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

UNEP/MAP
Athens, 2021

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REPORT

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

2020

Prepared in collaboration with:

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1. INTRODUCTION

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

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

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

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

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

2. SCOPE OF EXERCISE

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

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

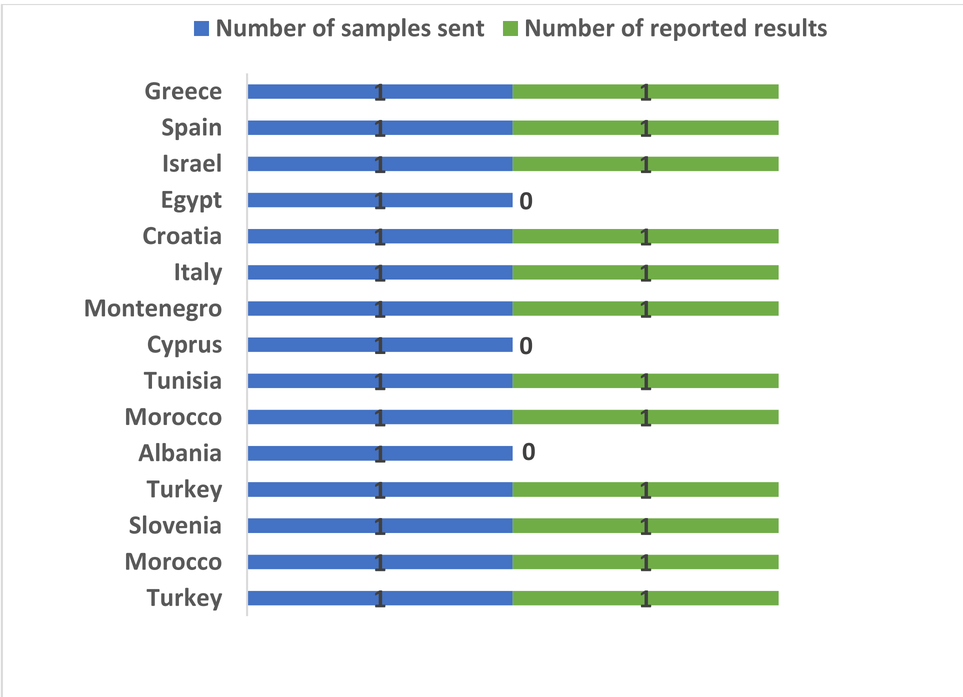

Figure. 1. Distribution per country of the MED POL PT sample

The deadline for reporting results was set for the 2 November 2020, but it was extended to the 15th of November 2020, after the request of several laboratories. Finally, 12 laboratories sent their results within the requested deadlines representing 80% of 15 participating laboratories that received the test sample reported results (see figure 1). Six laboratories reported results for both organochlorine pesticides, PCB congeners and PAHs, 4 laboratories reported results only for organochlorine pesticides and PCB congeners and 2 laboratory reported results only for PAHs.

3. <u>MATERIAL</u>

3.1. Preparation of the material

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

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

3.2. Assigned values and associated uncertainties of the PT sample

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

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

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

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

u_{hom} was set at 5%,

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

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

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

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

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

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

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

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

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

4. RESULTS AND EVALUATION

4.1. Data Reporting

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

4.2. Evaluation Criteria

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

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

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

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

Where:

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

Performance is considered satisfactory if $|z| \leq 2$.
The measurement is regarded as questionable if $2 < |z| < 3$.
The measurement is regarded as unsatisfactory when $|z| \geq 3$.
This score represents a simple method of giving each participant a normalized performance score for bias. The procedure has been accepted as a standard by ISO/IUPAC [3, 5, 6].

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

4.3. Overview of the reported measurement results and scoring

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

TABLE 6. Z-scores for PAHs

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

4.4. Analytical methodologies used by the participants

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

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

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

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

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

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

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

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

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

*With dual column confirmation

TABLE 9. Treatment of samples performed by participants for PAHs

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

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

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

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

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

TABLE 12. Quality parameters for PAHs.

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

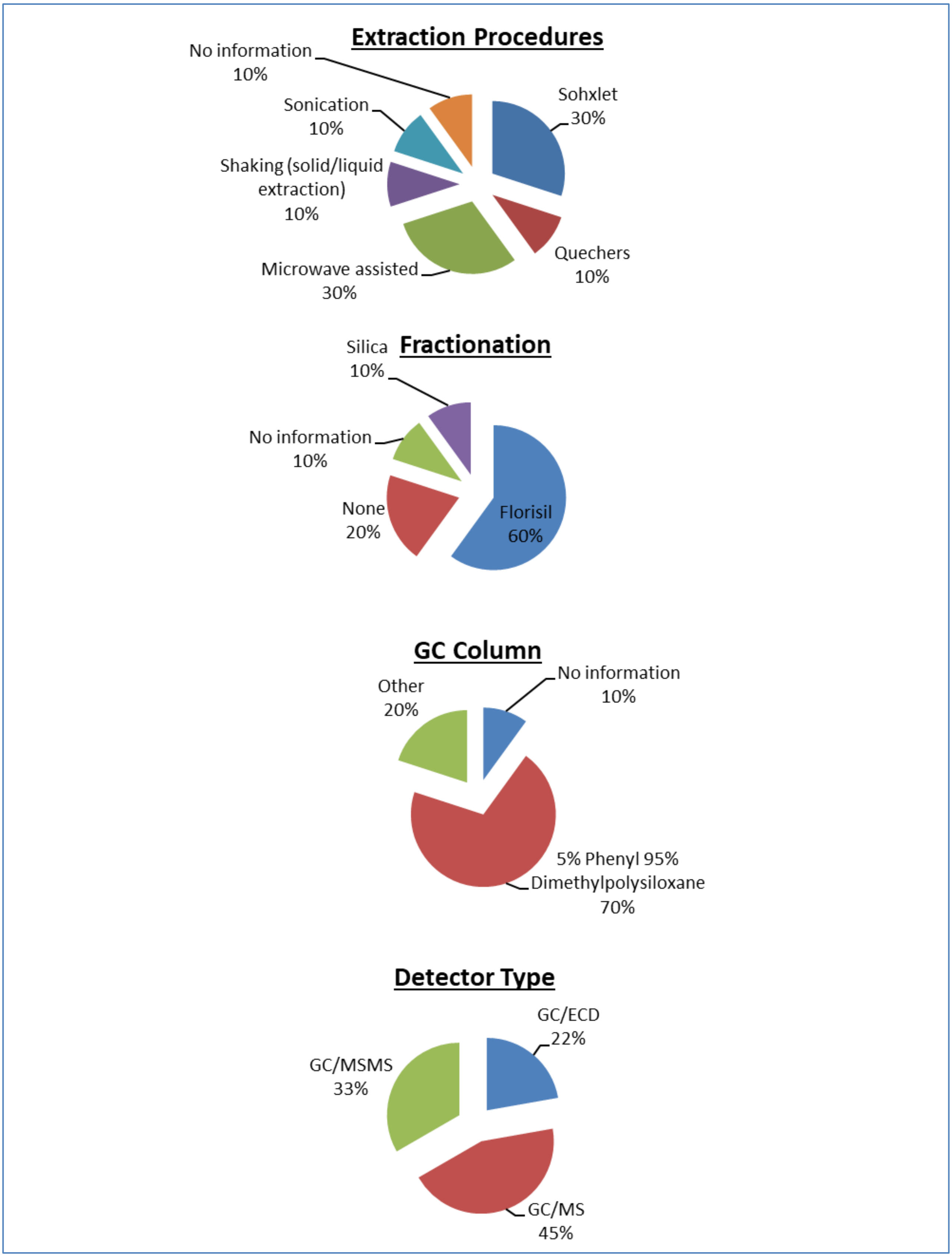

Figure 2. Graphic representation of sample treatment and instrumental conditions for organochlorine pesticides and PCB congeners.

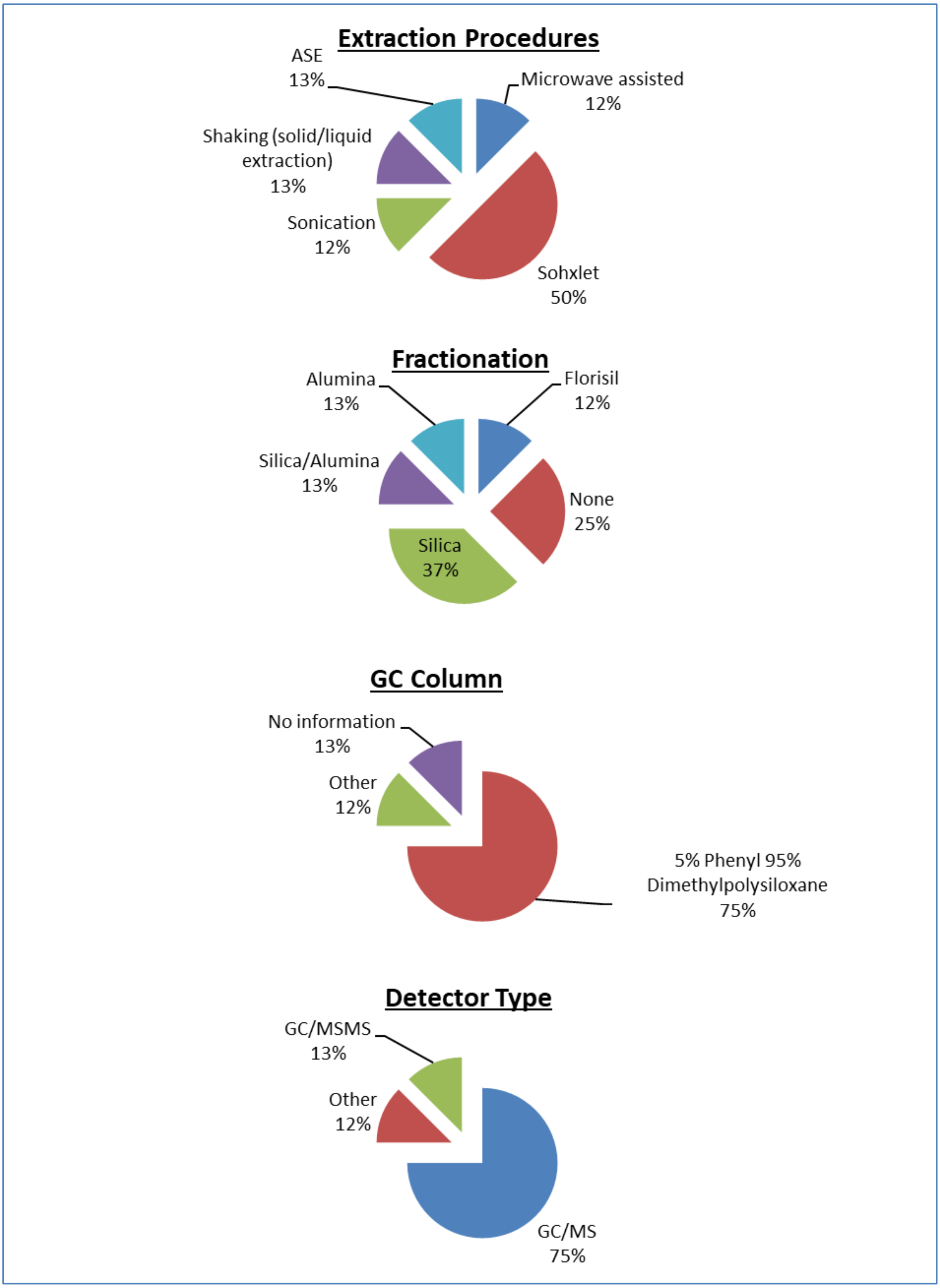

Figure 3. Graphic representation of sample treatment and instrumental conditions for PAHs

5. EVALUATION OF RESULTS

5.1. Organochlorine Pesticides and PCB Congeners

Among all designated laboratories, 67% submitted results for organochlorine pesticides and PCB congeners.
Table 13 reports the number of results and z-scores distribution per Participant for organochlorinated pesticides and PCB congeners.

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

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

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

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

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

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

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

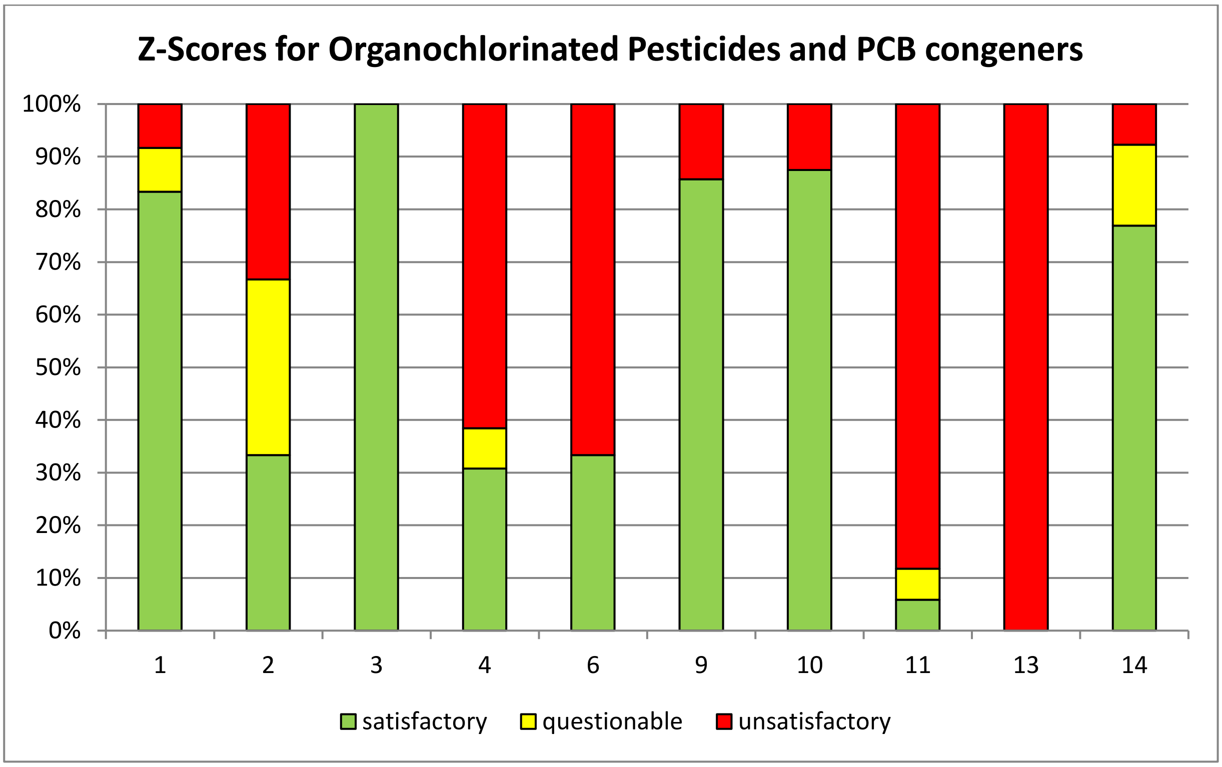

Figure 4. Graphic representation of laboratories z-scores for organochlorine pesticides and PCB congeners.

5.2. PAHs

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

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

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

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

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

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

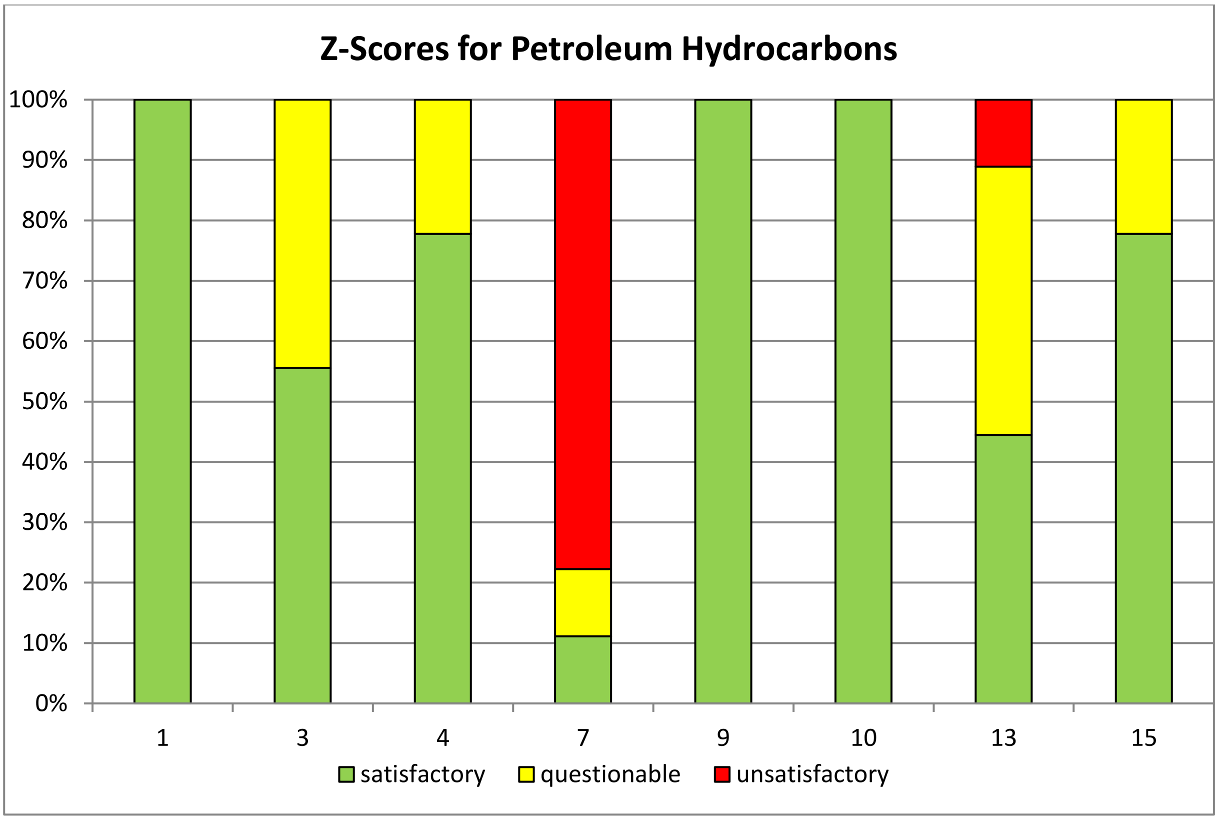

Figure 5. Graphic representation of laboratories z-scores for PAHs.

6. CONCLUSIONS AND RECOMMENDATIONS

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

7. REFERENCES

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

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

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

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

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

Annex 1:
List of Participants

Designated IMAP Competent laboratories that sent results

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

SLOVENIA	
National Laboratory of Health Environment and Food Prvomajska Ulica 1 2000 Maribor	OCs, PAHs

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

TUNISIA	
Institut National des Sciences et Technologies de la Mer (INSTM) Port de Pêche La Goulette 2060 La Goulette	PAHs

TURKEY	
Ministry of Environment and Urbanization Çevre Referans Laboratuvarı National Environmental Reference Laboratory Haymana Yolu 5. Km. 06830 Gölbaşı-Ankara	OCs, PAHs
Scientific and Technological Research Council of Turkey Marmara Research Center Environment and Clean Production Institute TUBITAK Gebze Yerleskesi Marmara Arastirma Merkeri Cevre ve Temiz Uretim Enstitusu 41470 Gebze/KOCAELI	OCs, PAHs

Designated IMAP competent laboratories that did not send

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

Annex 2:
Graphic Representation of Laboratories Performances

Graphic Representation of Laboratories Performances

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

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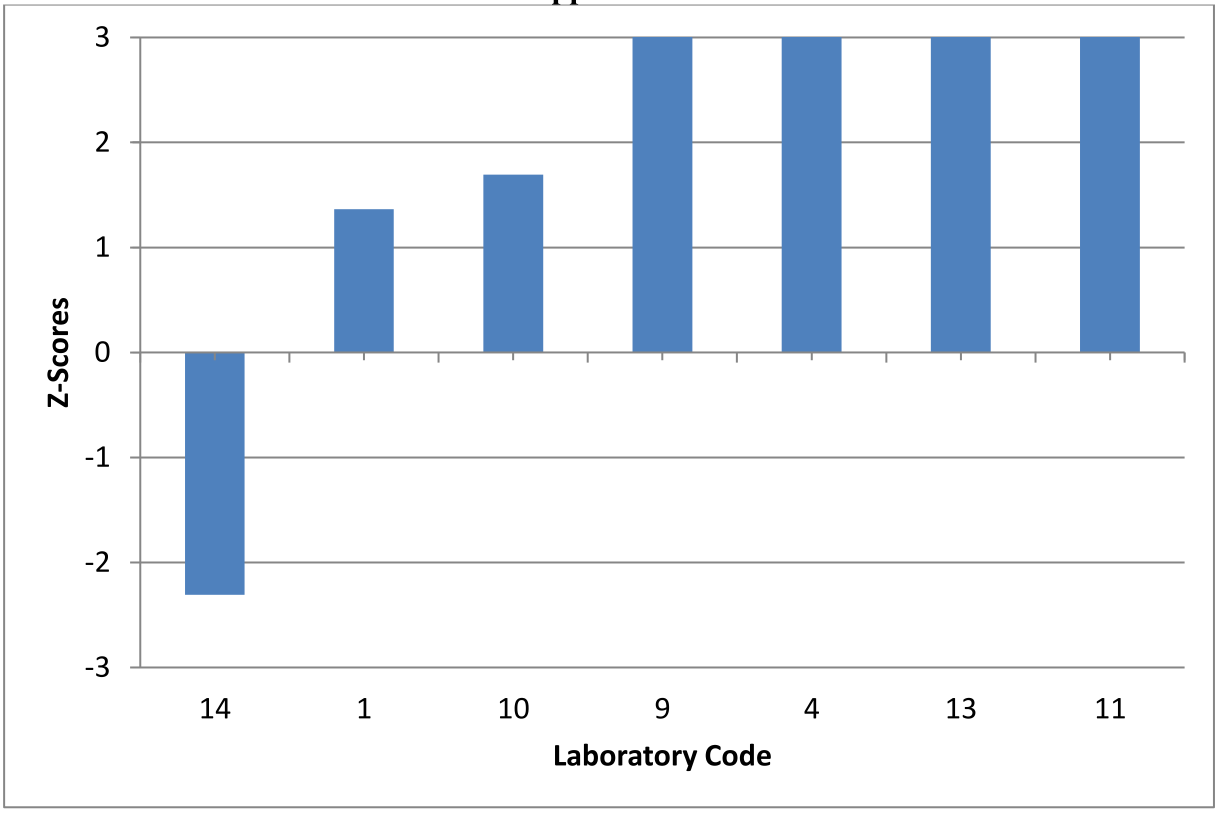

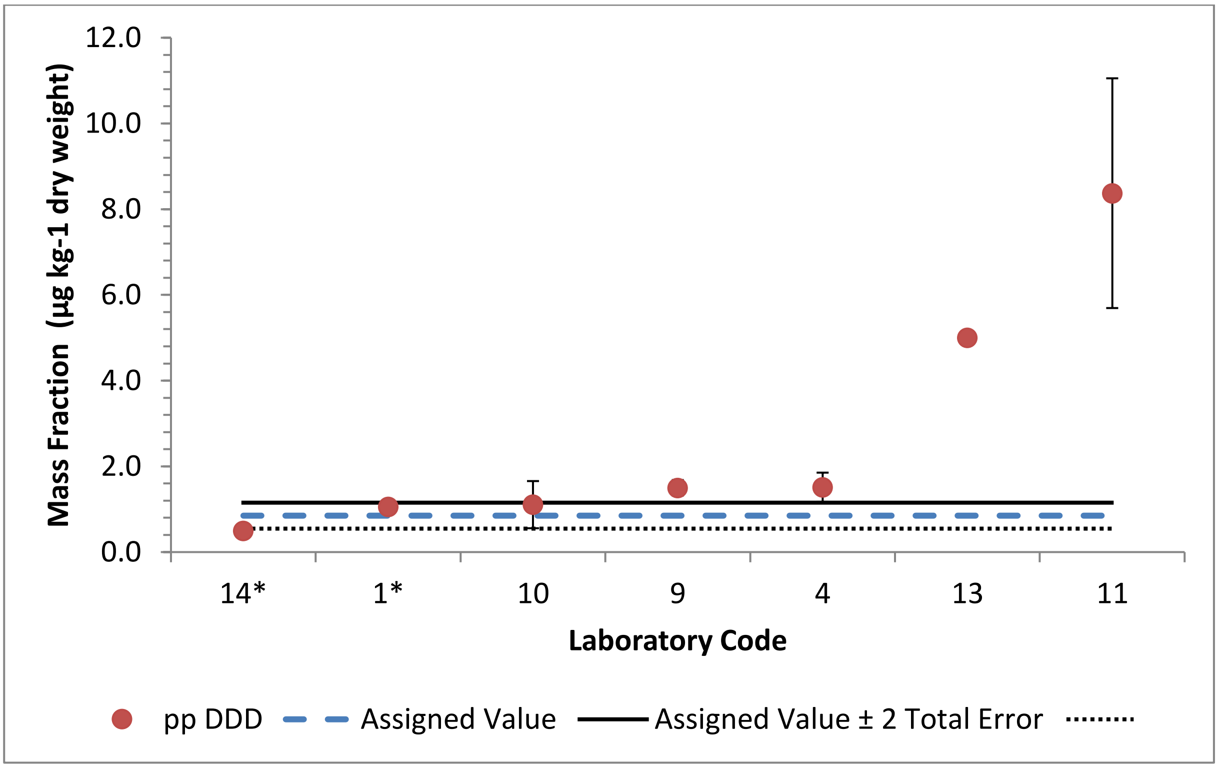

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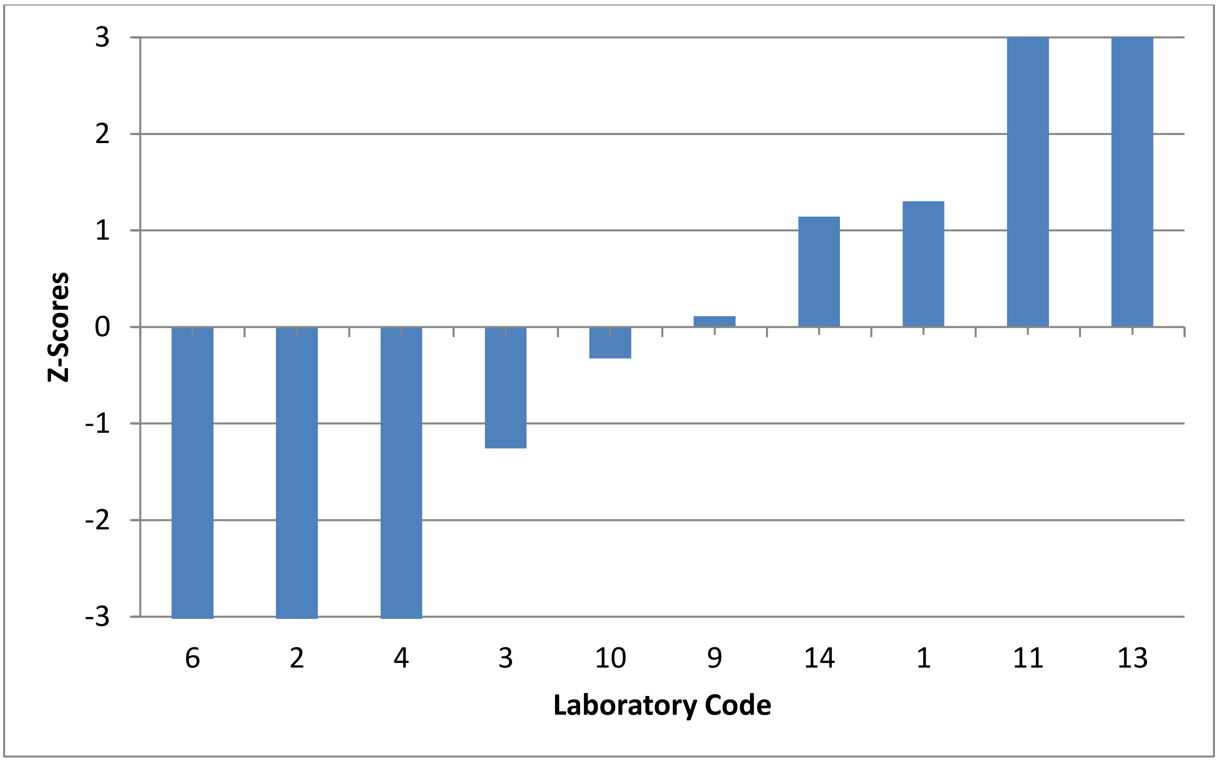

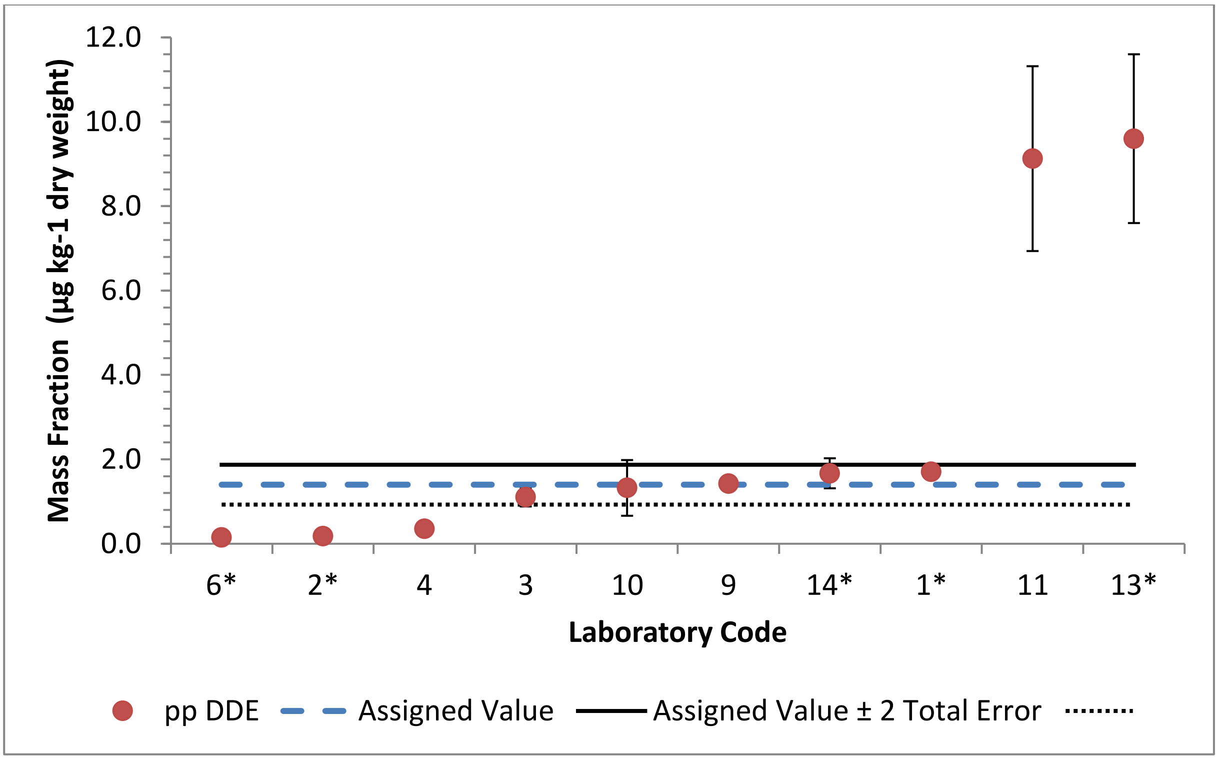

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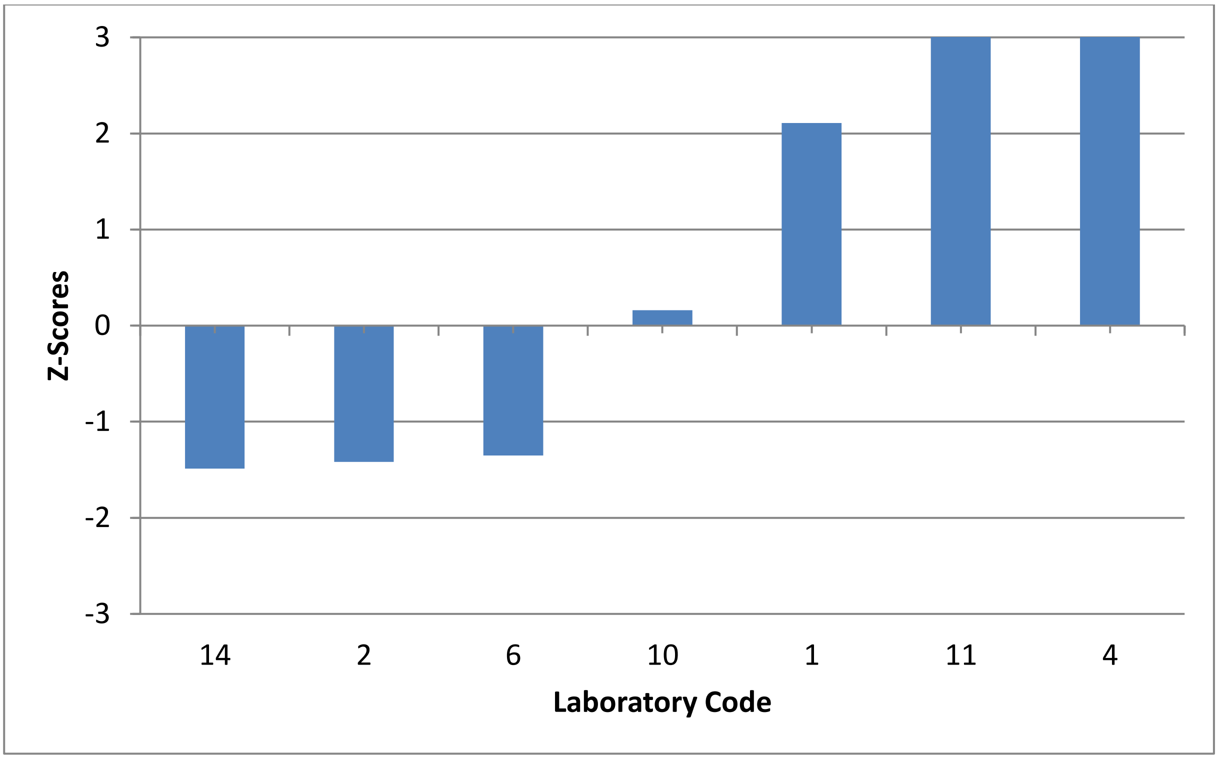

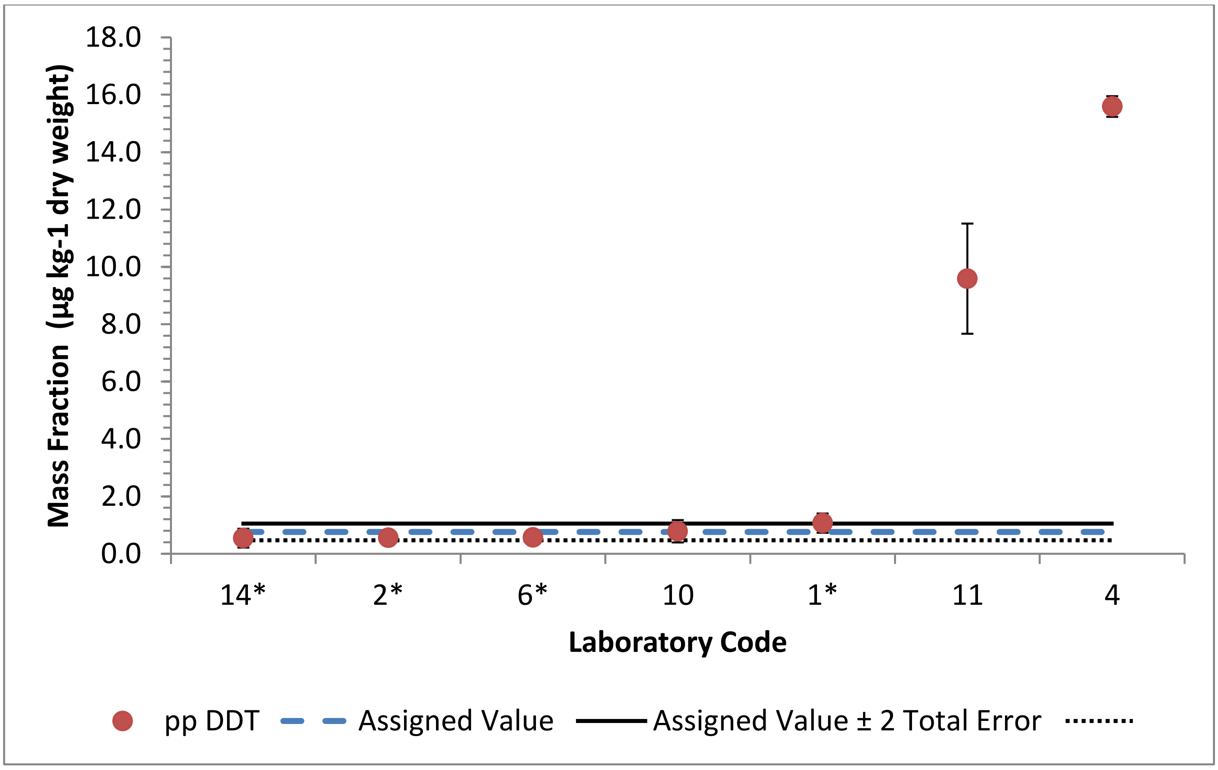

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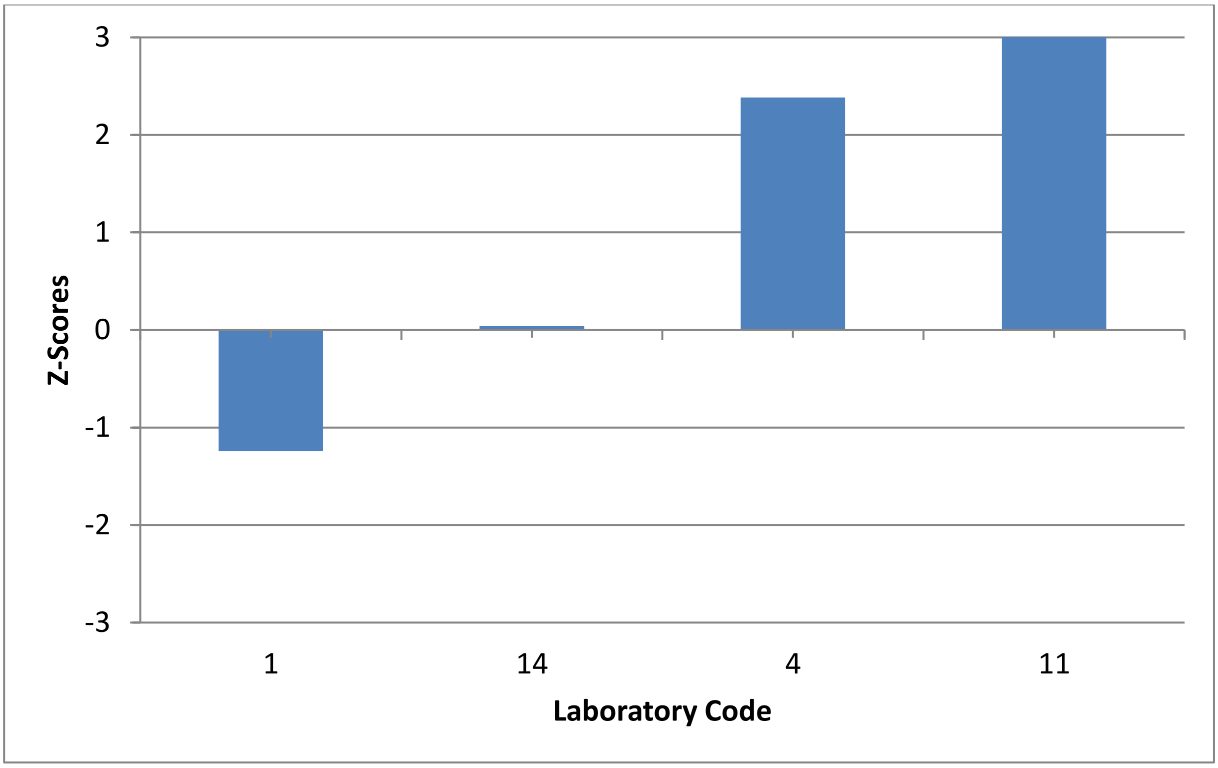

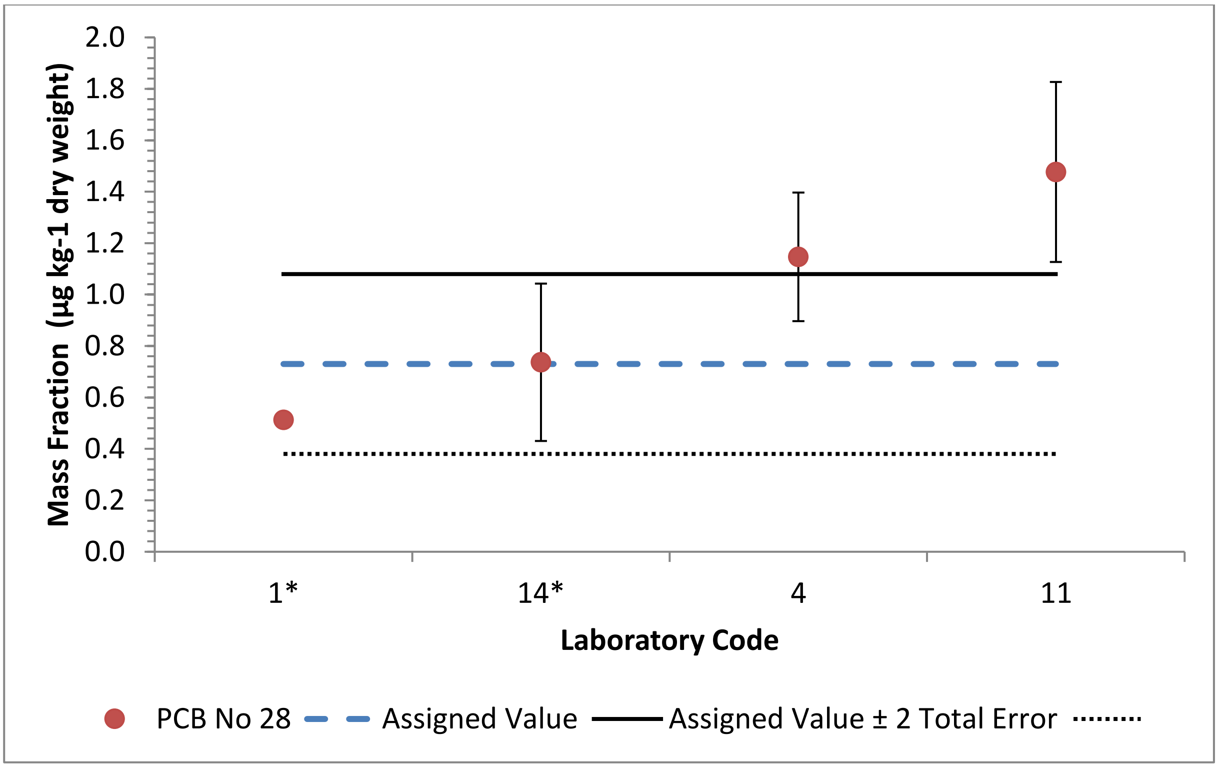

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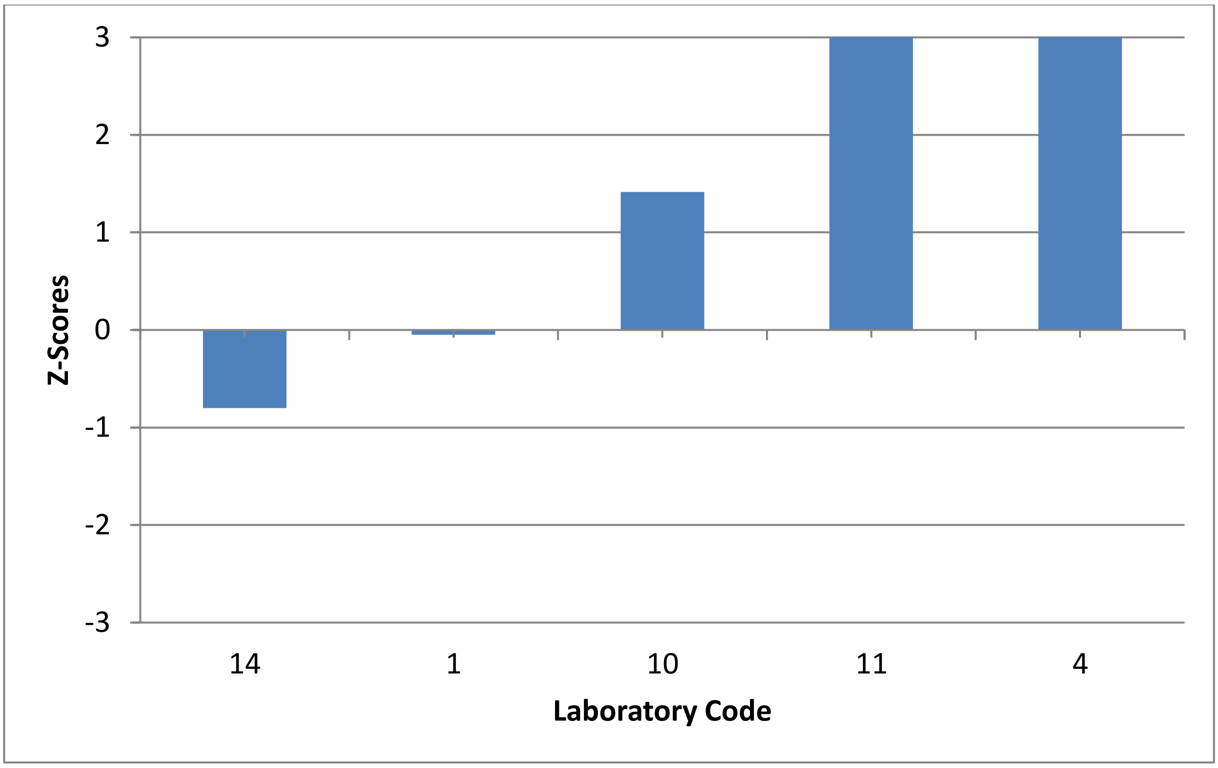

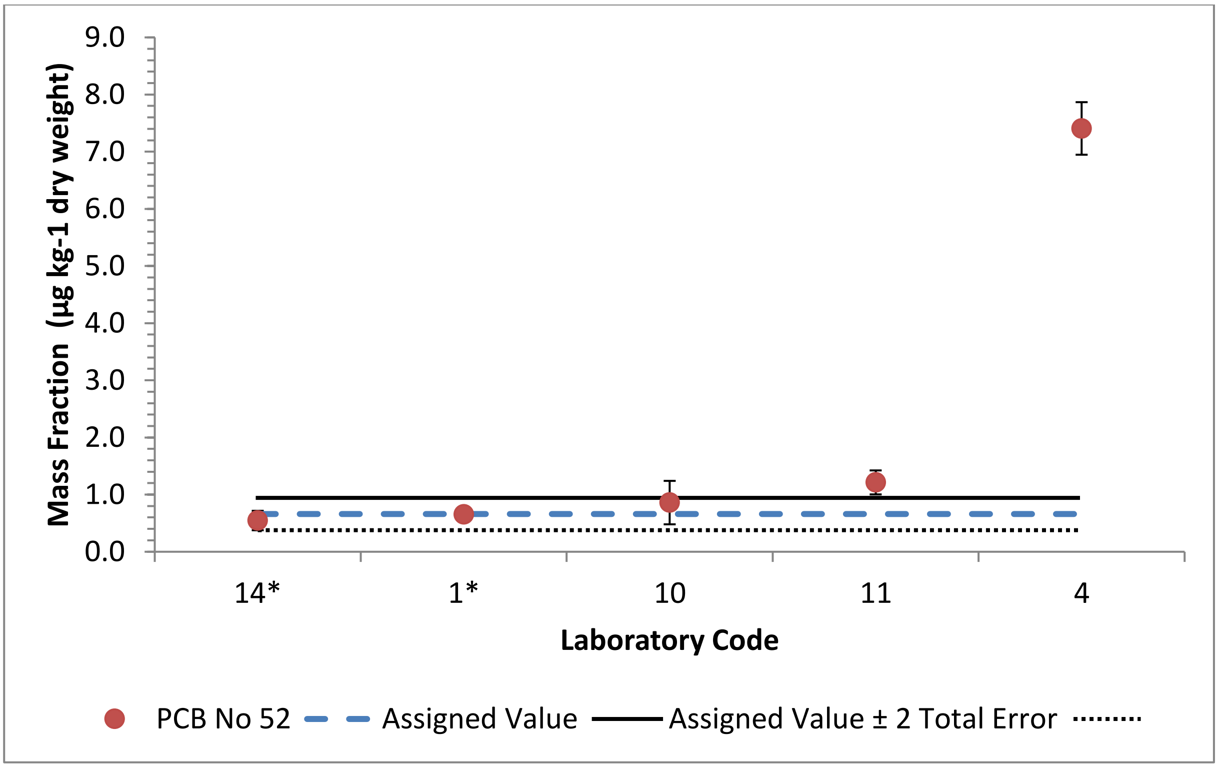

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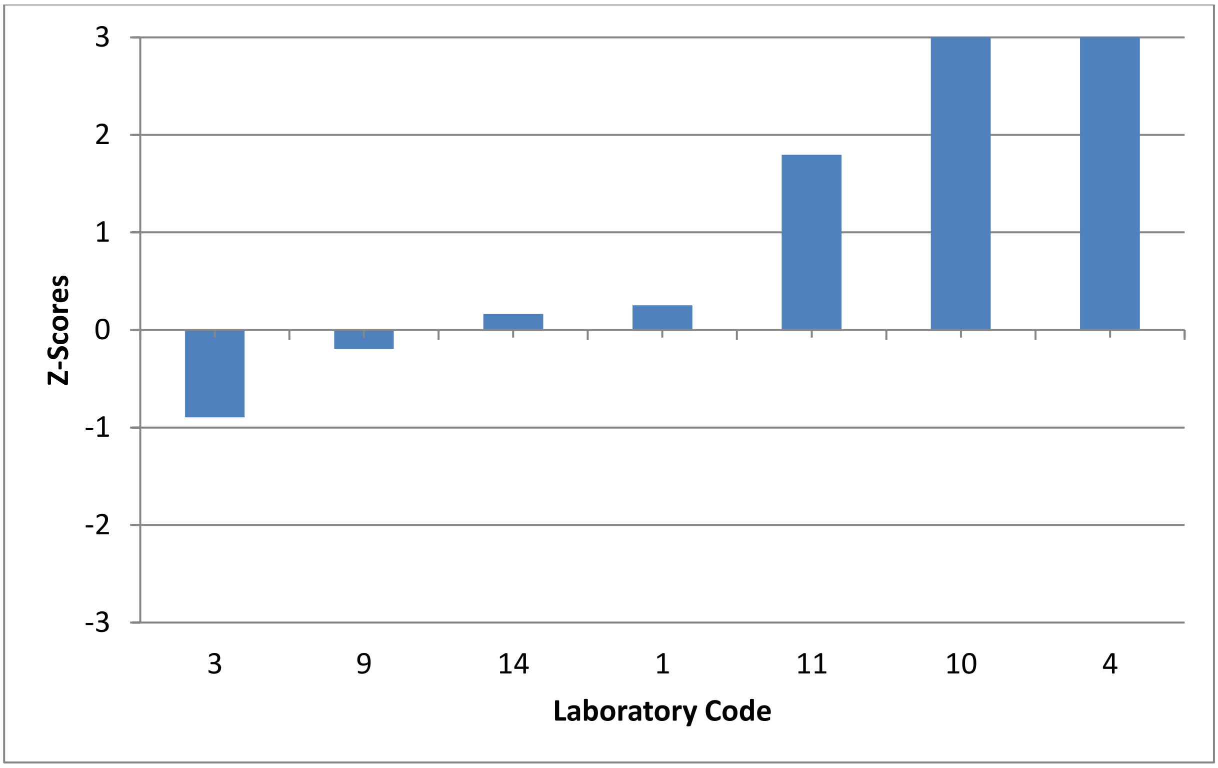

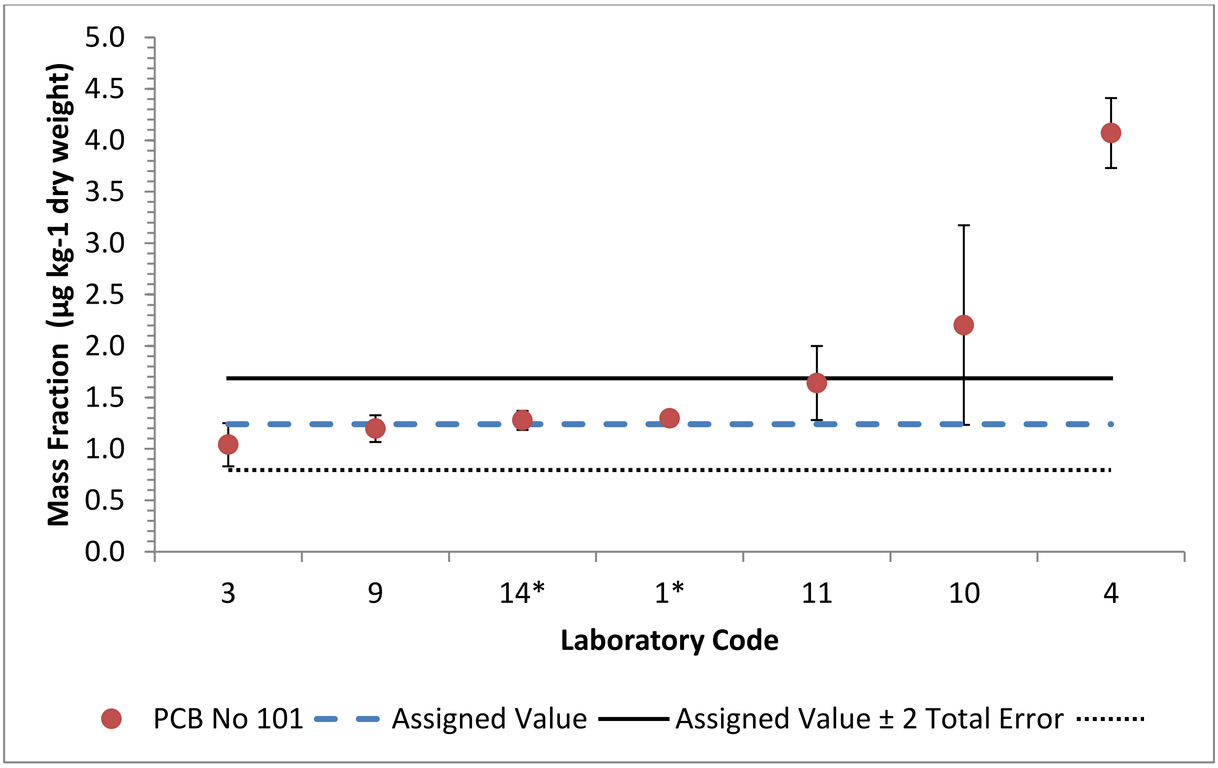

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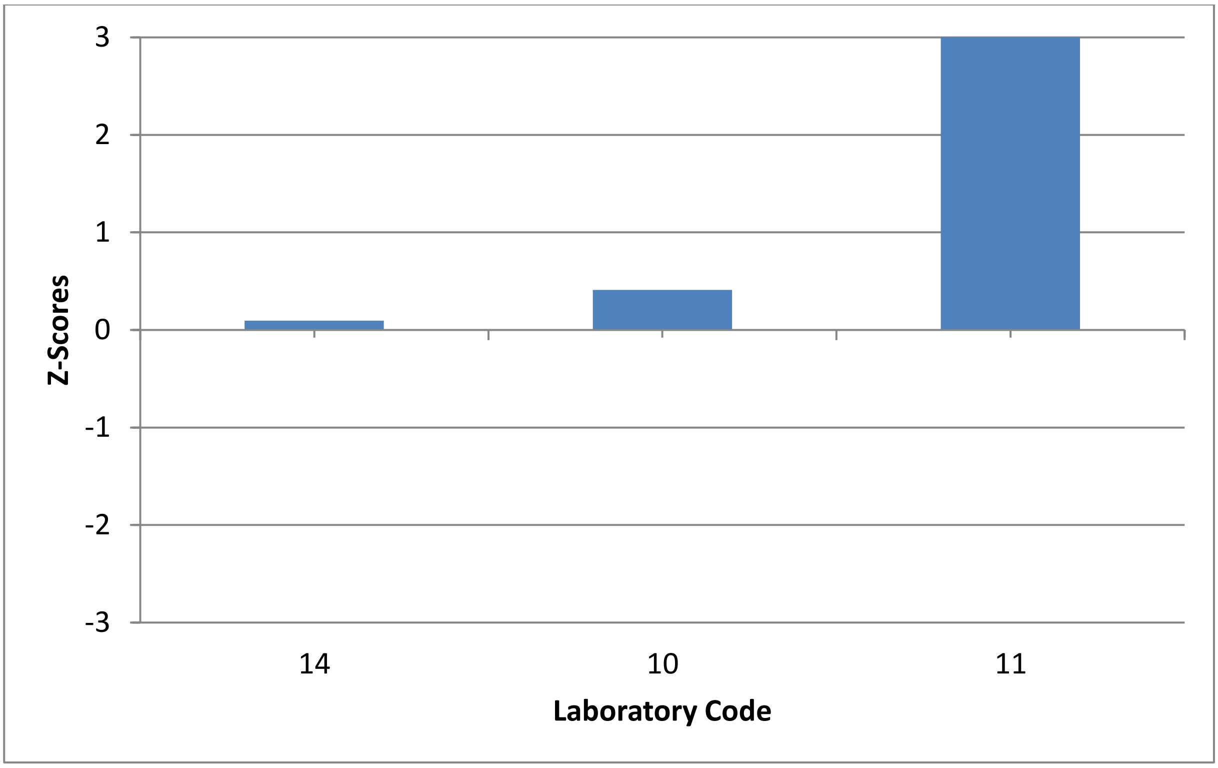

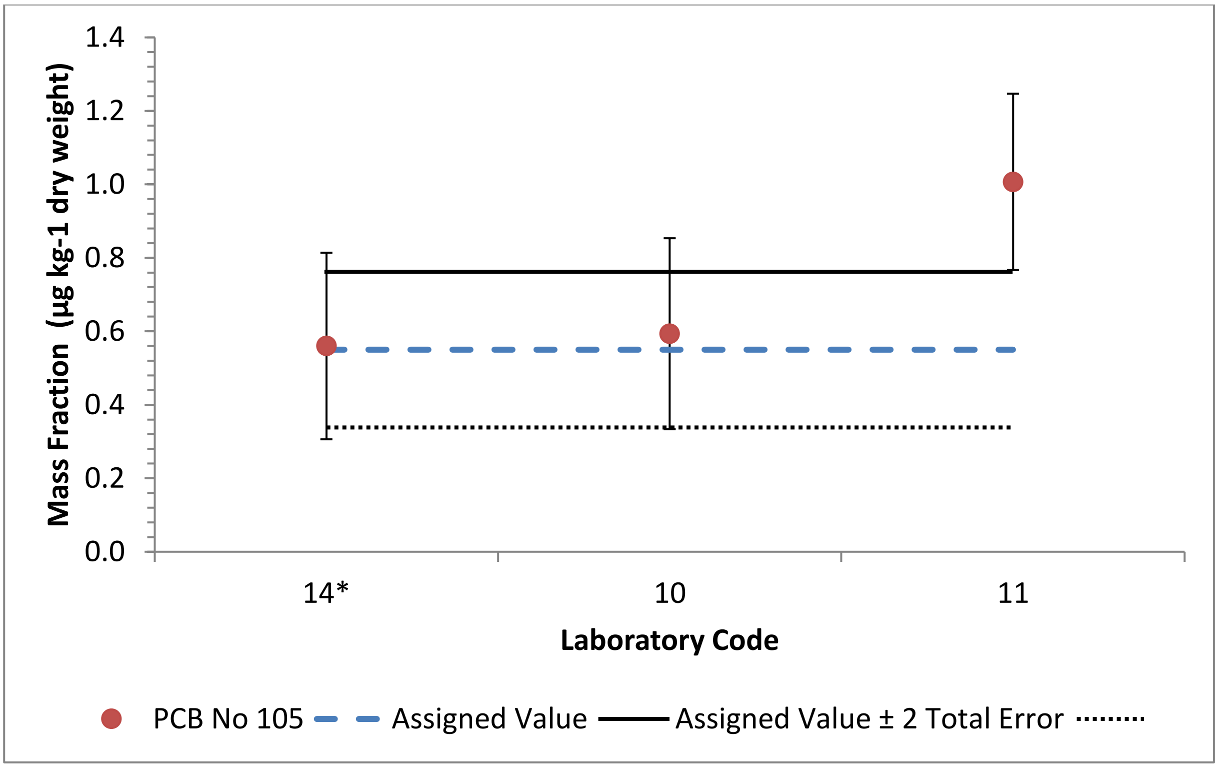

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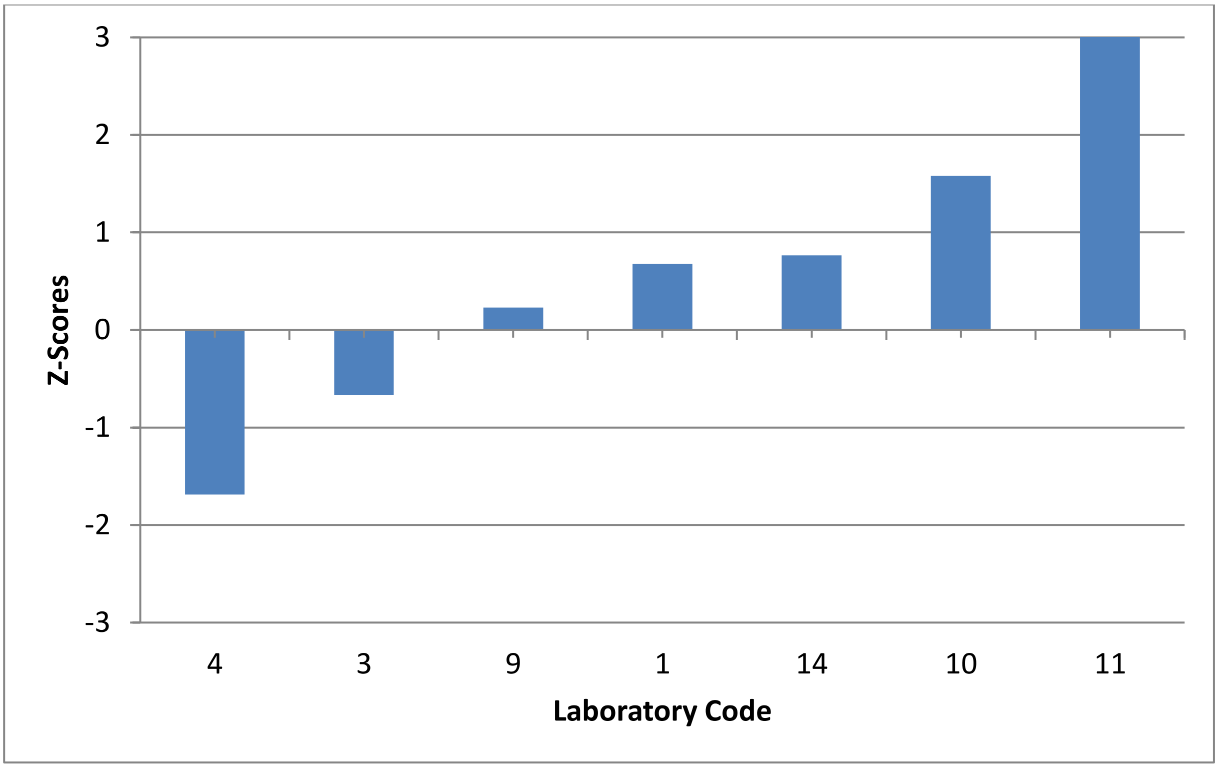

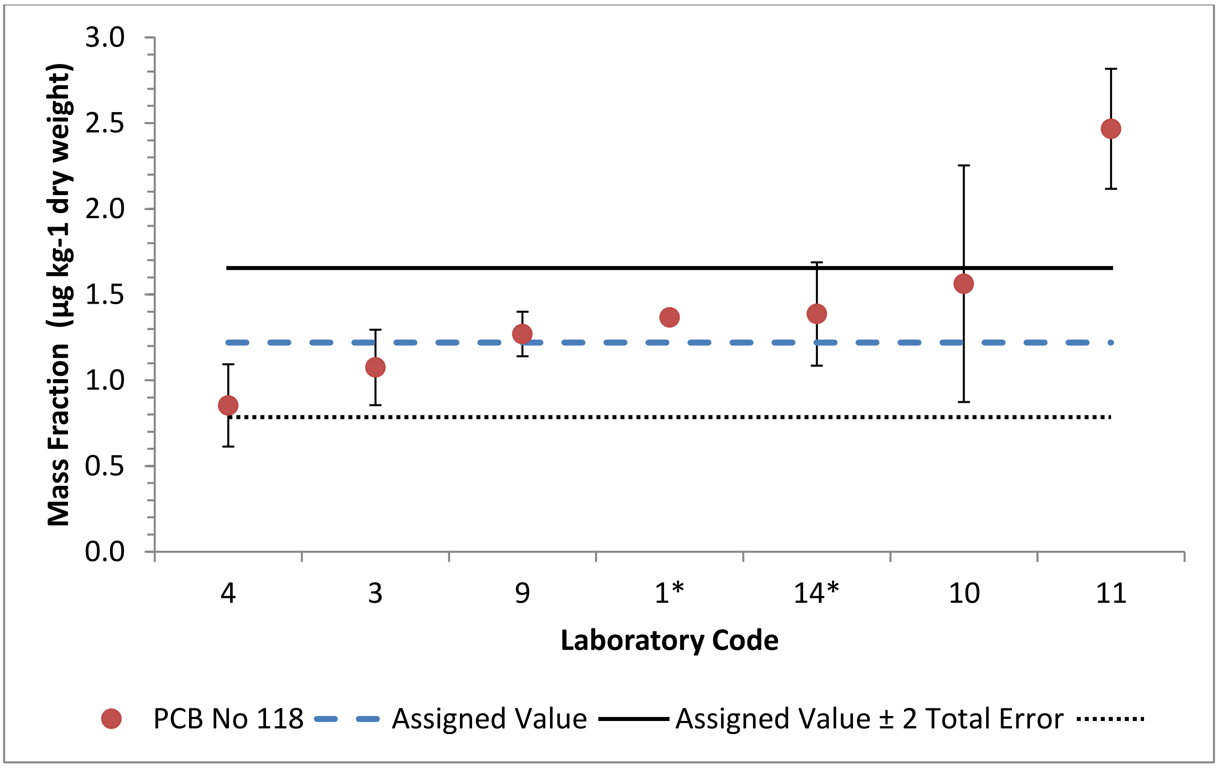

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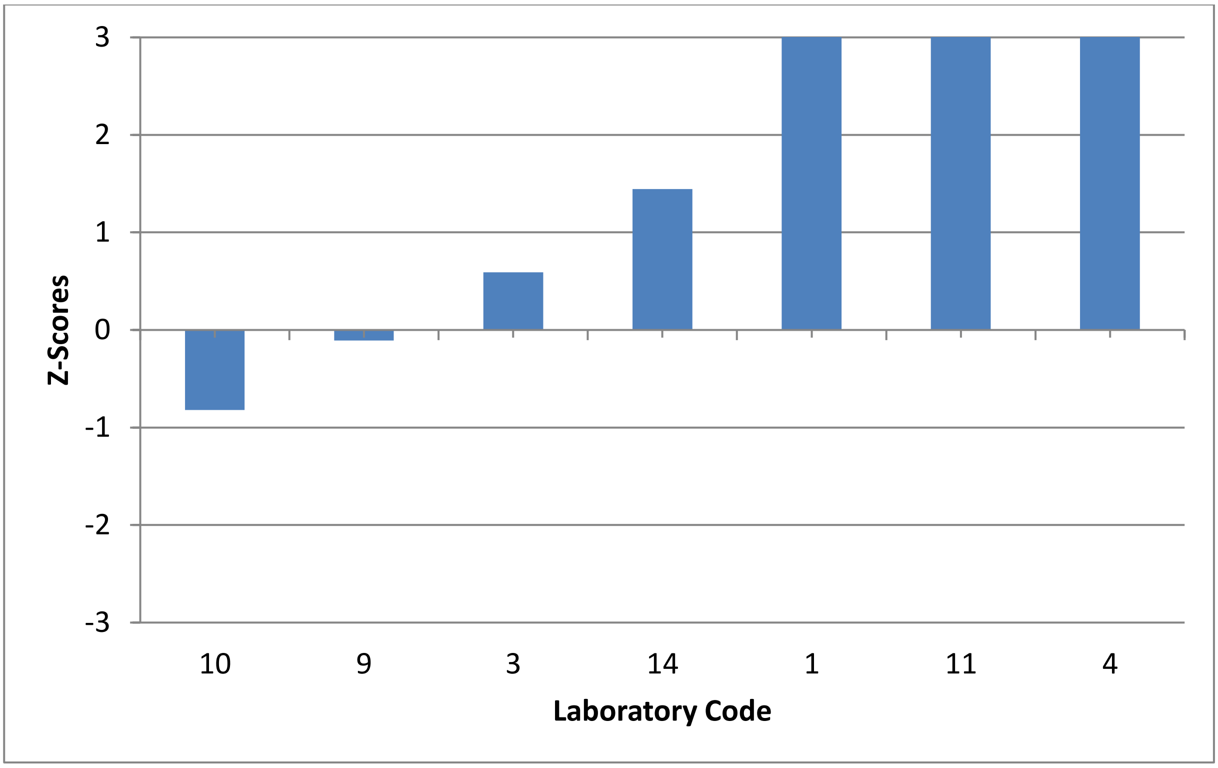

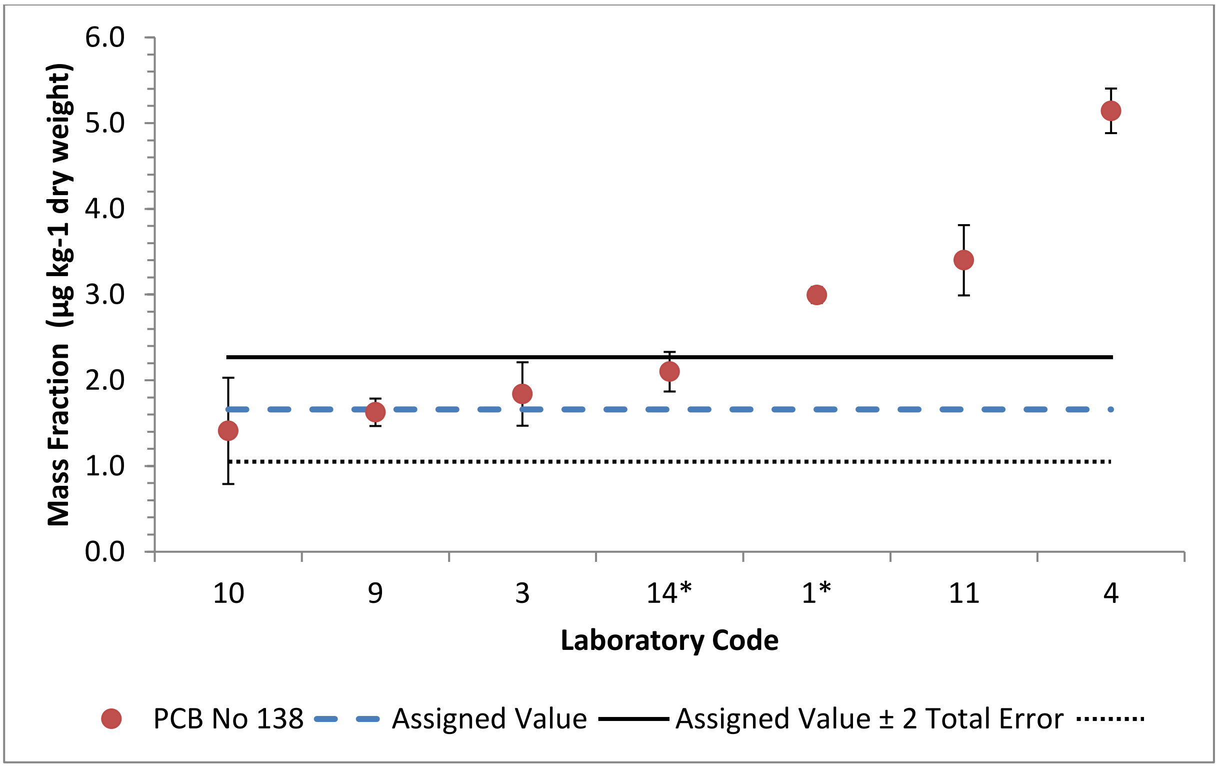

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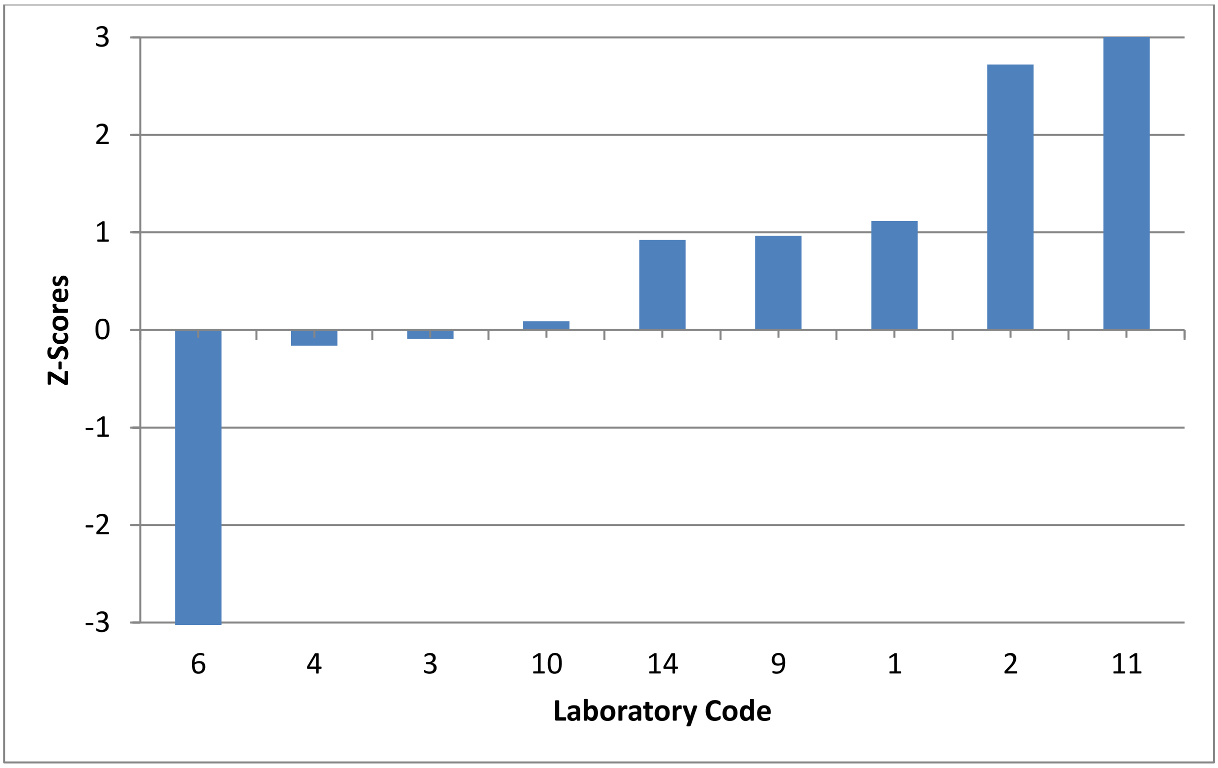

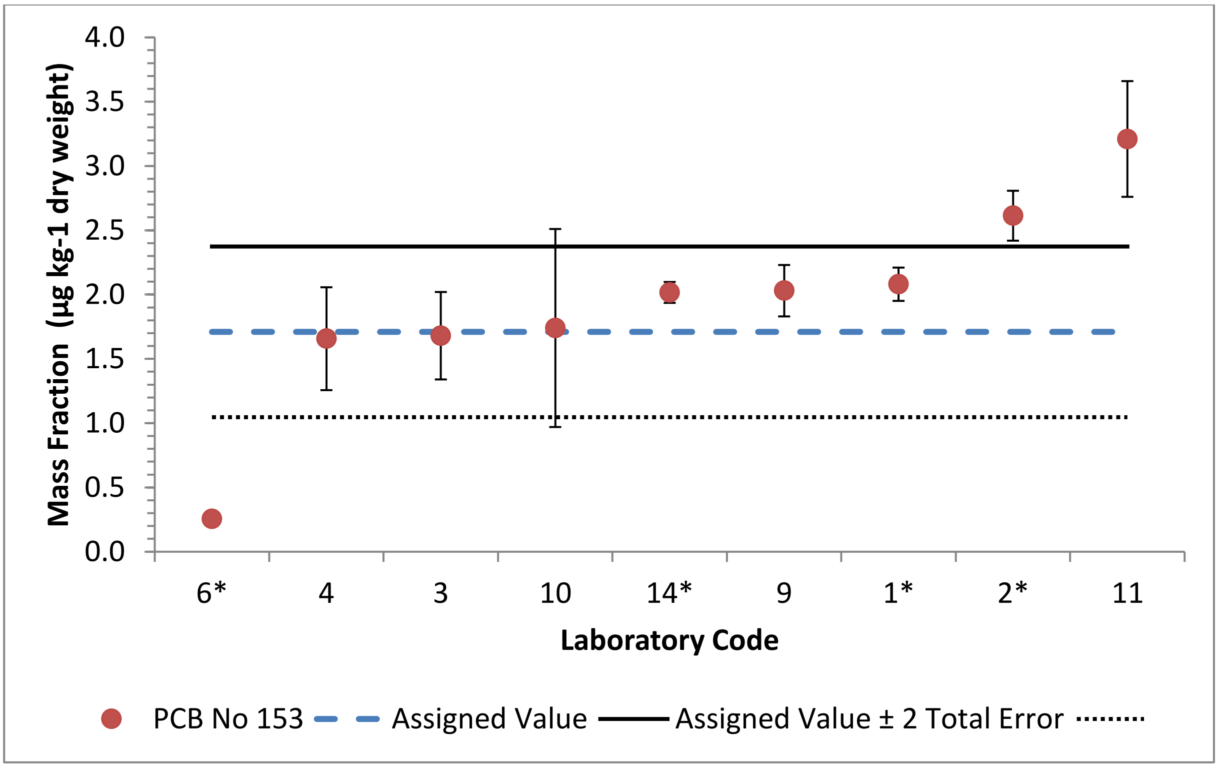

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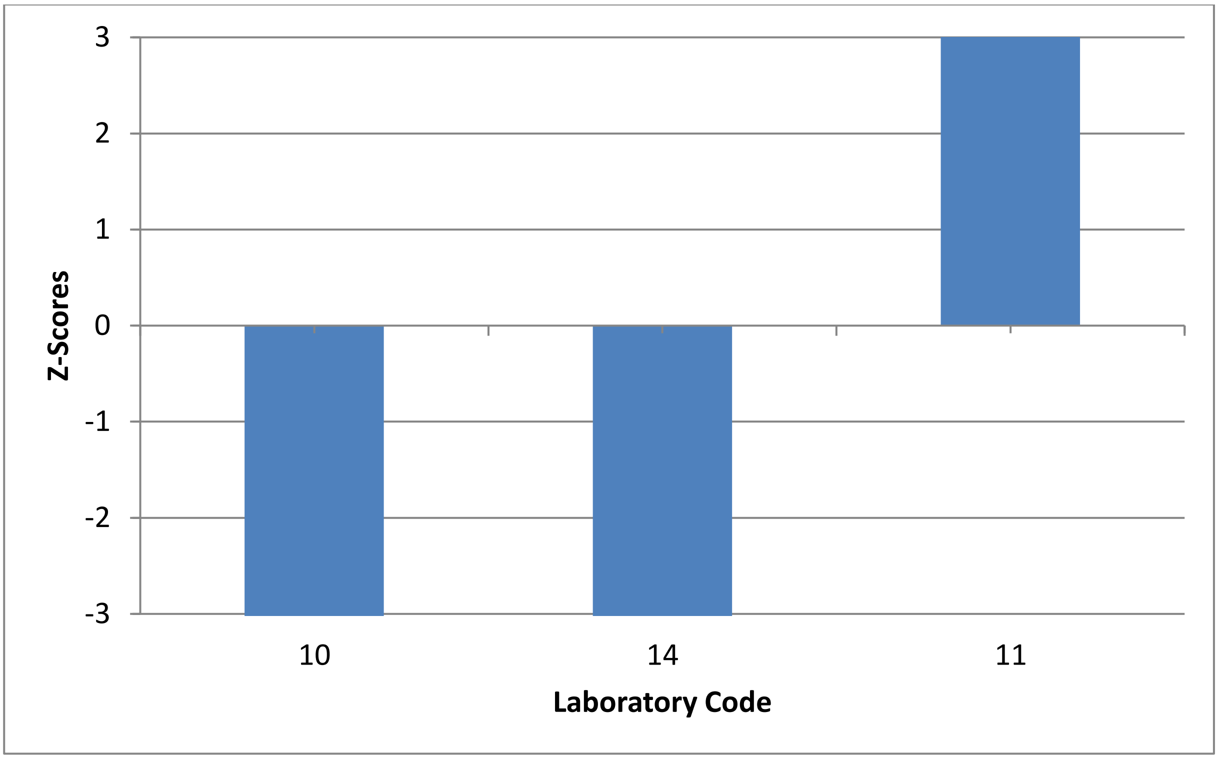

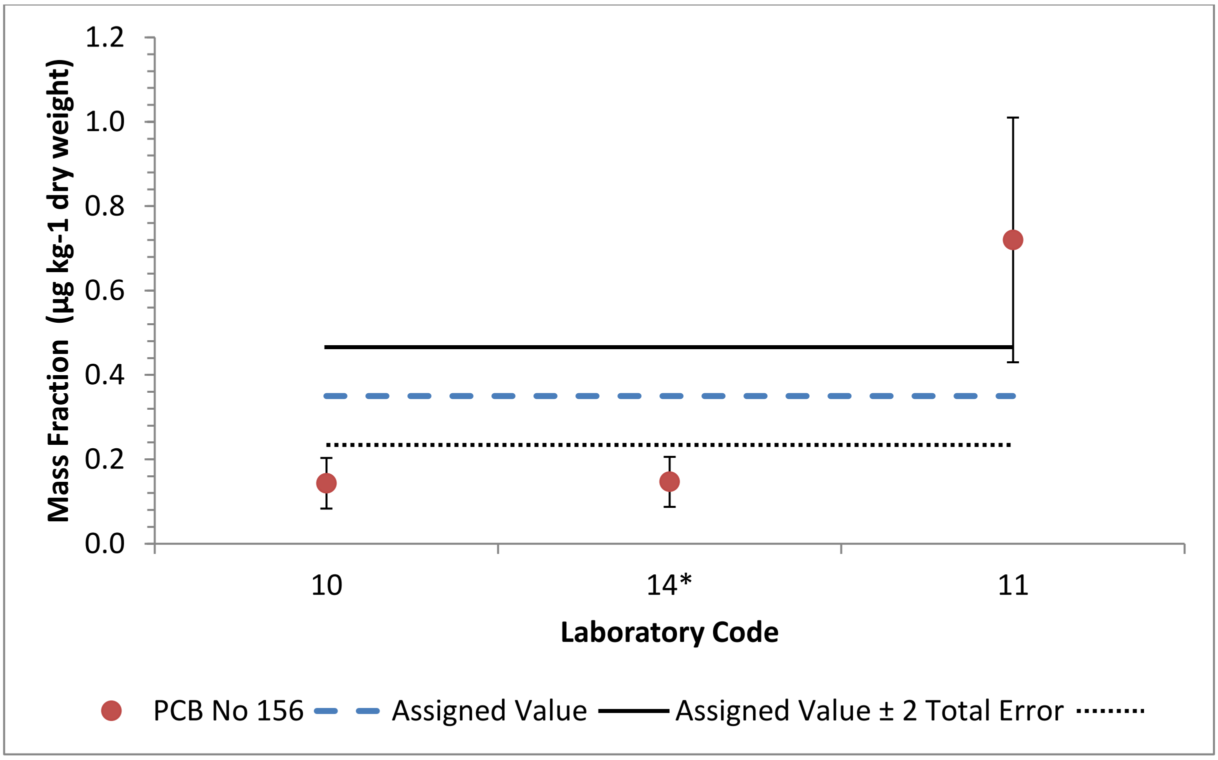

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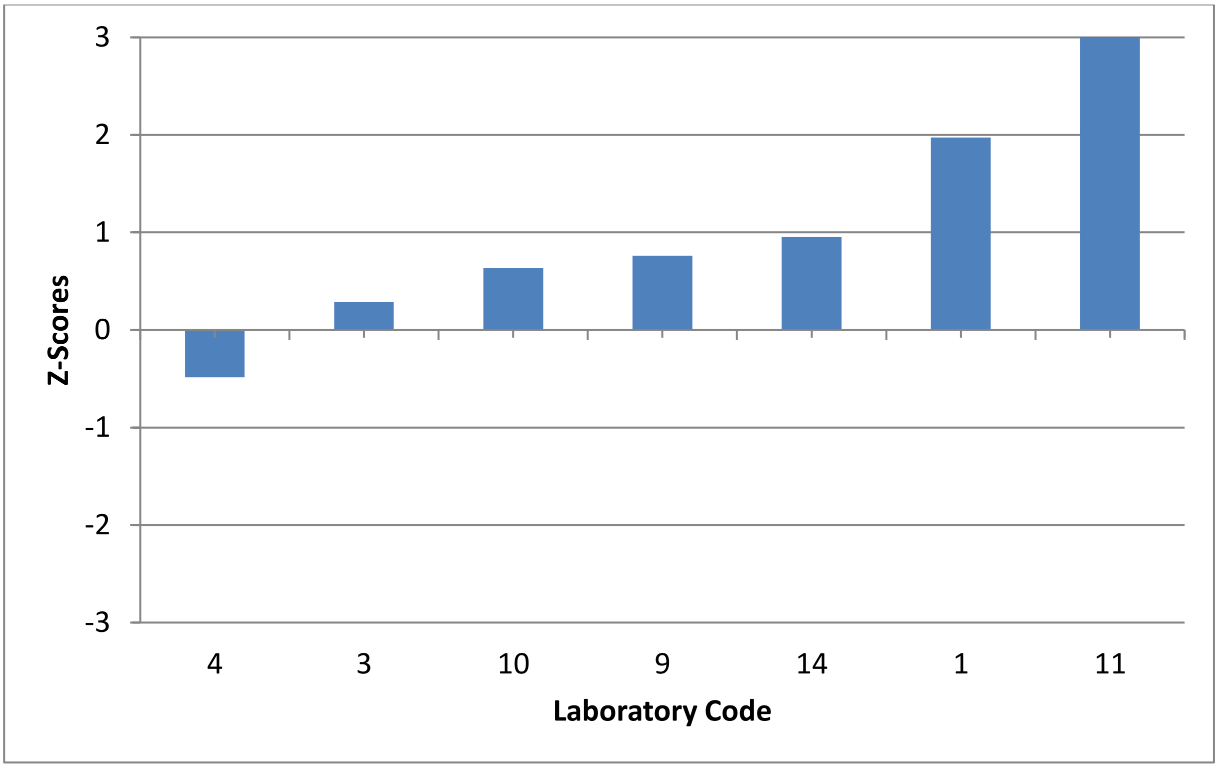

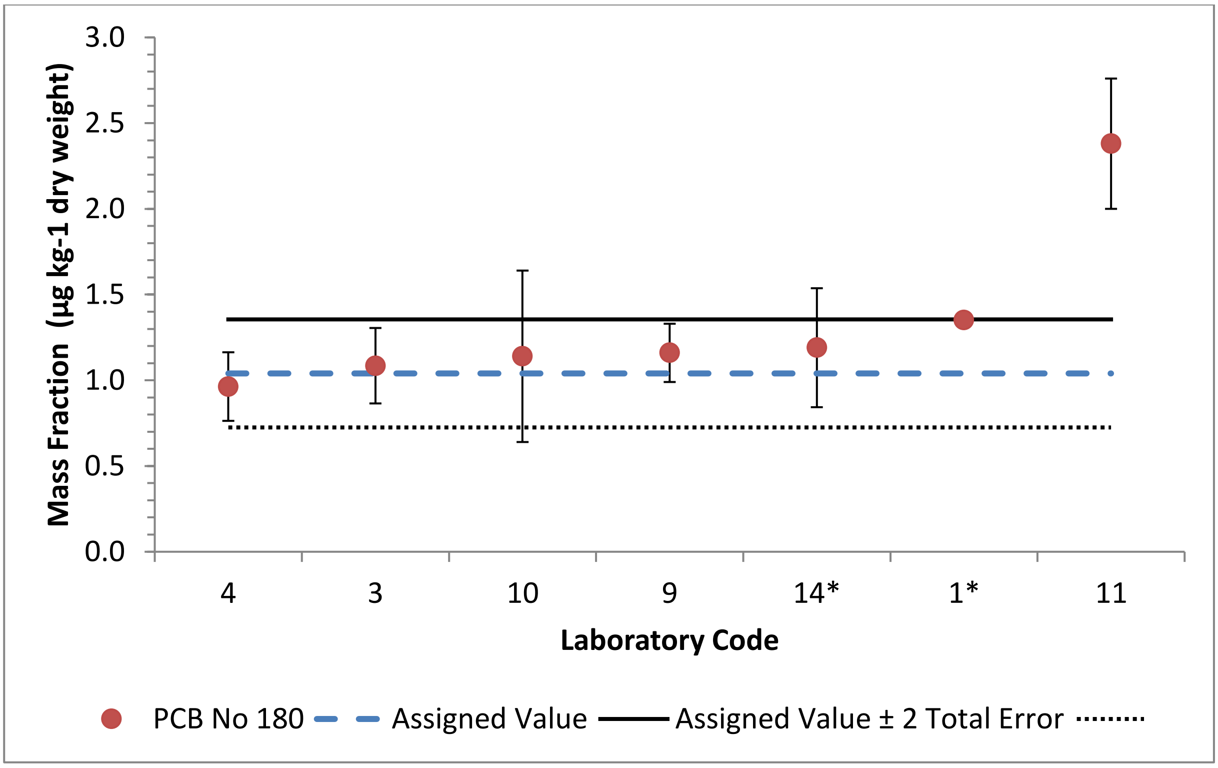

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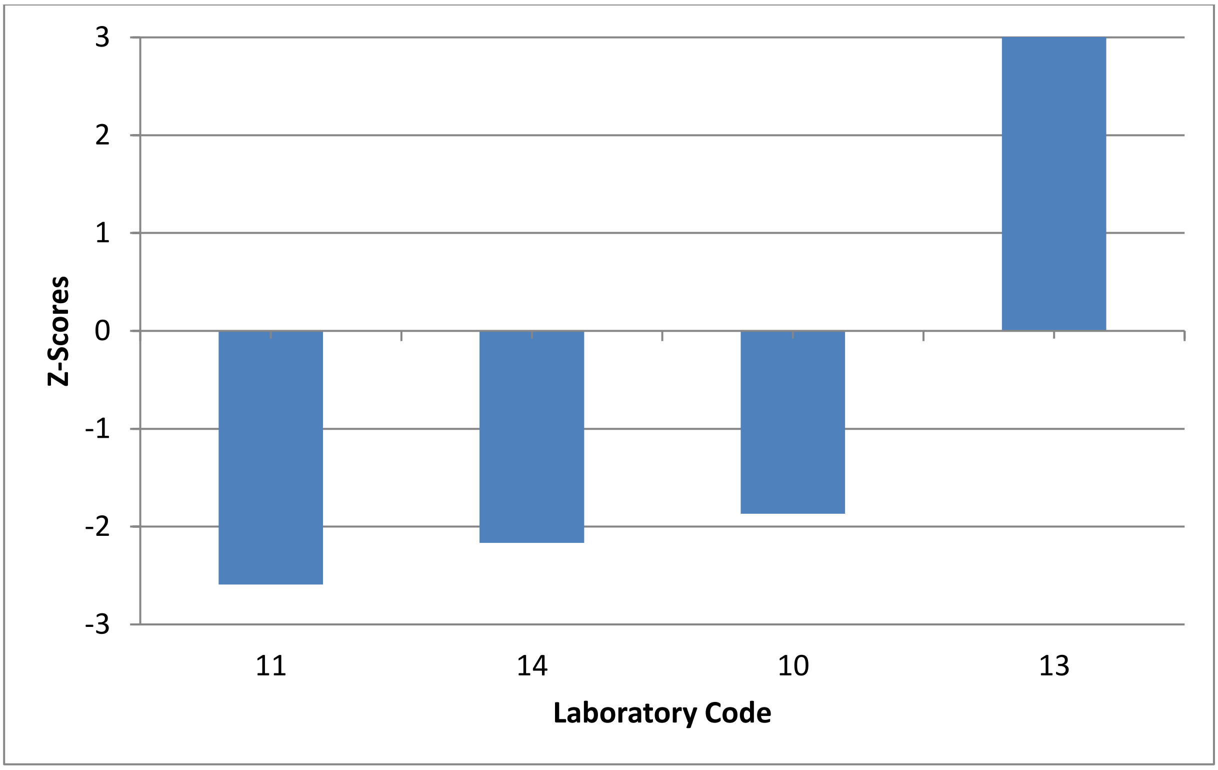

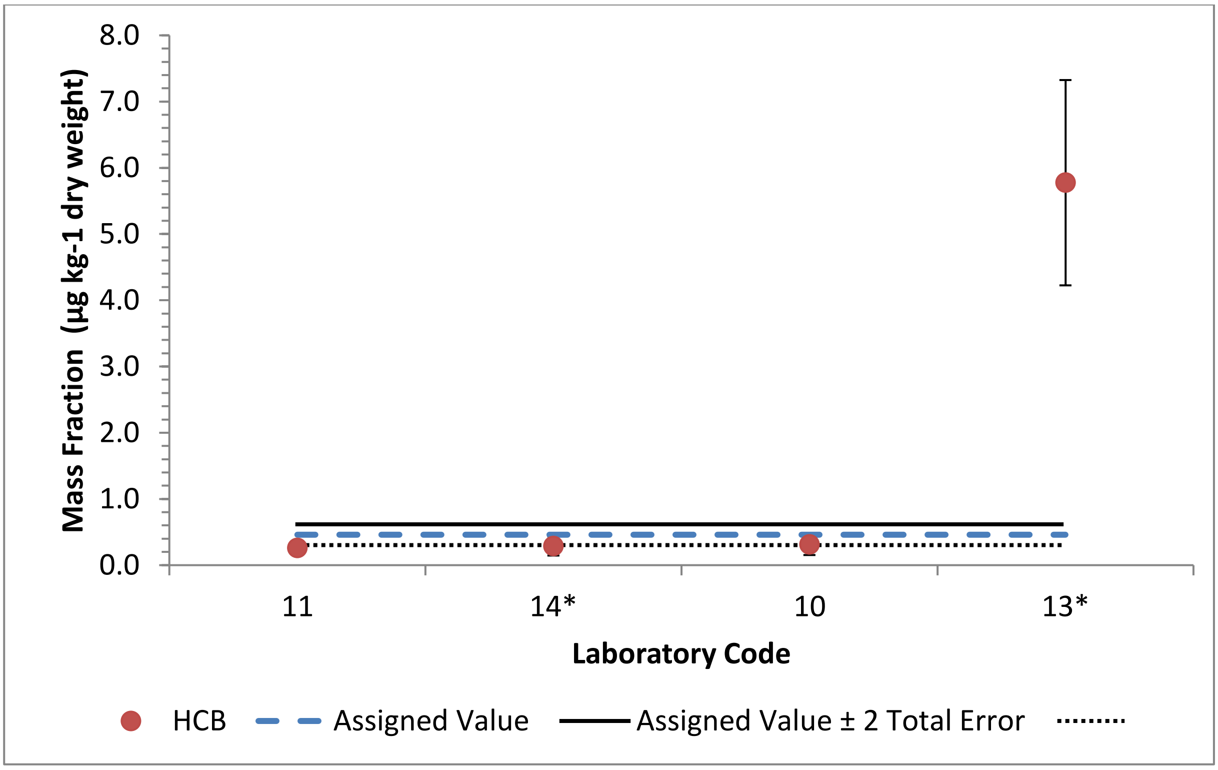

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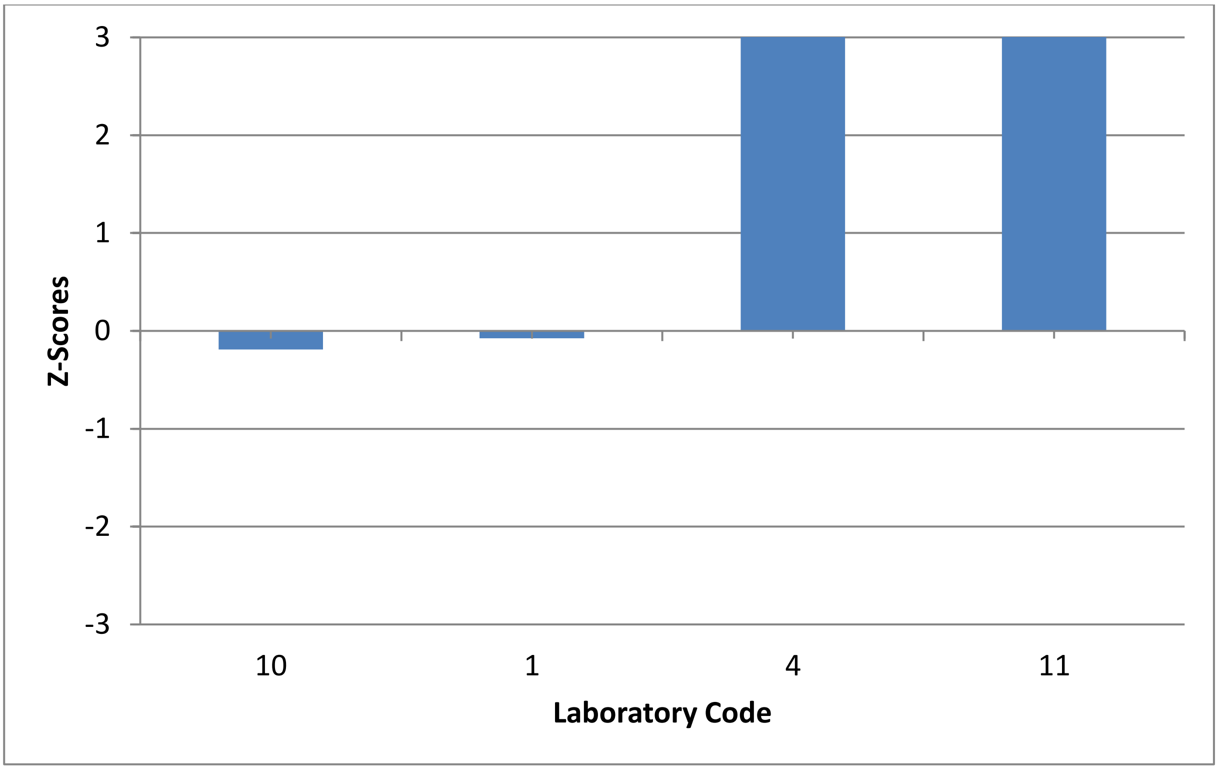

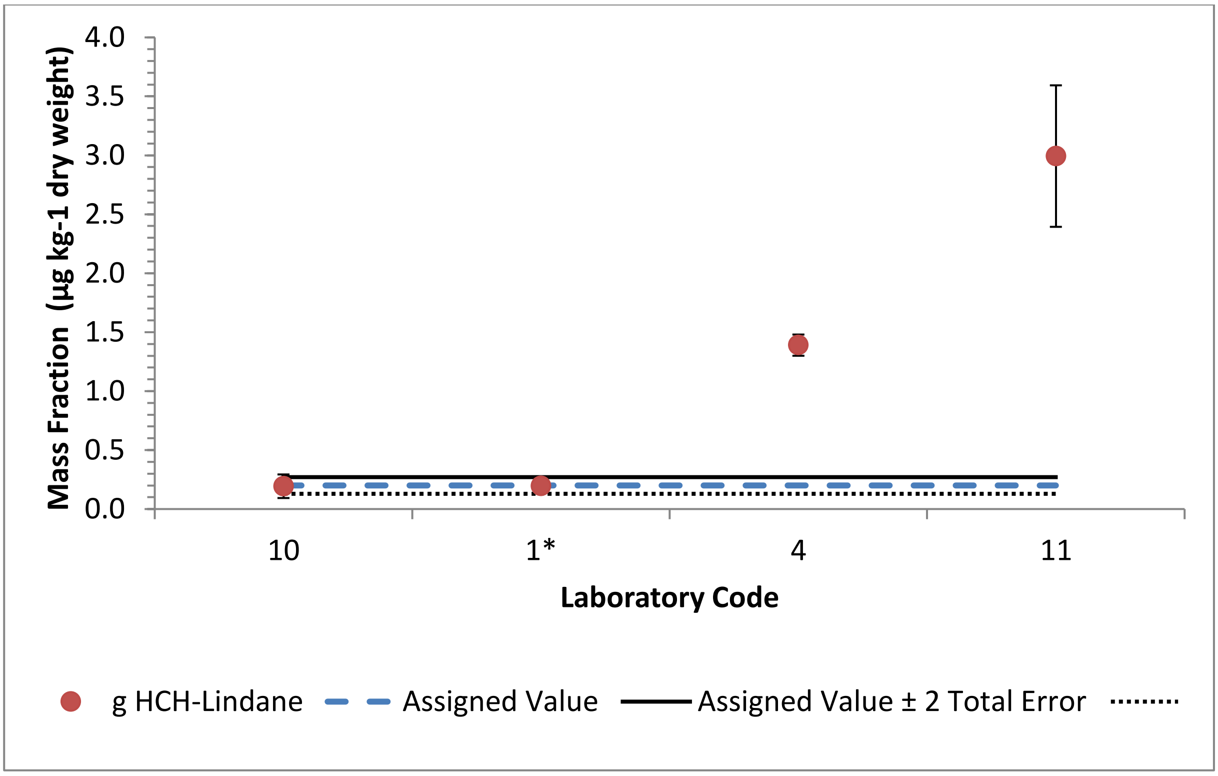

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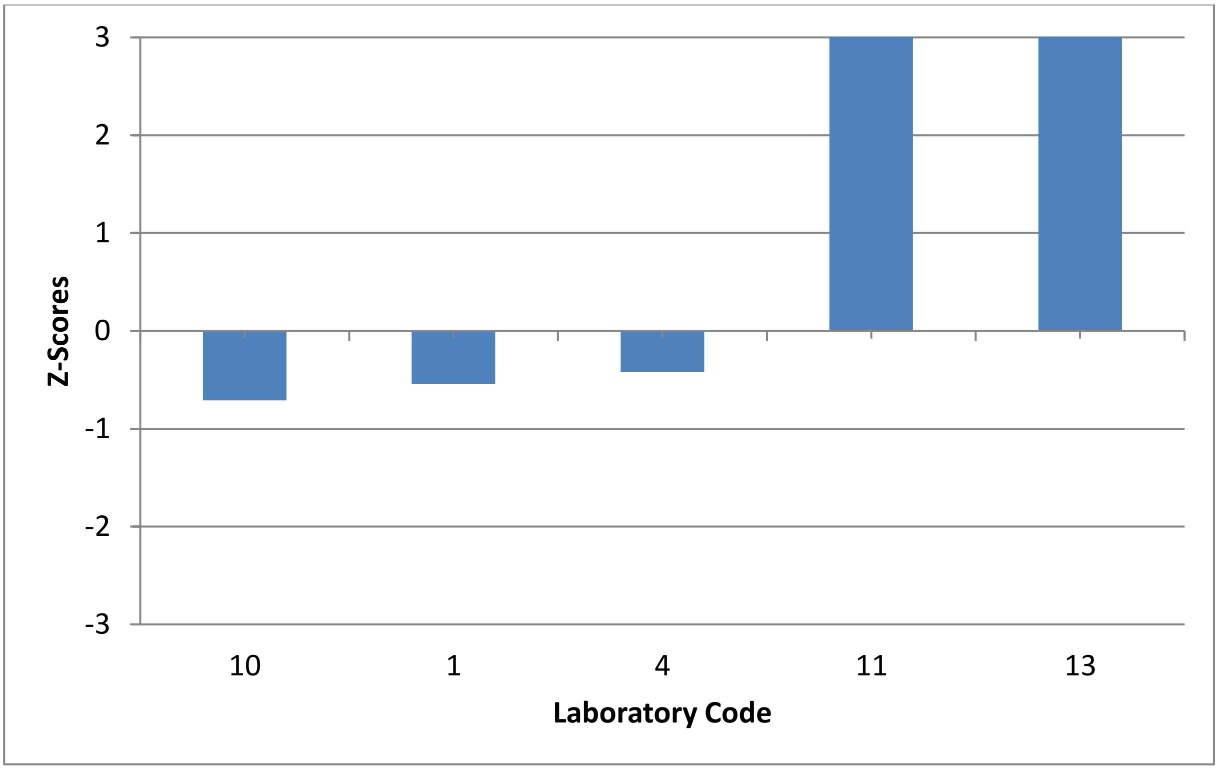

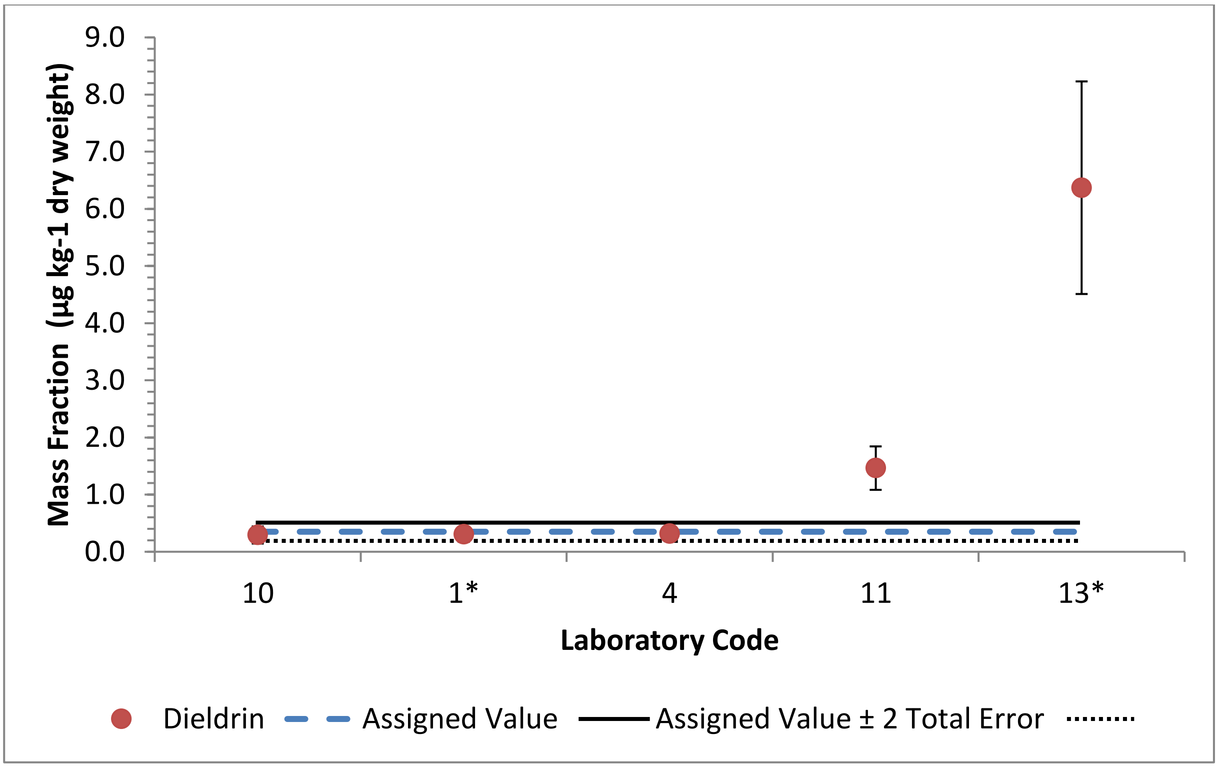

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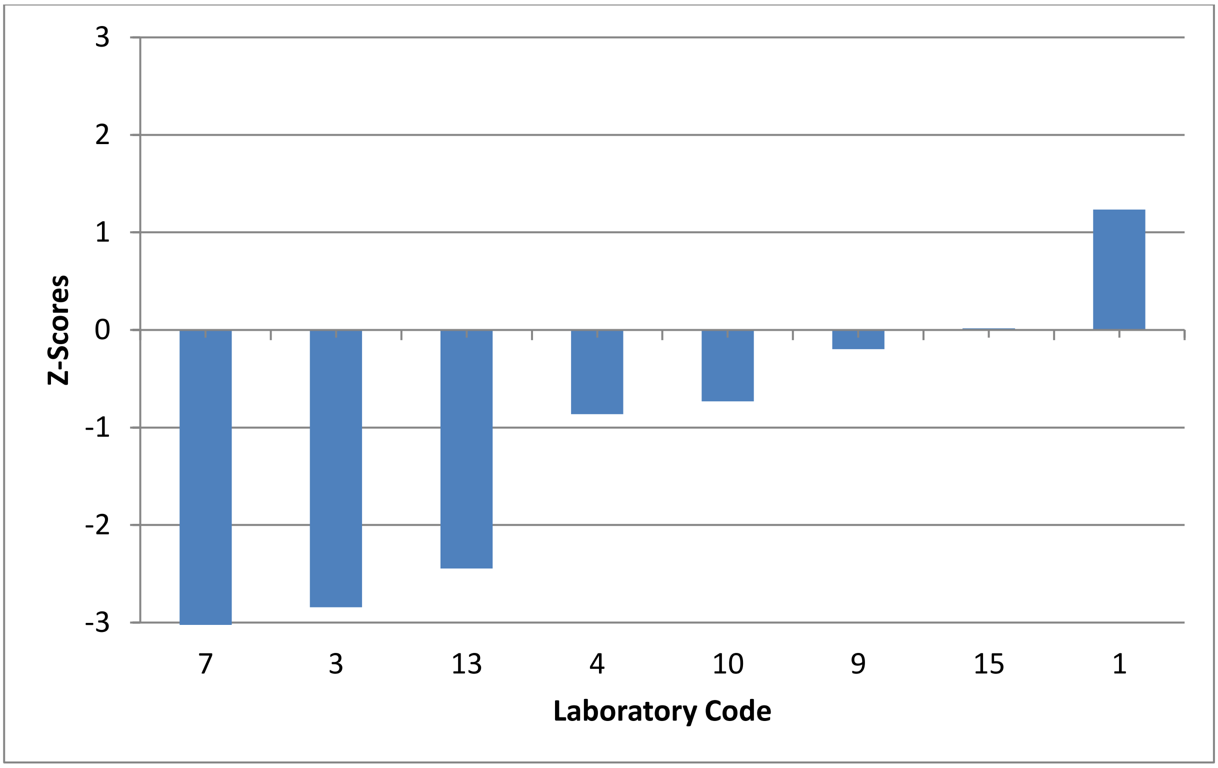

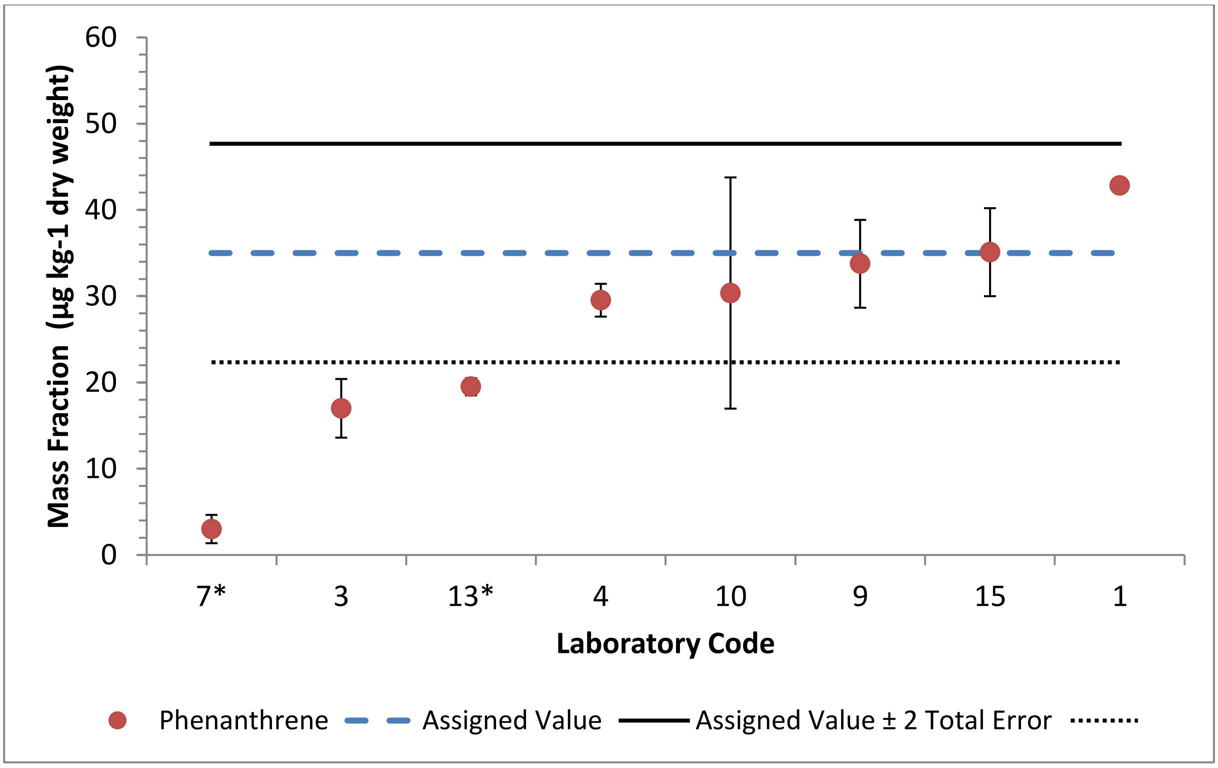

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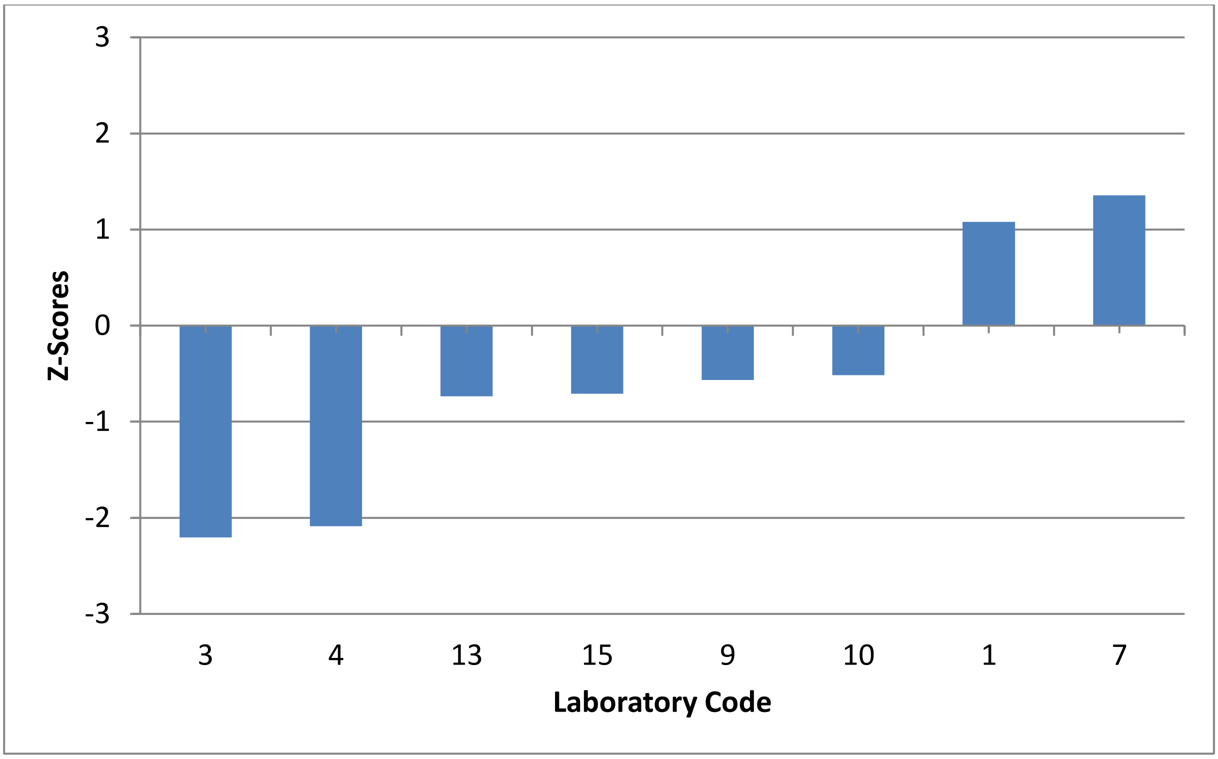

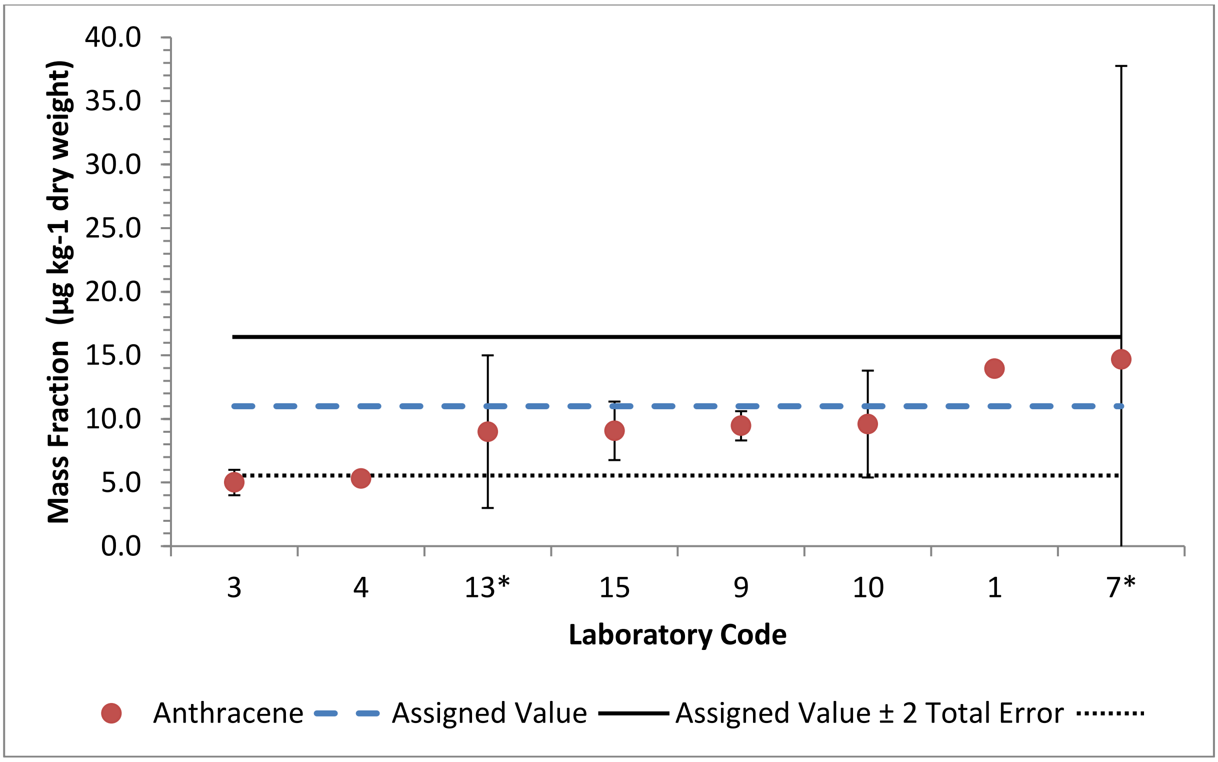

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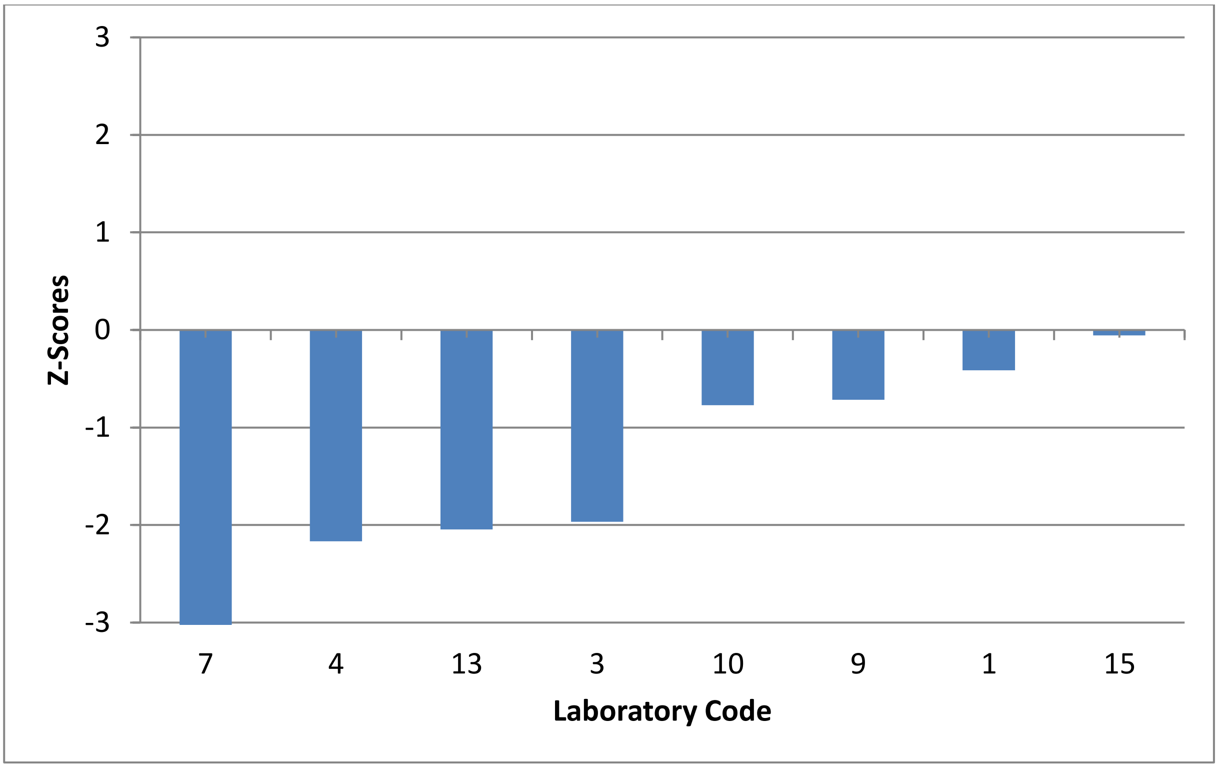

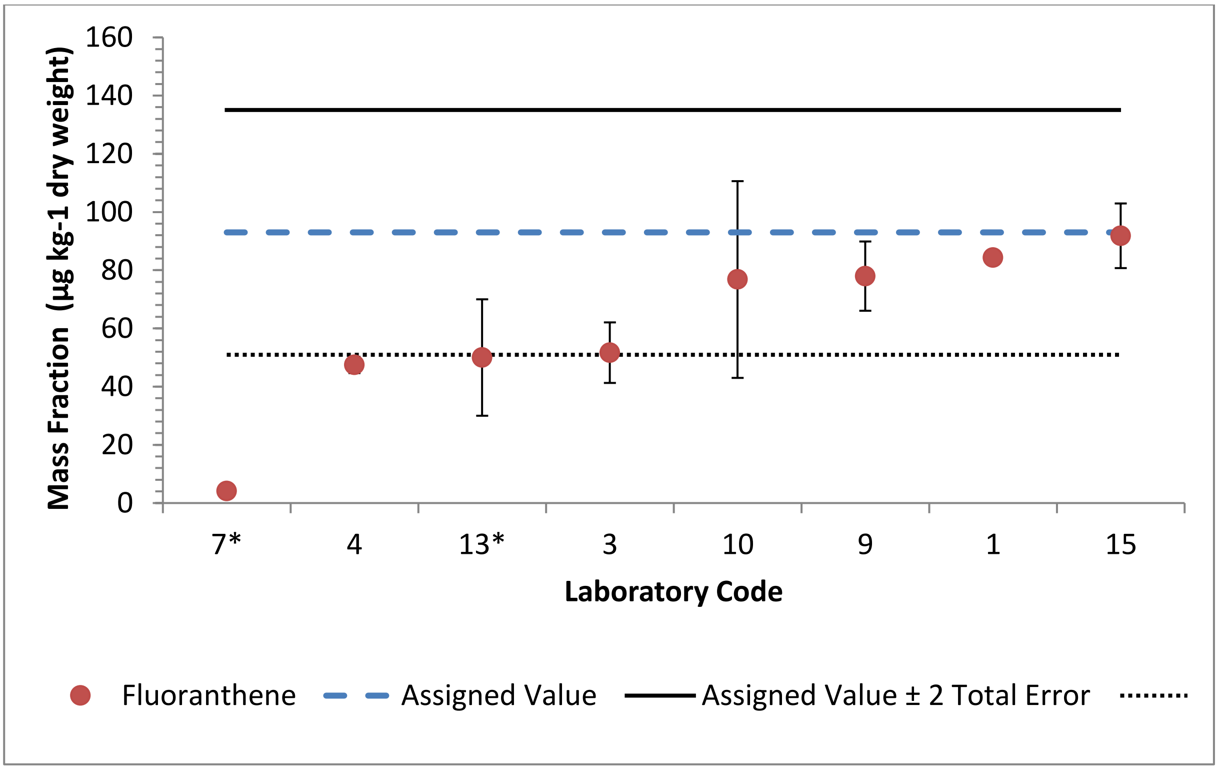

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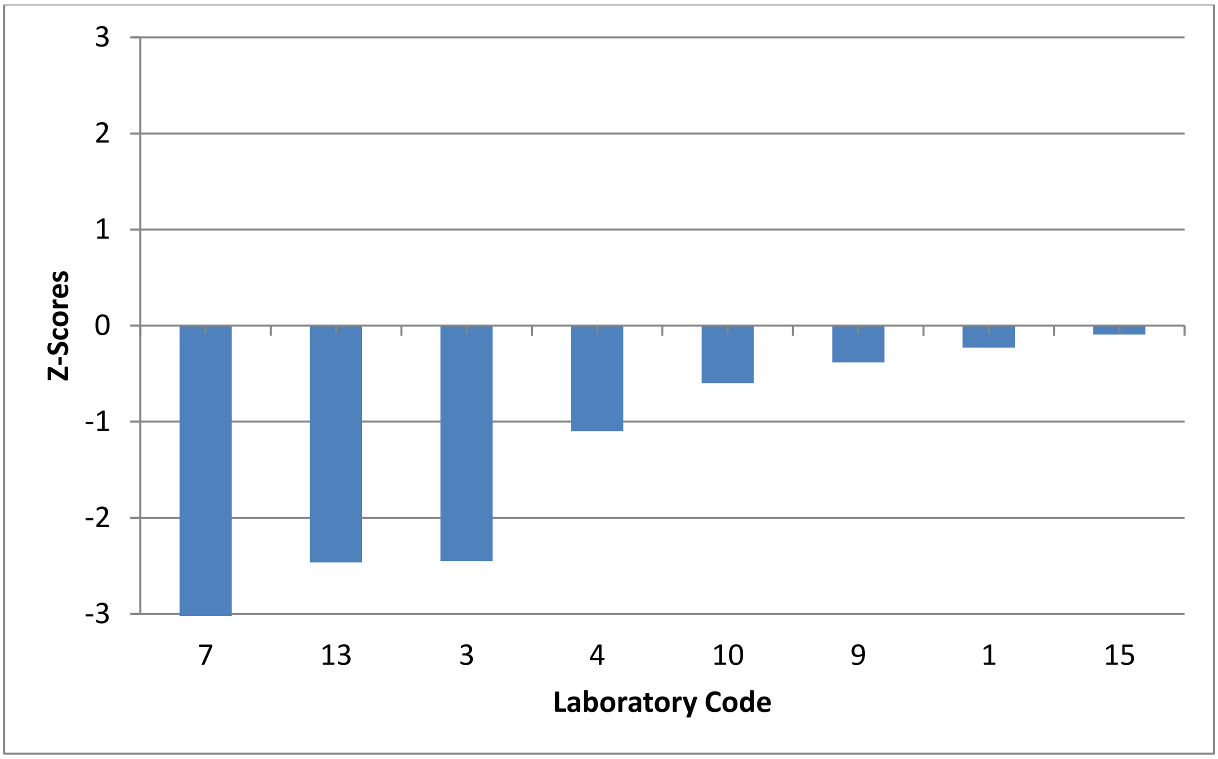
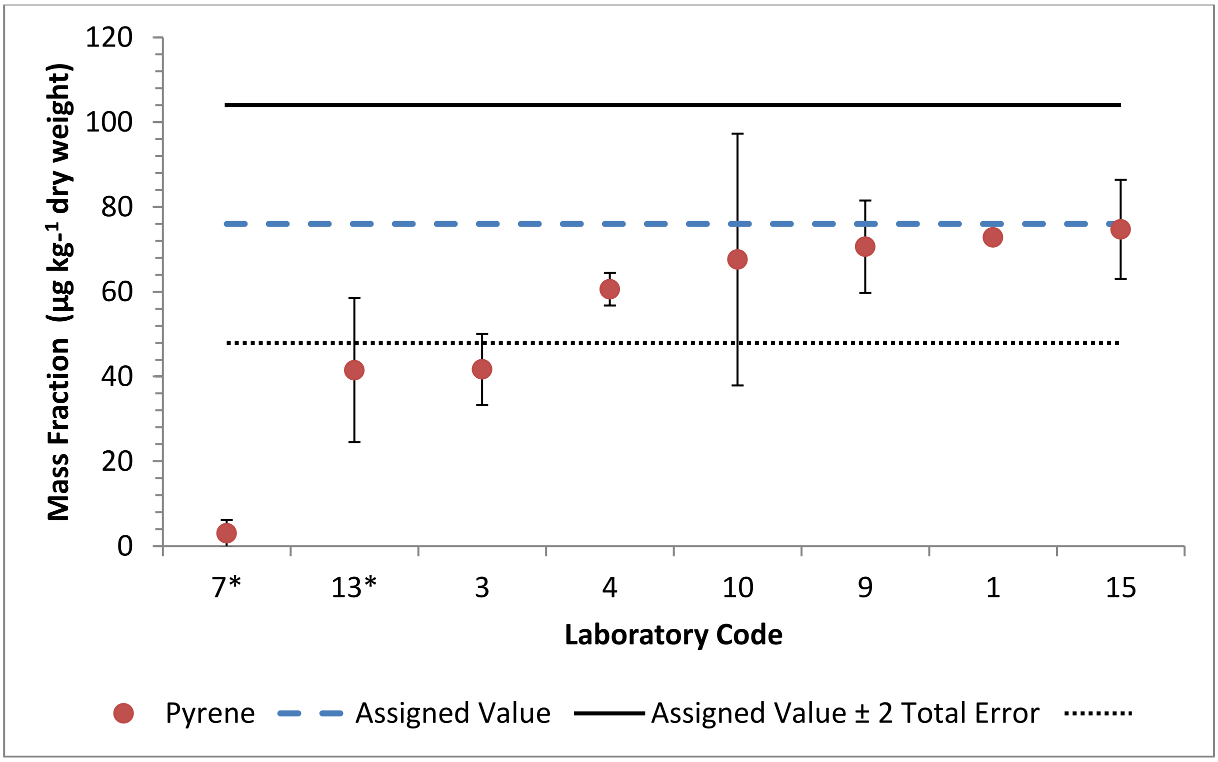
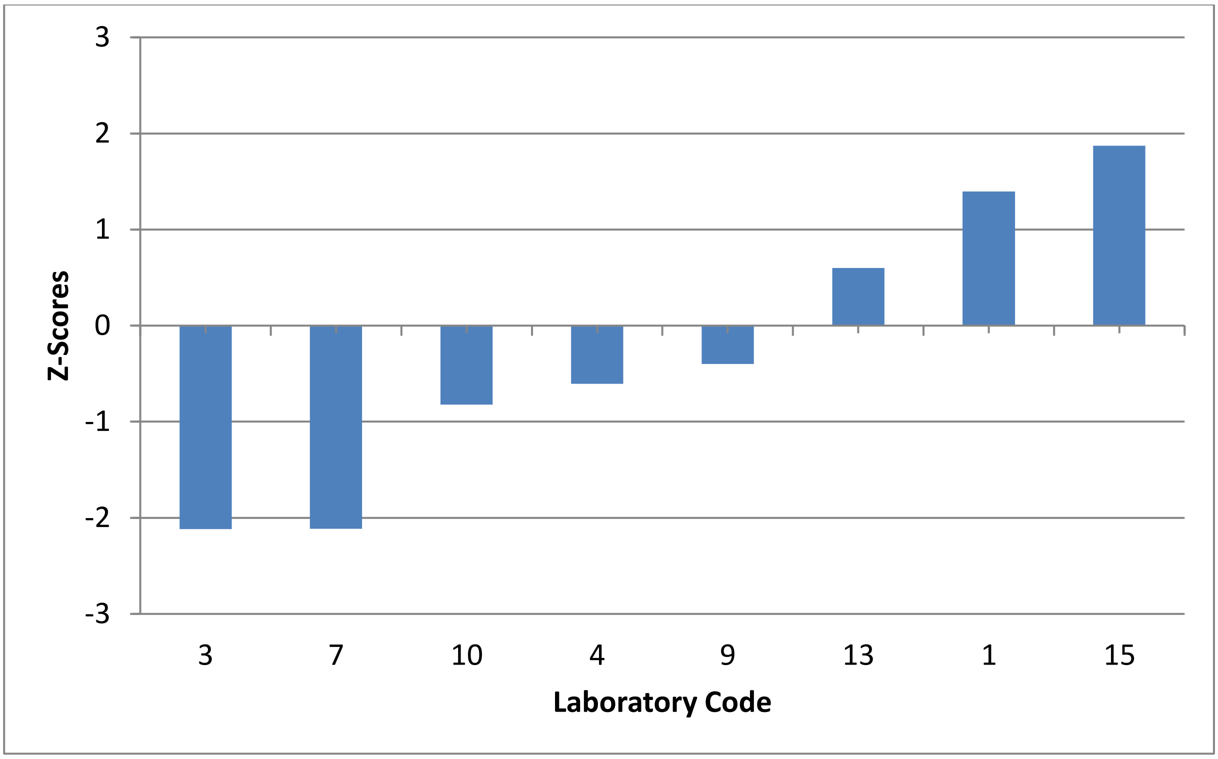
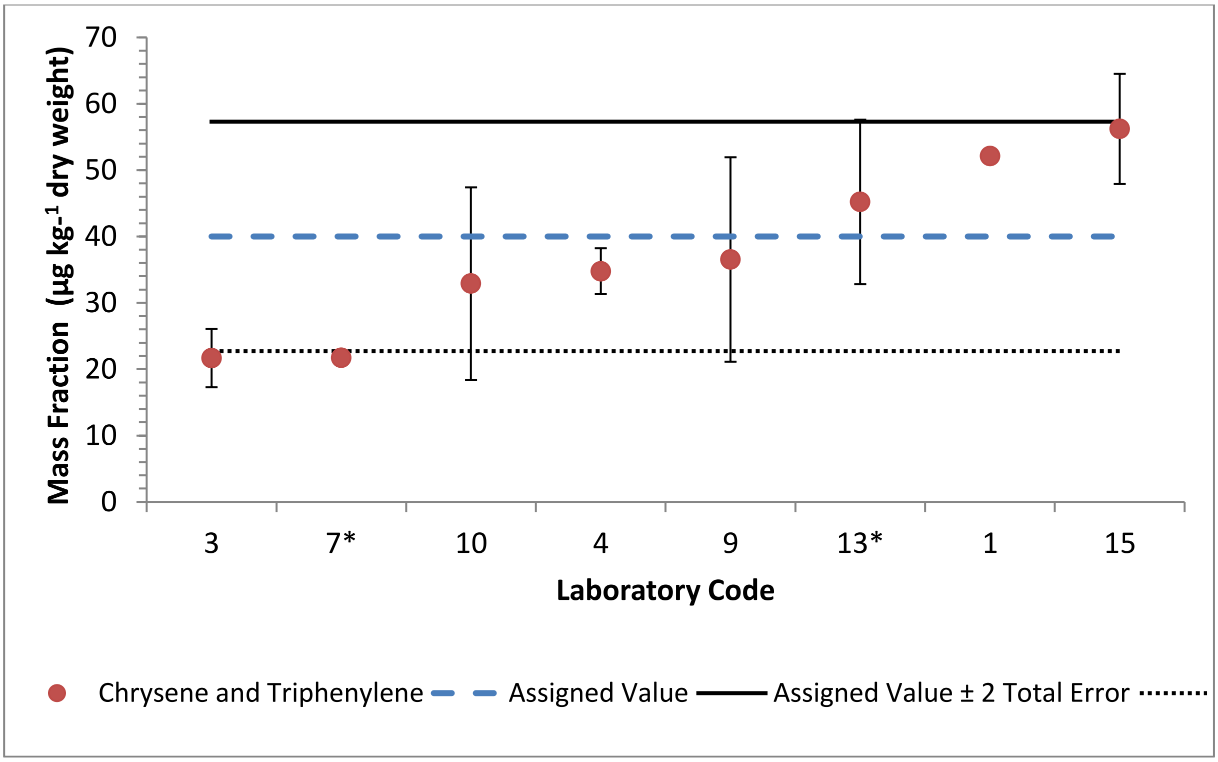


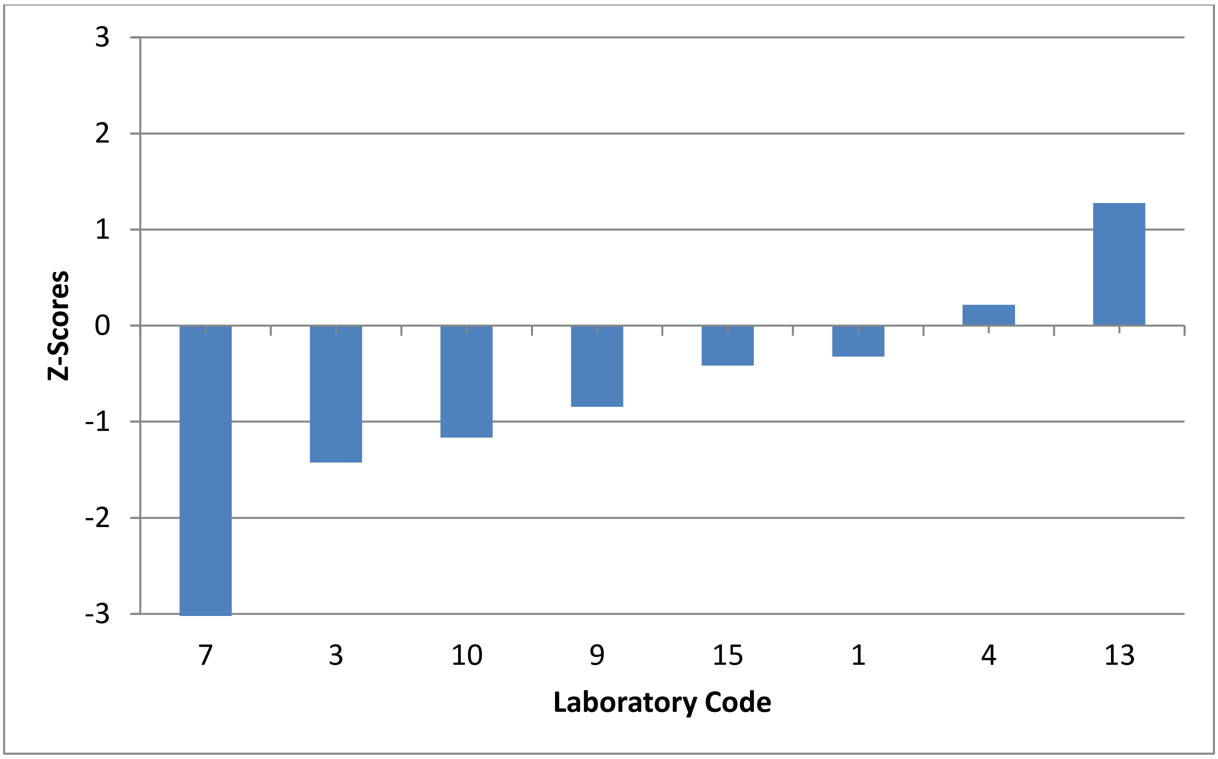


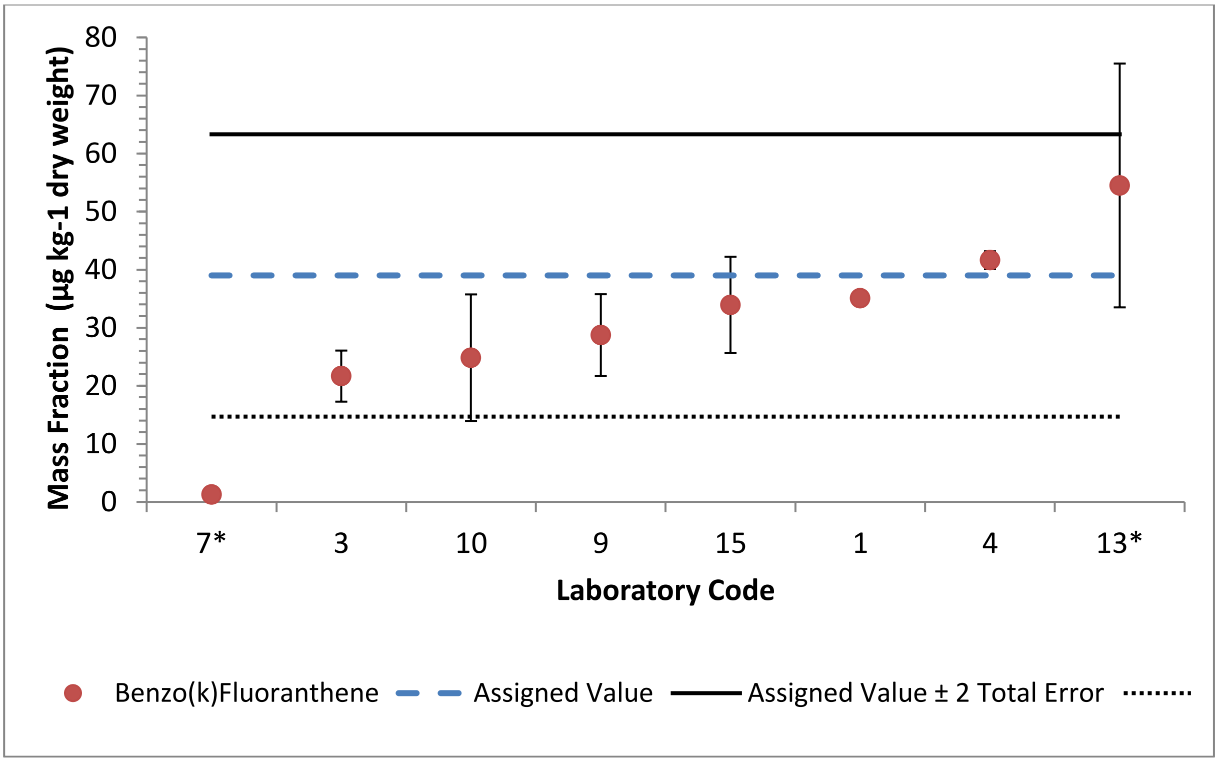
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR CHRYSENE (+ TRIPHENYLENE)



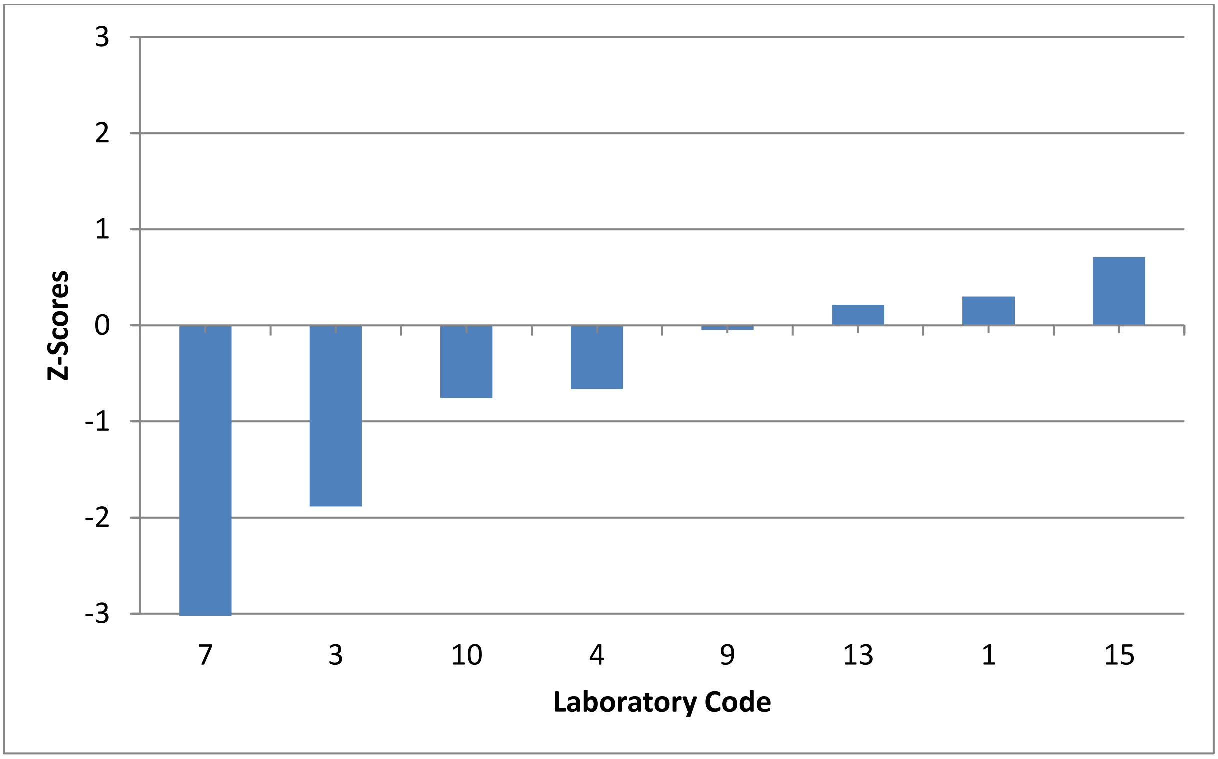


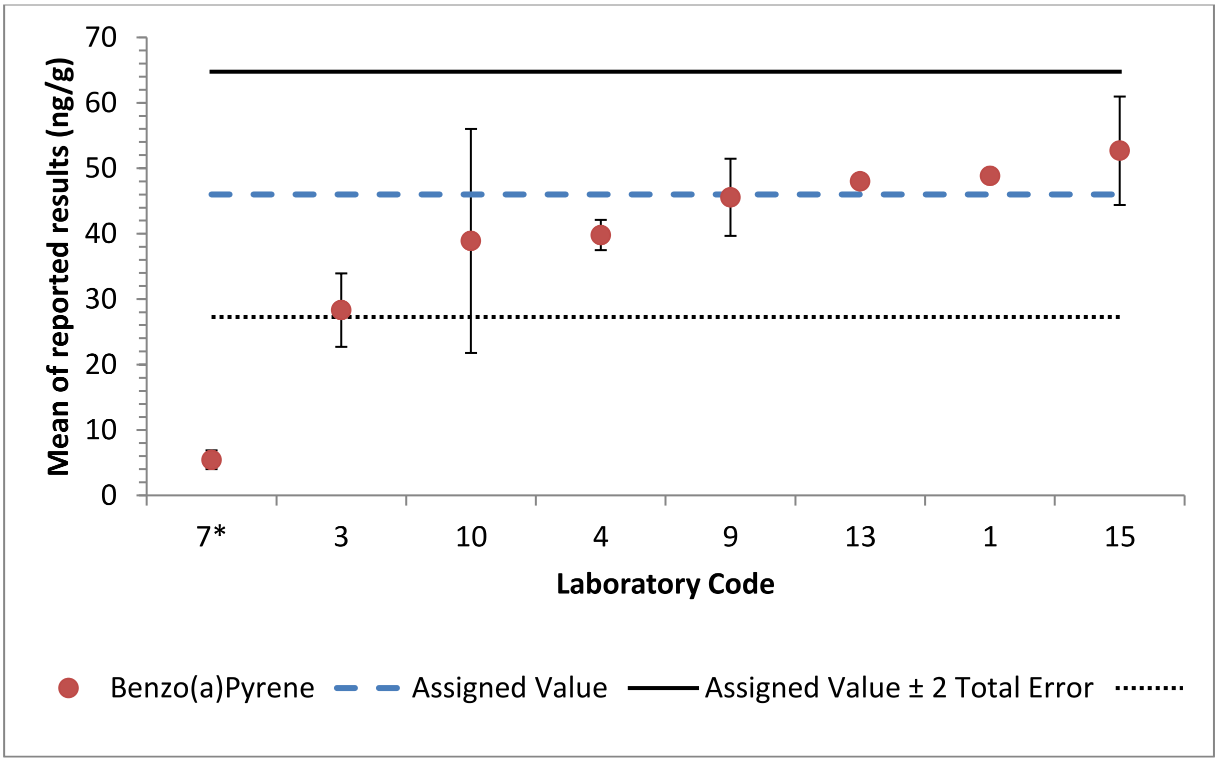
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [k] FLUORANTHENE



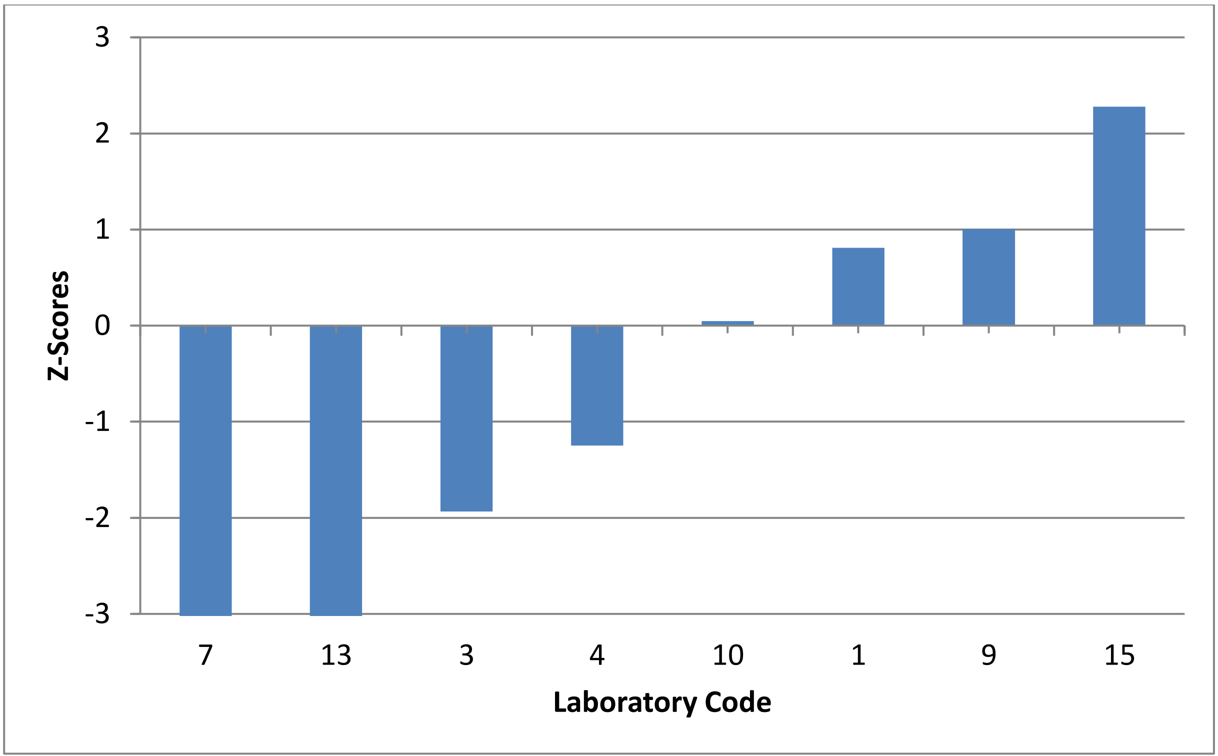


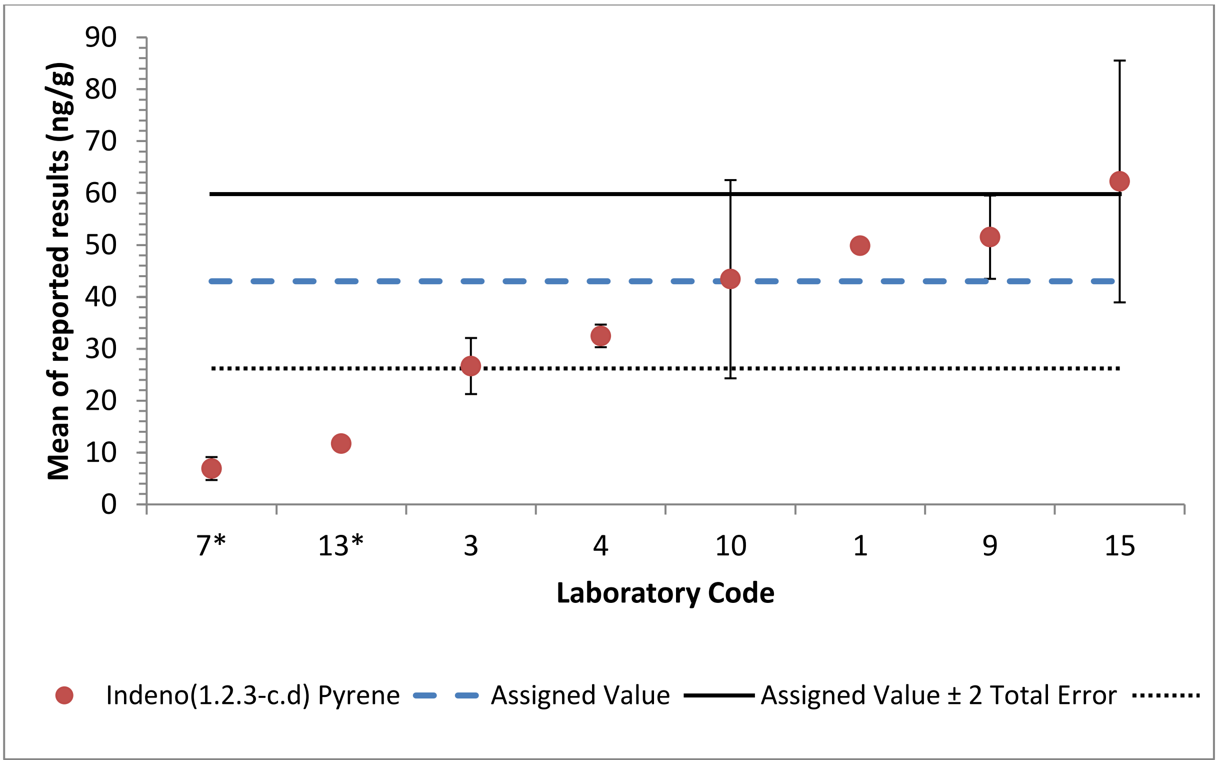
GRAPHIC REPRESENTATION OF LABORATORIES PERFORMANCES FOR BENZO [a] PYRENE





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





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