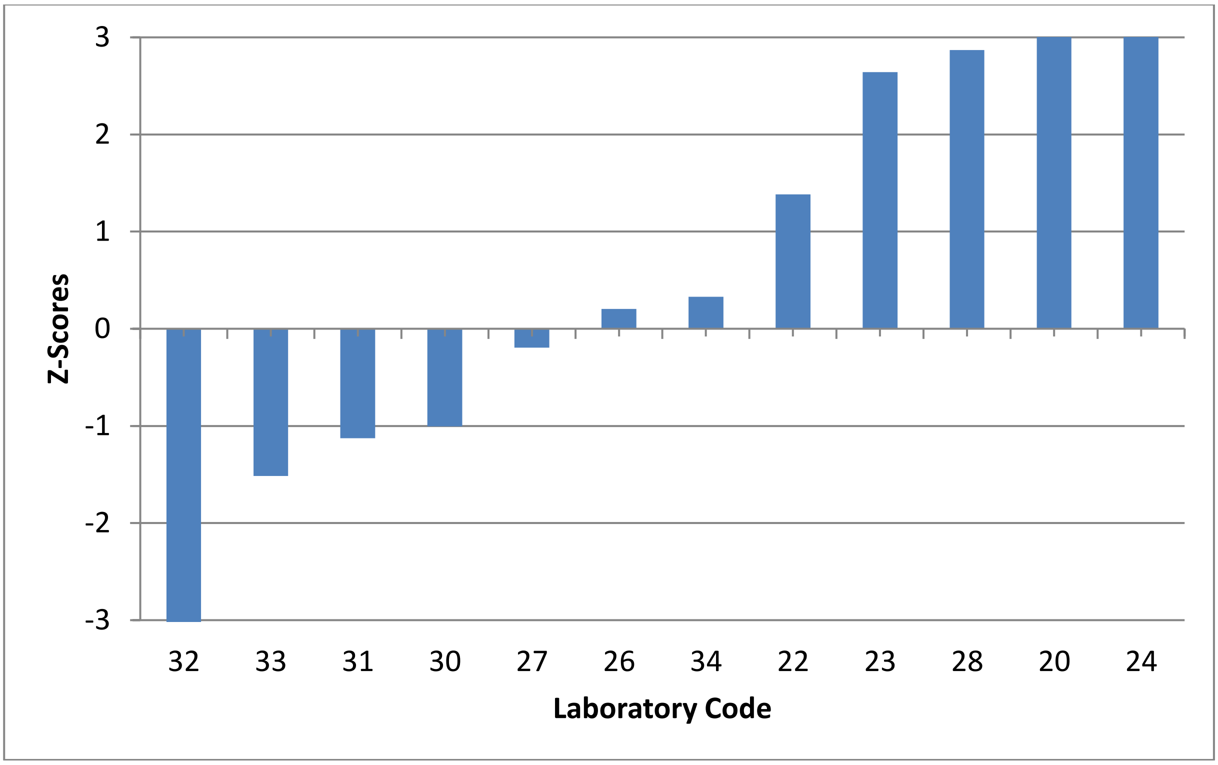

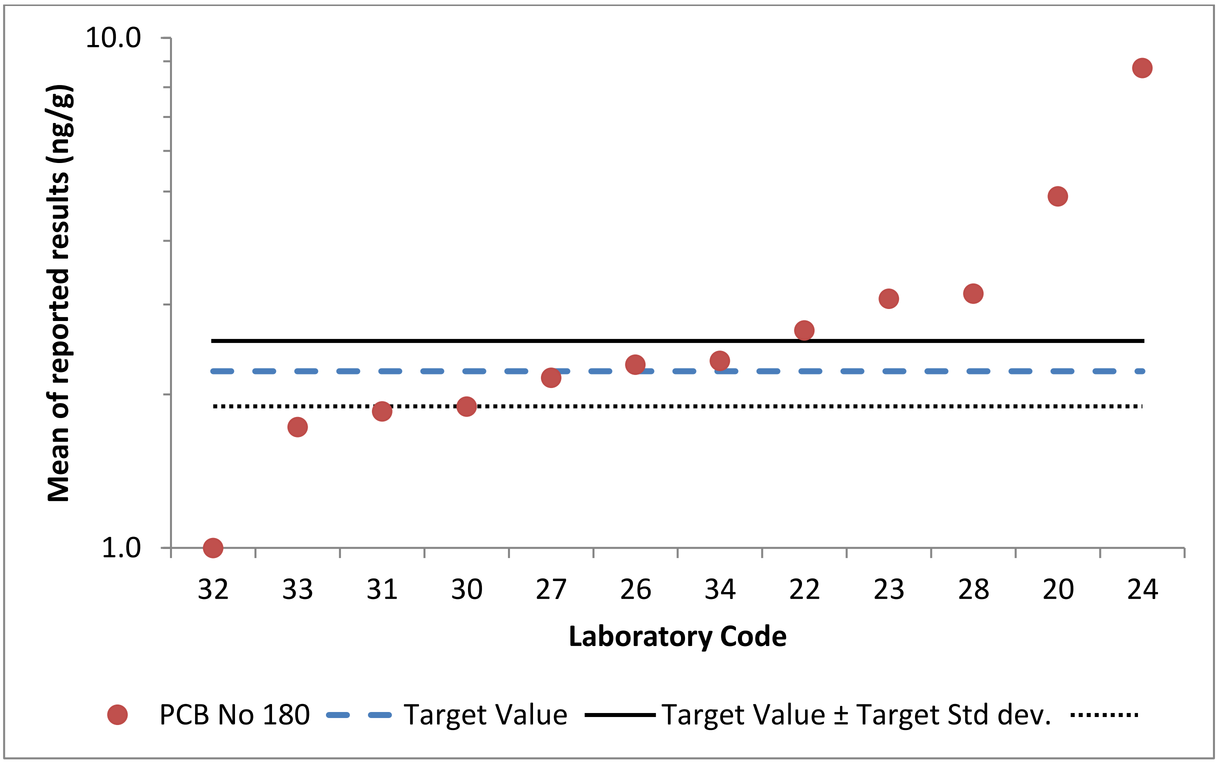

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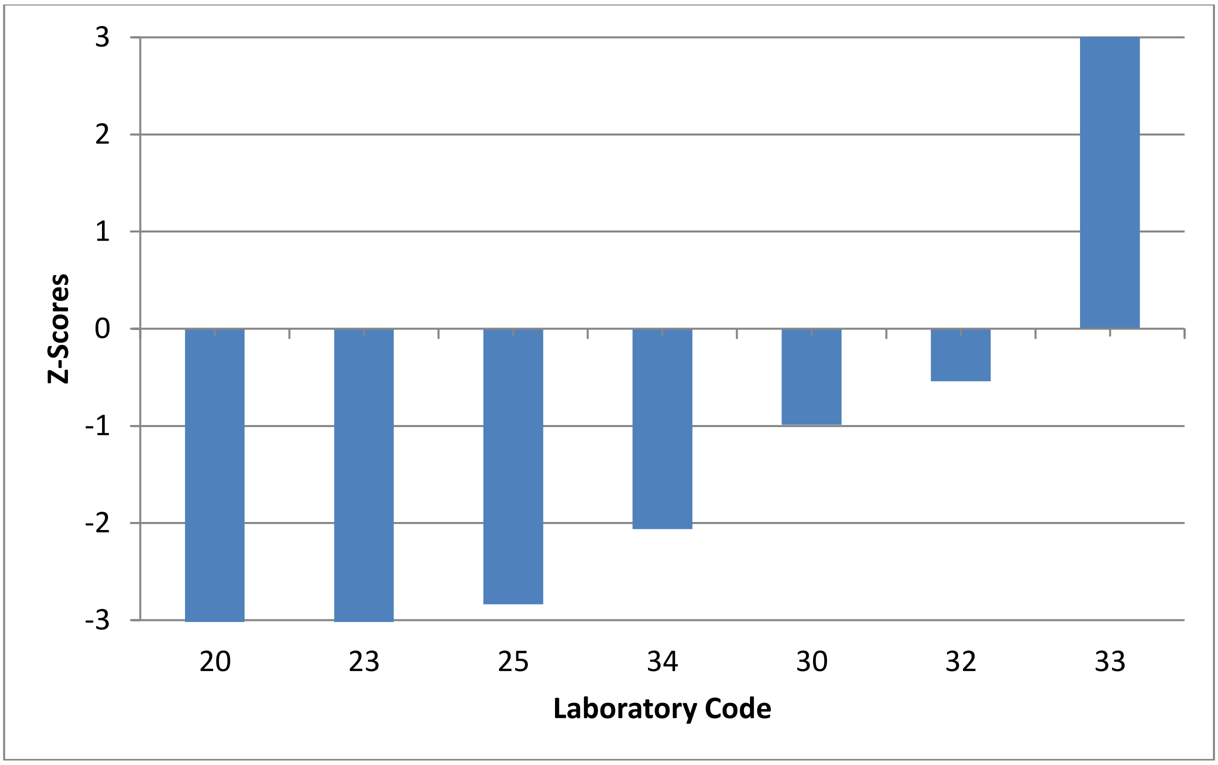

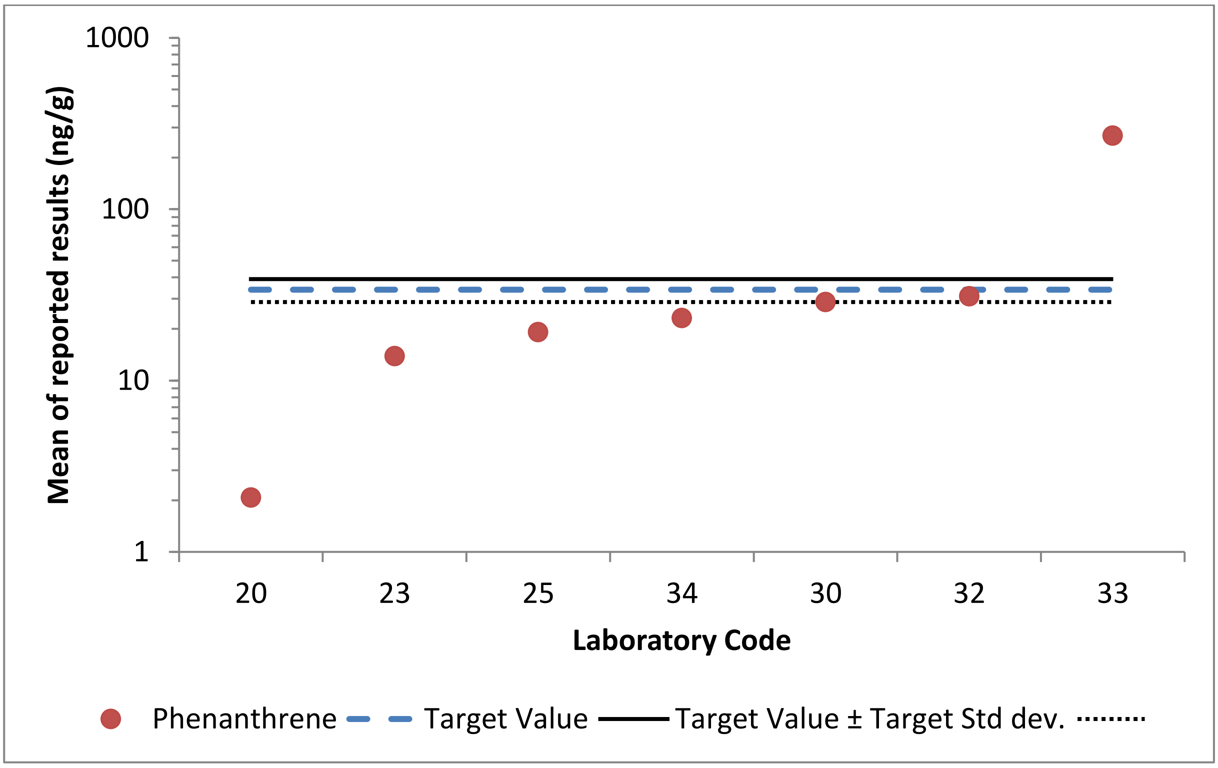

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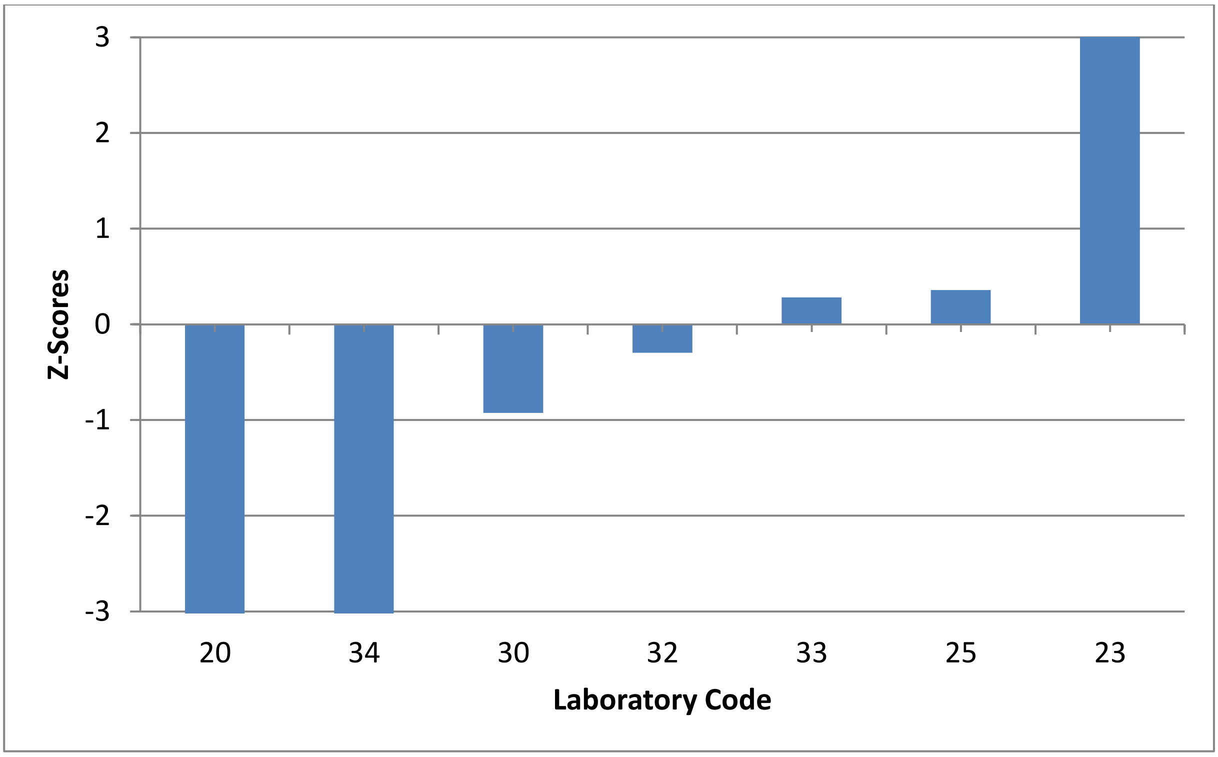

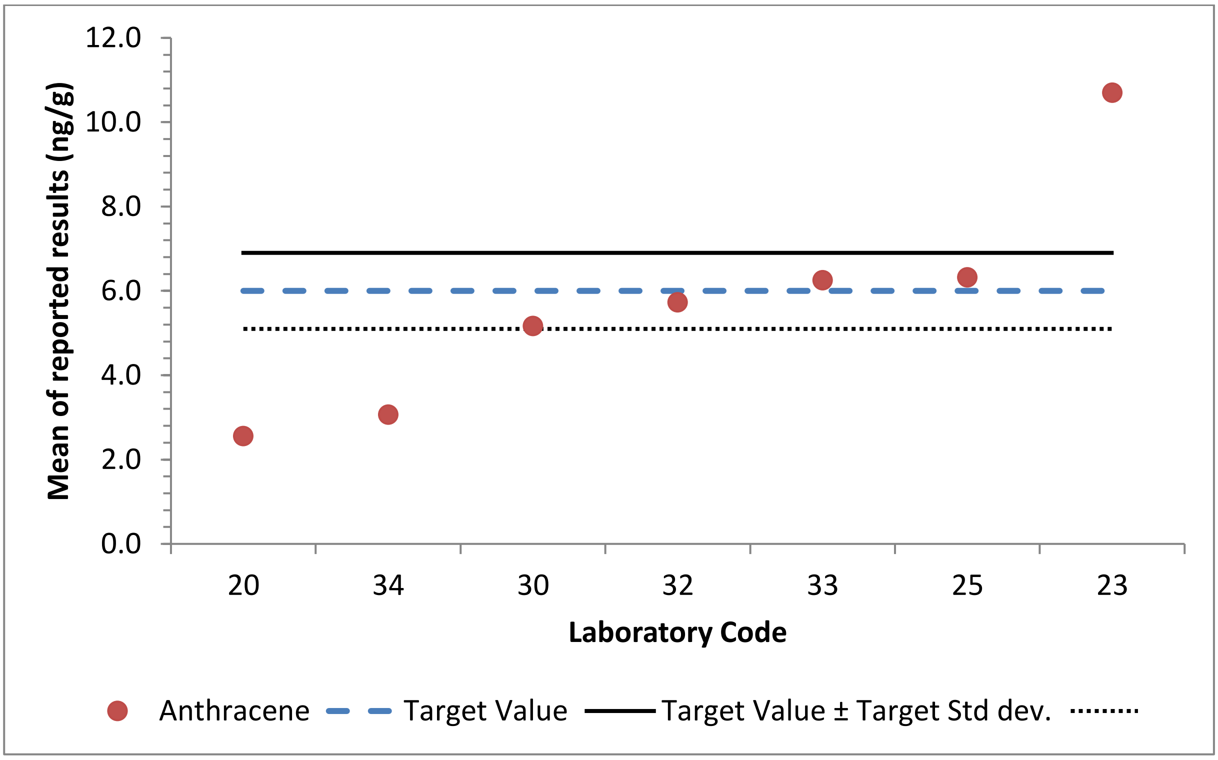

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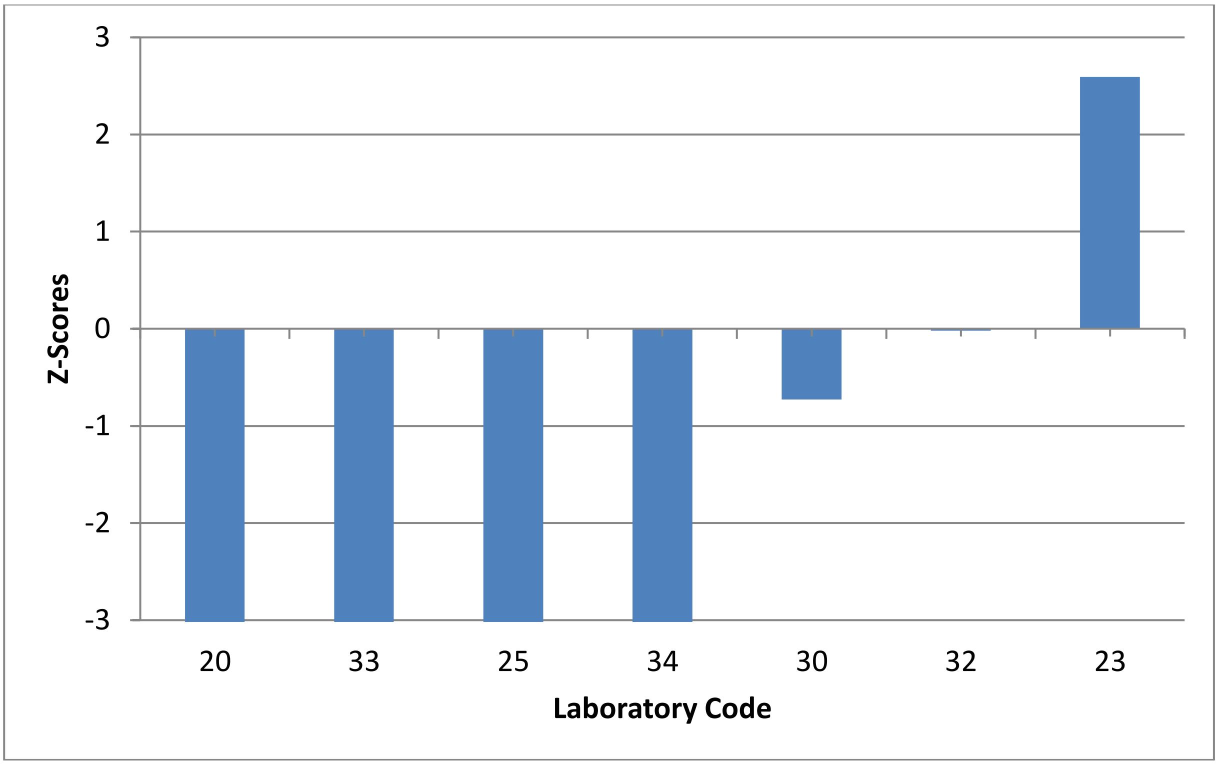

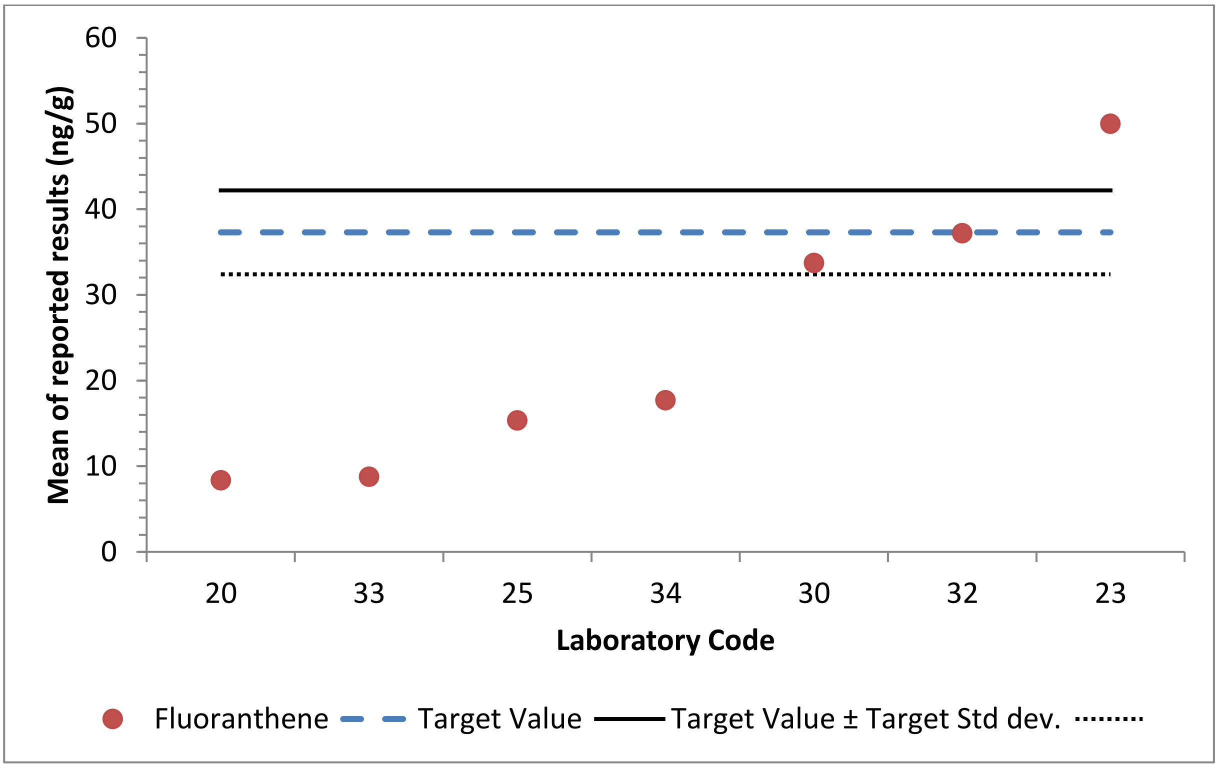

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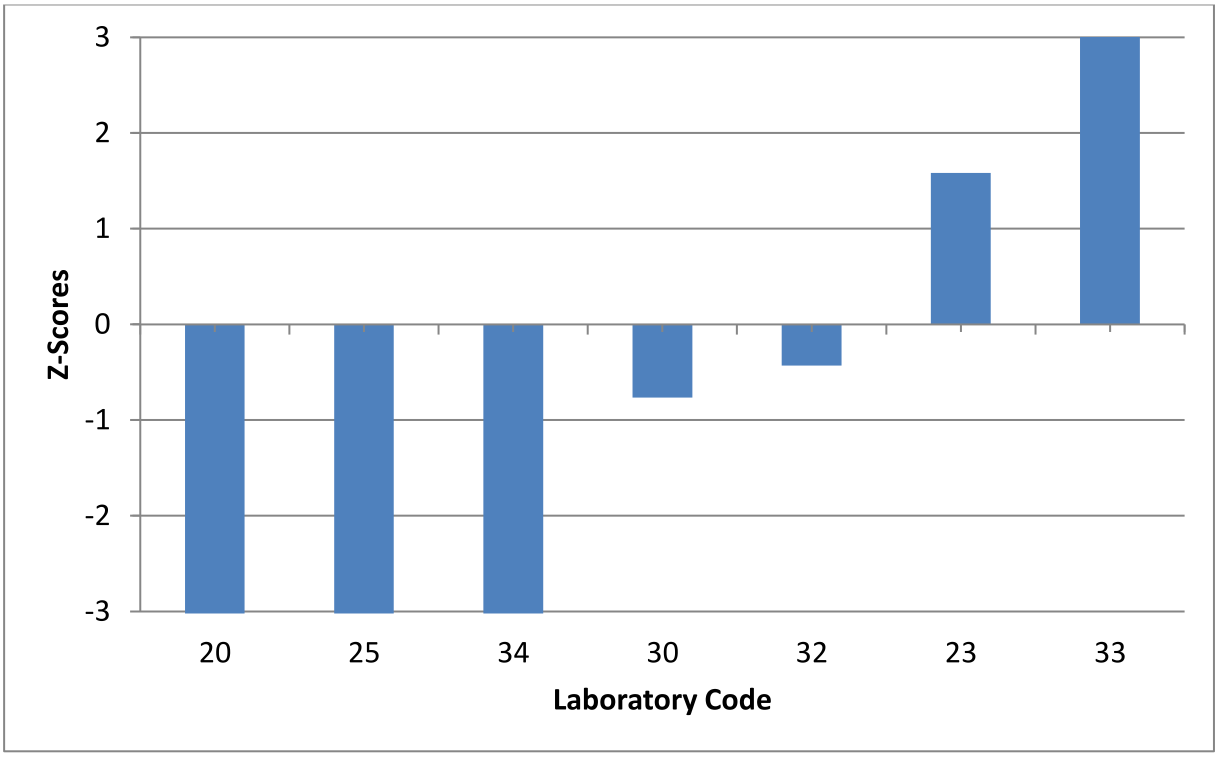

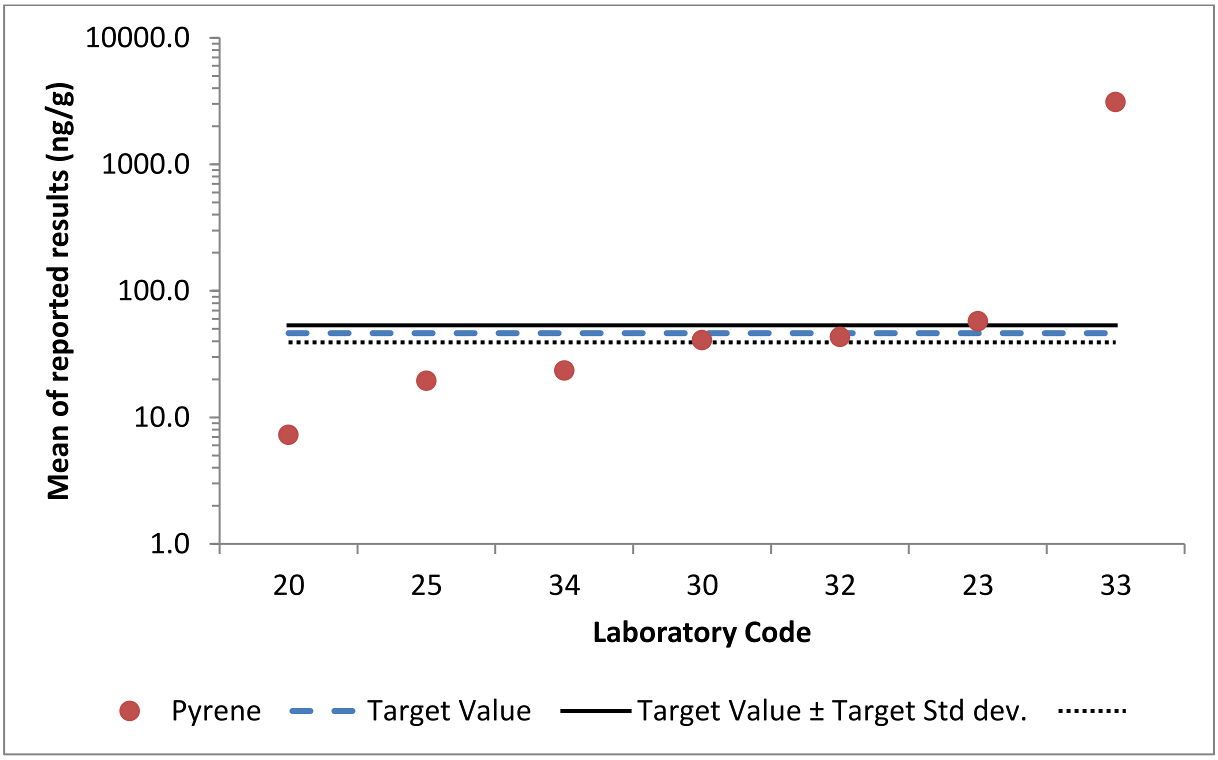

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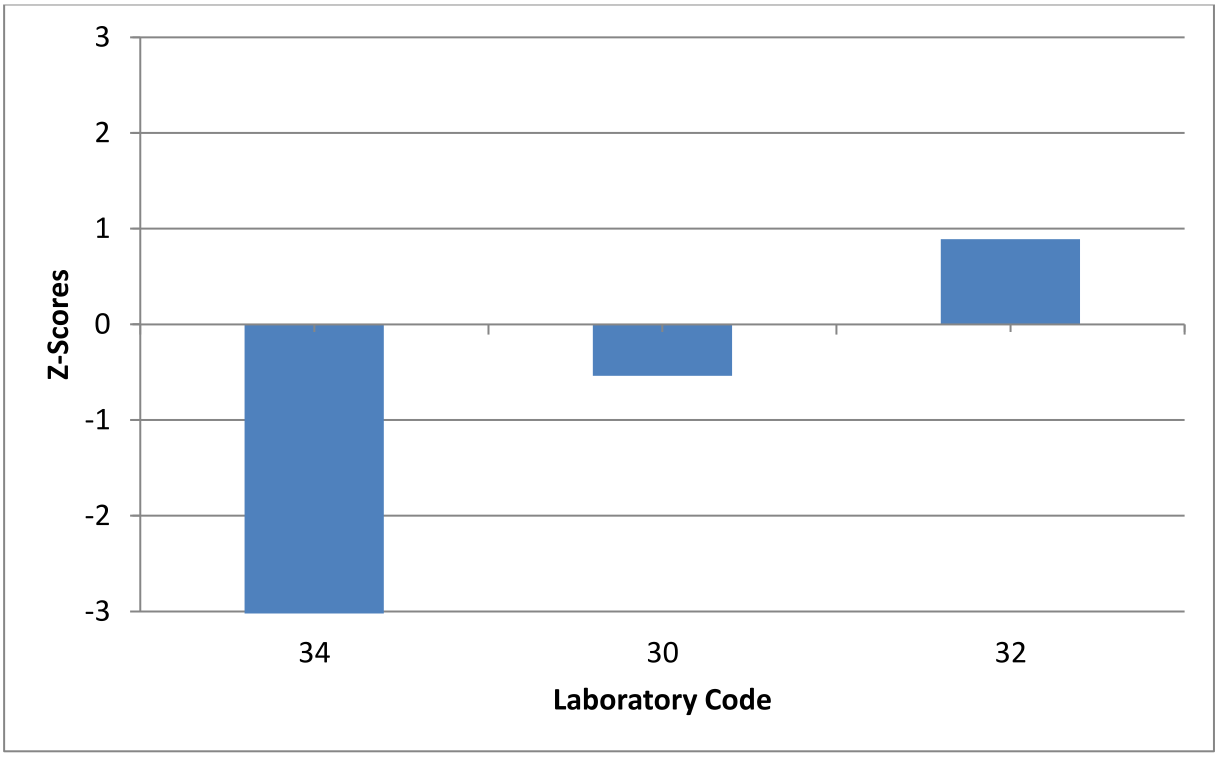

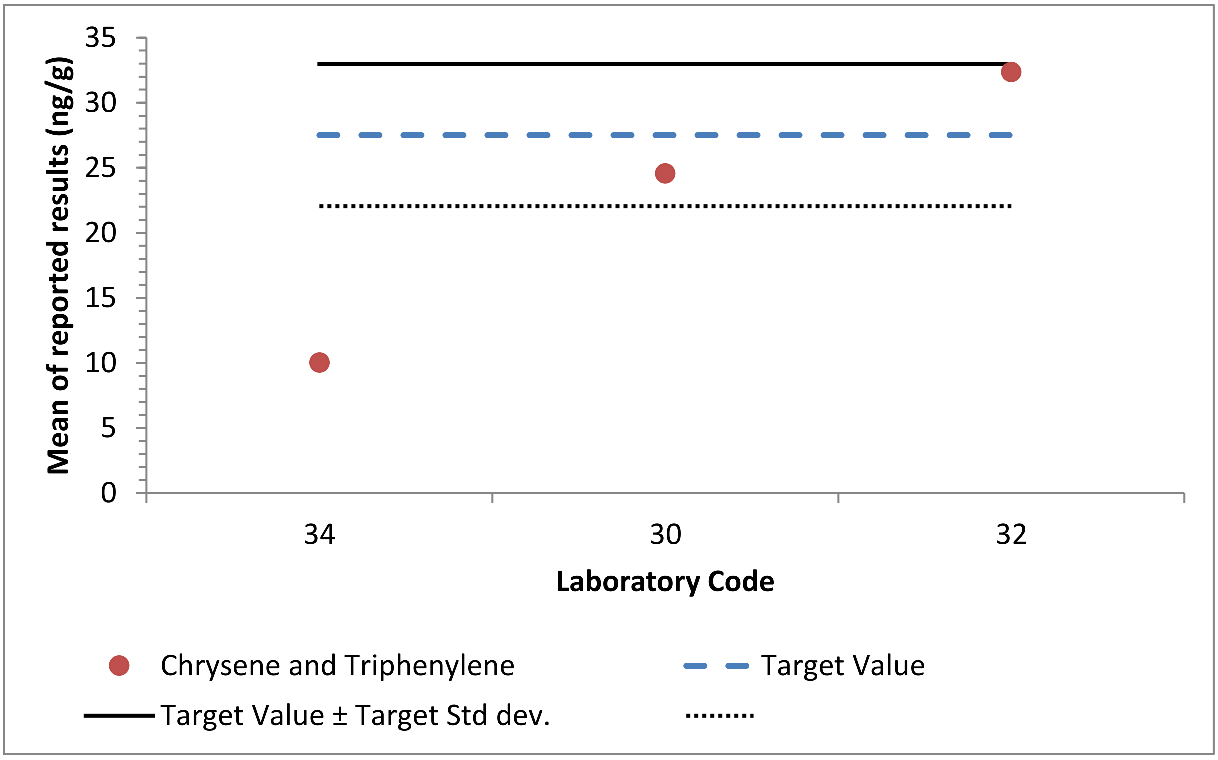

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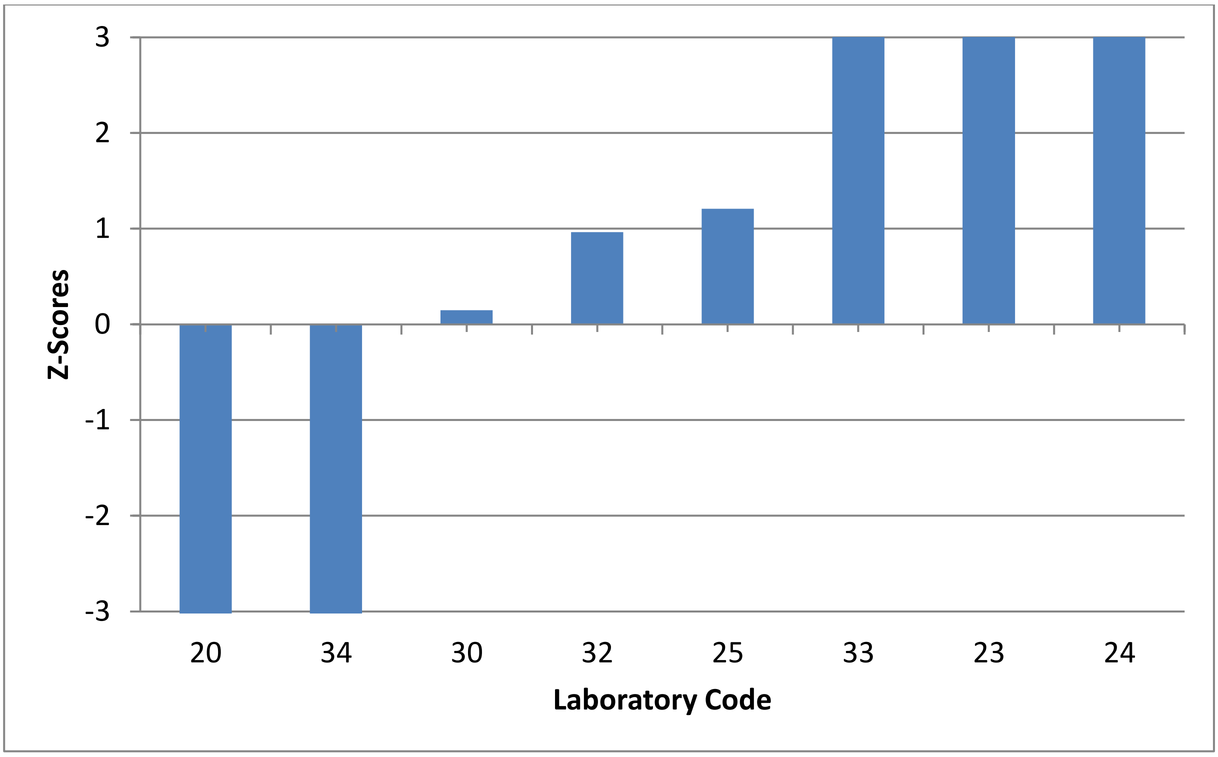

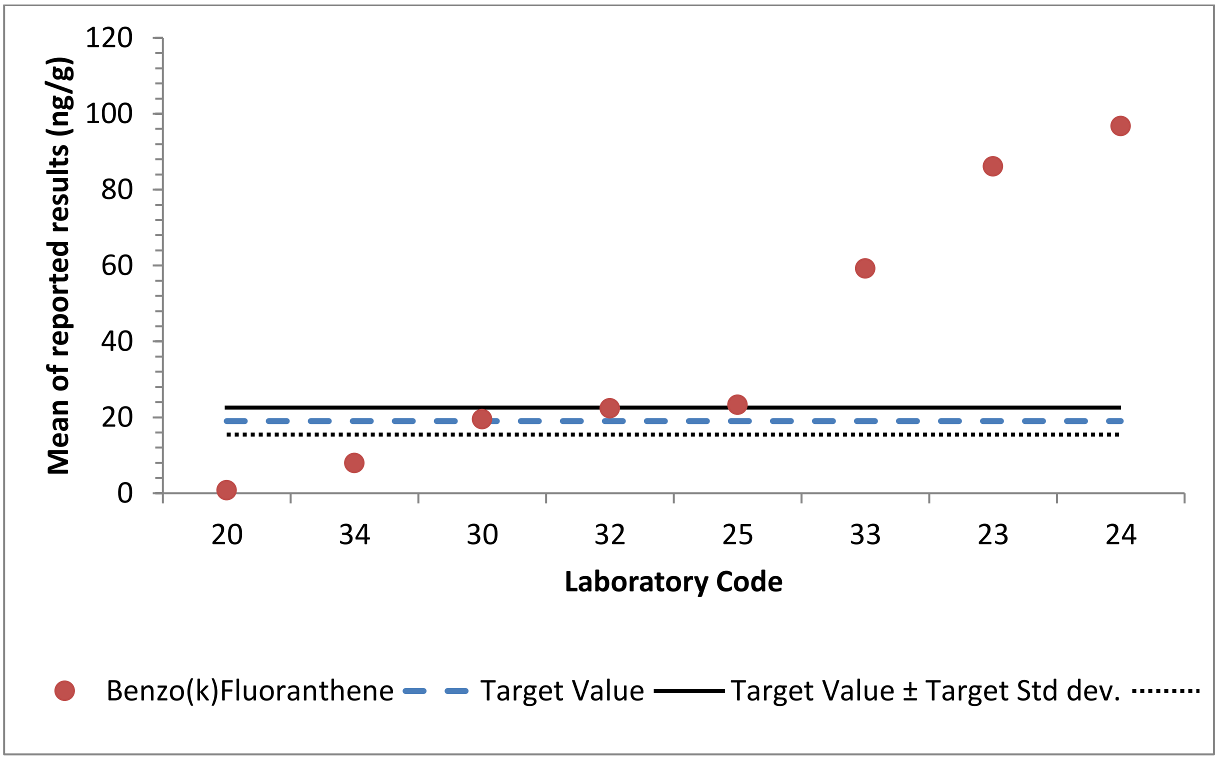

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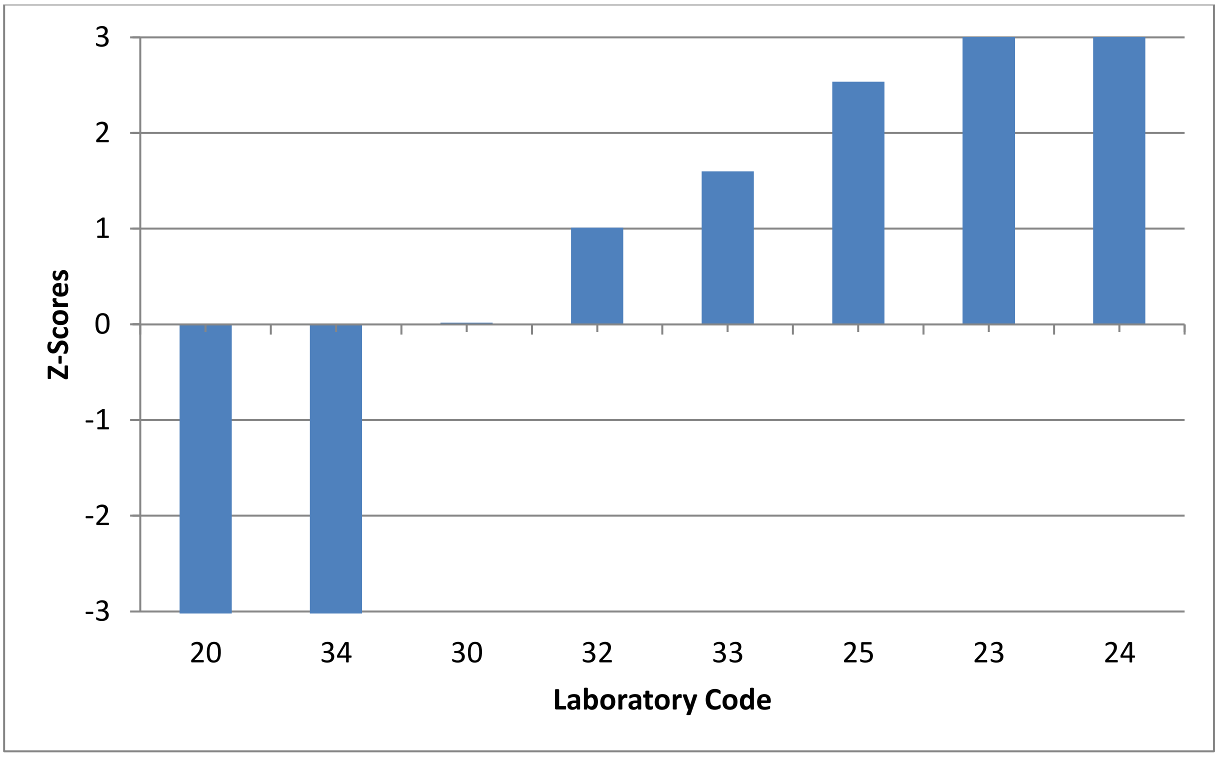
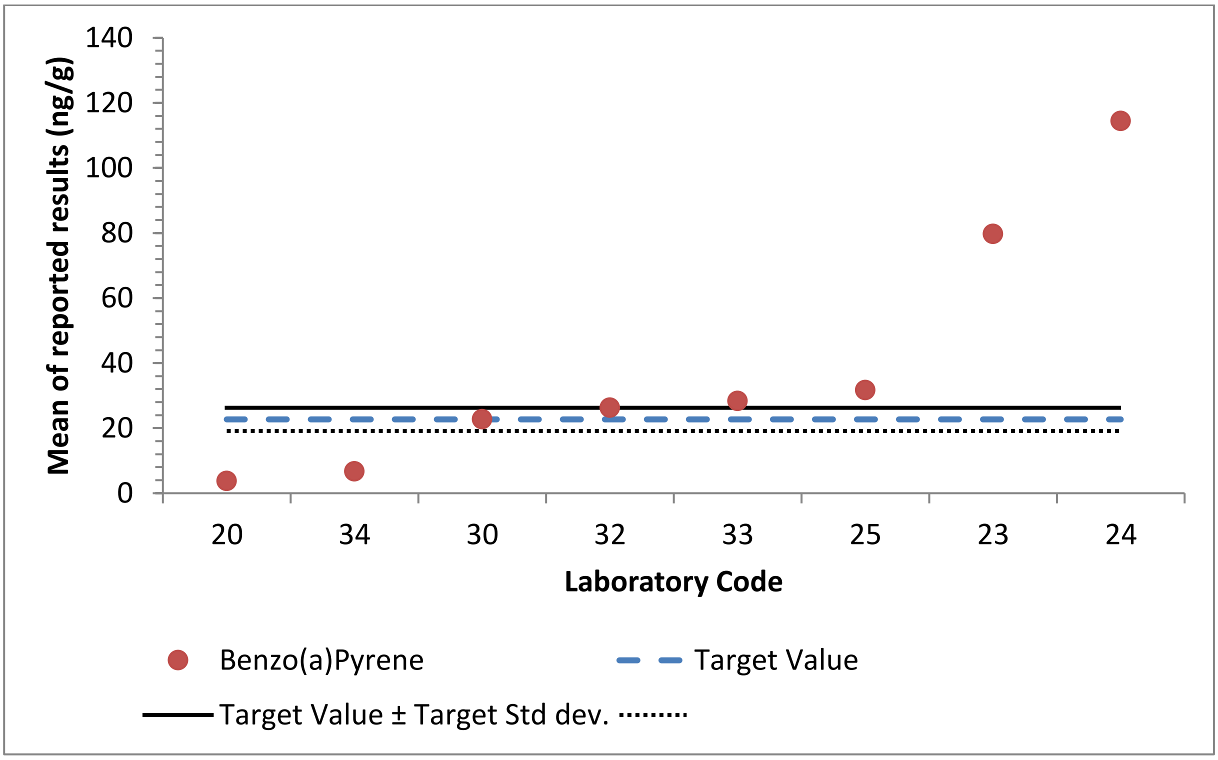
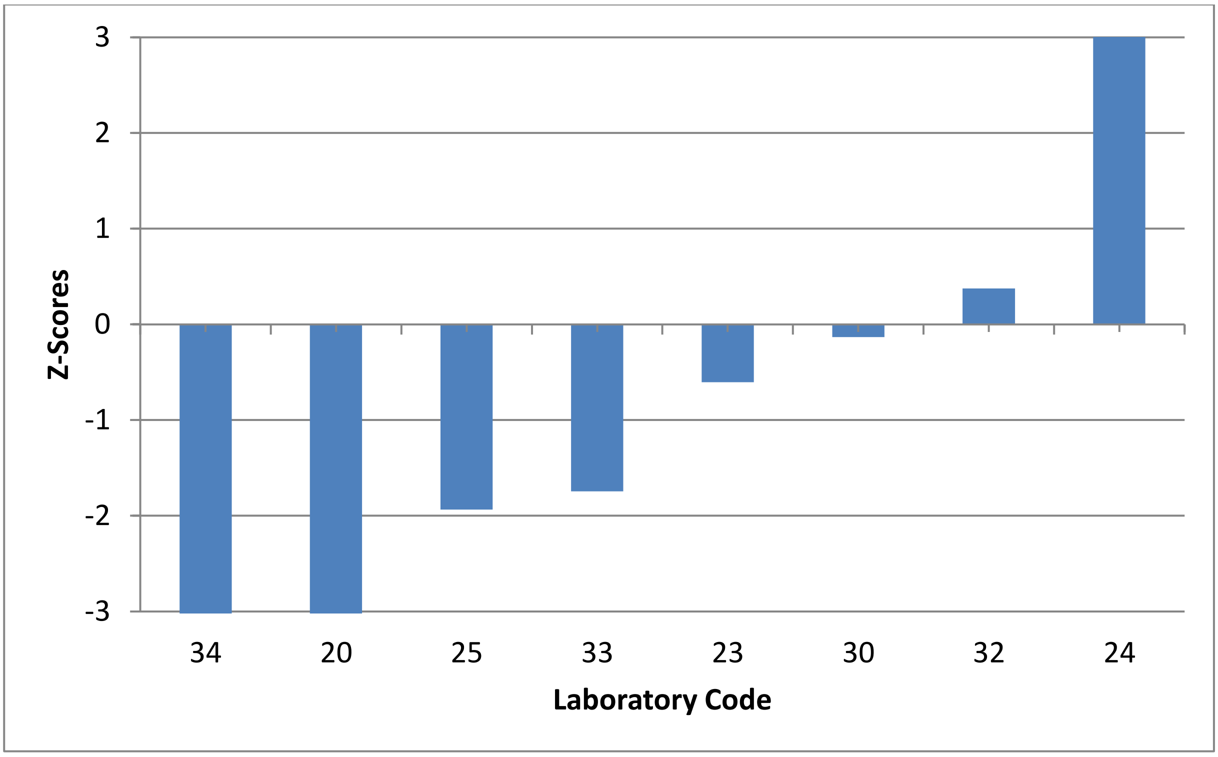
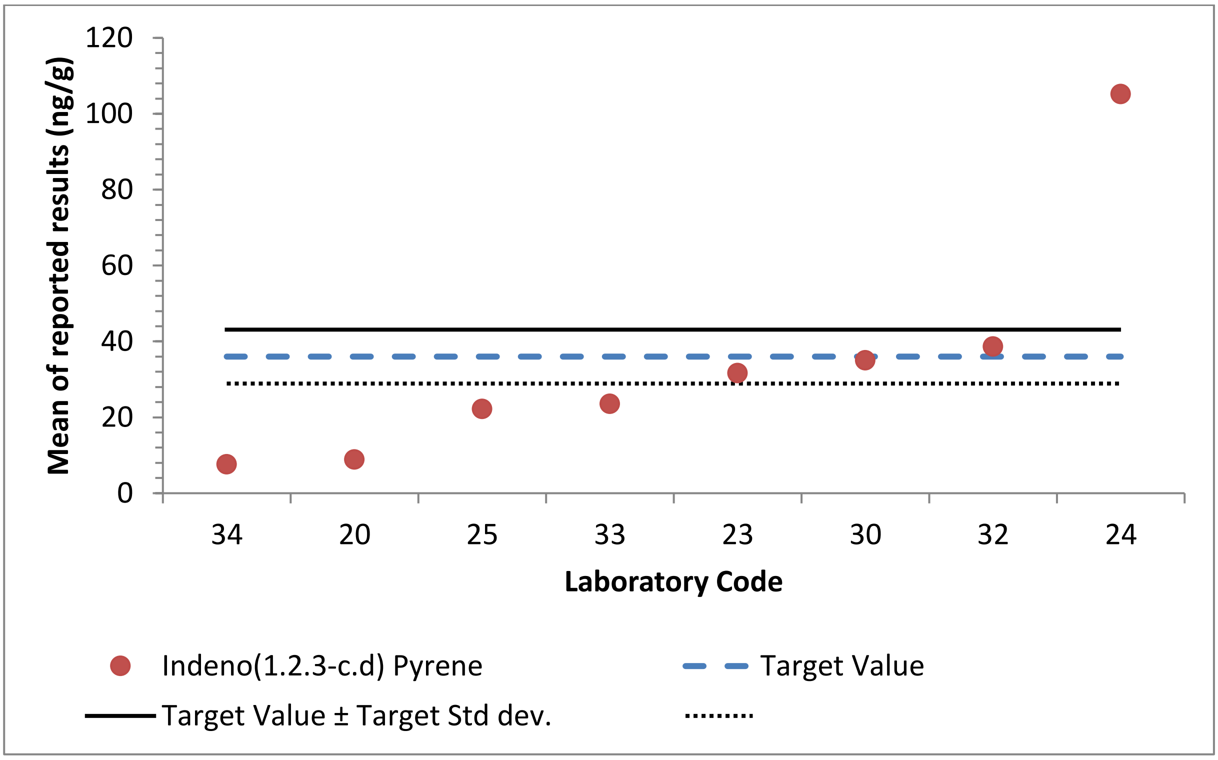




GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR INDENO (1.2.3-cd) Pyrene





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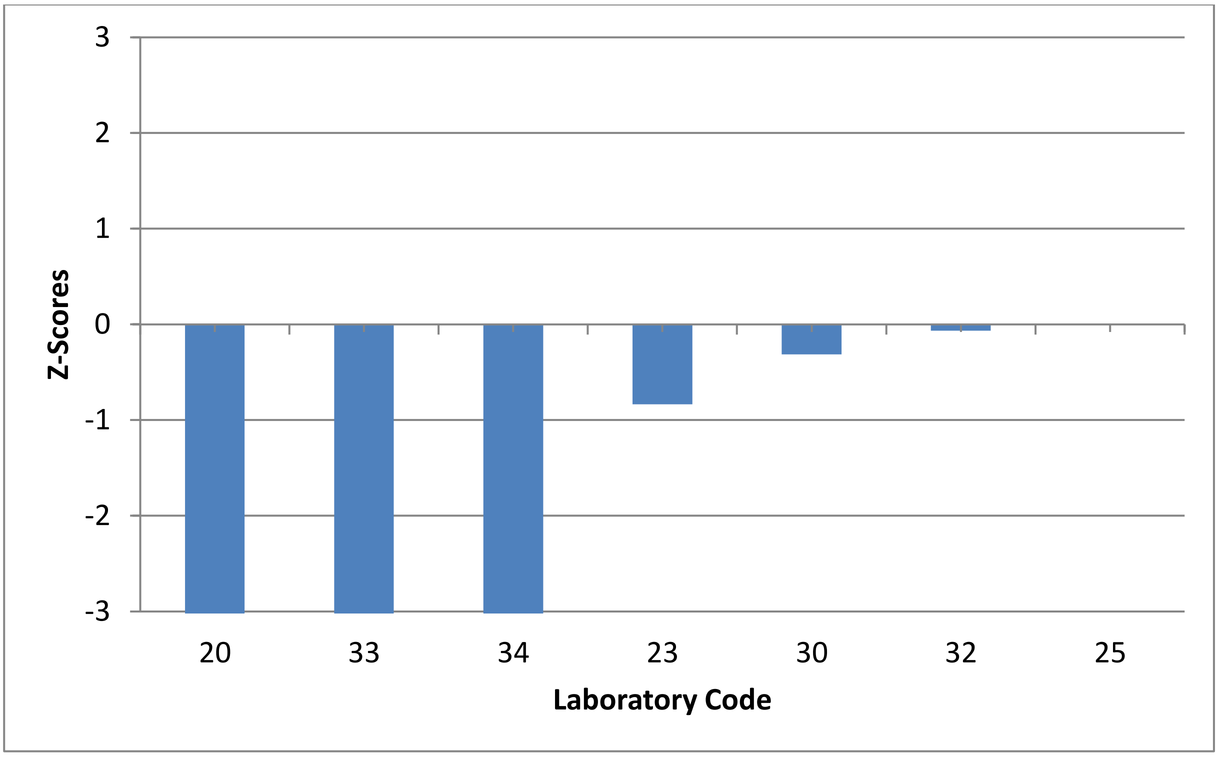

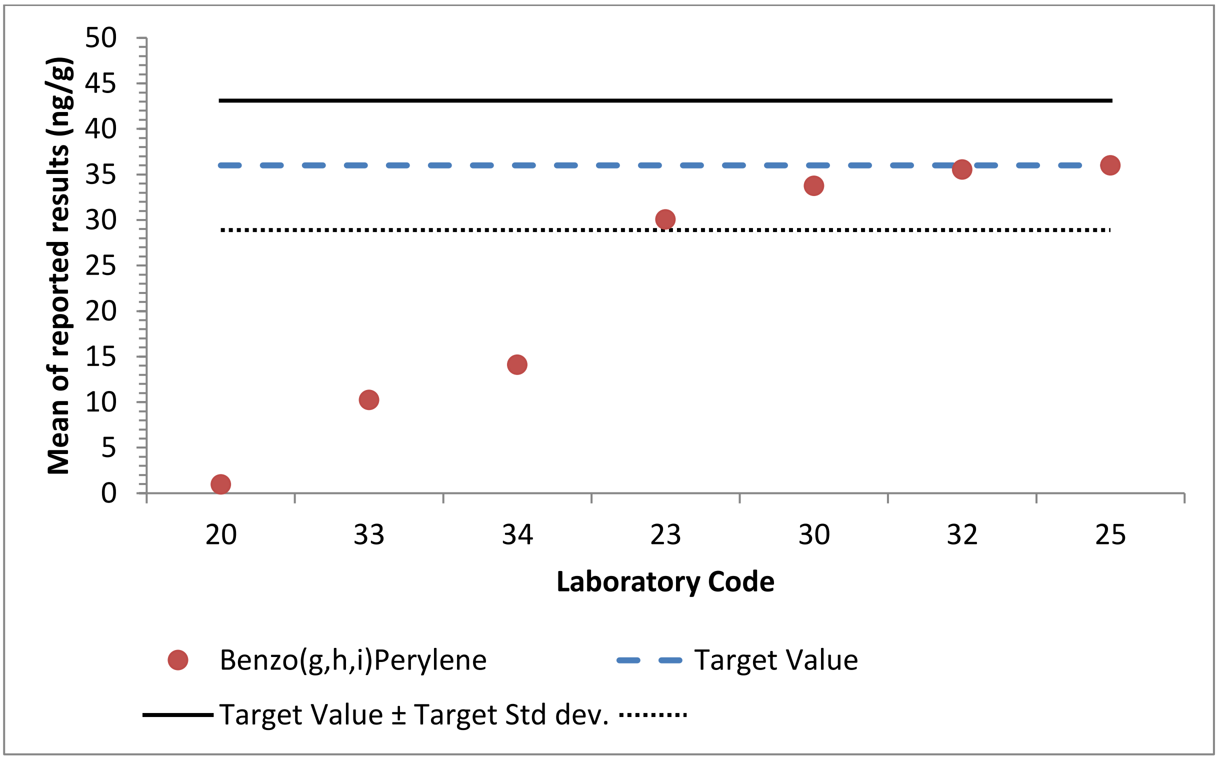

Annex 2: IAEA-459 Refence Sheet

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

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

REFERENCE SHEET

CERTIFIED REFERENCE MATERIAL

IAEA-459

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

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

Polycyclic Aromatic hydrocarbons

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

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

PCB congeners

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

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

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

Chlorinated pesticides

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

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

PBDE congeners

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

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

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

Polycyclic aromatic hydrocarbons

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

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

PCB congeners

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

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

Chlorinated pesticides

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

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

PBDE congeners

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

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

Origin and preparation of the material

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

Homogeneity of the material

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

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

Characterization study

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

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

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

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

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

Assignment of values – Certification procedure

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

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

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

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

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

Intended use

This certified reference material is intended to be used as a quality control material for the assessment of a laboratory's analytical work, for the development and validation of analytical procedures, and for quality assurance within a laboratory in the determination of chlorinated pesticides, PCBs, polybrominated diphenyl ethers and polycyclic aromatic hydrocarbons in sediment samples with very low concentration levels.

Instructions for use

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

Dry mass determination

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

Handling and storage

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

Issue and period of validity

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

Legal disclaimer

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

Compliance with ISO Guide 31:2000

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

Citation of this reference sheet

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

Note

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

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

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Mr Ales Fajgelj Chair, RM Certification Committee	Ms Imma Tolosa Project Officer, Marine Environmental Studies Laboratory

Annex 3: List of Participants:

MEDPOL designated participants that sent results

Institution	Parameters
ALBANIA	
Agjencia Kombetare e Mjedisit National Environment Agency (NEA) Ruga Sami Frasheri nr 23 godina nr 4 Tirana	OCs
BOSNIA & HERZEGOVINA	
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CROATIA	
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GREECE	
Hellenic Centre for Marine Research Institute of Oceanography 46.7km Athens-Sounio Av. Mavro Lithari 19013 Anavyssos	OCs, PAHs
ITALY	
ARPA Toscana Via G. Marradi 114 57126 Livorno	OCs, PAHs
LEBANON	
American University of Beirut CCC-SRB Bldg, 3rd Floor, Room 303c Bliss St Hamra PO Box 11.0236 Riad El Solh 1107-2020 Beirut	OCs, PAHs

MONTENEGRO	
Centre for Ecotoxicological Research Podgorica Bulevar Sarla de Gola 2 81000 Podgorica	OCs, PAHs
MOROCCO	
Office National de l'Electricité et de l'Eau Branche Eau Direction Contrôle et de la Qualité des Eaux Station de Traitement Avenue Mohamed Belhassan El Ouazzani 10002 Rabat-Chellah	OCs
SLOVENIA	
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SYRIA	
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